LUMINESCENCE OF BENZONITRILES

# LUMINESCENCE OF BENZONITRILE, MONODEUTEROBENZONITRILES, AND PERDEUTEROBENZONITRILE AT 77°K IN SOLID MATRICES

by

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#### CHAPTER I

#### INTRODUCTION

Determination of geometries of excited electronic states of molecules is one of the many aims of molecular spectroscopy. The application of absorption measurements for this purpose is well known ( $\underline{1},\underline{2},\underline{3}$ ), the required information being obtained from the analyses of the vibrational and/or rotational structure of absorption bands. The analysis of the vibrational structure permits identification of the vibrational modes and determination of force constants while the analysis of the rotational fine structure permits determination of rotational constants thus providing information about the geometry of the molecule in the excited state. The same type of information ( particularly of the excited triplet state since  $T_1 \leftarrow S_0$  absorption data are scarce ) can be obtained from emission spectra.

Qualitatively, from the Franck-Condon principle, the appearance of a prominent progression in a particular normal mode of vibration is indicative of a molecular distortion along that normal coordinate. Quantitative methods have been developed for calculation of geometry changes by relative intensity measurements on the members of the progression for absorption data (4.5) and emission data (6).

In this study, the vibrational analyses of benzonitrile, perdeuterated benzonitrile, and ortho-, meta-, and para-monodeuterated benzonitriles in rigid matrices ( both glassy and crystalline solutions ) at 77°K are presented.

The results of the vibrational analyses are interpreted in terms of excited state geometries. Benzene itself is known to be slightly expanded and hexagonal in the first excited singlet state (4), and hexagonal (7)or nearly so (6,8,9) in the lowest triplet state. Substitution of H by  $-C \equiv N$  on the benzene ring results in the donation of negative charge to the substituent, both by resonance and inductive effects ( 10 ). Nevertheless, Bak et al ( 11 ) have found by microwave spectroscopy that the ground state of benzonitrile is still nearly hexagonal, as in benzene. A recent rotational analysis of the  ${\rm S_0}{\twoheadrightarrow}\,{\rm S_1}$ absorption band of benzonitrile by Knight and Brand ( 12 ) has established that in the first excited singlet state, both the long and short axis of inertia are extended but not equally so. The vapor phase fluorescence has been reported by Bass ( 13 ) while the phosphorescence was first reported by Kowalski (14) in 1912 and again by Lewis and Kasha (15) in EPA at 90°K in 1943. The phosphorescence was more recently reported in ethanol at 77°K in 1962 by Takei and Kanda ( 16 ) and finally by Faure et al ( 17 )

in a solid nitrogen matrix in 1969.

The orbital symmetry of the lowest excited triplet state is assigned using polarization results obtained by the method of photoselection.

#### CHAPTER II

#### THEORETICAL

Molecular spectroscopy investigates the interaction between an ensemble of distinct particles (molecules) and an electromagnetic radiation field.

The total internal energy of an isolated molecule is given by the sum of the kinetic energy and the potential energy of all the electrons and nuclei present. A stationary state of the molecule, of energy  $E_t$ , may be represented by a wavefunction  $\psi_t$ , of the time independent wave equation

$$H \psi_t = E_t \psi_t$$
 II.1

where H , the total quantum mechanical operator, equals the kinetic energy operator of the nuclei ( $T_n$ ) and the electrons ( $T_e$ ), plus the operators for the coulombic interactions between electrons and nuclei ( $V_{en}$ ) and the internuclear and interelectronic repulsion operators ( $V_{nn}$ ,  $V_{ee}$ ),

 $H = (K.E. + P.E.) = T_e + T_n + V_{en} + V_{ee} + V_{nn}$  II.2

Since the motion of the electrons at any given instant is , to a first approximation, very rapid compared to the motion of the nuclei , the nuclei are assumed

to be in a fixed position for the purpose of calculating the energy of the electrons (  $\rm T_n$  and  $\rm V_{nn}$  are assumed constant ). One can also define an electronic Hamiltonian operator (  $\rm H_p$  ) as

$$H_e = T_e + V_{en} + V_{ee}$$
 II.3

The separation of nuclear and electronic motion implies that the total wavefunction can be written in a product form

$$\psi_{t} = \psi_{e} \psi_{n}$$
,

which implies that

$$H_e \psi_e = E_e \psi_e . \qquad II.4$$

The product wavefunction is commonly called the zero-order Born-Oppenheimer approximation and represents a good approximation to an eigenfunction of the Hamiltonian operator.

Born and Oppenheimer have also shown that the motion of a molecule can be separated into three types: electronic, vibrational, and rotational so that the total energy is represented by

$$E_t = E_e + E_v + E_r \qquad II.5$$

and the corresponding wavefunction

$$\Psi_{t} = \Psi_{e} \Psi_{v} \Psi_{r} . \qquad \text{II.6}$$

The molecules or particles will undergo spectroscopic transition from an initial state of energy  $E_1$ ( with respect to an arbitrary zero ) to a final state of energy  $E_f$  if energy  $|E_f - E_i|$  is absorbed or emitted by the molecules in the form of electromagnetic radiation. The frequency (f) of the radiation is given by

$$f = v_{fi}c = \frac{c}{\lambda} = \frac{|E_f - E_i|}{h}$$
 II.7

where  $\mathcal{V}_{\text{fi}}$  has wavenumber units ( cm<sup>-1</sup>), h is the universal Planck's constant (6.62 x 10<sup>-27</sup> erg-sec.) and c is the speed of light in vacuum (3.0 x 10<sup>-10</sup> cm/sec.). Since  $\mathcal{V}$  is proportional to the energy of the photon and is easily calculated as the reciprocal of the wavelength  $\lambda$ , the wavenumber is a very versatile unit extensively used in spectroscopy.

#### 2.1 Classification of States

Since spectroscopic electronic transitions occur between differing states, it is important to know which orbitals ( and types ) are available for the electrons to reside in. Several theories ( Huckel, Free-Electron, etc. ) have been developed to calculate the energies of the molecular orbitals. Since these theories are limited except for the simplest atoms, it is not possible to expect the theoretical approaches to predict exact quantities ( energies ) for the orbitals of polyatomic molecules.

Several approximations have to be made even for the simplest approaches:

a) the electronic Hamiltonian is a sum of effective oneelectron energy operators, H<sub>i</sub>, that is

$$H_{e} = \sum_{j} H_{j}; \qquad II.8$$

b) the  $\pi$ -electron system can be divided into core electrons and valence electrons, so that

 $H_{e} = \sum_{j} H_{j}(\text{core electrons}) + \sum_{k} H_{k}(\text{valence electrons}) \text{ II.9}$ in which  $\sum_{j} H_{j}(\text{core electrons})$  is assumed to provide a constant potential term in the electronic Hamiltonian  $H_{e}$ ;

c) it is usually assumed that the molecular orbitals are linear combination of the 2pz atomic orbitals located on the various nuclear centers.

Each molecular orbital then has a set of quantum numbers associated with it and the electrons are added to the orbitals in order of increasing energy and according to Pauli's exclusion principle, which states that all wavefunctions must be antisymmetric in the coordinates (spin as well as space coordinates) of all pairs of electrons. The states for the molecule are then determined by their orbital electronic configurations.

The molecular states of molecules are also usually classified by the symmetry of their space wavefunctions. The molecular orbitals transform as various irreducible representations of the point group to which the molecule belongs. The representations of the orbital configurations ( states of the molecule ) are then given by the direct product of these representations.

In addition to the symmetry of the space or orbital wavefunction, the total spin angular momentum  $[S(S+1)]^{\frac{1}{2}}h$ , or the spin multiplicity, 2S + 1, is also used to describe molecular states. Each electron in a molecule contributes a spin of 1/2. If the number of electrons is even and their spin are paired (anti-parallel) there will be no net spin (S) and the spin multiplicity (2S + 1) will be one, the resulting state being called a singlet state. (This is true for the ground state of most aromatic hydrocarbons.) However, if for example, one of the electron is promoted from a  $\pi$ -bonding orbital to a  $\pi$ -antibonding orbital and the electron spins are still anti-parallel, a singlet excited state is formed. If the spins of such an excited molecule are parallel, the spin multiplicity

will be three forming the excited triplet state. Likewise, doublet, quartet, etc., states will result from molecules ( or ions ) having an odd number of electrons.

#### 2.2 Vibrational Motions of Polyatomic Molecules

Molecules with N nuclei have 3N degrees of freedom of displacement. For nonlinear molecules, six of these are associated with translation and rotation motions of the molecule as a whole. Therefore, nonlinear molecules have 3N - 6 (33 for benzonitrile) degrees of freedom associated with the internal vibratory motions of the nuclei in the molecule and analysed into motions along separate normal coordinates and identified by energy and symmetry. (2,18,19)

The complex vibrational motion of the molecule can be decomposed in terms of normal modes, a normal mode being a mode of vibration in which each nucleus reaches its position of maximum displacement at the same time, and passes its equilibrium simultaneously.

The normal modes of vibration of benzonitrile with their frequencies and symmetries are given in Table ( 4.1 ).

### 2.3 Isotope Effect

When an atom of a molecule is replaced by an iso-

topic atom of the same element, it is assumed that the potential energy function and configuration are changed by negligible amounts (20). The frequencies of vibration may, however, be appreciably altered because of the change in mass involved. This is particularly true if hydrogen is the atom in question because of the large percentage change in mass. Therefore, a normal mode of vibration in which the hydrogen atom in question is oscillating with a large relative amplitude will suffer a greater isotopic change in frequency than a normal mode in which this hydrogen atom is moving with a relatively small amplitude.

If the isotopic shifts of the normal modes of vibration are known, the vibrational assignments of the electronic spectra will be helped by a vibrational analysis of the isotopic substituted analogue of a molecule.

#### 2.4 Electronic Transition

Transitions between different electronic states usually give rise to spectra in the visible and ultraviolet regions. In general, the electronic transition is composed of vibrational bands, each band being accompanied by a rotational fine structure which give rise to a certain bandwidth on the vibrational bands.

Although the energy difference between any pair

of states can be calculated, the spectroscopic transition between the two states cannot always be observed. The probability of a transition occuring depends on whether the incident radiation can change the electronic distribution of the ground state to that which is necessary for the excited state or vice versa. The expression for the probability of the transition between two states  $\psi_i$  and  $\psi_j$  is such that the probability depends on the square of the transition dipole moment integral

$$\mathbb{P} \propto \left| \int \Psi_{i} M \Psi_{j} d\tau \right|^{2} \qquad \text{II.10}$$

where M is the dipole moment operator and M = Mx + My + Mz =  $\sum_{i} er_{i}$  where e is the charge of the electron and  $r_{i}$ is the vector distance of the i<sup>th</sup> electron from an origin of a coordinate system fixed for the molecule.

The transition moment integral between the two states  $\Psi_{\rm i}$  and  $\Psi_{\rm j}$  is often denoted as  ${\cal R}_{\rm i,j}$  ,

$$R_{ij} = \int \Psi_i M \Psi_j d\tau \qquad \text{II.11}$$

or in the bra-ket notation as

$$\langle \Psi_{i}|M|\Psi_{j}\rangle$$
 II.12

where dT is over the whole configuration space of the 3N coordinates. If R = 0, the transition is forbidden as an

electric dipole transition. ( Quadrupole interaction and second order effects are not considered here. )

Restrictions on the value of R (transition moment) are imposed by symmetry. The application of group theory makes it possible to predict which transitions are allowed.

In any given electronic state, the molecule may be excited to any of the possible vibrational states. Each of these levels may be regarded as vibrational-electronic or vibronic state.

# 2.5 Vibronic Selection Rules

The vibronic wavefunction  $\psi_{\rm ev}$ , may be written as  $\psi_{\rm e}$   $\psi_{\rm v}$  , and the transition moment has the form

$$\mathcal{R}_{ev} = \int \psi'_{e} \psi'_{v} M \psi''_{e} \psi''_{v} d\tau_{ev} \qquad \text{II.13}$$

where the (') and (") denoted the initial and final states respectively.

A transition is allowed if the direct product of the vibronic species of the two states involved contains at least one component of the electric dipole moment ( Mx, My or Mz ). Thus while a pure  $A_2 \leftrightarrow A_1$  electronic transition in the  $C_{2v}$  point group is forbidden ( see Table (2.1a)), transitions to levels where various vibrations in the electronic states are excited may be allowed.

The intensity of an electronically forbidden transition ( such as  $A_2 \leftrightarrow A_1$  in  $C_{2v}$  ) depends on the proximity of a third electronic state to which a transition is allowed from the ground state ( <u>21</u> ). The forbidden transition can borrow intensity by a mixing of vibronic eigenfunction of the two states involved.

In principle, two electronic states of any species can perturb each other if vibrations of the right symmetry are excited, but this perturbation will be very weak unless the species of the two electronic states differ by only the species of one of the normal vibration ( $\underline{22}$ ). In other words, the product of species of a normal vibration and one of the electronic states must equal the species of the other electronic state.

# 2.6 Franck-Condon Principle

The shape of an absorption or emission band due to a single electronic transition may be considered to be determined by the spacing of the vibrational subbands and by the distribution of the total intensity among the vibrational subbands which is determined by the Franck-Condon principle. The Franck-Condon principle states that the most probable vibrational component of an electronic tran-

sition is one which involves no change in nuclear configuration since the electronic transition is much faster  $(10^{-15} \text{ sec.})$  than the nuclear motion  $(10^{-12} \text{ sec.})$ .

A potential energy diagram can be drawn for each of the vibrational modes in any given state (ground and excited), the whole of which will form the polydimensional potential energy diagram for the polyatomic molecule.

Assuming that the vibrational motion of the nuclei performs as oscillators ( harmonic and anharmonic ), the allowed energy levels ( solutions of the Schrodinger equation with potential energy  $V = \frac{1}{2}kr^2$  for the harmonic oscillator ) will be

 $E_{j} = h \mathcal{U}(j + \frac{1}{2}).$ 

Figure (2.1a) shows the energy levels, eigenfunctions, and probability density distributions for such an harmonic oscillator. Of course, the eigenfunctions and probability density distributions for an anharmonic oscillator will be similar except that they will be somewhat unsymmetrical and that the unequal spacing of the energy levels will be best described by a power series (Figure (2.1b)).

The most probable transition, according to the Franck-Condon principle, will then be the vertically up-



Fig. 2.1 Potential energy diagram with energy levels, eigenfunctions, and probability density distribution (---) for an harmonic (a) and anharmonic (b) oscillator.

ward ( absorption ) or downward ( emission ) transitions in the potential energy diagram. Since the internuclear separation in the j = 0 vibrational level is described by a probability distribution, the transitions will occur over a certain range of r, and therefore more than one band will originate from j = 0. But the most intense band will be where a maximum overlap of the eigenfunctions occur.

If upon excitation, the molecular geometry is not changed, i.e., the equilibrium nuclear separation is roughly the same as in the ground state, the most probable transition and most intense peak in the emission spectrum will be the 0,0 band with the progression falling off in intensity quite rapidly. This is depicted in figure ( 2.2a and 2.2b ). However, if the excited state geometry is quite different from that of the ground state, the minimum of the excited state potential energy curve will be displaced with respect to that of the ground state, and a longer progression will be expected since the j = 0 level of the excited state overlaps with more levels of the other state. This is shown in figure ( 2.2c and 2.2d ).

The most prominent vibrational progression provides important information about a change of geometry of the molecule since the progression due to the vibration



Figure 2.2 Franck-Condon potential curves for the ground and lowest excited states ( a,c ) and the resulting expected emission progression ( b,d ).

with respect to the normal coordinate whose equilibrium value is the most greatly changed by the electronic transition will appear prominently in the spectrum. Therefore, prominent progressions indicate the important distortions occuring upon electronic excitation.

Several methods have been developed to measure the magnitude of the molecular distortions. One of these, using the Franck-Condon factors (vibronic overlap intergrals) was first used for polyatomic molecules by Craig  $(\underline{4})$  who measured the distortion of benzene upon excitation. The method was further developed by Coon et al  $(\underline{5})$  and used for measuring the distortion from absorption data. The same type of information can be obtained from emission data  $(\underline{6})$ . The assessment of the distortion is permitted by a measurement of the relative intensities on the members of the progressions.

# 2.7 Electronic Absorption and Emission

Electronic absorption spectra of most saturated organic compounds occur in the far-UV region, i.e., below 200 nm. while absorption occuring in the near-UV and visible regions are due mostly to unsaturated compounds since less energy is required to promote  $\pi$ -electrons than  $\sigma$ -electrons.

Absorption electronic spectroscopy refers to a transition from a lower electronic state of a molecule to a higher electronic state. This can also be regarded as a promotion of one or more electrons from an occupied molecular orbital to a higher energy unoccupied orbital.

Once a molecule has been excited, several mechanisms are possible for losing the energy of the unstable excited molecule. One of these processes is the radiative mechanism, i.e., by fluorescence and phosphorescence. Other mechanisms are the radiationless process, photochemistry, etc.

Figure (2.3) shows the possible absorption transitions and the different types of mechanisms for the intramolecular loss of energy. A full line represent a radiative process between states of the same multiplicity and the dashed vertical lines those transitions between states of different multiplicity as they are, to a first approximation, forbidden. The nonradiative transitions are represented by a wavy arrow for the internal conversion and a horizontal dashed line for intersystem crossing. The internal conversion is defined as a radiationless passage between two different electronic states of the same spin multiplicity while intersystem crossing is the radiationless passage from an electronic state in the singlet mani-



Figure 2.3 Schematic energy levels with the possible absorption transitions and different types of mechanisms for intramolecular loss of energy.

fold to an electronic state in the triplet manifold or vice versa. Intersystem crossing is primarily responsible for the population of the triplet state of organic molecules.

Only two emissions are found to occur ( with a few notable exception, e.g., azulene ) between different electronic states, whereas absorption can occur between many electronic states. This former observation is summarized by the Kasha rule (23) which states that for organic molecules in condensed media, the emitting level of a given multiplicity is the lowest excited state of that multiplicity. This is because the internal conversion process is much shorter than the radiative process. ( A rate constant of  $10^{11}$  -  $10^{14}$  sec<sup>-1</sup> is associated with internal conversion whereas the fluorescence rate constant is approximately 10<sup>8</sup> sec<sup>-1</sup>.) It is an empirical fact that in condensed media, the excitation energy of  $S_2$ ,  $S_3$ ,... or any excited vibrational level of S1, S2,..., will rapidly be lost in inelastic collisions until the zero point vibrational level of S1 is achieved radiationlessly. Of course, for rarefied gases, emission can originate from any of the vibrational levels.

Similarly,  $S_1$  may have its energy degraded to  $S_0$  radiationlessly or it may be degraded to  $T_1$  through inter-

system crossing, or it may emit fluorescence which is formally known as the emissive passage between states of same multiplicity. Once the triplet state has been populated, it can lose its energy by intersystem crossing or by phosphorescence which is the emissive passage between two states of the same molecule which are of different multiplicity.

Any transition, radiative or non-radiative, between states of different spin multiplicity is highly forbidden but this forbiddenness is relaxed by the interaction between the magnetic dipole generated by the spin motion of the electron and the magnetic dipole generated by the orbital motion of the electron. This spin-orbit interaction has the effect of introducing singlet character into the triplet state and triplet character into the singlet state.

