THREE PHOTON SPECTROSCOPY OF MOLECULAR IODINE

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by

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A Thesis

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ABSTRACT

The construction and development of a laser spectrometer designed to generate multiphoton spectra is outlined. This apparatus has been used successfully to record the resonance enhanced three photon absorption spectrum of the isotopic molecules, ${}^{127}I_2$ and ${}^{129}I_2$.

Multiphoton spectra have been obtained under low $(\Delta v \sim 1.0 \text{ cm}^{-1})$ and high $(\Delta v \sim 0.12 \text{ cm}^{-1})$ resolution, by monitoring the undispersed fluorescence from highly excited states, following dye laser excitation over the green-red portion of the visible spectrum. The high resolution spectra were obtained either through the use of a single tunable dye laser or alternatively with the use of two dye lasers in tandem. In addition, spectra have been obtained for the first time using a dye laser configuration which allowed it to oscillate at two separate frequencies simultaneously, one of which was tunable.

The analysis of the high resolution spectra for both molecules has given evidence for at least five different excited states in the $50000-55000 \text{ cm}^{-1}$ region as being responsible for the observed spectrum. A detailed rotational analysis has been possible for three of these states, all of which are shown to be ion-pair in nature and of θ_u^+ symmetry. No prior rotational analysis has been given for one of these

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states (the $F0_u^+$ (${}^{3}P_0$)). The high resolution analysis was facilitated by measuring the polarization dependence of the rotational transitions under linearly and circularly polarized excitation. Isotopic substitution has allowed the assignment of absolute vibrational numbers.

The results of several investigations by previous workers are also incorporated into the analyses presented in this study. Conclusions are drawn that raise serious doubts about the validity of earlier reports concerning the existence of bound states Tying near 35000 cm^{-1} above the ground state.

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DEDICATION

To my wife, Ann-Marie and my daughters, Lindsay and Lauren in the hope they will finally discover just what it is I have been doing all these years.

CHAPTER 1

MULTIPHOTON SPECTROSCOPY

1.1 Introduction

Goppert-Mayer [1], was the first to show that the simultaneous absorption or emission of more than one photon in a spectroscopic transition was predicted by quantum mechanics. Her deduction was the result of an investigation into the consequences of Dirac's dispersion theory [2]. Dirac, himself had investigated, using second order perturbation theory, the theoretical possibility of observing optical phenomena due to the simultaneous absorption (at v_1) and emission (at v,) of a photon. The phenomena predicted by Dirac, (Raleigh ($v_1 = v_2$) and Raman ($v_1 > v_2$) scattering), though two photon events, are linear with respect to light intensity and were experimentally verified before 1930 [3]. On the other hand, the small magnitudes of multiphoton absorptivities (Chapter 1.2) thwarted attempts to observe non-linear absorption until the development of sufficiently high photon density light sources.

Not until 1961, after the development of the ruby laser was the first multiphoton (two photon) transition observed [4]. Initially, non-linear behaviour was monitored only in solid samples. The lower number densities of liquids and gases

hindered experimental observation of multiphoton transitions of samples in these states until much later. In 1974, the first two photon spectra for a gaseous molecular sample (benzene) were reported [5]. Rapid developments since that time have led to the observation of two photon transitions in a variety of atomic [6,7], diatomic [8,9] and polyatomic [10] species. In addition, other non-linear phenomena such as three photon absorption [11], second [12] and third harmonic generation [13], four wave sum mixing [14] and coherent anti-Raman scattering [15] are now routinely studied.

In the following section of this chapter, a brief discussion of the classical and quantum mechanical treatment of light absorption is given. This is followed by discussions of the selection rules governing multiphoton transitions as well as the polarization and power dependence of these transitions. A concluding section on some experimental aspects of multiphoton absorption work is also Aresented.

1.2 Classical and Quantum Mechanical Treatment of Multiphoton Absorption

The fundamental relationship in classical absorption spectroscopy is Lambert's Law (equation (1.1)), which states that the decrease in light intensity (dI) due to absorption is proportional to the product of the total absorption crosssection (σ_T) of the sample, the intensity of the incident radiation (I, photon cm⁻² s⁻¹), the population of the lower level (N) and the absorption path length, dx.

- dΙασ_TΙΝ dx

This equation can be generalized to treat non-linear absorption by considering $\sigma_{\rm T}$ to be the sum of the individual cross-sections (cm² molecule⁻¹) due to single photon and all possible higher order transitions, as given by equation (1.2).

$$\sigma_{\rm T} = \sigma^{(1)} + 2I\sigma^{(2)} + 3I^2\sigma^{(3)} + \dots \qquad (1.2)$$

In the above equation, $\sigma^{(1)}$ represents the single photon crosssection, which is typically 10^{-16} cm² molecule⁻¹ for relatively strong transitions. In comparison, the molecular absorptivities of two $(\sigma^{(2)})$ and three photon $(\sigma^{(3)})$ simultaneous transitions are on the order of 10^{-50} cm⁴ s photon⁻¹ and 10^{-80} cm⁶ s² photon⁻¹, respectively. Therefore, large photon fluxes are necessary before even the lowest order intensity dependent terms in equation (1.2) contribute to the absorption crosssection of the molecule. Hence in the majority of cases, where the incident radiation is of low intensity, these terms can be neglected and only the single photon contribution to or need be considered. As a result there is a first order dependence on the intensity for the absorptivity of the sample (equation (1.1)). This truncated form of equation (1.1) forms the basis of linear or classical spectroscopy. At large photon densities, contributions from the higher order terms in equation (1.2) result in a deviation from linearity, giving rise to non-linear, or, multiphoton spectroscopy.

(1.1)

Quantum mechanically, the radiation field and the irradiated sample can both be described by Hamiltonian operators. The absorption of light energy by the sample can be treated using perturbation theory by introducing a coupling Hamiltonian (H²),

$$H^{\prime} = -\mu \cdot E \tag{1.3}$$

where μ represents the electric dipole operator and E is the wave vector which describes the polarization state of the radiation field. It can be shown [16] that the absorptivity $(\sigma^{(n)})$ of an n photon transition is proportional to the square of the transition dipole moment $(M_{ab}^{(n)})$, which in turn can be expressed as the product of n individual matrix elements. Each matrix element is in the form of equation (1.4),

$$H_{ij} = \langle \psi_i | H^{\prime} | \psi_j \rangle \qquad (1.4)$$

where ψ_i and ψ_j are the zeroth order lower and upper state wave functions respectively. For an n photon absorption step between two real states (a+b), the molecule undergoes the transition via n-l intermediate states. In general, these states are non-stationary (virtual) in nature. The wave functions of such levels can be represented as a time dependent linear function of all the bound and continuous real eigenfunctions of the molecule. Hence, for example, the expression for the transition moment in the case of three photon absorption is given by equation (1.5),

$$\sigma(3) \propto (M_{ab}^{(3)})^2 = \left[\sum_{\ell m} \frac{H_{a\ell}}{(E_{a\ell} - h\nu)} \frac{H_{\ell m}}{(E_{\ell m} - h\nu)} \frac{H_{mb}}{(E_{\ell m} - h\nu)}\right]^2 \qquad (1.5)$$

where a and b are the initial and final (3 photon excited) states respectively, the summations represent the expansions of the one photon (L) and two photon (m) excited states. E_{ij} , is the energy difference between each pair of levels (i and j) in equation (1.5) and hv is the photon energy. The smaller the separation between E_{ij} and hv, the greater the contribution made by the real level being considered in the summation. In the case of exact resonance $(E_{ij} = hv)$, we have the special case of a real intermediate state. In this instance, the matrix element for the particular absorption step is given by equation (1.4). When the resonance condition is fulfilled at one or more of the intermediate levels, a significant enhancement in the absorption rate is observed.

Multiphoton transitions are classified as sequential (resonance enhanced), as simultaneous (virtural intermediates) or as a combination of each depending on the presence or absence of real intermediate states. The presence of both types of transitions allows the total absorptivity of the molecule to be expressed as the product of a sequential and a simultaneous term.

1.3 Selection Rules

For a heavy molecule such as iodine, Hund's coupling case 'c' is appropriate [17] to describe the interaction

between the various angular momentum vectors. Under this coupling case there are only three good quantum numbers: the internuclear projection of the electronic angular momentum (Ω) , the total angular momentum (J) and the 2J+1 components of J along a specified axis (M). In the absence of external fields, the M sublevels are degenerate.

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Application of the Born-Oppenheimer approximation allows electronic and nuclear motion to be considered separately. This permits the molecular Hamiltonian to be written as the sum of electronic and nuclear (vibrational and rotational) The associated wave function is then a product of an terms. expression describing electronic, vibrational and rotational motion respectively. With Handefined as in equation (1.3), the matrix elements of equations (1.4) and (1.5) and hence the absorption cross-section will be non-zero only if the selection rules regarding electronic and rotational transitions are obeyed. These rules are obtained by considering the symmetry properties of the above wave functions. Table 1.1 lists the selection criteria applicable to single photon transitions in homonuclear diatomic molecules which tend towards Hund's case 'c'

While no formal selection rule restricts vibrational transitions, the relative intensities of these transitions are governed by the overlap of the upper and lower state vibrational wave functions.

For a multiphoton transition, the selection rules given

in Table 1.1 are applied to each matrix element, H_{ij} in equations (1.4) and/or (1.5) to determine if $\sigma^{(n)}$ is non-zero (allowed transition). Though a transition may be for-bidden under the electronic dipole operator, it may be allowed under a higher order multipole operator. However in such cases the transition is usually very weak.

Table 1.1

Single Photon Selection Rules

Electr<u>ic</u> dipole selection rules for homonuclear diatomics I. Electronic transitions

 $\Delta \Omega = 0, -1$ $u \leftrightarrow g, u \leftrightarrow u, g \leftrightarrow g$ $+ \leftarrow +, - \leftrightarrow -, + \leftarrow +$

II. Rotational transitions

 $\Delta J = \stackrel{+}{-} 1 \quad \text{for an } 0 \stackrel{+}{\longrightarrow} 0 \stackrel{+}{\longrightarrow} \text{transition}$ $\Delta J = 0, \stackrel{+}{-} 1 \quad \text{for any other electronic transition}$ $\Delta M = -0 \quad \text{for linearly polarized light}$ $\Delta M = \pm 1 \quad \text{for circularly polarized light}$

Detailed electric dipole selection rules have been given for two [18,19], three [20-24] and four [24] photon simultaneous transitions, for a number of symmetry point groups.

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Of particular interest are molecules which belong to point groups exhibiting a center of symmetry. Absorption of an odd number of photons from a totally symmetric ground state allows excited states of ungerade (u) symmetry to be accessed, while excitation by an even number of photons enables upper states of gerade (g) symmetry to be probed.

1.4 Rotational Transition Probabilities.in Linearly and Circularly Polarized Light

A detailed discussion of the derivation of transitional amplitudes is beyond the scope of this work. As such discussions can be found in the literature [25-27], only those points salient to the present study will be noted.

With the proper selection of the form of the dipole moment operator [27,28], the rotational line strength for a given one photon transition can be factored into two terms. The first of these is dependent on the electronic transition (AQ for case 'c') and the second involves the variables of the rotating Hamiltonian (J and M) and also depends parametrically on Ω . Exact theoretical determinations of the first term are not generally possible as they require the knowledge of the upper and lower state electronic wave functions. Therefore. the matrix elements due to this term can be expressed as u_0 and u_1 to denote parallel ($\Delta\Omega$ = 0) and perpendicular ($\Delta\Omega$ = -1) transitions respectively. Values of u_0 and u_1 can be obtained from the experimentally observed line strengths. The matrix elements of the second, rotationally dependent term are, however,

well known functions of Ω , J, M, ΔJ , and ΔM [28].

One photon signal amplitudes are obtained by squaring (as $\sigma \alpha M_{ab}^2$) the product of the non-rotating component (represented by u_0 or u_1) and the appropriate tabulated rotational contribution. The sum of these squared products over all the lower state M values participating in the absorption transition gives the transitions probability. These probabilities are commonly known as the Hönl-London line strength factors [26].

In the case of multiphoton absorption the calculation of rotational line strengths is not as straightforward. All the possible excitation pathways that link a pair of upper and lower state rotational levels via allowed transitions through all the possible intermediate states must be taken into account. For example, Bray and Hochstrasser [27] have given the line strengths for the allowed rotational branches of a two photon 0^+ . 0^+ transition. As this case is relevant to this work, the treatment is briefly outlined below, for an $0^+_{\mu} = 0^+_{\mu}$ transition.

The two photon transition is assumed to be via a virtual intermediate state. Application of the selection rules in Table 1.1 to each of the resulting matrix elements (equation (1.5)) dictates that the intermediate state be a composite of real eigenstates of 0_g^+ and l_g symmetry only. This situation is clarified in Figure 1.1, which clearly demonstrates that the allowed two photon transitions are the

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Allowed two photon rotational branches for an $0^+_{\rm u}$ - $0^+_{\rm u}$ electronic transition Figure 1.1



O ($\Delta J=-2$), Q ($\Delta J=0$) and S ($\Delta J=+2$) branches. It is also clear that the transition probability calculation of a Q branch line, for example, will involve the squaring of a sum containing five separate contributions. Each of these contributions involves the sum of two (one photon amplitudes) terms each of which involves an electronic (u_0^{i} , u_0 , u_1^{i} or u_1) factor and a rotationally dependent term. The collective contributions of all real states of 0_g^+ character and the participation of all real states of 1_g symmetry to the non-stationary intermediate state are represented by u_0 (and u_0^{i}) and u_1 (and u_1^{i}) respectively.

The transition strengths for the two photon allowed rotational branches are given in Table 1.2 for excitation in linearly and circularly polarized light. These expressions were obtained by again summing over all the lower state M values (for absorption) following the squaring of the above summations for each branch.

Rather than considering absolute line strengths it is more instructive to consider the ratio (γ) of the transition probabilities in circularly polarized light to that in linearly polarized light as given in equation (1.6).

$$r = \frac{[M_{ab}^{(n)}]^2 \text{ cir.}}{[M_{ab}^{(n)}]^2 \text{ lin.}}$$
(1.0)

In the case of one photon absorption (n=1), it is always true that $\gamma = 1$. However, for multiphoton transitions, in general,

Table 1.2

Two Photon Line Strengths for an 0^+_{u} - 0^+_{u} Transition

Polarization

 Branch
 Linear
 Circular

 0
 $\frac{J^2(J-1)^2}{20J(J-1)(2J-1)}$ same x 3/2

 Q
 $\frac{(2J+1)}{9}$ $U_I^2 + \frac{(2J+1)(J(J+L))^2 U_S^2}{45J(J+1)(2J-1)(2J+3)}$ $\frac{(2J+1)(J(J+1))^2}{30J(J+1)(2J+3)(2J-1)}$

 S
 $\frac{(J+1)^2(J+2)^2}{20(J+1)(J+2)(2J+3)}$ same x 3/2

 U_S^2 = $|2u_0u_0' - u_1u_1'|^2$ same x 3/2

 U_I^2 = $|2u_0u_0' + u_1u_1'|^2$ for 0 and S branches $\gamma = 3/2$

for Q branch $Y = \frac{10J(J+1)(2J+3)(2J-1)}{3[J(J+1)]^2} (\frac{U_I}{U_S}) + \frac{2}{3}$

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 $\gamma \neq 1$. For the above $0_{u}^{+} - 0_{u}^{+}$ transition, Bray and Hochstrasser calculated a value of $\gamma = 3/2$ for the O and S branches, in accord with earlier investigations [29, 30]. However, for the Q branch (and in general for the Q branch of any $\Delta\Omega = 0$ two photon transition) the value of γ was predicted to be less than unity. The exact value of γ , while nominally a function of J, is more dependent on the electronic transition dipole factors denoted as U_S and U_I in Table 1.2. These factors are in turn functions of u_0 , u_0' , u_1 and u_1' (Table 1.2). Hence, an experimentally obtained value of γ of less than one in a two photon experiment indicates the presence of an $\Delta\Omega = 0$ transition. Conversely, measuring the polarization dependence of the resolved Q lines allows the relative contributions of real states of, in this case, 0_g^{+} and 1_g character to the intermediate state to be obtained.

1.5 Power Dependence

The number of absorped quanta (n) responsible for a particular multiphoton transition can be determined by considering equations (1.1) and (1.2), from which,

$$\Gamma \alpha \left(\sigma^{(n)} I^{n-1} \right) \text{ IN } dx \alpha I^{n} \tag{1.8}$$

$$\log \Gamma \propto n \log I \tag{1.9}$$

where Γ is the rate of absorption. Γ can be monitored by observing a related phenomena, such as fluorescence from the final state. A plot of log Γ (or related parameter) versus log I

gives, in principle, the value of n. Usually, however, the slope of the above plot is less than n because of optical saturation of one or more of the transition steps. Sequential transitions (real intermediate state) are particularly prone to saturation at the high photon fluxes required to observe non-linear behaviour.

Contributions to the total absorption cross-section from higher order terms (>n) in equation (1.2) are also a possibility at high light intensities and will increase the apparent value of n.

1.6 Experimental Techniques

1.6.1 Introduction

Non-linear spectroscopy using visible light can be used to study molecular states whose excitation energies lie in the ultraviolet. Dye lasers designed to give pulses of high intensity light are well suited to multiphoton studies. The tunability of these devices allows spectra to be recorded as a function of wavelength.

1.6.2 Detection of multiphoton transitions

Various means of detecting the occurrence of multiphoton transitions have been described in the literature [31, 32].

Non-linear transitions can be signaled by monitoring

the intensity of the radiation transmitted by the sample. This scheme has the advantage that it permits the direct calculation of multiphoton absorptivities (equation (1.2)).

A far more sensitive optical technique is the monitoring of the fluorescent light emitted by the high lying excited state. This can be accomplished by observing the emission at right angles to the exciting radiation. In cases where the multiphoton transition is resonance enhanced the term optical - optical double resonance (00DR) is often used to describe the experiment [33]. In general, fluorescence detection allows a determination of relative absorptivities only, though absolute values can be derived if the fluorescence quantum yield is known. Unfortunately, many excited states. do not fluoresce efficiently. This has lead to the development of a number of techniques that are not based on photon detection. Of these methods, only the one of interest to this study will be discussed here.

Excited electronic states often have relatively large ionization cross-sections that are independent of excitation wavelength over a large spectral range. The ionization potential of most molecules can usually be exceeded by the overall absorption of five photons or less in the visible region. As a result, the initial multiphoton transition is often accompanied by subsequent ionization of the molecule. Ions and electrons so produced can be collected across a pair of biassed electrodes with efficiencies approaching 100%, with a high signalto-noise ratio. This technique of monitoring multiphoton transitions was first reported almost simultaneously by Johnston et al. [34] and Petty et al. [35]. More complex experimental designs include the incorporation of a mass spectrometer to differentiate between the various atomic and molecular ions produced by the laser radiation.

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It has been found [36] that multiphoton transitions to states of Rydberg character are most likely to give rise to ionization spectra. On the other hand, fluorescence detection appears to be more selective to the observation of transitions to valence and ion-pair states.

CHAPTER 2

THE RELEVANT SPECTROSCOPY OF IODINE

2.1 Introduction

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Although the iodine molecule has been one of the most studied of all diatomic molecules [37], elucidation of its ultraviolet spectrum is far from complete. This is due in part to the heavy density of molecular eigenstates commencing near 40000 cm⁻¹ above the ground state, the region of interest in this work. The spectra produced by the molecule are strongly dependent on the experimental technique used, (absorption, condensed discharge, high frequency discharge, etc. ...) and the vapour pressure of, not only iodine but of inert gases, when added. Unfortunately, as a result the literature over the past half century or more has been filled with often confusing and contradictory analyses. Only recently, aided by a careful reexamination of earlier emission spectra, and laser based spectroscopy have definitive assignments been made and some of the earlier conflicts resolved.

As comprehensive reviews of the long and detailed spectroscopic background of iodine exist elsewhere [38-40], only those studies relevant to the present work will be discussed here.

As mentioned in Chapter 1.3, Hund's coupling case 'c' nomenclature [17] will be used to designate the molecular

terms, as is appropriate for a heavy molecule such as iodine. In some instances, to avoid ambiguity concerning spectral assignments, the Hund's case 'a' parent term will be given in parentheses after the term symbol. The alphabetic prefixes in common use for the better known states are also retained.

The above eigenstates can also be described in terms of the molecular orbital (MO) configuration from which they arise, and the dissociation products (separated atoms or_ ions) with which they correlate. Figure 2.1 shows the correspondence between the terms derived from the MO and separated atom approaches for the low lying valence states. These correlations can be made by application of the noncrossing rule for terms of like symmetry.

The ground state MO configuration of molecular iodine is given in equation (2.1).

 $(\sigma_{g}^{1s})^{2} (\sigma_{u}^{1s})^{2} \dots (\sigma_{g}^{5s})^{2} (\pi_{u}^{5p})^{4} (\pi_{g}^{5p})^{4} (\sigma_{u}^{5s})^{0}$ (2.1)

A convenient shorthand notation, denotes the occupation numbers of the four outer valence orbitals. The above configuration is labelled 2440 and gives rise to the totally symmetric ground state, $X \theta_g^+$. The ground state dissociates $(D_e = 12547 \text{ cm}^{-1})$ [41] into a pair of normal iodine atoms $({}^2P_{3/2})$. However, in the separated atom approximation, a pair of ground state iodine atoms can give rise to a total of ten molecular terms (Figure 2.1). All, but the $X \theta_g^+$ state
Figure 2.1

Correlation diagram for the low lying valence states of molecular iodine (not to scale) [40]



correspond to excited MO configurations (Figure 2.1). With the exception of the molecular ground state these valences states $({}^{2}P_{3/2} + {}^{2}P_{3/2})$ are expected to give repulsive or weakly bound potential curves [42]. An important exception are those states that are obtained from the case 'a' ${}^{3}\Pi$ (2431) term. These states are commonly denoted as; $A^{2}_{11}({}^{3}\Pi)$, $Al_{11}({}^{3}\Pi)$ and $O_{11}({}^{3}\Pi)$ respectively.

The next higher lying atomic asymptote is that corresponding to a ground state plus a spin orbit excited atom, ${}^{2}P_{1/2}$ ($\Delta E_{s.o} = 7603 \text{ cm}^{-1}$). Most of the terms arising from these separated atoms (Figure 2.1) again exhibit dissociative potential curves. A prominent exception is the remaining case 'c' component from the above ${}^{3}\Pi$ term, which is designated as the B0⁺_{\pi}.

The three terms derived from a pair of excited atoms $({}^{2}P_{1/2} + {}^{2}P_{1/2})$ (Figure 2.1) are also expected to be unbound [42].

Above the 23 low lying valence states, the next higher states are those that diabatically dissociate into the separated ions I⁺ (${}^{3}P_{2,1,0}$, ${}^{1}D$) + I⁻(${}^{1}S$). These deeply bound ($D_{e} > 30000 \text{ cm}^{-1}$) ion-pair states are expected to display very similar potential curves, as the dominant term in the potential function is simply $-e/r^{2}$ for such states. Hence, the states tending to each ionic asymptote will form a closely spaced cluster [43], with the energy levels of the positive ion determining the separation between adjacent groupings.

く The relative energy separation of the molecular states derived from the lowest lying ion pairs Figure 2.2

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Figure 2.2 shows the terms that arise from each pair of separated ions and the relative energy spacing of each cluster of charge-transfer states.

The first excited configuration of the iodine atom (5p,⁴6s) results in a number of atomic terms, the two lowest lying of which are the $({}^{3}P_{2})6s[2]_{5/2}$ and $({}^{3}P_{2})6s[2]_{3/2}$. Relative to the potential minimum of the molecular ground state the separated atoms ${}^{2}P_{3/2} + ({}^{3}P_{2})6s[2]_{5/2}$ and ${}^{2}P_{3/2} + ({}^{3}P_{2})6s[2]_{3/2}$ have energies of 67180.5 cm⁻¹ and 68639.9 cm⁻¹ respectively [44] (Figure 2.2).

The ground $(X3/2_g)$ and first excited state $(X1/2_g)$ of the I_2^+ molecule are obtained from the 2430 configuration. Rydberg series converging to both of these states are expected in the ultraviolet spectrum of iodine.

2.2 The Classical (One-Photon) Spectroscopy of Iodine

The room temperature absorption spectrum of iodine vapour shows a weak system in the near infrared (9600-8000Å), an intense banded region in the visible (6500-5000Å), a weak broad continuum near 2700Å, a strong series of bands with a maximum about 1825Å and below 1750Å, several Rydberg series [38].

The infrared system is due to the $Al_u({}^{3}\pi)-X0_g^+$ transition [45]. In emission this system has been recorded between 0.8 and 1.7 μ m [40].

The visible system, which is responsible for the characteristic color of iodine vapour, is due primarily to the $B0_u^+ - X0_g^+$ system. This system has been thoroughly investigated in absorption and emission since the end of the last century [38]. However, even for this well studied transition the correct upper state vibrational numbering was not determined until 1965 [47].

The strong ultraviolet band system was first photographed by Cordes [48] and now bears his name. Several other weaker systems were also observed in this region of the spectrum. Venkateswarlu [49] made the initial vibrational analysis of the Cordes bands, but it was later shown to be incorrect [38]. Nobs and Wieland [50] were the first to show that the bands recorded by Cordes and those photographed at much higher temperatures [51, 52] were in fact due to the same transition. Wieland, as quoted by Mulliken [38], found that all these bandheads could be adequately represented by the following quantum formula.

 $v = 40623.9 + 104.105v' - 0.2422405 v'^{2} + 0.453864 \times 10^{-5} v'^{5} - 0.70641 \times 10^{-6} v'^{4} + 6.41845 \times 10^{-10} v'^{5} - G''(v'') \\ 0 < v'' < 7 - 98 < v' < 259$

where v' is an arbitrarily assigned vibrational quantum number for the upper state and G''(v'') is the ground state

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(2,2)

vibrational term value relative to v" = 0. It has since been shown [53] that the upper state of this system is a member of the lowest ion-pair grouping $[I^+({}^{3}P_2) + I^-({}^{1}S))$, while the lower state is the ground state of the molecule. In keeping with the nomenclature proposed by Viswanathan et al. [54], this transition is denoted as the $D0^+_u({}^{3}P_2)-X0^+_g$. Recently, emission has been obtained on this system from the low (v' = 0-5) levels of the upper state [55, 56]. As a result, it has been suggested that the v' numbering in the above expression is either correct or too high by one unit [57].

Ultraviolet excitation ($\lambda < 2100\text{\AA}$) of iodine leads to the appearance of a long progression of diffuse bands in emission from 2000-5000 [58, 59]. At room temperature these so-called 'McLennan bands' exhibit a maximum intensity near 3250 Å, but these features exhibit a temperature and pressure dependence [60,61]. Mulliken [38], interpreted these bands as due to a bound-free transition. It was subsequently shown by Tellinghuisen [53] that these bands were indeed attributable to transitions from high lying levels of the $\text{D0}_{\rm u}^+$ (${}^{\rm J}\text{P}_2$) state to the continuum above the ground state dissociation limit.

The u.v.fluorescence spectrum excited by the 1830Å atomic iodine line was first studied by Verma [62] at high resolution. Five fluorescence series are stimulated by this emission line, enabling a calculation of the molecular constants characterizing the upper levels. A later reinvestigation

[63] showed that $D0_u^+$ (${}^{3}P_2$) was the excited state populated by the atomic line. Rigourous least squares analysis of the resolved line positions yielded a rotational constant of 0.012139 cm⁻¹ for v' = 204 (equation (2.2)) and a local value for the vibrational-rotational coupling constant of 3.43 x 10⁻⁵ cm⁻¹.

Oldenberg [64], was the first to show that upon the addition of inert foreign gases, the diffuse 'McLennan bands' are replaced by many series of sharp bands. This results from collisional population transfer from the $D0_{11}^+$ (${}^{3}P_{2}$) state to several nearby ion-pair states and their subsequent relaxation to the low lying valence states. By far the most intense of these systems extends from $3015-3460 \stackrel{0}{\text{A}}$ [39, 65, 66] and has recently been shown [67] to be due to the $D'2_{\sigma}({}^{3}P_{2}) - A'2_{\mu}({}^{3}\Pi)$ transition. Other prominent systems and their spectral assignments are given in Table 2.1. In addition to these transitions, Guy et al. [43] have reported several other weaker systems in the ultraviolet and claim.to have recorded emission from 12 of the 18 ion-pair states arising from $I^+({}^{3}P_{2,1,0}, {}^{1}D) + I^-({}^{1}S)$. Of particular interest to this current study is a system near 2380Å which was believed to be due to emission from the $0^+_{1,1}(^1D)$ ion-pair state ($T_{p} \sim 51720 \text{ cm}^{-1}$). Later, several members of the v' = 0 progression were photographed [75] in emission.

In 1958 Haranath and Rao [76] undertook a moderate dispersion $(6 \text{\AA}/\text{mm})$ study of the 1400-2400 region in emission. A total of 12 transitions were postulated to account for the

Table 2.1

Systems Observed in Emission in the Presence of Foreign Gases

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$\lambda(\hat{A})$	Transition	Reference
-5050	$D'2g({}^{3}P_{2})-2u({}^{3}\Delta)$	43, 64, 68, 69, 70
4000-4400	$E0_{g}^{+}(^{3}P_{2})-B0_{u}^{+}$	39, 43, 65, 66, 71, 72
3100-3300	$D0_{u}^{+}({}^{3}P_{2}) - X0_{g}^{+}$	55, 56
3015-3460	$D'2g(^{3}P_{2}) - A'2u(^{3}\Pi)$	39, 43, 56, 65, 66, 67, 73
2830-2890	$g_{g}^{-}({}^{3}p_{1}) - 0_{u}^{-}({}^{3}\pi)$	43,• 74
2712-2785	$lg({}^{3}P_{1}) - Al_{u}({}^{3}\pi)$	39, 43, 54, 66
2486-2730	$F0_{u}^{+}({}^{3}P_{0}) - X0_{g}^{+}$	39, 43, 65, 66, 71, 72
2380	$F'0_{u}^{+}(^{1}D) - X0_{g}^{+}$	43, 75

numerous bands that were photographed between 1450Å and 1790Å. A few of these appeared to be the same as the fragmentary systems first reported by Cordes [48] in absorption. Most of the upper states were assigned as Rydberg in nature and the remainder as ion-pair. A later attempt to rephotograph this region [77] failed to record any of the above bands, although it should be noted that a different excitation source was used. If the observations of Haranath and Rao are genuine however, a reanalysis of their data is in order, since several of the assumptions used in the original analysis are now known to be in error.

Although others have since reinvestigated the vacuum ultraviolet spectrum of iodine [78-80], by far the most comprehensive study was done by Venkateswarlu [81]. Analysis of high dispersion ($\sim 0.3 \text{\AA/mm}$) photographs taken between 1950Å and 1200Å in absorption resulted in the assignment of more than 30 previously unreported band systems. Again, the majority of the excited states were found to be Rydberg. Analysis of these series led to a determination of the ionpotential of the molecule (75814 \pm 10 cm⁻¹ or 9.399 \pm ization ev) and the magnitude of the spin orbit splitting in the ground state of I_2^+ (5081 cm⁻¹ or 0.63 eV). Although this latter figure is in good agreement with the result obtained from photoelectron [82] and electron impact studies [83], the value of the ionization potential (\sim 9.33 $\stackrel{+}{=}$ 0.02 eV) determined by these methods is not in accord with the ultraviolet study.

2.3 Laser Spectroscopy of Iodine

Many single photon laser induced fluorescence experiments have been conducted on the $B0_u^+ - X0_g^+$ transition. Recent high resolution Fourier-transform assisted studies [84-87] and the subsequent data reduction [88-89] have yielded very precise vibrational and rotational term values for the upper (v' = 0-80) and lower states (v'' = 0-9).

In multiphoton studies, high lying excited states are conveniently accessed by pumping the intense $B0_u^+ - X0_g^+$ transition, which is well matched to available dye and ion laser frequencies. Unless otherwise stated in the following discussion, the multiphoton transition is resonance enhanced via the $B0_u^+$ state.

In 1976, inspired by earlier preliminary work [90], an OODR study conducted by Danyluk and King [91] resulted in the observation of S states near 40000 cm⁻¹, which were arbitrarily labelled as the α , β , γ , δ and ε . Further experimental work [92] provided evidence that these states were separate and distinct. Vibrational and rotational constants were obtained for ${}^{127}I_2$ and ${}^{129}I_2$ [93]. Subsequently it was determined that these upper states belong to the lowest ionpair cluster. The correlation between the states labelled above and the terms belonging to the I⁺(${}^{3}P_2$) + I⁻(${}^{1}S$) asymptote is given in Table 2.2. The α , β and ε labelled states have been further investigated in a number of subsequent OODR studies [94-98]. In addition, ion-pair states correlating to

the $I^+({}^{3}P_{0,1}) + I^-({}^{1}S)$ ionic asymptotes have been observed [99-101]. The findings of these studies are summarized in Table 2.2.

Multiphoton ionization investigations have identified a pair of relatively low lying Rydberg states at 48426 cm⁻¹ [102]_and 53563 cm⁻¹ [103] with molecular symmetries of 2_g and 1_g respectively. In these particular studies, the excitation frequencies used ($v_1 > 22000 \text{ cm}^{-1}$) did not allow resonance enhancement via the B0⁺_u state (Figure 2.2). The observation of Rydberg states in this spectral region is at odds with the analysis of Venkateswarlu [81].

Lehmann, Goodman and Smolarek [102] recorded a second multiphoton spectrum (in addition to the 2_g Rydberg transition) while scanning between 5650Å and 5500Å (i.e. pumping the $B0_u^+ - X0_g^+$ transition). The increased ionization rate in this wavelength region was attributed to a second resonance enhancement via a real state at twice the photon energy. Analysis of the low resolution spectrum ($\Delta v=3.0 \text{ cm}^{-1}$) based on this assumption led to the following molecular constants for this state.

 $T_e = 35762 ~(4) ~cm^{-1} ~\omega_e = 104 ~(1) ~cm^{-1}$ (2.3)

Polarization measurements indicated that this intermediate state was totally symmetric. Although the existence of a repulsive state of 0_g^+ symmetry had long been known [104] in this region, this study provided the first evidence of a bound state in this portion of the electronic manifold of iodine.

In another MPI study, Zandee and Bernstein [105] employed a mass spectrometer to distinguish between I_2^+ and I_2^+ ions formed as a result of multiphoton absorption. The observed branching ratio when pumping in the region of the so-called 'Goodman bands' was reconciled with a six photon absorption mechanism. In the original work, Lehmann et al. [102] had measured a power index of less than two, thus indicating a high degree of saturation. Later De Vries et al. [106] measured the excess kinetic energy of iodine ions following multiphoton absorption in this same spectral region. Their observations supported the existence of the 'Goodman bands'. By using a dual laser experiment, with variable delay in the firing rates, they were able to determine a lifetime of 1.1 µs for this two photon excited state.

In 1978, Tai and Dalby [107] published the third harmonic generation (THG) spectrum of molecular iodine in the 5000-5400Å region. They also postulated that the signal intensity was enhanced by resonance at the two photon level. The following constants were calculated from an analysis of the spectrum for this intermediate state.

 $T_e = 35972.4$ (5) cm⁻¹ $w_e = 132.9$ (2) cm⁻¹ (2.4) As noted by the authors, the THG spectrum bears no resemblance to the MPI spectrum in this wavelength region. The THG spectrum, unlike the MPI spectrum, was found to be extinguished when the sample was irradiated with circularly polarized light. As the lowest ion-pair state has been convincingly shown to be

the D'2_g $({}^{3}P_{2})$ (T_e ~ 40387 cm⁻¹) [74], controversy has arisen concerning the possible existence of one or more bound states near 35800 cm⁻¹. This matter will be discussed later in this thesis.

Chen et al. [108] in 1978, recorded a low resolution $(\Delta \lambda = 2 \dot{A})$ three photon spectrum of iodine. Ultraviolet fluorescence was monitored following excitation in the visible (15000-17270 cm⁻¹). The broad bandwidth of the cw dye laser did not allow a satisfactory analysis. However, they believed they were accessing the D0⁺₁₁ (${}^{3}P_{2}$) state.

In 1979, Williamson and Compton [109], published the results of a sequential multiphoton ionization experiment. A narrowband dye laser (the pump) $(\Delta \lambda = 0.01\text{Å})$ was used to excite, various rovibronic levels of the B0^+_{u} state. A second, broadband dye laser $(\Delta \lambda = 0.25\text{\AA})$ (the probe) was scanned to induce ionization from the levels populated by the first laser. It was found that resonances upon the absorption of three photons (1 pump + 2 probe) significantly increased the ionization rate. Two long progressions were observed in the MPI spectrum, the stronger of which was fitted to the following empirical expression.

 $v = 58087.92 + 56.3701 \text{ n} - 0.13152 \text{ n}^2$ + 8.1193 x 10⁻⁴ n³ - 6.8462 x 10⁻⁶ n⁴ 0 < n < 58

(2.5)

These workers suggested that this series was attributable to resonances involving very high vibrational levels of the $F0_u^+$ (${}^{3}P_0$) state. The resonances recorded for the weaker progression agreed well with bandheads calculated from equation (2.2) and were therefore assigned as due to the $D0_{+}^+$ (${}^{3}P_2$) state.

High vibrational levels of the $F0_u^+$ (${}^{3}P_0$) state were also accessed by Cooper and Wessel [110] in the course of an ion dip experiment. Although no analysis of the three photon excited state was given, it appears that the vibrational levels involved were much lower in energy than those observed by Williamson and Compton [109].

Kawasaki et al. [111], in monitoring the dispersed fluorescence following multiphoton excitation in the 5400-4900Å region, observed four discrete systems centered near 3850Å, 3400Å, 2900Å and 2700Å. The first pair of transitions were assigned to double photon absorption events and designated as the $\beta_1 ({}^3P_2) - Al_u ({}^3\Pi)$ and $D'2_g ({}^3P_2) - A'2_u ({}^3\Pi)$ respectiveTy. However, the first assignment has since been challenged [43] as incompatible with the analysis of spectra taken in the presence of inert gases (Table 2.1). The other tables observed by Kawasaki et al. were unassigned, but attributed to three photon transitions. It seems probable though, that the 2700Å system corresponds to the well known $F0_u^+ ({}^3P_0) - X0_g^+$ transition. Tanaka [112] subsequently reinvestigated the 2900Å system and concluded it was in fact due to a two photon absorption, but no spectral assignment was made. Again, it is tempting to assign this transition to the recently observed $g_{g}^{-}({}^{3}P_{0}) \cdot v_{u}^{-}({}^{3}\Pi)$ system [74], which is centered near 2880Å in emission with added foreign gases. Further experimental work is necessary before a definite assignment can be made.

A similar study to those outlined above, by Kasatani et al. [113] resulted in the observation, in addition to the above systems, of a weak ultraviolet transition (2500-3500Å) at lower excitation wavelengths (5500-6100Å). However no analysis of this system was offered.

In 1984, a relatively narrowband ($\Delta v = 0.2 \text{ cm}^{-1}$) three photon spectrum of iodine was published by Ishiwata et al. [114]. Fluorescence between 2300Å and 2400Å was monitored as the dye laser was scanned. A total of eight spectral lines were recorded in the 17130 - 17370 cm⁻¹ region. Dispersion of the fluorescent light indicated the presence of two radiative decay channels, one to a shallowly bound valence state (${}^{2}P_{1/2} + {}^{2}P_{3/2}$) ($\lambda \sim 3100$ Å) and the other to high vibrational levels of the ground state ($\lambda \sim 2400$ Å). Polarization measurements determined that the three photon populated state was of 0⁺_u symmetry. It was therefore assigned as the F'0⁺_u (${}^{1}D$), the first state of this particular ion-pair cluster to be positively identified. Analysis of the spectra gave * estimates of the molecular constants for the weakly bound valence and the ion-pair state (Table 2.2).

Recently, a repulsive state of 1, symmetry

correlating to the $({}^{3}P_{2})6s[2]_{3/2} + {}^{2}P_{3/2}$ separated atoms has been observed using double resonance enhanced $(B0_{u}^{+}, E0_{g}^{+})$ three photon spectroscopy with the use of three separate dyc lasers [115].

