arbitrarily in this case.[24] This system also gave the interacting orbitals of similar patterns to the BH_3 addition. In this case, overlap repulsion was found to be very weak compared with the bonding interactions. The coefficients of electron configurations corresponding to I, II, III, and IV in Figure 4 (the $HTiCl_2^+$ fragment orbitals are 16a' and 18a' instead of 20a' and 21a') were calculated to be 0.3473, 0.2487, 0.1580, and −0.1194, respectively. The interaction is stronger and the interacting orbitals are more localized in this system than in the $CH_3TiCl_2^+ + C_2H_4$ system studied above, but we see no significant difference in the trend. The spherical 1s orbital of hydrogen seems to be somewhat more suited for electron delocalization in comparison with the methyl group. This means, however, that the reverse elimination through the four-membered cyclic transition state can also take place more easily.

The systems studied here may be oxidized too strongly. In more general cases, the Ti center has six coordination in an octahedral arrangement,[6,7] and the Ti–R bond will be broken more easily than in the present systems. The formation of the R–C bond and, consequently, the formation of the Ti–C bond will take place more readily. It is time-consuming at present to carry out calculations on other systems, but the influence of ligands is included directly in the bond-order matrix and consequently in the interacting orbitals. The polarizability of olefins is also of importance and, in addition, the metal–R moiety should be moderately electron deficient in order to suppress the overlap repulsion.

Conclusion

An application of the interacting orbital concept revealed some aspects of interactions in the insertion of $CH_2{=}CH_2$ to the C—Ti and H—Ti bonds. The concept of isolobal analogy appears to be more plausible here than it was with the highest occupied and lowest unoccupied frontier orbitals.[25] Though it is difficult to conclude whether a cyclic interaction is concerted or not or whether it is synchronous or asynchronous even in simpler organic reactions,[26] we suggest here that the presence of the low-lying unoccupied orbital having a large amplitude on the d orbitals of metal, and the high-lying occupied orbital having a large amplitude on R, is the requisite to facilitate insertion reactions via four-centered transitions states. The most important stage in olefin insertion is the activation of the C–C bond, as has been indicated by the significant contribution of the locally excited configuration and by the localized interacting orbitals of the olefin fragment in the ground state of the composite reacting system. Thus, as for the significance of the vacant d orbitals in the metal, our conclusion is obviously in line with that of Thorn and Hoffmann[16] and of Steigerwald and Goddard.[9]

Since there are a variety of molecules involved in reactions and since only some particular structural units in molecules participate actively in chemical interactions, recognition of the similarity and dissimilarity in reactivities of molecules by means of patterns will be helpful. Thus, the simple orbital transformations to give the orbitals that are localized specifically in the reactive regions of molecules would be suited for elucidating common features of interactions for the reagent and reactant of various sizes by means of theoretical calculations.

(24) The H–C bond in the model is about 1.47 times longer than the normal C-H bond. This compares roughly with the C(methyl)–C₂ bond which is 1.44 times that of the normal C-C bond length.

(25) Mingos, D. M. P. *Adv. Organomet. Chem.* **1977**, *15*, 1.
(26) See, for example: Komornicki, A.; Goddard, J. D.; Schaefer, H. F. *J. Am. Chem. Soc.* **1980**, *102*, 1763. Hiberty, P. C.; Ohanessian, G.; Schlegel, H. B. *Ibid.* **1983**, *105*, 719.

Line Shape of the Intervalence Transfer Band in Bridged Mixed-Valence Dimers: The Delocalized Case

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Abstract: An approximate method for the prediction of intervalence transfer (IT) band profiles for delocalized bridged mixed-valence dimers is given. The method is based on a three-site model, with the bridging ligand explicitly included. Potential energy surfaces along the totally symmetric vibrational sum coordinate are treated approximately as displaced harmonic oscillators. The force constants and displacements of the minima are obtained with second-order perturbation theory. We call this approximate procedure the second-order harmonic oscillator (SOHO) method. Transition intensities calculated from the SOHO method are in good agreement with those obtained numerically from the exact adiabatic potentials. The method is extended to include one coupled vibration on the bridging ligand. Simple expressions for the width of the IT absorption band at half-maximum are given. Implications for questions of electron delocalization in complexes of current interest in inorganic chemistry are discussed.

From the rich chemistry of bridged mixed-valence dimers and bridged metallic complexes, pioneered by Henry Taube and reviewed in volume 30 of *Progress in Inorganic Chemistry*,[1] there have emerged a number of interesting questions concerning electron delocalization in molecular electronic states. Considerable attention has been devoted recently to the questions of the extent and rate of spatial- and time-dependent delocalization of electrons in these complexes, the shape of the corresponding intervalence transfer (IT) band, and the role of the bridging ligand in the electron-transfer process.

One particular mixed-valence complex, the Creutz–Taube ion, a pyrazine-bridged mixed-valence complex of ruthenium

$$\left[(NH_3)_5RuN \bigcirc NRu(NH_3)_5 \right]^{5+}$$

has been the focus of considerable attention and controversy.

(1) (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1-73. (b) Haim, A. *Ibid.* 273-357. (c) Meyer, T. J. *Ibid.* 389-440. (d) Sutin, N. *Ibid.* 441-498.