The fluorescence spectra will then be the envelope of transitions from the zeroth vibrational level of the singlet state to various vibrational levels of the ground state whereas the phosphorescence spectra will consist of transitions from the zeroth vibrational level of the triplet state to the vibrational levels of the ground state.

Therefore, molecular distortions of both the singlet state and the triplet state can be determined by a

vibrational analysis of the fluorescence and phosphorescence spectra.

### 2.8 Symmetry Classification of Benzonitrile

Each isolated molecule can be classified by a symmetry point group, according to the symmetry elements its equilibrium nuclear configuration has.

The benzonitrile molecule in the ground state is planar (<u>11</u>) with the substituent,  $-C \equiv N$ , lying on a straight line bisecting the benzene ring. Benzonitrile has three symmetry elements in addition to the identity element, namely, a two-fold rotation axis and two reflection planes. These symmetry elements are shown in figure (2.4) in which the coordinate axes have been defined according to Mulliken's convention (<u>24</u>). The corresponding symmetry operations are:

 $C_2(z)$ , rotation about the z-axis through  $\pi$ ;

 $\sigma_v(xz)$ , reflection in a plane  $\perp$  to the molecular plane ;

 $\sigma'_{v}(yz)$ , reflection in the molecular plane.

These three symmetry operations together with the identity E comprise the  $C_{2v}$  point group to which benzonitrile belongs. Deuteration in the para position and



FIGURE 2.4 Symmetry Elements of Benzonitrile

C <sub>2v</sub>	E	C <sub>2</sub> (z)	$\sigma_{\rm v}({\tt xz})$	Ø'v(yz)		
A <sub>1</sub>	. 1	1	1	1	Mz	
A2	1	1	-1	-1	E	lz
<sup>B</sup> 1	1	-1	1	-1	Mx F	ly
<sup>B</sup> 2	1	-1	-1	1	My R	X

TABLE 2.1a Character Table of the  $\text{C}_{2\mathbf{v}}$  Point Group

TABLE 2.1 b Direct Product Table of the  $C_{2v}$  Point Group

C <sub>2v</sub>	A <sub>1</sub>	<sup>A</sup> 2	<sup>B</sup> 1	B <sub>2</sub>
A <sub>1</sub>	A <sub>1</sub>	A2	B <sub>1</sub>	B <sub>2</sub>
<sup>A</sup> 2	A <sub>2</sub>	A1	B <sub>2</sub>	B <sub>1</sub>
B <sub>1</sub>	<sup>B</sup> 1	<sup>B</sup> 2	A <sub>1</sub>	<sup>A</sup> 2
<sup>B</sup> 2	<sup>B</sup> 2	<sup>B</sup> 1	<sup>A</sup> 2	A <sub>1</sub>

perdeuteration does not alter the  $\rm C_{2v}$  symmetry but the deuteration in the meta and ortho position changes the symmetry to  $\rm C_{S}$  .

The character table and the direct product table of the  $C_{2v}$  point group are given in tables (2.1a and 2.1b). They are of use in assigning the orbital symmetry of the lowest triplet state as explained in the following sections.

#### 2.9 Polarization of Luminescence

It will be recalled that the electric dipole moment transition integral contains Mx, My, and Mz components. Therefore, it is possible that with an oriented molecule, a particular transition may occur only when the incident radiation is polarized along a certain direction. The molecular orientation can be accomplished by using single crystals. Another way is by the method of photoselection as described by Albrecht ( $\underline{24}$ ). In this method, the molecules are randomly 'frozen' in a glass and selectively excited by light having a particular oriented electric dipole, i.e., the molecules whose absorption transition moments are parallel to the electric vector of the exciting light will be excited preferentially and molecules with other orientations will contribute less to the total intensity of the transition. The degree of polarization is defined as

$$P = \frac{I_{VV} - I_{VH}}{I_{VV} + I_{VH}} = \frac{(3\cos^2 \alpha) - 1}{(\cos^2 \alpha) + 3}$$
 II.14

where  $I_{VV}$  is the intensity of emission as observed through a polarizer passing only vertical electric vector light after excitation by vertically polarized light.  $I_{VH}$  is the intensity of emission as observed through a polarizer passing only horizontal electric vector light after excitation by vertically polarized light.

 $\alpha$  is the angle between the emission and absorption transition moments. Therefore, parallel electric dipoles bring in a maximum contribution of + 1/2 to the degree of polarization while perpendicular electric dipoles contribute a maximum polarization of - 1/3. In practice, the maximum degree of polarization is rarely observed due to depolarization effects, such as glass strains, softness of glasses, and 'instrumental favoring'. Several techniques are employed to take care of these 'favoring factors'(<u>26</u>).

#### 2.10 Assignment of the Lowest Triplet State

The results of a polarization measurement can be used to assign orbital symmetry of electronic states. In planar aromatic hydrocarbons, the allowed  $\pi - \pi^*$  transitions are in-plane polarized. In C<sub>2v</sub> symmetry, these are  $A_1 \leftrightarrow A_1$  and  $A_1 \leftrightarrow B_2$ . As mentioned in the previous section, the degree of polarization is governed by the direction of the electric dipole moment of the absorbing and emitting states, e.g., in  $C_{2v}$ , a  ${}^1A_1 \rightarrow {}^1B_2$  absorption and a  ${}^1B_2 \rightarrow {}^1A_1$ fluorescence would produce a positive degree of polarization since the absorbing and emitting states have parallel transition moment (y). However, absorption in the  ${}^1A_1$  (z) followed with fluorescence from the  ${}^1B_2$  (y) state would result in a negative polarization.

Triplet to singlet transitions are not allowed to a first approximation. The transitions will become allowed if the triplet state has some singlet state character or the singlet state has some triplet state character mixed in it by the perturbing effect of spin- orbit interaction ( 26,27 ).

The wavefunction of the lowest triplet state, T<sup>1</sup>, perturbed by admixture with singlet states, s<sup>k</sup>, is expressed as

$$\Psi(T^{1}) = \Psi(t^{1}) + \sum_{k} \frac{\langle t^{1} | H_{so} | s^{k} \rangle}{E(t^{1}) - E(s^{k})} \Psi(s^{k})$$
 II.15

and the wavefunction of the singlet ground state, S<sup>0</sup>, perturbed by triplet states, t<sup>k</sup>, is expressed as
$$\Psi(s^{0}) = \Psi(s^{0}) + \sum_{k} \frac{\langle s^{0} | H_{s0} | t^{k} \rangle}{E(s^{0}) - E(t^{k})} \Psi(t^{k})$$
 II.16

where  $\Psi(t^1)$  and  $\Psi(s^0)$  are the unperturbed lowest triplet state and singlet ground state respectively and where  $H_{so}$  is the Hamiltonian operator for the spin-orbit interaction and has the form

$$H_{so} = -\left[\frac{h^2}{(2mc)^2}\right] (\nabla V \times p) \cdot s. \qquad II.17$$

McClure (  $\underline{28}$  ) has shown that the orbital part of  $H_{so}$  transform as axial rotation Rx, Ry, and Rz.

The transition moment of the singlet-triplet transition is then

$$M = \langle s^{0} | er | T^{1} \rangle = \sum_{k} \langle s^{0} | er | \frac{\langle t^{1} | H_{so} | s^{k} \rangle}{E(t^{1}) - E(s^{k})} s^{k} \rangle +$$
$$\sum_{k} \langle t^{1} | er | \frac{\langle s^{0} | H_{so} | t^{k} \rangle}{E(s^{0}) - E(t^{k})} t^{k} \rangle II.18$$

and the polarization of the phosphorescence is governed by the polarization of the transitions  $s^0 \leftrightarrow s^k$  and  $t^1 \leftrightarrow t^k$ .

For the transition moment of equation II.18 to be non-zero, one requires non-vanishing values for at least one of the 'k' mixing coefficients



No attention is paid to the absolute magnitude of mixing determined by these mixing coefficients.

If the lowest triplet state is of  ${}^{3}A_{1}$  orbital symmetry, then, recalling that the orbital part of  $H_{so}$ transforms as axial rotations, it is seen that the perturbing singlets to t<sup>1</sup> can be  ${}^{1}A_{2}$ ,  ${}^{1}B_{1}$ , and  ${}^{1}B_{2}$  and that the perturbing triplet states to s<sup>0</sup> may be  ${}^{3}A_{2}$ ,  ${}^{3}B_{1}$ , and  ${}^{3}B_{2}$ . However, the transition moment of equation II.18 is also governed by  $\langle s^{0} | er | s^{k} \rangle$  and  $\langle t^{1} | er | t^{k} \rangle$ . This reduces the s<sup>k</sup> to  ${}^{1}B_{1}$  and  ${}^{1}B_{2}$  and the t<sup>k</sup> to  ${}^{3}B_{1}$  and  ${}^{3}B_{2}$ . The polarizations of  ${}^{1}A_{1} \leftrightarrow {}^{1}B_{1}$  and  ${}^{1}A_{1} \leftrightarrow {}^{1}B_{2}$  are out-ofplane (x) and short axis in-plane (y) respectively as are the  ${}^{3}A_{1} \leftrightarrow {}^{3}B_{1}$  and  ${}^{3}A_{1} \leftrightarrow {}^{3}B_{2}$  transitions. These results are summarized in table (2.2). The direction of polarization of the transitions s<sup>0</sup> \leftrightarrow s^{k} and t<sup>1</sup> \leftrightarrow t^{k} which governs the polarization of the phosphorescence are written in parentheses.

For a  ${}^{3}B_{2}$  orbital symmetry for the lowest triplet state, different perturbing states and polarizations are expected; these are shown in table (2.2).

These considerations indicate that for both choices,

Lowest Triplet State t <sup>K</sup> (orbital symmetry)	H <sub>so</sub> (transform as R's)	Possible perturbing singlet states s <sup>K</sup> to the lowest triplet state and polarization of s <sup>K</sup> -> s <sup>O</sup>	Possible perturbing triplet states t <sup>k</sup> to the ground state and polarization of t <sup>k</sup> → t
<sup>3</sup> <sub>B2</sub>	A2	${}^{1}B_{1}$ (x)	${}^{3}A_{2}$ (x)
	B1	${}^{1}A_{2}$ (forbidden)	${}^{3}B_{1}$ (forbidden)
	B2	${}^{1}A_{1}$ (z)	${}^{3}B_{2}$ (z)
<sup>3</sup> A <sub>1</sub>	A2	${}^{1}A_{2}$ (forbidden)	${}^{3}A_{2}$ (forbidden)
	B1	${}^{1}B_{1}$ (x)	${}^{3}B_{1}$ (x)
	B2	${}^{1}B_{2}$ (y)	${}^{3}B_{2}$ (y)

TABLE 2.2 Spin-Orbital Mixing of Singlet and Triplet States

an out-of-plane polarization (x) contribution to the polarization of the 0,0 phosphorescence band is possible. But for  ${}^{3}A_{1}$ , a short axis in-plane (y) contribution is expected while for  ${}^{3}B_{2}$ , there can be a long axis in-plane (z) contribution. Thus, in principle, polarization measurements can assist in the triplet state orbital symmetry assignment; one merely excites into the 0,0 region of the  ${}^{1}A_{1} \rightarrow {}^{1}B_{2}$  (y) and  ${}^{1}A_{1} \rightarrow {}^{1}A_{1}$  (z) transitions and measures the relative degree of polarization of the 0,0 region of phosphorescence. For a  ${}^{3}A_{1}$  lowest triplet, the polarization ratio would be more positive for a (y) excitation while for a  ${}^{3}B_{2}$  assignment, the ratio would be more positive for the (z) excitation.

#### CHAPTER III

#### EXPERIMENTAL

### 3.1 Chemicals

 $C_6H_5CN$  - Commercial benzonitrile (Aldrich Chemical Co.) was purified by vacuum distillation. The emission spectra obtained from the non-redistilled benzonitrile was similar to that of the purified benzonitrile.

 $C_6D_5CN$  - Perdeuterated benzonitrile, of better than 99% isotopic purity, was obtained from Merck, Sharp and Dohme of Canada Limited and used as received.

0-, m-, p-D-C<sub>6</sub>H<sub>4</sub>CN - The monodeuterated benzonitriles were prepared by reductive removal of bromine from the corresponding bromobenzonitriles (Aldrich Chemical Co.) with powdered zinc in presence of acetic anhydride and deuterium oxide (29). Very low yields were obtained from this method. These were improved with a slight alteration to the procedure; a 1.5 : 1.0 molar ratio of deutetium oxide : acetic anhydride mixture was used instead of the recommended large excess of deuterium oxide. Also, much larger volumes (150 mls.) of benzene were used for extractions. This was done to avoid loss of the desired materials on the vessel walls and during each subsequent

transfer. The extract was then concentrated by the evaporation of benzene from a 250 mls. round-bottom flask, topped with a short tube ( 10 cm. long by 22 mm. o.d. ) to avoid possible evaporation of the product. The deuterated benzonitrile was then separated by fractional vacuum distillation.

The derivatives were analysed for purity by proton  $^{13}$ C magnetic resonance spectra (<u>30</u>) and found all to be obtained in close to 100% isotopic purity and with less than 5% of rearranged isomers.

3.2 Solvents

The following solvents were used to obtain solid (glass and polycrystalline ) matrices:

cyclohexane and <u>methylcyclohexane</u>, spectroquality products of Matheson, Coleman and Bell, were used without further purifications;

<u>isopentane</u> and <u>3-methylpentane</u>, pure grade products of Phillip 66, were used after shaking in Linde 10X molecular sieve;

<u>isooctane</u>, a spectranalysed Fisher reagent, <u>methanol</u>, a Shawinigan product and <u>absolute ethanol</u> were all used without further purifications.

None of the solvents employed showed detectable luminescence under the experimental conditions employed.

### 3.3 Apparatus

The basic apparatus used to obtain the emission spectra is shown schematically in figure (3.1).

The exciting light, provided from various sources ( Hanovia 150 Watt Xenon lamp or Osram 150 Watt Xenon lamp powered by a Bausch and Lomb power supply or a Osram 450 Watt Xenon lamp powered by a DC regulated universal lamp power supply, Model # C-72-50, from Oriel Optics Corporation ) was passed through a monochromator ( Bausch and Lomb 0.25 meter monochromator with a 1200 grooves/mm. grating or Jarrell-Ash 0.25 meter Ebert monochromator provided with a 2360 grooves/mm., 300 nm.blazed grating.) The monochromated light was then focussed by quartz lenses to irradiate the sample contained in a 11 mm. c.d. quartz tube immersed in a partially silvered quartz dewar containing boiling liquid nitrogen. The emitted light was detected by a dry-ice cooled photomultiplier ( RCA Type 8575 ) powered by a Power Design, Model HV 1544, power supply, after passing through a 0.5 meter Jarrell-Ash scanning monochromator ( provided with a 1180 grooves/mm. grating blazed at 400nm.) perpendicular to the direction of



a-LENSES

FIG. 3.1 APPARATUS FOR EMISSION EXPERIMENTS - BLOCK DIAGRAM

the exciting light. The resulting signal, amplified by a Keithley Model 610C solid state electrometer, was fed into a Varian Series G-2000 Recorder. The emission spectra thus obtained were uncorrected for instrumental response.

Phosphorescence lifetime measurements were obtained by feeding the signal directly from the photomultiplier tube ( or from the electrometer ) into an Hewlett-Packard 132A Dual Beam Oscilloscope. The decay of the 0,0 phosphorescence band, after mechanically shuttering the exciting light, was photographed by means of an Hewlett-Packard Model 196B Oscilloscope camera.

Polarized emission measurements were obtained by introducing a UV polarizing Glan prism between the exciting monochromator and the sample and one between the sample and the analysing monochromator. The instrumental favoring was minimized by executing the following procedure: the exciting polarizer was positioned to pass only vertical electric vector light ( V ) and the intensity of the emission was recorded for the horizontal ( H ) and vertical ( V ) position of the analysing polarizer. The uncorrected polarization ratio,  $I_{\rm VV}$  /  $I_{\rm VH}$ , was thus obtained . The correction factor,  $I_{\rm HH}$  /  $I_{\rm HV}$ , was obtained by positioning the exciting polarizer to pass only hori-

zontal electric vector light ( H ) and the intensity of emission again recorded for the horizontal and vertical position of the analysing polarizer. The product,  $I_{VV} \propto I_{HH} / I_{VH} \propto I_{HV}$ , was then the corrected polarization ratio, N , from which the degree of polarization, P = N - 1 / N + 1, was calculated.

#### 3.4 Preparation of the Solid Matrices

The luminescence spectra of the benzonitriles were obtained for both glassy and polycrystalline matrices. All spectra obtained using glassy solvents ( isopentane, 3-methylpentane, methylcyclohexane, isooctane, methanol, and ethanol ) were not well resolved; consequently, polycrystalline matrices, exhibiting the Shpolskii effect, were prepared.

As spectra of molecules dissolved in glasses are usually broad, it was found that different molecules show well resolved vibronic spectra in a Shpolskii matrix, a frozen normal alkane chosen so that the host molecule carbon skeleton chain length equals the largest dimension of the carbon skeleton of the solute aromatic molecule. The solute molecules would then fit exactly in "cages" formed by the frozen solvent.

In the case of benzonitrile, it is found that both

cyclohexane and methylcyclohexane polycrystalline matrices exhibited this Shpolskii effect.

The spectra obtained were very dependent on the cooling treatment of the sample. For a  $10^{-3}$  molar solution of benzonitrile in methylcyclohexane, rapid immersion of the sample in a dewar of boiling liquid nitrogen gave a clear or cracked glass giving broad peaks in both the fluorescence and phosphorescence spectra. When the sample was placed just above the liquid nitrogen level until a small portion crystallized, and then progressively lowered as a new region crystallized, until the entire sample appeared white, the spectra were very sharp. This type of cooling, referred to as slow cooling, should be contrasted with fast cooling. in which the sample was placed just above the liquid nitrogen until it turned completely white and then was plunged into the coolant. With fast or slow cooling, all main peaks were split in two ( 60 cm<sup>-1</sup> separation in phosphorescence and 100  $cm^{-1}$  in fluorescence.) The doublet nature of the spectrum was most obvious with fast cooling, i.e., the 0,0 region of phosphorescence had two peaks of comparable intensity. By the so-called slow cooling method, the member to the blue of the 0,0 region of phosphorescence was only about one-tenth as intense as its partner. The relative intensity of the blue to red

member can be controlled by varying the height of the sample tube resting over the liquid nitrogen in the fast cooling method.

In fluorescence, the split peaks that diminish with slow cooling were to the red.

For solutions of benzonitriles in cyclohexane, the appearance of the phosphorescence and fluorescence spectra also varied with the type of cooling employed. After plunging a  $10^{-4}$  molar solution of benzonitrile in cyclohexane ( more concentrated samples showed reabsorption of the 0,0 band due to the overlapping of the emission and absorption bands ) in boiling liquid nitrogen and waiting for fifteen minutes. the spectra consisted of broad doublets ( splittings of 40 cm<sup>-1</sup> in phosphorescence and 60 cm<sup>-1</sup> in fluorescence ). If the fast cooling method was employed, the red member was more intense than the blue one in fluorescence; in phosphorescence, the blue member was now a broad tail. With slow cooling, only red bands were present in both fluorescence and phosphorescence. If a slow cooled sample was warmed at room temperature for approximately five minutes and then slowcooled again, the spectra became sharper and the broadening of the 0,0 region were diminished. Fluorescence spectra obtained by this method were more resolved than in methylcyclohexane. Consequently, the vibrational analyses of the fluorescence were made using cyclohexane samples and that of the phosphorescence made using methylcyclohexane ones. It should be noted that the vibrational analysis in one solvent also applies for the other.

