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NORMAL-COORDINATE STRUCTURAL DECOMPOSITION AND THE VIBRONIC SPECTRA OF PORPHYRINS

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ABSTRACT

The connection is made between the normal-coordinate structural decomposition (NSD) and the vibronic molecular states and spectra of porphyrins. NSD is a procedure that provides a description of the distortion of a porphyrin from a D_{4h} symmetric reference structure in terms of equivalent displacements along the normal coordinates. Expressions for the optical absorption spectra with vibrational structure are developed with these NSD-determined deformations as parameters, and the expressions are applied to the UV-visible absorption spectra porphyrins.

INTRODUCTION

Normal-coordinate structural decomposition (NSD){Jentzen, 1998 #6367; Jentzen, 1997 #610} has become a powerful tool for the analysis of porphyrin structures, especially for quantifying out-of-plane distortion of the porphyrin macrocycle in heme proteins.{Jentzen, 1998 #6367; Jentzen, 1997 #610; Shelnutt, 1998 #127} The NSD analysis of the structure of a porphyrin macrocycle determines the deformations along the normal coordinates that optimally describe the distortion of the porphyrin molecule from of a square-planar reference structure. The description of the macrocycle distortion in terms of the normal coordinates provides a uniquely useful representation of the conformation given in terms of the vibrational modes and energies of the molecule. One outcome of the NSD analysis is that the description of the porphyrin distortion is greatly simplified. The simplification occurs because only a few displacements along the lowest-frequency vibration modes are required to accurately depict the structure. These lowest-frequency modes represent the most flexible ways for the molecule to distort, and these modes usually exhibit the largest deformations. The simple NSD description is an alternative to listing, for example, the out-of-plane displacements of all 24 atoms of the macrocycle. The latter description is not particularly informative, and even if the distortion is along only one of the normal modes one still has to give all 24 out-of-plane displacements.

Given the unique relationship between the molecular vibrations and the normal coordinates, one would expect that vibrational spectra might have a strong dependence on the normal-coordinate displacements determined in the NSD analysis. Certainly, when the ground-state distortion lowers the symmetry of the porphyrin from D_{4h}, vibrational modes of symmetries not normally Raman or IR active will be observed. Similarly, the vibrational structure in the electronic absorption bands of porphyrins is altered by the macrocyclic distortion, and expressions for the absorbance of the Q and B (Soret) bands, including the vibrational satellites, are easily obtained in the weak vibro-electronic (vibronic) coupling limit. Similar expressions for the Raman excitation spectra (RES) also follow from the analysis.

The crude Born-Oppenheimer approximation and vibronic coupling

The Born-Oppenheimer approximation provides a simplification of the molecular Hamiltonian based on the large difference in nuclear and electronic masses. Electrons are light and move much faster than the nuclei, thus we can effectively consider the nuclei fixed and calculate the motion of the electrons in the Coulomb field of the nuclei.

Consider a molecule consisting of N electrons and P nuclei with charges Z_p and masses M_p.

The Hamiltonian for this system is

$$H = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 - \frac{\hbar^2}{2}\sum_{p=1}^{P}\left(\frac{1}{M_p}\right)\nabla_p^2 - \sum_{i=1}^{N}\sum_{p=1}^{P}\frac{Z_p e^2}{r_{pi}} + \sum_{p>q}^{P}\frac{Z_p Z_q e^2}{R_{pq}} + \sum_{i>j}^{N}\frac{e^2}{r_{ij}}$$

$$= T_e + T_N + V(N-e) + V(N-N) + V(e-e), \qquad (1)$$

which can be rearranged as

$$H = \left[-\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 - \sum_{p}^{P}\sum_{i}^{N}\frac{Z_p e^2}{r_{pi}} + \sum_{i>j}^{N}\frac{e^2}{r_{ij}}\right] + \left[-\frac{\hbar^2}{2}\sum_{p=1}^{P}\left(\frac{1}{M_p}\right)\nabla_p^2 + \sum_{p>q}^{P}\frac{Z_p Z_q e^2}{R_{pq}}\right], \qquad (2)$$

where the terms in the first brackets include both electronic and nuclear coordinates and those in the last set of brackets are purely nuclear. The relative distances r_{pi}, r_{ij}, and R_{pq} are the distance between the p^{th} nucleus and the i^{th} electron, the distance between the i^{th} and j^{th} electrons, and the distance between the p^{th} and q^{th} nuclei, respectively.

Starting with the crude Born-Oppenheimer approximation, we assume solutions of the form

$$\psi\left(\vec{r}_i,\vec{R}_p\right)=\phi\left(\vec{r}_i\right)\chi\left(\vec{R}_p\right), \tag{3}$$

giving a complete separation of the electronic and nuclear motions. $\phi\left(\vec{r}_i\right)$ is a function of the electronic coordinates $\vec{r}_i$, which are related to the relative distances as indicated in Figure 1 for $\vec{r}_{pi}$. Similarly, $\chi\left(\vec{R}_p\right)$ is a function of only the nuclear coordinates $\vec{R}_p$ for each of the nuclei p. Substituting these molecular wavefunctions into the time-independent Schrödinger equation,

$$H\psi = E\psi, \tag{4}$$

we get

$$\chi\left(\vec{R}_p\right)\left(-\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2\right)\phi\left(\vec{r}_i\right)-\sum_{q=1}^{P}\sum_{i=1}^{N}\frac{Z_q e^2}{r_{qi}}\chi\left(\vec{R}_p\right)\phi\left(\vec{r}_i\right)+\chi\left(\vec{R}_p\right)\sum_{i>j}\frac{e^2}{r_{ij}}\phi\left(\vec{r}_i\right)$$

$$+\phi\left(\vec{r}_i\right)\left(-\frac{\hbar^2}{2}\sum_{q=1}^{P}\frac{1}{M_q}\nabla_q^2+\sum_{q>p}^{P}\frac{Z_q Z_p e^2}{R_{pq}}\right)\chi\left(\vec{R}_p\right)=E\chi\left(\vec{R}_p\right)\phi\left(\vec{r}_i\right). \tag{5}$$

Except for the second term on the left-hand side of the equation, the nuclear and electronic motions are separable.

The nuclear coordinate dependence comes in entirely through the terms,

$$-\sum_{q=1}^{P}\sum_{n=1}^{N}\frac{Z_q e^2}{r_{qi}}+\sum_{q>p}^{P}\frac{Z_q Z_p e^2}{R_{pq}}. \tag{6}$$

These potential energy terms contain all of the nuclear coordinate dependence of the Hamiltonian, and they can be expanded in a Taylor series about some zero point, which is usually taken to be the equilibrium geometry of the molecule in the ground state. That is, the full electronic part of the Hamiltonian can be written as

$$H^e = H_0^e\left(q_i, Q=0\right) + \sum_{K=1}^{3P} Q_K \left(\frac{\partial H^e}{\partial Q_K}\right)_{Q=0} + \frac{1}{2}\sum_{K,L=1}^{3P} Q_k Q_L \left(\frac{\partial^2 H^e}{\partial Q_K \partial Q_L}\right)_{Q=0} + \cdots, \qquad (7)$$

where we have made a coordinate transformation to the set of normal coordinates of the ground electronic state g that are zero at the equilibrium positions of the nuclei (Q = 0). The normal coordinates generally involve concerted motions of many of the nuclei of the macrocycle. H^e is the full Hamiltonian of the molecule missing only the term that is the kinetic energy of the nuclei,

$$-\frac{\hbar^2}{2}\sum_{K=1}^{3P}\frac{1}{\mu_K}\frac{\partial^2}{\partial Q_K^2},$$

as expressed in the new coordinates, where μ_K is the reduced mass for the coordinate Q_K. We can also show that both the kinetic and potential energies can be written in this diagonal form when the Q_K are the normal coordinates, though this is not obvious. Mixing the coordinate systems since we will ultimately solve parts of the problem independently, the full molecular Hamiltonian can be written as

$$H = \left[-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_p\sum_i \frac{Z_p e^2}{r_{0_{pi}}} + \sum_{i>j}\frac{e^2}{r_{ij}} + \sum_{p>q}\frac{Z_p Z_q e^2}{R_{0_{pq}}}\right]$$

$$+\left[\sum_{K=1}^{3P-6} Q_K\left(\frac{\partial H}{\partial Q_K}\right)_{Q=0} + \frac{1}{2}\sum_{L,K=1}^{3P-6} Q_K Q_L\left(\frac{\partial^2 H}{\partial Q_K \partial Q_L}\right)_{Q=0} + \cdots\right] + \left[-\frac{\hbar^2}{2}\sum_{K=1}^{3P-6}\frac{1}{\mu_K}\frac{\partial^2}{\partial Q_K^2}\right]. \qquad (8)$$

In this expression, we have separated the Hamiltonian into three terms.

The 0th order electronic states

The first term, $H_0^e\left(q_i, Q=0\right)$, has the nuclei fixed as indicated by the 0 of $r_{0_{pi}}$ and $R_{0_{pq}}$

in the denominators, and only the electrons move. This term gives the usual molecular orbital problem for a single-point calculation (with CI). We assume that we can solve this electronic part of the problem at least approximately. The solutions of the electronic Schrödinger equation with clamped nuclei, *i.e.*, the states $|l_\nu(\vec{r}_i)\rangle$ and energies $E^0_{l_\nu}$, satisfy

$$H^e_0|l_\nu(\vec{r}_i)\rangle = E^0_l|l_\nu(\vec{r}_i)\rangle, \tag{9}$$

Here, ν is a subscript that runs over all degenerate states with energy E^0_l.

The second term of Eq (8) couples the electronic and nuclear motion and we treat it as a perturbation. The third term is the kinetic energy of the nuclei.

