VIBRONIC MODEL FOR INTERCOMMUNICATION OF LOCALIZED SPINS VIA ITINERANT ELECTRON IN COMPLEX MIXED-VALENCE MOLECULES

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ABSTRACT

Here we propose a vibronic pseudo Jahn-Teller (JT) model for partially delocalized mixed valence (MV) molecules aimed to the description of the magnetic coupling between the localized spins mediated by the delocalized electron. The model involves the following key interactions: electron transfer in the spin-delocalized subsystem which is mimicked by a dimeric unit, coupling of the itinerant electrons with the molecular vibrations and isotropic magnetic exchange between the localized spins and delocalized electron. The pseudo JT vibronic coupling which is considered in the framework of the Piepho, Krausz and Schatz (PKS) model adapted to the case of partially delocalized MV molecules. It is revealed (qualitatively and quantitively) how the vibronic coupling affects the connection of the localized spins via the itinerant electron.

1. INTRODUCTION

In this article we focus on the magnetic MV clusters[1-13] in which localized spins are magnetically coupled through the spin-delocalized subsystem. Some examples of such partially delocalized inorganic MV molecules are provided by the reduced polyoxometalates (POMs) comprising mobile electrons interacting with the spin-localized subsystem.[12-16] Such molecular systems can be exemplified by the POMs $[PMo^{VI}_{11}Mo^{V}O_{40}(VO)_2]$ and $[PMo^{VI}_{11}Mo^{V}O_{40}\{Ni(phen)_2(H_2O)\}_2]$ in which the direct magnetic coupling between the two hosted remote V^{IV} ions (localized spins S=1/2) or two Ni^{II} ions (localized spins S=1) is constrained because of very large distances between the metal centers. At the same time the indirect coupling takes effect due to the presence of the extra electron delocalized over the central Keggin anion core,[12-13] which gives rise to a long-range interaction between the localized spins mediated by the mobile electron. One can also mention the tetranuclear valence-delocalized iron core coupled to the four outer localized spins of iron ions. [17-22] and multispin organic systems, which are of current interest in molecular spintronics. [23-32] Finally, some aggregate composed of quantum dots (which can be referred to as "physical molecules") accommodating different specific numbers of unpaired electrons can be also regarded as physical analogs of partially delocalized MV clusters.

The simplified recently proposed "toy" model[33] includes the electron transfer between the two metal centers of the central dimer and the exchange coupling

between the mobile electron and the outer spins. These two interactions was shown to result in spin-polarization mechanism that is similar to the double exchange (DE) [34,35]. According to this mechanism the spin of the excess electron is coupled via strong intra-center ferromagnetic Hund type exchange interaction with the spins of paramagnetic ions (spin cores), thus aligning them parallel to the spin of the mobile electron. Since the intra-ionic exchange produces the coupling of the spin of the extra electron and the spin-core belonging to the same metal ion, the spin-cores involved in the conventional DE can be also termed "internal spin cores". To distinguish this spin-polarization mechanism from the conventional DE mechanism we suggested to term it "external core double exchange" (ECDE). The two mentioned two spin-polarization mechanisms have at least two important differences features. *First*, as distinguished from the Hund-type intra-center exchange between the extra electron and the internal spin core that is always ferromagnetic, the inter-center exchange between the extra electron and the alien spin core can be either ferro- or antiferromagnetic . *Second*, is a rather strong mixing of Hund and non-Hund configurations.

A significant physical restriction of the toy model developed in Ref [33] is that this model involves only the electronic interactions. Meanwhile the vibronic coupling is known to reprsent an inherent ingredient of the description of the properties of MV systems [36-41] because it tends to create a barrier for tunneling of the extra electron. To overcome these limitations of the electronic model here we describe the vibronic toy model of partially delocalized MV systems with ECDE.

