VIBRONIC MODEL FOR LINEAR MIXED VALENCE TRIFERROCENIUM COMPLEX: ELECTRIC FIELD CONTROL OF SUPEREXCHANGE

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ABSTRACT

We develop a vibronic model for the electric field control of antiferromagnetic superexchange in mixed valence (MV) triferrocenium complex FeIII-FeII-FeIII proposed as possible candidate for the molecular implementation of quantum logic gate. Along with the electronic interactions such as electron transfer between the iron ions in different oxidation degrees and Coulomb repulsion of the extra holes, the proposed model of triferrocenium complex also takes into account the vibronic coupling as an inherent ingredient of the problem of mixed valency. The vibronic coupling is shown to play a key role in the degree of localization of the two holes among the three iron centers. This is shown to produce a pronounce influence on the electric field dependences the electronic density distributions and electrically switchable magnetic exchange in the considered linear triferrocenium complex.

1. INTRODUCTION

Responsive molecular materials whose properties can be tuned by applying different external stimuli, are of growing interest due to their important potential applications. Relevant examples of such materials in molecular magnetism are exemplified by spin-crossover [1] and bimetallic cyanide complexes [2] in which temperature, light or pressure can be used to control the spin states. Besides these stimuli, electric field or electric current can also be used to control the magnetic properties of some classes of systems admitting magnetoelectrical effects [3], [4]. It is to be noted in this context that the use of an electric field provides important advantages over the usage of the magnetic field [5], namely, an electric field can be easily obtained by means of gates or STM-tips, which provide a possibility of fast (picosecond) switching and selective addressing a single molecule.

The electric control of the spin states in single molecules is a topic of current interest in molecular spintronics [6]. Several classes of magnetic molecular systems have been proposed as electrically switchable systems [6-8]. Although the above mechanisms of the spin-switching in MV molecules are quite different in their nature, their common feature is that the applied electric field polarizes the itinerant electrons leading to a redistribution of its electronic density and thus causing a significant change in degree of delocalization. This modifies in its turn the magnetic properties, so the mentioned MV molecules exhibit magnetoelectrical effect peculiar to
multiferroics and, therefore, these systems can be regarded as single-molecule analogs of multiferroics [7b].

Besides the electronic and structural factors (electronic configurations, topology of the complexes, values of the electron transfer and exchange parameters, Coulomb repulsion energies, etc.), vibronic coupling plays a crucial role in the spin switching properties of MV molecules. Particularly, the interaction of the mobile electrons with the molecular vibrations tends to create a barrier for the tunneling which reduces the mobility of the electrons producing thus the self-trapping effect [9]. This means that the vibronic coupling can significantly change the electronic polarizability of the MV complexes and, thus, the spin-switching properties of such systems. In spite of the importance of the vibronic coupling in MV systems, which has been conceptually understood long time ago [9], this interaction has been often ignored [7c, 7e, 7f, 7j] mainly due difficulties in consideration of complex large scale MV systems. From this point of view modelling of relatively simple switchable MV systems admitting the precise solution of the vibronic problem is quite attractive as it provides a clear insight on the role of the vibronic coupling in the electric field control of the magnetic properties of such molecules.

The electronic model for the above mentioned electrically switchable molecule represented by the linear triferoceinium MV complex have been proposed in Ref. [7j]. Particularly, it has been indicated that such complex can be regarded as a molecular (chemical) implementation of “physical” trimeric two-electron linear molecules composed of quantum dots [10], which are of current interest due to their importance in quantum computing. Here in order to understand the mechanism of spin-switching caused by the electric field more in depth we develop a vibronic model of such triferoceinium complex.

2. THE MODEL FOR MIXED VALENCE TRIFEROCEINUM COMPLEX

The molecular structure of the MV triferoceinium complex in which three iron ions have linear disposition (in this sense we will refer them as linear trimers) is schematically shown in Figure 1a. The molecule includes two low-spin Fe\(^{\text{III}}\) ions each having spin \(S=1/2\) and one low-spin Fe\(^{\text{II}}\) ion that is diamagnetic. Such system possesses the electronic configuration \(d^5-d^6-d^5\) that is equivalent to the hole configuration \(d^1-d^0-d^1\) in the linear complex. For the sake of simplicity, the following discussion will be given in terms of hole configurations. We assume that each site in MV triferoceinium complex has a non-degenerate orbital (\(\varphi_1, \varphi_2, \varphi_3\)) which can accommodate one or two holes.

