Analytical and Structural Aspects of Vibronic Interactions in the Ultraviolet Spectra of Organic Molecules[1]

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The electronic and vibrational spectra of nonrotating molecules are normally regarded from the viewpoint of the Born–Oppenheimer approximation. A spectrum is thereby expected to display a number of electronic states, and each of these is expected to display a characteristic vibrational structure. The totality of these transitions exposes the spectrum of the vibronic eigenfunctions of the system.

The visible and uv spectra of organic molecules usually display a number of different electronic transitions, and these have vibrational structure, intensities, solvent effects, and energies that are frequently characteristic of the chromophoric composition of the molecules. Fundamentally these different properties arise because of electronic structural differences. On the whole many of the common spectral characteristics have been explained on an atomic orbital basis, and we generally understand the reasons why certain transitions are weak and others strong, why certain absorption bands shift to higher or lower energy on changing the solvent, or why certain bands are shifted more or less than others by substituents. The understanding of these and other spectral features is by no means complete or quantitative, but such effects are undeniably useful not only in expanding our knowledge of the electronic structures of complex molecules but also as empirical tools in many areas of experimental chemistry. It is therefore important to search for other, less conventional, aspects of the electronic spectrum that might readily expose new features of the electronic structure. One such aspect concerns the shape of electronic band spectra, or more specifically the band widths of the vibronic transitions. In this article we shall demonstrate that a very significant amount of information can be gleaned from casual observations of spectral band widths. Although most of the experiments offered in support of our contentions are of molecules in crystals or mixed crystals at 4.2°K, we also wish to make the point that the effects, once recognized, can often be seen in the room-temperature visible and uv spectrum.

The Born–Oppenheimer Approximation[2]

Each vibronic state $\Psi_{k\mu}(x,R)$ corresponds to a specific set of quantum numbers (k,μ) for the electronic (coordinates, x) and nuclear (coordinates, R) motions, respectively, with $\Psi_{k\mu}(x,R)$ given by eq 1. The

$$\Psi_{k\mu}(x,R) = \varphi_k(x,R)\chi_{k\mu}(R) \qquad (1)$$

adiabatic electronic states $\varphi_k(x,R)$ are eigenfunctions of a Hamiltonian that assumes the nuclei are fixed at a nuclear configuration R, and the electronic eigenvalues $E_k(R)$, one for each value of R, then determine the potential energy surfaces for the nuclear motion. The spirit of this discussion is to assume that the electronic functions are known from approximate theory, for example, in terms of molecular orbitals. The vibrational functions $\chi_{k\mu}(R)$ are harmonic oscillators having force constants $E_k''(R_0)$, with the equilibrium configuration defined by $E_k'(R_0) = 0$. This description of vibronic states is theoretically valid when the energy separation between successive electronic states, $|E_k(R_0) - E_l(R_0)|$, is large compared with vibrational frequencies. Still another necessary condition for the existence of the states in eq 1 is that the interaction energies between electronic states (so-called vibronic coupling) be vanishingly small compared with the separation between the states. If these conditions are not upheld, it becomes impossible to characterize each potential energy surface by a single electronic quantum number, and the electronic wave functions have to be regarded as functions of the nuclear displacements.

In real polyatomic molecules the vibronic coupling energies are about 10^2 to 10^4 cm^{-1} for each Å nuclear displacement. A typical vibrational displacement for a carbon-containing compound is $\sim$0.05 Å, so the net effect could approach the separation between successive low-energy excited states. Furthermore, because of the interpenetration of the various potential energy surfaces, there exists the certainty of many energy coincidences between vibronic states having *different* electronic quantum numbers. Since these potential surfaces do not in general have identical locations in nuclear configuration space (*i.e.*, $E_k'(R) \neq E_l(R)$), there will be interactions between energetically close states given by eq 1, and those will no longer be the proper eigenfunctions in that region. Each of the aforementioned effects represents a breakdown of the Born–Oppenheimer approximation, and the spectra of normal molecules should manifest such effects. As we shall see in the next section, one result of these interactions is a band broadening which may in many instances be quite revealing in terms of the electronic characteristics of the system. There are also energy shifts and modifications from expected vibrational

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(2) M. Born and K. Huang, "Dynamical Theory of Crystal Lattices," Oxford University Press, London, 1954, p 166 and Appendix VIII.

characteristics, but we will not discuss these aspects in this article.

General Considerations

The problem of relating the width of vibronic bands to theoretical quantities that expose known electronic characteristics can be dealt with if certain simplifying features are introduced. We consider first a molecule having two excited electronic states, and we represent the potential energy surfaces for these states by harmonic wells as shown in Figure 1. We now focus our interest on a particular vibronic state of the second excited electronic state, say Ψ_{2i}, corresponding to the ith vibrational excitation. We also suppose that transitions from the ground state to Ψ_{2i} are allowed, so that we expect to observe a sharp absorption line at the energy of the second electronic state *plus* the vibrational energy $h\nu_i$. Such a situation is shown in more detail in Figure 2a. It is apparent from Figure 1 that the vibronic states of the second excited electronic state lie in the same energy region as a highly dense set of vibronic states associated with the first excited state and an even more dense set of vibronic states from the ground state. To bring the problem around to a more specific situation we can consider the case where transitions to all of the vibronic levels having electronic quantum number $k = 1$ are forbidden under the experimental conditions. This could mean, for example, that the conditions of pathlength and concentration are such that transitions to the states $\Psi_{1\mu}$ (for all μ) are not seen, while those to Ψ_{2i} are seen (for a few special values of i).

