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Potential energy surfaces for a mixed-valence dimer in an applied electric field

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Summary. A mixed-valence dimer with an applied external field aligned along the internuclear axis is studied using a two-site small-polaron model. Potential energy surfaces are calculated in the adiabatic (Born–Oppenheimer) approximation. It is shown that two nuclear coordinates (one totally symmetric and the other antisymmetric) are coupled to the electronic motion, whereas only the antisymmetric coordinate is coupled in the absence of an electric field. For a strongly localized (valence trapped) system, the displacement along the totally symmetric coordinate is directly proportional to the applied field strength. For delocalized (valence-averaged) systems, there is significant displacement along the antisymmetric coordinate, an effect which also vanishes in the absence of an applied field. Contributions to the linewidth are estimated.

Key words: Mixed valence – Electrochromism – Stark effect – Vibronic coupling

1. Introduction

Recent work by the research groups of Boxer [1, 2] and of Hush [3–5] have established Stark effect spectroscopy as a valuable and definitive technique for the characterization of mixed-valence compounds. In particular, the response of the molecule to the applied electric field supplies good evidence for the assignment of the system to the proper Robin–Day [6] class. Correct Robin–Day classification has sometimes been difficult, even controversial, in mixed-valence chemistry [7].

Furthermore, Classes II and III mixed-valence compounds contain at least one spatially and/or temporally delocalized electron and therefore may have large hyperpolarizabilities. This opens possibilities for interesting and commercially useful electrochromic and nonlinear optical properties.

A number of authors [3–5, 8–10] have developed theory for the electrochromic properties (i.e. change in optical absorption as a function of applied field) of molecular electronic transitions.

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The purpose of the present work is to look at the vibrational modes of motion which are coupled to the electronic motion and to calculate the potential energy surfaces for a mixed-valence dimer in an applied electric field. One may then estimate changes in the absorption maximum $\nu_{\max}$ and the width $\Delta\nu_{1/2}$ as functions of the applied field.

2. The model

The total Hamiltonian for the system is that of the free molecule plus the interaction with the electric field, as

$$\boldsymbol{H} = \boldsymbol{H}_{\text{molecule}} + \boldsymbol{H}_{\text{field}}, \tag{1}$$

The molecular term is written in the usual fashion, as a sum of a purely electronic term, a vibrational term and a vibronic coupling term, as

$$\boldsymbol{H}_{\text{molecule}} = \boldsymbol{H}_{\text{e}} + \boldsymbol{H}_{\text{v}} + \boldsymbol{H}_{\text{e-v}}, \tag{2}$$

$$\boldsymbol{H}_{\text{e}} = E_1 \boldsymbol{a}_1^+ \boldsymbol{a}_1 + E_2 \boldsymbol{a}_2^+ \boldsymbol{a}_2 + B(\boldsymbol{a}_1^+ \boldsymbol{a}_2 + \boldsymbol{a}_2^+ \boldsymbol{a}_1), \tag{3}$$

$$\boldsymbol{H}_{\text{v}} = \boldsymbol{h}_1 + \boldsymbol{h}_2, \tag{4}$$

$$\boldsymbol{H}_{\text{e-v}} = A_1 q_1 \boldsymbol{a}_1^+ \boldsymbol{a}_1 + A_2 q_2 \boldsymbol{a}_2^+ \boldsymbol{a}_2, \tag{5}$$

where 1 and 2 are the two electronic states. One purely electronic basis state is located on each site and each electronic state is coupled to one local vibrational mode with coordinate q_i. The operators $\boldsymbol{a}_i^+$ and $\boldsymbol{a}_i$ are the creation and annihilation operators [11], respectively, for the ith electronic state. $\boldsymbol{h}_i$ represents the harmonic oscillator Hamiltonian for the ith vibrational mode. E_i is the energy of the ith electronic basis state and B is the transfer integral which arises from the coupling between these two states. For present purposes, we consider the symmetric case $E_1 = E_2$. A_i is the energy of the electron–vibrational coupling on the ith site. The above model for the zero-field molecule has been solved previously [12, 13] and has been used in the prediction of the spectroscopic properties of mixed-valence complexes [14–16].

