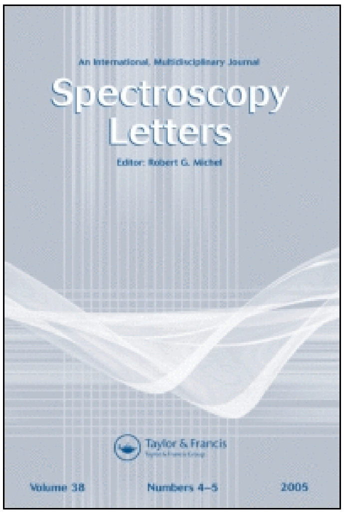

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Klokishner, S. I. and Tsukerblat, B. S.(1990) 'Charge Transfer Bands of Mixed Valence Molecular Crystals', Spectroscopy Letters, 23: 5, 637 — 647
To link to this Article: DOI: 10.1080/00387019008054445
URL: http://dx.doi.org/10.1080/00387019008054445

SPECTROSCOPY LETTERS, 23(5), 637-647 (1990)

CHARGE TRANSFER BANDS OF MIXED VALENCE MOLECULAR CRYSTALS

Key Words: Cluster,Transition Metal Ion, Vibronic Interaction,Dipole-Dipole Interaction,Dipole Moment,Order Parameter, Phase Transition,Absorption Band Shape.

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ABSTRACT

The electron-vibrational (vibronic)bands of light absorption by mixed valence molecular crystals containing clusters of transition metal ions in different states of oxidation as the structural units of lattice are considered. The absorption band shape calculation in different phase states is performed in the semiclassical limit for crystals consisting of trielectronic clusters of transition metals of the type of d^1-d^2. The band shape differs from the Gaussian and closely depends on the double-exchange and Heisenberg-type exchange parameters and on the temperature dependence of the average dipole moment playing the role of the order parameter.

1.Mixed valence (MV) molecular crystals contain clusters of same transition ions in different states of oxidation as the structural units of lattice. The important manifestation of MV is the occurence of so called optical charge transfer bands.These bands appear upon the electron transfer between the possible energetically equivalent localizations. Both the width and the maxima positions of these bands depend on the vibronic interaction parameter as well as on the exchange parameter[1].

The theory of charge ordering in MV molecular crystals based on the microscopic model[2,3] is developed in Refs[4,5]. The existence of charge ordered states was reliably proved in Refs[6,7] for some types of biferrocene crystals. In this article the theory of charge transfer bands in charge-ordered MV systems is suggested. While describing the electron-vibrational absorption spectra in passing the problem of charge ordering and phase transitions is decided simultaneously taking into account dipole-dipole interaction between clusters and the interaction of "extra" electrons with the molecular(localized) vibrations.

2.The Hamiltonian of the crystal consisting of dimeric clusters of the type of d^1-d^2 we write in the form:

$$\mathcal{H} = \sum_{\vec{n}} H_{\vec{n}} + H_{eL} + \sum_{\vec{n}} H_{\vec{n}}^{L} - \frac{1}{2}\sum_{\vec{n}\vec{m}} K(\vec{n}-\vec{m})\, d_{\vec{n}}^{z} d_{\vec{m}}^{z}, \qquad (1)$$

where $H_{\vec{n}}$ is the Hamiltonian of a isolated cluster, H_{eL} is the vibronic interaction, the third term in Eq.(1) describes the dipole-dipole interaction[4,5],and finally

$$H^{L}_{\vec n} = \sum_{\alpha} \frac{\hbar\omega_{\alpha}}{2}\left(Q^{2}_{\alpha\vec n} - \frac{\partial}{\partial Q^{2}_{\alpha\vec n}}\right) \qquad (2)$$

is the n-th cluster vibrational Hamiltonian, α numbers the normal modes. For clusters with an orbitally non-degenerate ground state the matrixes $H_{\vec n}$ and $d^{z}_{\vec n}$ have the form:

$$H_{\vec n} = \begin{bmatrix} P & -P & 0 & 0 \\ -P & P & 0 & 0 \\ 0 & 0 & \frac{3}{2}J+P & \frac{P}{2} \\ 0 & 0 & \frac{P}{2} & \frac{3}{2}J+P \end{bmatrix}, \quad d^{z}_{\vec n} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \qquad (3)$$

here J and P are the parameters of Heisenberg-type exchange interaction and transfer (double exchange) respectively, d_0 is the dipole moment of the cluster with the localized "extra" electron. While writing matrixes (3) use is made of the basis of the localized "extra" electron connected with the basis employed in Refs[4,5] with following relations:

$$|1(2)\rangle = (2)^{-1/2}\left(|{}^{4}A_{1g}\rangle (\pm) |{}^{4}A_{2u}\rangle\right),$$

$$|3(4)\rangle = (2)^{-1/2}\left(|{}^{2}A_{1g}\rangle (\pm) |{}^{2}A_{2u}\rangle\right).$$

Let us consider the lattice point interaction with the totally symmetric $Q^{\vec n a}_{A_1}$ and $Q^{\vec n b}_{A_1}$ displacements of the nearest environment of the each cluster ion. By introducing approximately normal coordinates $Q^{\vec n \pm}_{A_1} = (Q^{\vec n a}_{A_1} \pm Q^{\vec n b}_{A_1})/\sqrt{2}$ [8] we write the vibronic interaction of the cluster in the form:

$$H = V^{+} Q_{A_1}^{\vec{n}+} (I^{\vec{n}} \otimes I^{\vec{n}}) + + V^{-} Q_{A_1}^{\vec{n}-} (I^{\vec{n}} \otimes \sigma_z^{\vec{n}}), \tag{4}$$

where I and σ_z are the unit and the Pauli matrix correspondingly, $\otimes$ is the symbol of the direct matrix product, $V^{+} = V + 2V'$, $V^{-} = V - 2V^{-}$ .The parameters V and V^{-} can be expressed in terms of single-electronic matrix elements as follows:

$$V = (6)^{-1/2} \langle t_2 \| \frac{\partial W}{\partial Q_{A_1}^{a}} \| t_2 \rangle_0 , \quad V' = (6)^{-1/2} \langle t_2' \| \frac{\partial W}{\partial Q_{A_1}^{b}} \| t_2' \rangle_0 , \tag{5}$$

where W is the potential energy of electron-ligands interaction, $|t_2\rangle$ is the d-function of the single-electronic centre, $|t_2'\rangle$ is the same for the two-electronic centre. In accordance with (4) the interaction with the totally symmetric cluster vibration $Q_{A_1}^{\vec{n}+}$ can be excluded by the shift transformation. The $Q_{A_1}^{\vec{n}-} \equiv q_{\vec{n}}$ vibration in the isolated cluster mixes the exchange-resonance multiplets with different parity belonging to the same cluster spin S . This leads to the pseudo-Jahn-Teller effect.

3. We shall consider the vibrations as localized and neglect the interaction of clusters via the phonon field. Using the molecular field approximation for the Hamiltonian (1) one can get the adiabatic potentials for the states characterized by the total spin S:

$$U_{3/2}^{\pm}(q) = \pm W_1(q) + \frac{\omega}{2} q^2 ,$$

$$U_{1/2}^{\pm}(q) = \frac{3J}{2} \pm \frac{W_2(q)}{2} + \frac{\omega}{2} q^2 ,$$

$$W_1(q) = \left[P^2 + (D + v q)^2 \right]^{1/2} ,$$

$$W_2(q) = [P^2 + 4(D + \vartheta q)^2]^{1/2},$$

$$L = \sum_{\vec{n}} K(\vec{n} - \vec{m}),$$

$$D(T) = L\bar{d}(T)d_0, \quad \hbar = 1, \tag{6}$$

where $\vartheta \equiv V^-$. The essential peculiarity of the problem under consideration is the adiabatic potential dependence on the order parameter $\bar{d}$ in the space of the antisymmetric coordinate q. The thermal average of the dipole moment of crystal per one crystal cell (one cluster) plays the role of the order parameter. In the charge-ordered state the migrating electron is affected by the molecular field $-L\bar{d}$. In the case of $\vartheta^2/\omega \gg |P|$ the lower adiabatic potential sheets have the minima at the points

$$q_{1(2)} \simeq \underset{(-)}{+} \vartheta/\omega. \tag{7}$$

The adiabatic energy at points $q_{1,2}$ takes on the next approximate values:

$$U^-_{3/2}(q_{1(2)}) = \underset{(+)}{-} D - \frac{\vartheta^2}{2\omega}. \tag{8}$$