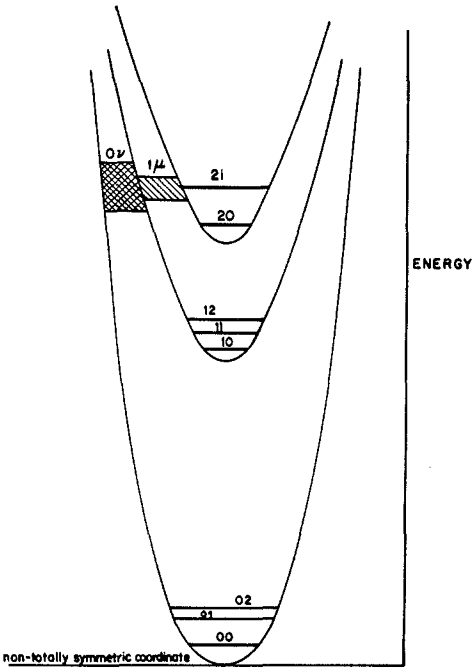

Figure 1. A schematic of the potential energy curves for the ground state and two excited states of a polyatomic molecule. Along the non-totally symmetric coordinate the potential curves are symmetric about the ground-state equilibrium position. Interactions neglected in forming Born–Oppenheimer states can modify this picture. The hatching and cross-hatching represent the vibrational sublevels from the lower energy potential surfaces. The states are labeled by two quantum numbers, $k\mu$, referring to the Born–Oppenheimer functions $\Psi_{k\mu}$ described in the text.

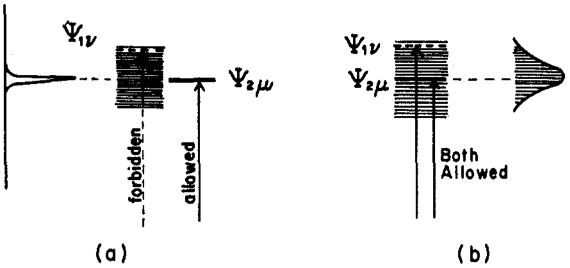

Figure 2. (a) Born–Oppenheimer scheme for Ψ_{2i} immersed in the sea of states $\Psi_{1\mu}$. The expected spectrum is displayed as a sharp line. (b) The electronic states are mixed by nuclear motions and the state Ψ_{2i} is no longer pure, but its character is spread over the nearby levels with which the interaction exists. The expected spectrum is displayed as a broad line. The spectral shifts that may arise if φ_1 and φ_2 are close together are not included.

The Born–Oppenheimer approximation, by definition, tells us that the state Ψ_{2i} does not interact with the states $\Psi_{1\mu}$ of the nearby quasi-continuum. Yet these states do interact to an extent that depends on the severity of the approximations involved in forming our original vibronic states. It follows that each state $\Psi_{1\mu}$ will, in reality, have acquired some Ψ_{2i} character, and transitions to many of the $\Psi_{1\mu}$ states will become allowed. The approximate manner in which the intensity of the transition to Ψ_{2i} becomes spread over the nearby $\Psi_{1\mu}$ states is readily discovered if we assume that the $\Psi_{1\mu}$ states are evenly spaced with a spacing Δ; then Δ^{-1} is the density of vibronic states $\rho(i)$ belonging to the first electronic state, found in the vicinity of the energy of Ψ_{2i}. The corrected wave function for the state $\Psi_{1\mu}$ is approximately given by $\Psi_{1\mu}'$, where

$$\Psi_{1\mu}' = N^{-1}(\Psi_{1\mu} + a\Psi_{2i} + \sum_{\nu} b_{\nu}\Psi_{1\nu}) \qquad (2)$$

The coefficients a and b are obtained from perturbation theory on the assumption that the energy gaps $(E_{1\mu} - E_{2i})$, $(E_{1\nu} - E_{2i})$ are large; the normalizing factor (N) is $(1 + a^2 + \Sigma b_{\nu}^2)^{1/2}$. The coefficients b_{ν} determine the interactions between states $\Psi_{1\mu}$ and $\Psi_{1\nu}$ of the quasi-continuum, and this interaction occurs through the intervention of the state Ψ_{2i}. In effect the b term indicates the manner in which the Ψ_{2i} character is distributed throughout the levels of the quasi-continuum. Since transitions to $\Psi_{1\mu}$, and also to all $\Psi_{1\nu}$, have been considered to be forbidden, the relative intensity of the transition to $\Psi_{1\mu}'$ is given by a^2/N^2. Introducing standard results from perturbation theory, and assuming Ψ_{2i} interacts with all the $\Psi_{1\nu}$ states equally, we can obtain an approximate result for the intensity, $I_{1\mu}$, of the transition to the state $\Psi_{1\mu}'$. The result is given below in terms of the constant interaction V, the energy spacing Δ in the form of $\rho(i)$, and the energy gap $\Delta E_{\mu i}$ between Ψ_{2i} and $\Psi_{1\mu}$

$$I_{1\mu} = \frac{V^2}{\Delta E_{\mu i}^2 + C^2V^4\rho^2(i)} \qquad (3)$$

this represents a Lorenzian distribution of intensity having a width at half-height of $CV^2\rho(i)$. The result in eq 3 is only valid in regions relatively far removed from the band center. The constant C is a numerical factor arising from the approximate sum over ν of inverse squared integers and is roughly of the order of unity. In general the states φ_1 and φ_2 will have different symmetry, so in the present example $\chi_{1\nu}$ must involve an odd number of non-totally symmetric vibrational modes. The interaction V depends on the manner that the electronic wave functions change with nuclear motions. V^2 can be written in terms of a product of the squared vibronic coupling energy, $E_v^2(n)$, and a Franck–Condon factor, F_n, representing the overlapping of vibrational eigenfunctions (except for the non-totally symmetric mode n) composing the two interacting vibronic levels. The energy $E_v(n)$ is defined for a particular normal mode, n, that has the proper symmetry to cause the electronic eigenfunctions to interact; thus we have, for the band width, very approximately

$$\Delta E_{1/2} = E_v^2(n)F_n\rho(i) \quad (4)$$

The quantity F_n is a controlling feature of the band width. The same term appears in the Robinson–Frosch,[3] Hunt–McCoy–Ross[4] theory of radiationless transitions. Byrne, *et al.*,[5] have made estimates of F_n, showing that it may vary from 1 to 10^{-20} depending on the situation. The foregoing formulas are obtained by Coulson and Zalewski[6] and by Bixon and Jortner[7] from rather different and more rigorous viewpoints. Like in the usual Franck–Condon effect, F_n depends critically on the displacement of the two potential energy surfaces along totally symmetric coordinates and on the number of totally symmetric coordinates. However in this case F_n also depends on the number of ways of making up the approximate vibronic energy gap, which depends on the number of appropriate non-totally symmetric modes available. Both of these factors depend on the vibronic energy gap $E_2(R_0) - E_1(R_0)$.