The model of the system takes into account the following basic interactions: 1) the Coulomb repulsion between the two holes shared among the three sites; 2) the hole transfer between the neighboring iron ions; 3) the interaction between the itinerant holes and external electric field; 4) the coupling between the holes and the molecular vibrations that is vibronic coupling. The first three ingredients can referred to as the electronic interactions.

1. *The Coulomb repulsion* tends to separate from each other the two extra holes and so the configuration \(d^1_1-d^2_2-d^1_3\) with the two holes localized on the terminal iron sites 1 and 3 and the empty central iron site 2 can be associated with the ground state of the complex as shown in Figure 1a. The double degenerate state in which the two holes occupy nearest neighboring positions (configurations \(d^1_1-d^2_2-d^1_3\) and \(d^0_1-d^1_2-d^1_3\)) is located above and separated from the ground level by the gap \(\delta\) which is approximately equal to the Coulomb repulsion energy for the neighboring
sites (see Figure 1b). The orbital schemes illustrating the distributions of the holes in different possible one-electron configurations and the corresponding Coulombic gaps are shown in Figure 2. For the sake of simplicity in the definition of the gap $\delta$ we have neglected the difference in the orbital energies of the holes on the terminal and central ions. The highest excited state of the complex corresponds to fully polarized hole configurations $d^2_1 - d^0_2 - d^0_3$, $d^0_1 - d^0_2 - d^2_3$, and $d^0_1 - d^2_2 - d^0_3$ which are separated from the ground state by the gap $U$, which can be estimated as the energy of Coulomb repulsion of the two holes occupying the same iron site. Such approximate consideration neglects the Coulomb energy for the ground $d^1_1 - d^1_2 - d^1_3$ configuration as compared with the on-site Coulomb energy $U$, as well as the difference in energies of the three fully polarized hole configurations which is also much smaller than $U$ (under the later assumption the highest excited level in Figures 1b and 2 is triply degenerate).

![Figure 1. Structure of linear triferrocenium MV complex (a); energy levels arising from the Coulomb repulsion of the mobile holes in the linear array (b).](image)

2. The electron (hole) transfer between the nearest neighboring iron sites switches the system between different localized configurations or, in other words, gives rise to mixing of the ground $d^1_1 - d^0_2 - d^0_3$ hole configuration with the excited $d^1_1 - d^1_2 - d^0_3$ and $d^0_1 - d^1_2 - d^1_3$ ones and also to mixing of these two configurations with the highest excited configurations involving doubly occupied iron sites. Such hole transfer is described by the transfer parameter $t = t_{ij} = t_{ji}$, along with the three above mentioned electronic interactions the electronic Hamiltonian includes the interaction of the trimer with the external electric field directed along the $Z$ axis of the linear molecule (Figure 1a). The measure of this interaction is the Stark energy $W = e F a$, where $a$ is the distance between the nearest iron sites, $F \equiv F_z$ is the projection of the electric field on the $Z$-axis, and $e$ is the hole charge. For the shortest Fe···Fe distance $a = 6.8$ Å (typical for such kind of complexes) the Stark energy $W = 3000$ cm$^{-1}$ corresponds to the electric field $F = 5.5 \times 10^6$ V/cm $= 0.055$ V/Å. This estimation shows that this strength of the field is rather strong but attainable and this value of $W$ falls into the scale for characteristic energies.

Let us denote the spin-function of the system as $\psi_{ij}(S)$ where $i$ and $j$ indicate the two iron sites populated by the holes as shown in Figures 1 and 2. In compliance
with the Pauli principle the two extra holes shared among three sites give rise to the three spin-triplets $\psi_{ij} (S = 1, M_S)$ with $i \neq j$ (singly occupied sites) and six spin-singlet states $\psi_{ij} (S = 0)$ with both $i \neq j$ and $i = j$ (doubly occupied sites). Using these states as a basis and taking into account that the above described interactions are independent of spin projection, one can define the matrix representation of the electronic Hamiltonian of the complex. Here we omit the details of calculations.