Table 2.2 lists all the known states (below 60000 cm⁻¹) of iodine and their principal constants prior to the commencement of this study. Table 2.2 Sumary of Known Holecular States of ¹²⁷13 Prior to Present Study (T₆ 40000 cm⁻¹)

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- -	•	-							•		-	given in cm	b - values in pare theses are est mates.								
Refs.	103	١١	102	51	n	И	100	91	91	91,98	55,56	86 ·	56,73	107	102	111	89	. 14	5	56,75	88
Sep. atoms		1 ⁺ (¹ ⁰)+1 ⁺ (¹ S)		(s ₁), 1•(¹ ₃ ₆), 1	1 ⁺ (³ P ₀)+1 ⁻ (¹ S)	1 ⁺ (³ P ₁)+1 ⁻ (¹ S)	1+(³ P ₀)+1 (¹ S)	1 ⁺ (³ P ₂)+1 ⁻ (¹ S)	-	-	-	•••	-			$1(2r_{3/2}) + 1(2r_{1/2})$		$1({}^{2}P_{1/2}) \cdot 1({}^{2}P_{1/2})$	* * *		-
, CN	[243]65		[243]6s		2332	•				•	1111						2131	2431	2131	- 1817	2440
r _e (γ)	2.57	3.48		3.53	(3.6)	(3.55)	3.57	4.04	3.67	3.65	3, 58	3,61	3.63	3.05		(3.65)	1.03	(1.2)	3.06	3.08	2.67
ackin ⁵		(1.1) ^b		10.3	•		5,728		2.72	5.419	(5)	5, 531	5.4				11.805		1.202.1	23.9	107.11
B _c x10 ²	4.029	2,190		2.131			2.08012	1.63	1.9702	1.99692	(2.0775)	2.0120	2,02	2.857			2.89/08		2.845	2.Anl	3, 73691
د x و د م	0.58	0.63		0.22	•36	0.49	0.2132	0.13	0, 222	0.20478	(91.0)	0. 22578	0.201	0,31		1.23	0.7526	0.29	r 2.429		0, 0.659
o D	211.4	131.1	251	9.901	95.96	105.7	101.180	1041.2	95.01	101.392	0.20	105.024	101	132.9	101	61.4	125.670	24.5	156.16	107	214.522
ر د	53562.8 ^a .	51707	48126	47559.1	. 47217.8	4 70 70	47025.92	41769.	41621.3	11111.764	1027.5	10.121.010	10187	15972.4	3576.2.0	19236.4	15769.046	12190	10946.81	10415	0.0
State		1.0.1		×	• • • • •	50°		4 5	.	• c] •	-	, n.	n () 2,	*	i				N		

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values in paren theses are esti-mates.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Excimer Laser

3.1.1 Introduction

The excimer laser for the multiphoton spectrometer which was constructed and developed during the course of this work was based on the 'Oxford' design [116, 117], utilizing XeCl as the gain medium. Previously, nitrogen lasers (a Molectron UV 500 and an NRG-0.6-8-500) had been employed in this laboratory in systems built to generate sequential absorption spectra. OODR studies (resonance enhanced two photon absorption) were successfully completed on I_2 [118], IBr [119], ICl [120] and Na₂ [121] with experimental designs incorporating the above nitrogen lasers. However, the higher peak powers offered by comparable excimer lasers permits an increase in signal strength relative ; to the earlier studies and enhances the probability of observing multiphoton simultaneous transitions.

An excimer is defined as a molecule that is bound in an excited state (with a typical radiative (τ) lifetime of 10^{-8} s) but which has a ground state that is dissociative or weakly bound ($\tau << 10^{-8}$ s). The relative lifetimes of the two electronic states allows the build-up of population inversion, a necessary prerequisite for the observation

of stimulated emission.

Although many classes of excimers have been shown to demonstrate gain on at least one transition, by far the most important, at this time are the rare gas halides. Since the first observation of stimulated emission in noble gashalogen donour mixtures [122], rapid development has been made in excimer technology, leading to the production of lasers with high peak and average powers in the ultraviolet. To date lasing has been reported using XeF (351 nm), XeCl (308 nm), XeBr (282 nm), KrF (248 nm), KrCl (222 nm), ArF (193 nm) and ArCl (175 nm) as the gain media.

3.1.2 Design and Construction of the Excimer Laser

Excimer lasers contain high pressure gas mixtures, and discharges through these media are inherently unstable. Under conditions of high number density (N) and large electric fields (E), the impedance of the discharge decreases due to the ionization of the gas. Regions of localized high E/N ratios will tend to draw more current leading to a further decrease in the resistance of that portion of the discharge. Uneven heating of the gas fill due to these striations creates inhomogenities in the gas density, predisposing the

discharge towards arcing with the next excitation pulse. Because of this arcing between the electrodes, the time in which electrical energy can be effectively channeled into the formation of electronically excited XeC2 is limited to a

few nanoseconds. This means that transverse electrical excitation and fast switching circuitry capable of delivering high voltages in a short period of time must be employed. The onset of arcing can be held off (typically by 20 - 30 ns) by homogeneously pre-ionizing the gas fill before the main discharge. Usually this is accomplished by using a series of spark gaps adjacent to the main electrodes, although many other schemes have been presented [123]. In the present design, a single charging network generates both the preionizing and main discharge, eliminating possible timing jitter that often plagued earlier schemes which employed two separate circuits.

The laser electrodes, internal capacitors and preionizing pins were mounted on a pair of parallel aluminum plates (80 x 13 x 0.1 cm), as illustrated in Figure 3.1. Support pillars of Perspex rods 5.5 cm in length, were positioned at each corner to separate the plates. An aluminum rod, 6 mm in diameter and 70 cm long attached along the centre of one plate served as the cathode. The anode was secured to the opposing plate and consisted of a 'half-round' crosssection of aluminum seated on an aluminum base 2.5 cm in height. A row of twelve barium titanate 'doorknob' capacitors (Steatite and Porcelain Products Ltd.) was mounted on either side of the anode. The separation between the electrode and capacitors was approximately 4 cm and the latter were equally distributed along the length of the anode (70 cm). A series

Figure 3.1 Cross-sectional view of the internal components of the excimer laser

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View of the internal ne excimer laser



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of screws protruded from the cathode supporting plate opposite each capacitor to serve as pre-ionizing electrodes. A gap of about 0.5 cm was maintained between each pin and its opposing capacitor. The main electrode spacing was approximately 2.0 cm.

The lower threshold voltage required to break down the gas in the pre-ionizing gap resulted in arc formation and subsequent discharging of the 'doorknob' capacitors before the breakdown of the gas between the main electrodes. The pre-ionizing radiation precedes the main discharge by typically 100 - 200 ns [117]. The initial population of electrons and ions which it induces dramatically stabilizes the subsequent discharge. The inductance of the pulse forming line (PFN) to allow as rapid a deposition of energy into was minimized the laser medium as possible. The reverse sides of both support plates were lined along their entire length with electrical grade Mylar, 35 cm in width, over which was placed a somewhat shorter and narrower section of aluminum foil (Figure 3.1). All screws used to secure the capacitors and electrodes to the support plates, and the pre-ionizing pins were inserted through the foil and insulating sheet. Once all components had been fastened in place, the Mylar sheet was folded over the foil to prevent accidental contact with the opposite electrode.

The entire internal assembly was placed, with the support plates positioned vertically, in a Pyrex pipe 36

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inches long and 6 inches in diameter (Corning 72-1410), with an aluminum flange (Corning 72-9450) at either end. Each flange was mated with a machined brass end plate 10.5 inches in diameter. All electrical and gas connections were made through these plates. TFE gaskets (Corning 72-9809) were used to give a positive high pressure seal.

Each internal support plate was fitted with a Perspex extension wrapped in copper foil. This foil in turn was in electrical contact with the aluminum sheet lining the reverse side of the support plate. These extensions enabled the anode to be in electrical contact with the front brass plate while the cathodic plate was positioned securely against the grounded rear plate.

Both terminating plates were machined with axial apertures 1.5 cm in diameter for optical access. Extensions of 1.75 inch O.D. brass tubing were brazed to the central apertures of each end plate. Quartz windows (5.0 cm in diameter) were sealed with O rings mounted on flanges at the end each brass appendage. In the case of the high voltage front plate the total length of the brass extension was 5 cm. This plate was also fitted with an adjustable pressure relief valve (Nupro B-6R-4M-10). The rear plate was provided with a longer arm of 15 cm to allow coupling with the vacuum line via a sidearm (Figure 3.2). Gas inlet connections were made through 0.25 inch O-ring sealed apertures in the earthed back plate.

The external circuitry is shown schematically in

Figure 3.2 Diagram of the external circuitry associated with the excimer laser



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Figure 5.2. A variable transformer (Powerstat 246-2-C) moderated the voltage from a 208V input line. The attenuated voltage was received by a dc oil immersed power supply (Universal Voltronics Corp. BPO-50-100) rated at 50 kV and a maximum current of 100 mA. Normally, an output voltage of 24 kV was used. The high voltage output charged a large storage capacitor (0.1 μ F (CSI 60W333)) rated at 60 kW via a pair of 100 k Ω ceramic resistors in series.

Switching of the PFN was accomplished using a grounded grid ceramic thyatron (EG & G HY3202). Voltage requirements for the cathode and reservoir heaters of the thyatron were met with separate circuits. Each circuit incorporated a variac (Powerstat 116), an isolation choke (EG & G TR-1724) and a transformer (EG & G TR-1863); collectively these elements for each heater are denoted as C and R in Figure 3.2. A water cooled aluminum platé (not shown in Figure 3.2) supported the thyatron via the earthed grid. A trigger box that generated 3.5 kV pulses of negative polarity superimposed on dc bias of + 200V switched the thyatron circuit. The constant dc potential held the cathode of the thyatron positive relative to the anode between trigger pulses. Closing of the circuit and subsequent discharging of the storage capacitor was only possible when a negative high voltage pulse appeared at the cathode tab. The trigger box enabled continuously variable pulse repetition rates of 0.5 to 5 Hz to be attained. Generally, the laser was operated at or near 3 Hz.

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This mid-range value represented a compromise between reduced peak power at higher-firing frequencies and the increased time required to scan a spectrum at lower rates.

The thyatron anode was connected to the charging terminal of the storage capacitor by a wide strip of copper foil. The energy released by the capacitor (26.5 J at 24 kV) was also conducted to the front brass plate of the laser housing by a broad strip of foil. The back plate of the laser cavity was earthed through a similar band of copper foil. An r.f coil was soldered between the Cu strip lines at both ends of the laser cavity to dissipate the storage capacitor when the laser was turned off.

The laser components with the exception of the trigger box and power supply were enclosed in a housing of aluminum sheeting. This was not only for safety considerations but to also limit the considerable r.f noise generated by the laser. A box fan was mounted in a side panel of the housing, orientated so as to cool the ceramic resistors and storage capacitor.

The entire laser assembly occupied one end of a 10' x 4' stainless steel table (NRC RS-410-12).

A concave reflector (radius of curvature = 0.93 m) held in an adjustable mount formed one end of the laser cavity. When properly aligned an intense rectangular lasing region (1 cm wide by 0.5 cm high), superimposed on a broad background of spontaneous emission was observed at the exit window. Reflection of light from this uncoated front window was

sufficient to provide the optical feedback necessary to .achieve stimulated emission.

The laser was found to generate pulses of about 1 MW peak power and of 15 ns duration (FWHM). The output was confined primarily to the 0-1 (3080.0Å) and the 0-2 bands (3082.5Å) of the $B(\frac{1}{2}) - X(\frac{1}{2})$ transition of Xe³⁵Cl. At a pulse repetition of 3 Hz, a mean output of 45 mW was calculated. Under a charging voltage of 24 kV and a storage capacitance of 0.1 µF this represents an efficiency of 0.2%, a value typical of lasers of this design [117].

3.1.3 Gas Fill

As mentioned above, XeCl was chosen as the gain medium for the laser. This decision was made for a number of reasons. Firstly, the relatively long wavelength emission minimizes photodegradation of the organic dyes and solvents employed in the dye lasers. Secondly, most dye molecules exhibit an absorption band in the vicinity of 308 nm. Thirdly, XeCl based lasers have consistently demonstrated the longest gas lifetimes before replacement is necessitated through the buildup of contaminants. Finally, the gas fill is much less corrosive than for the fluoride containing excimers.

The gas handling line was fabricated from copper tubing incorporating brass and stainless steel regulating valves. An isolation valve (Edwards 08-C333-04-000) separated the laser cavity from the vacuum line. The system could be evacuated to

a pressure of 100 m torr with a large capacity rotary pump (Sargent-Welch 1397). Once the laser cavity and gas handling line had been pumped down and the isolation valve closed, 25-35 torr of xenon (Matheson) and 3-5 torr of anhydrous hydrogen chloride (Canadian Liquid Air) were admitted to the cavity. High purity helium (Canadian Liquid Air) was then allowed to enter the laser until a total pressure of 33-36 psi was obtained. All gases were used without further purification.

In general, the gas fill was replaced once a week. While, it was possible to operate the laser for 3-4 weeks without changing the gas, it was found that the output power gradually decreased over this period.

The gas pressure fell by about 1 psi daily due to leakage but this had no discertible effect on laser performance over the lifetime of the gas fill. Gas heating was also minimal as evidenced by the small increase in pressure (~ 5 %) noted after continuous operation for several hours.

3.1.4 Maintenance

Once the initial debugging of the system had been completed, the laser displayed outstanding reliability. Over a three year period and an estimated 2×10^7 shots, only 3 major failures occurred that necessitated periods of extended down time. By far the most prevatent minor problem was the build-up of particulate matter on the quartz windows. Removal

of these deposits was imperative in order to obtain the high peak powers required to allow the subsequent observation of multiphoton phenomena. Cleaning was carried out as required, usually about once a month. While the windows were being replaced a positive pressure was maintained, by flowing helium through the laser cavity.

3.2 Grazing Incidence Dye Lasers

3.2.1 Introduction

The single pass spectral linewidth of a dye laser can be expressed as the product of two factors. The first of these is the inverse of the angular dispersion due to the dispersive elements in the laser cavity. An expression for the full angular dispersion due to a single grating is given by equation (3.1) [124];

$$\left(\frac{d\theta}{d\lambda}\right) = \frac{(\sin\theta + \sin\phi)}{\lambda \cos\theta} = \frac{m}{d \cos\theta}$$
(3.1)

where λ is the wavelength of the radiation, m the diffraction order, d represents the groove spacing, and the angles of incidence and diffraction relative to the grating normal are given by θ and ϕ , respectively.

The second factor is the divergence or angular spread of the beam emerging from the dye cell. Assuming a Gaussian beam profile, the divergence can be given in terms of its far field angle (equation (3.2))[125];

In the above expression w is the beam waist at the dye cell (typically 0.1 mm).

(3.2)

(3.3)

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Combining equations (3.1) and (3.2) leads to the following formula for the passive linewidth;

$$\Delta \lambda = \frac{\lambda^2 \cos \theta}{w \pi (\sin \theta + \sin \phi)} = \frac{\lambda d \cos \theta}{m w \pi}$$

Until 1978, by far the most popular dye laser design was that due to Hänsch [126]. The end reflector was a grating employed in high order (typically m = 5) and large angle of incidence (typically $\theta = 60^{\circ}$), which reduced the linewidth of the radiation in accord with equation (3.3). Further narrowing of the linewidth could be obtained by expanding the beam from the dye cell before it impinged on the grating. Expansion of the beam waist (typically done with a telescope) reduces the divergence and hence the spectral width of the radiation according to equation (3.4),

$$\Delta \theta_1 = \frac{\Delta \theta_2}{M}$$
(3.4)

where M is the magnification factor due to the telescope. The beam divergence before and after expansion is given by $\Delta \theta_1$ and $\Delta \theta_2$ respectively. In the Hansch scheme, tuning over the dye profile is accomplished through rotation of the Littrow configured ($\theta = \phi$) grating.

In 1978, two groups simultaneously developed a new dye laser geometry [127, 128] that has rapidly supplanted the Hänsch design. Their approach was to increase the angle of incidence (θ) at which the beam enters the grating. This so-called grazing incidence dye laser, operates with the dispersive element at angles approaching 90° relative to the incoming beam. The increase in angular dispersion due to this configuration allows the removal of the beam expanding element while maintaining a linewildth comparable to that obtained with the Hänsch design. No longer employed in Littrow, optical feedback into the cavity is provided by a mirror (or a second grating in Littrow) which redirects the dispersed light back onto the grating (Figure 3.3). The absence of the beam expanding telescope is additionally compensated for by the magnification that occurs whenever the angle of incidence (θ) is greater than the angle of diffraction (φ) as given by equation (3.5).

$M = \frac{\cos \phi}{\cos \theta}$

Rotation of the mirror (or the Littrow grating) tunes the laser by selecting a certain bandwidth of the diffracted radiation back along the optical axis for amplification.

Advantages of the grazing incidence design over that due to Hänsch are many, not the least of which is the ease of alignment. Enhancement of spectral purity and brightness

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(3.5)

accompanying the resulting shorter cavity are other advantages.

Large values of M are possible (equation (3.5)) as θ approaches 90°, resulting in a substantial reduction in the divergence of the beam. In addition the grating is used twice per pass in the grazing incidence configuration, giving a two-fold increase in the angular dispersion expected solely on the basis of equation (3.1).

Spectral linewidths were obtained with early cavity designs that rivalled or even surpassed those obtainable from comparable Hänsch dye lasers. However, the inherently low optical efficiency of the grazing incidence geometry resulted in relatively low intensity outputs. Reflective losses cause the efficiency of the grating to fall sharply as the angle of incidence (θ) approaches 90° . But such angles are required to give output of low bandwidth. A solution to this problem was offered by Duarte and Piper [129], who suggested the use of an intra-cavity prism assembly to anamorphically preexpand the beam waist prior to it striking the grating. Mannification of the beam afforded by the prism assembly allows the grating to be held at angles much less than 90°. The idea was not a novel one as prisms had long been advocated as replacements for the beam expanding telescope in Hänsch dye lasers [130]. Beam expansion due to a single prism follows equation (3.6), /

 $M = \frac{\cos \psi}{\cos \theta} = \left(\frac{n^2 - \sin^2 \theta}{n^2 - n^2 \sin^2 \theta}\right)^{1/2}$

(3.6)
where θ is angle of incidence and ψ the angle of refraction relative to the normal to the prism face. The right hand side of equation (3.6) is derived from Snell's Law, where n is the wavelength dependent refractive index of the prism substrate. If the angle of emergence is normal to the exit face (in practice accomplished by a careful selection of substrate and apex angle) the beam does not undergo demagnification upon leaving the prism. However, it has been shown [131], that the reduction in beam waist is within 5% of unity over a large range of conditions. As with gratings, large increases in the beam waist can be obtained when the prism is orientated at grazing incidence. Once again however, reflective losses from the entrance face of the prism become The coss incurred for p-polarized prohibitive at such angles. light (the component of the radiation whose electric vector lies in the plane of incidence) which is preferentially passed by the vertical grooves of the grating, is given by equation (3.7),

$$R_{p} = \frac{Tan^{2}(\theta - \psi)}{Tan^{2}(\theta + \psi)}$$
(3.7)

where θ and ψ are as defined above. In practice, usually two or more prisms with reduced angles of incidence are used in tandem. Such an arrangement enables a large overall magnification of the beam (the product of the individual expansion factors) and a substantial reduction in reflective losses compared to the use of **a** single prism. It has been shown [132]

that even at high angles of incidence the overall dispersion . due to a prismatic beam expander is typically only 1 - 2% of that due to the grating. However, the use of a multiple ... prism assembly affords the possibility of eliminating prismatic achromaticity, an additional advantage of employing more than one prism.

3.2.2 Narrowband Dye Laser Construction

The experimental design included a pair of grazing incidence dye lasers (Figure 3.4). One of these was designed to operate with a relatively narrow bandwidth of 0.1 cm⁻¹ and the other to give a broader spectral width of approximately 0.7 cm^{-1} . Both dye lasers were situated on the same optical table as the excimer laser. The narrowband dye laser (NDL), to be discussed below, is shown in Figure 3.3.

A portion of the excimer pump radiation was directed into the narrowband laser with a mirror (bsl in Figures 3.3 and 3.4). This reflector was mounted so that a portion of the pump beam passed beneath it and was used to either pump the second dye laser (Figure 3.4) or, as is shown in Figure 3.3, an amplifier cell associated with the narrowband dye laser. Vertical adjustment of the mirror allowed a continuous variation in the allocation of excimer radiation between the two dye cells employed.

That portion of the excimer beam used to pump the NDL was focussed to a horizontal line across the front face

Figure 3.3

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Schematic diagram of the narrowband dye laser. Amplifier cell is shown for completeness, in general it was not employed, see text

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of the dye cell (Hellma 131.037) via a cylindrical lens (f = 10 cm). The lens could be rotated in its mount to allow the angle of inclination of the pump beam on the dye cell to be varied. The lens mount also permitted fine adjustment along the x, y and z axes.

Dye solutions were circulated through the rigidly fixed quartz cells at rates of approximately 0.1 l/min by means of a magnetic drive gear pump (Micropump Corp.). Table 3.1 outlines the concentrations and wavelength range of the dyes employed during the course of this work.

A 1" diameter window formed one end of the optical cavity, through which the laser radiation exited. Optical feedback from the uncoated front surface of this window $(\sim 4\%)$ was sufficient to give stimulated emission. Like the dye cell, this window was wedged to prevent internal reflections along the optical path of the dye laser. As precise positioning of this element was crucial in the alignment of the laser, the window was secured in a high quality S-axis adjustable mount (NRC LP1).

The beam waist was magnified anamorphically with a prismatic expander consisting of a pair of right angle reflecting prisms (Oriel 4606, 4607) with hypotenuse length of 2.1 cm and 3.5 cm respectively. Both were constructed of crown glass (n = 1.5168 at $\lambda = 5876 \text{\AA}$). The prisms were arranged in the so called 'compensating pairs' mode to partially offset the dispersion due to each. Both were mounted on a compact

Table 3.1

Laser Dyes Used in this Work

Dye	Concentration (M)	Frequency Range (cm^{-1})
C-540A	1×10^{-2}	17600 - 18500
R6G	6×10^{-3}	17040 - 17380
	3 x 10 ⁻³	17250 - 17600
Kiton Red	2×10^{-3}	16400 - 17000
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All dyes in methanolic solution

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aluminum platform (7.5 cm x 4.5 cm) after the design of Kasuya et al. [133]. Orientation of the prisms was such that they presented approximately equal angles of incidence to the incoming beam. It has been shown [134] that such an arrangement gives minimum reflective losses for any given overall expansion factor. As angles of about 80° (0) were generally used in this work, the beam waist typically was enlarged by a factor of 20 (equation (3.6)), while reflective losses accounted for a 40% reduction in the p-polarized component of the radiation field (equation (3.7)), on transitting the prismatic assembly.

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. The pre-expanded beam was intercepted by a classically ruled grating (Jobin Yvon, 5M 25R), with a groove spacing of 1200 lines/mm, blazed at 10000Å in the first order at a blaze angle of $36^{\circ}52^{\circ}$. The total ruled length of the grating was 56 mm. A fabricated aluminum mount (7.5 cm x 7.5 cm) which secured this element could be manipulated to allow variation in the acceptance angle (6), the tilt and the inclination of the grating. By placing the mount on a translation stage, different segments of the magnified beam waist could be intercepted. The laser was operated using the grating in second (m=2) order. This enabled a twofold reduction in the line-width relative to the use of the first order output (equation (3.3)).

Diffracted light from the grating was reflected back along the optical axis of the dye laser with a 100% reflecting mirror (10 cm x 10 cm). This reflector was held in a mount that allowed the mirror to rotate about a vertical axis through its center. Precise movement of the mirror was accomplished using an Inchworm System (Burleigh Instruments PZ 557). A piezo-electrically actuated spindle was placed in contact with the rear of the mirror. The spindle was translated in discrete 6 nm steps at a selected rate (between 0.01 μ m s⁻¹ and 0.6 mm s⁻¹), usually about 0.1 μ m s⁻¹. A typical dye profile (~ 200 Å) could be scanned in less than 2 mm of spindle motion.

5.2.3 Alignment of Narrowband Dye Laser

Alignment of the optical cavity of the dye laser was based on the procedure outlined by Littman and Metcalf [127].

Once the ultraviolet radiation had been centered on the dye cell by manipulation of the front mirror (bsl), the cylindrical lens was introduced. The lens was rotated until the beam at the dye cell was approximately parallel to the surface of the table. Next, the output window was positioned by observing the single superradiant spot emerging from the far side of the dye cell when properly aligned. The intensity of this spot was then maximized by varying the separation between the cylindrical lens and the dye cell. Next the platform supporting the prisms was introduced. Rotational and lateral adjustment of each prism resulted in an expanded beam

of homogeneous intensity that filled the exit face of the The grating mount was then positioned to s ind prism. allow the incident beam to fall across the full width of the dispersive element. Light diffracted into second order by the grating was intercepted by the tuning mirror. Initially, to facilitate alignment, the reflector assembly was positioned "several centimeters from the grating. A pinhole placed between these elements aided in the simultaneous observation of the original and reflected beams. Vertical overlap was effected by adjustment of the inclination angle of the grating. Coarse horizontal correlation of the two beams through manual rotation of the entire mirror assembly was then usually sufficient to initiate lasing in the cavity. The reflector mount was then brought as close to the grating as feasible (\sim 1 cm). Usually, a slightly vertical adjustment of the grating was then necessary to maximize the intensity of the dye laser output.

The spectral purity and brightness of the dye laser emission were monitored by observing etalon fringes produced by the cavity output. An etalon having a free spectral range of 0.56 cm⁻¹ was mounted at the end of a telescope. The telescope was then trained on a white card which intercepted a spatially filtered portion of the lasing spot.

Adjustment of the cavity to generate stimulated emission of high intensity (bright etalon fringes) or of narrow linewidth (narrow fringes) could be readily accomplished. However, an arrangement that allowed both conditions to be met

simultaneously proved very difficult.

3.2.4 Broadband Dye Laser Construction and Alignment

The operating linewidth of the broadband dye laser (BDL) was almost an order of magnitude greater than that of the NDL. As a result construction and alignment of the cavity was not nearly as critical for optimum performance.

As the dye cavity was positioned further from the excimer laser than the NDL, a spherical quartz lens (f = 20 cm) condensed the highly divergent beam that passed beneath the front mirror (bsl):

The cylindrical lens, the exe cell and their respective mounts were as described earlier. A 5 cm diameter wedged window held in a gimbal mount (Burleigh Instruments SG-201) formed one end of the laser cavity. Only a single right angle prism was employed to expand the beam ($\theta \sim 70^{\circ}$). The grating, secured in a replica of the mount described earlier, was holographically ruled (ISA sp90 HM) with 1200 lines/mm. The first order beam, which was the most intense diffracted beam, was used for feedback. A broadband reflector of the same type as that employed in the NDL was used. Rotation of the mirror was again accomplished with the use of an Inchworm System (PI 550).

Alignment of the cavity was as outlined previously. Etalon fringes were not monitored, as our interest lay in obtaining maximum intensity (maximum signal strength), with the provision that the linewidth was to be less than 1 cm^{-1} . As a result, alignment of the dye laser was relatively simple, . rarely taking more than five minutes.

3.3 Wavelength Calibration of the Dye Lasers

3.3.1 Introduction

The different output bandwidths of the two lasers necessitated the use of separate wavelength calibration schemes. These are outlined in the following sections.

- 3.3.2 Narrowband Dye Laser

The output of the NDL was calibrated by simultaneous observation of the undispersed single photon laser induced fluorescence (LIF) of $^{127}I_2$. The high resolution (0.015 cm⁻¹) LIF spectrum of this molecule over the frequency range 14800-20000 has been accurately measured and listed [84-87]. Under the relatively broad bandwidth of the NDL (0.1 cm⁻¹) most of the individual spectral lines recorded above, are not resolved. This is especially so in the vicinity of bandheads, particularly those of the strong v" = 0 and v" = 1 progressions. In general however, an average of one calibration line every two wavenumbers could be identified.

For scans of the multiphoton spectrum of up to 20 cm⁻¹, a second order least squares fit satisfactorily described the relationship between the frequencies and positions of the assigned calibration lines. Longer traces of up to 50 cm⁻¹ required cubic and occasionally quartic expressions to describe the tuning curve of the dye laser.

The reproducibility of the frequency determinations of well resolved multiphoton lines from different runs were well within the bandwidth of the dye laser.

3.3.3 Broadband Dyc Laser

In earlier work in this laboratory the BDL was calibrated against the emission lines from an Fe/Ne lamp in conjunction with a monochromator. An alternative scheme with several advantages over the above method has been proposed [135] and is incorporated in the present design. This calibration technique is based on the opto-galvanic effect (OGE). This phenomena occurs when an electrical discharge is illuminated by an external source of resonant radiation. The energy levels of the gaseous species in the discharge which are coupled by the radiation generally exhibit different ionization cross-sections, resulting in a small but measurable impedance change across the discharge.

Our experimental arrangement was similar to that discussed by other workers [136, 137]. An Fe/Ne hollow cathode lamp operated at constant current (10 mA) served as . the discharge source. Dye laser emission (the zeroth order reflection from the grating) was directed and focussed down the bore of the hollow cathode (Figure 3.4). Care was taken to avoid contact of the beam with the electrode itself, as this

gave rise to large photo-electric signals. Opto-galvanic signals were generated when the frequency of the irradiating dye laser coincided with an atomic transition in the discharge region. Under constant current conditions, the impedance changes are manifested as voltage variations across the lamp electrodes. The OGE induced ac voltage was monitored at the anode of the lamp through a coupling capacitor which served to block the dc component due to the lamp power supply (Figure 3.4).

Three factors were found to be of importance in the generation and detection of the OGE induced signals. Firstly, the power supply had to be well regulated to keep the dc ripple to a minimum. Secondly, tight focussing of the laser radiation was necessary to generate detectable voltage changes. Lastly, and perhaps most importantly, the lamp discharge had to exhibit minimal electrical noise. Most of the OGE induced signals displayed maximum amplitudes of less than 50 mV and as a result were readily swamped by the noise generated by an unstable discharge. Of all the lamps available to us, only one proved satisfactory in this regard. Fortunately, this hollow cathode lamp had a Ne gas fill, well suited to the calibration of the spectra taken during the course of this work.

The most advantageous features of OGE calibration compared to the prior method used in this laboratory, lie in its simplicity and high accuracy.

Table 3.2

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Recorded OGE Calibration Lines for Ne Atom

<u>C-540A Dye</u>	R6G Dye	Kiton Red Dye
λ (vac) '	λ (vac)	λ (vac)
5363.7390 ^a	5749.8933	5936.102
5367.7150	5762.183	5940.965
5373.808 ^b	5766.017	5946.4812
5376.470	5771.907	5963.2748
5384.754	5806.0595	5967.1250
5402.0632	5813.028	5977.1892
5411.630	5818.258	5984.058
5414.163	5821.7699	5989.5664
5420.064	5830.526	5993.3132
5421.664	5854.1101	6002.613
5435.162	5870.044	6031.6667
5450.022	5874.4557	6047.8320
5495.930	5883.5254	6066.231
5535.208	5900.041	6076.0194 .
5564.3114	5904.428	6097.8507
5654.1352	5908.0666	
5664.1190	5915.2718	
5668.226	5920.5473	
5691.3955	,	
5654.1352		
5058.2024		
\$716.9250		
5720.8119		
5749.8933		

a wavelengths given to four decimal places obtained. from ref. 138

b wavelengths given to three decimal places obtained from ref. 139

All the OGE induced signals recorded in this study were found to be due to neon. The absence of any signals due to iron atomic transitions was compensated by the observation of many weak neon lines. In addition, several other lines were recorded which could not be reconciled with any known single photon Fe or Ne transition. These lines were found to be the result of two photon transitions in the rare gas. Such transitions have been recorded previously [137] under conditions of tight focussing. These transitions were not used in the calibration of the multiphoton spectra. In Table 3.2 are listed the single photon generated OGE signals observed during the course of this work.

The precision with which line positions could be determined varied because of the uneven distribution of the OGE induced signals across the spectra. Typically, however, a reproducibility of 0.5 cm⁻¹ was attained.

When the BDL was used in the static mode (dual beam experiments; Chapter 3.6.3) its output wavelength was determined with a 0.25 m monochromator (ISA HR320) (Figure 3.4). The wavelength was read directly from the wavelength dial, which was frequently recalibrated against the emission lines of an Fe/Ne hollow cathode lamp. In some instances the laser was calibrated by photographing the dye laser emission along with atomic lines from the above lamp on a 1.5 m spectrograph (Bausch/Lomb).

Another method of calibration took advantage of the



overlap of the dye laser outputs in the double beam studies. Both outputs could then be monitored simultaneously with the monochromator. Initially, the NDL would be set to the wavelength of interest, with reference to the ¹²⁷I, LIF The signal generated by a photomultiplier tube spectrum. (PMT) (not shown in Figure 3.4) attached to the exit slit , of the monochromator was then maximized by manually rotating the wavelength dial. At this point, the dial was locked to prevent further movement of the monochromator grating. The output from the NDL was then blocked and the BDL scanned until the signal from the monochromator indicated the frequencies of both dye lasers were identical (to within $\sim 0.5 \text{ cm}^{-1}$). This method had the advantage of not being dependent on the absolute accuracy of the wavelength dial of the monochromator.

3.4 Signal Generation and Detection

Radiation from the dye lasers (see Figure 3.4) was directed to a second optical table (Ealing 24-5183), on which the sample cells were mounted, by a series of mirrors (ml - m5) in kinematic mounts. An optical delay line (odl) was introduced when operating in the dual laser mode (Chapter 3.6.3) in order that the beams be in the desired temporal order.

The relatively small size of mirror ml (1 cm x 2 cm) allowed the outer portion of the NDL output to be transmitted

Figure 3.4 Schematic diagram of the multiphoton spectrometer. (not to scale)

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Irigger level shifter gated Integralor ref. channel chart recorder 1. 11) Is ref. cell Fe/No tamp 1 Ē 11 scope pre-and pholo-diode . 190 2 Ē / ni4 1.2 T Ê sfl --zerolh order output li i ş • monochromator polarizing optics s i 2 cell cell Fdb 11 m2 odt bredbeord dyo lasor шS ۰. 2 arrowband lsd dye laser 300 mm EXPERIMENTAL DESIGN excimer laser .

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directly into the $^{.127}I_{2}$ reference cell. At the same time however, the intense lasing region was intercepted by the mirror and directed towards m2. Before entering the iodine calibration cell the intensity of the beam was attenuated using a neutral density filter (1% T) and two strips of dichroic film orientated to discriminate against the appreciable background spontaneous emission associated with the dye laser. Single photon iodine fluoresence at 90° to the exciting radiation was monitored through a cutoff filter (Corning 2-64) via an RCA phototube (1P21). The anode signal was received by a preamplifier (Molectron LP143) which integrated and shaped the pulse to give a standard nuclear waveform (5us rise time, 50 us decay time). The output signal was then processed with a boxcar averager (unit #1 in Figure 3.4) which will be described later. The same boxcar channel was utilized to process the OGE calibration signal when the BDL was tuned.

In the double beam experiments; the laser outputs were counter propagated and focussed to the same spatial region with lenses (ll and l2) of long focal length (f \sim 50 cm). Once aligned, the beam from each dye laser could be followed along the optical path defined by the external mirrors (ml-m5) and lenses (ll and l2), into the cavity of the other laser and observed to exit via the zeroth order reflection from the grating. Optical coupling of the dye lasers was prevented by using long optical paths (\sim 6 m) and short pulse lengths

(∿ 10 ns).

A quartz cell (to be described later, Chapter 3.7). filled with the vapour of the iodine isotope of interest was positioned to straddle the focal region of the beam(s). It was found that spatial filters (sfl, sf2) placed directly in front of the iodine cell significantly increased the signal-tc-noise ratio (S/N). Fluorescent light emitted by the sample following multiphoton excitation was again monitored at 90° , over a solid angle of 10° . The filter assembly (fl) consisted of an interference filter centered at 310 nm $(\Delta \lambda = 20 \text{ nm}, \text{ Optics Technology Inc.})$ and a pair of glass \therefore filters, 6 mm thickness of UG-11 (Schott) and 4 mm thickness . of 7-54 (Corning). This combination of filters prevented the strong $B0_{11}^+ \cdot X0_{p}^+$ emission and the scattered laser light from reaching the photomultiplier tube (PMT) (EMI 9816QB), while transmitting radiation emitted in the 310 nm region. " This fluorescence corresponded to transitions from states in the 50000 $\rm cm^{-1}$ region to the shallow bound states correlating to the $I({}^{2}P_{1/2}) + I({}^{2}P_{3/2})$ separated atoms (Figure 2.1). The transmitted u.v light was focussed via a quartz lens (13) onto the front window of the PMT (S-20 response, 14 stage). The detector was enclosed in an electrothermically cooled (0° C) light tight housing (EMI D-50 MKIII) and was operated at voltages ranging from 1600 to 1900 volts depending on the signal strength. The output at the PMT anode was received by a fast broadband preamplifier (Ortec 9305) whose

output, in turn, was terminated into 50 ohms at the boxcar averager (unit #0).

Polarization studies of the individual multiphoton rotational lines were made using a rotatable double rhomb (Spectra-Physics 310-21)- as a broadband polarization rotator and a single Fresnel rhomb (Continental Optical Corp. FR8/33) to act as a 1/4 wave retarder. This combination (collectively denoted as 'polarization optics' in Figure 3.4) allowed the polarization of the beam to be changed from linear to circular and back again by simply rotating the double rhomb. In this manner, the polarization state of the radiation field could be altered without affecting the path length nor the intensity of the beam [140]. .Calibration of the double rhomb was done using a Glan laser polarizer (Karl Lambrecht Corp. MCSS 10-BB-550) which analysed the polarization state of the transmitted radiation. Polarization measurements were only conducted in association with the NDL, as will be discussed later.

3.5 Signal Processing

The boxcar assembly consisted of a pair of gated integrator and boxcar averager NIM modules (Stanford Research Systems SR-250) and a power supply/display module (SR-280) housed in a standard NIM bin. One of the boxcar modules (unit # 0) processed the input from the sample cell, while the other (unit # 1) handled the signal from the appropriate

69[°]

calibration channel. Each boxcar unit featured independently adjustable gate widths (2-15000 ns), delay times $(25 - 1.0 \times 10^8 \text{ ns})$ and gain (1-200). Signals on both channels were filtered, sampled over the duration of the respective gates, exponentially averaged and amplified prior to being output. Averaging was carried out over 30 laser pulses, for a time constant of 10 s at a repetition rate of 3 Hz.

The boxcar monitoring the multiphoton signal (unit # 0) was triggered by the output from a fast photodiode (EG & G SGD-040A) operated under a bias of -90 V (photoconductive mode). This photodiode (Figure 3.4) intercepted a portion of the spontaneous emission emanating from one of the dye lasers (usually the NDL). The adjacent boxcar (unit # 1) was then triggered via a TTL pulse internally generated by the first unit upon receiving the photodiode signal. An oscilloscope (Tektronix S61B), which was also triggered by this generated pulse, simultaneously monitored the signal waveform and the sampling gates of either channel (unit # 0 in Figure 3.4).

A level shifter consisting of a zener diode biassed operational amplifier converted the averaged output from the boxcars (0 - 10 V) to the ± 5 V input requirements of an . on-line minicomputer (Digital Corp. Minc-11 System). In addition it reversed the polarity of one of the output channels (unit \pm 1 in Figure 3.4) to permit the signal and

reference channels to oppose one another when displayed on the chart recorder (Linear 285).

The Minc-ll system consisted of a VT-105 video monitor, a dual floppy disk drive and a PDP-11/03 processor under the RT-ll operating system. In addition the system supported an analog/digital converter (A/D) and a digital/ analog (D/A) module as well as a clock unit. Collection, storage and subsequent processing of the boxcar outputs were effected through the use of the minicomputer employing software previously written [141].

As the dye lasers were scanned, the averaged outputs of both boxcar modules were sampled at a constant rate by the A/D converter. The resulting digitized spectrum was displayed (both channels) on the video monitor operated in the strip chart mode and simultaneously written to files on disks for later processing. In the case of the BDL a sampling rate of approximately 1 Hz was employed. Such a rate coupled with a scan speed of close to 8 cm^{-1}/min enabled a resolution of 0.08 $cm^{-1}/data$ point to be obtained. The boxcar units were interrogated approximately three times a second when the NDL was scanned. With a typical tuning rate of 0.7 $cm^{-1}/min.$, a resolution of nearly 0.004 $cm^{-1}/data$ point was obtained. This resulted in a well defined spectrum and enabled a single data file (maximum 15000 points per channel) to record a scan of up to 60 cm^{-1} . An algorithm based on that due to Stavitsky [142],

7-1

was utilized to find the positions of the peaks in the recorded data files. These positions were stored in a separate data file that was subsequently accessed by a least squares routine. Fits of peak position versus calibration wavelength (Ne lines, OGE) or frequency (I₂ lines, LIF) for the reference channel allowed subsequent frequency determination of the peaks found in the multiphoton spectrum.

·3.6 <u>Modes of Operation</u>

3.6.1 Introduction

The spectrometer could be operated in a variety of configurations to yield spectroscopic information. Nonlinear spectra could be generated with either dye laser singly and by using both lasers in tandem.