The 0th order vibrational states

We now consider the vibrational motion problem, which we solve in terms of the normal coordinates for the electronic ground electronic state, $|g\rangle$, which we just obtained formally in solving Eq (9). Thus, $|g\rangle$ satisfies

$$H^e_0|g\rangle = E^0_g|g\rangle. \tag{10}$$

Now, in the crude Born-Oppenheimer approximation, the molecular states are both Q_K and q_i dependent and are given by product states composed of an electronic wavefunction and a nuclear wavefunction, thus, for the molecular ground states,

$$\psi(\vec{r}_i,\vec{R}_p) = |g\rangle|\chi(Q_K)\rangle. \tag{11}$$

If we let the full molecular Hamiltonian, $H = H^e + T_N$, operate on this 0th order molecular state, we obtain

$$H\psi\left(\vec{r}_i,\vec{R}_p\right) = H|g\rangle\left|\chi_{\vec{v}}(Q_K)\right\rangle = \left(H^e + T_N\right)|g\rangle|\chi_{\vec{v}}\rangle, \tag{12}$$

where $\vec{v}$ is a vector of vibrational quantum numbers of dimension $3P$-6. If we now multiply on the left by the electronic state $\langle g|$ and integrate over the electronic coordinates, we have for the right side of equation (12),

$$\left(\left\langle g\middle|H^e\middle|g\right\rangle + T_N\langle g|g\rangle\right)|\chi_{\vec{v}}\rangle, \tag{13}$$

where,

$$\left\langle g\middle|H^e\middle|g\right\rangle = \left\langle g\middle|H_0^e\middle|g\right\rangle + \sum_{K=1}^{3N} Q_K\left\langle g\left|\left(\frac{\partial H^e}{\partial Q_K}\right)_0\right|g\right\rangle + \frac{1}{2}\sum_{K,L=1}^{3N} Q_K Q_L\left\langle g\left|\left(\frac{\partial^2 H^e}{\partial Q_K \partial Q_L}\right)_0\right|g\right\rangle + \cdots.$$

Truncating the series, we have the approximate expression,

$$\left\langle g\middle|H^e\middle|g\right\rangle \approx E_g^0 + \sum_K Q_K\left\langle g\left|\left(\frac{\partial H^e}{\partial Q_K}\right)_0\right|g\right\rangle + \frac{1}{2}\sum_K\sum_L Q_K Q_L\left\langle g\left|\left(\frac{\partial^2 H^e}{\partial Q_K \partial Q_L}\right)_0\right|g\right\rangle.$$

So we have,

$$\left(\left\langle g\middle|H^e\middle|g\right\rangle + T_N\langle g|g\rangle\right)|\chi_n\rangle =$$

$$\left[E_g^0 + \sum_K Q_K\left\langle g\left|\left(\frac{\partial H^e}{\partial Q_K}\right)_0\right|g\right\rangle + \frac{1}{2}\sum_K\sum_L Q_K Q_L\left\langle g\left|\left(\frac{\partial^2 H^e}{\partial Q_K \partial Q_L}\right)_0\right|g\right\rangle + T_N\right]|\chi_n\rangle \tag{14}$$

Usually we proceed by assuming that the Taylor expansion is about the equilibrium positions of the nuclei, and thus, the linear terms must vanish. That is, the slope at the bottom of the potential well in which the nuclei move must be zero. Said another way "expanding about the equilibrium position" means there can be no force on the nuclei at $Q_1 = 0, \cdots, Q_K = 0, \cdots$.[1] Defining the zero point in this way is not necessary however, and we will relax this condition later in the theory development. Alternatively, we might expand instead about the reference D_{4h} porphyrin macrocycle of the NSD analysis. Porphyrins that exhibit distortions from the reference structure will not have $\langle g|\left(\frac{\partial H^e}{\partial Q_L}\right)_0|g\rangle = 0$ for all normal coordinates, Q_L. These linear terms of the ground state are related to the displacements along the normal coordinates measured for a distorted porphyrin macrocycle by the NSD analysis of its structure. For now, we can neglect these terms and then include them later as part of the vibronic perturbation Hamiltonian for distorted porphyrins.

The quadratic term is diagonal in the normal coordinate system,[2] and we write this term for the ground electronic state as

$$\frac{1}{2}\sum_{K,L} Q_K Q_L \left\langle g\left|\left(\frac{\partial^2 H^e}{\partial Q_K \partial Q_L}\right)_0\right|g\right\rangle = \frac{1}{2}\sum_K Q_K^2 f_K, \tag{15}$$

where the f_K are the force constants of a harmonic oscillator,

$$f_K = \left\langle g\left|\left(\frac{\partial^2 H^e}{\partial Q_K^2}\right)_0\right|g\right\rangle. \tag{16}$$

Thus, finally we have for the ground electronic state,

$$\left(\left\langle g\left|H^e\right|g\right\rangle + T_N\langle g|g\rangle\right)|\chi_{\bar{v}}\rangle = \left[T_N + E_g^0 + \frac{1}{2}\sum_K Q_K^2 f_K\right]|\chi_{\bar{v}}\rangle. \tag{17}$$

The term in square brackets is the nuclear Hamiltonian for the ground state. We now see from Eq. (17) that the potential in which the nuclei move in the ground electronic state is the harmonic electronic potential energy,

$$E_g(Q_K) = E_g^0 + \frac{1}{2}\sum_K Q_K^2 f_K, \tag{18}$$

and the Schrödinger equation for the vibrational states $|\chi_{\vec{v}}(Q_K)\rangle$ of the ground electronic state is that for a collection of $3P$-6 independent harmonic oscillators,

$$\left[\sum_K \left(-\frac{\hbar^2}{2\mu_K}\frac{\partial^2}{\partial Q_K^2} + \frac{1}{2} f_K Q_K^2\right) + E_g^0\right]|\chi_{\vec{v}}\rangle = E_{g,\vec{v}}^0 |\chi_{\vec{v}}\rangle. \tag{19}$$

(Here we have ignored the rotational and translation motion.) The oscillators are independent because of the diagonal form.

The solutions of the independent harmonic oscillators problem are well known; the states $|\chi_{\vec{v}}\rangle$ are products of $3P$-6 Hermite polynomial functions of the normal coordinates with energies given by

$$E_{g\vec{v}} = E_g^0 + \sum_K \left(v_K + \frac{1}{2}\right)\hbar\Omega_K, \tag{20}$$

where the vibrational angular frequency is

$$\Omega_K = \sqrt{\frac{f_K}{\mu_K}}. \tag{21}$$

The vector $\vec{v}$ represents $3P$-6 integers giving the excitation level of each vibration,

$$|\chi_{\vec{v}}(Q_K)\rangle = |v_K \cdots\rangle = |v_1 \cdots, v_K, \cdots v_{3P-6}\rangle = |v_1\rangle |v_2\rangle \cdots |v_K\rangle \cdots |v_{3P-6}\rangle, \tag{22}$$

where we have dropped χ and labeled the vibrational state with the quantum numbers $\vec{v}$. The multimode vibrational state is simply a product of the Hermite polynomial states for each of the $3P$-6 oscillators.

The 0th order molecular states

Although these vibrational states are energy eigenstates only for the ground electronic state, nonetheless they form a basis (*i.e.*, they span the space) of the nuclear coordinates. Thus, we can take as our 0th order molecular states,

$$|\psi\rangle = |l_v\rangle|\vec{v}\rangle, \tag{23}$$

where the vibrational states are those of the ground state, and linear combinations of these states will provide improved first order solutions of the full molecular Hamiltonian, $H = H_0 + H'$. The 0th order states satisfy the 0th order Hamiltonian H_0, which has the form,

$$H_0 = \left[-\frac{\hbar^2}{2m_e}\sum_{i=1}\nabla_i^2 - \sum_p\sum_i \frac{Z_p e^2}{r_{o_{pi}}} + \sum_{i>j}\frac{e^2}{r_{ij}} + \sum_{p>q}\frac{Z_p Z_q e^2}{R_{o_{pq}}} \right] + \left[\frac{1}{2}\sum_K Q_K^2 f_K - \frac{\hbar^2}{2}\sum_K \frac{1}{\mu_K}\frac{\partial^2}{\partial Q_K^2} \right] \tag{24}$$

where the first bracket represents the 0th order *electronic* Hamiltonian and the second term is the 0th order *vibrational* Hamiltonian.

The Hamiltonian H' describing the interaction between the 0th order states is just $H' = H - H_0$, where from Eq (8),

$$\begin{aligned} H = &\left[-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_p\sum_i \frac{Z_p e^2}{r_{o_{pi}}} + \sum_{i>j}\frac{e^2}{r_{ij}} + \sum_{p>q}\frac{Z_p Z_q e^2}{R_{o_{pq}}} \right] \\ &+ \left[\sum_K Q_K \left(\frac{\partial H}{\partial Q_K}\right)_0 + \frac{1}{2}\sum_{K,L} Q_K Q_L \left(\frac{\partial H}{\partial Q_K \partial Q_L}\right)_0 - \frac{\hbar^2}{2}\sum_K \frac{1}{\mu_K}\frac{\partial^2}{\partial Q_K^2} \right]. \end{aligned} \tag{25}$$

Subtracting H_0 from H, we get

$$H' = \sum_K Q_K \left(\frac{\partial H}{\partial Q_K}\right)_0 + \frac{1}{2}\sum_{K,L}\left[Q_K Q_L \left(\frac{\partial H}{\partial Q_K \partial Q_L}\right)_0 - f_K \delta_{K,L} \right]. \tag{26}$$

H' is the vibronic interaction that mixes the 0th order product states of Eq (23) and couples the

0th order electronic states with the 0th order vibrational states. We can now use this vibronic interaction Hamiltonian to obtain perturbative solutions to the vibronic coupling problem.