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Although this complex has been studied by a variety of experimental techniques and theoretical models, it is not yet clear whether its ground state is a localized (valence trapped) or delocalized (valence averaged) structure.[2]

Mixed-valence complexes exhibit an IT band in the optical absorption spectrum. An IT transition has been defined as metal-to-metal charge transfer, but as we shall discuss below, this process in the delocalized case is perhaps described better as a bonding to less bonding transition. A description of the width of the IT band, the extent of electron delocalization, and the electron-transfer properties of mixed-valence dimers has been given by Hush.[3]   This work is based on classical electron-transfer models.[4] Hush has derived an expression for the bandwidth (in cm^{-1}) at half-maximum of the IT band of a localized, homonuclear mixed-valence dimer at 300 K as

$$\Delta\bar{\nu}_{1/2} = [2310\bar{\nu}_{max}]^{1/2} \qquad (1)$$

where $\bar{\nu}_{max}$ is the frequency in cm^{-1} of the absorption maximum. For a system with harmonic nuclear motion, the energy of activation ΔE^* is related to the energy of the IT band maximum ΔE_{IT} by the expression

$$\Delta E^* = (1/4)\Delta E_{IT} \qquad (2)$$

for the weak-electron-exchange coupling case. Note that eq 1 and 2 apply to localized, valence-trapped species, whose ground-state potential surfaces have double-minimum form. For delocalized dimers, both the ground and excited potential surfaces, corresponding to the initial and final states of the IT transition, have single-minimum form. The features of the potential surfaces for mixed-valence dimers have been reviewed by Ratner.[5] The manifestations of these features in the shape of the IT band in the visible or near-IR absorption spectrum are well-known: For localized dimers, the bands tend to be very broad and symmetrical, whereas the delocalized dimers have narrower profiles that are asymmetric (broader on the blue side than on the red side).[3]

Piepho, Krausz, and Schatz (PKS) were the first to calculate the full absorption band profile for mixed-valence dimers.[6] The PKS model treats a dimer consisting of two identical monomeric units labeled l and r. The model has two electronic states, $|l\rangle$ centered on the atom on the left and $|r\rangle$ centered on the atom on the right. Each of these electronic states is coupled to its own nuclear degree of freedom, assumed to be a harmonic oscillator with respective coordinates Q_l and Q_r and momenta P_l and P_r. The (local) electronic basis states $|l\rangle$ and $|r\rangle$ are assumed to be directly coupled to each other; the (off-diagonal) electron-exchange coupling between them is given the symbol ϵ. The coupling between the electronic and nuclear motion on each site is called λ. It is important to note that when the PKS Hamiltonian is transformed, the electronic motion is only coupled to one vibrational degree of freedom, the vibrational difference coordinate Q_-, which is defined as

$$Q_- = 2^{-1/2}(Q_l - Q_r) \qquad (3)$$

The vibrational sum coordinate Q_+, given by

$$Q_+ = 2^{-1/2}(Q_l + Q_r) \qquad (4)$$

is decoupled from the electronic operators. Thus the PKS model is a two-site, one-dimensional model with two parameters (ϵ and λ).

The PKS model has been widely applied.[1a,7-10] In general, the two parameters ϵ and λ are adjusted so that the position and width of the predicted spectrum match those of the observed spectrum. Buhks[11] and Wong and Schatz[12a] have extended the PKS model to incorporate the motion of the solvent as well as the internal motion.

Hush has critized the PKS model for excluding the totally symmetric vibrational sum coordinate[12b,d,13] (see eq 4). Hush's argument is based on a molecular orbital picture: when an electron makes a transition from a bonding molecular orbital to a less bonding or antibonding molecular orbital, the average bond distances should increase, and this corresponds to excitation of one or more totally symmetric vibrational modes. Furthermore, simple group theoretic arguments show that any totally symmetric vibrational mode is formally allowed to couple to an allowed electronic transition.[14] These simple MO and symmetry arguments made Hush's suggestion seem appealing, but some difficulties remained. First, the sum coordinate is in fact decoupled from the electronic motion within the framework of the two-site models.[12,13] Even if there is significant frequency shift between the ground and first-excited states along the totally symmetric vibrational coordinate, there is no displacement of the potential minimum along Q_+, and the contribution to the IT bandwidth is small.[12c] Second, there was no clear way to build the Q_+ coordinate into the two-site problem.

In recent papers, we have built the framework for resolution of the debate over the importance of the vibrational sum coordinate and for better understanding of the spectra of bridged mixed-valence dimers.[15-18] Our approach is based on a three-site model, in which one electronic basis state on the bridging ligand is explicitly included in addition to one basis state each on the donor and acceptor metal sites. We have shown that the potential surfaces depend on both the sum and difference coordinates.[15] When the metal–bridge electron-exchange coupling is strong, there is indeed displacement of the potential minimum in the first-excited state from that of the ground state along the Q_+ coordinate.[16] In the strong-electron-exchange coupling case, the IT band line shape function is dominated by the coupling to the sum coordinate, with little or no contribution to the bandwidth from the difference coordinate.[17] Thus, the two-site model of Schatz et al. is in fact a useful model for systems *where there are two and only two* important electronic states (namely, one parent state each on donor and acceptor sites). Indeed, the two-site model of PKS has achieved noteworthy success for nonbridged systems recently.[10] However, whenever there is significant through-bridge coupling, Hush's point regarding coupling to the vibrational sum coordinate is correct. Our model builds in the effects of coupling of the electronic motion to both the sum and difference coordinates in a rigorous way. In bridged systems where there is significant metal–bridge electron-exchange coupling, the two-site models do not contain the necessary information to incorporate the coupling to totally symmetric vibrational modes. Such complexes are beyond the range of applicability of the two-site models.

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(11) Buhks, E. Ph.D. Thesis, Tel-Aviv University, Tel-Aviv, Israel, 1980.
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Within the framework of our model, in complexes where the metal–bridge electron-exchange coupling is strong, the three electronic states of the molecular ion may be pictured qualitatively as bonding, nonbonding, and antibonding orbitals, resembling the three π molecular orbitals of the Hückel allyl radical represented by a view from above as

$$— \text{IA} > \quad \oplus \ominus \oplus$$
$$— \text{IN} > \quad \oplus \quad \ominus$$
$$— \text{IB} > \quad \oplus \oplus \oplus$$
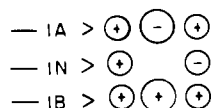
Analysis of the eigenfunctions in a recent electronic structure calculation on the Creutz–Taube ion confirms this qualitative picture.[19] For this ion, the coupled electronic state on the bridge is an unoccupied π^* orbital of pyrazine. In the mixed-valence species, the bonding orbital is fully occupied and the nonbonding orbital is half-occupied. Therefore, what has been termed an intervalence transfer (IT) transition may be visualized as a bonding-to-nonbonding transition in which charge density is transferred from the bridging ligand to the metal ions. When this transition takes place, one expects the metal–ligand bond distances to change (usually increase) slightly on both sides (corresponding to vibrational excitation along the Q_+ coordinate). There could also be nuclear reorganization in the bridging ligand caused by a decrease in charge density in the basis orbital that is coupled to the termini. This corresponds to excitation along one or more totally symmetric vibrational modes of the bridging ligand.