3.6.2 Single Colour Spectroscopy

Multiphoton spectra of iodine were initially observed using the BDL. Low resolution spectra from $16400-18700 \text{ cm}^{-1}$ were recorded for both isotopes using Kiton Red, Rhodamine 6G (R6G) and C-540A laser dyes (Table 3.1).

After completion of the broadband scans the NDL was employed to reexamine the multiphoton spectra under higher resolution. With this dye laser, scans for both isotopes were recorded over the R6G dye profile. Extensive scans over the higher frequency C-540A dye profile (17600-18200 cm⁻¹) were conducted for the lighter isotope, while a less exhaustive study was carried out for $129I_2$ (17600-17990 cm⁻¹). The

relative weakness of the multiphoton transitions recorded using Kiton Red necessitated the use of an amplifier dye cell (Figure 3.3) [143] to increase the intensity of the beam emitted by the NDL. Approximately 50% of the excimer beam was used to pump the oscillator cavity (NDL) while the remainder was diverted from the BDL cavity, and directed onto the front face of the amplifier cell. This radiation was focussed, being a cylindrical lens (Figure 3.3), to the same region on the dye cell as the incoming radiation from the oscillator cell. The increased spectral brightness enabled the observation of the stronger lines recorded previously with the BDL. Only spectra for the 12^7 I₂ molecule were recorded with this oscillator-amplifier arrangement.

High resolution single beam multiphoton spectra were recorded under linearly and circularly polarized excitation for both molecules over the R6G and C-540A dye regions scanned.

3.0.3 Two Colour Spectroscopy Using Two Dye Lasers

The multiphoton spectra of iodine, using two beams, were obtained in the following manner. The absorption of a single photon (c_1) from a fixed frequency beam (the pump) populated the $B0_u^+$ state. The spectral density of the $B0_u^+ \times 0_g^+$ spectrum assured that several transitions were pumped because of the finite bandwidth of the dye laser. A second, scanning (c_2) dye laser beam (the probe) then sampled the rovibronic population distribution.of the $B0_u^+$ state provided by the pump laser to effect two photon simultaneous transitions to states

in the 50000-55000 cm⁻¹ region $(\sigma_1 + 2\sigma_2)$.

In contrast to the sequential two photon experiments previously conducted in this laboratory, the BDL was used to pump the B0⁺ state and the NDL-utilized to act as the probe laser. This arrangement was employed here for a number of reasons. Unlike the earlier OODR studies discussed above, both lasers could independently generate multiphoton spectra, under the experimental conditions we employed. As the BDL mapped out an extensive multiphoton spectrum (see for example Figure 5.1), the observation of all but the strongest two beam transitions would have been obscured. Although the same situation existed when using the NDL as the probe laser, the increased resolving power of this laser significantly alleviated this problem. An additional advantage of the present experimental arrangement was that spectral lines originating from pumped levels of lower J could be resolved. Finally, the precision to which the line positions could be measured was much greater using the NDL $(^{127}I_{2})$ LIF calibration) than with the BDL (OGE calibration).

A disadvantage of this optical arrangement was the increased time required for data collection due to the respective scanning rates of the two dye lasers (Chapter 3.5). Offsetting this however, were the increased number of pumped $B\theta_{n}^{+}$ levels in each run which lead to a richer two beam spectrum.

The spectrometer was set up in this mode by first generating multiphoton spectra with the pump beam alone (EDL).

The portion of excimer radiation allocated to this laser was then decreased until the signal strength was barely discernible above the background. This ensured no contamination of the two colour (beam) spectrum from spectral lines due to the pump laser alone. The remaining excimer emission (\sim 70%) was directed into the optical cavity of the probe dye laser (NDL). Non-linear spectra were then obtained using this dye laser alone with an optical delay line (odl) , in the light path. This consisted of three planar mirrors (ml - m3 in Figure 3.4) spaced such that the pump beam preceded the probe beam by 2 ns as viewed from the center of the sample cell. Both beams were then carefully aligned for maximum overlap and focussed to a common focal spot. Next the pump beam frequency was set using one of the procedures outlined earlier (Chapter 3.3.3) and the probe laser scanned. Once a two beam signal was observed, the NDL was fixed and the signal strength maximized by slightly adjusting the focussing lenses (11 and 12 in Figure 3.4).

Two colour spectra were mainly obtained with RoG as the lasing medium in both dye lasers. Spectra were also recorded in this mode utilizing C-540A in the pump and probe lasers.

All dual beam spectra were recorded using the linearly polarized light emitted by the dye lasers. Runs with circularly polarized light were not done for two reasons. Firstly, the rhombic assembly introduced unavoidable attentuation of

the probe beam, severely reducing the two beam signal strength. Secondly, polarization measurements were not as critical in interpreting the spectra as in the one colour experiments, as will be discussed later.

5.6.4 <u>Two Colour Spectroscopy</u> Using a Single Dye Laser

The most intriguing of all the operating modes was the use of a single dye laser (NDL) to lase at two frequencies simultaneously and hence act as both the pump and the probe. This dual frequency configuration was first suggested by Prior [144]; however to the best of our knowledge, spectra obtained_from this optical arrangement have not previously been reported.

The dye laser was set up in the following manner. Moving the tuning mirror further back from the grating (\sim 10 cm) allowed light diffracted into the first order to be intercepted by a second mirror in a precision kinematic mount. Screening both mirrors in succession enabled the independent alignment of both optical cavities in the manner described earlier (Chapter 3.2.3). Slight adjustment of the second mirror was usually all that was required to provide overlap of the two output beams. The intensity of both beams suffered once the alternate optical channel was opened due to mode competition in the dye cell. To diminish the reduction in the probe beam intensity, the pump beam was attenuated by introducing a beam stopper to partially occlude the light diffracted

into first order. As the frequency separation of the two beams narrowed, the intensity of the weaker pump beam diminished and eventually fell to zero. Although this placed restrictions regarding selection of pump lines and the spectral regions that could be probed, the arrangement offered some advantages. Partitioning of the excimer radiation was no longer a concern as in the dual laser scheme. In addition alignment of the external optics was simplified; not only :were the number of mirrors and lenses halved, but the colinearity of the beams assured that they were focussed to the same spot (ignoring the achromaticity of the lens, £1).

The pump frequency was tuned by adjustment of the precision mirror mount. Wavelengths were determined with the ISA monochromator, which also served to show the presence of two frequencies in the dye laser output, and their relative intensities.

3.7 <u>Sample Cells</u> and Sample Preparation

The sample cells were constructed of quartz, as shown in Figure 3.5. The cells were fitted with sealed windows orientated normal to the incident radiation. A series of baffles were incorporated into each side arm to prevent light piping. Scattering of stray laser radiation was alleviated by a Wood's horn opposite the viewing window. Fluorescent light from the sample was monitored through this central window (diameter = 5 cm). To increase the S/N ratio, this

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Figure 3.5

r .

Sample cells used in this work

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window was fitted with a paper mask to restrict the viewing cone of the PMT (Figure 3.5). The opening in the mask (2 cm long x 1 cm high) allowed transmission of a significant portion of the emitted radiation while severely reducing the amount of scattered laser light reaching the detector. The total length of the cells was about 20 cm, giving a total volume of approximately 175 cm³.

In the case of the 127 isotope, iodine (BDH 99.9%) without further purification was sublimed into the cell in vacuo and condensed in the cold finger. Once a sufficient sample had been collected, the cell was isolated from the vacuum line and allowed to warm to room temperature. An ice bath was then placed around the cold finger and the cell pumped on for about a minute. The remaining sample (excess of $I_2(s)$) was recondensed under liquid N_2 and the cell permanently sealed.

The radioactive isotope (6 emitter, $t_{1/2} = 1.7 \times 10^{\circ}$ yr) was purchased as NaI in an NaHSO₃ solution (Oak Ridge National Laboratories). One millilitre of this sample (\sim 500 mCi) was oxidized with a solution of 0.1 M NaNO₂ in 1.0 M HNO₃. The nascent iodine was selectively extracted with ether. The organic layer was drawn off and placed on a vacuum line and the solvent distilled off at ice temperature. Prior to admission to the previously evacuated cell the iodine sample was dried over anhydrous P₂O₅. Once the isotope was in the cell it was permanently scaled.

CHAPTER 4

TREATMENT OF DATA

4.1 Dunham Coefficients

As mentioned in Chapter 1.3, the Born-Oppenheimer approximation [17] allows the energy of a molecule to be expressed as the sum of two contributions. These are terms due to purely electronic and nuclear (vibrational and rotational) motion.

The variation of the electronic energy with internuclear separation (r) gives (with the addition of a term due to nuclear repulsion at r) the form of the potential well within which the nuclei are constrained. The energy of an excited electronic state is conveniently measured by the separation between the minimum of its potential curve and that of the ground state curve. This difference is usually denoted as T_c .

Dunham [145], proposed that the distribution of quantized vibrational levels within a given potential well and the energy separation between adjacent rotational levels for a particular vibrational level be expressed by the eigenvalues of the vibrating rotor. This model is given in equation (4.1);

$$Y_{0,0} + E(v,J) = \sum_{m=0}^{\Sigma} \sum_{\ell=0}^{\Gamma} Y_{\ell,m} (v+\frac{1}{2})^{\ell} (J(J+1))^{m}$$
 (4.1)

Table 4.1

Correlation of Dunham Coefficients with Designations in Common Usage

Dunham Coefficient

Y _{0,0}	. ^т е
Y _{1,0}	ωe
Y _{2,0}	- e ⁻ ,
^Y 3,0	ωeye
Y4,0	^ω e ² e
Y0,1	Be
Y _{1,1}	- a e
Y2,1	^Y e
Y _{0,2}	-D _e
Y _{1,2}	. ⁻ 5
X _{0., 3}	н _е
Y _{0,4}	L _e
Y _{OS}	М

where the $Y_{l,m}$'s represent the eigenvalues (Dunham coefficients) which are to be determined from the experimental data. $Y_{0,0}$ is the electronic excitation end y and hence, to a first approximation, is equivalent to T_e . v and J in the above equation represent the vibrational and rotational quantum numbers respectively.

The correlation between the individual Dunham coefficients and the spectroscopic designations commonly used to denote molecular constants (as used in Chapter 2) are given in Table 4.1. Although the correspondences are not exact [145], for a heavy molecule such as iodine the differences are negligible.

4.2 Isotopic Relationships

Under the Born-Oppenheimer approximation, the form of the molecular potential curve is invariant with respect to isotopic substitution. Therefore, values of $Y_{0,0}$ are transferable from one isotopic molecule to another. This situation does not hold for the eigenvalues of the nuclear Hamiltonian as the vibrational and rotational Dunham coefficfents are dependent on the reduced mass of the molecule. However, the coefficients for a diatomic can be calculated from those derived from the analysis of an isotopic molecule by introducing the following mass scaling factor, c [140].

 $a = (\frac{\mu_{i/n}}{1/2})^{1/2}$

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(4.2)



Table 4.2

Mass Number	Atomic Mass (amu)
127	126 9041755 (36)
170	120.0044755 (50)
7 7 2	125.904989 (7)



a data taken from reference [147]
In equation (4.2), μ is the reduced mass of a reference molecule and μ_i the value for a given isotopic species. The reduced masses and values of ρ for the iodine molecule used in this work (relative to ${}^{127}I_2$) are listed in Table 4.2. The above definition of ρ allows the dependence on the reduced mass for vibration ($\mu^{1/2}$) and rotation (μ) to be factored from equation (4.1), to give the following expression for the total molecular energy, $E_{\rm T}$.

$$E_{T}(v,J) = \sum_{m=0}^{\infty} \sum_{\ell=0}^{\infty} Y_{\ell,m} (v+\frac{1}{2})^{\ell} (J(J+J))^{m} \rho^{(2m+\ell)}$$
(4.3)

Equation (4.3) allows the incorporation of data from different isotopic molecules, in a common least squares fit to yield a set of Dunham coefficients for the reference molecule.

For any Dunham coefficient of a given molecule, the corresponding value $(Y_{\ell,m}^{i})$ for any isotopic molecule can be obtained using equation (4.4)

$$Y_{\ell,m}^{i} = Y_{\ell,m} \rho^{(2m+\ell)} \qquad (4.4)$$

4.3 Least Squares Fitting of Spectroscopic Data

Observed spectral lines are the result of rovibronic transitions between a pair of electronic states. The energy levels of each state are described by a set of Dunham coefficients. Least squares fits in polynomials of $(v+\frac{1}{2})$, J(J+1) and ρ to the observed line positions allow estimates of the upper and lower state coefficients to be obtained. In some

cases, the Dunham coefficients associated with one of the electronic states involved in the transition (assumed to be the lower in the following discussion) were previously determined from other experimental work with greater precision than the present experiment can offer. In these instance, once the spectral assignments have been made, it is appropriate to add the lower state term value (as calculated from the more precise coefficients) to the observed transition frequency. This gives a set of term values for a particular range of upper state v and J values. A least squares fit based on equation (4.3) then yields estimates of the molecular constants that characterize the upper state (i.e. a single set of Dunham coefficients).

In matrix notation, the form of the linear regression equation can be written as,

$$Y = X S + \varepsilon \tag{4.5}$$

where y is a vector containing the n upper state term values and S is an array containing the k 'true' molecular parameters (Dunham coefficients). X represents an n x k matrix of known coefficients $(1, c(v+\frac{1}{2}), z^2(v+\frac{1}{2})^2, ...)$ that follow from expansion of equation (4.3), and c is a vector representing the error associated with each element of y. Under the assumption of linear regression theory these errors are normally distributed, have a mean of zero and a common but unknown variance. Minimization of the scalar sum of squares, resulting from equation (4.5) with respect to each element of ß gives an expression for the minimum-variance linear unbiassed.(MVLU) estimates of the 'true' molecular constants. After rearrangement, these MVLU estimates are given by the following equation;

$$b = (x^T x)^{-1} x^T y$$
 (4.6)

where the vector b contains the least squares estimate.

The variance-covariance matrix (V) of the least squares fit is given by;

$$V = \sigma^2 (X^T X)^{-1}$$
 (4.7)

where σ^{-} is the variance of the least squares fit. Thediagonal elements of the k x k V matrix are the standard errors of the corresponding element of the array, b. The off diagonal elements of V are the covariances associated with each pair of Dunham coefficients. In conjunction with the diagonal elements these values enable a calculation of the normalized correlation coefficients using equation (4.8).

$$C_{ij} = \frac{V_{ij}}{(V_{ii}V_{jj})^{1/2}} \quad i = 1, 2, 3...k \quad j=1, 2, 3...k \quad (4.8)$$

The values of C_{ij} are solely dependent on the extent of data and the model (number of vibrational, rotational and centrifugal distortion coefficients) used in the fit. A value of C_{ij} near $\stackrel{!}{\cdot}$ 1 indicates a strong correlation between the ith and jth Dunham coefficients and hence difficulty in obtaining accurate estimates of both. The unbiassed estimate of the variance (σ^2) can be shown to be given by the following formula [148];

$$\sigma^2 = \frac{1}{f} (y - Xb)^T (y - Xb)$$

where f, given by n-k, is the number of degrees of freedom of the least squares fit.

4.4 RKR Potential Curves

A method of obtaining internuclear potential curves from experimental data was first outlined by Rydberg in 1931 [149]. Soon after, Klein [150] showed that the classical turning points of vibration (for J=0) could be solved in terms of a pair of analytical expressions. The relationship of these so-called Klein action integrals (f and g) to the turning points (r_{t}) is;

$$r_{t} = \left[\frac{f}{g} + f^{2}\right]^{1/2} + f \qquad (4.10)$$

where the + sign refers to the maximum separation (r_{max}) and the - sign to the point of closest approach (r_{min}) of the nuclei. However the complexity of the functional forms of f and g discouraged the widespread use of this method.

Not until a further simplification of the technique by Rees [151], did RKR (Rydberg-Klein-Rees) curve fitting become commonplace. Rees showed that the action integrals

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(4.9)

could be expressed in terms of the experimentally determined vibrational $(Y_{\ell,0})$ and rotational $(Y_{\ell,1})$ Dunnam coefficients. The Klein action integrals can be expressed as;

$$f = \frac{h}{(8\pi^{2}cu)} \int_{v_{min}} \frac{dv'}{(E(v) - E(v'))^{1/2}}$$

$$g = \frac{h}{(8\pi^{2}cu)} \int_{v_{min}} \frac{B(v') dv'}{(E(v) - E(v'))^{1/2}}$$
(4.11)
(4.11)

where c is the velocity of light, v' is a continuous variable and v_{min} refers to the bottom of the potential well ($v_{min} \sim$ 0.5). E(v) and E(v') are determined from the vibrational Dunham coefficients as in equation (4.12);

$$E(a) = \sum_{\ell=1}^{\infty} Y_{\ell,0} (a + \frac{1}{2})^{\ell}$$
 where $a = v \text{ or } v'$ (4.12)

In equation (4.11), B(v') is the vibrationally dependent rotational constant and is given by equation (4.13);

$$B(v') = \sum_{\ell=0}^{\Sigma} Y_{\ell,1} (v' + \frac{1}{2})^{\ell}$$
(4.13)

The integrals in equation (4.11) were evaluated using Simpson's rule up to the point of singularity (v'=v). In the region of the discontinuity, Guassian quadrature was used to solve the expressions.

4.5 Franck-Condon Factor Calculations

It can be shown [17] that the intensity of a vibronic transition between a pair of molecular states is;

$$I_{v'v''} \alpha \left[\int \psi_{v'} \psi_{v''} d\tau \int \psi_{e}^{\dagger} u_{e} \psi_{e}^{\prime\prime} d\tau \right]^{2}$$

$$(4.14)$$

where v' and v" are the upper and lower state vibrational quantum numbers respectively. ψ_v represents the vibrational wavefunction associated with v and ψ'_e and ψ''_e are the electronic wavefunctions of the upper and lower state respectively. That part of the electronic dipole operator which depends on the electronic co-ordinates is given by, u_e . It is usually assumed that the electronic transition moment is a slowly varying function of r. This allows the second factor in equation (4.14) to be replaced by the average electronic transition strength as in equation (4.15);

$$I_{v'v''} \alpha \bar{u}^{2} [f\psi_{v'}\psi_{v''} d\tau]^{2}$$
(4.15)

The square of the vibrational overlap integral in equations (4.14) and (4.15), the Franck-Condon factor (FCF) determines the relative intensities of vibronic transitions within a given electronic transition.

The data required by the FCF routine consisted of the turning points (as determined by the RKR routine) for each vibrational level and U(r), the associated term values (evaluated at J=0) for the upper and lower states of the transition. This data was interpolated by the FCF routine using

the method of Lagrange to obtain values of the internuclear potential (U(r)) at closely separated intervals of r (spacing < 0.001Å).

The one dimensional radial Schrödinger equation given by equation (4.16)

$$\frac{d^2 \psi_V(r)}{dr^2} = (U(r) - E(v)) \psi_V(r)$$
(4.16)

was numerically solved using the Numerov method [152] to give the vibrational wavefunctions. The eigenvalues (E(v)) were determined in an iterative fashion using the input experimental -values as initial estimates. The consistency of the numerically calculated wavefunctions was tested by computing the rotational constant for each vibrational level from equation (4.17);

$$B_{v} = \frac{h}{8\pi^{2}cu} < \psi_{v} |r^{-2}| \psi_{v} >$$
 (4.17)

and comparing the result to the experimentally determined value.

Once the upper and lower state wavefunctions were numerically obtained, an array of FCF's was calculated. The overlap integrals (equation (4.15)) were solved using Simpson's rule.

CHAPTER 5

DESCRIPTION OF OBSERVED SPECTRA

5.1 Introduction

In this chapter, a description of the spectra obtained during the course of this work will be given. Comparison, where applicable, to the work of earlier workers will be made. The chapter is arranged in the chronological order in which the spectra were taken. which was in the following order with respect to the operating modes of the spectrometer;

- i) broadband single beam spectra
- ii) narrowband single beam spectra

iii) two beam spectra

While results are presented for the power and polarization dependence studies, the bulk of the analysis is given in the next chapter. The assignment of spectral lines, evident in the figures referred to in this chapter, will be discussed at that time.

5.2 Low Resolution Spectra

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As stated earlier (Chapter 3.6), multiphoton spectra were initially taken using the output from the broadband dye laser (BDL). Fluorescence from the highly excited final state(s) was monitored at 310 nm and recorded as a function

of laser wavelength. Spectra were obtained for both the $^{127}I_2$ and $^{129}I_2$ molecules. The laser dyes and the wavelength regions scanned were as follows; Kiton Red (6096-5946 Å), Rhodamine 590 (R6G) (5920-5749 Å) and Coumarin 540A (C-540A) (5700-5360 Å) for $^{127}I_2$ and (5700-5520) Å for $^{129}I_2$.

The multiphoton spectrum excited using Kiton Red was by far the weakest for the three dyes investigated. The frequencies of the more intense transitions are tabulated in Table 5.1 for both isotopic molecules. Figure 5.1 displays the recorded spectrum for the ${}^{127}I_2$ molecule.

Previously, this spectral region had been investigated under lower resolution ($\Delta\lambda=2A$) by Chen et al. [108]. Though the ultraviolet fluorescence following multiphoton excitation was observed in the same region (\sim 320 nm) as this work, none of the stronger features reported by these workers match the frequencies of the intense transitions observed in this study. They did, however, note a marked decrease in signal intensity relative to the spectral lines recorded over the R6G dye profile. This is in agreement with our findings. As a joulemeter or a similar device was not incorporated into the present experimental design, normalization of the spectra to correct for variations in the dye laser output power was not possible. The spectra recorded by Chen et al. also were not corrected for differences in laser intensity from one dye to another. It is probable however, that the relative weakness

•Ove	r Spectral Featu er the Kiton Red	res for ¹²⁷ I ₂ and _Dye Profile	i ¹²⁹ I ₂
127 ₁	2	1	29 ₁₂
frequency (cm ⁻¹	a) <u>remarks</u>	frequency (cm	-1) remarks
16779.8	~vs ,b	16854.2	. m
16774.7	s ·	16840.4	vs
16676.2	m,b	16834.5	\$
16614.2 /	m	16775.1	m,b
16523.8	m	16733.8	s
16443.8	m,b	16669.8	. m,b
· -		16651.6	s,b
	÷	16546.4	
		16488.1	m

Table 5.1

us, very strong

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s, strong π, medium b, broad

yery broad vb,

Figure 5.1

Low resolution trace of the multiphoton spectrum recorded over the Kiton Red dye profile for the ¹²⁷I₂ molecule. Also shown is the opto-galvanic calibration spectrum.



of the Kiton Red spectrum is due to a decrease in the multiphoton absorption cross-section rather than a reduction in the dye laser intensity.

The R6G multiphoton spectrum, like the Kiton Red spectrum, exhibited a seemingly random distribution of lines with no apparent bandheads or rotational branches. Table 5.2 lists the frequencies of the stronger features for both isotopes and Figures 5.2 and 5.3 display the spectra recorded in this region for $^{127}I_2$ and $^{129}I_2$ respectively. In this spectral region, better agreement was found between the spectra recorded in this work and those due to Chen and co-workers [108]. Strong lines observed by these authors are as follows, with our measurements in parentheses for comparison: 17060.7 cm^{-1} (17055.4 cm⁻¹), 17178.0 cm⁻¹ (17184.6 cm⁻¹) and 17267.0 cm⁻¹ (17262.4 cm⁻¹). However, other intense features which were previously observed near 17119 and 17225 cm⁻¹ do not correspond to strong transitions in our spectra.

Excitation spectra have also been obtained in this wavelength region by Kasatani et al. [113] as outlined in Chapter 2.3. Using an unspecified but very broadband $(\Delta v > 3 \text{ cm}^{-1})$ dye laser, they recorded a multiphoton spectrum between 16670 and 17540 cm⁻¹ by monitoring fluorescent light at 334 nm. Unfortunately, experimental frequencies were not listed, but they can be estimated from Figure 6 in reference [113]. Strong peaks were found near 16935, 17065, 17153 and 17270 cm⁻¹. The latter three of these lines appear to

Stronger S	pectral Feature for R6G Dye 1	es for ${}^{127}I_2$ and ${}^{129}I_2$ Profile	•
127 ₁₂	·····	129 ₁₂	•
frequency (cm ⁻¹)	remarks	frequency (cm ⁻¹)	remarks
17396.8	m	17379.9	s,b
17300.3	vs	17305.2	s
17289.6	S	17277.4	m,b
17262.4	s	17274.5	m,b
17214.1	m	4 17203.2	s
17184.6 •	vs	17193.5	s
17153.6	S	17173.7	s
17101.7	m	17170.8	s
17079.5	m,b	17152.9	s,b
- 17055.4	s	17147.5	vs
16952.2	m	17143.9	vs
		17068.7	S
• •		17064.4	m
		17048.8	m
		17045.0	s
•		17038.5	S
		10980.3	s,b
		16963.7	s,b
		10942.0	s,b
		10936.3	s,b

	T	a	b	1	e	5	•	2
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See Table 5.1 for explanation of symbols

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Figure 5.2

Low resolution trace of the multiphoton spectrum recorded over the R6G dye profile for the $^{127}I_2$ molecule

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Low resolution trace of the multiphoton spectrum recorded over the R6G dye profile for the $^{129}\mathrm{I}_2$ molecule

Figure 5.3



correlate with the strong features (Table 5.2) recorded during this work at 17055.4, 17153.6 and 17262.4 cm⁻¹ respectively. A signal of comparable intensity was not observed in our spectra in the vicinity of 16935 cm⁻¹. Additionally, a very intense feature near 17300.0 cm⁻¹, recorded in our laboratory did not have an analogue-in the spectrum recorded by Kasatani and co-workers (Chen et al. [108]), recorded only as far as 17270 cm⁻¹ in the blue).

The extensive wavelength profile of the C-540A dye laser requires two Figures (5.4 and 5.5) to display the entire spectrum. The measured line positions of the stronger peaks are listed in Table 5.3, for both isotopic molecules.

The most distinctive characteristic of the C-540A multiphoton spectrum is the occurrence of strong, generally broad features separated by approximately 50 cm⁻¹. Between these intense peaks appear only a few, much weaker multiphoton lines. For the lighter molecule, twenty-two such peaks were found, of varying separation (45-55 cm⁻¹) and intensity.

Lehmann, Smolarek and Goodman [102], scanned the 5500-5050 A region ($\Delta v = 3 \text{ cm}^{-1}$) of the $^{127}\text{I}_2$ molecule during the course of an MPI study. Though experimental frequencies were not given, except for the strongest observed peak (17881 (2) cm⁻¹), it is evident from their description of the MPI spectrum that the same system has been recorded here in fluorescence. Under low resolution, all their recorded features had the appearance of bandheads and were assigned as

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Stronger Sp	ectral Featur	es for $127I_2$ and	¹²⁹ I ₂
<u> </u>	for C-540A Dy	e Profile	
127 ₁₂	· •	12	⁹ 1 ₂
frequency (cm ⁻¹)	a <u>remarks</u>	frequency (cm ⁻¹) remarks
18607.8	m	18633.3	m,b
18549.2	S ,	17977.1	S
18504.7	m,b	17968.8	vs,b
18450.2	m	17920.3	s
18394.6	s	17874.4	vs `
18293.7	s	17867.6	vs,b
18238.2	vs .	17864.1	vs,b ·
18188.3	m	17814.1	S
18137.4	vs	17807.1	S
18090.3	s	17765.0	vs,b
18036.9	S	17761.5	vs,b
17983.4	S	17754.0	s,b
17937.4	S	17713.6	vs
17928.5	m	17671.5	m
17880.3	vs,b	17646.9	m
17827.1	s,b	17643.3	m
17779.8	s	17608.6	m
17767.0	vs		
17747.4	m,b	•	
17722.9	s,b		
17676.8	-S		-
17660.6	S	·	
17617.9	m	•	
17569.3	s		

TAULC J.J.J	Та	b 1	e	S,	•.	3
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See Table 5.1 for explanation of symbols

Figure 5.4

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Low resolution trace of the multiphoton spectrum recorded over the red end of the C-540A dye profile for the $12.7I_2$ molecule



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*****2.--

Figure 5.5

Low resolution trace of the multiphoton spectrum recorded over the blue end of the C-540A dye profile for the $12^{7}I_{2}$ molecule



such to a two photon transition. The observation of only two, much weaker peaks on the low energy side of the most intense peak ($\Delta v = 55 \text{ cm}^{-1}$ and 106 cm⁻¹ respectively) prompted these earlier investigators to assign the 17881 cm^{-1} transition as the origin band. The analysis of the spectrum based on this assignment led to the molecular constants given in equation (2.3). Although the strong peak noted by Lehmann and co-workers was recorded during this work (at 17880.3 cm⁻¹, Figure 5.4), other transitions of comparable intensity were observed, in contrast to the observations of the earlier investigators. Further, our study of the so-called 'Goodman bands' resulted in the recording of many additional groupings of lines to the red of the 'origin band'. While definite conclusions could not be drawn from these spectra, it seemed probable that either the 'origin band' was misassigned (making T_{μ} too high in equation (2.3)) or that extensive hot-band structure was being excited. This latter alternative is a possibility due to the significant Boltzmann population of the excited vibrational levels of iodine at room temperature. However, the recording of only a single progression of 'bandheads', albeit of varying separation, implies either the first alternative is correct (origin band not at 17881.0 cm^{-1}) or that the vibrational spacing of the upper state is about the same as in the ground state. The second alternative then suggests that the upper state is Rydberg in nature (ion-pair states being characterized by

much lower ω_e values). Such an assignment is in accord with the known propensity of MPI studies towards transitions involving Rydberg states as mentioned in Chapter 1.6.

The above interpretation is, however, based on the assumption that the strong features are indeed bandheads. Under the relatively higher resolution offered by our dye laser (BDL), it soon became apparent that most of the strong features did not display typical bandhead structure, but instead consisted of several closely grouped lines. Clearly, further investigation of this spectral region under the higher resolution offered by the NDL, was necessary before definite conclusions could be made regarding the 'Goodman bands'. In addition, it was felt that some of the earlier multiphotopwork, for example the studies conducted by Chen et al. [108], Kasatani and co-workers [113] and Tai, Dalby and Giles [107] merited further investigation.

5.3 Single Beam High Resolution Spectra

5.3.1 Introduction

Studies conducted using the NDL were not nearly as straightforward as with the BDL. The alignment of the dye laser to give output of high intensity and low bandwidth (< 0.15 cm⁻¹) simultaneously, proved difficult. The efficiency of the cavity dropped significantly when the prisms and grating were orientated to reduce the bandwidth of the -laser output. Even at linewidths approaching 0.1 cm⁻¹,

relatively few of the single photon rotational lines were resolved, to allow their use in calibrating the multiphoton spectra. Through a process of trial and error, the performance of the NDL was refined to give optimal resolution and signal to noise ratio (S/N).

5.3.2 Kiton Red Dye Profile

The relative weakness of the multiphoton lines recorded in the Kiton Red region made necessary the use of a passive amplifier cell (Chapter 3.6.2) to amplify the output of the NDL. This arrang**o**ment allowed the recording, under higher resolution, of the stronger features listed in Table 5.1 for the $^{127}I_2$ molecule. Figure 5.6, displays the observed multiphoton spectrum and the LIF calibration spectrum in the 16620 cm⁻¹ region. The difficulties mentioned above concerning calibration of the NDL scans can be put in perspective by noting that over the 28 cm⁻¹ region shown in Figure 5.6, Gersterkorn and Luc [86], assigned 135 individual single photon transitions. The bandwidth of our dye laser dictated that, of these Fines onIy 13 were resolved sufficiently to allow their use in calibrating the above multiphoton spectrum.

Over the regions scanned using this dye, a total of 21 multiphoton lines were recorded for the lighter molecule, and are tabulated in Appendix A. Spectra were not taken for the $^{129}I_2$ molecule in this region.



High resolution single beam trace of the 16606-16633 cm⁻¹ region (Kiton-Red dye) for the $^{127}I_2$ molecule. Spectrum was recorded using the amplifier dye cell (Figure 3.5). Also shown is the single photon $^{127}I_2$ LIF calibration spectrum.

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5.3.3 <u>R6G Dye Profile</u>

The multiphoton spectrum excited over the RoG dye profile was the most thoroughly studied of the three dye profiles investigated. The study of the 17000-17600 cm⁻¹ region necessitated the use of two different concentrations of laser dye (Table 3.1). Non-linear spectra of both isotopic molecules were investigated under linearly and circularly polarized radiation.

Spectra observed using the NDL enabled rotational resolution of the non-linear transitions previously obtained using the BDL. A striking example of this is given in Figure 6.6, which depicts the multiphoton scan near 17180 cm⁻¹ for the ¹²⁷I₂ molecule. This trace can be compared to the same region recorded under low resolution[•] (Figure 5.2). Though the enhancement in resolving power is obvious, it is also evident that not all features are fully resolved. Still, this trace serves to show that conclusions based solely on low resolution spectra must be regarded as tenuous.

A small region of the multiphoton spectrum in the R6G dye profile has been previously recorded by Ishiwata et al. [114] as described in Chapter 2.3. These workers noted eight . spectral lines between 17135 and 17372 cm⁻¹ as listed in Table 5.4. On the other hand, our spectra have revealed 69 transitions between these limits and a total of 130 lines over the entire dye profile for $\frac{127}{7}I_2^-$ alone. The measured

Comparison of OODR Lines Given by Ishiwata ______et al. [114] and This Study______

OODR Frequencies (cm⁻¹)

•	
<u>Ishiwata et al.</u>	<u>This Work (+ 0.08 cm +)</u>
17371 0	17372 205
1/5/1.9	17572.205
17368.8	17369.075
17301.2	17301.132
17299.5	17299.503
. 17220.6	•
17216.2	17216.172
17138.6	•
17135.3	- 1

line positions of these transitions can be found in Appendix A. While three of our experimental frequencies agree within our estimated uncertainty (10.08 cm^{-1}) . $(17216.172 \text{ cm}^{-1}, 17299.503 \text{ cm}^{-1} \text{ and } 17301.132 \text{ cm}^{-1}) \text{ with }$ those given by the earlier workers (Table 5.4), two others $(17368.975 \text{ cm}^{-1} \text{ and } 17372.205 \text{ cm}^{-1})$ lie outside these limits. These latter discrepancies can be explained by noting that Ishiwata et al. [114] did not quote experimental frequencies but instead listed the calculated frequencies of the $B0\dot{1}$ X04 transitions through which the upper state was allegedly pumped. However, the other lines observed by the previous workers at 17135.3 cm^{-1} , 17138.6 cm^{-1} and 17220.6 cm^{-1} were absent in our spectra. This is somewhat puzzling as both studies were conducted in a similar fashion, including monitoring the fluorescence at 310 nm. Further it is worth noting that many strong peaks, such as the lines in the 17180 ${\rm cm}^{-1}$ region (Figure 6.6) were not reported by the earlier workers.

Spectra were also obtained for ¹²⁹I₂ over this dye profile, and a total of 171 individual multiphoton transi-¹tions observed. A scan of the 17370 cm⁻¹ region for this molecule excited with circularly polarized light is given in Figure 6.8. All the recorded multiphoton lines for this. molecule are also listed in Appendix A.

5.3.4 C-540A Dye Profile

As mentioned previously (Chapter 5.2), the 'Goodman

bands' were reinvestigated using the NDL following preliminary observations with the BDL. Extensive scans of the 17600-18200 cm⁻¹ region were made for the ${}^{127}I_2$ molecule. A total of 173 multiphoton transitions were obtained and are listed in Appendix A.

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Figure 6.11, depicts the non-linear spectrum in the vicinity of the 'origin band' assigned by Lehmann and co-workers [102]. Though it clearly illustrates a high density of spectral lines, they are not indicative of a bandhead. Further evidence is given in Figure 6.12, which shows the rotational structure of the '1-1 band', 55 cm⁻¹ to the red of the 'origin band'. Quite clearly, there is no bandhead present but rather, several well spaced multiphoton In fact, the strongest of these lines can be dislines. cerned in Figure 4 of reference [102] as well as in Figure 5.4 in this work. Except in one instance, all the features observed under low resolution in this region were subsequently found to be due to localized congregations of spectral lines and not bandheads. The one exception was a broadband feature at 18239.1 cm^{-1} that quite clearly coincided with the head of the 24-0 band of the $B0_{11}^+ - X0_{12}^+$ system (Figure 6.10).

Spectra were also recorded using this dye for the. $^{129}I_2$ molecule between 17600 cm⁻¹ and 17990 cm⁻¹. A total of 83 multiphoton frequencies were observed and are listed in Appendix A. These spectra also served to show that the regularly occurring features listed in Table 5.5 were not, in general, bandheads. The multiphoton spectra were again recorded under both linearly and circularly polarized excitation.

5.3.5 Power Dependence

Following the discussion of Chapter 1.5, a study was conducted to determine the number of absorbed quanta responsible for the observed spectra. The dye laser was tuned so as to give maximum signal strength for the strong 17299.503 cm⁻¹ transition of the $^{127}I_2$ molecule (Figure 6.7). A series of neutral density filters were placed, in turn, in the optical path of the NDL and the averaged signal fromthe boxcar monitored. This was repeated several times for each filter, after which the mean fluorescence signal for each value of the dye laser attenuation was calculated. The fluorescence and laser intensities were then normalized such that the maximum value of each (obtained with the unattenuated beam) was 100. These findings are summarized in Table 5.5. In accord with equation (1.9), a plot of the logarithm of the normalized fluorescence signal (F) versus the logarithm of the normalized laser intensity (I) is displayed in Figure 5.7. A least squares fit, determined the slope of the line for this plot to be 1.93(11), thereby indicating absorption of at least two photons. Two photon absorption can be, however, definitely ruled out by noting that if this were the case the upper state would lie near 33000 cm^{-1} and be of gerade symmetry.

	Table 5.5	
£	Berren Berren terre	~

Data from Power Dependence Study

17299.523 cm⁻¹

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avr. output (dc volts)	\$Г	log(%Γ)	laser attenuation (%T)	log 3T
2.65 (5) ^a	100.0	2.00	100.0	2.00
).81 (3)	30.5	1.48	50.0-	1.70
.27 (2)	10.2	1.01	31.6	1.50
).08 (1)	3.0	0.48	15.8	1.20
0.00 (1)	0.0	1 <u>-</u> 1	0.0	

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estimated uncortainty in last figure

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Figure 5.7

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Plot of logarithm of the normalized fluorescence intensity versus the logarithm of the normalized laser intensity. Data for the plot is given in Table 5.5.


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As the excited state was monitored by observing radiation emitted at 310 nm (32250 cm^{-1}) it implies (Table 2.2), that the lower terminus could only be the ground state of the molecule. However, such a transition (g-g) is rigourously forbidden under the electric dipole selection rules outlined Therefore, the lowest possible number of in Chapter 1.3. photons absorbed to give rise to multiphoton transitions in this spectral region is three. This number can be reconciled with the slope determined from the above plot by assuming that the multiphoton transition is resonance enhanced via an optically saturated $BO_u^+ - XO_g^+$ single photon transition. This assumption is reasonable as the dye laser pulse intensity at the center of the sample cell approaches a calculated peak value of 500 kW/cm² (1.5 x 10^{24} photons cm⁻² s⁻¹ at 6000Å). In fact, an identical power dependence study using the Γ_2 . LIF reference cell showed that even the unfocussed dye laser emission was capable of inducing partial saturation of the BOu⁺-X0g⁺ transition.

A three photon absorption process places the highly excited state(s) near 50000.0 cm⁻¹. This is in good agreement with the energy of the fluorescent light (32250 cm⁻¹) plus the $I({}^{2}P_{1/2}) + I({}^{2}P_{3/2})$ dissociation limit (20147 cm⁻¹) (Figure 2.2). A finding of n=3 is in accord with the conclusions of Chen et al. [108] and with those of Ishiwata and colleagues [114].

Higher order nonlinear phenomena may account for some of the observed multiphoton lines, but they are expected

to be weak given the relative magnitudes of the absorptivities (Chapter 1.2) and the 'moderate' excitation intensities employed in this work. Analysis of the spectra proceeded on the assumption that the multiphoton lines were due to resonance enhanced three photon absorption. Hereafter, OODR spectra obtained with the use of a single dye laser are referred to as 3PIC (3 photon, single colour).

5.3.6 Polarization Dependence

Since fluorescence intensity is directly proportional to the rate of absorption of photons at a given frequency and thus to the square of the transition moment (Chapter 1.2), it can be used as a measure of the relative transition amplitudes of multiphoton lines in linear and circular polarized light.

