(975.5 cm^{-1} for $RbReO_4$ and 980 cm^{-1} for $TlReO_4$) is observed after annealing and might belong to the dimer species. Spoliti and Stafford[21] have studied the gas-phase IR spectra of the alkali perrhenates. These authors have observed a broad band extending from 800 to 1000 cm^{-1}. Our experiments show that the broad absorption quoted in that previous work is due to the overlap of the stretching vibrations assigned by us to the C_{2v} $MReO_4$ species. These authors have carried out extensive superheating experiments that, however, did not cause any change in frequencies or in band contours. Spoliti and Stafford came to the conclusion that the broad band observed during their experiments is due in part to the monomer and to the dimer whose frequencies are not much shifted from those of the monomer. We have also carried out superheating experiments on $LiReO_4$, $NaReO_4$, and $KReO_4$ whose vapor phases are supposed to consist of a nonnegligible concentration of dimers.[18,19] These perrhenates have been vaporized from an alumina double oven with an effusion hole of 1 mm. The top and the base of this oven have been kept at ca. 850 and 815 K, respectively. The vapors have been collected in N_2 and Ar matrices, and the observed spectra have been found identical with those obtained in the usual vaporization conditions.

We also conclude that the absorptions of the dimers might not be shifted much from those of the monomers, but they are not coincident with the bands of the $MReO_4$ species.

Acknowledgment. This work has been performed under the auspices of the R. A. Welch Foundation (Grant A-387).

Note Added in Proof. Meanwhile, we have completed our study on the $MReO_4$ molecules with Raman matrix-isolation measurements and with ^{18}O-enrichment experiments on $KReO_4$.[22] The latter ones confirm for $KReO_4$ the C_{2v} symmetry structure which is common for all the $MReO_4$ monomers.

Registry No. $LiReO_4$, 13768-48-4; $NaReO_4$, 13472-33-8; $KReO_4$, 10466-65-6; $RbReO_4$, 13768-47-3; $CsReO_4$, 13768-49-5; $TlReO_4$, 14013-75-3; ^{18}O, 14797-71-8.

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Charge-Transfer-Induced IR Absorptions in Mixed-Valence Compounds

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Received August 2, 1983

Prediction of the existence of tunneling transitions or charge-transfer-induced IR absorption in mixed-valence compounds has been made by Schatz et al. recently, on the basis of exact diagonalization of their PKS model. However, their claim has been disputed by Hush, who stated without proof that such transitions do not exist and are *artifacts* of the PKS model. To clarify this, the PKS model that describes a dimeric mixed-valence system is reexamined with use of linear response theory and a perturbative calculation. Both approaches give results that are consistent with Schatz et al.'s prediction. In addition, analytical expressions for the transition energies of the charge-transfer-induced IR absorption and the charge-transfer or intervalence absorptions are derived, together with expressions for their relative intensities. These are found to be in good agreement with that calculated by the numerical diagonalization method (PKS model). Applications of these expressions to some mixed-valence systems are also presented.

1. Introduction

Prediction of the existence of strong tunneling transitions[1] in the now famous Creutz–Taube ruthenium complex[3] is still a subject of controversy.[4,5] Schatz et al.[1] originally predicted that for this Ru complex there should be strong near-IR transitions at energies 131, 362, and 613 cm^{-1} with a combined dipole strength of 0.3 D^2 (D = Debye). However, Krausz et al.[6] recently reported that such transitions are not observed experimentally. In a recent review, Wong and Schatz[4] suggested that, by reducing the vibronic coupling parameter in the PKS model, the calculated tunneling transition intensities could be substantially reduced and become consistent with Krausz et al.'s result, as well as with the bond-length data of the complex. However, with such a reduced value, the predicted intervalence band contour would become narrower and hence fail to fit the experimental absorption band.

This discrepancy can be removed when solvent effects are introduced into the PKS model, as shown in a recent article by Wong and Schatz.[7] By introduction of an "effective" solvent vibronic coupling parameter λ_s and assumption of an effective solvent vibrational frequency of about 200 cm^{-1}, the observed absorption band shape of the Ru complex can be satisfactorily accounted for.

So far the existence of near-IR tunneling transitions is based entirely on exact numerical solution of the PKS model. In this approach, the vibronic Hamiltonian describing a dimer system is diagonalized with a large but truncated basis set. The resulting eigenfunctions are then used to calculate the transition intensities. Two types of transitions are predicted. One has transition energies $\gg \hbar w_\alpha$ (intervalence transitions) and the other $\lesssim \hbar w_\alpha$ (near-IR tunneling or charge-transfer-induced IR transitions), where w_α is the molecular vibrational frequency of the a_{1g} mode of the dimer system.

It is of interest to note that the Fourier transform method of Buhks,[8] the Hush treatment,[9-11] which is entirely based on

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the result of the Kubo and Toyozawa Laplace transform method,[12] and the most recent semiclassical treatment by Wong et al.[13] fail to predict the existence of the near-IR tunneling transitions.

Linear response theory was first developed by Kubo[14] and later discussed by Pines et al.[15] Recently, Rice et al.[16,17] applied this theory to systems of two sites and one or two electrons to describe some dimeric organic conductors. The IR enhanced absorptions related to a_{1g} vibrations of these systems, as well as charge-transfer absorptions, have been observed experimentally.