The 1st order vibronic molecular states

From time-dependent perturbation theory, the eigenstates to first order in the interaction, H', are as shown below:[3]

$$\left|l\right\rangle = \left|l_v\right\rangle\left|\vec{v}\right\rangle - \sum_{j,\alpha}\sum_{\vec{u}}\sum_{K=1}^{3N-6} \frac{\left\langle j_\alpha\right|\left(\frac{\partial H'}{\partial Q_K}\right)_0\left|l_v\right\rangle\left\langle\vec{u}\right|Q_K\left|\vec{v}\right\rangle}{E_{l_v\vec{v}} - E_{j_\alpha\vec{u}}}\left|j_\alpha\right\rangle\left|\vec{u}\right\rangle f_{j_\alpha\vec{u},l_v\vec{v}}(t_0)$$

$$-\sum_{j,\alpha}\sum_{\vec{u}}\sum_{K,L=1}^{3N-6} \frac{\left\langle j_\alpha\right|\left(\frac{\partial^2 H'}{\partial Q_K \partial Q_L}\right)_0\left|l_v\right\rangle\left\langle\vec{u}\right|Q_K Q_L\left|\vec{v}\right\rangle}{E_{l_v\vec{v}} - E_{j_\alpha\vec{u}}}\left|j_\alpha\right\rangle\left|\vec{u}\right\rangle f_{j_\alpha\vec{u},l_v\vec{v}}(t_0) \qquad (27)$$

+ *high order perturbation terms and high order Taylor series expansion terms,*

where $f_{j_\alpha\vec{u},l_v\vec{v}}(t_0) = 1 - e^{i\left(E_j^0 - E_l^0\right)\left(t_0 - t_0'\right)/\hbar}$. Notice that the first order states involve the energies only to 0th order. The molecular states, $\left|l\right\rangle$, are the approximate vibronic molecular states that we will use to introduce vibrational structure into our equations for the different types of electronic and vibrational spectra.

Evaluation of the vibrational matrix elements

Our next step is to evaluate the vibrational matrix elements in the above expression for the approximate vibronic states. The vibrational matrix elements can be evaluated by remembering that for a harmonic oscillator the coordinate can be expressed in terms of the creation and annihilation operators as

$$Q_K = \frac{1}{\sqrt{2f_K}}\left(A_K + A_K^\dagger\right). \tag{28}$$

Thus,

$$\left\langle \vec{u}\middle|Q_K\middle|\vec{v}\right\rangle = \left\langle u_1,\cdots,u_{3P-6}\middle|Q_K\middle|v_1,\cdots,v_{3P-6}\right\rangle = \frac{1}{\sqrt{2f_K}}\langle u_1|\cdots\langle u_{3P-6}|\left(A_K + A_k^\dagger\right)|v_{3P-6}\rangle\cdots|v_1\rangle$$

$$\left\langle \vec{u}\middle|Q_K\middle|\vec{v}\right\rangle = \begin{cases} \frac{1}{\sqrt{2f_K}}\left\langle v_K - 1\middle|A_K\middle|v_K\right\rangle, & \mathit{if}\ u_K = v_K - 1 \\ \frac{1}{\sqrt{2f_K}}\left\langle v_K + 1\middle|A_K^\dagger\middle|v_K\right\rangle, & \mathit{if}\ u_K = v_K + 1 \end{cases} \tag{29}$$

and all other $u_L = v_L$ for $L \neq K$. Now, using the relationships,

$$A_K\left|v_K\right\rangle = \left(v_K\hbar\Omega_K\right)^{1/2}\left|v_K - 1\right\rangle \tag{30}$$

and

$$A_K^\dagger\left|v_K\right\rangle = \left[\left(v_K + 1\right)\hbar\Omega_K\right]^{1/2}\left|v_K + 1\right\rangle, \tag{31}$$

we have

$$\left\langle \vec{u}\middle|Q_K\middle|\vec{v}\right\rangle = \begin{cases} \frac{1}{\sqrt{2f_K}}\left[v_K\hbar\Omega_K\right]^{1/2}, & u_K = v_K - 1\ \mathit{and}\ u_L = v_L,\ \forall L \neq K \\ \frac{1}{\sqrt{2f_K}}\left[\left(v_K + 1\right)\hbar\Omega_K\right]^{1/2}, & u_K = v_K + 1\ \mathit{and}\ u_L = v_L,\ \forall L \neq K \\ 0, & \mathit{otherwise.} \end{cases} \tag{32}$$

Similarly, the bilinear matrix elements are

$$\left\langle \vec{u}\middle|Q_K Q_L\middle|\vec{v}\right\rangle = \left\langle \vec{u}\middle|\left(A_K + A_K^\dagger\right)\left(A_L + A_L^\dagger\right)\middle|\vec{v}\right\rangle = \left\langle \vec{u}\middle|A_K A_L^\dagger\middle|\vec{v}\right\rangle + \left\langle \vec{u}\middle|A_K^\dagger A_L\middle|\vec{v}\right\rangle + \left\langle \vec{u}\middle|A_K A_L\middle|\vec{v}\right\rangle, \tag{33}$$

and the matrix elements that survive are

$$\langle \vec{u} | Q_K Q_L | \vec{v} \rangle = \frac{\hbar}{2\sqrt{\mu_K \Omega_K \mu_L \Omega_L}} \begin{cases} \sqrt{v_K (v_L + 1)}, & u_K = v_K - 1,\ u_L = v_L + 1 \\ \sqrt{(v_K + 1) v_L}, & u_K = v_K + 1,\ u_L = v_L - 1 \\ \sqrt{v_K v_L}, & u_K = v_K - 1,\ u_L = v_L - 1 \\ \sqrt{(v_K + 1)(v_L + 1)}, & u_K = v_K + 1,\ u_L = v_L + 1, \end{cases} \tag{34}$$

and for $K = L$ this reduces to

$$\left\langle \vec{u} \left| Q_K^2 \right| \vec{v} \right\rangle = \frac{\hbar}{2\mu_K \Omega_K} \begin{cases} \sqrt{v_K (v_L + 1)}, & u_K = v_K \\ v_K, & u_K = v_K - 2 \\ (v_K + 1), & u_K = v_K + 2. \end{cases} \tag{35}$$

Because the matrix elements like $\langle \vec{u} | \vec{v} \rangle$ and $\langle \vec{w} | Q_k | \vec{v} \rangle$ vanish for most cases, only a few terms of the U-matrix survive since $\langle \vec{u} | \vec{v} \rangle = \delta_{\vec{u},\vec{v}}$ and $\langle \vec{w} | Q_K | \vec{v} \rangle = 0$, unless $w_K = v_K + 1$ or $v_K - 1$ and $w_L = v_L \ \forall \ L \neq K$. In the case of $w_K = v_K + 1$,

$$\langle \vec{w} | Q_K | \vec{v} \rangle = \left[\frac{(v_K + 1)\hbar}{2\mu_K \Omega_K} \right]^{1/2}, \tag{36}$$

and for $w_K = v_K - 1$,

$$\langle \vec{w} | Q_K | \vec{v} \rangle = \left[\frac{v_K \hbar}{2\mu_K \Omega_K} \right]^{1/2}. \tag{37}$$

Thus, the matrix elements of the time evolution operator vanish for most final vibrational states.

The 0th order vibronic state energies

To completely evaluate the first order vibronic states (27), we also need the 0th order energies of the molecular states $E_{l_v \vec{v}}$, which are the sum of electronic energies $E_{l_v}^0$ plus the vibrational energies, $E_{\vec{v}}$, given by

$$E_{\vec{v}} = \sum_{K=1}^{3P-6} \left(v_K + \frac{1}{2} \right) \hbar \Omega_K . \tag{38}$$

Thus, the 0th order molecular state energies are

$$E_{l_v \vec{v}} = E_{l_v}^0 + \sum_{K=1}^{3P-6} \left(v_K + \frac{1}{2} \right) \hbar \Omega_K . \tag{39}$$

We may now use the 1st order vibronic molecular states and energies to evaluate the expressions for different types of molecular electromagnetic spectra.

Absorption spectra with vibrational structure

The probability amplitude for light absorption is given by

$$U_{f,n_k^\lambda - 1; i, n_k^\lambda} = -i \left[2\pi \hbar \omega_k n_k^\lambda \right]^{1/2} e^{i\vec{k}\cdot\vec{r}_0} \frac{\left\langle f \middle| \hat{e}^\lambda \cdot \vec{\mu} \middle| i \right\rangle}{\varepsilon_f - \varepsilon_i - \hbar \omega_k} \left(1 - e^{i(\varepsilon_f - \varepsilon_i - \hbar\omega)(t - t_0)/\hbar} \right), \tag{40}$$

where the states $|f\rangle$ and $|i\rangle$ are the exact molecular energy eigenstates. However, instead of the exact molecular eigenstates, we will use our first-order approximate vibronic states given in Eq (27). These vibronic states are better molecular states than the crude Born-Oppenheimer product states, $|l_v\rangle|\vec{u}\rangle$, which were our 0th order molecular stationary states.

We will assume the initial molecular state $|i\rangle$ is a ground state vibrational level with vibronic wavefunction,

$$|i\rangle = |g\vec{v}\rangle = |g\rangle|\vec{v}\rangle - \sum_{j,\alpha}\sum_{\vec{w}}\sum_{K} \frac{\left\langle j_\alpha \left| \left(\frac{\partial H}{\partial Q_K}\right)_0 \right| g \right\rangle \langle \vec{w}|Q_K|\vec{v}\rangle}{E_{g\vec{v}} - E_{j_\alpha\vec{w}}} |j_\alpha\rangle|\vec{w}\rangle f_{j_\alpha\vec{w},g\vec{v}}(t_0 - t_0')$$

$$-\sum_{j,\alpha}\sum_{\vec{w}}\sum_{K,L} \frac{\langle j_\alpha | \left(\frac{\partial^2 H'}{\partial Q_K \partial Q_L}\right)_0 |g\rangle \langle \vec{w}|Q_K Q_L|\vec{v}\rangle}{E_{g\vec{v}} - E_{j_\alpha\vec{w}}} |j_\alpha\rangle|\vec{w}\rangle f_{j_\alpha\vec{w},g\vec{v}}(t_0). \qquad (41)$$

We also need the arbitrary final state $\langle f| = \langle l_v\vec{u}|$, which is the adjoint of $|l_v\vec{u}\rangle$,

$$\langle f| = \langle l_v\vec{u}| = \langle l_v|\langle\vec{u}| - \sum_{j,\alpha}\sum_{\vec{w}}\sum_{K} \frac{\langle l_v | \left(\frac{\partial H'}{\partial Q_K}\right)_0 |j_\alpha\rangle \langle \vec{w}|Q_K|\vec{u}\rangle}{E_{l_v\vec{u}} - E_{j_\alpha\vec{w}}} \langle j_\alpha|\langle\vec{u}| f_{l_v\vec{u},j_\alpha\vec{w}}$$

$$-\sum_{j,\alpha}\sum_{\vec{w}}\sum_{K,L} \frac{\langle l_v | \left(\frac{\partial^2 H'}{\partial Q_K \partial Q_L}\right)_0 |j_\alpha\rangle \langle \vec{w}|Q_K Q_L|\vec{u}\rangle}{E_{l_v\vec{u}} - E_{j_\alpha\vec{w}}} \langle j_\alpha|\langle\vec{w}| f_{l_v\vec{u},j_\alpha\vec{w}}. \qquad (42)$$

The final state $|l_v\vec{u}\rangle$ at time t can be a *different* vibrational level of the electronic ground state (infrared, Raman) or an excited electronic and vibrational state (UV-visible absorption, NIR).

