MOLECULAR IMPLEMENTATIONS OF QUANTUM-DOT CELLULAR AUTOMATA: THE VIBRONIC PROBLEM IN MIXED-VALENCE TETRA-RUTHENIUM SPECIES

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ABSTRACT

Here we report the evaluation of the electronic and vibronic levels of mixed-valence tetra-ruthenium (2Ru(II)+2Ru(III)) systems assembled as two coupled Creutz-Taube complexes for which possible molecular implementations of quantum-dot cellular automata was proposed. In this view the main theoretical issue is related to the vibronic localization of the two holes whose positions are able encode information at the molecular level. These complexes are representatives of Robin and Day classes I, II, and III and therefore the vibronic coupling is crucially important for the adequate description of the magnetic characteristics and profiles of the intervalence optical bands.

1. INTRODUCTION

The structures of the tetra-ruthenium mixed-valence complexes suggested in Ref. [1,2] are shown in Fig. 1. These mixed-valence species consist of two Creutz-Taube complexes assembled in center-bridged and side-bridged tetramers within which two

Fig. 1. Examples of center-bridged and side-bridged mixed-valence Ru(II)2Ru(III)2 complexes (modified from refs. [1,2])
holes are shared between four sites as shown in Fig. 1. Due to Coulomb repulsion the energy of the system reaches minimum when the holes are instantly localized at the remote sites, i.e. along the diagonal of the square. The cell polarization was proposed to encode the binary information, thus,  \( P = +1 \) represents the binary \( 1 \) and \( P = -1 \) represents the binary \( 0 \) \cite{1,2} (Fig. 2). The theoretical background for the application includes evaluation of the energy levels of the two holes coupled to the vibrations, the barrier separating the two low lying states in Fig. 2 and the optical vibronically assisted bands accompanying the electron transfer processes. The intervalence optical absorption is peculiar for the mixed valence compounds and has been used to identify the key parameters of these systems, mainly the degree of the delocalization.

2. ELECTRONIC LEVELS

The Hamiltonian of the system is assumed to consist of three terms:

\[
H = H_e + \sum_i \hbar \omega_i \left( q_i^2 - \frac{\partial^2}{\partial q_i^2} \right) + \sum_i \nu_i O_i q_i.
\]

Here \( H_e \) is the electronic Hamiltonian, the next two terms (they will be specified later) are the Hamiltonian of the free vibrations and the vibronic interaction. The main factors controlling the electronic spectrum are the following \cite{3}: 1) Coulomb interaction between the itinerant holes that tends to instantly localize them as far as possible, i.e. on the sites located at opposite vertices (distant pair, two localized configurations). The difference in the energies of the Coulomb repulsion between the distant pairs (keeping binary information) and the neighboring ones (\( d \)- and \( n \)-pairs, the last have four possible configurations) will be denoted as \( U \); 2) the transfer of the two holes between four sites. The hole transfer parameters \( t_n \) and \( t_d \) correspond to the jumps between the distant and adjacent sites respectively. The energy pattern evaluated within the model involving the main interactions is the following (we omit here the details of calculations):

\[
E^{1}B_{1g}(d) = 0, \quad E^{1}B_{2g}(n) = E^{3}A_{2g}(n) = U - 2t_d, \\
E^{1}E_u(n) = U, \quad E^{3}A_{1u} = \frac{1}{2} \left( U + 2t_d \right) \pm \frac{1}{2} \sqrt{(U + 2t_d)^2 + 32t^2_n}, \\
E^{3}B_{1g}(n) = U + 2t_d, \quad E^{3}E_u = \frac{U}{2} \pm \frac{1}{2} \sqrt{U^2 + 16t^2_n}.
\]

The energy levels are labeled by the irreducible representations (irreps) of the point group \( D_{4h} \) of the molecule and by the quantum number of the full spin. The energies of the two terms \( 3E_u \) and two terms \( 1A_{1g} \) are marked by the symbols “+“ and “−“.

Fig. 2. Schematic quantum-dot cellular automata cell, \( P = +1 \) represents the binary 1 and \( P = -1 \) represents the binary 0.
The correlation diagrams (Fig. 3) give the pictures of the levels (in dimensionless units $E/U$ vs $t/U$) in the two limiting cases: $t_d = 0, t_n \neq 0$ and $t_d \neq 0, t_n = 0$. The case of strong transfer between the distant sites can probably be relevant to the center-bridge mixed-valence compound while for side-bridged mixed-valence the transfer between neighboring sites is undoubtedly dominant. One can see that the energies of the instantly localized system can be assigned to the two groups with the energies 0 (low-lying group) and $U$ (high-lying) accordingly the value of the Coulomb repulsion. The low-lying group contains spin-singlets and spin-triplets terms $^1B_{1g}, ^1A_{1g}, ^3E_u$ and the high-lying terms (originated from the manifold with the energy $U$) are $^1B_{2g}, ^1A_{1g}, ^3E_u, ^3A_{2g}, ^3B_{1g}, ^3E_u$. Providing $t_d = 0$ the system is always diamagnetic while in the case of $t_n = 0$ the ground state is accidentally degenerate and represented by a paramagnetic mixture of spin triplet and spin singlet terms. In the general case ($t_d \neq 0$ and $t_d \neq 0$) the energy pattern is more complicated but exhibits accidental degeneracy $^1B_{2g}, ^3A_{2g}$.

