LUMINESCENCE SPECTRA OF TOLUENE, BENZYL RADICAL AND SOME OF THEIR DEUTERATED ANALOGUES

LUMINESCENCE SPECTRA OF TOLUENE, BENZYL RADICAL AND SOME OF THEIR DEUTERATED ANALOGUES

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CHAPTER 1

INTRODUCTION

A number of methods are available for obtaining information about the ground state geometries of molecules. However, the accumulation of geometry data for molecules in excited electronic states has been hindered by a shortage of reliable methods for obtaining such information. If the rotational fine structure of a vibronic absorption band is resolved, it can be studied to obtain rotational constants and thus the geometry of a molecule in an electronically excited state can be deduced. In many instances, however, such fine structure cannot be resolved so observations of sub-bands or the overall shape of the rotational bands is used. The molecules being studied must be present in the gas phase, of course.

Excited state geometries can be inferred on the basis of the Franck-Condon principle. According to this principle, for a transition between electronic states, the most prominent vibrational progressions are those arising from normal modes which convert the geometry of one state into that of the other. The Franck-Condon principle has been applied quantitatively by measuring the relative intensities of the bands of a progression for both absorption[1,2] and emission[3] spectra.

In this study the vibrational fine structure of the fluorescence spectra of toluene and benzyl radical, along with the phosphorescence

spectrum of toluene were analyzed. The solutes were imbedded in polycrystalline matrices at 77°K.

The spectroscopically observable effects of chemical substitution of benzene have been of interest for some time. The particular case of methyl substitution of benzene has been the subject of U.V. absorption,[4,5,6] singlet-triplet absorption,[7] low temperature phosphorescence experiments[8,9,10] and fluorescence studies in both the vapour phase[11,12] and polycrystalline matrices.[13] These workers[10,13] have included deuterium substituted toluenes in their studies, using the deuterium shifts of vibrational frequencies as an aid in assigning the vibrational structure of their emission spectra. It is known that features of the vibrational structure vary from solvent to solvent. Along with the determination of the most important progressions in the fluorescence and phosphorescence of toluene, this work involves the study of the prominence of forbidden components in allowed transitions.

Benzyl radical is one of the simplest and, at the same time, one of the most experimentally accessible aromatic free radicals. Schüler and co-workers[14,15,16] were the first to prepare benzyl radical and obtain its emission spectrum using gaseous toluene with an electric discharge being passed through it. A number of other workers[17,18,19] also obtained spectra of benzyl radical in this manner. Use of the discharge method leads to production of side products, however, so Norman and Porter[20] used the method of preparing free radicals in situ by photolysis of the parent substance dissolved in a hydrocarbon glass at low temperatures. Porter and co-workers[20,21] observed the absorption spectrum of benzyl radical after photolyzing toluene in hydrocarbon solvents at 77°K. The low

temperature fluorescence spectrum of benzyl in a polycrystalline matrix has been the subject of investigation,[13,22] and the excitation spectrum of benzyl radical has been observed[23] using a hydrocarbon matrix at 77°K. Photoselection data[24] obtained using a hydrocarbon matrix at 77°K and rotational contour analyses of several bands of the gas phase emission spectrum[19] were required in order to confirm the symmetry of the first excited doublet state as A_2. Deuterated analogues of benzyl radical have been used[13,22] in assigning the vibrational structure of its fluorescence at low temperature in a polycrystalline matrix and it is known that these spectra also are solvent dependent. In this study, the prominence of forbidden components in the allowed electronic transition is also considered.

CHAPTER II

THEORETICAL

2.1 SYMMETRY CLASSIFICATION OF TOLUENE AND BENZYL RADICAL

Group theory has been a valuable asset in the understanding of spectral data. Examination of the symmetry elements of a molecule in its equilibrium nuclear configuration enables the assignment of the molecule to a symmetry point group.

Electron diffraction studies[25] indicate that the phenyl ring of toluene is essentially a planar hexagon. Microwave measurements show that the methyl group rotates quite freely, even in the condensed phase.[26] The incident electromagnetic radiation would therefore interact with the molecule with equal probability for all configurations of the methyl group with respect to the ring. Hence, the methyl group can be considered as an atom and the $CH_2\cdot$ group of benzyl is assumed to behave as a single atom also.

In addition to the identity element, toluene possesses three additional symmetry elements: a two-fold rotation axis and two reflection planes. These three symmetry elements are shown in Fig. 2.1 where the axes have been defined according to Mulliken's convention.[27] The corresponding symmetry operations are:

$C_2(Z)$: rotation through 180° about the Z axis;

$\sigma_v(XZ)$: reflection in a plane perpendicular to the molecular plane;

$\sigma_v'(YZ)$: reflection in a plane coincident with the molecular plane.

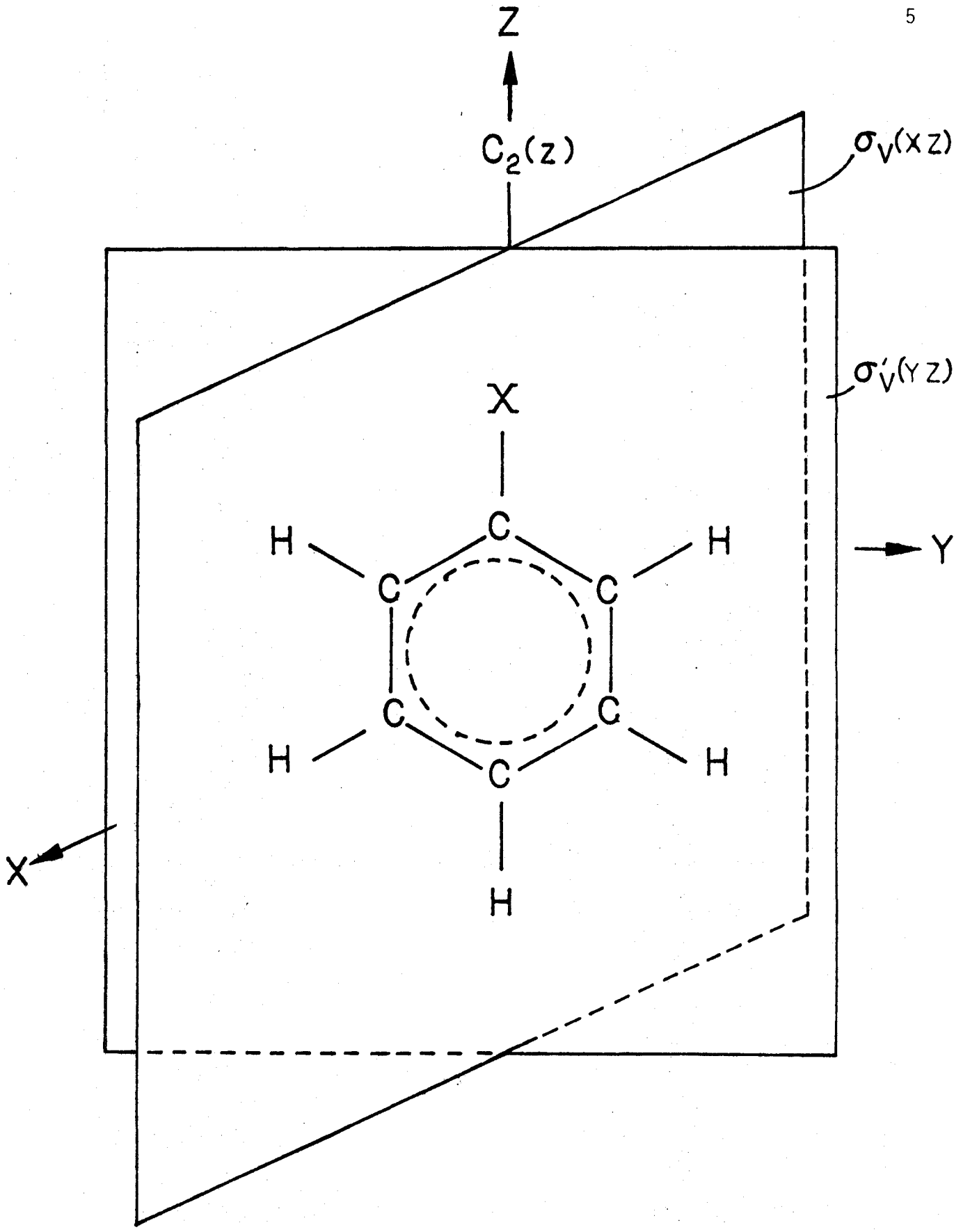

Figure 2.1 Symmetry elements of monosubstituted benzenes.

These symmetry operations are those of the point group C_{2v} and it is to that point group that toluene, toluene-α-d3, ring deuterated toluene-d5, toluene-d8 and the analogous benzyl radicals all belong. The same point group applies if there is monodeuteration in the para position but if the ortho or meta positions are deuterated, the resulting molecules can be considered as belonging to the point group C_s.

The character table and direct product table for C_{2v} are given in Tables 2.1 and 2.2. Such tables are helpful in determining which electronic transitions are symmetry allowed, and which vibrational modes are infrared and Raman active.

2.2 SPECTROSCOPIC TRANSITIONS

A spectroscopic transition can occur between two states E_i and E_f if

$$\Delta E = |E_f - E_i| = h\nu \tag{2.1}$$

where E_f and E_i are the energies of the final and initial states with respect to an arbitrary zero, ν is the frequency of the absorbed or emitted photon and h is Planck's Constant. Equation (2.1) can be written in the form

$$\bar{\nu} = \frac{|E_f - E_i|}{hC} \tag{2.2}$$

where h (Planck's constant) = 6.62×10^{-27} erg-sec and C is the speed of light in a vacuum = 3.00×10^{10} cm sec^{-1}. $\bar{\nu}$ is the wave number of the electromagnetic radiation absorbed or emitted when the transition occurs and is expressed in reciprocal centimeters. It is equivalent to the reciprocal of the wavelength, λ, and is proportional to the energy of the photon.

TABLE 2.1

Character Table for Point Group C_{2v}

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	
A_2	1	1	-1	-1		R_z
B_1	1	-1	1	-1	x	R_y
B_2	1	-1	-1	1	y	R_x

TABLE 2.2

Direct Product Table for Point Group C_{2v}

C_{2v}	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2	A_2	A_1	B_2	B_1
B_1	B_1	B_2	A_1	A_2
B_2	B_2	B_1	A_2	A_1

2.3 VIBRATIONS OF POLYATOMIC MOLECULES

For molecules having N nuclei, there are 3N degrees of freedom of motion. There are three rotational and three translational degrees of freedom for each molecule so there are 3N-6 vibrational degrees of freedom per molecule. (There are 3N-5 in a linear molecule which has only two rotational degrees of freedom.) Hence, in non-linear molecules, the vibrational motion can be resolved into 3N-6 normal modes, a normal mode being defined as a mode of vibration where each atom in the molecule reaches its position of maximum displacement at the same time and each atom passes through its equilibrium position at the same time.[28]

Including the methyl-ring torsional mode, there are thirty-nine normal modes in toluene (thirty-six in benzyl radical) and they are classified according to frequency and symmetry, the frequencies being called normal, or fundamental frequencies. There is a normal coordinate assigned to each normal mode and the vibrational motion of the molecule can be discussed in terms of these coordinates. The normal modes and frequencies for toluene are listed in Table 4.1. References (28), (29) and (30) treat the topic in detail.

2.4 ISOTOPE EFFECT

When an atom of a molecule is replaced by an isotopic atom of the same element, it is assumed that the potential energy function and configuration of the molecule are essentially the same.[28,31] The frequency of the vibration may be changed somewhat because of the change in mass. This is particularly true if hydrogen and deuterium are the atoms in question because there is a large percentage change in mass.

This frequency shift, or isotope effect, is useful in assigning spectral lines to modes of vibration. A given normal mode in which a hydrogen atom is oscillating with a relatively large amplitude, will undergo a greater change in frequency than a normal mode in which the hydrogen is vibrating with a smaller amplitude.

2.5 THE BORN-OPPENHEIMER APPROXIMATION

The operator form of the time-independent Schrödinger equation is

$$\hat{H}\psi_t = E_t\psi_t \tag{2.3}$$

where ψ_t is an eigenfunction corresponding to a stationary state of the system and is dependent upon the coordinates of all electrons and nuclei. The E_t values are the eigenvalues and correspond to the sum of potential and kinetic energies of the electrons and nuclei present. $\hat{H}$ is referred to as the Hamiltonian operator and has the form

$$\hat{H} = \text{kinetic energy} + \text{potential energy} = \hat{T}_E + \hat{T}_N + \hat{V}_{EN} + \hat{V}_{NN} + \hat{V}_{EE} \tag{2.4}$$

where $\hat{T}_E$ and $\hat{T}_N$ are operators representing, respectively, the total electronic and nuclear kinetic energies. $\hat{V}_{NN}$ is the potential energy operator including electrostatic repulsion of all nuclei and $\hat{V}_{EE}$ is a similar type of operator accounting for the repulsions of all electrons.

It is possible to simplify the solution of equation (2.3) by making an assumption which is explained classically in the following manner. Due to their relatively large masses, the motion of nuclei is much less rapid than that of the electrons. In a given instant, electron motion occurs as if the positions of the nuclei were fixed. It should, therefore, be possible to determine molecular properties by

calculating electron motions for fixed nuclear configurations.

This approximation is translated into quantum mechanical terms by assuming that, if the nuclei are in fixed positions (where $\hat{V}_N = 0$ and $\hat{V}_{NN}$ = constant) there is a set of electronic eigenfunctions, ψ_E, such that

$$\hat{H}_E\psi_E = E_E\psi_E \tag{2.4}$$

where

$$\hat{H}_E = \hat{T}_E + \hat{V}_{EN} + \hat{V}_{EE}. \tag{2.5}$$

Born and Oppenheimer[32] first showed that if ψ_E is only a slowly varying function of nuclear coordinates, the E_E can be thought of as being part of the potential field in which the nuclei move while $\hat{V}_{NN}$ supplies the other part of it. The equation for nuclear motion is, therefore

$$(\hat{T}_N + \hat{V}_{NN} + \hat{E}_E)\psi_N = E\psi_N. \tag{2.6}$$

The eigenvalues obtained are the eigenvalues of $\hat{H}$ in equation (2.3) and they are obtained by solving equation (2.4) over a range of values for the nuclear coordinates. Each E_E value is then used as a parameter in equation (2.6) in order to obtain the energies E and a set of wavefunctions, ψ_N, for the nuclear motion. Each electronic state of the molecule yields a different set of these functions and energies. The complete wavefunctions are obtained from

$$\psi = \psi_E\psi_N \tag{2.7}$$

where this product is referred to as the zero-order Born-Oppenheimer approximation. Spin and relativistic considerations are neglected,

but the approximation allows electronic wavefunctions of systems to be described independently of nuclear ones and it is valid as long as the electronic wavefunction is essentially independent of nuclear coordinates.

In the approximation previously discussed, it is possible to consider electronic, vibrational and rotational motions as being separate because of the different time frame involved with each type. The total wavefunction can be written approximately as

$$\psi = \psi_V \psi_r \psi_E \tag{2.8}$$

and the total energies can be written as the total of the different types of energies:

$$E = E_V + E_E + E_r \, . \tag{2.9}$$

2.6 CLASSIFICATION OF ELECTRONIC STATES

Electronic states are normally classified according to spin multiplicity and symmetry transformation properties of the electronic wavefunction.

Each electron has a spin of ½ and if the coupling of individual spins with orbital motion is small, the total of these spins is a resultant which is half integral for an odd number and integral for an even number of electrons.

Coupling of the total spin angular momentum with orbital angular momentum can cause the molecular electronic states to split into 2S+1 components, S being the total spin quantum number. The value 2S+1 is referred to as the spin multiplicity of the state and is written as a superscript before the symbol indicating the symmetry species to which

the electronic wavefunction for the state belongs.

When the spins of all electrons are paired S = 0 and singlet states arise. If electrons are located in orbitals in such a way that two electrons in different orbitals have their spins parallel, S = 1 and the resulting state is a triplet. Quartets, doublets, etc. can occur depending on the value of 2S+1. Most aromatic molecules have singlet ground states.

In linear polyatomic molecules, there is an axially symmetric electrostatic field about the nuclei and the electronic angular momentum about the molecular axis is conserved. Consequently, the classification of electronic states can be derived from vector models.

In non-linear molecules where symmetry is lower, electronic angular momentum is not conserved. The explanation of this, in classical terms, is that there is an exchange of angular momentum of nuclei and electrons due to the motion of the electrons in the electrostatic nuclear field. If the classification of states for such molecules is to be more thorough than that afforded by the multiplicity specification, group theory must be used. The states are then classified according to the transformation properties of their space wavefunctions when the symmetry operation of the point group to which the molecule belongs are applied. Each possible electronic wavefunction is a basis for one of the irreducible representations of the molecular point group and has the same symmetry species as the irreducible representation for which it is a basis. It is assumed that the nuclei are fixed in their equilibrium positions but this discussion also holds for non-equilibrium

nuclear configurations as long as they have the same symmetry as the equilibrium one.

For toluene and benzyl radicals (point group C_{2v}) the electronic wavefunctions form the bases of the irreducible representations of the point group C_{2v}. Each possible electron configuration corresponds to an irreducible representation and if the symmetries of the molecular orbitals which contain the electrons are known, their direct product gives the symmetry of the electronic state. It can be seen by looking up the C_{2v} point group in a character table that the wavefunctions for the different electronic states have the symmetry species A_1, A_2, B_1 and B_2.

2.7 THEORY OF ELECTRONIC TRANSITIONS

Electronic transitions normally give rise to spectra appearing in the ultraviolet and visible regions of the spectrum. Under high resolution it is possible to discern the vibrational and rotational structures of electronic spectra of molecules in the gas phase but in the condensed phase, electronic spectra are usually broad.

The energy separation of electronic states is of the order 10,000-100,000 cm^{-1} while the separations of vibrational and rotational states are 100-10,000 cm^{-1} and 0.1-100 cm^{-1}, respectively.[30]

The probability of transition between an upper and lower electronic state, the states being denoted by $\psi_{e'}$ and $\psi_{e''}$, respectively, is proportional to the square of the transition moment integral which is given by

$$R_{e'e''} = \langle \psi_{e'} | M | \psi_{e''} \rangle \quad , \tag{2.10}$$

M being the dipole moment operator. The transition is allowed only if $R_{e'e''}$ is non-zero and that condition will occur only if the product $\Gamma_{\psi_{e'}} \otimes \Gamma_M \otimes \Gamma_{\psi_{e'}}$ is totally symmetric for at least one component of M. It is assumed here that the states involved are non-degenerate and that the nuclei are fixed.