In section 2, we rewrite the PKS model Hamiltonian into an operator form that is very similar to that discussed by Rice[17] for a two-site, single-electron system. The results derived earlier by Rice can then be applied directly, and this leads immediately to the prediction of two charge-transfer-related transitions. In addition, the relative intensity ratio between the charge-transfer-induced IR absorption and the intervalence absorption is derived.

In section 3, we solve the PKS model Hamiltonian using perturbation theory in the nearly delocalized limit. Again, we are able to predict the existence of two charge-transfer-related absorptions and derive their relative intensity ratio.

In section 4, we compare the results obtained in sections 2 and 3 with those of the exact diagonalization method and the results obtained by Fourier transform and other related approaches.

In section 5, the analytical expressions are used to discuss some mixed-valence systems.

2. PKS Model in Operator Form

The Hamiltonian describing a dimer system in which an electron can transfer from one subunit to another is given by[2] (for a symmetric system)

$$H = \sum_i W_i^0 + \sum_{\alpha,i} P_i^{\alpha 2}/2M_i + \sum_{\alpha,i} \tfrac{1}{2}k_\alpha Q_i^{\alpha 2} + \sum_{\alpha,i} l_\alpha Q_i^\alpha + V_{12} \quad (1)$$

where i denotes the subunit and α denotes the αth normal mode of the subunit. W_i^0 is the energy of an electron in a subunit that is in a higher oxidation state. P_i^α and Q_i^α are respectively the momentum and normal coordinate of the subunit i, which has mass M_i. l_α is the displacement of the equilibrium position when an electron is transferred from one subunit to the other. k_α is the force constant of the harmonic vibration of the subunit, and V_{12} is the interaction between the two subunits that leads to the electron transfer.

Note that eq 1 is obtained for a symmetrical system with the assumption of an equal force constant in each subunit. Other approximations and assumptions are discussed in detail in ref 2 and will not be repeated here.

Equation 1 can be put into operator form by using[18]

$$\hat{F} = \sum_i \hat{f}_i = \sum_{\mu,\nu} a_\mu^+ \hat{f}_{\mu\nu} a_\nu^- \quad (2)$$

where $\hat{f}_{\mu\nu} = \int \varphi_\mu^*(i)\, f_i(\varphi_\nu(i))\, d\tau$ is the matrix element of the ith operator. a^+ and a^- are the electron creation and annihilation operators, respectively. The total Hamiltonian in the operator form is[18]

$$H_{\text{total}} = \sum_i E_0 n_i + \sum_{\alpha,i}(P_i^{\alpha 2}/2M_i + \tfrac{1}{2}k_\alpha Q_i^{\alpha 2}) + \sum_{\alpha,i} l_\alpha n_i\, Q_i^\alpha + \epsilon(a_1^+ a_2^- + a_1^- a_2^+) \quad (3)$$

Defining w_α as the vibrational frequency of the αth a_{1g} mode of a subunit and using the transformations $Q_i^\alpha = (\hbar/2Mw_\alpha)^{1/2} q_i$, $P_i^\alpha = (\hbar M w_\alpha/2)^{1/2} \dot{q}_i$, and $l_\alpha = \lambda_\alpha \hbar w_\alpha (2Mw_\alpha/\hbar)^{1/2}$, we obtain

$$H_{\text{total}} = \sum_i E_0 n_i + \epsilon(a_1^+ a_2^- + a_1^- a_2^+) + \sum_\alpha \hbar w_\alpha[\tfrac{1}{4}\dot{q}_+^{\alpha 2} + \tfrac{1}{4}(q_+^\alpha + 2^{1/2}\lambda_\alpha n)^2 - \lambda_\alpha{}^2 n^2/2] + \sum_\alpha \hbar w_\alpha[\tfrac{1}{4}(\dot{q}_-^{\alpha 2} + q_-^{\alpha 2}) + 1/2^{1/2}\lambda_\alpha q_-^\alpha \delta n] \quad (4)$$

where $q_\pm^\alpha = 1/2^{1/2}\,(q_1^\alpha \pm q_2^\alpha)$ are the dimeric normal coordinates and $\delta n = (n_1 - n_2)$.

The symmetric mode q_+^α with its harmonic Hamiltonian, $\sum_\alpha \hbar w_\alpha[{}^1/_4\dot{q}_+^{\alpha 2} + {}^1/_4(q_+^\alpha + 2^{1/2}\lambda_\alpha n)^2 - \lambda_\alpha{}^2 n^2/2]$, contains a constant of motion, n (the total number of electrons). Hence it can be decoupled from the remaining system. For a symmetrical system the first term is also a constant and hence can be dropped from further consideration. Thus the final Hamiltonian becomes

$$H_{\text{vib}} = \sum_\alpha \hbar w_\alpha[\tfrac{1}{4}(\dot{q}_-^{\alpha 2} + q_-^{\alpha 2}) + 1/2^{1/2}\lambda_\alpha q_-^\alpha \delta n] + \epsilon(a_1^+ a_2^- + a_1^- a_2^+) \quad (5)$$

It is seen that only the antisymmetry mode q_-^α interacts with the δn term, which is related to the charge-transfer interaction as will be shown later.

