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SPECTROSCOPY OF PORPHYRINS

Porphyrins are an important class of compounds that are of interest in molecular biology because of the important roles they play in vital biochemical systems such as biochemical energy conversion in animals, oxygen transport in blood, and photosynthetic energy conversion in plants. We are studying the physical properties of the energy states of porphyrins using the techniques of experimental and theoretical spectroscopy with the aim of contributing to a basic understanding of their biochemical behavior.

INTRODUCTION

Porphyrins are a class of complex organic chemical compounds found in such diverse places as crude oil, plants, and human beings. They are, in most cases, tailored to carry out vital chemical transformations in intricate biochemical or biophysical systems. They are the key constituents of chlorophyll in plants and of hemoglobin in animals. Without them, life would be impossible.

These molecules display a wide range of chemical and physical properties that depend on the structural details of the particular porphyrin molecule. All porphyrins are vividly colored and absorb light in the visible and ultraviolet regions of the spectrum. Some exhibit luminescence, paramagnetism, photoconduction, or semiconduction. Some are photosensitizers or catalysts. Scientists from several disciplines have been interested in unraveling the principles that cause this diversity of properties.

The simplest compound of all porphyrins is porphin. This aromatic molecule exists in two basic configurations (Fig. 1), depending upon the nature of the material at its center. When a metal ion (such as iron, magnesium, zinc, or cobalt) is attached at the center, the compound is said to be a "metalloporphin." When two hydrogen atoms are attached, the compound is termed "free base porphin." The periphery of these structures contains hydrogen atoms that can readily be displaced by one or more molecular groups, thus forming the general class of porphyrins. In some cases, these peripheral groups play a role in the particular properties of the porphyrin. In other cases, they serve to attach the porphyrin molecule to a chemically inert substrate such as a large protein molecule. In some highly sophisticated biochemical systems, the substrate places the chemically active porphyrin into a highly specific spatial position to permit its interaction with other chemically active species.

The metal ion in metalloporphyrins has a great influence on the properties of the particular porphyrin molecule. The iron porphyrin shown in Fig. 2a is called "heme" and is one of the most important porphyrins in molecular biology. Figure 2b shows schematically the structure of hemoglobin, which transports oxygen in the blood. There are four porphyrin groups attached to four protein chains. Other important heme-containing proteins are myoglobin, which stores oxygen in muscle, and the cytochromes, which perform many cellular functions involving oxygen metabolism and the production of stored biochemi-

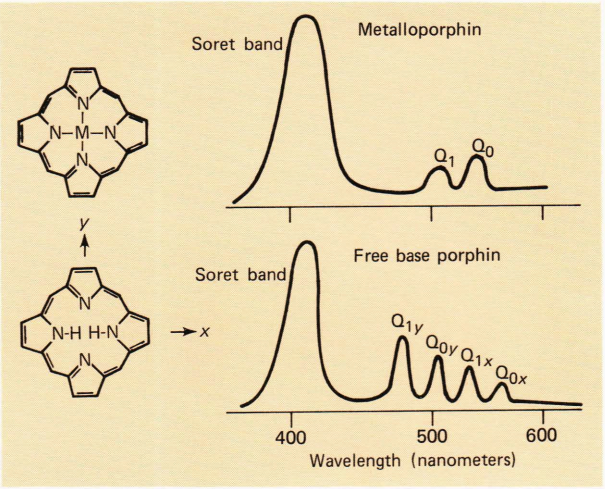

Fig. 1—The chemical structures for the two forms of porphin are shown on the left. A carbon atom and a hydrogen atom are understood to be at each apex not attached to a nitrogen atom. Metalloporphin has a metal atom (designated by M) complexed at the center of the molecule, while free base porphin has two hydrogen atoms in the center. The general class of porphyrins are obtained from porphin by replacing the peripheral hydrogen atoms with other chemical groups. The optical absorption spectra shown characterize these compounds when they are in solution at room temperature. Q_0 in metalloporphin is due to a pure electronic transition (no molecular vibrations) between the electronic ground state and the first electronic excited state; Q_1 is due to the same electronic transition but, in addition, molecular vibrations are involved. This band is called a vibronic band. The subscripts 0 and 1 for free base porphin carry a similar interpretation. The *x* and *y* subscripts refer to the orientation (polarization) of the electric vector of the absorbed light with respect to the axes shown on the chemical structure diagram for free base porphin.

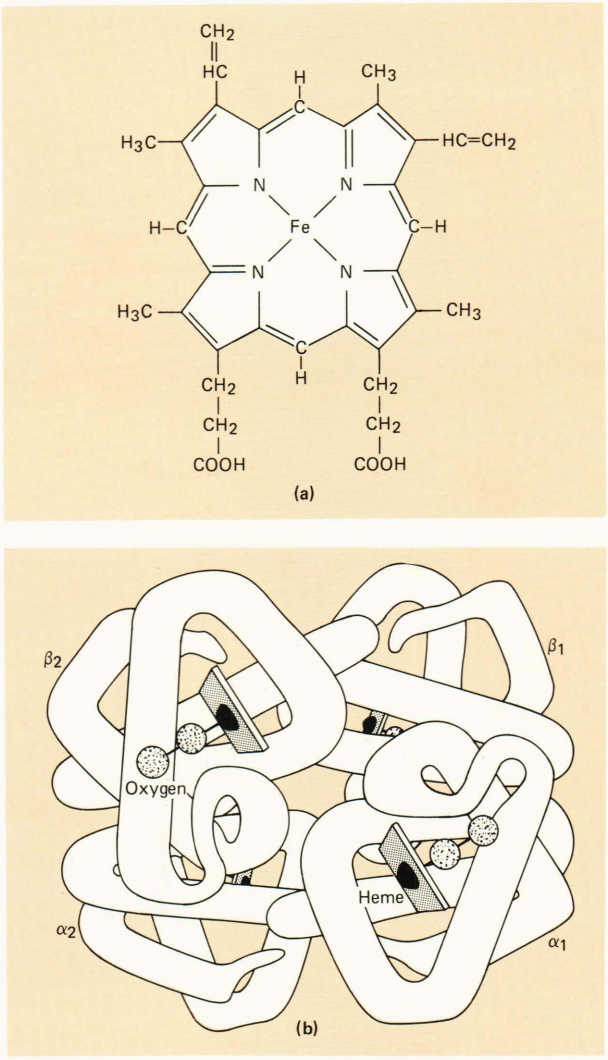

Fig. 2—(a) The chemical structure of heme (iron protoporphyrin); (b) a representation of the entire hemoglobin molecule, consisting of four protein chains denoted by α_1, α_2, β_1, and β_2. The four planar structures represent heme molecules to which oxygen binds in the lungs and which release oxygen in the capillaries.