Comparison of spectra recorded over the same spectral region with the output of the dye laser first linearly polarized and then circularly polarized indicated the presence of at least one upper state of $0u^+$ symmetry. This was shown by the reduction in intensity of certain prominent lines when excited with circularly polarized light. These could be identified as Q ($\Delta J=0$) branch transitions in a two photon $\Delta \Omega=0$ electronic transition from the B0u⁺ state. By far the majority of the stronger lines (in linearly polarized light) were subsequently found to belong to Q transitions (Figures 6.7 and 6.14). However, definitive assignments of the

spectral lines (Q or non-Q) were not always possible. This was especially the case with the weaker transitions, whose inten sities were particularly susceptible to short term fluctuations in the dye laser output power. Relatively large variations in peak amplitude were found for these lines. Other lines were blended, which made unambiguous branch assignments difficult. However, experiment indicated that the theoretical value of $\gamma = 3/2$ (Table 1.2) was not exhibited for some of the stronger 0 and S branch lines. For example, the intensity Fof the multiphoton transition observed at 17301.814 ${\rm cm}^{-1}$ (Figure 6.7) appeared invariant to the polarization state of the radiation field, even though an enhancement in signal strength is predicted based on the assignment of the when the multiphoton transition is excited by line, circularly polarized light. Repeated scans of the region shown in Figure 6.7 verified the relative magnitudes of all the transitions shown.

Many of the non-Q branch assignments based on the polarization dependence of the transition (as given in Appendix A) were only possible because the reduction in intensity when irradiated with circularly polarized light was so pronounced for the transitions which could be definitely identified as Q lines.

In agreement with Ishiwata et al. [114], our observations of the polarization dependence of the five lines in common with their study indicated they were due to $\Delta J=0$ transitions. The earlier workers quoted an average value of 0.2

for γ (equation (1.7)), by measuring the intensities of the eight lines (all Q branch) in linearly and circularly polarized light. Our study conducted on the five lines in common, resulted in a mean value of 0.22(3) for γ . A value of γ for the Q branch lines, though nominally J dependent (Table 1.2), could be determined prior to the analysis of the spectra . (i.e. the rotational analysis) by using the limiting form of the expression for γ valid at high J. Given in equation (5.1), this formula can be applied to a molecule such as iodine where high J levels (J>30) are routinely encountered.

 $\gamma = \frac{3}{\frac{U_{I}}{2+40(\frac{U_{I}}{U_{S}})^{2}}}$ (valid for Q branch transitions) (5.1)

The experimental value of γ enables the ratio of the square of the electronic transition amplitudes, $(U_I/U_S)^2$, to be estimated as 0.29. This value implies that the intermediate virtual state is predominantly of 0_g^+ character [27].

The reason why Bray and Hochstrasser's [27] relationships are obeyed qualitatively rather than quantatively may be as follows. In their study it was implicit that the M sublevels associated with the J level of the lower state were equally populated prior to the two photon excitation to the high lying states. In our case, however, the absorption of an initial photon to the $B0_{11}^{+}$ state gives rise to an

anistropic M population distribution due to the selection rules outlined in Table 1.1. If the simultaneous absorption of two photons should occur before the M sublevels can equilibrate then this would have to be taken into account inthe derivation of relative transition strengths in linear and circular polarized light. It has been suggested, that if the initial sequential absorption step is saturated then the population of the upper state levels becomes independent of M [153]. If this were the case then the theoretical values of y given in Table 1.2 should hold true in our work. The fact that they do not implies the initial absorption step plays some role in determining the relative transition amplitudes. While investigations of the polarization dependence of simultaneous three photon transitions have been conducted [22]. none have considered the role of resonance enhancement on individual rotational transitions.

5.3.7 Discussion of Single Beam Spectra

The total absorption cross-section (σ_T) , following the discussion presented in Chapter 1.2 for a resonance enhanced (at the single photon level) three photon transition, is given by the expression below;

$$\sigma_{\rm T} = \sigma_{\rm SEQ}^{(1)} \sigma_{\rm SIM}^{(2)}$$
(5.2)

In equation (5.2) $\sigma_{SEQ}^{(1)}$ is the cross-section of the $B0_u^+ - X0_g^+$ transition and $\sigma_{SIM}^{(2)}$ represents the cross-section for the two photon simultaneous transition out of the real intermediate state. To be allowed, transicions must satisfy two sets of selection rules (Table 1.1) such that the sequential and the simultaneous cross-sections are non-zero. A further constraint on possible 3P1C transitions is the requirement that the resonance criterion, given in equation (5.3), must be fulfilled.

 $2(E_{2}(v_{2},J_{2}) - E_{1}(v_{1},J_{2})) = E_{3}(v_{3},J_{3}) - E_{2}(v_{2},J_{2})$ $2\sigma_{21} = \sigma_{32}$

In the above equation, E_1 , E_2 and E_5 are the term values of the ground, intermediate and final states respectively. These energies are functions of the vibrational (v_1, v_2, v_3) and rotational (J_1, J_2, J_3) quantum numbers (equation (4.1)). The single photon transition frequency (which is also the frequency at which the non-linear transition is observed in the spectrum) is given by σ_{21} , and σ_{32} represents the frequency of the two photon transition from the $B0_u^+$ state to the higher lying states. The selection rule's and resonance criterion combine to give rise to the seemingly random frequency distribution of the observed SPIC lines, which is particularly evident in the spectra in the RoG and Kiton Red dye regions.

(5.3)

The analysis of classical (linear) spectra is based on the separation of regular spectral features, be they bandheads (vibrational analysis) or adjacent lines within a given rotational branch. Such features are usually readily discernible and offer a relatively straightforward analysis of the spectrum to yield molecular constants (Dunham coefficients) for the upper and lower electronic states. The situation is much more complicated in multiphoton spectra when one or more of the absorption steps is resonance enhanced. Although relationships can be derived to calculate the frequency distribution of the allowed rotational branches, they are of limited use in the direct analysis of the spectra due to the paucity of observed lines in any given branch. Ιt is instructive, however, to see how these formulae are developed through consideration of the rotational selection rules applicable to the observed absorption pathway and the resonance constraint (equation (5.3)). For example, a single photon R transition followed by a two photon Q transition would be given as in equation (5.4);

 $E_{3}(v_{3},J_{1}+1) = 5(E_{2}(v_{2},J_{1}+1) - E_{1}(v_{1},J_{1})) + E_{1}(v_{1},J_{1})$ (5.

The term values can be expressed in terms of the molecular constants of each state following equation (4.1). Upon substitution into the appropriate equation (5.4)-like expression and subsequent rearrangement, the branch relationships for

Table 5.6

3-Photon Branch Relationships

ч Э Coefficient

			<u> </u>	·	-,7					· -		
	$A^{C} - 144D_{3} + 12D_{2}$	-6B3+6B2	$\Lambda + 4D_3$	- 2B ₃ .	A - 128D2	- 6B ₂	$A + 4D_3$	- 2 ^B 3		V	$\Lambda + 36D_3$	-6B ₃
	168D ₃ - 36D ₂	$-7B_3 + 9B_2 - 2B_1$	12D ₃ -36D ₂	$-3B_3 - 3B_2 - 2B_1$	- 36D2	$+B_3+9B_2-2B_1$	12D ₃	-6B ₃ -3B ₂ -2B ₁		$B_3 - 3B_2 - 2B_1$	-60D3	$+5B_3 - 3B_2 - 2B_1$
	$73 n_3 - 39 n_2 + 2 n_1$	$-B_3 + 3B_2 - 2B_1$	$13h_3 - 39h_2 + 2h_1$	$-B_3 + 3B_2 - 2B_1$	$1_{3} - 391_{2} + 20_{1}$	$-B_{3}+3B_{2}-2B_{1}$	$13D_2 - 3D_2 + 2D_1$.	$-B_3 + 3B_2 - 2B_1$	$1)_3 - 31)_2 + 210_1$	$-B_3 + 3B_2 - 2B_1$	$370_3 - 30_2 + 20_1$	$-B_3 + 3B_2 - 2B_1$
· ($14D_3 - 18D_2 + 4D_1$		$6D_3 - 18D_2 + 4D_1$		$2D_3 - 18D_2 + 4D_1$		$(0)_3 + (0)_2 + (0)_1$		$-2D_3 + 6D_2 + 4D_1$		$-100_3+60_2+40_1$	
-	R S		(, К,Q	R.0		, p`S			ь , ,	p.0	

T_i, B_i and D_i represent the vibrational term values and the rotational and centrifugal distortion constants respectively, for each value of v_i (i=1 $i \cdot e \cdot E(v_{i}, J_{i}) = T_{i} + B_{i}(J_{i}(J_{i}+1) - D_{i}(J_{i}(J_{i}+1))^{2})$ $\Lambda = -T_{\tau} + 3T_{\gamma} - 2T$

the six allowed branches (Figure 1.1) of an $0_g^+ - 0_u^+ - 0_u^+$ three photon transition (0,0, or S two photon line preceded by either an R or P pump transition) can be evaluated. These expressions are listed in Table 5.6.

The initial step in the analysis was to calculate all the possible resonance $BO_u^+ - XO_g^+$ transitions within a certain bandwidth of each experimental 3PlC frequency. This was conveniently done using a Fortran routine (SORTCH) that calculated single photon transition frequencies and compared these values with the observed 3P1C transition energies. Transition frequencies were calculated using the ground state Dunham coefficients given by Tromp and Le-Roy [89] and the constants of Hutson et al. [88] for the BO_{ii}^+ state. The validity of using sets of parameters from different sources was checked by comparing calculated line frequencies against the experimental values listed by Gerstenkorn and Luc [86]. Excellent agreement; to within $\frac{1}{2}$ 0.005 cm⁻¹ was found in all cases. This finding is not surprising as both studies used the same set of measured line positions with which to determine molecular parameters. The corresponding Dunham coefficients for the $129I_2$ molecule were derived from the above constants using equation (4.4) and the appropriate value of the mass scaling factor from Table 4.2.

In selecting possible resonance lines, single photon transitions were considered from $v_1=0-4$. Transitions originating from excited ground state vibrational levels were considered

, for two reasons. First, an appreciable fraction of the molecules are vibrationally excited at room temperature . $(\sim 35\%)$ and secondly, transitions from these excited levels. to the $B0_{11}^+$ state are favored on Franck-Condon grounds in this region of the spectrum. This latter point is especially relevant with respect to the multiphoton spectrum recorded with Kiton Red dye. For well-determined, unblended 3P1C lines a tolerance of $\stackrel{+}{\sim}$ 0.15 cm⁻¹ was used in selecting possible pump levels. This arbitrary limit not only took into account the bandwidth of the dye laser but also acknowledged the possibility that in some instances, perhaps the pump frequency was slightly off resonance. With the above tolerance limit (ranging to ± 0.3 cm⁻¹ for broad 3P1C features) an average of ten possible pump lines was found for every experimental frequency.

As traditional methods of analysis were of little use in unraveling the 3P1C spectrum, a variety of novel approaches were tried in an attempt to assign spectral features. While tentative assignments could be made for localized regions of the spectra, an overall, consistent analysis was not found. Aside from the overwhelming number of possible J assignments for each 3P1C line, the main obstacle lay in not knowing the number of upper states contributing to the observed spectra.

5.4 <u>Two Beam Spectra</u>

Only one report of two beam multiphoton absorption (n>2) had been published concerning the iodine molecule [109] prior to this study. Despite the high resolution of this MPI study, a rotational analysis of the spectrum was not offered. More recently, OODR studies of a similar nature as those discussed here have been reported for the Br₂ [154] and Cl₂ [155] molecules.

As stated earlier (Chapter 3.6.3), the BDL was used to pump the $B0_u^+$ state while the NDL was scanned to induce two photon absorption from the populated intermediate levels to the higher lying states. Hereafter, the two beam spectra are denoted as 3P2C (3 photon, 2 colour). The advantage in employing two beams to stimulate multiphoton transitions is the extra experimental degree of freedom it offers relative to the single beam work, since the pump and probe frequencies can be varied independently.

Extensive spectra were taken using a common dye (R6G or C-540A) in each laser. The details regarding the spectral regions covered by these scans are given in the next chapter.

Double beam spectra were not easy to obtain experimentally. This was primarily because of the limited amount of excimer radiation available for distribution between the two dye lasers. Unless both lasers were operated near maximum efficiency, 3P2C signals were not observed. Indeed, it was often difficult to record even 3P1C lines generated

by the probe laser alone when the excimer radiation was divided between the two dye lasers. The problems in obtaining 3P2C spectra are clearly demonstrated by the few, relatively weak traces recorded for the 129 I₂ molecule. This was in spite of the fact that the single beam spectra were quite intense. Experimental difficulties in the preparation of the radioisotopic molecule were believed responsible for the relative weakness of the double beam spectra. It is well known that the $B0^+_{11}$ state is efficiently quenched by foreign gases [156], particularly large polar molecules [157] such as ether, which was used to extract the nascent $^{129}I_{2}$ sample. Trace amounts of this solvent would tend to depopulate the B0⁺ state and hence reduce the three photon signal strength. This would in particular, adversely affect the two beam transition amplitude because of the temporal delay between the pump and probe pulses. In addition, as outlined in Chapter 1.2, the ion-pair states of iodine also undergo rapid collisional energy transfer when excited in the presence of foreign gases. Indeed even trace amounts of impurities have been shown to be effective in bringing about population redistribution [56].

In general, the double beam spectra exhibited much lower S/N ratio than the narrowband single beam studies, because of the lower intensity of the NDL output and the unavoidable jitter in the overlap of the two beams. The later introduction of an amplifier cell into the probe beam and the resulting case with which 3P2C spectra were obtained (after

completion of this work) unequivocally showed that the attenuated NDL output was mainly responsible for the difficulty in observing 3P2C transitions. On average, the 3P2C lines were found to be less intense than the 3P1C transitions recorded on the same trace. However, the relative signal strengths were found to be reversed when the system was operated in the alternate two colour mode (i.e. single dye laser). This is perhaps because factors influencing the relative spatial orientation of the two beams (i.e. thermal gradients in dye cell) affected both beams in a similar fashion thus increasing the observed 3P2C signal intensity relative to the dual dve laser approach. The reversal of the relative signal strengths of the 3PIC and 3P2C lines when operating in this mode is clearlyshown in Figure 6.5, in which the probe laser scan includes the 3P1C lines near 17180 cm^{-1} (Figure 6.6). However only a few traces were recorded with this configuration owing to experimental difficulties associated with mode competition between the two beams along the common optical path through the dye cell. The following description refers then, to the dual dye laser approach, unless otherwise stated.

Many 3PIC transitions, excited by the NDL alone, were conspicuous in the double beam spectra. The frequencies of these lines, in contrast to the 3P2C lines, were of course invariant with respect to the pump laser frequency. The single colour lines could also be readily identified by comparison of 3P1C and 3P2C spectra recorded over the same spectral region.

Those 3P2C transitions originating from a common $B0_u^+$ rovibrational level consisted of a strong line flanked on either side by a much weaker line (Figure 6.3). The observed triplet structure was consistent with the 0_u^+ symmetry assignment of the three photon excited state(s) from the polarization analysis of the 3P1C spectra.

When the lasers were operating satisfactorily, 3P2C spectra could be obtained for any given pump laser frequency within the dye profile. Indeed, if the NDL scan was extensive (>30 cm⁻¹), at least two B0⁺_u rovibronic levels could usually be identified as giving rise to two beam spectra. This was a consequence of the high density of lines in the B0⁺_u-X0⁺_g single photon spectrum and the relatively large bandwidth of the BDL. At any one pump frequency, a bandwidth of 0.7 cm⁻¹ enabled, in principle, the simultaneous pumping of about 20 individual B0⁺_u-X0⁺_u transitions (for v₁ = 0-2, J₁ = 0-150). Most of these pumped transitions did not give rise to subsequent two photon transitions due to such reasons as selection rules, Franck-Condon factors and the limited spectral region covered by the probe laser.

Generally, for each pump frequency, the NDL was scanned over as long a wavelength interval as possible. This greatly facilitated the subsequent analysis of the spectra, as each O, Q, S line grouping was separated from the adjacent triplet structure (due to the next vibrational level of the upper state) by approximately one half the energy difference

of the rotationless levels.

The most useful of the 3P2C experiments were those conducted with the pump laser set at a frequency corresponding to the bandhead of a $B0_{u}^{+}-X0_{g}^{+}$ vibronic transition. Each bandhead consists of a number of closely spaced lines of low J, and when these lines were pumped simultaneously, the \checkmark corresponding 3P2C spectra showed a series of broad head-like features which could be easily distinguished from lines due to transitions between levels of high J. The most comprehensive of these studies were performed pumping the heads of the 14-0 (Figure 6.1) and 20-0 (Figure 6.2) bands of $^{127}I_{2}$ as well as the 15-0 band of $^{129}I_2$. These readily discernible features enabled the vibrational intervals of the three photon excited states to be approximately determined. This was to prove invaluable to the analysis of the single and double beam spectra, as will be made evident in the next Chapter.

CHAPTER 6 -

RESULTS AND DISCUSSION

6.1 3P2C Bandhead Analysis

As mentioned in Chapter 5.4, the 3P2C spectra obtained with the pump laser set at the low J-value heads of various $B0_u^+-X0_g^+$ bands showed a number of head-like features. The lower energy 3P2C heads for both molecules were observed while pumping the respective 14-0 bands. An example is shown in Figure 6.1, in which three such features are evident for the $^{127}I_2$ mecule. The higher energy OODR heads for the lighter molecule were recorded when the 20-0 band was pumped, as shown in Figure 6.2.

Almost all of these characteristically broad 3P2C features (listed in Table 6.1) were identified as components of one of two main progressions. Both of these series were observed for each isotopic molecule.

The most extensive progression of 3P2C heads (for convenience, temporarily denoted as the ϕ system) demonstrated an average spacing of 37 cm⁻¹ for the ${}^{127}I_2$ molecule. Eleven, non-consecutive, members of this system were observed for ${}^{127}I_2$ and three for the heavier molecule as listed in Table 6.2. One of the lower lying 3P2C heads of this system is shown in Figure 6.1, while Figure 6.2 depicts the four highest lying members of this system. These latter heads were separated by

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Observed 3P2C Head-like Features

Pump Band	σpump (cm ⁻¹)	$\sigma_{\text{probe }(\text{cm}^{-1})}$	$E_3(cm^{-1})$
14-0	17315.8	17517.8	52058.4
	**	17304.0	520-30.9
· • •	· • • • • •	17292.5	52007.9
11 .	11	17279.5	51981.8
**	6 . 4	17243.5	51909.8
11	· · · · · · · · · · · · · · · · · · ·	17240.7	51904.2
. **	11	17239.1	51901.3
tt -		17174.6	- 51772.1
* *	11 •	17167.2	51757.4
**	11	- 17163.9	51750.7
••	e tt	17124.7	51672.3
11	11	17091.3	51005.4
** .	tt .	17086.0	51594.9
15-0	17416.7	17345.6	52214.9
20-0	17892.9	17884.3	53768.9
11	11	3,7848.8	53697.6
**		17812.8	53625.5
/	11	17776.4	53552.8
		•	
129 _{I2}		•	
<u> </u>			
14-0	17305.2	17311.8	52035.0
· 11	"	17307.7	52026.8
**		17305.4	52022.1
15-0	17405.4	17384.6	52280.8
**		17364.7	52240.9
	11	17369.7	52251.0
** .) 11	17331.7	52174.9

Figure 6.1

3P2C spectrum of the 127 I_2 molecule. Pump frequency = 17315.81 cm⁻¹ (14-0 $B0_u^- \times 0_{\sigma}^+$ bandhead). Indicated are 3P2C heads originating from the ϕ (Table 6.2), ζ (Table 6.4) and F'0⁺ (Table 6.3) upper states.

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·	<u> </u>	•	<u> </u>	
a <u>n</u>	E ₃ (cm ⁻¹)	<u>n</u>	E ₃ (cm ⁻¹)	
Û	51594.9	b k	52022.2	
1	51672.3	k+2	52174.9	с
2	51750.7	k+3	52251.0	- .
4	51904.2		•	•
5	51981.8		•	
6	\$2058.4			
8	52214.9			
2 ó	53552.8			
27	53625.5	• •	•	,
28	53697.6	•	•	
29	53768.5			
а	n is an arbitrarv integ	er.		

Table 6.2

р.

k is an unknown integer to be determined.

132

Figure 6.2

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5P2C spectrum of the 127 I₂ molecule. Pump frequency = 17892.9 cm⁻¹ (20-0 B0⁺_u-X0⁺_g bandhead). Indicated are the four highest observed 3P2C heads originating from the ϕ state. As will be shown in Chapter 6.3.4, they are due to emission from v=78-81 of the F0⁺_u state. Note the interrupted frequency scale.



about 36 cm⁻¹ in the double beam spectrum, corresponding to an upper state vibrational interval of approximately 72 cm⁻¹. Most of the intervening 3P2C heads were not observed using the above $B0_u^+ - X0_g^+$ bands, due to the limited extent of the probe Frequency scans. Unfortunately, pumping intermediate v_2 levels at low J was not very successful in giving 3P2C head-like features, as the required pump frequencies could not be pumped strongly. This was a consequence of the dye concentrations employed (R6G and C-540A) and the resulting wavelengths over which the cavity lased efficiently.

The upper state term values given in Table 6.1 were calculated (using equation (6.1)) from the positions of the 3P2C heads, on the assumption that the high frequency edge of the feature coincided with the two photon band origin, -

$$E_3 = 2 (\sigma_{probe}) + E_2 (v_2, 0)$$
 (6.1)

where σ_{probe} was the frequency of the NDL at which a given 3P2C bandhead was observed. $E_2(v_2,0)$ represents the $B0_u^+$ state rotationless term value (equation (4.12)) relative to the potential minimum of the ground state. A least squares fit to the $^{127}I_2$ data in Table 6.2 yielded the following constants with a standard deviation of 0.86 cm⁻¹;

 $E_3(n) = 51594.18(69) + 78.24(19) n - 0.12(6) n^2$ (6.2) where n is an arbitrary integer (n=0-29). The relatively low value of the vibrational interval suggests that this progression is due to transitions that terminate on highly excited levels of a lower lying $(T_e < 51594 \text{ cm}^{-1})$ electronic state, such as one of the ion-pair states correlating to the $I^+({}^{3}P_2 \text{ or } {}^{3}P_1) + I^-({}^{1}S)$ diabatic dissociation limit. As only three 3P2C heads were observed for the ${}^{129}I_2$ molecule, the assignment of absolute vibrational quantum numbers was not possible on the basis of these spectra alone.

A second series of 3P2C heads exhibited a spacing of about 65 cm^{-1} in the OODR spectrum for both molecules. This corresponds to an actual energy separation of approximately 130 cm⁻¹ between adjacent vibrational levels in the final state. Three members of this system were observed for each isotopic molecule, as listed in Table 6.3. These heads were accessed via the respective low v_2 bandheads of both molecules. Comparison of the 3P2C head frequencies to the values derived from the vibrational term values calculated using the constants given by Ishiwata et al. [114] for the I_2^{127} molecule, identified the upper state of this progression as F'0⁺. The lowest lying member of our series of heads (shown in Figure 6.1) was. tentatively assigned to $v_3=0$ (in agreement with Ishiwata and co-workers), as no member of this progression was observed to the red of this feature. This was despite the fact what strong heads were recorded for other systems in this region of the spectrum using the same pump frequencies. All E_3 values calculated from the observed 3P2C heads of this progression for both isotopic molecules were fitted to a common expression (using

	<u> </u>		'u ^{otate}		<u> </u>	
	<u>127</u> ₁₂	•			¹²⁹ I ₂	
v	•	E ₃ (cm ⁻¹)		<u>v</u>	•.	E ₃ (cm ⁻¹)
0		51772.1		2		52026.8
1		51901.2		3	• •	52153.9
2		52030.9		4	_	52280.8
			-			

Table 6.3

Assigned 3P2C Heads for Transitions to the F'0, State

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the mass reduced scaling factor, ρ) to give the following constants (applicable to the $^{127}I_2$ molecule);

 $E_3(v_3) = 51707(1) + 129.85(92)(v_3+0.5) - 0.32(18)(v_3+0.5)^2$

Although experimental evidence strongly supported the above vibrational numbering scheme $(v_3=0-4)$, a rotational analysis was necessary to unequivocally determine absolute assignments. For instance, it was found by trial and error, that incrementing the numbering by one unit yielded a slightly lower standard deviation for the fit.

Aside from the above systems, several other heads were observed in the 3P2C spectra for both molecules. Three such features separated by about 150 cm⁻¹ were observed for 'the ¹²⁷I₂ molecule (Table 6.4). These bands were nearly coincident with every other transition of the \diamond system, as can be seen in Figure 6.1. Another very intense feature, for which E₃ = 52007.9 cm⁻¹ was also recorded for the ¹²⁷I₂ molecule. For the ¹²⁹I₂ molecule, two unassigned bands were observed which gave E₃ values of 52035.0 and 52240.9 cm⁻¹ respectively. It could not be determined on the basis of these spectra if one or the other belonged to either of the fragmentary systems of the lighter molecule.

With a preliminary vibrational (low J) analysis completed, assignment of the high J lines in both the 3PlC and 3P2C spectra could be attempted. The remainder of this Chapter is subdivided into sections dealing with each of the observed

 $(6.3)^{-1}$

Table 6.4

Assigned 3P2C Heads for Fragmentary system of ¹²⁷I₂

•			
n			$E_3 (cm^{-1})$
0		<u></u>	51605.4
1			51757.4
2			51909.8
	•		

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3-photon excited states.

The F'0⁺_u State

6.2.1 The High J 3P2C Analysis

The first of the three photon excited states to be discussed will be the one designated as $F^*0^+_u$ by Ishiwata and co-workers [114]. A presentation of the double beam analysis will be given prior to the discussion of the 3P1C results, as the spectra were interpreted in this order. Much of the discussion given in the two following sections will be pertinent to the analyses of the other three photon states to be presented in subsequent sections of this Chapter.

All of the observed 3P2C transitions terminating on the $F'O_u^+$ state were found to be the result of using pump and probe frequencies within the R6G dye profile. The strongest of these OODR lines originated from individual rotational transitions comprising the respective 14-0 bands. A summary of the 3P2C spectra collected for the $F'O_u^+$ state is given in Appendix B which includes the BDL frequency and the pumped single photon lines as well as the probe frequencies for which assignments were made.

As noted in Chapter 5.4, the 3P2C high J transitions were assigned to line triplets, corresponding to the $\Delta J=-2$ (O branch), $\Delta J=0$ (Q branch) and $\Delta J=2$ (S branch) two photon

139.

transitions from the pumped $B0_u^+$ level. The probe frequencies of the assigned transitions, in conjunction with the calculated energy [88] of the rovibronic level of the $B0_u^+$ level being pumped ($E_2(v_2,J_2)$), were used to calculate the upper state term value for each value of J_3 from the rotationally dependent form of equation (6.1).

As the BDL frequency decreased (pumping higher J for a given $B0_u^+-X0_g^+$ band) the strong, readily discernible, Q branch lines of a given $v_3 - v_2 - v_1$ transition were observed to shift to the red. This indicated that the rotational constants of the pumped vibronic levels of the $B0_u^+$ state were greater than those of the vibrational levels of the $F'0_u^+$ state accessed by the probe laser. An example of this behaviour is shown in Figures 6.1 and 6.3 and 6.4, for which the pump frequencies are 17315.8, 17282.1 and 17248.5 cm⁻¹, respectively. These frequencies excite successively higher J values of the 14-0 $B0_u^+-X0_g^+$ band, from which subsequent two photon transitions are observed to the corresponding rotational levels of the upper state ($v_3=0$).

Figure 6.5 shows a 3P2C spectrum obtained using the NDL alone to generate the pump and probe beams, which clearly shows the O, Q and S two photon branch lines to the first excited vibrational level of the $F'O_u^+$ state following single photon excitation of the $v_2=14$, $J_2=98$ rovibronic level of the BO_u^+ state.

The broad bandwidth of the BDL (dual dye laser mode) when pumping in the range $J_1 = 25-100$, usually resulted in one R and one P branch line being excited simultaneously for each Figure 6.3 3P2C spectrum of the $127I_2$ molecule.

pump frequency	(cm ⁻¹)	v ₂	v ₁	J_2	J _l	$E_{2} (cm^{-1})$
17282.193		14 _	0	52	53 -	17388.941
17282.080	*	14	0	59	58	17409.706



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			· · · · · · · · · · · · · · · · · · ·	*		
				•		•
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				:		•••••
· ·		•		•		
				· · · ·	1	
•						
•	•			· · ·		
	- • •				•	
•				4 1 1 1 1	•	
-					· · · · ·	
r			•	·		
	Figure 6.4	■ 3P2C spe	ctrum of the	127 In mole	ecule.	
n an	-			-2		
	pump fr	eauencv (cm ⁻¹) v	vI.	T E (cm ⁻	1,

-	pump	frequency	(cm *)	v2	vı	J ₂	Jl	$E_2 (cm^{-1})$	
		17248.672	•	14	0	75	76	17466.862	•
		17248.475		14	0	82	81	17496.096	
			· .	• •			•	•	
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pumped $B0_u^+ - X0_s^+$ vibronic transition as evidenced by Figures 6.3 and 6.4

Due to the uncertainty in the determination of the pump laser frequency with the usual method of calibration (via monochromator, Chapter 3.3.3) at least two alternative sets of J values for these P and R lines could be initially assigned as serving to populate the intermediate state. It was therefore possible at this stage to be in error by one, or even, two quanta in J_1 (and hence J_2 and subsequently J_3) in the assignment of pump lines. Fortunately, any such misassignment had only a small effect on the calculated upper state molecular constants. This was because an increase (or decrease) in the assigned value of J_3^- relative to the actual value results in a compensating decrease (or increase) in the $B0_{u}^{+}$ state contribution $(E_{2}(y_{2},J_{2}))$, equation (6.1)) to the calculated energy of the upper state level. As the analysis proceeded the probability of such errors was reduced by.considering the following tests. First, the tentative pump assignments for a particular 3P2C spectrum were required to correspond to single photon transition frequencies that differed by no more than the linewidth of BDL. Additionally as more 3P2C lines for a given upper state vibrational, level were assigned, plots of $E_3(v_3, J_3)$ versus $J_3(J_3+1)$ could be made. For the purpose of these plots a value of $Y_{0,2} = -3.0 \times 10^{-9} \text{ cm}^{-1}$. was assumed to correct for non-linearity due to centrifugal distortion. However, such corrections were very small, (0.3 cm⁻¹

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	· · · · ·	••••
Figure 6.5	3P2C spectrum of the ${}^{127}I_2$ molecule obtained using a single dye laser.	••••••••••••••••••••••••••••••••••••••
pump	frequency (cm^{-1}) v ₂ v ₁ J ₂ J ₁	E ₂ (cm ⁻¹)

	-	-	÷-	T	- · - · -
17317.,168	 14_	0	98.	97	17671.437

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at J_3 =100) for the range of J_3 values encountered in the analysis. In order to obtain the best linear fit, a renumbering of one or more of the triplet clusters (0, Q and S lines) was sometimes in order. These plots were most useful if the vibrational level had been previously recorded as a head-like feature in the low J 3P2C scans. Though there existed a high degree of uncertainty in the pump line assignment for these scans, it made insignificant changes (>0.2 cm^{-1}) to the upper state term values (and hence the band origin) over a large range of J₁ values. Indeed, it was this fact that enabled the head-like features to display their characteristically broad structure. These runs allowed the band origin, and hence the absolute J3 numbering to be well determined. As a final check on the 3P2C assignments, the Dunham coefficients obtained from the concurrent 3PlC analysis (in conjunction with the constants given earlier for the BO_{11}^+ [88] and XO_{12}^+ [89] states) were used to predict the position of the 3P2C lines for each pump line used and, where necessary, reassignments of the observed double beam lines were made. The whole analysis consisted of successive minor refinements that converged upon a self-consistent set of J_3 values and their associated \bullet rotational term values. In this respect, it was analogous. to the classical analysis of a high resolution single photon spectrum.

Table 6.5 gives the number of 3P2C lines and the range of J values assigned for each vibrational level of the

Table 6	.5 ·	Summary	of the 3P2C	Assignments
		for the	F'0 State	

¹²⁹I₂

0

¹²⁷1₂

4

<u>v</u>

0

1

2-

3

•4

S

6

Number of Assignments Range of J Number of Assignments Range of J 81 2-84 0. 40 2-128. ν Ο 2-112 37 • ·10 6-40 22 14-112 -11 6-93 17 10-52 8 6-24 0 2 93-95 28 6-79 80-87

4 . 24-90 0

respective $F'O_u^+$ states of both isotopic molecules. The upper state term values $(E_3(v_3,J_3))$ were fitted to yield the low order Dunham coefficients (equation (4.1)) by means of a multivariate least squares routine (MULREG) which was based on the principles outlined in Chapter 4.1. As the 3P2C data was not extensive enough to yield a precise determination of the first order centrifugal distortion constant $(Y_{0,2})$, this parameter was constrained to its theoretical value, given in the Dunham approximation by equation (6.4);

 $Y_{0,2} = -4(Y_{0,1})^3 / (Y_{1,0})^2 = -2.5 \times 10^{-9} \text{ cm}^{-1}$ (6.4)

The Dunham coefficients obtained from the 3P2C analysis of both molecules for the F'0⁺_u state are listed in Table 0.0. To facilitate comparison of the constants obtained from the separate analyses, the parameters given are applicable to the normal molecule. The relative imprecision of the constants derived from the ¹²⁹I₂ analysis is a direct result of the dearth of 3P2C data garnered for this molecule. A calculation. of the normalized correlation coefficients indicated a high degree of correlation between each pair of coefficients, again a result of the limited extent of the data for this molecule. The results of the combined 3P2C analysis (incorporating data for both molecules) are also given in Table 0.6. As expected, these constants bear close resemblance to those obtained from the more extensive ¹²⁷I, analysis.

	The 3P2C Analysis o			
Dunham Coefficient (cm ⁻¹)	. 127 ₁₂	129 ₁₂ 2	¹²⁷ ₁₂ + ¹²⁹ 1 ₂	
Y _{0,0}	51706.360(56) ^b	51705.4(13)	51706.331(62)	
Y _{1,0}	130.790(36)	131.01(66)	130.750(37)	
Y _{2,0}	- 0.4400(50)	- 0.460(83)	- 0.4327(53)·	
Y _{0,1}	0.021942(11)	0.02210(14)	0.021969(11)	
Y _{1,1} .	-8.19(44)x10 ⁻⁵	-1.20(33)×10 ⁻⁴	-9.39(40)x10 ⁻	
с Ү _{0,2}	-2.5x10 ⁻⁹	-2.5x10 ⁻⁹	-2.5x10 ⁻⁹	
σ^{d} (cm ⁻¹)	0.29	0.34	0.34	
a constant molecule	s refer to $127I_2$ motion can be calculated u	lecule, constants f using equation (4.4	or ¹²⁹ I ₂	
b numbers deviatio	in parentheses corre n	espond to one stand	ard	
c Y _{0,2} was -2.5x10 ⁻	constrained to its 9 cm ⁻¹ (equation (6.	theoretical value	of	
d standard	deviation of fit as	s calculated from e	quation (4.9)	

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Table 6.6

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6.2.2 The 3P1C Analysis

The analysis of the complex 3P1C spectra was facilitat. ed through the use of a Fortran routine (FINDI2). This program, using (initially) the upper state constants obtained from the prior 3P2C analysis, calculated (using equation (4.1)) three photon term values over an appropriate range of v_3 values and compared these values to those derived using the appropriate form of equation (5.4) for all the possible J_3 assignments $(J_3=J_2-2, J_2, J_2+2)$ for each $B0_u^+ - X0_g^+$ resonance transition, as found by SORTCH, for every observed 3P1C frequency. If the difference between a derived and a calculated term value for particular values of v_3 and J_3 was less than . a specified limit, the resonance transition was selected for further scrutiny before a definite spectral assignment was In searching for likely single photon pump transitions, made. account was taken of the polarization analysis of the 3P1C line. For example, only term values for which $J_3=J_2$ were calculated if the multiphoton line had previously been designated as belonging to a two photon Q transition.

Several criteria were used when assigning one or more resonance lines to an experimental 3P1C frequency. The first, as mentioned above, was the difference (ΔE_3) between the derived and calculated three photon term values. This limit was arbitrarily set to $\Delta E_3(\text{cm}^{-1}) \leq |1.0+0.01 J_3|$. A sliding scale was used to recognize the fact that the 'true' and calculated three photon energies may well deviate as J increased, where

any discrepancies in the 3P2C derived constants would become more evident. Also taken into account was the energy difference (ΔE_1) between the single photon resonance frequency and the measured 3P1C frequency. For example, strong lines were not normally assigned to pump transitions for which $|\Delta E_1| > 0.15 \text{ cm}^{-1}$. The value of v_1 and J_1 from which the resonance line originated was also considered. Thus, intense 3P1C lines were not assigned to single photon pump lines that emanated from $v_1 > 2$ or from $J_1 \ge 120$, even if the values of ΔE_1 and ΔE_3 favored the designation.

In many instances more than one assignment could be made for a given 3PlC frequency that satisfied the above selection criteria. If, as was often the case, the line was broad, all of these assignments were incorporated into the subsequent reduction of the data. If, however, the multiphoton line was not noticeably broad the assignment was generally made to the $\mathrm{B0}^+_{\mathrm{u}}$ -X0⁺_g resonance line of lowest v₁.

Once resonance frequencies for several 3P1C lines had been assigned, it became apparent that each measured transition energy was consistently either slightly higher (or lower) than the calculated single photon transition frequency (i.e. pump lines slightly off resonance). It was the experimental frequencies, therefore, rather than the calculated pump frequencies that were used to determine the upper state term values, from equation (6.5);

 $E_3(\hat{v}_3, J_3) = 3 \sigma_{21} + E_1(v_1, J_1)$

(6.5)

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where σ_{21} is the dye laser frequency at which the 3P1C line was observed. As more 3P1C transitions were assigned, the values of v_3 , J_3 and E_3 (v_3 , J_3) were entered, along with the previous single beam assignments and the 3P2C data, into the data file used by the least squares fitting program (MULREG). The slightly revised Dunham coefficients obtained from the subsequent multivariate fit were then used by the FINDI2 routine to search for further 3P1C transitions terminating in the rovibronic manifold of the $F'0_u^+$ state. This iterative procedure was repeated many times before arriving at the final set of assignments.

The assignment of the 3P1C lines was aided by the fact that multiphoton lines originating from a common $BQ_u^+ - XO_g^+$ vibronic transition, if observed, fell with 0-20 cm⁻¹ (depending on J₁) of each other (Figures 6.6, 6.7 and 6.8). The relative magnitudes of the respective rotational constants $(B_1 > B_2 > B_3)$ dictated that these lines usually occurred in the following order with increasing laser frequency: $(R,0)^*$, (P,0), (R,Q), (P,Q), (R,S), and (P,S). As noted previously (Chapter 5.4), the strongest of these transitions were those that were associated with the two photon Q branch ((R,Q) and (P,Q)), as evidenced by the spectra shown in Figures 6.6 and 6.7.

^t i.e. a single photon R branch transition followed by a two photon O transition.

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Figure 6.6

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High resolution 3PlC trace for the 127_{I_2} molecule over the 17175-17205 cm⁻¹ 2^{I_2} region in linearly polarized light. Assignments are indicated for transitions to the F'0⁺_u (v=1) and F0⁺_u (v=56,58) states.



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Figure 6.7 High res molecule

High resolution 3P1C trace for the 127 I molecule over the 17290-17300 cm⁻¹ 2 region in linearly and circularly polarized light.

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As also observed in the 3P2C spectra, the O and S two photon branch lines were, to a first approximation symmetrically positioned about the Q line. At low J (Jx15) many transitions of a given branch (e.g. (R,S)) became simultaneously possible. Coupled with the relatively small separation between the pump lines, this resulted in giving rise to a 3P1C head-like feature. One such feature was observed near 17193 cm⁻¹ for the $129I_{2}$ molecule for the 1-15-1 $(v_{3}-v_{2}-v_{1})$ transition. Resonances at slightly higher J values (J=15-25), while permitting the excitation of multiple transitions of a given type, resulted in a much more extended spectral feature due to the increased separation between adjacent pump lines. These easily recognized resonances typically displayed two broad, closely spaced peaks sometimes followed at slightly lower energies by one or more narrower transitions of much weaker intensity. These features, such as the one observed for the 129 L₂ molecule near 17595 cm⁻¹ (9-17-0), proved 'invaluable to the analysis of the 3P1C spectrum. As J_1 increased, the individual 3P1C branches became resolved, due in part to the fact that fewer resonances occurred: the relatively large energy separations between the respective adjacent rotational levels in the $X0_e^+$, $B0_u^+$ and $F'0_u^+$ states precluded the simultaneous fulfillment of the resonance requirement (equation (5.3)) and the rotational selection rules for all six branches. As J_1 further increased, fewer and fewer of the three photon branch lines from a common $B0_{11}^+ - X0_{c}^+$

vibronic transition were observed. Above $J_1 v120$, usually just one of the possible 3P1C lines was observed. This made assignments involving high J transitions tenuous. Slight changes in the assumed value of the centrifugal distortion constant resulted in a completely new set of high J assignments. For any reasonable value of $Y_{0,2}$, a set of 3P1C assignments could be made that appeared to support this value. So, the same approach as adopted for the two beam analysis was used, and $Y_{0,2}$ was held to its theoretical value (equation (0.4)) of -2.5 x 10^{-9} cm⁻¹.