Since the analyses of the phosphorescences will be presented for a medium which gives splittings on all the major bands, the transitions originate from the vibrationless triplet states favored by both 'fast' and 'slow' cooling. Consequently, the origins will be denoted as  $0_{\rm f}$  and  $0_{\rm s}$  in tables ( 4.2 ) to ( 4.6 ).

#### CHAPTER IV

#### RESULTS

The phosphorescence and fluorescence spectra result from a radiative loss of energy from the zeroth vibrational levels of the first excited singlet state and first excited triplet state respectively. ( By the Boltzmann distribution, if the vibrational level spacing is much larger than kT, no appreciable population in vibrationally excited  $S_1$  and  $T_1$  is expected; at 77°K, kT is equal to 54 cm<sup>-1</sup>.)

The ground state fundamentals of benzonitrile- $h_5$ (<u>29,31</u>) and benzonitrile- $d_5$ (<u>32</u>) are presented in table (4.1) with the fundamentals labelled after Herzberg (<u>33</u>). Whiffen's designations (<u>34</u>) for monosubstituted benzenes are also included. Figure (4.1) shows some schematic normal vibrations appearing in this study.

Bak and Neilsen ( $\underline{29}$ ) have also made some tentative partial assignments for para-, meta-, and orthomonosubstituted benzonitriles from infrared studies. Using these, the infrared absorption analysis of monodeuterated pyridines ( $\underline{35}$ ), and the similarity of the fluorescences and phosphorescences of the benzonitriles, entries in the last three columns of table (4.1) are made. The shifts

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Desi	gna- Description o	f	Symme	try		Fre	quency	.(cm <sup>-1</sup> )	)
t	C6H5CN Mode <sup>a</sup>		C <sub>2v</sub>	Cs	Нp	Dp	Pc	Mc	0 <b>c</b>
$\nu_1$	VC-H		a <sub>1</sub>	a	3080	2305			
$\nu_2$	VC-H		a <sub>1</sub>	a	3062	2286			
$v_3$	<i>U</i> С-H		a <sub>1</sub>	a	3042	2283			
$v_4$	VCEN		<sup>a</sup> 1	a'	2232	2226	2250 <sup>d</sup>	2245 <sup>d</sup>	2250 <sup>d</sup>
$v_5$	VC-C	k	a <sub>1</sub>	a'	1599	1568	1595	1592	1593
VG	Vc-c	m	a <sub>1</sub>	a'	1492	1378	1482	1474	1472
$v_7$	$\chi$ -sens( $\mathcal{V}$ C-CN)	q	a <sub>1</sub>	a١	1192	1123	1190	1196	1192
$v_8$	βс <b>-</b> н	a	a <sub>1</sub>	a	1178	871	1180 <sup>d</sup>	1175 <sup>d</sup>	1115 <sup>d</sup>
$v_9$	βс <b>-</b> н	Ъ	a <sub>1</sub>	a'	1027	845	1023	1037	1042
$v_{10}$	ring	p	a <sub>1</sub>	a	1001	959	980	999	985
$v_{11}$	X-sens(QC-C-C)	r	a1	a'	769	718	760 <sup>d</sup>	740 <sup>d</sup>	760 <sup>d</sup>
$v_{12}$	$\chi$ -sens( $\alpha$ C-C-C)	t	a <sub>1</sub>	a	461	452	450 <sup>d</sup>	450 <sup>d</sup>	460 <sup>d</sup>
$v_1$	ус-н	h	a2	a"	978	780			
VIL	Ус-н	g	a2	a"	848	695			
$v_1$	φc-c	W	a2	a"	401	(382)			
$v_{16}$	ус-н	j	b <sub>1</sub>	a"	(989)	(830)			
$v_{17}$	, Ус-н	i	b <sub>1</sub>	a"	925	769			
$v_{18}$	Ус-н	f	b <sub>1</sub>	a"	758	643			

TABLE 4.1

Ground State Fundamentals in the Benzonitriles

TADLE 4.1 (Continued	(b
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Designa	- Description o	of	Symme	try		Fre	quency,	(cm <sup>-1</sup> )	
tior	C6H5CN Mode		C <sub>2v</sub>	Cs	Н	D	P	M	0
$v_{19}$	фс-с	V	b <sub>1</sub>	a"	686	572			
$v_{20}$	$\chi$ -sens( $\phi$ C-C)	x	<sup>b</sup> 1	a"	548	488	51 5 <sup>d</sup>	525 <sup>d</sup>	535 <sup>d</sup>
$v_{21}$	$\chi$ -sens( $\gamma$ C-CN)	У	<sup>b</sup> 1	a"	172	170	з <i>к</i>		
$v_{22}$	Yc≡n		<sup>b</sup> 1	a"	162	160	(150) <sup>d</sup>	(150) <sup>d</sup>	(155)
$v_{23}$	<b>ИС-</b> Н		<sup>b</sup> 2	a'	3072	2286			
$v_{24}$	VC-H		<sup>b</sup> 2	a'	3027	2283			
$v_{25}$	Vc-c	1	<sup>b</sup> 2	a	1584	1568			
$v_{26}$	VC-C	n	Ъ <sub>2</sub>	a	1448	1330			
V27	Vc-c	0	<sup>b</sup> 2	a	1337	1289			
$v_{28}$	ВС-н	е	<sup>b</sup> 2	aı	1289	1040		(	1280) <sup>d</sup>
V29	Вс-н	С	<sup>b</sup> 2	a'	1163	838			
V30	<b>β</b> с-н	d	Ъ <sub>2</sub>	ai	1071	823		(880) <sup>d</sup>	
$v_{31}$	ac-c-c	S	b2	at	629	599	615 <sup>d</sup>	615 <sup>d</sup>	615 <sup>d</sup>
V32	βc≡n		<sup>b</sup> 2	a١	551	552	540 <sup>d</sup>	525 <sup>d</sup>	530 <sup>d</sup>
V33	$\chi$ -sens( $\beta$ C-CN)	u	b2	a'	381	357	365 <sup>d</sup>	365 <sup>d</sup>	365 <sup>d</sup>

a. The second column correlates the vibrational modes of benzoni-trile with the labelling of vibrational modes of monosubstituted benzenes by Whiffen (34)

b. From Reference 31

c. From Reference 29, except as noted.

d. From this work; see text.



















V30









Figure 4.1 Some schematic vibrational modes of benzonitrile

of the observed vibrational fundamentals help in making assignments in the vibrational analyses.

### 4.1 Vibrational Analyses of Phosphorescence

The phosphorescence spectra were obtained after slow cooling of  $10^{-3} - 10^{-4}$  molar samples in cyclohexane and methylcyclohexane; but the latter were slightly more structured. Consequently, even if the spectra were more complicated due to the appearance of split peaks on all major bands, the vibrational analysis of the phosphorescences was made in that particular solvent. The analyses given for the benzonitriles in methylcyclohexane are also valid in cyclohexane.

### a- Benzonitrile-H5

The phosphorescence spectrum of benzonitrile-H<sub>5</sub> is shown in figure ( 4.2 ), and the vibrational analysis listed in table ( 4.2 ). The strong band at 27 010 cm<sup>-1</sup> is assigned as the origin band for molecules in the environment produced by slow cooling. This band and all the other main bands in the spectrum have weak intensity splitting of about 60 cm<sup>-1</sup> to the blue; these are attributed to transitions from the triplet state to the ground state by molecules in environment enhanced by fast cooling. These splittings tend to complicate the spectrum but their

assignments are ascertained by running the spectrum of a fast-cooled sample.

In cyclohexane, the 0,0 band was observed at 26 760  $\text{cm}^{-1}$  as compared to 26 780  $\text{cm}^{-1}$  obtained by Takei and Kanda ( 16 ). In ethanol, the 0,0 band was found at 26 985  $\text{cm}^{-1}$  compared to 26 910  $\text{cm}^{-1}$  found by these authors. Of the series of very weak peaks in the region 0-700 cm<sup>-1</sup>, only that at  $465 \text{ cm}^{-1}$  was reported in the low resolution work of Takei and Kanda. However, all except the 610 cm<sup>-1</sup> band were detected in a solid nitrogen matrix reported by Faure, Valadier and Janin ( 17 ). The band assigned as 2 x 170  $cm^{-1}$  there fits better with 2 x 160  $\rm cm^{-1}$  in this work for all the benzonitriles. The appearance of a band at 540 cm<sup>-1</sup> does not permit a distinction to be made between 0,  $v_{20}$  and 0,  $v_{32}$ . However, in the phosphorescence of benzonitrile-D\_5 , where  $\,{\cal V}_{\,20}$  shifts down to 488 cm<sup>-1</sup>, both seem to be present, justifying the double assignment for the 540  $\rm cm^{-1}$  peak. Bands appearing at 765, 1000, 1185, 1610, and 2245 cm<sup>-1</sup> are interpreted as a1 fundamentals. The outstanding feature of the spectrum is the long progression of  $\, {\cal V}_{5}$  and of  $\, {\cal V}_{8}$  plus the building up of  $\, {\cal V}_{\, 5}$  on the other fundamentals and combinations. The assignment of 2 x  ${\mathcal V}_8$  cannot be distinguished from  $v_5$  +  $v_{11}$ , therefore both assignments are entered.

Here again, the isotope effect will justify these alternate assignments.

### b- Benzonitrile-D5

The analysis of phosphorescence of benzonitrile-D<sub>5</sub>, figure ( 4.3 ), is contained in table ( 4.3 ). The analysis of this compound greatly helps the justification of the assignment of certain peaks in benzonitrile-H5 because the deuterium shifts would be expected to be the largest here. The perdeuteration moves the 0,0 band 100  $\rm cm^{-1}$  to higher energy ( blue ). The peak at 540  $\rm cm^{-1}$  in benzonitrile-H<sub>5</sub> is now split into two peaks assigned as 0,  ${\cal V}_{20}$ and 0,  ${\cal V}_{32}$  substantiating the double assignment for benzonitrile-H<sub>5</sub>. The most dramatic change in the spectrum is the shift of the 1185  $\rm cm^{-1}$  peak to 870  $\rm cm^{-1}$ , consistent with a 0,  ${m 
u}_8$  assignment. This shift has now revealed a new band at 1115 cm<sup>-1</sup>, assigned as the 0,  $v_7$  transition. This band (  $1192 \text{ cm}^{-1}$  in benzonitrile-H<sub>5</sub> ) was probably hidden by the 0,  $\mathcal{V}_8$  band at 1178 cm<sup>-1</sup>. Many of the bands in the spectrum are only slightly deuterium sensitive but their assignments serve as a check for the assignments of benzonitrile-H<sub>5</sub>. The 1610  $\text{cm}^{-1}$  in H<sub>5</sub> is now shifted down to 1565  $\text{cm}^{-1}$  and the 1000  $\text{cm}^{-1}$  peak has shifted to 960  $\text{cm}^{-1}$ ; these are assigned as 0,  ${m 
u}_5$  and 0,  ${m 
u}_{10}$  respectively. Here again , the main progressions are in  ${\cal U}_5$  ( up to 4 x  ${\cal U}_5$  )

and  $v_8$ . In perdeuterated benzonitrile, one can now distinguish between 0.2 x  $v_8$  and 0.  $v_5 + v_{11}$ , therefore, the progression in  $v_8$  is observed. The main part of the spectrum consists of transitions of  $v_5$  built on other fundamentals and progressions. Generally, the assignments of benzonitrile-D<sub>5</sub> follow those of benzonitrile-H<sub>5</sub> quite well.

### c- <u>Para-deuterated benzonitrile</u> ( p-DC6H4CN )

The general appearance of the phosphorescence spectrum of p-monodeuterated benzonitrile, figure ( 4.4 ), is very similar to that of benzonitrile-H5. The analysis given in table ( 4.4 ) differs from that of table ( 4.2 ) only in very few minor details. This is expected since the para hydrogen does not play a great part in the frequencies involved in the major part of the spectrum, i.e., in the  ${\cal V}_5$  and  ${\cal V}_8$  fundamentals ( see figure ( 4.1 )). The greatest expected shift would be in  $\, {\cal V}_{10}^{}$  where it occurs at 990 cm<sup>-1</sup> in  $p-DC_6H_4CN$  , down from 1000 cm<sup>-1</sup> in  $H_5$  . This has the effect of closing the gap between the peaks involving the 0,  $\mathcal{V}_8$  +  $\mathcal{V}_{11}$  and 0,2 x  $\mathcal{V}_{10}$  transitions from 60 cm<sup>-1</sup> in  $H_5$  to 25 cm<sup>-1</sup> in this compound. This feature appears again when  ${\mathcal V}_5$  is added to these combinations. Except for these two regions, the spectrum can almost be superimposed on the spectrum of benzonitrile-H<sub>5</sub>. It should also be noted that the para isomer gives the largest blue shift of the 0,0 band (  $40 \text{ cm}^{-1}$  ) for the three monosubstituted benzonitriles.

# d- <u>Meta-deuterated benzonitrile</u> ( $m-DC_6H_4CN$ )

The 0,0 transition of the phosphorescence of metamonodeuterated benzonitrile, figure ( 4.5 ), is blue shifted by 10 cm<sup>-1</sup> with respect to the 0,0 band of  $H_5$ . One of the few minor differences in the spectrum is the appearance of a weak band at 880 cm<sup>-1</sup> which seems to be absent in  $H_5$ ,  $D_5$  and  $p-DC_6H_4CN$ . This could be due to a b2 fundamental, since the change in symmetry upon introduction of D in the meta and ortho positions makes both the a1 and b2 fundamentals of C2 now totally-symmetric a' fundamentals. This band is assigned as 0,  ${\cal U}^{}_{
m 30}$  with other alternate assignments as 0,  $v_{32}$  +  $v_{33}$  or 0,  $v_{20}$  +  ${\cal V}_{33}.$  This peak has the effect of changing the appearance of the spectrum, which is basically that of benzonitrile-H  $_5$ plus combinations of  ${\cal V}_{10}$ ,  ${\cal V}_8$ , and  ${\cal V}_5$  with the 880 cm<sup>-1</sup> band to give peaks at 1890, 2050, and 2480 cm<sup>-1</sup> respectively. The series is repeated with the combination of  $\, 
u_{\, 5} \,$ and 2 x  $\mathcal{V}_5$  on the previous peaks, i.e.,  $\mathcal{V}_5$  +  $\mathcal{V}_{10}$  ,  ${\mathcal V}_5$  +  ${\mathcal V}_8$  , 2 x  ${\mathcal V}_5$  combines with the 880 cm<sup>-1</sup> band to give peaks at 3475, 3650, and 4070 cm<sup>-1</sup> respectively. But the main features are still the progressions in  ${\mathcal V}_5$  and

 $v_8$  plus the combinations of  $v_5$  with the other fundamentals and combinations.

### e- Ortho-deuterated benzonitrile ( $O-DC_6H_4CN$ )

The variations between the phosphorescence spectrum of ortho-monodeuterated benzonitrile, figure ( 4.6 ), and benzonitrile-H5 are minimal. The 0,0 band lies at higher energy by 15 cm<sup>-1</sup>. ( It should be noted that the total blue shift on perdeuteration of 100  $\rm cm^{-1}$  is nearly equal to the para-substitution shift plus twice the sum of the meta and ortho shifts. ) The shoulder on the 1000  $cm^{-1}$  of benzonitrile-H<sub>5</sub> is now clearly resolved, and assigned as 0,  $\mathcal{V}_9$  . The 1185 cm<sup>-1</sup> band has lost considerable intensity; part of this is attributed to the deuterium isotope effect shift of  $\mathcal{V}_8$  to 1115 cm<sup>-1</sup>. There is also a weak sharp band at 1280  $cm^{-1}$ , which is very weak or appears as shoulder in all the other spectra. In the infrared absorption of ortho, a band at 1294  $cm^{-1}$  has been attributed to 746 cm<sup>-1</sup> + 540 cm<sup>-1</sup> ( 0,  $\mathcal{V}_{11}$  +  $\mathcal{V}_{32}$  ). A band in the same region for the ortho deuterated pyridine with anomalously high intensity has been observed. This band could be due to the b2 fundamental  $\, {\cal V}_{28} \,$  with alternate assignments of 0,  $\mathcal{V}_{11}$  +  $\mathcal{V}_{32}$  or 0,  $\mathcal{V}_{10}$  + 2 x  $\mathcal{V}_{22}$  . The assignments proposed in table ( 4.6 ) indicate that this band appears in combinations with  ${\mathcal V}_5$  and  ${\mathcal V}_{10}.$  This behavior is not found

for the other molecules included in this study.

There seems to be a loss of the  $\mathcal{V}_8$  progression but the  $\mathcal{V}_5$  progression plus the combinations of multiples of  $\mathcal{V}_5$  on the other fundamentals and combinations remain.

# Figure 4.2

Phosphorescence of  $10^{-3}$  M benzonitrile in polycrystalline methylcyclohexane at  $77^{\circ}$ K.



