Coordination Chemistry Reviews, 14 (1975) 357—412
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

THE JAHN—TELLER EFFECT IN CRYSTAL CHEMISTRY AND SPECTROSCOPY

I.B. BERSUKER

Department of Quantum Chemistry, Academy of Sciences, Moldavian SSR, 277028 Kishinev (USSR)

(Received May 6th, 1974)

CONTENTS

A. INTRODUCTION

The so-called Jahn—Teller effects at present form a new trend in the physics and chemistry of molecules and crystals, joining together all the manifestations of interactions in degenerate and pseudo-degenerate states of polyatomic systems. Although the Jahn—Teller theorem[1] was formulated* in 1937, its development began in the late 1950s and early 1960s, when experiments became available to substantiate the effects predicted by the theory.

Most Jahn—Teller systems are coordination compounds, almost all of which have an electronic degenerate or nearly degenerate (pseudo-degenerate) term in the ground or the first excited state. These degeneracies are due to their unfilled central atom *d* (or *f*) shells combined with a high-symmetry environment. As is shown below, small deviations from high symmetry, which formally remove the electronic degeneracy, do not necessarily remove the Jahn—Teller effects, and therefore practically all coordination compounds may be subjects of Jahn—Teller investigations.

Manifestations of the Jahn—Teller effect cover a wide range of physical and chemical properties and may be divided into two parts.

(a) Manifestations in the resonance methods of investigation (i.e. in the whole range of spectroscopy).

(b) Manifestations in non-resonance investigations (i.e. in stereochemistry, crystal chemistry, chemical reactivity, magnetic and electric polarizability and so on)

In the present paper, the theory of the main part of these effects, excluding chemical reactions (see Section G), is briefly considered. Attention will be paid to the basic ideas and their qualitative elucidation which lead to a proper understanding of the phenomenon as a whole and to its application. For well-known reasons, we shall try to avoid bulky mathematical deductions, bearing in mind, nevertheless, that mathematical language is a most adequate one for the physics and chemistry of molecules.

It is obvious that in a short review of the theory of the Jahn—Teller effect, it is impossible to present in detail all the material (in particular experimental) on this topic; it might constitute the material of a full (and perhaps more than one) monograph. The experimental papers mentioned below only serve as illustrations of the theoretical results, and therefore their choice may have an accidental character.

The outline of the subject and especially of its applications is given here from two aspects. After a brief consideration of the theoretical basis of the Jahn—Teller effect (Section B) the main corollaries of this effect — the complicated adiabatic potentials — are derived (Section C). Then a qualitative (and partly semiclassical) aspect of its applications to stereochemistry, crystal chemistry and spectroscopy (band shapes and polarized luminescence) is presented (Section D). This part of the treatment, though approximate, gives a good basis for a qualitative understanding of the Jahn—Teller effect. The more rigorous consideration is based on the solution of the vibronic equations (Section E), the two main results of which — tunneling splitting and vibronic

---

* In "A historical note", given as a preface to Englman's book[2], Teller acknowledged that the idea behind the Jahn—Teller effect belonged rightfully to Landau. More general proofs of this theorem were obtained recently[3].

reduction — lead to a series of observable effects (microwave and ultrasonic absorption, characteristic EPR and Mössbauer spectra, zero-phonon line splitting, a new kind of rotational spectrum and polarizability of highly symmetric molecules, and so on) (Section F).

B. THE FORMULATION AND THE MEANING OF THE JAHN—TELLER THEOREM. VIBRONIC EQUATIONS

There are few cases where the names of effects, scientific rules or laws do not reflect their meaning sufficiently. However, in the case of the Jahn—Teller theorem its commonly used formulation may lead to misunderstanding, and even give rise to a notion which is contrary to its real meaning. The widely accepted formulation of this theorem, initiated by its authors[1] and presented in monographs and textbooks, affirms that in an electronic degenerate state the nonlinear symmetrical nuclear configuration is unstable, and as a result of this instability the nuclei displace themselves in order to destroy the symmetry of their configuration and to remove the electronic degeneracy, until a non-degenerate ground state is achieved.

As one can see, this formulation contains two very important statements about the properties of polyatomic systems in the electronic degenerate states, namely, about (1) the spontaneous distortion of the nuclear configuration and (2) the removal of the ground state degeneracy. It is highly dramatic to note that both these statements, if taken literally, are incorrect and differ from what is really proved in the Jahn—Teller theorem[4,5].

In order to clarify this statement, let us start from first principles. The Hamiltonian of the system can be divided into three parts.

$$H = H_q + H_Q + V(q_\nu, Q_\alpha) \tag{1}$$

where the H_q and H_Q operators include all the interactions in the electronic and nuclear subsystems respectively, while $V(q_\nu, Q_\alpha)$ is the electron—nuclei (vibronic) interaction operator (hereafter q_ν and Q_α denote the total electronic and nuclear normal coordinates respectively).

In the adiabatic approximation, the solution of the Schrödinger equation for the system

$$H\Psi(q_\nu, Q_\alpha) = E\Psi(q_\nu, Q_\alpha) \tag{2}$$

is carried out in two successive steps. First the electronic part of eqn. (2)

$$[H_q + V(q_\nu, Q_\alpha)]\,\psi_i(q_\nu, Q_\alpha) = \epsilon'_i(Q_\alpha)\,\psi_i(q_\nu, Q_\alpha) \tag{3}$$

for the fixed nuclear coordinates Q is solved. The electronic energy $\epsilon'_i(Q_\alpha)$ as a function of Q_α together with the nuclear interaction term from H_Q (for details see Section C) form the so-called adiabatic potential $\epsilon_i(Q_\alpha)$.

What is really proved in the Jahn—Teller theorem refers to these adiabatic potentials: if there is a point $Q_\alpha = Q_{\alpha 0}$, $\alpha = 1,2,\ldots,N$ (N is the whole number of nuclei) where the values of several (f) adiabatic potentials coincide, $\epsilon_i(Q_{\alpha_0}) = \epsilon(Q_{\alpha_0})$, $i = 1,2, \ldots, f$ (i.e. if Q_{α_0} is a point of f-fold degeneracy), then none of the $\epsilon_i(Q)$ surfaces has a minimum at this point.

The proof of this statement is simple. Expanding the $V(q_\nu, Q_\alpha)$ operator in a series of small displacements from the point $Q_\alpha = Q_{\alpha_0}$ we have

$$V(q_\nu, Q_\alpha) = V(q_\nu, Q_{\alpha_0}) + \sum_\alpha \left(\frac{\partial V}{\partial Q_\alpha}\right)_0 (Q_\alpha - Q_{\alpha_0})$$

$$+ \frac{1}{2}\sum_{\alpha,\beta} \left(\frac{\partial^2 V}{\partial Q_\alpha \partial Q_\beta}\right)_0 (Q_\alpha - Q_{\alpha_0})(Q_\beta - Q_{\beta_0}) + \ldots \tag{4}$$

A minimum of the $\epsilon_i(Q_\alpha)$ surface at the point $Q_\alpha = Q_{\alpha_0}$ can be achieved only when all the electronic matrix elements of the linear terms of eqn. (4)

$$A = \int \psi_i^* \left(\frac{\partial V}{\partial Q_\alpha}\right)_0 \psi_i \, \mathrm{d}q_\nu \tag{5}$$

vanish, i.e. $A = 0$. Using symmetry considerations and group theoretical methods, one can easily show that, for any symmetry point group which admits degenerate terms, there are definite normal displacements Q_α for which the matrix element (5) does not vanish, i.e. $A \neq 0$. These coordinates Q_α, along which the surface $\epsilon_i(Q_\alpha)$ at the point Q_{α_0} has no minimum, are named Jahn—Teller active coordinates.

What conclusions can be drawn from the proved absence of minima of the adiabatic surfaces at the point of degeneracy?

For a non-degenerate electronic term, the full wave function in the adiabatic approximation (in the second step after solving eqn. (3)) is represented as a product of the electronic and nuclear wave functions.

$$\Psi_i(q_\nu, Q_\alpha) = \psi_i(q_\nu, Q_\alpha)\,\chi_i(Q_\alpha) \tag{6}$$

where the following equation for $\chi_i(Q_\alpha)$ can be derived.

$$\left[\sum_\alpha \left(-\frac{h^2}{2M_\alpha}\right)\frac{\partial^2}{\partial Q_\alpha^2} + \epsilon_i(Q_\alpha) - E_i\right]\chi_i(Q_\alpha) = 0 \tag{7}$$

Hence for the non-degenerate case, as is easily seen from eqn. (7), the adiabatic potential $\epsilon_i(Q_\alpha)$ plays the role of the potential energy of the nuclei (in the field of the electrons). Then the derivative $(\partial\epsilon/\partial Q_\alpha)_0$ has the physical sense of the generalized force, acting on the nuclei at the point Q_{α_0}, and its non zero value proves that the nuclear configuration will be distorted by this force till the point where $(\partial\epsilon/\partial Q_\alpha) = 0$ is reached. For this case, a classical (or semiclassical) approach in considering nuclear motions may be very useful for many problems.

But for degenerate electronic terms, the situation is more complicated. In the common formulation of the Jahn—Teller theorem, given at the beginning of this section, it is implicitly assumed that for a degenerate term the adiabatic potential has the same physical sense as for a non-degenerate term and, hence, the absence of a minimum on the $\epsilon_i(Q_\alpha)$ surface at the degeneracy point leads to a spontaneous distortion of the nuclear configuration. In fact, however, near the degenerate point there are several closely lying and intersecting surfaces $\epsilon_i(Q_\alpha)$ and therefore each loses any physical sense, becoming a formal notion.

It can be shown[5,8] that in this case the usual adiabatic approximation is not valid. In an approximation similar to the adiabatic one, in the case of electronic degeneracy the full wave function, instead of eqn. (6), takes the form

$$\Psi(q_\nu, Q_\alpha) = \sum_{j=1}^{f} \psi_j(q_\nu, Q_\alpha)\chi_j(Q_\alpha) \tag{8}$$

where the f nuclear coordinate functions $\chi_j(Q_\alpha)$ obey a system of f coupled equations,

$$\left[\sum_\alpha \left(-\frac{h^2}{2M_\alpha}\right)\frac{\partial^2}{\partial Q_\alpha^2} + \epsilon_i(Q_\alpha) - E_i\right]\chi_i(Q_\alpha) + \sum_{\substack{j=1\\ j\neq i}}^{f} A_{ij}\chi_j(Q_\alpha) = 0 \tag{9}$$

and A_{ij} are the electronic non-diagonal matrix elements of the Hamiltonian.

From these equations, it is easily seen that in the case of electronic degeneracy under consideration, the electronic and nuclear motions are essentially mixed (eqn. (8)) and $\epsilon_i(Q_\alpha)$ no longer plays the role of pure nuclear potential energy, so the concept of classical motions of the nuclei on the $\epsilon_i(Q_\alpha)$ surfaces becomes invalid (at least near the point of degeneracy; see Section D).

Thus in the case of electronic degeneracy, it is impossible to draw definite conclusions concerning the properties of the system knowing only some features of the adiabatic potentials near the point of degeneracy, supplied by the Jahn—Teller theorem. For such conclusions, the potentials $\epsilon_i(Q_\alpha)$ in the whole space of the Q_α coordinates and the solutions of eqns. (9) must be known.

It will be shown below that, strictly speaking, the solutions of eqns. (9) give neither nuclear configuration distortion nor ground state degeneracy removal, vibronic effects being of a dynamic nature and hence more complicated. The characteristic distortions as well as degeneracy removal for the Jahn—Teller system as a whole can be revealed only when an external influence is present. The Jahn—Teller theorem is essential in stimulating the investigation of potential surface and the solution of eqns. (9) which lead to extremely interesting new effects for electronically degenerate polyatomic systems.

A special vibronic case is supplied by the systems with so-called electronic pseudo-degeneracy (pseudo-Jahn—Teller effect). The vibronic coupled eqns. (9) decouple and become the usual eqn. (7) if the last terms, containing the

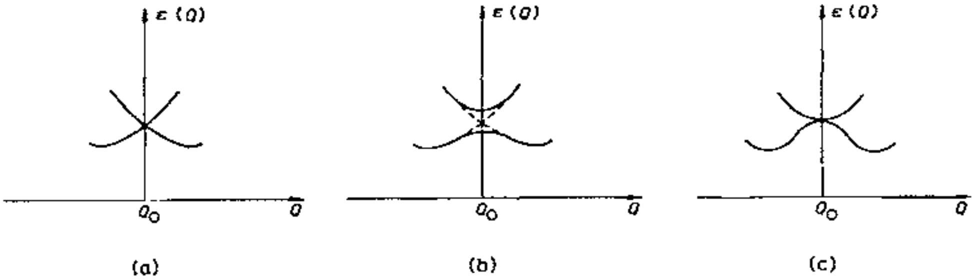


Fig. 1. The adiabatic potential behaviour near the point of degeneracy (or pseudo-degeneracy) for (a) strong Jahn—Teller, (b) pseudo-Jahn—Teller and (c) Renner-type vibronic coupling.

electronic non-diagonal matrix element of the Hamiltonian A_{ij} are omitted. If there is no degeneracy and the energy difference $\epsilon_i - \epsilon_j$ is great enough, the A_{ij} terms may be neglected compared with $\epsilon_i - \epsilon_j$ (a quantitative criterion is given in Section C).

In the case of exact degeneracy $\epsilon_i = \epsilon_j$, these terms cannot be neglected. However, there are intermediate cases when there is no degeneracy, i.e. $\epsilon_i \neq \epsilon_j$ in the whole region of Q_α coordinates, but for some points the difference $\epsilon_i - \epsilon_j$ is small or comparable with the A_{ij}'s. For these cases, the terms A_{ij} cannot be omitted and thus, although the electronic term is non-degenerate, the vibronic problem reduces to the same system of coupled vibronic eqns. (9). As will be shown below, the vibronic effects arising here, known as the pseudo-Jahn—Teller effects, are similar to ones for the case of exact degeneracy (the Jahn—Teller effects), though some additional specific features are possible.

In Fig. 1, the distinction in the adiabatic potential behaviour near the point of degeneracy or pseudo-degeneracy for these two cases, Jahn—Teller and pseudo-Jahn—Teller, is illustrated (for simplicity only one active coordinate is taken into account). The Renner-type behaviour[7] is also shown for comparison. As one can see, there is a real intersection of the two adiabatic potentials in the Jahn—Teller case, while there is only a pseudo-intersection in the pseudo-Jahn—Teller case. But, in the case of a strong vibronic interaction, in the region far enough from the point $Q = Q_0$, this distinction is lost and the adiabatic potentials behaviour in the two cases become quite similar.

C. ADIABATIC POTENTIALS FOR ORBITALLY DEGENERATE AND PSEUDO-DEGENERATE STATES

The conclusion from the discussion given above is that, if by solving eqn. (3) coinciding (at the point $Q_\alpha = Q_{\alpha_0}$) adiabatic potential values $\epsilon_i'(Q_{\alpha_0}) = \epsilon'(Q_{\alpha_0})$, $i = 1,2, \ldots, f$ (f-fold degeneracy) are obtained, then the properties of the molecule under consideration can be determined by a subsequent solution of the system of coupled eqns. (9). For this purpose, the adiabatic potentials have first to be determined, which will be done in this section. As will be shown in the next section, knowledge of the adiabatic potentials is also important as such, since many qualitative deductions can be derived from the $\epsilon(Q_\alpha)$ surface shape without solving eqns. (9).

For the coordination compounds in question, only twofold ($f = 2$) and threefold ($f = 3$) orbital degeneracies (E and T electronic terms, respectively) are required, the T terms being inherent only for cubic systems (octahedral, tetrahedral, cubic). A higher-fold degeneracy, say $f = 5$, might occur for an icosahedral molecule which will not be considered here, since it is a very uncommon case.

Calculation of the adiabatic potentials is not complicated. First we divide the electronic subsystem, as usual, into two parts, the valence electrons and those of the atomic core. The vibronic interaction $V(q_\nu, Q_\alpha)$ is assumed to involve only the valence electrons, while the atomic core interactions can be approximated by means of a harmonic term $\frac{1}{2}\sum_\alpha K_\alpha Q_\alpha^2$, where $K_\alpha = M_\alpha\omega_\alpha^2$ is the force constant for the Q_α normal vibration (M_α is the reduced mass and ω_α is the frequency).