In so doing one of the adiabatic potential minima corresponding to the "extra" electron localization along the mean field direction occurs deeper (Fig.1a). With temperature increase the molecular field decreases, the adiabatic potential minima flatten, and finally at the phase transition point the minima become energetically equivalent. In the opposite case $\vartheta^2/\omega < |P|$ the lower adiabatic potential sheets have only one minimum.

The eigen-functions have the form:

$$\Psi^{\underset{(-)}{+}}_{3/2} = \left[\frac{1}{2}\left(1 \underset{(+)}{-} \frac{D+\vartheta q}{W_1(q)}\right)\right]^{\frac{1}{2}}|1\rangle \underset{(-)}{+} \left[\frac{1}{2}\left(1 \underset{(-)}{+} \frac{D+\vartheta q}{W_1(q)}\right)\right]^{\frac{1}{2}}|2\rangle,$$

$$\Psi^{\pm(-)}_{1/2} = \left[\frac{1}{2}\left(1 \mp_{(+)} \frac{2(D+vq)}{W_2(q)}\right)\right]^{\frac{1}{2}}|3\rangle \pm_{(-)} \left[\frac{1}{2}\left(1 \pm_{(-)} \frac{2(D+vq)}{W_2(q)}\right)\right]^{\frac{1}{2}}|4\rangle . \qquad (9)$$

In the case of ferroelectric type of ordering for the order parameter we get the equation $(L>0,\ k_B=1)$:

$$\frac{\bar{d}}{d_0} = Tr_L\left\{\exp\left(-\frac{\omega q^2}{2T}\right)(D+vq)\left[W^{-1}(q)\times\right.\right.$$
$$\times \sinh\left[\frac{W_1(q)}{T}\right]+\exp\left(-\frac{3J}{2T}\right)W_2^{-1}(q)\times$$
$$\left.\left.\times \sinh\left[\frac{W_2(q)}{2T}\right]\right]\right\}\left\{Tr_L\left[\exp\left(-\frac{\omega q^2}{2T}\right)\times\right.\right.$$
$$\times\left[\cosh\left[\frac{W_1(q)}{T}\right]+\frac{1}{2}\exp\left(-\frac{3J}{2T}\right)\times\right.$$
$$\left.\left.\left.\times\cosh\left[\frac{W_2(q)}{2T}\right]\right]\right]\right\}^{-1}. \qquad (10)$$

The equation (10) is obtained in the semiclassical approximation[9], wherein the adiabatic potential represents the total energy. In Eq.(10) Sp_L means the integration over the vibrational coordinates. This integral can be evaluated only in some limiting cases. The system behaviour is determined by four dimensionless parameters $|P|/Ld_0^2$, $J/|P|$, $|v|/\omega$, $|v|/|P|$. Expanding the right side of Eq.(10) in a series in degrees of $\vec{d}$ we get the equation for the phase transition temperature T_c. This equation is not listed here. Provided that $J<0$, $|J|>|P|$, $|P|/2Ld_0^2-2v^2/\omega|P|<1$