### TABLE 4.2

Vibrational Analysis of Phosphorescence of  $C_{6}H_{5}CN$  in

Polycrystalline Methylcyclohexane at  $77^{\circ}$ K

Ia	Positic	n	$\Delta V(cm^{-1})$	Assignment
- Convertigence - Marcal Annual - Marcal	$\lambda$ (nm x 10)	$v(cm^{-1})$	and and and the second second second second	
W	3694	27 070	-60	0 <sub>f</sub> ,0
S	3702	27 010	0	0 <sub>s</sub> ,0
VW	3735	26 775	235	0 <sub>f</sub> ,2 x 22
W	3745	26 700	310	0 <sub>s</sub> ,2 x 22
VW	3754	26 640	370	0 <sub>s</sub> ,33
W	3767	26 545	465	0,12
VW	3778	26 470	540	0 <sub>s</sub> ,20 ;0 <sub>s</sub> ,32
WW	3788	26 400	610	0,31
W	3801	26 310	700	0 <sub>f</sub> ,11
m	3810	26 245	765	0,,11
VW	3820	26 180	830	0 <sub>s</sub> ,11 + 33 ;0 <sub>s</sub> ,20 + 2 x
W	3836	26 070	940	0 <sub>f</sub> ,10
m	3845	26 010	1000	0,10
VW	3848 sh <sup>b</sup>	25 990	1020	0,9
W	3862	25 895	1115	0 <sub>1</sub> ,8
n	3872	25 825	1185	0 <sub>s</sub> ,8
VW	3880 sh	25 775	1235	0 <sub>s</sub> ,11 + 12
VW	3889 sh	25 715	1295	$0_{s}, 10 + 2 \times 22$ ;
				$0_{s}, 11 + 20$

TABLE 4.2 (Continued)

I	Positi	.on	$\Delta v(cm^{-1})$	Assignment
en de setter de sette	$\lambda$ (nm x 10)	V(cm <sup>-1</sup> )	1946 - 1976 - 1976 - 1976 - 1976 - 1976 - 1976 - 1976 - 1976 - 1976 - 1976 - 1976 - 1976 - 1976 - 1976 - 1976 -	
ww	3900	25 640	1370	0 <sub>s</sub> ,10 + 33
VW	3915	25 545	1465	0 <sub>s</sub> ,10 + 12
W	3927	25 465	1545	$0_{f},5;0_{s},10+20$
S	3937	25 400	1610	0 <sub>s</sub> ,5
W	3948 sh	25 330	1680	0 <sub>f</sub> ,10 + 11
W	3960	25 255	1755	0 <sub>s</sub> ,10 + 11
W	3974	25 165	1845	0 <sub>s</sub> ,10 + 12 + 33
WW	3981	25 120	1890	0 <sub>f</sub> ,8 + 11
W	3990	25 065	1945	0 <sub>s</sub> ,8 + 11 ;0 <sub>f</sub> ,2 x 10
W	3999	25 005	2005	0 <sub>s</sub> ,2 x 10 ;0 <sub>s</sub> ,9 + 10
WV	4008	24 950	2060	0 <sub>s</sub> ,5 + 12
W	4018	24 890	2120	$0_{f}, 8 + 10$
m	4028	24 825	2185	0 <sub>s</sub> ,8 + 10 ;0 <sub>f</sub> ,4
m	4038	24 765	2245	0 <sub>s</sub> ,4
W	4047	24 710	2300	0 <sub>f</sub> ,2 x 8 ;0 <sub>f</sub> ,5 + 11
m	4057	24 650	2360	0 <sub>s</sub> ,2 x 8 ;0 <sub>s</sub> ,5 + 11
WV	4070 sh	24 570	2440	0 <sub>s</sub> ,5 + 12 + 33
W	4087	24 470	2540	$0_{f}, 5 + 10$
m	4097	24 410	2600	0 <sub>s</sub> ,5 + 10
WV	4102 sh	24 380	2630	°s,5 + 9
W	4116	24 295	2715	0 <sub>f</sub> ,5 + 8
m	4127	24 230	2780	0 <sub>s</sub> ,5 + 8
vw	4154	24 075	2935	0 <sub>f</sub> ,3 x 10 ;0 <sub>f</sub> ,4 + 11

I	Positi	on	$\Delta v(cm^{-1})$	Assignment
46471-06212-072-004	$\lambda$ (nm x 10)	$\nu(cm^{-1})$		
W	4165	24 010	3000	$0_{s}, 3 \ge 10; 0_{s}, 4 + 11$
VW	4178	23 935	3075	$0_{s}, 5 + 10 + 12$
WV	4186 sh	23 890	3120	$0_{s}, 2 \times 8 + 11$ ;
				$0_{s,5} + 2 \times 11$
W	4190	23 865	3145	0 <sub>f</sub> ,2 x 5
W	4197 sh	23 825	3185	$0_{s}, 8 + 2 \times 10$
m	4201	23 805	3205	0 <sub>s</sub> ,2 x 5
W	4206 sh	23 775	3235	0 <sub>s</sub> ,4 + 10
WV	4217	23 715	3295	$0_{f}, 5 + 10 + 11 ;$
				$0_{f}, 2 \ge 8 + 10$
W	4229	23 645	3365	$0_{s}, 5 + 10 + 11 ;$
				0 <sub>s</sub> ,2 x 8 + 10
W	4239	23 590	3420	0 <sub>s</sub> ,4 + 8
WW	4250	23 530	3480	$0_{f}, 5 + 8 + 11 ; 0_{f}, 3 \ge 8$
W	4260	23 475	3535	$0_{s}, 5 + 8 + 11 ; 0_{s}, 3 \times 8$
W	4271	23 415	3595	$0_{s}, 5 + 2 \times 10$
WW	4294	23 290	3720	$0_{f}, 5 + 8 + 10$
W	4303	23 240	3770	$0_{s,5} + 8 + 10$
W	4317	23 170	3840	0 <sub>s</sub> ,4 + 10
WW	4326	23 115	3895	$0_{r}, 5 + 2 \ge 8$
W	4338	23 050	3960	$0_{s}, 5 + 2 \times 8$
W	4340	23 040	3970	$0_{s}^{2} \times 5 + 11$
VW	4372	22 875	4135	$0_{f}, 2 \ge 5 + 10$

TABLE 4.2 (Continued)

I	Position		$\Delta V(cm^{-1})$	Assignment		
true all and the second	$\lambda$ (nm x 10)	$\nu(cm^{-1})$	an a state the later later to state the state			
W	4385	22 805	4205	$0_{s}^{2}$ , 2 x 5 + 10		
W	4390	22 780	4230	$0_{s}^{2} \times 5 + 9$		
WV	4405	22 700	4310	0 <sub>f</sub> ,2 x 5 + 8 ;0 <sub>s</sub> ,3 x 8 +		
				11 ;0,5 + 8 + 2 x 11		
W	4418	22 635	4375	$0_{s}, 2 \ge 5 + 8$		
VW	4424	22 605	4405	$0_{s}, 4 + 8 + 10$		
VW	4432	22 565	4445	$0_{f}, 3 \ge 8 + 10; 0_{f}, 5 + 8$		
				10 + 11		
VW	4450	22 470	4540	$0_{s}, 3 \ge 8 + 10; 0_{s}, 5 + 8$		
				10 + 11 ;0 <sub>f</sub> ,4 + 5 + 11		
VW	4462	22410	4600	$0_{s}, 5 + 3 \times 10; 0_{s}, 4 + 5$		
				11		
W	4476	22 340	4670	$0_{s}^{2} \times 5 + 10 + 12$		
TW	4485	22 290	4720	$0_{s}, 4 \ge 8; 0_{s}, 5 + 2 \ge 8 +$		
TW	4490	22 270	4740	0 <sub>f</sub> ,3 x 5		
w	4497	22 235	4775	$0_{s}, 5 + 8 + 2 \times 10$		
J	4502	22 210	4800	0 <sub>s</sub> ,3 x 5		
<i>r</i> w	4509	22 180	4830	$0_{s}, 4 + 5 + 10$		
ΓW	4521	22 120	4890	$0_{f}, 5 + 2 \ge 8 + 10^{-1}$		
TW	4534	22 055	4955	$0_{s}, 5 + 2 \ge 8 + 10$ ;		
				$0_{s}^{2}, 2 \ge 5 + 10 + 11$		
TW	4546	21 995	5015	0 <sub>s</sub> ,4 + 5 + 8		
W	4558	21 940	5070	$0_{f}, 5 + 3 \ge 8_{0_{f}}, 2 \ge 5 +$		
				8 + 11		

TABLE 4.2 (Continued)

TABLE 4.2 (Continued)

I	Positi	on	$\Delta V(cm^{-1})$	Assignment
A NET THE OWNER WATER	$\lambda$ (nm x 10)	$v(cm^{-1})$	Najmada Alexandrova da da comencia da c	
W	4570	21 880	5130	0 <sub>s</sub> ,5 + 3 x 8 ;0 <sub>s</sub> ,2 x 5 +
				8 + 11
ww	4584	21 815	5195	$0_{s}^{2} \times 5 + 2 \times 10$
vw	4607	21 705	5305	$0_{f}, 2 \ge 5 + 8 + 10$
ww	4621	21 640	5370	$0_{s}^{2} \times 5 + 8 + 10$
W	4637	21 565	5445	$0_{s}, 4 + 2 \ge 5$
W	4658	21 470	5540	$0_{s}, 3 \ge 5 + 11 ; 0_{s}, 2 \ge 5$
				2 x 8
ww	4713	21 220	5790	$0_{\rm s}, 3 \ge 5 + 10$
WW	4722	21 175	5835	$0_{s}, 3 \ge 5 + 9$
W	4737	21 110	5900	$0_{f}, 3 \ge 5 + 8$
vw	4751	21 050	5960	$0_{s}, 3 \ge 5 + 8$
vw	4761	21 005	6005	$0_{s}, 4 + 5 + 8 + 10$
VW	4789	20 880	6130	$0_{s}, 5 + 3 \ge 8 + 10$
VW	4803	20 820	6190	$0_{s}^{2} \times 5 + 2 \times 10$ ;
				$0_{s}, 4 + 2 \ge 5 + 11$
VW	4829	20 710	6300	$0_{s}, 3 \ge 5 + 2 \ge 11$ ;
				$0_{s}^{2}$ , 2 x 5 + 2 x 8 + 11
W	4847	20 630	6380	$0_{\rm s}, 4 \ge 5$

<sup>a</sup>Intensities uncorrected for instrumental response; s= strong; m= moderate; w= weak; v= very.

<sup>b</sup>sh= shoulder

<sup>c</sup> For all assignments of tables ( 4.2 ) - ( 4.11 ), only the subscript i of  $\nu_{\rm i}$  are presented.

Figure 4.3

Phosphorescence of  $10^{-3}$  M perdeuterated benzonitrile in polycrystalline methylcyclohexane at  $77^{\circ}$ K.



# TABLE 4.3

Vibrational Analysis of Phosphorescence of  $C_{6}D_{5}CN$  in Polycrystalline Methylcyclohexane at 77°K

Ia	Positi	on	av(cm <sup>-1</sup> )	Assignment
Standardianet	$\lambda$ (nm x 10)	$\nu(cm^{-1})$		1
W	3681	27 170	-60	0 <sub>f</sub> ,0
S	3689	27 110	0	0 <sub>s</sub> ,0
WV	3719	26 890	220	0 <sub>f</sub> ,2 x 22
W	3728	26 825	285	0 <sub>s</sub> ,2 x 22
WV	3737	26 760	350	0 <sub>s</sub> ,33
W	3748	26 680	430	0 <sub>s</sub> ,12
W	3756	26 625	485	0 <sub>s</sub> ,20
WV	3767	26 545	565	0 <sub>s</sub> ,32
WV	3780	26 455	655	0 <sub>s</sub> ,31;0 <sub>f</sub> ,11
W	3789	26 390	720	0 <sub>s</sub> ,11
W	3801	26 310	800	0 <sub>f</sub> ,8
m	3811	26 240	870	°,8
WV	3813 sh <sup>b</sup>	26 225	885	0 <sub>f</sub> ,10
m	3824	26 150	960	0 <sub>s</sub> ,10
WV	3838	26 055	1055	0 <sub>f</sub> ,7
W	3847	25 995	1115	0 <sub>s</sub> ,7
W	3850	25 975	1135	0 <sub>s</sub> ,11 + 12
VW	3860	25 910	1200	0 <sub>s</sub> ,11 + 20

TABLE 4.3 (Continued)

I	Posit	lon	$\Delta V(cm^{-1})$	Assignment
CELL COLOR DE LA COLOR DE L	$\lambda$ (nm x 10)	$\nu(cm^{-1})$		
VW	3866	25 865	1245	$0_{s}, 10 + 2 \ge 22$
WV	3876	25 800	1310	$0_{s}, 10 + 33$
WV	3887	25 725	1385	$0_{s}, 10 + 12$
W	3905	25 610	1500	$0_{s}, 10 + 20; 0_{f}, 5$
S	3915	25 545	1565	0 <sub>s</sub> ,5
W	3930 sh	25 445	1665	0 <sub>s</sub> ,10 + 11
W	3942	25 370	1740	0 <sub>s</sub> ,2 x 8
vw	3945 sh	25 350	1760	$0_{f}, 8 + 10$
W	3955	25 285	1825	0 <sub>s</sub> ,8 + 10
WV	3958 sh	25 265	1845	0 <sub>f</sub> ,2 x 10
VW	3969	25 195	1915	0 <sub>s</sub> ,2 x 10
VW	3981	25 120	1990	0 <sub>s</sub> ,7 + 8
W	3984	25 100	2010	$0_{s}, 8 + 10 + 33 ; 0_{s}, 5 + 12$
VW	3993	25 045	2065	0 <sub>s</sub> ,7 + 10
WV	3996	25 025	2085	$0_{s}, 2 \ge 10 + 33$
WV	4010 sh	24 940	2170	0 <sub>f</sub> ,4
W	4021	24 870	2240	0 <sub>s</sub> ,4
W	4026	24 840	2270	0 <sub>s</sub> ,5 + 11
W	4043	24 735	2375	° <sub>f</sub> ,5 + 8
m	4053	24 675	2435	0 <sub>s</sub> ,5 + 8
W	4055 sh	24 660	2450	$0_{f},5 + 10;0_{s},2 \ge 8 + 11$
m	4067	24 590	2520	$0_{s,5} + 10$
WV	4083	24 490	2620	0 <sub>5</sub> ,3 x 8

TABLE 4.3 (Continued)

I	Positi	on	$\Delta V(cm^{-1})$	Assignment
Statution and Street	$\lambda$ (nm x 10)	$\nu(cm^{-1})$		
W	4094	24 425	2685	°s,5 + 7
W	4097	24 410	2700	$0_{s}, 5 + 11 + 12$
W	4109	24 335	2775	$0_{s}, 8 + 2 \times 10$
vw	4127	24 230	2880	$0_{f}, 4 + 11$
vw	4139	24 160	2950	$0_{s}, 4 + 11$
W	4159	24 045	3065	$0_{f}, 2 \ge 5$
m	4171	23 975	3135	$0_{s}, 2 \ge 5; 0_{s}, 5 + 8 + 11$
				0 <sub>s</sub> ,4 + 8
vw	4182 sh	23 910	3200	$0_{s}, 4 + 10$
VW	4188 sh	23 880	3230	$0_{s}, 5 + 10 + 11$
ww	4201	23 805	3305	$0_{s}, 5 + 2 \times 8$
W	4216	23 720	3390	$0_{s}, 5 + 8 + 10$
VW	4220 sh	23 695	3415	0 <sub>f</sub> ,5 + 2 x 10 ;0 <sub>f</sub> ,4 x 8
vw	4232	23 630	3480	$0_{s}, 5 + 2 \times 10 ; 0_{s}, 4 \times 8$
WV	4247	23 545	3565	$0_{s}, 5 + 7 + 8$
WV	4259	23 480	3630	$0_{s}, 5 + 7 + 10$
W	4263	23 460	3650	$0_{s}, 5 + 10 + 11 + 20$
WV	4280 sh	23 365	3745	0 <sub>f</sub> ,4 + 5
W	4292	23 300	3810	0,4 + 5
W	4295 sh	23 285	3825	$0_{2}, 2 \ge 5 + 11$
vw	4315	23 175	3935	$0_{s}, 2 \ge 5 + 8$
W	4329	23 100	4010	$0_{2}, 2 \ge 5 + 8$
W	4343	23 025	4085	$0_{2} \times 5 + 10$
I	Positi	on	$\Delta v(cm^{-1})$	Assignment
----	----------------------	----------------	---------------------	------------------------------------
-	$\lambda(nm \ge 10)$	$\nu(cm^{-1})$		
WV	4358	22 945	4165	$0_{s}, 5 + 3 = 8$
W	4374	22 860	4250	$0_{s}^{2} \times 5 + 7$
vw	4378	22 840	4270	$0_{s}^{2} \times 5 + 11 + 20$
ww	4392	22 770	4340	$0_{s}, 5 + 8 + 2 \times 10$
vw	4411	22 670	4440	$0_{f}, 4 + 5 + 11$
vw	4424	22 605	4505	$0_{s}, 4 + 5 + 11$
WV	4447	22 485	4625	0 <sub>f</sub> ,3 x 5
W	4460	22 420	4690	$0_{s}, 3 \ge 5; 0_{s}, 4 + 5 + 8$
				$0_{s}^{2} \times 5 + 8 + 11$
vw	4474 sh	22 350	4760	$0_{s}^{2}$ x 5 + 10 + 11 ;
				$0_{s}, 4 + 5 + 10$
WW	4497	22 235	4875	$0_{s}^{2} \times 5 + 2 \times 8$
ww	4512	22 165	4945	$0_{s}^{2} \times 5 + 8 + 10$
W	4515	22 150	4960	$0_{f}^{2} \times 5 + 2 \times 10$
WV	4530	22 075	5035	$0_{s}, 2 \ge 5 + 2 \ge 10$
WV	4547	21 995	5115	$0_{s}, 2 \ge 5 + 7 + 8$
ww	4560	21 930	5180	$0_{s}, 2 \ge 5 + 7 + 10$
vw	4564	21 910	5200	$0_{s}^{2}$ , 2 x 5 + 10 + 11 + 20
VW	4590	21 785	5325	$0_{f}, 2 \ge 5 + 4$
vw	4599	21 745	5365	$0_{s}, 2 \ge 5 + 4$
VW	4603	21 725	5385	$0_{s}, 3 \ge 5 + 11$
WW	4625	21 620	5490	$0_{f}, 3 \ge 5 + 8$
VW	4641	21 545	5565	$0_{s}, 3 \ge 5 + 8$

TABLE 4.3 (Continued)

I	Positi	on	$\Delta V(cm^{-1})$	Assignment
Constant of Designation	$\lambda$ (nm x 10)	$\nu(cm^{-1})$		
ww	4656	21 480	5630	$0_{s}, 3 \ge 5 + 10$
W	4678	21 375	5735	0 <sub>s</sub> ,2 x 5 + 3 x 8
VW	4696	21 295	5815	$0_{s}, 3 \ge 5 + 7$
W	4716	21 205	5905	$0_{s}^{2} \times 5 + 8 + 2 \times 10$
W	4743	21 085	6025	$0_{s}^{2} \times 5 + 4 + 11$
vw	4777	20 935	6175	$0_{f}, 4 \ge 5$
W	4793	20 865	6245	$0_{s}, 4 \ge 5; 0_{s}, 2 \ge 5 + 4 + 8$
W	4808	20 800	6310	$0_{s}^{2}, 2 \ge 5 + 4 + 10;$
				$0_{s}, 3 \ge 5 + 10 + 11$
W	4838	20 670	6440	$0_{s}, 3 \ge 5 + 2 \ge 8$
W	4852	20 610	6500	$0_{s}, 3 \ge 5 + 8 + 10$

TABLE 4.3 (Continued)

<sup>a</sup>Intensities uncorrected for instrumental response; s= strong; m= moderate; w= weak; v= very.

<sup>b</sup>sh= shoulder

Phosphorescence of  $10^{-3}$  M para-monodeuterated benzonitrile in polycrystalline methylcyclohexane at  $77^{\circ}$ K.