In the next section, we shall discuss first the complexes where all vibrational motion on the bridging species may be neglected. Then we extend the treatment to include one totally symmetric mode on the bridging ligand.

Our previous work has focused on the features of the potential surfaces[15,16] and on the calculation of the IT absorption band line shape for bridged dimers using a two-dimensional finite element method.[17] The aim of the present paper is to present a significantly simpler approximate method for calculating the IT band line shape for delocalized complexes (i.e., for the case where the metal–bridge coupling is large).

The third section analyzes the moments for the absorption spectra and a simple expression for the IT bandwidth is derived.

In the final section, we discuss the scope and limitations of our model and the approximations used therein.

Applications of the Three-Site Model

A. Model. In the present paper, attention will be given exclusively to delocalized complexes for which ground and first- and second-excited potential surfaces all have single-minimum form. First we present a general three-site model. Next we discuss its application to complexes that have no important bridge vibrations. Then we show how the model may be applied to complexes that have one totally symmetric vibrational motion on the bridge coupled to the electronic motion. The goal is to calculate the energies and nuclear eigenfunctions for the vibronic levels of the three potential surfaces and to use them to predict the intensities of the transitions between these levels and the corresponding absorption band profiles.

We begin with the three-site, three-mode Hamiltonian

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_e + \hat{\mathcal{H}}_v + \hat{\mathcal{H}}_{e-v} \tag{5}$$

$$\hat{\mathcal{H}}_e = J(a_1{}^\dagger a_2 + a_2{}^\dagger a_3 + a_2{}^\dagger a_1 + a_3{}^\dagger a_2) + \alpha a_2{}^\dagger a_2 \tag{6}$$

$$\hat{\mathcal{H}}_v = \sum_{i=1}^{3} \left(\frac{P_i{}^2}{2m_i} + \frac{1}{2}m_i\omega_i{}^2 q_i{}^2 \right) \tag{7}$$

$$\hat{\mathcal{H}}_{e-v} = \sum_{i=1}^{3} A_i q_i a_i{}^\dagger a_i \tag{8}$$

where $a_i{}^\dagger$ and a_i are the creation and annihilation operators for the ith electronic state, P_i and q_i are the momentum and coordinate

(19) Ondrechen, M. J.; Ellis, D. E.; Ratner, M. A. *Chem. Phys. Lett.* **1984,** *109,* 50–55.

for the ith nuclear degree of freedom, site 2 is the parent bridge state, and sites 1 and 3 are the parent terminal states, which are assumed to be degenerate.

Note that J is the electron-exchange coupling between the bridge and each terminal state. It is assumed that the two termini are separated sufficiently in space so that the direct electron-exchange coupling between them may be taken to be zero. The energy difference between the parent bridge state 2 and the parent terminal states is given by α. It is assumed that each of the three vibrations is harmonic with reduced mass m_i and frequency ω_i. In the present work, we are concerned exclusively with the symmetric case: $m \equiv m_1 = m_3$, $\omega \equiv \omega_1 = \omega_3$, and $A \equiv A_1 = A_3$. The electronic–nuclear coupling is taken to be of the polaron type, i.e., linear in the nuclear coordinate q_i and linear in the electron number operator $a_i{}^\dagger a_i$. In the case of the Creutz–Taube ion, sites 1 and 3 correspond to $4d_{xz}$ orbitals on the two Ru ions and site 2 corresponds to the lowest π^* orbital on the pyrazine ring which has the right symmetry for back-bonding with the metal $4d_{xz}$ orbitals. We assume that only one vibration on each site is important. The electronic part of the Hamiltonian is taken to be of the one-electron type, and spin–orbit coupling is neglected. Coupling to the motion of the solvent is neglected in the present case. The spatial redistribution of charge and its interaction with the polar medium, which is very important in the localized case, are not so significant in the delocalized case to be considered here.

We next transform the Hamiltonian into the basis set appropriate for the case where the electron-exchange coupling is strong $(|J| > A^2/2m\omega^2)$ and where the three parent states are nearly degenerate (α small)

$$a_b{}^\dagger = \frac{1}{2}(a_1{}^\dagger + 2^{1/2}a_2{}^\dagger + a_3{}^\dagger) \tag{9}$$

$$a_n{}^\dagger = 2^{-1/2}(a_1{}^\dagger - a_3{}^\dagger) \tag{10}$$

$$a_a{}^\dagger = \frac{1}{2}(a_1{}^\dagger - 2^{1/2}a_2{}^\dagger + a_3{}^\dagger) \tag{11}$$

For this case, the electronic and nuclear motions occur on such different time scales that the Schrödinger equation may be solved in the adiabatic approximation.