The result expressed in eq 4 presupposes that the states Ψ_{2i}, namely the electric-dipole-allowed vibronic states of the second electronic state, are far apart compared with $\Delta E_{1/2}$. If this is not the case the spectrum should become quite diffuse. It is also assumed that $E_2(R_0) - E_1(R_0)$ is large compared with the interaction energy, and if this condition is not upheld the vibrational wave functions will be severely modified by the influence of electronic interactions on the potential energy surfaces. It should be relatively common to to find band widths of $\sim$100 cm^{-1} in molecules for which the "background" states are spaced 10^{-2} cm^{-1} apart. Should an electronic transition display such a band width, for the reasons given here, then the mean time for internal conversion between the two electronic states can be considered as the time uncertainty associated with such an energy, namely 10^{-14} sec. In condensed media the heat sink surrounding the excited molecule will rapidly absorb all the vibrational energy in excess of the zero-point energy of the first excited electronic state.

Other Factors Determining Line Width

Because of spontaneous emission the energy states of a molecule are not stable, but decay with a definite probability per unit time. If one of the states involved in the transition is the ground state of the molecule, then the spectral band width is determined by the energy uncertainty associated with a given excited-state lifetime. In the visible and uv spectral regions these lifetimes range from 10 to 10^{-9} sec, providing band widths from $\sim 10^{-13}$ to 10^{-3} cm^{-1}. In low-pressure gas-phase spectra these natural widths are swamped by the Doppler effect which provides band widths of $\sim$0.05 cm^{-1} regardless of the line strength.

In the condensed phase there are two important kinds of contributions to the band widths of the spectra of rigid molecules; the first involves the presence of multiple sites, and the second involves the influence of lattice vibrations of the solid. The former effect vanishes if mixed crystals or pure crystals are used, since in that case the molecules of interest are each occupying identical sites. However the spectra of glasses and solutions will always display broad bands (10–100 cm^{-1}) because of this effect. The influence of lattice vibrations on the shapes and widths of vibronic bands is not understood in any detail, but experimental observations have yielded a few generalities. For example, the vibronic band width is temperature dependent; the width at very low temperatures is seldom greater than kT. The latter means that widths of $\sim$2 cm^{-1} at 4.2°K are about maximal. In this laboratory we have observed band widths of considerably less than 0.5 cm^{-1} in mixed crystals at 4.2°K. As we shall see in what follows, these considerations usually only apply to the spectra of the lowest electronic states of a given multiplicity.

Spectral Consequences of Vibronic Interactions

Before presenting descriptions of some spectra we shall list here in general terms some of the consequences of vibronic interactions of the type described above.

(1) The absorption spectrum of the second excited state (of a given multiplicity) of a polyatomic molecule should be broader than that of the first. This principle presupposes that the two excited states are energetically closer to one another than to the ground state. The effect is not qualitatively dependent on the electric dipole allowedness of *either* of the states, although in the example used in the foregoing development we assumed that transitions to the second state were allowed.

(2) The absorption spectrum of the first excited

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[3] (a) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); (b) G. W. Robinson, *ibid.*, **38**, 1187 (1963).

[4] G. R. Hunt, E. E. McCoy, and I. G. Ross, *Australian J. Chem.*, **15**, 591 (1962).

[5] J. P. Byrne, E. F. McCoy, and I. G. Ross, *ibid.*, **18**, 1589 (1965).

[6] C. A. Coulson and K. Zalewski, *Proc. Roy. Soc.* (London), **A268**, 437 (1962).

[7] J. Jortner and M. Bixon, *J. Chem. Phys.*, **48**, 715 (1968).

electronic state should become broader as the energy region of the second excited state is penetrated, although the transitions to the second state should be even broader.

(3) Internal conversion rates between excited states should be obtainable directly from the band widths ($\Delta E_{1/2}$) in the electronic spectrum, by means of the uncertainty relation $\tau^{-1} = \Delta E_{1/2}/\hbar$. (Contributions to the line width by the inhomogeneous broadening mechanisms mentioned above would have to be subtracted out.)

(4) Maximal effects of band broadening should be manifest when the terms in eq 4 are maximal: (a) $E_V(n)$: this term could be considered roughly constant at 10^3–10^4 cm^{-1}/Å, although simple molecular orbital considerations, and symmetry considerations, can sometimes suggest a lower value on the grounds that the two electronic wave functions are not readily coupled by the available nuclear motions, or that the molecule has no (or at least a dearth of) vibrational modes of the proper type n for a given energy gap; (b) $\rho(i)$: the density of background states in the neighborhood of the active level depends on the symmetry, the number of atoms in the molecule, and the energy gap between the two electronic states (for a molecule like benzene it is estimated[3] that $\rho(i)$ would be roughly 10^4 states/cm^{-1} for an energy gap of 8570 cm^{-1}); (c) F_n: this factor is strongly dependent on the energy gap and on the same factors that influence $\rho(i)$; in addition it is very dependent on the relative geometries of the two states. The possible range of values for F_n is so great that this term can dominate comparative features of internal conversion[4] and band width. F_n will be small when the two states involve similar electronic configurations, it will be large when these are very different. Thus, two $n\pi^*$ states would interact much less than would a $\pi\pi^*$ and an $n\pi^*$ state, other things being equal. Similarly a bent excited state should interact strongly with an unbent state.

(5) When two states are very close in energy (say within a few hundred reciprocal centimeters), then the interactions described here cannot lead to band broadening in the low-energy region of the spectrum since there are an insufficient number of background states. However in this case the present description is invalid since the Born–Oppenheimer states are not even a good first approximation to the actual ones. Discrete perturbations should be observable in the gas-phase spectrum. In condensed media the spectrum may still be broad in the overlapping region because of the coupling with lattice states, and because the electronic potential surfaces are strongly distorted by the vibronic interaction (as in the Jahn–Teller effect, which occurs when the two electronic states become degenerate).