3. VIBRONIC MODEL FOR A MIXED-VALENCE SPECIES WITH SQUARE TOPOLOGY

The second term in the full Hamiltonian describes the free harmonic vibrations of the system, $q_i$ are the dimensionless vibrational coordinates, $\omega_i$ are the vibrational frequencies. We shall employ the conventional vibronic model for mixed valence systems formulated by Piepho, Krausz and Schatz [4] (referred to as PKS model) which deals with the independent “breathing” displacements (that are assumed to be the normal coordinates) of the ions around the sites of the electron localization. Using the projection operator one can obtain the following explicit expressions for the PKS coordinates for a tetrameric system belonging to the point group $D_{4h}$. The vibronic coupling is linear with respect to the vibrational coordinated as assumed in the PKS model. The matrices $O_{ij}$ are defined in the basis of the electronic wave functions (in terms of the Slater’s determinants) belonging to the definite irreps for spin triplet and
spin singlet terms so far indicated. For the sake of brevity the 6x6-matrices $O_i$ are not given in this article. The coupling with the full-symmetric mode is described by the unit matrix and therefore can be ruled out from the further consideration by a simple shift of the equilibrium position along this coordinate which does not affect any physical properties. Finally one arrives at the independent (but complicated) pseudo JT problems for spin-singlets and spin-triplets terms mixed by the vibronic interaction: $\left( B_{1g}, 2A_{1g}, B_{2g}, E_u \right) \otimes \left( b_{1g} + e_u \right)$ and $\left( 3A_{2g}, B_{1g}, 2E_u \right) \otimes \left( b_{1g} + e_u \right)$. One can see that we face a complicated dynamic pseudo JT problems of six electronic states coupled to the three vibrational modes.

4. SYMMETRY ASSISTED APPROACH

The full JT Hamiltonian can diagonalized in the basis composed as a direct product of the electronic wave-functions $\left| \Gamma_f \gamma_f \right\rangle$ and the states $|n_i\rangle$ ($n_i = 0, 1, 2...$) of the harmonic oscillators:

$$\begin{align*}
|\Gamma_f \gamma_f \rangle |n_1\rangle |n_2\rangle \cdots |n_k\rangle &= |\Gamma_f \gamma_f \rangle |n_1, n_2 \cdots n_k\rangle. 
\end{align*}$$

The electronic levels are labeled by the irreps $\Gamma_1, \Gamma_2 \cdots \Gamma_r$ of the actual point group, while the basis functions are denoted by the symbols $\gamma_1, \gamma_2 \cdots \gamma_l$ correspondingly.

Due to sizeable electronic basis (six electronic functions in the problem under consideration) and multiple degeneracy of the excited vibrational levels in multimode JT systems (three modes in the present case) the sizes of the matrices of the full Hamiltonian prove to be rather large even if the basis is restricted to a relatively small number of the harmonic oscillator levels. On the other side, the truncation of the vibronic matrices can result in a dramatic lack of precision which essentially refers to the evaluation of the profiles of the optical bands for which highly excited vibronic levels are involved.

Recently we presented a powerful computational approach to the dynamic JT/pseudo JT systems [5, 6] aimed to overcome these difficulties. The approach is based on the concept of the evaluation of the symmetry adapted vibronic basis that allows to essentially reduce the vibronic JT matrices. The algorithm for the solution of the eigen-problem takes full advantage of the point symmetry arguments and thus allows to reduce the vibronic matrices to full extent. The group-theoretical assignment of the vibronic states allows to predict the symmetry labels for the vibronic levels in advance, that means before evaluation, and therefore to optimize the required computational resources. The general procedure of the symmetry assisted evaluation is described in Ref [5]. The way of calculations for the $\left( B_{1g}, 2A_{1g}, B_{2g}, E_u \right) \otimes \left( b_{1g} + e_u \right)$ and $\left( 3A_{2g}, B_{1g}, 2E_u \right) \otimes \left( b_{1g} + e_u \right)$ pseudo JT problems in the system under consideration are quite similar to those previously reported for some other mixed-valence systems [5,6] and for this reason here we omit the details of calculations.