We define H_D as the sum of $\tilde{\mathcal{H}}_e$ and $\tilde{\mathcal{H}}_{e-v}$ transformed into the new basis set

$$H_D = \tilde{H}_e + \tilde{H}_{e-v} \tag{12}$$

H_D is then expressed as

$$H_D = H_0 + V \tag{13}$$

where H_0 and V are given by

$$H_0 = 2^{1/2}J(a_b{}^\dagger a_b - a_a{}^\dagger a_a) \tag{14}$$

$$V = ((1/2)\alpha + (1/2)A_2q_2)(a_b{}^\dagger a_b + a_a{}^\dagger a_a - a_b{}^\dagger a_a - a_a{}^\dagger a_b) + 2^{-3/2}AQ(a_b{}^\dagger a_b + a_a{}^\dagger a_a + a_b{}^\dagger a_a + a_a{}^\dagger a_b) + 2^{-1/2}AQa_n{}^\dagger a_n + (1/2)Aq(a_n{}^\dagger a_b + a_b{}^\dagger a_n + a_a{}^\dagger a_n + a_n{}^\dagger a_a) \tag{15}$$

and where we have also transformed the nuclear coordinates as

$$Q = 2^{-1/2}(q_1 + q_3) \tag{16}$$

$$q = 2^{-1/2}(q_1 - q_3) \tag{17}$$

$$q_2 = q_2 \tag{18}$$

Adiabatic potentials are obtained by the method of ref 16, which utilizes second-order perturbation theory. The three adiabatic potential energy surfaces calculated through second order are given by

$$U_B = 2^{1/2}J + (1/2)\alpha + 2^{-7/2}\alpha^2/J + 2^{-3/2}AQ + 2^{-9/2}A^2Q^2/J - (1/8)(A\alpha Q/J) - (1/8)(AA_2Qq_2/J) + 2^{-5/2}A_2\alpha q_2/J + (1/2)A_2q_2 + 2^{-7/2}A_2{}^2q_2{}^2/J + 2^{-5/2}A^2q^2/J + (1/2)(Kq^2) + (1/2)(KQ^2) + (1/2)(K_2q_2{}^2) \tag{19}$$

$$U_N = 2^{-1/2}AQ + (1/2)(Kq^2) + (1/2)(KQ^2) + (1/2)(K_2q_2{}^2) \tag{20}$$

$$U_A = -2^{1/2}J + (1/2)\alpha - 2^{-7/2}\alpha^2/J + 2^{-3/2}AQ -$$
$$2^{-9/2}A^2Q^2/J + (1/8)(A\alpha Q/J) + (1/8)(AA_2Qq_2/J) -$$
$$2^{-5/2}A_2\alpha q_2/J + (1/2)(A_2q_2) - 2^{-7/2}A_2^2q_2^2/J -$$
$$2^{-5/2}A^2q^2/J + (1/2)(Kq^2) + (1/2)(KQ^2) + (1/2)(K_2q_2^2)$$
$$(21)$$

where $K = m\omega^2$ and $K_2 = m_2\omega_2^2$. These second-order expressions are valid for small vibrational displacements and for $|J| > A^2/2K$, $|J| > A_2^2/2K_2$, and $|J| \gtrsim |\alpha|$. The three surfaces are labeled B, N, and A because when A and α are small relative to the electron-exchange coupling $|J|$, the three molecular states resemble the three π molecular orbitals of the Hückel allyl system.

Whenever the above perturbative treatment is valid, the ground (B) surface has single-minimum form.[16] The transition that is generally called IT is actually in this limit a transition from the vibronic levels of the B surface to the vibronic levels of the N surface, analogous to the bonding-to-nonbonding transition in the Hückel allyl radical.

B. Application to Complexes without a Coupled Vibration on the Bridge. To utilize the above approximate potential surfaces to calculate the line shape of the so-called IT band for delocalized bridged complexes, let us first consider the case where none of the vibrational modes on the bridging ligand are coupled to the electronic transition of interest ($A_2 = 0$).

When $A_2 = 0$, the potential energy surfaces depend upon two coordinates, the vibrational sum and difference coordinates (Q and q). Along the sum coordinate, the minimum for the first-excited (N) surface is displaced from that of the ground surface (B)[16]

$$Q_{min}(B) = A(2^{1/2}\alpha - 4J)(A^2 + 2^{7/2}JK)^{-1} \quad (22)$$

$$Q_{min}(N) = -2^{-1/2}A/K \quad (23)$$

Along the sum coordinate, the effective harmonic force constant $(\partial^2 U/\partial Q^2)_{q=0}$ is slightly larger in the first-excited surface than in the ground surface

$$K_{eff}(Q;B) = K + 2^{-7/2}A^2/J \quad (24)$$

$$K_{eff}(Q;N) = K \quad (25)$$

Note that the last term on the right-hand side of eq 24 is small, so that the force constants along Q are approximately equal to that of the monomer K for both surfaces.

Along the difference coordinate q the minimum for the ground and first-excited surfaces coincide

$$q_{min}(B) = q_{min}(N) = 0 \quad (26)$$

and the corresponding effective harmonic force constants are given by

$$K_{eff}(q;B) = K + 2^{-3/2}A^2/J \quad (27)$$

$$K_{eff}(q;N) = K \quad (28)$$

We have already demonstrated[17] that for the strongly delocalized case and for $A_2 \approx 0$, the width of the IT band arises entirely from coupling to the vibrational sum coordinate and not to the difference coordinate. Since the sum coordinate alone determines the width of the IT band for this case, the energies and intensities of the transitions between the vibronic levels of the upper and lower surfaces may be calculated from one-dimensional slices of the potential surfaces along the sum coordinate Q with the difference coordinate q fixed at its potential minimum value $q_{min}(B) = q_{min}(N) = 0$. The energies and eigenfunctions for these one-dimensional slices may be obtained by a one-dimensional finite difference method.[17]

Alternatively, one could treat the B and N surfaces approximately as two displaced one-dimensional harmonic oscillators along the sum coordinate Q with respective harmonic force constants given by eq 24 and 25 and with respective minima given by eq 22 and 23. We shall refer to this method as the second-order harmonic oscillator (SOHO) approximation because the potentials are taken to be harmonic oscillators whose force constants and

potential minima were obtained from second-order perturbation theory.

