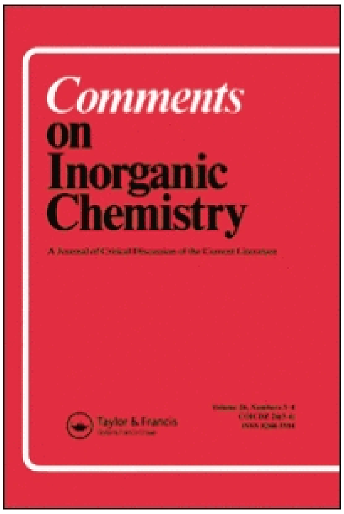

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Electronic Absorption Spectroscopy-Vibronic Coupling and Band Shape Analysis

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A parallel analysis of the hyperfine parameters for Cu doped into a K_2PdCl_4 lattice [C. Chow, K. Chang, and R. D. Willett, J. Chem. Phys. **59**, 2629 (1973)] gives results similar to those presented here.

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VIII. ELECTRONIC ABSORPTION SPECTROSCOPY—VIBRONIC COUPLING AND BAND SHAPE ANALYSIS

From Section III, for D_{4h}–$CuCl_4^=$, the parity forbiddenness of the $d \rightarrow d$ transitions in this centrosymmetric complex is overcome by vibronic or Herzberg-Teller coupling to odd parity vibrations of the nuclear framework. In addition, absorption bands in metal complexes can be greatly broadened (relative to the < 1 cm^{-1} expected on the basis of their lifetimes) due to coupling of the electronic transitions to distortions of the molecular framework. Both effects require two new terms in the molecular Hamiltonian which relate to nuclear motion.

For a complex with N atoms there are $3N - 6$ normal modes of vibration Q_i which are given for D_{4h}–$CuCl_4^=$ by

$$Q_i(D_{4h}\text{–}CuCl_4^=) = a_{1g} + b_{1g} + b_{2g} + a_{2u} + b_{2u} + 2e_u. \qquad \text{(VIII-1)}$$

We must then add a term to the Hamiltonian for each Q_i to account for the potential energy associated with the nuclear vibration[1]

$$H_{\text{nuc vib}} = \tfrac{1}{2}k_i(Q_i - Q_i^0)^2,\ i = 1 \cdots 3N - 6. \qquad \text{(VIII-2)}$$

The nuclei vibrate about equilibrium position Q_i^0 with a harmonic oscillator restoring force given by the force constant $k_i = 4\pi^2 m_i c^2 \nu_i^2$ where ν_i is the frequency given in cm^{-1} for a force constant expressed in dynes/cm. This term converts the energy levels discussed in the text (Figure III-2A) into potential energy surfaces as shown in Figure VIII-1, where, for the time being, we assume that the excited state is not displaced relative to the gound state. There are $3N - 6$ of these, one for each normal mode of vibration. A quantum-mechanical treatment of the vibrations leads to discrete solutions with energies $E_m = (m + \frac{1}{2})\nu_i$, where m is the vibrational quantum number of the ground state ($= 0,1,2 \ldots$). Analogous solutions exist for the excited state, described by the vibrational quantum number n. Each vibrational energy level has associated with it a vibrational wavefunction, $\chi_m(Q_i)$, which is a Hermite polynomial function. Finally, in the Born-Oppenheimer approximation[2] the total wavefunction can be written as a product of electronic and nuclear wavefunctions:

$$\begin{aligned} \psi_g^{\text{tot}} &= \psi_g^{\text{elec}}\, \chi_m(Q_i) \\ \psi_e^{\text{tot}} &= \psi_e^{\text{elec}}\, \chi_n(Q_i). \end{aligned} \qquad \text{(VIII-3)}$$

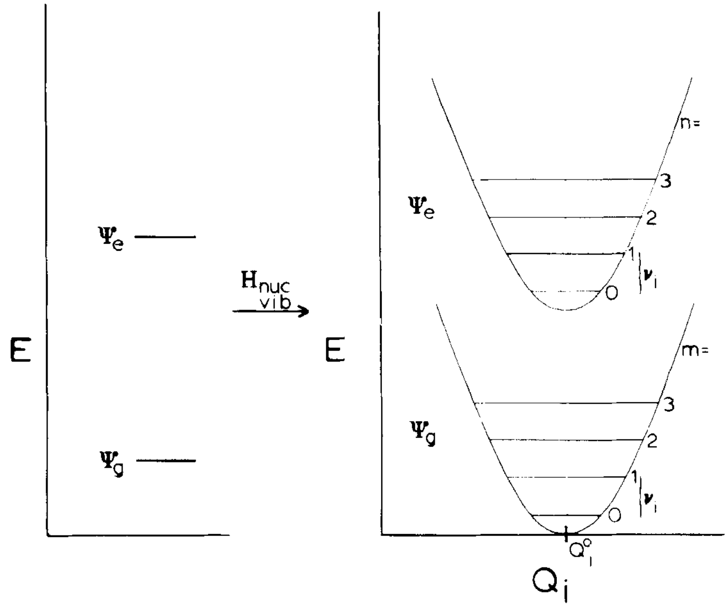

FIGURE VIII-1 Potential energy surfaces generated by the inclusion of $H_{\substack{\text{nuc}\\\text{vib}}}$ in the ground and electronic states of a metal complex.

