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Optical Manifestation of Jahn-Teller Effect in Square-Planar Complexes

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The optical band shape singlet-doublet transition in the square-planar complexes has been investigated in the framework of the quasiclassical approach, the spin-orbit coupling has been included. The optical band shape has been examined in the cases of static and dynamic Jahn-Teller effect.

In den Grenzen der quasi-klassischen Näherung werden die optischen Singulett-Dublett-Übergänge für quadratische Komplexe untersucht. Dabei wird auch der Einfluß der Spin-Bahn-Kopplung auf die Form der Banden untersucht. Das Verhalten der optischen Bande wird für den statischen und dynamischen Jahn-Teller-Effekt untersucht.

La forme de la bande de transition singlet-doublet a été étudiée dans les complexes quadratiques-planes, en utilisant l'approximation quasiclassique. On tient compte des effets de l'intéraction spine-orbitale. La forme de la bande a été étudiée dans les cas des effets statique et dynamique de Jahn-Teller.

Introduction

At present there is considerable interest in Jahn-Teller effect (JTE) and related problems (see [1, 2]). The JTE in two-fold degenerate electronic level is qualitatively different for the cubic and trigonal systems on the one hand and for the tetragonal systems from the other hand. In the first case the two-fold degenerate *e*-mode is active in the JTE and the matrix Hamiltonian of vibronic interaction with such mode

$$\hat{H} = c(\boldsymbol{\sigma}_z q_1 + \boldsymbol{\sigma}_x q_2)$$

contains only one constant c (q_1, q_2 and $\boldsymbol{\sigma}_x$, $\boldsymbol{\sigma}_z$ are the normal coordinates and the Pauli matrixes respectively). By contrast in the second case nondegenerate modes b_{1g} and b_{2g} are active in the JTE, so that in the case of square-planar complex the vibronic Hamiltonian

$$\hat{H} = c_1 \boldsymbol{\sigma}_z q_1(b_{1g}) + c_2 \boldsymbol{\sigma}_x q_2(b_{2g})$$

contains two independent constants c_1 and c_2. This last circumstance gives the opportunity to examine so the dynamic JTE ($c_1 \neq 0$ and $c_2 \neq 0$) as the static JTE (c_1 or c_2 is equal zero) varying the values of constants c_1 and c_2.

The case of static JTE was investigated by Hougen in his important paper [3]. The general case of dynamical JTE in square-planar complexes was examined in details by Ballhausen [4]. On the basis of numerical methods he obtained the optical spectra for ${}^2A \rightarrow {}^2E$ transition in the case of intermediate coupling ($\Delta E_{\text{JT}} \sim 3\hbar\omega$) and at $T = 0°K$ when the quantum effects in the optical band structure may be observed. The envelope curve of optical band may be received by quasiclassical approximation in the another limit case of the high temperature and strong coupling $\Delta E_{\mathrm{JT}} \gg \hbar\omega$. Such investigation we give in this note for $A \rightarrow E$ transition in square-planar complexes.

General Expressions

As it is mentioned above for doublet ^2E term in square-planar complexes two nondegenerate mode b_{1g} and b_{2g} are JT active. The secular equation including spin-orbit coupling has the form [4]:

$$\begin{array}{c|cccc|}
\varphi_x\alpha & -c_1q_1-\varepsilon & 0 & c_2q_2+\frac{1}{2}i\lambda & 0 \\
\varphi_x\beta & 0 & -c_1q_1-\varepsilon & 0 & c_2q_2-\frac{1}{2}i\lambda \\
\varphi_y\alpha & c_2q_2-\frac{1}{2}i\lambda & 0 & c_1q_1-\varepsilon & 0 \\
\varphi_y\beta & 0 & c_2q_2+\frac{1}{2}i\lambda & 0 & c_1q_1-\varepsilon
\end{array} = 0\,. \tag{1}$$

The solutions are

$$\varepsilon = \pm\sqrt{c_1^2q_1^2+c_2^2q_2^2+\frac{\lambda^2}{4}} \equiv \pm\varepsilon_0\,. \tag{2}$$

the eigenfunctions can be written as

$$\left.\begin{aligned}
\Psi_+(r,q,\sigma) &= N\left[\left(c_2q_2+i\frac{\lambda}{2}\right)\varphi_x+(c_1q_1+\varepsilon_0)\varphi_y\right]\chi(\sigma)\\
\Psi_-(r,q,\sigma) &= N\left[-(c_1q_1+\varepsilon_0)\varphi_x+\left(c_2q_2-i\frac{\lambda}{2}\right)\varphi_y\right]\chi(\sigma)\\
N &= \left[2\left(c_1^2q_1^2+c_2^2q_2^2+\frac{\lambda^2}{4}+c_1q_1\varepsilon_0\right)\right]^{-1/2}
\end{aligned}\right\} \tag{3}$$

where $\sigma=\pm\frac{1}{2}$, $\chi(\frac{1}{2})=\alpha$, $\chi(-\frac{1}{2})=\beta$.