3. The vibronic coupling will be treated in the framework of the Piepho-Krausz-Shatz (PKS) model [9, 11]. The model assumes that the extra hole occupying a non-degenerate orbital located at the site $i$ interacts with the full-symmetric ("breathing")

![Figure 2. Orbital scheme for the triferrocenium complex indicating the hole populations.](image)

displacements $q_i$ of the first coordination sphere of this site. The coupling parameter $\nu_i$ and frequencies $\omega_i$ for all redox sites are equal and will be denoted as $\nu$ and $\omega$. We will use the dimensionless vibrational coordinates $q_i$. The free harmonic vibrations are described by:

$$H_\omega = \frac{\hbar \omega}{2} \sum_{i=1}^{3} \left( q_i^2 - \frac{\partial^2}{\partial q_i^2} \right),$$

(3)

A partial contribution to the total coupling from the hole localized at a certain site $i$ (i.e. occupying orbital $\varphi_i$) can be expressed as $\langle \varphi_i | \hat{V} | \varphi_i \rangle = \nu q_i$. The matrix of the vibronic interaction is diagonal within the basis functions $\psi_{ij}(S)$:

$$\langle \psi_{ij}(S) | \hat{V} | \psi_{ij}(S) \rangle = \nu (q_i + q_j).$$

(4)

The new collective non-symmetric coordinates are found as:

$$q_g = \frac{1}{\sqrt{6}} (2q_2 - q_1 - q_3), \quad q_u = \frac{1}{\sqrt{2}} (q_1 - q_3).$$

(5)

The occurrence of the two active modes is peculiar for the trimeric systems [11], which distinguish them from the basic dimeric MV clusters in which the only antisymmetric PKS mode is active in the transfer processes [9].

3. THE ELECTRONIC ENERGY PATTERN OF TRIFERROCENIUM COMPLEX
The electronic energy levels of the system are the eigen-values of the matrices of the full electronic Hamiltonian. Throughout the paper we will use the same set of the electronic parameters as in Ref. [7] dealing with the electronic model of triferoceenium complex: $\delta \approx 0.12 \text{ eV} \approx 968 \text{ cm}^{-1}$ [13a], $t \approx 50 \text{ meV} \approx 400 \text{ cm}^{-1}$ [13b], $U \approx 4 \text{ eV} \approx 32000 \text{ cm}^{-1}$ [13c]. An example which allows to reveal the main features of the energy pattern is given in Figure 4 in which the above mentioned numerical values of the parameters are used. One can see that the first order transfer processes shift and split the two Coulomb energy levels (Figure 3a) corresponding to hole configurations in Figure 2 but are unable to discriminate spin-singlets and spin-triplets (Figure 3b). The degeneracy over full spin quantum number is removed by the second order transfer terms (Figure 3c), which thus lead to a long-range antiferromagnetic exchange coupling in linear three-site two-electron array of redox sites. The spin-dependent splitting of the ground manifold, which is one of the main feature of the energy pattern, can be described in terms of spin-1/2 operators $\hat{S}_1$ and $\hat{S}_3$ by the Heisenberg type exchange Hamiltonian: $\hat{H}_{\text{eff}} = -2J_{\text{eff}} \hat{S}_1 \cdot \hat{S}_3$, where $J_{\text{eff}}$ is the effective parameter of the antiferromagnetic exchange between the terminal iron ions. If the energy gap $\delta$ between the two isomers of triferoceenium complex strongly exceeds the transfer integral $t$ between the nearest neighboring iron sites ($\delta \gg t$), the effective transfer parameter $t_{13}$ between the two terminal sites 1 and 3 is given by the second order expression $t_{13} = -t_{12}t_{23}/\delta = -t^2/\delta$ and hence the parameter $J_{\text{eff}}$ is given by the approximate fourth-order expression $J_{\text{eff}} \approx -t_{13}^2/U \approx -2t^4/(U\delta^2)$. One can see that the combined action of the hole transfer between the redox sites and on-site and intersite Coulomb repulsion between the two holes results in the long-range antiferromagnetic kinetic superexchange (by analogy with the Anderson’s mechanism) mediated by the virtual hole transfer.

