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Electric Field Control of the Optical Properties in Magnetic Mixed-Valence Molecules

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We propose the use of an electric field stimulus to strongly affect the optical properties of ferromagnetic mixed-valence (MV) dimers. This proposal is based on the prediction of an anomalous Stark effect in the intervalence absorption bands of these multi-electron MV systems. As distinguished from the conventional Stark effect observed in one-electron dimers, a strong change of the intervalence bands is accompanying the crossing of the different spin levels caused by the application of an electric field. This new effect can be referred to as giant spin-dependent Stark effect. In spintronics this opens the possibility for an optical detection of the spin state in these magnetic molecules.

One of the current challenges in molecular spintronics is that of controlling the spin state of a molecule by applying a physical stimulus different from a magnetic field.¹ An attractive possibility is that of using an electric field, instead of a magnetic field, as the former is easier to obtain, it undergoes fast switching and can be applied at the nanoscale. Some interesting experiments on the electrical control of the spin state have recently been reported in spin-crossover nanoparticles,² and even in individual spin-crossover molecules.³ On a theoretical basis several magnetic molecules have been proposed to be electrically switchable. One can mention the following: 1) spin-crossover metal complexes,⁴ 2) valence-tautomeric metal complexes,⁵ 3) dipolar metal complexes, as for example asymmetric dimers⁶ or molecular triangles formed by three antiferromagnetically coupled spins,⁷ and 4) magnetic mixed-valence metal complexes.^{8,9} In this last class of systems we have recently shown that ferromagnetic MV magnetic dimers stabilising a high-spin ground state as a consequence of the electron delocalization occurred over the two spin cores can be good candidates for the electric control of the spin states and for this reason they can be referred to as single-molecule multiferroics.⁸ In fact, in these systems the electron

delocalization, and hence the ground spin state, are expected to be extremely sensitive to the electric field, which progressively reduces the electron delocalization while inducing a large dipole moment in the molecule. Since this degree of delocalization is directly connected with the Stark spectroscopy of the intervalence (charge-transfer) absorption bands,¹⁰ one should also expect an influence of the electric field on the optical properties of these molecules. Still, this conventional Stark effect, already known for the one-electron MV systems, is expected to be a small effect.

In this work we show that, in contrast to what happens in one-electron MV systems, in multi-electron MV systems the external electric field can give rise to a dramatic change in the position and shape of the intervalence optical absorption bands and, therefore, may change the color of these materials if the intervalence absorption is located in the visible region. This is due to a new Stark effect referred to as giant spin-dependent Stark effect. Quantitative consideration is based on a model of a MV binuclear unit consisting of two spin-sites (magnetic ions) and an electron delocalized over these two ions.⁸ The total Hamiltonian is represented in the following matrix form within the basis of the electronic states $\psi_A(S, M_S)$, $\psi_B(S, M_S)$ corresponding to the extra electron localization on the sites *A* and *B*:

$$H(S) = t_S \sigma_x - JS(S+1) + vq\sigma_z + \frac{\hbar\omega}{2} \left(q^2 - \frac{\partial^2}{\partial q^2} \right) - d_0 E \sigma_z, \quad (1)$$

This parametrized model includes the double exchange, t_S , the Heisenberg-Dirac-van Vleck (HDVV) exchange interaction, J , the Piepho-Krausz-Schatz (PKS) vibronic coupling, v , the Hamiltonian of the free out-of-phase PKS vibrations, q , with the frequency ω and the coupling with an external electric field, E (along the metal-metal axis). The Hamiltonian in Eq. (1) is blocked (σ_x and σ_z are the Pauli matrices) accordingly to the