Since the nuclei of molecules are actually in motion, it is necessary to re-state the selection rule using eigenfunctions involving nuclear coordinates. Using the Born-Oppenheimer approximation, the total eigenfunction can be written as:

$$\psi_{ev} = \psi_e \psi_v = \psi_e(q,Q)\psi_v(Q). \tag{2.11}$$

Q denotes all nuclear coordinates and q, all electronic coordinates. Rotational motion is neglected. The finer interaction of electronic and vibrational motion is also neglected but the part of the interaction which is expressed by having ψ_e as a function of Q is retained.[29]

As before, the transition probability is proportional to the square of the transition moment, given by

$$R_{e'v'e''v''} = \langle \psi_{e'v'} | M | \psi_{e''v''} \rangle . \tag{2.12}$$

Let the dipole moment operator, M, be separated into electronic and nuclear parts:

$$M = M_e + M_N . \tag{2.13}$$

The equation

$$R_{e'v'e''v''} = R_{e'e''} \langle \psi_{v'} | \psi_{v''} \rangle \tag{2.14}$$

is arrived at by substituting (2.13) into (2.12) and simplifying. $R_{e'e''}$ varies slightly with Q since the electronic wavefunction, ψ_e,

contains nuclear as well as electronic coordinates. The transition between two states $\psi_{e'}$ and $\psi_{e''}$ is permitted if $R_{e'e''}$ is non-zero. In the case of toluene and benzyl radical (point group C_{2v}) electronic transitions from a totally symmetric singlet ground state, $^1A_1$, to singlet excited states of A_1, B_1 and B_2 symmetries are permitted; for benzyl radical (C_{2v}) transitions from the ground doublet state $^2B_1$ to doublet excited states A_1, A_2 and B_1 are symmetry allowed.

The intensity of transitions between the vibrational levels of the electronic states is governed by the magnitude of the overlap integral $\langle\psi_{v'}|\psi_{v''}\rangle$ and the selection rule is that the direct product $\Gamma_{\psi_{v'}} \otimes \Gamma_{\psi_{v''}}$ must be totally symmetric for the integral to be non-zero. $\psi_{v'}$ and $\psi_{v''}$ must therefore belong to the same irreducible representation. Hence, transitions can only occur between vibrational states belonging to the same symmetry species.

The vibrationless levels of the electronic states can always combine to give the 0,0 band if the transition is electronically allowed. In either electronic state, transitions can occur between states in which any number of quanta of a totally symmetric vibration are excited. That is,

$$\Delta V_s = V_{s'} - V_{s''} = 0, \pm 1, \pm 2, \pm 3, \ldots \quad . \tag{2.15}$$

In the case of non-totally symmetric vibrations, however, only the changes

$$\Delta V_a = V_{a'} - V_{a''} = 0, \pm 2, \pm 4, \ldots \quad . \tag{2.16}$$

can occur in the quantum number.

2.8 VIBRONIC COUPLING

The dependence of the electronic wavefunction upon nuclear

coordinates, Q, permits the interaction of electronic and vibrational motion in polyatomic molecules so that factoring of $R_{e'v'e''v''}$ in the manner of equation (2.14) is no longer valid. When the nuclei are in a displaced position of a non-totally symmetric vibration, the molecule has lower symmetry than it would have in the equilibrium position and states which have different species in the equilibrium position can have the same species under reduced symmetry. The result is the mixing of the zeroth order vibrational levels of the electronic states involved and this type of interaction is known as the Herzberg-Teller effect. Therefore, transitions which were previously forbidden electronically, can occur between the perturbing states each of which has assumed properties of the others. The Herzberg-Teller theory[33] treats the change in nuclear coordinates as a perturbation in the electronic Hamiltonian since the potential energy term, $\hat{V}_{EN}$, and the operator, $\hat{H}_E$, vary with change of nuclear coordinates in higher approximation.

In principle, two electronic states of any species can perturb each other if suitable vibrations are excited. In fact, such perturbations are very weak unless the species of the two electronic states do not differ by more than the species of one of the normal vibrations. This condition may be written as:

$$\Gamma_{\psi_a} \otimes \Gamma_{\psi_b} = \Gamma_Q \qquad (2.17)$$

where ψ_a is the perturbed state, ψ_b is the perturbing state and Q is the normal coordinate representative of the vibration causing the perturbation.[29]

2.9 THE FRANCK-CONDON PRINCIPLE

The shape and intensity of an electronic absorption or emission spectrum is governed by the relative intensities of the vibrational substructure of the electronic transition. The Franck-Condon principle provides an understanding of these relative intensities and it is based on the fact that an electronic transition occurs much more rapidly (10^{-15} sec) than oscillation of the nuclei (10^{-12} sec) so the nuclear configuration remains essentially the same immediately before and immediately after the electronic transition.

If the electronic transition moment is considered to be approximately constant and if the total wavefunction can be considered as being composed of vibrational, rotational and electronic components, the intensity of the transition is dependent upon the extent to which the eigenfunctions of the participating vibrational levels overlap. That is, the intensity of the transition is proportional to the square of the vibrational overlap integral. This integral is termed the Franck-Condon factor.

Within a given vibrational level the most probable nuclear configuration is dependent upon the square of the vibrational eigenfunction for that level. There is, therefore, a probability distribution as a function of r within the level. Thus, in the case of emission at low temperature, a number of transitions can originate in the zeroth vibrational level of the excited electronic state.

In the approximation of constant nuclear configuration during an electronic transition, the most probable transition would correspond to a vertical line on the potential energy diagram, as in Figures 2.2a , 2.2c .

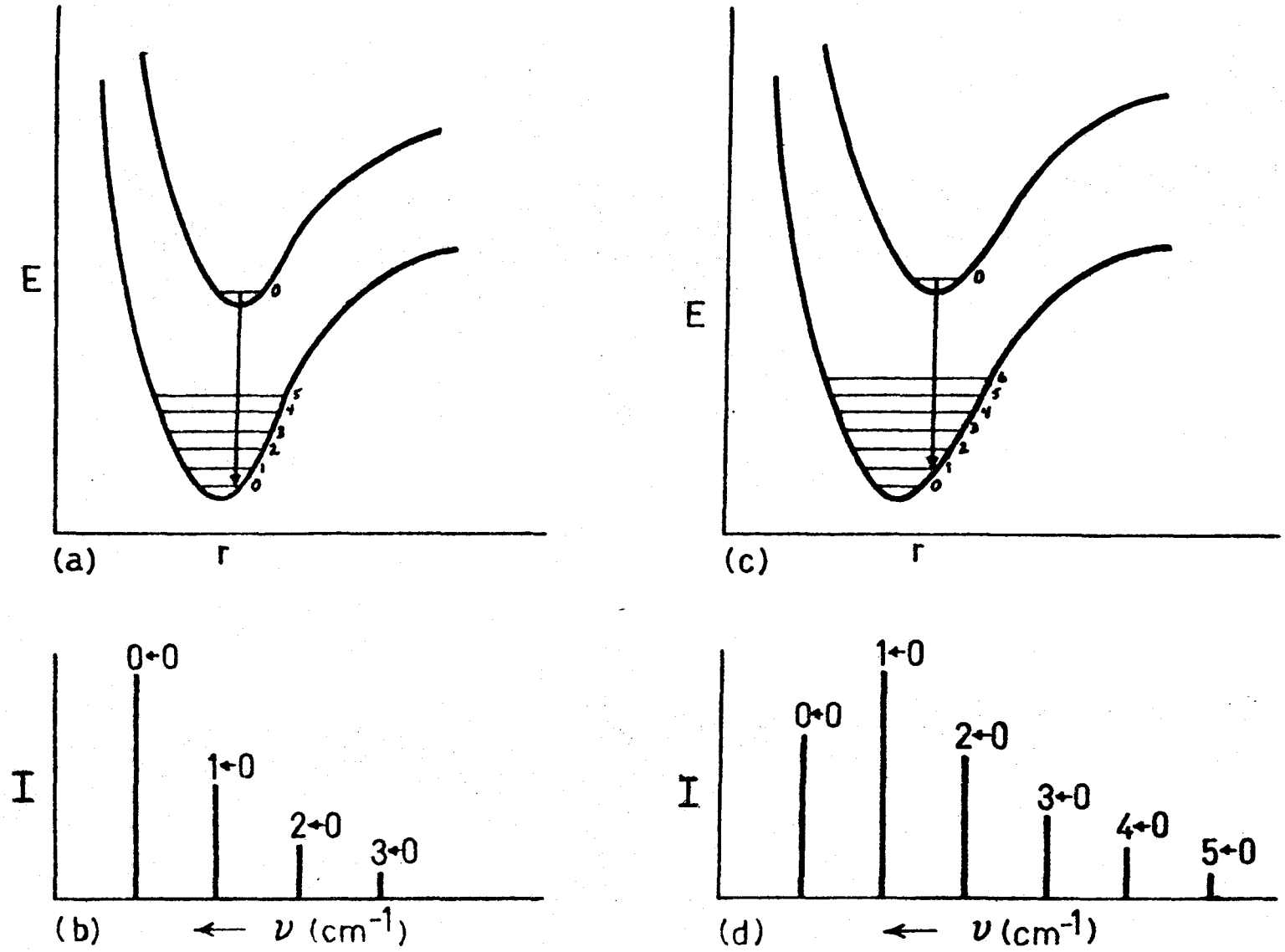

Figure 2.2 Franck-Condon potential curves for the ground and first excited states (a,c) and the resulting emission progression (b,d) .

If the minima of the potential energy curves are not displaced with respect to each other, the 0,0 transition is the most intense and the intensity of the bands lessens gradually toward longer wavelengths, as shown in Figures 2.2a and 2.2b . This is the case for molecules which do not distort upon entering the excited electronic state. If the molecule does distort when so excited, the potential energy minima are displaced with respect to each other and the eigenfunctions of the zeroth vibrational level now overlaps more effectively with some other vibrational level of the ground state and the transition to this level will be most intense, as depicted in Figures 2.2c and 2.2d . There is also overlap with the eigenfunctions of a larger number of ground state vibrational levels so the spectral progressions involved are longer. Therefore, information concerning the excited state geometry of a molecule can be deduced from the most prominent vibrational progressions.

2.10 FLUORESCENCE AND PHOSPHORESCENCE

After a molecule has become excited due to absorption of radiation, the extra energy can be lost through various radiative and non-radiative processes. Figure 2.3 ,referred to as a Jablonski diagram, indicates the types of processes involved. Solid, vertical lines represent spin allowed absorption and emission transitions while dashed vertical lines indicate spin forbidden absorption and emission. Horizontal dashed arrows represent intersystem crossing, while wavy, vertical lines indicate vibrational relaxation.

If a molecule is excited into one of the higher excited states of the singlet manifold, S_i, the energy can be degraded by internal

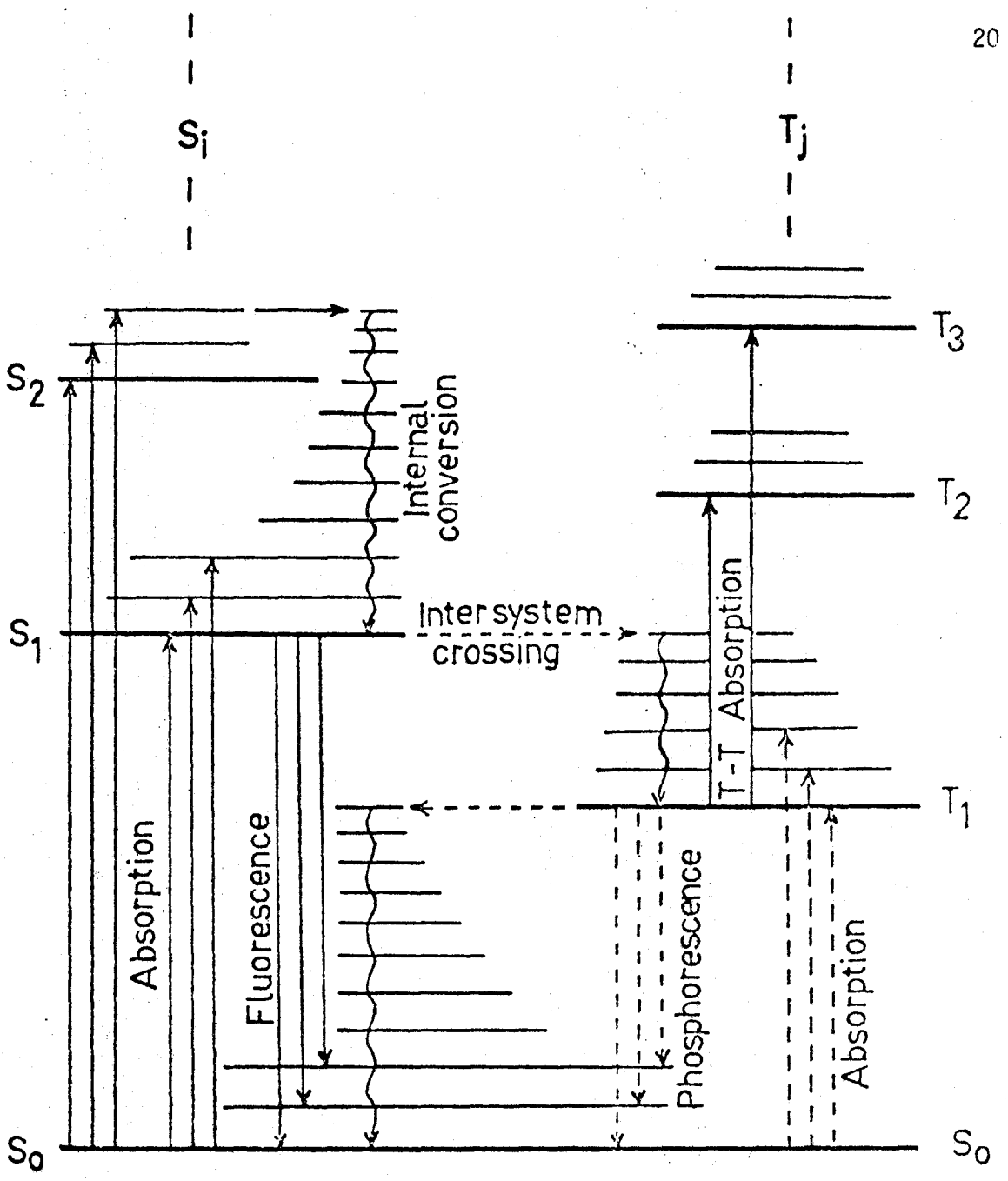

Figure 2.3 Schematic view of energy levels with possible absorption transitions and different types of mechanisms for intramolecular loss of energy.

conversion and vibrational relaxation. Internal conversion is defined as a non-radiative passage between electronic states of the same multiplicity. When the molecule undergoes internal conversion from S_i to S_1 it can still be vibrationally excited within S_1 and this excess vibrational energy is removed by the intermolecular process of vibrational relaxation so that, relative to the minimum of the S_1 potential energy surface, a thermally equilibrated collection of S_1 molecules is produced. In fact, emission from excited states above the zeroth vibrational level of S_1 is seldom observed with molecules in rigid hydrocarbon glasses or polycrystalline matrices at 77°K. This is also the case for the triplet manifold. It is a general rule, known as Kasha's Rule,[34] that emission occurs from the S_1 or T_1 state, and not from higher excited states.

A molecule in the S_1 state can undergo one of several possible processes:

(i) Fluorescence, which is the radiative passage between states of the same multiplicity;

(ii) Internal conversion and vibrational relaxation from S_1 to S_0;

(iii) Intersystem crossing from S_1 to T_1 which is defined as the non-emissive passage between two states of different multiplicity.

If process (iii) occurs, vibrational relaxation then follows so the molecule is in the lowest vibrational level of the T_1 state and one of the following processes happens:

(i) Phosphorescence, which is the radiative passage between

states of different multiplicity ($T_1 \rightarrow S_0$ in this study);

(ii) $T_1 \rightsquigarrow S_0$ intersystem crossing, followed by vibrational relaxation within S_0.

Virtually all phosphorescence spectra are due to efficient intersystem crossing since singlet-triplet absorption is forbidden and T_1 must be populated in some other manner. If the $T_1 \rightsquigarrow S_0$ process was of comparable efficiency, phosphorescence would be observed only in rare cases. The disparity in the $S_1 \rightsquigarrow T_1$ and $T_1 \rightsquigarrow S_0$ rate constants can be as large as 10^9 and several workers have offered explanations for it. Kasha[35] proposed that the probability of $S_1 \rightsquigarrow T_1$ increased as the energy difference between S_1 and T_1 decreased. Robinson[36,37,38] formulated a theory which embodies the idea of the intersystem rate constant k_{isc} for $T_1 \rightsquigarrow S_0$ being very sensitive to the energy gap T_1-S_0. The sensitivity to the energy gap is contained in the overlap integrals of the two states between which energy is being non-radiatively transferred. The sensitivity of k_{isc} should be common to both intersystem crossing and internal conversion, and should be independent of spin reorientation processes.

Although intersystem crossing and direct absorption involving states of different multiplicity are both spin forbidden, their probabilities of occurrence are not equal. Spin orbit coupling is inversely proportional to the energy differences between the triplet and singlet states concerned. When the T_1-S_1 energy differences ($\sim$ 3000-9000 cm^{-1}) are considered, the probability for intersystem crossing should be larger than that for direct transition between the ground singlet and lowest triplet state. The S_1 to T_1 intersystem crossing process is slow compared

to the S_1 and S_0 fluorescence, but it competes well enough to populate the triplet state. See Table 2.3 where the processes and their rate constants are listed.

The degree to which the spin forbiddenness of singlet-triplet transitions is relaxed depends upon the magnitude of the interaction between the magnetic dipole generated by spin motion of the electron and that produced by its orbital motion. Such spin-orbit coupling, as the interaction is termed, causes the introduction of triplet character into singlet states and vice-versa.

In summary, the spectra which are obtained are the result of the collection of transitions from the zeroth vibrational level of the excited state. If the upper state is singlet, the spectra obtained are fluorescence and if the upper electronic state is a triplet, the spectra are termed phosphorescence spectra.

Molecular distortions of the singlet and triplet can be studied by examination of the vibrational structure of the relevant electronic transition.

2.11 CHARACTERISTICS OF POLYCRYSTALLINE MATRICES

In gas phase spectroscopy, emission from a higher vibrational level which has previously taken part in an absorption process frequently occurs. This phenomenon is termed resonance fluorescence and according to Kasha's rule does not occur in solid solutions at low temperatures. Kasha's rule also eliminates "hot bands" from consideration since no transitions having energy greater than that of the 0,0 can occur. The spectra obtained at low temperature using solid solutions are, therefore, much less complicated than their gas phase counterparts.

TABLE 2.3

Rate Constants for Radiative and Non-Radiative Processes in Rigid Media at 77°K.