Substituting these expressions for the initial and final states $|g\vec{v}\rangle$ and $\langle l_v\vec{u}|$ into the expression (40) for the absorption probability amplitude, we have

$$U_{l_v\vec{u},g\vec{v}}^{n_k^\lambda - 1, n_k^\lambda} = -i\left[2\pi\hbar\omega_k n_k^\lambda\right]^{1/2} e^{i\vec{k}\cdot\vec{r}_0} \left[\frac{\left\langle l_v \left| \hat{e}^\lambda \cdot \vec{\mu} \right| g \right\rangle \langle\vec{u}|\vec{v}\rangle}{E_{l_v\vec{u}} - E_{g\vec{v}} - \hbar\omega_k} \left(1 - e^{i\left(E_{l_v\vec{u}} - E_{g\vec{v}} - \hbar\omega_k\right)(t - t_0)/\hbar}\right) \right.$$

$$-\sum_{j_\alpha}\sum_{\vec{w}}\sum_{K} \frac{\left\langle l_v \left| \left(\frac{\partial H'}{\partial Q_K}\right)_0 \right| j_\alpha \right\rangle \langle \vec{w}|Q_K|\vec{u}\rangle f_{l_v\vec{u},j_\alpha\vec{w}}(t_0 - t_0')}{E_{l_v\vec{u}} - E_{j_\alpha\vec{w}}} \frac{\left\langle j_\alpha \left| \hat{e}^\lambda \cdot \vec{\mu} \right| g \right\rangle \langle\vec{w}|\vec{v}\rangle}{E_{l_v\vec{u}} - E_{g\vec{v}} - \hbar\omega_k} \left(1 - e^{i\left(E_{l_v\vec{u}} - E_{g\vec{v}} - \hbar\omega_k\right)(t - t_0)/\hbar}\right)$$

$$-\sum_{j_\alpha}\sum_{\vec{w}}\sum_{K}\frac{\left\langle j_\alpha\left|\left(\frac{\partial H'}{\partial Q_K}\right)_0\right|g\right\rangle\langle\vec{w}|Q_K|\vec{v}\rangle f_{j_\alpha\vec{w},g\vec{v}}\left(t_0-t_0'\right)}{E_{g\vec{v}}-E_{j_\alpha\vec{w}}}\frac{\left\langle l_v\left|\hat{e}^\lambda\cdot\vec{\mu}\right|j_\alpha\right\rangle\langle\vec{u}|\vec{w}\rangle}{E_{l_v\vec{u}}-E_{g\vec{v}}-\hbar\omega_k}\left(1-e^{i\left(E_{l_v v}-E_{g\vec{v}}-\hbar\omega_k\right)(t-t_0)/\hbar}\right)$$

$$+\ terms\ in\ Q_K Q_L\cdots\Big]. \tag{43}$$

We neglect the fourth term with factors like $\langle\vec{w}|Q_K|\vec{v}\rangle\langle\vec{u}|Q_K|\vec{x}\rangle$ and other terms in $Q_K Q_L$.

Here, we have approximated $\langle\vec{u}|\left\langle l_v\left|\hat{e}^\lambda\cdot\vec{\mu}\right|j_\alpha\right\rangle|\vec{w}\rangle$ by $\left\langle l_v\left|\hat{e}^\lambda\cdot\vec{\mu}\right|j_\alpha\right\rangle\langle\vec{u}|\vec{w}\rangle$. The dipole operator is defined by $\vec{\mu}\equiv\sum_\alpha Z_\alpha e\vec{r}_\alpha$, where α includes all charged particles of the molecule (electrons and nuclei), thus, we have ignored the nuclear coordinate dependence of $\vec{\mu}$. In this case, nuclear coordinate dependence will come entirely through the Q_K-dependence of the energy eigenstates. This is reasonable for optical frequencies of light since the field primarily interacts with the light electrons, but not the heavy and shielded nuclei. On the other hand for IR absorption, this approximation is not sufficient and we must keep the explicit nuclear coordinate dependence of $\vec{\mu}$.

Each state absorbs independently of the other states, thus the probability of absorption to all of the molecular states in terms of the *U*-matrix is

$$P(\hbar\omega_k)=\sum_{l_v,\vec{v}}\left|U_{l_v\vec{u},g\vec{v}}^{n_k^\lambda-1,n_k^\lambda}\right|^2. \tag{44}$$

Evaluating the vibrational matrix elements and molecular state energies in Eq (43), we obtain non-vanishing terms for only three final vibrational states.

(1) First, consider the case when $\vec{u}=\vec{v}$ and l is an electronic excited state; this is called the purely electronic or 0-0 transition. In this case, we have

$$U_{l_v\vec{v},g\vec{v}}^{n_k^\lambda-1,n_k^\lambda}=i\left[2\pi\hbar\omega_k n_k^\lambda\right]^{1/2}e^{i\vec{k}\cdot\vec{r}_0}\frac{\left\langle l_v\left|\hat{e}^\lambda\cdot\vec{\mu}\right|g\right\rangle}{E_{l_v}^0-E_g^0-\hbar\omega_k}\left(1-e^{i\left(E_{l_v}^0-E_g^0-\hbar\omega_k\right)(t-t_0)/\hbar}\right), \tag{45}$$

where the second and third terms vanish for $\vec{u}=\vec{v}$ because

$$\left\langle\vec{w}\left|Q_K\right|\vec{v}\right\rangle\left\langle\vec{w}\middle|\vec{v}\right\rangle=\left\langle\vec{w}\left|Q_K\right|\vec{v}\right\rangle\delta_{\vec{w},\vec{v}}=\left\langle\vec{v}\left|Q_K\right|\vec{v}\right\rangle\delta_{\vec{w},\vec{v}}=0. \tag{46}$$

(2) Next, consider the case, $\left|\vec{u}\right\rangle=\left|v_1,\cdots,v_{L-1},v_L+1,\cdots,v_{3N-6}\right|\equiv\left|v_L+1\right\rangle$, for which we get

$$U_{l_v v_L+1,g v_L}^{n_k^\lambda-1,n_k^\lambda}=i\left[\frac{2\pi n_k^\lambda\hbar\omega_k\left(v_L+1\right)\hbar}{2\mu_L\Omega_L}\right]^{1/2}e^{i\vec{k}\cdot\vec{r}_0}\frac{\left(1-e^{i\left(E_{l_v}^0-E_g^0+\hbar\Omega_L-\hbar\omega_k\right)(t-t_0)/\hbar}\right)}{\left(E_{l_v}^0-E_g^0+\hbar\Omega_L-\hbar\omega_k\right)}$$

$$\times\sum_{j_\alpha}\left[\frac{\left\langle l_v\left|\left(\frac{\partial H'}{\partial Q_L}\right)_0\right|j_\alpha\right\rangle\left\langle j_\alpha\left|\hat{e}^\lambda\cdot\vec{\mu}\right|g\right\rangle f_{l_v v_L+1,j_\alpha v_L}}{E_{l_v}^0-E_{j_\alpha}^0+\hbar\Omega_L}+\frac{\left\langle j_\alpha\left|\left(\frac{\partial H'}{\partial Q_L}\right)_0\right|g\right\rangle\left\langle l_v\left|\hat{e}^\lambda\cdot\vec{\mu}\right|j_\alpha\right\rangle f_{j_\alpha v_L+1,g v_L}}{E_g^0-E_{j_\alpha}^0-\hbar\Omega_L}\right]. \tag{47}$$

(3) The only other case in which an element of U survives is when the final vibrational state is $\left|\vec{u}\right\rangle=\left|v_1,\cdots,v_{L-1},v_L-1,\cdots,v_{3N-6}\right|=\left|v_L-1\right\rangle$. In this case, we have

$$U_{l_v v_L-1,g v_L}^{n_k^\lambda-1,n_k^\lambda}=i\left[\frac{2\pi n_k^\lambda\hbar\omega_k v_L\hbar}{2\mu_L\Omega_L}\right]^{1/2}e^{i\vec{k}\cdot\vec{r}_0}\frac{\left(1-e^{i\left(E_{l_v}^0-E_g^0-\hbar\Omega_L-\hbar\omega_k\right)(t-t_0)/\hbar}\right)}{\left(E_{l_v}^0-E_g^0-\hbar\Omega_L-\hbar\omega_k\right)}$$

$$\times\sum_{j_\alpha}\left[\frac{\left\langle j_\alpha\left|\left(\frac{\partial H'}{\partial Q_L}\right)_0\right|l_v\right\rangle\left\langle j_\alpha\left|\hat{e}^\lambda\cdot\vec{\mu}\right|g\right\rangle f_{l_v v_L-1,j_\alpha v_L}}{E_{l_v}^0-E_{j_\alpha}^0-\hbar\Omega_L}+\frac{\left\langle j_\alpha\left|\left(\frac{\partial H'}{\partial Q_L}\right)_0\right|g\right\rangle\left\langle l_v\left|\hat{e}^\lambda\cdot\vec{\mu}\right|j_\alpha\right\rangle f_{j_\alpha v_L-1,g v_L}}{E_g^0-E_{j_\alpha}^0+\hbar\Omega_L}\right]. \tag{48}$$