values of the full spin S and its projection M . The double exchange represents a spin-dependent electron delocalization phenomenon accompanied by the ferromagnetic spin arrangement as was first proposed by Zener and Anderson&Hasegawa¹¹ to explain the properties of MV manganites with perovskite structure. The ferromagnetic intercenter coupling through the double exchange is induced by the itinerant electron which moves keeping its spin orientation parallel to that of the spin cores in the on-site Hund's configurations.¹¹ Microscopic approaches to the electron transfer parameters are developed and reviewed in ref.¹² In the dimer, the double exchange parameter t_S is a linear function of the total spin S , $t_S = t(S+1/2)/(2s_0+1)$ where t is the one-electron transfer integral, and s_0 is the spin of the core (ion without the extra electron). On the contrary, the isotropic HDVV exchange acts within each localized configuration of a MV system and in most cases proves to be antiferromagnetic, thus stabilizing the minimum S values.¹³ The vibronic coupling tends to localize the system competing thus with the electron transfer processes which are spin-dependent due to the presence of the double exchange. Finally, the effect of an electric field on the spin states of the dimer is described through the Hamiltonian: $H = -d_0 E \sigma_z$, where $d_0 \sigma_z$ is the matrix of the electric dipole moment operator and $d_0 = eR/2$ (e is the electron charge and R is the distance between metal sites). This effect is quite similar to that produced by the internal asymmetry,¹⁴ or alternatively by the action of the molecular field in charge ordered systems.¹⁵ It tends to trap the electron at a definite site and therefore acts as an additional factor (along with the PKS vibronic coupling) that quenches the ferromagnetic double exchange.

As a model system to study this magneto-electric effect we have chosen the d^2 - d^3 MV dimer for which a real example formulated as $[(PY_5Me_2)_2V_2(\mu-5,6\text{-dimethylbenzimidazolates})](PF_6)_4$ has been reported by Long et al. (Figure 1). In this MV dinuclear vanadium(II)-vanadium(III) complex double exchange stabilizes the high-spin state with $S = 5/2$ with respect to the lower-spin states with $S = 3/2$ and $S = 1/2$, which are excited states lying around 100 cm^{-1} above the ferromagnetic ground state.¹⁶ Hence, this system represents the simplest magnetic MV dimer in which, along with the ferromagnetic, $S = 5/2$, and the antiferromagnetic, $S = 1/2$, states, an intermediate spin value $S = 3/2$ can be stabilized under some special conditions.

Recently Suzuki and Satoko¹⁷ evaluated the electronic structure of this MV vanadium dimer with the aid of broken symmetry (BS) density functional theory (DFT) calculations. This study confirmed our earlier prediction concerning the possibility to control the spin state of the vanadium dimer by an external electric field.⁸ Although this study neglected the vibronic coupling effects, it has been useful to confirm the validity of the electronic parameters. Thus, the values of the exchange parameter and the transfer integral were found to be $|J| = 0.00776 \text{ eV} \approx 62.58 \text{ cm}^{-1}$ and $t = 0.1474 \text{ eV} \approx 1188.78 \text{ cm}^{-1}$, respectively. These values are of the same order of magnitude as the values $|J| = 100 \text{ cm}^{-1}$ and $t = 2000 \text{ cm}^{-1}$ we used in our previous study.⁸ Note that the ratio between the transfer and exchange parameters is nearly the same in both studies ($t/|J| \approx 20$). As the properties of a MV dimer are determined by this ratio, we will keep the values of these electronic parameters in the analysis reported in the present work. Still, to quantitatively account for the electro-optical properties of this system we will

also need to take into account the effect of the vibronic coupling, as these properties directly depend on the degree of electron delocalization

In the absence of the vibronic coupling and electric field ($q = 0$ in Fig. 2a), the ground state possesses the maximum spin $S = 5/2$ due to the strong ferromagnetic effect of the double exchange which in the present case exceeds the HDVV coupling. On the other side, the vibronic PKS interaction is known to suppress the double exchange but does not affect the HDVV coupling so that in the limit of strong PKS coupling the energies of the minima of the adiabatic curves (associated with the spin levels) should obey the Lande's rule.

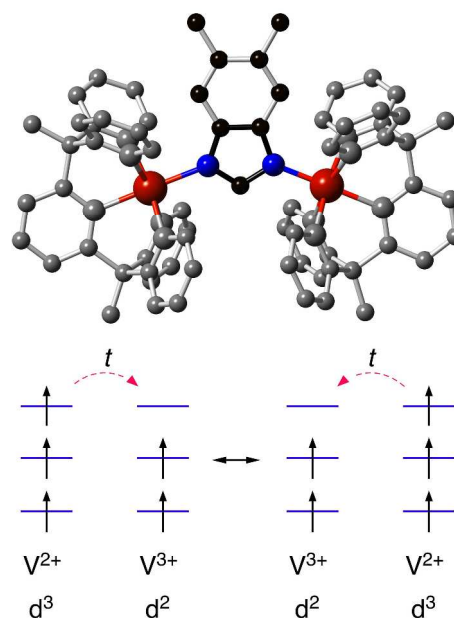


Figure 1. Schematic structure of a dinuclear vanadium (d^2 - d^3) MV system (ref. 16) and an orbital scheme of the spin-dependent electron transfer (double exchange).