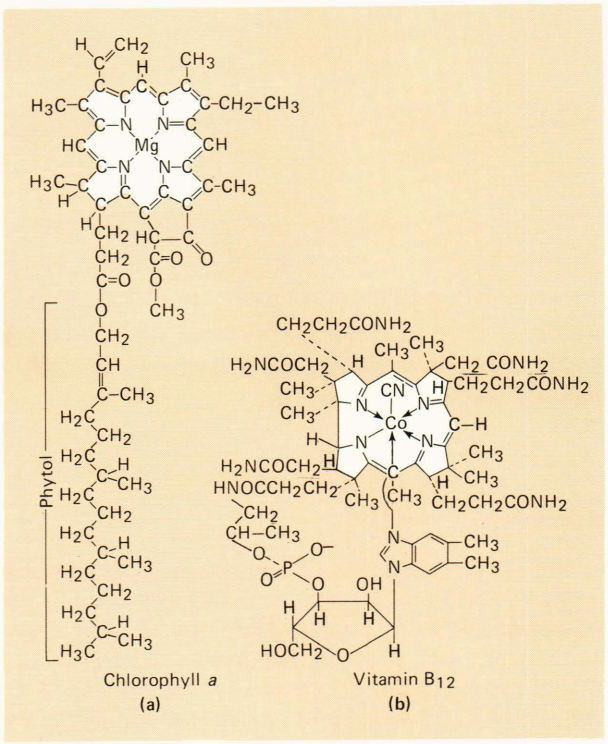

Fig. 3—The chemical structures of two important molecules that contain a metalloporphyrin, chlorophyll *a*, and vitamin B_{12}.

cal energy from foodstuffs. The heme group is usually attached to a large protein molecule by a bond between the iron atom and a nitrogen atom of a histidine amino acid residue of the protein. The chemical activity is due to the heme group. Two other important porphyrin derivatives, as seen in Fig. 3, are magnesium-containing chlorophyll and cobalt-containing vitamin B_{12}.

We are interested in the quantum structure of porphyrins. Atoms and molecules are comprised of bound particles, which can be described by standing wave functions using the theoretical methodology called quantum mechanics. The conditions to which the standing wave modes correspond are called "states." The quantum structure of molecules in solids or liquids may be considered to consist of their electronic and vibrational structures. The electronic structure is determined by the distribution of electronic charge in the molecule and by its electronic energy states. The vibrational modes of the molecule and their corresponding vibrational energy states comprise the vibrational structure. Collectively, these structures are referred to as "vibronic structure."

The basis for the chemical action of porphyrins is founded in their quantum structure. Although a detailed and valid theory that relates structure to activity does not yet exist, in a few cases the relationship of structure to the chemical role of porphyrins is understood, as, for example, in recent reports of photodestruction of malignant tissue by a hematoporphyrin derivative.[1] Its role is understood in terms of its quantum structure, which permits absorption of light in the red region of the spectrum of the molecule and subsequent transfer of the excitation energy to a triplet oxygen molecule. This, in turn, forms excited singlet oxygen molecules that attack and destroy the malignant tissue. In another example, two hydrogen atoms on the periphery of the porphyrin structure in chlorophyll change the electronic structure of the molecule sufficiently so that it absorbs more light in the red/green region of the spectrum, causing the molecule to perform photosynthesis more efficiently.

The overall objective of the porphyrin spectroscopy project at APL is to advance the state of knowledge of the electronic and vibrational energy structure of porphyrins and to study the effects of chemical perturbations on this structure. Implicit in this objective is a desire to contribute to the understand-

ing of the relationship between structure and chemical and biological function.

Optical and microwave spectroscopies are the experimental methods that are used to probe the quantum structure of porphyrins. In optical spectroscopy, changes in quantum states are detected when the molecule absorbs energy to achieve a higher excited energy state or when it loses energy as it decays into a lower energy state. The energy is related to the frequency of the radiation by the Einstein relation

$$E = h\nu,$$

where h is Planck's constant and ν is the frequency. Figure 4 is a diagram of typical energy levels. For porphyrins, the light absorption at Q_0 (see Fig. 1) corresponds to the E_1 energy level in Fig. 4. In absorption spectra, one observes transitions from the ground state (E_0) to the various excited vibronic states of the molecule ($E_1 + e_1$, $E_1 + e_2$, etc.). Thus, the absorption spectra reveal excited electronic energy levels (E_1, E_2,...) and associated vibrational energy levels (e_1, e_2,...). The molecule will eventually release the excitation energy and return to its electronic ground state (E_0). When the molecules are in a solid or liquid phase, which is the case in these studies, an excited molecule (in E_2, for example) will decay to the first (or lowest) excited state (E_1), with the energy loss being released in the form of heat. The subsequent decay from this state to the ground electronic state is often accompanied by the emission of electromagnetic radiation, which is referred to as "luminescence." The transition from the lowest excited state, E_1, to the electronic ground state, E_0, may terminate on a ground-state vibrational level as shown in Fig. 4. Thus, it follows that the luminescence spectra can yield vibrational energy levels in the ground electronic state.

Electron spin resonance is a microwave spectroscopic technique that is used when the molecular species in its ground state contains a magnetic moment. Here, the ground state consists of a pair of states (doublet), each with a magnetic moment oriented in opposition to the other. In the absence of a magnetic field, the two states have the same energy. However, in the presence of a magnetic field, the energies of the two states are different. If microwave energy of the proper frequency is imposed on the sample, the energy will be absorbed by the molecules, causing a transition from the lower energy component of the doublet to the higher energy component. This technique can give valuable information about the local environment of such paramagnetic species.

Much work has been done in the field of porphyrin spectroscopy. The optical spectra shown in Fig. 1, obtained in solution at room temperature, are typical of most metalloporphyrin and free base porphyrin spectra. The strong band at approximately 400 nanometers, called the Soret band, is common to all porphyrins. The weaker bands in the region of 500 to 600 nanometers are called "Q bands." Free base porphyrins have four bands in this region, while metalloporphyrins have only two. The structure of the spectra in this region is similar for most porphyrins although the reduced porphyrins, such as chlorophyll, exhibit the departures from this structure described previously. The region of the Q bands has been the principal focus of spectroscopic study in our laboratory.