Process	Rate Constant (sec^{-1})
Absorption, $S \rightarrow S_1$	10^{15}-10^{16}
Internal Conversion, $S_2 \rightsquigarrow S_1$	$> 10^{12}$
Vibrational Relaxation within S_1, T_1 or S_0	$> 10^{12}$
Fluorescence, $S_1 \rightarrow S_0$	10^{6}-10^{9}
Internal Conversion, $S_1 \rightsquigarrow S_0$	10^{6}-10^{12}
Intersystem Crossing, $S_1 \rightsquigarrow T_1$	10^{4}-10^{12}
Phosphorescence, $T_1 \rightarrow S_0$	10^{-2}-10^{4}
Intersystem Crossing, $T_1 \rightsquigarrow S_0$	10^{-1}-10^{5}

The solvent-solute system can be thought of as being an infinitely dilute cold gas.[39] In such a system, the guest molecules are isolated from each other so there is little guest-guest interaction. The solvent is considered to be virtually inert and host-guest interaction is minimized. Spectra obtained from such guests are characteristic of the free molecule because there is little interaction between the molecule and the environment to cause distortion of the energy level system. Absorption or emission of the host does not occur because the energy levels of such molecules are well above those of the guest. Both polycrystalline matrices and organic-glass solvents manifest these solvent characteristics.

Typically, the wavelength of electronic and vibrational transitions changes by less than one percent on going from the gas phase to the solid. This slight shift arises from the fact that the excited state of the guest interacts with the host system to a different extent than in the case with the guest ground state, as shown in Figures 2.4a and 2.4b. The shift is an indicator of the relative difference in interaction energy on going from one phase to the other. The wavelength of the transition may be blue or red shifted depending on the relative magnitudes of the interactions involved.

Usually, the 0,0 transition of fluorescence does not coincide with the 0,0 of absorption in the solid phase. This is expected because each solute molecule is rigidly surrounded by solvent molecules. Upon absorption of light, the solute molecule is in an unstable excited state configuration relative to the surrounding solvent molecules. However, the solute molecule usually has time to achieve a stable, equilibrium

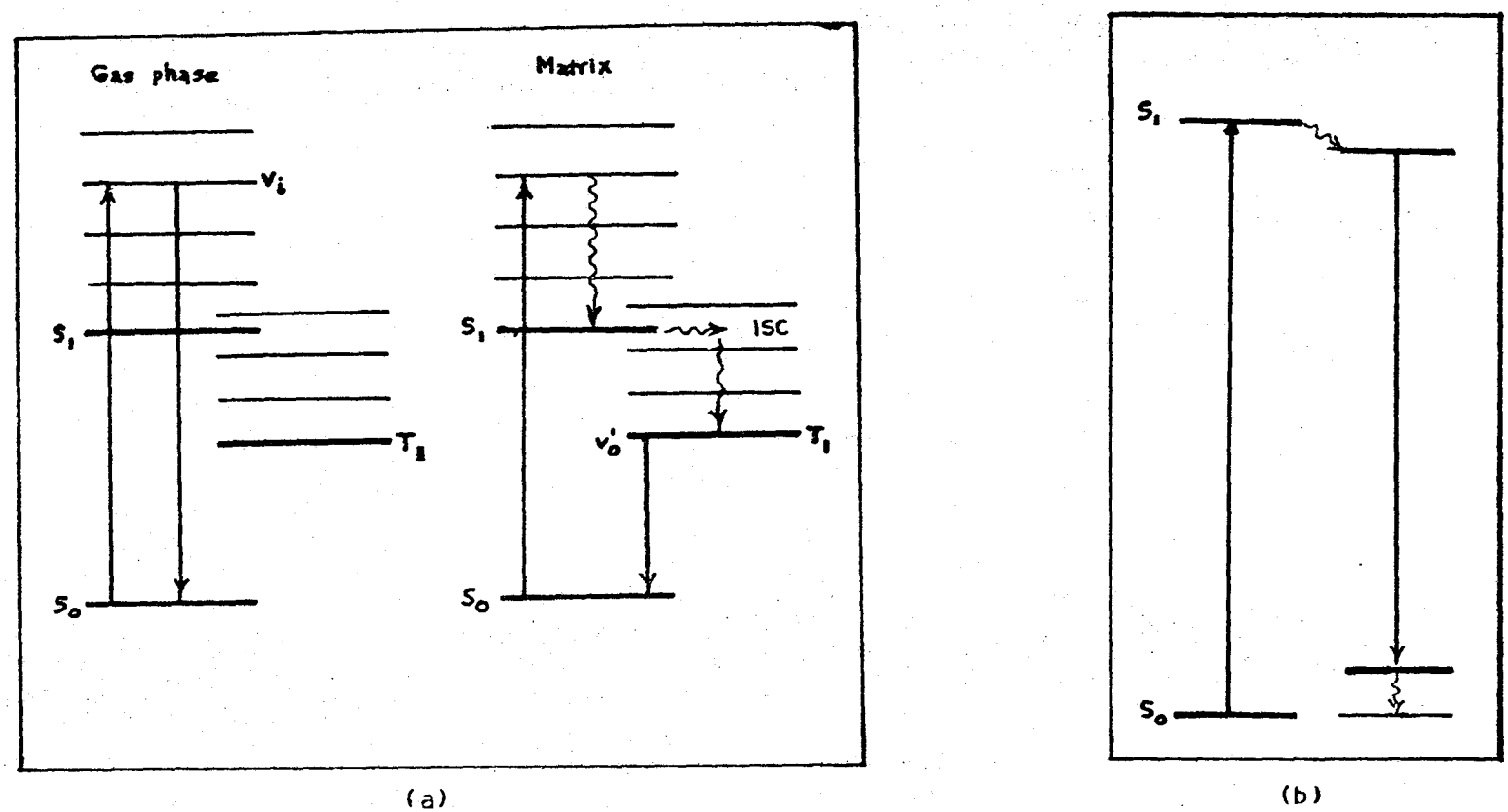

Figure 2.4a Comparison of gas phase and matrix emission.
2.4b Difference of 0,0 energies for absorption and emission.

configuration before emitting. When emission has occurred, the guest molecule will be in an unstable configuration with regard to the ground state and will undergo relaxation. Thus, the 0,0 transition of emission is of lower energy than the absorption one in solid phase spectra.

When a solvent whose molecular dimensions closely match those of the solute is chosen and a polycrystalline matrix is formed, sharp spectra are often obtained. This phenomenon is called the Shpol'skii effect.[39] When solute and solvent are not matched in that manner, poorly resolved spectra usually result. Careful choice of solvent and the use of polycrystalline samples can lead to much sharper spectra being obtained.

It occasionally happens that spectra obtained using Shpol'skii solvents exhibit peak splitting which is due to multiple site emission. If cyclohexane , for example, is frozen too rapidly, two crystalline modifications of the solvent will appear in the same sample and two similar spectra corresponding to the emission of the solute from the cubic and monoclinic environments will be obtained. The separation of corresponding peaks can be as much as 100 cm.[40] Slow cooling of the sample eliminates this problem by allowing cyclohexane to solidify in monoclinic form only.

Splitting of spectral peaks can also be caused by emission from guest molecules having several preferred orientations in the sample.[41] Again, cooling the sample slowly in the best preventative measure.

CHAPTER III

EXPERIMENTAL

3.1 CHEMICALS

$C_6H_5CH_3$ of scintillation quality was purchased commercially from Matheson, Coleman and Bell. It was vacuum distilled before use but the emission spectra obtained before and after this distillation were virtually identical.

$C_6D_5CH_3$ of greater than 99% isotopic purity was obtained from Merck, Sharp and Dohme of Canada. Vacuum distillation of it was carried out but this was found to have been unnecessary since emission spectra taken before and after the distillation were identical.

$C_6H_5CD_3$ was bought from Stohler Isotope Chemicals. It was also more than 99% isotopically pure and was used as received.

$C_6D_5CH_3$ was prepared according to the method of Werstiuk and Kadai[42] involving acid catalyzed exchange of aromatic protons by deuterium at high temperature.

The o, m and p-deuterotoluenes were obtained from the corresponding mono-brominated toluenes (British Drug Houses, Laboratory Reagent) by preparing the corresponding Grignard reagent and hydrolyzing it with D_2O. The product was then purified by distillation using a Vigreux column.

The deuterated derivatives were all checked for isotopic purity

by Carbon-13 magnetic resonance.[43] Toluene-d8, toluene α-d3 and toluene-d5 were checked by this method and they were found to have deuterium incorporations in the desired positions in excess of 95%.

The ortho-, meta- and para-monodeuterated toluenes had deuterium incorporations of 92%, 92% and 82%, respectively, as estimated by Carbon-13 n.m.r.

The benzyl radicals were produced from the analogous toluenes in 10^{-2}-10^{-3} M solutions by 15-20 minutes irradiation with 270 nm. light provided by an Osram 450 watt Xe lamp. Samples which were prepared in this way and kept frozen in liquid nitrogen gave reproducible spectra as long as thirty-six hours after preparation.

3.2 SOLVENTS

Methylcyclohexane, cyclohexane, hexane and heptane were Matheson, Coleman and Bell "spectroquality" chemicals and were used without further purification.

3-Methylpentane (3-MP) was pure grade Phillip 66 and was passed through a Linde 10X molecular sieve before being used.

These materials all failed to show detectable luminescence under the conditions employed in obtaining spectra.

3.3 APPARATUS

Figure 3.1 provides a schematic illustration of the apparatus used to obtain the emission spectra.

The exciting light was obtained from a low pressure mercury lamp or from a high pressure 450 watt xenon lamp powered by a D.C. regulated Universal lamp power supply Model #C-72-50 from Oriel Optics

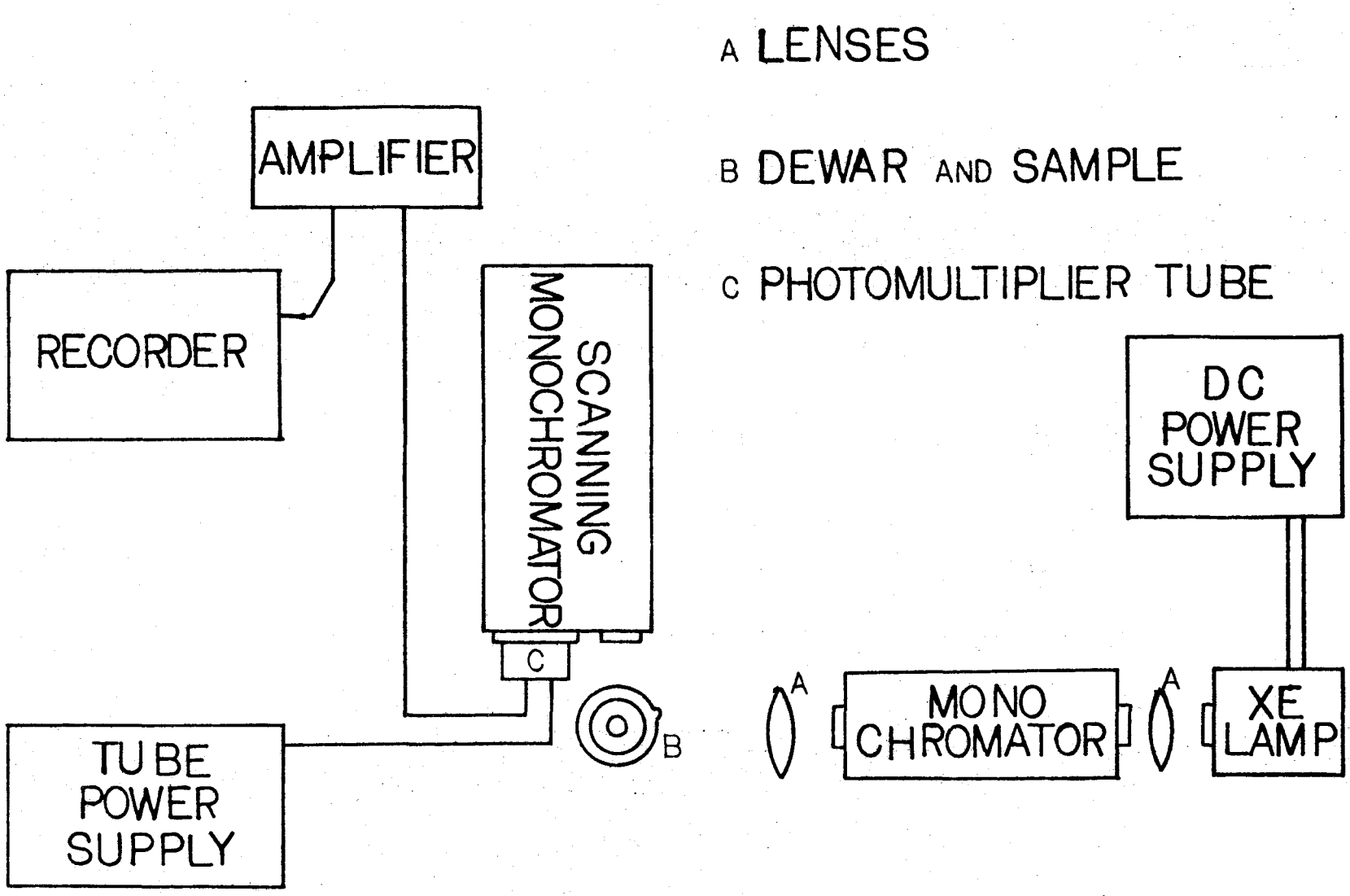

FIG. 3.1 APPARATUS FOR EMISSION EXPERIMENTS BLOCK DIAGRAM

Corporation. Most of the intensity of the mercury lamp emission was concentrated at 253.7 nm and it was this wavelength which was used to excite toluene. The 450 watt xenon lamp has a white emission so it was necessary to pass the light from it through a Jarrell-Ash 0.25 meter Ebert monochromator whose grating, blazed at 300 nm, has 2360 grooves/mm. This light source was used in obtaining benzyl radical spectra, the excitation wavelength being 317 nm.

The exciting light was then focussed by quartz lenses on the sample within an 11 mm O.D. quartz tube which was submerged in a partially silvered dewar containing liquid nitrogen.

The light emitted by the sample was passed through a 0.5 meter Jarrell-Ash scanning monochromator whose grating, blazed at 400 nm, has 1180 grooves/mm. This monochromator was mounted at right angles to the direction of the exciting light and was equipped with an RCA 8575 photomultiplier tube powered by a Power Design Model HV1544 power supply.

The photomultiplier output signal was then amplified in one of two ways:

(1) by a Keithley Model 610C electrometer;

(2) by an Ortec Model 454 Timing Filter Amplifier used with an Ortec photon counting system consisting of a Model 421 Integral Discriminator, a Model 441 Ratemeter, and a 9201 Photomultiplier base.

The spectra were obtained using 10^{-2}-10^{-4} M solutions and were uncorrected for instrumental response. The estimated accuracy of the luminescence spectra is ± 1 Å. The spectra were calibrated using mercury emission lines.

CHAPTER IV

RESULTS AND DISCUSSION

At 77°K, the Boltzmann factor, kT, is approximately 50 cm^{-1}. This value is somewhat smaller than the spacing between vibrational levels so there is little thermal population of higher vibrational levels in the excited states. Consequently, transitions occur from the zeroth vibrational level of S_1 or T_1 and terminate at some vibrational level in the ground state.

The ground state fundamentals used in this work are portrayed schematically in Figure 4.1, where they are designated by Whiffen's notation for monosubstituted benzenes. The complete set of toluene fundamental frequencies is given in Table 4.1, where the Whiffen,[44] Wilson[45] and Herzberg[29] designations are shown.

The resolution of the toluene fluorescence and phosphorescence spectra and benzyl radical fluorescence spectra was rather poor with most solvents used (such as hexane or cyclopentane) although the main features of the spectra were similar from solvent to solvent at 77°K. Polycrystalline methylcyclohexane was the solvent used in obtaining the spectra analyzed in this study, since well resolved spectra were recorded for the fluorescence and phosphorescence of toluene and for the fluorescence of benzyl radical at 77°K. In cases where the methylcyclohexane solvent was present as a glass or cracked glass, the overall appearance of a spectrum was the same as observed with the polycrystalline matrix but resolution was much poorer.

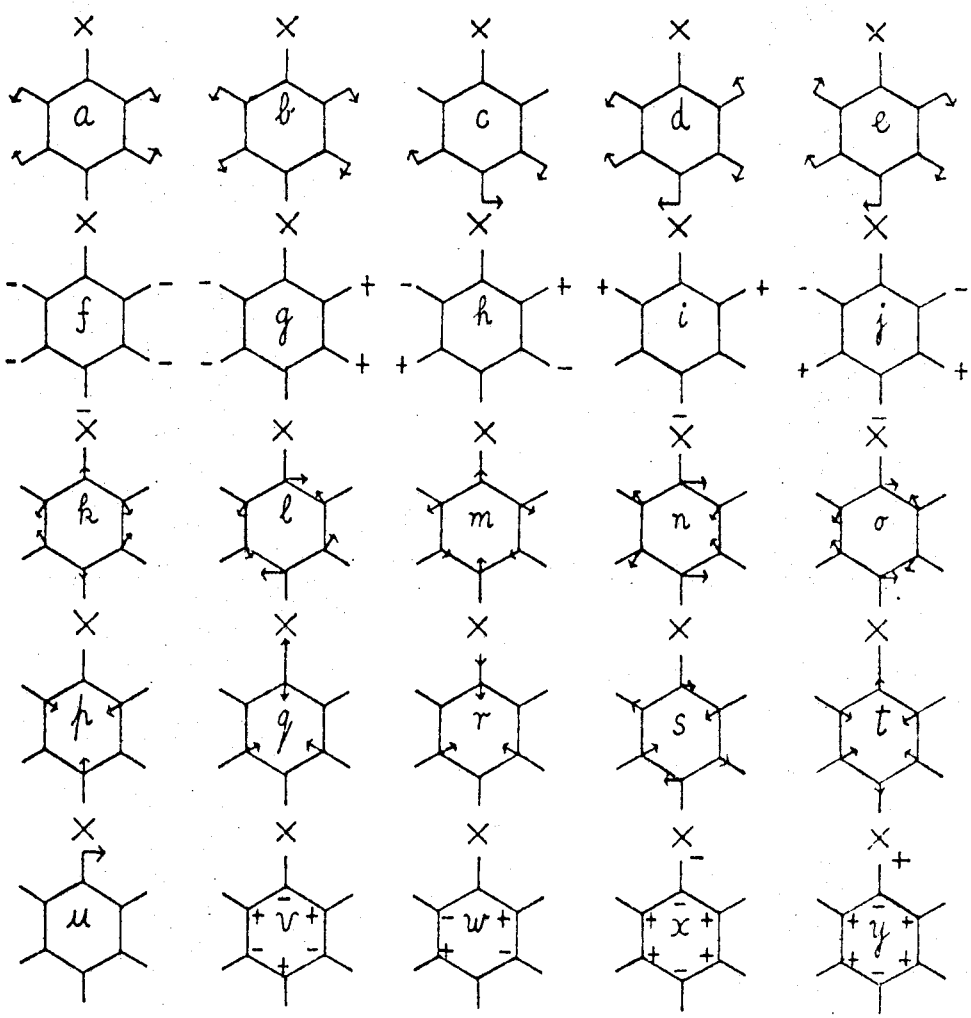

Figure 4.1 Schematic illustrations of some vibrational modes of mono-substituted benzenes.

TABLE 4.1

Ground State Fundamentals in Toluene and Some of its Deuterated Derivatives.