In the presence of an electromagnetic field, the total Hamiltonian can be written[16]

$$H_{\text{total}} = \sum_\alpha \hbar w_\alpha[\tfrac{1}{4}(\dot{q}_-^{\alpha 2}) + 1/2^{1/2}\lambda_\alpha q_-^\alpha \delta n] + \epsilon(a_1^+ a_2^- + a_1^- a_2^+) - \tfrac{1}{2}(e\cdot\mathbf{a})(n_1 - n_2)\cdot\mathbf{F} \quad (6)$$

where $\mathbf{F}$ denotes an externally applied electric field. $(e\cdot\mathbf{a})(n_1 - n_2)$ represents the electric dipole moment of the dimer, and the vector length $\mathbf{a}$ is of the order of the separation between the subunits.

Equation 6 is identical with that for a two-site, single-electron organic conductor system described by Rice et al. earlier.[17] The frequency-dependent conductivity is thus given by[16,17]

$$\sigma(w) = -iw\left(\frac{1}{4}e^2\mathbf{a}\cdot\mathbf{a}\right)\left[X(w) + \frac{X(w)\,\bar{X}(w)\,D(w)}{1 - \bar{X}(w)\,D(w)}\right] \quad (7)$$

where $\bar{X}(w) = X(w)/X(0)$; $X(w)$ is defined as

$$X(w) = \sum_\beta |\langle\beta|\delta n|0\rangle|^2 2w_{\beta 0}/[w_{\beta 0}{}^2 - (w + i\delta)^2] \quad (8)$$

where $|\beta\rangle$ denotes the eigenstate. $\beta = 0$ denotes the ground state. $D(w)$ is defined as

$$D(w) = \sum_\alpha X(0)\, g_\alpha{}^2 w_\alpha/(w_\alpha{}^2 - w^2) \quad (9)$$

Note that the real part of the conductivity $\sigma(w)$ gives the charge-transfer absorption. From (7) it can be seen that there are two types of transitions. One is centered at $\sim w_{\beta 0}$ and is the charge-transfer or intervalence transition due to electron transfer from one subunit to the other. Notice that $w \approx w_{\beta 0} >> w_\alpha$. The second transition given by the second term in the brackets is in the vibrational energy region (mid- to far-IR). It is seen to be proportional to $D(w)$ and $X(w)$. The proportionality to $X(w)$ implies that its intensities are derived from the charge-transfer transition and should therefore have the

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same polarization properties as the charge-transfer transition. From (9) it is readily seen that the mid-IR transition intensity is proportional to g_α^2 (where $g_\alpha = \lambda_\alpha \hbar w_\alpha$), which is a measure of the electron–phonon coupling.

Under normal circumstances, the a_{1g} molecular vibration of the individual subunit is IR inactive. However, in the present dimeric system described by eq 6, where we have strong electronic interaction between the subunits, the coupled a_{1g} vibrations become IR active. A similar intensity mechanism has been discussed by Ferguson and Matsen and others for isolated charge-transfer complexes.[19–23] Hence we may regard the mixed-valence dimer complex, or more generally mixed-valence compounds, and certain types of organic conductors as other classes of charge-transfer complexes.

The transition energies are found by evaluating the roots of the equation $0 = 1 - \tilde{X}(w)\,D(w)$ in eq 7. For simplicity, we consider only one vibration, i.e., $w_\alpha = w_0$. Also for a nearly delocalized system, the transition dipole moment $|\langle\beta|\delta n|0\rangle| \approx 1$, and $w_{\beta 0} = (2\epsilon_0)w_0$.[13] We have

$$\frac{w_0}{(w_0^2 - w^2 - iw\gamma_0)} = \frac{4\epsilon_0^2 w^2 - (w + i\delta)^2}{4\epsilon_0\lambda_0^2 w_0^3} \qquad (10)$$

In (10) a damping term has been added to $D(w)$ to prevent a divergence at $w \approx w_0$. From (10) we obtain (defining $\delta = \delta_0 w_0$, $\gamma_0 = \gamma_{00}w_0$, and $\epsilon_0 \hbar w_0 = \epsilon$)

$$(w/w_0)^2 = \tfrac{1}{2}(4\epsilon_0^2 + 1 + 2\delta_0\gamma_{00}) + \tfrac{1}{2}[(1 + 4\epsilon_0^2 + 2\delta_0\gamma_{00})^2 - 16\epsilon_0^2(1 - \lambda_0^2/\epsilon_0)]^{1/2} \qquad (11)$$

If $\delta_0 \approx \gamma_{00} \approx 0$ and $\epsilon_0 >> \lambda_0^2$

$$\begin{aligned}(w/w_0)^2 &= 4\epsilon_0^2 + \lambda_0^2/\epsilon_0 + \lambda_0^2/4\epsilon_0^3 + \ldots \\ &= 1 - \lambda_0^2/\epsilon_0 + \lambda_0^2/4\epsilon_0^3 + \ldots \qquad (12)\end{aligned}$$

The charge-transfer absorption occurs at

$$w_{\mathrm{IT}} \approx w_0(2\epsilon_0)(1 + \lambda_0^2/8\epsilon_0^3)^{1/2} \qquad (13)$$

whereas the mid-IR charge-transfer-induced absorption occurs at

$$w_{\mathrm{IR}} \approx w_0(1 - \lambda_0^2/\epsilon_0)^{1/2} \qquad (14)$$

Notice that both expressions are valid at temperature $T = 0$ K. Note also that w_{IR} given by (14) is the frequency of vibration on the lower potential surface which is slightly distorted by the vibronic interaction and $w_{\mathrm{IR}} \leq w_0$. However, one must be cautious in distinguishing w_{IR} and w_0. The former is the antisymmetric combination of the subunit symmetric vibrations whereas the latter is the symmetric vibration of each *uncoupled* subunit. In other words, they refer to different entities and should not be confused. (Strictly speaking, one should not talk about any frequency reduction at all.)