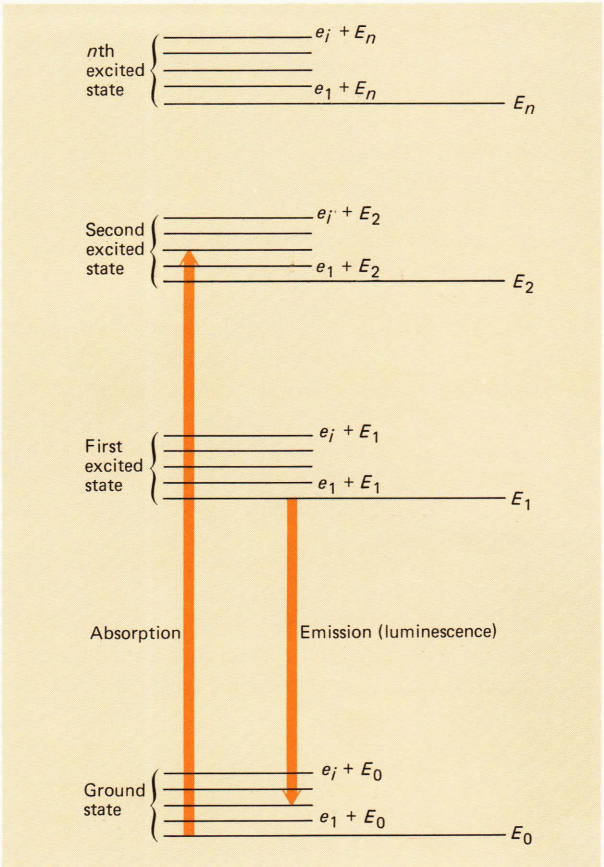

Fig. 4—Absorption and emission processes. The *E*'s are electronic energy levels, typically greater than 16,000 cm^{-1} for porphyrins. The *e*'s are vibrational energy levels superimposed on the *E*'s. For porphins (porphyrins with no side groups on their periphery) the *e*'s are less than 3600 cm^{-1}. For metalloporphyrins, transitions to E_1 correspond to Q_0 while transitions to E_2 correspond to the Soret band in Fig. 1.

The apparent simplicity of the spectra is surprising for a molecule with the structural complexity of porphyrin. The spectra should be rich in spectral components (lines) due to energy transitions between vibronic states. In fact, there are many such components in porphyrin spectra, but they are masked or hidden beneath the broad spectral structure shown in Fig. 1, obscuring the details of the quantum structure of the molecules. Following is a description of how we resolved the sharp spectral components contained in the broad bands and how this information is being used to probe the quantum structure of porphins.

EXPERIMENT

Initially, our work on porphyrin spectroscopy focused on two main areas. First, we wanted to ob-

tain high-resolution, sharp-line optical spectra instead of the broad structureless spectra observed in solutions at room temperature. Thermal line broadening and inhomogeneous broadening due to nonuniform interactions between solvent and porphyrin are the two main mechanisms that must be reduced or eliminated before sharp-line spectra can be obtained. Thermal broadening can be eliminated by recording spectra with the sample immersed in liquid helium at 4.2 K. Inhomogeneous broadening can be a more difficult problem. This type of broadening is shown schematically in Fig. 5a. Basically, it results from the porphyrin molecules being in a random environment. Each porphyrin experiences slightly different perturbing forces from the neighboring solvent molecules. The resulting spectrum can be thought of as a continuous distribution of sharp-line spectra of porphyrins in nonequivalent solvent environments, leading to a broad band.

One way of reducing spectral broadening due to nonuniform solvent interactions is to use frozen inert gas matrices as the solvent,[2] which reduces solvent interactions to a minimum. A second approach (Fig. 5b) involves the use of a single crystal host lattice, which, in an ideal case, makes each site equivalent to any other because of the periodic array of atoms or molecules in the structure and results in a single spectral line.

Although rare gas matrices are more generally applicable, crystalline hosts offer the advantage of providing spatially oriented guest molecules so that polarization characteristics of the spectra can be studied. Russian workers[3] had reported the use of normal alkane hosts, primarily *n*-octane, for obtaining porphyrin spectra. These hosts are liquids at room temperature and usually yield polycrystalline samples upon cooling. We found that the aromatic hydrocarbon triphenylene would accept small amounts of porphin molecules as guest molecules.[4] Single crystals of triphenylene, which is a solid at room temperature, containing trace amounts of various porphins, were grown from solution. We have used crystalline hosts of this type exclusively. Figure 6 shows the absorption spectrum of zinc porphin in an amorphous matrix compared to the polarized absorption spectrum of zinc porphin in triphenylene at 4.2 K. The sharp lines are apparent in the single crystal spectra.

The second main thrust of our effort concerned the observation, by Russian workers and at APL, of multiplets in the spectra. A multiplet is the occurrence of several spectral lines in a region of the spectrum where only a single line is expected. The question arose of whether the multiplets were an intrinsic property of a single type of porphyrin site or if they resulted from the existence of several types of non-

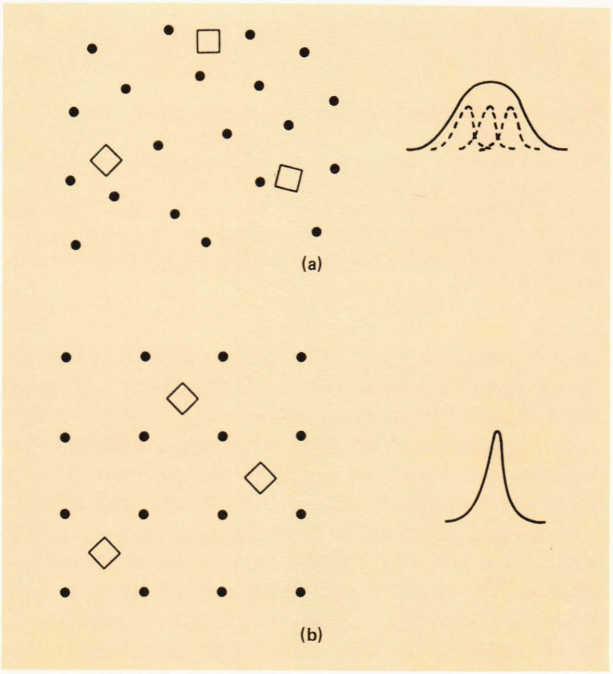

Fig. 5—The effect of host lattice symmetry on spectral linewidth. (a) In a random lattice, the guest molecules reside in lattice sites that are each different from one another. This causes the energies of the guest porphyrins in nonequivalent host lattice sites to be slightly different, resulting in slightly displaced spectral lines. The observed spectrum is a superposition of slightly displaced lines, and a broad band is observed. (b) In a periodic matrix or lattice, guest porphyrin molecules reside in equivalent host sites. Therefore, each guest porphyrin has the same energy and a spectral line at the same wavelength, resulting in the observation of a single sharp line.