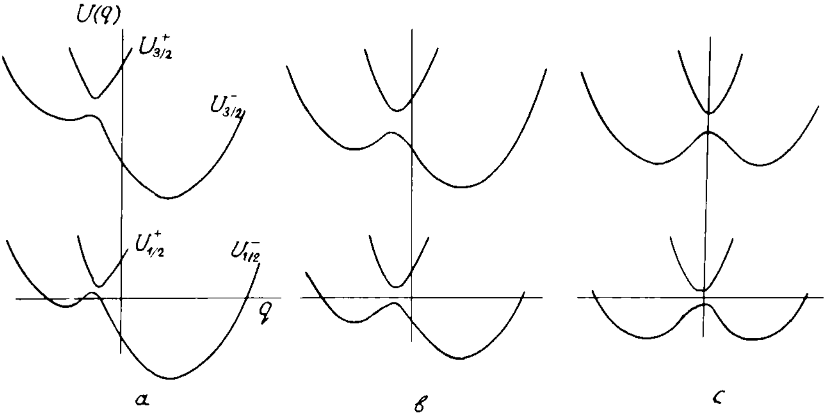

Fig.1.Temperature dependence of the adiabatic potentials in the mean field approximation in the case $|V|/\omega=3,2$, $P/Ld_0^2=0,2$, $|P|/\omega=1$. a)$T/T_c=0,3$;b)$T/T_c=0,9$;c)$T/T_c=1$.

one can get for the phase transition temperature the approximate expression

$$T_c=\frac{|P|}{2\,\mathrm{arctanh}\left(\frac{|P|}{2Ld_0^2}-\frac{2V^2}{\omega|P|}\right)} \qquad (11)$$

It is seen from Eq.(11) that in this limiting case the electron-phonon interaction rises the phase transition temperature.In the case of ferromagnetic intracluster exchange the phase transition temperature is also determined by formula (11) wherein it is necessary to replace $|P|/2$ by $|P|$. In the case of strong electron-phonon interaction $V^2/\omega|P|>1$ the order parameter equation transforms to:

$$\frac{\bar{d}}{d_0}=\tanh\frac{D}{T} \qquad (12)$$

Here the phase transition temperature is determined by the next relation $T_c = L\alpha_0^2$.

4. The semiclassical approximation is used also for calculation of absorption band shapes. In the dipole approximation only the transitions between the adiabatic potential sheets corresponding the same spin multiplet are allowed. Since the transition is accompanied by the electron transfer the so called charge transfer bands (or intervalence transition bands[1]) correspond to the transitions above mentioned. The absorption band shape is determined by the relation

$$F_S(\Omega) = Z^{-1}\int dq\,\left|\langle \Psi_S^{+}(q)|d|\Psi_S^{-}(q)\rangle\right|^2 \times$$

$$\exp\left[-U_S^{-}(q)/T\right]\delta\left[U_S^{+}(q) - U_S^{-}(q) - \Omega\right], \qquad (13)$$

where Z is the statistical sum. Carrying out the integration in Eq. (13) we get:

$$F_S(\Omega) = \exp\left(\frac{\Omega}{2T}\right)\Omega^{-1}\eta(S)\left[X(S)\right]^{-1} \times$$

$$\left\{\exp\left[-\frac{\omega}{8T\upsilon^2}\left(X(S)+2D\right)^2\right] + \right.$$

$$\left. + \exp\left[-\frac{\omega}{8T\upsilon^2}\left(X(S)-2D\right)^2\right]\right\},$$

$$\eta\left(\tfrac{3}{2}\right) = 1, \quad \eta\left(\tfrac{1}{2}\right) = \frac{1}{8}\exp\left(-\frac{3J}{2T}\right), \qquad (14)$$

where $X\left(\frac{3}{2}\right) = \left(\Omega^2 - 4P^2\right)^{1/2}$, $X\left(\frac{1}{2}\right) = \left(\Omega^2 - P^2\right)^{1/2}$. In the case of $\Omega \gg 2|P|$ for $S=3/2$ and $\Omega \gg |P|$ for $S = 1/2$ the charge transfer band extrema are determined from the transcendental equation:

$$\Omega^2 - 2\Omega\left[\frac{\upsilon^2}{\omega} + D\tanh\left(\frac{\omega D\Omega}{2T\upsilon^2}\right)\right] + \frac{8T\upsilon^2}{\omega} = 0. \tag{15}$$

In the frequency range $\Omega \gg \frac{2T\upsilon^2}{\omega D}$ the absorption band has one maximum at the point

$$\Omega_m = \frac{\upsilon^2}{\omega} + D + \left[\left(\frac{\upsilon^2}{\omega} + D\right)^2 - \frac{8\upsilon^2 T}{\omega}\right]^{1/2}. \tag{16}$$

From Eq.(16) it is seen that the band maximum disappears and the absorption intensity monotonically decreases when $(\upsilon^2\omega^{-1} + D)^2 \leq 8T\upsilon^2\omega^{-1}$.