2. HAMILTONIAN OF PARTIALLY-DELOCALIZED MIXED VALENCE MOLECULE

The main idea of the toy model is to imitate a complex multiroute spin-delocalized subsystem of partially delocalized MV molecule by a dimer in which the extra electron is delocalized over two spinless sites *B* and *C*, as schematically shown in Figure 1a. The localized spins S_A=S_D=S_0 occupy the two terminal positions *A* and *D* adjacent to the two sites *B* and *C* of the MV dimer. The Hamiltonian corresponding to the vibronic model is the following:

$$\hat{H} = \hat{H}_{tr} + \hat{H}_{ex} + \hat{H}_{vib} \equiv t \sum_{\sigma=\pm\frac{1}{2}} (\hat{c}^{+}_{B\sigma}\hat{c}_{C\sigma} + \hat{c}^{+}_{C\sigma}\hat{c}_{B\sigma}) \pm 2J\left(\hat{n}_B\hat{S}_A\hat{s}_B + \hat{n}_C\hat{S}_D\hat{s}_C\right)$$

$$+ \frac{\omega}{2}\left(q^2 - \frac{\partial^2}{\partial q^2}\right) + vq\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}. \quad (1)$$

The term $\hat{H}_{tr}$ represents the one-electron transfer over two orbitals φ_B and φ_C located on the sites *B* and *C* of the MV dimer, where $\hat{c}^{+}_{i\sigma}$ and $\hat{c}_{i\sigma}$ are the creation and annihilation operators, $t \equiv t_{BC}$ is the transfer integral which is assumed to effectively incorporate all multiroute transfer pathways in real complex systems. Figure 1a illustrates the transfer processes in the dimeric *B*-*C* subunit of the system.

The term $\hat{H}_{ex}$ describes exchange coupling between the localized spins S_A and S_D and the spin of the mobile electron, $s_B = 1/2$ and $s_C = 1/2$, $S_A = S_D \equiv S_0$, $\hat{n}_B$ and $\hat{n}_C$ are the operators of the site populations, $\hat{n}_B + \hat{n}_C = 1$. HDVV coupling gives rise to the two spin states for each localization, $S_{AB} \equiv S^* = S_0 \pm 1/2$ for the *A*-*B* pair and $S_{CD} \equiv S^* = S_0 \pm 1/2$ for the *C*-*D* pair. The two states with maximal spin $S^* = S_0 + 1/2$

appear when the itinerant electron instantly residing at the sites *B* and *C* is coupled ferromagnetically. These states can be referred as Hund type states. Alternatively, the case of antiferromagnetic coupling, $S^* = S_0 - 1/2$, corresponds to the non-Hund states for the *C*-*D* pair.

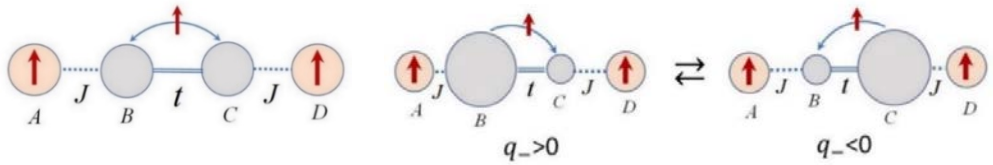


Figure 1. The model spin sites in partially delocalized system: *B*-*C*-unit-MV dimer separating two localized spins *A* and *D* (left); image of the out-of-phase PKS vibration q_-. Expanded and compressed (as compare to their average sizes, left) sites are denoted by the enlarged and decreased balls (right).

The vibronic coupling in the PKS model [36-39] takes into account the interaction between the extra electron and the fully symmetric ("breathing") vibrations q_A and q_C of the ligand surroundings. Only the antisymmetric vibration $q_- = (1/\sqrt{2})(q_B - q_C)$, is interrelated with the electron transfer processes. The image of the "out-of-phase" vibration of spin-delocalized dimeric fragment is shown in Figure 1, right. Refinement of the PKS model with due account for displacements of the metal sites is given in [40,41], but here we will use the basic version in order to avoid excessive complications. In Eq. (1) the 3rd term is the Hamiltonian of the harmonic oscillator, $q_- \equiv q$ is the dimensionless coordinate of the active "out-of-phase" vibration, ω is the frequency, is the vibronic interaction ($\hat{H}_{ev}$) which is defined by the 2×2-matrix in the basis of the one-electron orbitals φ_B and φ_C of MV unit, v is the vibronic coupling parameter. Since the sign of v does not influence the physical results, for the sake of definiteness we assume that $v > 0$. PKS model is essentially simplified, but the most important issue, is that the PKS model is able to describe the main physical factor that determines the properties of MV compounds, namely, the barrier between localized configurations and degree of localization which is manifested in all physical properties of such type of compounds. Here we omit the details of the evaluation of the matrix elements of different part of the Hamiltonian.