For present purposes, vibrational anharmonicities, frequency shifts, non-Condon effects, electron–electron repulsion and spin–orbit coupling are neglected in the molecular Hamiltonian. It is assumed that the coupling between the electronic motion and the nuclear motion is linear in the vibrational coordinate.

We shall designate the internuclear axis as the x axis and thus it is convenient to assume that the applied electric field is aligned along the x-axis. The Hamiltonian for the interaction with an applied electric field therefore may be written as

$$\boldsymbol{H}_{\text{field}} = -e E_x \boldsymbol{x}, \tag{6}$$

where $\boldsymbol{x}$ is the position operator for the electron in the molecule, e is a constant and E_x is the applied field.

In the homonuclear case, it is convenient to express the nuclear coordinates in terms of sum and difference combinations, given by

$$Q_+ = 2^{-1/2}(q_1 + q_2), \tag{7}$$

$$q_- = 2^{-1/2}(q_1 - q_2). \tag{8}$$

Rewriting Eq. (5) in terms of these transformed coordinates, one obtains

$$\boldsymbol{H}_{e-v} = 2^{-1/2} A q_{-} (\boldsymbol{a}_1^+ \boldsymbol{a}_1 - \boldsymbol{a}_2^+ \boldsymbol{a}_2) + 2^{-1/2} A Q_{+} \tag{9}$$

for the case where $A = A_1 = A_2$.

Noting that the local vibrational coordinates q_1 and q_2 represent stretching motions of the coordination shell about each metal ion, then we may write the positions x_1 and x_2 of the two metal nuclei as

$$x_1 = -x_{01} - q_1, \tag{10}$$

$$x_2 = x_{02} + q_2, \tag{11}$$

where x_{0i} represents the equilibrium distance between the ith nucleus and the origin. In the homonuclear case, $x_0 = x_{01} = x_{02}$. Equation (6) may now be rearranged to obtain a new expression for the $\boldsymbol{H}_{\text{field}}$ operator as

$$\begin{aligned}\boldsymbol{H}_{\text{field}} = e E_x [& x_0 (\boldsymbol{a}_1^+ \boldsymbol{a}_1 - \boldsymbol{a}_2^+ \boldsymbol{a}_2) + 2^{-1/2} q_{-} \\ & + 2^{-1/2} Q_{+} (\boldsymbol{a}_1^+ \boldsymbol{a}_1 - \boldsymbol{a}_2^+ \boldsymbol{a}_2)].\end{aligned} \tag{12}$$

Note that Eq. (12) is valid for the homonuclear case. It is readily apparent from Eqs. (9) and (12) that, within the confines of the present model, the totally symmetric vibrational coordinate Q_+ is only coupled to the electronic motion in the presence of an applied external field.

In the present work, results obtained in the adiabatic (Born–Oppenheimer) approximation (BOA) are presented. The BOA potentials enable one to see how an additional vibrational mode (Q_+) becomes coupled to the electronic transition, and also how the coupling to the antisymmetric coordinate (q_-) is changed as the external field is applied. The full vibronic coupling treatment without the BOA will be presented elsewhere.

3. Parameters

The parameters appearing in the present model Hamiltonian are B, k, A, eE_x, and x_0. All of our parameters are given in units of eV and Angstroms. We now discuss some specific molecules, to show how certain sets of parameters correspond to particular types of physical systems.

The resonance integral B is on the order of -0.1 eV for a typical localized (valence-trapped) dimer and on the order of -1.0 eV for a typical delocalized (valence-averaged) dimer. Some examples are given in Table 1. For long distance electron transfer, where donor and acceptor sites are separated by a few tens of Ångstroms, the resonance integral is much smaller in magnitude. For example, the electron transfer kinetics studies on the derivatized metalloprotein ruthenium pentaamine histidine-33–zinc-substituted cytochrome c estimated $|B|$ to be 1×10^{-5} eV [21].