(6) The range of band-broadening effects expected depends critically on the factors described in (5), but generally we expect 1–10 cm^{-1} for weak interactions (*e.g.*, weak vibronic coupling and small density of background states), 10–100 cm^{-1} for intermediate interactions, and >100 cm^{-1} for strong interactions (large Franck–Condon factors). The latter are comparable with or greater than multiple site band widths in solution spectra, and so these effects should be observable in room-temperature uv spectra. All other things being equal, these coupling cases place the Franck–Condon factor between $10^{-4}\Delta E_{1/2}$ and $10^{-6}\Delta E_{1/2}$, which yields values of F in the range of 10^{-4}–10^{-2} (weak interactions) and 10^{-4} to 10^{-2} or greater for strong interactions. These values fall in the range of F values calculated by Hunt, *et al.*,[5] for typical molecules.

(7) Besides the effects explicitly worked out here, one has to consider the influence of the background states from the lattice (medium). Even when electronic states are quite near, the state densities can be large due to the presence of low-frequency lattice modes. Electronic intensity can be spread over a quasi continuum of lattice states in much the same manner as described for vibronic states. In order to have a coupling between lattice-vibronic states (three quantum number states) it is required that the vibronic eigenfunctions be sensitive functions of the lattice displacements; that is, the vibronic energies must depend significantly on the molecular motions in the lattice. Thus a vibronic level of the second electronic state can mix with the background lattice states. In this manner we obtain line broadening even when the density of background vibronic states is as low as $\sim(kT)^{-1}$ at low temperatures.

Band-Width Studies in the Ultraviolet Spectra of Organic Molecules

Aromatic Hydrocarbons. The effects described above are rather strikingly exemplified by the linear polyacenes, as well as by the other aromatics. The second excited *singlet states* of benzene (2000 Å), naphthalene (2900 Å), and anthracene (probably at ~3650 Å) are quite broad. Usually the first excited state of a given multiplicity is sharp regardless of the type (*i.e.*, L_b or L_a) that happens to be lowest (see Figure 3). Although these features are clearly manifest in the low-temperature crystal spectra, one can see the effect in solution spectra[8] since the band widths in the second states of ~250 cm^{-1} are often noticably larger than in the first. The same features appear in the spectra of the *triplet states* of benzene[9,10] and naphthalene[11] and of benzene and naphthalene derivatives.[12,13] The absorption spectra of the second states, although broad, show distinct vibronic bands and can be understood in terms of the Born–Oppenheimer approach in the sense that the line widths do not completely obscure the vibrational structure.

(8) E. Clar, "Polycyclic Hydrocarbons": Vol. I, Academic Press Inc., New York, N. Y., 1964; Vol. II, Springer-Verlag, Vienna, 1964.

(9) S. D. Colson and E. R. Bernstein, *J. Chem. Phys.*, **43**, 2661 (1965).

(10) G. W. Robinson, *ibid.*, **47**, 1967 (1967).

(11) D. M. Hanson and G. W. Robinson, *ibid.*, **43**, 4171 (1965).

(12) G. Castro and R. M. Hochstrasser, *ibid.*, **47**, 2241 (1967).

(13) Unpublished results from this laboratory. These transitions are readily seen in *para*-dihalogenated benzenes, trichloro- and tribromobenzenes, and tetraphenyl group IV compounds, and in halogenated naphthalenes.

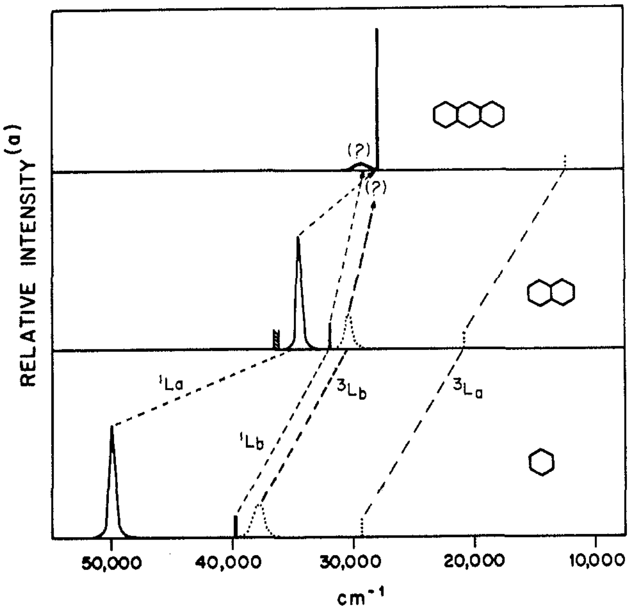

Figure 3. A schematic of the band widths of aromatic hydrocarbon spectra, illustrating that the second states give broad spectra regardless of orbital type. In the case of naphthalene the vibronic levels of state 1 remain sharp beyond the origin of state 2. In the case of anthracene the location of the second state is not confirmed.

Reference 7 contains the spectra of a hundred or so aromatic molecules. The longest wavelength bands are sharpest for the spectra of all molecules except those that have aromatic chromophores mixed by carbon–carbon single bonds, for example, phenylnaphthalene, *p*-terphenyl, etc. With the confidence that the lowest energy excited states should be sharpest, the explanation of these anomalies is clear: the relative dispositions of the chromophores in such molecules probably change during low-frequency vibrations such that in solutions at room temperature the ground-state molecular geometries vary considerably from molecule to molecule. The dependence of the excited-state energy on these nuclear displacements must be much more severe. This contention is confirmed by the observation of sharp low-temperature spectra of solids containing multiple chromophoric molecules. For these exceptional cases it often arises that higher excited states show relatively sharp spectra, and this is presumably explained by the fact that we do not expect the interchromophore interactions to be identical for every excited state.

The case of azulene is particularly interesting since the line widths are narrower in the second state ($\sim$3300 Å) than they are in the first (at 6800 Å). McCoy and Ross[14] have emphasized this feature and its importance to understanding the special internal conversion properties of azulene. From our viewpoint, if the line width of the second state equals that of the first, then the internal conversion rate from state 2 to state 1 must be comparable with that from state 1 to state 0, assuming the line-broadening mechanism is of the type under discussion. The line width of the first transition is greater than that of the second transition by about 0.3 cm^{-1}, thus the internal conversion lifetime, or emission lifetime, of azulene $1 \rightarrow 0$ must be $\sim 10^{-11}$ sec.