The intensity ratio R is defined as the ratio of the IR transitions to the intervalence transitions. To a first approximation, this is given by the ratio of the second term in (7) to the second term of the same equation:

$$R = \frac{I_{\mathrm{IR}}}{I_{\mathrm{IT}}} = \frac{\left\langle \dfrac{X(w)\,\tilde{X}(w)\,D(w)}{1 - [\tilde{X}(w)\,D(w)]} \right\rangle}{\langle X(w)\rangle} \qquad (15)$$

Note that the numerator and the denominator in (15) refer to integrated values over the respective regions. It is readily shown that

$$R = 2\sum_\alpha \lambda_\alpha^2(w_\alpha^2/w_{\beta 0}^2) \qquad (16)$$

Equation 16 is further simplified if only one mode is considered, i.e., $w_\alpha = w_0$:

$$R = 2\lambda_0^2 w_0^2/w_{\beta 0}^2 = \lambda_0^2/(2\epsilon_0^2) \qquad (17)$$

It is seen that, in a nearly delocalized system, the ratio R increases with increasing λ_0^2. Thus I_{IR} is more likely to be observed when there is substantial electron–vibrational coupling. Conversely, if I_{IR} is not observed in a delocalized system despite the presence of a fairly strong intervalence band, then it is most likely that the electron–vibrational coupling is small.

3. Perturbative Solution for the Nearly Delocalized System

We can solve the vibronic Hamiltonian (5) using perturbation theory. Define a new basis set as

$$|+\rangle = 1/2^{1/2}(|1\rangle + |2\rangle) \qquad |-\rangle = 1/2^{1/2}(|1\rangle - |2\rangle) \qquad (18)$$

where $|1\rangle = a_1^+|0\rangle$ and $|2\rangle = a_2^+|0\rangle$ and $|0\rangle$ is some zero state.[18] The vibronic Hamiltonian becomes ($q_0 = q_-$)

$$H_{\mathrm{vib}}/\hbar w_0 = \begin{bmatrix} \tfrac{1}{2}(\dot{q}_0^2 + q_0^2) + \epsilon_0 & \lambda_0 q_0 \\ \lambda_0 q_0 & \tfrac{1}{2}(\dot{q}_0^2 + q_0^2) - \epsilon_0 \end{bmatrix} \qquad (19)$$

This is identical with that in the PKS model.[2] The zeroth-order wave function is[1,24]

$$|\mu_\pm^{(0)}\rangle = 1/2^{1/2}[|1\rangle \pm (-1)^\mu|2\rangle]\,\chi_\mu(q_0) \qquad (20)$$

with the corresponding zeroth-order energy

$$E_\pm^{(0)}(\mu) = \mu + \tfrac{1}{2} \mp (-1)^\mu|\epsilon_0| \qquad (21)$$

The perturbation $\lambda_0 q_0$ mixes the vibrational states:

$$\lambda_0 q_0\,\chi_\mu(q_0) = 1/2^{1/2}\lambda_0[\mu^{1/2}\,\chi_{\mu-1}(q_0) + (\mu + 1)^{1/2}\,\chi_{\mu+1}(q_0)] \qquad (22)$$

Thus the first-order wave function is

$$|\mu_\pm^{(1)}\rangle = |\mu_\pm^{(0)}\rangle + 1/2^{1/2}\lambda_0[\mu^{1/2}|(\mu - 1)_\pm^{(0)}\rangle/(1 \mp 2(-1)^\mu|\epsilon_0|) + (\mu + 1)^{1/2}|(\mu + 1)_\pm^{(0)}\rangle/(-1 \mp 2(-1)^\mu|\epsilon_0|)] \qquad (23)$$

Note that the corrections to the zeroth-order wave functions are of the same signs as the zeroth-order wave functions. With use of (23) the transition matrix element can be evaluated:

$$\begin{aligned}\langle\nu_+^{(1)}|\delta n|\mu_-^{(1)}\rangle = &\left[1 + \frac{1}{2}\lambda_0^2\left(\frac{(\mu\nu)^{1/2}}{(1 - 2|\epsilon_0|(-1)^\mu)(1 + 2|\epsilon_0|(-1)^\nu)}\right) + \frac{(\nu + 1)^{1/2}(\mu + 1)^{1/2}}{(-1 - 2|\epsilon_0|(-1)^\mu)(-1 + 2|\epsilon_0|(-1)^\nu)}\right]\delta_{\nu\mu} + \\ &\frac{1}{2}\lambda_0^2\left[\frac{\nu^{1/2}(\mu + 1)^{1/2}\delta_{\mu+1,\nu-1}}{(1 - 2|\epsilon_0|(-1)^\mu)(-1 + 2|\epsilon_0|(-1)^\nu)} + \frac{\mu^{1/2}(\nu + 1)^{1/2}\delta_{\mu-1,\nu+1}}{(-1 - 2|\epsilon_0|(-1)^\mu)(1 + 2|\epsilon_0|(-1)^\nu)}\right] \qquad (24)\end{aligned}$$