#### TABLE 4.4

Vibrational Analysis of Phosphorescence of  $p-D-C_6H_4CN$  in Polycrystalline Methylcyclohexane at  $77^{\circ}K$ 

Ia	Positi	on	△V(cm-1)	Assignment
	$\lambda$ (nm x 10)	$\nu(cm^{-1})$		
W	3688	27 115	-60	0 <sub>f</sub> ,0
S	3696	27 055	0	0,0
W	3728	26 825	230	0 <sub>f</sub> ,2 x 22
W	3738	26 750	305	0 <sub>s</sub> ,2 x 22
W	3747	26 690	365	0 <sub>s</sub> ,33
W	3759	26 605	450	0 <sub>s</sub> ,12
W	3768	26 540	515	0 <sub>s</sub> ,32;0 <sub>s</sub> ,20
WV	3782	26 440	615	0 <sub>s</sub> ,31
VW	3795	26 350	705	0 <sub>f</sub> ,11
W	3803	26 295	760	0 <sub>s</sub> ,11
VW	3813 sh <sup>b</sup>	26 225	830	$0_{s}, 20 + 2 \ge 22; 0_{s}, 12 + 3$
VW	3827	26 130	925	0,10
m	3837	26 065	990	0,10
vw	3846 sh	26 000	1055	0,9
VW	3851	25 965	1090	$0_{s},11 + 2 \ge 22$
W	3856	25 935	1120	0,,8
m	3865	25 875	1180	0,8
W	3871 sh	25 840	1215	0,11 + 12

Position		av(cm <sup>-1</sup> )	Assignment
nm x 10)	$\nu(cm^{-1})$		
880 sh	25 775	1280	$0_{s},10 + 2 \times 22 ;0_{s},12$
892 sh	25 695	1360	0 <sub>s</sub> ,10 + 33
905	25 610	1445	0 <sub>s</sub> ,10 + 12
919	25 515	1540	0 <sub>s</sub> ,10 + 32 ;0 <sub>f</sub> ,5
929	25 450	1605	0 <sub>s</sub> ,5

TABLE 4.4 (Continued)

I

Galacoulous	$\lambda$ (nm x 10)	$\nu(cm^{-1})$	ing states and the state of the st	
WV	3880 sh	25 775	1280	$0_{s},10 + 2 \ge 2;0_{s},11 + 20$
W	3892 sh	25 695	1360	0 <sub>s</sub> ,10 + 33
W	3905	25 610	1445	$0_{s}, 10 + 12$
W	3919	25 515	1540	0 <sub>s</sub> ,10 + 32 ;0 <sub>f</sub> ,5
S	3929	25 450	1605	0 <sub>s</sub> ,5
WV	3941	25 375	1680	0 <sub>f</sub> ,10 + 11
W	3950	25 315	1740	0 <sub>s</sub> ,10 + 11
VW	3963	25 235	1820	$0_{s}, 10 + 12 + 33;$
				$0_{s}, 10 + 20 + 2 \times 22$
W	3977 sh	25 145	1910	$0_{f}^{2} \times 10$
W	3983	25 105	1950	0 <sub>s</sub> ,8 + 11
W	3987	25 080	1975	0 <sub>s</sub> ,2 x 10
W	4000	25 000	2055	0 <sub>s</sub> , 5 + 12
W	4008	24 950	2105	0 <sub>f</sub> ,8 + 10
W	4018	24 890	2165	0 <sub>s</sub> ,8 + 10
W	4031	24 805	2250	0 <sub>s</sub> ,4
WV	4040	24 750	2305	$0_{f}, 2 \ge 8; 0_{f}, 5 + 11$
m	4049	24 695	2360	$0_{s}, 2 \ge 8; 0_{s}, 5 + 11$
W	4062 sh	24 620	2435	$0_{s}, 5 + 12 + 33;$
				$0_{s}, 5 + 20 + 2 \ge 22$
VW	4076	24 535	2520	$0_{f}, 5 + 10$
m	4087	24 470	2585	$0_{s}, 5 + 10$
WV	4103	24 370	2685	0 <sub>s</sub> ,5 + 9

I	Positi	on	av(cm <sup>-1</sup> )	Assignment
ensistantiawa	$\lambda$ (nm x 10)	V(cm <sup>-1</sup> )		the the stand of the stand stands and a flar that an advertise of the stands of the stands of the stands
vw	4108	24 345	2710	0 <sub>f</sub> ,5 + 8
m	4118	24 285	2770	0 <sub>s</sub> ,5 + 8
VW	4125 sh	24 240	2815	$0_{s}, 5 + 11 + 12$
vw	4134 sh	24 190	2865	$0_{s}, 5 + 11 + 20;$
				$0_{s}, 5 + 10 + 2 \ge 22$
VW	4143	24 135	2920	0 <sub>f</sub> ,3 x 10 ;0 <sub>f</sub> ,4 + 11
VW	4156	24 060	2995	$0_{s}, 3 \ge 10; 0_{s}, 4 + 11$
VW	4165	24 010	3045	$0_{s}, 5 + 10 + 12$
vw	4183	23 905	3150	0 <sub>f</sub> ,2 x 5
n	4193	23 850	3205	0 <sub>s</sub> ,2 x 5
vw	4197 sh	23 825	3230	$0_{s}, 4 + 10$
VW	4205	23 780	3275	$0_{f}, 2 \ge 8 + 10; 0_{f}, 5 +$
				10 + 11
M	4216	23 720	3335	0 <sub>s</sub> ,2 x 8 + 10 ;0 <sub>s</sub> ,5 +
				10 + 11
N	4231	23 635	3420	° <sub>s</sub> ,4 + 8
vw	4245	23 555	3500	$0_{f}, 5 + 2 \ge 10$
N	4251	23 <b>52</b> 5	3530	$0_{s}, 3 \ge 8; 0_{s}, 5 + 8 + 11$
Ŵ	4256	23 495	3560	$0_{s}, 5 + 2 \times 10$
N	4282	23 355	3700	$0_{f}, 5 + 8 + 10$
W	4293	23 295	3760	$0_{s}, 5 + 8 + 10$
v	4307	23 220	3835	0 <sub>s</sub> ,4 + 5
ww	4317	23 165	3890	$0_{f},5 + 2 \ge 3;0_{f},2 \ge 5 +$

TABLE 4.4 (Continued)

I	Positi	on	$\Delta V(cm^{-1})$	Assignment
	$\lambda$ (nm x 10)	$v(cm^{-1})$	CR - Spin a start for a start of the	
W	4329	23 100	3955	$0_{s,5} + 2 \times 8 ; 0_{s,2} \times 5 + 1$
VW	4344	23 020	4035	$0_{s}, 2 \ge 5 + 12 + 33$
vw	4358	22 945	4110	$0_{f}, 2 \ge 5 + 10$
W	4371	22 880	4175	$0_{s}^{2}, 2 \ge 5 + 10$
vw	4377	22 845	4210	$0_{s}^{2}, 2 \ge 5 + 9$
WW	4396	22 750	4305	$0_{s}, 3 \ge 8 + 11 ; 0_{s}, 5 + 8 +$
				2 x 11
W	4407	22 690	4365	$0_{s}, 2 \ge 5 + 8$
vw	4414 sh	22 655	4400	$0_{s}, 4 + 8 + 10$
W	4424	22 605	4450	$0_{f}, 3 \ge 8 + 10;$
				$0_{f}, 5 + 8 + 10 + 11$
ww	4437	22 540	4515	0 <sub>s</sub> ,3 x 8 + 10 ;0 <sub>s</sub> ,5 + 8 +
				10 + 11 ;0 <sub>f</sub> ,4 + 5 + 11
VW	4452	22 460	4595	$0_{s}, 5 + 3 \ge 10; 0_{s}, 4 + 5 + 1$
W	4466	22 390	4665	$0_{s}^{2}, 2 \ge 5 + 10 + 12$
W	4481	22 315	4740	0 <sub>f</sub> ,3 x 5
W	4493	22 255	4800	0 <sub>s</sub> ,3 x 5
VW	4497 sh	22 235	4820	$0_{s}, 4 + 5 + 10$
W	4508	22 185	4870	$0_{f}, 5 + 2 \ge 8 + 10$ ;
				$0_{f}, 2 \ge 5 + 10 + 11$
W	4520	22 125	4930	$0_{s}, 5 + 2 \ge 8 + 10$
				$0_{s}^{2}$ , 2 x 5 + 10 + 11
VW	4537	22 040	5015	0 - 4 + 5 + 8

TABLE 4.4 (Continued)

TABLE 4.4 (Continued)

I	Positi	on	$\Delta V(cm^{-1})$	Assignment
eterntecompany	$\lambda$ (nm x 10)	$\nu(cm^{-1})$		
vw	4546	21 995	5060	$0_{f}, 5 + 3 \ge 8;$
				$0_{f}, 2 \ge 5 + 8 + 11$
W	4559	21 935	5120	$0_{s}, 5 + 3 \ge 8;$
				$0_{s}^{2} \times 5 + 8 + 11$
WW	4566	21 900	5155	$0_{s}^{2} \times 5 + 2 \times 10$
WV	4594	21 765	5290	$0_{f}, 2 \ge 5 + 8 + 10$
W	4606	21 710	5345	$0_{s}^{2} \times 5 + 8 + 10$
wv	4625	21 620	5435	$0_{s}, 4 + 2 \ge 5$
ww	4647	21 520	5535	$0_{s}^{2}$ , 2 x 5 + 2 x 8 ;
				$0_{s}, 3 \ge 5 + 11$
W	4666	21 430	5625	$0_{s}, 3 \ge 5 + 12 + 33$
WV	4684	21 350	5705	$0_{f}, 3 \ge 5 + 10$
VW	4698	21 285	5770	$0_{s}, 3 \ge 5 + 10$
W	4740	21 095	5960	$0_{s}, 3 \ge 5 + 8$
VW	4750	21 055	6000	$0_{s}, 4 + 5 + 8 + 10$
W	4770	20 965	6090	$0_{s}, 5 + 3 \times 8 + 10;$
				$0_{s}^{2} \times 5 + 8 + 10 + 11$
AM	4792	20 870	6185	$0_{s}^{2} \times 5 + 3 \times 10$ ;
				$0_{s}, 4 + 2 \ge 5 + 11$
WW	4822	20 740	6315	$0_{s}^{2} \times 5 + 2 \times 8 + 11;$
				$0_{s}, 3 \ge 5 + 2 \ge 11$
VW	4840	20 660	6395	0 <sub>s</sub> ,4 x 5

a, b See subscripts in TABLE 4.2

Phosphorescence of  $10^{-3}$  M meta-monodeuterated benzonitrile in polycrystalline methylcyclohexane at  $77^{\circ}$ K.



### TABLE 4.5

Vibrational Analysis of Phosphorescence of  $m-D-C_6H_4CN$  in

Polycrystalline Methylcyclohexane at 77°K

Ia	Positi	on	av(cm <sup>-1</sup> )	Assignment
Cashing Street Barriel	$\lambda$ (nm x 10)	ν(cm <sup>-1</sup> )		
W	3692	27 085	-65	0 <sub>f</sub> ,0
S	3701	27 020	0	0,,0
W	3734	26 780	240	0 <sub>f</sub> ,2 x 22
WV	3743	26 715	305	0 <sub>s</sub> ,2 x 22
ww	3752	26 655	365	0 <sub>s</sub> ,33
W	3765	26 560	460	0 <sub>s</sub> ,12
WV	3774	26 495	525	0 <sub>s</sub> ,32
WV	3786	26 415	605	0,31
WV	3797	26 335	685	0 <sub>f</sub> .11
W	3805	26 280	740	0,11
WV	3815	26 210	810	$0_{s}, 12 + 33; 0_{s}, 20 + 2 x$
W	3826	26 140	880	0 <sub>s</sub> ,20 + 33 ;0 <sub>s</sub> ,32 + 33 ;
WV	3834	26 080	940	01.10
m	3843	26 020	1000	0,10
WV	3849 sh <sup>b</sup>	25 980	1040	0,9
VW	3859	25 915	1105	0 <sub>f</sub> ,8
m	3869	25 845	1175	0 <sub>s</sub> ,8
WW	3888 sh	25 720	1300	$0_{s},10 + 2 \ge 22;0_{s},11 + 2$
WW	3901	25 635	1385	0 <sub>s</sub> ,10 + 33

TABLE 4.5 (Continued)

I	Positi	on	av(cm <sup>-1</sup> )	Assignment
	$\lambda(nm \times 10)$	ν(cm <sup>-1</sup> )		
W	3914 sh	25 550	1470	$0_{s}, 10 + 12$
W	3925	25 480	1540	$0_{s}, 10 + 20; 0_{f}, 5$
S	3934	25 420	1600	0 <sub>s</sub> ,5
W	3947 sh	25 335	1685	0 <sub>f</sub> ,10 + 11
WV	3955	25 285	1735	0 <sub>s</sub> ,10 + 11
ww	3966	25 215	1805	$0_{f}$ ,10 + 20 + 33 ; $0_{f}$ ,10 + 30
WV	3979	25 130	1890	$0_{s},10 + 20 + 33;0_{s},10 + 30$
W	3984	25 100	1920	0 <sub>s</sub> ,8 + 11
WV	3996	25 025	1995	0 <sub>s</sub> ,2 x 10
W	4005	24 970	2050	$0_{s}, 8 + 20 + 33 ; 0_{s}, 5 + 12$
WV	4015	24 905	2115	$0_{f}, 8 + 10$
W	4026	24 840	2180	0 <sub>s</sub> ,8 + 10
W	4036	24 775	2245	°s,4
WV	4043	24 735	2285	$0_{f}, 2 \ge 8; 0_{f}, 5 + 11$
W	4052	24 680	2340	$0_{s}^{2}$ x 8 ; $0_{s}^{5}$ + 11
WW	4062	24 620	2400	$0_{f}, 5 + 20 + 33; 0_{f}, 5 + 30$
WW	4075	24 540	2480	$0_{s}, 5 + 20 + 33; 0_{s}, 5 + 30$
VW	4084	24 485	2535	$0_{f}, 5 + 10$
m	4094	24 425	2595	0,5 + 10
WW	4101	24 385	2635	0,5+9
WV	4112	24 320	2700	0 <sub>f</sub> ,5 + 8
m	4124	24 240	2780	0 <sub>5</sub> ,5 + 8
WV	4148	24 110	2910	$0_{f}, 3 \ge 10; 0_{f}, 4 + 11$

I	Positi	on	$\Delta V(cm^{-1})$	Assignment
λ	(nm x 10)	$\nu(cm^{-1})$	na film and all days and a state of the state	
VW	4160	24 040	2980	$0_{s}, 3 \ge 10; 0_{s}, 4 + 11$
ww	4175	23 950	3070	$0_{s}, 2 \ge 8 + 11;$
				$0_{s}, 5 + 10 + 12$
WV	4186	23 890	3130	$0_{f}, 2 \ge 5$
m	4197	23 825	3195	$0_{s}, 2 \ge 5; 0_{s}, 8 + 2 \ge 10$
vw	4201 sh	23 805	3215	0 <sub>s</sub> ,5 + 11 + 20 + 33 ;0 <sub>s</sub> ,5
WW	4212	23 740	3280	$0_{f}^{2} \times 8 + 10;$
				$0_{f}, 5 + 10 + 11$
W	4224	23 675	3345	$0_{s}^{2}$ x 8 + 10 ;
				$0_{s}, 5 + 10 + 11$
WW	4236	23 605	3415	0 <sub>s</sub> ,4 + 8
VW	4247	23 545	3475	$0_{s}, 5 + 10 + 20 + 33; 0_{s}, 5$
VW	4254	23 510	3510	0 <sub>s</sub> ,3 x 8 ;0 <sub>s</sub> ,5 + 8 + 11
VW	4268	23 430	3590	$0_{s}, 5 + 2 \ge 10$
WV	4279	23 370	3650	$0_{s}, 5 + 8 + 20 + 33; 0_{s}, 5 + 8$
W	4290	23 310	3710	$0_{f}, 5 + 8 + 10$
W	4301	23 250	3770	$0_{s}, 5 + 8 + 10$
W	4313	23 185	3835	$o_{s}, 4 + 5$
VW	4320	23 150	3870	$0_{f}, 5 + 2 \ge 8; 0_{f}, 2 \ge 5 + 3$
W	4333	23 080	3940	$0_{s}, 5 + 2 \ge 3; 0_{s}, 2 \ge 5 + 2$
VW .	4357	22 950	4070	$0_{s}^{,2} \times 5 + 20 + 33; 0_{s}^{,2} \times 5$
VW I	4368	22 895	4125	$0_{f}, 2 \ge 5 + 10$
vw 1	4381	22 825	4195	$0_{s}^{2} \times 5 + 10$

TABLE 4.5 (Continued)

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TABLE 4.5 (Continued)

I	Position	The disc strategy of the state of the	(cm <sup>-1</sup> )	Assignment
halper all has represented in the	(nm x 10)	(cm <sup>-1</sup> )	11-14-15-10-10-10-1-1-1-1-1-1-1-1-1-1-1-1-1-1	
W	4389	22 785	4235	$0_{s}^{2}, 2 \ge 5 + 9$
WW	4400	22 725	4295	$0_{f}^{2} \times 5 + 8$
VW	4413	22 660	4360	$0_{s}^{2} \times 5 + 8$
W	4442	22 510	4510	$0_{s}, 3 \ge 8 + 10; 0_{f}, 5 +$
				3 x 10 ;0 <sub>f</sub> ,4 + 5 + 11
VW	4457	22 435	4585	$0_{s}, 5 + 3 \times 10; 0_{s}, 4 + 5 + 11$
vw	4470	22 370	4650	$0_{s}, 4 \ge 8; 0_{s}, 5 + 2 \ge 8 + 11$
VŴ	4485	22 295	4725	0 <sub>f</sub> ,3 x 5
W	4498	22 230	4790	$0_{s}, 3 \ge 5; 0_{s}, 5 + 8 + 2 \ge 10$
VW	4505	22 200	4820	$0_{s}^{2}, 2 \times 5 + 11 + 30;$
				$0_{s}^{2} \times 5 + 11 + 32 + 33$
WW	4529	22 080	4940	$0_{s}, 5 + 2 \times 8 + 10$
WV	4543	22 010	5010	0 <sub>s</sub> ,4 + 5 + 8
WV	4553	21 965	5055	$0_{s}^{2} \times 5 + 10 + 30$ ;
				$0_{s}^{2}$ , 2 x 5 + 10 + 32 + 33
WV	4562	21 920	5100	$0_{s}^{2} \times 5 + 8 + 11$
WW	4579	21 840	5180	$0_{s}, 2 \ge 5 + 2 \ge 10$
WV	4591	21 780	5240	$0_{s}^{2}, 2 \ge 5 + 8 + 30;$
				0 <sub>s</sub> ,2 x 5 + 8 + 32 + 33
WV	4602	21 730	5290	$0_{f}, 2 \ge 5 + 8 + 10$
WV	4616	21 665	5355	$0_{s}^{2} \times 5 + 8 + 10$
WW	4633	21 585	5435	$0_{s}, 4 + 2 \ge 5$

I	Positic	on	(cm <sup>-1</sup> )	Assignment
	(nm x 10)	(cm <sup>-1</sup> )	<b>₩₩₽_₽~₩₽</b> ₽₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩	
WV	4639	21 555	5465	$0_{f}, 2 \ge 5 + 2 \ge 8;$
				$0_{f}, 3 \ge 5 + 11$
WV	4653	21 490	5530	$0_{s}^{2} \times 5 + 2 \times 8;$
				$0_{s}, 3 \ge 5 + 11$
WV	4683	21 355	5665	$0_{s}, 3 \ge 5 + 30;$
			8	0 <sub>s</sub> ,3 x 5 + 32 + 33
WW	4707	21 245	5775	$0_{s}, 3 \ge 5 + 10$
vw	4733	21 130	5890	$0_{f}, 3 \ge 5 + 8$
WV	4746	21 070	5950	$0_{s}, 3 \ge 5 + 8$
vw	4754	21 035	5985	$0_{s}, 5 + 3 \ge 8 + 10$
VW	4797	20 845	6175	$0_{s}^{2} \times 5 + 3 \times 10$ ;
				$0_{s}, 4 + 2 \ge 5 + 11$
WV	4845	20 640	6380	0 <sub>s</sub> ,4 x 5
VW	4857	20 590	6430	$0_{s}^{2} \times 5 + 2 \times 8 + 10;$
				$0_{s}, 3 \ge 5 + 10 + 11$

TABLE 4.5 (Continued)

<sup>a</sup>Intensities uncorrected for instrumental response; s= strong; m= moderate; w= weak; v= very.