![Figure 3. Low-lying energy levels (in cm$^{-1}$) of triferoceenium complex evaluated with allowance for the Coulomb repulsion (a), Coulomb repulsion and first order transfer (b), Coulomb repulsion, first and second order transfer (c). Only the main interconnections between the levels in the cases (a), (b) and (c) are indicated.](image)

The electric field has been shown [7] to result in the considerable enhancement of the antiferromagnetic exchange interaction between the two hole spins due to the field induced redistribution of the hole density resulting in the transformation of the isomeric forms $\text{Fe}^{III}-\text{Fe}^{II}-\text{Fe}^{III} \leftrightarrow \text{Fe}^{III}-\text{Fe}^{III}-\text{Fe}^{II}$ and, as a result, to the transition from
the case of weak next-neighbors superexchange to the case of much stronger exchange coupling between the nearest iron ions. The value \( W = \delta = 968 \text{ cm}^{-1} \) corresponds to the field of \( 1.8 \times 10^6 \text{ V/cm} \), so that an attainable field can produce significant effect on the energies of the holes. Thus, if the electric field is strong enough \((\delta, t << W << U)\) to overcome the difference in energies of two isomers, it can stabilize the isomeric form Fe\textsuperscript{III}-Fe\textsuperscript{III}-Fe\textsuperscript{II}. Applying perturbation theory, one can show that the effective exchange parameter can be expressed as \( J_{\text{eff}}(W \gg \delta) = -\frac{2t^2}{U} \). The value \( J_{\text{eff}}(W \gg \delta) \) represents the parameter of the kinetic exchange between the nearest neighboring holes which apparently strongly exceeds the parameter \( J_{\text{eff}} \) for the long range superexchange in the absence of the field. It is to be noted that in the case of triferrocenium complex the inequality \( \delta >> t \) does not hold and the approximate expression for zero field parameter \( J_{\text{eff}} \) is given here only to demonstrate the physical origin of the long range superexchange. The exact expressions (in the framework of the adapted model) can be obtained by the diagonalization of the energy matrices. The above expression represents a rather good approximation for the Stark energy within the range \( \delta << W << U \). Being purely electronic in its nature the approach proposed in Ref. [7j] neglects the vibronic coupling which, in general, cannot be regarded as weak interaction in majority of MV compounds.

4. VIBRONIC APPROACH: POTENTIAL SURFACES AND HOLE LOCALIZATION

We will first consider the vibronic effects within the frame of the semiclassical adiabatic approximation. For the numerical estimation, the above mentioned set of the electronic parameters will be used. For the vibrational quantum we will use a typical value \( \hbar \omega = 200 \text{ cm}^{-1} \) and the parameter \( \nu \) will be varied in the subsequent analysis. The lowest sheet of the adiabatic surface with \( S=0 \) calculated at zero electric field is represented in Figure 4 by the contour plots and some characteristic vertical sections. Inspecting the contour plots in Figures 4a and c one can distinguish the two qualitatively different cases of potential surfaces. Providing relatively weak (or moderate) vibronic coupling \( \nu = 3\hbar \omega = 600 \text{ cm}^{-1} \) the lower sheet of the surface possesses the only minimum (Figures 5a), while in the case of a strong coupling \( (\nu = 7.5\hbar \omega = 1500 \text{ cm}^{-1}) \) the lower sheet exhibits three deep minima (Figures 4c).

The only minimum in the case of moderate coupling \( (\nu = 3\hbar \omega) \) is located at the point \( q_g^{\min} = 2.3, \quad q_u^{\min} = 0 \). The adiabatic potential surface near the minimum exhibits two gentle slopes which are symmetric with respect to the mirror plane passing through the axis \( q_u = 0 \). The vertical section of the adiabatic surface along the line passing through the minimum and one of the slope is shown in Figure 4b. It is seen that the minimum near which the system performs harmonic oscillations is deep enough (approximately \( 2\hbar \omega \)) to confine the configurations of the system to the vicinity of this minimum, and therefore, to interrelate the physically justified electronic densities with the adiabatic wave functions evaluated at the minimum point. Inspection of the wave-function in the point of minimum shows that \( \psi_{13}(0) \) produces a dominant contribution to the full wave-function indicating that in this minimum the two holes are mainly localized on the two terminal sites. In this minimum the molecule in distorted along the vibrational coordinate \( q_g \), which corresponds to the
compression of ligand surrounding of the sites 1 and 3 and expansion surrounding of the first coordination sphere of the site 2.