For vibronic coupling an additional term must be included in the Hamiltonian which will couple the electron and nuclear motions.[3] This is obtained from a Taylor expansion of the ligand-field (or a more general molecular) potential H_{LF} (which operates on electron coordinates) in terms of the nuclear coordinates Q_i

$$H_{\mathrm{elec\ nuc}} = Q_i \frac{\partial H_{\mathrm{LF}}}{\partial Q_i}. \qquad \text{(VIII-4)}$$

We proceed by using Eq. (VIII-4) as a perturbation to mix higher energy odd-parity Laporté allowed excited states ψ_u^{elec} into the Laporté-forbidden ψ_e^{elec} giving Eq. (VIII-5), where Q_i has been removed from the electronic integral as it operates only on nuclear coordinates.[4]

$$|\psi_e^{\mathrm{elec}'}\rangle = |\psi_e^{\mathrm{elec}}\rangle + Q_i \frac{\langle \psi_e^{\mathrm{elec}} | \frac{\partial H_{\mathrm{LF}}}{\partial Q_i} | \psi_u^{\mathrm{elec}} \rangle |\psi_u^{\mathrm{elec}}\rangle}{E_e - E_u}. \qquad \text{(VIII-5)}$$

We can now evaluate the transition moment integral [Eq. (III-1B)] for the transition $\psi_g^{\mathrm{tot}} \rightarrow \psi_e^{\mathrm{tot}}$ where Eqs. (VIII-3) are used with $|\psi_e^{\mathrm{elec}}\rangle$ given by Eq. (VIII-5) to obtain Eqs. (VIII-6)

$$f^{1/2} \propto \langle \psi_g^{\mathrm{elec}} \chi_m(Q_i) | M(x,y,z) | \psi_e^{\mathrm{elec}'} \chi_n(Q_i) \rangle \qquad \text{(VIII-6a)}$$

$$\propto \frac{\langle \psi_e^{\mathrm{elec}} | \frac{\partial H_{\mathrm{LF}}}{\partial Q_i} | \psi_u^{\mathrm{elec}} \rangle \langle \psi_g^{\mathrm{elec}} | M(x,y,z) | \psi_u^{\mathrm{elec}} \rangle \langle \chi_m(Q_i) | Q_i | \chi_n(Q_i) \rangle}{E_e - E_u}. \qquad \text{(VIII-6b)}$$

The first two integrals in Eq. (VIII-6b) give the electronic selection rules for vibronic coupling. For the first integral to be group theoretically different from zero, $\Gamma_e \times \Gamma_{\partial H_{\mathrm{LF}}/\partial Q_i} \times \Gamma_u = A_1$; similarly, $\Gamma_g \times \Gamma_{x,y,z} \times \Gamma_u = A_1$ for the second integral to be nonzero. Combining the two expressions gives $\Gamma_g \times \Gamma_{x,y,z} \times \Gamma_e \times \Gamma_{\partial H_{\mathrm{LF}}/\partial Q_i} = A_1$. Finally, as Eq. (VIII-4) is a term in the molecular Hamiltonian it must be totally symmetric, which requires that $\Gamma_{\partial H_{\mathrm{LF}}/\partial Q_i} = \Gamma_{Q_i}$. Therefore, the electronic selection rules associated with vibronic coupling are given by

$$\Gamma_g \times \Gamma_{x,y,z} \times \Gamma_e \times \Gamma_{Q_i} = A_1. \tag{VIII-7}$$

Application of Eq. (VIII-7) to the $d \rightarrow d$ transitions in D_{4h}–CuCl$_4^{=}$ [using the Q_i given in Eq. (VIII-1) and the fact that in D_{4h} M(x,y) has E_u symmetry and $M(z)$ has A_{2u} symmetry] leads to the vibronic polarizations given in Table VIII-1 and included in Figure III-3. All transitions become allowed by odd parity vibrations except the ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition in z polarization. The molecularly polarized single crystal absorption spectrum[5] of D_{4h}–CuCl$_4^{=}$ is given in Figure VIII-2. Clearly the band at 12,500 cm^{-1} has no z intensity and thus can be assigned as the ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition. It should be noted that the band between 14,000 and 16,000 cm^{-1} is split in x and y polarizations indicating that this is doubly degenerate ${}^2B_{1g} \rightarrow {}^2E_g$ transition, split because the actual geometry of CuCl$_4^{=}$ in the crystal is closer to D_{2h}. Finally, in Figure VIII-2, all intensity is significantly lower in z polarization. This would appear to indicate that the dominant Laporté allowed excited states (ψ_u^{elec}) mixed into the $d \rightarrow d$ transitions are the Cl → Cu charge-transfer transitions, which probably results from the energy denominator in Eq. (VIII-6b). As discussed in Section IV and observed in Figure IV-3, only one charge-transfer transition is allowed in z polarization (${}^2B_{1g} \rightarrow {}^2B_{2u}$) and this has no theoretical or experimental absorption intensity.[6]

Returning to Eq. (VIII-6b), the last integral determines the vibrational selection rules for vibronic coupling. Based on the properties of Hermite vibrational functions[1] this integral is equal to zero unless

TABLE VIII-1
Vibronic polarizations of $d \rightarrow d$ transitions in D_{4h}–CuCl$_4^{=}$

$d \rightarrow d$ transition	Q_i allowing x,y polarization	Q_i allowing z polarization
${}^2B_{1g} \rightarrow {}^2B_{2g}$	e_u	—
${}^2B_{1g} \rightarrow {}^2E_g$	a_{2u}, b_{2u}	e_u
${}^2B_{1g} \rightarrow {}^2A_{1g}$	e_u	b_{2u}

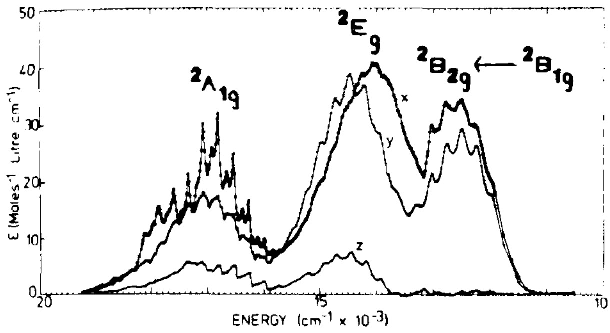

FIGURE VIII-2 Polarized absorption spectra of the ligand field region for a single crystal of D_{4h}-$CuCl_4^=$ at 10 K (from Ref. 5).

