

# A Model for the Optical Absorption Spectrum of ( $\mu$ -Pyrazine)decaamminediruthenium(5+): What Hath Creutz and Taube Wrought?

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**Abstract:** Application of a three-site vibronic coupling model is made to the Creutz-Taube ion, a pyrazine-bridged mixed-valence compound of ruthenium. We argue that one totally symmetric metal-ligand stretch mode and one totally symmetric pyrazine ring mode dominate the line shape of the intervalence transfer band. By using only one adjustable Hamiltonian parameter, we account for the observed absorption band profile. We report our predicted profile for the z-polarized part of the metal-to- $\pi^*$  charge-transfer band and argue that this (previously neglected) band also contains information about the metal-metal coupling. A new five-mode model is also presented, in which the Ru-NH<sub>3</sub> and Ru-N<sub>pyz</sub> vibrations are treated separately. We then show that for the Creutz-Taube ion, the Ru-N vibrations may be treated to good approximation as a single mode on each metal site. The nature of the groundstate of the Creutz-Taube ion is discussed in light of our results. On the basis of evidence in the literature to date, we conclude that the complex is delocalized, with strong metal-bridge coupling.

## I. Introduction

We report here the first treatment of the line shape of the near IR absorption band of the Creutz-Taube ion<sup>1-3</sup> which explicitly includes important features of the bridging ligand. We show that it is possible to account for the shape of the near IR band by using a delocalized model for the ground state. Our model correctly predicts the solvent independence of the line shape and the absence of tunnelling transitions in the far IR. We also comment on the shape of the higher frequency metal-to- $\pi^*$  charge-transfer band, which has been largely ignored in the literature but which, we argue, also contains important information on the metal-metal interaction.

The Creutz-Taube ion, a pyrazine-bridged mixed-valence dimer of ruthenium [(NH<sub>3</sub>)<sub>5</sub>Ru]<sub>2</sub>(pyz)<sup>5+</sup>, has been the center of intense attention and controversy since it was reported in 1969<sup>1</sup> and up to the present.<sup>2,3</sup> The most striking feature of its optical absorption spectrum is a broad, strong transition in the near IR ( $\bar{\nu}_{\max} = 6400$  cm<sup>-1</sup>;  $\Delta\bar{\nu}_{1/2} = 1200$  cm<sup>-1</sup>;  $\epsilon = 5500$  m<sup>-1</sup> cm<sup>-1</sup>) which is not present in the corresponding +4 and +6 ions.<sup>1</sup> The controversies surrounding this transition have centered on the following: (1) How to account for both the width of the near IR absorption band<sup>4</sup> and the absence of tunnelling transitions in the far IR;<sup>5</sup> (2) Whether or not totally symmetric vibrational modes of motion contribute to the absorption band profile;<sup>6</sup> (3) The role of the nuclear motion of the medium in the transition,<sup>6a,7</sup> in light of the observed solvent independence of the absorption band line shape;<sup>1</sup> and (4) Whether the near IR band corresponds to a net metal-to-metal transfer of charge density, characteristic of a localized (valence-trapped) ground state, or to a transition from a symmetric to an antisymmetric combination of electronic basis orbitals on the two metal ions, characteristic of a delocalized (valence-averaged) ground state.<sup>2a</sup>

We have addressed these questions in recent papers,<sup>8-11</sup> in which we have developed a three-site model with explicit inclusion of the bridging ligand. These papers all have dealt with a general bridged dimer with an arbitrary bridging ligand. The present paper represents the first application of our model to a specific mixed-valence system. Application of this model to complexes of interest is somewhat more difficult than that of the earlier two-site models<sup>4</sup> containing two adjustable Hamiltonian parameters. In the model of Piepho, Krausz, and Schatz (PKS), the two parameters  $\epsilon$  (an electron exchange coupling) and  $\lambda$  (a vibronic coupling constant) were found by an iterative fit of the predicted

absorption band profile to the observed profile.<sup>4</sup> Since our three-site model contains at least four Hamiltonian parameters, most (or preferably all) of them must be calculated in advance from available experimental data and from an electronic structure computation. We are now able to calculate all but one of the Hamiltonian parameters for our model and for the moment leave the remaining one as an adjustable parameter. The near IR band line shape of the Creutz-Taube ion is analyzed by using only one fit Hamiltonian parameter.