There is no first-order correction to the energy as can be seen from (22). The second-order energy can be shown to be

$$E_\pm^{(2)}(\mu) = \mu + \tfrac{1}{2} \mp (-1)^\mu|\epsilon_0| - \lambda_0^2[(2\mu + 1)(-1)^\mu|\epsilon_0|/(1 - 4|\epsilon_0|^2 - \tfrac{1}{2}(1 - 4|\epsilon_0|^2)] \qquad (25)$$

Note that $|\mu_+^{(1)}\rangle$ and $|\mu_-^{(1)}\rangle$ are associated with energies $E_+^{(1)}(\mu)$

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Table I. Comparison of W_{IR} Calculated by Analytical Methods with the Exact Diagonalization Results[a]

λ_0	$W_{\mathrm{IR}}{}^{\mathrm{PKS}}$	$W_{\mathrm{IR}}{}^{\mathrm{LRT}}$	$W_{\mathrm{IR}}{}^{\mathrm{PER}}$
0.01	499.995	499.996	499.996
0.10	499.580	499.580	499.580
0.50	489.452	489.473	489.510
1.00	457.075	456.435	458.042
2.00	314.270	288.675	332.168

[a] All W values are in cm^{-1}. Abbreviations: PKS = exact diagonalization method; LRT = linear response theory; PER = perturbation method. In all cases $|\epsilon_0| = 6.00$.

Table II. Comparison of W_{IT} Calculated by Analytical Methods with the Exact Diagonalization Results[a]

λ_0	$W_{\mathrm{IT}}{}^{\mathrm{PKS}}$	$W_{\mathrm{IT}}{}^{\mathrm{LRT}}$	$W_{\mathrm{IT}}{}^{\mathrm{PER}}$	$W_{\mathrm{IT}}{}^{\mathrm{KTH}}$
0.01	6000.004	6000.003	6000.004	6000.004
0.10	6000.42	6000.035	6000.42	6000.42
0.50	6010.62	6000.87	6010.42	6010.62
1.00	6041.25	6003.47	6041.67	6045.64
2.00	6222.78	6013.87	6166.67	6288.68

[a] All W values are in cm^{-1}. Abbreviations: PKS = exact diagonalization method; LRT = linear response theory; PER = perturbation method; KTH = Kubo-Toyozawa-Hush method. In all cases $|\epsilon_0| = 6.00$.

Table III. Comparison of Relative Intensity Ratios for a Nearly Delocalized System[a]

λ_0	R^{PKS}	R^{LRT}	R^{PER}
0.01	1.408×10^{-6}	1.39×10^{-6}	1.408×10^{-6}
0.10	1.409×10^{-4}	1.39×10^{-4}	1.049×10^{-4}
0.50	3.571×10^{-3}	3.47×10^{-3}	3.527×10^{-3}
1.00	1.497×10^{-2}	1.39×10^{-2}	1.418×10^{-2}
2.00	7.772×10^{-2}	5.56×10^{-2}	5.795×10^{-2}

[a] Abbreviations: PKS = exact diagonalization method; LRT = linear response theory; PER = perturbation method. In all cases $|\epsilon_0| = 6.00$.

and $E_-^{(1)}(\mu)$, respectively. From (25) we can obtain the transition energy

$$w_{\mathrm{IT}}/w_0 = E_+^{(2)}(\mu) - E_-^{(2)}(\nu) = (\mu - \nu) - [1 + (-1)^{\nu-\mu}] \times (-1)^{\mu}|\epsilon_0| + \lambda_0{}^2|\epsilon_0|\{[(2\mu + 1)(-1)^{\mu} - (2\nu + 1)(-1)^{\nu}]/(1 - 4|\epsilon_0|^2)\} \quad (26)$$

Notice that when λ_0 is small, the transition matrix element given by (24) approaches unity. In addition, when T approaches 0 K, the transition from $\nu = 0$ to $\mu = 0$ predominates and $w_{\mathrm{IT}}/w_0 = 2|\epsilon_0|$. These facts have been used in section 2 to derive expressions for the transition energies and the intensity ratio R. At $T = 0$ K, (26) gives ($\nu = \mu = 0$)

$$w_{\mathrm{IT}}/w_0 = 2|\epsilon_0| + 2\lambda_0{}^2|\epsilon_0|/(4|\epsilon_0|^2 - 1) \approx 2|\epsilon_0| + \lambda_0{}^2/2|\epsilon_0| \quad (27)$$

This gives the transition energy of the intervalence absorption at 0 K. For the IR charge-transfer-induced transition, its energy is also obtained from (26):

$$E_-^{(2)}(1) - E_+^{(2)}(0) = 1 - 2|\epsilon_0|\lambda_0{}^2/(4|\epsilon_0|^2 - 1) \quad (28)$$

The intensity ratio R discussed in section 2 can be obtained as follows. From (24), the intervalence transition intensity is

$$I_{\mathrm{IT}} = |\langle 0_-^{(1)}|\delta n|0_+^{(1)}\rangle|^2 = \left\{1 - \frac{\frac{1}{2}\lambda_0{}^2}{4|\epsilon_0|^2 - 1}\right\}^2 \quad (29)$$

To obtain the charge-transfer-induced IR transition intensities, we have to use the wave functions in (23) and obtain

$$\langle \mu_+^{(1)}|\delta n|(\mu + 1)_-^{(1)}\rangle = -1/2^{1/2}\lambda_0(-1)^{\mu}4|\epsilon_0|(\mu + 1)^{1/2}/(4|\epsilon_0|^2 - 1) \quad (30)$$

from which we obtain

$$\begin{aligned} I_{\mathrm{IR}} &= |\langle 0_+^{(1)}|\delta n|1_-^{(1)}\rangle|^2 \\ &= \{8\lambda_0{}^2|\epsilon_0|^2/(4|\epsilon_0|^2 - 1)^2\} \end{aligned} \quad (31)$$

$$R = 8\lambda_0{}^2|\epsilon_0|^2/[4|\epsilon_0|^2 - 1 - \tfrac{1}{2}\lambda_0{}^2]^2 \quad (32)$$

Note that (32) can be simplified to ${}^1/{}_2\lambda_0{}^2/|\epsilon_0|^2$, and this is identical with the result obtained earlier in (17).