Vibrational force constants k are roughly of order 10 eV/Å^2 for an intramolecular mode, although a wide range of values is possible. For instance, the totally symmetric metal-ligand stretch mode in $\mathrm{Ru(NH_3)_6^{2+/3+}}$ has been calculated to be 16 eV/Å^2 [20]. k is a couple of orders of magnitude smaller for an intermolecular mode.

The vibronic coupling parameter A is proportional to and on the order of $k\,\Delta r$, where Δr is the change in equilibrium bond distance for each local oscillator upon

Table 1. Values[a] for the resonance integral B and vibronic coupling parameter A in some typical dimer systems

Dimer	B (eV)	$\|A\|$ (eV/Å)	Conclusion	References
$((NH_3)_5Ru)_2(4,4'bipy)^{5+}$	− 0.3	8.4	Loc	[17]
Wolffram's red salt	− 0.6	17	Loc	[18]
Benzene dimer cation	− 0.6	10	Loc; low barrier	[19]
$((NH_3)_5Ru)_2(pyz)^{5+}$	− 0.9	1.5	Deloc	[20]

[a] All values for B and A are estimated by a PKS [15,16] method, except for those for $((NH_3)_5Ru)_2(pyz)^{5+}$. For this latter compound, B is a bridge-mediated resonance integral, and was calculated by an electronic structure method. A was calculated from vibrational and X-ray crystallographic data on the monomer

change in oxidation state. Some examples of calculated and estimated values for A are given in Table 1.

For the applied electric field strength, we use the value 0.2 eV/Å, which corresponds to a very intense, but attainable, laser field.

For x_0, we use the value 2.0 Å for the delocalized cases and 5.0 Å for the localized cases, which correspond to typical values for the position of donor and acceptor atoms in a mixed-valence compound.

4. Results

Using the BOA, two two-dimensional potential energy surfaces $U_+(Q_+, q_-)$ and $U_-(Q_+, q_-)$ are obtained as

$$U_-(Q_+, q_-) = kq_-^2/2 + kQ_+^2/2 + 2^{-1/2}AQ_+ + 2^{-1/2}eE_xq_- - [B^2 + 1/2(Aq_- + 2^{1/2}eE_xx_0 + eE_xQ_+)^2]^{1/2}, \tag{13}$$

$$U_+(Q_+, q_-) = kq_-^2/2 + kQ_+^2/2 + 2^{-1/2}AQ_+ + 2^{-1/2}eE_xq_- + [B^2 + 1/2(Aq_- + 2^{1/2}eE_xx_0 + eE_xQ_+)^2]^{1/2}, \tag{14}$$

for the homonuclear case. Each of the two sites are assumed to be coupled to harmonic vibrations. These two local vibrational modes are assumed to have equal force constant k; note that k is contained in Eq. (4).

The lower potential surface, represented by Eq. (13), may have either single-minimum or double-minimum form, depending upon the relative sizes of the parameters. Figure 1 depicts contours of equal potential for the lower (ground state) surface along the two nuclear coordinates Q_+ and q_- for the case where $B = -1.0$ eV, $A = -9.0$ eV/Å, $k = 3.5$ eV/Å^2, $eE_x = 0.2$ V/Å and $x_0 = 5.0$ Å. This corresponds to a localized (valence-trapped) ground state where the two local states, which are degenerate in the absence of an applied field, have become nondegenerate. In the lower of the two wells, the innermost contour is at − 13.1 eV and the next-innermost is at − 13.0 eV. For the localized case in zero field, there is a maximum along q_- located at $q_- = 0$. However in the presence of an external field, this maximum corresponds to a saddle point and is shifted away from $q_- = 0$, as shown in Fig. 1. For the case shown in Fig. 1, the saddle point is located