Due to the spin dependence of the double exchange, the degree of localization increases with the decrease of the full spin. In particular, in the ferromagnetic $S = 5/2$ state the electron is almost delocalized while for the remaining spin states an activation barrier appears at $q = 0$, leading to an electron localization (Figure 2a). In the present case the vibronic coupling is intermediate so that the double exchange is not fully suppressed and the ferromagnetic $S = 5/2$ level remains the ground state. However, at the same time the excited adiabatic potential minima ($S = 3/2$ and $S = 1/2$) are close in energy to the ground one and the influence of an electric field may be sufficient to produce a spin crossover as it tends to stabilize the adiabatic potential minima associated to the lower spin states (Figure 2b).

It is to be noted that at zero field the $S = 5/2$ ground state of the system is nearly delocalized in the shallow minima (i.e. belongs to class III in the Robin&Day scheme). Therefore, at low temperature the intervalence optical absorption is expected to show a relatively narrow band characteristic for Class III (or for the borderline II/III).

In presence of an electric field the electron-localized lower spin states get stabilized with respect to the $S = 5/2$ high spin state. Therefore, this electrically-induced spin crossover leads to an electron localization of the MV system, which passes from Class III to Class II (Figure 2b). Under this condition the intervalence band is expected to become much broader and shifted to the blue side.

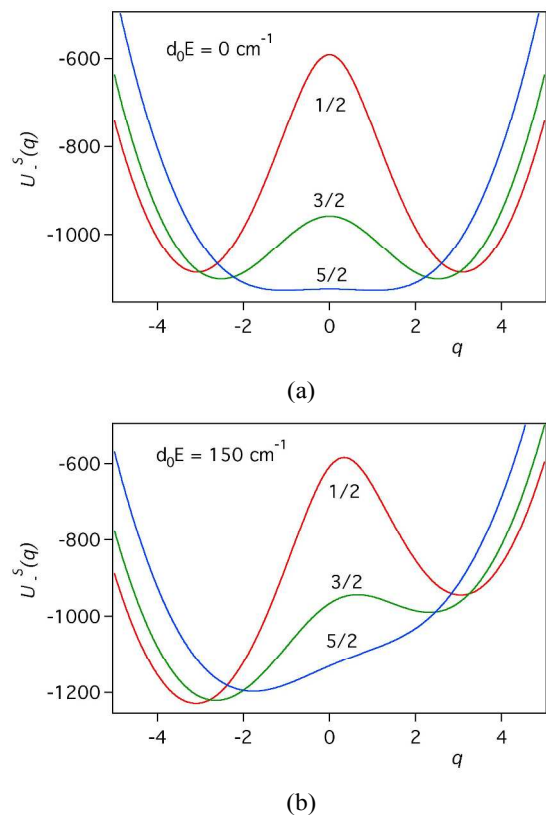


Figure 2. Lower branches of the adiabatic surfaces for a d^2-d^3 MV dimer described by the parameters $J = -100 \text{ cm}^{-1}$, $t = 2000 \text{ cm}^{-1}$, $\nu = 650 \text{ cm}^{-1}$ and $\hbar\omega = 200 \text{ cm}^{-1}$, where ω and q represent the vibrational frequency and the corresponding dimensionless normal coordinate for the out-of-phase vibrational mode, respectively: (a) without electric field, (b) with an electric field along the molecular axis $d_0E = 150 \text{ cm}^{-1}$ that corresponds to $E = 0.0606 \text{ V/nm}$ for $R = 6.19 \text{ \AA}$ (intermetallic distance in vanadium complex¹⁶).

Notice that the arguments so far discussed have only illustrative meaning. In fact, to quantitatively model this effect the use of a dynamic (quantum-mechanical) vibronic approach becomes mandatory. That is so because in the present case the field should be able to induce a crossing of the low-lying vibronic levels with different spins. It is well-known that just in this spin-crossover case the adiabatic approximation loses its accuracy even for an adequate description of the low lying levels and is absolutely invalid for the highly excited vibronic levels contributing to the intervalence absorption spectra.