Within the semiclassical approximation the line shape function of the optical absorption is given by

$$\begin{aligned}
K(x) = {} & \frac{1}{\pi\hbar}\left(\frac{k_1k_2\vartheta_1\vartheta_2}{\omega_1\omega_2}\right)^{1/2}\sum_{\pm}\iint_{-\infty}^{\infty} dq_1\,dq_2\,|\langle\Psi_0|d|\Psi_\pm\rangle|^2\\
& \cdot\exp\left(-\frac{k_1\vartheta_1}{\hbar\omega_1}q_1^2-\frac{k_2\vartheta_2}{\hbar\omega_2}q_2^2\right)\delta(\hbar x\pm\varepsilon_0)\,,
\end{aligned} \tag{4}$$

$$\vartheta_i = \tanh\frac{\hbar\omega_i}{2k_B T}, \qquad x = \Omega-\Omega_0$$

where d is the dipole moment operator, Ψ_0 is the orbital singlet ground state wavefunction, Ω is the light frequency, $\hbar\Omega_0$ is the energy gap between the electronic terms when the nuclear configuration is fixed in the high symmetry point $q_1=q_2=0$. Introducing ϱ and φ coordinates by the relations

$$c_1q_1=\varrho\cos\varphi, \qquad c_2\,q_2=\varrho\sin\varphi \tag{5}$$

one can obtain for K_+ following expression

$$\begin{aligned} K_+(x) = {} & \frac{1}{2\pi\hbar c_1 c_2}\left(\frac{k_1 k_2 \vartheta_1 \vartheta_2}{\omega_1 \omega_2}\right)^{1/2} \int_0^{2\pi} d\varphi \int_0^{\infty} \varrho \, d\varrho \\ & \cdot \frac{\exp\left[\left(-\frac{k_1 \vartheta_1}{\hbar\omega_1 c_1^2}\cos^2\varphi - \frac{k_2 \vartheta_2}{\hbar\omega_2 c_2^2}\sin^2\varphi\right)\varrho^2\right]}{\varrho^2 + \frac{\lambda^2}{4} + \varrho\cos\varphi\sqrt{\varrho^2 + \frac{\lambda^2}{4}}} \\ & \cdot \left[d_{0x}^2\left(\varrho^2\sin^2\varphi + \frac{\lambda^2}{4}\right) + d_{0y}^2\left(\varrho^2\cos^2\varphi + \varrho^2 + \frac{\lambda^2}{4} + 2\varrho\cos\varphi\sqrt{\varrho^2 + \frac{\lambda^2}{4}}\right)\right] \\ & \cdot \delta\left(\hbar x \pm \sqrt{\varrho^2 + \frac{\lambda^2}{4}}\right). \end{aligned} \tag{6}$$

The expression for K_- looks similarly. For nonpolarised light $d_{0x}^2 = d_{0y}^2 \equiv d^2$ and the expression (6) becomes more simply

$$\begin{aligned} K_\pm(x) = {} & \frac{d^2}{\pi\hbar c_1 c_2}\left(\frac{k_1 k_2 \vartheta_1 \vartheta_2}{\omega_1 \omega_2}\right)^{1/2} \int_0^{2\pi} d\varphi \int_0^{\infty} \varrho \, d\varrho \\ & \cdot \exp\left[\left(-\frac{k_1 \vartheta_1}{\hbar\omega_1 c_1^2}\cos^2\varphi - \frac{k_2 \vartheta_2}{\hbar\omega_2 c_2^2}\sin^2\varphi\right)\varrho^2\right] \delta\left(\hbar x \pm \sqrt{\varrho^2 + \frac{\lambda^2}{4}}\right). \end{aligned} \tag{7}$$

Performing the integration we get

$$\begin{aligned} K(x) = {} & \frac{2d^2}{c_1 c_2}\left(\frac{k_1 k_2 \vartheta_1 \vartheta_2}{\omega_1 \omega_2}\right)^{1/2} \\ & \cdot |x| \exp\left[-\frac{1}{2}\left(\frac{k_1 \vartheta_1}{\hbar\omega_1 c_1^2} + \frac{k_2 \vartheta_2}{\hbar\omega_2 c_2^2}\right)\left(\hbar^2 x^2 - \frac{\lambda^2}{4}\right)\right] \\ & \cdot I_0\left[-\frac{1}{2}\left(\frac{k_1 \vartheta_1}{\hbar\omega_1 c_1^2} - \frac{k_2 \vartheta_2}{\hbar\omega_2 c_2^2}\right)\left(\hbar^2 x^2 - \frac{\lambda^2}{4}\right)\right]\left[\Theta\left(x - \frac{|\lambda|}{2\hbar}\right) + \Theta\left(-x - \frac{|\lambda|}{2\hbar}\right)\right]. \end{aligned} \tag{8}$$

In Eq. (8) I_0 and Θ are the Bessel function of image argument and the step function respectively.