	Designation [a]		Symmetry		Description	Frequency (cm^{-1})						
			C_{2v}	C_s	of h8 mode	h8 [b]	α-d3 [b]	d5 [c]	d8 [b]	p-d1 [b]	m-d1 [b]	o-d1 [b]
	ν_1	7a	a_1	a'	νC-H	3085 [d]	3087 [d]	2300		2262	2266	2985
	ν_2	20a	a_1	a'	νC-H	3063	3063	2285	2293	3079	3087	2259
	ν_3	2	a_1	a'	νC-H	3055	3056	2271	2286	3054	3056	3044
	ν_4	ν_s	a_1	a'	νCH_3	2921	2130	2920	2121	2898	2923	2920
k	ν_5	8a	a_1	a'	νC-C	1605	1606	1569	1583	1601	1600	1600
m	ν_6	19a	a_1	a'	νC-C	1494	1495	1390	1388	1491	1482	1477
	ν_7	δ_s	a_1	a'	δCH_3	1379	1045	1378	1041	1380	1378	1380
q	ν_8	13	a_1	a'	X-sens(νC-Me)	1208	1225	1144	1180	1211	1205	1203
a	ν_9	9a	a_1	a'	βC-H	1175	1180	871	880	1179	1155 [e]	1156
b	ν_{10}	18a	a_1	a'	βC-H	1030	1026	842	840	1029	1025	1033
p	ν_{11}	12	a_1	a'	Ring	1003	1003	961	961	986	1002	991
r	ν_{12}	1	a_1	a'	X-sens(αC-C-C)	784	758	741	717	785	763	788
t	ν_{13}	6a	a_1	a'	X-sens(αC-C-C)	521	498	507	490	517	520	525
h	ν_{14}	17a	a_2	a"	γC-H	964	966	790		917	889	914
g	ν_{15}	10a	a_2	a"	γC-H	843	840	660			836	834
w	ν_{16}	16a	a_2	a"	φC-C	408	361	355	349	411	389	398
	ν_{17}	ν_a''	b_1	a"	νCH_3	2979	2230	2970	2241	2959	2976	2975
	ν_{18}	δ_a''	b_1	a"	δCH_3	1460	1050	1448	1049	1450	1462	1465
	ν_{19}	r"	b_1	a"	rCH_3	1040	845	1035	770	1040	1046	1040
j	ν_{20}	5	b_1	a"	γC-H	978	980	816	785	947	917	943
i	ν_{21}	10b	b_1	a"	γC-H	893	917	735	735	834	800	765
f	ν_{22}	11	b_1	a"	γC-H	728	709	621	541	608	646	636
v	ν_{23}	4	b_1	a"	φC-C	695	698	551		710	695	720
x	ν_{24}	16b	b_1	a"	X-sens(φC-C)	464	446	413	390	453	453	461
y	ν_{25}	17b	b_1	a"	X-sens(γC-Me)	217	206	208	197	208	215	218

TABLE 4.1 (Continued)

	Designation [a]		Symmetry		Description	Frequency (cm^{-1})						
			C_{2v}	C_s	of h8 mode	h8[b]	α-d3[b]	d5[c]	d8[b]	p-d1[b]	m-d1[b]	o-d1[b]
	ν_{26}	7b	b_2	a'	νC-H	3039	3038	2255	2260	3042	3033	3067
	ν_{27}	20b	b_2	a'	νC-H	3029	3029	2265	2250	3024	3020	3019
	ν_{28}	ν_a'	b_2	a'	νCH_3	2952	2209	2948	2211	2959	2948	2950
l	ν_{29}	8b	b_2	a'	νC-C	1586	1586	1556	1570	1579	1582	1590
n	ν_{30}	19b	b_2	a'	νC-C	1468	1448	1322	1332	1420	1450	1450
	ν_{31}	δ_a'	b_2	a'	δCH_3	1460	1050	1448	1049	1450	1462	1464
e	ν_{32}	3	b_2	a'	βC-H	1331	1300	1071	972	1317	1290	1284
o	ν_{33}	14	b_2	a'	νC-C	1318	1261	1284	1270	1319	1315	1298
c	ν_{34}	9b	b_2	a'	βC-H	1154	1154	838	869	866	1165	1126
d	ν_{35}	18b	b_2	a'	βC-H	1080	1073	816	819	1105	1100	867
	ν_{36}	r'	b_2	a'	rCH_3	1040	845	1035	770	1040	1046	1040
s	ν_{37}	6b	b_2	a'	αC-C-C	623	623	597	605	616	618	619
u	ν_{38}	15	b_2	a'	X-sens(βC-Me)	344	307	335	298	338	344	348

a Designations of modes of those of Whiffen,[44] Herzberg[29] and Wilson,[45] respectively.

b From Varsanyi.[46]

c From Hitchcock and Laposa.[47]

d From Fuson et al.[48]

e From this work.

TABLE 4.2

Description of the Benzene Ring and Ring-Substituent Vibrations of Toluene.

Abbreviated Form	Description
νC-H	C-H stretching.
βC-H	C-H in-plane deformation.
γC-H	C-H out-of-plane deformation.
νC-C	C-C stretching.
αC-C-C	Ring in-plane deformation.
ϕC-C	Ring out-of-plane deformation.
Ring	Ring breathing mode.
νC-Me	C-C stretching between benzene ring and substituent group.
βC-Me	C-C in-plane deformation between benzene ring and methyl group
γC-Me	C-C out-of-plane deformation between ring and methyl group.
X-sens	Substituent, X, sensitive vibrations in which X moves with substantial amplitude so that the frequencies are sensitive to the mass of X.
νCH_3	Symmetric (ν_s) and antisymmetric (ν_a',ν_a''). C-H stretching modes within the methyl group.
δCH_3	Symmetric (δ_s) and antisymmetric (δ_a', δ_a'') bending modes within the methyl group.
rCH_3	Rocking movements the methyl group in the molecular plane (r') and out of the molecular plane (r'').

4.1 VIBRATIONAL ANALYSIS OF PHOSPHORESCENCE OF TOLUENES

a. Toluene-h8

The phosphorescence spectrum of toluene is shown in Figure 4.2 and the vibrational analysis is presented in Table 4.3. Kanda and Shimada[8] observed the 0,0 transition of toluene phosphorescence at 28,920 cm^{-1}, using cyclohexane as solvent at 77°K, while Kanda and Sponer[9] who studied the triplet singlet emission of toluene crystals at 4°K, and of toluene in ether-isopentane-alcohol (EPA) solvent at 77°K, found the 0,0 transitions at 28,789 cm^{-1} and 28,889 cm^{-1}, respectively. With the exception of an out-of-plane b_1 mode at 440 cm^{-1}, Kanda and Shimada observed no bands between the 0,0 transition and 660 cm^{-1}. With the EPA solvent, Kanda and Sponer observed no peaks in the low frequency region and those noticed by them in their study of toluene crystal at 4°K were assigned as lattice vibrations. Recently, Haaland and Nieman[10] studied toluene phosphorescence in a benzene matrix at 4°K and assigned the 0,0 transition as 28,994 cm^{-1} while observing peaks at 228 cm^{-1} and 454 cm^{-1} which were assigned as out-of-plane fundamentals. In addition, an out-of-plane fundamental was observed at 475 cm^{-1} along with two weaker bands which were assigned as 0,2 x 228 and 0,3 x 228, respectively. The progression in 228 cm^{-1} was not observed in this work where methylcyclohexane was the solvent at 77°K. However, the 0,0 value obtained in this study was 29,010 cm^{-1} which is in very good agreement with that found when benzene was used as the matrix. Evans[7] also obtained a value of 29,000 cm^{-1} using oxygen perturbation, to effect singlet triplet absorption. The 200 cm^{-1} and 445 cm^{-1} modes, which were assigned as 0,y and 0,x, respectively, did not combine with the main progressions in the spectrum. The b_1 mode v also

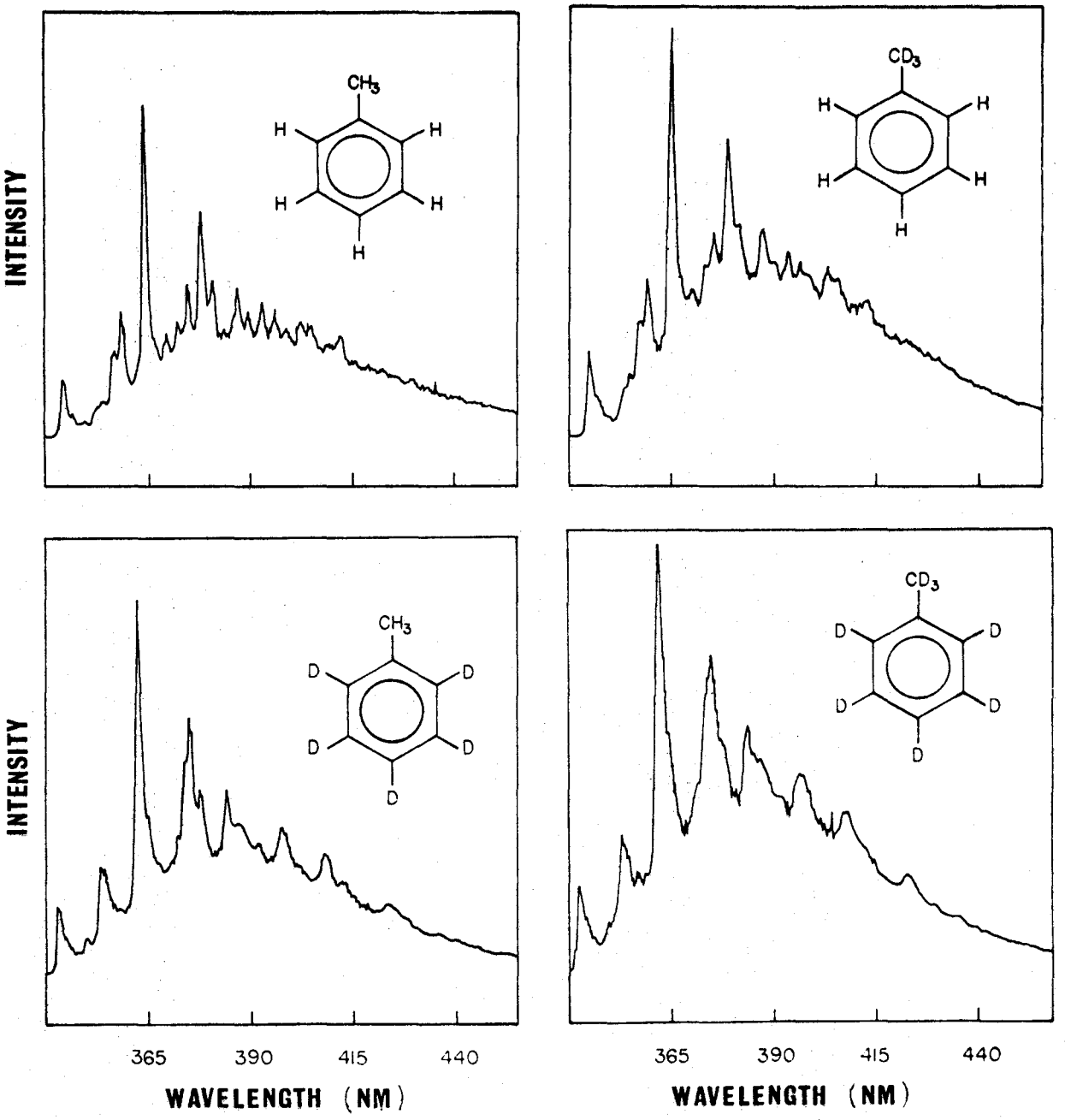

Figure 4.2 Phosphorescence spectra of (clockwise from upper left) toluene-h8, toluene-α-d3, toluene-d8 and toluene-d5, all solutions 10^{-3}M in methylcyclohexane matrices at 77°K.

TABLE 4.3

Vibrational Analyses of Phosphorescences of 10^{-3}M $C_6H_5CH_3$ and 10^{-3} M $C_6H_5CD_3$ in Polycrystalline Methylcyclohexane Matrices at 77°K.

Toluene-h8		Toluene-α-d3		Assignment[a]
$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	
29010	0	29020	0	0,0
28810	200	28835	185	0,y
28565	445	28615	405	0,x
28315	695	28335	685 sh	0,v
28210	800	28210	810	0,r
28005	1005	28010	1010	0,p
27845	1165	27855	1165	0,a
27795	1215 sh[b]	27795	1225 sh	0,q
27430	1580	27435	1585	0,ℓ
27415	1595 sh	27420	1600 sh	0,k
27220	1790 sh	27225	1795 sh	0,p+r
27000	2010	27025	2000	0,2xp
26,830	2180	26815	2205	0,a+p
26,640	2370	26655	2365	0,ℓ+r;0,k+r
26625	2385			0,k+r
26420	2590	26435	2585	0,ℓ+p
26390	2650 sh	26415	2605 sh	0,k+p
26225	2775	26280	2740	0,ℓ+a
26205	2805 sh	26240	2780	0,k+a
26010	3000			0,3xp
25820	3190	25835	3185	0,k+ℓ
25800	3210 sh	25805	3215 sh	0,2xk
25635	3375	25675	3345	0,ℓ+p+r;0,k+p+r
25415	3595	25430	3590	0,ℓ+2xp;0,k+2xp
25220	3790	25240	3780	0,a+ℓ+p;0,a+k+p
25040	3970	25055	3965	0,k+ℓ+r;0,2xk+r
24845	4165	24850	4170	0,k+ℓ+p;0,2xk+p
24675	4335	24665	4355	0,a+k+ℓ;0,a+2xk

TABLE 4.3 (Continued)

Toluene-h8		Toluene-α-d3		Assignment[a]
$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	
24420	4590	24420	4600	0,ℓ+3xp;0,k+3xp
24250	4760	24280	4740	0,2xk+ℓ;0,3xk
24055	4955	24205	4925	0,k+ℓ+p+r;0,2xk+p+r
23845	5165	23855	5165	0,k+ℓ+2xp;0,2xk+2xp
23640	5370	23675	5345	0,a+k+ℓ+p;0,a+2xk+p
23465	5545			0,2xk+ℓ+r;0,3xk+r
23255	5755	23250	5770	0,2xk+ℓ+p;0,3xk+p
23085	5925	23070	5950	0,a+2xk+ℓ;0,a+3xk

[a] Designation of normal modes according to Whiffen.

[b] sh = shoulder

TABLE 4.4

Vibrational Analyses of Phosphorescences of 10^{-3} M $C_6D_5CH_3$ and 10^{-3} M $C_6D_5CD_3$ in Polycrystalline Methylcyclohexane Matrices at 77°K.

Toluene-d5		Toluene-d8		Assignment[a]
$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	
29145	0	29145	0	0,0
28995	150	29010	135	0,y
28795	350	28820	325	0,x
28570	575	28565	580	0,v
28410	735 sh[b]	28410	735 sh	0,r
28290	855	28295	850	0,b
28225	920	28250	895 sh	0,a
28170	975 sh	28170	975 sh	0,p
27995	1150	27980	1165	0,q
27600	1545	27610	1535	0,ℓ;0,k
27440	1705 sh	27450	1695 sh	0,p+k
27210	1935 sh	27210	1935 sh	0,2xp
27005	2140	26985	2160 sh	0,p+q
26855	2290	26870	2275 sh	0,ℓ+r;0,k+r
26725	2420	26740	2405 sh	0,a+ℓ;0,a+k
26645	2500	26655	2490	0,ℓ+p;0,k+p
26455	2690	26455	2690 sh	0,2xp+r
26035	3110	26060	3085	0,k+ℓ:0,2xk
25820	3325	25840	3305	0,2xa+ℓ;0,2xa+k
25510	3635	25495	3650	0,ℓ+p+q;0,k+p+q
25330	3815	25330	3815	0,k+ℓ+r;0,2xk+r
25145	4000	25185	3960	0,k+ℓ+p;0,2xk+p
24905	4240			0,ℓ+2xp+r;0,k+2xp+r
24500	4645	24530	4610	0,2xk+ℓ;0,3xk
24295	4850			0,2xa+k+ℓ;0,2xa+2xk
23655	5490	23680	5465	0,a+2xk+ℓ;0,a+3xk

[a] Designation of normal modes follows Whiffen.

[b] sh = shoulder

appeared at 695 cm^{-1} but was weak and rather broad. This assignment was made on the basis of the isotope shift upon perdeuteration since the value for the corresponding peak in toluene-d8 is 580 cm^{-1}.