The three minima (Figure 4c) in the case of strong vibronic coupling are inequivalent in energy. The deeper minimum corresponds to the configuration in which the two holes are mostly located on the terminal sites, while the two equivalent in energy shallow minima correspond to $d_1^1 - d_2^1 - d_3^0$ and $d_1^0 - d_2^1 - d_3^1$ configurations. The shape of the potential surface is also illustrated by the two characteristic sections, along the line connecting deep and shallow minima (Figure 4a) and along the line connecting two equivalent shallow minima (Figure 4e). In both sections the maxima of the curves approximately correspond to the saddle-points of the low sheet of the bi-dimensional potential surface. The image of the potential surface qualitatively demonstrates that in the case of strong vibronic coupling the transfer processes are strongly quenched in such a way that the system predominantly resides in localized configurations performing slow tunneling between them. At the same time the

![Figure 4. Adiabatic surfaces of the triferrocenium complex: countour plot in the case of weak vibronic coupling (a), vertical section passing through the minimum and one of the slopes in the case of weak vibronic coupling (b); countour plot in case of strong vibronic coupling (c); countour plot in the case of strong vibronic coupling (d); countour plot in the case of strong vibronic coupling (e).](image-url)
vibronic coupling (c) and two sections (see text) in the case of strong vibronic coupling (d and e). The cases of weak (moderate) and strong vibronic coupling are defined by the parameters $\nu = 3\hbar\omega = 600 \text{ cm}^{-1}$ and $\nu = 7.5\hbar\omega = 1500 \text{ cm}^{-1}$ respectively.

Coulomb repulsion proves to be unquenched so that the difference in energies between deeper minimum ($d_{1}^0 - d_{2}^0 - d_{3}^0$) and two shallow ones ($d_{1}^1 - d_{2}^1 - d_{3}^1$ and $d_{1}^0 - d_{2}^1 - d_{3}^1$) remains approximately equal to the same value $\delta$ as in electronic energy pattern.

Finally, considering the case of strong vibronic coupling it is worth to underline a pivotal role of the vibronic coupling in the insight at the localization of the itinerant holes. In fact, the two configurations $d_{1}^1 - d_{2}^1 - d_{3}^0$ and $d_{1}^0 - d_{2}^1 - d_{3}^1$ in the electronic problem give rise to a doubly degenerate level for each spin (that are the energies evaluated at the symmetric reference configuration of the atoms) and therefore the transitions between these two configurations are barrierless. On the contrary, the vibronic interaction leads to the self-trapping of these configurations which are separated by a potential barrier (Figure 4e) and therefore become physically localized. In the electronic pattern the two configurations $d_{1}^1 - d_{2}^1 - d_{3}^0$ and $d_{1}^0 - d_{2}^1 - d_{3}^1$ are separated by the Coulomb gap $\delta$ from the ground one $d_{1}^1 - d_{2}^1 - d_{3}^1$. Although these configurations are different in energy, the excitation is barrierless. In contrast, in the presence of the vibronic coupling the thermal excitation energy exceeds the Coulomb gap $\delta$ due to the potential barrier as shown in the section connecting the corresponding minima of the adiabatic surface (Figure 4d). Now the energy, which is approximately the gap between the minima, defines the equilibrium Boltzmann population in the system relaxed to the minima. An essential physical difference in the character of the localization between the cases of moderate and strong vibronic coupling should be emphasized. While in the last case all three low lying hole configurations are separated by the potential barriers (Figures 4a-c), in the former case the transition between the two neighboring configurations is barrierless because the system possesses one potential minimum only (Figures 4a,b).