Extension of the 3P1C analysis above $v_5=4$ (the highest vibrational level observed in the 3P2C bandhead traces) was also difficult. Without 3P2C determined band origins to anchor the 3P1C analysis, a number of plausible assignment pathways were evident. Hampering the analysis above $v_3=4$ was the fact that only a few OODR lines were observed for each value of v_3 (with the exception of the low J assignments for $v_3=9$, $\frac{129}{I_2}$. The final analysis was arrived at by considering the selection criteria carefully for each 3PlC frequency and deciding on which of the possible assignment routes best described the data. In the end, the final analysis incorporated data ranging up to v_3 =11. Most of the 3P1C assignments (Appendix A) involved lines recorded in the R6G dye region. Only for the higher levels $(v_3>9)$ were transitions excited by the C-540A dye laser assigned as terminating on the $F'0_{tt}^+$ state.

Figure 6.8

High resolution 3P1C trace for the $\frac{129}{12}$ molecule over the 17350-17385 cm⁻¹ region in circularly polarized light.



	Ta	b1	e	6	•	7
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Summary of 3P1C Assignments for $F'0_u^+$ State

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		127 ₁₂		129 ₁₂	·
	<u>v</u>	Number of Lin es Found	Range of J	Number of Lines Found	Range of J
	0	2	38-91	6	82-120
	1	. 9	36-99	19	0-91
	2	8	33-132	6	40-93
-	3	5	58-110	9	43-138
	4	4	60-117	7	45-110
	5	0	-	• 5	02-135
	Ó	2	77	3 ·	75-109
	7	2	120-128	5	75-122
	S	0	-	1.	123
	9	2	33-50	13	17-85
	10	0	-	2	90-93
	11		ø2-70	2	57-58

Total

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	Ta	b:	le	6	.8

The 3P1C Analysis of the $F'0_{u}^{\dagger}$ State

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Dunham Coeffici (cm ⁻¹)	ent 127 ₁₂	129 ₁₂	127 ₁₂ +129 ₁₂
Y _{0,0}	\$1706.07(23) ^b	51705.95(18)	51705.98(14)
Y _{1,0}	130.84(11)	130.937(82)	130.911(62)
Y _{2,0}	-0.455(78)	-0.462(68)	-0.4599(49)
	 .		•
Y _{0.1}	0.021966(28) 0.021971(20)	0.021970(16)
Y _{1,1}	-9.59(60)x10	-5 -9.97(39)x10	$5 - 988(32) \times 10^{-5}$
Y _{0,2} c	-2.5x10 ⁻⁹	-2.5x10 ⁻⁹	-2\5x10 ⁻⁹
o(cm ⁻¹)	0.41	0.49	0.46

a constants are given w.r.t. normal moleculeb uncertainty in the last digits that correspond to

uncertainty in the last digits that correspond to one standard deviation

c

parameter constrained to theoretical value (equation (6.4)).

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A summary of the 3P1C analysis of both molecules is given in Table 5.7. The Dunham coefficients gained from the least squares analysis is presented in Table 68, where as before, the molecular parameters are expressed for the normal The excellent agreement between the two sets of molecule. data indicated that the tentative vibrational numbering scheme presented in Chapter 6.1 was correct. The ¹²⁹I, assignments (such as those shown in Figure 6.8) were compatible with the criteria given earlier regarding spectral designations and fully supported the above vibrational analysis. More than twice as many 3P1C lines were assigned to this upper state for the 129_{1} , molecule compared to the 127_{1} , molecule. This was primarily because of the two sets of low J assignments for $v_3=1$ and 9, respectively, for the heavier diatomic.

6.2.3 Discussion of the 3P1C and 3P2C Analyses

Despite the relatively poor S/N ratio of the 3P3C spectra, the standard deviations of the least squares fits using the two beam data alone (Table 5.6) were lower than those using only the 3P1C data (Table 5.8). This was the result of a number of factors. First, the inclusion of many low J(J=0-10) assignments for each vibrational level enabled more precise vibrational energies (and hence vibrational Dunham coefficients) to be calculated from the 3P2C than from the 3P1C lines. This explains the relatively poor agreement between the $Y_{i,0}$ (i=0-2) constants obtained from the combined

•	Final	Dunham Coefficients	for F'0 State
Dunham Coefficient (cm ⁻¹)		127 ₁₂	129 ₁₂
Y _{0,0} ^b		51706.129 (59) ^c	51706.129 (59)
Y _{1,1}		130.932 (26)	129.912 (26)
Y _{2,0}		-0.4614 (25)	-0.4542 (25)
Y _{0,1}		0.0219750 (92)	0.0216340 (91)
Y _{1,1}	·	$-1.008(22) \times 10^{-4}$	-9.846(21)x10 ⁻⁵
Y _{0,2} d		-2.5x10 ⁻⁹	-2.4x10 ⁻⁹

Table 6.9

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 σ (cm⁻¹) 0.41

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constants valid for v = 0-11

a calc. from those given for normal molecule using equation (4.4)

b rel. to pot. min. of ground state

- c uncertainty in last digits corresponding to one standard deviation
- d coefficient constrained to its theoretical value (equation (6.4)).

 $(^{129}I_2 + ^{127}I_2)$ single beam analysis and those from the overall double beam analysis. The two beam operating mode also allows the resonance requirement (equation (5.3)) to be satisfied exactly, hence the observed-minus-calculated three photon energies would be expected to be lower on average than those differences based on the 3P1C assignments. In instances where relatively large deviations were observed, the 3P2C assignment in question was often excluded from subsequent fits, especially if it was a weak (usually 0 or S) line. On the other hand, there was more confidence in the assignments of the generally more intense 3P1C frequencies as most were recorded and measured on at least two separate traces. As a result, larger values of ΔE_3 were more likely to be tolerated, which tended to increase the standard deviation of the fit.

The results of a global fit, which included the 3P1C and 3P2C data gathered for both molecules are given in Table 0.9. Prior to this fit, the ${}^{129}I_2$ data were mass scaled (equation (4.3)) to allow the melding of the data sets. The resulting ${}^{127}I_2$ Dunham coefficients were then converted to the corresponding constants for the ${}^{129}I_2$ molecule using equation (4.4), and these parameters are also listed in Table 6.9.

6.2.4 RKR and FCF Calculations

The vibrational and rotational constants in Table 6.9 were used to generate an RKR potential curve (Chapter 4.4) for the $F'0_{ii}^+$ state. The derived semi-classical turning

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points and the associated energies for each vibrational level $(v_3=0.11)$ are given in Table 6.10.

The potential curve obtained, in conjunction with the corresponding curve for the ${\tt B0}_{\rm u}^+$ state generated from. the data of Hutson [88], was used to calculate a set of FCF's for the two photon $F'0_{u}^{+}-B0_{u}^{+}$ transition. The potential curves of both states are plotted in Figure 6.9. As this electronic transition is not saturated under the experimental conditions employed in this study, (Chapter 5.3.5) the FCF's are useful in determining which spectral transitions will be observed. An array of FCF's for this system is given in Table 6.11 for $v_3=0-11$ and $v_2=10-26$ (the levels involved in this study). These values were calculated for the hypothetical $J_2=0-J_3=0$ transition, and in the following discussion are assumed to be independent of J. The relative magnitudes of the FCF's in Table o.-11 for the most part describe the observed 3PIC and 3P2C spectra. For example, a decrease in the transition strength is predicted between $v_3=2$ and 3 when pumping $v_2=14$. It was indeed found that transitions to $v_5=0$, 1 and 2 gave rise to 3P2C bandhead formation while pumping this intermediate level (via the $1\overline{4}$ -0 B0⁺_u-X0⁺_g band). No such head was observed for $v_3=3$, despite the fact that the probe dye (R6G) laser was still operating efficiently in the region (17367 cm^{-1}) for which the transition to $v_3=3$ was expected to occur.

From Table 6.11, the value of v_3 which gives the maximum overlap for a given v_2 level rises at a much slower

		•3	-	K
	x	Table 6.10	•	
-	RKR	Turning Points fo e F'0 ⁺ u State	r .	· · · · · · · · · · · · · · · · · · ·
<u>v</u>	<u>U(r)</u>	r _{min} (A)	-	r _{max} (A)
5	0.0	3.	477 (15)	
0	65.405	3.417		3.544
1	195.414	3.376		3.598
2	324.501	3.350	•	- 3.037
3	452.664	3.330	× ×	3.070
4	579.905	3.313		3.700
5	706.223	3.299		3.728
Ö	\$51.619	3.280	·	3.754
7	956.091	3.274		3.779
S	1079.641 🔍	3.264		3.803
9	1202.268	3.255	.	3.820
10	1323.973	3.246		3.849
11	1444.754	3.238		3,871

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rate than that with which the dye laser scales the vibrational.manffold of the $F'0_u^+$ state. For example, pumping the rotational levels of v_2 =14 allows the possibility of recording, in the 3P1C mode, transitions to v_3 =0 ($J_3 \sim 130$), v_3 =1 ($J_3 \sim 95$) and v_3 =2_($J_3 \sim 40$). These upper and lower state levels are also coupled by relatively large FCF's (Table 6.11). However, when pumping v_2 =20, the single beam study results in the accessing of $v_3 \sim 15$ (from v_1 =0), well above the FCF maximum at v_3 =3. This explains the absence of bandhead features for this system in the 3P2C spectra when pumping v_2 =20 in this study. During this work, for those pump lines which excited transitions to the v_2 =20 level (Appendix B), the probe laser was only scanned over the 17770-17900 cm⁻¹ region, whereas to observe the 3-20 $F'0_u^+$ -B0 $_u^+$ transition would have required a probe frequencynear 17080 cm⁻¹.

The FCF's of the $F'0_{u}^{+}-B0_{u}^{+}$ system are not, alone, however, sufficient to explain the occurrence or absence of transitions in the multiphoton spectra. Two further points were found to be of importance and are discussed below. Firstly, the two photon transition to a given v_3 level might not be energetically permitted from the pumped v_2 level (i.e. $E_3 \ge 3 \sigma_{21} + E_1$). In the 3P2C mode, of course, this point can be surmounted by simply increasing the probe laser frequency. Secondly, if the multiphoton transition is energetically possible but involves resonances at high J (J \gtrsim 130), the low Boltzmann population of the J₁ level and the fact that relatively

System		-
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		FCF's for	$r F!0_u^+-B0$	u^{+} 127 I_{2}	¹²⁷ I ₂ System		
,	0	1	_ 2	3	4		
	.0668	3 .1047	.0725	.0208	.0000		
	.1256	51040	.0220	.0017	.0278		

 v_2/v_3

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÷

Table 6.11

	11	.1256	.1040	.0220	.0017	.0278	.0419
	12	.1858	.0505 气	.0024	.0429	.0472	.0160
	13	.2131	.0011	.0538	.0544	.0073	.0057
-	14	.1851*	.0405*	.0804*	.0056	.0175	.0417
	15	.1171*	.1518*	.0201*	.0262*	.0521*	.0113
	16	.0507	.2100*	.0184*	.0732*	.0070*	.0158*
	17	.0132	.1535	.1533	.0143	.0289*	.0450*
	18	.0015	.0593	.2295	.0434	.0586	_0004*
	19	.0000	.0094	.1386	.2194	.0000	.0450
	20	.0000	.0001 '	.0307	.2249	.1438	.0190
	21	.0000	.0002	.0005	.0703	.2840	.0628
	22	.0000	.0000	.0009 -	.0166	.1273	.3001
	23	.0000	.0000	.0003	-0027	.0042	.1940
	24	.0000	.0000	.0000	.0010	.0065	.0083
	25	.0000	.0000	.0000	.0000	.0025	.0135
	26	.0000-	0000	.0000	.0000	.0002	.0052
							•

indicates those levels which can be accessed from $v_1=0,1$ ($J_1<140$) in a 3P1C study. ×

Table 6.11 (continued)

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v ₂ /v ₃	antibert 6 an	7	8	9	10	11	
· 10	.0294	.0335	.0233	.0090	.0008	.0013	
11	.0282	.0076	.0000	.0067	.0171	.0217	
12	.0000	.0102	.0242	.0297	.0142	.0033	
13	.0283	.0303	.0132	.0007	.0033	.0132	
14	.0219	.0010	.0063	.0204	0222	.0119	
15	.0032	.0245	.0268	.0100	.0000	.0055	
16	.0378*	.0163	.0000	.0102	.0217	.0173	
17	.0046	.0086*	.0275*	.0192*	.0025	.0021	
18	.0275*	.0315*	.0045*	.0039	.0192*	.0195*	
19	.0271	.0005×·	.0227*	.0246*	.0053*	.0012*	
20	.0084	.0400	.0119	.0014*	.0183*	.0203*	
21	.0376	.0024	.0197	.0276	.0062	.0017	
22	.0150	.0282	.0230	.0013	.0198	.0202	
23	. 2759	.0008	.0077	.0381	.0039	.0040	
24	.2590	. 2296	.0009	.0002	.0339	.0149	
25	.0132	.3111	.1792	.0014	.0131	.0192	
20	.0253	.0175	.3421	.1362	.0000	.0385	

few three photon resonances occur between such highly excited rotational levels (as discussed in Chapter 6.2.2) lessens the probability of observing these transitions in the 3P1C and 3P2C spectra. The interplay between the FCF's, energetics and resonance J values is best illustrated through a few examples. While the FCF for the 0-13 $F'0_{11}^+-B0_{11}^+$ transition is relatively large, it can be shown using equation. (6.5) that it is not possible to access any vibronic levels of the $F'0_{u}^{+}$ state (let alone $v_{3}=0$) from $v_{2}=13$ when operating in the 3P1C mode. However, in pumping v_2 =13 and scanning the probe laser to higher frequencies this transition can be observed in the dual beam mode. While the 0-14 $F'0_{ij}^+$ -B0, transition is energetically possible in a 3P1C scan and also exhibits a large FCF, the resonance condition (equation (5.2)) is fulfilled near J=130. Hence these transitions are expected to be few and of weak intensity. Indeed none were observed in this study.

Those v_3 levels that can be accessed from each v_2 level in a 3P1C study have been marked with an asterisk in Table 6.11 (for transitions from $v_1=0-1$ and $J_1=0-140$).

6.2.5 Dissociation Products

As outlined in Chapter 2, earlier studies [91] have shown the existence of many lower lying $(Y_{0,0} \sim 40000 - 47000 \text{ cm}^{-1})$ ion pair states correlating to one or the other of the $I^{-}({}^{1}S) \leq I^{+}({}^{5}P_{2,1,0})$ dissociation limits. The question arises; can

the $F'0_{u}^{+}$ state also be confidently assigned to ionic atomic products at large internuclear separations, based on data obtained at small values of r?

A simple but accurate method of determining dissociation energies from an analysis involving the vibrational levels near the bottom of the potential well has been given [158], and is outlined below. It has been shown to be particularly accurate when applied to electronic states that dissociate ionically.

Long range theory [159,160] predicts that near dissociation, the attractive (right hand) limb of an ion-pair potential curve is given by the following equation;

$$U(r) = D - \frac{C_1}{r}$$
 (6.6)

where D is the dissociation energy relative to the potential. minimum, C_1 is a known constant $(1.16141 \times 10^5 \text{ cm}^{-1} \text{ Å})$, and r is the internuclear separation. This theory also predicts that the vibrational term values (G(v)) in this region can be represented as in equation (6.7);

$$G(v) = D - X_0(1)(v_D - v)^{-2}$$
 (6.7)

where $X_0(1)$ is a constant $(1.2693 \times 10^{10} \text{ cm}^{-1} \text{ for } {}^{127}\text{I}_2)$ and v_D is a negative integration constant.

In the general treatment for the determination of dissociation energies [158], an auxillary function is introduced in equation (6.7) to describe the behaviour of the

vibrational levels further down the potential well. However, for a heavy molecule such as iodine, this factor is effectively unity [158].

For levels well removed from dissociation, equation (6.7) can be expanded in terms of v to give equation (6.8);

$$G(v) = D - X_0(1) v_D^{-2} - 2 X_0(1) \cdot v_D^{-3} v - 3 X_0(1) v_D^{-4} v^2$$
(6.8)

The experimentally observed vibrational term values can also be expressed in terms of powers of v as in equation (6.9);

$$S(\mathbf{v}) = \sum_{i=0}^{N} G_{i} \mathbf{v}^{i}$$
(6.9)

Each expansion coefficient, G_i , can be expressed in terms of the vibrational Dunham coefficients $(Y_{i,0}, i=0,1,...)$. By equating like powers of v in equations (6.8) and (6.9), a set of simultaneous equations are obtained which can be solved to yield D. A simplification of this method, which has been shown to lead to little loss in accuracy [158], is to truncate the above expressions at N=2 (i.e v²). This approach (the so-called G3 approximation) leads to the following expression for D;

$$D = G_0 + X_0(1) v_D^{-2} = Y_{0,0} + \frac{1}{2} Y_{1,0} + \frac{1}{4} Y_{2,0} + X_0(1) v_D^{-2}$$
(6.10)

where v_{D} is given by equation (6.11);

$$x_{1} = - \left[2X_{0}(1)/G_{1} \right]^{1/3} = - \left[2X_{0}(1)/(Y_{1,0} + Y_{2,0}) \right]^{1/3}$$
(6.11)

From the data given in Table 6.9, a value of $v_D = -579.5$ was obtained from equation (6.11), which enabled a diabatic dissociation energy, D, of 89570 cm⁻¹ to be calculated. This value is about 4% larger than the nearest ion-pair asymtote limit, $I^+(^1D) + I^-(^1S)$ at 85930 cm⁻¹. As the next possible set of ionic dissociation products occurs near 104000 cm⁻¹, (all the 0_u^+ states having been assigned to the lower lying D < 85930 cm⁻¹ ionic limits), the assignment of this state as $F^*0_u^+(^1D)$ is reasonable. This conclusion was also reached by Ishiwata et al. [114].

The possibility exists, however, that the $F'O_u^+$ is covalent or Rydberg in nature, though the observed vibrational frequency argues against the latter alternative. The method presented above does not give accurate values of D for states that dissociate covalently. In fact the approach fares little better than the Birge-Sponer [17] method of extrapolating to the dissociation limit. Application of this treatment allows D to be calculated from equation (6.12);

$$D = \frac{Y_{1,0}^2}{4Y_{2,0}} + Y_{0,0}$$
(6.12)

Using this formula and the data in Table 6.9 a value of 60995 cm^{-1} is obtained for D. The nearest atomic asymtote (Figure 2.2) is the ${}^{2}P_{3/2} + ({}^{3}P_{2})6s[2]_{5/2}$ limit which occurs

at 67180 cm⁻¹ relative to the potential minimum of the ground state. Given the fact that the Birge-Sponer approach invariably leads to an overestimation of D [17] (for example, a value of 18890 cm⁻¹ for D was calculated using equation (6.12) for the $X0_g^+$ ground state, whereas the actual value is 12547 cm⁻¹), the assignment of the F' 0_u^+ state to the $I^-(I^-S) + I^+(I^-D)$ ionic products is all but certain.

6.2.6 Discussion

Subsequent to the preliminary report of this work [161], a further study by Ishiwata et al. [162] appeared in the literature concerning the $F'0_{tr}^+$ state. A two beam study conducted in a similar manner as our investigation resulted in levels as high as $v_5 = 38$ being accessed for the $\frac{127}{1}$, molecule. No spectra were recorded for the ¹²⁹I, molecule nor were the frequencies of further 3P1C lines in addition to those given earlier [114] reported. The Dunham coefficients quoted by these workers are listed in Table 6.12. Comparison of the vibronic energies and rotational constants for the levels (0-11) common to our and the above study showed good agreement (Table 6.13), especially for the lower (v < 4)levels for which the bulk of our assignments were made. A spectral simulation, which utilized the latest Dunham coefficients for the $F'0_{U}^{+}$ state (Table 6.12), and the relevant constants of the $B0_{u}^{+}$ [88] and $X0_{g}^{+}$ [89] states, was used to calculate the frequency distribution of the 3PlC spectrum.

Table	6.	12
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Dunham	Coefficient	ts for the	$F'0_{u}^{+}$	State
from th	e Work of	<u>Ishiwata</u> et	<u>al.</u>	[162]

(cm⁻¹)

ΰ.

Y _{0,0}	51706.237 (2)
Y 1,0	131.00041 (83)
Y _{2,0}	-0.516270 (143)
Y _{3,0}	4.2640 (104) x 10^{-3}
Y 4,0	-4.5797 (330) x 10 ⁻⁵
Y _{5,0}	2.8381 (376) x 10^{-7}
Y _{0,1}	0.02194899 (46)
Y _{1,1}	-9.2508 (99) x 10 ⁻⁵
Y _{2,1}	8.359 (79) x 10^{-7}
¥3,1	-8.550 (167) x 10 ⁻⁹
Y _{0,2}	-2.632 (37) x 10^{-9}

 σ (cm⁻¹) = 0.031

Digits in parentheses correspond to one standard deviation in the last quoted digits

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Comparison of Calculated Vibrational and Rotational Constants Obtained from our Study and that of Ishiwata et al. for $F'0^+_u$ State

	Our Stu	dy	Ishiwata	a et al.
v	$\frac{E_3(cm^{-1})^a}{2}$	$B_{3} \times 10^{2} (cm^{-1})$	E ₃ (cm ⁻¹)	$B_3 x 10^2 (cm^{-1})$
0	51771.480 (50) ^b	2.1925 (8)	c 51771.609(2)	2.190294(46)
1	51901.489 (38)	2.1824 (7)	51901.590(2)	2.181208(48)
2	² 52030.575 (34)	2.1723(6)	52030.576(3)	2.172281(52)
ī.	_52158.739 (36)	2.1622 (5)	52158.590(4)	2.163509(58)
4	52285.980 (40)	2.1521(6)	52285.655(5)	2.154885(66)
5	52412.298 (44)	2.1421 (7)	52411.791(7)	2.146406(75)
6 ·	52537.693 (49)	2.1320 (9)	52537.020(9)	2.138066(86)
7	52662.165 (55)	2.1219(10)	52661.361(11)	2.129859(98)
8	52785.715 (66)	2.1118 (12)	52784.832(14)	2.121782(112)
9	52908.342 (82)	2.1017 (14)	52907.452(18)	2.113827(127)
10	53030.046 (104)	2.0917(16)	53029.238(22)	2.105992(145)
11	53150.827 (133)	2.0816 (18)	53150.206(27)	2.098269(163)

a rel. to pot. min. of ground state

b uncertainties (lo) calculated by propagating uncertainty associated with the Dunham coefficients in Table 6.9 and Table 6.12-

c uncertainties were calculated neglecting the cross terms in the error calculation as the covariances between the Dunham coefficient were not listed by these authors

While not all these predicted transitions were observed in our study (because of Boltzman and Franck-Condon reasons), those that were, had been assigned in accord with the calculated spectrum.

The present study of the $F'0_u^+$ state has incorporated experimental data obtained in the 3P1C and 3P2C operating modes for ${}^{127}I_2$ and ${}^{129}I_2$. While Ishiwata et al. [114], made a strong case for the assignment of absolute vibrational quantum numbers on the basis of the agreement between the observed and calculated FCF distribution for the $F'0_u^+-X0_g^+$ system, only through studies involving isotopic substitution can the numbering be absolutely determined.

The present isotopic study has also confirmed the provisional numbering $(v_3=0)$ given by Viswanathan [75] for the upper level observed in emission to several high lying levels of the ground state.

6.5 Upper State of the ϕ System

6.3.1 Introduction

The analysis of the high resolution spectra of the ϕ system was aided by the inclusion of a 3P1C head-like feature (Figure 6.10) near 18239 cm⁻¹ (24-0, single photon bandhead) for the ¹²⁷I₂ molecule into the previously given 3P2C bandhead analysis (Chapter 6.1). An excellent fit resulted when the upper state vibrational level for this head was assigned as n=44 (equation (6.2)). Excited state vibrational term

Figure

Figure 6.10 3P1C bandhe molecule ne onance with

3PlC bandhead recorded for the $^{127}I_2$ molecule near 18239.1 cm⁻¹ (in resonance with the 24-0 B0u-X0g bandhead). Upper level assigned to n=44 of the ϕ state. As will be explained in Chapter 6.3.4 this level corresponds to v=96 of the F0⁺_u state.



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values could then be calculated over a large range of frequencies (51500-54800 cm⁻¹) for the normal molecule. These rotationless energies (E₃) were compared to those calculated ⁻ previously from all the numerous local fits to the 3PIC line frequencies. Two of these earlier analyses were found to give vibrational term values that agreed well with those generated when the 3PIC bandhead was included in the above fit. A local fit to six 3PIC lines in the vicinity of 17780 cm⁻¹ resulted in an E₃ value of 53479.61 cm⁻¹ and a rotational constant (B₃) of 0.01844 cm⁻¹. The former value agreed well with the interpolated energy of the n=25 level (E₃=53480.1 cm⁻¹). Another group of five 3PIC lines clustered about 18290 cm⁻¹ could be assigned as terminating on n=47. A least squares analysis of these lines lead to a rotational constant of 0.01678 cm⁻¹.

Preliminary Dunham coefficients obtained from the bandhead data and the above pair of local fits were then employed in the FINDI2 program to search for further 3PIC transitions terminating on the upper state of the ϕ system. As the bandhead data had fortuitously included both the low and high energy regions of the recorded spectrum, the 3PIC analysis did not involve extensive extrapolation of the observed low J heads. The analysis was therefore much more straightforward than that of the F'0⁺_u state, where only data at low v were available from the bandhead runs.

6.3.2 The 3PIC Analysis of the 127 I₂ Molecule

Due to the extensive and advantageous distribution of the head-like three photon features, the 3PlC analysis could be conducted without an initial 3PZC high J analysis. Indeed, most of the 3PlC assignments were made prior to the commencement of the analysis of the two beam high J spectra.

Initially, an assumed value of $Y_{0,2} = -5x10^{-9}$ cm⁻¹ was used as calculated from equation (6.4) in searching for further 3P1C assignments. Unlike the corresponding analysis of the F'0⁺_u state, this Dunham coefficient was statistically determined, albeit poorly, due to the large number of high J₃ assignments which could be made. However, whether this least squares value was an accurate estimate of the 'true' distortion coefficient or simply a reflection of the high J assignments made using the original assumed value, is unknown.

By far the majority of the 3P1C frequencies assigned to this upper state were excited using C-540A dye. Of the 173 single beam OODR transitions recorded over this particular dye profile, 106 were eventually assigned to the upper state of the ϕ system (some more than once). Examples of spectra recorded over this dye profile are shown in Figures 6.11 and 0.12. A further 54 3P1C frequencies in the R6G dye region were also assigned to this state, a few of which are evident in Figure 6.6. In assigning the single beam transitions, the selection criteria given previously (Chapter 6.2.2) were followed.

Data were collected for all but 10 vibrational levels

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Figure 6.11

High resolution 3P1C trace for the $^{127}I_2$ molecule recorded in the region of Goodman's 'origin band' [102] with linearly polarized light. D0⁴ vibrational numbering made using Wieland's [38] scheme. All other assignments are due to the F0⁴ state which will be shown (Chapter 6.3.4) to be the identity of the ϕ state (v=n+52). The D0⁺ state will be discussed in Chapter 6.4.





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High resolution 3PlC trace for the 127_{I_2} molecule recorded over the 17815-17840 2 cm⁻¹ region in linearly polarized light. D0^u state numbering made using Wieland's [38] scheme. All other assignments are due to the F0^u state which will be shown (Chapter 6.3.4) to be the identity of the Φ state (v₂=n+52). The D0^u state will be discussed in Chapter 6.4.



over the range, n=-1-50. A summary of the 3PlC assignments for the normal molecule is given in Table 6.14. The molecular constants, obtained from the 3PlC assignments to this state are listed in Table 6.15. These parameters are given with tespect to the lowest observed level for which data was collected (n=-1). As this level, in all probability, did not correspond to v=0, the constants in Table 6.15 are not, strictly speaking, Dunham coefficients. This has been indicated by using lower case letters to denote these quantities in this table.

6.3.3 The 3P2C Analysis of the $127I_2$ Molecule

With the single colour analysis well underway before the start of the 3P2C analysis, the initial uncertainty in the pump assignments was not as great as had been the case for the $F'0_{u}^{+}-B0_{u}^{+}-X0_{g}^{+}$ system. The 3P2C lines were again observed to occur in triplets, verifying the 0_{u}^{+} electronic symmetry assignment made on the basis of the 3P1C polarization measurements. As with the single beam spectra, the 3P2C analysis spanned the R6G and C-540A (Figure 6.13) dye profiles. In the former dye region, the probe laser often excited transitions from a common pumped $B0_{u}^{+}$ level to both the $F'0_{u}^{+}$ (¹ D) state and the upper state considered here, as for example, shown in Figures 6.1, 6.4 and 6.5.

The pump and probe frequencies for which 3P2C lines were assigned as terminating on the upper state are given in

	Su Assign	mmary of the $3Pl$ ments for the 12		
	<u>3P1C</u>		<u>3P2C</u>	•
	Number of Assignments Made	Range of J	Number of Assignments <u>Made</u>	Range of J
L	. 1	131	0 -	-
)	4	43-54	6	6 -10
L	ο .	-	6	6-62
2	2	54-64	34、	2-62
5	0	-	21	2-61
Ļ	8	36-139	8	2-61
5	1	66	-11	2 - 54
)	3	53-100	9	4 - 7 5
	0	- .	0	-
	2 `	37-134	5	34-44
-	2	64-73	15	15-50
	1	. 28	4	10-43
	0	- '	2	41-98.
	15	10-101	6	6-51
	0	· -	3	6-10
	0.	-	•	
	· 1	68	•	
	1	79	-	
	5	47-64		
	1	62		
	0 .	-		
	1	81 ;		
•	7	48-103	-	-
	1	72		
	6	34-108		
	3	84-116		
	9	39-138		
	6	70-148	8	0 - 2 2

Table 6.14

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		· ·	·	. ,
27	19		6-130	22
28	5		68-77	. 33
29 .	9		26-123.	30
30	5		48-87	5
31	• 10		60-120	. 8
32	7 .	•	54-68	10
33	1		95	. 0
34	5		29-99	1
35	5		29-86	
36	ົ 6		48-137	
37	4		52-117	
38	4		52-155	
39	6		23-138	
40	6		33-86	·
41	0			
42	2		100-139	
43	2		56	
44	1		121	•
45	1		99	
46	0		-	
47	• 6	•	41-121	
48	0		- ·	
49	1	-	88	
50	3	1	95-121	

Total 188

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0-59 0-92 1-96 65-98 65-86 72-118 -105

Table (5.15
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Molecular Constants from the 3PlC and 3P2C Analysis of ${}^{127}I_2$ Molecule for the Upper State of the Φ System (rel. to n = -1) -184

Molecular Constants			
(cm ⁻¹)	3P1C	3P2C	3P1C + 3P2C
У _{0,0}	51477.62(23) ^a	51477.76(12)	51477.890(95)
`y _{1,0}	78.107(32)	78.142(31)	78.098(18)
У _{2,0}	-0.0910(14)	-0.0945(22)	-0.09166(83)
^y 3,0	-0.191(17)x10 ⁻³	-0.132(45)x10 ⁻³	-0.177(11)x1
^y 0,1	0.019647(26)	0.019683(28)	0.019659(16
^y 1,1	$-0.6243(58) \times 10^{-4}$	-0.620(11)x10 ⁻⁴	-0.6190(44)x
^y 0,2	-0.42(11)x10 ⁻⁸	-0.67(26)x10 ⁻⁸	-0.522(77)x1
σ (cm ⁻¹) 0.53	0.37	0.46

figures in parentheses correspond to one standar deviation in the last quoted digits.

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Figure 6.13

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3P2C trace for the $^{127}I_2$ molecule in the C-540A dye region. The assignments are all made to the F0⁺ state which will be shown (Chapter 6.3.4) to be the identity of the ϕ state (v_3 =n+52)

pump freq. (cm ⁻¹)	v ₂	vl	J ₂	J_1 .	$E_2(cm^{-1})$
17888.342	20	0	16	i7	. 17899.659
17888.441	20	0	22	21	17905.678
17888.405	21	0	84	85	18160.908
17888.496	21	0	90	89	18187.067



Appendix B. The summary of the 3P2C assignments is included in Table 6.14. The derived molecular constants from the 3P2C analysis are listed in Table 6.15, again with respect to n = -1.

6.3.4 Spectral Assignment of the Upper State

An independent analysis (3P2C and δ P1C) of the ¹²⁹I₂ spectra was not feasible due to the small number of observed 3P2C head-like features for this three photon excited state. Mass scaling of the ¹²⁷I₂ constants was also not possible as the vibrational numbering was not known. Therefore, as a precursor to the ¹²⁹I₂ analysis, a study was undertaken to attempt to assign the upper state to the excited vibrational levels of a lower lying ion-pair state. In particular, the 0_u^+ states $(D0_u^+({}^{3}P_2))$ and $F0_u^+({}^{3}P_0))$ were considered as likely candidates in view of the polarization analysis.

Previous work concerning the $D0_u^+$ state [38, 48] suggested the vibrational spacing of this state to be much less than the $\sim 75 \text{ cm}^{-1}$ observed in this region of the spectrum. Hence our attention was concentrated on the $F0_u^+$ as the probable assignment of the upper state of the ϕ system. Spectroscopic data for the low vibrational levels of the $F0_u^+$ state has been obtained in emission by a number of workers for the ${}^{127}I_2$ molecule [39, 66, 72]. A previous investigation had also studied this system ($F0_u^+$ - $X0_g^+$) in emission for the ${}^{129}I_2$ molecule [72]. An MPI study by Williamson and Compton [109] resulted in the recording of an extensive series of bands that they tentatively assigned to resonances involving very highly excited levels of the $F0_u^+$ state (equation (2.3)). The vibrational spacing ($\sqrt{75}$ cm⁻¹) observed in our work fell between those reported at low v ($\sqrt{97}$ cm⁻¹) and at very high v ($\sqrt{58}$ cm⁻¹). In view of this, attempts were made to match our data with that of Viswanathan [75], obtained at low v (0-8) and with that of Williamson and Compton [109] at high v (m=(0+k)- (58+k) , where m is the absolute vibrational quantum number and k is an integer constant to be determined).

As an initial step, the low v_5 data were integrated into our analysis. The experimental term values given by Viswanathan [75] are given in Table 6.16. Polynomial fits were made for a number of alternative numbering schemes (by letting the level designated as n=0 assume the values v=40-60 inclusively). The fits were judged not only on their standard deviations but also on how well the calculated values of $Y_{0,0}$ and $Y_{1,0}$ compared with the values obtained from the low v data alone (Table 6.16). While increasing the order of the polynomials in (v+1/2)had little effect on reducing the standard deviation, better agreement for the above constants was found compared to the values returned by the lower order $(3^{rd} and 4^{th})$ expressions. In the end, a sixth degree fit was found to best represent the amalgamation of both sets of data with n=0 set equal to v=52. The results of this final fit are listed in Table 6.17. To avoid listing a large number of insignificant figures for the higher order terms (to ensure the faithfulness of the equation

Table 6.16

Viswanathan's [75] Low v Data for the F0⁺ State

Dunham Coefficient (cm⁻¹)

Y _{0,0}		47217.64 (38)
Y _{1,0}		96.53 (20)
Y _{2,0}		0.477 (21)
· ·	σ = 0.37	cm ⁻¹

Experimental data:

•	·===1,
<u>v</u> ~	E(Cm)
0 .	47158.52
1 .	47254.22
2	47349.18
3	47442.92
4	47534.79
5	47626.89
Ó	47717.47.
7	47808.12
8	47896.42

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Dunham Coefficients Resulting from Amalgamation of the Low v(0-8) and Intermediate v(52-102) Data for the F'0⁺_u State

•	5	
Dunham Coefficient	(cm ⁻¹	<u>)</u> .
Y _{0,0}		47217.707 (31)
Y _{1,0}		96.967 (5)
Y _{2,0}		-0.64303 (6)
, ^Y 3,0		0.01408 (2)
Y _{4,0}	. ·	-0.182 (7) x 10^{-3}
¥5,0		• 0.117 (3) x 10^{-5}
^Y 6,0		-0.3 (1) x 10^{-8}
Y _{0,1}		0.022855 (22)
Y _{1,1}	·	-0.6248 (26) x 10
Y0,2		-0.483 (63) × 10 ⁻⁸
c	= 0.	46 cm^{-1}

 $Y_{1,0} - Y_{0,0}$ inclusive were constrained in fit, see text.

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in reproducing the upper state energies, the following approach, originally due to Le-Roy (as quoted in reference [57]) was used. The highest order term was successively rounded off to the least significant figure, and with this term held fixed, the data were refitted, and the procedure was repeated until only $Y_{0,0}$ was allowed to float.

The conclusion regarding the absolute numbering of the upper state was the same whether all the ${}^{127}I_2$ data (as in Table 6.17) or just the bandhead data were used. In addition, the calculated ${}^{129}I_2$ vibronic energies (equation (4.4)) based on this numbering scheme were in good agreement with the previously obtained experimental results [72] at low v. As a result of these findings, the φ state was assigned as being the F0⁺_u (${}^{3}P_0$). This assignment meant that the current study represented the first rotational analysis of this ion-pair state, as all previous work had been confined to vibrational analyses.

The Dunham coefficients listed in Table 6.17 glso enabled the calculation of the higher lying $^{129}I_2$ vibrational term values. Comparison of these calculated vibronic energies with the observed values (Table 6.2) fixed the upper state vibrational quantum numbers of the recorded $^{129}I_2$ 3P2C bandheads as v=58, 60 and 61 respectively.

6.3.5 <u>3PlC and 3P2C Analysis of ${}^{129}I_2$ Molecule for $F0_u^+$ State With the absolute vibrational numbering determined, the</u>

3P1C transitions terminating on the $F0_u^+$ (3P_0) state could be readily determined using the mass scaled Dunham coefficients derived from the analysis of the ${}^{127}I_2$ spectra. Again, most of the assigned 3P1C lines were due to lines excited over the C-540A dye profile. Figure 6.14 shows the spectral assignments made in the 17710 cm⁻¹ region in linearly and circularly polarized light. Assignments were also made in the R6G dye region as evidence by Figure 6.8.

The assignments appeared to confirm the adopted vibrational numbering scheme, as evidenced, for example by the observation of a strong 3PlC line where a (P,Q) or (R,Q) transition was predicted on the basis of the $^{127}I_{2}$ constants.

A summary of the ${}^{129}I_2$ single beam assignments is given in Table 6.18, and the derived constants are listed in Table 6.19. The Dunham coefficients were calculated relative to $v_3=0$, and since the lowest vibrational level for which data were obtained was $v_3=52$, the vibrational constants, particularly Y_{0-0} , are poorly determined.

The 3P2C analysis of the $F0_u^+$ state for the ${}^{129}I_2$ molecule was again hindered by the lack of experimental data. The pump and probe frequencies at which 3P2C transitions were observed are again listed in Appendix B. The limited extent of two beam data necessitated the constraining of the centrifugal distortion constant to its theoretical value $(5x10^{-9} \text{ cm}^{-1})$, as it was not statistically determined when allowed to float. The Dunham coefficients returned by the

Figure 6.14

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High resolution 3P1C trace for the $^{129}I_{2}$ molecule over the 17705-17730 cm⁻¹ $^{-2}$ region in linearly and circularly polarized light. All assignments are made to the F0⁺_u state.