## II. The Three-Mode Model

We utilize a three-site, three-mode model Hamiltonian given by<sup>10,11</sup>

$$\hat{H} = \hat{H}_e + \hat{H}_v + \hat{H}_{e-v} \quad (1)$$

$$\hat{H}_e = J(a_1^+ a_2 + a_2^+ a_3 + a_2^+ a_1 + a_3^+ a_2) + \alpha a_2^+ a_2 \quad (2)$$

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

$$\hat{H}_{e-v} = \sum_{i=1}^3 A_i q_i a_i^+ a_i \quad (4)$$

where  $a_i^+$  and  $a_i$  are the creation and annihilation operators for

- (1) (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988-3989. (b) Creutz, C.; Taube, H. *Ibid.* **1973**, *95*, 1086.
- (2) (a) Fürholz, U.; Bürgi, H.-B.; Wagner, F. E.; Stebler, A.; Ammeter, J. H.; Krausz, E.; Clark, R. J. H.; Stead, M. J.; Ludi, A. *J. Am. Chem. Soc.* **1984**, *106*, 121-123. (b) Krausz, E.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 939-943. (c) Fürholz, U.; Joss, S.; Bürgi, H.-B.; Ludi, A. *Ibid.* **1985**, *24*, 943-948. (d) Joss, S.; Bürgi, H.-B.; Ludi, A. *Ibid.* **1985**, *24*, 949-954.
- (3) Dubicki, L.; Ferguson, J.; Krausz, E. R. *J. Am. Chem. Soc.* **1985**, *107*, 179-182.
- (4) Peipho, S. B.; Krausz, E. R.; Schatz, P. N. *J. Am. Chem. Soc.* **1978**, *100*, 2296-3005.
- (5) Krausz, E.; Burton, C.; Broomhead, J. *Inorg. Chem.* **1982**, *20*, 434-435.
- (6) (a) Wong, K. Y.; Schatz, P. N. *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; American Chemical Society: Washington, DC, 1982; pp 281-296. (b) Hush, N. S. *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; American Chemical Society: Washington, DC, 1982; pp 301-331.
- (7) Buhks, E. Ph.D. Thesis, Tel-Aviv University, Tel-Aviv, Israel, 1980.
- (8) Root, L. J.; Ondrechen, M. J. *Chem. Phys. Lett.* **1982**, *93*, 421-424.
- (9) Ondrechen, M. J.; Ko, J.; Root, L. J. *J. Phys. Chem.* **1984**, *88*, 5919-5923.
- (10) Ko, J.; Ondrechen, M. J. *Chem. Phys. Lett.* **1984**, *112*, 507-512.
- (11) (a) Ondrechen, M. J.; Ko, J.; Zhang, L.-T. *Int. J. Quantum Chem.: Quantum Chem. Symp.* **1986**, 393-401. (b) Ko, J.; Ondrechen, M. J. *J. Am. Chem. Soc.* **1985**, *107*, 6161-6167. (c) Ko, J. Ph.D. Dissertation, Northeastern University, 1986.

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Table I.

parameter	ref	method
$A = -1.52 \text{ eV}/\text{\AA}^a$	17	X-ray crystallography
$K = 15.6 \text{ eV}/\text{\AA}^2$	15	Raman <sup>d</sup>
$m = 1.76 \cdot 10^{-27} \text{ eV s}^2/\text{\AA}^2$ (= 17 amu)		
$A_2 = -2.4 \text{ eV}/\text{\AA} (?)$	this work	(fit parameter)
$K_2 = 7.0 \text{ eV}/\text{\AA}^2$	14, 16	force field <sup>b</sup>
$m_2 = 5.27 \cdot 10^{-28} \text{ eV s}^2/\text{\AA}^2$ (= 5.08 amu)	14, 16	force field <sup>b</sup>
spin down $\downarrow$ (B $\rightarrow$ N) <sup>c</sup>		
$J = -0.85 \text{ eV}$	13	HFS-DVM
$\alpha = 0.93 \text{ eV}$	13	HFS-DVM
spin up $\uparrow$ (N $\rightarrow$ A) <sup>c</sup>		
$J = -0.86 \text{ eV}$	13	HFS-DVM
$\alpha = 1.73 \text{ eV}$	13	HFS-DVM

<sup>a</sup>Using  $A = \sqrt{6K\Delta r}$ , where  $\Delta r$  is the difference in bond distances between Ru(II) and Ru(III) hexammines; equal to 0.04 Å. <sup>b</sup> $\nu_2 = 609 \text{ cm}^{-1}$ . <sup>c</sup>The HFS-DVM calculation is spin unrestricted. Therefore, the values for  $\alpha$  differ for the two spin states due to exchange splitting. <sup>d</sup>Using  $\nu = 500 \text{ cm}^{-1}$ .