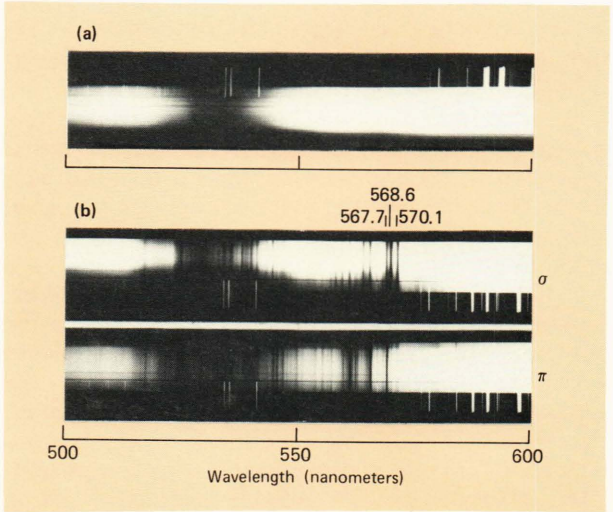

Fig. 6—The absorption spectrum of zinc porphin at low temperature, showing the effect of the host lattice on spectral bandwidth. In (a), zinc porphin is in an amorphous (random) matrix. The spectra are broad. In (b), zinc porphin is in triphenylene, a crystalline (periodic) matrix. The spectra consist of sharp lines. The symbols σ and π refer to the polarization of the light relative to the optic axis of the triphenylene crystal; σ refers to the case when the electric vector of the absorbed light is perpendicular to the optic axis; π designates light absorption with the electric vector parallel to the optic axis.

equivalent sites, each giving rise to a sharp spectral line. If the multiplets were due to porphyrins in nonequivalent lattice sites, there was then a problem of separately recording the spectra of these nonequivalent porphyrin site species. Our solution was to use selective excitation techniques involving a scanning tunable dye laser pumped by a nitrogen laser.[5] First, one obtains the conventional sharp-line absorption and fluorescence spectra. Then the fluorescence spectrum corresponding to a particular site is recorded by exciting a single sharp absorption line of the multiplet. The process is repeated for the other lines in the multiplet. Then the spectrograph is tuned to the wavelength of a single sharp fluorescence line in the fluorescence spectrum, and the excitation source, i.e., the dye laser, is scanned through the region of the absorption spectrum. Whenever the excitation wavelength matches that of an absorption line of the site species being detected, fluorescence is observed. Thus, the absorption spectrum corresponding to the site species is obtained. The two procedures give the absorption and fluorescence spectra of a single type of porphin site. The results for the case of zinc porphin in triphenylene are shown in Fig. 7. There were three strong absorption lines in the conventional spectrum in the region near 570 nanometers. Figure 7a shows the conventional fluorescence spectrum taken with broadband excitation. Figures 7b, 7c, and 7d show the fluorescence spectra upon exciting each of the three strong absorption lines. One sees that the top spectrum is a superposition of the lower three spectra. Excitation spectra were also recorded. The results prove that the multiplet structure of zinc porphin in triphenylene is due to three nonequivalent sites and is not an intrinsic property of a single type of porphyrin site species. The results also demonstrate a method for separately recording their spectra.

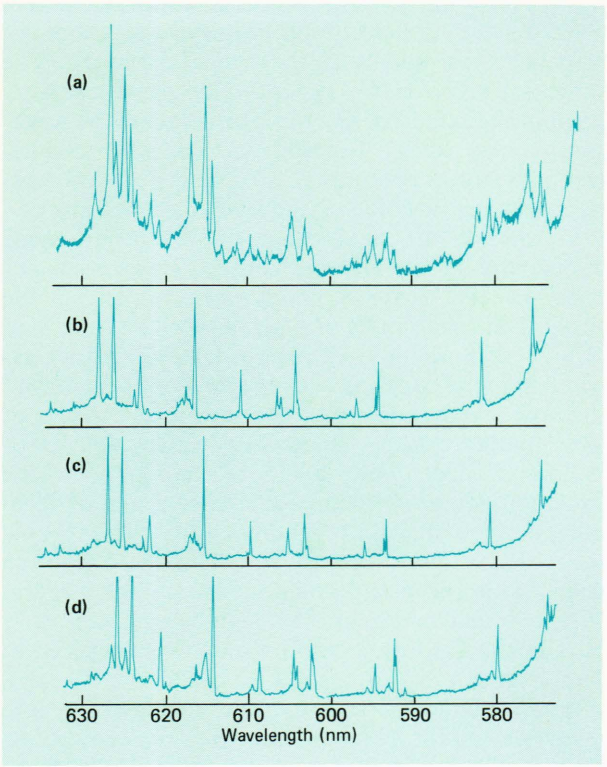

Fig. 7—Luminescence spectra of zinc porphin in triphenylene at 4.2 K, illustrating the effects of broadband excitation and narrow-band (line) excitation on the fluorescence spectra: (a) broadband excitation; (b), (c), and (d), narrow-band excitation at 570.1, 568.6, and 567.7 nanometers, respectively. Note that (a) is a superposition of (b), (c), and (d). Narrow-band excitation excites fluorescence from porphyrins that reside in equivalent lattice sites. These results show that the three spectra shown in (b), (c), and (d) correspond to porphyrins in three nonequivalent types of host lattice sites.

Our current interest centers around the vibronic structure of porphins as modified by external forces or perturbations. They fall into two classes: those due to the host solvent or matrix and those due to discrete chemical species, particularly biologically important species, such as oxygen, that interact with some of the porphyrin molecules. Our interest in the effects of the host solvent on the guest porphyrin molecules arises from our desire to characterize the structure of unperturbed porphyrin molecules. Because it is very difficult to obtain suitable spectra of porphyrins in the free (vapor phase) state (because of their very low vapor pressure), a solvent or host material is necessary. Therefore, it is important to determine the extent of the perturbation of the guest porphyrin molecule by the host material.

The effects of discrete chemical species on the structure of porphyrins are of fundamental interest. The observation and interpretation of spectral shifts that can be correlated with the addition of specific chemical species are pertinent to the relationship between chemical and physical properties and molecular structure. This information is of interest because it will aid in the understanding of the fundamental basis of the chemical behavior of porphyrins in biologically significant processes such as the oxygenation of hemoglobin. An important incentive for this avenue of study is our observation of additional lines in porphyrin spectra that could be attributed to the presence of small amounts of impurity molecules that had been introduced into the host. The additional lines are interpreted to result from a zinc porphyrin that is interacting with a nearby impurity species. A full exploitation of these experimental observations, however, will also require a detailed theory for the interpretation of sharp-line porphyrin spectra.

Effects of the host lattice on porphyrin spectra were observed in crystalline samples of the aromatic host, anthracene, containing small amounts of free base porphin. Polarized sharp-line absorption spectra were obtained at 4.2 K.[6] Selective excitation techniques gave single site absorption and fluorescence spectra. Absorption lines associated with Q_{0x} and Q_{0y} (see Fig. 1) were identified on the basis of the similarity of the vibronic (electronic-vibrational) spectra of

the Q_x and Q_y spectral systems. (The Q_x system refers to the pure electronic transition, Q_{0x}, and the associated vibronic transitions contained in Q_{1x}. The same holds for the Q_y system.) The excitation spectrum in the region of Q_y was characterized by weak, sharp lines, called "quasilines," superimposed on top of a strong continuum. Conversely, the Q_x system had strong quasilines and a weak continuum.