5.In the case of relatively strong interaction $|P|/\omega = 1$ $|\upsilon|/\omega = 3.2$, $|P|/L\alpha_0^2 = 0.2$ the intervalence transition bands for the spin multiplet $S = 3/2$ are presented in Fig.2. For these parameter values the order parameter temperature dependence was numerically found and with help of formula (14) the shape of optical curve was calculated (Fig.2). At low temperature T/T_c=0,3 the optical curve has a pronounced maximum in the range $\Omega \simeq 26\omega$. It is seen from Fig.1a that the position of this maximum is close to the energy of the Franck-Condon transition to the upper adiabatic potential sheet. In so doing the adiabatic potential maximum corresponding to the unprofitable electron localization is not populated and does not contribute in absorption. The band peculiarity on the left edge is stipulated by the transitions in the region of strong non-adiabatic term's mixing. At low temperatures the relative intensity of this spectra range is small.The divergence in the expression for the band form-function results from the classical consideration of the nuclei motion. With temperature increase the band ma-

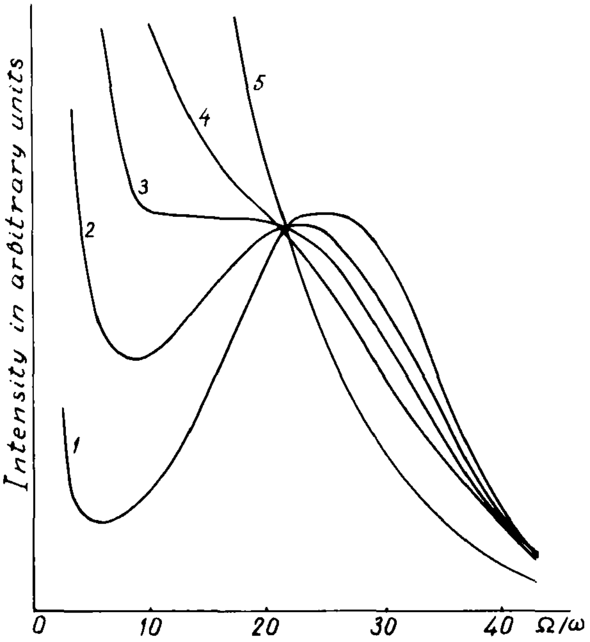

Fig.2.Temperature dependence of charge transfer band-shape $F_{3/2}(\Omega)$ in the case $|\vartheta|/\omega = 3,2$; $|P|/Ld_0^2 = 0,2$; $|P|/\omega = 1$.
1.$T/T_c = 0,3$;2.$T/T_c = 0,4$;3.$T/T_c = 0,5$;4.$T/T_c = 0,6$;
5.$T/T_c = 1$.

ximum intensity decreases and the maximum position shifts to the range of low energies due to the fact that with temperature increase the decrease of the molecular field leads to the flattening of the adiabatic potential minima and reduces the Franck-Condon transition energy from the deep minimum. Finally,at sufficiently high temperature the main maximum vanishes and the peak at the left edge is the most intensive. In the disordered state in the case of sufficiently strong vibronic coupling the Franck-Condon transitions are forbidden as the dipole moment operator does not mix the states with different localizations $\langle d_a^1 - d_b^2 | d | d_a^2 - d_b^1 \rangle$.

It should be noted that the semiclassical approximation[9] describes the principal broad maximum sufficiently well. At the same time the semiclassical approximation is the unfavourable for the describing of the left band edge which corresponds to the transitions of the range of strong non-adiabatic term's mixing. The results obtained evidence about the pronounced manifestations of charge ordering and phase transitions in MV molecular crystals.

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Date Received: 01/15/90
Date Accepted: 02/21/90