3. GENERAL EXPRESSIONS FOR THE ADIABATIC ENERGIES

In the framework of PKS model the adiabatic potentials *U*(*q*), which can be associated with the energies of the system within the adiabatic approximation, can be found analytically. The final results of calculations are the following:

$$U_{\pm}\left(q,\ S^* = S_0 + \tfrac{1}{2}, S = S_{max} = 2S_0 + \tfrac{1}{2}\right) = \tfrac{1}{2}\omega\ q^2 - JS_0\ \pm\sqrt{v^2q^2 + t^2}\ ,$$

$$U^-_{\pm}(q, S < S_{max})$$

$$= \frac{1}{2}\left[\omega\ q^2 J \sqrt{J^2(2S_0+1)^2 + 4v^2q^2 + 4t^2 - 4J\sqrt{9\ v^2q^2 + t^2\left(S+\frac{1}{2}\right)^2}}\right]. \quad (2)$$

The superscripts "−" and "+" in $U^-_{\pm}$ and $U^+_{\pm}$ mean that the corresponding adiabatic levels originate from the non-Hund's and Hund's configurations, while the subscripts "$\pm$" denote the upper and lower branches for each pair of the levels with a certain spin *S*. The results can be illustrated by a particular case of $S_A = S_D = S_0 = 1$ which preserves all main features of the basic model. In Sections 4 and 5 we will

give a detailed analysis of the adiabatic potentials for the limiting cases of strong exchange coupling ($|J|>>|t|$) and strong electron transfer ($|J|<<|t|$) in order to reveal the physical roles of the vibronic interaction included in the generalized toy model.

4. STRONG EXCHANGE LIMIT WITHIN THE ADIABATIC PICTURE

The physical properties of the system are determined by the three parameters U, t and υ (and also $\hbar\omega$ which can be used as an energy unit to scale the parameters to the dimensionless values). We will consider the two limits having clear physical sense: (i) strong inter-atomic exchange, $|J|>>|t|$ and (ii) strong transfer, $|J|<<|t|$. We assume that the exchange is antiferromagnetic, $J < 0$, and $t > 0$. The electronic levels (eigenvalues of $\hat{H}_{tr} + \hat{H}_{ex}$) in these two limits [33] can be subdivided into two groups, namely, the exchange multiplets (separated by the gap $3|J|$) split by the transfer processes in the case (i), and the resonance multiplets (separated by the gap $2|t|$) split by the exchange coupling in the case (ii).

The manifestation of the ECDE can be illustrated by the series of the adiabatic potentials as shown in Figure 2 illustrating the strong exchange coupling limit. Simple visual expressions for the positions of the minima can be found in the strong exchange limit and also providing moderate vibronic coupling ($\upsilon/\hbar\omega < 3|J|$) when the two groups (Hund's and non-Hund's) of the adiabatic levels are well separated.

If the vibronic coupling is strong enough or/and the transfer parameter is relatively small, $\upsilon^2 > \hbar\omega\, t\,(2S+1)/6$, the adiabatic potential possesses two minima in which the mobile electron is mostly localized on the sites B and C, while in the opposite case of weak coupling/strong transfer the system preserves symmetric configuration and fully delocalized, $q_{min}(S) = 0$. The positions $q_{min}(S)$ as well as the conditions for localization are spin-dependent (which is a common consequence of the double exchange), so that the conditions of instability for $S = 1/2,\ 3/2$ and $5/2$ are $\upsilon^2 > \hbar\omega\, t\,/3$, $\upsilon^2 > 2\hbar\omega\, t\,/3$ and $\upsilon^2 > \hbar\omega\, t$ correspondingly. This instability can be referred to as spin-dependent pseudo JT effect which has been recognized in MV systems exhibiting DE (see [1, 2]). Since the vibronic coupling and electron transfer are competitive, the states with a larger spin are more stable with respect to nuclear reorganization to the self-consistent states or, in other words, less localized.

