

# Theory of Electroabsorption Spectroscopy in Pyrazine-Bridged Ru Dimers

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**Abstract:** A theoretical study of near-IR–vis electroabsorption spectroscopy (Stark effect) for the Creutz–Taube ion, a pyrazine-bridged mixed-valence Ru dimer, and for its homovalent +4 analogue is presented. A vibronic model that takes into account correlation effects is considered for the calculation of absorption line shape profiles, also in the presence of an external static electric field. The model also incorporates the orientation of molecules with respect to the applied field and the polarization of the incident light and accounts for the essential features of the difference spectra that have been observed experimentally.

## Introduction

Mixed-valence compounds are of interest particularly for the study of intramolecular charge transfer. Many properties which originate from the mobility of their electrons make them also interesting for potential applications in molecular electronics and photonics. Depending on the time scale of such mobility one then has delocalized or localized compounds, which can be classified, according to the Robin and Day scheme,<sup>1</sup> respectively as class III and class II.

A valuable probe for electron delocalization is the Stark effect spectroscopy (electroabsorption) technique, in which the modifications of the absorption spectra induced by an applied static electric field allow one to distinguish between localized and delocalized systems.<sup>2–5</sup>

The effect of an electric field on the position and shape of optical spectral lines finds further application in the development of electrochromic materials and in the study of biological systems. It has been argued that local field effects represent one of the most convincing explanations for the occurrence of unidirectional electron transfer in the photosynthetic reaction center.<sup>6</sup>

In the present paper, we focus on perhaps the most extensively studied mixed valence compound, the Ru(II)/Ru(III) bridged dimer  $[(\text{NH}_3)_5\text{Ru-pyz-Ru}(\text{NH}_3)_5]^{5+}$  (pyz = pyrazine), first synthesized and studied by Creutz and Taube<sup>7</sup> and now known to be delocalized,<sup>8</sup> as well as on its homovalent companion  $[(\text{NH}_3)_5\text{Ru-pyz-Ru}(\text{NH}_3)_5]^{4+}$ . These compounds have been

widely studied and several theoretical models have been considered for the explanation of their near-IR–vis optical properties.<sup>9–17</sup> To date, it is known that the bridge (pyz)  $\pi^*$  and the Ru  $4d_{xz}$  orbitals (pyz in the yz plane) play a central role,<sup>12</sup> that correlation effects are needed in a model that correctly describes the whole series of  $[\text{Ru-pyz-Ru}]^{m+}$  ( $m = 4, 5, \text{ and } 6$ ) ions,<sup>14–16</sup> and finally, that vibronic coupling plays a secondary role although the inclusion of nuclear degrees of freedom is necessary for accurate line shape profiles.<sup>17</sup>

Electroabsorption spectra in the near-IR–vis for the Creutz–Taube (+5) ion, as well as for its homovalent (+4) analogue, have been measured.<sup>3</sup> Earlier work<sup>18,20</sup> has discussed electronic effects in Stark effect spectra, but did not take into account the vibronic effect, which is essential to describe the line shape of these systems with spatial or temporal electron delocalization. In a previous paper<sup>21</sup> we have shown that a vibronic model that does not include correlation and which invokes the adiabatic approximation is able to account for the observed behavior of the near-IR intervalence (IT) transition for the +5 species. The present work incorporates correlation effects into a vibronic coupling model,<sup>17</sup> so that we can now study the behavior of the system as a function of the total charge. In addition, we now employ an exact nonadiabatic method; a nonadiabatic model is essential in order to treat the full range of coupling strengths observed in mixed-valence systems. Furthermore, the

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present work examines the entire near-IR–vis electroabsorption spectrum.