5. ELECTRIC FIELD EFFECTS WITHIN THE ADIABATIC APPROACH

When considering the influence of an external field, we restrict ourselves to the case of a moderate vibronic coupling assuming that $\nu = 3\hbar\omega = 600 \text{ cm}^{-1}$. Figure 6 shows the evolution of the lowest adiabatic potential surface having $S=0$ with the increase of the Stark energy $W$. External electric field leads to the shift of this minimum towards the slope and also to the appearance of the second (excited) minimum disposed on one or another slope depending on whether the electric field is parallel or antiparallel to the Z-axis of the complex. At relatively weak electric field this additional minimum is much shallower than the main minimum (Figure 5a). The wave-function in this shallow minimum corresponds to the presumable localization of the two holes in nearest neighbor sites. The further increase of the Stark energy results in stabilization of the excited minimum with respect to the ground one (Figures 5c, d) accompanied with the decrease of the weight of the state $\psi_{13}(0)$ in the ground minimum and increase of the weight of the state $\psi_{12}(0)$ in the excited minimum. At some critical value of the Stark energy (that is around 990 cm$^{-1}$) the two minima become equivalent which corresponds to the coexistence of the $\{1,3\}$ and
\( \{1,2\} \) localizations of the two holes. After this value of the Stark energy the first minimum corresponding to the presumable localization of the two holes on the remote sites 1 and 3 becomes excited, while the second minimum in which the two holes occupy the nearest neighboring positions 1 and 2 becomes the ground one (see Figure 5d). Further increase of the electric field leads to the stabilization of the second minimum with respect to the ground one (Figure 5e) and finally, at strong enough field the first minimum disappears, while in the second minimum the two holes are almost fully localized on the sites 1 and 2 (Figure 5f). Therefore, Figure 5 show the variation of the adiabatic potential surface accompanying the field induced transformation from the isomer Fe\(^{\text{III}}\)-Fe\(^{\text{II}}\)-Fe\(^{\text{III}}\) to the isomer Fe\(^{\text{III}}\)-Fe\(^{\text{III}}\)-Fe\(^{\text{II}}\). It is to be noted that the critical value of the Stark energy at which the two minima becomes energetically equivalent proves to be slightly larger than the gap \( \delta \) because of the electron delocalization which hinders the transition between the two isomers.

Figure 5. Contour plots of the lowest adiabatic potential surface with \( S = 0 \) calculated at \( \nu = 600 \text{ cm}^{-1} \) and: \( W = 600 \text{ cm}^{-1} \) (a), \( 968 \text{ cm}^{-1} \) (b), \( 980 \text{ cm}^{-1} \) (c),
The analysis of the coordinates of the minima shows that in all cases they lie on the approximately straight line described by the equation \( q_u = 0.591 q_g - 1.397 \). The sections of the adiabatic potential surface along this line clearly display the above described evolution of the minima with the change of the electric field. The plots of these sections at the same values of \( W \) as in Figure 5 are shown in Figure 6. One can see that the increase of the electric field changes the shape of the adiabatic potential from the single well one (case of small \( W \)) to that having two non-equivalent minima, namely, right deep minimum and left shallow minimum. These minima are being equalized until they become energetically equivalent at some critical value of the Stark energy. The further increase of the field leads to the reversed energy gap between the two minima (right shallow minimum and left deep minimum) which increases when the electric field is enhanced until the right shallow minimum disappears.

**6. SUMMARY OF THE RESULTS**

In this article we have developed a vibronic model for a linear MV triferrocenium complex \( \text{Fe}^{III}-\text{Fe}^{II}-\text{Fe}^{III} \) proposed as possible candidate for the molecular...
implementation of quantum logic gate and magnetic switching system. The model takes into account the following electronic interactions and corresponding parameters underlying the vibronic problem: hole transfer (parameter $t$) between the iron ions in different oxidation degrees, difference in energies (gap $\delta$) of two isomeric forms $\text{Fe}^{\text{III}}$-$\text{Fe}^{\text{II}}$-$\text{Fe}^{\text{III}}$ and $\text{Fe}^{\text{III}}$-$\text{Fe}^{\text{III}}$-$\text{Fe}^{\text{II}}$ arising mainly from the Coulomb repulsion of the extra holes in nearest neighboring types of hole localizations $d_{1}^{0}-d_{2}^{0}-d_{3}^{0}$, $d_{1}^{0}-d_{2}^{1}-d_{3}^{1}$ and also on-site Coulomb energy (parameter $U$) for fully polarized configurations $d_{1}^{1}-d_{2}^{0}-d_{3}^{0}$, $d_{1}^{0}-d_{2}^{1}-d_{3}^{2}$, $d_{1}^{0}-d_{2}^{0}-d_{3}^{1}$.