$n = m \pm 1$, and then its value is proportional to $\sqrt{m}$ or $\sqrt{n}$, whichever is larger. Therefore, as shown in Figure VIII-3, at low temperatures only the $m = 0 \rightarrow n = 1$ transition is vibronically allowed and will contribute to the absorption intensity. As the temperature is increased, a Boltzmann population of higher odd-parity vibrational levels of the ground state occurs. This leads to two effects: (1) the $m = 1 \rightarrow n = 0$ transition (called a hot band) will appear in the absorption spectrum at an energy $-\nu_i$ relative to the $m = 0 \rightarrow n = 0$ transition, and (2) the total intensity of the transition increases with temperature. A quantitative treatment of the latter effect gives

$$f(T) = f(T = 0\ \text{K}) \coth(\nu_i/2kT). \qquad \text{(VIII-8)}$$

The temperature dependence of the $d \rightarrow d$ transitions of D_{4h}-$CuCl_4^=$ is reproduced in Figure VIII-4a and contrasted to the temperature-independent integrated transition intensity for the noncentrosymmetric D_{2d}-$CuCl_4^=$ in Figure VIII-4b. Note that one should be cautious in applying Eq. (VIII-8) in that several Q_i with different ν_i can in general contribute to vibronic coupling and application of Eq. (VIII-8) simply gives an effective value of ν_{obs}.

Thus far we have only considered excited states which have the same equilibrium geometry as the ground state (Q_i^0 which will now be defined as zero). However, excited states can in general be distorted

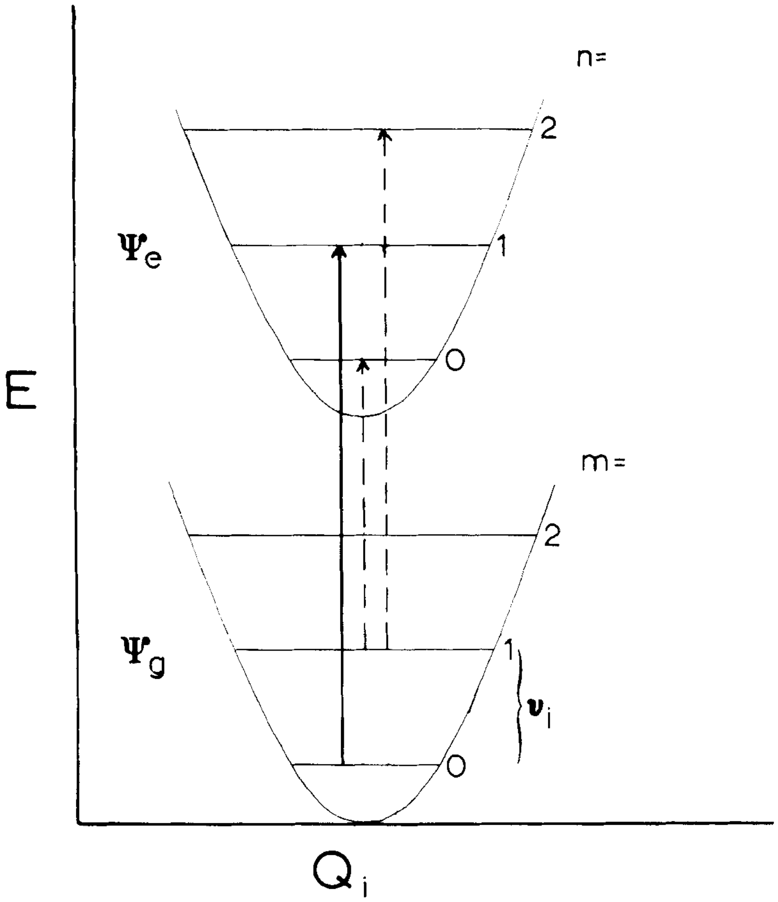

FIGURE VIII-3 Vibronically allowed transitions. Low temperature: solid arrow. High temperature: dashed arrows.

relative to the ground state along specific normal modes Q_i which are not those involved in vibronic coupling in centrosymmetric complexes.[8] In Figure VIII-5 the distortion of the excited state relative to the ground state is ΔQ_i which lowers the energy of the excited state by the value $E_i = \frac{1}{2}k_i\Delta Q_i^2$ relative to its value at the ground state equilibrium geometry. These excited state distortions determine the absorption bandshape. Considering again the expression for the

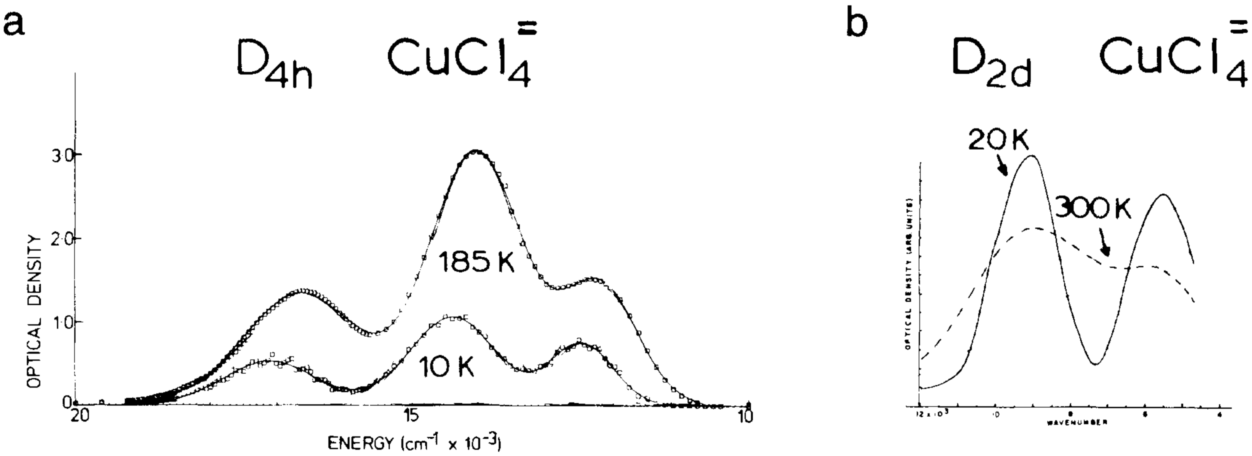

FIGURE VIII-4 Temperature dependence of the ligand field absorption spectra of (a) D_{4h} and (b) D_{2d}–$CuCl_4^{=}$. [For (a) see Ref. 5, and for (b) see Ref. 7.]