Discussion

If $\lambda = 0$ the optical band is splitted into two components with zero intensity at $x = 0$. (Fig. 1a.) This line shape resembles that of $A \to E$ transitions in cubic and trigonal cases [5] and coincides with the last when $\frac{k_1 \vartheta_1}{\hbar\omega_1 c_1^2} = \frac{k_2 \vartheta_2}{\hbar\omega_2 c_2^2}$. Note, that at the high temperature ($k_B T \gg \hbar\omega_1, \hbar\omega_2$) the condition $\frac{k_1 \vartheta_1}{\hbar\omega_1 c_1^2} = \frac{k_2 \vartheta_2}{\hbar\omega_2 c_2^2}$ transforms into the condition $\frac{k_1}{c_1^2} = \frac{k_2}{c_2^2}$ when the lowest potential sheet surface possesses the continuum of minima, i.e. the complex can "rotate" freely between an "elongate" and "rhombic" configuration [4].

The interaction with one of the active mode becoming weaker the splitting is decreasing, when $c_2 = 0$ the dip of the optical curve at $x = 0$ disappears, and the optical band becomes the Gaussian one with the maximum at the Franck-Condon frequency $x = 0$.

$$K(x) = \frac{d^2\hbar\sqrt{\vartheta_1}}{c_1\sqrt{2\pi}} \exp\left(-\frac{\vartheta_1\hbar^2x^2}{2c_1^2}\right). \tag{9}$$

The appearance of the Gaussian curve in this case may be easily understood. Indeed in $q_2 = 0$ section the potential surfaces are two intersecting parabolas; so the dynamic JTE becomes the static one. Then point $q_1 = 0$ turns out to be the turning point for the nuclear motion, so the absorption intensity has maximum at $x = 0$.

The account of the spin-orbit interaction gives the following expression for the absorption coefficient in the case $c_2 = 0$:

$$\begin{aligned} K(x) = \frac{2d^2}{c_1}\left(\frac{\hbar k_1\vartheta_1}{\pi\omega_1}\right)^{1/2} \frac{|x|}{\left(\hbar^2x^2 - \frac{\lambda^2}{4}\right)^{1/2}} \\ \cdot \exp\left[-\frac{k_1\vartheta_1}{\hbar\omega_1c_1^2}\left(\hbar^2x^2 - \frac{\lambda^2}{4}\right)\right]\left[\Theta\left(x - \frac{|\lambda|}{2\hbar}\right) + \Theta\left(-x - \frac{|\lambda|}{2\hbar}\right)\right]. \end{aligned} \tag{10}$$

Eq. (10) describes the optical band with two sharp peaks at $x = \pm\frac{\lambda}{2\hbar}$, separated by the zero absorption range (Fig. 1b). Absence of the absorption in the range $|x| < \frac{|\lambda|}{2\hbar}$ takes place in the case of dynamic JTE ($c_2 \neq 0$) too. In this case, however, the optical band shape is more smoothed and its two peaks may be placed at $x \neq \frac{\lambda}{2\hbar}$. So, in the case $\frac{k_1\vartheta_1}{\omega_1c_1^2} = \frac{k_2\vartheta_2}{\omega_2c_2^2} \equiv \frac{k\vartheta}{\omega c^2}$ we get

$$K(x) = \frac{2d^2\hbar\vartheta}{c^2}|x| \exp\left[-\frac{\vartheta}{c^2}\left(\hbar^2x^2 - \frac{\lambda^2}{4}\right)\right]\left[\Theta\left(x - \frac{|\lambda|}{2\hbar}\right) + \Theta\left(-x - \frac{|\lambda|}{2\hbar}\right)\right]. \tag{11}$$