The zero-temperature approximation

Before we examine what these three expressions say about the vibrational structure in electronic absorption spectra, let's make one additional simplification. At absolute zero temperature, only the lowest lying vibrational state will be populated, *i.e.*, $\left|\vec{v}\right\rangle = \left|\vec{0}\right\rangle$, and under these conditions the three expressions become

$$U_{l_v\bar{0},g\bar{0}}^{n_k^\lambda-1,n_k^\lambda} = i\left[2\pi n_k^\lambda \hbar\omega_k\right]^{1/2} e^{i\vec{k}\cdot\vec{r}_0} \left\langle l_v\middle|\hat{e}^\lambda\cdot\vec{\mu}\middle|g\right\rangle \frac{\left(1-e^{i\left(E_{l_v}^0-E_g^0-\hbar\omega_k\right)(t-t_0)/\hbar}\right)}{\left(E_{l_v}^0-E_g^0-\hbar\omega_k\right)} \tag{49}$$

$$U_{l_v 1_L,g0_L}^{n_k^\lambda-1,n_k^\lambda} = i\left[\frac{\pi n_k^\lambda \hbar\omega_k\hbar}{\mu_L\Omega_L}\right]^{1/2} e^{i\vec{k}\cdot\vec{r}_0} \frac{\left(1-e^{i\left(E_{l_v}^0-E_g^0+\hbar\Omega_L-\hbar\omega_k\right)(t-t_0)/\hbar}\right)}{\left(E_{l_v}^0-E_g^0+\hbar\Omega_L-\hbar\omega_k\right)}$$

$$\times\sum_{j_\alpha}\left[\frac{\left\langle j_\alpha\middle|\left(\frac{\partial H'}{\partial Q_L}\right)_0\middle|l_v\right\rangle\left\langle j_\alpha\middle|\hat{e}^\lambda\cdot\vec{\mu}\middle|g\right\rangle f_{l_v 1_L,j_a 0}}{E_{l_v}^0-E_{j_\alpha}^0+\hbar\Omega_L}+\frac{\left\langle j_\alpha\middle|\left(\frac{\partial H'}{\partial Q_L}\right)_0\middle|g\right\rangle\left\langle l_v\middle|\hat{e}^\lambda\cdot\vec{\mu}\middle|j_\alpha\right\rangle f_{j_\alpha 1_L,g0}}{E_g^0-E_{j_\alpha}^0-\hbar\Omega_L}\right], \tag{50}$$

and for the third case

$$U_{l_v(-1_L),g0}^{n_k^\lambda-1,n_k^\lambda} = 0\,. \tag{51}$$

Locations of the absorption band maxima

We now use these three expressions to evaluate vibronic effects on optical absorption spectra. First, we will look at the 0°K approximation. Then we evaluate what the expression for case (3), which vanishes in the 0°K approximation, says about absorption spectra in cases where the temperature is not zero.

When absorption is to an excited electronic state $|l_v\rangle$, one absorption band is given by Eq (49). $U^{n_k^\lambda-1,n_k^\lambda}_{l_v\bar{0},g\bar{0}}$ peaks at $E^0_{l_v}-E^0_g=\hbar\omega_k$, that is, when the frequency of the incident light matches the purely electronic transition energy. (The intensity does not diverge at the resonance because of the imaginary line width term that should also appear in the denominator in Eq (49). The intensity at this peak is determined by the transition dipole matrix element, $\left\langle l_v \middle| \hat{e}^\lambda\cdot\bar{\mu} \middle| g\right\rangle$, the incident light intensity $I_0=n_k^\lambda\hbar\omega_k$, and the other factors in Eq (49). For an A_{1g} ground state $|g\rangle$, it is sufficient for $|l_v\rangle$ to transform as *x*, *y*, or *z* so that the dipole matrix element does not necessarily vanish. In the D_{4h} molecular symmetry of porphyrin for example, that would be either an E_u or an A_{2u} state. We get a 0-0 absorption band for each electronic state with non-vanishing dipole matrix element.

Additional vibronic peaks appear in the absorption spectrum as determined by $U^{n_k^\lambda-1,n_k^\lambda}_{l_v1_L,g0}$ given by Eq (50). The peaks occur when the frequency of the incident light is $\hbar\omega_k=E^0_{l_v}-E^0_g+\hbar\Omega_L$. This is when the light energy corresponds to the energy separation of the ground and excited electronic levels *plus* the energy of the vibrational quantum for the L^{th} normal mode. These vibrational side bands thus occur on the high-energy side of the 0-0 band, and the intensity at resonance depends on the dipole matrix element, the same as the 0-0 absorption band. However, the intensity of this so-called 0-1 absorption band also depends on the magnitude of the vibronic coupling matrix elements, $\left\langle j_\alpha \middle| \left(\frac{\partial H'}{\partial Q_L}\right)_0 \middle| l_v \right\rangle$.

Absorption processes are independent events so the spectrum is the sum of all such transitions, *i.e.*,

$$P\left(\hbar\omega_k\right)=\sum_{l_v}\sum_{\vec{u}}\left|U_{l_v\vec{u},g\vec{v}}^{n_k^\lambda-1,n_k^\lambda}\right|^2=\sum_{l_v}\sum_{K}\left|U_{l_v 1_L,g\vec{0}}^{n_k^\lambda-1,n_k^\lambda}\right|^2. \qquad (52)$$

(See equations (11) and (12) in a paper by Shelnutt.){Shelnutt, 1981 #16132} Vibrational side bands are illustrated in Figure 2.

Thus, the absorption spectrum, which is proportional to the probability of absorption, is composed of the 0-0 transition for each electronic state and a vibrational satellite band composed of the 0-1 absorptions from each of the allowed normal coordinates, that is, normal coordinates for which the vibronic coupling matrix elements do not vanish. The normal coordinates that contribute to the spectrum are determined by the symmetry properties of the vibronic coupling matrix elements.

Intensity borrowing in absorption spectra

Ignoring the *t*-dependent factors, the intensity of the 0-0 absorption band is

$$I_{l_v\bar{0},g\bar{0}}=\frac{2\pi\hbar\omega_k n_k^\lambda\left|\left\langle l_v\left|\hat{e}^\lambda\cdot\bar{\mu}\right|g\right\rangle\right|^2}{\left(E_{l_v}^0-E_g^0-\hbar\omega_k\right)^2}, \qquad (53)$$

and the intensity of the contribution of L^{th} normal mode to the vibrational side band is

$$I_{l_v 1_L,g0} = \frac{\pi n_k^{\lambda} \hbar \omega_k}{\mu_L \Omega_L} \frac{1}{\left(E^0_{l_v} - E^0_g + \hbar\Omega_L - \hbar\omega_k\right)^2}$$
$$\times \left| \sum_{j_\alpha} \left[\frac{\left\langle j_\alpha \middle| \left(\frac{\partial H'}{\partial Q_L}\right)_0 \middle| l_v \right\rangle \left\langle j_\alpha \middle| \hat{e}^{\lambda} \cdot \vec{\mu} \middle| g \right\rangle f_{l_v 1_L, j_\alpha 0}}{E^0_{l_v} - E^0_{j_\alpha} + \hbar\Omega_L} + \frac{\left\langle j_\alpha \middle| \left(\frac{\partial H'}{\partial Q_L}\right)_0 \middle| g \right\rangle \left\langle l_v \middle| \hat{e}^{\lambda} \cdot \vec{\mu} \middle| j_\alpha \right\rangle f_{j_\alpha 1_L, g0}}{E^0_g - E^0_{j_\alpha} - \hbar\Omega_L} \right] \right|^2 \quad (54)$$

For electronic absorption by D4h metalloporphyrins, the energy denominator of the second term in the numerator is large, since

$$E^0_{j_\alpha} - E^0_g + \hbar\Omega_L > E^0_{j_\alpha} - E^0_g >> \hbar\Omega_L, \quad (55)$$

for $j_\alpha \neq g$. In the case $j_\alpha = g$, the matrix elements $\left\langle g \middle| \left(\frac{\partial H'}{\partial Q_L}\right)_0 \middle| g \right\rangle$ all vanish since the ground-state matrix elements are all zero. Thus, if we neglect the vibronic coupling to the ground state, then we have only the first term that survives with $j_\alpha \neq g$,

$$I_{l_v 1_L,g0} = \frac{2\pi n_k^{\lambda} \hbar \omega_k \hbar}{\mu_L \Omega_L} \left| \sum_{j_\alpha} \frac{\left\langle j_\alpha \middle| \left(\frac{\partial H'}{\partial Q_L}\right)_0 \middle| l_v \right\rangle \left\langle j_\alpha \middle| \hat{e}^{\lambda} \cdot \vec{\mu} \middle| g \right\rangle}{E^0_{l_v} - E^0_{j_\alpha} + \hbar\Omega_L} \right|^2 \frac{1}{\left(E^0_{l_v} - E^0_g + \hbar\Omega_L - \hbar\omega_k\right)^2}. \quad (56)$$

Usually, the largest term in the sum of Eq (56) will be from vibronic coupling within an excited electronic state $\left|l_v\right\rangle$, *i.e.*, the term for which $j_\alpha = l_v$, since this allows the denominator to get as small as $\hbar\Omega_L$. However, nearby electronic states for which $E^0_{j_\alpha} - E^0_{l_v} \approx \hbar\Omega_L$ can also give a very large contribution.