Let us assume that by solving the electronic eqn. (3) for the point $Q_\alpha = Q_{\alpha_0}$ we obtain a twofold degenerate E term or a threefold degenerate T term. For small deviations of Q_α from Q_{α_0}, the potential energy $V(q_\nu, Q_\alpha)$ after eqn. (4) differs little from the $V(q_\nu, Q_{\alpha_0})$ value and hence the magnitude

$$V' = V(q_\nu,Q_\alpha) - V(q_\nu,Q_{\alpha_0})$$

$$= \sum_\alpha \left(\frac{\partial V}{\partial Q_\alpha}\right)(Q_\alpha - Q_{\alpha_0}) + \frac{1}{2}\sum_{\alpha,\beta}\left(\frac{\partial^2 V}{\partial Q_\alpha \partial Q_\beta}\right)_0 (Q_\alpha - Q_{\alpha_0})(Q_\beta - Q_{\beta_0}) + \ldots \quad (10)$$

may be considered as a small perturbation. The perturbation problem for a degenerate term is reduced to the following secular equation.

$$\| V'_{ij} - \epsilon'\delta_{ij} \| = 0, \; i,j = 1,2, \ldots, f \quad (11)$$

from which f roots $\epsilon'_k(Q_\alpha)$ can be obtained. Together with the core interaction terms these form the required adiabatic potentials.

$$\epsilon_k(Q_\alpha) = \frac{1}{2}\sum_\alpha K_\alpha Q_\alpha^2 + \epsilon'_k(Q_\alpha), \; k = 1,2, \ldots, f \quad (12)$$

(i) The E term (the "Mexican hat" and tetragonal minima)

In a general form the two electronic functions of the degenerate E term may be denoted as $|\theta\rangle$ and $|\epsilon\rangle$, their symmetry properties being determined by the well-known coordinate functions $\theta \sim 3z^2 - r^2$ and $\epsilon \sim x^2 - y^2$ (respectively d_{z^2} and $d_{x^2-y^2}$ functions after the transition metal d-function nomenclature). To calculate the V'_{ij} matrix elements, we take into account the group theoretical condition $[E^2] = A_1 + E$ due to which only the a_1-type (totally

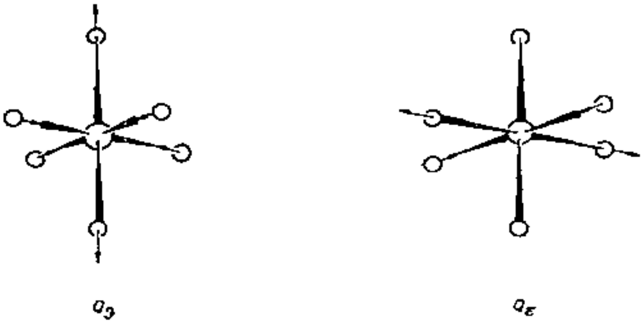


Fig. 2. Q_θ and Q_ϵ components of the tetragonal e_g-type vibrations for an octahedral system.

symmetric) and the e-type (twofold degenerate) vibration terms in eqn. (10) give non zero V'_{ij} values (hereafter we use small letters for vibration symmetry, as distinguished from the capital letters used for the electronic and full terms). Since the totally symmetric coordinate a_1 can be excluded by means of an appropriate choice of its zero reading, the only active coordinates in the vibronic interaction (the Jahn—Teller active coordinates) remain e type. Therefore the E term vibronic problem denotation can be abbreviated as the E—e problem.

Thus a vibronic correction term $\epsilon'_k(Q_\alpha)$ in eqn. (12) is present only for the coordinates Q_α of the e-type vibrations. For others, the adiabatic potential keeps the simple form

$$\epsilon(Q_\alpha) = \left(\frac{1}{2}\right)\sum_\alpha K_\alpha Q_\alpha^2$$

common to the non-degenerate case.

The twofold degenerate e-type vibrations may be represented by two coordinates Q_θ and Q_ϵ (Fig. 2). Assuming the point $Q_{\theta_0} = Q_{\epsilon_0} = 0$ to be zero reading, and taking into account only the linear and second-order terms of eqn. (10), one can obtain from eqn. (11) the secular equation[5,8—10]

$$\begin{vmatrix} A_1 Q_\theta + A_2(Q_\theta^2 - Q_\epsilon^2) - \epsilon' & -A_1 Q_\epsilon + 2A_2 Q_\theta Q_\epsilon \\ -A_1 Q_\epsilon + 2A_2 Q_\theta Q_\epsilon & -A_1 Q_\theta - A_2(Q_\theta^2 - Q_\epsilon^2) - \epsilon' \end{vmatrix} = 0 \tag{13}$$

where the quantities

$$A_1 = \left(\frac{\partial V_{\theta\theta}}{\partial Q_\theta}\right)_0 \text{ and } A_2 = \frac{1}{2}\left(\frac{\partial^2 V_{\theta\theta}}{\partial Q_\theta^2}\right)_0 \tag{14}$$

are the so-called linear (A_1) and second-order (A_2) vibronic coupling constants in the E—e problem. The solution of eqn. (13) is more convenient when written down in polar coordinates.

$$Q_\theta = \rho \cos\phi, \quad Q_\epsilon = \rho \sin\phi \tag{15}$$

Then

$$\epsilon'_\pm (\rho,\phi) = \pm\, \rho\, [A_1^2 + A_2^2\rho^2 + 2A_1A_2\rho \cos 3\phi]^{\frac{1}{2}} \tag{16}$$

and

$$\epsilon_\pm (\rho,\phi) = \tfrac{1}{2} K_e\rho^2 \pm \rho[A_1^2 + A_2\rho^2 + 2A_1A_2\rho \cos 3\phi]^{\frac{1}{2}} \tag{17}$$

If the second-order vibronic coupling terms are negligible, i.e. if $A_2 = 0$, then

$$\epsilon_\pm (\rho,\phi) = \tfrac{1}{2} K_e\rho^2 \pm A_1\rho \tag{18}$$

In this case the adiabatic potential in the space of the Q_θ and Q_ϵ coordinates is independent of ϕ and has the form of a rotation figure named "the Mexican hat" (Fig. 3).

When the second-order terms are taken into account, some warping ("crimping") of this surface occurs resulting in regularly alternating humps and wells along the bottom of the trough (Fig. 4). The turning points of the surface are

$$\rho_0 = \frac{\pm A_1}{K_e \mp (-1)^n 2A_2}, \quad \phi_0 = \frac{n\pi}{3}, \quad n = 0,1,\ldots,5 \tag{19}$$

the upper and lower signs corresponding to the cases $A_1 > 0$ and $A_1 < 0$ respectively. If $A_1/A_2 > 0$ the minima points occur for $n = 0,2,4$ and saddle-points for $n = 1,3,5$, while for the case $A_1/A_2 < 0$ the two types of points

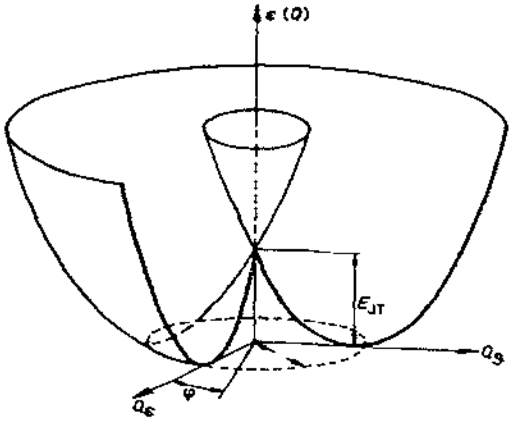


Fig. 3. The "Mexican hat"-like adiabatic potential in the space of Q_θ and Q_ϵ e-type displacement for an E-term system (E—e problem) in the linear approximation.

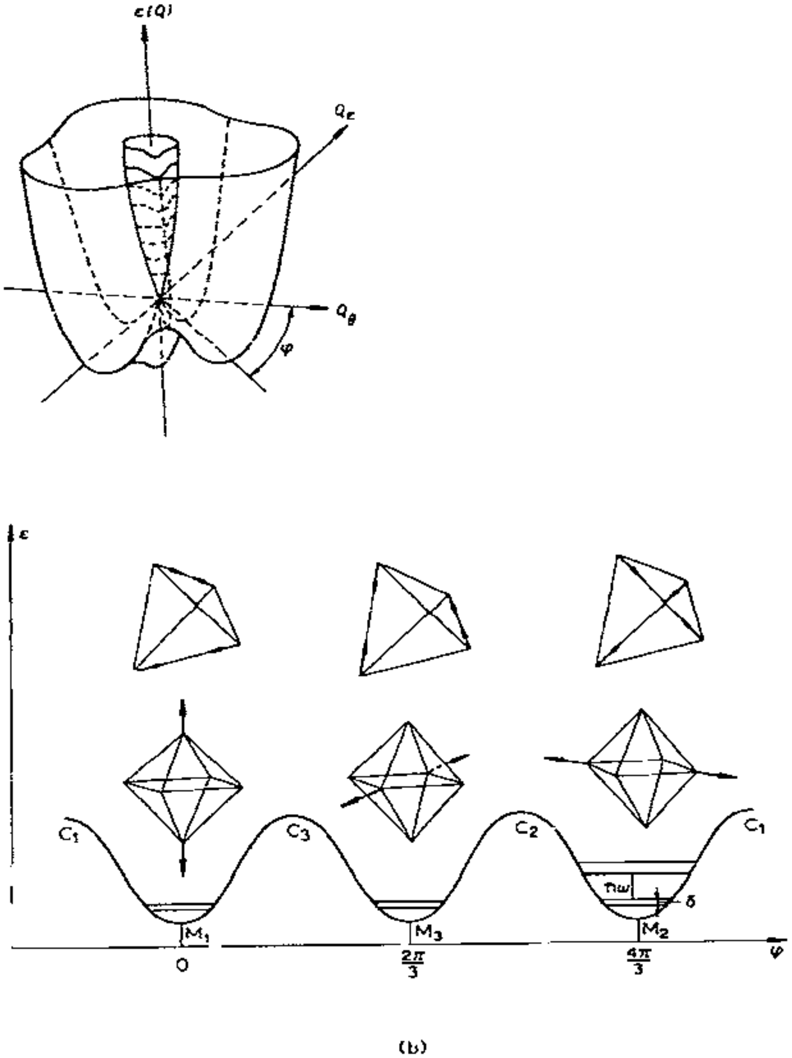


Fig. 4. The adiabatic potential (a) and its ϕ coordinate angular dependence along the bottom of the lower sheet (b) for an E-term system (E—e problem) in the second-order approximation. The directions of distortion of octahedral and tetrahedral systems in the minima points are also shown for illustration.

interchange (for all the cases it is assumed that $K_e > 2A_2$). The minima depths read off from the electronic degeneracy point — the Jahn—Teller stabilization energy E_{JT} — are determined by the expression

$$E_{JT} = \tfrac{1}{2}A_1^2/(K_e - 2A_2) \tag{20}$$

and the (minimal) barrier height between the minima is

$$\Delta = 4A_2E_{JT}/(K_e - 2A_2) \tag{21}$$

The two electronic wave functions corresponding to the two solutions of eqn. (13) (two sheets of the surface (17)) take the form

$$\begin{aligned}\Psi_- &= \cos\frac{\Omega}{2}|\theta\rangle - \sin\frac{\Omega}{2}|\epsilon\rangle\\ \Psi_+ &= \sin\frac{\Omega}{2}|\theta\rangle + \cos\frac{\Omega}{2}|\epsilon\rangle\end{aligned} \tag{22}$$

where

$$\tan\Omega = \frac{A_1\sin\phi - A_2\rho\sin 2\phi}{A_1\cos\phi + A_2\rho\cos 2\phi} \tag{23}$$

Note that in all publications on this topic until ref. 11, it was assumed that $\Omega \equiv \phi$, which is correct only in the linear approximation when $A_2 = 0$.

Taking into account the nuclear displacements for the normal coordinates Q_θ and Q_ϵ (Fig. 2) and their values in the minima points (19), one can easily determine the Jahn—Teller distortions of the nuclear configuration illustrated in Fig. 4.

(ii) The T term, linear approximation (tetragonal and trigonal minima)

The T terms are of two kinds, T_1 and T_2, for which the vibronic problem is rather similar. Therefore we shall consider here only one case, say, the T_2 term. The basic three wave functions for the electronic T_2 term $|\xi\rangle$, $|\eta\rangle$ and $|\zeta\rangle$, can be taken to transform as the Cartesian coordinate products yz, xz and xy, respectively. According to the group theoretical condition $[T^2] = A_1 + E + T_2$, in the T-term case there are two types of totally/symmetric vibrations, e and t_2, which are active in the Jahn—Teller effect (the denotation of the problem is abbreviated as T—$(e + t_2)$). The t_2 type is threefold degenerate, its three components Q_ξ, Q_η and Q_ζ involving nuclear displacements shown in Fig. 5. The secular eqn. (11) is of the third order and has

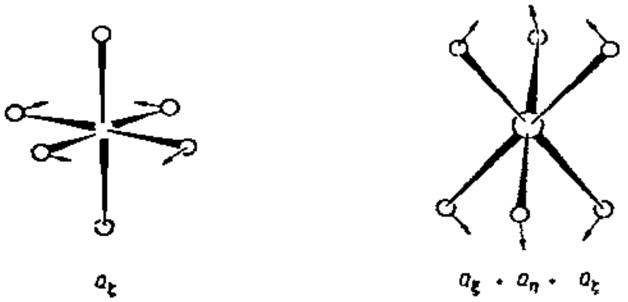


Fig. 5. Trigonal t_2-type Q_ζ and $Q_\xi + Q_\eta + Q_\zeta$ displacements for an octahedral system.

three solutions $\epsilon'_k(Q_\alpha)$ which represent three sheets of the adiabatic potential in the five-dimensional space of the Q_α coordinates, $\alpha = \theta,\epsilon,\xi,\eta,\zeta$. ($Q_\alpha = 0$ is the point of intersection of all the three sheets). The T—$(e + t_2)$ problem is therefore much more complicated than the E—e, and there are no simple analytical expressions for the T-term adiabatic potentials similar to eqn. (17) for the E-term case.

In particular, when only linear vibronic terms in eqn. (10) are taken into account, the secular eqn. (11) for the T-term case is[12] (see also ref. 13):

$$\begin{vmatrix} C\left(-\frac{1}{2}Q_\theta + \frac{(3)^{\frac{1}{2}}}{2}Q_\epsilon\right) - \epsilon' & BQ_\zeta & BQ_\eta \\ BQ_\zeta & C\left(-\frac{1}{2}Q_\theta - \frac{(3)^{\frac{1}{2}}}{2}Q_\epsilon\right) - \epsilon' & BQ_\xi \\ BQ_\eta & BQ_\xi & CQ_\theta - \epsilon' \end{vmatrix} = 0 \quad (24)$$

where

$$B = \left(\frac{\partial V_{\eta\zeta}}{\partial Q_\xi}\right)_0 \text{ and } C = \left(\frac{\partial V_{\zeta\zeta}}{\partial Q_\theta}\right)_0 \quad (25)$$

are the trigonal and tetragonal linear vibronic constants, respectively. Although it is very difficult to obtain convenient expressions for ϵ', solutions of eqn. (24), the turning points of the surface (12) can be determined using the procedure suggested by Opik and Pryce[12] (which avoids the complete solution of these equations). Omitting the calculations, we give here the results.

The three sheets of the surface are

$$\epsilon_i = \tfrac{1}{2}\,K_e\,(Q_\theta^2 + Q_\epsilon^2) + \tfrac{1}{2}K_t\,(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2) + \epsilon'_i,\ i = 1,2,3 \quad (26)$$

where ϵ'_k are the solutions of eqn. (24) and $K_t = M_t\omega_t^2$, ω_t being the frequency of the trigonal vibrations. The surface (26) has three types of turning point. (1) Three tetragonal points for which, similar to the E-term case, only the tetragonal coordinates Q_θ and Q_ϵ are displaced from their high-symmetry $Q_\theta = Q_\epsilon = 0$ values; (2) four trigonal points for which only the trigonal Q_ϵ, Q_η and Q_ζ coordinates are displaced (see Table 1 and Fig. 6); (3) six orthorhombic points for each of which one tetragonal and one trigonal coordinate is displaced (Table 1).

The depths of these points are respectively

$$E^e_{JT} = C^2/2K_e,\ E^t_{JT} = 2B^2/3K_t,\ E^o_{JT} = \tfrac{1}{4}\,E^e_{JT} + \tfrac{3}{4}E^t_{JT} \quad (27)$$

and if

$$C^2/2K_e > 2B^2/3K_t \quad (28)$$

TABLE 1

Turning points of the adiabatic potential for an electronic T term, linearly coupled to e and t_2 vibrations (*linear* $T-(e+t_2)$ *problem*)

Number of equivalent points r	Nature	Coordinates in five-dimensional space $(Q_\theta, Q_\epsilon, Q_\xi, Q_\eta, Q_\zeta)$
3	Tetragonal minima or saddlepoints	$(C/K_e, 0, 0, 0, 0)$
		$(-3C/2K_e, C/2K_e, 0, 0, 0)$
		$(-3C/2K_e, -C/2K_e, 0, 0, 0)$
4	Trigonal minima or saddlepoints	$(0, 0, 2B/3K_t, 2B/3K_t, 2B/3K_t)$
		$(0, 0, -2B/3K_t, -2B/3K_t, 2B/3K_t)$
		$(0, 0, -2B/3K_t, 2B/3K_t, -2B/3K_t)$
		$(0, 0, 2B/3K_t, -2B/3K_t, -2B/3K_t)$
6	Orthorhombic saddlepoints	$(-C/2K_e, 0, 0, 0, B/K_t)$
		$(-C/2K_e, 0, 0, 0, -B/K_t)$
		$(3C/4K_e, -C/4K_e, 0, B/K_t, 0)$
		$(3C/4K_e, -C/4K_e, 0, -B/K_t, 0)$
		$(3C/4K_e, C/4K_e, B/K_t, 0, 0)$
		$(3C/4K_e, C/4K_e, -B/K_t, 0, 0)$

then the tetragonal points are absolute minima (and the trigonal ones are saddle points), but for the opposite inequality, the trigonal ones become absolute minima, whereas the orthorhombic turning points in the linear approximation under consideration are always saddle points.

In particular, when $C^2/2K_e = 2B^2/3K_t$, all the extrema points are at the same depth. This case was shown to have a continuum of minima points

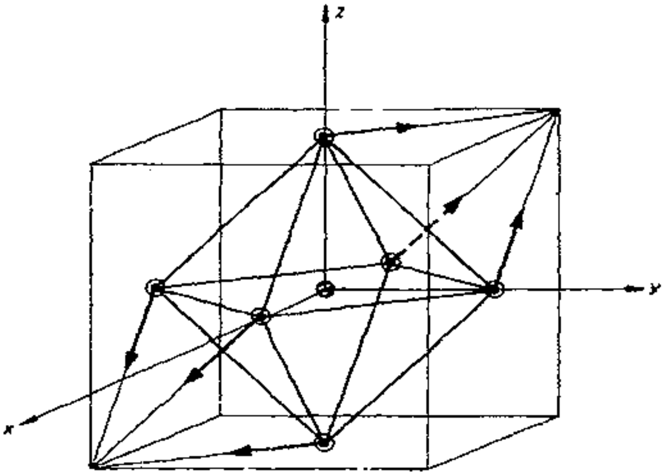


Fig. 6. Illustration of a trigonal distortion of an octahedral system (cf. the $Q_\epsilon + Q_\eta + Q_\zeta$ displacement in Fig. 5).