One revealing feature of the present analysis involves the possible identification of the hitherto unobserved second excited state (^1L_b) of anthracene which is predicted by theory[15] to lie at 1400 cm^{-1} above the well-known 3800-Å state. The polarized spectra of Bree and Katagiri[16] show the onset of a very broad weak absorption at 2800 cm^{-1} above the 3800-Å state. This weak absorption has the proper polarization characteristics to be assigned ^1L_b. Only the foreknowledge that such a transition is expected to be quite diffuse makes possible even this tentative assignment.[17]

The spectrum of naphthalene in durene[18] shows some interesting features in the region of the second electronic state: the use of polarized light permits observations of two excited states in the overlapping region. The vibronic bands of the first state (0,0 at 31654 cm^{-1}) remain quite sharp beyond the commencement of the second transition (0,0 at 34,410 cm^{-1}), and it is only at $\sim$1000 cm^{-1} beyond this origin that the lines broaden significantly. Also there appear to be some rather diffuse bands in the same region. The second transition is broad and complex, having band widths of $\sim$100 cm^{-1}. These features are qualitatively understood on the basis of the notions presented above.

Nitrogen Heterocycles. The electronic spectra and structure of these molecules are complicated by the presence of nonbonding (n) electrons that can be promoted into π^* orbitals, thereby producing a new manifold of states—the $n\pi^*$ states—that can interact with one another and with the $\pi\pi^*$ states. An $n \rightarrow \pi^*$ transition is usually readily characterized[19,20] when it is the lowest excited state of a molecule. The vibronic structure of an $n \rightarrow \pi^*$ transition is usually quite different from that of a $\pi \rightarrow \pi^*$ transition, indicating that the changes in nuclear configuration (however slight)[20] compared with the ground state are quite different for the $n\pi^*$ and $\pi\pi^*$ states. It follows that the Franck–Condon factor between $n\pi^*$ and $\pi\pi^*$ states must be relatively large compared with the factor between more similar types of states. We therefore expect the band-broadening effects to be more pronounced in nitrogen heterocycles, and we can use this effect to identify the relative positions of $n\pi^*$ and $\pi\pi^*$ states.

Perhaps the most apparent result that *could* be due to this effect involves the well-known uv spectrum of pyridine in hydrocarbon and hydroxylic solvents. These spectra are shown in Figure 4. In pentane the 2600-Å $\pi\pi^*$ absorption region is quite diffuse, whereas

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(14) G. R. Hunt and I. G. Ross, *Proc. Chem. Soc.*, 11 (1961).

(15) R. Pariser, *J. Chem. Phys.*, **24,** 250 (1956).

(16) A. V. Bree and S. Katagiri, *J. Mol. Spectry.*, **17,** 24 (1965).

(17) R. M. Hochstrasser and C. A. Marzzacco, *J. Chem. Phys.*, in press.

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(19) M. Kasha, *Discussions Faraday Soc.*, **9,** 14 (1950).

(20) K. K. Innes, J. P. Byrne, and I. G. Ross, *J. Mol. Spectry.*, **22,** 125 (1967).

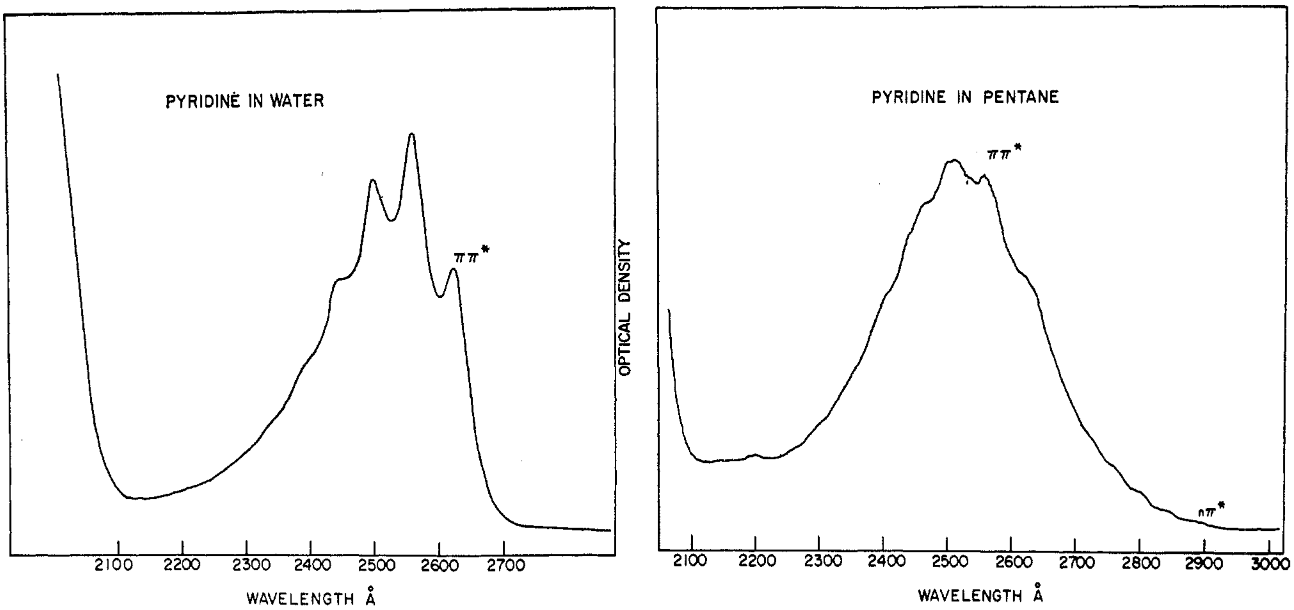

Figure 4. Absorption spectra of pyridine in pentane (right) and water (left). The spectrum in water is considerably sharper in the sense that the vibronic bands are better resolved. In this case the solvent broadening would be expected to be greatest in water.