Providing weak coupling, $\upsilon = 0.6\,\hbar\omega$ (Figures 2a), the system is stable in the symmetric configuration for all spin states and consequently delocalized. In the case of the JT instability the energy levels of the system can also be associated with the minima of the adiabatic potentials, which give also a visual representation of the character and nature of localization of the mobile electron. In the case of intermediate (closer to weak) coupling $\upsilon = 1.1\hbar\omega$ (Figure 2b) the lower sheet of the adiabatic potentials possesses two shallow minima only for $S = 1/2$, while in the remaining spin states $(S > 1/2)$ the system is fully delocalized. This result remarkably demonstrates some of physical consequences of spin dependence of the degree of localization in the partially delocalized MV system comprising spin-delocalized unit.

With the further increase of the vibronic coupling from intermediate $\upsilon = 2.2\hbar\omega$ to strong $\upsilon = 4.0\hbar\omega$ (Figures 3c to 3f) the lower branches of the adiabatic curves acquire distinct minima of the increasing depth. The two peculiarities of this transformation are to be mentioned. The gap between the low lying $S = 1/2$ and $3/2$ levels in the minima point decreases with the increase of υ , so that finally in the limit of strong vibronic coupling these two levels become degenerate. Further increase of the vibronic coupling results in an usual

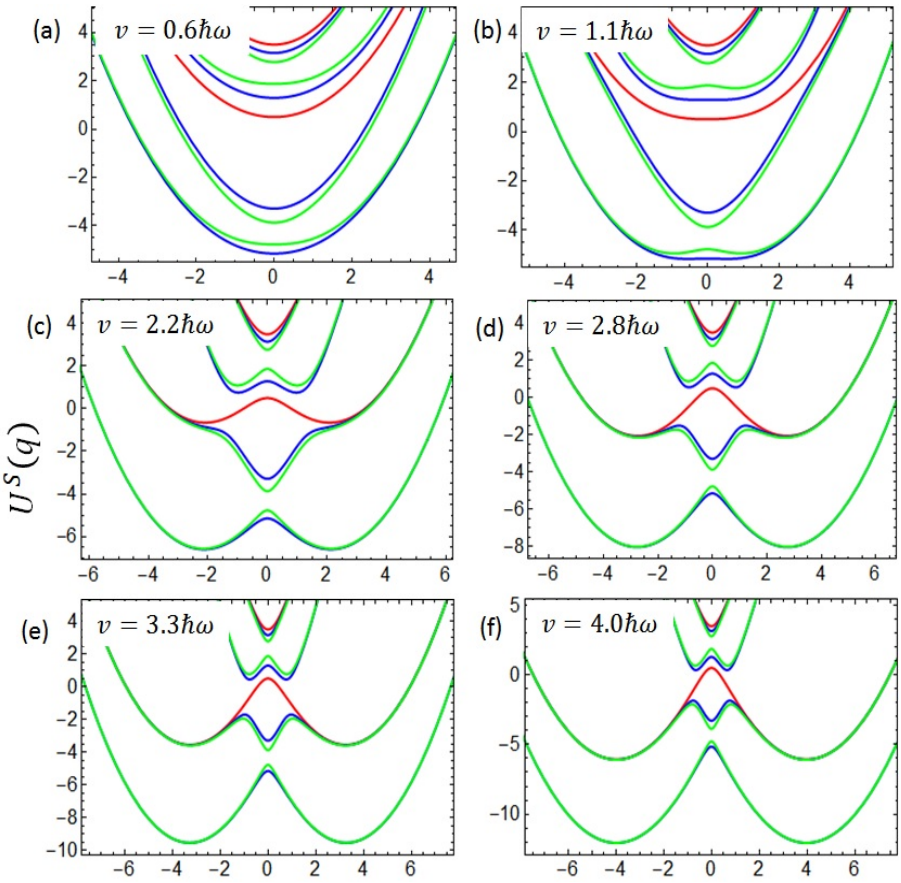


Figure 2. Adiabatic energy levels calculated in the strong exchange limit with the parameters $\hbar\omega = 200cm^{-1}, t = 0.2\ \hbar\omega, J = -0.5\hbar\omega$. Coloring: *S*=3/2 – blue, *S*=5/2 – red, *S*=1/2 – green.