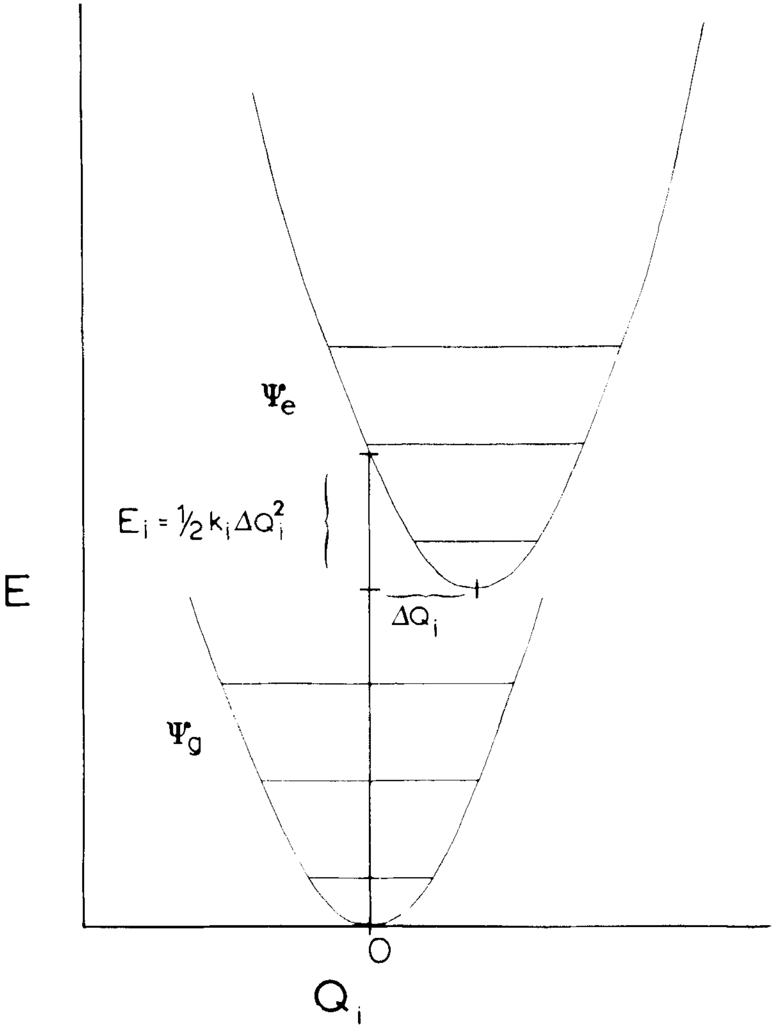

FIGURE VIII-5 Excited state potential energy surface relative to ground state along normal mode Q_i.

oscillator strength in terms of the total electronic-vibrational wavefunctions in Eq. (VIII-3) one obtains

$$f^{1/2} \propto \langle \psi_g^{\text{elec}}\, \chi_m(Q_i) | M(x,y,z) | \psi_e^{\text{elec}}\, \chi_n(\overline{Q}_i) \rangle \qquad \text{(VIII-9a)}$$

$$\propto \langle \psi_g^{\text{elec}} | M(x,y,z) | \psi_e^{\text{elec}} \rangle \langle \chi_m(Q_i) | \chi_n(\overline{Q}_i) \rangle \qquad \text{(VIII-9b)}$$

where in (VIII-9b) the integrals over the electronic and nuclear coordinates have been separated. The electronic integral in Eq. (VIII-9b) is simply some source of intensity for an electronic transition (Laporté allowed charge-transfer intensity, or a forbidden $d \rightarrow d$ transition made allowed by either static distortion or vibronic coupling to $Q_j \neq Q_i$ for a centrosymmetric complex). It should be emphasized that it is the vibrational integral in Eq. (VIII-9b) which determines the bandshape. $\chi_m(Q_i)$ is a Hermite function centered at the ground state equilibrium position while $\chi_n(\overline{Q}_i)$ is a Hermite function centered at the excited state geometry ΔQ_i. Therefore the absorption bandshape derives from the overlap of these displaced Hermite functions. First we consider the solutions at $T = 0°\text{K}$. If there is no distortion of the excited state, $\Delta Q_i = 0$ and only the $m = 0 \rightarrow n = 0$ transition is allowed by the orthogonality of the $\chi(Q_i)$. Hence only an intense, sharp line will appear in the absorption spectrum as shown in Figure VIII-6. However, if the excited state is distorted relative to the ground state $\Delta Q_i \neq 0$ and the $\chi_n(\overline{Q}_i)$ are no longer orthogonal to $\chi_m(Q_i)$ with $m = 0$. This leads to a Franck-Condon progression of peaks separated by ν_i with an intensity distribution given by the ratio

$$\frac{I_{0n}}{I_{00}} = \frac{S_i^n}{n!} \qquad \text{(VIII-10)}$$

which derives from the overlap integrals of the displaced Hermite functions in Eq. (VIII-9b). The absorption bandshape given by Eq. (VIII-10) is a Poisson distribution which becomes Gaussian at large values of S_i. S_i is the Huang-Rhys parameter[9] which is given by