the  $i$ th electronic state and where  $p_i$  and  $q_i$  are the momentum and coordinate for the  $i$ th nuclear degree of freedom, assumed to be a harmonic oscillator with reduced mass  $m_i$  and frequency  $\omega_i$ . Sites 1 and 3 are the parent metal states, assumed to be degenerate, and site 2 is the parent bridge state, whose energy is different by  $\alpha$  from that of the metal basis states.  $J$  is the electronic exchange coupling between the bridge and each metal state. Since the present compound is homonuclear, we take  $m \equiv m_1 = m_3$ ;  $\omega \equiv \omega_1 = \omega_3$  and  $A \equiv A_1 = A_3$ . For 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  $\pi^*$  orbital on the pyrazine ring which has the right symmetry for backbonding with the metal  $4d_{xz}$  orbitals. We assume that only one vibration on each site is important, and the vibronic coupling is assumed to be linear in the vibrational displacement  $q_i$  with vibronic coupling constant  $A_i$ . In section III, we relax the assumption that only one vibrational mode per site is important, and we use a new five-mode model to treat the Ru-N (pyz) stretch modes separately from the Ru-N(NH<sub>3</sub>) stretch modes.  $\hat{H}_e$  is taken to be of the one-electron type and spin-orbit coupling is neglected. It is assumed that only one electronic state on each site is important, consistent with our electronic structure results.<sup>13</sup>

The values for the parameters used here are given in Table I. Note that the unsubscripted parameters  $A$ ,  $K(=m\omega^2)$  and  $\nu(=\omega/2\pi)$  pertain to the vibrations on the metal sites. For now we approximate this motion about each metal ion in the Creutz-Taube complex by the symmetric stretch in the Ru hexammines Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+/3+</sup>. In section III we show that when this approximation is eliminated, the predicted absorption band profile is not changed significantly. The terms in the purely electronic Hamiltonian  $J$  and  $\alpha$  were obtained from a Hartree-Fock-Slater discrete variational method (HFS-DVM)<sup>12</sup> calculation. Details of the calculation of the parameters  $\alpha$  and  $J$  are given in the preceding paper.<sup>13</sup>

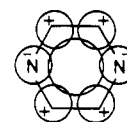
In our three-site scheme, the approximate criterion for localization (valence-trapping) was reported to be<sup>9</sup>

$$\frac{A^2}{2^{3/2}K|J|} > 1 \quad (5)$$

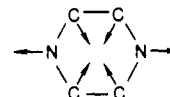
Utilizing the values for  $A$ ,  $K$ , and  $J$  given in Table I, the lhs of 5 equals 0.06, which corresponds to a delocalized ground state.

Note that our model builds in features of the bridge state which were hidden in or absent from the previous two-site models. The information about the bridge is contained in the parameters  $\alpha$ ,  $J$ ,  $A_2$ ,  $K_2$ , and  $\nu_2$ . State 2, the pyrazine  $\pi^*$  orbital responsible for

the metal-metal coupling in the Creutz-Taube ion, may be represented by a view from above as

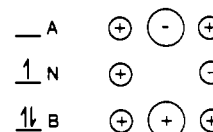


One would expect that if an electron is added to this  $\pi^*$  orbital, the C-C bond distances would shorten and the C-N bond distances would lengthen. Indeed, the vibrational mode which undergoes the largest frequency shift on going from free pyrazine<sup>14</sup> to the Creutz-Taube ion<sup>2a,15</sup> is the 6a mode<sup>14</sup> represented by



which contains exactly the displacements expected from the changes in bond order resulting from occupation of the above  $\pi^*$  orbital. This mode of motion is the one most likely to be strongly coupled to the intervalence transfer (near IR) transition.  $K_2$  (obtained from ref 46) and  $m_2$  given in Table I are for the 6a mode of pyrazine.  $m_2$  was calculated by using the frequency  $\nu_2 = 609 \text{ cm}^{-1}$ , given in ref 14.

The electronic structure calculations have shown that three of the molecular orbitals of the Creutz-Taube ion are bonding, nonbonding, and antibonding combinations of Ru(1) ( $4d_{xz}$ ),  $\pi^*$  and Ru(2) ( $4d_{xz}$ ).<sup>13</sup> These combinations may be depicted by



and in a qualitative way resemble the three Hückel MO's of the allyl radical. This is the only significant coupling between Ru(1) and Ru(2). The transition of the spin down  $\downarrow$  electron from the bonding orbital to the nonbonding orbital is the near IR transition. Note that it has a dual character: It contains both intervalence transfer character [in that the complex goes from a sum combination of Ru(1) ( $4d_{xz}$ ) and Ru(2) ( $4d_{xz}$ ) to a difference combination] and  $\pi^*$ -to-metal charge-transfer character.

With the exception of  $A_2$ , all of the Hamiltonian parameters have been obtained either from literature data or from the HFS-DVM calculation.  $A_2$  is the vibronic coupling parameter for the coupled vibrational mode on the pyrazine ring. The corresponding parameter  $A$  for the metal sites may be estimated easily, since the changes in bond distance on going from Ru<sup>3+</sup> to Ru<sup>2+</sup> are known. However, neither X-ray diffraction data nor vibrational spectra (from which one might infer changes in the geometry from frequency shifts) have been reported for the pyrazine radical anion pyz<sup>-</sup>, to our knowledge. Thus  $A_2$  for now remains the only adjustable parameter in our model; its value in Table I was obtained by a fit of our predicted near IR absorption band profile to the observed profile.