Using the dynamic vibronic approach we obtain the set of vibronic eigen-values ε_v^S and the corresponding eigen-vectors c^A, c^B belonging to each allowed spin value, S :

$$\Psi_v(SM_S) = \psi_A(SM_S) \sum_n c_{nv}^A(S) \Phi_n(q) + \psi_B(SM_S) \sum_n c_{nv}^B(S) \Phi_n(q) \quad (2)$$

where $\Phi_n(q)$ are the wave-functions of the harmonic oscillator. The vibronic wave-functions in eq. (2) are obtained by diagonalizing the matrix of the Hamiltonian, eq. (1) in the basis composed of the product of electronic states and harmonic oscillator states. The truncated basis for the numerical diagonalization of the vibronic matrix includes 800 unperturbed functions that guaranty high accuracy in the evaluation of the vibronic levels and wave-functions $\Psi_v(SM_S)$ (v enumerates the vibronic states).

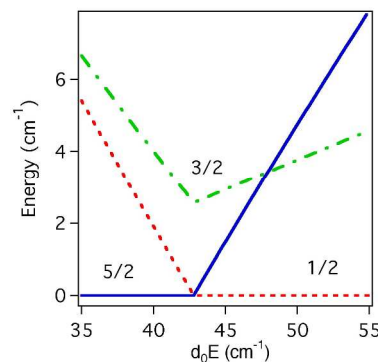


Figure 3. Low-lying vibronic energy levels of the d^2-d^3 dimer calculated for $t = 2000 \text{ cm}^{-1}$, $J = -100 \text{ cm}^{-1}$, $\nu = 680 \text{ cm}^{-1}$ and $\hbar\omega = 200 \text{ cm}^{-1}$ as a function of the external electric field. $S = 5/2$ - blue, $S = 3/2$ - green, $S = 1/2$ - red.

The crossing of the low-lying vibronic levels caused by the external electric field is shown in Fig. 3 for the parameters indicated in the caption. One can see that at low electric fields the system is ferromagnetic ($S_g = 5/2$), while at some critical values of the field ($d_0E_c \approx 43 \text{ cm}^{-1}$ for the parameters in the plot) the system exhibits stepwise switch to the antiferromagnetic ($S_g = 1/2$) ground state in Fig. 3. Notice that, in contrast to what is predicted by the simplified adiabatic picture, for the set of parameters of choice the dynamic model never allows the intermediate spin state $S = 3/2$ to be the ground state. The enveloping profile of the intervalence charge transfer absorption band for a magnetic MV dimer is calculated by:

$$F(\Omega) = \hbar\Omega Z^{-1} \sum_S (2S+1) \sum_{v' < v} (N_{v'}^S - N_v^S) \times \left[\sum_n (c_{nv'}^A(S) c_{nv}^A(S) - c_{nv'}^B(S) c_{nv}^B(S)) \right]^2 f(\varepsilon_v^S - \varepsilon_{v'}^S - \hbar\Omega) \quad (3)$$

where $N_v^S = \exp(-\varepsilon_v^S/kT)$, Z is the partition function, and $f(x)$ is the shape-function of the individual vibronic line which is assumed to be a normalized Gaussian, $f(x) = (2\pi\Delta^2)^{-1/2} \exp(-x^2/2\Delta^2)$ with the broadening parameter Δ which should be of the order of $\hbar\omega$ in order to ensure a continuous spectral distribution.

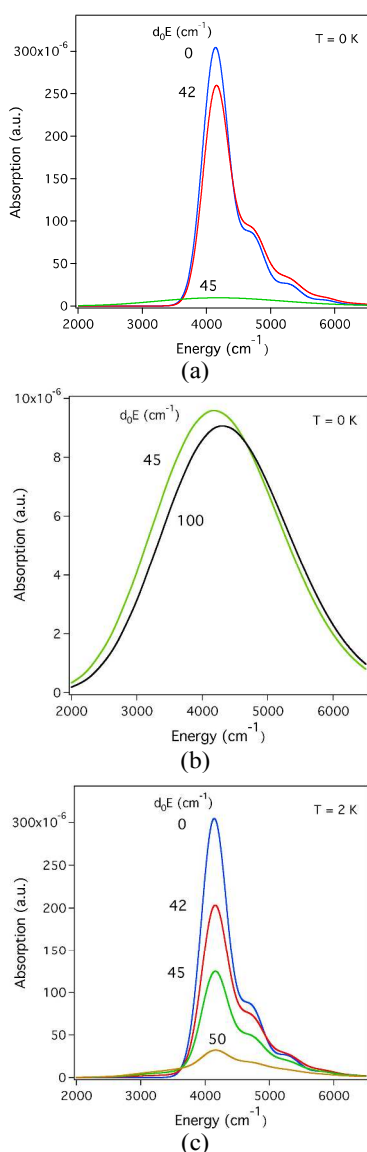


Figure 4. Intervalence transfer bands calculated at $T=0$ (a,b) and $T=2\text{K}$ (c) for the values of t , ν , J , and $\hbar\omega$ reported in Fig. 3, and for different values of the external electric field, $\Delta = 1.0\hbar\omega$.