$$S_i = E_i / \nu_i. \qquad \text{(VIII-11)}$$

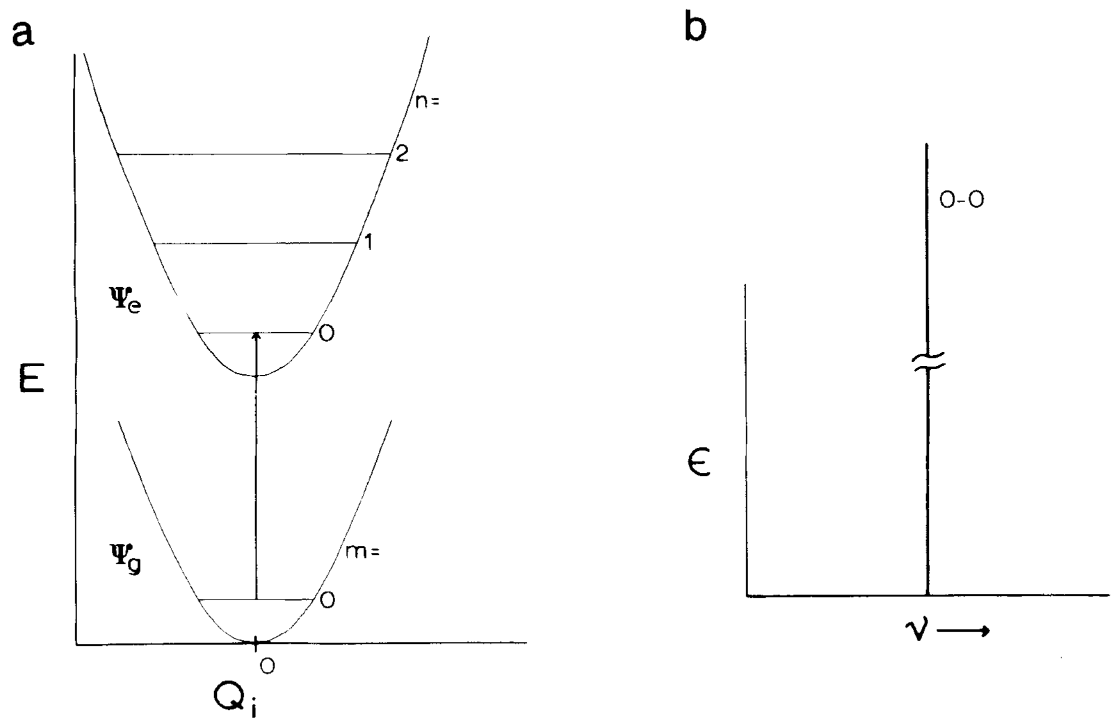

FIGURE VIII-6 Electronic-vibrational transition allowed for undistorted excited state at $T = 0$ K.

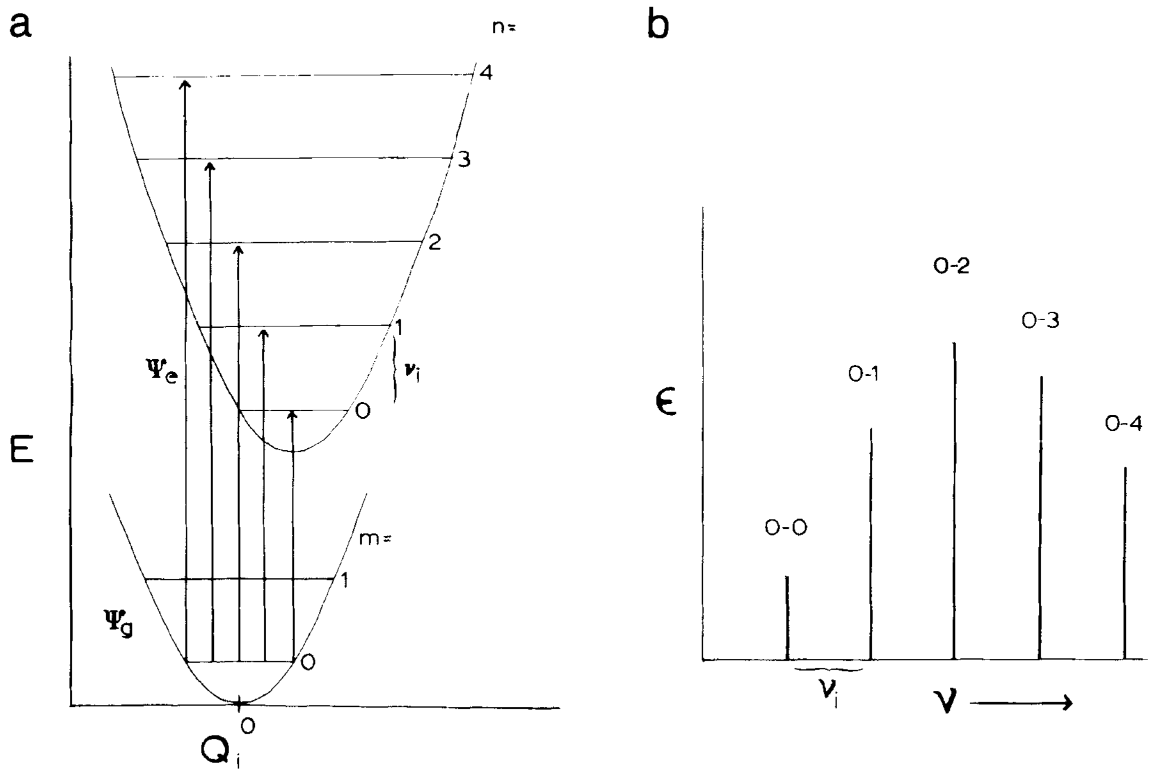

FIGURE VIII-7 Electronic-vibrational transitions allowed for excited state distorted by ΔQ_i in normal mode Q_i at $T = 0$ K. $S_i = 2.75$ is used in (b).