The predicted spectrum is calculated by using a method similar to that detailed in ref 11b. Since the ratio on the lhs of eq 5 is smaller than unity, the delocalized limit applies. The gap between the ground and first-excited potential surfaces is large relative to the vibrational spacings for the parameters given in Table I, so the adiabatic approximation is valid. The exact adiabatic potentials are three-dimensional and depend on the three coordinates  $q_2$ ,  $q_+$ , and  $q_-$  with

$$q_{\pm} = 2^{-1/2}(q_1 \pm q_3) \quad (6)$$

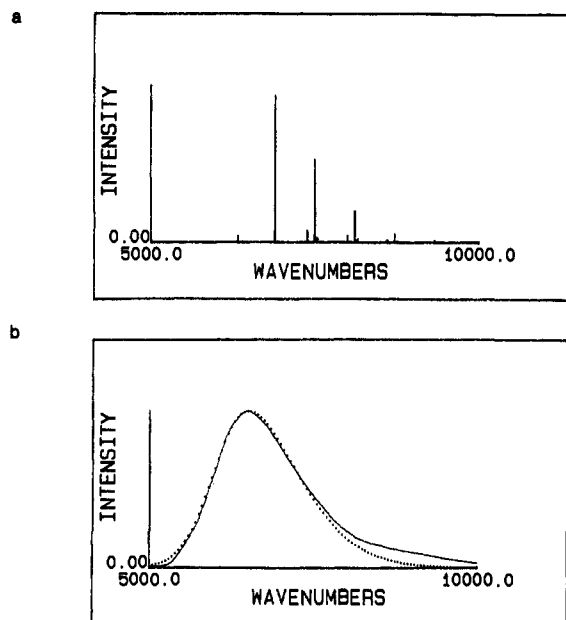
However, in the delocalized case, the  $q_-$  coordinate is not important,<sup>10,11</sup> and it may be frozen at its potential minimum value  $q_- = 0$ .<sup>11b</sup> The resulting potential surfaces depend upon the two

(12) Delley, B.; Ellis, D. E. *J. Chem. Phys.* 1972, 76, 1949.

(13) Zhang, L.-T.; Ko, J.; Ondrechen, M. J., the preceding paper in this issue.

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

(15) Strekas, T. C.; Spiro, T. G. *Inorg. Chem.* 1976, 15, 974-976.



**Figure 1.** (a) Predicted intensity as a function of frequency for the vibronic transitions for the B  $\rightarrow$  N (IT) band in the near IR region at 300 K. (b) Dotted curve: predicted IT band profile for the IT transition of the Creutz-Taube ion. (A smooth version of Figure 1a, with the horizontal axis shifted by 575  $\text{cm}^{-1}$ .) Solid curve: observed single-crystal polarized spectrum (ref 2a). Both spectra at 300 K.

totally symmetric displacements  $q_+$  and  $q_2$ , which may be treated as nearly independent oscillators.<sup>11b</sup> The nuclear eigenfunctions used in the present work are obtained from one-dimensional slices of the potential surfaces along each of the two totally symmetric coordinates with the other one held constant at its value at potential minimum. The one-dimensional nuclear wave functions  $\phi_n$  (where  $l = \text{B, N, or A}$  and  $n$  is the vibrational quantum number) are then calculated by a finite difference method. The Franck-Condon factors for the IT transition are given approximately by

$$S(\text{B}_{nl} \rightarrow \text{N}_{n'l'}) \approx \langle \phi_{\text{N}l'}(q_+) | \phi_{\text{B}n}(q_+) \rangle \langle \phi_{\text{N}l'}(q_2) | \phi_{\text{B}n}(q_2) \rangle \quad (7)$$

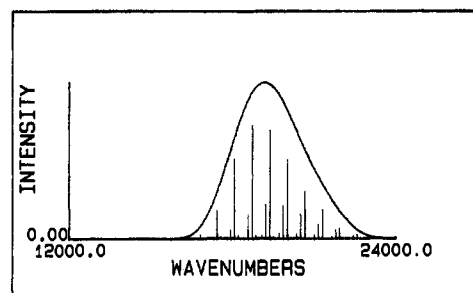
where the terms on the rhs of eq 7 are obtained by direct numerical integration. Intensities for the B  $\rightarrow$  N transition at temperature  $T$  are given by

$$I(\text{B}_{nl} \rightarrow \text{N}_{n'l'}) \propto \left( \sum_i \sum_j e^{-E_{ij}/kT} \right)^{-1} e^{-E_n/kT} |S(\text{B}_{nl} \rightarrow \text{N}_{n'l'})|^2 \quad (8)$$

where  $E_{ni}$  is the vibrational energy of the initial state.