The eigenfunctions and energies for these approximate one-dimensional potentials are now, of course, very well-known. Expressions for the integral of the product of two displaced harmonic oscillators with two different force constants have been given previously in a number of sources and have been applied in a variety of problems.[20] For instance, Siders and Marcus recently have applied these expressions to the problem of outer-sphere electron transfer in solution.[21]

For a harmonic oscillator function $\phi_n(k,Q)$ with n quanta of excitation and force constant k whose minimum is displaced by Q_0 from the HO function $\phi_m(k',Q + Q_0)$ with m quanta of excitation and with force constant k', the overlap integral may be obtained from expressions given previously in the literature.[21] Note that for our displaced potentials along the sum coordinate, the harmonic force constants are nearly identical for the B and N surfaces. We can neglect the second (small) term on the right-hand side of (24) and take both surfaces to have force constant K. In this case where the two displaced oscillators have identical frequency, the overlap integral may be written as[20-22]

$$\int_{-\infty}^{+\infty} \phi_l^*(k,Q + Q_0)\phi_n(k,Q)\,dQ =$$
$$\left(\frac{p^{l-n}n!}{l!}\right)^{1/2} e^{-p/2}L_n^{l-n}(p), \quad \text{for } l > n \quad (29)$$

where L_n^{l-n} is an associated Laguerre polynomial and p is given by

$$p = (Km)^{1/2}Q_0^2/2\hbar \quad (30)$$

Equation 29 gives the Franck–Condon factor for a transition from the nth vibronic level of the ground surface to the lth vibronic level of the excited surface. Under low-temperature conditions, one need only consider excitations from the $n = 0$ level, and the relative intensities to the final vibrational states ϕ_l obey a Poisson distribution[20-22]

$$|\langle\phi_l(k,Q + Q_0)|\phi_0(k,Q)\rangle|^2 = \frac{e^{-p}p^l}{l!} \quad (31)$$

Utilizing the SOHO approximation, the displacement Q_0 between the minima of the B and the N surfaces along the sum coordinate is given by

$$Q_0 = A(2^{1/2}\alpha - 4J)(A^2 + 2^{7/2}JK)^{-1} + 2^{-1/2}AK^{-1} \quad (32)$$

Equations 30–32 provide a simple method for predicting the intensities of the transitions between the vibronic levels of the B and the N surfaces of a delocalized bridged dimer at low temperature.

To test the accuracy of the SOHO method, we compare the Franck–Condon factors squared (which are proportional to the transition intensities at low temperature) obtained from this approximate method to those obtained numerically from a finite difference calculation on one-dimensional slices of the exact adiabatic potentials given in ref 17. We calculate the square of the vibrational overlap integral for a transition from the lowest vibrational level of the B surface to the lth level of the N surface. Table I gives the values obtained from both methods for the square of this integral for the case where $A = -1.0$ eV/Å, $J = -0.5$ eV, $\alpha = 0.0$, $K = 10.0$ eV/Å^2, and $m = 1.0 \times 10^{-26}$ eV s^2/Å^2. These values were selected to correspond to a strongly delocalized bridged complex. The electronic coupling $J = -0.5$ eV corresponds to a strong back-bonding interaction between the transition-metal terminus and the bridge. The vibronic coupling parameter A is of order 10^0–10^1 eV/Å for transition-metal complexes. We have

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Intervalence Transfer Band in Bridged Dimers

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Table I. Comparison of SOHO Transition Intensities with Those Obtained from Numerical Solutions of the Exact Adiabatic Potentials[a]

	$|\langle l|0\rangle|^2$	
l	SOHO approx	exact adiabatic potl
0	0.740 612	0.748 312
1	0.222 389	0.215 844
2	0.033 389	0.032 192
3	0.003 342	0.003 342

[a] Transition intensities calculated for the case $A = -1.0$ eV/Å, $J = -0.5$ eV, $K = 10.0$ eV/Å², $\alpha = 0$ and $m = 1.0 \times 10^{-26}$ eV/s²/Å². Transitions are from the $n = 0$ level of the B surface to the lth level of the N surface. Squares of the vibrational overlap integrals are calculated (a) in the SOHO approximation and (b) from numerical integration of the nuclear wave functions obtained numerically from one-dimensional slices (along the sum coordinate) of the exact adiabatic potentials. In the present example $A_2 = 0$, i.e., there are no coupled bridge modes.

selected A on the low end of this range, to correspond to the strongly delocalized case. K and m correspond to a vibrational frequency of ~200 cm⁻¹. We take $\alpha = 0$ for the present example, which means that the parent bridge and terminal basis states are degenerate.

Notice in Table I that the relative transition intensities obtained by the SOHO method differ only by 3% or less from the numerical results calculated from the exact adiabatic potentials. Additional trials were made with different values for the parameters and the SOHO results showed about the same degree of accuracy. Equations 30–32 have given the intensities of the transitions between the vibronic levels of the B and N surfaces of this hypothetical bridged dimer at low temperature with quite reasonable accuracy and with substantial savings of computational time.

C. Application to Complexes with One Coupled Bridge Vibration. We now extend the above method to complexes where one mode of vibrational motion on the bridging ligand is coupled to the electronic motion. To see how this might occur, let us use the Creutz–Taube ion as an example. In this complex, the terminal metal ions are coupled via a π^* state on the pyrazine bridge represented by this view from above
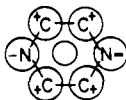
When charge density is removed from this orbital, the C–C bonds are expected to lengthen and the C–N bonds are expected to shorten. The vibrational mode corresponding to these nuclear displacements is the one that exhibits the largest frequency shift on going from free pyrazine[23,24] to the Creutz–Taube complex[2a,25] and is expected to be the mode most strongly coupled to the increase in C–C and decrease in C–N bond orders. Therefore, the IT transition should be accompanied by the excitation of one (or possibly more) totally symmetric vibrational mode(s) on the pyrazine ring. This type of coupling to the bridge modes may be important in many of the bridged dimers of interest.

To incorporate one bridge vibrational mode, we return to the original three-site, three-mode Hamiltonian of eq 5–8 and transform it into the Q, q, and q_2 (sum, difference, and bridge, respectively) nuclear coordinates given by eq 16–18. Solving the Schrödinger equation in the adiabatic approximation, three adiabatic potential surfaces are obtained as

$$V_1 = -R^{1/3}(\cos\theta + 3^{1/2}\sin\theta) + V' \tag{33}$$

$$V_2 = -R^{1/3}(\cos\theta - 3^{1/2}\sin\theta) + V' \tag{34}$$

$$V_3 = 2R^{1/3}\cos\theta + V' \tag{35}$$

(23) Lord, R. C.; Marston, A. L.; Miller, F. A. *Spectrochim. Acta* **1957**, *9*, 113.