The main features of the toluene-h8 spectrum in methylcyclohexane solvent include the very intense band at 1580 cm^{-1}, which is attributed to one quantum of a b_2 vibration, the C-C stretching mode ℓ. There appears a shoulder at 1595 cm^{-1}. The shoulder is not sharp but is definitely present for all toluenes in this study at 77°K and is clearly present at 4°K in crystalline benzene. It is assigned as the a_1 C-C stretching mode k. The 1580 cm^{-1} band serves as a false origin and its shoulder combines with a_1 modes r, p, a and k to account for the majority of the bands. No progressions in non-totally symmetric modes are observed. The bands $0,2 \times \ell$ and $0,3 \times \ell$ seem to be absent, as well as progressions in the low frequency out-of-plane b_1 modes, as mentioned above. Mode p also forms a progression. No methyl modes seem to be present in the spectrum, neither for toluene-h8 nor for any of its deuterated relatives.

b. Toluene-α-d3

The phosphorescence spectrum of toluene-α-d3 is quite similar to that for toluene-h8. The 0,0 transition appears at 29,020 cm^{-1} and the most intense peak in the spectrum is assigned as $0,\ell$ with 0,k appearing as a slight shoulder on this bond. The a_1 mode a appears as a band of medium intensity and the a_1 modes r, p and a appear in combinations with the progression in k. There is a progression in p but it is very weak and $0,3 \times p$ does not appear. The phosphorescence spectrum of this mole-

cule is presented in Figure 4.2 and the vibrational analysis is given in Table 4.3.

c. Toluene-d8

The phosphorescence spectrum and vibrational analysis for toluene-d8 are given in Figure 4.2 and Table 4.4, respectively. The 0,0 transition was observed at 29,145 cm^{-1} indicating that perdeuteration of toluene shifts this transition 135 cm^{-1} to the blue. The totally symmetric mode a is again prominent but is shifted to 850 cm^{-1}. This large isotope shift is expected for mode a when toluene is perdeuterated so that the assignment of the 0,a transition in toluene is substantiated. The presence of the a_1 fundamental q which appears as a shoulder at 1215 cm^{-1} in toluene-h8 is also affirmed since it appears in the toluene-d8 spectrum as a weak band at 1165 cm^{-1}. As was the case with toluene-h8 and toluene-α-d3, the most intense band of the spectrum is due to the 0,ℓ transition and it appears at 1535 cm^{-1} in toluene-d8. Modes a, p and r, the latter two of which shift to 975 and 735 cm^{-1}, respectively, combine with the false origin ℓ and the progression in k. Mode a also combines with the progression in k and there is a weak progression in p. The low frequency out-of-plane modes v, x and y are shifted quite dramatically with x moving from 445 cm^{-1} to 325 cm^{-1} and y from 200 to 135 cm^{-1}. These shifts are as expected on the basis of infrared frequencies reported for toluene-d8. As was mentioned previously, the most intense band in the spectrum of toluene-h8 was due to 0,ℓ at 1580 cm^{-1}. It was possible to resolve a shoulder at 1595 cm^{-1} which was assigned as a quantum of the a_1 mode k. According to infrared data (see Table 4.1), perdeuteration affects both

both transitions to the same extent, shifting them approximately 30 cm^{-1} to the blue. However, in the spectrum of toluene-d8 in methylcyclohexane, the two bands were so close together that they could not be resolved. Since the b_2 mode ℓ was found to be much more intense in the spectra of the monodeuterated toluenes, toluene-h8 and toluene-α-d3, the most intense band of the toluene-d8 and toluene-d5 spectra was assigned as 0,k also.

d. Toluene-d5

The phosphorescence spectrum of toluene-d5 is almost identical to that of toluene-d8, and the vibrational analysis presented for the latter is quite valid for toluene-d5 also. The only difference in the spectra of the two molecules is that the band at 920 cm^{-1} in toluene-d5 appears as a doublet with the lower frequency member being assigned as 0,b (850 cm^{-1}) while the 920 cm^{-1} component was assigned as a quantum of the a_1 mode a. There is the usual intense band at 1545 cm^{-1} assigned as 0,ℓ and the fundamentals p, r and a combine with k. The 0,0 transition was observed at 29,145 cm^{-1}, this value being identical to that obtained for toluene-d8. The phosphorescence spectrum of toluene-d5 is presented in Figure 4.2 and the vibrational analysis is given in Table 4.4.

e. Para-Deuterated Toluene

The overall appearance of the phosphorescence spectrum of para-deuterated toluene is similar to that of toluene-h8. The vibrational analyses, as expected, are also similar for both molecules. Vibrational mode p involves the para position and it is shifted from 1000 cm^{-1} in toluene-h8 to 985 cm^{-1} in para-deuterated toluene. For this molecule, the 0,0 transition was assigned as 29,020 cm^{-1}. The

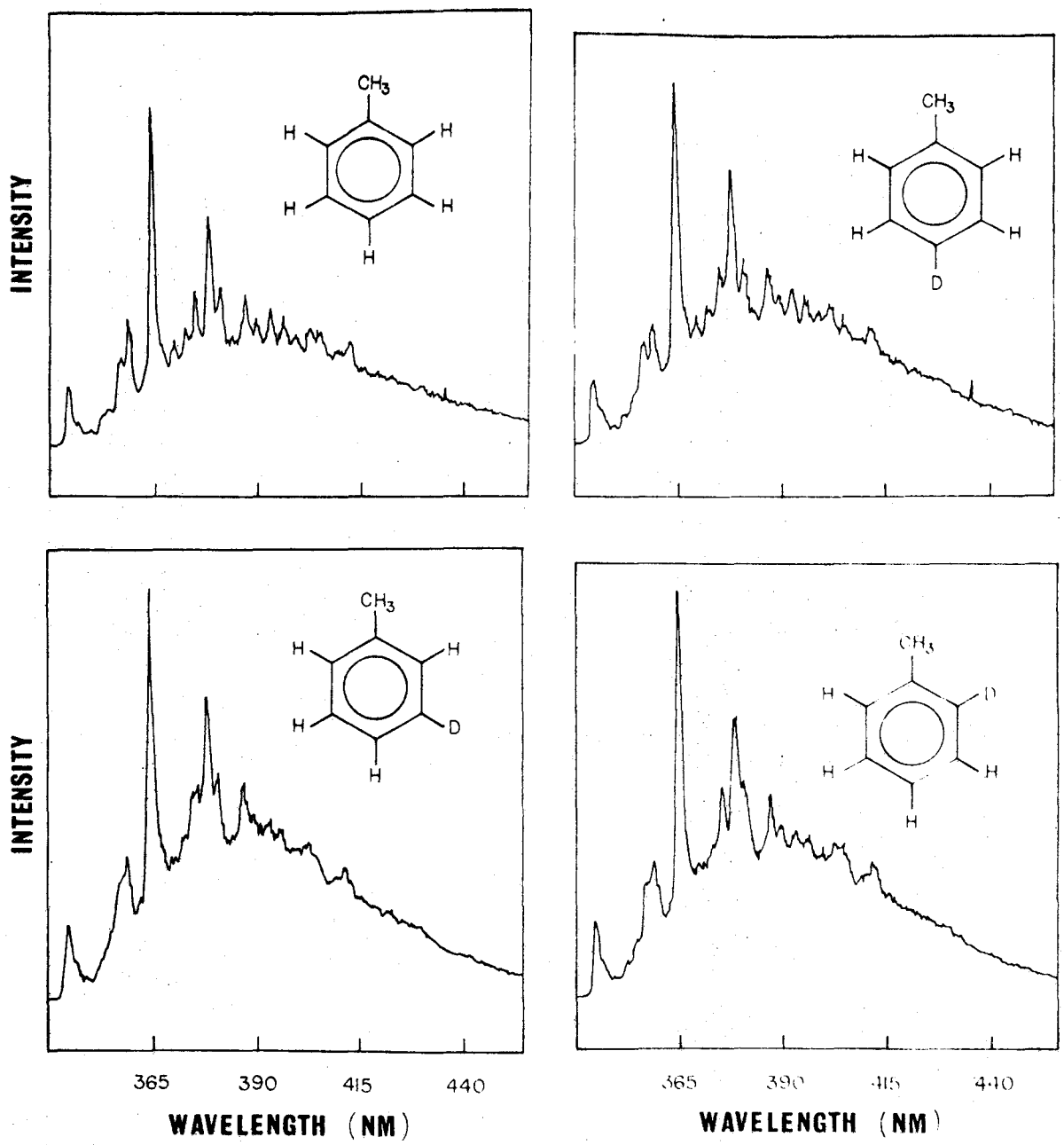

Figure 4.3 Phosphorescence spectra of (clockwise from upper left) toluene-h8, para, ortho and meta deuterated toluenes, all solutions 10^{-3}M in methylcylcohexane matrices at 77°K.

TABLE 4.5

Vibrational Analyses of Phosphorescences of 10^{-3} M para-D-$C_6H_4CH_3$, 10^{-3} M meta-D-$C_6H_4CH_3$, and 10^{-3} M ortho-D-$C_6H_4CH_3$ in Polycrystalline Methylcyclohexane Matrices at 77°K.

para-d-Toluene		meta-d-Toluene		ortho-d-Toluene		Assignment[a]
$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	
29020	0	29020	0	29020	0	0,0
28850	170	28835	185	28845	175	0,y
28615	405	28605	415	28605	415	0,x
28435	585	28395	625	28395	625	0,f
		28345	675			0,v
28210	810	28210	810	28210	810	0,r
28035	985	28020	1000	28020	1000	0,p
27955	1165	27865	1155	27895	1125	0,a
27810	1210 sh[b]	27810	1210	27810	1210	0,q
27450	1570	27450	1570	27450	1570	0,ℓ
27430	1590 sh	27425	1595 sh	27425	1595 sh	0,k
27065	1955	27020	2000	27025	1995	0,2xp
26855	2165	26860	2170	26890	2130	0,a+p
26665	2355	26665	2355	26655	2365	0,ℓ+r;0,k+r
		26590	2430			0,f+p+r
26475	2545	26450	2570	26450	2570	0,ℓ+p
26450	2570 sh	26420	2600 sh	26425	2595 sh	0,k+p
26275	2745	26280	2740	26335	2685	0,ℓ+a;0,k+a
26060	2960	26035	2985	26010	3010	0,3xp
25875	3145	25865	3155	25865	3155	0,k+ℓ
		25815	3205 sh	25800	3210 sh	0,2xk
25705	3315	25685	3335	25700	3320	0,ℓ+p+r;0,k+p+r
25485	3535	25445	3575	25445	3575	0,2xp+ℓ;0,k+2xp
25290	3730	25255	3765	25280	3740	0,a+ℓ+p;0,a+k+p
25055	3965	25055	3965	25080	3940	0,k+ℓ+r;0,2xk+r
24895	4125	24845	4175	24875	4145	0,k+ℓ+p;0,2xk+p
24675	4345	24710	4310	24765	4255	0,a+k+ℓ;0,a+2xk

TABLE 4.5 (Continued)

para-d-Toluene		meta-d-toluene		ortho-d-toluene		Assignment[a]
$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	
		24400	4620			0,3xp+ℓ;0,k+3xp
24315	4705	24295	4725	24295	4725	0,2xk+ℓ;0,3xk
23920	5100					0,k+ℓ+2xp;0,2xk+2xp
23705	5315	23725	5295	23795	5225	0,a+k+ℓ+p;0,a+2xℓ+p
		23485	5535			0,2xk+ℓ+r;0.3xk+r
23350	5670	23255	5755	23300	5710	0,2xk+ℓ+p;0.3xk+p

[a] Designation of normal modes follows Whiffen.

[b] sh = shoulder

spectrum is depicted in Figure 4.3 and the vibrational analysis is presented in Table 4.5.

f. Meta-Deuterated Toluene

The vibrational analysis presented for meta deuterated toluene in Table 4.5 is almost identical to that for toluene-h8, and the spectra are similar in appearance. The 0,0 transition was observed at 29,020 cm^{-1} and the spectrum is depicted in Figure 4.3 .

g. Ortho-Deuterated Toluene

The spectrum of ortho-deuterated toluene, Figure 4.3 is not significantly different from that of toluene-h8 either. The 0,0 band was assigned as 29,020 cm^{-1}, a value which is slightly to the blue of that for toluene-h8 and the wavenumber values of the 0,0 bands for the three monodeuterated toluenes are the same. The band assigned to the 0,a transition is shifted, appearing at 1125 cm^{-1} while the same transition appeared at 1165 cm^{-1} in toluene-h8. In the meta deuterated toluene, this transition is shifted only slightly, appearing at 1155 cm^{-1}. The vibrational analysis of ortho-deuterated toluene is given in Table 4.5.

4.2 DISCUSSION OF PHOSPHORESCENCE OF TOLUENE

The phosphorescence spectra of all the toluenes considered here are similar in appearance and the vibrational analysis of the parent is strongly reinforced by the analyses of the other molecules.

However, the phosphorescence spectra were quite different in appearance from the fluorescence (see Section 4.3). In the phosphorescence spectra, p forms only a very short progression while the longest progression is

in k. Schematic diagrams of both vibrational modes are presented in Figure (4.1) and it can be seen that they are somewhat complementary. For a molecule having an excited state geometry different from that of the ground state, the most prominent progression is in that mode which transforms the molecule from one geometry to the other.

The progressions in modes k and p, together with the lack of any progression in out of plane vibrations, imply that the excited triplet state is planar. The appearance of the progression in k is consistent either with a quinoidal geometry, i.e., the benzene ring having two short and four long bonds, with the methyl group at the apex of two of the long bonds, or with an antiquinoidal geometry. For toluene in a benzene matrix at 4°K, Haaland and Nieman[10] reported that the triplet state was quinoidally distorted, with a difference in length between long and short bonds of 0.035 Å. The lower resolution of the present spectra preclude a quantitative treatment as presented by these authors. Haaland and Nieman also estimated that the methyl group of toluene was out-of-the-plane of the ring by 3.6° in a benzene matrix at 4°K. The absence of out-of-plane vibrational progressions in methylcyclohexane matrix at 77°K suggests that the triplet state geometry of toluene is solvent-sensitive, as has been reported for benzene in various matrices. The main progression in toluene's phosphorescence is different from benzene's. There the main progression is in the breathing mode, indicating a hexagonal geometry with an overall increase in size.

Next, the prominence for the b_2 false origin, mode ℓ, in the phosphorescence spectrum of toluene will be discussed. It is necessary

first to recall the mechanism proposed for the phosphorescence of the parent, benzene. It has been suggested by Albrecht, that the $T_1 \rightarrow S_0$, $^3B_{1u} \rightarrow {}^1A_{1g}$ radiative transition in benzene arises from a second order mechanism,[49] wherein the lowest triplet state, $^3B_{1u}$, vibronically couples with a higher triplet state $^3E_{1u}$, which in turn spin-orbit couples with a $^1A_{2u}$ singlet state, whose transition to the ground state is allowed. This pathway gives the lowest triplet state some $^1A_{2u}$ character (the mixing of triplets into the ground singlet state is regarded as energetically unfeasible) and confers out-of-plane polarization on the phosphorescence. In other words, the phosphorescence is polarized like the singlet-singlet transition(s) that the triplet state "borrows" or "steals" intensity from. In-plane polarized phosphorescence is accounted for by replacing $^1A_{2u}$ by $^1E_{1u}$ in the above scheme. Experimentally, the phosphorescence of benzene is mainly out-of-plane polarized, suggesting the importance of the $^1A_{2u}$ pathway. Direct first-order spin-orbit coupling in benzene is forbidden.

Turning to toluene, the first-order spin-orbit coupling term between the singlet states Γ_i and T_1 (assumed to be $^3A_1$, as for other monosubstituted benzenes) is no longer forbidden. The transition moment due to this first order term is of the form

$$R^{I}_{T_1 \rightarrow S_0} = \sum_i R_{S_0 \rightarrow {}^1\Gamma_i} \times \frac{\langle {}^1\Gamma_i | H_{SO} | {}^3A_1 \rangle}{E({}^3A_1) - E({}^1\Gamma_i)} \times \langle \Phi_k | \Phi_0 \rangle \qquad (4.1)$$

where $R_{S_0 \rightarrow {}^1\Gamma_i}$ represents the transition moment of the $S_i \rightarrow \Gamma_i$ process and $\langle \Phi_k | \Phi_0 \rangle$ is the overlap integral between the k^{th} vibrational level of S_0 and the zeroth vibrational level of the lowest triplet state. The latter integral vanishes unless the vibrational wavefunction Φ_k be-

longs to the totally symmetric representation. It should be noted that this type of term can only be responsible for transitions from T_1 to totally symmetric vibrational levels of S_0 or to vibrational levels of S_0 where even multiples of non-totally symmetric vibrational are excited. The $^1\Gamma_i$ states can be $^1B_1$ and/or $^1B_2$.

The large intensity of one quantum of the non-totally symmetric b_2 mode ℓ in the phosphorescence spectrum has to be accounted for by a second order term in the spin-orbit coupling mechanism. If the second order mechanism for benzene mentioned above also holds for toluene, then one can write the transition moment due to this second order term as:

$$R^{II}_{T_1\rightarrow S_0}(k) = \sum_{i,j} R_{S_i\rightarrow {}^1\Gamma_i} \times \frac{\langle {}^1\Gamma_i | H_{SO} | {}^3\Gamma_j \rangle}{E({}^3\Gamma_j) - E({}^1\Gamma_i)} \times \frac{\langle {}^3\Gamma_j | \frac{\partial H_0}{\partial Q,a} | {}^3A_1 \rangle}{E({}^3A_1) - E({}^3\Gamma_j)} \times \langle \Phi_k | Q,a | \Phi_0 \rangle \qquad (4.2)$$

where Q,a represents the perturbing normal coordinate in the vibronic interaction, in this case mode ℓ. The symmetry identification (b_2) of mode ℓ requires $(\frac{\partial H_0}{\partial Q,a})$ to be of B_2 symmetry and therefore $^3\Gamma_j$ to be $^3B_2$. If $^1\Gamma_i$ is $^1B_1$, which is the $^1A_{2u}$ state of benzene lowered from D_{6h} to C_{2v} symmetry, then the intensity of mode ℓ in the phosphorescence spectrum can be accounted for by a large contribution from $R^{II}(\ell)$:

$$^3A_1 \xrightarrow[\text{coupling}]{\text{vibronic}} {}^3B_2 \xrightarrow[\text{coupling}]{\text{spin orbit}} {}^1B_1 \,. \qquad (4.3)$$

The total transition probability P of the phosphorescence transition is:

$$P\alpha[\sum_k R^I(k)_{T_1\rightarrow S_0} + \sum_k R^{II}(k)_{T_1\rightarrow S_0}] \,. \qquad (4.4)$$

The summation occurs over all the vibrational bands of S_0, such as those presented in the vibrational analyses of the phosphorescence of toluene.

R^{II} accounts for all the intensity in benzene and, in toluene, this term is also of prime importance, as can be seen by investigating the intensity of the R^{I} contributions versus that of the R^{II} contributions. Of course, it is impossible to give a quantitative evaluation to R^{I}/R^{II} from this work since bands do overlap and a given one can still have several contributions. The vibrational analysis lists the main contributions to the band. Nevertheless, qualitatively, R^{II} plays a much greater role than R^{I} in toluene. For example, the $0,\ell$ band is about four times as intense as the 0,0 band. Methyl perturbation while giving a non-zero R^{I} contribution, still does not drastically change the fact that the vibronic spin-orbit pathway is still the dominant triplet intensity route. This result is in marked contrast to the phosphorescence of C_6H_5CCH,[50] C_6H_5CN,[41] and C_6H_5NC[51] studied in our laboratory, where the 0,0 transitiion is very intense, and the $0,\ell$ transition was not observed. These latter three substituents seem to perturb benzene's triplet state much more than methyl does.

4.3 VIBRATIONAL ANALYSIS OF FLUORESCENCE OF TOLUENES

It was found that 10^{-3}-10^{-4} M solutions of the toluenes in methylcyclohexane provided the sharpest spectra. At higher concentrations, the spectra were not well resolved and there was a decrease in intensities of the 0,0 bands due to self-absorption caused by the overlap of emission and absorption regions of the molecule. Spectra involving cyclohexane as solvent were quite resolved also but were not as detailed as those obtained with methylcyclohexane. The vibrational analyses presented here are for the toluenes in methylcyclohexane but the overall appearance of the spectra is not very different if cyclohexane is used as solvent.

a. Toluene-h8

The 0,0 band was of medium intensity and was assigned as 37,320 cm^{-1}. The first intense band at 775 cm^{-1} was assigned to the totally symmetric mode r and the most intense band in the spectrum was observed at 985 cm^{-1}. It was assigned to the 0,p transition. The totally symmetric mode, q, was observed as a strong band at 1220 cm^{-1}. At lower frequencies, two bands at 520 cm^{-1} and 625 cm^{-1} were attributed to a quantum of the totally symmetric mode, t, and a quantum of the b_2 vibration s, respectively. The b_2 mode u was observed at 355 cm^{-1} but it was of very low intensity. The longest progression is in the ring breathing mode, p, up to 0,5 x p and there is another quite strong progression in r. Mode q enters into combinations with both progressions while the transition 0,s acts as a false origin for progressions in p and r. For example, four quanta of mode p are based on s.