Thus, the progression spacing in Figure VIII-7 gives ν_i, the intensity distribution gives S_i, and then through the relationship $E_i = \frac{1}{2}k_i(\Delta Q_i)^2$ one obtains the excited state distortion ΔQ_i in normal mode Q_i. For D_{4h}-$CuCl_4^{=}$ the low-temperature structured absorption of the ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition shown in Figure VIII-2 gives $\nu_i = 265$ cm^{-1}, $S_i \cong 2.75$, therefore $\Delta Q_i = 0.14$ Å.[10]

As the temperature increases a Boltzman population of the higher ground state vibrational levels in Figure VIII-7 occurs, leading to overlapping intensity distributions from each level. The situation becomes complicated and the vibrational structure on the electronic transition is lost. The temperature dependence and, in general, the analysis of unstructured absorption bands is then best approached through a moment analysis of the bandshape.[8a] Theory demonstrates that the parameters which relate to the bandshape are given by the second moment, m_2, of a transition

$$m_2 = S_i(\nu_i)^2 \coth(\nu_i/2kT). \qquad \text{(VIII-12)}$$

Experimentally [Eq. (VIII-13)], the zeroth moment m_0 of an absorption band is the integrated intensity, the first moment m_1 the average energy, and the second moment m_2 the bandshape which for a Gaussian is related to the full width at half-maximum.

$$m_0 = \int \epsilon(\nu)d\nu \qquad \text{(VIII-13a)}$$

$$m_1 = \frac{1}{m_0}\int \epsilon(\nu)\nu d\nu \qquad \text{(VIII-13b)}$$

$$m_2 = \frac{1}{m_0}\int \epsilon(\nu)(\nu - m_1)^2 d\nu \qquad \text{(VIII-13c)}$$

$$= (\text{f.w.h.m.})^2/8 \ln 2. \qquad \text{(VIII-13d)}$$

Thus, from the temperature dependence of the second moment one can obtain approximate values of ν_i and S_i and hence ΔQ_i even for an unstructured absorption band.[12]

We can now consider the information content of these experimentally obtained excited-state distortions in terms of changes in bonding upon excitation. As has been discussed, the contribution to the total energy of the ground state due to nuclear motion is given by Eq. (VIII-14a)

$$E^{g}_{\text{nuc}} = \tfrac{1}{2}k_iQ_i^2 \qquad \text{(VIII-14a)}$$

which converts ψ_g into a potential energy surface as in Figure VIII-8a. For the excited state we must include an additional term in the Hamiltonian (relative to the ground state) $H_{\substack{\text{elec}\\ \text{nuc}}} = Q_i \dfrac{\partial H_{\text{LF}}}{\partial Q_i}$. This term was used earlier for vibronic coupling to mix ψ_e^{elec} with ψ_u^{elec} through odd parity vibrations Q_j. Now we evaluate the effects of this term directly on ψ_e^{elec}. This generally involves a different set of Q_i. Thus the effect of electron-nuclear coupling in the excited state gives a contribution to the energy

$$E^{e}_{\text{elec -nuc}} = \langle \psi_e^{\text{elec}} | \left(\frac{\partial H_{\text{LF}}}{\partial Q_i}\right)_0 | \psi_e^{\text{elec}} \rangle Q_i, \qquad \text{(VIII-14b)}$$

where the integral is a constant, evaluated at the equilibrium position of the ground state. This is known as the "linear coupling term" which, when the integral is nonzero, should be viewed as a distorting force in the excited state relative to the ground state along normal mode Q_i. Thus, this term must be equal to zero in the ground state which is at its equilibrium geometry. A contribution to the energy of ψ_e, linear in Q_i with a slope of $\langle \psi_e | (\partial H_{\text{LF}} / \partial Q_i)_0 | \psi_e \rangle$ is indicated at the top of Figure VIII-8a. The contribution to the total energy due to nuclear motion for ψ_e is given by the sum of the above two terms.

$$E^{e}_{\text{nuc}} = \langle \psi_e | \left(\frac{\partial H_{\text{LF}}}{\partial Q_i}\right)_0 | \psi_e \rangle Q_i + \tfrac{1}{2}k_iQ_i^2. \qquad \text{(VIII-14c)}$$

This is equivalent to graphically adding the ground state potential energy surface to the linear coupling term in Figure VIII-8a to obtain

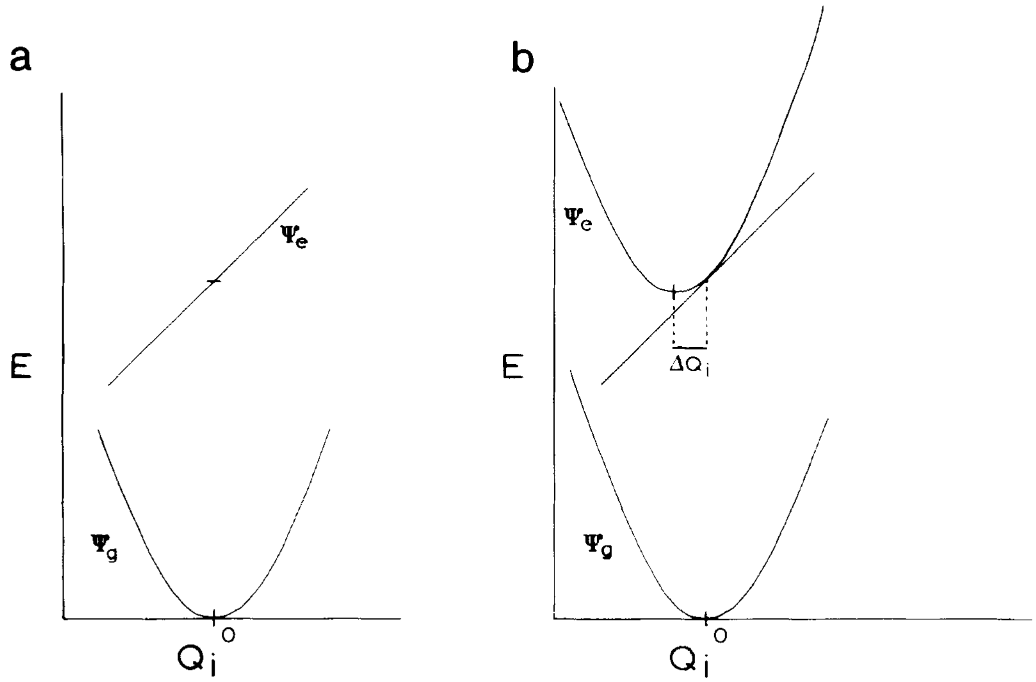

FIGURE VIII-8 Effects of a linear coupling term on the excited state: (a) Ground state potential energy surface at equilibrium $Q_i = 0$. Excited state with nonzero linear term $= \langle\psi_e|(\partial H_{\mathrm{LF}}/\partial Q_i)_0|\psi_e\rangle Q_i$ (b) Distorted excited state geometry obtained by adding the ground state potential energy surface to the linear coupling term in (a).