To discuss the significance of this result, some understanding of the mechanisms responsible for quasilines and continua is necessary. In general, the spectral characteristics of a given vibronic transition of a guest molecule imbedded in a frozen matrix depend upon the coupling between the guest species and the host matrix.[7] The vibronic transition consists of two components: a sharp line called the "zero phonon" line; and a broad component—the "phonon wing"—which is due to coupling of local host lattice vibrations (phonons) to the vibronic state. Thus, quasilines are the sharp zero phonon lines, while the broad components are the phonon wings, which occur on the high-energy side of a quasiline in absorption and on the low-energy side in fluorescence. Figure 8 shows an example of these spectral characteristics. At low temperature, the relative strength of the phonon wing with respect to the zero phonon line in a given transition is a measure of the guest/host coupling for that transition. If a region contains many vibronic transitions that have strong phonon wings, the phonon wings can superimpose upon one another to form a broad continuum in this region. On this basis, the Q_x and Q_y transitions of free base porphin in anthracene exhibit weak and strong guest/host coupling, respectively. This conclusion was also supported by theory based upon a simple model of porphyrin (the cyclic polyene model). That model of porphyrin has been successful in describing the qualitative character of porphyrin electronic spectra.

The relative strengths of the broad and sharp components provide a qualitative indication of the appropriateness of particular experimental spectra for comparison with theoretical results. If the spectra in a region consist of strong quasilines with little continua or phonon structure, the transitions in this region can be judged to be weakly coupled to the host matrix and, thus, to approach those of a free porphyrin molecule. Most theoretical studies of porphyrins deal with models of free porphyrins. Thus, experimental spectra that consist of weak quasilines with strong continua or phonon structure may represent a physical system that cannot be described by theoretical studies that do not account for guest/host coupling. The relative intensities of the pure electronic transitions, Q_{0x} and Q_{0y}, provide an illustration of the importance of accounting for strong guest/host coupling when it exists. The broad spectra (Fig. 1) indicate that Q_{0y} is stronger than Q_{0x}. Therefore, theories that predict this have been considered to be in agreement with experiment. Our results, however, indicate that the observed strength of Q_{0y} in broadband spectra is due in large measure to the guest/host interaction (which provides the continuum in this region). When the intensities of the sharp components (quasilines) of Q_{0x} and Q_{0y} are compared, the Q_{0x} component is stronger. Thus, for a free porphin species, our results indicate that Q_{0x} is stronger than Q_{0y}, in contradiction to broadband spectra.

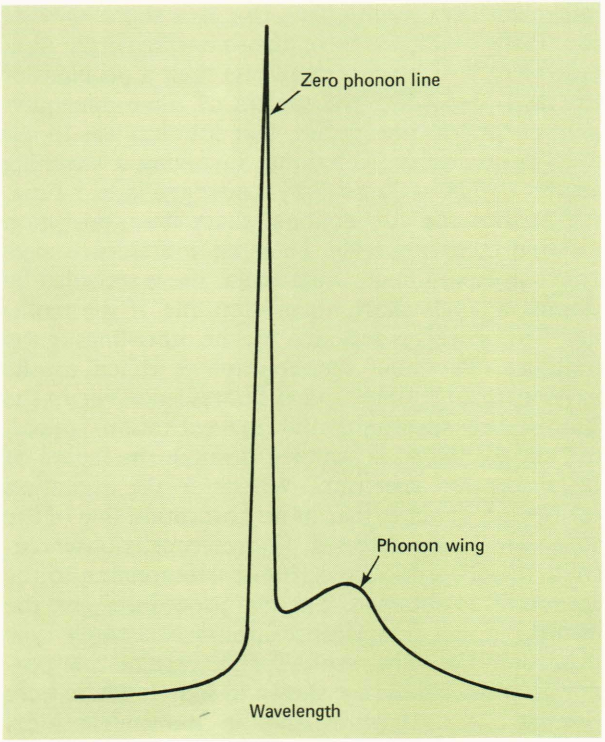

Fig. 8—Spectral structure of a vibronic transition of a guest molecule in a host lattice at low temperature. The zero phonon line is associated with the guest porphyrin molecule, while the phonon wing is due to the interaction of the host lattice vibrations with the guest porphyrin.

Another system that we have studied is magnesium porphin in triphenylene.[8] The temperature dependence of the lowest pure electronic fluorescence transition (also called the 0-0 transition) is shown in Fig. 9. At low temperature, a sharp zero phonon line lies on the high-energy side of a broad phonon wing. As the temperature is increased, the intensity of the zero phonon line relative to the phonon wing decreases, the line shifts to higher energy, and, above 40 K, the zero phonon linewidth increases. These temperature effects are of great interest because they can be analyzed in terms of coupling between the lattice phonons and the electronic state of the guest, thereby allowing a quantitative assessment of guest/host coupling.

Figures 10a and 10b show plots of the temperature dependence of the shift of the zero phonon line from its unshifted position at low temperature and of the zero phonon linewidth of magnesium porphin in triphenylene. These quantities may be calculated theoretically; the pertinent equations are given

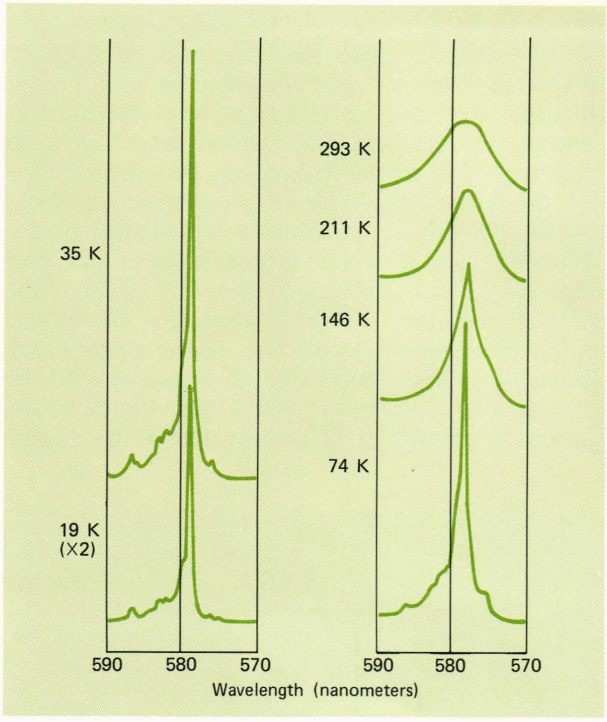

Fig. 9—Temperature dependence of the 0-0 fluorescence transition of magnesium porphin in triphenylene. The broadening of the line at higher temperatures is due to the increase in the lattice vibrations at high temperature.