In Figure 4 the calculated profiles of the intervalence absorption bands are shown for different values of the electric field and the temperature. Let us first consider the low temperature limit ($T = 0$). In this case the vibronic transitions exclusively come from the ground vibronic level. At zero field, the optical band is relatively narrow, asymmetric and centered near the energy $2t$ (Fig. 4a), as predicted from the qualitative PKS picture (Fig. 2a). We will conventionally assign these spectra to the type [5/2] (accordingly to the spin of the initial vibronic level which uniquely contributes to the absorption at $T = 0$).

In presence of an electric field the spin of the system switches from $S = 5/2$ to $S = 1/2$ (Fig. 3) and at the same time the degree of localization increases stepwise (Fig. 2) at a critical value E_c . When this spin crossover occurs the intervalence band becomes wider, much less intense and shifts towards high energy as illustrated in Fig. 4 for $d_0E \approx 45\text{ cm}^{-1}$ ([1/2]-type spectra). At

this point one can distinguish the two types of the intervalence Stark effects, namely a conventional field dependence of the band at fields below the critical value ($E < E_c$), exhibited by [5/2]-spectra, and an anomalous intervalence Stark effect in the vicinity of the critical field ($E \approx E_c$). In this last case the band undergoes an abrupt change from [5/2] to [1/2]-type spectra. At higher fields ($E > E_c$), the ground spin state $S = 1/2$ does not change anymore and therefore a conventional Stark effect is observed (see Fig. 4b).

Notice that the conventional Stark effect is characterized by a weak field dependence of the intervalence band. In contrast, the anomalous Stark effect that accompanies the crossing of the vibronic levels with different spins is comparatively very abrupt. Thus, it can be referred to as spin-dependent or giant Stark effect. By analogy with the conventional Stark spectroscopy¹⁰ providing information about the degree of localization, the anomalous Stark effect so far described can be proposed as an efficient tool to study the degree of spin-dependent localization and double exchange in multi-electron MV systems.

Increase of the temperature results in the population of the excited vibronic levels and consequently the band acquires contributions from different spin-states, i.e. the full band is represented by the thermally weighted superposition of the [5/2] and [1/2] (and partially the [3/2]) sub-bands. As a result, the transition between the two types of spectra as function of the field becomes gradual (Fig. 4c). Thus, even above the critical point ($d_0E \approx 45\text{ cm}^{-1}$) the intervalence band is dominated by a [5/2]-type spectrum, which is much more intense and sharp than the [1/2]-type spectrum, although the ground vibronic level belongs to $S = 1/2$. One needs to be well above the critical point to observe a broad and weak [1/2]-type spectrum ($d_0E \approx 50\text{ cm}^{-1}$). We can thus conclude that the variation of the temperature can be considered as a tool for an additional control of the intervalence absorption.

Finally, it should be noted that the possibility to electrically control the optical properties of MV compounds relies on the fine tuning of both the vibronic and the magnetic interactions in the molecule. The magnetic MV molecules of interest are those characterized by a moderate vibronic coupling and a dominant double exchange. This means that the system should be almost delocalized in the high-spin state and weakly localized in the remaining spin states, i.e. it should be in the niche between classes II and III in the Robin&Day classification. At the same time the spin structure of the system should exhibit a ferromagnetic ground spin state, but the lower spin states should be sufficiently close in energy so as to undergo a spin crossover under the influence of an electric field. In this context, the electric field should be able to partially reduce the double exchange in order to stabilize the antiferromagnetic spin state, which will become the ground state.

Conclusions

In summary, here we have predicted that the optical properties of ferromagnetic MV molecules should strongly change in presence of an external electric field. Such anomalous effect should appear when the ground state of the MV molecule changes from high spin to low spin. In these circumstances the effect is much stronger than the conventional Stark effect and has been named as giant spin-dependent Stark effect. Owing to

the large intensity of the intervalence (charge-transfer) bands, this new effect opens the possibility for an optical detection of the spin state in these molecular systems.

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