(24) Simmons, J. D.; Innes, K. K.; Begun, G. M. *J. Mol. Spectrosc.* **1964**, *14*, 190–197.

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where

$$V' = (1/3)(2^{1/2}AQ + \alpha + A_2q_2) + (1/2)K(q^2 + Q^2) + (1/2)(K_2q_2^2) \tag{36}$$

$$R^{1/3} = (1/3)[(2^{-1/2}AQ - \alpha - A_2q_2)^2 + 6J^2 + (3/2)(A^2q^2)]^{1/2} \tag{37}$$

and where θ is an angle between 0 and $\pi/3$ given by

$$\theta = (1/3)\cos^{-1}\{-R^{-1}[3^{-3}(2^{-1/2}AQ - \alpha - A_2q_2)^3 + (1/6) \times (2^{-1/2}AQ - \alpha - A_2q_2)(2J^2 + (1/2)(A^2q^2)) + (1/4)(A^2q^2(\alpha + A_2q_2)) - 2^{-5/2}A^3q^2Q]\} \tag{38}$$

K_2 and A_2 denote the force constant and vibronic coupling constant for the bridge mode and the other symbols retain their previous meanings. In eq 38, $\cos^{-1}$ denotes the principal value of the arccos function $(0,\pi)$. Notice that the three adiabatic potentials of eq 33–35 are three-dimensional potential surfaces.

We have shown previously that for delocalized complexes, coupling to the difference coordinate q may be neglected:[17] there is no displacement of the minimum along q, and the frequency shift between the ground and first-excited potential surfaces is very small. Therefore, we shall project these potentials in three-dimensional space onto the two-dimensional space defined by $q = 0$ ($q = 0$ is the value for the difference coordinate at the potential minimum). The resulting two-dimensional potentials are given by

$$W_1 = 2^{-3/2}AQ + (1/2)\alpha + (1/2)A_2q_2 - (1/2)[(2^{-1/2}AQ - \alpha - A_2q_2)^2 + 8J^2]^{1/2} + W' \tag{39}$$

$$W_2 = 2^{-1/2}AQ + W' \tag{40}$$

$$W_3 = 2^{-3/2}AQ + (1/2)\alpha + (1/2)(A_2q_2) + (1/2)[(2^{-1/2}AQ - \alpha - A_2q_2)^2 + 8J^2]^{1/2} + W' \tag{41}$$

$$W' = (1/2)(KQ^2) + (1/2)(K_2q_2^2) \tag{42}$$

Energy levels and eigenfunctions in the adiabatic approximation for these three two-dimensional potentials (eq 39–41) may be obtained numerically with a two-dimensional finite element method.[26] As a far simpler alternative to such a numerical solution, we employ the SOHO approximate method, taking the motions along the sum coordinate and along the bridge coordinate to be two independent harmonic oscillators. Thus the nuclear wave function is given by a product of two harmonic oscillator functions as

$$\Phi_{ij} = \phi_{+i}\phi_{2j} \tag{43}$$

and the total vibrational energy is the sum of the contributions from the sum and bridge coordinates, given by

$$E_{ij} = (i + 1/2)\hbar\omega_+ + (j + 1/2)\hbar\omega_2 \tag{44}$$

Again, second-order perturbation theory is used to obtain expressions for the minima in the B and N surfaces. Along the sum coordinate, the difference $Q_{\min}(N) - Q_{\min}(B)$ in the potential minima between N and B surfaces was found to be

$$\Delta Q_{\min} = -2^{-1/2}A/K + \frac{2^{1/2}AA_2^2(\alpha + 2^{3/2}J)}{(A^2 + 2^{7/2}JK)(A_2^2 + 2^{5/2}JK_2) - A^2A_2^2} \frac{A(A_2^2 + 2^{5/2}K_2J)(2^{1/2}\alpha - 4J)}{(A^2 + 2^{7/2}JK)(A_2^2 + 2^{5/2}JK_2) - A^2A_2^2} \tag{45}$$

The corresponding displacement in the potential minima along the bridge coordinate q_2, $q_{2\min}(N) - q_{2\min}(B)$, is given by

$$\Delta q_{2\min} = A_2[2^{-1/2}A\Delta Q_{\min} + (1/2)(A^2/K) + \alpha + 2^{3/2}J] \times (A_2^2 + 2^{5/2}K_2J)^{-1} \tag{46}$$

As before, the force constants for both surfaces may be taken to

(26) TWODEPEP, IMSL, Inc., Houston, Texas.

Table II. Comparison of SOHO Transition Energies and Relative Intensities with the Numerical Results from the Exact Adiabatic Potentials for a Complex with One Coupled Bridge Vibration[a]

	SOHO approx		exact adiabatic potl	
lm	$\Delta E_{lm,00}$	$|\langle lm|00\rangle|^2$	$\Delta E_{lm,00}$	$|\langle lm|00\rangle|^2$
00	6 370.6	0.329 109	6 370.7	0.333 963
10	6 891.2	0.049 412	6 891.5	0.045 761
01	6 924.8	0.316 349	6 925.2	0.302 624
20	7 411.8	0.003 709	7 412.5	0.003 415
11	7 445.4	0.047 496	7 445.8	0.045 288
02	7 479.0	0.152 041	7 479.9	0.150 238
30	7 932.4	0.000 186	7 934.7	0.000 160
21	7 966.0	0.003 566	7 595.8	0.003 496
12	7 999.6	0.022 827	8 000.9	0.024 326
03	8 033.2	0.048 715	8 036.2	0.053 890
40	8 452.9	0.000 007	8 458.0	0.000 006
31	8 486.6	0.000 178	8 489.0	0.000 210
22	8 520.2	0.001 714	8 522.9	0.001 943
13	8 553.8	0.007 314	8 556.6	0.009 311
04	8 587.4	0.011 707	8 593.7	0.015 507