The temperature dependence of the near-IR charge-transfer-induced transition can be readily calculated from (25) and (30). It can be shown that its intensities decrease as the temperature increases.

4. Comparison of Results in the Nearly Delocalized System

In Table I, a comparison of w_{IR} calculated with use of analytical expressions derived by using linear response theory and the perturbation method with that of the PKS exact diagonalization is presented. Here $w_0 = 500$ cm^{-1}. It is seen that for small electron-vibrational coupling, both analytical results ($w_{\mathrm{IR}}{}^{\mathrm{LRT}}$ and $w_{\mathrm{IR}}{}^{\mathrm{PER}}$) agree very well with the exact diagonalization results. However, when λ is large, the disagreement becomes large. For the case $|\epsilon_0[= 6.0$ and $\lambda_0 = 2.0$ the deviation is still less than 10%. Thus either eq 28 or 14 can be used as a good approximation to calculate the frequency of the charge-transfer-induced IR absorption.

The intervalence transition energies can also be obtained by the Laplace transform method first developed by Kubo and Toyozawa[12] and later applied by Hush[9] to treat a mixed-valence system. The result is[9,25]

$$w_{\mathrm{IT}}(T \rightarrow 0\ \mathrm{K}) \approx 2\epsilon_0 w_0 + \tfrac{1}{2}w_0(\lambda_0{}^2/\epsilon_0)(1 - \lambda_0{}^2/\epsilon_0)^{-1/2} \quad (33)$$

Equation 33 has also been obtained by Buhks[8] more recently. However, its lack of validity in describing the actual temperature dependence of the absorption band of a delocalized mixed-valence system has been discussed by Wong and Schatz elsewhere.[13]

Table II presents a comparison of w_{IT} calculated by the PKS exact diagonalization and various analytical methods. It is seen that the perturbation method gives the best approximation compared with other analytical methods. Linear response theory, however, fares poorly when compared with the exact diagonalization.

It should be stressed here that the Kubo-Toyozawa-Hush (KTH) treatment and the treatment by Buhks[8] using the Fourier transform method, though they give fairly accurate results for w_{IT}, all fail to predict the existence of the near-IR transition so important in understanding this system.

Table III presents a comparison of the relative intensity predicted by the analytical methods with the exact diagonalization. It is seen that the perturbation method consistently

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(25) The mean transition energy of a vibronic transition from a ground potential surface with the force constant Ω' to an excited potential surface with the force constant Ω'' is given by the Kubo and Toyozawa Laplace transform method as[12]

$$E = E_0 + \tfrac{1}{2}\Delta\Omega''^2\Delta + \hbar/4\ \mathrm{trace}[1/\Omega' \coth(\hbar\Omega'/2kT)\ \Gamma] \quad \text{(i)}$$

where E_0 is the separation between the two potential surfaces at their potential minima, Δ is the displacement of the minimum of the excited potential surface from that of the ground potential surface, and $\Gamma = (\Omega''^2 - \Omega'^2)$ is the difference in the force constants. For a delocalized mixed-valence system, $\Delta = 0$, $E_0 = 2\epsilon_0\hbar w_0$, $\Omega'' = w_0(1 + \lambda_0{}^2/\epsilon_0)^{1/2}$, $\Omega' = w_0(1 - \lambda_0{}^2/\epsilon_0)^{1/2}$, and $\Gamma = w_0{}^2[2\lambda_0{}^2/\epsilon_0]$. Hence

$$\hbar w_{\mathrm{IT}} = 2\epsilon_0\hbar w_0 + \hbar/4[w_0{}^2(2\lambda_0{}^2/\epsilon_0)(1/w_0) \times (1 - \lambda_0{}^2/\epsilon_0)^{-1/2}] \coth[\hbar w_0(1 - \lambda_0{}^2/\epsilon_0)^{1/2}/2kT] \quad \text{(ii)}$$

from which eq 33 can be derived.

Table IV. Comparison of Analytical Methods

	LRT	PER	KTH
wave function	implicit	explicit (first-order)	explicit (classical)
prediction	two charge-transfer-related transitions	two charge-transfer-related transitions	one charge-transfer-related transition (IT band)
accuracy with respect to PKS for w_{IR}	good	good	not available
accuracy with respect to PKS for w_{IT}	poor	excellent	good
accuracy with respect to PKS for R	good	good	not available

gives better results than those by linear response theory. However, both become inaccurate when λ_0 is large.

Finally, an overall comparison of the analytical approaches with the exact diagonalization method is presented in Table IV. It is noted that the perturbative approach gives better agreement with the exact diagonalization method. Several points are to be noted below.