Table ·	6.18
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Summary of the 3P1C and 3P2C Assignments for the ¹²⁹I₂ Molecule

•	<u>3P1C</u>		<u>3P2C</u>	
<u>v</u> 3	Number of Assignments Made	Range of J	Number of Assignments Made	Range of J
52	. 1	109		
53	1 /	78		•
54	0	• -	•	
55	1	. 80		
56	2	40-49	•	•
57	¥ 0	-	1	57
58	1	56	2	5-10
59	1	118	0	-
60	7	31-145	9	2-26
61	· 2	75-76	10	0-93
62	4	32-130	1	93
63	: 1	69		
64	7	17-102		
65	4	71-121	•	
66	l	131		
67	- 2	104-i11	•	
68	4	88-124		
69	1	114		
70	- 4	83-148		
71	6	51-103		
72	1 [']	79		
73	0	-		
74	1	105		
75	0 · .			
76	0			
77	5	41-52		
78	0	-		

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Table	6.18	(continued)
· · · ·		•
79	2	95
80	3	70-79
81 [.]	5	_ 30-125
82	- 3	60-108
83	. 3	64-88
84	1	92
85	5	8-90
86	2	68-86
87	7	43-109
88	1	25
89	2	84-119
91	1	90
92	3	87-129
93.	1	59
96	_1	118 •

Total 115

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Results of the 3P1C and 3P2C Analysis of the $F0_u^+$ State, $^{129}I_2$

Dunham Coefficient	•		· · ·
(cm ⁻¹)	3P1C	3P2C	Overall
Y _{0,0}	47283, (13) ^a	47311. (144)	47280.(12)
Y _{1,0}	85.90(55)	85. (5)	86.03(52)
Y _{2,0}	-0.062(76)	-0.076(41)	-0.064(71)
^Y 3,0	-0.187(34)x10 ⁻³	•	-0.177(32)x10 ⁻³
Y _{0,1} .	0.023038(69)	0.0239(20)	0.023022(55)
Y _{1,1}	~ -0.6538(87)x10 ⁻⁴	-0.77(33)x10 ⁻²	• 0.6518(75)x10
Y _{0,2}	-0.31(13)x10 ⁻⁸	-0.500x10 ⁻⁸	-0.30(12)x10 ⁻⁸
σ(cm ⁻¹)	0.47	0.24	0.44
•	· •		•

Dunham coefficients evaluated with respect to $v_3=0$ and are. applicable to the $12^{7}I_2$ molecule and are valid for $v_3 = 52-96$

a figures in parentheses correspond to one standard deviation in the last digits

b value fixed due to limited amount of data

MULREG routine are listed in Table 6.19.

6.3.6 Overall Fit of the 3P1C and 3P2C Data

A least squares fit that incorporated the single and double beam data of both molecules yielded the Dunham coefficients shown in Table 6.20. As before, the ${}^{129}I_2$ data was mass scaled before the global fit that included a total of 583 individual assignments. The resulting Dunham coefficients, applicable to the ${}^{127}I_2$ molecule, were then converted to the corresponding values of the ${}^{129}I_2$ molecule using equation (4.4). The relatively large uncertainty in the vibrational coefficients is again the result of the extrapolation from the lowest level for which data was collected (v=51) to the bottom of the potential well.

It was found that the variation of the rotational constant with v+1/2 could be described well by a first order fit even though data was collected over a range of 51 upper state vibrational levels. Extrapolation to the bottom of the well predicted a rotational constant (0.022867 (27) cm⁻¹) somewhat larger (\sim 15%) than the other known values for the ion-pair states of I₂ (Table 2.2).

6.3. Incorporation of Data from Some Previous Studies into the Current F0, State Analysis --

Following the completion of the 3PlC and 3P2C analysis for both molecules, an attempt was made to incorporate the MPI data of Williamson and Compton [109] into the analysis

Table (5.2	0 f
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Dunham Coefficients for ${}^{127}I_2$ and ${}^{129}I_2$ for the F0⁺_u State, Relative to v₃ = 0

	- 2	12
Y. 0,0	47282. (4)	47282 (4)
Y _{1,0} -	_ 85.95 (15)	85.28 (15)
Y _{2,0}	-0.630(20)x10 ⁻¹	-0.620(20x10 ⁻¹
^Y 3,0	-0.1835(87)x10 ⁻³	-0.179(85)x10 ⁻³
1	х. 19. С	
^Y 0,1	0.022867 (27)	0.022512 (27)
Y _{1,1}	$-0.6264(35) \times 10^{-4}$	-0.6119(34)x10 ⁻
N.	$-0.471(64) \times 10^{-9}$	$-0.456(67) \times 10^{-9}$

a constants valid for v=51-102

b coefficients calculated from ${}^{127}I_2$ results using equation (4.4)

-

С

uncertainty corresponding to one standard deviation in the last quoted digits.

of the $F0_u^+$ state. As a preliminary step, only our bandhead data and the calculated frequencies of the highly excited vibrational term values from the formula given by these workers (equation (2.5) and in Table 6.21) were used in the fits. Excellent low order (4th and 5th) polynomial fits were obtained when the lowest level observed in the MPI study was assigned to v_3 =150. The same conclusion was reached when the bandhead data was replaced by the ${}^{127}I_2$ 3P1C and 3P2C data. These particular fits were far more convincing than the similar study conducted previously on-the low v data [75] and our data.

Following this encouraging initial fit. the data of Viswanathan [75], all our data for both molecules and the high vibrational data were fitted to a common expression in polynomials of v+1/2. Instead of using the calculated term values to represent the MPI data, another approach was used. The calculated vibrational energies were taken as exact, and to each term value was added a randomly generated, normally distributed error consistent with the quoted standard deviation of $\sim 0.5 \text{ cm}^{-1}$ [109]. Several sets of data synthesized in this manner were constructed, and the conclusions to be discussed below were found to be invariant with respect to which set of high v data was used. Each generated array of term values was fitted to a polynomial, of the same order (5th) used originally by Williamson and Compton to represent their experimental findings, as a check on the validity of the data set. Table 6.21 shows the result of one such fit, and for comparison the

Table 6.21

A Sample Synthesized Data Set for Williamson and Compton's MPI Data [109]

Calcu <u>Gener</u>	lat ate	ed Coefficients from d Data (cm ⁻¹)	Williamson-Compton		
y _{0,0}	=	58166.86 (29)	58166.84*		
y _{1,0}	Ξ	56.508 (68)	56.3701		
У _{2,0}	=	-0.1331 (47)	-0.13152		
y _{3.0} ;	=	0.84×10^{-3} (12)	+0.8119x10 ⁻³		
У. _{4,0}	÷	-0.71x10 ⁻⁵ (10)	-0.68462x10 ⁻⁵		

 $\sigma = 0.44 \text{ cm}^{-1}$

 $\sigma < 0.5 \text{ cm}^{-1}$

19

Williamson and Compton gave the 0-0 bandhead frequency $(58087.92 \text{ cm}^{-1})$, the above value of $y_{0,0}$ is relative to the potential minimum of the ground state

values given by Williamson and Compton are also displayed.

A series of polynomial fits ranging from 4th to 9th order in (v+1/2) were conducted using the low v(0-8) data, our intermediate v (3P1C and 3P2C data for both molecules, with numbering fixed such that n=0 equaled v=52) data, and a synthesized set of high v data (for which the lowest level was allowed to assume the values v=140-'55 inclusively). The minimum standard deviation for each degree of fit was consistently given with the lowest member of the MPI progression set at v=150. It was found that an 8th order fit best described the variation of the above data with v+1/2, as determined by the criteria outlined in Chapter 6.3.4. The results of one overall fit (utilizing the high v data set summarized in Table 6.21) are given in Table 6.22. As done previously, the higher order vibrational coefficients were rounded off successively and the data refitted.

In conclusion, the MPI data almost certainly represent an extension of the upper state of ϕ system, with a separation between the respective lowest observed levels of $\Delta v=99$ (150-51). Less certain, but highly likely was the assignment of this upper state to the FO_u⁺ (³P₀) ion-pair state. The difficulty in being more certain was mainly due to the paucity of data at low v (Table 6.16).

In the course of a multiphoton ionization dip study of the ${}^{127}I_2$ molecule, Cooper and Wessel [110] observed four single beam transitions that were resonance enhanced at the

Table 6.22

Results of 1s Fit to All the Available Data for the $F0^+_u$ State

Dunham Coefficients (cm⁻¹)

	•
Y _{0,0}	47218.419 (29)
Y _{1,0}	96.588 (3)
Y ₂ _0	-0.6036 (4)
Y _{3,0}	0.0131131 (2)
Y4,0	-0.18331 (7) x 10^{-3}
Y _{5,0}	0.149 (1) x 10^{-5}
Y _{6,0}	-0.710 (8) x 10 ⁻⁸
Y _{7,0}	0.184 (3) x 10^{-10}
Y _{8,0}	-0.2 (1) x 10^{-13}
Y _{0,1}	-0.022835 (30)
Y, 1,1	-6.221 (38) x 10 ⁻⁵
Y _{0,2}	-4.61 (72) x 10^{-9}

Vibrational constants valid for v=0-208 Rotational constants valid for v=51-103 Higher order vibrational coefficients constrained. See text.

Table 6.23

Assignment of Multiphoton Ionization Dip Transitions Observed by Cooper and Wessel [110]

Observed freq. (cm ⁻ 1) ⁺	d Single P Resona Assignm		Photon Ou ance ec ment ⁺ of		Our ed Va of v	Assign alue 5, J ₃	Three Photon Energy		
	<u>J</u> 2	<u>J</u> 1	<u>v</u> 2	<u>v</u> 1	<u>v</u> 3	J ₃	E _{obs}	Ecalc	
Ì8395.1	16	17	26	0	103	16	55304.315	55304.244	
18393.9	24	23	26	0	103	24	55309.456	55309.625	
18350.4	58	59	26	0	102	58	55288.404	55288.957	·
18347.0	65	64	26	0	102	65	55304.130	55303.219	
•		x					. •	-	

values given are from Table 1, reference [110]

- derived from single photon resonance assignment using equation (6.5), energy rel. to pot. min. of ground state
- b. calculated energy from our ^{127}I molecular constants for the F0_u state (Table 6.15)². Estimated uncertainty in each of the calculated energies is $^{+}$ 0.5 cm⁻¹.

one photon $(B0_{\rm u}^+)$ and three photon levels. The unknown three photon state was labelled as k. The frequencies and the single photon assignments of the above lines are listed in – Table 6.23. At the time of their study, these workers postulated that the intermediate (4 photon absorption process overall) k state was, in fact, high vibrational levels of the $F0_{\rm u}^+$ state. Our extensive rotational analysis has allowed the verification of this assumption. After consideration of the calculated three photon term values (equation (6.5)) based on their assignments and the range of permissible J_3 values $(J_3=J_2+2, J_2+1)\ldots J_2-2)$, it was concluded that the resonant transitions involved. $v_3=102$ and 103 of the $F0_{\rm u}^+$ state (Table 6.23).

6.3.8 <u>Discussion</u>

After our conclusion had been reached regarding the absolute vibrational numbering of the $F0_u^+$ state levels, we received a preprint of a further MPI study of the ${}^{127}I_2$ molecule. In this work, Hoy and Brand [163] were able to gather rotationally resolved spectra for a large range of upper state vibrational levels, which they tentatively numbered from v=0 to v=220. They were able to show that this upper state was the same one responsible not only for the ϕ system 3P2C bandhead observed in this work [161], but also the multiphoton resonances first reported by Williamson and Compton [109]. In accord with our conclusions, Hoy and Brand labelled this upper state as the $F0_u^+$ (${}^{3}P_0$). Their analysis also confirmed the relative vibrational numbering scheme we had determined for the low, intermediate and high v_3 data. But, as with the $F'0_u^+$ (${}^{1}D$) state analysis, only our isotopic work was able to confirm the absolute vibrational assignments.

This latest MPI study also gave evidence for a strong perturbation in the range v_3 =15-40, as indicated by anomalous values of E_3 and B_3 in this region. This explained the high order fit needed to merge the low v_3 data with those gained from this work. It also explained the difficulty we experienced in assigning the 3PIC lines excited in the Kiton Red region. Several attempts were made to assign these transitions to the $F0_{u}^{+}$ state with several different vibrational numbering schemes . (besides the one adopted above) but with no success. As Hoy and Brand [163] were not able to record resolved rotational structure in this region, their results were not directly applicable to our Kiton Red analysis. In connection with the previously mentioned relative weakness of the Kiton Red excited transitions, it is interesting to note that the cut off in emission for the $F0_{u}^{+}-X0_{g}^{+}$ system occurs near v=15 [72], just at the onset of the perturbation.

By default, the perturbing state responsible for the anomalies in the rovibronic manifold of the $F0_u^+$ state was assigned to the higher lying $F'0_u^+$ (¹D) state by Hoy and Brand. Their spectral simulations predicted that while the $F0_u^+$ state is heavily perturbed due to this interaction, the $F'0_u^+$ state

exhibits a smooth variation of T_{1} and B_{2} with y. They did, however, expect that the analysis of the Fiou state would yield relatively large values for the Dunham coefficients $Y_{3,0}$ ($v9x10^{-3}$ cm⁻¹) and $Y_{2,1}$ ($v1x10^{-6}$ cm⁻¹). While our data were not extensive enough for the $F'0_{11}^+$ state to permit a. valid test of this expectation, the data obtained by Ishiwata et al. [162] were. Their analysis yielded a Y3.0 value of 4.3x10⁻³ cm⁻¹ and a $Y_{2,1}$ value of 8.4x10⁻⁷ cm⁻¹. These results can be compared to those gained from an extensive analysis of a typical ion-pair state, the $EO_g^+({}^{3}P_2)$; for which $Y_{3,0}=5.7 \times 10^{-5}$ cm^{-1} and $Y_{2,1}=2.4x10^{-8}$ cm^{-1} . As can be seen, the comprehensive analysis of the $F'0_{ij}^+$ state appears to support the suspicions of Hoy and Brand, regarding the perturbing state. However, as these workers mentioned, interaction with a state of Rydberg character rather than with the $F'0_{11}^+$ state cannot be ruled out.

6.3.9 RKR and FCF Calculations.

An RKR curve for the $F0_u^+$ state was obtained using the vibrational constants given in Table 6.22. Rotational data were available only for the limited range of v_3 values 51-103, and hence turning points could only be determined for these v_3 values. In order to extend the potential curve to the true minimum ($r_e=3.58\text{Å}$), the value of $Y_{0,1}$ as found by Hoy and Brand [163] was constrained in a least squares fit of all the data; and the higher order rotational coefficients

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up to and including $Y_{3,1}$ were determined, to smooth the variation of B_3 with v_3 . The resulting turning points are listed in Table 6.24. These values are in good agreement (within $\frac{1}{2}$ 0.02A) with those given by Hoy and Brand [163]

The wavefunctions describing the excited $F0_u^+$ vibrational levels observed in this study are highly oscillatory. These excited levels also span (r_{max}, r_{min}) a relatively large interval of r. Together, these facts result in the fluorescence from the excited v_3 levels being more or less evenly distributed over an extensive range of lower state levels. As a consequence, the individual FCF's are expected to be small and to show relatively little variation with v_2 for a given v_3 progression. These expectations were borne out when the FCF's for transitions between v_3 =51-103 and v_2 =10-27 ($B0_u^+$ state) were calculated. In contrast to the FCF's determined for the F' 0_u^+ - $B0_u^+$ transition (Table 6.11), for a given v_3 progression the maximum FCF was, typically, >0.01 and the difference between the largest and smallest values was only about two orders of magnitude.

It was found that for the $F0_u^+ - B0_u^+$ system, it was not the FCF but rather whether or not a transition was energetically possible that determined the form of the observed spectrum. For example, in the single beam spectra for which the rotational transitions of the 20-0 band were in resonance with the dye laser frequency, only transitions to v_3 =76-81 were energetically possible (over the range J=0-150). The analysis of the 3P1C traces resulted in the assignment of transitions to v_3 =77-81
Table 6.	24
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RKR Turning Points for the $F0_u^+$ (${}^{3}P_0$);State

•		. 0		ò
<u>v</u> ·	$U(r) cm^{-1}$	r _{min} (A)		$r_{max}(A)$
-0.5	0.0	• •	3.582	•
· · · · 0	47.994	3.508		3.656
10	960.609	3.236		3.945
20	1811.732	3.102		4.117
30	2631.755	3.010	· · ·	4.265
40	3433.697	2.942	•	4.403
50	4220.990	2.892		4.536
60	4992.587	2.853		4.609
70	5446.030	2.823	•	4.803
80	6479.049	2.800		4.939
90	7190.154	≈ 2.781		5.076
100	7878.631	2.764		. 5.214

c

from the pumping of various J_2 values within the 20-0 band. The 76-20-0 three photon transition involves transitions near J \sim 150, and these were not observed due to their sparcity and relative weakness.

6.3.10 Reinterpretation of the "Goodman" Bands

There has been considerable controversy in the literature over the past few years concerning the existence of bound states of $^{127}I_2$ between 30000 and 40000 cm⁻¹. excited electronic While some experimental evidence has implied that such states exist, as outlined in Chapter 2,3, other work has resulted in conclusions to the contrary [74]. One of the more prominent studies that claimed to give proof for bound states in this region was the MPI study of Lehmann, Smolarek and Goodman [102]. The apparent bandhead features recorded under low resolution by these workers have been found in this study under high resolution to be composed of individual transitions in the main involved high $(J_3>25)$ rotational excitation. which These groupings of spectral lines have been shown in the preceding sections to be attributable to three photon transitions terminating on excited vibrational levels of the $F0_{11}^+$ $({}^{5}P_{0})$ state. For example, Goodman's 'origin band' at 17881.0 cm⁻¹ has been shown to be primarily due to the 81-20-0 transition, for which 8 3P1C lines were assigned over the range $J_{3}=26-36$ (Figure 6.11).

However, it remains to show how the characteristic

appearance of the low resolution single beam MPI (and fluorescence) spectra arises, which led the earlier investigators to erroneous conclusions. The following argument has been found satisfactory in explaining the appearance of the $F0_u^+-B0_u^+-X0_g^+$ spectrum recorded over the C-540A dye profile.

For any 3P1C transition, the resonance requirement must hold (equation (5.3)), which can be expressed as below,

$$2 [T_2 + B_2 J_A^* - (T_1 + B_1 J_A^*)] = T_3 + B_3 J_A^* - (T_2 + B_2 J_A^*)$$
(6.13)

where J_A^* represents the product, $J_A(J_A+1)$, and J_A is the J value of the hypothetical three photon Q branch transition, i.e. $J_A-J_A-J_A$. The following treatment ignores the small effects of centrifugal distortion. Expansion of equation (6.13) leads to an expression (equation (6.14)) for J_A^* .

$$J_{A}^{*} = \frac{3T_{2}^{-2}T_{1}^{-}T_{3}^{-}}{-3B_{2}^{+}2B_{1}^{+}B_{3}^{-}}$$
(6.14)

If this value. is negative, then the transition $v_3 - v_2 - v_1$ is not energetically possible.

It will be assumed that each of the rotational constants is invariant over a few adjacent vibrational levels and that the respective vibrational separations are also constant over this limited range. These approximations allow the rotational term values of any neighbouring vibrational level to be given with respect to a chosen reference level as in equation (6.15);

$$E_{i}(v_{i}+n_{i},T_{i}) = \tilde{E}_{i}(v_{i},J_{i}) + n_{i} \Delta G_{i}$$
 (6.15)

i = 1,2 or 3

where n_i is the difference between the respective vibrational numbers of a given level and the reference level, and ΔG_i represents the local vibrational separation for state i. The above definitions allow the J value (J_B) for which any other three photon resonance transition occurs, to be calculated with respect to an arbitrarily chosen v_3 - v_2 - v_1 transition;

$$J_{B}^{\star} = \frac{3T_{2}^{-2}T_{1}^{-T_{3}^{+}} - 3n_{2}\Delta G_{2}^{-2}n_{1}\Delta G_{1}^{-n_{3}} - n_{3}\Delta G_{3}}{(-3B_{2}^{+2}B_{1}^{+}B_{3}^{-})}$$
(6.16)

This equation correctly predicts that for a specific $B0_u^+ \cdot X0_g^+$ transition (i.e. $n_1 = n_2 = 0$), the J value at which resonance occurs in the upper state decreases (due to the last term in the numerator) as v_3 (n_3) increases, when the denominator is positive.

The expressions for J_A^* and J_B^* can then be substituted separately into the following expression to give the single photon frequency (σ_{21}) at which the three photon resonance occurs.

$$\sigma_{21} = E_2 - E_1 = T_2 + B_2 J_x^* - [T_1 + B_1 J_x^*]$$
(6.17)

where x = A or B

The energy difference, α , between the reference 3P1C $v_3(J_A) - v_2(J_A) - v_1(J_A)$ frequency and the general $v_3 + n_3(J_B) - v_2 + n_2(J_B) - v_1 + n_1(J_B)$ single beam three photon transition frequency is given by equation (6.18).

$$\alpha = n_1 \Delta G_1 - n_2 \Delta G_2 + (B_2 - B_1) \left[\frac{-3n_2 \Delta G_2 + 2n_1 \Delta G_1 + n_3 \Delta G_3}{-3B_2 + 2B_1 + B_3} \right]$$
(6.18)

Equation (6.18) allows the study of the relative separation of 3PlC transitions (with respect to a chosen reference transition) as a function of n_1 , n_2 and n_3 . For example, if we consider the $v_3+1-v_2-v_1$ three photon transition (i.e. $n_3=1$, $n_2=n_1=0$) the spacing of the 3PlC line groupings will be given by (for $v_1=0$, $v_2=20$ and $v_3=80$)

$$\alpha = 0 - 0 - 0.012 \left[\frac{0 + 0 + 72}{0.0165} \right] = -52 \text{ cm}^{-1}$$
(6.19)

Hence the 81-20-0 and 80-20-0 transitions are predicted to be separated by approximately 52 cm⁻¹, in good agreement with the experimentally observed value of 50.9 cm⁻¹ between the respective (P,Q) transitions.

Of further interest is the case where $n_1=0$, $n_2=1$ and $n_3=2$, which results (again for the above reference level) in a value of 1.6 cm⁻¹ for α . Therefore the $v_3+2-v_2+1-v_1$ transition will lie in the same spectral region as the $v_3-v_2-v_1$ transition. This can be seen in Figures 6.11 and 6.12. The combination of the above examples predicts a series of 3PIC lines separated by approximately 50 cm⁻¹ for transitions

emanating from a common value of v_1 . Further, if we consider the $v_3^{+2} - v_2^{+2} - v_1^{+1}$ transition, a value of 11 cm⁻¹ for a is calculated from equation (6.18). Hence, at least a partial overlap of the reference 3PIC transitions from $v_1^{=0}$ is expected with those that originate from $v_1^{=1}$ for which $n_2^{=2}$ and $n_3^{=1}$. An example of this is given in Figure 6.12, in which 3PIC lines due to the 80-20-0 and 82-22-1 transitions are identified. Although only a single reference level has been considered in this discussion, the extent of the observed spectra (Figures 5.4 and 5.5) argues that equation (6.18) holds over a large range of v_3 and v_2 values.

Equation (6.18) predicts a separation of $\sim 80 \text{ cm}^{-1}$ between the $v_3+1-v_2-v_1$ and $v_3-v_2-v_1$ transitions for the $F'0_u^+-B0_u^+-X0_g^+$ system. Such a progression was not observed for at least two reasons. First, the single beam energetically accessible v_3 levels did not, in general, exhibit large FCF's for the two photon transition from a given v_2 level. In other words the FCF parabola did not coincide with the v_3-v_2 transitions marked with an asterisk in Table 6.11. Second, the overlap with the $F0_u^+-B0_u^+-X0_g^+$ system and the fragmentary systems in the R6G dye region obscured any regular structure due to the $F'0_u^+-B0_u^+-X0_g^+$ system alone.

Other experimental evidence has been offered for the existence of a stable electronic state between 30000 and 40000 cm⁻¹. In particular, a third harmonic generation (THG) spectrum obtained by Tai et al. [107] over the 17900-18600 cm⁻¹

region for the $127I_2$ molecule was proposed to have involved resonances at the one photon $(B0_{11}^{+} \text{ state})$ and the two photon level with a bound state. Based on this assumption, molecular constants were derived (equation (2.4)) for the two photon _excited 0_{σ}^{+} state. Although the THG spectrum recorded by Tai et al. was not duplicated in this laboratory, a couple of points concerning their analysis are worth noting. First, the bandwidth of the dye laser used in their single beam study was $\sim 0.5 \text{ cm}^{-1}$, almost as broad as the output of the BDL employed in our low resolution studies. We have already shown that spectral analyses based on such investigations are suspect. A review of the spectral assignments (single photon resonance frequencies) in Table I of reference [107], shows that several. of their pump assignments differ from the observed resonance frequency (ΔE_1) by more than 1.5 cm⁻¹ or 3 times the laser On the other hand, the pump assignments made in linewidth. the present study were usually, within one and certainly no greater than two linewidths of the NDL, of the experimental 3P1C frequency. Our calculations show that on average, 40 individual pump assignments are possible within $\frac{1}{2}$ 1.5 cm⁻¹ of the observed multiphoton frequency, in this region of the spectrum, if transitions from $v_1 = 0-2$ and $J_1 = 10-150$ are considered. In our experience, any one of a number of sets of results are possible when the number of plausible resonance assignments is so large. A least squares fit of Tai and coworkers data based on their assignments (ignoring the obvious

typographical errors) showed that almost 30% of the assignments resulted in observed-minus-calculated values of $\Delta E_{2} \ge |1.0 \text{ cm}^{-1}|$, which was the arbitrary cutoff limit used in the present study.

An alternative interpretation of the THG offered by Tai et al. was the possibility of a virtual two photon state and a real three photon terminus. However, this was rejected by these workers on the grounds that the Cordes bands (Chapter 2.2) do not occur in the spectral region probed by the dye laser ($\sqrt{53700-55800}$ cm⁻¹). However, it is well known that they do extend into this region [38]. These workers also failed to comment on the possibility of another ion-pair or a Rydberg state serving as a final bound state. However, in all fairness, extensive data were not available for these states at the time of their THG study.

Much was made of the 100 cm⁻¹ separation between the stronger features in the THG spectrum, which was attributed to hot band structure arising from the ground state (\sim half the vibrational interval of 213 cm⁻¹) and cited as evidence for a real two photon excited state. But, as was shown above, the separation of spectral features in a low resolution resonance enhanced single beam study must be regarded cautiously.

Tai et al. also recorded an MPI spectrum of this region (17900-18600 cm⁻¹), which curiously bears no apparent resemblance to the MPI spectrum observed by Lehmann et al. 1 [102] and which was later recorded during the present study using fluorescence detection. A preliminary analysis of this spectrum by Tai and colleagues on the assumption the upper terminus was the $D0_{u}^{+}$ (${}^{3}P_{2}$) state resulted in a B₅ value of $0.0338 \stackrel{+}{} 0.0010 \text{ cm}^{-1}$ for $\dot{v}_{3} = 15$. But, it is now well established that the rotational constant ($Y_{0,1}$) for the $D0_{u}^{+}$ state is >0.021 cm⁻¹ [57]. Hence, it would seem that a reinvestigation of the THG and MPI spectra recorded by Tai et al. under high resolution is in order.

A strong, broad feature in the THG spectrum near 18064 cm⁻¹ (Figure 2 of reference [107]) has the appearance of a bandhead. This frequency coincides with the low J transitions of the 22-0 $B0_u^+ \cdot X0_g^+$ band. Based on this pump assignment an E_3 value of about 54210 cm⁻¹ (relative to $v_1=0$, $J_1=0$) is obtained, in good agreement with the calculated E_3 value of 54204 cm⁻¹ for v=194 of the upper state of the Cordes bands, as given by Wieland's [38] quantum formula (equation (2.2)).

In summary, while a number of investigations (outlined in Chapter 2,3) have purported to show the existence'of stable electronic states in the 30000-35000 cm⁻¹ region for the iodine molecule, they are all dependent on the validity of the conclusions reached by Lehmann et al. [102] and Tai et al. [107]. In this work, it has been shown unequivocally that the analysis of Lehmann and colleagues is in error. Further, serious doubts can be raised about the analysis of the THG spectrum offered by Tai and co-workers.

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6.4 The $D0_u^+$ State 6.4.1 Introduction

Following the conclusion of the single beam analyses of the F'0⁺_u and F0⁺_u ion-pair states there remained many unassigned 3PIC lines. Attempts were made to assign these lines to three photon transitions terminating on other electronic states. In particular, the third and last remaining low lying ion-pair state of 0⁺_u symmetry $(D0^+_u({}^{3}P_2))$ was considered a likely candidate. Certainly other studies [109, 163] have demonstrated that multiphoton resonances can be observed to populate the F0⁺_u and D0⁺_u states under the same experimental conditions.

Due to the relatively low electronic excitation energy of the $D0_u^+$ state $(Y_{0,0} \sim 41027 \text{ cm}^{-1})$ [57], three photon transitions within the range of single photon frequencies used in this study would result in high vibrational excitation $(v_3 > 150$, based on Wieland's bandhead formula given in equation (2.2)). The only previous rotational analysis involving these high lying levels was made possible by calculating the energies of the upper state levels populated by the 1830.4Å atomic iodine line [62, 63]. As only five $D0_u^+$ rovibronic levels are excited (Table 6.25), a rigourous least squares analysis to yield vibrational and rotational Dunham coefficients was not possible. However, these studies offered a convenient starting point for the present analysis.

2.16



Table 6.25



a original numbering of Wieland [38]. b rel. to pot. min. of ground state.

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c _one standard deviation in last quoted figures.

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6.4.2 The 3P1C Analysis of the $D0_u^+$ State

The unassigned 3P1C lines in the high frequency (C-540A) end of the OODR spectrum recorded for the $\frac{1277}{12}$ molecule were the initial target of our investigation. The preliminary stage of the analysis involved looking for pairs of closely spaced unassigned 3PIC transitions. On the assumption they were due to (R,Q) and (P,Q) branch lines, values of T_3 and B_3 were calculated for plausible pump assignments. The value of B3 was then compared to the corresponding value estimated by Tellinghusien et al. [63] which was 0.012139 cm⁻¹ for $v_3 = 204$ (equation (2.2)). A few such sets of assignments gave rotational constants that were of similar magnitude to the above value. However, one particular pair of assignments merited further consideration. The OODR lines recorded at the frequencies 17921.545 cm^{-1} and 17910.816 cm^{-1} were assigned to the (P(68),Q) and (R(78),Q) transitions respectively (pumped via $B0_u^+ - X0_g^+$ 21-0 band). A two point fit gave a B_3 value of 0.012784 cm⁻¹ and a T₃ result of 53881.11 cm⁻¹. The latter value was found to be in very good agreement with the calculated value of T_3 for $v_3 = 187$ ($T_3 = 53882.50$ cm⁻¹) from Wieland's [38] bandhead formula (equation (2.2)). These two assignments in conjunction with the three photon term values in Table 6.25 allowed the calculation of a preliminary set of Dunham coefficients. For the purpose of this and all succeeding fits, $Y_{0,2}$ was constrained to the theoretical value of -4×10^{-9} cm⁻¹ (equation (6.4)). The preliminary coefficients

were used by the FINDI2 program to search for further 3PlC transitions involving the $D0_{11}^+$ state for $v_z = 185-208$. Once all plausible assignments were made for the intervening $v_{\overline{3}}$ levels, the search was gradually extended to encompass lower and higher levels. In making 3P1C assignments, the criteria outlined in Chapter 6.2.2 were again followed. A total of 31 assignments were made for the $^{127}I_2$ molecule, most of which involved weak, previously unassigned multiphoton lines. Two of these assignments are evident in Figure 6.11. A summary of the single beam assignments is given in Table 6.26. The results of the least squares analysis on the E_3 values derived from the above OODR transitions plus the five upper state term values given by Tellinghuisen et al. (Table 0.25), are presented in Table 6.27. The first column of results in this table is based on Wieland's numbering scheme (equation (2.2)) for the v_3 levels. The second column gives the calculated parameters that were obtained from the same data when the lowest observed level ($v_3 = 170$) was designated as v=0. These latter constants are differentiated from the Dunham coefficients given in the first column, by the use of lower case letters.

No lines in the ${}^{129}I_2$ single beam spectra could be definited assigned to the $D0_u^+$ state, though there remained many unassigned 3PIC frequencies. In view of the relative weakness of the 3PIC lines assigned for the ${}^{127}I_2$ molecule and the limited extent of the high resolution C-540Å spectrum recorded for

Ta	ble	: 6.	26.
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Summary of 3P1C Assignments for the D0⁺ State of ¹²⁷I₂

ν ^a	Numbe	r of Lines A	ssigned	Range of J
170	•	1		69
171	* .x	4		26-42
175	·	3		85-98
176		4	• *	58-71
178		1	,	67
179		3		32-44
180	· · ·	2	•	75-110
182	۰.	2		46-46
185		. 2	•	107-119
187	. ·	2		67-79
188		4	•	33-46
211	· •	2		25-37
214		1		87
		· · ·		

Total .31

а

numbering according to Wieland [38].

	3P1C Lines of the	$= \frac{12}{12}$ I 2 Mo	olecule
Relati	ve to $v_3 = 0 \ (cm^{-1})$	Relativ	$ve to v_3 = 170 (cm^{-1})$
Y _{0,0} ª	41558. (258) ^b	у _{0,0}	53144.56 (22)
Y _{1,0}	88.3 (41)	У _{1,0}	49.905 (40)
Y _{2,0}	-0-130 (21)	^y 2,0	$-0.957(24) \times 10^{-2}$
Y _{3,0}	$0.67(38) \times 10^{-4}$	y _{3,0}	0.62(39)x10 ⁻⁴
Y _{0,1}	0.01852(27)	У _{0,1}	0.013269 (65)
Y _{1,1}	-0.311(15)x10 ⁻⁴	_ ^y 1,1	-0.312(15)x10 ⁻⁴
Y _{0,2} d	-0.4×10^{-8}	^y 0,2	-0.4x10 ⁻⁸
	$\sigma = 0.33 \text{ cm}^{-1}$		$r = 0.33 \text{ cm}^{-1}$

Table 6.27

Dunham Coefficients from Analysis of the

a rel. to pot min. of ground state. Fit used original numbering given by Wieland ($v_3=170-214$). Fit includes upper state term values given by Tellinghuisen et al. [63] for $v_3=204$, 205 and 208.

b: numbers in parentheses correspond to one standard deviation

c constants evaluated relative to the lowest observed level, i.e., $v_3=170$ becomes v=0. Constants rel. to pot. min. of ground state.

d value constrained to theoretical value (equation (6.4)).

the $^{129}I_2$ molecule, this was not surprising.

The selection of pump and probe frequencies used in the double beam experiments did not allow the sampling of the v_3 levels (170 $\leq v_3 \leq$ 214) observed in the 3P1C study. Careful scrutiny of the 3P2C spectra failed to give evidence for unassigned 0, Q, S lines separated by approximately 25 cm⁻¹ (probe dye laser frequency) from similar triplet sequences.

6.4.3 Incorporation of the Results of Emission Studies

Tellinghuisen [55] and Koffend et al. [56] have published investigations of the $D0_{11}^+$ -X0_{d}^+ system in which emission from the low vibrational devels of the upper state has been observed. The former study also included observation of the corresponding transitions for the $^{129}I_2$ molecule. Table 6.28 summarizes the findings of these two studies. The result of an unweighted least squares fit in powers of $v_3 + 1/2$ is also given in Table 6.28. A weighted fit was not possible as Koffend et al. [56] did not quote the standard errors of their results. On the basis of the number of significant figures quoted, their values were apparently an order of magnitude more precise than Tellinghuisen's. Presumably this was because Koffend et al. did a rotational analysis and thus gave the positions of the band origins, whereas Tellinghuisen's analysis was based on bandhead data. In the combined least squares fit, presented in Table 6.28, and in all subsequent fits incorporating the emission data this distinction was ignored (separation of bandhead and band origin $\sim 0.05 \text{ cm}^{-1}$).

Table 6.28

Summary of Previous Work Concerning $D0_{u}^{+}-X0_{e}^{+}$ System in Emission

Dunham Coefficient (cm⁻¹)

Y 0,0	a		41027.3	(1.3)
Y _{1,0}			95.32	(96)
. ^Y 2,0			-0.16	(13)
	σ	=	2.03	1

¹²⁷₁₂

	Rollend et al. [50]	<u>Terringnuisen [55]</u>	
	$\frac{E_3 (cm^{-1})}{E_3 (cm^{-1})}$	$E_{3} (cm^{-1})$	E_3 calc. (cm ⁻¹)
•	-	41074.9(6) b	41074.9
	- ·	41169.5(4)	41169.9
	41266.49	41264.2(7)	41264.0
•		41358.0(7)	41359.0
	-	-	41453.0
	41545.29	-	41546.8
	41641.23	-	41640.2

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	- <u>Te</u> llinghuisen [55]	
v	$E_{3} (cm^{-1})$	E_3 calc. (cm ⁻¹)
0	41074.8(4)	41074.6
1	41167.3(5)	41168.8
2.	41264.7(15)	41262.8

results of unweighted fit to data below, $^{129}I_2$ data mass scaled, coefficients applicable to $^{127}I_2$ molecule. Uncertainties correspond to one standard deviation.

uncertainty (one standard deviation) as quoted by Tellinghuisen [55].

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Subsequent to his emission study of the $D0_u^+ \cdot X0_g^+$ system, Tellinghuisen [57] concluded on the basis of spectral simulations of the $D0_u^+ - X0_g^+$ bound-free emission and Wieland's analysis [38], that the numbering used in the latter work was either correct or too high by a single unit. Although he was unable to determine which of the alternative schemes was correct, he slightly favoured the lower numbering scheme.

In an attempt to determine the true absolute numbering of the upper state levels, least squares fits in $v_3 + 1/2$ were undertaken, which incorporated the low v_3 emission data (Table 6.28) and those obtained for high v_3 , i.e. the results given by Tellinghuisen (Table 6.25), those obtained in this study and the bandhead data obtained from Wieland's absorption work.

Synthetic data sets were generated, in the manner previously given (Chapter 6.3.7), for Wieland's bandhead frequencies. These data sets were obtained by setting the desired standard deviation of the generated values in the range $1.0 - 1.5 \text{ cm}^{-1}$, following the example of Tellinghuisen [57]. Again, the synthetic sets of data were fitted to polynomials in $v_3 + 1/2$, and the least squares coefficients compared to the original constants given by Wieland [38]. Table 6.29 displays the results of one such fit The apparent lack of agreement between the two sets of constants can be traced to the extrapolation involved from the lowest observed level, $v_3=98$, to $v_3=0$.

In the least squares fits that encompassed all the

Table 6.29	
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Synthetic Data Set for $D0_u^+$ Levels $v_3 = 98-259$ Based on Formula Given by Wieland [38] 225

	l s. Fit to Syn- thesized Data Set	Wieland's Constants
Y _{0,0}	40492. (105) ^b	40731.0
Y`1,0	110.2 (32)	104.165
Y _{2,0}	-0.314 (38)	-0.2422465
Y _{3,0}	$0.88(22) \times 10^{-3}$	0.453864x10 ⁻³
Y _{4,0}	-0.195(63)x10 ⁻⁶	-0.70641x10 ⁻⁶
^Y 5,0	$0.206(71) \times 10^{-8}$	0.641845x10 ⁻⁹ -

 $\sigma = 1.20 \text{ cm}^{-1}$

a rel. to pot. min. of ground state.

1

b numbers in parentheses represent one standard deviation.

Table 6.30

Dunham Coefficients from Simultaneous Fit of All Data Pertaining to $D0^+_U$ State and Comparison to Parameters Obtained by Tellinghuisen [57]

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	,	
	This Study	Tellinghuisen [57]
Dunham	Coefficients (cm ⁻¹)	Dunham Coefficients (cm ⁻¹)
Y _{0,0} a	41027.363 (249) ^b	41026.4 (4)
Y _{1,0}	-94.9875 (14)	95.66 (21)
Y _{2,0}	-0.10777 (2)	-0.1345 (50)
Y ₃ ,0	-0.599(3)x10 ⁻³	-0.214(43)x10 ⁻³
Y _{4,0}	0.388(6)x10 ⁻⁵	$0.13(2) \times 10^{-5}$
Y _{5,0}	-0.99(1)x10 ⁻⁸	$-0.17(2) \times 10^{-8}$
Y _{6,0}	$0.10(2) \times 10^{-10}$	-
Y _{0,1}	0.020775	0.020775
Y _{1,1}	$-0.514(2) \times 10^{-4}$	-0.5×10^{-4}
Y _{2,1}	$0.4(2) \times 10^{-7}$	0.372×10^{-7}
Y _{0,2} d	-4.0x10 ⁻⁹	$\sqrt{-4.8 \times 10^{-9}}$ for $v_3^{e} = 203$
σ = 1.1	4 cm^{-1}	

- a rel. to pot. min. of ground state, all vibrational coefficients constrained except Y_{0,0} and Y_{1,0}.
- b uncertainty in final digits that corresponds to one standard deviation.
- c fixed to value given by Tellinghuisen [57].
- d theoretical value (equation (4.4)).
- e numbering adopted in this study and [57]; i.e. reduction by one unit of that used by Wieland [38]. D₃ given by Tellinghuisen et al. [63].

available data for the $D0_{11}^+$ state, the numbering at low v_{3} was kept fixed and the relative numbering of the high v--levels varied. . While a fifth order fit for the vibrational coefficients (the same degree fit as used by Wieland) was inconclusive as to the correct numbering, a sixth degree fit slightly favoured the reduction by one unit of the numbering used by Wieland [38]. This was indicated by comparison of the standard deviations of the fits employing different numbering schemes and the agreement of the least squares estimates of $Y_{0,0}$ and $Y_{1,0}$ with those values determined from the low v_3 data (Table 6.28). This preferred numbering scheme was invariant with respect to which of the synthesized data sets were used. It also made no difference if the $Y_{0,1}$. coefficient was held fixed to the value given by Koffend et al. [56] and Tellinghuisen [57] or allowed to float. The results of a typical sixth order fit, which used the synthesized data given in Table 6.29, are presented in Table 6.30. As done previously, the higher order terms have been rounded off to the least significant digit and constrained to those values in all subsequent fits. For comparison the constants obtained by Tellinghuisen [57] are also displayed on Table 6.30.