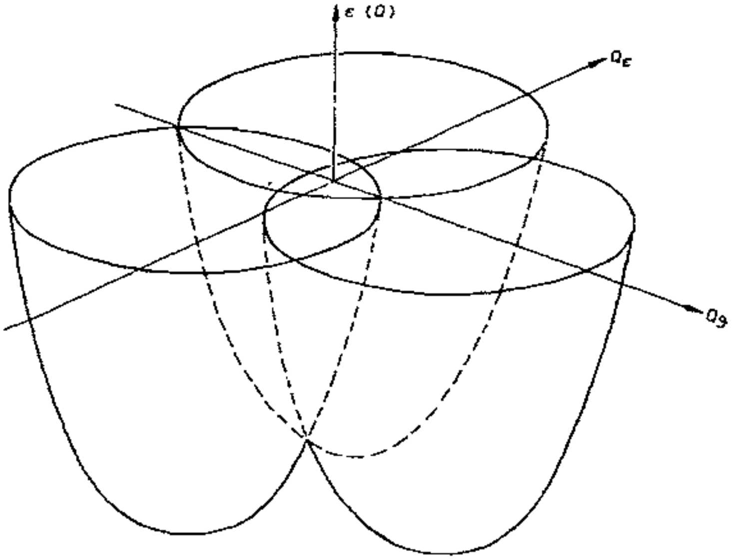


Fig. 7. The adiabatic potential for a T-term system linearly coupled to tetragonal e-type vibrations only (T—e problem) — three equivalent paraboloids.

forming a two-dimensional trough in the five-dimensional space[14] (in principle similar to the Mexican hat in the E-term case).

Since the two vibronic coupling constants, B and C, in the T—$(e + t_2)$ problem are independent, a situation is possible when one of them is negligibly small. If $B = 0$ then the linear trigonal displacements from the $Q_\alpha = 0$ point disappear and eqn. (24) can be solved directly. The adiabatic potential of the T term in the space of only e displacements (T—e problem) consists of three equivalent paraboloids intersected in the point of degeneracy (Fig. 7). In each of them the system under consideration is tetragonally distorted, quite similar to the E—e case (Fig. 4). But the electronic states in these paraboloids, described by the $|\xi\rangle$, $|\eta\rangle$ and $|\zeta\rangle$ functions respectively, as distinguished from the E-term case, are mutually orthogonal and, therefore, completely "isolated" (the system once placed in a definite paraboloid state cannot by itself pass to another one).

Another particular case, $C = 0$, $B \neq 0$ (the T—t_2 problem), leads to four equivalent trigonal minima of the adiabatic potential (Fig. 6).

(iii) The T term, second-order approximation (orthorhombic minima)

As has recently been shown[15], the result obtained above, that in the T—$(e + t_2)$ problem the adiabatic potential minima can be only either tetragonal or trigonal, is specific for the linear vibronic coupling approximation used, and when the second-order vibronic coupling terms are taken into account, a new type of absolute minima may occur, namely, orthorhombic (which in the linear approximation can only be saddle points).

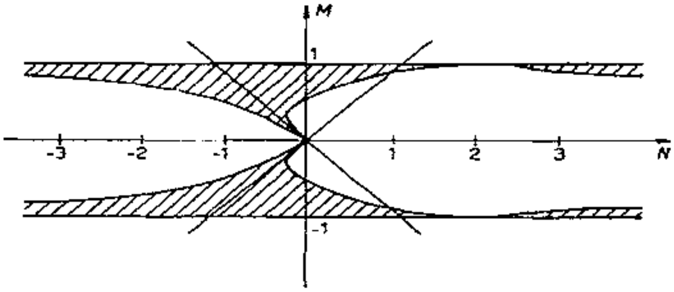


Fig. 8. The orthorhombic minima "occurrence zone" on the MN plane for a T-term system coupled to both e and t_2-type vibrations (T—$(e + t_2)$ problem) in the second-order approximation.

The most important second-order vibronic terms are of the $E \times T_2$ type mixing the e and t_2 displacements. Taking them into account and denoting the appropriate vibronic coupling constant by D, one has to deal with five parameters of the problem, K_e, K_t, B, C and D. However, the main characteristic features of the vibronic properties can be described by means of only two dimensionless combinations of these parameters, $M = D/(K_e K_t)^{\frac{1}{2}}$ and $N = CD/BK_e$ (it is assumed that $M < 1$).

From the results obtained in the second vibronic coupling approximation[15] the most important seems to be the relationship between the parameters for which the orthorhombic extrema points become absolute minima. It may be represented by means of the "occurrence zone" on the MN plane (Fig. 8). Along the lines $M = \pm N3^{½}/2$ the depths of the tetragonal and trigonal turning points concide, $E^{e}_{JT} = E^{t}_{JT}$, but as the point $N = M = 0$ (which corresponds to the linear approximation $D = 0$) the same depths have the orthorhombic points too, $E^{e}_{JT} = E^{t}_{JT} = E^{o}_{JT}$, so the two-dimensional trough in the five-dimensional space is realized.

Out of this point $E^{o}_{JT} \neq E^{e,t}_{JT}$ and hence the trough is warped ("crimped") in principle similar to the E—e case (Fig. 4) but in a more complicated fashion. Two cases dependent on the D values are possible here, $E^{o}_{JT} < E^{e,t}_{JT}$ and $E^{o}_{JT} > E^{e,t}_{JT}$. In the latter the orthorhombic extrema points become absolute minima, and the appropriate parameter values for this case can be found from the shaded area ("occurrence zone") in Fig. 8.

The coordinates of one of these orthorhombic minima are

$$\begin{aligned} Q_{\theta 0} &= -C\,(N - 2M^2)/2K_e N\,(1 - M^2) \\ Q_{\zeta 0} &= B\,(2 - N)/2K_t(1 - M^2),\ Q_{\epsilon 0} = Q_{\eta 0} = Q_{\xi 0} = 0 \end{aligned} \tag{29}$$

(the others can be determined by symmetry operations) and their depth is

$$E^{o}_{JT} = C^2(N^2 + 4M^2 - 4M^2N)/8K_e N^2(1 - M^2) \tag{30}$$

Together with this essential change of orthorhombic point behaviour, the account of the second-order vibronic terms also reveals some new types of less symmetrical twelve-equivalent extrema points which, however, have been shown never to become absolute minima[15].

(iv) Pseudo-degenerate states

Consider first the simplest case[12] of two non-degenerate states, Ψ_1 and Ψ_2, divided by an energy interval 2Δ. Taking, as above, the linear vibronic interaction terms of eqn. (10) as perturbation and assuming that there is only one vibronic active coordinate Q, we obtain the following perturbation theory secular equation (the energy is read off from the middle of the two levels).

$$\begin{vmatrix} \Delta - \epsilon' & aQ \\ aQ & -\Delta - \epsilon' \end{vmatrix} = 0 \tag{31}$$

where

$$a = \left(\frac{\partial V_{12}}{\partial Q}\right)_0$$

is the vibronic coupling constant (cf. eqn. (14)).

The solution of eqn. (31) — the vibronic corrections to the electronic energies — can be obtained immediately

$$\epsilon'_{1,2} = \pm\,(\Delta^2 + a^2Q^2)^{\frac{1}{2}} \tag{32}$$

Together with the core interaction term from eqn. (12), we obtain the following expression for the adiabatic potentials.

$$\epsilon_{1,2}\,(Q) = \tfrac{1}{2}\,KQ^2 \pm (\Delta^2 + a^2Q^2)^{\frac{1}{2}} \tag{33}$$

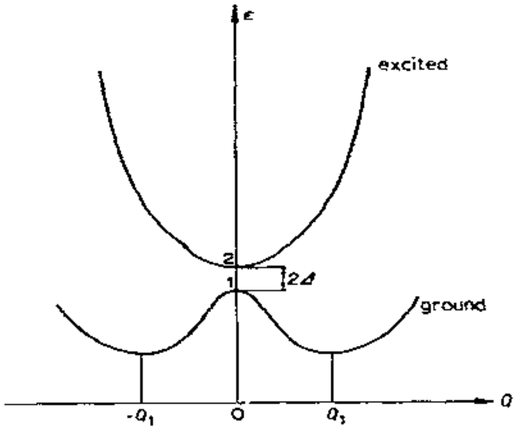
where it is assumed that the core force constant K is the same in the two states under consideration.

Expression (33) shows clearly that, under the influence of the vibronic coupling $a \neq 0$, the two states change differently: the curvature of the upper curve increases whereas that of the lower one decreases and becomes zero when $a^2 = \Delta K$. If

$$\Delta < \frac{a^2}{K} \tag{34}$$

the curvature of the lower curve becomes negative, i.e. the system in the lower (ground) state becomes unstable with regard to the Q displacements. The adiabatic potential in this case has two equivalent minima at the points $\pm\,Q_0$ (Fig. 9)

$$Q_0 = (a^2/K^2 - \Delta^2/a^2)^{\frac{1}{2}} \tag{35}$$



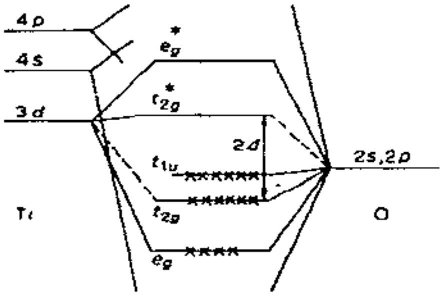


Fig. 9. Illustration to a two-level (and one active coordinate) pseudo-degenerate case. The two minima at the points $\pm Q_1$ may be of dipolar type.

Fig. 10. One electron level scheme and their electron population for a d^0 complex of TiO_6 type[16] in $BaTiO_3$.

Consider now a more complicated case of d^0 coordination compounds with a non-degenerate ground state, e.g. an octahedral complex of tetravalent titanium with, say, an oxygen-type environment[16]. Its simple one-electron energy level scheme is illustrated in Fig. 10 where the electronic population is also shown (the one-electron levels are denoted by small letters). For the ground state adiabatic potential analysis, the vibronic mixing of the nearest six $2p_\pi$ oxygen functions and three $3d_\pi$ titanium functions which together form the t_{2g}, t_{1u} and t_{2g}^* electronic levels must be taken into account. The ground electronic term of the system as a whole is ${}^1A_{1g}$ and the first excited term (of the same spin multiplicity) is ${}^1T_{1u}$.

The only active coordinates mixing the ground and excited terms are of the T_{1u} type. Taking into account its three components, Q_x, Q_y and Q_z, each of which removes the inversion center and moves the Ti atom along the appropriate fourfold axis, one can obtain the vibronic secular eqn. (11) of the ninth order (according to the nine functions involved in the vibronic mixing mentioned above) which in the linear approximation of eqn. (10) has the following roots[16].

$$\epsilon'_{1,2} = \pm\,[\Delta^2 + a^2(Q_x^2 + Q_y^2)]^{\frac{1}{2}}, \quad \epsilon'_{3,4} = [\Delta^2 + a^2(Q_x^2 + Q_z^2)]^{\frac{1}{2}},$$

$$\epsilon'_{5,6} = \pm\,[\Delta^2 + a^2(Q_y^2 + Q_z^2)]^{\frac{1}{2}}, \quad \epsilon'_{7,8,9} = -\Delta\,,$$

where

$$a = \langle 2p_y \left| \left(\frac{\partial V}{\partial Q_x}\right)_0 \right| 3d_{xy} \rangle \qquad (37)$$

Then for the adiabatic potential of the ground state in the space of the coordinates Q_x, Q_y and Q_z we obtain the following approximate expression.

$$\epsilon\,(Q_x, Q_y, Q_z) = \tfrac{1}{2}\,K(Q_x^2 + Q_y^2 + Q_z^2) - 2\,[\Delta^2 + a^2(Q_x^2 + Q_y^2)]^{\frac{1}{2}} + [\Delta^2 + a^2(Q_x^2 + Q_z^2)]^{\frac{1}{2}} + [\Delta^2 + a^2(Q_y^2 + Q_z^2)]^{\frac{1}{2}} \qquad (38)$$

The shape of this surface is determined by the relation of its three parameters Δ, K and a. If $\Delta > 4a^2/K$, then the surface (38) has a single minimum at the point $Q_x = Q_y = Q_z = 0$ for which the system is not distorted from its initially assumed high symmetry configuration. But if

$$\Delta < \frac{4a^2}{K} \qquad (39)$$

the surface (38) has four types of extrema points.

(1) One maximum is at the point $Q_x = Q_y = Q_z = 0$.

(2) Eight minima are at the points $Q_x = Q_y = Q_z = Q_0{}^{(1)}$

$$Q_0^{(1)} = (8a^2/K - \Delta^2/2a^2)^{\frac{1}{2}} \qquad (40)$$

and at a depth (read off the point (1))

$$E_{\mathrm{PJT}}^{(1)} = 3\,[4a^2/K + \Delta^2 K/4a^2 - 2\Delta] \qquad (41)$$

In these minima, the Ti atom is displaced along the trigonal axes toward three oxygen atoms simultaneously.

(3) Twelve saddlepoints at $Q_p = Q_q \neq 0$, $Q_r = 0$ ($p, q, r = x, y, z$) are minima in the p and q directions and maxima along Q_r. In these points, the titanium atom is displaced towards two oxygen atoms situated on the p and q axes.

(4) Six saddlepoints are at the points $Q_p = Q_q = 0$, $Q_r = Q_0^{(2)}$

$$Q_0^{(2)} = (16a^2/K^2 - \Delta^2/a^2)^{\frac{1}{2}} \qquad (42)$$

and at a depth

$$E_{\mathrm{PJT}}^{(2)} = 2\,[4a^2/K + \Delta^2 K/4a^2 - 2\Delta] \qquad (43)$$

For tetrahedral systems, a similar treatment is possible[17]. Here one may expect four equivalent minima, in each of which there is one non-equivalent (the other three remaining equivalent) metal—ligand bond, shortened or elongated.

Thus the examples considered in this section make it clear that the vibronic interaction for electronic states energetically close enough (pseudo-degeneracy) leads to the same kind of effects inherent to states of exact degeneracy, namely nuclear configuration instability and the presence of several adiabatic potential minima.

The condition of pseudo-degeneracy obtained above (eqn. (34) or eqn.

(39)) in principle has the same form for other cases too. It must be emphasized that since it contains three competing magnitudes, the condition for one of them, say Δ, may be very soft, i.e. there may be cases when the pseudodegeneracy condition is fulfilled for great absolute values of Δ.

More exciting than the similarity is the distinction between the degeneracy (Jahn—Teller) and pseudo-degeneracy (pseudo-Jahn—Teller) cases. Whereas in the Jahn—Teller case the vibronic active coordinates can be only of the even type, in the pseudo-Jahn—Teller case they may be of the odd type as well. An example of the latter was considered above for the d^0 octahedral complex of titanium[16]. The odd-type distortion leads to dipole moment formation and, hence, the pseudo-Jahn—Teller systems may be dipolar unstable[16—18], the effect being impossible for a Jahn—Teller system possessing a center of inversion. For a system without an inversion center (e.g. tetrahedral complex) the Jahn—Teller distortions in the T—t_2 problem may also be of a dipolar type.

D. SOME QUALITATIVE RESULTS

The adiabatic potentials obtained above can be used for the solution of the coupled eqns. (9) containing all the information about the properties of the Jahn—Teller or pseudo-Jahn—Teller systems under consideration. However, solution of eqns. (9) is very difficult practically and is available now only for a limited number of particular cases (see Section E). Therefore one must recover and withdraw maximum information about these systems using only the knowledge of the adiabatic potentials without complete solution of eqns. (9).

As was mentioned above (Section B) in the non-degenerate state, the adiabatic potential has the meaning of nuclear potential energy in the averaged field of the electrons. Its surface consists of a single sheet, at every point of which the derivative has the sense of a generalized force acting upon the nuclei. In this instance, the nuclear motion can be described well enough in a classical way considering the nuclei moving along the potential surface. Such a classical (more precisely, semiclassical) approach is very useful in a series of applications, e.g. for investigations of chemical reaction dynamics.

But in the case of orbital degeneracy, as shown above, the potential surface has several intersected sheets and, strictly speaking, the classical notions become invalid. However, analysing the adiabatic potentials obtained for the general cases (see Figs. 3, 4, 7, 9), one can see that when the vibronic interaction is strong enough, the area near the point of intersection (where the surface sheets are close) is relatively small. Far from this point of degeneracy and near the bottom of the minima, the energy distance between the surface sheets becomes appreciably great (e.g. $4E_{JT}$ in the E—e problem). Therefore in the case of very deep adiabatic potential minima (strong Jahn—Teller effect), the states near the bottom of them can be treated approximately the same as non-degenerate cases, i.e. considering the nuclear motion in a semiclassical way. In so doing, caution must be taken, bearing in mind the quantum effects which are lost in this semiclassical treatment.

In this section an attempt is made to draw some general conclusions about the Jahn—Teller and pseudo-Jahn—Teller effects only on the basis of the known adiabatic potentials without solving the vibronic eqns. (9), but using semiclassical notions and some obvious quantum effects.

(i) The "relativity rule" concerning the means of observation

Let us consider the possibility of experimental detection of the distorted nuclear configurations for a free Jahn—Teller or pseudo-Jahn—Teller system. First we should clarify what physical sense has the notion of nuclear configuration. According to wave mechanics, the nuclear coordinates are operators and only their wave-mechanical averages can have observable magnitudes. As we have seen from the adiabatic potentials obtained in the previous section, in all the cases there are several (or an infinite number) of equivalent minima points, which are completing one another up to the high symmetry initially assumed for the undistorted system. Therefore the averaged nuclear coordinates for an unperturbed system in the vibronic problem under consideration will always correspond to the undistorted configuration. This result is quite general and is due to the symmetry of the Hamiltonian used (it fully supports the statement made in Section B).