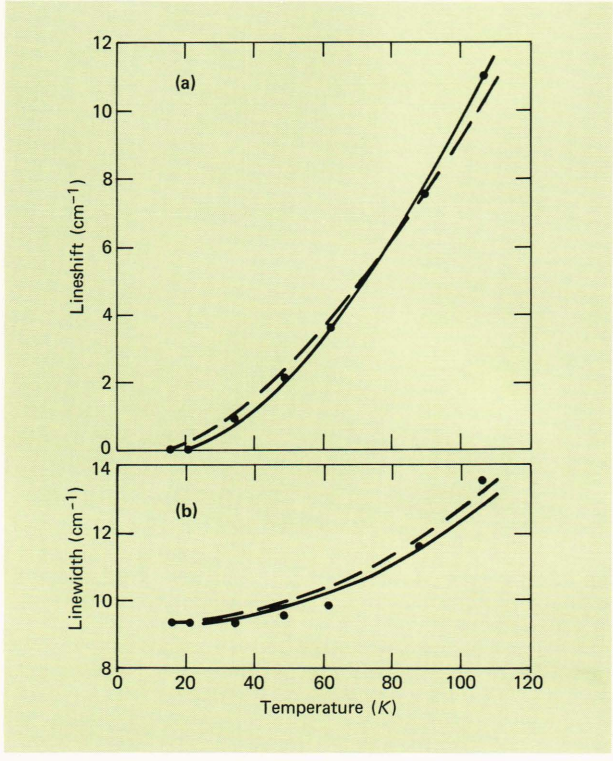

Fig. 10—Temperature dependence of (a) the zero phonon lineshift and (b) the zero phonon linewidth of the 0-0 fluorescence transition of magnesium porphin in triphenylene. The solid and dotted lines represent two fits of theoretical calculations to the data points.

elsewhere.[8] For the purposes of our discussion, the important parameters are θ_D, the Debye temperature of the host; $\Omega(T)$, the line position at temperature T; $\Gamma(T)$, the linewidth at temperature T; and β and γ, which are average coupling parameters for the shift and width of the line, respectively. The two curves in Figs. 10a and 10b were obtained by numerically fitting the data to theoretical expressions, using two different Debye temperatures to get the values of β and γ. Although 144 K is a typical θ_D value for organic materials, the value of 200 K provided a slightly better fit to the data, giving values for β and γ of 133 and 73.3 cm^{-1}, respectively. The lattice coupling parameters, β and γ, give a measure of the strength of the guest/host interaction in doped crystal systems. The measured values are small and indicate a weak coupling between magnesium porphin and the triphenylene lattice.

Everything else being equal, for spectroscopic studies one would choose a host lattice with minimal guest/host interaction. The expressions that describe the temperature dependence of the intensity, linewidth, and lineshift of the zero phonon line in terms of average coupling parameters involve several approximations. However, the formalism allows one to compare quantitatively the guest/host interactions of various similar host crystals and to choose the host that has minimum effect on the spectra of the guest porphin molecules. The small values of the coupling parameters of triphenylene provide some justification for our approach to the investigation of porphyrin spectra.

Another way to assess the effects of the host lattice on the spectra of the guest porphyrin is to compare the spectra of porphyrins in different hosts. To this end, the spectra of zinc porphin in anthracene were studied. Conventional polarized optical absorption spectra at 4.2 K revealed multiplet structure, which made the identification of the 0-0 transition difficult. Site-selective techniques were employed again to record the single site absorption and fluorescence spectra. The vibrational frequencies obtained for this system could be compared to those of zinc porphin in triphenylene. The patterns of vibrational frequencies were consistent in the two systems, indicating minimal host/lattice perturbations on the spectra.

A complete and detailed theory of porphyrin spectra is not yet available. In past work, interpretation of spectra was based upon available theory. For example, group theory and the polarization characteristics of the absorption spectra were used to classify prominent vibrational transitions according to their symmetry type. In zinc porphin, the vibrational frequencies were assigned to recently calculated frequencies of a similar metalloporphin, copper porphin.[9] Interpretation of spectra was also aided by comparisons of spectra of metalloporphin and free base porphin. For example, by comparing the zinc porphin frequencies to those observed for free base porphin in the same host, we were able to assign lines that occurred in zinc porphin but could not do so in

free base porphin to vibrations that involve the central metal

THEORY

A theory that describes the spectra of free porphyrins is necessary to interpret changes in the spectra that are due to external perturbations on the molecules. An effort is under way to establish a suitable model to describe experimental spectra. Such a model should be capable of predicting both the positions and strengths of spectral lines. We will review briefly the nature of our theoretical work and its relationship to existing theories.

The physical principles that govern the emission and absorption of light by molecules are based upon classical concepts of electromagnetic radiation. In particular, light can be emitted (or absorbed) by a molecule when it changes states if the distribution of electronic charge averaged between the two states is a dipole distribution. The strength of the emission is proportional to the square of the magnitude of the dipole. The electronic charge distribution can be determined by calculating the electronic energy states of the molecule, the distribution being embodied in the electronic wave functions. There are many methods for performing electronic energy calculations, and indeed, many calculations have been performed for porphyrins.

The spectra are further complicated, however, because the nuclear constituents are not fixed but can move relative to one another, setting up vibrational modes in the molecule. These vibrations affect the spectra in two ways. First, the positions of the spectral lines reflect the total energy of each state involved in the transition and thus must include the vibrational energy. Second, the vibrations affect the strengths of the spectral lines in which they are involved. Figure 11 shows the effect of a vibration on the spectra. The result of a vibration is a vibronic line displaced from that corresponding to a vibrationless transition by the energy $h\nu$. The frequency ν and the relative nuclear displacements can be calculated by well established methods of vibrational analysis. Present theoretical methodology is sufficient to describe the position of the vibronic spectral lines and the strengths and positions of lines due to pure electronic transitions, which involve no vibrational modes. No detailed calculations of the strengths of vibronic lines have been made, however, and it is in this area that our present effort lies. Figure 12 illustrates schematically the present state of theory and

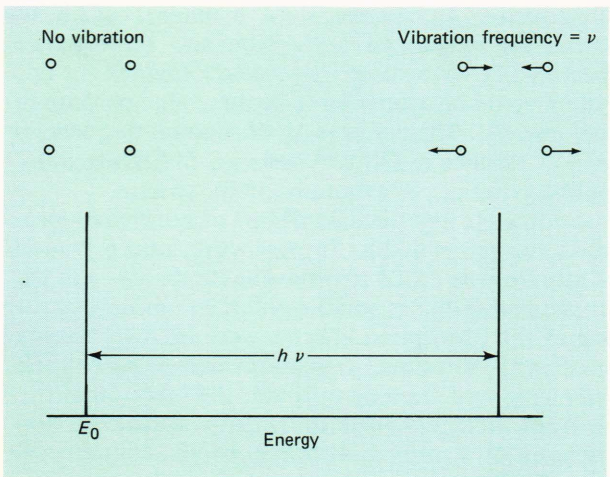

Fig. 11—The effect of a molecular vibration on the spectrum. E_0 is a pure electronic transition. A molecular vibration will introduce an additional line in the absorption spectrum at energy $E_0 + h\nu$ for a vibration in the excited state and an additional line in the fluorescence spectrum at $E_0 - h\nu$ for a vibration in the ground state (see Fig. 4).