5. DISCUSSION

Within the PKS model the frequencies of all active vibrations are equal to the frequency $\omega$ of the local “breathing” mode and therefore the electronic system is
effectively coupled to a three-dimensional oscillator for which the degeneracies \( g(n) \) of each level with the number \( n \) can be expressed as: \( g(n) = (1/6)(n+1)(n+2) \). Therefore the dimension of the vibrational space \( G(N) \) including the six-dimensional electronic space is the following:

\[
G(N) = 6 \sum_{n} g(n) = (N+1)(N+2)(N+3).
\]  

(4)

For example, if \( N=16 \) oscillator levels are involved in the vibrational basis the size the truncated vibronic matrix (without symmetry based simplifications) is rather large \( G(16) = 5814 \). As one can see from Table the symmetry adapted approach is advantageous and leads to an essential simplification of the computational problem by blocking the vibronic matrices accordingly to the irreps of the point group \( D_{4h} \). For instance, the maximal size of the vibronic matrix in this case is 1458 (for \( ^3E_u \)) which is more than three times less than the size of the full vibronic matrix. When \( N=20 \) vibrational levels are included the size is increased, \( G(20) = 10626 \), and the problem becomes more complex. From Table one can see again that the use of symmetry simplifies the solution and at the same time the advantages of the approach are more pronounced. In fact, the maximal size of the sub-matrix is 2662 (for \( ^3E_u \)) which is approximately four times smaller than the size of the initial matrix.

This choice of the basis \( N=16 \) can ensure a reasonable accuracy in the description of the vibronic levels required for the adequate evaluation of the profiles of the intervalence optical bands in the system under consideration. Some examples of the intervalence absorption bands are given in Fig. 4 providing \( t_d = 0 \) for the cases of the typical values of the transfer parameters \( t_n = -500 cm^{-1} \) and \( t_n = -2000 cm^{-1} \) (temperature \( T = 2K \)). It is assumed that we are dealing with the case of intermediate coupling \( \nu = 1200 cm^{-1} \equiv 2\hbar \omega \). Occurrence of the structureless intervalence bands in mixed valence compounds reflects mainly the effects of the dispersion of the active modes in crystals (or polarization of solution) and also the broadening of the discrete lines due to relaxation processes. For this reason in Fig. 4 we do not show the palisade of the discrete lines corresponding to the individual transitions and present only enveloping curves. To obtain the enveloping curves the shapes of the individual lines are assumed to be Gaussians \( \left(2\pi\sigma^2\right)^{-1/2}\exp\left(-x^2/2\sigma^2\right) \) with the broadening parameter \( \sigma = 0.4\hbar \omega \). This smoothing procedure hides the individual lines but keeps
the general structure of the band as shown in Fig. 4. It is to be noted that the justification of the procedure of the transformation of the discrete spectral distribution into the continuous one (in order to get experimentally observed enveloping curve) is not trivial. This question is discussed in Ref. [7] where the additional interaction with the acoustic phonons (along with the coupling with the local vibration) has been assumed to lead to the smoothed absorption band. The optical profiles of the whole bands (obtained in the framework of the simplest Gaussian broadening model) have complicated structure and they are far from being Gaussians. Providing relatively weak transfer $t_n = -500\,\text{cm}^{-1}$ the band is strongly asymmetric with a long high frequency structured shoulder and abrupt low energy part. There is a similarity between this band that in the dimers. In the case of relatively strong transfer $t_n = -2000\,\text{cm}^{-1}$ the band is asymmetric and double headed that is similar to the $A \rightarrow E(e)$ bands in the JT centers with cubic and trigonal symmetry. A more detailed analysis of the vibronic spectra and intervalence optical absorption along with the question about the relevance of the present theory to the experiment will be given elsewhere. We will also analyze the conditions (localization degrees) under which the complexes can be used as quantum-dot cellular automata.

**ACKNOWLEDGMENTS**

B.T. acknowledges financial support of the Israel Science Foundation (ISF, grant no. 168/09). B.T and A.P. and. are grateful to COST Action CM1203 “Polyoxometalate Chemistry for molecular Nanoscience (PoCheMon)” for supporting this work. E.C. and J.M.C-J thank EU (Project ELFOS and ERC Advanced Grant SPINMOL), the Spanish MINECO (grants MAT2011-22785, the CONSOLIDER project on Molecular Nanoscience), and the Generalidad Valenciana (Prometeo and ISIC Programmes of excellence) for the financial support of this work. A.P. acknowledges the University of Valencia for a visiting research grant and the Supreme Council for Science and Technological Development of the Republic of Moldova (project 11.817.05.03A) for financial support.
REFERENCES