The inability of the KTH method to predict the charge-transfer-induced transition is due to its use of the Fermi golden rule for calculating the absorption profile. In this approach, explicit potential energy difference between the ground and excited potential surfaces has to be used and consequently any consideration of possible charge-induced transition is ruled out. On the other hand, linear response theory considers the linear response of the dimeric system to the external perturbation represented by δn and is thus able to predict the presence of two charge-transfer-related transitions.

The perturbative method employs explicit vibronic wave functions and uses them to calculate transition dipole moments and thus offers a better physical insight into the nature of the two charge-transfer-related transitions (see eq 24 and 30). In this regard, the perturbation method appears to be the best among the analytical methods; i.e., it is able to predict fairly accurately the transition energies of both the charge-transfer-induced IR transition and the intervalence transition.

We have demonstrated in this section that the analytical expressions agree closely with the numerical diagonalization results except for cases that have large vibronic coupling. In the following section, we apply them to discuss some mixed-valence systems.

The analytical methods are readily extendible to include more than one vibrational mode. The PKS exact diagonalization method, however, becomes intractable as the number of vibrational modes increases beyond 1. This is because the vibronic basis set and hence the size of the vibronic matrix to be employed become too large for most computers to handle. For a two-mode system, the size of the matrix is $n(n + 1)$, where n is the number of phonons for each mode.[7] It is seen that the size could easily exceed several hundred with small number of phonons. It is thus unrealistic to employ the exact diagonalization to cases of several vibrational modes.

5. Application to the Creutz-Taube Ruthenium Complex

The Creutz-Taube ruthenium complex has been a subject of much discussion and controversy.[1,4,5] Its intense intervalence band at ~6000 cm^{-1} has a high-energy shoulder whose origin remains unresolved.

By fitting the band contour with their PKS model, Piepho et al.[2] concluded that the complex is a delocalized system with $|\epsilon_0| = 6.0$ ($w_0 = 500$ cm^{-1}) and the high-energy shoulder is caused by a large vibronic coupling with $\lambda_0 = 2.7$. Later, they predicted that there should be strong near-IR transitions at 131, 362, and 613 cm^{-1}, with a combined dipole strength of 0.3 D^2 at 300 K.[1]

Employing expression 17, we obtain $2.7^2/2 \times 6^2 \approx 0.10$; i.e., the IR transitions should be at least $^1/_{10}$ of the intervalence absorption. This value is consistent with the PKS model, which gives $R = 0.2$.[1] Since the intervalence band is intense, the IR transitions should be measurable according to the prediction. However, Krausz et al.[6] have conducted a search for these predicted IR absorptions and failed to observe them. They concluded that if the IR transitions were to exist, they must be about 100 times less intense than the predicted intensity ratio, i.e., R should be about 10^{-3}.

In a recent review, Wong and Schatz[4] suggested that, by reducing λ_0 to 1.1 and increasing $|\epsilon_0|$ to 6.35, the PKS model would fit the intervalence band position while keeping the IR transition intensities to a level consistent with Krausz et al.'s result. Again employing (17), we see that $R = 1.1^2/2 \times 6.35^2 = 1.5 \times 10^{-2}$, which is about 1 order of magnitude smaller than that in the previous case. Unfortunately such a reduced λ_0 value would give a much narrower intervalence absorption contour and hence fail to account for the high-energy shoulder.[4]

Another attempt to explain the high-energy shoulder is to include solvent effects into the PKS model.[7] By introduction of an effective solvent vibronic coupling parameter λ_s and assumption of an effective solvent vibrational frequency w_s of about 200 cm^{-1}, the observed intervalence absorption band contour can be satisfactorily accounted for. However, we shall show below that, even with such a modified PKS model, the predicted IR transition intensities are still to large to be unobservable.

Since we have two vibrational frequencies w_0 and w_s, eq 16 should be used for R. With the parameters $|\epsilon_0| = 6.0$, $\lambda_0 = 1.1$, $w_0 = 500$ cm^{-1}, $\lambda_s = 3.9$, and $w_s = 200$ cm^{-1}, which give a good fit to the observed intervalence absorption band,[7] we obtain $R \approx 0.05$. This is considered too large compared with $R \lesssim 0.001$ required by the experimental work by Krausz et al.[6]

We conclude that the shoulder of the intervalence absorption band of the Ru complex is not entirely caused by vibronic couplings. Perhaps an explanation in terms of the presence of other electronic transitions should be seriously considered. It is of interest to note that the splitting of the energy levels for Os(III) by spin-orbit coupling gives rise to absorption in the region of 2000 nm. That for Ru(III) complexes is expected to be about one-third as large and might be a factor in determining the shape of the intervalence band of the Creutz-Taube complex. Furthermore, the effect of low-symmetry crystal fields at the Ru sites might not be negligible.

6. Conclusion

We have solved the PKS vibronic Hamiltonian using linear response theory and the perturbative method in the nearly delocalized limit. Both methods predict the existence of charge-transfer-induced IR transitions. They also give results for the transition energies and relative intensity ratio, and these are in good agreement with that by the exact diagonalization. We wish to emphasize that the IR transitions are not *artifacts* of the numerical calculation or of the PKS model, as stated recently without proof in the literature.[11] These expressions have been employed for some mixed-valence systems to shed light on their properties.