Even if an electronic state $|j_\alpha\rangle$ is farther away in energy (*i.e.*, $E^0_{j_\alpha} - E^0_{l_v} > \hbar\Omega_L$), vibronic coupling to $|j_\alpha\rangle$ will contribute if its transition dipole $\langle j_\alpha|\hat{e}^\lambda \cdot \vec{\mu}|g\rangle$ is large enough to make up for the large denominator. When this occurs, it is called *intensity borrowing* and intensity borrowing plays an important role in the absorption spectra of porphyrins.

Interference effects on the relative intensities of the 0-0 and 0-1 bands

Another feature of the absorption spectra of porphyrins is that the intensity factor of Eq (56) may contain more than one term. In this case, cancellation or addition of the contributions to the vibrational side band from both the intra-state and inter-state terms may occur. Interference is important in determining a particular vibration's contribution to the 0-1 absorption band. These effects are most noticeable when the magnitudes of the terms are nearly equal. Their influence is even more apparent for the resonance Raman excitation profiles than for the absorption spectra.

Optical absorption spectra of metalloporphyrins

The UV-visible absorption spectra of metalloporphyrins, illustrated in Figure 3 provide a good example of intensity borrowing. Part of the intensity in Q_V-band is due to vibronic coupling among the Q_x and Q_y components of the doubly degenerate E_u state (D_{4h} molecular symmetry), *i.e.*,

$$j_\alpha = l_v = Q_x, Q_y \quad (j = \mathrm{Q};\ \alpha = x, y), \tag{57}$$

through matrix elements such as

$$\left\langle Q_x \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| Q_x \right\rangle . \qquad (58)$$

Another part of the intensity is a result of coupling of the Q states to the B_x and B_y states, *i.e.*, $j_\alpha = B_x, B_y$ and $l_v = Q_x, Q_y$ by matrix elements like

$$\left\langle B_y \left| \left(\frac{\partial H'}{\partial Q_L} \right)_0 \right| Q_x \right\rangle . \qquad (59)$$

Even though the separation between the Q and B states is large (~7000 cm^{-1}) compared to typical fundamental vibrational frequencies (~1500 cm^{-1}), the large extinction coefficient of B still allows it to contribute sometimes on par with the inter-Q state coupling.

Symmetry considerations in the absence of ground-state distortion of the porphyrin

For a D_{4h}-symmetric porphyrin, the totally symmetric representation must belong to $\Gamma_{l_v} \times \Gamma_{j_\alpha} \times \Gamma_L$ if the vibronic coupling matrix elements of the type (58) and (59) are to be nonzero. Since the Q and B states are of (transform according to) E_u symmetry in D_{4h}, we can see from the character table (Table 1) that $E_u \otimes E_u$ contains A_{1g}, A_{2g}, B_{1g}, and B_{2g}. For the x- and y-components of *the same electronic state*, the A_{2g} symmetry representation must be omitted from these representations of the group since A_{2g} does not transform like x^2, y^2, or xy (see Table 1). Therefore, for the vibronic coupling matrix element to survive, Γ_L crossed with one of these four (or three) representations must give the totally symmetric representation. This occurs only when the symmetry of the L^{th} normal mode is itself of one of these symmetries because the totally symmetric representation is obtained when one of these symmetry representations is crossed with itself. Thus, only the A_{1g}, A_{2g}, B_{1g}, and B_{2g} vibrational modes contribute to the absorbance of the vibration side band. Vibrations with all four of these symmetries contribute for coupling between the Q and B states; only A_{1g}, B_{1g}, and B_{2g} vibrational modes contribute by vibronically coupling within the (Q_x,Q_y) and (B_x, B_y) pairs. Since the same vibronic and electronic matrix elements also determine the symmetries of the vibrations that are active in the resonance Raman spectra, the same selection rules determine the Raman active modes.

Connection with the ground-state deformations of porphyrin from NSD

The displacements along the normal coordinates for the ground state structures of porphyrins can be explicitly represented in the above-described development of the vibronic states of molecules. Remember that these displacements are measured from a D_{4h}-symmetric porphyrin reference structure, and the displacements are for the ground state of the porphyrin. This situation is treated by carrying out the Taylor series expansion about the reference structure instead of the equilibrium structure of the molecule. In this case, the linear matrix elements of the type $\langle g|\left(\frac{\partial H}{\partial Q_L}\right)_0|g\rangle$ no longer vanish. We will also make the approximation that keeping one or several of these linear matrix elements adequately describes the distortion in the ground state. This means that the development of the vibronic theory up to this point is valid as long as we now include these ground-state vibronic matrix elements.

The connection with NSD is made if the reference structure for the expansion is the same as the NSD reference structure. Before we continue we must first understand the meaning of the normal coordinates in this instance. The NSD displacements are along the coordinates of the "bare" metalloporphyrin macrocycle, i.e., the copper porphyrin macrocycle for which the masses of the 12 hydrogen atom substituents and the metal atom are set to zero. For all substituted porphyrins these bare macrocycle normal coordinates are mixed with the substituent and metal motions to give the true normal coordinates of the particular substituted porphyrin. Thus, our expressions in terms of the macrocycle modes describe how a normal mode of the substituted porphyrin responds to a macrocycle distortion to the extent that it contains contributions from the normal coordinates of the bare macrocycle. We will often find that the ground state distortion occurs along only one or two macrocycle normal coordinates. The analysis that we now describe strictly only applies for a distortion of our bare reference macrocycle, which has no physical reality; however, mixing of the macrocycle and substituent (and metal) motions insures that the actual porphyrin normal modes behave similarly. If the normal coordinate vectors are know for the porphyrin, then we can used NSD to project out the contributions of the bare macrocycle modes.

We must remember that the Hamiltonian itself is no longer totally symmetric because of the inclusion of the symmetry-lowering terms. For the ground-state vibrational states, the Hamiltonian is now given by

$$H^e = T_N + E_g^0 + \sum_L Q_L \langle g | \left(\frac{\partial H^e}{\partial Q_L}\right)_0 | g \rangle + \tfrac{1}{2} \sum_L Q_L^2 f_L \tag{60}$$

instead of the Hamiltonian in Eq (17), which applies when the expansion is about the equilibrium undistorted structure. The state $|g\rangle$ is the electronic ground state of the D_{4h} reference structure in the NSD analysis and is assumed to be A_{1g}. At first it might seem that the matrix elements $\langle g | \left(\frac{\partial H}{\partial Q_L}\right)_0 | g \rangle$ actually vanish since the 0th order electronic state $|g\rangle$ is A_{1g} in D_{4h}, thus the matrix element would vanish unless $\left(\frac{\partial H}{\partial Q_L}\right)_0$ is also A_{1g}. This seems to allow only totally symmetric deformations and no symmetry lowering. However, remember that H^e is no longer totally symmetric when there is a deformation along a particular asymmetric coordinate Q_L. This means that $\left(\frac{\partial H}{\partial Q_L}\right)_0$ contains A_{1g} as long as Γ_L is contained in the representations of the Hamiltonian. If the distortion is along only one normal coordinate, say Q_K, then the Hamiltonian contains $A_{1g} \oplus \Gamma_K$, and thus $\Gamma_L \otimes \Gamma_{H^e} = \Gamma_L \otimes (A_{1g} \oplus \Gamma_K)$ will contain A_{1g} if Γ_L is either A_{1g} or Γ_K. That is, the matrix element will not vanish for normal modes of the same symmetry as the normal coordinate along which the ground state distortion occurs.

The molecular symmetry of the porphyrin is lowered by the distortion, and if the distortion is along a single non-totally symmetric normal coordinate Q_K, then the molecular symmetry is that of the highest symmetry point group for which Γ_K becomes totally symmetric. This point group can be determined using the correlation table for the D_{4h} point group and its subgroups (Table 2). For example, consider a purely ruffled porphyrin that is distorted along the lowest-frequency normal coordinate of B_{1u} symmetry. Examination of the correlation table shown in Table 2 indicates that the point group $D_{2d}(C_2')$ has B_{1u} alone of all the non-totally symmetric modes going into A_1. Thus, pure ruffling gives D_{2d} for the macrocycle symmetry. If the ground-state distortion is along more than one normal coordinate, then the distortion is lowered to the point group for which the symmetries of all of these normal modes become totally symmetric. For example, the gabled porphyrin structure involves deformations along both the ruffling and doming coordinates with symmetries B_{1u} and A_{2u}, respectively. From the correlation table, the point group $C_{2v}(C_2,\sigma_d)$ has both B_{1u} and A_{2u} as A_1. Thus, the symmetry of the macrocycle and of course its molecular Hamiltonian are C_{2v}.

The equations we have derived for UV-visible absorption spectra by expanding about the equilibrium structure of the molecule are almost the same as those needed for an expansion about the D_{4h} reference structure. However, there are more nonvanishing matrix elements to be concerned with, mainly the linear terms of the ground electronic state. These matrix elements are directly related to the deformation along the normal coordinates. From Eq (17), the minimum of the potential energy (where the slope is zero) is at $Q_L = 0$ for all L. In contrast, the minimum in the potential energy for Eq (60) occurs where the condition

$$\frac{\partial H^e}{\partial Q_K} = \left\langle g \middle| \left(\frac{\partial H^e}{\partial Q_K}\right)_0 \middle| g \right\rangle + Q_K^0 f_K = 0 \tag{61}$$

is met. Thus, the deformation along the K^{th} normal coordinate Q_K^0 is

$$Q_K^0 = \frac{-\left\langle g \middle| \left(\frac{\partial H^e}{\partial Q_K}\right)_0 \middle| g \right\rangle}{f_K}. \tag{62}$$

The energy of the equilibrium point of the potential energy is lower than E_g^0 by

$$\frac{\left| \left\langle g \middle| \left(\frac{\partial H^e}{\partial Q_K}\right)_0 \middle| g \right\rangle \right|^2}{8 f_K}. \tag{63}$$

The deformations Q_K^0 are determined in the NSD analysis. However, keep in mind that these are the displacements along the normal coordinates of the reference macrocycle (no substituents or metal), not the normal coordinates of a particular substituted porphyrin. Strictly speaking, since no quadratic terms are added in Eq (60), then the normal coordinates of the bare macrocycle are unaltered by the distortion.