the $n\pi^*$ region commencing at ~2900 Å is quite well defined vibronically, as evidenced by the weak series of bands on the long-wavelength tail of the spectrum. By contrast, with water as solvent the $\pi\pi^*$ region becomes relatively well defined vibronically, and the $n\pi^*$ absorption is no longer apparent. These results can be interpreted as manifestation of $n\pi^*$–$\pi\pi^*$ vibronic mixing, which causes extreme diffuseness in the $\pi\pi^*$ bands when the $n\pi^*$ state is at *lower* energy. The hydrogen bonding in water shifts the $n\pi^*$ state *above* the $\pi\pi^*$ state, thereby permitting the $\pi\pi^*$ state to become the lowest excited singlet state and enabling the recovery of the vibronic patterns. Actually the spectrum of benzene in water is not much sharper than that of pyridine in water. It should be remembered that molecular spectra in polar and other solvents will be broadened by a number of other effects, and only dramatic changes in the vibronic interactions will show up in solution spectra.

The absorption spectra of the triplet states of pyrazine, dimethylpyrazine, tetramethylpyrazine, quinoxaline, diazaphenanthrene, and phenazine all display marked $n\pi$–$\pi\pi^*$ perturbations.[17] The pyrazine derivatives are intriguing since the methyl substitution ultimately inverts the ordering of the lowest $^3\pi\pi$ and $^3n\pi^*$ states. Thus the spectrum of pyrazine is sharp until about 2000 cm^{-1} into the transition, at which point the lines start to broaden, indicating that by then the origin of the $^3\pi\pi^*$ state has been passed. In dimethylpyrazine the broadening is more severe and commences after about 200 cm^{-1} beyond the $^3n\pi^*$ origin. In tetramethylpyrazine the much weaker $^3\pi\pi^*$ state is lowest, and the $^3n\pi^*$ state displays only a diffuse spectrum (see Figure 5).[17] The $^3n\pi^*$ states of the nitrogen heterocycles mentioned above are never the lowest energy states, since each has a $^3\pi\pi^*$ state (that shows very sharp absorption spectra) relatively close to the lowest triplet state of the parent hydrocarbon. In every case the $n \rightarrow \pi^*$ transitions are diffuse, but less diffuse when the $^3n\pi^*$– $^3\pi\pi^*$ energy gap is largest (*cf.* phenazine). It is interesting to recall that the lowest energy singlets are of $^1n\pi^*$ type: they are sharp in every case, and the higher energy $^1\pi\pi^*$ states are diffuse.[17,21,22]

A contrasting situation is evident in the spectrum of phthalazine (2,3-diazanaphthalene) which shows two sharp electronic transitions both of which are $^1A_2$ $(n\pi^*) \leftarrow {}^1A_1$ transitions.[23] Here then is another potential candidate for anomalous fluorescence of the azulene type, but unfortunately the molecule does not fluoresce from either state. Again we can qualitatively understand the sharpness of both states: since their Franck–Condon patterns in absorption are identical, it follows that the Franck–Condon factor between them is close to zero.

The singlet states of quinoxaline show an effect similar to that described above for naphthalene. The lower energy $^1n\pi^*$ state gives a very sharp transition; the $^1\pi\pi^*$ bands are very broad but one can clearly see the sharp $^1n\pi^*$ bands superimposed on the $^1\pi\pi^*$ state bands. Again this interesting phenomenon demonstrates the effectiveness of vibronic interactions between two states of different orbital type (see Figure 6)[17] although in this case the vibronic interactions do not result in the complete destruction of the vibronic patterns of the upper state.

An over-all view of the perturbative effects described above can be obtained from a careful comparative study of the low-resolution vapor spectra of pyridine and dichloropyridine (see Figure 7). The $^1n\pi^*$ state

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(21) R. M. Hochstrasser and C. A. Marzzacco, *J. Chem. Phys.*, **45,** 4681 (1966).

(22) R. M. Hochstrasser and C. A. Marzzacco, *ibid.*, **46,** 4155 (1967).

(23) R. M. Hochstrasser and C. A. Marzzacco, *ibid.*, in press.

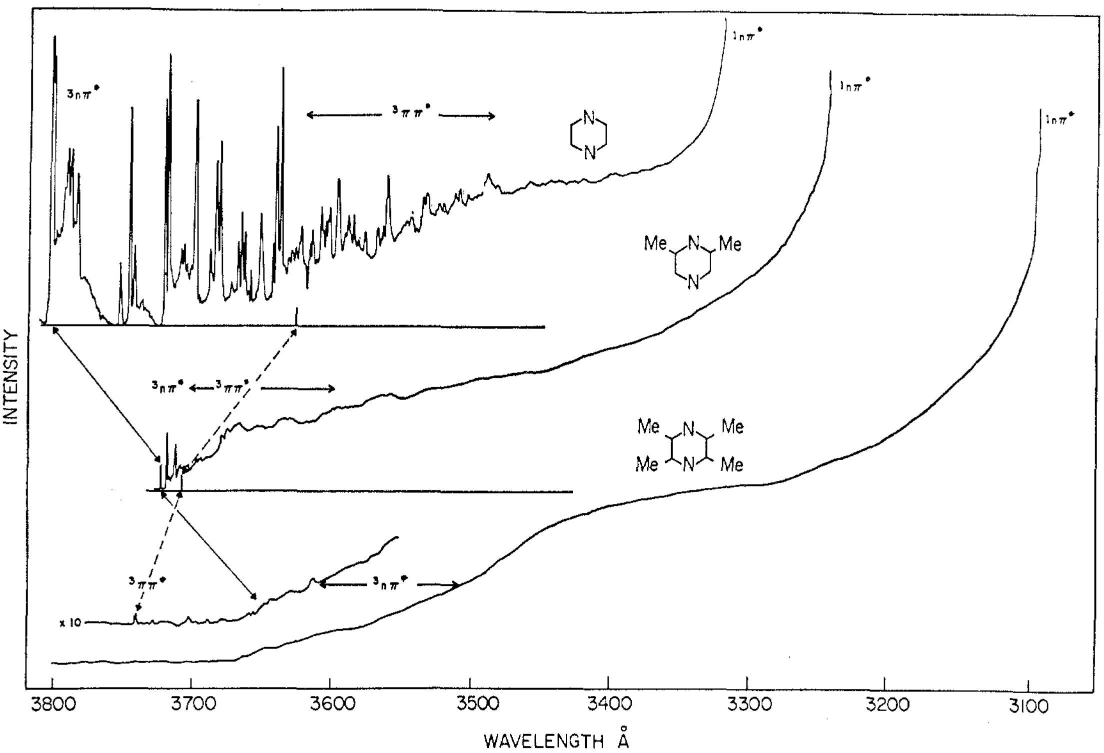

Figure 5. Absorption spectra of crystals of pyrazine and derivatives at 4.2°K. The π* ← n transition has about the same intensity in each case (integrated intensity). Notice the blue shift of the ^{3}nπ* and ^{1}nπ* (cut-off) under methyl substitution.