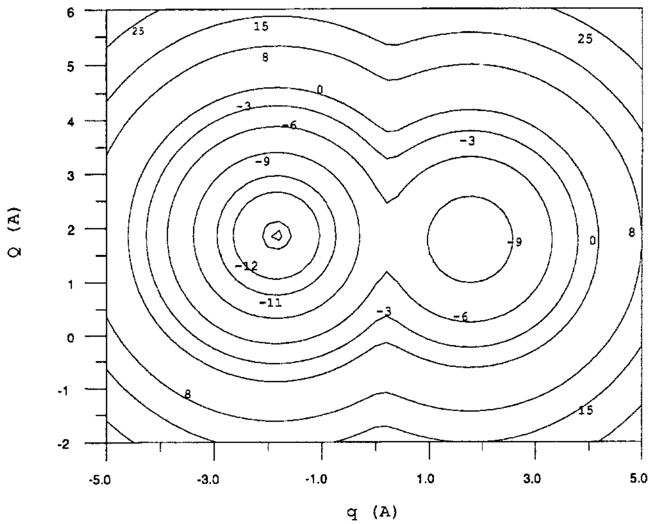


Fig. 1. Contours of equal potential in the ground state in the presence of an applied electric field along the two coupled coordinates Q_+ and q_- for the case $B = -1.0$ eV, $A = -9.0$ eV/Å, $k = 3.5$ eV/Å^2, $eE_x = 0.2$ eV/Å and $x_0 = 5.0$ Å. This corresponds to a mixed-valence dimer with a localized (valence-trapped) ground state. In the lower of the two wells, the innermost contour is at -13.1 eV and the next-innermost is at -13.0 eV

at $(Q_+, q_-) = (2.016, 0.199)$, while the two minima are located at $(Q_+, q_-) = (2.061, -2.057)$ and $(1.980, 1.974)$. The minimum for the corresponding upper surface is at $(2.016, 0.167)$.

In the absence of an applied field, there is no interaction between the electronic motion and the totally symmetric vibration Q_+. However in the present system, there is a finite displacement of the minima between the upper and lower surfaces along Q_+. In the limit $2k|B|/A^2 \ll 1$, the displacement of the minima along Q_+ is directly proportional to the applied field, as

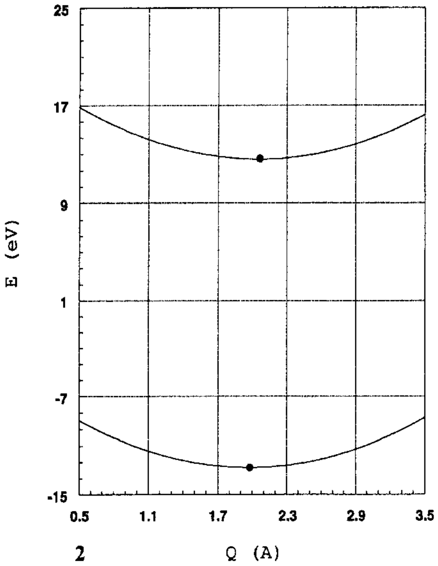
$$\lim_{2k|B|/A^2 \to 0} \Delta Q_+ = 2^{1/2}\, eE_x/k. \tag{15}$$

Figure 2 depicts a slice of the upper and lower potential surfaces along Q_+, with the coordinate q_- fixed at one of its minimum values of 1.974 Å for the case where $B = -1.0$ eV, $A = -10.0$ eV/Å, $k = 3.5$ eV/Å^2, $eE_x = 0.2$ V/Å and $x_0 = 5.0$ Å. Note that these parameters correspond to a localized, double-well ground state, similar to the case shown in Fig. 1. The minima for the two surfaces in Fig. 2 are marked with solid dots. These two minima are displaced by 0.08 Å along Q_+.

As the ratio $2k|B|/A^2$ becomes large, the displacement along Q_+ between the upper and lower surfaces becomes dependent upon the square of the applied field. For $2k|B|/A^2$ large and along the $q_- = 0$ plane, ΔQ_+ is given approximately by

$$\Delta Q_+ \cong (eE_x)^2[A/k - 2x_0]/2^{1/2}kB. \tag{16}$$

Figure 3 shows slices of the upper and lower surfaces along Q_+, with q_- fixed at a value of -0.35 Å which corresponds to the ground state minimum, for the