Effects of ground-state distortion on the UV-visible absorption spectra

At first order, the 0-0 transition is unaffected by the distortion in the ground state because the vibronic matrix elements do not appear in Eq (53). At higher orders of the expansion in Eq (43), new bilinear terms will introduce distortion effects on the 0-0 absorption bands.

For the 0-1 transitions of excited electronic states $|l_v\rangle$ such as Q and B for porphyrins, the intensity factor for Eq (54) contains the term,

$$\frac{\langle g|\left(\frac{\partial H}{\partial Q_L}\right)_0|l_v\rangle\langle g|\hat{e}^{\lambda}\cdot\vec{\mu}|g\rangle f_{l_v 1_L,g0}}{E_l^0-E_g^0+\hbar\Omega_L}+\frac{\langle g|\left(\frac{\partial H}{\partial Q_L}\right)_0|g\rangle\langle l_v|\hat{e}^{\lambda}\cdot\vec{\mu}|j_\alpha\rangle f_{g1_L,g0}}{-\hbar\Omega_L} \tag{64}$$

when $j_\alpha = g$ in the sum. Usually, the first term is small because the electronic states l_v (Q_x, Q_y, B_x, B_y) are far above the ground state, making the denominator large. In addition, the second term usually vanishes in the absence of ground state distortion because the vibronic matrix elements $\langle g|\left(\frac{\partial H}{\partial Q_K}\right)_0|g\rangle$ vanish. However, when there is ground state distortion, the matrix elements $\langle g|\left(\frac{\partial H}{\partial Q_K}\right)_0|g\rangle$ do not vanish, and the modes along which the distortion occurs then contribute to the absorbance of the vibrational side band of the electronic transition by way of the last term in Eq (64). The new vibrations that are activated by this mechanism contribute peaks at the frequency of the 0-0 transition plus the vibrational frequency of the normal mode. For porphyrins, the symmetry of these new normal modes are not restricted to those that couple E_u electronic states, but are of the symmetry of the deformations contributing to the ground state distortion. For example, porphyrin doming is an A_{2u} deformation, thus A_{2u} normal coordinates containing the *dom* vibration can contribute to the vibrational satellites of the Q and B absorption bands of the domed porphyrin. The magnitude of the contribution depends on the magnitude of $\langle g|\left(\frac{\partial H}{\partial Q_L}\right)_0|g\rangle$ and thus the displacement along the L^{th} normal coordinate, *i.e.*, the *dom* deformation in this case. Physically, this just expresses the obvious result that the totally symmetric modes in the lowered symmetry of the distorted porphyrin are allowed.

Other than the addition of the $j_\alpha = g$ term of Eq (64), the expression for the 0-1 term remains formally the same as given in Eq (56). However, the distortion introduces additional nonzero matrix elements in the sum that mix $|j_\alpha\rangle$ and $|l_\nu\rangle$ and thus alter the contributions of the normal modes to the absorption and resonance Raman spectra. In the case of D_{4h}-symmetric porphyrins, only in-plane vibrations of A_{1g}, A_{2g}, B_{1g}, and B_{2g} influence the vibrational side bands, because these symmetries are contained in $E_u \otimes E_u$. That is, $\left(\frac{\partial H}{\partial Q_L}\right)_0$, which transforms like Γ_L, must have one of these symmetry classifications if the L^{th} mode is to contribute by mixing two E_u states like Q and B.

On the other hand, if the molecule is distorted along say the *K*th normal coordinate, then H has the symmetry $A_{1g} \otimes \Gamma_K$. Thus, $\left(\frac{\partial H}{\partial Q_L}\right)_0$ has the symmetry $\Gamma_L \otimes \Gamma_H = \Gamma_L \otimes (A_{1g} \oplus \Gamma_K) = \Gamma_L \oplus (\Gamma_L \otimes \Gamma_K)$. The matrix elements coupling the Q and B E_u-symmetry transitions, $\langle l_\nu|\left(\frac{\partial H}{\partial Q_L}\right)_0|j_\alpha\rangle$, to be allowed also require that $\Gamma_L \oplus (\Gamma_L \otimes \Gamma_K) = E_u \otimes E_u = A_{1g} \oplus A_{2g} \oplus B_{1g} \oplus B_{2g}$. This condition is satisfied if

$$\Gamma_L = A_{1g}, A_{2g}, B_{1g}, \text{ or } B_{2g} \tag{65}$$

or

$$\Gamma_L \otimes \Gamma_K = A_{1g}, A_{2g}, B_{1g}, \text{ or } B_{2g} \tag{66}$$

The former case is just the usual selection rule making the A_{1g}, A_{2g}, B_{1g}, and B_{2g} modes active for the vibronic side bands of the Q and B transitions. In the latter case, Eq (66), the modes that can contribute depend on the symmetry of the deformation Γ_K. Since any of the representations A_{1g}, A_{2g}, B_{1g}, and B_{2g} crossed with itself or one of the other members of this collection also gives one of this set, then any of these in-plane vibrations, which are already active in D_{4h} symmetry, will have additional nonzero matrix elements brought about by the distortion. Furthermore, if the ground state deformation Γ_K is of E_u in-plane symmetry, then E_u normal modes will contribute to the Raman and absorption spectra because Eq (66) is then satisfied. Similarly, if the distortion is an out-of-plane E_g distortion (*e.g.*, a wave deformation), the E_g modes are activated. Lastly, for the other out-of-plane modes of A_{1u}, A_{2u}, B_{1u}, and B_{2u} symmetries, we get one of A_{1g}, A_{2g}, B_{1g}, and B_{2g} by crossing any one of the out-of-plane symmetries with one of the other members of this set. Thus, a distortion of one these types activates all of the other out-of-plane modes of this set of symmetries.

As a concrete example, doming is a deformation along the lowest frequency mode of A_{2u} symmetry, giving $\Gamma_K = A_{2u}$. This activates all A_{2u} modes since $\Gamma_L \otimes \Gamma_K = A_{2u} \otimes A_{2u} = A_{1g}$. However, B_{1u} modes are active as well since $\Gamma_L \otimes \Gamma_K = B_{1u} \otimes A_{2u} = B_{2g}$. Similarly, doming activates the other nondegenerate out-of-plane modes.

Summarizing, A_{1g}, A_{2g}, B_{1g}, and B_{2g} modes are always active in vibronically coupling Q and B transitions of porphyrins, but deformation along one of these in-plane modes alters their contribution to the vibrational side bands of Q and B. Normal modes of A_{1u}, A_{2u}, B_{1u}, and B_{2u}

symmetries will contribute if the ground state deformation is along a normal coordinate of one of these symmetry types. E_u normal modes become active if the deformation is along a E_u mode, and E_g modes become active if the deformation is E_g. These contributions from matrix elements like $\left\langle l_\nu \left| \left(\frac{\partial H}{\partial Q_L} \right)_0 \right| j_\alpha \right\rangle$ are independent of the contributions from the ground state matrix elements $\left\langle g \left| \left(\frac{\partial H}{\partial Q_L} \right)_0 \right| g \right\rangle$ that will also be present as describe above. Notice that the former contributions are not directly related to the latter ground-state distortion given by the NSD deformations.

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REFERENCES AND FOOTNOTES

1. Thus, the force given by

$$F_K = -\frac{\partial E_g(Q_K)}{\partial Q_K}$$

must vanish for all K at the equilibrium point.

$$0 = F_L = -\frac{\partial}{\partial Q_L}\left(E_g^0 + \sum_K Q_K \left\langle g \left| \left(\frac{\partial H}{\partial Q_K} \right)_0 \right| g \right\rangle + \frac{1}{2} \sum_K Q_K^2 \left\langle g \left| \left(\frac{\partial^2 H}{\partial Q_K^2} \right)_0 \right| g \right\rangle \right)$$

$$= -\left\langle g \left| \left(\frac{\partial H}{\partial Q_K} \right)_0 \right| g \right\rangle - Q_L \left\langle g \left| \left(\frac{\partial^2 H}{\partial Q_L^2} \right)_0 \right| g \right\rangle$$

at $Q_L = 0$, the force will vanish if and only if we have

$$\left\langle g \left| \left(\frac{\partial H}{\partial Q_L} \right)_0 \right| g \right\rangle = 0, \quad \forall L.$$

2. We must still show that a set of coordinates Q_K can be found for which both the kinetic energy operator and the potential energy $E_g(Q_K)$ can be simultaneously written in the diagonal forms, *i.e.*,

$$-\frac{\hbar^2}{2} \sum_K \frac{1}{\mu_K} \frac{\partial^2}{\partial Q_K^2}$$

and

$$E_g^0 + \frac{1}{2} \sum_K Q_K^2 f_K \ )$$

3. In the above we have used a result from perturbation theory. The state $|i(t_0)\rangle$ of the molecule at time t_0 after the vibrational-electronic interaction H' is turned on at t_0' is

obtained from the coefficients

$$\langle f|i(t)\rangle = \langle f|U|i\rangle = U_{fi}.$$

This is the amplitude for the probability of starting in an initial 0^{th} order eigenstate i and evolving to a 0^{th} order eigenstate f in time t_0' to t_0, at which time the interaction with the field is turned on. The 0^{th} order state i evolves according to

$$|i(t)\rangle = \sum_j |j\rangle\langle j|i(t)\rangle = \sum_j |j\rangle\langle j|U|i\rangle = \sum_j U_{ji}|j\rangle.$$

Now from our earlier result, to first order

$$U_{ji} = \delta_{ji} + \frac{\langle j|H'|i\rangle}{E_j - E_i}\left(1 - e^{i(E_j - E_i)(t_0 - t_0')/\hbar}\right);$$

therefore, to first order the state at time t_0 is

$$|l(t_0)\rangle = \sum_j U_{jl}|j\rangle = \sum_j \left[\delta_{jl} + \langle j|H'|l\rangle \frac{\left(1 - e^{i(E_j - E_l)(t_0 - t_0')/\hbar}\right)}{E_j - E_l}\right]|j\rangle$$

$$= |l\rangle + \sum_j \langle j|H'|l\rangle \frac{\left(1 - e^{i(E_j - E_l)(t_0 - t_0')/\hbar}\right)}{E_j - E_l}|j\rangle.$$

Substituting for the vibronic Hamiltonian leads to the improved molecular eigenstates given above.