The physical requirements for which the predicted charge-transfer-induced IR absorptions could be observed are briefly summarized below. The system should be nearly delocalized (i.e., borderline of class II and class III according to the Robin and Day classification[26]) with substantial electron-vibrational coupling λ_0 and sufficiently low electronic coupling strength ϵ_0. The latter condition implies that the charge-transfer band at $\sim 2\epsilon_0$ should be located close to the energy range of the predicted charge-transfer-induced IR absorptions. This proximity would increase the intensity of the induced IR absorption, as indicated in (17) or (32). A system with symmetrical vibrations of high frequencies (w_α) would have large vibronic coupling (see (9) and note that $g_\alpha = \lambda_\alpha \hbar w_\alpha$) and hence would be expected to give stronger induced IR absorptions. It is of interest to note that the organic semiconductor MEM(TCNQ)$_2$, in which strong charge-transfer-induced IR absorptions are observed, possesses a charge transfer or intervalence band at ~ 3500 cm^{-1}, which is indeed very close to the induced IR absorptions (~ 2200–100 cm^{-1}).[7]

We wish to point out that the PKS model is in fact a vibronic model for a two-site, single-electron system. A similar model has recently been proposed by Rice et al.[17] to describe some dimeric organic semiconductors in which *both* the IR enhanced absorptions related to a_{1g} vibrations as well as the charge-transfer absorption have been observed. It is of great interest to be able to observe the charge-transfer-induced IR transitions in mixed-valence compounds. In this regard, Fourier transform IR spectroscopic technique should prove particularly valuable, as demonstrated by Clark and Swanson recently.[27]

Acknowledgment. It is a pleasure to thank Professor P. N. Schatz, of the Chemistry Department at the University of Virginia, for support, discussion, and useful comments on the manuscript. Special thanks go to Dr. M. J. Rice, of Webster Research Center, Xerox Corp., for sending reprints of his works and giving comments. Comments and suggestions by the reviewers are gratefully acknowledged. This work is in part supported by the National Science Foundation under Grant CHE8025608.

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Rh–Rh Bond Protonation in [$Rh_2Cl_2(\mu\text{-}CO)(Ph_2PCH_2PPh_2)_2$] and the Structure of an Unusual Oxidative-Addition Product, [$Rh_2Cl_3(\mu\text{-}H)(\mu\text{-}CO)(Ph_2PCH_2PPh_2)_2$]·$H_2O$

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Received December 21, 1982

The reaction of [$Rh_2Cl_2(\mu\text{-}CO)(DPM)_2$] (DPM = $Ph_2PCH_2PPh_2$) with protonating acids, HA (A = Cl, $SO_3C_6H_4CH_3$, BF_4), yields [$Rh_2Cl_2(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2(A)$], in which protonation of the Rh–Rh bond and coordination of the A^- anion to one of the Rh centers have occurred. The products are either nonelectrolytes or weak electrolytes in CH_2Cl_2 solution. $^{31}P\{^1H\}$ and ^1H NMR spectra of these products indicate that they are symmetrical on the NMR time scale owing to fluxional processes that result either from anion dissociation and recoordination or from reversible loss of HA; in both processes the result is anion transfer from one rhodium center to the other. The BF_4^- anion in the HBF_4 adduct can be displaced by THF to yield [$Rh_2Cl_2(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2(THF)$][$BF_4$], which it seems has a structure similar to that of the HBF_4 adduct but with THF instead of BF_4^- coordinated to one metal. An X-ray structure determination of the HCl adduct, [$Rh_2Cl_3(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2$], confirms that the chloride ion is coordinated to one rhodium atom and that Rh–Rh bond protonation has occurred. This product has bridging hydride and carbonyl groups, two terminal chloro ligands on one metal and one on the other, and two mutually trans, bridging DPM groups. [$Rh_2Cl_3(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2$] crystallizes with one hydrogen-bound H_2O of crystallization per complex molecule in the space group $I2/a$ with $a = 25.021$ (3) Å, $b = 14.697$ (2) Å, $c = 27.486$ (3) Å, $\beta = 107.57$ (1)°, and $Z = 8$. Refinement has converged to $R = 0.052$ and $R_w = 0.058$ for 227 parameters varied and 5535 unique observed reflections.

Introduction

We have undertaken an investigation into the Rh–Rh bond protonation in [$Rh_2Cl_2(\mu\text{-}CO)(DPM)_2$] (**1**) because of the implications regarding carbonyl activation and ligand coupling reactions. Insertion of acetylenes into the Rh–Rh bond of **1** has previously been observed to result in Rh–Rh bond cleavage and concomitant rehybridization of the carbonyl group toward sp^2 with lowering of the CO bond order.[1] This rehybridization and the movement of the metals apart also bring the carbonyl group into closer contact with the inserting group, a transformation that may lead to ligand coupling reactions. Protonation of the Rh–Rh bond in **1**, it was felt, might lead to partial rehybridization of the carbonyl group owing to lengthening of the Rh–Rh bond to a distance intermediate between those in **1** and in the acetylene-inserted product. We were interested in the possibility of stabilizing a bridging-carbonyl geometry that was intermediate between those observed at the limits of a "normal" metal–metal bond[2] and the nonbonded extreme.[1,3,4]

A comparison of the chemistry of **1** with acids having coordinating and noncoordinating anions was also of interest owing to the potential of the former to undergo oxidative-addition reactions, at either or both metal centers. In particular, the addition of HX across the Rh–Rh bond yielding a Rh(II)–Rh(II) species (viewing the CO group as a neutral one-electron donor to each metal) having a bridging CO and

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