In practice, however, the free system may happen to be at the very beginning (ab initio) in a distorted configuration, appropriate to one of the adiabatic potential minima (as a result of chemical reaction, collisions and so on). Since there are other equivalent minima, this configuration is not stationary and after a certain time τ (the mean lifetime), it turns into another equivalent minimum configuration by means of tunneling, for example (see Section E). During the time τ, the system is vibrating near the minimum position with a period $T = 2\pi/\omega$, where ω is the vibration frequency determined by the adiabatic surface curvature at the minimum point.

Now it is obvious that if $\tau \lesssim T$ the notion of a minimum distorted configuration loses its real meaning; the general consideration given above has a physical sense only when $\tau \gg T$, i.e. when the system is performing many (at least several) vibrations in the given (distorted) configuration before transition to another one[5].

The distorted configuration mean lifetime τ can be determined as a magnitude inversely proportional to the tunneling frequency (see Section E). It follows that the deeper are the minima and the greater is the barrier between them the greater is τ. Therefore the distorted configuration assumes a physical sense only in the limit of a sufficiently strong Jahn—Teller effect.

But even having a physical sense, can the distorted configurations be observed experimentally and under what conditions? To answer this question we have to introduce a characteristic time of interaction of the system with experimental means of observation (an effective "time of measurement") τ'.

Then if

$$\tau' \ll \tau \tag{44}$$

a distorted configuration (one of several equivalent ones) will be observed, whereas for $\tau' \gg \tau$ an average over all the minima undistorted configuration will occur in the experiment. When $\tau \sim \tau'$, a more rigorous consideration is needed (see Section F).

Thus, performing the measurement with different means of observation having different τ', one can perceive essentially different information about the nuclear configuration of the same system: distorted and undistorted. In other words, the nuclear configuration is not an absolute feature of the Jahn—Teller systems — it depends upon the means of observation. We come to the "relativity rule" concerning the means of observation which can be formulated as follows[5,19,20]: in a free Jahn—Teller system with strong vibronic coupling, the observable nuclear configurations are dependent on the means of observation and may vary by changing the method of measurement.

This rule may be of practical significance for qualitative analysis of the manifestations of the Jahn—Teller effect contributing to a better understanding of their origin. Some difficulties may be encountered in the τ' value determination which may involve the solution of the problem of the measurement perturbation of the system. As seen in Section F in the EPR measurements the magnitude of τ' is inversely proportional to the Zeeman interaction with the external field. Since this interaction is proportional to the field intensity H, the τ' value can be easily changed: for values of H great enough, the relation $\tau' \ll \tau$ may be fulfilled, so that the distorted configuration (an anisotropic spectrum) is observed, while for small H values the inverse relation may take place, $\tau' \gg \tau$, and an averaged spectrum is to be expected. A similar transition from an anisotropic spectrum to an isotropic one can be obtained for the same τ' value (the same H) by changing the τ value with temperature, since the tunneling frequency is temperature dependent (Section F).

Another example of the "relativity rule" manifestation is provided by the polarized luminescence considered below. There τ' is determined by the lifetime of the excited electronic state relative to spontaneous irradiation. In the polarizability measurements (Section F), τ' is determined by the rate of molecular orientation in the applied electric field.

(ii) Vibronic amplification of distorting perturbations

So far we have considered only free Jahn—Teller or pseudo-Jahn—Teller systems. For stereochemistry and crystal chemistry, the behaviour of these systems under small perturbations distorting the nuclear configuration is of great importance. Such perturbations may arise, for instance, either from small differences in the ligands which lower the initially assumed (Jahn—Teller) symmetry, or from the influence of the next coordination spheres in the crystal structure.

If these low-symmetry perturbations are great enough when compared with the vibronic interaction (i.e. if they produce an energy splitting greater than the Jahn—Teller stabilization), they may completely reduce (quench) the Jahn—Teller effects. In the other limit when the perturbations are smaller than the vibronic interaction, they do not remove the Jahn—Teller effects but modify them. Let us deal now with this latter case.

Consider the simplest E—e problem in the linear approximation, i.e. a system with an adiabatic potential in the form of a Mexican hat (Fig. 3). As was discussed above for the free system, the average picture, to be seen in the experiment, gives an undistorted nuclear configuration. Under the influence of a small distorting perturbation, say elongating the system in the Q_θ direction, the circular trough will be distorted, namely an additional potential well in the Q_θ direction (and a hump in the opposite $-Q_\theta$ direction) will appear. If the depth of the well is greater than the kinetic energy of the circular motion in the trough (in a wave-mechanical approach this condition may be softer), then the nuclear motions are localized in this well and an appropriate distorted nuclear configuration will be observed in the experiments.

The most exciting result in this picture is that the magnitude of the distortion is determined mainly by the vibronic interaction and is almost independent of the perturbation magnitude[21]. Indeed, the additional well is formed at a point on the circular trough with coordinates (ρ_0, ϕ_0) from which only ϕ_0 depends on the perturbation, and therefore the magnitude of the distorted configuration, determined by the ρ_0 value, is independent of the perturbation (in fact the perturbation distorts the trough circle too, so the ρ_0 value becomes perturbation dependent, but for small perturbations it is a second-order effect). This ρ_0-value distortion is often called the static limit of the Jahn—Teller effect.

Thus, a small perturbation acting upon a Jahn—Teller system produces a distortion which is determined by the static Jahn—Teller effect. Since the kinetic energy of the motion along the trough $a = h^2/8M\rho_0^2$ is of the order[22] of several cm^{-1} perturbation of the order a in the absence of the Jahn—Teller effect will produce a very small distortion. Meanwhile the static Jahn—Teller effect distortion may be great enough. Hence, we come to the "amplification rule" in Jahn—Teller distortions: a small distorting perturbation may be amplified by vibronic interactions.

Let us make some qualitative (or semi-quantitative) estimations of the coefficient of vibronic amplification K_a. In the absence of vibronic interactions, the distortion magnitude Q_0' can be found from comparison of the perturbation energy W with elastic distortion, $W = \frac{1}{2} KQ_0'^2$, $Q_0' = (2W/K)^{\frac{1}{2}}$. If $W = a$, then

$$Q_0' = (2a/K)^{\frac{1}{2}} = h\omega/2A_1,$$

where ω is the frequency of the Q vibration, A_1 is the vibronic coupling constant, and it is taken into account that $a = h^2/8M\rho_0^2$, $K = M\omega^2$, $\frac{1}{2} K\rho_0^2 = E_{JT} = A_1^2/2K$ (see Section C). On the other hand, when vibronic interactions are taken into account the distortion value is $Q_0 \approx \rho_0 = A_1/K = 2E_{JT}/A_1$. The coefficient of vibronic amplification can be obtained directly as the ratio Q_0/Q'_0.

$$K_a = \frac{Q_0}{Q'_0} \approx \frac{4\,E_{JT}}{\hbar\omega} \tag{45}$$

This K_a value may be very great, since for coordination compounds with an E term (say, for octahedral Cu^{II} or Mn^{III}) the $E_{JT}/\hbar\omega$ ratio is of the order 5—10, which gives $K_a \sim 20$—40 (the minimal ratio $E_{JT}/h\omega$ appropriate to the strong limit Jahn—Teller effect gives $K_a \sim 5$). These figures, however, are the upper limits since eqn. (45) has been obtained for a minimal perturbation magnitude $W \sim a$. Indeed, if $W = pa$ with $p > 1$, then $Q'_0 = (p)^{\frac{1}{2}}\,\hbar\omega/2A_1$ and instead of eqn. (45) we obtain

$$K_a \approx \frac{4E_{JT}}{(p)^{\frac{1}{2}}\hbar\omega} \tag{46}$$

In particular, when $(p)^{\frac{1}{2}} = 4E_{JT}/h\omega$, $K_a \sim 1$, i.e. there is no amplification. For this case $W = pa = E_{JT}$, and the Jahn—Teller effect is completely quenched by the perturbation, so the distortion $Q'_0 \sim \rho_0$ is of perturbational origin only.

So far we have considered the simplest case of the linear E—e problem. For more complicated cases the estimations obtained above have to be modified (there may also be other means of estimation including the temperature effect[21]). But the general conclusion about the abnormal great "distortional susceptibility", and about the vibronic amplification of distorting perturbations (having an energy $W < E_{JT}$) is valid for all the Jahn—Teller and pseudo-Jahn—Teller systems.

The notion of vibronic amplification essentially contributes to a better understanding of the manifestations of the Jahn—Teller effect. In particular, it removes completely as incorrect the statements, often met in the literature, that the Jahn—Teller effects are not to be expected in systems where the differences in the ligands, or other low-symmetry perturbations, formally remove the electronic orbital degeneracy (e.g. see ref. 23). On the contrary, as shown in this section it is only such low-symmetry perturbations (small but vibronically amplified) which lead to observable distortions. In the absence of these perturbations, the Jahn—Teller distortions are of a dynamic nature and do not manifest themselves in an absolute way in stereochemistry and crystal chemistry (in the absence of phase transitions due to cooperative Jahn—Teller effect, considered in the next section).

(iii) Cooperative Jahn—Teller effect and structural phase transitions

Of great importance for crystal chemistry of coordination compounds is the so-called cooperative Jahn—Teller effect. Consider a crystal structure containing orbitally degenerate coordination centers which possess characteristic adiabatic potentials described in Section C. Without interaction between the centers, the nuclear motion for each is appropriate to its adiabatic potential and is independent of the motions in the other centers. Hence the dynamic distortions (dynamic Jahn—Teller effect) for different centers are not correlated. When interaction of the Jahn—Teller centers is taken into account, the "molecular field" formed by the environment acting upon the given center is not isotropic. In this case, the energetically most advantageous is the crystal state with correlated (ordered) static distortions. The structure of such a crystal will obviously be different from that expected for the same crystal without taking account of vibronic interactions.

The effect of the correlated Jahn—Teller distortion on the crystal structure is often called the cooperative Jahn—Teller effect.

It is obvious that the crystal vibrations and temperature fluctuations will tend to destroy Jahn—Teller distortion correlation. Therefore for a given energy of distortion interaction there is (at least in principle) a definite temperature for which the correlation breaks down and the centers become independent (with a dynamic Jahn—Teller effect on each), the crystal as a whole becoming more symmetric. This temperature-dependent breakdown of the correlation of center distortions is nothing more than a structural phase transition.

The qualitative picture given above in fact, was obtained on the basis of rigorous mathematical deductions. Structural phase transitions due to cooperative Jahn—Teller and pseudo-Jahn—Teller effects were considered in a series of papers[16,17,24–31]. Different classes of crystals (spinels, perovskites, orthovanadates, and others) were studied from this point of view, and the critical Curie temperature, as well as other characteristic features, were derived as a function of the vibronic coupling and other crystal parameters.

Special cases of structural phase transitions are provided by the ferroelectric effects, which were shown to be due to the cooperative pseudo-Jahn—Teller effect[16,26]. Since this latter may give rise to the dipolar instability and dipolar distortions[16–18] mentioned above, their correlation and ordering in crystals lead to a spontaneous polarized state and ferroelectric phase transitions. Several classes of ferroelectric crystal structures of pseudo-Jahn—Teller origin were successfully studied[16,17,26,30,31].

The cooperative Jahn—Teller (or pseudo-Jahn—Teller) effect provides the only cases where the absolute static Jahn—Teller distortion of the nuclear configuration manifests itself directly. For orbitally degenerate coordination centers in crystals, the environment is always expected to be distorted, either statically (below the Curie temperature) or dynamically (above it). Thus, if the Jahn—Teller effect is known to be strong for a given atom, ion or coordination center, the knowledge of the environmental nuclear configuration at a definite temperature may indicate whether the Jahn—Teller phase transition has already taken place below this temperature or not. Of course, all the additional effects, such as low-symmetry distorting perturbations (considered in the previous section), spin—orbit interaction (for T terms), etc., must also be taken into account.

'ABLE 2

xamples of ordered distortions in crystals at room temperatures (cooperative Jahn—Teller ffect) (see ref. 5)

rystal	Tetragonal distortions of the transition metal environment MA_6	
	$R(M{-}A_1)$ (Å)	$R(M{-}A_2) = R(M{-}A_3)$ (Å)
$\mathrm{uF_2}$	2.27	1.93
$\mathrm{uCl_2}$	2.95	2.30
$\mathrm{uBr_2}$	3.18	2.40
$\mathrm{_2CuF_4}$	1.95	2.08
$\mathrm{lnF_3}$	2.09	1.8
$\mathrm{u_2(OH)_2CO_3}$	2.41	2.01
lnO(OH)	2.03	1.9

The strongest Jahn—Teller effect (the greatest vibronic constant) is known be incidental to transition metal coordination systems with an orbitally egenerate electronic E term. Therefore these cases are the best known Jahn—'eller subjects. The stronger is the Jahn—Teller effect and the greater are the oordination center interactions in the crystal, the higher is the Curie temperaıre for the phase transition. In Table 2 are given some examples of crystals, r which the room temperature is below the Curie temperature and there-re the Jahn—Teller ion environment is statically distorted. For these crystals, ıe Curie temperature is expected to be very high since they contain the rongest Jahn—Teller ions ($\mathrm{Cu^{II}}$, $\mathrm{Mn^{III}}$), subjected to very strong interactions ue to the presence of common shared ligands. Other examples, including ıhn—Teller phase transition Curie temperatures, are available[16,17,24–31].

v) The shape of electronic absorption and luminescence broad bands

Light absorption and luminescence in coordination compounds are usually udied at room temperature where the spectra consist of broad bands ithout vibrational (or rotational) structure. These conditions are very favourle for the use of the semiclassical approach in which the nuclear motions e considered as classical ones along the adiabatic potential surface.

Consider an electronic transition between two coordination compound rms, 1 and 2, one or both of which being orbitally degenerate. For the coficient of light absorption as a function of the frequency $K_{12}(\Omega)$ (in the pression $I = I_0 \exp[-K_{12}(\Omega) l]$, where I and I_0 are the intensities of the ansmitted and incident light respectively and l is the layer thickness) we ıve (see ref. 5, p. 282)

$$_{12}(\Omega) = N \frac{4\pi^2 \Omega}{3c} F_{12}(\Omega) \qquad (47)$$

where N is the number of absorption centers in unit volume and $F_{12}(\Omega)$ is the so-called band shape factor. In the semiclassical approach the latter is given by the expression[5,32]

$$F_{12}(\Omega) = \int dQ_\alpha \, |M_{12}(Q_\alpha)|^2 \rho_1(Q_\alpha) \, \delta \, [\Delta\epsilon(Q_\alpha) - \hbar\Omega] \tag{48}$$

where

$$\mathrm{M}_{12}(Q_\alpha) = \int \Psi_1^*(r_\nu, Q_\alpha) \, \mathrm{M} \, \Psi_2(r_\nu, Q_\alpha) \, d\tau_\nu \tag{49}$$

$$\Delta\epsilon(Q_\alpha) = \epsilon_2(Q_\alpha) - \epsilon_1(Q_\alpha) \tag{50}$$

$$\rho_1(Q_\alpha) = \frac{\exp\,[-\epsilon_1(Q_\alpha)/kT]}{\int dQ_\alpha \exp\,[-\epsilon_1(Q_\alpha)/kT]} \tag{51}$$

$\epsilon_1(Q_\alpha)$ and $\epsilon_2(Q_\alpha)$ are the adiabatic potentials for the two states under consideration and M is the dipole moment operator.

Thus, knowing the adiabatic potentials $\epsilon_i(Q_\alpha)$ (Section C), one can calculate the absorption coefficient as a function of the incident light frequency, i.e. the shape of the absorption band. For equilibrium luminescence (for which the vibrational relaxation takes place before spontaneous irradiation) the formula for the band shape is similar to eqn. (48), in which one has to insert the expression $\rho_2(Q_\alpha) \exp(-\hbar\Omega/kT)$ instead[33] of $\rho_1(Q_\alpha)$.

The first semiclassical calculations of the absorption band shapes expected for electronic transitions to degenerate states were carried out by O'Brien[34], Moran[35] and Toyozawa and Inoue[36]. Examples of results obtained for the A—E and A—T transitions in the linear approximation are illustrated in Figs. 11(a) and 12. The shape of the A—E transitions band obeys the expression

$$F_{12}(\Omega) = \frac{|M_{12}|^2 \hbar |\Omega - \Omega_0|}{4E_{JT}kT} \exp\left[-\frac{\hbar^2(\Omega-\Omega_0)^2}{4E_{JT}kT}\right] \tag{52}$$

and has a dip at $\Omega = \Omega_0$, where Ω_0 is the A—E energy interval at the point $Q_\theta = Q_\epsilon = 0$. It may surely be interpreted as due to a characteristic Jahn—Teller splitting which after eqn. (52) is temperature dependent (proportional to $(T^{1/2})$.

For the A—T transition the band shape is very simple, Gaussian-like and not split, when the coupling with the e vibrations is dominant in the T term (T—e problem) and its adiabatic potential has the form shown in Fig. 7. If the t_2 vibrations are dominant (T—t_2 problem), then the band shape becomes like that shown in Fig. 12.