situation of the coexistence of the localized and delocalized minima (Figures 2e). In the limit of strong coupling, $\upsilon = 4.0\hbar\omega$, the system has two energetically equivalent lowest minima comprises $S = 1/2,\ 3/2$ states, while the first excited minima comprise $S = 1/2, 3/2, 5/2$ levels. The system in this case can be imagined as a superposition of the two disconnected isomers *A*-*B**-*C*-*D* and *A*-*B*-*C**-*D* in which the itinerant electron is localized on the sites *B* (*C*) and coupled to the metal ions *A* (*D*), while the spins *D* (*A*) are magnetically independent. Therefore, the vibronic coupling can be attributed to the factors interfering the magnetic coupling mediated by the itinerant electron due to loss of its mobility. This phenomenon has a direct analogy with the concept of polaron in dielectric crystals. In fact, a mobile electron in crystals shifts the neighboring atoms from their equilibrium positions and moves together with the polarization produced by its field which, in turn, increases the effective mass of the electron and reduces its mobility. The "molecular polaron" considered here has the same physical root and behaves in a similar manner, while an essential feature of "molecular polaron" in MV systems is the existence (along with the ionic polarization) of the vibronically-dependent spin polarization effect.

5. ADIABATIC VIBRONIC PROBLEM IN THE CASE OF STRONG TRANSFER

The adiabatic potentials evaluated in the strong transfer limit $|J|<<|t|$ for S_0=1 are shown in Figures 3a-f. In the case of weak vibronic coupling (case of $\upsilon =$

$0.25\hbar\omega$ in Figure 3a) the condition of stability is fulfilled and, therefore, the energies of the minima simply represent the pattern of the electronic energy levels unaffected