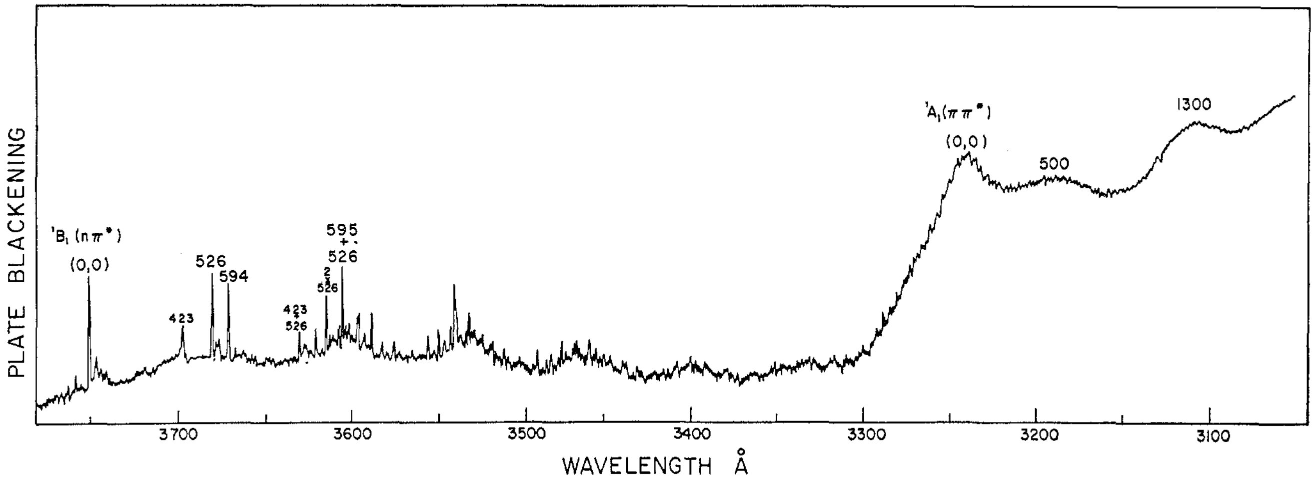

Figure 6. Absorption spectrum of quinoxaline in durene at 4.2°K. The lower energy sharp lines are the vibronic bands of the π* ← n transition. The broad stronger bands are the π* ← π transition, but the sharp structure overlying these broad bands corresponds to vibronic components of the ^{1}nπ* state.

of pyridine at 2900 Å is very sharp, but the ^{1}ππ* state at ~2600 Å gives only diffuse bands. The stronger ππ* state at ~2000Å is quite well defined vibronically, as if it were some considerable energy away from any lower energy ^{1}nπ* state. The chloro substitution shifts the ^{1}nπ* state to higher energy—possibly to around 2300 to 2600 Å—while the ππ* states are shifted to lower energy. Now the ^{1}ππ* state shows a sharp spectrum (at ~2750 Å), and the higher energy ^{1}ππ* state gives a diffuse band. Note that the dichloropyridine spectrum is recorded at a considerably lower pressure than used for pyridine.

Organic Ketones. The relative energies of ^{3}ππ* and ^{3}nπ* states of aromatic carbonyl compounds is a feature that is of great importance to organic photochemistry. Recently a number of experimental studies on acetophenone derivatives[24-26] have pointed to the fact that solvent interactions and substituent effects are capable of interchanging to the order of close-lying ^{3}ππ* and ^{3}nπ* states. As we have pointed out,[17,26] band-width studies on acetophenone and its derivatives can indi-

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(25) H. A. Lamola, *J. Chem. Phys.*, 47, 4810 (1967).

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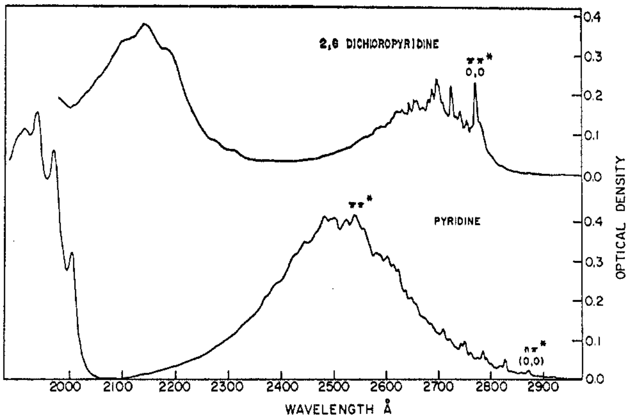

Figure 7. Absorption spectra of pyridine and dichloropyridine vapors. These spectra were recorded on a Cary spectrophotometer at 300°K. The intensity scales are roughly comparable since the path length used for dichloropyridine was ten times that for pyridine and the vapor pressures at 300°K are roughly in this ratio.

cate which state is of lowest energy and also give the approximate location of the higher energy state regardless of the state ordering. The rationale is comparable with that used in describing the pyrazine spectrum; even though the $^3\pi\pi^*$ state has vanishingly small intensity and its presence is swamped by absorption to the lower energy $^3n\pi^*$ state, the presence of the weaker state is detected through changes in the band width in the allowed spectrum.