Figure 1a shows the predicted intensities of the transitions from the vibronic levels of the B surface to those of the N surface at 300 K. The predicted frequency of the absorption maximum is governed primarily by the parameters  $a$  and  $J$  and deviates from the experimental maximum of about 6400  $\text{cm}^{-1}$  by 575  $\text{cm}^{-1}$  or 0.07 eV. This is about the limit of accuracy on the values for  $\alpha$  and  $J$ , which were obtained by the HFS-DVM method. One could adjust  $\alpha$  and  $J$  slightly to eliminate this small deviation, but we have chosen instead to leave  $\alpha$  and  $J$  at their calculated values and to move the scale of the predicted spectrum by 575  $\text{cm}^{-1}$  to compare with experiment. On each stick of Figure 1a, we place a Gaussian function<sup>4</sup> with width  $\sigma = 420 \text{ cm}^{-1}$  (the minimum width needed to eliminate structure in the band) in order to compare with the unresolved crystal spectrum.<sup>2a</sup> This Gaussian width represents a composite of several effects, including medium vibrational motion, counterion motion,  $\text{NH}_3$  internal rotation, and thermal population of any of the other 150 normal modes of the ion. Figure 1b shows the experimental spectrum<sup>2a</sup> (solid curve) and our prediction (dotted curve) for the near IR absorption band.

The observed band at 2.2 eV, assigned to metal-to- $\pi^*$  charge transfer,<sup>1</sup> contains components with different polarizations,<sup>13</sup> one of which is the  $z$ -polarized N  $\rightarrow$  A transition for the spin up  $\uparrow$  electron. Figure 2 shows our prediction for the  $z$ -polarized component of the band, arising from  $d_{xz}$ -to- $\pi^*$  charge transfer, by using our parameters from Table I. We hope that single-crystal po-



**Figure 2.** Predicted shape of the N  $\rightarrow$  A or  $z$ -polarized component of the metal-to- $\pi^*$  charge-transfer band at 300 K.

larization spectra will be performed on this band.

The three potential surfaces calculated from the present parameters all have single-minimum form. No tunnelling transitions<sup>5</sup> are predicted. The predicted line shapes are also independent of solvent.

### III. The Five-Mode Model

Thus far we have adopted an admittedly simplistic view of the coupled vibrations on the metal sites, in that we have treated the two metal ions as though they were octahedrally symmetric and with only one coupled vibrational mode per metal ion. In the X-ray crystallographic work of Gress, Creutz, and Quicksall on  $[\text{Ru}(\text{NH}_3)_5(\text{pyz})]^{2+/3+}$  it was shown that the change in electron occupation leads to nuclear displacements which are not octahedrally symmetric.<sup>18</sup> In particular, the Ru-to- $\text{N}_{\text{pyz}}$  bond length changes in a direction opposite to the usual and by a distance greater than that for Ru-to-*cis*- $\text{NH}_3$  ( $-0.07 \text{ \AA}$  vs.  $+0.04 \text{ \AA}$ ). This suggests that there are two coupled vibrational modes per Ru ion in the Creutz-Taube ion. To treat this, we propose the model below. We treat the Ru- $\text{NH}_3$  vibrations separately from the Ru-pyz vibrations and assume that the Ru-*trans*- $\text{NH}_3$  vibrations and the Ru-*cis*- $\text{NH}_3$  vibrations have about the same coupling strength. This latter assumption is consistent with the X-ray data of ref 18 and 2a. Equations 1 and 2 remain the same, but equations 3 and 4 are replaced by

$$\hat{H}_n = \sum_{i=1\text{C},1\text{B},2,3\text{C},3\text{B}} \left( \frac{P_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 q_i^2 \right) \quad (9)$$

$\hat{H}_{e-n} =$

$$A_C(q_{1\text{C}}a_1^\dagger a_1 + q_{3\text{C}}a_3^\dagger a_3) + A_B(q_{1\text{B}}a_1^\dagger a_1 + q_{3\text{B}}a_3^\dagger a_3) + A_2 q_2 a_2^\dagger a_2 \quad (10)$$

Now C labels the Ru- $\text{NH}_3$  vibrations and B labels the Ru-bridge vibrations. The new vibronic coupling constants are given by

$$A_C = \sqrt{5} m_C \omega_C^2 \Delta r_C \quad (11)$$

$$A_B = m_B \omega_B^2 \Delta r_B \quad (12)$$

We may then define new coordinates  $q_{+C}$ ,  $q_{-C}$ ,  $q_{+B}$ ; and  $q_{-B}$ . Since  $\omega_C \neq \omega_B$  and since  $m_C \neq m_B$ , this five-dimensional problem may be treated as a product of five one-dimensional problems. The two antisymmetric coordinates  $q_{-C}$  and  $q_{-B}$  may be dropped, in a manner analogous to the earlier case. Thus effectively we have a product of three one-dimensional problems.