Figure VIII-8b. Proceeding from Eq. (VIII-14c) and setting $\partial E^{e}_{\text{nuc}}/\partial Q_i = 0$, one obtains the expression for ΔQ_i given by

$$\Delta Q_i = -\frac{\langle \psi_e | (\partial H_{\text{LF}}/\partial Q_i)_0 | \psi_e \rangle}{k_i}. \qquad \text{(VIII-15)}$$

Therefore the excited state will distort when $\langle \psi_e | (\partial H_{\text{LF}}/\partial Q_i)_0 | \psi_e \rangle \neq 0$. From group theory this will be the case[13] if $[\Gamma_e \times \Gamma_e] = \Gamma_{Q_i}$, where [ ] indicates the symmetric direct product of ψ_e with itself and the characters of the symmetric direct product for symmetry operation $\hat{R}$ are given by

$$[\chi^2](\hat{R}) = \tfrac{1}{2}([\chi(\hat{R})]^2 + \chi(\hat{R}^2)) \qquad \text{(VIII-16)}$$

For a nondegenerate ψ_e, $[\Gamma_e \times \Gamma_e]$ gives only the totally symmetric irreducible representation; hence excited state distortions are only allowed in totally symmetric normal modes Q_i. For a degenerate excited state $[\Gamma_e \times \Gamma_e]$ will again contain the totally symmetric irreducible representation, but it will also contain additional even parity vibrations. These correspond to nontotally symmetric, Jahn-Teller distortions of the excited state. These are discussed in detail in Refs. 11 and 14.

Finally, we need to relate Figures VIII-8a,b to inorganic bonding theory. For excited state distortions which involve the totally symmetric normal mode, this is most clearly accomplished through correlation to the Tanabe-Sugano (T&S) diagrams.[15] Thus we consider here only the limit of an octahedral geometry, which for a d^9 Cu(II) complex corresponds to the T&S type diagram given in Figure VIII-9a: one $^2E_g \rightarrow {}^2T_{2g}$ transition at an energy of 10 Dq. The totally symmetric normal mode of vibration of an octahedron ($Q_{a_{1g}} = 1/\sqrt{6}\,(\vec{R}_1 + \vec{R}_2 + \vec{R}_3 + \vec{R}_4 + \vec{R}_5 + \vec{R}_6)$) is pictured in Figure VIII-10. During the time course of the $Q_{a_{1g}}$ vibration, the ligand-field strength decreases when all the ligands go out and increases when all the ligands approach the metal. Quantitatively, one can convert

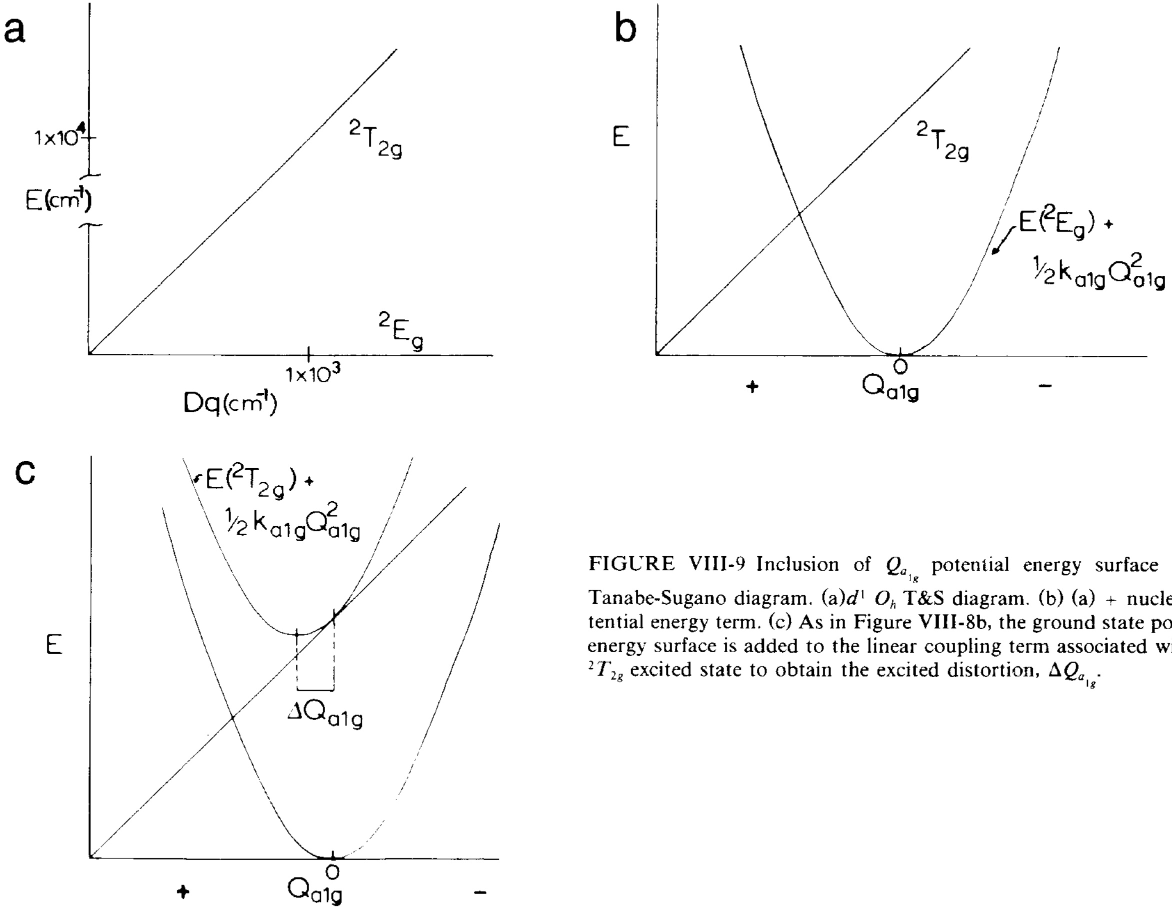

FIGURE VIII-9 Inclusion of $Q_{a_{1g}}$ potential energy surface in the Tanabe-Sugano diagram. (a)d^1 O_h T&S diagram. (b) (a) + nuclear potential energy term. (c) As in Figure VIII-8b, the ground state potential energy surface is added to the linear coupling term associated with the $^2T_{2g}$ excited state to obtain the excited distortion, $\Delta Q_{a_{1g}}$.