### The Model

To predict the near-IR–vis optical properties, the pyz-bridged Ru(II)/Ru(III) and Ru(II)/Ru(II) dimers can be modeled by taking into account only the pyz  $\pi^*$  and the Ru  $d_{xz}$  orbitals (with pyz in the plane  $yz$  and  $z$  being the Ru-pyz-Ru axis). Ru(II) and Ru(III) have respectively  $4d^6$  and  $4d^5$  configuration and the ligand field is nearly octahedral. The bridging ligand breaks the degeneracy of the  $t_{2g}$  orbitals, so that the  $d_{xz}$  is the highest in energy and is then occupied by two electrons for Ru(II) and one for Ru(III). The Ru-pyz back-bonding interaction, the source of the electron delocalization, must be taken into account, as well as the energy difference between pyz  $\pi^*$  and metal orbitals and the on-site Coulomb repulsion. We can therefore write a Hubbard Hamiltonian<sup>22</sup> for the electronic part:

$$H_{el} = \sum_{j,\sigma} \epsilon_j n_{j,\sigma} + t \sum_{j,\sigma} (a_{j,\sigma}^+ a_{j+1,\sigma} + h.c.) + U \sum_{j(M \text{ only})} n_{j,\uparrow} n_{j,\downarrow} \quad (1)$$

where the rightmost summation is over  $M$  atoms only and where  $a_{j,\sigma}^+$  ( $a_{j,\sigma}$ ) is the creation (annihilation) operator for one electron in the orbital of site  $j$  with spin  $\sigma$ ,  $n_{j,\sigma} = a_{j,\sigma}^+ a_{j,\sigma}$  is the number operator for the spin orbital  $j\sigma$ ,  $\epsilon_j = \epsilon_{pyz}$ ,  $\epsilon_{Ru}$  ( $\Delta = \epsilon_{pyz} - \epsilon_{Ru}$ ) is the site energy ( $N_{site} = N_{Ru} + N_{pyz}$  is the total number of sites and also the number of orbitals),  $U$  is the on-site repulsion term, and  $t$  is the  $d_{xz}$ – $\pi^*$  resonance integral.

Nuclear degrees of freedom are then taken into account, as in ref 17, considering only one significant vibration for each site, e.g. the symmetric 6a stretch for pyz and the Ru–NH<sub>3</sub> symmetric stretch of the octahedral coordination shell for each Ru site. These are modeled by harmonic oscillators, and vibronic coupling is considered in its simplest form, linear in the vibrational coordinate. Then the following vibronic molecular Hamiltonian may be written as:

$$\begin{aligned} H_{mol} &= H_{el} + H_v + H_{el-v} \\ H_v &= \sum_j \omega_j \left( b_j^+ b_j + \frac{1}{2} \right) \\ H_{el-v} &= \sum_{j,\sigma} \lambda_j n_{j,\sigma} (b_j^+ + b_j) \end{aligned} \quad (2)$$

where  $H_{el}$  is the electronic Hamiltonian of eq 1 and  $b_j^+$  ( $b_j$ ) is the creation (annihilation) operator for one-quantum excitation in the oscillator  $j$  with frequency  $\omega_j$  ( $\hbar = 1$ ).  $H_{el-v}$  is the vibronic interaction, which is expressed as:

$$H_{el-v} = \sum_{j,\sigma} A_j q n_{j,\sigma}$$

with the substitution

$$q_j = \frac{1}{\sqrt{2m_j \omega_j}} (b_j^+ + b_j) \quad (3)$$

The values of the optimal parameters<sup>16,17</sup> of the Hamiltonian of eqs 1 and 2 are (in eV)

$$\begin{aligned} t &= -0.73, \Delta = 5.06, U = 4.62 \\ \lambda_1 &= \lambda_3 = -0.1, \lambda_2 = -0.16 \\ \omega_1 &= \omega_3 = 0.0619776 \text{ (}\sim 500 \text{ cm}^{-1}\text{)} \\ \omega_2 &= 0.0754887 \text{ (}\sim 609 \text{ cm}^{-1}\text{)} \end{aligned}$$

where  $\lambda_j$  is the vibronic coupling constant for the  $j$ -th mode.

The effects of a static electric field are then included in the form:

$$\begin{aligned} H &= H_{mol} - \mu F \\ \mu &= \sum_{j,\sigma}^{N_{site}} n_{j,\sigma} \left( j - \frac{N_{site} + 1}{2} \right) \end{aligned} \quad (4)$$

Here  $\mu$  is the dipole moment operator and  $F$  is the electric field vector.