The following values for the parameters were used:  $A_C = -1.40 \text{ eV/\AA}$ ,  $A_B = 1.24 \text{ eV/\AA}$ ,  $K_B = 17.7 \text{ eV/\AA}^2$ ,  $K_C = 15.6 \text{ eV/\AA}^2$ ,  $m_B = 4.64 \cdot 10^{-27} \text{ eV s}^2/\text{\AA}^2$ , and  $m_C = 1.76 \cdot 10^{-27} \text{ eV s}^2/\text{\AA}^2$ . Values for the parameters  $K_2$ ,  $m_2$ ,  $A_2$ ,  $J$ , and  $\alpha$  remain the same as before. The force constant and reduced mass  $K_B$  and  $m_B$  correspond to the literature value for the Ru-N(pyz) stretch mode of 328  $\text{cm}^{-1}$ .<sup>15</sup> Figure 3 shows the predicted intensities of the transitions from the vibronic levels of the B surface to the vibronic levels of the N surface at 300 K. Note that it is very similar to Figure 1a.

(16) Scully, D. B. *Spectrochim. Acta* **1961**, *17*, 233-237.

(17) Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304.

(18) Gress, M. E.; Creutz, C.; Quicksall, C. O. *Inorg. Chem.* **1981**, *20*, 1522-1528.

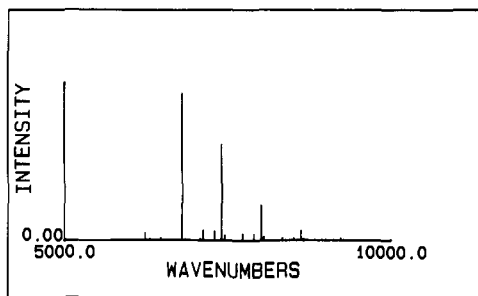


Figure 3. Intensity as a function of frequency of the vibronic transitions for the B  $\rightarrow$  N (IT) band in the near IR region at 300 K, calculated by using the five-mode model.

When Gaussian width is placed on each of the "sticks" in the spectrum of Figure 3, the line shape is identical with the predicted line shape curve of Figure 1b. Thus the original single-mode-per-site approximation of eq 3 and 4 is quite good. The net effect of this more refined model is to shift some of the vibronic intensity by a small amount. That  $A_C$  and  $A_B$  have opposite signs does not matter. The magnitude of the displacement along  $q_+$  is governed primarily by the magnitude of the coupling  $A$  and not by its sign.<sup>9</sup> It is the magnitude and not the sign of this displacement which determines the absorption band profile.

#### IV. Discussion

The spectral line shapes predicted herein are the first for the Creutz-Taube ion to be based on the totally symmetric vibrational modes ( $q_+$  and  $q_2$ ), rather than on one antisymmetric mode ( $q_-$ ). In a delocalized bridged dimer, it is the totally symmetric modes which can couple to the IT band and dominate the IT band line shape.

We have shown that approximating the vibrational modes at each metal site as one single mode is quite reasonable; we have also shown how to go beyond this approximation.

Tunnelling transitions in the far IR are not predicted by the present model. The ground-state surface has single-minimum form along  $q_-$  and  $q_+$  is uncoupled to the IT transition. By using the present model Hamiltonian we performed non-Born-Oppenheimer calculations<sup>19</sup> which show transitions with about 1% of the intensity of the IT at about 500  $\text{cm}^{-1}$ . However, our model predicts no transitions in the frequency range studied in ref 5.

We have assumed the coupling of the intervalence transfer transition to bridge ring modes is dominated by coupling to the  $6a$  mode of pyrazine, based on simple, intuitive bond order-bond length and  $\pi$ -MO arguments. In the absence of polarized resonance Raman data, these intuitive arguments are our best guide at the present time. Earlier Raman results showing resonance enhancement<sup>15</sup> were later shown to be caused by photodecomposition products.<sup>2a</sup> Three Raman active modes were shown to be resonance enhanced by the *visible* electronic transition. However, as we have shown previously<sup>13,20</sup> this transition contains multiple components, and only one of these components involves the (through-bridge) metal-metal coupling. Thus there are no experimental data to date which indicate which pyrazine ring mode(s) is/are coupled to the near IR band, so we have fallen back on our (reasonable) bond order-bond length arguments.

While we cannot calculate  $A_2$  (the ring mode vibronic coupling constant) from experimental data available at this time, we have some indications that the fit value of  $A_2$  is about the right size. First of all, the fit value of  $A_2$  corresponds to a bond angle change of a few degrees upon reduction of  $\text{pyz}$  to  $\text{pyz}^{\cdot-}$ , which is reasonable. Also, vibrational studies on the benzene radical anion<sup>24</sup> yielded displacements of roughly 1–2  $\text{eV}/\text{\AA}$  (vs. our value of 2.4  $\text{eV}/\text{\AA}$  for pyrazine).