The 0,0 band of the gas phase emission spectrum of toluene was

observed at 37,474 cm^{-1} by Kahane-Paillous and Leach.[11] With the exception of some low frequency vibrations, most fundamentals observed in that spectrum were also seen in this study. Watmann-Grajcar[13] assigned the 0,0 band of the toluene fluorescence spectrum with cyclohexane solvent as 37,161.5 cm^{-1} at 77°K. Bands at 123, 223, 286 and 405 cm^{-1} to the red of the origin were also observed in that spectrum but were not corraborated by this study. The 123 cm^{-1} band was attributed to a carbon-methyl torsional mode in their analyses. In the spectra of this study, where methylcyclohexane was used as solvent, a weak broad band was observed at 355 cm^{-1} and was assigned to the transition 0,u. In the spectra of toluene-h8 no splitting of spectral peaks due to solvent effects was observed. This state of affairs contrasts with the observations of workers who noticed splittings due to either the presence of the solvent in two crystalline modifications,[29] or to emission from solute molecules having different orientations within the solvent.[26] The spectrum is depicted in Figure 4.4 and the vibrational analysis is presented in Table 4.6 .

b. Toluene-α-d3

There is minimal difference between the fluorescence spectra of toluene-α-d3 and toluene-h8 The vibrational analysis of the former is also presented in Table 4.6 . In the spectrum of toluene-α-d3 the band assigned as 0,q (1225 cm^{-1}) is not as intense as in toluene-h8 and bands arising from combination of q with other progressions are weakened slightly. Secondly, the frequencies at 1555 cm^{-1} (assigned as 0,2 x r) and 1605 cm^{-1} (0,p + s) of toluene-h8 are more widely separated

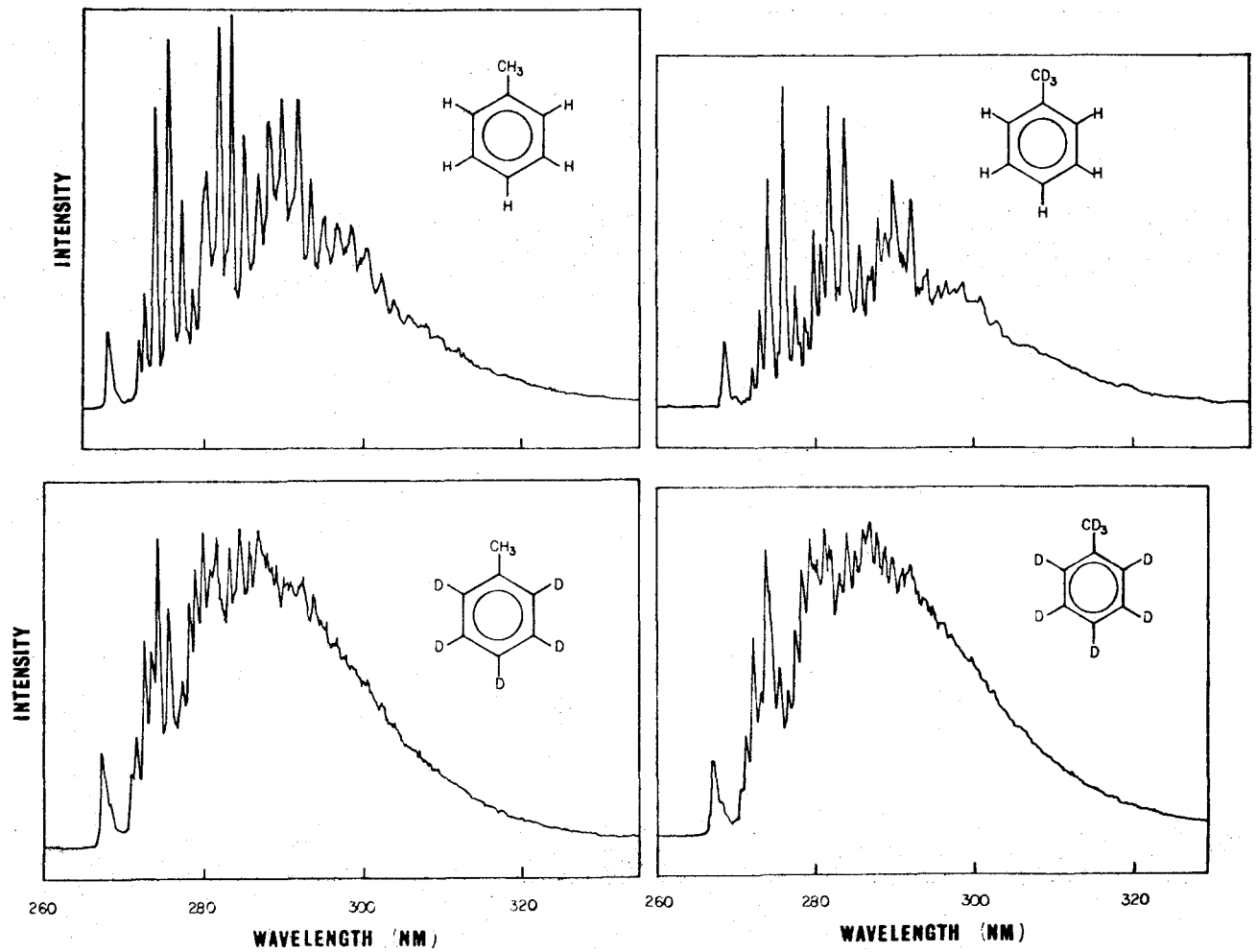

Figure 4.4 Fluorescence spectra of (clockwise from upper left) toluene-h8, toluene-α-d3, toluene-d8 and toluene-d5, all solutions 10^{-3} M in methylcyclohexane matrices at 77°K.

TABLE 4.6

Vibrational Analyses of Fluorescences of 10^{-3}M $C_6H_5CH_3$ and 10^{-3} M $C_6H_5CD_3$ in Polycrystalline Methylcyclohexane Matrices at 77°K.

Toluene-h8		Toluene-α-d3		
$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	Assignment[a]
37230	0	37260	0	0,0
36875	355	36930	330	0,u
36710	520	36750	510	0,t
36605	625	36645	615	0,s
36455	775	36510	750	0,r
		36445	815	0,r'
36245	1000	36260	1000	0,p
36010	1205	36035	1225	0,q
35930	1300 sh[b]	35995	1265 sh	0,r+t
35830	1400	35880	1380	0,r+s
35715	1515			0,p+t
35675	1555	35755	1505	0,2xr
35625	1605	35640	1620	0,p+s
35575	1655 sh	35615	1645 sh	0,s+2xt
35450	1780	35500	1760	0,p+r
		35425	1835 sh	0,p+r'
35300	1930	35335	1925	0,r+s+t
35235	1995	35260	2000	0,2xp;0,q+r
		35235	2025 sh	0,b+p
35075	2155 sh	35150	2110	0,2xr+s
35040	2190	35025	2235	0,p+q
34955	2275	35000	2260 sh	0,p+r+t
34830	2400 sh	34870	2390	0,p+r+s
34805	2425	34830	2430	0,2xq
34785	2445 sh			0,r+s+2xt
34650	2580	34745	2515	0,2xr+p

TABLE 4.6 (Continued)

$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	Assignment[a]
34625	2605	34640	2620	0,2xp+s
		34600	2660	0,p+s+2xt
34520	2710	34530	2730 sh	0,p+q+t
34470	2760	34495	2765	0,2xp+r;0,q+2xr
34445	2785	34470	2790	0,b+p+r
34225	3005	34260	3000	0,3xp;0,p+q+r
34210	3020	34235	3025	0,b+2xp
34035	3195	34015	3245	0,2xp+q
33840	3390	33820	3440	0,p+2xq
33625	3605	33740	3520	0,2xp+2xr
		33600	3660	0,3xp+s
33445	3785	33500	3760	0,3xp+r
33235	3995	33245	4015	0,4xp;0,2xp+q+r
33035	4195	33025	4235	0,3xp+q
32860	4370	32840	4420	0,2xp+2xq
32650	4580			0,4xp+s
32445	4785	32540	4720	0,4xp+r
32230	5000			0,5xp;0,3xp+q+r

[a] Designation of normal modes follows Whiffen.

[b] sh = shoulder

in toluene-α-d3 because the former shifts to 1505 cm^{-1} in this molecule. Of course, the 0,r transition is shifted from 775 cm^{-1} in toluene-h8 to 750 cm^{-1} in toluene-α-d3 so the assignment of 0,2 x r is substantiated. A third difference is the appearance of a distinct shoulder at about 815 cm^{-1} in toluene-α-d3 . The transition causing it would have to undergo a dramatic shift in order to appear at 815 cm^{-1} since, in toluene-h8 , the peak assigned to 0,r is very sharp with no shoulders being evident. It is believed that the mode causing it is a ring-substituent rocking mode which can be either an out-of-plane mode, or a non-totally symmetric in-plane one. For toluene-h8 the infrared frequency for this mode is $\sim$ 1030 cm^{-1} (refer to Table 4.1) and since vibration p(1000 cm^{-1}) is very intense in the fluorescence spectrum, the rocking mode frequency is probably buried under it. When the spectra of the two molecules are run at comparable signal to noise ratios, the toluene-α-d3 spectrum shows a peak at 1000 cm^{-1} which is much sharper than that of the toluene-h8 spectrum. It is therefore believed that the ring substituent bending mode shifts to 815 cm^{-1} upon deuteration of the methyl group. In spite of these differences, the overall appearances of the fluorescence spectra is similar for both molecules. The 0,0 transition for the toluene-α-d3 spectrum was assigned as 37,260 cm^{-1} and the spectrum is depicted in Figure 4.4 .

c. Toluene-d8

The fluorescence spectrum of toluene-d8 is shown in Figure and the vibrational analysis is listed in Table 4.7 . The 0,0 transition was observed at 37,410 cm^{-1} which is to be compared with the

TABLE 4.7

Vibrational Analyses of Fluorescences of 10^{-3} M $C_6D_5CH_3$ and 10^{-3} M $C_6D_5CD_3$ in Polycrystalline Methylcyclohexane Matrices at 77°K.

Toluene-d5		Toluene-d8		
$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	Assignment[a]
37385	0	37410	0	0,0
37245	140	37245	165	0,lattice
36875	510	36915	495	0,t
36790	595	36820	590	0,s
36655	730	36700	710	0,r
		36670	740 sh	
36535	850	36565	845	0,b or 0,r' in toluene-d-8
36430	955	36455	955	0,p
		36415	995 sh	0,2xt
36245	1140	36245	1165	0,q
36050	1335	36100	1310	0,r+s
36025	1360			0,b+t
35930	1455	35995	1415	0,2xr
35830	1555	35870	1540	0,p+s
35805	1580 sh[b]			0,b+r
35700	1685	35755	1655	0,p+r
35675	1710 sh	35665	1745	0,q+s
35575	1810	35625	1785	0,b+p
35485	1900	35525	1885	0,2xp
35425	1960 sh	35425	1985	0,b+q
35300	2085	35275	2135	0,p+q
35110	2275	35150	2260	0,p+r+s
35090	2295			0,2xq
34975	2410	35025	2385	0,p+2xr
34855	2530	34905	2505	0,2xp+s
34830	2555			0,b+p+r

TABLE 4.7 (Continued)

$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	Assignment[a]
34785	2600	34805	2605	0,2xp+r
34700	2685			0,p+q+s
34640	2745	34685	2725	0,b+2xp
34555	2830	34565	2845	0,3xp
34425	2960	34445	2965	0,b+p+q
34340	3045	34330	3080	0,2xp+q
34175	3210	34210	3200	0,2xp+r+s
		34095	3315	0,2xp+2xr
33990	3395	33965	3445	0,3xp+s
33840	3545	33840	3570	0,3xp+r
		33695	3715	0,b+3xp
33590	3795	33615	3795	0,4xp
33435	3950			0,3xp+q
33265	4120	33255	4155	0,3xp+r+s
33035	4350			0,4xp+s
32875	4510	32895	4515	0,4xp+s
		32660	4750	0,5xp

[a] Designation of normal modes follows Whiffen.

[b] sh = shoulder

37,351.0 cm^{-1} value assigned by Watmann-Grajcar, who used cyclohexane solvent at 77°K.[13] Fundamental frequencies at 102, 198, 297, 337 and 400 cm^{-1} were also observed in that work but no definite bands appeared below 500 cm^{-1} in the toluene-d8 fluorescence spectrum of this study. The band at 845 cm^{-1} could be assigned to the methyl group rocking mode r', but mode b is probably a larger contributor. As is the case in toluene-h8 , the main progressions are in the a_1 modes p and r but the bands are broadened and somewhat less intense than their counterparts in toluene-h8 . The 0,p transition moves from 1000 cm^{-1} in toluene-h8 to 955 cm^{-1} in this molecule while 0,r shifts from 775 cm^{-1} to 710 cm^{-1} in toluene-d8 . Perdeuteration also caused the bands at 625 and 520 cm^{-1} to shift to 590 and 495 cm^{-1}, respectively. These isotope shifts are consistent with those expected on the basis of infrared and Raman data for toluene-h8 and toluene-d8 (refer to Table 4.1) and serve to substantiate the assignments presented here for toluene-h8 fluorescence.

d. Toluene-d5

The fluorescence spectrum of toluene-d5 is similar to that of toluene-d8 . It should be noted, however, that the toluene-d5 spectrum is sharper and that the band assigned to mode q is not only sharper but much more intense than it was in toluene-d8 . The band assigned to 0,p is very sharp and there are no shoulders associated with it. The principal features of the spectrum are the intense progressions in r and p, with the b_2 mode s acting as a false origin. The vibrational analysis is given in Table 4.7 and the spectrum is depicted in Figure 4.4. The 0,0 band appears at 37,385 cm^{-1}.

e. Para-deuterated toluene

Deuteration at the para position causes the 0,0 value to change only slightly from 37,230 cm^{-1} to 37,245 cm^{-1}. The overall appearance of the spectrum is similar to that of toluene-h8 because the progressions in p and r remain the most prominent feature of the spectrum. There are shoulders at 790, 830, 1015 and 1235 cm^{-1} which could be caused by the glass emissions if the sample is not totally polycrystalline. However, it is more likely that they are due to emission from toluene-h8 impurity because the wavelength values of the shoulders correspond, within experimental error, to those of toluene-h8.

The h8 transition 0,b could be contributing intensity to the shoulder at 1015 cm^{-1} since, according to infrared data (Refer to Table (4.1)), it has a wavenumber value in this region. Other prominent bands in the spectrum had shoulders which were attributed to toluene-h8. The vibrational analysis is presented in Table 4.8 and the spectrum is shown in Figure 4.5.

f. Meta-deuterated toluene

The wavenumber value of the 0,0 transition of meta-deuterated toluene is 37,260 cm^{-1} which is 30 cm^{-1} to the blue of that for toluene-h8. The spectrum resembles that of para-deuterated toluene with only minor differences. The shoulders which appeared at 790 and 830 cm^{-1} in para-deuterated toluene, are resolved as individual peaks in the spectrum of the meta compound where they appeared at 790 and 855 cm^{-1} respectively. The 0,r transition appears at 750 cm^{-1} and 0,2 x r is also shifted so that it overlaps with 0,p + t at 1520 cm^{-1}. Many of the shoulders which were assigned to toluene-h8 in the para fluorescence

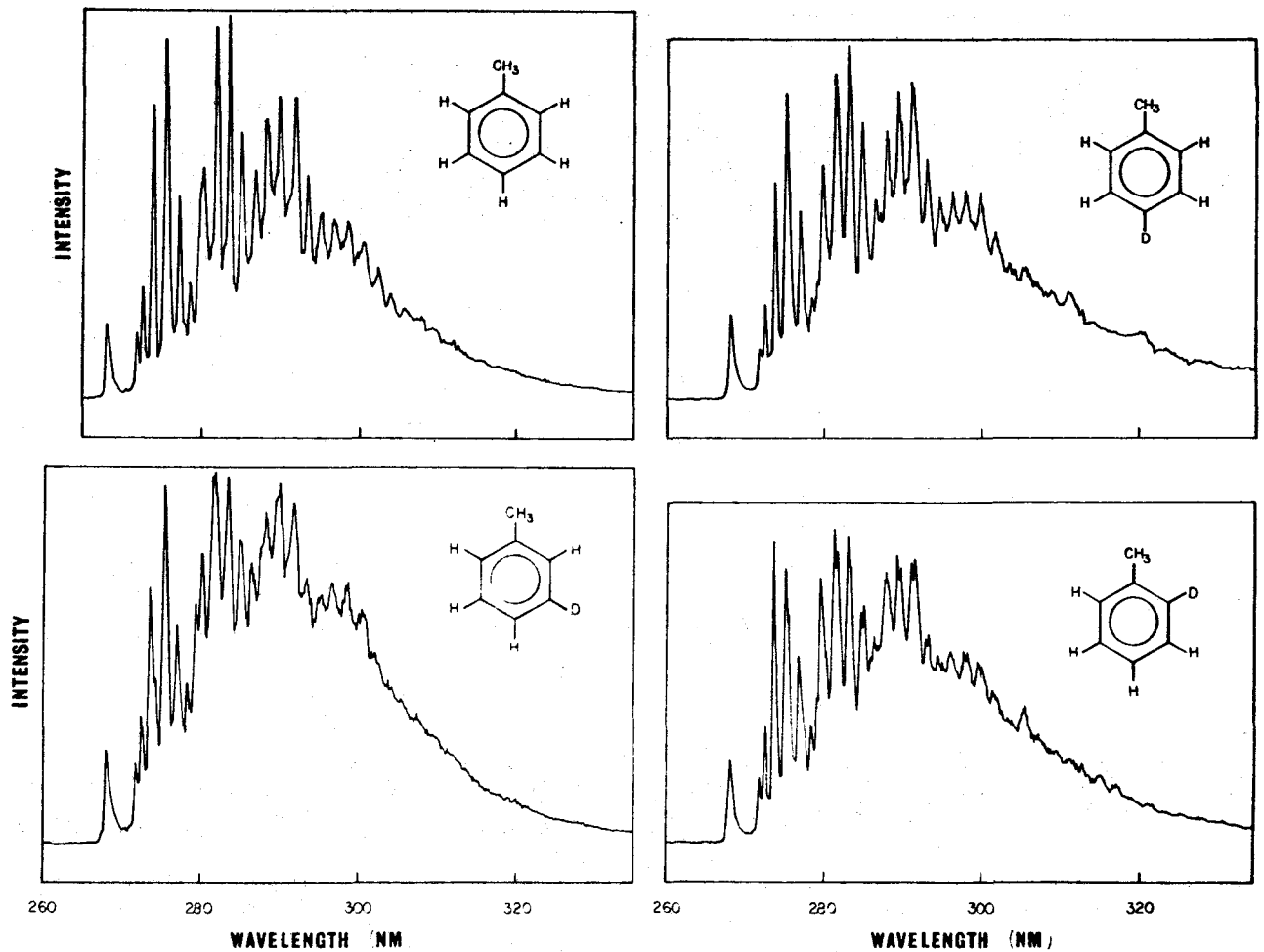

Figure 4.5 Fluorescence spectra of (clockwise from upper left) toluene-h8, para, ortho and meta-deuterated toluenes, all solutions 10^{-3} M in methylcyclohexane matrices at 77°K.