<sup>b</sup>sh= shoulder

Phosphorescence of  $10^{-3}$  M ortho-monodeuterated benzonitrile in polycrystalline methylcyclohexane at  $77^{\circ}$ K.



### TABLE 4.6

Vibrational Analysis of Phosphorescence of o-D-C<sub>6</sub>H<sub>4</sub>CN in Polycrystalline Methylcyclohexane at 77°K

Ia	Positi	.on	sv(cm <sup>-1</sup> )	Assignment
gusetile and an day	$\lambda$ (nm x 10)	v(cm-1)	an a	an a
W	3692	27 085	-60	0 <sub>f</sub> ,0
S	3700	27 025	0	0 <sub>s</sub> ,0
W	3733	26 790	235	0 <sub>f</sub> ,2 x 22
WW	3743	26 715	310	0 <sub>s</sub> ,2 x 22
VW	3751	26 660	365	0 <sub>s</sub> .33
WW	3764	26 565	460	0,12
VW	3775	26 490	535	0 <sub>s</sub> ,20 ;0 <sub>s</sub> ,32
VW	3789	26 390	635	0 <sub>s</sub> ,31
W	3799	26 325	700	0,11
m	3807	26 265	760	0 <sub>s</sub> ,11
WV	3815 sh <sup>b</sup>	26 210	815	0 <sub>s</sub> ,12 + 33
VW	3823	26 160	865	$0_{s}, 12 + 2 \ge 2; 0_{s}, 20 + 33$
W	3832	26 095	930	0,10
m	3841	26 035	990	0,10
W	3849	25 980	1045	0,9
m	3860	25 910	1115	0,8
WW	3865 sh	25 875	1150	$0_{s}, 20 + 31 ; 0_{f}, 7$
WV	3872	25 825	1200	0 <sub>s</sub> ,7

I	Position		$\Delta v (cm^{-1})$	Assignment	
fational 2011 million - partitu dan	$\lambda$ (nm x 10)	$v(cm^{-1})$	o Gan Ann Gangara (gan Grint an an San Jan San San San San San San San San San S		
W	3884	25 745	1280	$0_{s},10 + 2 \ge 22;0_{s},11 +$	
				20 ;0 <sub>s</sub> ,11 + 32 ;0 <sub>s</sub> ,28	
W	3903	25 620	1405	$0_{s}, 10 + 33$	
VW	3914 sh	25 550	1475	0 <sub>s</sub> ,10 + 12	
W	3924	25 485	1540	$0_{s}, 10 + 20; 0_{f}, 5$	
S	3934	25 420	1605	0 <sub>s</sub> ,5	
W	3955	25 285	1740	$0_{s}, 10 + 11$	
vw	3965 sh	25 220	1805	$0_{s}, 9 + 11$	
W	3982	25 115	1910	$0_{s}, 8 + 11 ; 0_{f}, 2 \times 10$	
Ň	3992	25 050	1975	$0_{s}^{2}$ x 10	
W	4001	24 995	2030	$0_{s},9 + 10$	
N	4013	24 920	2105	$0_{s}, 8 + 10; 0_{s}, 2 \ge 9$	
W	4026	24 840	2185	$0_{s}, 7 + 10; 0_{f}, 4$	
n	4036	24 775	2250	0 <sub>s</sub> ,4	
VW	4042 sh	24 740	2285	$0_{s}^{,2 \times 10 + 2 \times 22}; 0_{s}^{,10}$	
n	4053	24 675	2350	$0_{s}, 5 + 11$	
7W	4070	24 570	2455	$0_{s}, 5 + 20 + 33$	
N	4081	24 505	2520	$0_{f}, 5 + 10$	
n	4092	24 440	2585	0 <sub>s</sub> ,5 + 10	
/W	4101	24 385	2640	0 <sub>s</sub> ,5 + 9	
Ţ	4113	24 315	2710	0 <sub>s</sub> ,5 + 8	
rw	4126 sh	24 235	2790	0 <sub>8</sub> ,5 + 7	
T	4140	24 155	2870	$0_{a},5 + 10 + 2 \times 22 ;0_{a},5^{+}$	

TABLE 4.6 (Continued)

TABLE 4.6 (Continued)

I	Positi	on	$\Delta V(cm^{-1})$	Assignment
	$\lambda$ (nm x 10)	V(cm <sup>-1</sup> )		
W	4153	24 080	2945	$0_{f}, 4 + 11$
VW	4168	23 990	3035	$0_{s}, 4 + 11$
W	4180 sh	23 925	3100	$0_{s}, 8 + 2 \times 10$
W	4186	23 890	3135	$0_{f}, 2 \ge 5$
m	4196	23 830	3195	0 <sub>s</sub> ,2 x 5
vw	4201 sh	23 805	3220	$0_{s}, 4 + 10$
VW	4222	23 685	3340	$0_{s}, 5 + 10 + 11$
vw	4233 sh	23 625	3400	$0_{s}, 5 + 9 + 11$
vw	4250	23 530	3495	$0_{s}, 5 + 8 + 11$
ww	4261	23 470	3555	$0_{s}, 5 + 2 \ge 10$
W	4274	23 395	3630	$0_{s}, 5 + 9 + 10$
WW	4287	23 325	3700	$0_{s}, 5 + 8 + 10$
W	4301	23 250	3775	$0_{s}, 5 + 7 + 10; 0_{f}, 4 + 5$
W	4312	23 190	3835	0 <sub>s</sub> ,4 + 5
VW	4334	23 075	3950	$0_{s}^{2}, 2 \ge 5 + 11$
wv	4354	22 965	4060	$0_{s}^{2}, 2 \ge 5 + 20 + 33$
vw	4363	22 920	4105	$0_{f}^{2} \times 5 + 10$
W	4376	22 850	4175	$0_{s}^{2}, 2 \ge 5 + 10$
W	4387	22 795	4230	$0_{s}^{2}, 2 \ge 5 + 9$
VW	4400	22 725	4300	$0_{s}^{2}$ , 2 x 5 + 8
vw	4407 sh	22 690	4335	$0_{f}, 2 \ge 5 + 7$
vw	4416	22 645	4380	$0_{s}^{2} \times 5 + 7$
vw	4431	22 570	4455	$0_{s}^{2}$ , 2 x 5 + 10 + 2 x 22
				$0_{s}^{2}, 2 \times 5 + 28$

TABLE 4.6 (Continued)

I	Positi	on	$\Delta V(cm^{-1})$	Assignment
orano.cotose	$\lambda$ (nm x 10)	V(cm-1)	un des ritur des automatics statutes and an	
W	4448	22 480	4545	$0_{f}, 4 + 5 + 11$
WV	4460	22 420	4605	$0_{s}, 4 + 5 + 11$
W	4477	22 335	4690	$0_{s}, 5 + 8 + 2 \times 10$
W	4484	22 300	4725	0 <sub>f</sub> ,3 x 5
W	4497	22 235	4790	0 <sub>s</sub> ,3 x 5
vw	4502 sh	22 210	4815	$0_{s}, 4 + 5 + 10$
VW	4515	22 150	4875	$0_{f}^{2} \times 5 + 10 + 11$
ww	4529	22 080	4945	$0_{s}^{2}$ , 2 x 5 + 10 + 11
W	4557	21 945	5080	$0_{s}^{2}, 2 \ge 5 + 8 + 11$
W	4570	21 880	5145	$0_{s}^{2}$ , 2 x 5 + 2 x 10
W	4584	21 815	5210	$0_{s}^{2}$ x 5 + 9 + 10
W	4599	21 745	5280	$0_{s}^{2}, 2 \ge 5 + 8 + 10$
W	4617	21 660	5365	$0_{s}^{2}$ , 2 x 5 + 7 + 10
VW	4631	21 595	5430	$0_{s}, 4 + 2 \ge 5$
W	4654	21 485	5540	$0_{s}, 3 \ge 5 + 11$
WV	4702	21 270	5755	$0_{s}, 3 \ge 5 + 10$
WV	4711	21 225	5800	$0_{s}, 3 \ge 5 + 9$
WV	4730	21 140	5885	$0_{s}, 3 \ge 5 + 8$
WV	4764	20 990	6035	$0_{s,3} \ge 5 + 10 + 2 \ge 22$
WV	4799	20 840	6185	$0_{2},4+2 \ge 5+11$
VW	4843	20 650	6375	0,4 x 5
vw	4851	20 615	6410	$0_{s}, 4 + 2 \ge 5 + 10$

a, b See subscripts in TABLE 4.2

#### 4.2 Vibrational Analyses of Fluorescence

The fluorescence spectra were obtained with  $10^{-3}$ -10<sup>-4</sup> molar solutions of the benzonitriles in cyclohexane and methylcyclohexane. With higher concentrations, the 0,0 region intensity was diminished due to self-absorption ( overlapping of the emission and absorption bands ) and there also appeared a very broad structureless band with  $\lambda$  max. at around 325 nm . This was probably due to a dimer or excimer formation in the concentrated solution. The analyses presented below are for twice cooled cyclohexane solutions ( see p. 40 ) but the analyses are also valid for methylcyclohexane solutions although the spectra obtained in the latter solvent are not as detailed and are complicated by the appearance of splittings masking some very weak peaks.

a- Benzonitrile-H5

The 0.0 band of fluorescence at 36 075 cm<sup>-1</sup> is weak in benzonitrile-H<sub>5</sub>, figure (4.7), and in all the benzonitriles. It is shifted 445 cm<sup>-1</sup> to lower energy as compared to the vapor 0.0 band reported by Bass (<u>13</u>). In methylcyclohexane, the split 0.0 bands are at 36 165 cm<sup>-1</sup> and 36 050 cm<sup>-1</sup>. The former is predominant for a slow-cooled sample. The analysis is given in table (4.7). The first transition after the 0,0 band occurs at 450 cm<sup>-1</sup> and is assigned as 0,  $\mathcal{V}_{12}$ . Bass has reported three fundamentals at lower energy, i.e., at 173, 270, and 382 cm<sup>-1</sup> respectively. The next band at 540 cm<sup>-1</sup> is assigned as 0,  $\mathcal{V}_{32}$  since perdeuteration, see figure (4.8), does not indicate the presence of 0,  $\mathcal{V}_{20}$  which would underlie the 0,  $\mathcal{V}_{32}$  band in H<sub>5</sub>. The first major bands of the spectra appear at 1000 cm<sup>-1</sup> and 1195 cm<sup>-1</sup> assigned as 0,  $\mathcal{V}_{10}$  and 0,  $\mathcal{V}_{7}$  respectively. The main feature of the spectrum is the long progression in  $\mathcal{V}_{10}$  (up to 5 x  $\mathcal{V}_{10}$ ) plus the progressions in  $\mathcal{V}_{7}$  and  $\mathcal{V}_{12}$ . The great majority of the rest of the bands is due to transitions to vibronic states involving combinations of these three fundamentals. All the fundamentals reported in table (4.7) appear in the vapor fluorescence of Bass (13).

b- Benzonitrile-D5

Perdeuteration increases the 0,0 energy gap by 155 cm<sup>-1</sup>. An analysis, table (4.8), of the fluorescence spectrum shown in figure (4.8) indicates that the strong 1000 cm<sup>-1</sup> in benzonitrile-H<sub>5</sub> is shifted to 970 cm<sup>-1</sup> and the 1195 cm<sup>-1</sup> band has moved down to 1155 cm<sup>-1</sup>. These observations are consistent with the H<sub>5</sub> assignments of 0,  $\mathcal{V}_{10}$  and 0,  $\mathcal{V}_{7}$  for these bands. The 775 cm<sup>-1</sup> band has now shifted to 720 cm<sup>-1</sup>, consistent with a 0,  $\mathcal{V}_{11}$  assignment. Similarly, the appearance of a weak band at 855 cm<sup>-1</sup> and a strong one at 1385 cm<sup>-1</sup> fits the expected deuteration effects on  $\mathcal{V}_9$  and  $\mathcal{V}_6$ . The spectrum is very similar to that of benzonitrile-H<sub>5</sub> except for the increased intensity of the 1280 cm<sup>-1</sup> and 1385 cm<sup>-1</sup> bands. The main feature still remain the long progression of  $\mathcal{V}_{10}$  plus  $\mathcal{V}_{10}$  and  $\mathcal{V}_7$  combining with other fundamentals and combinations.

### c- <u>Para-deuterated benzonitrile</u> ( p-DC6H4CN )

Deuterium substitution in the para position of benzonitrile blue-shifts the origin band by about 40 cm<sup>-1</sup>. The general appearance of the spectrum is very much the same as benzonitrile-H<sub>5</sub>. As can be seen from a comparison of figure (4.9) with figure (4.7), there is only one small difference in the entire 0-2500 cm<sup>-1</sup> region, namely that the band at 2405 cm<sup>-1</sup> and 2475 cm<sup>-1</sup> in H<sub>5</sub> now appears as one broader band at 2435 cm<sup>-1</sup> from the 0.0 band. Based on the assignment for these bands in H<sub>5</sub>, one would expect them to move closer to each other in para-, meta-, and ortho-monodeuterated benzonitrile. From table (4.1), calculations would expect the separations between 0.2 x  $V_7$ and 0.2 x  $V_{10} + V_{12}$  transitions to be 30 cm<sup>-1</sup>, 65 cm<sup>-1</sup> and 45 cm<sup>-1</sup> respectively. In meta, the two bands are clearly resolved, figure (4.10), and in ortho, one appears as a shoulder on the other band. The analysis of para-monodeuterated benzonitrile is consequently very similar to that of benzonitrile-H<sub>5</sub>.

### d-<u>Meta-deuterated</u> benzonitrile ( $m-DC_6H_4CN$ )

The spectrum in figure (4.10) is again very similar to that of benzonitrile-H<sub>5</sub> as is the vibrational analysis in table (4.10). The 0,0 band is now shifted 25 cm<sup>-1</sup> to higher energy. One of the few differences is that on an expanded scale, the 1025 cm<sup>-1</sup> band seems to be resolved from the 1000 cm<sup>-1</sup> band; these are assigned as 0,  $\nu_9$  and 0,  $\nu_{10}$  respectively. Also, as mentioned for paradeuterated benzonitrile, the 0,2 x  $\nu_7$  and 0,2 x  $\nu_{10}$  +  $\nu_{12}$  bands are now separated. This adds weight to the proposed assignment of  $\nu_9$  to the shoulders on 1000 cm<sup>-1</sup> in H<sub>5</sub> and para-deuterated benzonitrile. None of the bands seems to be very sensitive to deuterium substitution.

## e- Ortho-deuterated benzonitrile ( $o-DC_6H_4CN$ )

Replacement of hydrogen in the ortho position by deuterium alters the fluorescence spectrum only negligibly as seen from figure (4.11). The assignments proposed in table (4.11) agree quite well with those for the other benzonitriles. The 0.0 transition band has shifted to higher energy by 40 cm<sup>-1</sup>. As in the phosphorescence, the sum of the 0,0 shifts in the monosubstituted species ( counting meta and ortho twice ) adds up to the total shift in benzonitrile-D<sub>5</sub>, within experimental error. It is to be noted that the separation between 0,  $\mathcal{V}_9$  and 0,  $\mathcal{V}_{10}$ is now greater and the two bands are now resolved at 990 cm<sup>-1</sup> and 1040 cm<sup>-1</sup>. The shift in  $\mathcal{V}_{10}$  from 1000 cm<sup>-1</sup> to 990 cm<sup>-1</sup> has the effect of changing slightly the position of the bands in the 3000 cm<sup>-1</sup> region. The two series of peaks at 2920, 2965 cm<sup>-1</sup> and 3005, 3040 cm<sup>-1</sup> in benzonitrile-H<sub>5</sub> have now combined to form a triplet of which 3 x  $\mathcal{V}_{10}$  pays the major contribution at 2960 cm<sup>-1</sup>.

#### 4.3 Phosphorescence Polarization Measurements

The lowest triplet state is assigned by using polarization results of the pure electronic transition between the triplet state and the ground state. The intensities of the vertically and horizontally polarized emission of the 0,0 band of phosphorescence of a  $10^{-3}$  molar solution of benzonitrile-H<sub>5</sub> in 3-methylpentane glass at 77°K were measured following excitation with vertically and horizontally polarized light. The degree of polarization P was determined from P = N - 1 / N + 1 where N = I<sub>VV</sub> · I<sub>HH</sub> / I<sub>VH</sub> · I<sub>HV</sub>; this result contains correction factors due to instrument favoring, glass strains, etc. The subscripts in the intensities I refer to the orientation of the exciting and analysing polarizers in that order respectively. The wavelengths of excitation were 277 nm. and 230 nm., corresponding to the 0,0 region of the  ${}^{1}A_{1} \rightarrow {}^{1}B_{2}$  ( $S_{0} \rightarrow S_{1}$ ,  ${}^{1}L_{b}$  band in Platt's notation ) and  ${}^{1}A_{1} \rightarrow {}^{1}A_{1}$  ( $S_{0} \rightarrow S_{2}$ ,  ${}^{1}L_{a}$  band ) transitions respectively.

When exciting in the  ${}^{1}L_{b}$  band, the degree of polarization was found in the range of -5% to -12%, whereas excitation in the  ${}^{1}L_{a}$  band produced a degree of polarization in the range of -15% to -27%. For a given experiment, the degree of polarization was always more negative when exciting in the  ${}^{1}L_{a}$  band than when exciting in the  ${}^{1}L_{b}$  band; but the results from day to day varied somewhat probably due to the method of glass preparation, freshness of sample, etc. The above results, that the degree of polarization was less negative for the  ${}^{1}A_{1} \rightarrow {}^{1}B_{2}$  than for  ${}^{1}A_{1} \rightarrow {}^{1}A_{1}$  transition, allows one to assign the orbital symmetry of the phosphorescent  $\pi - \pi^{*}$  state as  ${}^{3}A_{1}$  for benzonitrile having a  $C_{2v}$  symmetry. A similar assignment was proposed earlier (<u>16</u>) although its justification is not obvious.

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Fluorescence of  $10^{-4}$  M benzonitrile in polycrystalline cyclohexane at  $77^{\circ}$ K.