In a delocalized system, there is very little displacement of charge density through space, and solvent effects can be neglected. As shown by Buhks,<sup>7</sup> in a delocalized complex the only effect of

the polar medium is to place width on each of the vibronic "sticks" which arise from coupling to high-frequency intramolecular vibrational modes. In the present case, solvent motion, counterion motion,  $\text{NH}_3$  internal rotation, etc., all serve to eliminate vibrational structure in the absorption spectrum but otherwise do not affect the line shape. Therefore, we prefer not to include these effects in the Hamiltonian and simply eliminate vibrational structure by placement of width on each vibronic transition, as in the PKS model.<sup>4</sup>

Application of our three-site model to the IT transition of the Creutz-Taube ion has been reported very recently by Wong.<sup>21</sup> However, Wong has assumed that (in the present notation)  $A = A_2$  and that  $\alpha = 0$ . Because of the assumption that  $\alpha = 0$ , the results of ref 21 and the present results are significantly different, although both lead to the same conclusion that the C-T ion is strongly delocalized. If  $\alpha$  is taken to be zero, then  $J$  must be adjusted (rather artificially) in order to place the IT transition maximum at the correct frequency. This has significant effect on the predicted line shape and also places the  $t_{2g}$ -to- $\pi^*$  transition at the wrong frequency.

Presently, most of the evidence points to a delocalized ground state for the Creutz-Taube ion. Our present and recent<sup>13,20</sup> work is able to account for the EPR data and almost all of the observed absorption and MCD features in terms of a delocalized structure. Averaging of infrared vibrational frequencies also suggests delocalization on the vibrational time scale.<sup>1b</sup> The equivalence of the two Ru ions, together with very well-refined Ru-N bond distances in the X-ray structures of halide salts of the C-T ion<sup>22,2</sup> likewise serve as evidence for valence averaging.

Studies by X-ray photoelectron spectroscopy and by Mössbauer spectroscopy we take to be inconclusive.

The one piece of evidence which suggests valence trapping and which we are unable to account for at the present time is the observed near coincidence of infrared bands at 700, 1230, and 1585  $\text{cm}^{-1}$  with Raman bands at 699, 1232, and 1594  $\text{cm}^{-1}$ .<sup>2a</sup> This has been interpreted as evidence that the ion is not centrosymmetric.<sup>2a</sup> These vibrations are probably ring modes of pyrazine.<sup>2a</sup> Because assignments and intensities for these modes have not been reported to date, we do not wish to advance an explanation for this observation but can offer some speculation. Even if the valence is averaged, the two Ru ions are not necessarily formally equivalent in all media. This was observed in X-ray diffraction studies of the C-T ion with a tosylate counterion.<sup>2</sup> One of the Ru ions in this crystal is lifted slightly out of plane and this breaks the center of symmetry. In addition, the appearance of totally symmetric monomer modes in the infrared absorption spectrum has been observed in some charge-transfer complexes, when these modes are coupled to the charge-transfer transition.<sup>23</sup> Careful assignments and intensity measurements on these modes might prove to be interesting in the Creutz-Taube ion.

In addition to the near coincidence of IR and Raman frequencies, the C-T ion has one additional mystery which our models cannot solve, and that is the MCD feature<sup>2b</sup> at 12 800  $\text{cm}^{-1}$  and the (possibly related) shoulder in the absorption spectrum<sup>1</sup> at about 12 000  $\text{cm}^{-1}$ . While these may be (a) doublet  $\rightarrow$  quartet transition(s), we are unable to speculate about the exact nature of transition(s) involved.

It is hoped that the present model will be subjected to further experimental tests, including: (1) vibrational spectra of the pyrazine radical anion, (2) polarization spectra on the metal-to- $\pi^*$  charge-transfer band, (3) polarized resonance Raman work, (4) careful single-crystal studies on bridged dimers which are less controversial than the Creutz-Taube ion.

(20) Ko, J.; Zhang, L.-T.; Ondrechen, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1712–1713.

(21) Wong, K. Y.; *Chem. Phys. Lett.* **1986**, *125*, 485–489.

(22) Beattie, J. K.; Hush, N. S.; Taylor, P. R.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1977**, 1121–1124.

(23) Girlando, A.; Marzola, F.; Pecile, C.; Torrance, J. B. *J. Chem. Phys.* **1983**, *79*, 1075–1085.

(24) Moore, J. C.; Thornton, C.; Collier, W. B.; Devlin, J. P. *J. Phys. Chem.* **1981**, *85*, 350–354.

(19) This calculation was done without the bridge motion, since the bridge motion does not couple to tunnelling transitions in the present model.

We conclude that the Creutz-Taube ion is electronically sort of a fancy version of the allyl radical, with the two termini coupled strongly via the bridge and with two allowed transitions ( $B \rightarrow N$  and  $N \rightarrow A$ ) arising from this coupling. The strong degree of delocalization might lead one to speculate about potentially exciting conductive properties of extended linear chains of this or related bridged species. However, more importantly, this piece of synthetic art of Creutz and Taube has in the last 17 years raised many important and fundamental questions about the way we interpret the results of a variety of common spectroscopic techniques and about the way we think of the very basic phenomena of spatial and temporal electron delocalization.