TABLE 4.8

Vibrational Analyses of Fluorescences of 10^{-3} M para-D-$C_6H_5CH_3$, 10^{-3} M meta-D-$C_6H_5CH_3$ and 10^{-3} M ortho-D-$C_6H_5CH_3$ in Polycrystalline Methylcyclohexane Matrices at 77°K .

para-d-Toluene		meta-d-Toluene		ortho-d-Toluene		
$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	Assignment[a]
37245	0	37260	0	37260	0	0,0
36915	315	36915	345	36930	330	0,u
36740	505	36740	520	36750	510	0,t
36645	600	36655	605	36645	615	0,s
36485	760	36510	750	36485	775	0,r
36455	790 sh[b]	36470	790	36445	815 sh	h8 imp.[c]
36415	830 sh	36405	855	36405	855 sh	
36260	985	36260	1000	36260	1000	0,p
36230	1015	36230	1030	36230	1030	h8 imp.;0,b
36035	1210	36060	1200	36060	1200	0,q
36010	1235 sh	36035	1225 sh	36025	1235 sh	h8 imp.
35985	1260 sh	35995	1265 sh	35985	1275 sh	0,r+t
35870	1375	35895	1365	35870	1390	0,r+s
35755	1490	35740	1520	35755	1505 sh	0,p+t
35665	1580 sh			35690	1570	0,2xr
35650	1595	35640	1620	35640	1620	0,p+s
35585	1660 sh	35615	1645 sh	35615	1645 sh	h8 imp.
35475	1770	35500	1760	35485	1775	0,p+r
35450	1795 sh	35460	1800	35450	1810	h8 imp.;0,b+r
		35410	1850 sh	35400	1860 sh	

TABLE 4.8 (Continued)

$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	Assignment[a]
		35300	1960 sh			
35285	1960	35275	2005	35275	1985	0,2xp;0,q+r
35260	1985 sh	35235	2025	35250	2010	h8 imp.;0,b+p
35050	2195	35050	2210	35075	2185	0,p+q
35025	2220 sh	35015	2245	35015	2245	h8 imp.
34975	2270 sh					
34870	2375	34880	2380	34880	2380	0,p+r+s
34845	2400	34845	2415 sh	34870	2390	0,2xq
		34770	2490 sh	34805	2455	h8 imp.
34710	2535	34745	2515	34700	2560	0,p+2xr
34685	2560	34660	2600	34640	2620 sh	0,2xp+s
34625	2620 sh	34625	2635 sh			h8 imp.
34540	2705 sh	34540	2720 sh	34555	2705 sh	0,p+q+t
34505	2740	34505	2755	34505	2755	0,2xp+r;0,q+2xr
34470	2775	34445	2815	34460	2800	0,b+p+r;0,p+q+s
		34410	2850	34410	2850 sh	h8 imp.;0,b+q+s
34315	2930 sh	34315	2945	34315	2945 sh	
34280	2965 sh	34245	3015	34270	2990	0,3xp;0,p+q+r
34235	3010 sh	34210	3050 sh	34235	3025	h8 imp.;0,b+2xp
				34200	3060 sh	h8 imp.
34085	3160	34070	3190	34085	3175	0,2xp+q
34050	3195 sh	34025	3235	34050	3210	h8 imp.;0,b+p+q
33850	3395	33850	3410	33875	3385	0,p+2xq
33820	3425 sh			33840	3420	h8 imp.

TABLE 4.8 (Continued)

$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	Assignment[a]
				33705	3555	0,2xp+2xr
33695	3550	33680	3580	33635	3625 sh	0,3xp+s
33510	3735	33510	3750	33510	3750	0,3xp+r
33480	3765 sh	33465	3795	33465	3795	h8 imp.
33290	3955	33245	4015	33780	3980	0,4xp
33235	4010 sh					h8 imp.
		33090	4170			
33080	4165	33035	4225	33080	4180	0,3xp+q
33035	4210 sh					h8 imp.
32875	4370	32860	4400	32875	4385	0,2xp+2xq;0,3xp+r+s
32660	4585	32690	4570	32680	4580	0,4xp+s
32530	4715	32500	4760	32500	4760	0,4xp+r
32330	4915	32250	5010	32280	4970	0,5xp;0,3xp+q+r

[a] Designation of normal modes follows Whiffen.

[b] sh = shoulder

[c] Toluene-h8 impurity.

spectrum were also seen in the spectrum of the meta compound. The vibrational analysis, which is much like that of para-deuterated toluene is presented in Table 4.8 and the spectrum is presented in Figure 4.5 .

g. Ortho-deuterated toluene

Placing deuterium in the ortho position causes the 0,0 transition to shift 40 cm^{-1} to the blue of that for toluene-h8 so that it is at 37,260 cm^{-1}. The band at 775 cm^{-1}, assigned as 0,r, is slightly more intense than that due to 0,p whereas in all other molecules of this study mode p was the most intense of the fluorescence fundamentals. The vibrational analysis of this molecule is also given in Table 4.8 and the fluorescence spectrum is illustrated in Figure 4.5 .

4.4 DISCUSSION OF FLUORESCENCE OF TOLUENE

According to the vibrational analyses of the fluorescence spectra, the most prominent progression involves the ring breathing mode, p. There is also a moderately long progression in r, and q combines with both progressions. The schematic representations of r and p in Figure 4.1 show that these two modes are complementary to each other. The length of the progression in these two modes implies that, in the first excited singlet state, toluene has a slightly expanded regular hexagon structure. The lack of progression in out-of-plane vibrations implies that the molecule is planar in the first excited singlet state. This behaviour is similar to that reported for benzene whose C-C bond length increases by 0.037 Å when the molecule enters the first excited singlet state.

In Section 2.8, it was stated that in cases where an electronic transition was forbidden, the symmetry selection rule (equation (2.14))

was not valid. The more general vibronic selection rule

$$R_{e'v'e''v''} = \langle \psi_{e'v'} | M | \psi_{e''v''} \rangle \tag{2.12}$$

$R_{e'v'e''v''}$ being the vibronic transition moment, applies in such instances. If the vibronic transition moment is to be non-zero, the direct product of the irreducible representations of the two vibronic states must contain the irreducible representation of at least one of the components of M. In order to obtain the irreducible representation of the vibronic state, one takes the direct product of the irreducible representations of the electronic state and of the vibrational normal mode involved.

In benzene (point group D_{6h}), the first excited singlet, or S_1 state, is of B_{2u} symmetry while S_3 transforms as E_{1u}. The direct product of the former with e_{2g} yields the latter representation so that, if an e_{2g} vibration is excited, the two electronic states mix and transitions between the totally symmetric ground state and S_1, which is now a vibronic state, can occur. This can be written as,

$$R_{e'v'e''v''} = \langle A_{1g} a_{1g} | M | B_{2u} e_{2g} \rangle \neq 0 \tag{4.5}$$

and

$$A_{1g} \otimes a_{1g} \otimes B_{2u} \otimes e_{2g} = \Gamma_{M_x, M_y} \tag{4.6}$$

In this manner, absorption from the zeroth vibrational level of $S_0(^1A_{1g})$ to vibronic states of S_1 that have a symmetry of $B_{2u} \otimes e_{2g} = E_{1u}$ is accounted for.

The fluorescence of benzene, from the zeroth vibrational level of $S_1(^1B_{2u})$ to vibronic levels of S_0 is also allowed according to the following integral:

$$R_{e'v'e''v''} = \langle A_{1g}e_{2g}|M|\ B_{2u}a_{1g}\rangle \neq 0. \tag{4.7}$$

For benzene the e_{2g} ground state vibration required occurs at 606 cm^{-1} and the fluorescence spectrum includes this vibronic component. The pure electronic component is rigorously forbidden, but may in fact occur very weakly if the molecule is in a crystal or lattice where field effects could cause slight relaxation of symmetry restrictions.

The methyl group in toluene does not represent a strong perturbation on the ring but the overall symmetry of the molecule has decreased (point group C_{2v}); the pure electronic component of the spectrum is allowed and equation (2.14) can be written:

$$R_{e'e''} = \langle\psi'|M|\psi''\rangle \neq 0 \tag{2.14}$$

where $\Gamma_{\psi'} \otimes \Gamma_{\psi''} = A_1$, B_1 or B_2. The $S_0 \leftrightarrow S_1$, $^1A_1 \leftrightarrow {}^1B_2$ transition is allowed via M_y which transforms as B_2. Nevertheless, the vibronic character inherited from the parent benzene is still evident as the intensity of the 0,0 transition is equal to that of the false origin at 620 cm^{-1}. This band is due to normal mode s which transforms as b_2. Then,

$$A_1 \otimes a_1 \otimes B_2 \otimes b_2 = \Gamma_{M_z}. \tag{4.8}$$

In other words, the vibronic false origin band is z-polarized while the 0,0 band is y-polarized. The b_2 band does not appear in the toluene fluorescence spectrum, a situation which contrasts with that observed in the phosphorescence spectrum of that molecule.

It is true that the "allowedness" of transitions is governed

by rules formulated from group theory. However, the intensity of a forbidden component is determined, in part, by the size of the energy gap between the excited electronic states which are mixing. For example, in ethynylbenzene the mixing of excited states S_1 and S_2 is strong because the S_1-S_2 energy gap is only 0.65 e.v. The corresponding energy gap in phenylisocyanide is 0.83 e.v. so S_1 and S_2 are perturbing each other strongly in this molecule also. However, in benzonitrile and toluene, the difference in energy between S_1 and S_2 is approximately 1 e.v. so the vibronic components of the spectra of these two molecules are reduced in intensity compared with the corresponding component in the fluorescence spectrum of ethynylbenzene and phenylisocyanide.

4.5 VIBRATIONAL ANALYSIS OF FLUORESCENCE OF BENZYL RADICALS

a. Benzyl-h7

The 0,0 transition of h7 is of medium intensity and in this study was observed at 21,655 cm^{-1}. Watmann-Grajcar[13] analyzed the fluorescence spectrum of h7 using cyclohexane as solvent at 77°K and found that the 0,0 band appeared at 21,666.9 cm^{-1}. The fluorescence spectra of benzyl-α-d2 and benzyl-d7 were obtained under the same conditions and analyzed but the vibronic structure was complicated in all three molecules by the presence of peak splittings due to solute molecules emitting from the monoclinic and cubic environments which coexist in the sample. Furthermore, Watmann-Grajcar observed nine low frequency vibrations between the 0,0 (monoclinic) and 531 cm^{-1}. One of those bands was assigned as the 0,0 transition from solute molecules trapped in a cubic lattice while several more transitions were attributed to lattice vibrations. The weak band at 230 cm^{-1} was ascribed to benzyl radicals trapped in an environment containing predominantly toluene molecules. Three fundamentals were assigned at 361 cm^{-1}, 393 cm^{-1} and 435 cm^{-1} with the band at 361 cm^{-1} being the most intense of the three. Furthermore, there were bands which were described as "satellite bands", that is bands arising from the coupling of lattice vibrations with vibrational modes of the solute. Ripoche,[22] however, observed the 0,0 at 21,647 cm^{-1} for the benzyl-h7 fluorescence and recorded only one low frequency band at 362 cm^{-1} when methylcyclohexane was used as solvent at liquid air temperature. In addition, Lloyd and Wood[52] recently reported the 21,682 cm^{-1} band as the fluorescence 0,0 for benzyl-h7 in an adamantane matrix. The only low frequency vibrational mode noticed

in their work was assigned at 365 cm^{-1}. A similar result was obtained in this study where the band at 355 cm^{-1} was assigned as 0,u. The two most intense bands of the spectrum, at 525 cm^{-1} and 620 cm^{-1} were assigned as 0,t and 0,s respectively while the 0,ℓ transition also gives rise to a prominant band in the spectrum. Bands due to modes r, p and q also appear but they are of low intensity. Modes r, p, t and ℓ form short progressions with no more than two quanta of any of these vibrations appearing.

The allowed component of the spectrum includes the moderately intense 0,0 band, the 0,t transition (very intense) and 0,p (weak). The forbidden, or vibronic component is based upon the very intense 0,s transition at 620 cm^{-1} which transforms as b_2. Finally the b_2 model ℓ enters into combinations with modes t, s, r and p. The fluorescence spectrum of benzyl-h7 is shown in Figure 4.6 and the vibrational analysis is presented in Table 4.9. The results of that analysis tend to confirm the work of Ripoche[22] and Lloyd et al.[52]

b. Benzyl-α-d2

There is little difference between the vibrational analysis of benzyl-α-d2 and that of benzyl-h7. The use of methylcyclohexane as solvent enabled relatively uncomplicated spectra to be acquired because, in contrast with cyclohexane systems, there were fewer peak splittings and "satellite" bands present. Watmann-Grajcar[13] observed the 0,0 transition at 21,645.8 cm^{-1} and assigned three low frequency modes at 321 cm^{-1}, 354 cm^{-1}, and 411 cm^{-1} respectively where cyclohexane was used as the solvent at 77°K. In the spectra studied here, the 0,0 band as assigned as 21,630 cm^{-1} and it was

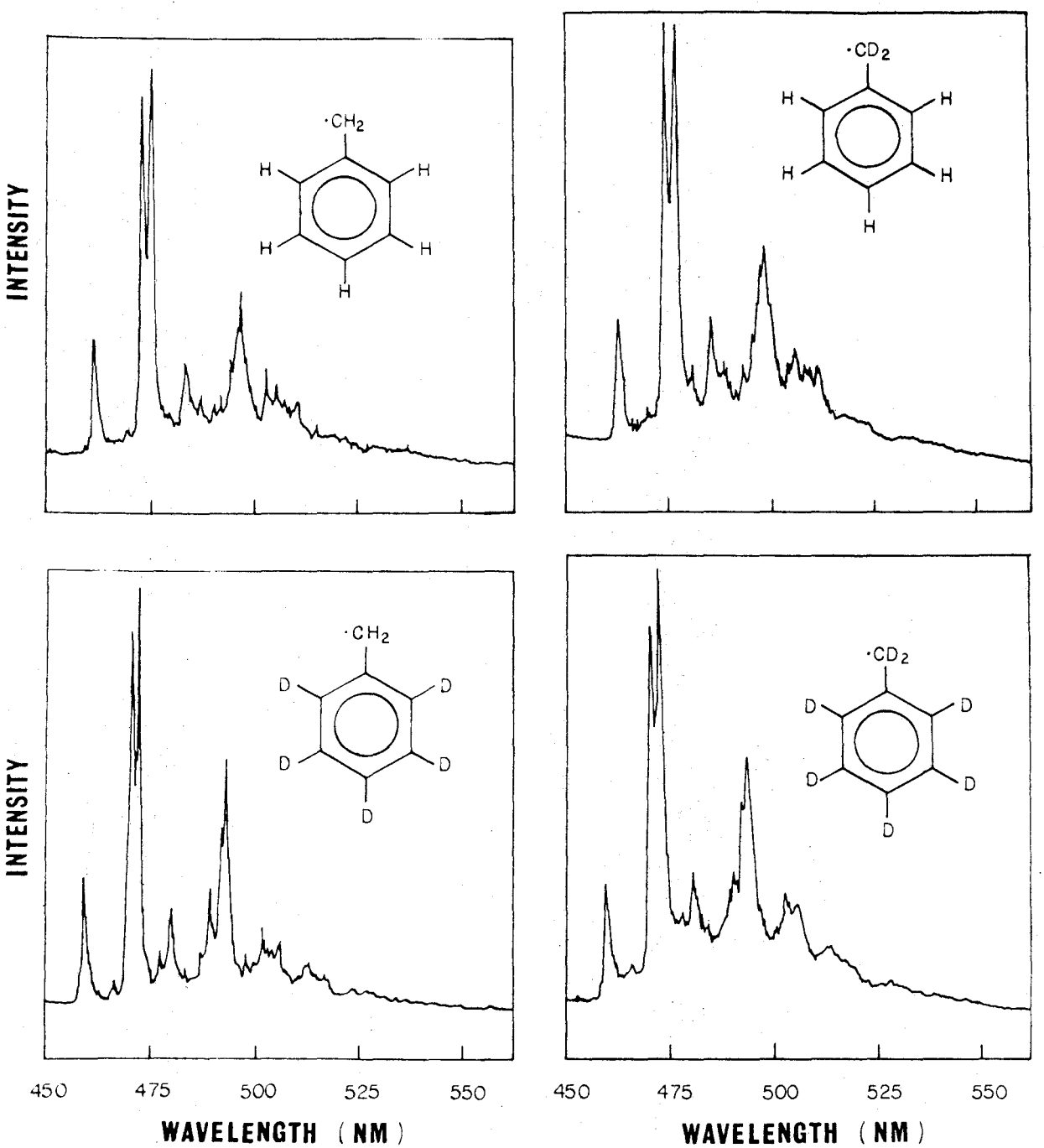

Figure 4.6 Fluorescence spectra of (clockwise from upper left) benzyl -h7, benzyl-α-d2, benzyl-d7 and benzyl-d5 radicals in methylcyclohexane matrices at 77°K.

TABLE 4.9

Vibrational Analysis of Fluorescences of $C_6H_5CH_2\cdot$, and $C_6H_5CD_2\cdot$ in Polycrystalline Methylcyclohexane Matrices at 77°K.

Benzyl Radical-h7		Benzyl Radical-α-d2		Assignment[a]
$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	
21655	0	21630	0	0,0
21610	50	21585	45	lattice
21485	170			lattice
21405	250	21390	240	
21300	355	21310	320	0,u
21130	525	21125	505	0,t
21035	620	21025	605	0,s
20845	810	20850	780	0,r
20805	850			0,t+u
20665	990	20650	980	0,p
20625	1030	20600	1030	0,b;0,2xt
20515	1140	20505	1125	0,s+t
20385	1270	20360	1270	0,q
20315	1340	20315	1315	0,r+t
20220	1435	20220	1410	0,r+s
20145	1510	20140	1490	0,p+t
20115	1540	20090	1540	0,ℓ
20035	1620sh[b]	20045	1585	0,p+s
19865	1790	19860	1770	0,p+r;0,q+t
19780	1875	19805	1825	0,q+s
19690	1965	19675	1955	0,2xp
19595	2060	19580	2050	0,ℓ+t
19510	2145	19525	2105	0,p+s+t;0,ℓ+s
19420	2235			0,p+q
19300	2355	19325	2305	0,ℓ+r
19140	2515	19130	2500	0,ℓ+p
18875	2780	18865	2765	0,2xp+r

[a] Designation of normal modes follows Whiffen.