These results were refined and developed by several authors[2,37–42]. In

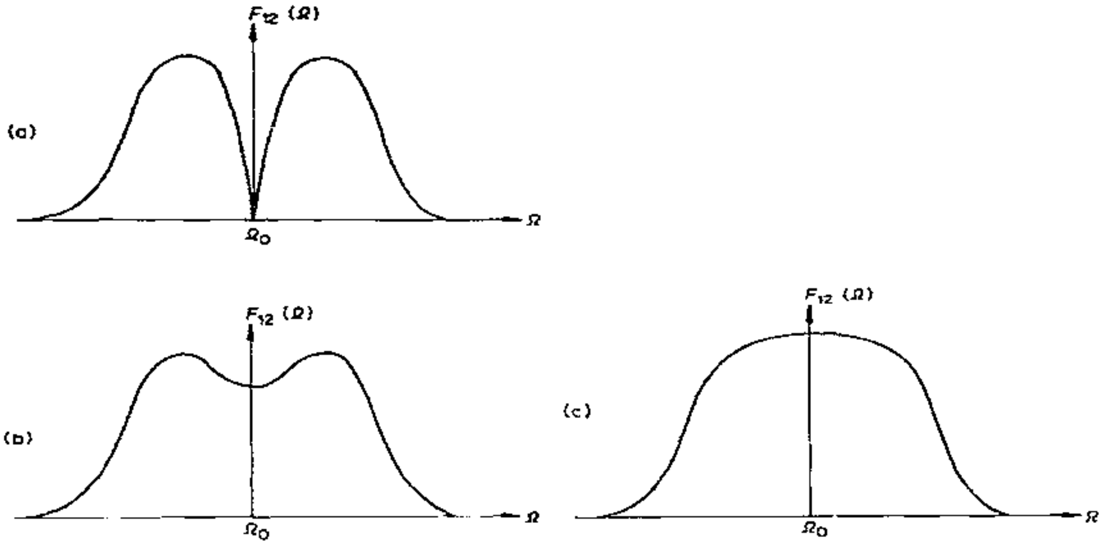


Fig. 11. Electronic absorption band shape for an $A \rightarrow E$ transition taking into account vibronic coupling to both e and a_1 vibrations[40] (a and ω_a are respectively the coupling constant and frequency of the totally symmetrical vibrations a_1): (a) $a = 0$, (b) $A_1^2X_1 > a^2X$; (c) $A_1^2X_1 < a^2X$ $\left(X = \coth\frac{\hbar\omega_a}{2kT}, X_1 = \coth\frac{\hbar\omega_\rho}{2kT}\right)$.

particular, it was shown[39] that by taking into account the totally symmetrical vibrations, the "acute elements" of the absorption band (e.g. the sharp dip in Fig. 11(a)) are smoothed and flattened (Fig. 11(b)). In the case of very strong coupling with these totally symmetrical vibrations, they may even quench

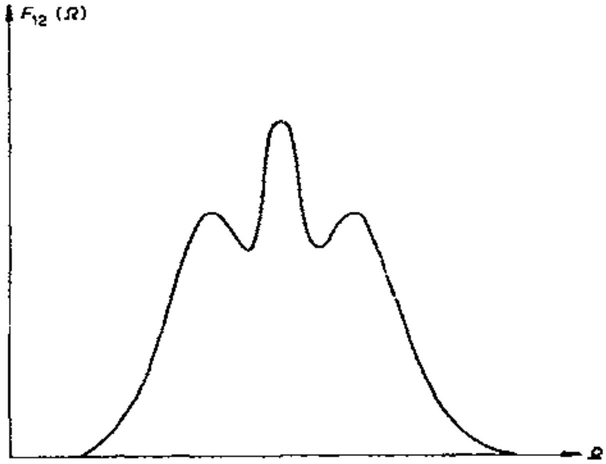


Fig. 12. Electronic absorption band shape for an $A \rightarrow T$ transition, the T term being dominantly (linearly) coupled to t_2 vibrations (T—t_2 problem).

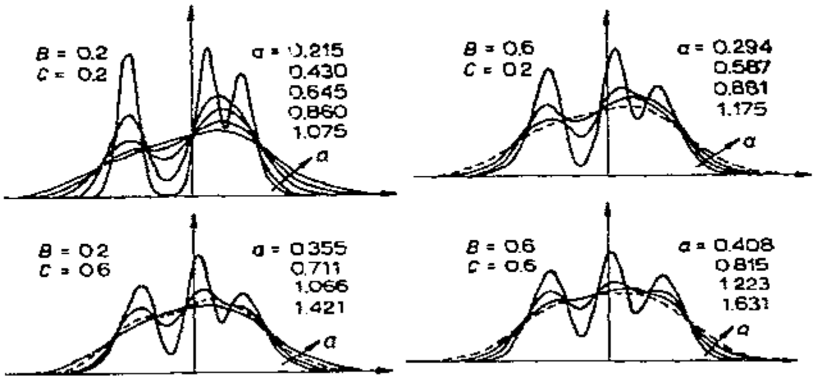
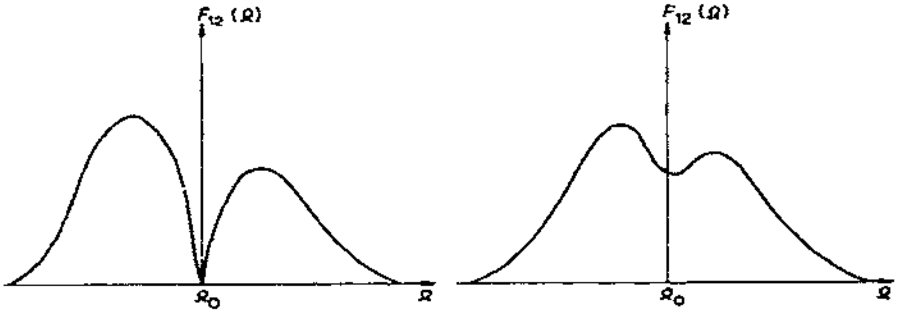
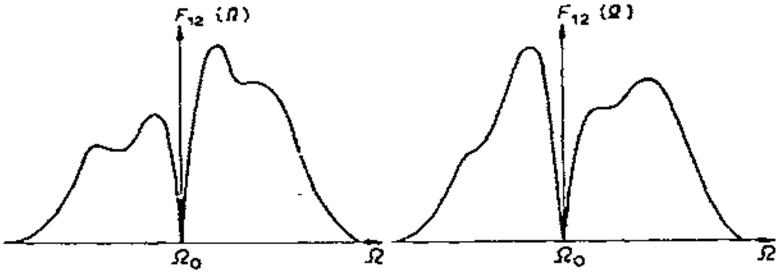


Fig. 13. Electronic absorption band shape for an $A \rightarrow T$ transition, the T term being coupled to both e and t_2 vibrations, taking into account the influence of totally symmetric a_1 vibrations (the curves for several values of B, C and α are shown[37]).



(a) (b)

Fig. 14. Electronic luminescence band shape for an $E \rightarrow A$ transition (in the linear E—e problem approximation): (a) $\alpha = 0$; (b) $\alpha \neq 0$.



(a) (b)

Fig. 15. Electronic absorption band shape for an $E \rightarrow E$ transition (in the linear E—e problem approximation[39]): (a) $A_1' > A_1''$; (b) $A_1' < A_1''$ (A_1' and A_1'' are the vibronic coupling constants for the ground and excited states respectively).

completely the Jahn—Teller splitting[39,40] (Fig. 11(c)). The same picture is expected for the $A \to T$ transition[37] (Fig. 13). Luminescence curves are given in ref. 39 (see Fig. 14). The $E \to E$ transition band shape[39—41] is illustrated in Fig. 15. Examples of pseudo-Jahn—Teller influence on band shapes are seen in ref. 42.

For all these cases, the band shape expected depends essentially on the relation between adiabatic potential parameters and other vibration coupling constants. It was also shown[39,40] that quantum corrections to the semi-classical band shape curves are essential. (Absorption and luminescence band shapes in Renner-type systems are given in refs. 33, 41.)

(v) Polarized luminescence

Significant information about the nature of the degenerate electronic state adiabatic potential minima can be obtained from the investigation of polarized luminescence[43,44]. This opportunity is based upon selection rules which determine that electronic transitions between the initial and final minima states are allowed only for a definite light polarization.

For instance, a dipole type (electric or magnetic) transition from a non-degenerate state to the tetragonal [100] minimum of an excited T term is allowed only for the [100] polarization, but for incident light polarized along [111] the transition is allowed for all three minima simultaneously. From the tetragonal [100] minimum of the ground T term, the transition to the [100] minimum of the excited T term is forbidden, whereas the transition to the [010] and [001] minima is allowed only for light polarization of the [001] and [010] directions respectively. For transitions to trigonal minima the polarization prohibitions are quite different (Tables 3—5 provide some examples).

Assume now that in accordance with the "relativity rule" discussed above (Section (i)) the lifetime in the minimum τ is greater than the lifetime of the excited electronic state relative to the spontaneous optical transition to the ground τ'. If this is the case, the luminescence should have a definite polarization determined by the polarization of the incident light. Indeed,

TABLE 3

Matrix elements of the electric dipolar moment $\vec{d}$ components for $A_{1g(u)} \to T_{1u(g)}$ transitions, the T term having three tetragonal minima oriented along the fourfold axes.

T-term minima	100	010	001
d_x	d	0	0
d_y	0	d	0
d_z	0	0	d

TABLE 4

Matrix elements of the electric dipolar moment d components for $A_{1g(u)} \to T_{1u(g)}$ transitions, the *T* term having four trigonal minima oriented along the threefold axes

T-term minima	111	$\bar{1}11$	$1\bar{1}1$	$11\bar{1}$
d_x	d	$-d$	d	d
d_y	d	d	$-d$	d
d_z	d	d	d	$-d$

dependent on this, the excited state minima will be differently populated, the population relationship being easily obtained from the known electronic minima wave functions (see Section C and Tables 3—5) and, again, each of these minima gives rise to a definite polarization of the luminescence light.

Some general conclusions concerning the nature of the adiabatic potential minima in an excited *T*-term state (when the ground state is non-degenerate) based upon the analysis given above may be formulated as follows.

(1) If for absorption light polarized in the direction [100] the luminescence is polarized in the same direction, and for incident light polarized along [111] the luminescence is completely depolarized, then in the excited state tetragonal absolute minima occur.

(2) If for incident light polarized along [111] the luminescence is partly polarized in the same direction, and for [100] polarized light the luminescence is completely depolarized, then trigonal minima occur in the excited *T*-term state.

(3) If for the [100] polarization of absorption light the luminescence light is partly depolarized with an intensity relation $I_x : I_y : I_z = 2 : 1 : 1$, but for the [110] polarization this latter becomes $I_x : I_y : I_z = 3 : 2 : 2$, being completely depolarized for incident light polarized as [111], then the six orthorhombic minima occur in the excited state.

TABLE 5

Matrix elements of the electric dipolar moment d components for $A_{1g(u)} \to T_{1u(g)}$ transitions, the *T* term having six orthorhombic minima oriented along the twofold axes

T-term minima	110	$1\bar{1}0$	101	$10\bar{1}$	011	$01\bar{1}$
d_x	d	d	d	d	0	0
d_y	d	d	0	0	d	d
d_z	0	0	d	d	d	d

For transitions between two degenerate electronic terms the polarization relationship becomes more complicated.

When the lifetime of the minimum state is shorter than the lifetime of the excited electronic state, $\tau \ll \tau'$, then during the time τ' the populations of the equivalent minima equalize, and (in accordance with the general "relativity rule") a completely depolarized luminescence will be observed in all cases.

E. SOLUTIONS OF THE VIBRONIC EQUATIONS

(i) General solutions

Until now, only two particular cases of the vibronic eqns. (9) are known to have been solved numerically — the linear E—e problem[45] and the linear T—t_2 problem[46]. In the former, tables of energy levels and wave function coefficients for different vibronic coupling constant values have been obtained, and by means of these data the band shape for the electronic $A \rightarrow E$ and $E \rightarrow A$ transitions were calculated. Some of these results are illustrated in Fig. 16. One can see that for the $A \rightarrow E$ transition, the band is split and its main features are similar to those obtained in the semiclassical approximation (Fig. 11). For the $E \rightarrow A$ transition, the band is not split, and this result

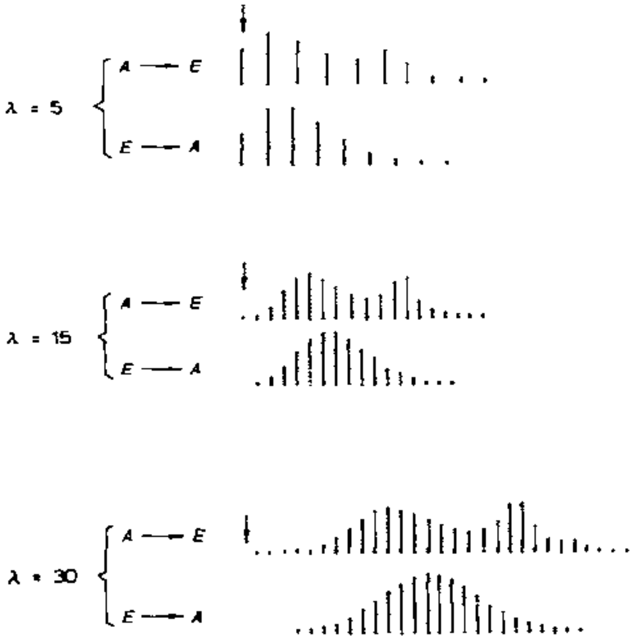


Fig. 16. Electronic absorption and luminescence intensities for $A \rightarrow E$ and $E \rightarrow A$ transitions as a function of frequency calculated by the numerical data obtained from the solution of the linear vibronic E—e problem[45]. (The arrows indicate the zero-phonon line position.)

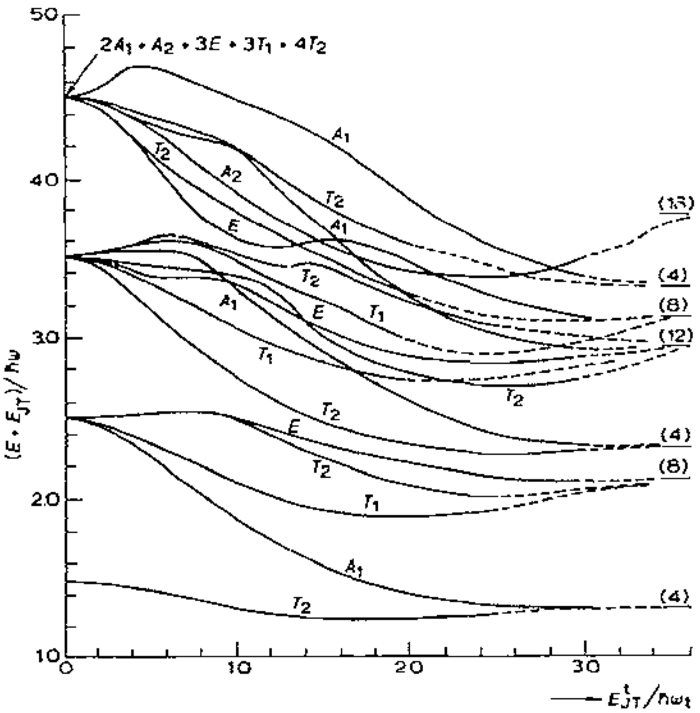


Fig. 17. Vibronic energy levels as a function of the ratio $E^t_{JT}/\hbar\omega_t$ obtained by numerical solution of the vibronic equations of the T—t_2 in the linear approximation[46].

at first sight contradicts that obtained in the semiclassical approach where a Jahn—Teller splitting of the band is also expected (Fig. 14). In fact, however, there is no contradiction between the two appoaches, since the band shape based upon the numerical results of the vibronic equation solutions[45] is calculated without taking account of the excited vibronic state population, i.e. for $T = 0$, for which the semiclassical approximation also gives no splitting.

The energy level scheme obtained by Caner and Englman[46] for the linear T—t_2 problem as a function of the vibronic coupling constant values is shown in Fig. 17. Using these data, a band shape calculation was also performed[47]. The results are given in Fig. 18.

Along with the exact numerical solutions of eqns. (9) available for these particular cases, different approximate and semi-empirical solutions including the other Jahn—Teller cases may be of great importance. In the case of a very weak vibronic coupling, a perturbation calculation of the energy levels and wave functions may be performed[48,49].