[a] Transition energies and intensities are calculated for the case $A = -1.5$ eV/Å, $J = -0.6$ eV, $K = 15.0$ eV/Å², $A_2 = -3.0$ eV/Å, $\alpha = 0.2$ eV, $K_2 = 17.0$ eV/Å², and $m = m_2 = 1.56 \times 10^{-27}$ eV s²/Å². Transitions are from the 00 level of the B surface to the *lm* level of the N surface. Calculations were performed (a) with the SOHO method, and (b) from numerical integration of the nuclear wave functions obtained numerically by a two–dimensional finite element method from the exact adiabatic potentials. Transition energies are in wavenumbers (cm⁻¹).

be approximately equal to those of the isolated species, i.e., K_2 for the bridge coordinate and K for the sum coordinate. This second-order treatment is valid provided the vibrational displacements are not too large and for $|J| > A^2/2K$, $|J| > A_2^2/2K_2$, and $|J| \gtrsim |\alpha|$.

The harmonic force constants obtained from second-order perturbation theory along the sum coordinate are the same as those for the previous example and are given in eq 24 and 25. Along the bridge coordinate the force constants were obtained as

$$K_{eff}(q_2;B) = K_2 + 2^{-5/2}A_2^2/J \qquad (47)$$

$$K_{eff}(q_2;N) = K_2 \qquad (48)$$

As before the second term on the right-hand side of (47) is small so the harmonic frequencies of the B and N surfaces along any one coordinate will again be taken to be identical.

For this two-mode problem, we must calculate the product of the squares of the overlap integrals

$$|\langle \Phi_{lm}|\Phi_{ij}\rangle|^2 =$$
$$|\langle \phi_{+l}(Q + \Delta Q_{min})|\phi_{+i}(Q)\rangle|^2|\langle \phi_{2m}(q_2 + \Delta q_{2min})|\phi_{2j}(q_2)\rangle|^2 \quad (49)$$

This product will give the relative intensities of the transitions between the vibronic levels of the B and N surfaces if the system is initially in the state Φ_{ij}, which is defined by eq 43. At low temperatures, the transition intensities are given by a product of two Poisson distributions

$$|\langle \Phi_{lm}|\Phi_{00}\rangle|^2 = \frac{r^l e^{-r}}{l!} \frac{s^m e^{-s}}{m!} \qquad (50)$$

where r and s are given by

$$r = (K_+ m)^{1/2}(\Delta Q_{min})^2/2\hbar \qquad (51)$$

$$s = (K_b m_2)^{1/2}(\Delta q_{2min})^2/2\hbar \qquad (52)$$

and where K_+ and K_b are the harmonic force constants for the sum and bridge coordinates, respectively, with $K_+ \approx K$ and $K_b \approx K_2$. (In the example below, we have used the average of eq 24 and 25 for K_+ and the average of eq 47 and 48 for K_b.)

In Table II the transition energies and intensities obtained from the SOHO approximate method (eq 50) are compared to the energies and intensities obtained from a numerical solution to the Schrödinger equation for the adiabatic potentials of eq 39–42 (by a two-dimensional finite element method[26]) for the case $A = -1.5$
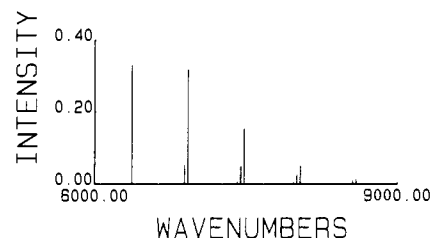
Figure 1. Low-temperature absorption spectrum for the case given in Table II predicted with the SOHO method.
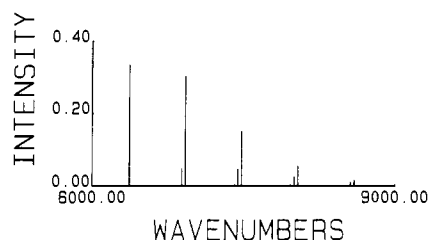
Figure 2. Low-temperature absorption spectrum for the case given in Table II obtained numerically from the exact adiabatic potentials.

eV/Å, $J = -0.6$ eV, $K = 15.0$ eV/Å², $A_2 = -3.0$ eV/Å, $\alpha = 0.2$ eV, $K_2 = 17.0$ eV/Å², and $M = M_2 = 1.56 \times 10^{-27}$ eV s²/Å². (This reduced mass corresponds to 15 amu.) In this particular example, we have taken the vibronic coupling on the bridge to be somewhat stronger than that on the termini ($|A_2| > |A|$) and have taken the parent bridge state to be 0.2 eV higher in energy than the parent terminal states. These parameters were chosen to correspond to a typical strongly delocalized bridged dimer.

Again, the SOHO method proves to be quite a reasonable approximate procedure. The transition energies are in agreement with the numerical results to within a few wavenumbers or less. The relative intensities are in agreement to within a few percent, at least for the more intense transitions. The corresponding low-temperaure absorption spectrum obtained from the SOHO method is shown in Figure 1. Figure 2 gives the low-temperature spectrum obtained from the numerical results given in Table II for the exact adiabatic potential. Comparing Figures 1 and 2, the difference between the SOHO and numerical results for this complex with one coupled bridge mode are barely discernible.

Moment Analysis

Next the moments for the distribution of transition intensities will be analyzed in order to obtain an expression for the width of the absorption envelope at half-maximum.

For the complex with one coupled bridge vibration discussed in the preceding section, the *k*th moment is defined as[20]

$$M_k = \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} (E^0 + E_{lm} - E_{00})^k \frac{r^l e^{-r}}{l!} \frac{s^m e^{-s}}{m!} \qquad (53)$$

where E^0 is the energy difference between the minimum of the upper surface and the minum of the lower surface. The width of the absorption envelope at half-maximum is given by

$$\Delta E_{1/2} = 2(M_2 - M_1^2)^{1/2} \qquad (54)$$

For the present example, the width at half-height is derived as

$$\Delta E_{1/2} = 2\hbar[(rK_+/m) + (sK_2/M_2)]^{1/2} \qquad (55)$$

where r and s are given in eq 51 and 52. Thus, the width of the low-temperature absorption band at half-maximum may be predicted without the use of a computer.