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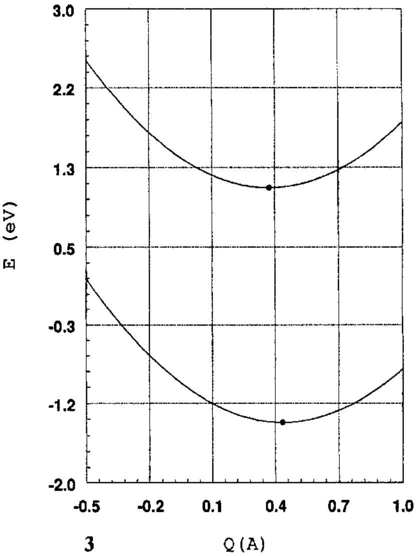

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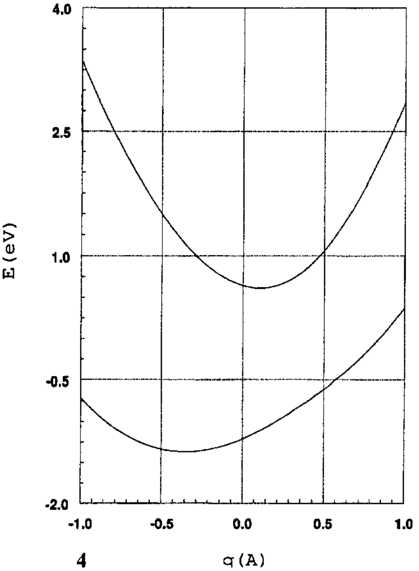

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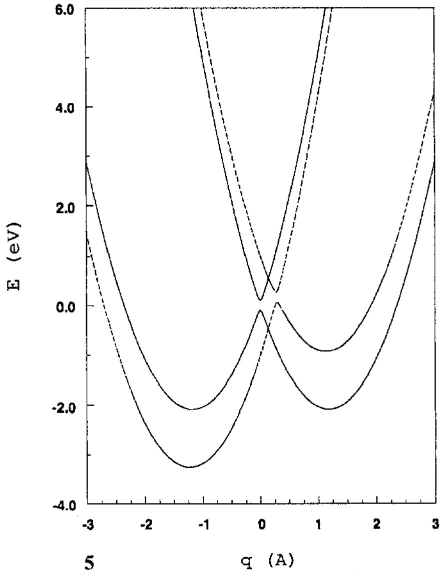

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Fig. 2. Cross sections of the potential energy surfaces along the Q_+ coordinate with the q_- coordinate held fixed at its minimum value of 1.974 Å for the case where $B = -1.0$ eV, $A = -10.0$ eV/Å, $k = 3.5$ eV/Å^2, $eE_x = 0.2$ eV/Å and $x_0 = 5.0$ Å. These parameters correspond to a localized, double-well ground state

Fig. 3. Cross sections of the potential energy surfaces along the Q_+ coordinate with the q_- coordinate held fixed at a value of -0.4 Å for the case $B = -0.8$ eV, $A = -2.0$ eV/Å, $k = 3.5$ eV/Å^2, $eE_x = 0.2$ eV/Å and $x_0 = 2.0$ Å. These parameters correspond to a delocalized, valence-averaged, single-minimum ground state

Fig. 4. Cross sections of the potential energy surfaces along the q_- coordinate with the Q_+ coordinate held fixed at the value of 0.44 Å for the case $B = -0.8$ eV, $A = -2.0$ eV/Å, $k = 3.5$ eV/Å^2, $eE_x = 0.2$ eV/Å and $x_0 = 2.0$ Å. These parameters correspond to a delocalized ground state

Fig. 5. The ground potential energy surfaces for along q_- for the case where $B = -0.1$ eV, $A = -5.0$ eV/Å, $k = 3.0$ eV/Å^2 and $x_0 = 5.0$ Å for the zero-field (solid line) and the finite field of $eE_x = 0.2$ eV/Å (dashed line) cases

case $B = -0.8$ eV, $A = -2.0$ eV/Å, $k = 3.5$ eV/Å^2, $eE_x = 0.2$ V/Å and $x_0 = 2.0$ Å. These parameters correspond to a delocalized, valence-averaged, single-minimum ground state. Again the two minimum points, which in this case are displaced from each other by 0.05 Å along Q_+, are marked with solid dots. As $|B|$ approaches infinity, the displacement along Q_+ approaches zero. In the absence of an applied electric field, all displacements along Q_+ are zero.