In the other limiting case of strong coupling, eqns. (9) can also be simplified. For the E—e problem, only the lower sheet of the adiabatic potential (Fig. 3) may be taken into account (at least when the ground and several low-lying excited states localized near the bottom of the trough are considered). This

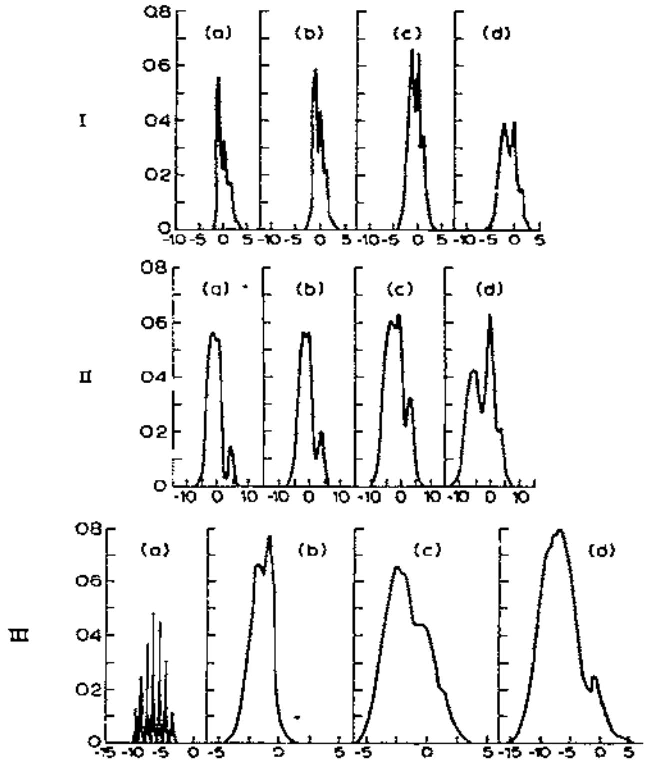


Fig. 18. Electron $A \to T$ transition intensities for a T—t_2 system as a function of light frequency, temperature, linear coupling constant B and broadening parameter α (all energies in units of $\hbar\omega_t$)[47]. I (absorption): $B = -(6)^{1/4}$, $\alpha = 0.5$; (a) $kT = 0$; (b) $kT = 0.5$. (c) $kT = 1$; (d) $kT = 4$. II (absorption): $B = -6$, $\alpha = 1$, and kT values the same as in I. III (emission): (a) $B = -6$, $\alpha = 0.1$, $kT = 0$; (b) $B = -(6)^{1/4}$, $\alpha = 0.5$, $kT = 4$; (d) $B = -6$, $\alpha = 0.5$, $kT = 4$.

case was investigated by O'Brien[22]. The motion in the trough was approximately divided into a radial one along ρ and an angular one along the ϕ coordinate. The radial motion was assumed to be harmonic with an energy $h\omega_\rho(n + \frac{1}{2})$, while the angular one was assumed rotational with an energy $m^2(h\omega_\rho)^2/4E_{\mathrm{JT}}$, where m is the rotational quantum number which is here only half-integral. The full expression for the level energies is therefore

$$\epsilon_{nm} = -E_{\mathrm{JT}} + \hbar\omega_\rho(n + \tfrac{1}{2}) + m^2\hbar^2\omega_\rho^2/4E_{\mathrm{JT}}, \quad m = \pm\tfrac{1}{2}, \pm\tfrac{3}{2}, \ldots, \quad n = 0,1,2,\ldots \tag{53}$$

When second-order vibronic coupling terms are taken into account, the problem becomes rather complicated (see eqn. (17)). O'Brien[22] suggested a solution in which it is supposed that the second-order terms may be regarded as small perturbations to the ground vibrational state. Then the angular motion is no longer purely rotational but obeys the approximate equation

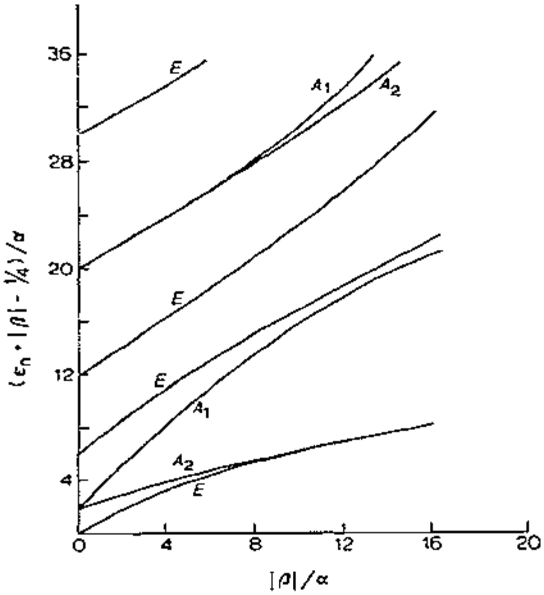


Fig. 19. Vibronic energy levels as a function of the ratio $|\beta|/\alpha$ obtained by numerical solution of eqn. (54) for the second order E—e problem[22].

$$\left[-\alpha \frac{\partial^2}{\partial\phi^2} + \beta \cos 3\phi\right] \chi_m(\phi) = \epsilon_m \chi_m(\phi),\ \alpha = \hbar^2/3M\rho_0^2,\ \beta = A_2\rho_0^2 \tag{54}$$

The results of the numerical solution of this equation for different parameter relations β/α are given in Fig. 19.

It should be noted that in the solution given above, there are some unproved approximations. Indeed, the β value is shown to be greater than $\hbar\omega_\rho$, and therefore perturbation theory which takes into account only the ground vibrational state is invalid. There are also other approximations made in ref. 22 (e.g. the centrifugal terms in the potential energy are omitted).

Another solution based on the variation principle has recently been suggested[11]. As trial wave functions for the ground vibronic E and first excited A_1 levels one may choose

$$\left.\begin{aligned} \psi_E(\rho,\phi) &= N_E \begin{Bmatrix} \cos\dfrac{\phi}{2} \\ \\ \sin\dfrac{\phi}{2} \end{Bmatrix} \exp(\nu\cos 3\phi)\, q^{\frac{1}{2}} \exp\left[\tfrac{1}{2}u(q-1)^2\right] \\ \psi_{A_1}(\rho,\phi) &= N_{A_1} \cos\frac{3\phi}{2} \exp(\nu\cos 3\phi)\, q^{\frac{1}{2}} \exp\left[\tfrac{1}{2}u(q-1)^2\right] \end{aligned}\right\} \tag{55}$$

where ν and u are variational parameters ($q = \rho/\rho_0$). Some results obtained

TABLE 6

Dimensionless variational parameter values for tunneling level wave functions (55), energies and the tunneling splitting δ (in $\hbar\omega/2$ units), $\lambda = 4$

γ	E level			A level			tunneling splitting $\delta = \epsilon_A - \epsilon_E$
	ν	u	ϵ_E	ν	u	ϵ_A	
0.0							
0.2	0.071	4.774	−2.590	0.036	4.544	−2.208	0.382
0.4	0.140	4.908	−2.456	0.071	4.619	−2.134	0.322
0.6	0.206	5.019	−2.332	0.105	4.694	−2.062	0.270
0.8	0.269	5.104	−2.218	0.138	4.755	−1.993	0.225
1.0	0.329	5.165	−2.111	0.170	4.815	−1.926	0.185
1.2	0.385	5.219	−2.013	0.201	4.870	−1.861	0.152
1.4	0.438	5.271	−1.921	0.231	4.926	−1.799	0.122
1.6	0.489	5.298	−1.835	0.260	4.974	−1.738	0.097
1.8	0.536	5.336	−1.753	0.289	5.018	−1.679	0.075
2.0	0.581	5.356	−1.677	0.317	5.059	−1.621	0.056
2.2	0.623	5.374	−1.604	0.344	5.096	−1.565	0.039
2.4	0.663	5.400	−1.535	0.370	5.130	−1.511	0.024
2.6	0.701	5.415	−1.469	0.396	5.168	−1.457	0.012

for definite values of the adiabatic potential parameters $\lambda = 2E_{\mathrm{JT}}/\hbar\omega_\rho$ and $\gamma = 2\Delta/\hbar\omega_\rho$ are illustrated in Table 6.

Approximate solutions of the vibronic problem for some other particular cases may be found in refs. 14, 50—53.

(ii) Tunneling splitting

Another approach to the problem which allows one to obtain the ground and several excited state vibronic levels in the case of a strong Jahn—Teller effect was suggested earlier[54,55]. In this approach, the adiabatic potential minimum states are taken as a starting approximation, and then the interaction between them, assumed to be small, is taken into account as a perturbation, leading to tunneling transitions between the minimum configurations through the potential barriers.

The initial minimum states are taken in the adiabatic approximation as a product of the electronic $\psi_i(r_\nu, Q_\alpha^{(i)})$ and nuclear $\chi_\kappa(Q_\alpha^{(i)})$ wave functions

$$\Phi_{i\kappa}(r_\nu, Q_\alpha^{(i)}) = \psi_i(r_\nu, Q_\alpha^{(i)})\,\chi_\kappa(Q_\alpha^{(i)}),\ i = 1,2,\ldots,r \tag{56}$$

where the $Q_\alpha^{(i)}$ are the normal coordinates in the ith minimum, which can easily be obtained by symmetry considerations, κ characterizes the vibration state in the minimum and r is the number of equivalent minima. In the harmonic approximation, $\chi_\alpha(Q_\alpha^{(i)})$ can be taken as a product of harmonic

$$\chi_\kappa(Q_\alpha^{(i)}) = \chi_{\kappa_1}(Q_1^{(i)})\,\chi_{\kappa_2}(Q_2^{(i)})\ldots\chi_{\kappa_K}(Q_K^{(i)})$$

oscillator functions where K is the number of Jahn—Teller active coordinates (equal to 2,3,5 for tetragonal, trigonal and orthorhombic minima respectively).

The energies of the minima states are

$$E_\kappa = -E_{\mathrm{JT}} + \sum_{j=1}^{k} \hbar\omega_j(\kappa_j + \tfrac{1}{2}) \tag{57}$$

where ω_j is the appropriate vibration frequency. Since E_κ does not depend on the minimum index i (whereas the wave function (56) does) the energy states (57) are r-fold degenerate. This degeneracy may be removed by taking into account the non-orthogonality of the minima states.

The full wave function of the system can be sought for as a linear combination of the minima functions (56).

$$\Psi_\kappa(r_\nu, Q_\alpha) = \sum_{i=1}^{r} c_{i\kappa}\Phi_{i\kappa}(r_\nu, Q_\alpha^{(i)}) \tag{58}$$

the coefficients $c_{i\kappa}$ being determined by the minimum variation condition for the full energy (calculated by this function). This leads to a secular equation of the rth order

$$\|H_{ij}^\kappa - \epsilon_\kappa S_{ij}^\kappa\| = 0 \tag{59}$$

where H_{ij}^κ are the full Hamiltonian matrix elements, and S_{ij}^κ are overlap integrals for the functions (56). Owing to the equivalency of the minima we have $H_{ij}^\kappa = H_{12}^\kappa$ and $S_{ij}^\kappa = S_{12}^\kappa$, $i, j = 1,2,\ldots,r$, and eqn. (59) is esssentially simplified. Its solutions — the ϵ_κ and $c_{i\kappa}$ values as functions of the H_{12}^κ and S_{12}^κ values for tetragonal, trigonal and orthorhombic minima — are given in Table 7.

In the limiting case of a strong Jahn—Teller effect (very deep minima) the H_{12}^κ and S_{12}^κ values can be calculated directly. For the E—e problem (Section C, Fig. 4), assuming the electronic functions (in the minima) ψ_i to be independent of the nuclear coordinates (appropriate to the so-called simple adiabatic approximation[6]), we have

$$\begin{aligned} S_{12}^\kappa &= -\tfrac{1}{2}\gamma_\kappa \\ \gamma_\kappa &= \int \chi_{\kappa\theta}(Q_\theta^{(1)})\,\chi_{\kappa\epsilon}(Q_\epsilon^{(1)})\,\chi_{\kappa\theta}(Q_\theta^{(2)})\,\chi_{\kappa\epsilon}(Q_\epsilon^{(2)})\,\mathrm{d}Q_\theta\,\mathrm{d}Q_\epsilon \end{aligned} \tag{60}$$

For the ground state $\kappa_\theta = \kappa_\epsilon = 0$, and taking, approximately, $\omega_\theta \approx \omega_\epsilon = \omega$ (note that in polar coordinates $\omega_\theta \equiv \omega_\rho$ and $\omega_\epsilon \equiv \omega_\phi$, cf. Section C), we obtain

$$\gamma_0 = \exp(-3E_{\mathrm{JT}}/2\hbar\omega) \tag{61}$$

TABLE 7

Energies and wave function coefficients $C_{i\alpha}$ (after eqn. (58)) for tunneling levels in three, four and six minima model systems; the coefficients $C_{i\alpha}$ are given in the form N_α $(C_{1\alpha}, C_{2\alpha}, \ldots, C_{r\alpha})$, $\alpha = 1, 2, \ldots, r$, where N_α is a common multiplier ($S \equiv S^K_{12}$, $H_{12} \equiv H^K_{12}$)

r	Symmetry	Energy	$C_{i\alpha}$
3	E	$-\frac{H_{12}}{1-S}$	$\frac{1}{[6(1-S)]^{\frac{1}{2}}}(2, -1, -1)$
	A	$\frac{2H_{12}}{1+2S}$	$\frac{1}{[2(1-S)]^{\frac{1}{2}}}(0, 1, -1)$
			$\frac{1}{[3(1+2S)]^{\frac{1}{2}}}(1, 1, 1)$
4	T	$-\frac{H_{12}}{1-S}$	$\frac{1}{2(1-S)^{\frac{1}{2}}}(1, -1, -1, 1)$
			$\frac{1}{2(1-S)^{\frac{1}{2}}}(1, 1, -1, -1)$
			$\frac{1}{2(1-S)^{\frac{1}{2}}}(1, -1, 1, -1)$
	A	$\frac{3H_{12}}{1+3S}$	$\frac{1}{2(1+3S)^{\frac{1}{2}}}(1, 1, 1, 1)$
6	T_1	$\frac{2H_{12}}{1+2S}$	$\frac{1}{2(1+2S)^{\frac{1}{2}}}(1, 1, 1, 1, 0, 0)$
			$\frac{1}{2(1+2S)^{\frac{1}{2}}}(1, 0, -1, 0, 1, 1)$
			$\frac{1}{2(1+2S)^{\frac{1}{2}}}(0, -1, 0, 1, 1, -1)$
	T_2	$-\frac{2H_{12}}{1-2S}$	$\frac{1}{2(1-2S)^{\frac{1}{2}}}(1, -1, 1, -1, 0, 0)$
			$\frac{1}{2(1-2S)^{\frac{1}{2}}}(-1, 0, 1, 0, 1, 1)$
			$\frac{1}{2(1-2S)^{\frac{1}{2}}}(0, -1, 0, 1, -1, 1)$

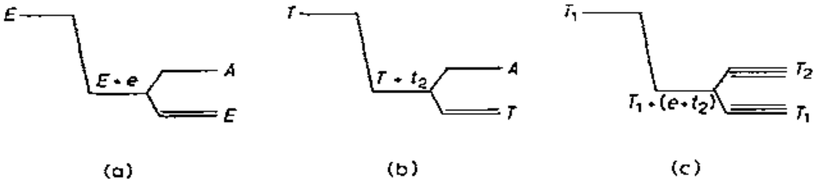


Fig. 20. The tunneling splitting vibronic energy levels for the second-order E—e problem (a), linear T—t_2 problem (b) and second-order T—$(e + t_2)$ problem (c).

If $\omega_\theta \neq \omega_\epsilon$, then introducing the quantity $p = \omega_\epsilon/\omega_\theta$, one can obtain

$$\gamma_0 = \left(\frac{16p}{3p^2 + 10p + 3}\right)^{\frac{1}{2}} \exp\left(-6\frac{p^2 + 3}{3p^2 + 10p + 3}\frac{E_{JT}}{\hbar\omega_\theta}\right) \tag{62}$$

In the same approximation

$$H^0_{12} = \tfrac{3}{4}E_{JT}\,\gamma_0\left(1 + \frac{1}{2}\frac{A_2}{K_e - 2A_2}\right) \tag{63}$$

Since $H^0_{12} > 0$, the ground vibronic (tunneling) state is twofold degenerate E (Fig. 20(a)). (In the first publications on this topic[54,55] there was an error in the sign of the splitting.)

In the linear T—e problem (Section C, Fig. 7) the electronic states in the three tetragonal minima are mutually orthogonal and therefore $S^\kappa_{12} = H^\kappa_{12} = 0$, and hence there is no tunneling splitting. In the T—t_2 case (four trigonal minima) the tunneling splitting can be obtained in a similar manner to the E term case discussed above. The fourfold degenerate vibronic states in the minima are split into two levels, T and A (Table 7) by tunneling, the former being lower (Fig. 20(b)) and

$$H^\kappa_{12} = \tfrac{2}{3}E^t_{JT}\,\gamma_\kappa \tag{64}$$

$$\gamma_0 \ = \exp\left(-4E^t_{JT}/3\hbar\omega_t\right) \tag{65}$$

When the second-order vibronic coupling terms are taken into account, six orthorhombic minima occur (see Section C, eqn. (29) and (30)). This being the case, tunneling between them leads to a splitting of the sixfold degenerate level into two, T_1 and T_2 (Table 7, Fig. 20(c)), with an energy interval[15]

$$\delta = \frac{3}{2}E^0_{JT}\,\frac{24 - 28N - 2N^2 + 9N^3}{(4 - 3N)(4 - 3N^2)}\,\frac{S}{1 - S^2} \tag{66}$$

$$S = \exp\left[-\frac{3}{2}\frac{E^0_{JT}}{\hbar\omega}\,\frac{12 - 20N - 11N^2}{(4 - 3N)(4 - 3N^2)}\right] \tag{67}$$

In all cases, the tunneling splitting approach is valid only when the splitting magnitude is much smaller than the vibration quantum in the minimum

$$\delta \ll \hbar\omega \tag{68}$$

(iii) The reduction of electronic magnitudes

The solutions of the vibronic equation obtained above — the lowest energy levels — show that in all cases the ground state remains of the same multiplicity (the same degeneracy and symmetry) as the initial electronic term (cf. the formulation of the Jahn—Teller theorem and its discussion in Section B). Therefore one may expect that the qualitative features of the observable properties of the system determined by the ground state only will also be unchanged by vibronic effects. It will be shown below in this section that, indeed, the vibronic interaction reduces quantitatively all the ground state physical magnitudes of electronic origin without changing their qualitative aspect. This reduction effect was seen for the first time in our calculation of the spin—orbit splitting of the T term[56] and afterwards generalized by Ham[57] for any physical electronic magnitude.

The reduction theorem may be formulated as follows: let the wave function for the electronic degenerate Γ term be $\psi_{\Gamma\gamma}(r_\nu)$ (γ denotes the component of the representation Γ) and for the appropriate vibronic term be $\Psi_{\Gamma\gamma}(r_\nu, Q_\alpha)$. Then for matrix elements of any electronic operator $F_{\bar{\Gamma}\bar{\gamma}}(r_\nu)$, transforming as the $\bar{\gamma}$ component of the $\bar{\Gamma}$ representation, the following relationship holds.

$$\begin{aligned}&\langle\Psi_{\Gamma\gamma_1}(r_\nu, Q_\alpha)|F_{\bar{\Gamma}\bar{\gamma}}(r_\nu)|\Psi_{\Gamma\gamma_2}(r_\nu, Q_\alpha)\rangle\\ &\quad = K_\Gamma(\bar{\Gamma})\,\langle\psi_{\Gamma\gamma_1}(r_\nu)|F_{\bar{\Gamma}\bar{\gamma}}(r_\nu)|\psi_{\Gamma\gamma_2}(r_\nu)\rangle\end{aligned} \tag{68}$$

where the constant $K_\Gamma(\bar{\Gamma}) < 1$, and (for a given term, Γ) depends only on the representation $\bar{\Gamma}$ of the electronic operator F. For proof of this theorem see, for instance, ref. 52.