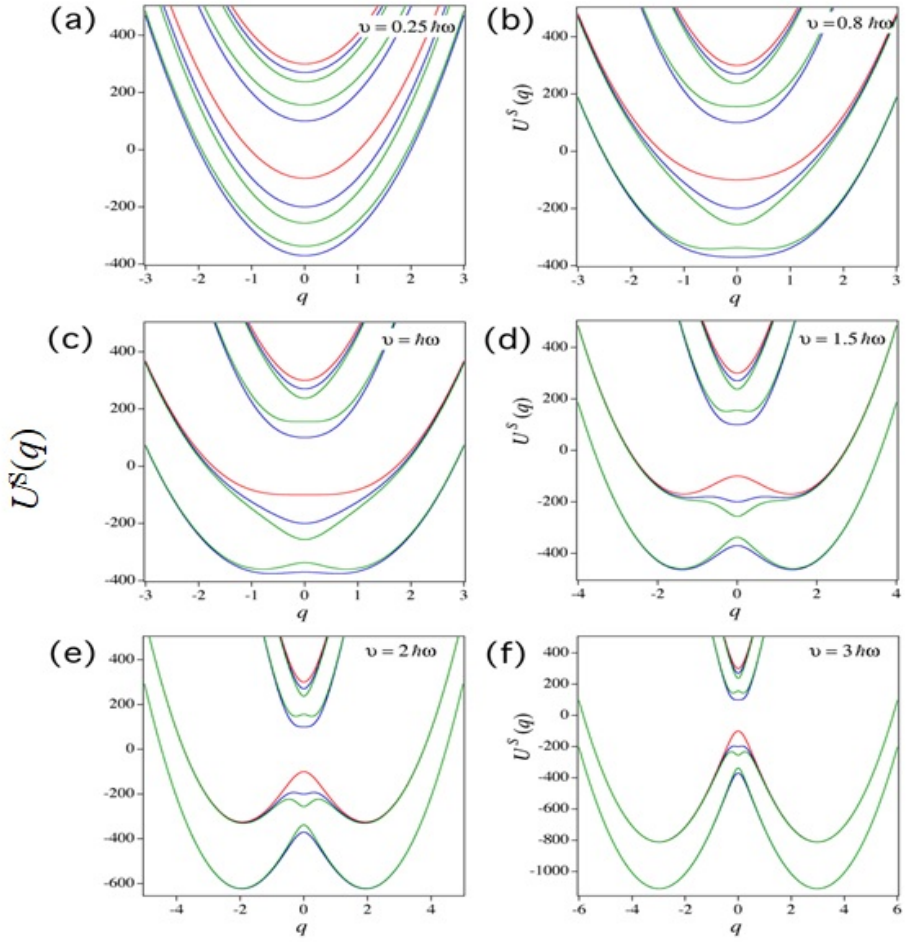


Figure 3. Adiabatic energy levels in the case strong transfer limit. $\hbar\omega = 200cm^{-1}, t = 1.0\ \hbar\omega, J = -0.5\hbar\omega$. Coloring is the same as in Figure2.

by the vibronic coupling. This energy pattern can be regarded as a result of the splitting of the two levels with the energies $+t$ and $-t$ (bonding and antibonding orbitals) by the intraatomic exchange. It is remarkable that the last proves to be twice smaller compared with the initial exchange due to the fact that in the case under consideration the electronic density in MV unit is evenly distributed between the two centers. Such energy pattern is peculiar for the splitting produced by the indirect exchange coupling between the two localized spins (mediated by the mobile electron) and so the strong transfer limit has been also termed "indirect exchange limit" in Ref. [33] With the increase of υ the instability appears in the lower branch of $S = 1/2$ potential ($\upsilon = 0.8\ \hbar\omega$, Figure 3b) giving rise to the excited partially localized (at *B* or *C*) minima. The further increase of υ also gives rise to the instability in the states with higher spin values (Figures 3c, d). It is to be noted that the energies of the minima in Figures 3b, c correspond to the electronic energy pattern in the case of strong exchange because the transfer processes in these cases are strongly suppressed by the vibronic self-trapping. This reflects the transition from the case of strong transfer (i. e. indirect exchange limit) to the case of strong exchange (i. e. DE limit) with the increase of the vibronic coupling. Finally, in the limit of strong vibronic coupling the

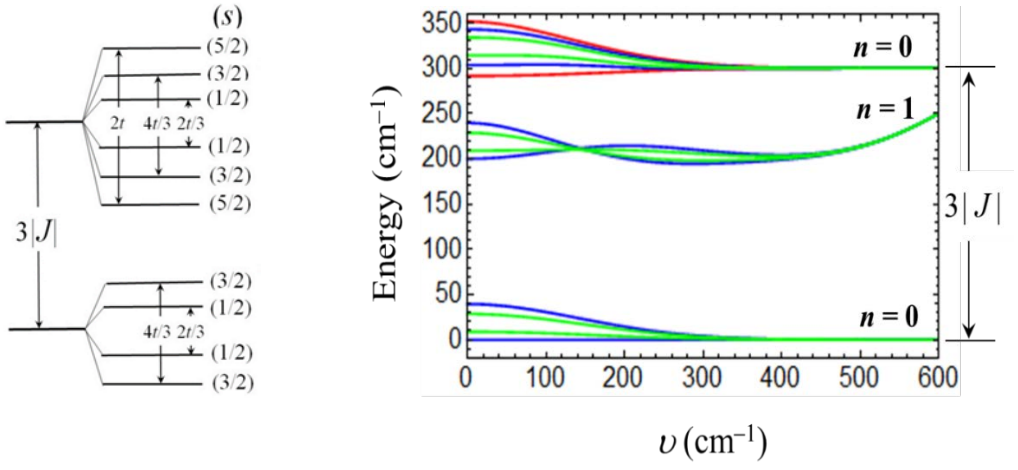
positions of the minima (for each localization) become equal and they are separated by the gap 3|*J*| which is peculiar for the case of strong exchange (Figures 3e, f). In this case the energy pattern includes the two exchange levels corresponding to the superpositions of the two uncoupled isomers *A-B*-C-D* and *A-B-C*-D* with trapped electron. It should be also noted that although the vibronic coupling produces the trapping effect the vibronic reduction of transfer cannot be interpreted as a simple rescaling of the parameter *t*.