### TABLE 4.7

# Vibrational Analysis of Fluorescence of C<sub>6</sub>H<sub>5</sub>CN in Polycrystalline Cyclohexane at 77°K

Ia	Position		AV(cm <sup>-1</sup> )	Assignment
000000000000000000000000000000000000000	$\lambda$ (nm x 10	) v(cm <sup>-1</sup> )		
W	2772	36 075	0	0,0
W	2807	35 625	450	0,12
WW	2814	35 535	540	0,32
WV	2821	35 450	625	0,31
WW	2823	35 300	775	0,11
W	2845	35 150	925	0,2 x 12
S	2851	35 075	1000	0,10
W	$2853 \text{ sh}^{b}$	35 050	1025	0,9
WV	2857 sh	35 000	1075	0,12 + 31
S	2867	34 880	1195	0,7
W	2870 sh	34 845	1230	0,11 + 12
WV	2875 sh	34 785	1290	0,11 + 32
WV	2883	34 685	1390	0,3 x 12 ;0,11 + 31
m	2890	34 600	1475	0,10 + 12
W	2892 sh	34 580	1495	0,6 ;0,9 + 12
W	2897	34 525	1550	0,10 + 32
W	2903 sh	34 445	1630	0,10 + 31
m	2905	34 425	1650	0.7 + 12

TABLE 4.7(Continued)

I	Position		$\Delta V (cm^{-1})$	Assignment
decomparizioni de la comparizione d	$\lambda$ (nm x 10	)) $V(cm^{-1})$	and a state of the	
W	2908 sh	34 390	1685	0,11 + 2 x 12
W	2913	34 330	1745	0,7 + 32
W	2921	34 235	1840	0,7 + 31
W	2929	34 140	1935	0,10 + 2 x 12
m	2936	34 060	2015	0,2 x 10
W	2943	33 980	2095	0,10 + 12 + 31
S	2952	33 875	2200	0.7 + 10
m	2955	33 840	2235	0,10 + 11 + 12 ;0,
m	2959	33 795	2280	0,7 + 12 + 31
m	2970	33 670	2405	0,2 x 7
m	2976	33 600	2475	0,2 x 10 + 12
W	2983 sh	33 525	2550	0,2 x 10 + 32
W	2986 sh	33 490	2585	0,2 x 10 + 31
m	2993	33 410	2665	0,7 + 10 + 12
W	2996	33 380	2695	0,10 + 11 + 2 x 12
W	3001	33 320	2755	0,7 + 10 + 32
W	3009	33 235	2840	0,7 + 10 + 31
				0,2 x 7 + 12
VW	3016 sh	33 155	2920	0,2 x 10 + 2 x 12
A.M.	3021	33 110	2965	0,2 x 7 + 32
W	3024	33 070	3005	0,3 x 10
vw	3027 sh	33 035	3040	0,2 x 7 + 31
7W	3030 sh	33 005	3070	0,2 x 10 + 12 + 31

TABLE4.7(Continued)

I	Position		$\Delta V(cm^{-1})$	Assignment
(das a Grand Ange Marco and	$\lambda$ (nm x 1	$(cm^{-1})$	under State of the	
W	3043	32 860	3215	0,7 + 2 x 10
W	3047	32 820	3255	0,2 x 10 + 11 + 12
				0,4+10
VW	3050 sh	32 785	3290	0,7 + 10 + 12 + 31
W	3060	32 680	3395	0,2 x 7 + 10
W	3065	32 625	3450	0,3 x 10 + 12
W	3080	32 470	3605	0,3 x 7
W	3086	32 405	3670	0,7 + 2 x 10 + 12
W	3090 sh	32 365	3710	0,7 + 2 x 10 + 32
W	3102	32 235	3840	0,2 x 7 + 10 + 12
WW	3107	32 185	3890	0,3 x 10 + 2 x 12
VW	3118	32 070	4005	0,4 x 10
VW	3125	32 000	4075	0,3 x 10 + 12 + 31
W	3138	31 865	4210	0,7 + 3 x 10
W	3142	31 825	4250	0,3 x 10 + 11 + 12
				0,4 + 2 x 10
7W	3156	31 685	4390	0,2 x 7 + 2 x 10
7W	3161	31 635	4440	0,4 x 10 + 12
TW	3176	31 485	4590	0,3 x 7 + 10
WW	3183	31 415	4660	0,7 + 3 x 10 + 12
VW	3206	31 190	4885	0,4 x 10 + 2 x 12
WW	3217	31 085	4990	0,5 x 10
VW	3224	31 015	5060	0,4 x 10 + 12 + 31

TABLE 4.7(Continued)

I	Position		av(cm <sup>-1</sup> )	Assignment
State Collection with the	$\lambda$ (nm x 10)	V(cm <sup>-1</sup> )		a san dan daga dan dan dan dan dan dan dan dan dan da
WW	3239	30 880	5195	0,7 + 4 x 10
W	3244	30825	5250	0,4 x 10 + 11 + 12

<sup>a</sup>Intensities uncorrected for instrumental response; s= strong; m= moderate; w= weak; v= very.

<sup>b</sup>sh= shoulder

Fluorescence of  $10^{-4}$  M perdeuterated benzonitrile in polycrystalline cyclohexane at  $77^{\circ}$ K.


# Vibrational Analysis of Fluorescence of $C_6D_5CN$ in Polycrystalline Cyclohexane at $77^{\circ}K$

Ia	Positio	<u>n</u>	av(cm <sup>-1</sup> )	Assignment
10.20.20.00 Tool Found School School	$\lambda$ (nm x 10)	$\nu(cm^{-1})$		
W	2760	36 230	0	0,0
W	2795	35 775	455	0,12
W	2801	35 700	530	0,32
W	2806	35 625	605	0,31
W	2816	35 510	720	0,11
W	2827	35 375	855	0,9
WW	2832	35 310	920	0,2 x 12
S	2836	35 260	970	0,10
W	2840 sh <sup>b</sup>	35 210	1020	0,12 + 32
W	2844	35 160	1070	0,12 + 31
S	2851	35 075	1155	0,7
W	2854 sh	35 040	1190	0,11 + 12
m	2861	34 950	1280	0,9 + 12
S	2870	34 845	1385	0,6 ;0,3 x 12
S	2873	34 805	1425	0,10 + 12
W	2880	34 720	1510	0,10 + 32
M	2886 sh	34 650	1580	0,10 + 31
m	2888	34 625	1605	0,7 + 12

TABLE 4.8(Continued)

I	Positic	Position		Assignment
and an and a second	$\lambda(nm \times 10)$	$\nu(cm^{-1})$		an fan de service de s
W	2892 sh	34 580	1650	0,11 + 2 x 12
W	2895 sh	34 540	1690	0,7 + 32
m	2900	34 480	1750	0,7 + 31
W	2907	34 400	1830	0,6 + 12 ;0,9 + 10
W	2910	34 365	1865	0,10 + 2 x 12
m	2915	34 315	1915	0,2 x 10
W	2920 sh	34 245	1985	0,10 + 12 +32
W	2924	34 200	2030	0,7 + 9 :0,10 + 12 +3
W	2929 sh	34 140	2090	0,7 + 2 x 12
S	2932	34 105	2125	0,7 + 10
W	2934 sh	34 085	2145	0,10 + 11 + 12
W	2942 sh	33 990	2240	0,4 ;0,7 + 12 + 31
W	2944 sh	33 965	2265	0,9 + 10 + 12
S	2947	33 935	2295	0,2 x 7
S	2951	33 885	2345	0,2 x 10 + 12
W	2953 sh	33 865	2365	0,6 + 10
N	2959	33 795	2435	0,2 x 10 + 32
n	2967	33 705	2525	0,2 x 10 + 31 :0,6 +
n	2970 sh	33 670	2560	0,7 + 10 + 12
N	2980	33 555	2675	0,7 + 10 + 32
n	2986	33 490	2740	0,2 x 7 + 12
v	2991 sh	33 430	2800	0,2 x 10 + 2 x 12
v	2999	33 345	2885	0,3 x 10

TABLE 4.8(Continued)

I	Posit	lon	$\Delta v(cm^{-1})$	Assignment
diss.clovefibilition	$\lambda$ (nm x 10)	√(cm <sup>-1</sup> )		
VW	3006	33 265	2965	0,7 + 9 + 10
W	3015	33 170	3060	0,7 + 2 x 10
W	3019 sh	33 125	3105	0,2 x 10 + 11 + 12
VW	3029 sh	33 015	3215	0,9 + 2 x 10 + 12 ;
				0,4 + 10
m	3032	32 985	3245	0,2 x 7 + 10
W	3037	32 925	3305	0,3 x 10 + 12
VW	3043	32 860	3370	0,2 x 7 + 12 + 31
W	3047	32 820	3410	0,3 x 10 + 32
W	3053	32 755	3475	0,3 x 7
W	3056 sh	32 720	3510	0,7 + 2 x 10 + 12
W	3063 sh	32 650	3580	0,7 + 2 x 10 + 32
N	3072	32 550	3680	0,7 + 2 x 10 + 31 ;
				0,6 + 2 x 7
VW	3077	32 500	3730	0,2 x 7 + 10 + 12
W	3080	32 465	3765	0,3 x 10 + 2 x 12
W	3091	32 350	3880	0,4 x 10
VW	3106	32 195	4035	0,7 + 3 x 10
vw	3119	32 060	4170	0,7 + 2 x 10 + 11 + 12
				0,4 + 2 x 10
JW	3123	32 020	4210	0,2 x 7 + 2 x 10
TW	3128	31 970	4260	0,4 x 10 + 12
JW	3140	31 845	4385	0,4 x 10 + 32

TABLE 4.8 (Continued)

I	Position		$\Delta V(cm^{-1})$	Assignment
talan 10 metatak kerjad	$\lambda$ (nm x 10)	$\nu(cm^{-1})$	Nang Sawa Million (January Construction)	
W	3144	31 805	4425	0,3 x 7 + 10
VW	3162	31 625	4605	0,7 + 3 x 10 + 12
W	3183	31 415	4815	0, 5 x 10
WW	3225	31 005	5225	0, 2 x 7 + 3 x 10

<sup>a</sup>Intensities uncorrected for instrumental response; s= strong; m= moderate; w= weak; v= very.

<sup>b</sup>sh= shoulder.

Figure 4.9

Fluorescence of  $10^{-4}$  M para-monodeuterated benzonitrile in polycrystalline cyclohexane at 77°K.



Vibrational Analysis of Fluorescence of  $p-D-C_6H_4CN$  in

Ia	Positio	on	$\Delta V(cm^{-1})$	Assignment
incriting differ the station days	$\lambda$ (nm x 1)	)) $V(cm^{-1})$	manadynes klann-da fillefalas - figan manadhas dana agun ata y dan	
VW	2769	36 115	0	0,0
W	2805	35 655	460	0,12
VW	2811	35 575	540	0,32
WV	2817	35 500	615	0,31
VW	2827	35 370	745	0,11
WW	$2842 \text{ sh}^{b}$	35 185	930	0,2 x 12
S	2847	35 125	990	0,10
W	2850 sh	35 090	1025	0,9
W	2854 sh	35 040	1075	0,12 + 31
S	2864	34 915	1200	0,7
W	2866 sh	34 890	1225	0,11 + 12
W	2871 sh	34 830	1285	0,11 + 32
WV	2880 sh	34 720	1395	0,11 + 31;3 x 12
m	2885	34 660	1455	0,10 + 12
W	2889 sh	34 615	1500	0,6 ; 0,9 + 12
W	2892	34 580	1535	0,10 + 32
W	2898	34 505	1610	0,10 + 31
m	2902	34 460	1655	0,7 + 12
W	2904	34 435	1680	0.11 + 2 X 12

Polycrystalline Cyclohexane at 77°K

TABLE 4.9(Continued)

I	Positi	Position		Assignment
	$\lambda$ (nm x 10)	$\nu(cm^{-1})$		an a gan a gan a gan a gan a gan gan gan
W	2909 sh	34 375	1740	0,7 + 32
W	2917	34 280	1835	0,7 + 31
W	2925	34 190	1925	0,10 + 2 x 12
m	2930	34 130	1985	0,2 x 10
W	2934 sh	34 085	2030	0,9 + 10
W	2938	34 035	2080	0,10 + 12 + 31
W	2948	33 920	2195	0,7 + 10
W	2953 sh	33 865	2250	0,7 + 9 ; 0,4
W	2957 sh	33 820	2295	0,7 + 12 + 31
S	2969	33 680	2435	0,2 x 7 ;0,2 x 10 + 12
m	2972 sh	33 645	2470	0,9 + 10 + 12
W	2977 sh	33 590	2525	0,2 x 10 + 32
WV	2984	33 510	2605	0,2 x 10 + 31
S	2989	33 455	2660	0,7 + 10 + 12
m	2991	33 435	2680	0,10 + 11 + 2 x 12
W	2994 sh	33 400	2715	0,7 + 10 + 32
W	3004	33 290	2825	0, 7 + 10 + 31
W	3010	33 225	2890	0,2 x 7 + 12 ; 0,2 x 10
				+ 2 x 12
W	3015	33 170	2945	0,3 x 10
W	3018 sh	33 130	2985	0,9 + 2 x 10
WW	3025	33 055	3060	0,2 x 10 + 12 + 31
W	3037	32 925	3190	$0.7 + 2 \times 10$

TABLE 4.9(Continued)

I	Positi	on	$\Delta V(cm^{-1})$	Assignment
No. of Street	$\lambda(nm \ge 10)$	$\nu(cm^{-1})$	na tin bayan kina da dina madakina na dina m	
W	3043	32 860	3255	0,7 + 9 + 10 ;0,4 + 10
VW	3047 sh	32 820	3295	0,7 + 10 + 12 + 31
W	3056	32 720	3395	0,2 x 7 + 10
W	3061 sh	32 670	3445	0,3 x 10 + 12
W	3073	32 540	3575	0,3 x 10 + 31
W	3080	32 470	3645	0,3 x 7 ;0,7 + 2 x 10
				+ 12
WW	3086 sh	32 405	3710	0,7 + 2 x 10 + 32
W	3103	32 225	3890	0,3 x 10 + 2 x 12 ;
				0,2 x 7 + 10 + 12
W	3107	32 180	3935	0,4 x 10
W	3130	31 950	4165	0,7 + 2 x 10
W	3137	31 880	4235	$0,7 + 9 + 2 \times 10$ ;
				0,4 + 2 x 10
WV	3150	31 745	4370	0,2 x 7 + 2 x 10
W	3156	31 685	4430	0,4 x 10 + 12
W	3164	31 565	4550	0,3 x 7 + 10
WV	3175	31 495	4620	0,7 + 3 x 10 + 12
WV	3199	31 260	4855	0,4 x 10 + 2 x 12
WV	3211	31 145	4970	0,5 x 10
W	3224	31 015	5100	0.7 + 4 x 10

<sup>a</sup>Intensities uncorrected for instrumental response; s= strong; m= moderate; w= weak; v= very

<sup>b</sup>sh= shoulder

## Figure 4.10

Fluorescence of  $10^{-4}$  M meta-monodeuterated benzonitrile in polycrystalline cyclohexane at  $77^{\circ}$ K.



Vibrational Analysis of Fluorescence of  $m-D-C_6H_4CN$  in

Ia	Positio	n	$\Delta V(cm^{-1})$	Assignment
	$\lambda$ (nm x 10)	$V(cm^{-1})$		
W	2770	36 100	0	0,0
W	2805	35 650	450	0,12
vw	2811	35 575	525	0,32
<b>W</b>	2818	35 485	615	0,31
W	2830	35 335	765	0,11
W	2843 sh <sup>b</sup>	35 175	925	0,2 x 12
S	2849	35 100	1000	0,10
m	2851 sh	35 075	1025	0,9
W	2855 sh	35 025	1075	0,12 + 31
S	2865	34 905	1195	0.7
W	2871 sh	34 830	1270	0,11 + 32
W	2876 sh	34 770	1330	0,3 x 12
W	2881	34 710	1390	0,11 + 31
m	2887	34 640	1460	0,10 + 12 ;0,9 + :
W	2890 sh	34 600	1500	0,6
W	2894	34 555	1545	0,10 + 32
W	2900 sh	34 485	1615	0,10 + 31
m	2903	34 445	1655	0,7 + 12
W	2910	34 365	1735	0.7 + 32

Polycrystalline Cyclohexane at  $77^{\circ}$ K

I	Position	$\Delta V (cm^{-1})$	Assignment
And and the second s	$\lambda (nm \times 10) \vee (cm^{-1})$	and a state of the	
W	2919 34 260	1840	0,7 + 31
W	2927 34 165	1935	0,10 + 2 x 12
m	2934 34 085	2015	0,2 x 10
m	2937 34 050	2050	0,9 + 10
W	2940 sh 34 015	2085	0,10 + 12 + 31
S	2950 33 900	2200	0,7 + 10
S	2953 33 865	2235	0,7 + 9 ;0,4
m	2957 sh 33 820	2280	0,7 + 12 + 31
S	2966 33 715	2385	0,2 x 7
m	2973 33 635	2465	0,2 x 10 + 12
W	2977 sh 33 590	2510	0,6 + 10
W	2981 33 545	2555	0,2 x 10 + 32
W	2987 sh 33 480	2620	0,2 x 10 + 31
m	2991 33 435	2665	0,7 + 10 + 12
W	2998 sh 33 355	2745	0,7 + 10 + 32
m	3006 33 265	2835	0,7 + 10 + 31 ;
			0,2 x 7 + 12
W	3014 33 180	2920	0,2 x 10 + 2 x 12
W	3022 33 090	3010	0,3 x 10
W	3026 33 045	3055	0,9 + 2 x 10
W	3030 sh 33 005	3095	0,2 x 10 + 12 + 31
m	3040 32 895	3205	0,7 + 2 x 10
m	3045 32 840	3260	0,7 + 9 + 10 ;0,4 +

TABLE 4.10(Continued)

TABLE 4.10 (Continued)

I	Position	n	۵۷(cm <sup>-1</sup> )	Assignment
	$\lambda$ (nm x 10)	$\nu(cm^{-1})$		
W	3048 sh	32 810	3290	0,7 + 10 + 12 + 31
m	3057	32 710	3390	0,2 x 7 + 10
m	3062	32 660	3440	0,3 x 10 + 12
W	3075	32 520	3580	0,3 x 7
W	3083	32 435	3665	0,7 + 2 x 10 + 12
W	3088	32 385	3715	0,7 + 2 x 10 + 32
W	3099	32 270	3830	0,7 + 2 x 10 + 31
W	3105	32 205	3895	0.3 x 10 + 2 x 12
W	3114	32 115	3985	0,4 x 10
W	3121	32 040	4060	0,3 x 10 + 12 + 31
W	3134	31 910	4190	0,7 + 3 x 10
W	3140	31 845	4255	$0.7 + 9 + 2 \times 10$ ;
				$0,4 + 2 \times 10$
VW	3152	31 725	4375	0,2 x 7 + 2 x 10
VW	3159	31 655	4445	0,4 x 10 + 12
W	3171	31 535	4565	0,3 x 7 + 12
VW	3179	31 455	4645	0,7 + 3 x 10 + 12
WW	3199	31 260	4840	0,4 x 10 + 2 x 12
WW	3213	31 125	4975	0,5 x 10
W	3222	31 035	5065	0,4 x 10 + 12 + 31
WW	3229	30 970	5130	0,7 + 4 x 10
WW	3241	30 855	5245	0,7 + 9 + 3 x 10 ;
				0,4 + 3 x 10

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Figure 4.11

Fluorescence of 10<sup>-4</sup> M ortho-monodeuterated benzonitrile in polycrystalline cyclohexane at 77°K.