[b] sh = shoulder

noted that modes u, t, s and r shifted slightly to 320 cm^{-1}, 505 cm^{-1}, 605 cm^{-1} and 780 cm^{-1} respectively. In spite of such shifts, the overall appearance of the fluorescence spectrum is similar to that of benzyl-h7. The vibrational analysis of the benzyl-α-d2 fluorescence spectrum is also contained in Table 4.9 and the spectrum is presented in Figure 4.6.

c. Benzyl-d7

The fluorescence spectrum of this molecule is presented in Figure 4.6 and Table 4.10 contains the vibrational analysis. The 0,0 transition shifts 120 cm^{-1} to the blue upon perdeuteration of benzyl-h7, so that this band appears at 21,735 cm^{-1}. This value compares favorably with those determined by Ripoche[22] and Watmann-Grajcar[13] who observed the 0,0 bands of their systems at 21,737 cm^{-1} and 21,756.6 cm^{-1} respectively. Watmann- Grajcar noticed several low frequency modes below 400 cm^{-1} but Ripoche observed only the 0,u transition at 300 cm^{-1}. The appearance of 0,u at that frequency is affirmed by this study but no other low frequency modes were observed in the benzyl-d7 spectra considered here. The overall appearance of the spectrum is not very different from that of benzyl-h7 although all fundamentals present are shifted considerably. The 0,b transition, which appears at 1030 cm^{-1} in benzyl-h7, shifts to 835 cm^{-1} in the benzyl-d7 spectrum while modes t, s, r and p shift from 525 cm^{-1}, 620 cm^{-1}, 810 cm^{-1} and 990 cm^{-1} to 495 cm^{-1}, 580 cm^{-1}, 770 cm^{-1} and 940 cm^{-1} respectively. The 0,ℓ transition shifts from 1540 cm^{-1} in benzyl-h7 to 1480 cm^{-1} in benzyl-d7. The magnitudes of these shifts are similar to those observed for the corresponding modes of toluene when it is perdeuterated. As in benzyl-h7, the 0,t and 0,s transitions are the

TABLE 4.10

Vibrational Analysis of Fluorescences of $C_6D_5CH_2\cdot$ and $C_6D_5CD_2\cdot$ in Polycrystalline Methylcyclohexane Matrices at 77°K.

Benzyl Radical-d5		Benzyl Radical-d7		Assignment[a]
$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	
21765	0	21735	0	0,0
21580	185	21565	170	lattice
		21490	245	
21425	340	21435	300	0,u
21255	510	21240	495	0,t
21180	585	21155	580	0,s
20995	770	20965	770	0,r
20925	840	20900	835	0,b
20815	950	20795	940	0,p
20665	1100	20660	1075	0,s+t
20505	1260	20480	1255	0,r+t
20455	1310	20415	1320	0,b+t
20415	1350	20375	1360	0,r+s
20310	1455	20295	1445	0,p+t
20270	1495	20255	1480	0,ℓ
		20235	1500	
20245	1520sh[b]	20220	1515	0,p+s
20145	1620	20125	1610	0,b+r
20045	1720			0,p+r
19970	1795			0,b+p
19895	1870	19865	1870	0,2xp
19865	1900	19840	1895	
19820	1945	19840	1895	0,b+s+t
		19785	1950	
19745	2020	19745	1990	0,ℓ+t
19725	2040	19700	2035	0,p+s+t
19660	2105	19645	2090	0,b+r+t
19480	2285	19455	2280	0,ℓ+r
19325	2440	19315	2420	0,ℓ+p
18920	2845			0,3xp

[a] Designation of normal modes follows Whiffen.

[b] sh = shoulder

most intense in the spectrum and the transition due to the ring breathing mode p is weak. There are progressions in modes r, p and ℓ but they are very short.

d. Benzyl-d5

The fluorescence spectrum of benzyl-d5 is almost identical to that of benzyl-d7 (see Figure 4.6). The vibrational analysis is presented in Table 4.10 and it is quite similar to the one provided for benzyl-d7. The 0,0 band was observed at 21765 cm^{-1} and fundamental modes u, t, s, r, b and p appear. The most intense bands are due to the 0,t and 0,s transitions while 0,p is quite weak.

e. Para-Deuterated Benzyl Radical

Placing a deuterium atom in the para position in benzyl radical causes negligible change in the frequency of the 0,0 band which appears at 21660 cm^{-1}. The overall appearance of the spectrum is similar to that of the benzyl-h7 fluorescence although the peaks are broadened slightly in the region between 1300 cm^{-1} and 1600 cm^{-1}. There are several shoulders in the spectrum which are believed to be due to benzyl-h7 impurity emission. The most intense bands in the spectrum are again due to the totally symmetrical mode t and the non-totally symmetric, in-plane mode s. The frequency values of the fundamental modes are shifted only slightly in para-deuterated benzyl radicals so the vibrational analysis presented for benzyl-h7 is still essentially valid. The analysis is given in Table 4.11 and the fluorescence spectrum is depicted in Figure 4.7.

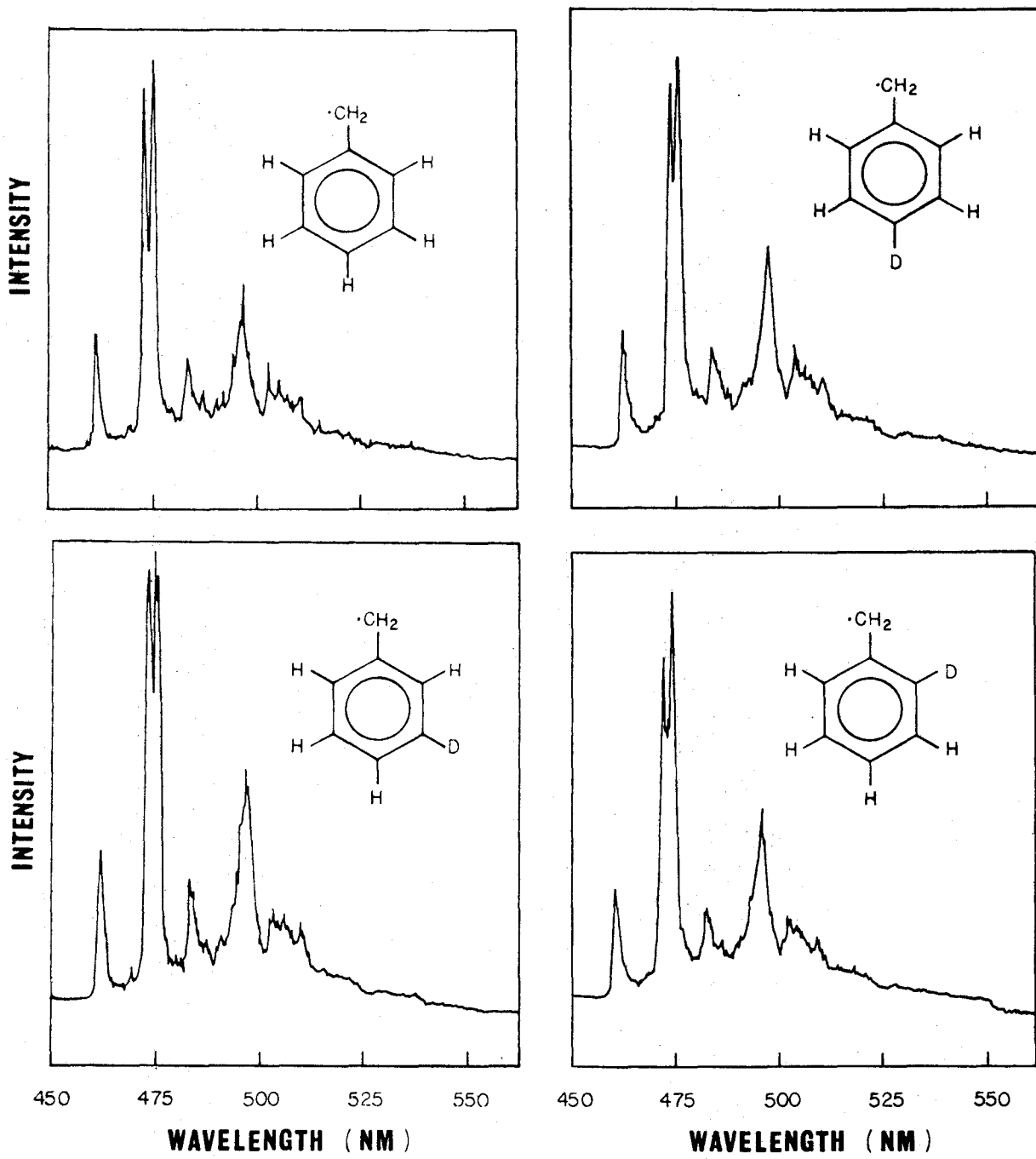

Figure 4.7 Fluorescence spectra of (clockwise from upper left)benzyl-h7, para, ortho and meta-deuterated benzyl radicals in methylcyclohexane matrices at 77°K.

Table 4.11

Vibrational Analysis of Fluorescences of p-D-$C_6H_4CH_2$·, m-D-$C_6H_4CH_2$· and O-D-$C_6H_4CH_2$· in Polycrystalline Methylcyclohexane Matrices at 77°K.

para-d-Benzyl Radical		meta-d-Benzyl Radical		ortho-d-Benzyl Radical		Assignment[a]
$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	
21660	0	21670	0	21685	0	0,0
		21655	15	21665	20	h7 imp[c]
21605	55sh[b]	21610	60	21620	65	lattice
21515	145	21515	155	21515	170	lattice
21300	360	21305	365	21325	360	0,u
21135	525	21140	530	21165	520	0,t
		21130	540	21135	550sh	h7 imp.
21045	615	21660	610	21070	615	0,s
		21045	625			h7 imp.
20860	800	20885	795	20885	800	0,r
20685	975	20685	985	20700	985	0,p
20625	1035sh	20625	1045sh	20645	1040sh	0,b;0,2xt
20535	1125	20530	1140	20545	1140	0,s+t
20405	1255	20395	1275	20410	1275	0,q
20340	1320	20365	1305	20345	1340	0,r+t
20220	1440	20270	1400	20265	1420	0,r+s
		20220	1450sh	20220	1465sh	h7 imp.
20160	1500sh	20165	1505sh	20175	1510sh	0,p+t

Table 4.11 (cont'd)

para-d-Benzyl Radical		meta-d-Benzyl Radical		ortho-d-Benzyl Radical		Assignment
$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	$\nu(cm^{-1})$	$\Delta\nu$	
20135	1525	20140	1530sh	20145	1540	0,ℓ
20115	1545sh	20115	1555sh	20115	1570sh	H7 imp.
20085	1575sh	20085	1585sh	20085	1600	0,p+s
20030	1630sh	20055	1615			H7 imp.
19875	1785	19900	1775	19895	1790	0,p+r;0,q+t
		19865	1805	19860	1815	H7 imp.
19805	1855	19780	1875	19800	1885	0,q+s
19720	1940	19720	1950	19710	1975	0,2xp
19615	2045	19620	2050	19620	2065sh	0,ℓ+t
19590	2070sh	19585	2085sh	19585	2100sh	H7 imp.
19530	2130	19535	2135	19540	2145	0,p+s+t
19435	2225	19400	2270	19435	2250	0,p+q
				19325	2360	0,ℓ+r
19170	2490	19155	2515	19180	2505	0,ℓ+p
18910	2750	18915	2755	18925	2760	0,2xp+r

[a] Designation of normal modes follows Whiffen.

[b] sh - shoulder

[c] Benzyl-h7 impurity

f. Meta-Deuterated Benzyl Radical

The vibrational analysis of the fluorescence of this molecule is also contained in Table 4.11 and the spectrum is shown in Figure 4.7 . The 0,0 transition is slightly blue shifted to 21,670 cm^{-1}. In the spectrum of this molecule, peaks due to benzyl-h7 impurity emission are more noticeable than was the case with the para-deuterated benzyl radical spectrum. The appearance of the spectrum is similar to that of the fluorescence of the para compound since bands due to the 0,t and 0,s transition remain the most intense ones. The vibrational analysis is very much like that for the para deuterated benzyl radical fluorescence.

g. Ortho-Deuterated Benzyl Radical

The 0,0 band is blue shifted by 30 cm^{-1} so it appears at 21,685 cm^{-1} in the fluorescence of this molecule. However, the other fundamentals present in the spectrum are shifted only slightly, if at all, from their frequency values in the benzyl-h7 spectrum. In the spectra of the benzyl radical molecules considered here, the bands assigned to transition 0,t (520 cm^{-1}) and 0,s (615 cm^{-1}) are of comparable intensity. In ortho-deuterated benzyl radical however, the 0,t band is somewhat less intense than that assigned to 0,s. Table 4.11 contains the vibrational analysis while the fluorescence spectrum is the subject of Figure 4.7.

4.6 DISCUSSION OF FLUORESCENCE OF BENZYL RADICAL

Bindley and Walker[17] investigated the emission spectrum observed between 4400Å and 5000Å after treatment of toluene by an electric discharge. They were able to show that the spectrum was due to benzyl radical emission. They observed isotope shifts in some bands of the radical emission spectrum

when toluene-α-d3 was used in the discharge instead of toluene itself. The radical substituents were found to be $-CH_2^{\cdot}$ when toluene-h8 was used in the discharge and $-CD_2^{\cdot}$ if toluene-α-d3 was employed.

The ground state of benzyl radical is a doublet and has B_1 symmetry. For a time there was some argument as to whether the first excited state had A_2 or B_1 symmetry. The photoselection experiments of Johnson and Albrecht[53] indicated that the symmetry of this state was B_1 but Cossart-Magos and Leach[19] performed rotational contour analyses on several bands of the gas phase emission spectra of benzyl-h7, benzyl-α-d2 and benzyl-d7, concluding that the first excited state of benzyl was of A_2 symmetry. Friedrich and Albrecht,[24] after further photoselection measurements, reached the same conclusion.

Longuet-Higgins and Pople[54] predicted qualitatively that there should be two absorption systems in the visible and near UV regions of the spectrum and that the higher energy one, involving a $^2B_1$-$^2B_1$ transition should have the greater intensity. Baudet[55] calculated the oscillator strength of the $^2B_1$-$^2B_1$ transition as 1.8×10^{-2} while that of the $^2A_2$-$^2B_1$ transition was found to be 3.2×10^{-3}. An approximate calculation of the oscillator strength of the $^2A_2$-$^2B_1$ transition was carried out by Laposa and Morrison[56] who used fluorescence lifetime data as the basis of the calculation and a value of $\sim 8 \times 10^{-4}$ was determined by them. These oscillator strength values indicate that, while the pure electronic transition $^2A_2$-$^2B_1$

is allowed on group theoretical grounds, it will be of very low intensity. In addition, a portion of the intensity of the transition can be accounted for in terms of a vibronic factor:

$$R_{e'v'e''v''} = \langle A_2 a_1 | M | B_1 b_2 \rangle \neq 0 \tag{4.9}$$

and

$$A_2 \otimes a_1 \otimes B_1 \otimes b_2 = A_1 \equiv \Gamma_{M_z}. \tag{4.10}$$

This can account for the presence of mode s, acting as a false origin.

The main features of the benzyl radical fluorescence spectrum, then, are the weakly allowed 0,0 transition, the very strong 0,t (525 cm^{-1}) transition which is allowed in the same sense as the 0,0 one and the 0,s (620 cm^{-1}) transition, which serves as a false origin. The fundamental frequencies of benzyl radical are not very different from those of other monosubstituted benzenes, particularly toluene. They can therefore be assigned quite reliably,[17] although the benzyl radical itself cannot be produced in the large concentrations required to obtain the vibrational fundamental frequencies from infrared and Raman experiments. According to the selection rules given previously, the vibronic contribution to the spectrum can be due to b_1, b_2 or a_1 vibrational modes if the first excited electronic state is of B_1 symmetry. If that state is an A_2 state, then the vibrations contributing to the vibronic term can be of a_1, a_2 or b_2 symmetry. All bands in the benzyl radical spectra of this study were assigned to a_1 or b_2 vibrational modes while neither b_1 nor a_2 modes appeared. It is known that at 77°K most transitions involved in emission spectra originate at the lowest vibrational level of the first excited

electronic state (see section 2.10). Unfortunately, the vibrational analysis of benzyl radical fluorescence presented here cannot distinguish between A_2 or B_1 symmetry for the first excited state although work previously mentioned has established it as A_2. The results presented here are consistent with that result although the a_2 vibrations cited by Watmann-Grajcar[13] as a basis for assigning that symmetry according to vibronic selection rules did not appear in the spectra studied here. Ripoche[22] observed an a_2 vibration at 865 cm^{-1} for benzyl-h7 in cyclopentane, methylcyclopentane and methylcyclohexane solvent but was unable to affirm it in the corresponding benzyl-d7 spectra. The bands assigned to a_2 transitions with cyclohexane solvent could be due to other fundamentals coupling with lattice modes.

It is interesting to compare the benzyl radical fluorescence spectrum with that of toluene. In both molecules, the pure electronic transition is only weakly allowed. In toluene, however, the 520 cm^{-1} and 625 cm^{-1} bands are roughly equal in intensity to that of the 0,0 transition whereas in the benzyl radical spectrum, the bands at 520 and 625 cm^{-1} are much more intense than the 0,0 transition. The second excited state is much closer in energy to the first one in benzyl radical than it is in toluene so that the first order vibronic term could become relatively large and this fact is reflected in the intensity of the vibronic part of the spectrum. In toluene, totally symmetric modes p and r give rise to strong bands and there is a long progression of up to five quanta involving the o,p transition. In the benzyl radical fluorescence, the o,r transition is very weak and o,p does not originate long progressions although it is

of noticeable intensity. As was mentioned in the discussion of toluene fluorescence (section 4.4), the long progression in the ring breathing mode, p, enables one to argue, on the basis of the Franck-Condon principle that in the first excited singlet state, the molecule is planar but expanded slightly. A similar conclusion cannot be achieved regarding the geometry of benzyl radical in the first excited doublet state as the progressions in the fluorescence spectrum involved are very short. The conclusions arrived at on the basis of the spectra analyzed in this study are similar to those obtained by Watmann-Grajcar[13] and Ripoche.[22]

CHAPTER V

SUMMARY

The phosphorescence and fluorescence spectra of toluene and some of its deuterated analogues in polycrystalline methylcyclohexane matrices at 77°K were recorded. The phosphorescence spectra and their corresponding vibrational analyses are similar for all these toluenes but differ from the fluorescence spectra and vibrational analyses obtained under the same conditions.

The vibrational analyses of the fluorescence spectra are consistent with a planar, slightly expanded hexagon structure for the toluenes in the first excited singlet state.

The phosphorescence spectra indicate that the triplet state geometry of toluene is planar in polycrystalline methylcyclohexane matrix. As in the case of benzene, the lowest triplet state geometry of toluene is solvent sensitive.

The fluorescence spectra of benzyl radical and its deuterated analogues in polycrystalline methylcyclohexane matrices were also recorded. The progressions in these spectra were quite short and the vibrational analyses were obtained by using fundamental modes and frequencies analogous to those observed in toluene fluorescence under the same conditions.

Forbidden components were prominent in the spectra of all three systems. In the toluene phosphorescence, and also in the benzyl radical

fluorescence, the vibronic origin was found to be much more intense than the pure electronic one. In the toluene fluorescence spectra, on the other hand, the vibronic and electronic origins were of comparable intensity.

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