6. DYNAMIC VIBRONIC PROBLEM, ENERGY LEVELS

The adiabatic approximation (Born−Oppenheimer paradigm) so far exploited allowed us to give a qualitative and imaginative analysis of the vibronic trapping and its magnetic consequences. Nevertheless, the adiabatic description (based on classical representation of the atomic movement) has significant limitations. That is why in this Section we give a quantum-mechanical solution of the vibronic pseudo JT problem. As a basis we will use the products of the electronic wave-functions with a definite localization of the mobile electron and the wave functions of the free harmonic vibrations $\chi_n(q)$ ($n = 0, 1\ldots$) that is, the basis includes the following states:

$$\left|(S_{AB})S, M_S, n\right\rangle \equiv \left|(S_{AB})S, M_S\right\rangle \chi_n(q), \qquad \left|(S_{CD})S, M_S, n\right\rangle \equiv \left|(S_{CD})S, M_S\right\rangle \chi_n(q). \quad (3)$$

Figures 4 a,b show the two patterns of the low-lying energy levels. The vibronic energy levels (Figure 7b) calculated providing relatively strong exchange coupling. For comparison the corresponding electronic energy pattern is shown in Figure 7a.



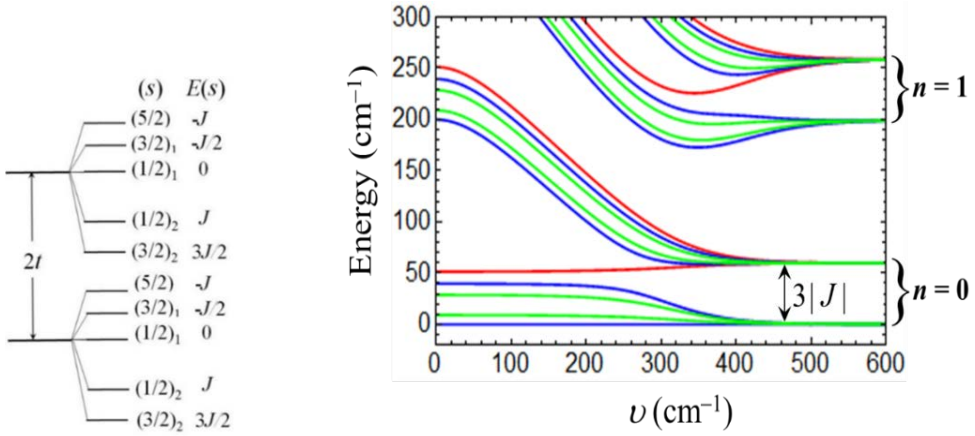
(a) (b)

Figure 4. Electronic energy levels in the strong exchange limit (a), and vibronic energy levels calculated at $\hbar\omega = 200\ \mathrm{cm}^{-1}$, $t = 0.15\ \hbar\omega$, $J = -0.5\hbar\omega$ (b). Coloring is the same as in Figure 3.

Although the vibronic coupling mixes the unperturbed levels of the Harmonic oscillator, one can see that in the case under consideration we can trace the evolution of vibronic levels with a certain number *n*. It is seen that in this case the vibronic coupling reduces the double exchange splitting. In the strong vibronic coupling limit when the electron transfer is fully quenched both the ground and excited vibronic levels with *n* = 0 are degenerate with respect to the total spin values (the ground level comprises *S* =1/2 and 3/2 and excited level comprises *S* = 1/2, 3/2 and 5/2, where the state with S=5/2 comes from the excited Hund's configuration) and separated from

each other by the gap $3|J|$. Such composition of the spin-vibronic levels exactly reproduces the pattern of the electronic levels at $t = 0$. The energy pattern in this case can be imagined as a result of paramagnetic mixture of the energy levels of two disconnected isomers *A-B*-C-D* and *A-B-C*-D* in which the mobile electron is localized on the sites *B* (*C*) and coupled to the metal ions *A* (*D*), while the localized spins of the terminal sites *A* and *D* prove to be magnetically independent.