6.4.4 RKR Curve of the DO, State

The vibrational and rotational constants given in Table 6.30 were used to construct an RKR curve for the $D0_u^+$ state. The RKR turning points and associated energies (for

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J=0) for selected vibrational levels in the range $v_3=0-210$ (new numbering) are listed in Table 6.31.

The comments made earlier (Chapter 3.9) regarding the calculation of FCF's for the $F0_u^+-B0_u^+$ system are even more pertinent to the $D0_u^+-B0_u^+$ transition and hence these values were not determined for the latter system.

	KKK Turning Poin	nts for the DO State	· · ·
<u>ې</u> د 10	$\frac{\mathrm{U}(\mathrm{r})\mathrm{cm}^{-1}}{\mathrm{O}\mathrm{O}\mathrm{O}}$	r _{min} (Å)	r _{max} (A)
-0 . 5		5,576	
- 10 -	47.605	3.504	3.653
10	989.378	3.277	3.967 -
20	1902.895	3.179	4.158
30	2787.528	3.110	4.320
40	3642.721	3.055	4.470
50	4468.166	3.010	4.613
60	5263.784	2.971	4.753
70	6029.707	2.936	4.890
80	6766.255	2.904	5.027
90	7473.913	2.876	5.163
100	8153.319	2.850	5.301
110	8805.234	2.826	5,439
120 .	9430.530	2.803	5.579
130	10030.161	2.782	5.721
140	10605.151	2.762	5.864
150	11156.568	2.743	6 010
160	11685.505	2.725	6 157
170	12193.061	2.709	6 307
180	12680.319	2.693	6 150
190	13148 327	2 678	- 6 617
200	13598 077	2.670	0.013
- 210			0.769
	14030.482	2.031	6.928

KR Turning Points for the DO State

Table 6.31

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CHAPTER 7 CONCLUSIONS

In this chapter, the conclusions derived from this study will be summarized, and some suggestions for future work outlined.

A laser spectrometer has been developed that has proven to be a useful tool for the study of non-linear transitions in gaseous species. . Specifically, this system has been employed to obtain the most extensive three photon excitation spectrum of molecular iodine yet reported. Rotationally resolved single (3P1C) and double (3P2C) beam spectra have been observed for $^{127}I_{2}$ and $^{129}I_{2}$. Analysis of the high resolution traces has resulted in a combined total of nearly 1000 3P1C and 3P2C assignments, which have enabled the three lowest lying 0, ion-pair states to be characterized. In addition, the results of several investigations by prior workers have been incorporated, to extend and consolidate the present ana-The three photon spectra of the $129I_2$ molecule are ... lvsis. reported for the first time, and have enabled absorbute vibrational quantum numbers to be assigned. This work has also resulted in the building of a strong case against the existence of bound states lying between the ${}^{2}P_{1/2} + {}^{2}P_{1/2}$ asymptotic limit and the lowest cluster of ion-pair states [Figure 2.2]. Much work remains to be done, however. From the

3P2C bandhead data alone (Chapter 6.1), at least three more highly excited states are contributing to the observed spectra. Our attempts to correlate the unassigned heads to the undesignated 3P1C and 3P2C lines were not conclusive. Further work is already underway in this laboratory to characterize these unknown states. The complexity of the three photon excitation spectrum is born out by the fact that monitoring the fluorescence from the upper states at a different wavelength has resulted in the observation of at least six new 3P2C progressions [164]. Two of these exhibit a separation of about 75 cm⁻¹ between consecutive heads similar to the spacing of the fragmentary system recorded during this work (Table 6.4).

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Besides further investigation into the three photon spectrum, a study of the four photon absorption spectrum would be very interesting and is quite feasible. The BDL output could be set to a frequency corresponding to an assigned SPIC transition. Fluorescence from the populated three photon level can be blocked using a filter assembly that only transmits below 200 nm. The NDL could then be scanned over the 14000-20000 cm⁻¹ region (using ${}^{127}I_2$ frequency calibration [84-87]) to induce single photon transitions from the three photon levels pumped by the BDL. This 4P2C experiment would result in the observation of fluorescence from molecular states in the 70000 cm⁻¹ region. While this region is well known to be spectrally dense (Chapter **3**.2), few definite assignments

have been made. Spectra obtained in the above manner will, however, be simple and easily interpreted. This would be because, despite the relatively broad bandwidth of the BDL, only a few 3P1C lines are pumped at any given frequency. In some cases, only a single three photon level would be photoselected. If the pump lines are chosen carefully, and the output power of the NDL is minimised, there should be no interference due to 4P1C transitions. As the NDL is scanned, allowed single photon transitions (Table 1.1) will be induced from the 3P1C levels pumped by the BDL. The spectrum will consist of groups of lines (2 or 3 depending on the symmetry of the four photon state), separated by the vibrational interval of the terminating state. The assignment of rotational quantum numbers will be simple as the pumped 3P1C assignment will be known. Conversely, once the four photon states have been identified, unassigned 3P1C lines can be pumped, and the spacing of the resulting 4P2C lines can be used to determine the three photon pump energy and hence assign the pump line. Another advantageous feature of this experiment is that the peak power of the NDL is not of critical importance; on the contrary, it would be kept as low as possible to avoid inducing multiphoton absorption of higher orders (5P2C, 6P2C, etc..). Any such higher order processes could be studied separately by using an appropriate interference filter.

Three photon resonance enhanced spectra in other molecules are also a possibility. Unfortunately, the number

of diatomics that can be studied in a static cell at room temperature is limited. It may be possible to use part of the excimer emission to volatize a solid sample such as Se, in a sealed cell. However, such studies would probably be limited to single beam work due to the finite amount of excimer radiation available. Future experimental designs could include a flow system and a discharge region to allow the study of transient species. Polyatomics are also a possibility for study; certainly a few have visible absorption systems (e.g. $Cr0_2Cl_2$ and $N0_2$) suitable for single photon pumping. A drawback to polyatomic studies would be the increased complexity of the multiphoton spectrum under high resolution. Another important consideration would be the accuracies with which the spectroscopic constants of the ground and intermediate states are known. Without well-determined Dunham coefficients for the calculation of possible pump frequencies, the analysis of the single beam spectrum would be extremely difficult.

A suggested equipment change is the replacement of the red sensitive FMT (EMI 9816QB) now used, with a solar blind or equivalent PMT. This would allow the removal of the glass filters currently required to block the scattered laser light and the intense single photon fluorescence. The absence of these filters would more than compensate for the generally lower gain of the uv - only detector.

In summary, the prognosis for future work appears promising based on the results obtained in this study.

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APPENDIX A

 127_{I_2} , 129_{I_2} 3P1C Lines and Assignments

Legend:

symbol		meaning
vw .	1 5	very weak
W		weak
m -		medium
s		strong
vs		very strong
₫Ъ ≁	`	double
b		broad -
vb		very broad
NQ		non-Q line as indicated by po £. analysis
Q		Q line as indicated by pog. analysis

Vibrational numbering of $D0_u^+$ upper state assignments based on Wieland's [38] scheme.

127₁₂

3P1C LINES AND ASSIGNMENTS

LINE(cm ⁻¹)	v3	v2	vı	ΰ₃	J2	J1 .	STATE	REMARKS
18308.527	211	25	0	25	. 27	28	D(0u+)	w
18304.840	211	25	0	37	37	36	D[0u+) ·	m 🕳
18300.676							• '	s,Q?
18296.486	101	26	0	[°] 88	90	89-	F(0u+)	m, NQ?
18295.276	214	26	0	87	85	86	D(0u+)	w,Q?
18294.636	99	25	0	41	41	42_	F(0u+)	m,Q?
18294.300	99	25	С	49	47	46	F(0u+)	m,Q?
1829 2. 551	<u>5</u> 5	25	0	41	43	44	F(0u+)	m, NQ
18291.919	. 99	25	0	49	49	48	F(0u+)	s.Q
18291.250								w,Q?
18289.510	ð ð.	25	0	49	51	50	F(0u+)	— m, NQ
18255.996						•	· ·	w, NQ - 2
18254.783							•	m,Q
18216.813	• •							* ₩
18210.995								vw,b
18209.343								vw,b
18202.436	ġ ġ	26	Ċ	121	123	122	F(0u+)	m, b, NQ
18196.981	o –	25	ð	<u>ğ</u> ğ	õõ	98	E(01+)	W
18193.262	95	24	0	56	56	57	E.eu+)	m , Ç
18190.335	95	24	0	56	58	59	E(0u+)	1 m, 22
18189.741	95	24	C	64	÷6 +	63	훈(3년+)	w
18140.470	92 102	23 31	0	33 121	31 119	52 118	F(Cu+) F(Cu+)	W.N.2 7
18138.810	900	23 23	0 0	33	33 39	34	F(0u+) F(0u+)	w, 5, N2 ?
18136.710	92 · 92 ·	23	0 C	(1) -4 (1) -7	35 41	36 40	ア(0ビナ) ア(0ビナ)	w,vc,N <u>C</u>

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LINE(cm ⁻¹)	v3	v ₂	vl	J3	J2	. J1	STATE /	REMARKS
18094.080	91	23	o	68	66	67	F(0u+)	w,b,NQ ?
18090.801	91	23	0	68	68	69	F(0u+)	s,Q
18086.475	91 103	23 33	0 3	76 107	76 105	75 106	F(Ou+) F(Ou+)	m,b,Q ?
18039.319	88 197	22 23	0 0	48 92	46 92	48 93	F(0u+) D(0u+)	w,b,NQ
18036.915	88 88	22 22	0	48 56	48 54	49 53	F(0u+) F(0u+) _	s,Q
18034.400		· .			-			w,NQ
18033.387	102	35	4	95	93	94	F(0u+)	w,b,Q ?
17998.440	91	24	0	138 -	138	137	F(0u+)	w,b,NQ ?
17994.596	94 96	27 29	1 2	139 121	137 123	138 122	F(0u+) F(0u+)	m,Q ?
17991.424	91	24	0	138	140	139	F(0u+)	w,b,NQ ?
17987.492	89	23	0	117	117	116	F(0u+)	s,Q
17986.885	87	22	0		84	83	F(0u+)	m,NQ ·
17986.510	89 94	24 28	1 2	52 100	52 98	53 99	F(0u+) F(0u+)	W,NQ ? W,NQ ?
17983.311	89 8	24	1	60	60	59	F(Ou+)	m,NQ ?
17982.716	s7	22	C	86	86	85	F(0u+)	vs,Q
17978.430	87	22	O	86	88	S 7	F(0u+)	m, NQ
17967.652								w,Q ?
17965.971	188	21	0	33	33	34	D(0u+)	w.C ?
17965.543	98 98	27 32	1 13	79 ↓20	77 122	78 123	F(0u+) F(0u+)	w,Q ? w,Q ?
17962.305	188 92	21	0 2	45 86	43 84	42 83	D(Cu+) F(Ou+)	w,b,NQ ?
12960-139								w,NQ ?
17959.492	188	21	С	46	46	45	D(02+)	m,Q

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	$LINE(cm^{-1})$	v3	v 2	vl	J3	J2	Jl	• STATE	REMARKS
۰	17957.117	188	21	0	46	48	47	D(0u+)	m,Q ?
	17947.53Ì	90	25	1	105	107	108	F(0u+)	m,b,Q
•	17943.633	86 90	22 26	0 2	99 53	97 51	98 50	F(0u+) F(0u+)	m, NQ
,	17940.221	88	23	0	132	132	131	F(0u+)	m.Q ?
}	17939.441	90	26	2	52	54	53	F(0u+)	w,Q
	17938.742	86 88 93	22 24 28	0 1 2	99 79 121	99 79 119	100 80 118	F(0u+) F(0u+) F(0u+)	m,b,Q ?
	17937.391	84	21	0	` 59	57	58	F(0u+)	m,b,NQ
	17936.565								w,b,NQ
	17934.404	84-	21	0	59	59	60	F(0u+)	s,Q
	17933.549	88	23	. 0	132	134	133	F(0u+)	·m,NQ ?
	17932.738								w.C ?
	17931.398	84	21	0	59	61	62	F(0u+) *	m , NQ
	17930.934	86	23	1	29	27	28	F(0u+) ·	W, NQ
	17930.100	84	21	0	68	68	67	F(0u+)	vs.Q
	17929.172	36	23	1	- 29	29	30	.F(0u+)	" , b, Q ?
	17927.148	86	23	1	37	37	36	F(0u+)	w.2.3
	17926.660	84	21	0	68	70	69	F(0u+)	m (2) 2
	17925.738								s, N <u>C</u>
	17921.545	187	21	С	67	67	68	D(0u+)	
	17910.816	187	21	e	79	79	÷8	D(0u+)	- m, Ω ?
	17907.467	91	28	3	23	23	24	F(0u+)	w, vb; Ng 2
	17888.430	83	21	e	86	84	85	F(0u+)	m,:::Ç
	17884.169	83	21	0	86	86	87	F(0u+)	s,
	17883.625	81 37	20 25	0 2	26 29	24 27	25 20 7	F(0u+) F(0u+)	π

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LINE	1)			₹-	•	•.		246
LINE (Chi	-) v3	v2	v1	73	- J2	71	STATE	REMARKS
17882.2	45 81 87	20 -25	0 2	. 26 .36	26 34	- 27 33	. F(Ou+) . F(Ou+)	VS
17881.8	57 · 81 81 87 87	20 20 24 25	0 0 1 2	27 35 106 29	27 33 108	28 32 107	F(Ou+) F(Ou+) F(Ou+) F(Ou+)	, m
17880.8	59 81 87	20 25	- 0 2	26 28	28 30	2.9 31	F(0u+) F(0u+) F(0u+)	s,b
17880.1	98 81 81	20 20	0 0	27 35	29 35	30 34	F(0u+) F(0u+)	vs,Q
17879.7	13 81 83	20 21	0 0	36 86	36 88	35 89	F(0u+) F(0u+)	W
17865-69	93 182	20	0	. 46	44	45	D(0u+)	w, NQ
17863.3.	49 182	20	0	46	46	47	D(0u+)	m,Q
- 17834.71	15 80 . 82	20 21	00	68 106	66 106	67 107	F(0u+) F(0u+)	vs,Q ?
17832.2;	38 86	25	2	72	72	71	F(0u+)	W,Q ?
17831.3:	26 80	20	0	68	68	69	F(0u+)	vs,Q
17829.2.	17 82	21	0	106	108	109	F(0u+)	w, NC
17827.81	16 80	20	0	68	70	71	F(0u+)	m, NQ
- 17826.48	51 80 82	20 22	0 1	77 48	77 46	76 47	F(Ou+) F(Ou+)	s,NQ
17823.99	91 82, 82	22 22	1	48 56	48 54	49 53	F(0u+) F(0u+)	π, Q
17822.53	30 80 89	20 28	0 3	77 82	79 80	78 81	F(0u+) F(0u+)	m , NQ
17820.93	185	21	0	119	117	116	D(0u+)	w,NC -:
17788.18	10 85	25	2	95	93	92	F(0u+)	w,vb
17784.90	94 79 83	20 23	0 1	93 108	91 108	92 109	F(0u+) F(0u+)	.s,NQ
17781.84	9 77	19	0	39	37	38	F(0u+)	m,NQ
17780.31	.0 .79	20	С		93	94	F(0u+)	vs,Q

	•	•		- *,	.		•	247`
LINE(cm ⁻¹)	v3. ⊿	· v 2	v1	J3,	' J ₂	Jl	STATE	REMARKS
177 79. 899	77	19	ĨO	3.9	39	100	F(0u+)	vs,Q
17779.318	77 83 ₋	19 23	0 1	48 108	46 (110	111	F(0u+) F(0u+)	s,NQ
17778.695	81 81. 、83	21 [°] 22 23	0 •1 1	123 78 116	125 76 116	126 77 115	F(0u+)	m,b,NQ
17777.809	77	19	0	39	41	42	F(0u+)	m
17776.965		_	(s,Q
17776.387	77	19	_ کو	- 49	. 49	48	F(0u+)	m,b,Q
17775.565	79	20	0	93	95 95	96	F(0u+)	m,b,NQ ·
17774.555	81 83 83	22 24 24	1 2 2	78 52 60	78 52 58	79 53 57	F(Ou+) F(Ou+) F(Ou+)	π, Q
17773.855	77	19	0	49	51	50	F(0u+)	s,NQ
17772.881	83	23	1	-116	118	117	F(0u+)	vw,vb,NQ
17770.650								W,NQ ?
17770.041	-		•		-	•		w,Q
17768.652	79 83	20 24	0 2	102 60	104 62_	103 61	F(0u+) F(0u+)	m,NQ
17767.745	79999999 777777	21 21 21 21 21 21 21	1 . 1 1 1 1	796 85 15	77 88 13 14	S 999 123	F(0u+) F(0u+) F(0u+) F(0u+) F(0u+) F(0u+) F(0u+)	s,vb,Q?
17767.050	999999 777777	21 21 21 21 21 21	1 1 1 1	7 9 8 17 16	9 9 10 15 16	10 10 11 14 15	F(0u+) F(0u+) F(0u+) F(0u+) F(0u+)	s,vb,Q?
17766.022	79 79 81	21 21 22	1 - 1 I	15 17 86	13 19 58	14 18 87	F(0u+) F(0u+) F(0u+)	m
17765.754			•	~				m
17757.695				Ń		•		w,Q ?

.

	LINE(cm ⁻¹)	. V 3	٧o	vi	Ja	Jo	JI	STATE	DEMARKC	
	17756.838	176	2. 19	0	· i 58	58	59	D(0u+)	w.b.0 ?	
	17753.791	176 179	19 21	0 1	58 32	60 32	61 33	D(0u+) D(0u+)	w, NQ	
	17750.883	176 90	19 30	03	70 146	68 144	67 145	D(0u+) F(0u+)	w,NQ	
	17748.311	179	21	1	44	44	43	D(0 <u>u</u> +)	w,b,Q ?	
	17746.404	176 179-	19 21	0 1	71 44	71 46	70 45	.D(0u+) D(0u+)	w,NQ ?	
	17742.111	80	21	0	138	136	137	F(0u+)	w, 5.10	
	17735.368								m,NQ ?	
	17731.796	84	26	3	54	52	- 51	F(0u+)	w,b,NQ	
:	17729.004	78 84	20 26	0 3	121 54	119 54	118 53	F(0u+) F(0u+)	w,b	
	17728.055								s,Q	
	17726.977	76	19-	,0	84	84	82	F(0u+)	s,Q —	~~
	17726.815	.82	24	2	87	85	84	F(0u+)	s,NQ	
	17722.751								s,Q .	
	17721.682	78	21	ĺ	61	59	60	- F(Ou+)	m,Q ?	
	17718.258	82	24	2	87	89	88	F(0,u+)	s,Q	
	17717.378	76	19	0	. 85	87	86	F(0u+)	s,NQ	
	17714.373	88	29 -	3	137	137	138	F(0u+)	w	
	17713.921	78	21	1	70	70	69.	F(0u+)	s,Q	
	17712.950								w	
	17712.016	175	21	1	67	65	66	D(0u+)	w	
	17710.423	78	21	1	70	72	71	F(0u+)	w, NQ	
	17710.217	85	26	2	143	143	142	F(0u+)	w	
	17708.654	175	19	o	85	85	86	- D(0u+)	m , Q	
	17704.240	175	19 `	0	85	87	58	D(0u+)	~	
·										-

LINE(cm ⁻¹)	٧a	V2	۷ı		Ja	.Th	STATE	- 249 -
17698.791	2	•••		- 3	- <u>-</u> <u>-</u>	1	JIRIE	KEMAKAS
17698.270	- 175	19	0	98	96	95	- D(0u+)	т. ЪО2
17697.563								w
17697.048				•		•		s.0 ?
17696.536	83	25	2	120	120	121	F(0u+)	m.0 ?
17696.033					·			w.b
17695.604	171	18	0	27	29	30	D(0u+)	w
17693.888	175	19	0	98 -	.98	97	D(0u+)	m, NO
17693.613	171	18	0	4,0	7 38	37	D(0u+)	w,sh
17691.630								w,db
17691.055	171	18	0	41	41	40	D(0u+)	s,Q
17690.456				-			·	m,b,Q
17689.740								* W
17689.041					•			w
17688.338	171	18	0	42	44	43	D(0u+)	w. NQ 2
17679.469	73	18	0	48	46	47	F(0u+)	m, NQ
17676.992	73	15	0	4 S	48	49	F(0u+)	vs,Q
17676.293	73	18	0.	57	55	54	F(Ou+)	m,NQ ?
17674.600	73 81	18 23	0	48 99	50 101	51 102	F(0u+) F(0u+)	m,b,NQ
17673.580								m,b,Q
17673.050								s,Q
17670.750								m, Ç
17670.003	73 75	18 19	0	- 58 108	60 108	59 107	F(0u+) F(0u+)	s,NÇ ·
17667.668								
17664.434	75 -	20	1	34	32	33	F(0u+)	m,b

···				• •		(2) .	- ``.	•
•	LINE(cm ⁻¹)	v ₃	v2	v1	J3	J2	/ · J1	STATE	250 REMARKS
	17663.770	77 75	20 20	0 1	138- 35	140 33	139 34	F(Ou+) F(Ou+)	w,vb
v	17662.706	75 77	20 21	1 1	34 96	34 96	35 95	F(Ou+) F(Ou+)	vs,Q
	17661.199	11	18	0.	62	60	61	F ⁽ (0u+)	w,NQ ?
	17660.758	79	23	2	77	77	76	F(0u+)	m,b,NQ ?
	17660.133	75 75	20 20	1 1	35 43	37 43	38 42	F(Ou+) F(Ou+)	m,db
	17658.195	11 75	18 20	0 1	62 43	 62 45 	63 44	F ^(0u+) F(0u+)	s,Q
	17655.717	. 11	18	0	70	70	69	F [*] (0u+)	s,Q
	17654.981	11	18	0	62	64	65	F'(0u+)	m, NQ
	17646.924			•		•			m,Q
	17643.369	170	18	0	69	71	72	D(0u+)	w,b,NQ
	17634.859	78	22	1	132	130	131	F(0u+)	m,Q -
	17628.772	72	18	0	81	79	80	F(0u+)	,m,Q ?
	17624.334								w,Q?
	17623.209								m,Q ?
	17620.648	78	22	1	140	140	139	F(0u+)	w,b,Q ?
	17617.664	72 76 76	15 21 21	0 1 1	91 108 116	91 108 114	90 109 113	F(0u+) F(0u+) F(0u+)	s,Q
	17611.589	74	20	1	72	72	73	F(0u+)	s,Ç .
	17590.357								w
	17587.564	à	17	0	50	50	49	F ⁽ (0u+)	S
	17585.591								
	17584.967					•			m
	17579.492								-
	17575.683								s >
					. -				-
			•					ه	

				•			•	•
LINE(cm ⁻¹)	v 3	v2	vı	J3	J2	J ₁ .	STATE	251 REMARKS
17573.620	69	17	 0	55	55	- 56	F(Ou+)	S
17572.802	69	17	0	64	62	61 -	F(0u+)	m
17570.752	69	17	0	55	57	58	F(0u+)	w
17568.988	- 79	25	3	97	97	96	F(0u+)	w,b —
17568.026								w
17563.580	•							m
17556.718	71	19	1	_ 48	48	49	F(Ou+)	m,b
17554.140	73	20	1	105	105	104	F(0u+)	w,b
17532.902							-	S
17470-137	65	16	. 0	60	60	61	F(0u+)	w, Q?
17468.857					•	·		w, NQ
17465.252	65	16	· 0	70	70	69	、 F(Ou+)	m,Q?
17460.900								vw, NQ
17455.977								W
17455.295								W
17452.344	69 78	19 26	1 3	104 148	104 150	105 150	F(0u+) F(0u+)	w w
17450.055	9	20	2	33	35	36	F ^(0u+)	, w
17442.813	6 67	16 18	0 1	77 68	. 77 70	78 69	F (0u+) F (0u+)	5,0
17439.843	69	20	2	47	45	46	F(0u+)	s, <u>[</u> ?
17438.760	6	16	0	77	79	80	F ^(0u+)	m,NQ
17437.661	7 69	17 20	0 2	120 55	120 53	121 52	F ^(0u+) F(0u+)	s,Ç
17433.276	ī	17	0	128	128	127	F ^(0u+)	s, <u>î</u>
17415.013								S
17410.926	70	20	1	. 154	152	151	F(0u+)	ww.
1740 F 928						·		m

LI 1 1 1 1 1 1 1 1 1 1 1 1 1	INE(cm ⁻¹) 17404.735 17404.078 17403.111 17397.311 7396.313 7396.025 7390.580 7378.309 7377.681 7373.279	• V3 66 64 64 64 64 64 64 64 64 64	v2 16 17 17 17 17 17 17 17 17 17 17	0 1 1 1 1 1 1 2 3	J3 101 10 10 12 11 19 11 20 12 21 79 62	J2 103 10 10 11 17 13 20 14 21 77	J1 102 11 12 16 14 19 15 20 78	STATE F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+)	252 REMARKS vw m m vs s,b s,b
LI 1 1 1 1 1 1 1 1 1 1 1 1 1	INE (cm ⁻¹) 17404.735 17404.078 17403.111 17397.311 7396.313 7396.025 7390.580 7378.309 7377.681 7373.279	 • V3 66 64 64 64 64 64 64 64 64 68 70 4 73 	v ₂ 16 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 17 15 15	0 1 1 1 1 1 1 1 2 3	J3 101 10 10 12 11 19 11 20 12 21 79 62	J2 103 10 10 11 17 13 20 14 21 77	J1 102 11 12 16 14 19 15 20 78	STATE F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+)	REMARKS VW m m vs s,b s,b
	17404.735 17404.078 17403.111 17397.311 17396.313 7396.025 7390.580 7378.309 7377.681 7373.279	66 64 64 64 64 64 64 64 68 70 43	16 17 17 17 17 17 17 17 17 20 22	0 1 1 1 1 1 1 1 2 3	101 10 12 11 19 11 20 12 21 79 62	103 10 10 11 17 13 20 14 21 77	102 11 12 16 14 19 15 20 78	F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+)	vw m m vs s,b s,b
	17404.078 17403.111 17397.311 17397.311 17396.313 17396.025 17396.025 17390.580 17378.309 17377.681 17373.279	66 64 64 64 64 64 64 68 70 43	16 17 17 17 17 17 17 17 17 20 22	0 1 1 1 1 1 1 1 2 3	101 10 12 11 19 11 20 12 21 79 62	103 10 10 11 17 13 20 14 21 77	102 11 12 16 14 19 15 20 78	F(0u+) F(0u+) F(0u+) F(0u+) F(0u+) F(0u+) F(0u+) F(0u+) F(0u+) F(0u+)	m m vs s,b s,b
	17403.111 17397.311 17397.311 17396.313 17396.025 7390.580 7378.309 7377.681 7373.279	66 64 64 64 64 64 64 68 70 73	16 17 17 17 17 17 17 17 17 17 20 22	0 1 1 1 1 1 1 1 2 3	101 10 10 12 11 19 11 20 12 21 79 62	103 10 10 11 17 13 20 14 21 77	102 11 12 16 14 19 15 20 78	F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+) F(Ou+)	m vs s,b s,b
	7397.311 7396.313 7396.025 7390.580 7378.309 7377.681 7373.279	64 64 64 64 64 64 68 70 43	17 17 17 17 17 17 17 17 17 20 22	1 1 1 1 1 1 2 3	10 12 11 19 11 20 12 21 79 62	10 10 11 17 13 20 14 21 77	11 12 16 14 19 15 20 78	F(0u+) F(0u+) F(0u+) F(0u+) F(0u+) F(0u+) F(0u+) F(0u+) F(0u+)	vs s.b s.b
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	7396.313 7396.025 7390.580 7378.309 7377.681 7373.279	64 64 64 68 70 43	17 17 17 17 20 22	1 1 1 2 3	11 20 12 21 79 62	13 20 14 21 77	14 19 15 20	F(Ou+) F(Ou+) F(Ou+) F(Ou+)	s,b s,b
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	7396.025 7390.580 7378.309 7377.681 7373.279	64 64 68 70 4 73	17 17 20 22	1 1 2 3	12 21 79 62	14 21 77	15 20 78	F(0u+) F(0u+)	s,b
1 1 1 1 1 1 1 1 1 1 1 1 1 1	7390.580 7378.309 7377.681 7373.279	68 70 4 73	⁻ 20 22 15	2 3	79 62	77	78	•	
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	7378.309 7377.681 7373.279	70 4 73	22	3	62		• •	F(0u+)	w
1 1 1 1 1 1 1 1 1 1 1 1 1	7377.681 7373.279	4 73	15			64	65	F(0u+)	w., Q?
1 1 1 1 1 1 1 1 1 1	7373.279	4 73	15						w,Q?
1 1 1 1 1	200 005		24	0 3	68 133	66 131	65 132	F ^(0u+) F(0u+)	w, NQ
1 - 1 1 1 1	1012.200								s,Q
- 1 1 1 1	7369.075	4	15	0	60	62	63	F(Ou+)	m,Q?
1	7368.975								w,NQ
1	7366.394								m , Q
11	7365.723	-61 -	15 15	0 0	73 - 69	71 71	70 70	F(Ou+) F ⁽ (Ou+)	m,NQ
	7365.438	· .	•					•	π,Q
1.	7362.955	61	15	0	64	66	67	F(0u+)	w, NQ
17	7361.193	61	15	0	74	74	73	F(0u+')	s,Q
17	7302.827	2	14	0	33	31	32	F F (Ou+)	m,NQ
17	7301.814	2	14	0	.41	39	38	F ⁽ (0u+)	w, NQ
17	7301.132 -	2	14	0	33	33	34	$F^{-}(0u+)$	s,Q
17	7299.503	2	14	0	42	42	41	F ⁽ (0&+)	vs,Q
17	7299.051								m,NQ
					,				
				-	•				

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• •					-			253 -	
$LINE(cm^{-1})$	<u>v</u> 3	v2 7	v1	J3	J2 ·	Jl	STATE	REMARKS	·
17296.909	2	14	0	43	45	44	F (0u+)	m,Q?	÷
17294.842	3 66	15 19	0 1	110 152	108 154	107 155	F (Qu+) F(Qu+)	W, NQ	•
17293.028	•		r×					m,Q?	
17291.486						-		m', Q?	
17289.482	60	16	1	37	. 37	36	F(0u+)	m,Q?	
17289.047								m , Q -	
17271.459	62	18	2	28	28	29	F(0u+)	w,Q	
17266.324						`		w,Q?	
17263.057	57	14	0	66	66	6-7	F(0u+)	m,Q?	
17262.944	57	14	0	75	73	72	F(0u+)	m,Q?	
17261.543								m,NQ	
17261.158	3	16	-1	66	64	63	F ^(0u+)	w, NQ	
17260.234	• 3	16	1	58	.58	59	F ⁻ (0u+)	s,Q.	
17259.638	4	17	1	116	114	113	F ^(0u+)	w, NO	
17258.712		,						w, NQ	
17258.027							•	s,Q	ì
17257.078	-,							m,NQ	
17254.084	3	16	1	67	69	68	F ^(0u+)	m, NQ	
17246.512	4	17	1	117	119	118	F´(0u+)	w,Q?	
17236.772		•						m , Q	
17231.159	59	16	1	83	83	82	F(0u+)	s,Q	
17216.172	. 1	14	0	99	99	-98	F ¹ (0u+)	s,Q?	
17206.731	2	1.5	0	132	134	135	- F ¹ (Ou+)	w,NQ	
17205.746								s, 🖓	
17198.213								m,Q?	
17187.742	1 56	15 15.	1 1	3 6 36	34 34	35 35	F ^(0u+) F(0u+)	m,NQ	
						-	-		

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, \					×.	. •	•	_ •	254
•		×3	· v ₂	v <u>1</u>	33	J.2	Jl	STATE	REMARKS
	1/18/.115	56	15 - 15	- 1 1	37 37	35 35	36 36	F [*] (0u+) F(0u+)	w, NQ
	17186.703	1	15 😌	1	44.	42	41	F (0u+)	m,b,NQ
•	17185.902	1	15	1	45	43	42	F (0u+)	s,NQ?
	17185.604								S,NQ
	17185.402	1 56 ⁻	15 15	1	37 37	* 37 37	38 38	F ⁽ 0u+) F(0u+)	S,NQ?
	17185.076	56	15	1(.	46	- 44	43	F(0u+)	W,NQ?
•	17184.406								vs
-	17184.248	~ `1	15	1	45	45	44	F (Ou+)	v'S,Q
	17183.811			١				•	w.b.Q
	17183.375	- 1 56	15 15	1 1	37 37	39 39	40 40	F ^(0u+) F(0u+)	ww.b.NQ
	17182.682	58	16	1	100	100	101	F(0u+)	m
	17181.746								m
•	17181.500	1	15	1	46	48	47	F ⁻ (0u+)	m
	17179.756					•			₩.
•	17179.400	56.	15	1	48	50	- 49	F(0u+)	w, NQ?
	17162.845	53	13	0	67	65		F(0u+)	• s,Q?
	17159.373	58	17	2	53	53	52	F(0u+)	w, Q
	17158.712			•	,				w, Q
	17155.090	53 ·	13	0	68	70	71	F(0u+)	s,NQ?
ŕ	17154.651								π,Q
(-	17153.404						-		m , Q
-1	17149.954								w.c
	17148.841	53 2	13 17	0 2	79 55	81 55	80 56	F(0u+) F ⁽ (0u+)	vs,Ç
	17146.867							e*	s, Ç
							•		•
	. •	·						•	
							-	•	· ` `

·				_					255
,	LINE(cm ⁻¹)	183-	^v 2	vī.	. J3	J2	Jl	STATE	REMARKS
	17146.328	×.		• •	•				s,Q
	17144.345				•.			•	. m,Q
	17143.203		••			, ·	• '		m,Q
	17105.535	0	15	1	91	. 91	92	F ^{`*} (0u+)	m
	17100.888							· •	- w
	17099.047		•	-					w
•	17092.051		•						vw
	17090.569		(<u> </u>					w
•	17084.764			X				F F	w,NQ
	17081.827	52	14	1	42	- 40	41	F(0u+)	m
	17079.297	52	14	1	43	43	44	F(0u+)	m,Q
	\$7078.944	52	14	1	52	50	49	F(0u+)	m, NQ
	17076.961	52	14		43	45	46	F(0u+)	w, NQ
	17075.824	52	14	1	- 53	53	52	F(0u+)	·s,Q
	17075.246	\ 56	16	1	139	139	·140	_F(Ou+)	
	17072.473	52	14	1	54	56	55	F(0u+)	m,NQ
	17071.255	U	16	2	38	38	39	F ⁽ (0 <u>u</u> +)	π,Q
	17069.825	0	16	2	46	46	45	F ^(0u+)	m,Q
	17066.088								w,NQ?
	17059.322								w, NQ?
	17053.501	54 54	16 16	2	54	54 61	55 J 60	F(0u+) F(0u+)	w
	17049.442	54	16	2	64	64	63	F(0u+)	m .
	17048.776	58	19	- 3	99	97	<u>9</u> 8	F(0u+)	ω •
	17044.248	51	13	G	131	- +20:	128	F(0u+)	
	17041.539					`			×
	16692.126							•	w,b
								`	
		-							

		· · ·	•	•	•	•	
	· •.		•		•		256
LINE(cm ⁻¹)	v ₃ v ₂	vı	J3	J2	Jl	STATE	REMARKS
16691.053					• 、		w,b
16681.109	•		•			.`	m,b
16680.535		н Н	. •			4	.m,b
16678.835	 	•					• m
16677.136	•				· - ``		S
16676.796					1	•	m
16676.438	•	. •				•	m.
(16675.721		•		•			w,b
16625.801	Υ.						S
16620.324	•		•.				S
16616.451							m
16615.498	· •	·					VW
16613.949							·S
16542.016							W
16538-592							vs
16534.815	· (w 、 .
16530.375	-	•					m
16530.084			•				
16524.656							m
16520.797							w vb
							·· / · ·

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3P1C LINES AND ASSIGNMENTS

									-
•	_LINE(cm ⁻¹)	v ₃	v2	vl	J3	J ₂ .	Jl	STATE	REMARKS
	17985.586								vw,b
	17981.983	:						· ·	vw,b
	17976.984	91	25	1	90	92	93	F(0u+)	w ·
	17974.822								w,b
	17970.329	89	23	0	119	119	118	F(0u+)	s m,b
	17970.214	87	22	0	80	80	81	F(Ou+)	S
e R	17966.864	85 85 85	21 21 21	0 0 0	6 8 16	8 8 14	9 9 13	F(Ou+) F(Ou+) F(Ou+)	s,b
	17965.906	85 85 87	21 21 22	0 0 0	9 17 80	11 17 82	12 16 83	F(Ou+) F(Ou+) F(Ou+)	s,vb
	17965.527	85 · 85	21 21	0 0	18 10	18 12	17 13	F(0u+) F(0u+)	m
	17875.864	89	26	2	84	84	83	F(Ou+)	w
	17874.551	87	24	1	101	101	102	F(0u+)	vw
	17874.070) 87	24	1	109	107	106	F(0u+)	w
	17873.729								vw
	17872.604								vw
	17871.891	93	21	0	SS	86	87	F(0u+)	• 1 11
	17870.267	92	31	3	131	129	130	F(Ou+)	w,b
	17868.832	87 92	24 29	1 3	109 94	109 92	108 91	F(0u+) F(0u+)	w,b
	17868.268	92 •	29	3	87	87	. 88	F(0u+)	
	17867.482	81 83	20 21	0 0	30 88	28 88	29 89	F(0u+) F(0u+)	::s
	17866.029	81	20	0	30	30	31	` F(0u+)	۳s
۲.	17865.598	87	25	2 `	42	44	39	F(0u+)	

	LINE(cm ⁻¹)	V 2	٧o	۷ı	Ja	Jo	٦٦	STATE	258 REMARKS
	17864.464	81 87	20	, 0 2	30	32 41	33	F(0u+) F(0u+)	w
·	17863.717	81 87	20 25	0 2	39 34	- 39 - 36	38 37	F(0u+) F(0u+)	vs
	17863.255	87	24	1	109	111	110	F(0u+)	m
	17824.157	88	27	3	25	25	24	F(0u+)	w
	17823.249				-			· .	m _
,•	17818.609	80 86	20 25	0 2	70 68	68 68	69 69	F(0u+) F(0u+)	s
	17818.320	82	21	0	108	108	109	F(0u+)	s
	17818.067	86	25	2	76	74	. 73	F(0u+)	m
	17815.220	80	20	0	70	70	71	F(0u+)	vs
	17814.011	-80	20	0	79	77	76	F(0u+)	w,b
	17812.644	82	21	0	108	110	111	F(0u+)	w,b
	17811.560	84	23 ·	1	92	94	95	F(0u+)	w
	17810.320	80	20 ·	0	79	-7,9	78	F(0u+)	vs
	17803.994	82	22	1	60	`60	59	F(Ou+)	m
	17772.291	85	25	2	90	90	91	F(0u+)	m
۰ ۱	17768.779	79	20	0	95	93	94	F(0u+)	m,b
1.	17768.570	81	21	0	125	125	126	F(0u+)	w
	17767.571	\$5	25	2	90	92	93	F(0u+)	w
	17766.261	77	19	0	42	40	41	F(0u+)	m
	17764.167	77 79	19 20	0 0	42 95	42 95	43 96	F(Ou+) F(Ou+)	vs,b
	17763.515	77	19 *	С	51	49	48	F(0u+)	w
	17761.059	77	19	0	51	51	50	F(0u+)	w,vb
	17757.796	77 83	19 24	0 2	52 64	54 62	53 61	F(0u+) F(0u+)	w w
	17732.359	86	26	2	133	135	134	F(0u+)	w
		•							-

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•									259	
	$LINE(cm^{-1})$	v3	v2	. v 1	J3	J2	J 1	STATE	REMARKS	· •.
	17731.750								w,b	
	17730-908	86	27	3	82	84	85	F(0u+)	w	
	17727.445	86	27	3	89	91	90	F(0u+)	w .	
	17726.389								m,b	
	17724.373								m,b	
	17720.318								m '	•
	17719.315			•					m', b	
	17718.455	80	21	0	148	146	145	F(0u+)	w, NQ	
	17718.096								m,Q	
	17716.297								m,b,Q	
	17713.348	82	23	1	134	134	133	F(0u+)	w,b	
	17712.576	76	19	0	77	77	78	F(0u+)	vs,Q	
	17711.363	76	19	0	86	84	83	.F(Ou+)	vs,NQ	
	17709.850					4			w,vb,NO	
	17707.914								w,NQ	
	17707.284	78	20	0	123	123	122	F(Ou+) -	s,Q	
	17706.441	•							vs,Q	
	17702.254	78	21	1	64	64	65	F(0u+)	m.NO?	
	17697.943								m , NO	
	17694.229	78	21	1	73	· 75	74	F(0u+)	m.NO?	
	17669.629	83	26	3	85	83	82	F(0u+)	т.b	•
	17665.467	83	26	3	85	- 85	84	F(0u+)	··· , ~	
	17661.670	11	18	0	57	• 57	56	F ⁽ (0u+)	 m . C	۲
	17660.902	75	19	0	101	101	102	$\Xi(0n+)$	e 0	
	17660.684	- 11	18	0	58	58	57	F ((0 1) +)	e ()	
		79	22	ĩ	119	119	120	F(0u+)	9 / Y	
	17658.506								s,0	·
								~		
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, ,	LINE(cm ⁻¹)	٧3	V2	۲v	٦٦		Jı	STATE	260 REMARKS
	17658.030	73	18	0	60	60	59	F(0u+)	vs.0
·	17657.442	77 81	20 24	02	131 102	133 104	134 105	F(0u+) F(0u+)	m,Q
	17656.653	77	- 21	1	90	88	U . 89	F(0u+)	w,NO
	17655.072				•				m,vb,Q?
	17652.145		•						w, NQ
-	17651.058								w,NQ
	17647.371	75	2 Q	1	38	38	39	F(0u+)	s,Q
	17646.889					١.			s,Q
	17646.286	•						· ~	w,NQ
	17598.022	72	18	0	93	95	94	F(0u+)	w,NQ
	17595.742	, 9 9 9 9 74	17 17 -17 17 20	0 0 0 - 0 1	- 1 7 19 25 26 83	17 17 23 24 81	18 18 22 23 80	F ^(0u+) F ^(0u+) F ^(0u+) F ^(0u+) F(0u+)	s,b,NQ?
	17595.407	9 9	17 17	0 0	18 26	18 24	19 23	F ^(0u+) F ^(0u+)	s,b,NQ?
	17595.057	9	17	0	27	25	24	F´(0u+)	s,db,Q .
	17594.860 ۲	9 9	17 17	0 0	17 19	19 19	20 20	F ^(0u+) F ^(0u+)	. <i>'</i>
	17593.977	9	17	ر0	27	27	26	F ⁽ (0u+)	vs,Q
	17593.449	9 74 -	17 20	0 1	26 74	28 76	27 77	F ^(0u+) F(0u+)	w,NQ
	17593.070	9 10	17 18	0 0	27 93	29 91	28 92	F´(0u+) F´(0u+)	w,NQ
	17592.334	9 76	17 22	0 2	28 57	30 55	29 56	F ^(0u+) F(0u+)	m,b,NQ
	17591.764	74	20	1	83	83	82	F(0u+)	s,db,Q
	17591.545			•	• •			،	s,db,Q
	17591.150								s,Q?