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## Rehybridization and $\pi$ -Orbital Overlap in Nonplanar Conjugated Organic Molecules: $\pi$ -Orbital Axis Vector (POAV) Analysis and Three-Dimensional Hückel Molecular Orbital (3D-HMO) Theory

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**Abstract:** Nonplanarity in conjugated organic molecules such as the bridged annulenes, strained cycloalkenes, cyclophanes,  $\pi$ -complexes of organometallic and surface-bound alkenes and aromatics, and the transition states of most chemical transformations (particularly substitutions, additions, eliminations, and pericyclic reactions) plays a fundamental role in determining their chemistry. The primary response of conjugated systems to nonplanarity is a change in the balance between the  $\sigma(\text{sp}^2)$  and  $\pi(\text{p})$  hybridization which is the rule in planar situations. In previous publications on this subject we have reported the development of the  $\pi$ -orbital axis vector (POAV) analysis which preserves  $\sigma$ - $\pi$  separability in nonplanar geometries by appeal to the orbital orthogonality relationships. It is the primary hypothesis of the POAV analysis that the  $\sigma$ -bonds lie along the internuclear axes of the molecule. Thus, after structural adjustment, the remaining dislocations are construed to occur among the  $\pi$ -electrons. In the present paper a detailed analysis of these questions is presented in terms of electronic structure calculations on torsionally ( $C_2$ ) twisted ethylene. The results are in excellent agreement with the assumptions and predictions of the POAV model and lend credence to the idea that torsionally twisted  $\pi$ -systems may be adequately mapped onto a minimal sp basis set (for analytical purposes) by the POAV theory. In the second part of the paper a number of nonplanar conjugated systems are analyzed with the three-dimensional (3D-) HMO theory. The 3D-HMO theory further quantifies the POAV analysis by utilizing the local POAV hybrids to calculate overlap integrals between pairs of conjugated atoms. Suitably scaled, the overlap integrals provide reduced resonance integrals which allow a unified treatment of conjugated systems-planar and nonplanar. A natural definition of homoconjugation emerges from the analysis: the homoconjugate bond is characterized by an overlap integral between a pair of conjugated atoms in which the  $p_\pi$ ,  $p_\pi$  contribution does not predominate.

Although planarity is considered to be the normal state of conjugated organic molecules containing formally  $\text{sp}^2$  hybridized carbon atoms, reference to the literature shows that (with some notable exceptions) nonplanarity is the norm.<sup>1</sup> In many cases, the absence of a molecular symmetry plane containing the conjugated fragment of a molecule is of little consequence. The chemical ramifications of nonplanarity in conjugated organic molecules such as bridged annulenes,<sup>2,3</sup> strained cycloalkenes,<sup>4-8</sup>

cyclophanes,<sup>5</sup>  $\pi$ -complexes<sup>6</sup> of organometallic<sup>7</sup> and surface-bound<sup>8</sup> alkenes and aromatics, and the transition states<sup>9</sup> of most chemical transformations (particularly substitutions, additions, eliminations and pericyclic reactions) are not so easily dismissed.

The primary response of conjugated systems to nonplanarity is a change in the balance between the  $\sigma(\text{sp}^2)$  and  $\pi(\text{p})$  hybridization which is the rule in planar situations. In previous publications on this subject we have reported the development of the

(1) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978.

(2) Boekelheide, V. In *Proceedings of the Robert A. Welch Foundation*; Milligan, W. O., Ed.; Robert A. Welch Foundation: USA, 1968; p 83.

(3) Vogel, E. In *Proceedings of the Robert A. Welch Foundation*; Milligan, W. O., Ed.; Robert A. Welch Foundation: USA, 1968; p 215.

(4) (a) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683. (b) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem.* **1981**, *103*, 1891. (c) *Stereochemistry and Reactivity of Systems Containing  $\pi$ -Electrons*; Watson, W. H., Ed.; Veerlag Chemie International: Florida, 1983. (d) Nakazaki, M.; Yamamoto, K.; Naemura, K. *Top. Curr. Chem.* **1984**, *125*, 1. (e) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312. (f) McEwen, A. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 3951.

(5) (a) *Cyclophanes*; Kelhn, P., Rosenfeld, S. M., Ed.; Academic: New York, 1983. (b) *Top. Curr. Chem.* **1983**, *113*, 115.

(6) Dewar, M. J. S. *Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969.

(7) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980.

(8) (a) Stuve, E. M.; Madix, R. J. *J. Phys. Chem.* **1985**, *89*, 3183. (b) Van Hove, M. A.; Lin, R. F.; Samorjai, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 2532. (c) Hills, M. M.; Parmeter, J. E.; Mullins, C. B.; Weinberg, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 3554.

(9) (a) March, J. *Advanced Organic Chemistry*; McGraw-Hill: New York, 1985. (b) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146. (c) Burgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153.