The vibronic coupling (parameter $\nu$ which has been regarded as the adjustable parameter of the theory because no value of this parameter is available) and free harmonic vibrations has been taken into account within the PKS model adapted to the linear trimeric $\text{Fe}^{\text{III}}$-$\text{Fe}^{\text{II}}$-$\text{Fe}^{\text{III}}$ MV system. The bi-dimensional vibronic problem has then been treated both within the adiabatic approximation and in the framework of a more precise comprehensive quantum-mechanical approach. The main effects of the vibronic coupling are summarized below:

First, it has been demonstrated that depending on the relative strength of the vibronic coupling and the hole transfer, the system can possess two qualitatively different types of the adiabatic potential surfaces. Thus, in the case of moderate or weak vibronic coupling and zero electric field the lower sheet of the potential surface with $S=0$ has been shown to possess a single minimum that corresponds to the most favorable Coulomb configuration of the two holes, which in this case are predominantly localized at the terminal ferrocenium sites. In the case of strong vibronic coupling the lower sheet of the adiabatic surface at zero field has three minima, one of which is deeper than the remaining two energetically equivalent minima. Evaluated hole distributions in the minima evidence that the low-lying minimum corresponds to the prevailing $\text{Fe}^{\text{III}}$-$\text{Fe}^{\text{II}}$-$\text{Fe}^{\text{III}}$ configuration, while in the remaining excited equivalent shallow minima the two holes are mostly localized at the neighboring sites. Electric field considerably changes the picture of the adiabatic potential surfaces leading to the appearance (in case of weak vibronic coupling) and stabilization (in cases of both weak and strong vibronic interaction) of the excited minimum corresponding to nearest neighbor disposition of the two holes. The increase of the electric field tends to equalize the energies of the two minima until at some critical value of the electric field the minimum with nearest neighbor disposition becomes the ground one. This corresponds to the transition between the two isomeric forms induced by the electric field.

Second, the examination of the difference in energies of the minima of the lowest surfaces with $S=0$ and $S=1$ found from the semiclassical adiabatic approach and also the energy gap between the lowest spin-vibronic levels with $S=0$ and $S=1$ found from the numerical solution of the dynamic vibronic problems led us to conclude that the vibronic coupling results in the JT/pseudo JT reduction of the antiferromagnetic exchange coupling between the remote $\text{Fe}^{\text{III}}$ sites.

Third, the vibronic coupling has been shown to play a crucial role in the efficiency of the electric field control of the antiferromagnetic exchange and magnetic properties of the triferrocenium complex. Thus, vibronic coupling has been shown to produce a significant effect on the field induced stepwise transformation $\text{Fe}^{\text{III}}$-$\text{Fe}^{\text{II}}$-$\text{Fe}^{\text{III}} \leftrightarrow \text{Fe}^{\text{III}}$-$\text{Fe}^{\text{III}}$-$\text{Fe}^{\text{II}}$ increasing the abruptness of the field dependences of singlet-triplet gap and the hole densities which are of primary importance when considering the molecule as a magnetically switchable system. Finally, providing strong vibronic coupling the efficiency of the electric field control of the magnetic properties is
shown to be significantly increased even in spite of the fact that in this case such control is possible in a narrower range of the electric field strengths. This result is of primary importance while considering the molecule as a magnetically switchable system.

The results so far discussed are based on the parametric electronic and vibronic Hamiltonians containing a set of the adjustable parameters whose values are estimated from the previous studies of triferrocenium complexes. For the further progress in the study of this system it would be desirable independent ab initio evaluation of the key parameters. The current state of the theoretical approaches for the evaluation of the electronic and vibronic parameters is given in the review articles [15] and [16].

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