It follows from this theorem (eqn. (68)) that, if the constants $K_\Gamma(\bar{\Gamma})$, called reduction factors, are known, then all the ground state electronic magnitudes can be determined directly from the matrix elements calculated by the initial basic electronic functions of the degenerate term, i.e. without solution of the vibronic problem. In particular, the reduction factors $K_\Gamma(\bar{\Gamma})$ can be obtained from a definite experimental observation and then used for prediction of all the others.

The $K_\Gamma(\bar{\Gamma})$ constants can also be calculated when the solutions of the vibronic equations are known. For the linear E—e problem, the two reduction constants, $K_E(A_2)$ and $K_E(E)$, can be calculated from the numerical data available[58] as a function of the vibronic coupling constant (or the ratio $E_{\mathrm{JT}}/\hbar\omega$). In Fig. 21, the results obtained are shown together with the curves for approximate analytical expressions useful in applications[57,59].

$$\left.\begin{aligned}&K_E(A_2) \approx \exp(-4E_{\mathrm{JT}}/h\omega)\\ &K_E(E) = \tfrac{1}{2}[1 + K_E(A_2)]\end{aligned}\right\} \tag{69}$$

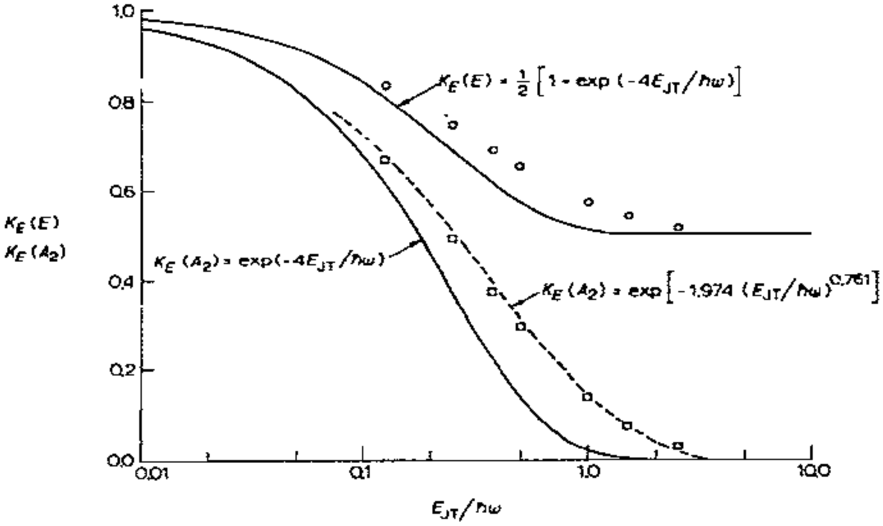


Fig. 21. Reduction factors $K_E(E)$ and $K_E(A_2)$ as a function of the ratio $E_{JT}/\hbar\omega$ for the linear E—e problem[59]. The points are exact values calculated from the data of ref. 58, while the continuous curves show the approximate expressions (69) (the broken line is chosen to fit the calculated points over the range[59] $0.1 \lesssim E_{JT}/\hbar\omega \lesssim 3.0$).

For the linear T—e problem, the following approximate expressions are valid[57,59].

$$\left.\begin{aligned} &K_T(T_1) \approx K_T(T_2) \approx \exp(-3E^e_{JT}/2\hbar\omega_e) \\ &K_T(E) = 1 \end{aligned}\right\} \tag{70}$$

More exact values, taking account a small t_2 vibration influences, were obtained in ref. 52. For the linear T—t_2 problem we have[57,59] (Fig. 22)

$$\left.\begin{aligned} &K_T(T_1) \approx K_T(E) \approx \exp(-9E^t_{JT}/4\hbar\omega_t) \\ &K_T(T_2) = \tfrac{1}{3}\,[2 + K_T(T_1)] \end{aligned}\right\} \tag{71}$$

These expressions are in good accordance with the numerical data available from solution of the vibronic equations[46].

For orthorhombic minima of the T—$(e + t_2)$ second-order problem the approximate formulae are[15]

$$\begin{aligned} &K_T(E) = (1 + 8S + 6\widetilde{S})/(4 + 8S) \\ &K_T(T_1) = (3S + \widetilde{S})/(1 + 2S),\ K_T(T_2) = (1 + 6S)/(2 + 4S) \end{aligned} \tag{72}$$

where

$$\begin{aligned} &S = \tfrac{1}{2}\exp\left[-\frac{K_t}{4\hbar\omega_t}\,(3Q^2_{\theta_0} + 2Q^2_{\zeta_0})\right] \\ &\widetilde{S} = \tfrac{1}{2}\exp(-K_t Q^2_{\zeta_0}/\hbar\omega_t) \end{aligned} \tag{73}$$

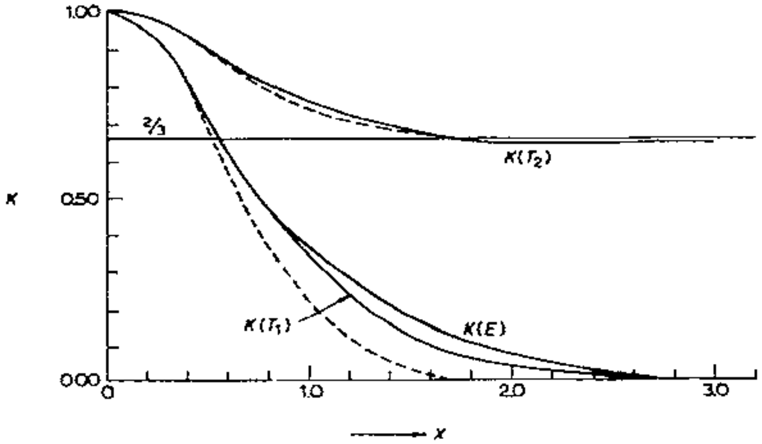


Fig. 22. Reduction factors $K_T(E)$, $K_T(T_1)$ and $K_T(T_2)$ in the linear T—t_2 problem as a unction of $x = [3\,E^{t}_{JT}/2\hbar\omega_t]^{\frac{1}{2}}$. The continuous lines show the results obtained from the umerical solution of the vibronic equations[46], while the broken lines follow the approxinate expressions (71)[59].

he equilibrium coordinates Q_{θ_0} and Q_{ζ_0} being given by eqn. (29).

As is seen from eqns. (69) — (73) the reduction of electronic characteristics lue to vibronic interactions is exponentially dependent on the ratio $E_{JT}/\hbar\omega$ vhich determines the magnitude of the Jahn—Teller effect, and it may be ery great for a strong Jahn—Teller effect. The most strongly reduced (of ll the cases) are T_1-type operators, to which the electron orbital moment nd hence the spin—orbit interaction belong. The essential reduction of the pin—orbit splitting (sometimes by one to two orders of magnitude[56,60]) is ne of the most pronounced manifestations of the Jahn—Teller effect in T erm systems (the E term is not split by spin—orbit interaction in the firstrder approximation).

Other reduced magnitudes are, for example, the anisotropic (orbital) part f the Zeeman interaction, all the (non-totally symmetric) interactions beween the electrons and nuclei (say, dipole—dipole, quadrupole, etc.), the Coulomb and exchange interactions between Jahn—Teller centers in crystals[61] nd so on.

It must be emphasized that the reduction picture described above loses its implicity and attractiveness when the physical magnitude is not only deternined by the ground state. In particular, for a strong Jahn—Teller effect there s another tunneling level which lies close to the ground state (see Figs. 17 nd 19) and may essentially influence the observable effects. In other cases, vhen $K_\Gamma(\overline{\Gamma}) \approx 0$, second-order reduction factors have to be taken into ccount[62].

F. SPECTROSCOPIC MANIFESTATIONS OF TUNNELING SPLITTING AND REDUCTION EFFECTS

There are two somewhat different areas of manifestation of the Jahn—Teller effect based on the solutions of the vibronic equations discussed above: the tunneling splitting and the reduction effects. Whereas the former are essential only in the case of strong vibronic coupling (great $E_\pi/\hbar\omega$ ratio), the latter are most essential for weak (or intermediate) coupling when the energy difference between the ground and excited states is very large and the observable magnitudes are determined only by the ground state.

Before going on to consider these effects in detail, it must be noted that, since the tunneling splitting is small and of vibronic origin, observable spectroscopic properties may be essentially affected by small perturbations which are always present in real samples. In the case of a Jahn—Teller center in a crystal, the role of such perturbations may be lattice vibrations and random strain resulting from inhomogeneities, dislocations or nearby point defects.

The vibronic problem of a Jahn—Teller center in crystals in which lattice vibrations are taken in account is not yet solved, although some attempts have been made[63]. Some qualitative conclusions about the lattice vibration influence upon the Jahn—Teller center tunneling splitting may be made on the basis of a model in which the surrounding crystal is regarded as a viscous continuum[64]. In this model, the tunneling transitions between the equivalent (but differently oriented) distorted nuclear configurations are hindered not only by the internal potential barrier, but by the viscosity of the environment as well. Since the viscosity decreases with temperature rise, the tunneling frequency should also increase by increasing the temperature.

Qualitatively, the same conclusion can be obtained from a more rigorous treatment of the problem in the approximation of the so-called "triple adiabatics" in which three subsystems are separated: the quick one, i.e. the electronic motions, the slow one, i.e. the coordination (Jahn—Teller) center vibrations, and the slowest one, i.e. the lattice vibrations[65].

The effect of random strain on the observable properties of Jahn—Teller systems was investigated in a limited number of cases[57,59,66,67]. It was shown that, although the splitting produced by these strains can be greater than the tunneling splitting (or Zeeman splitting), in most cases only the line shapes (but not positions) are affected (an effect obviously due to the random nature of the strains and their mutual compensation when averaged upon the overall crystal). In other cases, random strain also decreases the line intensity[67].

(i) Microwave and ultrasonic absorption

Microwave absorption may be predicted as a consequence of direct transitions between the tunneling levels (Fig. 20) under the electromagnetic perturbation[68]. These transitions in the general case are magnetic dipolar allowed, and for systems without an inversion center they are also electric dipolar allowed. Taking account of the comment made above concerning the lattice vibration and the influence of random strain, as well as the small value of the tunneling splitting, one may expect the absorption line to be very broad (and even similar to relaxation type absorption, see ref. 69).

The observed additional microwave loss due to Mn^{3+} ions (E term) in yttrium—iron garnets[70] seems to be of the tunneling nature under consideration. Indeed, this absorption has clear-cut frequency dependence with a temperature-dependent maximum position ($\nu_{\max} = 15$ kMc at 37°K and $\nu_{\max} \approx$ 56 kMc at 58° K) in accordance with the strong dependence of the tunneling splitting on crystal temperature described above.

In a similar way, transitions between the tunneling levels under acoustic perturbations which lead to ultrasonic absorption can be considered[71,72]. For the $E \to A$ transition between the tunneling levels of the E—e problem we obtain the following expression for the absorption coefficient as a function of the absorption frequency[71] ω

$$\sigma_{E-A}(\omega) = \frac{\pi}{3} \frac{N R^2 A_1 \nu^2}{kT \theta^3 d} g(\omega) L \tag{74}$$

where N is the number of absorption (Jahn—Teller) centers in a unit volume in the crystal, d being its density, R is the minimal metal—ligand distance, A_1 is the linear vibronic coupling constant (see eqn. (14)), v is the velocity of sound, $g(\omega)$ is the form factor of the line determining its shape and depending on the relaxation processes in the crystal,

$$\int_0^\infty g(\omega)\, \mathrm{d}\omega = 1,$$

and L is the factor which takes into account the sound propagation direction $\mathbf{n}$ and polarization $\mathbf{m}$.

$$L = \sum_i m_i^2 n_i^2 - \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} m_i n_i m_j n_j, \; i,j = x,y,z \tag{75}$$

(m_i and n_i are the direction cosines).

Estimates, say, for hydrated copper complexes (taking $A_1 = 2.5 \times 10^{-4}$ dyn) give $\sigma \approx 3 \times 10^{-11} \omega^2 (4\pi^2 T)^{-1}$, which (without account of random strain, see below) is several orders greater than the so-called magnetic acoustic resonance absorption[73]. The absorption frequency can be regulated by means of magnetic fields[72].

Introducing the relaxation time τ, we can express the line shape by means of the expression

$$g(\omega) = \frac{2}{\pi} \frac{\tau}{1 + (\omega - \omega_0)^2 \tau^2} \tag{76}$$

where $h\omega_0 = \delta$ is the tunneling splitting. As τ is strongly temperature dependent, $g(\omega)$ has a maximum as a function of temperature which can be obtained from the expression $(\omega - \omega_0)\tau\,(T_{\max}) = 1$ if the temperature dependence of δ is neglected.

Acoustic loss due to Jahn—Teller tunneling was observed experimentally by Sturge and coworkers[74,75] in an electronic E-term system Ni^{3+}: Al_2O_3 (see also ref. 76). The author[75] claims that this loss is due to relaxation processes, involving the tunneling effects, but not to resonance transitions between the tunneling levels, the motivation being that the random strain causes much greater splitting, $\Delta \sim 2\ cm^{-1}$, than the tunneling (estimated as $\delta \sim 10^{-1} cm^{-1}$).

However, these objections are not convincing since it can be shown[67] that the sound absorption intensity is strongly dependent on the influence of the crystal lattice defect and decreases with its increase in the ratio $\delta^2/(\delta^2 + \Delta^2)$. It follows that the centers which are strongly affected by random strain do not, in effect, absorb the sound, and only those centers which are not distorted (or are only slightly distorted) by the lattice defect do absorb the sound. The number of resonance-absorbing centers and hence the total absorption intensity is, thereby, strongly decreased by random strain; however, this has little effect on the experimental observations since, as shown above, the effect itself is very strong. For reasons, similar to those discussed above for microwave absorption[69], the ultrasonic absorption lines are expected to be broad and relaxation-like.

(ii) Electron paramagnetic resonance

In an overwhelming majority of cases, electronically degenerate terms in coordination compounds are formed by unpaired electrons with a total spin $S \neq 0$. This fact together with the small magnitude of the tunneling splitting (which often falls in the radiowave range) predetermines the actuality and usefulness of the EPR method in investigation of the Jahn—Teller effect.

Many papers have been devoted to the Jahn—Teller effect in EPR spectra (see reviews in refs. 59,75,77 and the appropriate chapters in monographs cited in refs. 2,5,78). The physical picture of the phenomenon can be clarified by considering the results for the three minima model of the second-order E—e problem first obtained in ref. 64. One can obtain the following expressions for the tunneling state energies in the E—e problem (say, for octahedral complexes of Cu^{II}) as a function of the magnetic field intensity $H \parallel Oz$, by solving the second-order perturbation problem for the Zeeman and spin—orbit interaction.

$$\begin{aligned}
\epsilon^{\pm}_{1\kappa} &= \frac{1}{6}\delta_\kappa \pm \left(1 - \frac{5}{2}\frac{\lambda}{\Delta}\right)\beta H - \frac{1}{2}\left[\left(\delta_\kappa \pm \frac{\lambda}{\Delta}\beta H\right)^2 + \frac{8\lambda^2}{\Delta^2}\beta^2 H^2\right]^{\frac{1}{2}} \\
\epsilon^{\pm}_{2\kappa} &= \frac{1}{6}\delta_\kappa \pm \left(1 - \frac{5}{2}\frac{\lambda}{\Delta}\right)\beta H + \frac{1}{2}\left[\left(\delta_\kappa \pm \frac{\lambda}{\Delta}\beta H\right)^2 + \frac{8\lambda^2}{\Delta^2}\beta^2 H^2\right]^{\frac{1}{2}} \qquad (77) \\
\epsilon^{\pm}_{3\kappa} &= -\frac{1}{3}\delta_\kappa \pm \left(1 - \frac{\lambda}{\Delta}\right)\beta H
\end{aligned}$$

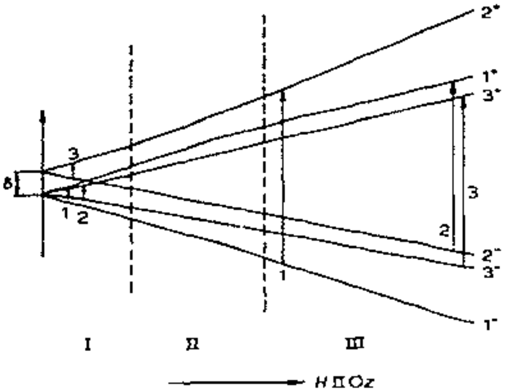


Fig. 23. Tunneling energy level dependence on the magnetic field intensity H∥Oz for an *E*-term case and magnetic dipolar allowed transitions between them.

where λ is the spin—orbit interaction constant, Δ is the energy interval between the ground E_g term and first excited T_{2g} term, and δ_κ is the tunneling splitting.