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LINE(cm ⁻¹)	v3	v ₂	v 1 ~	΄J3	J2	J <u>1</u>	STATE	REMARKS
17588.961						,	•	s,Q
17546.717	73	20	ĺ	98	98	99	F(0u+)	w
17545.718								w,b
17544.482				•			· ·	·s,Q
17542.178	71	19	1	51	51	52	F(0u+)	m
17541.484	71	19	l	60	58	57	F(0u+)	
17539.520					2	`		w
17538.596								m,b
17537.991		~			,			w
17534.527						-	- .	w
17531.828								m
17524.547					•	· 5		w,b
17523.639	·\							m
17520.891		\checkmark				•		m,b,NQ
17519.686							•	w,b,Q?
17518.772								vw,b
17515.740								w
17514.768		•					•	w,b
17512.911								w,b
17511.316	8	17	· 0	õõ.	92	91	F ⁽ ()u÷)	s,NQ?
17510.191	68	17	0	88	86	87	F(0u+)	m
17508.129								ď,m
17506.076	-68	17	0	- 88	88	89	F(04+)	Sw.b
17501.914	68	17	• o •	- 88	90	91 -	、 F("0u+)	C, W
17498.960							· ·	vs,0
17497.326								w.b

	•			•		•			262
	LINE(cm ⁻¹)	`_ v 3_	~~v2	vı	J3	J2	J _l	STATE	REMARKS
	17496.824				•	•			w -
•	17496.706	74	22	2	105	103	104	F(0u+)	w
	17494.260	70 72	19 20	1	83 126	81 124	82 123	F(0u+) F(0u+)	w
	17492.890		•						w,b
	17490.233	70 9	19 19	1 1	83 85	83 83	84 84	F(0u+) F (0u+)	m,b,NQ3
-	17486.228	70 9	19 19	1 1	83 85	85 85	86 86	F(0u+) F(0u+)	m,b
	17484.674	70	19	1	92	92	91	F(0u+)	s,b
	17483.811					•	•		w,NQ?
	17483.087								w,b
	17481.733								s,Q
	17480.995	72	21	2	79	77	76	F(0u+)	m,b,NQ?
•	17479.555					•			vw
	17478.936			. •					w, NQ
	17476.227								vw, NQ
	17472.766				•			·	s,Q
	17471.635								w,b
•	17470.106								VW
	17469.065		•						W
	17468.203								w,b
	17465.890	4							m,Q
	17463.355							· •	s,Q
	17460.068	10	21	2	90	88	87	F ^(0u+)	w,Q?
	17459.270								w,Q?
	17458.621	,							, Q, d, m
								•	ł
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LINE(cm ⁻¹)	v3	v2	vl	J3	J2	Jl	STATE	REMARKS	•
17456.473	· 9	20- 20	2 2	2	4 4	5	F´(Ou+)	m,Q	
	9	20. 20	2	6	4.	5.		•	
- - .	9 9	20 · 20	22	- 5 7	5 5	6			•
17455.697	65	16	0	71	69.	68	F(0u+)	w,b,NQ	
	· 9	20	0	14	14	13	F (Ou+) F (Ou+)	-	
17453.235	. 6	16	0	66	64	65	F ^(0u+)	vs,NQ?	
17452.368				·				w,b	
17451.918							,	w,Q	
17451.529			:	•				s,Q	
17451.024								m,b,NQ?	
17449.899							•	s,b,Q?	
17449.277						•		w,NQ?	
17447.550	7	17	0	·115	113	114	F ^(0u+)	w,NQ?	
17446.867	6	16	0	. 75	75	74	F (Ou+) .	vs,Q	
17446.259	67	17	0	120	120	119	F(0u+)	s,Q	
17446.000							· ·	m,NQ	
17444.307							-	.w,b	
17443.430	6	16	0	75	77	76	F'(Ou+)	m,b,Q	
17442.445					-			m,NQ	
17440.191								w	
17439.221								m,b	
17438.717	69	19	1	- 114	112	111	F(0u+)	w	
17438.289								m	
17436.523	67	18	1	61	61	62	F(0u+)	s	
17435.787								m,ò	
17433.022	69	19	.1.	106	108	109	F(Ou+)	w (
						\		<i>,</i> .	•
).			

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LINE(cm ⁻¹)	v3	v ₂	vı	J3	J ₂	Jl	STATE	REMARKS
17432.351	7	17	0	123	125	124	F ^(0u+)	m,vb
17431.873								W
17431.488	71	21	2	103	101	100	F(0u+)	w,vb,NQ
17428.104							•	w,b,NQ-
17426.869	71	21	2	103	103	102	F(0u+)	m,Q
17422.690			-					vw,NQ
17415.221							·	w,b
17413.857	_7	18	1	75	75	76	F ⁽ 0u+)	s,Q
17411.105	7	18	1	83	83	82	F´(0u+)	s,Q
17409.943	7	18	1	75	77	78	F ^(0u+)	w,b,NQ
17409.425	8	19	1	123	123	122	F (0u+)	m,Q
17408.010	7	18	1	76	78	79	F´(0u+)	vw,vb,Q
17406.834							1	m,b,NQ
17405.399	66	17	0	130	128	129	F(0u+)	w
17403.482	70	20	1	148	146	147	F(0u+)	۰vw
17401.219								w,b
17396.639		-						vw
17395.803		·		•				VW
17395.248								vw ·
17391.324								VW
17390.670								s
17390.102								W
17389.310			•	•	•			s,vb
17388.990								m
17388.381	68 9	19 21	1 2	124 120	124 118	125. 117	F(0u+) F(0u+)	vw,b
17387.709								1.7

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	•				`		•		265
	LINE(cm ¹)	v3	v2	vl	J3	J2	J_1^{-}	STATE	REMARKS
	17384.910	64	17	1	17	15	16	F(0u+)	m ·
	17384.079	64 64	17 17	1	17 26	17 24	18 23	F(0u+) F(0u+)	vs,b,NQ2_
	17382.562	64	17	1	27	27	26	F(0u+)	s,vb,Q
	17380.666	4 64	15 17	0 1	53 / 28 .	51 30	50 29	`F´(Ou+) · F(Ou+)	s,NQ
	17379.800	4	15	0	45	45	46	F ^(0u+)	vs,Q
	17378.055								m
	17377.425	4 4	15 15	0 0	45 54	47 54	48 53	F'(0u+) F'(0u+)	s,db,NQ
	17376.978				•		•		m,NQ?
	17375.984						\$		vs,Q
	17374.825				· ·				s,Q
	17374.000		-						w,b,Q ~
	17373.158		•						w,b
	17372.129				-	•		. *	w,b
	17370.207								Ŵ
	17364.745			•	•				m,Q
	17363.670								w
	17362.370							•	vw,b
	17361.577								w
	17361.125								.vv y
	17359.038							•	 m
	17358.486								w,NQ
	17357.246								s,Q
	17356.429					÷			m,NQ
	17354.669								m,Q
	17354:016			١.	· .				m) Q
•			÷.			e.			

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	LINE(cm ⁻¹)	. v 3	v2	v _l .	. J3	J ₂	J	STATE	REMARKS
	17353.472						. -	•	m.
	17352.566			٠			· .		m, NQ
	17349.410	61	15	0.	75	75	74	F(0u+)	m,Q
	17348.932	-							w
	17348.061	•							m,Q
	17347.435							•	vw,NQ
	17344.783	61 6	15 18	0 1	76 109	78 107	77 108	F(0u+) F´(0u+)	w,b
	.17343.936	5	17	1	62	60	61	F (0u+)	m
	17341.127	5	17 `	1	62.	62	63	F (0u+)	S .
·	17338.925	5	17,	1	70	70	69	F ^(0u+)	vs,Q
	17337.884	5	17	1	62	64	65	F ^(0u+)	m,NQ
•	17337.232	•					. `		W,NQ
•	17336.899								w,b,Q?
	17336.184								w
	17335.441								w
•	17332.672					•			m,Q
	17332.006	6 65	18 18	1 1	110 1 1 2	112 112	113 113	F´(Ou+) F(Ou+)	w
	17330.472								d,m
	17329.719	63	15	0	78	80	81	F(0u+)	w,b,NQ
Á	17328.840			ć					vw,b,Q?
	17327.615	67	20	2	104	102	1.0 3	F(Ou+)	w,NQ
	17326.925	63 65	17 18	1	69 112	71 114	72 115	F(0u+) F(0u+)	
	17325.930							、	m
	17325.012								vw,Q
	17321 -157	63	17	1	79	81	80	F(Ou+)	m,NQ?
-			•						

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	· 	•		-			· ·		267	-
	LINE(cm ⁻¹)	· 🗸 🗸 3	v2 ·	v1	. J3	J2	Jl	STATE	REMARKS	•
	17306.430	• . 	_			1		•	vw,b,Q	
	17306-010	_			-				vw,b,Q	•
	17305.638	•						•	m,NQ	
	17305.081				•				s,Q	
	17304.161		. •						vs,Q	
	17304.016								vs,Q	-
	17302.248	7	20	2	-116	118	117	F ^(0u+)	w	• .
	17297.048	3	15	0	103	103	102	F´(0u+)	s,Q	
	17295.652	3	15	0	95	97	98	F ^(0u+)	w,Q?	
	17293.775							· ·	w, NQ	•
	17292.854								₩.Q? /	
	17290.509	a 3	15	0	104	106	105	F ^(0u+)	s,NQ?	
	17285.082								w,vb,NQ	
•	17282.924	62	17`	l	96	94	95	F (0u+)	w,b,NQ	
	17280.650	60	16	1	• 31	29	30	F(0u+)	w,NQ	
	17279.095	60	16	1	31	31	32	F(Ou+)	m,sh,Q	
	17278.867	60	16	1	40	38	37	F(0u+)	s,NQ	
	17277.430	60 62	16 17	1 1	31 105	33 103	34 102	- F(θu+) F(θu+)	w,NQ w,NQ	
	17276.492	60	16	1	41	41	40	F(Ou+)	s,b,Q	
	17273.954	60	16	1	42	44	43	F(0u+)	m,NQ? -	
	17271.605	5	18	1	135	133	134	F´(Ou+)	w,NQ?	
	17270.401	3	16	1	4,3	41	42	F ⁽ (0u+)	m,NQ	
	17269.103	3	16	1	51	49	48	F ⁽ (0u+)	w,Q	
	17268.270	- 3	16	1	43	43	44	F ⁽ (0u+)	s,NQ?	
	17266.253	3	16	1	43	45	46	F ⁽ (0u+)	s,Q	
	17264.685	1	17	1	102	102	103	F ¹ (Gu+)	s,Q	*
								•		
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	. .		•	*		·			26.9
•	$LINE(cm^{-1})$	۲V	Vэ	עו	Ja	ป้ว	J	STATE	208 REMARKS
	17264.264	J	- Z 	. T	- 3	•2	.^	UINIL	m.NO?
	17261.051	4	17	1	110	110	109	$F^{(0)}$	m.b
	17258.935	62	18	2	32	32	33	F(0u+)	m
	17256.731						,	- ((,	S
•	17254.590								
	17250.519			,		•			-
	17246.949								
•	17245.273								e
	17244.426	59	15	σ	118	פוו	ورز	下(02+)	5 W
	17240.481								w
	17239.748								
	17233.139	4	18	2	56	56	57	- Ε ⁽⁰ 11+)	m đh
	17231.158	4	18	2	64	64	63	• F ⁽⁰ 0+)	
	17230.602	4	18	2	56	58	59	F'(0u+)	m b
	17228.793	5 .	19	2	104	106	107	F(0u+)	, <i>2</i>
	17224.573	59	16	1	75,	75	76	E(0n+)	с. С
	17218.943			-	. 2			1(04)	5
	17198.164							•	
	17193-956	ı	15	٦	0	0	٦	21(0):1)	w
	1,1,0,1,0,0	1	15	1	2	0	1	F(0u+) F(0u+)	s,2,Q
		1	15	1	2	2	1	F (0u+) F (0u+)	,
		1	15 15	1	4	2 3	1 2	F´(Ou+) F´(Ou+)	
	•	1 1	15 15	1 1	3	3	2.2	デ〔(0u+) 〒〔(0u+)	
		1	15	1	2	4	3	F'(0u+)	
		i	15	1	6	4	3	F (00+)	
		1	15 15	1 1	3 5	5 5	4	F ⁽ (0u+) F ⁽ (0u+)	
		1 1	15 15	1 1	7 4	5 6	4 .	F (0u+) F (0u+)	
		1 1	15 15	1	6	6	555	F(0u+)	5

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	LINE(cm ⁻¹)	v3	v ₂	v1	J3	J2.	. J ₁	. STATE	REMARKS
	17192.434	1	15	. 1	13	15	14	F ⁽ 0u+).	m,NQ
	17192.164				-		• •		m,Q?
	17191.279 -				•				w, NQ
	17190.811	•		:			۰.		' m
	17190.101	2	16 /	1	93	93	94	F ^(0u+)	s,Q
	17188.964			•	м.				s,Q
	17188.301	56	14	0	99	101	102	F(0u+)	w,NQ
	17186.981			•	C				w, NQ
	17183.381 ·								W, NQ
	17179.663								s.d
	17176.607					·			w
	17176.034	56	15	l	39	37	38	F(0u+)	m, NQ
	17174.029					-		,	s,Q —
	17173.609								m,db
	17173.246	56	15	1	49	47	46	. F(0u+)	w, NQ
	17171.508	56	15	1	40	42	43	F(0u+)	w, NQ
	17170.923							•	m,db,Q [°] .
	17170.371								m
	17169.927								m,db
	17168.518								w, NQ
	17162.369	58	16	1	112	112	111	F(0u+)	
	17159.238	2	17 ;	2	40	38	39	F ⁽ (0u+)	n
	17158.140	2	17	2	48	46	45	F ⁽ (0u+)	w
	17157.358	29	17 18	2 2	4 C 9 S	40 98	41 99	F ⁽ (u+) F ⁽ (u+)	S
	17156.811	60	17	1	145	147	146	F(0u+)	w
-	17155.851			•					s .
							*	¢	

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	· . •	_	-	•				•	270	
	LINE(cm ⁻¹)	v3	` v ₂	Vl	J3	J ₂	. J1	🝠 STATE	REMARKS	
•	17155.506	2 62	17 19	2 2	40 130	42 132	43 133	F´_(0u+) F(0u+)	m,b	
	17154.721	0	14	0	117	115	116	F ^(0u+)	s	
• • •	17153.146	2	17	2 `	49	51	50	F´(0u+)	m,vb	
.	17147.782	53 58	13 17	0 2	78 47	76 49	75 50	F(0u+) F(0u+)	S S	
	17147.525	58 .	17	2	. 56	56	55	F(0u+)	S	
.*	17144.416								m	
•	17143.886	0	14	́ о	126	126	125	F ^(0u+)	m	
	17142.693				•	\sim			w	
۰ ~_	17118.572	0	15	1.	82	80	81	F ⁽⁰ u+)	d, m	
	17116.434	0	15	1	90	88	87	F ⁽ (0u+)	m	
	17114.816	0 ⁻ 55	15 15	1 1	82 .80	82 82	83 83	F ^(0u+) F(0u+)	S	
. •	17112.475	••	. –						w	
	17107.033	. 0	15	1	91	93	92	F ⁽ (0u+)	m	-
•	17090-324	52	13	0	109	107	106	F(0u+)	S	

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APPENDIX B

127_{I_2} , 129_{I_2} 3P2C Lines and Assignments

PUMP (cm ⁻¹) v ₂	v1	J2	Jl	J ₃ =J ₂ -2	PROBE (cm^{-1} J ₃ =J ₂) J ₃ =J ₂ +2	. ∨ 3 <i>€</i> ,	Śtate
17248.475	14	0	82	81	17219.820	17223.369	17226.856	. 1	F´(Ou+)
17248.475	14	Ö	82	81	17284.000	17287.599	17291.236	2	F(()u+)
17248.475	14	. 0	82	81	17155.123	17158,695	17162.320	- 0	F'(0u+)
17248.672	1_4	0	75	76	17222.690	17225.934	17229.293	1	F´(0u+)
17248.672	14	0	75	76	17286.963	17290.180	17292.537	2	F ^(0u+)
17248.672	14	0	75	76	17157.924	17161.227	17164.756	0	F (0u+)
17248.672	14	0	.75	76	·	17296.930		58	F(0u+)
17248.672	14	0	75	76		17220.389		56	F(0:1+)
17248.672	- 14	0	75	. 76	17157.947	17161.197	17164.522	0	F ^(0u+)
17249.435	15	0	126	125	17148.082	17153.463	17158.695	1	F´(0u+)
17265.986	14.	0	71	70	17159.553	17162.553	17165.713	0	F ⁽ (0u+)
17265.986	14	0	71.	70	17288.629	17291.586	17294.742	2	F ⁽ (0u+)
17266.138	14	0	64	65	17161.738	:17164.389	17167.287	d l	F´(0u+)
17266,138	14	0	64	65	17291.260	17293.941	17296.647	2	F´(0u+)
17267.447	14	0	70	69	17289.055	17291.920	17295.082	2	F´(0u+)
17279.615	14	0	61	60	17162.895	17165.502	17168.488	0	F´(0u+)
17279.615	14	0	61	60	17163.264	17165.576	17168.580	0	F´(0u+)
17279.615	14	υ	61	60	17162.943	17165.602	17168.565	0	F´(0u+)
17279.734	14	0	54	55	17165.111	17167.463	17169.889	0	F (0u+)
17279.734	14	0	54	55	17165.091	17167.458	17169.808	0	F (0u+)
17279.734	1.4	0	54	55	17150.628	17152.872	17154.883	54	F(0u+)
17279.734	14	0	54	55	17165.072	17167.471	17169.922	0	F´(0u+)
17280.636	15	0	114	113	17154.883	17159.695	17165.091	1	F ^(0u+)
17280.859	14	0	60	59	17109.412	17111.705	17114.193	53	
17280.859	14	0	60	59	17163.264	17165.889	17168.580	0	F´(0u+)
17280.859	14	0	60	59	17163.255	17165.910	17168.488	0	F´(0u+)

	•	•		-			• • •	×	.	272
	PUMP(cm ⁻¹)	v 2	v1	` J <u>2</u>	J _l	J3=J2-2	PROBE(cm ⁻⁾ J ₃ =J ₂	J ₃ =J ₂ +2	v3	State
	17280.859	14	0	60	59	17292.467	17295.051	17297.738	2	F (Ou+)
	17280.859	14	0	-20	59	17148.109	17150.332	17152.863	54	F(0u+)
	17280.859	14	0	60	59	17163.264	17165.875	17168.565	. 0	F (0u+)
•	17280.859	14	0	60	59	17148.030	17150.220	17153.120	54	F(0u+)
	17280.975	14	0	53	54	17165.602	17167.721	17170.131	0	F'(0u+)
	17280.975	14	0_0	53	5,4	17294.404	17296.699	17299.088	2	F ⁽ (0u+)
	17280.975	14	0	53.	54	17165.502	17167.664	17170.006	0	F ⁽ (0u+)
•	17280.975	14	0	53	54	17165.404	17167.721	17170.107	0	F'(0u+)
·	17281.331	15	0	107	108	17158.848	17162.916	17167.940	1	F~(0u+)
	17282.080	14	0	59	58	17226.120	17228.450	17230.600	56	, F(Ou+)
لہ	17282.080	14	0	59	58	17163.924	17166.453	17169.023	0	F ^(0u+)
	17282.080	14	0	59	58	17148.900	17151.199	17153.637	54) F(Ou+)
	17282.080	14	0 -	59	58	17187.730	17189.780	17192.050	55	F(0u+)
	17282.080	14	0	59	58	17228.450	17231.290	17233.860	1	F´(0u+)
	17282.193	14	0	52	53	17230.600	17233.090	17235.240	1	F´(Ou+)
	17282.193	14	0	52	53	17267.130	17269.490	17271.490	57	F(0u+)
•	17282.193	14	0	52	53	17165.961	17168.199	17170.490	0.	F´(Ou+)
•	17282.193	14	0	52	53	17190.720	17192.660	17194.640	55	F(0u+)
	17282.193	14	0	52	53	17152.086	17154.051	17156.000	54	F(0u+)
	17284.565	14	<u>.</u> 0	50	51	17166.516	17168.611	,17170.797	. <u>`</u> 0	F ¹ (0u+)
¥.	17284.565	14	0	50	51	17295.688	17297.721	17299.514	2	F´(0u+)
	17284.565	14	0	50	51		17231.781		56	F(Ou+)
	17284.565	14	0	50	51	17231.119	17233.484	17235.738	1	∑ F´(0u+)
	17284.565	14	0	50	51	17152.793	17154.543	17156.607	54	F(0년+).
	17284.565	14	Ō	50	51	17191.002	17193.359	17195.146	<u>র্</u> জু	F(0u+)
	17284.883	16	1	36	37	17199.510	17200.990	17202.717	2	F ⁽ (0u+)
	17284.883	16	1	36	37	17263.281	17264.908	17266607	3	F´(Ou+)
	. N			5		•				

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	•, ••,				•	•••		· · · ·		273	
•	PUMP(cm ⁻¹) v ₂	vl	J2	J1	J ₃ =J ₂ -2	PROBE(cm ⁻ J ₃ =J ₂	1 ₎ J ₃ =J ₂ +2	۳з	State	
4	17284.883	16	1	36	37	17288.395	17289.797	17291.500	60	F(0u+)	
0	17284.883	16	i	36	37	17211.652	17213.315	17214.572	58	F(0u+)	
, · · gur	17284.883	16	- 1	36	37	17326.130	17327.529	17328.902	61	F(0u+)	
	17285.512	16	1	42	41	17286.648	17288.147	17289.797	60	F(0u+)	
٠.	17285.512	16	1	42	41	17324.162	17325.607	17327.254	61	F(0u+)	
	17285.512	16	1	42	41	17325.607	17327.529	17329.268	4	F´(0u+)	
	17285.512	16	1	42	41	17171.461	17173.350	17174.961	57	F(0u+)	
	17285.512	16	·l	42	41	17198.092	17199.898	17201.663	2	F ⁽ 0u+)	
	17285.519	15	0	112	111		17298.918		60	F(0u+)	
	17285.519	15	0	112	111		17160.475		l	F´(0u+)	
	17285.519	15	0	112	111		17288.395		3	F ^(0u+)	•
	17285.519	15	0	112	111		17224.900		2	F´(0u+)	
	17285.615	14	0	56	55	17164.520	17166.910	17169.426	0	F (0u+)	
	17285.754	16	1	35	36	17327.254	17328.902		4	F'(0u+)	
	17289.567	16	1	37	36	17263.332	17264.873	17266.461	3	F ^(0u+)	
-	17289.776	16	l	30	31	17264.502	17265.900	17267.041	3	F ^(0u+)	
	17297.972	16	1	23	22	17265.807	17266.752	17267.742	3	F´(0u+)	
	17297.972	16	l	23	22	17265.785	17266.750	17267.723	3	F´(0u+)	•
	17298.092	16	1	16	17	17266.752	17267.311	17268-039	3	F ⁻¹ (0u+)	
	17298.092	16	1	16	17	17266.750	17267.371	17268.053	3	F ⁽ (0u+)	
	17302.020	14,	0	32	33	17274.481	17275.658	17276.703	57	F(0u+)	
•	17305.574	14	0	34	33	17197.008	17198.236	17199.578	55	F(0u+)	
	17305.574	14,	0	340	-32	17158.375	17159.566	17160.902	54	F(0u+)	
	17305.626	14	0	27	28	17198.236	17199.764	17200.818	55	F(Ou+)	
	17305.626	14 •	0	27	28	17159.566	17161.137	17162.188	54	F(Ou+)	
	17305.626	14 -	0	.27	28	17171.192	17172.656	17173.863	0	F ⁽ (0u+)	
•	17306.232	14.	0	33	32	17170.305	17171.699	171,73.246	, 0	F ^(0u+)	
			>			•					
				•			•				
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· .	PUMP(cm ⁻¹)	¥2	vı J	J2	J.	J3=J2-2	PROBE(cm^{-1} J ₃ =J ₂	J ₃ =J ₂ +2	v3	'State
	17306.283	14	0	26	27	17171.359	17172.682	17173.867	0	F ⁽ (0u+)
	17306.283	14	· 0	26	27 [.]	17198.453	17199.797	17200.793	55	F(0u+)
	17306.371	15	0	103	102	17160.477	17164.99.6	17169.510	1	F [*] (0u+)
	17306.869	14	Ö	32	31	17170.406	17171.840	17173.221	0	F'(Ou+)
	17306.869	14	0	32	31	17158.430	17159.768	17161.125	54	F(0u+)
	17306.959	15	•0	96	9 <u>7</u>	17163.902	17168.012	17172.379	1	F ⁽ 0u+)
	17315.053	15	0	99	9.8	17162.350	17166.826	17171.381	1	F´(Ou+)
•	17315.422	14	0	10	9	17173.658	17174.115	17174.578	0	F ⁽ 0u+)
	17315.422	14	0	10	9	17162.635	17162.859	17163.397	54	F(0u+)
	17315.682	14	0	8	7	17085.197	17085.596	17086.076	52	F(0u+)
	17315.682	14	Ō	8	7	17162.545	17162.947	17163.430	54	F(0u+)
	17315.682	14	0	8	7	17317.434	17317.654	17318.000	58	F(0u+)
	17315.682	14	0	8	7	17085.563	17085.781	17086.017	52	F(0u+)
	17315.682	14	0	8	7.	17124.030	17124.428	17124.721	53	F(0u+)
	17315.943	14	0	4	3	17240.393	17240.664	17240.800	56	F(0u+)
	17315.943	14	0	4	3	17303.332	17303.641	17304.031	2	F (0u+)
	173 5.943	14	0	4	3	17174.111	17174.305	17174.584	0	F ^(0u+)
	17315.943	14	0	4	3	17279.301	17279.451	17279.931	57	F(0u+)
	17315.943	14	0	4	3	17291.398	17291.506	17291.873		
	17315.943	14	0	4	3	17202.010	17202.350	17202.400	55	ອ F(Ou+)
	17315.943	14	0	4	3	17238.828	17239.131	17239.574	1	F ^(0u+)
	17315.943	14	0	4	3	17163.443	17163.607	17163.875	54	F(0u+)
	17315.943	14	0	4	43	17317.950	17317.950	17317.950	58	F(0u+)
	17317.167	15	0	98	97	17162.861	17167.225	17171.186	1	F ¹ (0u+)
	17317.167	15	0	98	97	17227.484	17231.242	17236.127	2	F ⁽ (0u+)
	17392.413	15	0	50	49	17373.160	17375.287	17377.406	4	F ^(0u+)
	17409.858	15	0	~28	27	17378.256	17379.410	17380.447	4	F [*] (0u+)

		•			. `	•	,* <u>-</u> *			• - •
	PUMP (cm^{-1})) v ₂	vl	J2	Jŀ	Jan Jan 2	PROBE(cm ⁻	L) .	v3	275 State
	17409,968	15	0	21	22	17379 106	J3-J2	J3=J2+2	•	· ·
	17413-996	15	ů n	12	12	17390 330	17300.119	1/380.918	4	F (0u+)
	17414,190	16	• n		13	1/000.000	17373 266	1/381-300	4	F (0u+)
•	17414.589	15	n	17	16	17380 330	17390 934	17201 400	63	F(0u+)
	17414.650	15	0	10	יי	17/10 561	17300.024	1/381.400	61	£ (0u+)
	17454 171	16		10	. 76	17419.001	17419.893		62	F(0u+)
	17473 004	10	0	~	70	17440.391	1/443.598	17446.875	6	F´(Ou+)
	17475.904	10	0	64	63	1/445.187	17447.803	17450.525	6	F (Ou+)
	17474.374	16	U	57	58	17447.803	17449.787	17452.205	6	F'(Ou+)
	1/484.550	16	D	49	50	17450.076	17451.674	17453.717	6	F´(Ou+)
	17484.702	18	1	26	27	17421.088	17422.109	17423.402	- 7	F (Ou+)
	17487.621	16	0	53	52	17433.883	17436.244	17438.225	64	F(0u+)
•	17487.621	16	0	53	52	17448.621	17450.754	17452.973	[.] 6	F´(Ou+)
	17487.996	16	0	46	47	17450 😴 54	17452.332	17454.260	6	F´(0u+)
	17492.955	16	0	48	47	17321.909	17323.759	17325.970	61	F(0u+)
	17493.266	18	1	8	9	17387.168	17387.516	17387.936	65	F(0u+)
	17493.266	18	1	8	9	17349.322	17349.722	17350.195	64	, F(Ou+)
	17493.266	18	1	-8	9	17360.864	17361.178	17361777	6	F´(Ou+)
	17493.289	16	` 0	41	42	17362.996	17364.344	17365.660	62	F(0u+)
	17493.289	16	0	41	42		17401.762		63	F(Ou+)
	17493.289	16	0	41	42	17324.833	17326.268	17327.685	6]	F(01+)
	17501.143	16	0	39	38	17452.365	17453.925	17455.375	6	E(0u+)
	17502.195	16	0	31	32	17453.654	17454_873	17456.184	- -	E (011+)
	17512.466	16	0	20	19	17455.654	17456-369	17457 496	ں د	
	17512.571	17	0	90	91	17449.350	17452 268	17456 764	- -	
	17512.587	16	0	13	14		17457 141	x/7JU1/04	i e	
•	17512.587	16	0	13	14	17445 197	17445 057		0	
	17856.216	23	1		84		17075 600	17000	ъ4 о :	r(Uu+)
			- .		04	ì	T/032.009	1/838.527	84	F(0u+)
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	PUMP(cm ⁻¹)	v ₂ ,	vı	J ₂	Jl		PROBE (cm-1)	V3	Z76 State
	17056 500		_			J3=J2-2	J3≕J2	J3=J2+6		
	1/856.508	23	1	79	80	• 2	17803.219	. (83	F(0u+)
•	17856.508	23	1	· 79	80	17836.061	17838.527	.17841.193	84	F(0u+)
	17857.110	. ²⁰	0	51	52	17872.641	17874.570	17876.943	81	F(0u+)
	17857.110	20	0	51	52	17836.920	17838.527	17840.492	80	F(0u+)
	17857.110	20	0	51	52	17800.842	17802.498	17804.779	79	F(0u+)
	17857.361	20	0	57	56	17798.447	17800.410	17802.498	79	F(0u+)
•	17857.361	20	0	57	56	17870.525	17872.443	17874.570	81	F(0u+)
	17857.361	20	0	57,	56		17836.529	17838.498	80	F(Ou+)
	17860.724	21	0	96	97	•	17806.170		81	F(0u+)
	17860.724	21	0	96	97	17838.965	17841.975	17845.438	82	F(0u+)
•	17860.945	20	0	48	49.	17801.910	17803.580	17805.380	.79	F(Ou+)
	17860.945	20	0	48	49	17838.020	17839.729	17841.975	80	F(0u+)
	17877.696	23	1	74	73	17838.617	17841.440	17844.231	84	F(0u+)
	17877.727	20	0	32	33	17879.756	17880-897	17882.078	81	F(0u+)
	17883.271	20	0	31	30	17879.736	17880.940	17881.902	81	F(0u+)
	17883.271	20	0	31	30	17843.957	17845.084	17846.240	80.	F(0u+)
	17885.211	20	0	28	27	17844.686	17845.678	17847.002	80	F(0u+)
	17885.687	20	0	21	22	17846.260	17847.002	17847.559	80	F(0u+)
	17885.810	20	0	27	26	17844.686	17845.861	17847.002	80	F(0u+)
	10888.104	23	1	68	67		17809.262		83	F(0u+)
	17888.405	21	0	84	85	17882.756	17885.291	17888.279	83	F(0u+)
	17888.405	.51	0	84	85	17775.426	17778.268	17781.295	80	F(0u+)
	17888.405	21	0	84	85	17846.982	17849.850	17853.063	82	F(0u+)
	17888.405	21	0	84	85		17813.757	17816.709	81	E(0u+)
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	PUMP(cm ⁻¹)	. v ₂	v 1	J2	Jl	Ja=Ja-2	PROBE(cm ⁻	l) .Ta=.Ta+2	¥3	277 State
•	17888.405	21	0	84	85	17811.102	17814.117	17817,172	81	. √ F(0n+)
,	17888:496	21	0	90	89	17807 373	17810 301	17813 527	ີຄາ	F(01+)
	17888.496	21	ů N	90	89	· 17771 295	17774 529	17777 770	90	F(0u+)
•	17889.342	20 0	-0	16	17	17774 688	17775 426	17776 066	78	F(0u+)
	17889.342	20	0	16	17	17811_102	17811 816	17812 389	79	- T(Ou+)
	17889.441	20	· 0	22	21	17810 310	17811 020	17811 816	70	F(01+)
	17889.441	20	n	 22	21	17773 810	17774 688	17775 426	70	F(0u+)
	17889.731	20	0	19	18	17846 565	17847 307	17847 000	, 0 0 U	F(01+)
	17889_731	20	n	19	19	17810 244	17811 0/0	17811 020		
•	17889 731	20	ں م	19	18	17882 856	17993 111	17002 004	13	
	17889 749	20	י. ו	67	55	17807 039	17005.111 , 17000 EA1	17003.304	0.7	
	17890 027	21	יד ד	105	104	17007.035	17052 014	1/811.830	ده	F(0u+)
•	17990.027	24	- -	100	104	17011.115	17011.000		ğθ Ξ0	r(Uu+)
	17000.034	20	0	12	12	178112115	1/811:830	1/812.459	79	F(Ou+)
	17090.034	20	U	12	13 . ~	1/84/.30/	1/84/.998	17848.584	80	F(Ou+)
	17890.034	20	U	12	51	<	17883.904	17884.300	81	F(0u+)
	17890.914	22	U	.116	117	17850.842	17854.754	17859.264	84	F(0u+)
	17892.582	20	0	2	3	17776.178	17776.379		78 •	F(0u+)
•	17892.582	20	0	2	3	•	17884.856	•	81	F(0u+)
	17892.582	20	0	2	3	17812.436.	17812.742		79	F(Ou+)
	17892.582	20	0	2	.9	17848.529	17848.777		80	F(Cu+) 🖌 .
	. (ζ.	-	• •	=	• • • • • • • • • • • •
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				127	I ₂ (Exc	3P2C LIN	ES AND ASSI	GNMENTS			
						•	gie dye las	er)			
	$PUMP(cm^{-1})$	v2	vl	J2	Jl	ч.	PROBE (cm ⁻¹)	v3	State	
<i></i>						J3=J2-2	J3=J2	J3=J2+2	•		
	17317.168	15	0	98	97	17162.926	17167.193	17171.533	۱	R〔())+)	
	17317.168	15	0	98	97		17193.799	17197.522	57	ר (טעיי) ד(ומ+)	
										r(00+)	
	17317.711	15	0	91	92	17166.205	17170.082	171741121	1	F ⁽⁰ u+)	
	17317.711	15	0	91	92		17198.574	17202.090	57	F(Ou+)	
	17317.711	15	0	91 [:]	9 Ż		17234.209	· ·	2	F ^(0u+)	
									۰.		
	17415.419	15	0	14	13	17316.452	17316.967	17317.531	3 ~	F [*] (0u+)	
	17415.419	15	0	14	13	17343.589	17343.074	17342.590	60	F(0u+)	
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3P2C LINES AND ASSIGNMENTS

$PUMP(cm^{-1})$. * 2	v1	J ₂	Jl	J ₃ =J ₂ -2	PROBE(cm ⁻¹ J ₃ =J ₂) J ₃ =J ₂ +2	v3	State
17304.044	15	0	93	94	17297.709	17301.592		3	F (0u+)
17304.044	15	0	93	94	·	17338.722	١	Ġ1	F(0u+)
17304.762	14	0	10	9		17305.426.		58	F(Ou+)
17304.762	14.	0	10	9		17307.719		2	F´(0u+)
17304.771	14	0	3	4	· •	17267.668		57	F(Ou+)
17304.771	14	0	3	4		17306.113		58	F(Ou+)
17400.714 -	18	1	82	83	17346.553	17350.023	17353.969	6	F[(0u+)
17400.731	15	0	24	23	17319.301	17320.121	17321.662	3	F'(0u+)
17400.731	15	0	24	23	17366.216	17367.464	17368.534	61	F(Ou+)
17400.731	15	0	24	23	17328.514	17329.633	17330.699	60	F(0u+)
17400.731	15	0	24	23	17382.208	17383.222		4	F (Ou+)
17400.814	15	0	-17	18	17320.121	17320.893	17321:662	3	.F ^(0u+)
17400.814	15	0	17	18		17368.534		61	F(0u+)
17400.814	15	0	17	18		17330.699		60	F(0u+)
17403.385	15	0	17	16	17367.797	17368.459	17369.420	61	F(0u+)
17403.385	15	0	17	16	17383.410	17384.124	17384.818	4	F ^(0u+)
17403.513	18	1	87	86		17348.225		6	F´(0u+)
17405.246	15	0	ક્	7	17384.107	17384.606	17384.908	4	F´(0u+)
17405.246	15	0	8	7	17321.080	17321.193	17321.450	3	F ^(0u+)
17405.478	15	0	5	4	17331.504	17331.703	17331.900	60	F(0u+)
17405.516	15 ·	0	2	1		17331.703	17331.900	60	F(Ou+)
17405.516	15	0	2	1	17369.732	17369.732	17369.732	61	F(0u+)
17414.475	16	0	93	92	•	17365.216		63	F(0u+)
17414.475	16	0	93	92		17378.025	17382.208	5	F ^(0u+)