The alternative case is shown in Figure 5a,b. Figure 5b shows the low-lying vibronic levels for the opposite case of relatively strong electron transfer and their comparison with the corresponding electronic levels shown in Figure 5a. It is seen that in this case the vibronic reduction of the electron transfer cannot be regarded as a simple rescaling of the parameter *t*.



(a) (b)

Figure 8. Electronic energy levels in the strong transfer limit (a), and vibronic energy levels calculated at $\omega = 200\ \mathrm{cm}^{-1}$, $t = 0.8\ \omega$, $J = -0.1\ \omega$ (b).

double exchange) and finally to the limit of full localization when the system at low temperature is represented by the uncorrelated spins $s_0 \pm 1/2$ and s_0.

7. CONCLUDING REMARKS

In summary we have proposed a vibronic toy model aimed at the description of the main physical mechanisms and interactions governing the indirect magnetic coupling between the localized spins through the mobile electron in partially delocalized MV systems. It should be underlined in this context that the problem of evaluation of the energy patterns and the physical properties of polynuclear partially delocalized MV systems (e. g. such complex systems as MV polyoxometalates) admits numerical solution with the aid of well-elaborated computational approaches [19,42] and related computer programs MVPACK [20] and VIBPACK [42, 43]. These powerful theoretical tools allows to evaluate the electronic and vibronic levels of nanoscopic systems giving the detailed description in terms of the adjustable parameters. The analysis of the properties and physical phenomena in these systems is hindered by the complications that are peculiar for the large systems having (in most cases) rather complicated energy pattern which obscure the main features. On the contrary, the basic model proposed here has an important advantageous features as compared to the mentioned more sophisticated approaches. Indeed, in spite of the fact that this basic model is rather simplified and neglects the details of the real complex systems, it

involves a lot of physics which cannot be directly seen from the results of calculations performed for real complex systems with the aid of the mentioned computer programs. Another advantage of the proposed vibronic model is that it is not limited to a specific system (or systems) but can be used to gain insight into the key features of a wide class of MV molecules combining in their structures spin-localized and spin-delocalized subunits.

We have demonstrated that along with the electronic interactions (electron transfer within the spin-delocalized subunit and exchange coupling between the localized and delocalized subunits) the vibronic self-trapping effect plays a decisive role in the magnetic coupling between the localized spins (external spin-cores) mediated by delocalized electron. Thus, at strong vibronic coupling the electron delocalization is strongly reduced which gives rise to breaking down the indirect coupling between the localized spins. As a result, the localized spins prove to be uncorrelated and the system at low temperatures behaves as paramagnet consisting of two spins S_0 and S_0-1/2. Also, even if the electron transfer is much stronger than the exchange coupling (this is a case of indirect exchange in the model neglecting the vibronic coupling) one can expect the appearance of the energy pattern typical for the double exchange limit provided that the vibronic coupling is strong enough. This means that vibronic interaction tends to cause the transition from the limit of indirect exchange to the limit of double exchange.

Vibronic effects have been analyzed both within the semiclassical adiabatic approximation and performing the numerical solution of the dynamic spin-dependent pseudo-JT vibronic problem. While the adiabatic approximation adequately describes the distribution of the electronic densities, it fails (especially providing moderate vibronic coupling) in the description of the intervalence absorption profiles. That is why we have used the results of the solution of the dynamic vibronic approach to evaluate the vibronically assisted of the optical absorption spectra of the partially delocalized MV systems. In course of this solution we establish the main peculiarities of such spectra arising from the two kinds of symmetry selection rules, namely, the by the parity rule and by the law of the intermediate spin conservation. As the first rule, it is common for both conventional MV dimers and the MV molecules with partial electron delocalization. Contrary, the second rule involving the intermediate spins is a specific feature of partially delocalized systems exhibiting ECDE.

Finally, the results of the present study are closely related to the problem of the electric field control of the magnetic coupling between the localized spins. [33] Particularly, they allow us to establish the criteria for the rational design of electrically switchable devices based on the partially delocalized MV molecules. According to these criteria the electric field control of correlation between the localized spins proves to be more efficient in the case of weak electron transfer and/or strong vibronic coupling which are the prerequisites for more ease polarization of the spin-delocalized subunit by the external electric field. The detailed study of such electrically controlled molecules is under way.

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