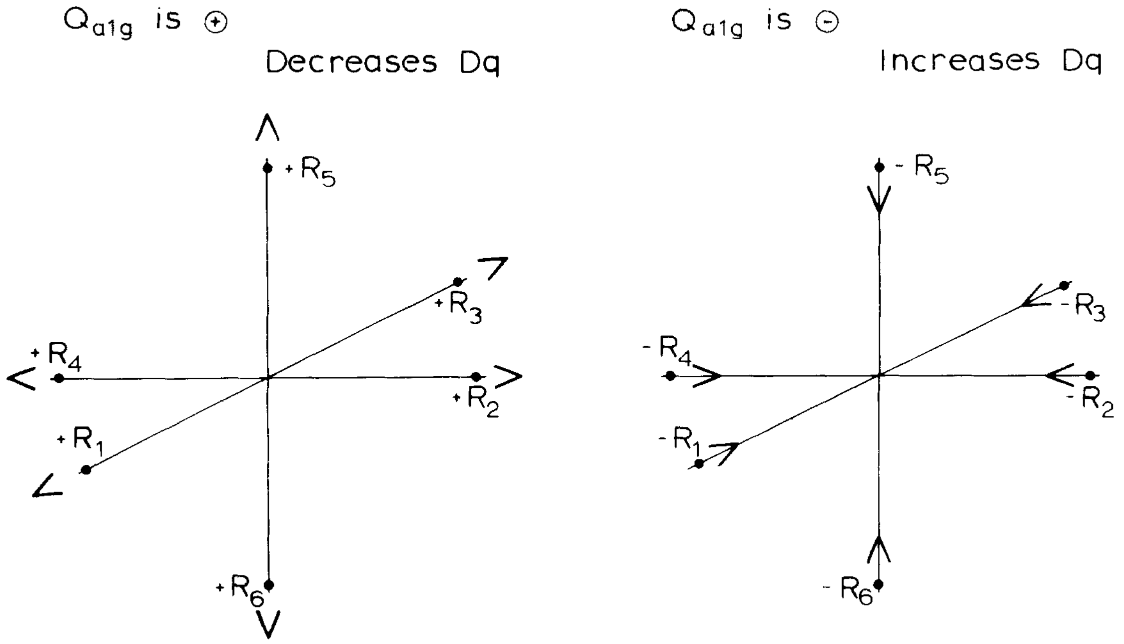

FIGURE VIII-10 Totally symmetric ($Q_{a_{1g}}$) normal mode of vibration of an octahedron. + and − phases of the vibration are on the left and right, respectively.

the ground-state potential energy term in Eq. (VIII-14a) into a function of Dq using

$$\delta Dq = \left(\frac{\partial Dq}{\partial R}\right)\left(\frac{\partial R}{\partial Q_{a_{1g}}}\right)\delta Q_{a_{1g}} \qquad \text{(VIII-17a)}$$

$$= \left(\frac{-5Dq}{R}\right)\left(\frac{1}{\sqrt{6}}\right)\delta Q_{a_{1g}}. \qquad \text{(VIII-17b)}$$

(where $Dq = Ze^2\langle r^4\rangle/6R^5$ and R is the M-L distance).[16] This nuclear potential energy term can now be added to the ^2E_g electronic ground state energy in the T&S diagram, where $Q_{a_{1g}} = 0$ corresponds to the actual Dq value of the complex (Figure VIII-9b). It should now be observed that Figure VIII-9b corresponds to Figure VIII-8a in the sense that the slope of the $^2T_{2g}$ excited state energy relative to the ground state corresponds to a nonzero value of the linear coupling term. As described above, graphical addition of the ^2E_g potential energy surface to this $^2T_{2g}$ linear coupling term produces the excited state distortion, $\Delta Q_{a_{1g}}$, shown in Figure VIII-9c. The $^2T_{2g}$ excited state undergoes a distortion which lowers Dq, hence the ligands expand along the a_{1g} normal mode ($\Delta Q_{a_{1g}}$ is positive as indicated on the left of Figure VIII-10). In terms of one-electron orbitals this distortion derives from the fact that the $^2E_g \rightarrow {}^2T_{2g}$ transition involves excitation of an electron from a t_{2g} metal orbital which is π^* into an e_g metal orbital which is σ^* and thus more strongly antibonding with the ligands.[11,14e] One can graphically estimate a quantitative value of $\Delta Q_{a_{1g}}$ from Figure VIII-9c. Alternatively, expressions for the octahedral $\partial H_{\mathrm{LF}}/\partial Q_i$ operators are available.[17] For $Q_i = a_{1g}$, this is given by

$$\frac{\partial H_{\mathrm{LF}}}{\partial Q_{a_{1g}}} = \frac{175Ze^2}{4\sqrt{6}\,R^6}\left(x^4 + y^4 + z^4 - \frac{3r^4}{5}\right). \qquad \text{(VIII-18)}$$

Evaluation of this operator over the excited state ψ_e, in Eq. (VIII-15) then gives $\Delta Q_{a_{1g}}$. For the $^2T_{2g}$ excited state of octahedral Cu(II), this gives

$$\Delta Q_{a_{1g}} = \frac{50Dq}{\sqrt{6}\,R\,k_{a_{1g}}}. \qquad \text{(VIII-19)}$$

To summarize, the excited state has a distorting force, relative to the ground state, along specific group-theoretically-allowed normal modes which derives from the change in electronic transition energy with distortion.

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