Table 1. Character table for the D_{4h} molecular point group.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0		(xz,yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	-1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x,y)	

Table 2. Correlation table for the D4h point group and its subgroups. (Fateley, W.G., Golish, F.R., McDevitt, N.T., Bentley, F.F. *Infrared and Raman Selection Rules for Molecular and Lattice Vibrations: The Correlation* Methods, Wiley-Interscience: New York, 1972; Salthouse, J.A. Ware, M.J., *Point Group Character Tables,* University Press: Cambridge, 1972.)

D_{4h}	D_4	D_{2h}		D_{2d}		C_{4h}	C_{4v}	C_4	S_4	D_2		C_{2v}	
		C'_2	C''_2	C'_2	C''_2					C'_2	C''_2	C_2,σ_v	C_2,σ_d
A_{1g}	A_1	A_g	A_g	A_1	A_1	A_g	A_1	A	A	A	A	A_1	A_1
A_{2g}	A_2	B_{1g}	B_{1g}	A_2	A_2	A_g	A_2	A	A	B_1	B_1	A_2	A_2
B_{1g}	B_1	A_g	B_{1g}	B_1	B_2	B_g	B_1	B	B	A	B_1	A_1	A_2
B_{2g}	B_2	B_{1g}	A_g	B_2	B_1	B_g	B_2	B	B	B_1	A	A_2	A_1
E_g	E	$B_{2g}+B_{3g}$	$B_{2g}+B_{3g}$	E	E	E_g	E	E	E	B_2+B_3	B_2+B_3	B_1+B_2	B_1+B_2
A_{1u}	A_1	A_u	A_u	B_1	B_1	A_u	A_2	A	B	A	A	A_2	A_2
A_{2u}	A_2	B_{1u}	B_{1u}	B_2	B_2	A_u	A_1	A	B	B_1	B_1	A_1	A_1
B_{1u}	B_1	A_u	B_{1u}	A_1	A_2	B_u	B_2	B	A	A	B_1	A_2	A_1
B_{2u}	B_2	B_{1u}	A_u	A_2	A_1	B_u	B_1	B	A	B_1	A	A_1	A_2
E_u	E	$B_{2u}+B_{3u}$	$B_{2u}+B_{3u}$	E	E	E_u	E	E	E	B_2+B_3	B_2+B_3	B_1+B_2	B_1+B_2

D_{4h}	C_{2v}		C_{4h}			C_2			C_S			C_i
	C'_2	C''_2	C_2	C'_2	C''_2	C_2	C'_2	C''_2	σ_h	σ_v	σ_d	
A_{1g}	A_1	A_1	A_g	A_g	A_g	A_g	A_1	A	A'	A'	A'	A_g
A_{2g}	B_1	B_1	A_g	B_g	B_g	A_g	A_2	A	A'	A''	A''	A_g
B_{1g}	A_1	B_1	A_g	A_g	B_g	B_g	B_1	B	A'	A'	A''	A_g
B_{2g}	B_1	A_1	A_g	B_g	A_g	B_g	B_2	B	A'	A''	A'	A_g
E_g	A_2+B_2	A_2+B_2	$2B_g$	A_g+B_g	A_g+B_g	2B	A+B	A+B	$2A''$	$A'+A''$	$A'+A''$	$2A_g$
A_{1u}	A_2	A_2	A_u	A_u	A_u	A	A	A	A''	A''	A''	A_u
A_{2u}	B_2	B_2	A_u	B_u	B_u	A	B	B	A''	A'	A'	A_u
B_{1u}	A_2	B_2	A_u	A_u	B_u	A	A	B	A''	A''	A'	A_u
B_{2u}	B_2	A_2	A_u	B_u	A_u	A	B	A	A''	A'	A''	A_u
E_u	A_1+B_1	A_1+B_1	$2B_u$	A_u+B_u	A_u+B_u	2B	A+B	A+B	$2A'$	$A'+A''$	$A'+A''$	$2A_u$

FIGURES

Figure 1. Definitions of distance in Eq (2).

Figure 2. Vibronic structure in absorption spectra.

Figure 3. Typical metal porphyrin absorption spectrum illustrating the observed vibronic structure for the Q transition. The intensity of the vibrational side band is partly a consequence of intensity borrowing from the strong B transition. It is also influenced by distortion in the ground electronic state as quantified by normal-coordinate structural decomposition.

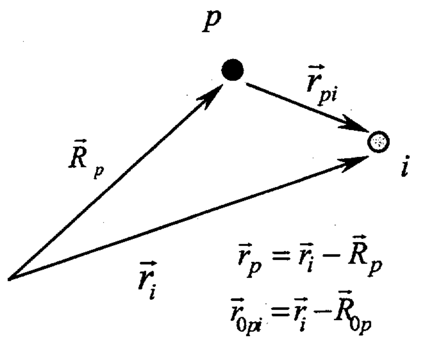
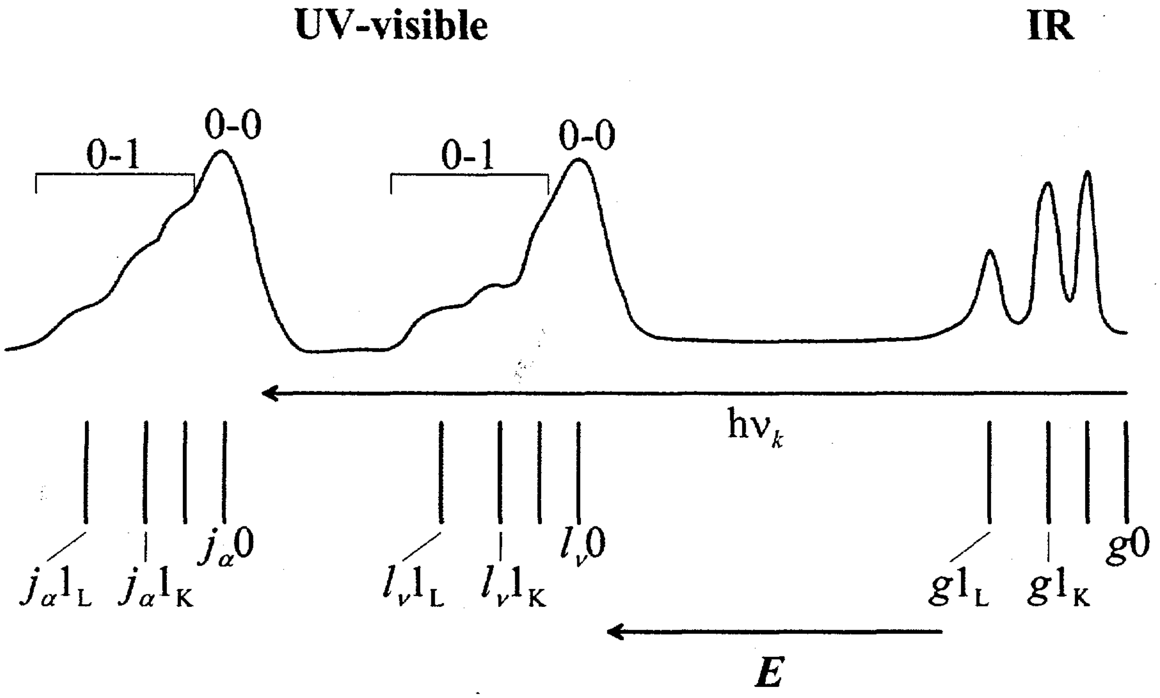

p
$\vec{r}_{pi}$
i
$\vec{R}_p$
$\vec{r}_i$
$\vec{r}_p = \vec{r}_i - \vec{R}_p$
$\vec{r}_{0pi} = \vec{r}_i - \vec{R}_{0p}$

Figure 1.


UV-visible
IR
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0-0
0-1
0-0
hν_k
j_α1_L
j_α1_K
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l_ν1_L
l_ν1_K
l_ν0
g1_L
g1_K
g0
E

Figure 2.

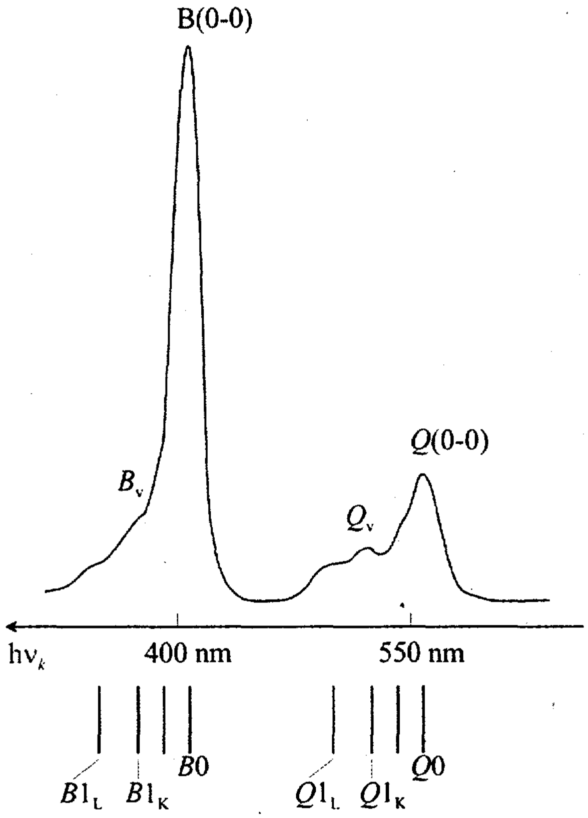

Figure 3.