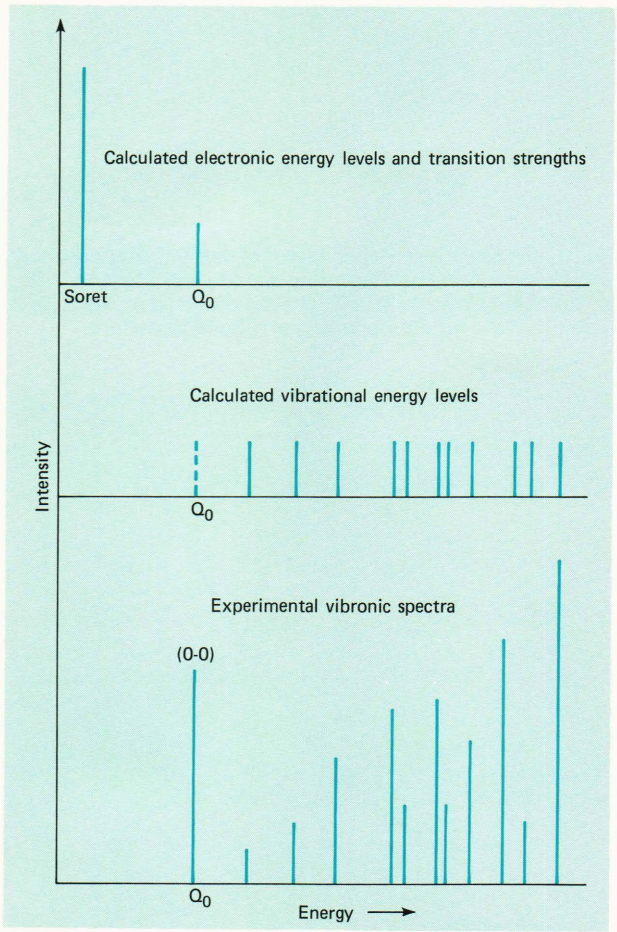

Fig. 12—Present status of theoretical and experimental porphyrin vibronic spectra. The lower spectrum indicates an experimental fluorescence spectrum consisting of a pure electronic transition (0-0) and a number of vibronic lines. The two top spectra indicate the present theoretical capability. The line positions and intensities of pure electronic transitions (Soret band and Q_0) can be calculated if molecular vibrations are not included. The positions of vibronic lines can be calculated (middle spectrum) by classical vibrational analysis while ignoring the electronic structure of the molecule. Intensities of vibronic lines have not been calculated previously. To do so, the interaction between the pure electronic structure of the molecule and the molecular vibrations must be taken into account.

experimental results. The top row illustrates the results of theory in which the electronic energy levels (in the visible region) and transition strengths have been calculated. The middle row exemplifies results of vibrational analyses of porphyrins. In that case, only the energy levels are calculated. The bottom row illustrates a fluorescence spectrum that contains the Q_0 transition and the vibronic lines that are due to transitions from Q_0 to the vibrational states in the ground electronic state. The lack of theoretical vibronic line strengths greatly restricts valid interpretation of experimental spectra.

The effect of molecular vibrations on spectral line strengths can be determined by assessing the effect of the vibrations on the molecular electric dipole moments. There are two ways in which the displaced nuclei in a vibration affect the dipole moment. The first is a geometrical effect in which a dipole moment is induced because of the changes in distances between the charges, q, that are centered on the constituent atoms. This is illustrated for a particular example in Fig. 13. Figure 13a shows the molecule with the nuclei in their equilibrium positions (no vibration). The dipole moment is zero in this nuclear configuration and charge distribution. In Fig. 13b, the nuclei are displaced a distance $d/4$ from their equilibrium positions, corresponding to a particular vibrational mode. A dipole moment of magnitude qd exists when the molecule is in this nuclear configuration. The second effect occurs because the distances between the nuclei have changed, resulting in a change in the electronic energy of the molecule. This change in energy will change the distribution of electronic charge on the nuclei, thus changing the dipole moment.

Our effort in this area has been to incorporate these ideas within the framework of quantum mechanics and the theory of vibrations of polyatomic molecules. This problem is split into three parts in practice: the electronic structure calculation, the vibrational analysis, and the calculation of the interaction of the electronic states and vibrational modes

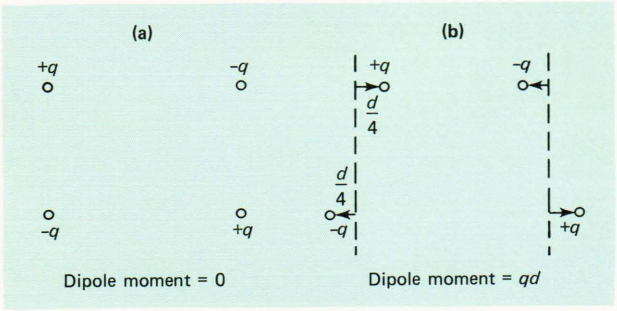

Fig. 13—The effect of a vibrational distortion of a molecule on the molecular dipole moment. In (a), the electric dipole moment is zero. In (b), the atoms are displaced as in a molecular vibration, and a dipole moment of magnitude qd is induced as a result of the change in interatomic distances. The charges on each atom in this example are assumed to be unchanged during the displacement of the atoms.

to account for the vibronic transition strengths. The electronic and vibrational structures, therefore, must be determined first. Electronic structure calculations have been done for porphyrins at APL and other laboratories. The general method that we used for calculating electronic structure is π-electron molecular orbital theory. The principal results of interest for porphyrin spectroscopy are the energy levels and transition intensities for the Soret band and Q_0 states and their corresponding wave functions.

The vibrational analysis is the classical problem of finding the frequencies and normal modes of a system of coupled oscillators. The normal modes are the relative displacements of the components of the oscillator system (the nuclei) for a given vibration frequency. The two essential ingredients for an oscillator system, masses connected by forces that have the characteristics of mechanical springs, are provided by the nuclear masses and the forces that hold the adjacent nuclei together. The model that we used takes into account stretching forces (between two nuclei) and bending forces (torques). This type of force field, called a valence field, is in common use for vibrational analyses of polyatomic molecules.

The results of a recent vibrational analysis of free base porphin by our group are given in Tables 1 and 2,[10] which show the force constants used and the vibrational energies. The normal modes are not listed because of the great amount of detail involved; instead, the principal components in the potential energy distributions, which are related to the normal mode coordinates, are shown. The distribution indicates the percentage contribution of each force

Table 1

FORCE CONSTANTS FOR FREE BASE PORPHIN

1.	NH stretch	6.86 mdyn/Å
2.	CN stretch	6.82
3.	CH stretch	5.12
4.	$C_\alpha C_\beta$ stretch	5.41
5.	$C_\beta C_{\beta'}$ stretch	6.87
6.	$C_\alpha C_m$ stretch	5.62
7.	C_αNH bend	0.45 mdyn·Å
8.	CCH bend	0.43
9.	$C_\beta C_\alpha$N bend	1.02
10.	$C_m C_\alpha$N bend	1.27
11.	$C_\alpha NC_{\alpha'}$ bend	2.00
12.	$C_\alpha C_\beta C_{\beta'}$ bend	1.24
13.	$C_\alpha C_m C_{\alpha'}$ bend	1.37
14.	$C_\beta C_\alpha C_m$ bend	0.98
15.	CC,CC; CC,CN; CN,CN stretch-stretch	0.42 mdyn/Å
16.	CC,CCH stretch-bend	0.18 mdyn
17.	CC,CCC; CC,CCN; CN,CCN; CN,CNC stretch-bend	0.21