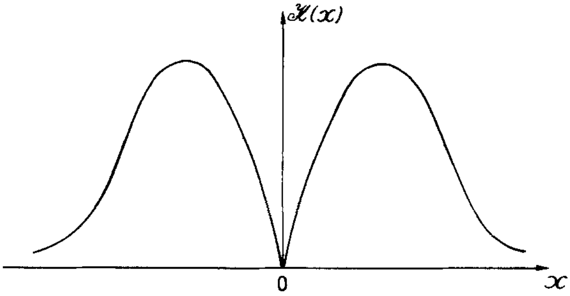

Fig. 1a

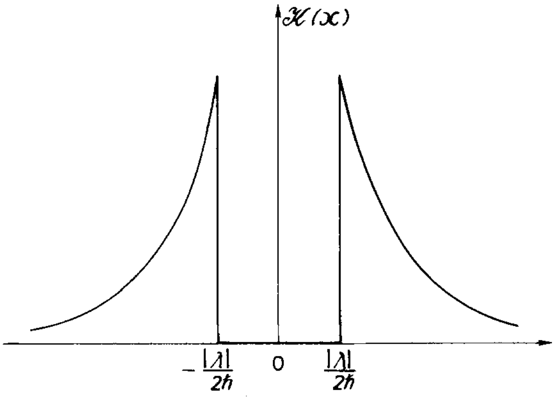

Fig. 1b

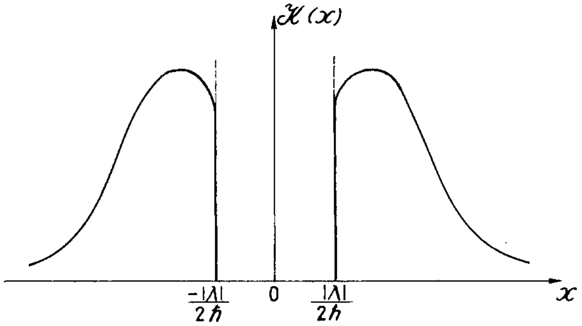

Fig. 1c

Fig. 1. The optical absorption band shape of $^2A \to {}^2E$ transition: a $\lambda = 0$, $c_1 \neq 0$, $c_2 \neq 0$; b $\lambda \neq 0$, $c_1 \neq 0$, $c_2 = 0$; c $\lambda \neq 0$, $\frac{k_1 \vartheta_1}{\omega_1 c_1^2} = \frac{k_2 \vartheta_2}{\omega_2 c_2^2} \equiv \frac{k \vartheta}{c \omega}$

The maxima of curve (11) are either at

$$x_{\max} = \pm \sqrt{\frac{c^2}{2\hbar^2 \vartheta}}, \quad \text{if} \quad \sqrt{\frac{c^2}{2\hbar^2 \vartheta}} > \frac{|\lambda|}{2\hbar},$$

or at (12)

$$x_{\max} = \pm \frac{|\lambda|}{2\hbar}, \quad \text{if} \quad \sqrt{\frac{c^2}{2\hbar^2 \vartheta}} < \frac{|\lambda|}{2\hbar}.$$

In the first case (12) (Fig. 1c) when the vibronic interaction exceeds the spin-orbit one maxima positions are temperature dependent, and the splitting of two peaks is proportional to $\sqrt{T}$ (at high temperature). This temperature dependence of the splitting takes place only in the temperature range $\vartheta < \vartheta_0 \equiv \frac{2c^2}{\hbar^2 \lambda^2}$. In this connection it is interesting to note the difference in the shapes of optical bands splitted by spin-orbit interaction in two cases: 1) the active modes forming the band shape are total symmetrical, 2) the JT b_{1g} and b_{2g} – modes are active. In

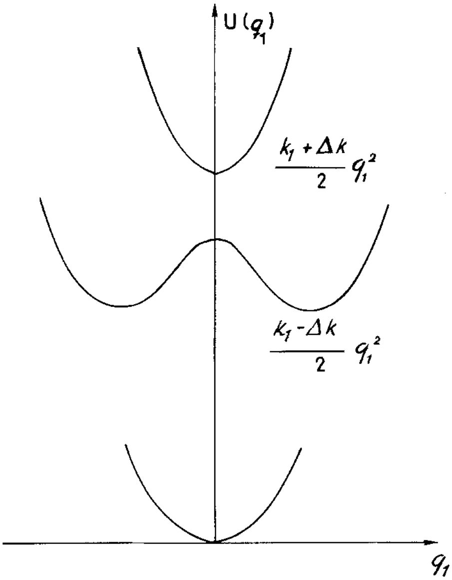

Fig. 2. Adiabatic potentials in the case $c_2 = 0$, $\lambda \neq 0$

the case 1) the spin-orbit interaction manifests itself as a "rigid" shift of Gaussian bands, and the structure of whole band may be not observe if λ is small enough. In contrary, in the case 2) the zero intensity range is appeared and two peaks are easily resolved. This result may be easily understood in the case $c_2 = 0$. Such form of the optical band results from the frequency shift of square-complex vibrations due to the simultaneous action of spin-orbit interaction and vibronic coupling (Fig. 2). Optical Franck-Condon transitions on the upper surface occurs at the $x > \frac{|\lambda|}{2\hbar}$, whereas the transitions on the lower surface leads to the absorption at $x < -\frac{|\lambda|}{2\hbar}$, so in the region $|x| < \frac{|\lambda|}{2\hbar}$ the absorption is absent.

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