Discussion

Beginning with a three-site model for bridged mixed-valence dimers, we have shown how delocalized complexes may be treated with second-order perturbation theory to give expressions for the intensities of the transitions between the vibronic levels of the upper and lower surfaces. The SOHO method is quite simple and has

been shown to give reasonably accurate transition energies and intensities.

Although the present method incorporates effects that are not present in the previous two-site models (including the totally symmetric vibrations along Q and q_2, the metal–bridge coupling J, and the energy gap α), it is still an overly simple picture. It is assumed that there are three and only three coupled electronic states. Obviously the present model does not apply to complexes in which other states mix appreciably with the orbitals containing the unpaired electron. The electronic Hamiltonian is taken to be of the one-electron type. Hückel Hamiltonians have been used previously for transition-metal complexes of the type discussed here, for example in the PKS model and the Beratan–Hopfield[27] model for transition-metal dimers with rigid polymeric bridges. However, a one-electron Hamiltonian is admittedly a simplistic one for transition-metal systems, where repulsion occurs between electrons of opposite spin occupying the same orbital on a given metal ion. Therefore, the parameters in $\hat{\mathcal{H}}_e$ (J and α) obtained for the N-electron system will not be valid for the $(N + 1)$- or $(N - 1)$-electron system. One could introduce electron–electron repulsion terms into $\hat{\mathcal{H}}_e$, but this has the disadvantage of bringing still more parameters into the problem.

Because the applicability of the present work is limited to delocalized complexes, we are able to neglect solvent effects and to obtain the nuclear eigenfunctions in the adiabatic approximation. A more general treatment of systems with weaker electron-exchange coupling (smaller $|J|$) would have to include solvent effects and would have to solve the full vibronic problem without the adiabatic approximation.

There has been interest recently in the osmium analogues of the ruthenium complexes discussed above.[28] To apply the present model to these osmium complexes, the effects of spin–orbit coupling would have to be incorporated.

Recently, Dubicki, Ferguson, and Krausz[29] have proposed a crystal-field type model for the Creutz–Taube ion which incorporates spin–orbit coupling and the tetragonal and rhombic splittings of the metal t_2 orbitals. Using fit parameters, the model successfully interprets the anisotropy of the EPR g values and the MCD spectrum. However, this model utilizes an effective direct metal–metal coupling and does not explicitly include the bridging ligand. Such an effective Hamiltonian has its value in describing properties arising solely from the purely electronic subsystem, but inclusion of the bridging species is necessary to incorporate properly the important coupled vibrational motion.

In the past, through-bridge coupling in bridged dimers has been described in terms of a superexchange mechanism.[30] One can write an effective terminus–terminus electronic coupling constant (called ϵ in the PKS model) in terms of the terminus–bridge electronic coupling (J of the present model). However, such a projection of the 3 × 3 problem onto a 2 × 2 space is based on

perturbation theory, which is valid for α very large or for $|J|$ small but which breaks down for large $|J|$. For complexes with strong metal–bridge coupling, the two-site descriptions break down. This is illustrated most dramatically by the qualitative differences in the potential energy surface.

In the present paper, we have emphasized the transition from the B surface to the N surface. The same method may also be applied to the N → A transition, which the experimentalists call $t_{2g} \rightarrow \pi^*$.[31] In a delocalized complex, the two termini are equivalent and the B → A transition is symmetry forbidden.

Transition intensities at low temperature were obtained from the squares of the vibrational overlap integrals. For the complexes of interest, the frequencies of the internal vibrations involved are sufficiently high so that at room temperature, there is not significant thermal population of excited vibrational levels. Therefore, it is expected that the low-temperature limit should provide a good approximation to the room-temperature spectrum. Of course, the high-temperature case may be treated by using eq 29 and multiplying by the thermal population weighting factor appropriate for the initial state.[17]

Since several parameters are contained in the present model, they are best obtained a priori rather than by a fit to the observed spectrum. K and K_2 are readily available from vibrational spectra. J and α may be obtained from electronic structure calculations, which are currently in progress on a variety of bridged dimers. A may be calculated from crystallographic data on the oxidized and reduced forms of the monomeric terminal metal ion. A_2 is the one parameter that is not as straightforward to estimate with accuracy, since crystallographic data are usually available on the free bridge but not on the corresponding radical anion. There are a number of possible means of estimating A_2,[32] but at worst our model contains one parameter to be fit, A_2.

It is important to note that the line-broadening mechanism is completely different for a two-site delocalized complex vis-a-vis a three-site delocalized complex. In the two-site case, the absorption bandwidth (for the IT transition, which is really a bonding-to-antibonding transition in the delocalized case) arises from differences in shape and force constant (second derivative) of the upper and lower surfaces, because the minima of these two surfaces coincide. In the three-site system, the IT absorption bandwidth occurs primarily because the minimum of the upper surface is displaced from the minimum in the lower surface, with both surfaces nearly harmonic. Thus, the SOHO approximation is a viable one for predicting the IT band line shape for delocalized bridged dimers.

(27) Beratan, D. N.; Hopfield, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1584–1594.

(28) Dubicki, L.; Ferguson, J.; Krausz, E. R.; Lay, P. A.; Maeder, M.; Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.*, **1985**, *107*, 2167–2171.

(29) Dubicki, L.; Ferguson, J.; Krausz, E. R. *J. Am. Chem. Soc.* **1985**, *107*, 179–182.

(30) For example: Halpern, J.; Orgel, L. E. *Discuss. Faraday Soc.* **1960**, *29*, 32.

(31) For example: Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988–3989.

(32) For instance, A_2 may be estimated from force constant–bond length relationships if vibrational data are available on the free bridge and the corresponding anion. Alternatively, A_2 may be calculated by electronic structure calculations with geometry optimization on the free bridge and the corresponding anion.