Optical spectra, with and without the field, are computed by the Lanczos technique described elsewhere.<sup>14–16</sup> The electronic basis set is made by all configurations with minimal  $S_z$  (1/2 and 0 for the +5 and +4 ions respectively), obtained filling the three orbitals (one  $d_{xz}$  for each Ru and the pyz  $\pi^*$ ) with three or four electrons (two from Ru(II) and one from Ru(III)). The vibrational basis set is the direct product of all combinations of local oscillator wave functions, up to a maximum excitation; in the present case we have taken 25 states for each oscillator on Ru and 15 for that on pyz, and have verified that a slight decrease in those values does not cause differences in the spectra. Finally, the total basis set is made by the direct product of electronic and vibrational basis, giving rise to a total number of 84 375 vibronic configurations.

We note that the spectra are observed in a glassy matrix and it is assumed that the molecules are aligned randomly with respect to the applied field. Here we examine the case where the polarization of the incident light is in a plane perpendicular to the axis of the applied field.

Letting the  $z$  axis be the axis of the applied field, let  $\theta$  and  $\varphi$  be the azimuthal and polar angles of the molecule. Let  $\varphi_E$  be the angle between the polarization of the incident light and the  $x$  axis. The spectral function  $S$  for an individual molecule then depends on  $\theta$ ,  $\varphi$ , and  $\varphi_E$ . For a random distribution of molecular orientations, the observed spectrum is a convolution of the molecular spectra  $S(\theta, \varphi, \varphi_E)$  given by:

$$\langle S \rangle = \frac{1}{8\pi^2} \int \int \int S(\theta, \varphi, \varphi_E) \sin \theta \, d\theta \, d\varphi \, d\varphi_E \quad (5)$$

The spectrum of an individual molecule  $S(\theta, \varphi, \varphi_E)$  may be written as:

$$S(\theta, \varphi, \varphi_E) = \sin^2 \theta \cos^2(\varphi_E - \varphi) S_\theta \quad (6)$$

where  $S_\theta$  is the molecular spectrum computed in the usual fashion by using the operator  $\mu F \cos \theta$ . The spectral function for a random set of molecular orientations is then given by:

$$\langle S \rangle = K \int_0^\pi S_\theta \sin^3 \theta \, d\theta \quad (7)$$

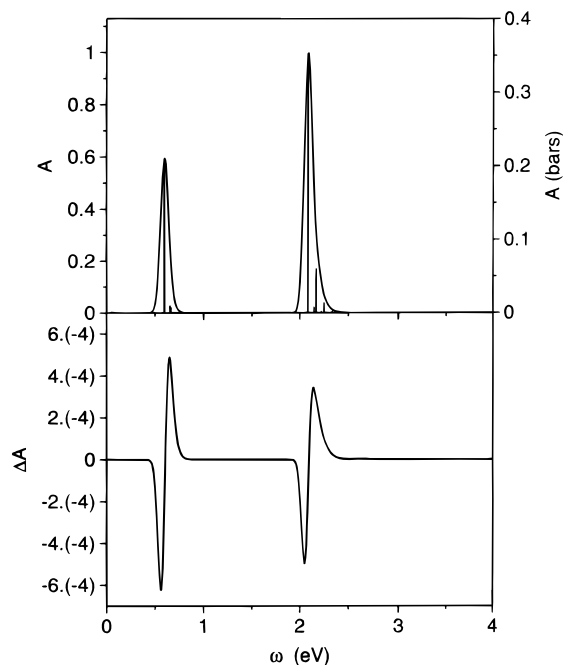
where  $K$  is given by:

$$K = \frac{1}{8\pi^2} \int \int \cos^2(\varphi_E - \varphi) \, d\varphi_E \, d\varphi \quad (8)$$

However,  $K$  is not important for the present purposes, since the intensities are normalized so that the calculated zero-field spectrum is normalized to the observed spectrum.