Table 2

CALCULATED AND OBSERVED FREQUENCIES OF IN-PLANE VIBRATIONS OF FREE BASE PORPHIN

Symmetry	Frequency (cm^{-1}) Obs.	Obs.	Calc.	Potential Energy Distribution* (%)
A_g			3531	99(1)
			3076	99(3)
			3075	99(3)
			3071	99(3)
	1607 s		1599	41(2) + 13(10) + 11(14) + 10(4)
	1595 vs	1600 vs	1593	48(6) + 29(4) + 11(11) + 11(10)
	1529 vw		1540	36(5) + 31(4) + 14(6) + 12(8)
		1490 m	1516	33(2) + 30(5) + 18(8)
	1400 vw		1418	40(5) + 31(6) + 28(2)
	1348 m	1358 w	1346	42(5) + 30(6)
	1174 s	1219 m	1188	82(8)
		1128 w	1107	80(8) + 11(5)
		1057 w	1103	80(8) + 12(5)
	972 w		968	53(4) + 13(2)
	950 s	950 m	952	32(4) + 20(2) + 15(11)
			748	22(13) + 20(4) + 17(2) + 17(10)
	719 m	720 w	704	27(11) + 18(9) + 15(6) + 15(14)
	272 w	309 w	292	39(6) + 13(11)
	151 vw	152 vw	172	45(10) + 28(14) + 12(2)
B_{1g}			3073	99(3)
			3071	99(3)
			3069	99(3)
	1688 vw		1714	48(7) + 37(2) + 12(6)
	1575 w	1616 vs	1575	58(2) + 26(6)
	1490 m		1481	37(4) + 36(6) + 20(8)
			1469	41(4) + 28(2) + 13(8)
	1383 s	1387 s	1388	28(8) + 26(7) + 22(4) + 19(6)
	1314 m	1318 m	1325	77(8) + 11(6) + 10(4)
	1223 m	1178 m	1193	59(8) + 13(6)
	1137 w		1133	75(8) + 14(4)
	1051 m		1041	30(2) + 28(6)
	986 w	974 w	991	31(2) + 18(8) + 16(6)
			864	45(12) + 14(8) + 11(13)
	722 m	787 w	722	40(12) + 18(9)
	488 w		506	48(10) + 36(14)
		420 vw	407	28(6) + 23(14) + 16(4)
	118 w		124	51(13) + 23(10) + 11(14)

Symmetry	Frequency (cm^{-1}) Obs.	Calc.	Potential Energy Distribution* (%)
B_{2u}		3076	99(3)
		3072	99(3)
		3070	99(3)
		1715	47(7) + 37(2) + 13(6)
		1575	33(2) + 21(4) + 15(10) + 10(11)
		1559	40(6) + 21(5) + 18(4) + 13(8)
		1479	34(4) + 21(5) + 20(8) + 14(2)
	1406	1412	32(6) + 24(2) + 22(7) + 18(5)
	1352	1374	37(8) + 17(4) + 16(7) + 15(6)
	1252	1257	56(8) + 19(6)
	1137	1144	74(8) + 12(4)
		1106	80(8) + 11(5)
	995	991	34(2) + 18(6) + 11(8)
	970	966	37(4) + 18(2) + 10(11)
	841	835	32(12) + 15(10) + 13(4) + 13(13)
	719	710	17(9) + 15(14) + 13(12) + 13(11)
		368	39(10) + 27(14)
		344	30(6) + 15(14)
B_{3u}		3531	99(1)
		3075	99(3)
		3072	99(3)
		3069	99(3)
	1589	1602	36(2) + 25(6) + 16(4) + 10(10)
		1570	32(6) + 22(5) + 15(2) + 14(4)
		1521	59(2)
		1474	36(4) + 23(5) + 21(6) + 21(8)
		1385	26(8) + 25(5) + 23(4) + 20(6)
	1262	1260	64(8) + 15(6)
	1158	1151	74(8) + 13(4)
	1098	1104	80(8) + 11(5)
	1033	1032	30(2) + 27(6) + 13(8)
	951	958	40(4) + 17(2)
	809	822	29(12) + 16(4) + 15(10) + 13(13)
	690	708	17(9) + 17(12) + 11(11) + 11(6)
		370	39(10) + 27(14)
		340	30(6) + 15(14)

*Percentage contribution of each force constant (in parentheses) shown in Table 1.

constant in Table 1 to the potential energy of each vibration. The energies (which are related to the frequencies by $E = h\nu$) are given in wave numbers (cm^{-1}) and compared with experimental results.

The intensities of vibronic transitions are determined by the dipole moment average between the two states involved in the transition. When the molecule undergoes a vibration characterized by a normal coordinate, Q, the dipole transition moment may be written as

$$\bar{M}(Q) = \bar{M}(Q_0) + \left(\frac{\partial \bar{M}}{\partial Q}\right)_{Q_0} Q, \qquad (1)$$

where $\bar{M}(Q_0)$ is the dipole moment when the molecule is in the equilibrium nuclear configuration. The calculation of this expression, using quantum mechanics, involves the electronic wave functions and energy levels and the normal mode vibration coordinates and vibrational wave functions. The mathematical procedure, the details of which will not be discussed here, has been established with computer programs and tested recently for a simple case. The calculation was shown to be resolvable into two parts. One part corresponded to the change in molecular dipole moment due to the altered charge distribution in the molecule during a vibration. The second part was due to the changes in interatomic distances during a vibration. For the test case (a hypothetical four-atom molecule), both parts were of comparable importance. This was considered to be a significant result because the second part is not normally taken into account in calculations of this type.

SUMMARY

The porphyrin spectroscopy project at APL involves both experimental and theoretical work. The initial work was heavily oriented toward experiment because of the lack of available detailed porphyrin spectra. The spectra now available, resulting in large measure from the work at APL, exceed the present theoretical description of porphyrin spectra. Recent work here has been directed toward establishing a theoretical procedure that can describe porphyrin spectra in sufficient detail to match the experimental spectra. Such a procedure has been established, but its validity has not yet been completely tested.

When the theoretical development is completed, it will be used to study the effects of perturbations on porphyrin quantum structure that might be ascribed to discrete impurity species. The specific changes in the spectra that the theory will address are changes in line positions and line intensities. This theory will complement experimental spectra obtained from porphyrin specimens in which small amounts of impurity species have been introduced to produce observable changes in the spectra. In this way, the spectroscopic studies will bear directly on the chemistry of porphyrins in a fundamental manner by correlating changes in porphyrin quantum structure to interactions of porphyrins with other species.

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