# Vibrational Analysis of Fluorescence of $o-D-C_6H_4CN$ in Polycrystalline Cyclohexane at $77^{\circ}K$

Ia	Positio	n	$\Delta V(cm^{-1})$	Assignment
Strain Statistics	$\lambda$ (nm x 10)	V(cm <sup>-1</sup> )	an standar of the standard of t	10-20-01-10-01-01-01-01-01-01-01-01-01-01-01
W	2769	36 115	0	0,0
W	2804	35 660	455	0,12
W	2810	35 585	530	0,32
W	2817	35 500	615	0,31
W	2829	35 350	765	0,11
WV	2842 sh <sup>b</sup>	35 185	930	0,2 x 12
S	2847	35 125	990	0,10
m	2851	35 075	1040	0,9
W	2853 sh	35 050	1065	0,12 + 31
W	2856 sh	35 015	1100	0,8
S	2864	34 915	1200	0,7
W	2867 sh	34 880	1235	0,11 + 12
W	2872 sh	34 820	1295	0,11 + 32
VW	2879 sh	34 735	1380	0,11 + 31 ;0,3 x 12
m	2885	34 660	1455	0.10 + 12
m	2890	34 600	1515	0.6 :0.9 + 12
m	2892 sh	34 580	1535	0,10 + 32
W	2896 sh	34 530	1585	0.9 + 32

TABLE 4.11(Continued)

I	Position		ΔV (cm-1)	Assignment
Borne grad and grad	$\lambda(nm \times 10) \nu($	(cm <sup>-1</sup> )		n <mark>den skille gan gen den skille skil</mark>
W	2899 34	+ 495	1620	0,10 + 31
m	2902 34	+ 460	1655	0,7 + 12
W	2906 sh 34	+ 410	1705	0,11 + 2 x 12
W	2909 34	+ 375	1740	0,7 + 32
VW	2917 34	280	1835	0,7 + 31
W	2924 34	1 200	1915	0,10 + 2 x 12
m	2930 34	+ 130	1985	0,2 x 10
m	2935 34	070	2045	0,9 + 10
W	2939 sh 34	025	2090	0,10 + 12 + 31
W	2942 33	990	2125	0, 9 + 12 + 31
S	2948 33	920	2195	0,7 + 10
m	2952 33	875	2240	0,7 + 9 ;0,4
m	2956 sh 33	830	2285	0.7 + 12 + 31
W	2962 sh 33	760	2355	0,9 + 11 + 32
W	2966 sh 33	715	2400	0,9 + 11 + 31
m	2968 33	695	2420	0,2 x 7
m	2971 sh 33	660	2455	0,2 x 10 + 12
W	2974 sh 33	625	2490	0,9 + 10 + 12 ;0,6 + 10
W	2981 sh 33	545	2570	0,2 x 10 + 32
W	2985 sh 33	500	2615	0,2 x 10 + 31
m	2989 33	455	2660	0,7 + 10 + 12
W	2994 33	400	2915	0,7 + 9 + 12
W	2998 sh 33	355	2760	0,7 + 10 + 32

TABLE 4.11 (Continued)

I	Position		$\Delta V(cm^{-1})$	Assignment
	$\lambda$ (nm x 10) $\nu$	(cm-1)	an daga attir diga sagan yaka sa ayan daga daga daga daga saga	
W	3003 sh 3	33 300	2815	0,7 + 10 + 31
W	3009 3	33 235	2880	0,2 x 10 + 2 x 12
W	3016 3	33 155	2960	0,3 x 10
A	3022 3	33 090	3025	0,9 + 2 x 10
Ā	3037 3	32 925	3190	0,7 + 2 x 10
W	3042 3	32 875	3240	0,7 + 9 + 10 ;0,4 +
W	3048 sh 3	32 810	3305	0,7 + 10 + 11 + 12
W	3057 3	32 710	3405	0,2 x 7 + 10
M	3062 3	32 660	3455	0,3 x 10 + 12
W	3080 3	32 470	3645	0,7 + 2 x 10 + 12 ;
				0,3 x 7
Ň	3084 3	12 425	3690	0,7 + 9 + 10 + 12
N	3100 3	2 260	3855	0,2 x 7 + 10 + 12
N	3106 3	12 195	3920	0,3 x 10 + 2 x 12
Ň	3112 3	12 135	3980	0,4 x 10
7W	3120 3	2 0 50	4065	0,2 x 9 + 2 x 10
w.	3131 3	1 940	4175	0,7 + 3 x 10
W	3137 3	1 880	4235	0,7 + 9 + 2 x 10 ;
				0,4 + 2 x 10
y W	3144 3	1 805	4310	0,7 + 2 x 10 + 11 +
7W	3151 3	1 735	4380	0,2 x 7 + 2 x 10
7W	3157 3	1 675	4440	0,4 x 10 + 12
TW	3174 3	1 465	4650	$0,7 + 3 \times 10 + 12$

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TABLE 4.11 (Continued)

Position		$\Delta V(cm^{-1})$	Assignment
$\lambda$ (nm x	10) $V(cm^{-1})$		ng an an air an
3181	31 440	4675	0,7 + 9 + 2 x 10 + 12
3201	31 240	4875	0,4 x 10 + 2 x 12
3208	31 170	4945	0,5 x 10
3230	30 960	5155	0,7 + 4 x 10
	<u>Posi</u> λ(nm x 3181 3201 3208 3230	Position $\lambda$ (nm x 10) $\nu$ (cm <sup>-1</sup> )318131 440320131 240320831 170323030 960	Position $\Delta V(cm^{-1})$ $\lambda (nm \times 10) V(cm^{-1})$ 318131 440320131 2404875320831 1704945323030 9605155

<sup>a</sup>Intensities uncorrected for instrumental response; s= strong; m= moderate; w= weak; v= very.

<sup>b</sup>sh= shoulder

#### CHAPTER V

### DISCUSSION

The luminescence spectra obtained in this investigation were very dependent on the method of sample cooling. The doublet nature of the phosphorescence and fluorescence in cyclohexane has also been observed for benzene (36), and attributed to emission of the solute in two different crystalline environments of cyclohexane, the high temperature cubic form and the low temperature monoclinic form. Evidently, with rapid immersion of the benzonitriles in cyclohexane into the liquid nitrogen, some of the high temperature modification is present. By cooling more slowly, more of the monoclinic phase is formed; after thawing and 'slow-cooling' again, only the red partner of the doublet bands is observed. This is the behavior found by Spangler and Kilmer ( 37 ) for benzene. Hence the spectra shown in figures (4.7) - (4.11) are considered to be fluorescences of the benzonitriles in the monoclinic form of cyclohexane. The broad background still present under all the main bands may be unresolved multiplet structure due to various orientations of the solute, or to lattice vibrations of the solvent.

Heat capacity measurements (<u>38</u>) indicate the presence of only one crystalline phase for methylcyclo-

hexane in the region 12°K - 298°K ; therefore, other factors need be considered as candidates responsible for the doublet splittings in methylcyclohexane. Martin and Kalantar ( 39 ) have noted that cooling methylcyclohexane produces a glass plus a crystalline mass. The phosphorescence 0,0 electronic band for benzonitrile-H5 in methylcyclohexane glass was found in the present study to be at 26 910 cm<sup>-1</sup> which is quite distinct from the doublet bands at 27 010  $cm^{-1}$  and 27 070  $cm^{-1}$ . The concentrations used here are so dilute that microcrystal benzonitrile emission is ruled out; for benzene in cyclohexane, this becomes important only at 0.1 M ( 37 ). It seems likely that the phosphorescences shown in figures (4.2) - (4.6)result from benzonitriles in two different orientations in a single crystalline modification of the solvent. Differing solute-solvent interactions would explain the observed splittings. The ratio of molecules in the two orientations would be expected to vary with cooling. Fast cooled method spectra mirror the populations at a higher temperature, frozen in to some extent by immersion in the liquid nitrogen. Slow cooling allows the more favorable orientation at 77°K to predominate. Ethynylbenzene, which is slightly larger than benzonitrile, shows no splittings in the luminescence spectra in methylcyclohexane ( 40 ). Presumably in this case there is only one preferred or

possible solute orientation. The phosphorescence lifetimes of the doublet 0,0 band of phosphorescence in methylcyclohexane were measured; both are about three seconds and exponential. In cyclohexane, both are about ten percent longer and exponential. This is to be contrasted with benzene in cyclohexane in which Martin and Kalantar ( $\frac{41}{1}$ ) have found that the phosphorescence lifetime in the monoclinic form of cyclohexane ( slow-cooling ) was longer than that in the cubic form ( fast cooling ) by a ratio of about 4 : 1.

The shapes and the vibrational analyses for the phosphorescences of all the benzonitriles are very similar but distinct from the fluorescences, which are also very nearly identical. The agreement of the data for the deuterated benzonitriles with those for ordinary benzonitrile lends considerable support to the proposed assignments.

In the phosphorescence, the main progressions are in  $\mathcal{V}_5$  and  $\mathcal{V}_8$ .  $\mathcal{V}_5$  involves C - C stretching and  $\mathcal{V}_8$  is concerned with in-plane C - H bending. An approximate pictorial representation of these mode of vibration can be found in figure (4.1). From these pictures, it is seen that these two modes are somewhat complementary. Their prominence in long progressions is consistent with a planar, non-regular hexagon ring triplet state geometry. The absence of long progressions of out-of-plane vibrations lends support to the proposed planar geometry. Intensity measurements on the 1600 cm<sup>-1</sup> progression in the phosphorescence of toluene ( $\underline{6}$ ) indicate that the ring has four short bonds and two long ones (antiquinoid). The resolution at which the spectra of this study were taken is not sufficient to warrant such calculations; contribution of underlying bands would give a relatively large error to such measurements.

The same progressions are also evident in the rigid glass matrices, i.e., isopentane, methylcyclohexane, 3-methylpentane, ethanol and methanol. Of course, the spectra in such glasses look much simplified due to the low resolution obtained but the  $v_5$  progression is still observed.

The orbital symmetry of the lowest triplet state was assigned as  ${}^{3}A_{1}$  ( ${}^{3}A^{*}$  for meta and ortho) on the basis of the polarization of the 0.0 transition band of phosphorescence. With such an assignment, two triplet sublevels,  $T_{x}$  and  $T_{y}$ , (of symmetry  $b_{1}$  and  $b_{2}$ ) are dipole emissive. The appearance of strong  $a_{1}$  fundamentals in progressions and combinations does not permit a partitioning to be made of the relative contributions of the sublevels to the observed bands. Accurate polarization measurements throughout the phosphorescence region would be of help in that respect. The weak presence of nontotally symmetric vibrations in the phosphorescence indicates that vibrational perturbations are very small. To account for their presence, several routes can be considered for combining spin-orbit and vibrational effects, such as spin-vibronic coupling ( 1<sup>st</sup> order perturbation ), vibronic coupling among triplets with spin-orbit coupling, and vibronic coupling among singlets with spin-orbit coupling ( 2<sup>nd</sup> order perturbation ). All of these pathways predict that b1 vibrations can be evident in the spectra due to  ${}^{1}A_{1}$  (z) and  ${}^{1}B_{2}$  (y) singlet admixture, and  $b_{2}$ vibrations due to  ${}^{1}A_{1}$  and  ${}^{1}B_{1}$  (x) mixing. Polarization measurements throughout the entire phosphorescence spectrum could help settle the question of the nature of the perturbing singlets, but could not distinguish between the three aforementioned mechanisms.

The fluorescence analyses show that the main progression is in  $\mathcal{V}_{10}$ , the ring breathing mode. Two other prominent fundamentals appearing in the spectra are  $\mathcal{V}_7$ and  $\mathcal{V}_{12}$ , from which the progressions and combinations with  $\mathcal{V}_{10}$  comprise almost the entire spectra. A glance at figure (4.1) shows that  $\mathcal{V}_7$  and  $\mathcal{V}_{12}$  are quite related to the breathing mode. Therefore, their appearance is interpreted to signify that the excited singlet state is nearly hexagonal but slightly expanded. In contrast to the phosphorescence, no progressions in  $v_5$  and  $v_8$  are observed. In benzene and methylbenzene (<u>6</u>), the main progression in absorption and fluorescence is also the ring breathing mode. In benzene, there is an increased C - C bond distance of 0.037 A<sup>o</sup>.

The predominance of the a1 modes in progressions and combinations, built on the 0,0 band of fluorescence suggests that the mixing of  $S_1$  with  $S_2$  (  ${}^1B_2$  with  ${}^1A_1$  ), giving rise to the b2 forbidden components, is small ( refer to section 2.5 ). The intensity of the forbidden transition will depend on the proximity of a third electronic state, in this case  ${}^{1}A_{1}$  (  $S_{2}$  ). In fact, the intensities of the b2 forbidden transitions (  ${m v}_{31}$  and  ${m v}_{32}$  ) are very weak compared to the same modes (  ${m v}_{34}$  and  ${m v}_{35}$  ) for ethynylbenzene ( 40 ), where the mixing of S<sub>1</sub> with S<sub>2</sub> is strong ( 42 ) and where the main features of the fluorescence are a1 progressions built on one quantum of nontotally symmetric b2 vibrations. The weak mixing for benzonitrile as compared to ethynylbenzene is explained by the fact that the energy gap between  $S_1$  and  $S_2$  is much larger for benzonitrile ( $\sim 7400 \text{ cm}^{-1}$ ) than for ethynylbenzene  $(\sim 5200 \text{ cm}^{-1})$ .

### CHAPTER VI

### SUMMARY

The vibrational analyses and spectra for the phosphorescences of all the benzonitriles in methylcyclohexane are quite similar but very different from the vibrational analyses and spectra for the fluorescences of the benzonitriles in cyclohexane.

The nature of the splittings in methylcyclohexane is attributed to two different orientations of the solute molecules in a single crystalline form whereas, in cyclohexane, it is attributed to solute in two different ( cubic and monoclinic ) crystalline forms.

The vibrational analyses of the phosphorescences are consistent with a planar, non-hexagonal ring triplet state geometry and that of the fluorescences consistent with a planar, slightly expanded ring excited singlet state geometry.

The lowest triplet state orbital symmetry is assigned as  ${}^{3}A_{1}$  on the basis of polarization of the phosphorescence 0.0 band.

#### REFERENCES

- 1. H.Suzuki, <u>Electronic Absorption Spectra and Geometry of</u> <u>Organic Molecules</u>, Academic Press, New York, 1967.
- 2. G.Herzberg, <u>Electronic Spectra of Polyatomic Molecules</u>, Van Nostrand, Princeton, New Jersey, 1966.
- 3. J.B.Birks, <u>Photophysics of Aromatic Molecules</u>, Wiley-Interscience, New York, 1970.
- 4. D.P.Craig, J. Chem. Soc. 1950, 2146.
- 5. J.B.Coon, R.E.DeWames, and C.M.Loyd, J. Mol. Spectrosc. <u>8</u>, 285 (1962).
- 6. G.C.Neiman, J. Chem. Phys. <u>50</u>, 1674 (1969).
- S.Leach and R.Lopez-Delgado, J. Chim. Phys. <u>61</u>, 1636 (1964).
- 8. M.S. de Groot and J.H. van der Waals, Mol. Phys. <u>6</u>, 545 (1963).
- 9. G.C.Neiman and D.S.Tinti, J. Mol. Spectrosc. <u>46</u>, 1432 (1967).
- J.March, <u>Advanced Organic Chemistry</u>; <u>Reactions</u>, <u>Mecha-</u> nisms and <u>Structure</u>, p.232, McGraw-Hill, New York, 1968.
- 11. B.Bak, D.Cristensen, W.B.Dixon, L.Hansen-Nygaard, and J.Rastrup-Andersen, J. Chem. Phys. <u>37</u>, 2027 (1962).
- 12. J.C.D.Brand and D.P.Knight, J. Mol. Spectrosc. <u>36</u>, 328 (1970).
- 13. A.M.Bass, J. Chem. Phys. <u>18</u>, 1403 (1950).
- 14. J. von Kowalski, Physik Z. 12, 956 (1912).
- 15. G.N.Lewis and M.Kasha, J. Am. Chem. Soc. <u>66</u>, 2100 (1943).
- 16. K.Takei and Y.Kanda, Spectrochim. Acta, 18, 1201 (1962).
- 17. E.Faure, F.Valadier, and J.Janin, Compt. Rend. <u>269</u>, Series B, 431 (1969).
- 18. G.W.King, <u>Spectroscopy and Molecular Structure</u>, Holt, Rinehart and Wilson, New York, 1964.

- 19. E.B.Wilson, J.C.Decius and P.C.Cross, <u>Molecular Vibra-</u> <u>tions</u>, McGraw-Hill, New York, 1955.
- 20. G.Herzberg, <u>Electronic Spectra of Diatomic Molecules</u>, Table 39, Van Nostrand, Princeton, New Jersey, 1950.
- 21. See reference 2, p. 139.
- 22. See reference 2, p. 67.
- 23. M.Kasha, Discussions Faraday Soc. 2, 14 (1950).
- 24. R.S.Mulliken, J. Chem. Phys. 23, 1997 (1955).
- 25. A.C.Albrecht, J. Mol. Spectrosc. 6, 84 (1961).
- 26. T.Azumi and S.P.McGlynn, J. Chem. Phys. 37, 2413 (1962).
- 27. S.P.McGlynn, T.Azumi, and M.Kinoshita, <u>Molecular Spec-</u> <u>troscopy of the Triplet State</u>, Prentice-Hall, Englewood Cliffs, New Jersey, 1969.
- 28. D.S.McClure, J. Chem. Phys. 17, 665 (1949).
- 29. B.Bak and J.T.Neilsen, Z. Elektrochem. 64, 560 (1960).
- 30. G.L.LeBel, J.D.Laposa, B.G.Sayer, and R.A.Bell, Anal. Chem., In press.
- 31. J.H.S.Green, Spectrochim. Acta, 17, 607 (1961).
- 32. R.J.Jakobsen, Spectrochim. Acta, 21, 127 (1965).
- 33. G.Herzberg, <u>Infrared and Raman Spectra</u>, pp.271-272, Van Nostrand, Princeton, New Jersey, 1945.
- 34. D.H.Whiffen, J. Chem. Soc. 1956, 1350.
- 35. F.A.Andersen, B.Bak, S.Brodersen, and J.Rastrup-Andersen, J. Chem. Phys. 23, 1047 (1955).
- 36. J.D.Spangler and H.Sponer, Spectrochim. Acta, <u>19</u>, 169 (1963).
- 37. J.D.Spangler and N.G.Kilmer, J. Chem. Phys. <u>48</u>, 698 (1968).
- 38. D.R.Douslin and H.M.Huffman, J. Am. Chem. Soc. <u>68</u>, 173 (1946).

- 39. T.E.Martin and A.H.Kalantar, J. Chem. Phys. <u>49</u>, 244 (1968).
- 40. H.Singh and J.D.Laposa, to be published.
- 41. T.E.Martin and A.H.Kalantar, J. Chem. Phys. <u>50</u>, 1486 (1969).
- 42. G.W.King and S.P.So, J. Mol. Spectrosc. 33, 376 (1970).