### Results and Discussion

In the upper part of Figure 1 we report the computed near-IR–vis spectra of the +5 species. The vibronic transitions are represented by the sticks (right scale) and the introduction of a phenomenological Gaussian width for each line generates the overall line shape profile (left scale). The agreement with the experimental spectrum of ref 3, as far as position, intensity ratio, and asymmetric profile, is very good; the intensity of the metal-to-ligand charge transfer (MLCT) band has been normalized to that of Figure 5 of ref 3. Switching on a static electric field of  $4 \times 10^5$  V/cm, one obtains the difference spectra shown in the lower part of Figure 1. For both the near-IR (known as IT) and MLCT bands, the agreement with the experimental results of ref 3 is good although the computed difference spectrum is a

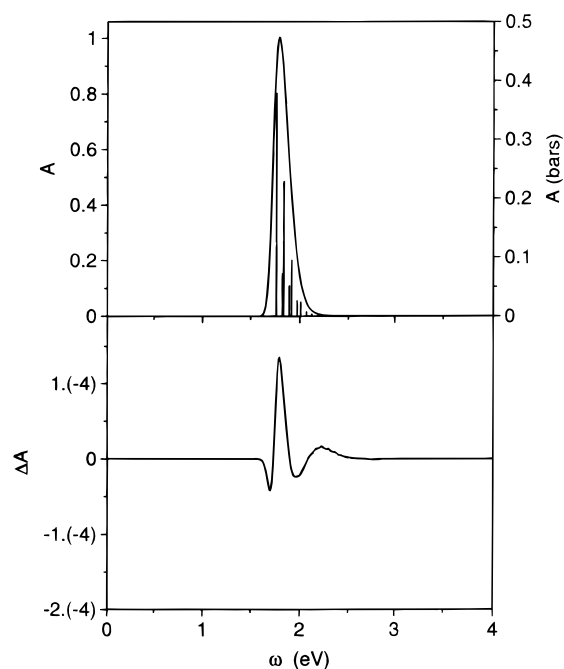


**Figure 1.** Computed near-IR-vis absorption spectra for the Creutz-Taube (+5) ion (upper part). Computed difference spectra (spectrum with the field minus spectrum with no field) for the Creutz-Taube (+5) ion in the near-IR-vis (lower part).

little more intense than in the experiment. This is to be expected since the  $4 \times 10^5$  V/cm field applied in the experiment is not the field actually experienced by the molecule, embedded in a water/glycerol matrix at 77 K. An estimate of the real field on the molecule cannot be obtained easily. Furthermore, the difference spectrum is a small difference between two larger numbers at each value for the frequency, so that an error (resulting from, e.g., a local field correction) of a few percent in the field-on spectrum may lead to a large error in the intensity in the difference spectrum. With this considered, the agreement between the calculated and observed difference spectra is quite good for the (unscaled) line shape function and reasonable for the scaled intensity.

We obtain similar results for the +4 ion. Upper and lower parts of Figure 2 show the absorption and the difference spectra, respectively. Again, the qualitative agreement with the experimental results is very good, although the experimental MLCT band reported in Figure 4 of ref 3 is slightly more symmetric than the one we calculated. Quantitatively the calculated difference spectrum is more intense than in the experiment for the same reasons as for the +5 species.

Note that the basic profiles of our spectra are in agreement with experiment. The near-IR band in the difference spectrum of the +5 species has a minimum (corresponding to negative  $\Delta A$ ) on the red side and a less intense maximum on the blue side. This is because the asymmetric intervalence band of a delocalized complex blue shifts slightly when an electric field is applied. The metal-to-ligand charge-transfer band in the



**Figure 2.** Computed near-IR-vis absorption spectra for the +4 homovalent analogue of the Creutz-Taube ion (upper part). Computed difference spectra (spectrum with the field minus spectrum with no field) for the +4 homovalent analogue of the Creutz-Taube ion in the near-IR-vis (lower part) spectrum.

difference spectrum of the +4 species has a minimum on the red side, a maximum in the middle, and another minimum on the blue side.

## Conclusions

We have reported model calculations of the electroabsorption spectra for pyz-bridged Ru(II)/Ru(III) and Ru(II)/Ru(II) dimers for which experimental results are available.<sup>2,3</sup> The two species have been modeled, according to previous studies,<sup>14-17</sup> taking into account the Ru-pyz back-bonding interaction and energy difference, Coulomb repulsion, and vibronic interaction. This is the first time that electroabsorption line shapes have been predicted taking into account both vibronic coupling and Coulomb repulsion. The vibronic coupling enables us to calculate the absorption profile with and without the applied electric field, and the Coulomb repulsion allows us to compare the different charge states of the dimer. The results obtained for the line shape for both the mixed-valent and the homovalent species are in good agreement with experimental findings in the entire near-IR-visible region.

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