Crystalline acetophenone provides a perfect example[26] of a lower energy $^3n\pi^*$ state the origin of which (at 26115 cm^{-1}) is sharp (line widths ~2–3 cm^{-1} at 4.2°K), while at about 440 cm^{-1} from this origin the line widths start to increase (~10 cm^{-1}), thus exposing the presence of the underlying $^3\pi\pi^*$ state. Presumably these line-width increases can only occur fairly well beyond the origin of $^3\pi\pi^*$ state even in a condensed medium.

The benzophenones offer interesting examples of $n\pi^*$ perturbative interactions. The spectrum of crystalline benzophenone in the $^3n\pi$ region shows sharp (~0.3 cm^{-1}) bands over the spectral range up to the singlet cut-off point.[27] This important feature most probably indicates that there is no $^3\pi\pi^*$ state at lower energy than the $^1n\pi^*$ state of benzophenone. Accordingly the very fast (~10^{11} sec^{-1}) intersystem crossing in benzophenone must occur because of direct mixing of singlet and triplet $n\pi^*$ states.[26] Such mixing can be understood to be efficient if the vibronic interaction between $^3n\pi^*$ and $^3\pi\pi^*$ (at higher energy) is large. An additional feature of the benzophenone spectrum is that the line width of the $n \rightarrow \pi^*$ singlet transition (~1–2 cm^{-1}) is larger than that for the singlet–triplet transition (~0.3 cm^{-1}), suggesting that intersystem crossing, or intersystem mixing, is very efficient in this case. According to these estimates the fluorescence lifetime of benzophenone should be ~10^{-11} sec.

Experimental Usefulness of Band-Width Studies

The descriptions of uv spectra of organic molecules summarized above have suggested to us that there are a number of important benefits to be gained by regarding spectra from the viewpoint of shape and band width, in addition to the more conventional viewpoint of intensity and spectral location. Some of the more prominent aspects of our interpretative notions are now summarized.

(1) An increase of band width with increasing energy in what appears to be a single electronic transition provides a strong indication of the presence of an underlying less-allowed state. This effect can usually be clearly seen in low-temperature spectra and is worth looking for in room-temperature solution spectra. If the perturbation is clearly seen, there is a strong likelihood that the two states have different orbital character, for example, an $n\pi^*$ and $\pi\pi^*$, or any kind of state and charge-transfer state.

(2) A spectrum that commences with a broad, vaguely structured, band system often seems to give clue to the presence of a weaker, lower energy, state that would have different orbital origin. Certainly for states of photophysical interest in nitrogen heterocycles and ketones this criterion has been unfailingly useful to us when applied to low-temperature melts or single crystals.[17,26] Of course at room temperature there are a number of transitions that are intrinsically broad; such transitions are found in molecules containing coupled chromophoric groups, especially when the relative dispositions of these groups is changed during low-frequency vibrations; also charge-transfer transitions tend to be broad even if they are the lowest states, although the reasons for this are not so clear, especially in solids.

(3) We have found that nearby electronic transitions can often be distinguished from one another by bandwidth observations even when other factors such as polarization and vibrational analysis fail to aid in the distinction. Biphenylene is an example where we have used this principle,[28] and in this case the inferences confirmed in the gas-phase spectrum could be clearly drawn from the solution spectrum. When the higher energy transition is severely broadened, again we have invariably discovered that the two states have different orbital character.

(4) The absorption spectrum appears to provide very strong indications of the important internal conversion processes in the molecule. When the upper states are broadened measurably, the absorption of light in condensed media must lead very rapidly to the population of thermally accessible vibronic states of the lowest excited (sharp) electronic state. The observation in the absorption spectrum of more than one sharp state of a given multiplicity appears to be strongly suggestive of unusual internal conversion properties. In this event the internal conversion, and therefore the luminescence

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(27) S. Dym, R. M. Hochstrasser, and M. Schafer, *J. Chem. Phys.*, **48**, 646 (1968).

(28) R. M. Hochstrasser and R. D. McAlpine, *ibid.*, **44**, 3325 (1966).

and photochemical properties, are expected to display isotope effects. There is also a possibility that these molecules will show luminescence corresponding to the electronic transition *between* the two excited states, although this effect has not yet been observed in large molecules.

(5) When two electronic states are very close (~1000 cm^{-1} or less) the structure and sharpness of the spectrum is quite unpredictable. In the case of the diazines where the states are of different orbital type the upper state is rendered completely diffuse, and all hint of the quantization of vibronic states is absent from the spectra in the overlapping region (*e.g.*, dimethylpyrazine, quinoxaline, diazaphenanthrene). Since sometimes this annihilation of the Born–Oppenheimer states is not observed, we have supposed that the vibronic coupling matrix element is the crucial factor and that in certain molecules this may turn out, for reasons given above, to be extremely small. The band broadening increases with the number of atoms in the molecule, as evidenced by the methylpyrazines. In smaller molecules, *e.g.*, aliphatic ketones or smaller enones, these interactions will probably lead to modifications of the spectral intervals rather than band broadening. The role of the medium on this kind of extreme broadening is not quantitatively clear.

Conclusions and Cautions

A proper theory of band widths in polyatomic molecular spectra has not yet been worked out. In addition to the assumptions made in this article there are problems associated with introducing ground vibronic states. These are omitted here because it is expected that, although the state density will be large, the F values will be very small indeed because of the very large vibrational quantum numbers involved. There is further the problem of the vibronic states Ψ_{2j} (with $j \neq i$) which may also be dense unless the zero-point level is being considered. Thus the present approach is really only valid for the 0,0 band of the second excited state.

As mentioned in the text there are a number of different influences on the band width of a vibronic transition that are dependent not only on perturbations between electronic states, as described here, but also on the character of the transition and the nature of the molecule.

The objective of this article was not to explain all band-width phenomena in molecular spectra but simply to point out with documentation that research along these lines is very likely to expose a number of additional and invaluable features for molecular structure determination and analysis.

The views expressed in this article are a consequence of seeing the low-temperature spectra of a large number of molecules and crystals. I am indebted to my students and postdoctorals who have, mainly for reasons other than those given here, studied these systems. In particular I wish to acknowledge the assistance of C. A. Marzzacco, who has helped in the crystallization of a number of the ideas expressed here.