In the case where the ground state is delocalized (valence-averaged), both surfaces possess a minimum at $q_- = 0$ when the external field is off. However, the application of the external field introduces a substantial shift of minimum between the ground and excited surfaces along the antisymmetric coordinate q_-, even in the delocalized case. Slices of the upper and lower potential surfaces along the q_- coordinate for such a case are shown in Fig. 4. Parameters used in Fig. 4 are: $B = -0.8$ eV, $A = -2.0$ eV/Å, $k = 3.5$ eV/Å^2, $eE_x = 0.2$ V/Å, $x_0 = 2.0$ Å and Q_+ is fixed at the value of 0.435 Å. As is apparent from the single-minimum lower surface, these parameters correspond to a delocalized ground state. In sharp contrast to the zero-field case, there is substantial displacement, in this case 0.5 Å, between the minima of the two surfaces along the antisymmetric q_- coordinate. Thus, the delocalized dimer should exhibit significant broadening and blue-shifting of the "intervalence" band upon application of the electric field.

For the preceding delocalized case, the contribution to the linewidth from the field-induced coupling to q_- may be written approximately as

$$\Delta\nu = c^{-1}\left[(k/m)^{1/2}\, k/\pi h\right]^{1/2} |\Delta q_-| \tag{17}$$

Here m is the reduced mass, c is the speed of light and h is Planck's constant. Equation (17) makes use of an approximate method in which the upper and lower surfaces are treated as displaced, equal-frequency, harmonic oscillators along the coordinate of interest [20–22]. For the parameters used in Figs. 3 and 4 and using a value of 0.5 Å for $|\Delta q_-|$ and a typical value of 1×10^{-27} eV s^2/Å^2 ($\cong 10$ amu) for m [20, 22, 23], the contribution to the linewidth from q_- alone is about 2000 cm^{-1}. This contribution is expected to be considerably larger for systems with a larger force constant.

It is also of interest to look at the shifts in absorption maximum for the intervalence band. Symmetric, localized compounds become asymmetric in the presence of an external field, with one ground-state minimum shifting up in energy and the other shifting down. For typical values of the parameters for such a system, these shifts in energy can be substantial, as shown in Fig. 5. Figure 5 plots the ground-state potential energy surfaces along q_- for the case where $B = -0.1$ eV, $A = -5.0$ eV/Å, $k = 3.0$ eV/Å^2 and $x_0 = 5.0$ Å for the zero-field (solid line) and the finite field of $eE_x = 0.2$ V/Å (dashed line) cases. With the field switched on, the lower of the two ground-state minima is significantly stabilized relative to the excited state, and a large blue shift is expected in the Intervalence band.

5. Discussion

From the present work, one can calculate values for the spectral shifts (electrochromic effect) upon application of an electric field, and also estimate changes in the linewidths.

For both localized and delocalized mixed-valence dimers, substantial changes in the spectrum are predicted when the system is placed in an applied electric field.

Localized systems should exhibit a large blue shift when the field is switched on. Some small additional broadening is expected, caused by induction of coupling of the electronic motion to the totally symmetric coordinate. Delocalized systems are expected to show considerable broadening upon application of an external field, due to induced shifts of minima along the antisymmetric coordinate.

In an earlier study of the CO molecule, Hush and Williams [24] obtained expressions for the ground-state equilibrium bond distance as a function of applied electric field. For the field not too large and for parameters corresponding to a localized case, their expression for the equilibrium bond distance in this limit is proportional to the applied field to the first power. For parameters corresponding to the delocalized case and for the field not too large, the equilibrium bond distance is proportional to the square of the applied field. The present results for the displacement associated with the intervalence transition show the same general type of field dependence in the two limiting cases.

Application of an electric field is one, but not the only [20, 22, 25–29], mechanism by which additional totally symmetric modes become coupled to the electronic motion in a donor–acceptor couple.

The adiabatic approximation used here is very good for the delocalized systems. It is less accurate for the localized systems, but still gives a reasonable picture of their behaviour. A full nonadiabatic treatment is currently in progress.

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