The $\epsilon_i^\mp$ dependence on H is illustrated in Fig. 23. The allowed magnetic dipolar transitions between these levels, shown by arrows, are more conveniently described by dividing the H range into three: I, the low-frequency range $((\lambda/\Delta)\beta H \ll \delta_\kappa)$; II, the intermediate range $((\lambda/\Delta)\beta H \sim \delta_\kappa)$; III, the high-frequency range $((\lambda/\Delta)\beta H \gg \delta_\kappa)$. In ranges I and III, the $\epsilon_i^\mp$ dependence on H is almost linear, so the electromagnetic wave absorption can be characterized by means of g factors. In range I they are $(\lambda < 0)$

$$g_1 = 2 - \frac{\lambda}{\Delta}(6 + 3\gamma_\kappa),\; g_2 = 2 - \frac{\lambda}{\Delta}(2 - 3\gamma_\kappa),\; g_3 = 2 - \frac{4\lambda}{\Delta} \tag{78}$$

while in range III, three other transitions are allowed.

$$g_1 = 2 - \frac{8\lambda}{\Delta},\; g_{2,3} = 2 - \frac{\lambda}{\Delta}(2 \pm 3\gamma_\kappa) \tag{79}$$

where γ_κ, given by eqns. (60) — (62), is, in most cases, small and may be omitted. In the intermediate range, the intensities of the lines (78) decrease and those for the lines (79) increase when going from I to III. For the angular dependence, say, of the low-frequency spectrum, we have[79]

$$\begin{aligned} g_{1,2} &= 2 - \frac{4\lambda}{\Delta} \pm \frac{2\lambda}{\Delta}\left[1 - 3\left(l^2m^2 + l^2n^2 + m^2n^2\right)\right]^{\frac{1}{2}} \\ g_3 &= 2 - \frac{4\lambda}{\Delta} \end{aligned} \tag{80}$$

where l, m and n are the H direction cosines (without taking into account the vibronic coupling, the angular dependence of the spectra is essentially different[79,80]). The characteristic angular dependence of the Jahn—Teller EPR spectrum was a subject of multiple experimental verification[2,5,59,78,79,81].

Note that, on the assumption of a strong temperature dependence of the tunneling splitting δ, one can obtain the transition from spectrum I to spectrum III considered above by keeping the H value constant but changing the temperature, the low-frequency range, I, being appropriate to high temperatures, while the high-frequency range, III, is appropriate to low temperatures. (If range I is reached at high temperature for which there are quick relaxation processes, the appropriate spectra should be completely isotropic.) Such temperature transitions in the EPR spectra had been observed in a series of compounds before the tunneling splitting effect was revealed[82—85], but were subsequently interpreted on the basis of tunneling splitting[64].

The effect of tunneling on the hyperfine splitting of the EPR spectra is also essential[59,86].

For large tunneling splitting δ the influence of the upper A_1 level on the ground E-level characteristics becomes negligible and the expected EPR spectrum may be determined easily using reduction factors obtained in Section E. If this is the case, the following two lines, each with hyperfine structure (ν is the appropriate hyperfine quantum number), are expected[57,59].

$$h\omega_{\pm} = (g_1\beta H + P_1\nu) \pm K_E(E)\,(g_2\beta H + P_2\nu) \times [1 - 3\,(l^2m^2 + l^2n^2 + m^2n^2)]^{\frac{1}{2}} \qquad (8)$$

where

$$g_1 = 2 - \frac{4\lambda}{\Delta}\,,\; g_2 = -\frac{4\lambda}{\Delta}$$

$$P_1 = -P\left(k + \frac{4\lambda}{\Delta}\right),\; P_2 = -P\left(\frac{4}{7} + \frac{34}{7}\frac{\lambda}{\Delta}\right)$$

$P = 2\gamma\beta\beta_N\,\langle r^{-3}\rangle$, γ is the nuclear g factor, β and β_N are the electronic and nuclear Bohr magnetons, and k is the contact hyperfine interaction constant. As was shown by Ham[67] and Chase[66], strong (as well as weak) random strain does not affect the line positions but their shapes. Expressions analogous to eqn. (81) were also obtained for T-term case spectra[59].

The tunneling splitting also affects the rate of the relaxation processes[87—89], since the probability of relaxation transition between non-Kramers conjugated levels is greater than for conjugated ones, and some new channels of relaxation occur (through the higher tunneling level) which lead to another temperature dependence of the relaxation rate ($\sim e^{-(\delta/kT)}$ and $\sim T^5$ instead of $\sim T$ and $\sim T^7$ for direct and Raman processes, respectively).

(iii) Zero-phonon line splitting

In the electronic spectroscopy of coordination compounds, as already mentioned in Section D, the high-temperature broad-band absorption and luminescence are often investigated. In this case, fine structure due to tunneling splitting is not expected to be observed. It is well known, however, that at low temperatures there may be the so-called zero-phonon lines in crystals (an optical analogue of the Mössbauer effect), which are very narrow and sharp (see, for instance, the appropriate chapter in ref. 90). For these lines the tunneling splitting, say, in the excited electronic state can be ovserved experimentally (if greater than the linewidth). Difficulties may be caused by the fact that the transition to one of the tunneling levels is usually forbidden and becomes allowed only in the next approximation, or in the presence of distorting perturbations.

Caplianskii and Przevusskii[91] have observed the splitting of the zero-phonon line of the $A \rightarrow E$ electronic transition in Eu^{2+}: CaF_2, Eu^{2+}: SrF_2, Sm: CaF_2, and Sm^{2+}: SrF_2 (the splitting being of the order of 15.3, 6.5, 27 and 26 cm^{-1}, respectively) and Chase[92] interpreted these splittings as due to tunneling. One of the lines, as expected, is not seen until appropriate external stress is applied. A splitting of 40 cm^{-1} in the electronic ${}^4A_1 \rightarrow {}^4T_2$ transition in V^{2+}: MgO was observed by Sturge[60], but its interpretation as due to tunneling splitting of the excited T term is still not definite, although its Jahn—Teller origin is beyond doubt.

(iv) Hyperfine structure of Mössbauer spectra

It is quite obvious that the Jahn—Teller dynamic processes in the electronic shell and nuclear configuration directly affect the positions and shapes of the Mössbauer resonance γ-quanta absorption lines. Consider the E-term case with strong vibronic coupling and let the Mössbauer nucleus be in a symmetric coordination complex which in the absence of vibronic interactions has no quadrupole splitting. Using the wave functions of the tunneling levels given[11] in eqn. (55), it was shown[93] that for a transition $I = 1/2 \rightarrow I = 3/2$ (say, for the iron nucleus; I is the nuclear spin) six lines are expected in the spectrum, their frequencies (read off from the undisplaced line) and intensity relations being as follows.

$$h\omega_{1,4} = -\frac{\delta}{2}\,[1 \pm (1+x)^{\frac{1}{2}}]\,,\ h\omega_{2,5} = \mp 2a,\ h\omega_{3,6} = \frac{\delta}{2}\,[1 \mp (1+x)^{\frac{1}{2}}]\,, \qquad (82)$$

$$I_{1,6} : I_{2,5} : I_{3,4} = \frac{2x}{x + [1 + (1+x)^{\frac{1}{2}}]^2} : 1 : \frac{2\,[1 + (1+x)^{\frac{1}{2}}]^2}{x + [1 + (1+x)^{\frac{1}{2}}]^2} \qquad (83)$$

Here $a = K_E(E) \cdot a'$, where a' is the usual quadrupole coupling constant and $K_E(E)$ is the reduction factor given in eqn. (69), $x = 2(B/\delta)^2$, $B = ba$, b being a coefficient of the order of unity depending on the second-order potential barrier height (δ is the tunneling splitting magnitude).

It is seen from the expressions (82) and (83) that the six lines in the Mössbauer spectrum under consideration are of two groups, three in each,

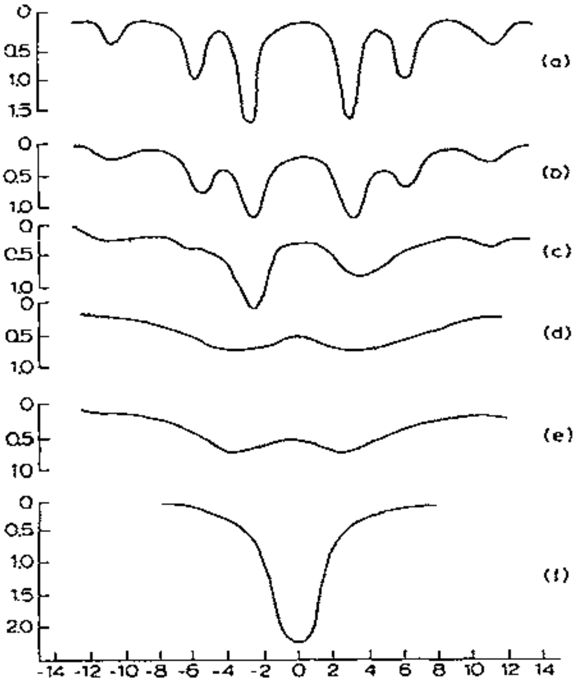


Fig. 24. Mössbauer absorption line shapes as a function of relaxation parameters λ_1 and λ_2 for an E—e problem system: (a) $\lambda_1 = \lambda_2 = 0$; (b) $\lambda_1 = \lambda_2 = 0.1$; (c) $\lambda_1 = 1$, $\lambda_2 = 0.01$, (d) $\lambda_1 = 0.01$, $\lambda_2 = 1$; (e) $\lambda_1 = \lambda_2 = 1$; (f) $\lambda_1 = \lambda_2 = 10$ (all magnitudes in linewidth units).

symmetrical in position and intensities (Fig. 24(a)). For very deep adiabatic potential minima when $\delta \ll a$, the lines in each group have close frequencies (and intensities) and are situated near the points $\pm 2a$. The picture of the spectrum as a whole is like the usual quadrupole splitting in a static distorted complex, but with twice as small a magnitude of the splitting (this is due to the reduction factor value $K_E(E) = 1/2$).

By increasing the tunneling splitting δ, two lines (from each group of three) split off, one displacing towards the center of the spectrum and increasing its intensity, the other moving away from the center and simultaneously lowering its intensity. If the individual lines are not resolved completely, the resulting spectrum as a whole manifests a quadrupole splitting, the magnitude of which decreases when δ increases. Taking into account the increase of δ with temperature mentioned above, one may make a general qualitative conclusion that at low temperatures in the systems under consideration a quadrupole splitting in the Mössbauer spectrum is expected which decreases its magnitude by a temperature increase. Such a temperature behaviour of the quadrupole splitting was observed in crystals containing $FeCl_4^{2+}$ groups[94], and in $FeCr_2O_4$ (ref. 95).

The picture discussed above is incomplete since the relaxation processes, essential in the temperature dependence of the line shapes, have not been taken into account. In order to do so, let us introduce two relaxation transition probabilities, λ_1 and λ_2, which characterize the relaxation rates between the two states of the ground E level and between the E and A_1 tunneling levels, respectively. The line shapes taking these relaxations into account were calculated numerically using a stochastic model[93]. Some results for several λ_1 and λ_2 values and $a = 3$, $b = 4$, and $\delta = 8$ (all magnitudes in line width units) are illustrated in Fig. 24(a) — (f).

As one can see, by increasing the relaxation probabilities (which for a given system is equivalent to an increase of the temperature) the spectrum first turns from the sextet to a doublet and then to a common singlet for an undistorted system. Note that the two constants, λ_1 and λ_2, affect the characteristic features of the spectrum differently[93].

The T-term case may be even more important in the Mössbauer spectra problem than the E-term, since it is appropriate for the commonly investigated octahedral complexes of high-spin Fe^{2+} and low-spin Fe^{3+}. For this case, the effect of tunneling splitting on the hyperfine structure of the Mössbauer spectra was evaluated taking into account the magnetic hyperfine interaction with the electronic spins $S = 0$, 1/2 and 2 as well, but without taking account of relaxation in the electronic subsystem[96,97]. Unfortunately, the influence of the random strain on the Mössbauer spectra of Jahn—Teller systems has not yet been investigated. The question was considered in ref. 98 without taking into account the Jahn—Teller effect.

(v) Pure rotational spectra of symmetrical molecular systems[99]

As was discussed in Section C, some of the Jahn—Teller distortions are of a dipolar type. The latter may occur either as pseudo-Jahn—Teller distortions for any system, or as Jahn—Teller distortions for systems without inversion centers in a T-term state. It is well known that high-symmetry systems, say, of cubic type, without a proper dipole moment have no pure rotational absorption. It will be shown below that such high-symmetry molecules, being dipolar unstable, may have a characteristic pure rotational absorption spectrum, as well as other properties, inherent in molecules having proper dipole moments[16—18,99,100].

Let us assume that the system under consideration has four equivalent dipolar type minima of the adiabatic potential, as in the T_2—t_2 problem of a tetrahedral coordination compound (Section C). The tunneling states for this case are T_2 and A_1 with wave functions and energies given in eqn. (58) and Table 7.

Taking into account the rotations (but not vibronic—rotational interaction) one has to add to every vibronic level a series of rotational levels. This results in

$$E_{T_2 J} = BJ(J+1),\ E_{A_1 J} = BJ(J+1) + \delta \tag{84}$$

where B is the rotational constant, the wave functions being a product of the function (58), $\Psi_\kappa{}^\Gamma(r_\nu, Q_\alpha)$, $\Gamma = T_2, A_1$, and of the rotational function of a spherical top, ϕ_{JKM}, $K, M = 0, \pm 1, \pm 2, \ldots, \pm J$. With the known functions one can calculate the intensities of the induced dipolar transition $\Gamma J \to \Gamma' J'$, which for each unit of incident radiation density and N absorbing centers in a volume unit are[99]

$$I_{\Gamma J \to \Gamma' J'} = \frac{8\pi^3 p_0^2}{9\hbar^2 c^2} \frac{N}{Z} (E_{\Gamma' J'} - E_{\Gamma J}) \left[\exp\left(-\frac{E_{\Gamma J}}{kT}\right) - \exp\left(-\frac{E_{\Gamma' J'}}{kT}\right)\right] C_{JJ'} \quad (85)$$

where Z is the statistical sum

$$Z = \sum_J (2J+1)^2 \left[3 g^I_{T_2 J} + g^I_{A_1 J} \exp\left(-\frac{\delta}{kT}\right)\right] \exp\left[-\frac{\hbar c\, BJ(J+1)}{kT}\right]$$

g^I_J being the statistical weight due to the nucleus spin I

$$C_{JJ'} = \begin{cases} (2J+1)(2J+3) \ , & J' = J+1 \\ (2J+1)^2 \ , & J' = J \\ (2J+1)(2J-1) \ , & J' = J-1 \end{cases} \quad (86)$$

and p_0 is the absolute value of the dipole moment of the system in the dipolar minimum.

As is seen from the expressions obtained, the transition with $J' = J + 1$ (R branches) can be of three types: $T_2 J \to T_2(J+1)$ (R), $A_1 J \to T_2(J+1)$ (R') and $T_2 J \to A_1(J+1)$ (R''), while the Q transitions ($J' = J$) and the P transitions ($J' = J - 1$) are allowed only as $T_2 J \to A_1 J$ (Q branch) and $T_2 J \to A_1(J-1)$ (P branch). The conditions for these branches to occur, their frequency and intensity dependence on temperature, as well as on the δ and B constant relationship are given in ref. 99. In particular, for high tunneling splitting values, δ, and $\delta > B$, all the branches R, R', R'', P and Q may occur in the experiment. (Note that in the common pure rotational spectra for systems with a proper dipolar moment, only one R branch occurs, three branches R, P and Q being incidental only for the rotational structure of the vibrational spectrum.) An example is illustrated in Fig. 25.

The intensity of this new spectrum is proportional to p_0^2 and, hence, it is $(p_0/p_M)^2$ times weaker than the common pure rotational spectra, where p_M is the dipolar moment of a usual rigid dipole molecule. Although quantitative numerical estimates of the p_0 value are not yet available, it seems to be of the order of 0.1 debye (higher limit) for strong dipolar unstable systems, which value leads to $(p_0/p_M)^2 \sim 10^{-2}$. Experimentally, it is possible to check such an absorption and even much weaker ones (the observed Coriolis interaction induced absorption is of the order of 10^{10} times weaker than usual[101]).

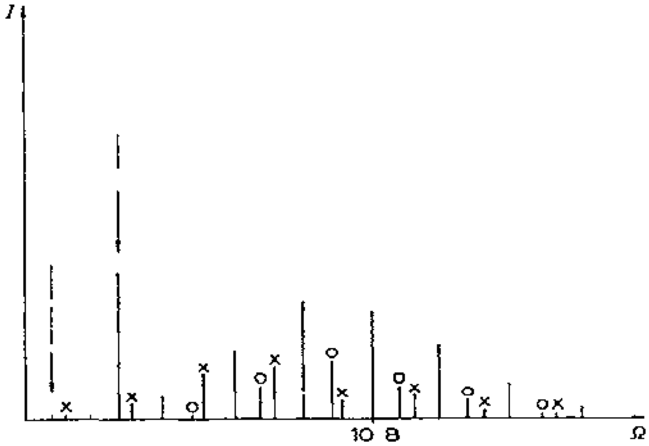


Fig. 25. The calculated (eqn. (85)) pure rotational (infrared) spectrum of a four minima T—t_2 problem tetrahedral system with $\delta = 15$, $B = 5.24$ and $kT = 50$ (all in cm^{-1}). The R-branch lines are not marked, while the R' and R'' lines are marked by crosses and rings, the Q and P lines being shown by full and broken arrows respectively.

(vi) The polarizability of dipolar unstable symmetrical systems

As is well known, two types of molecular behaviour in an external electric field are known: (1) for rigid dipole molecules, which have a temperature-dependent polarizability $\alpha = P_M^2/3kT$, and (2) for highly symmetric non-dipolar molecules where polarizability is independent of temperature. For dipolar unstable molecules, as will be shown below, the polarizability behaviour is quite unusual involving both types of temperature dependence.

Consider a two (dipolar) minimum system with a tunneling splitting 2δ and energy levels

$$E_{\Gamma JKM} = \pm\,\delta + E_{JK} = \pm\,\delta + BJ(J+1) + (A - B)K^2 \qquad (37)$$

where E_{JK} are the rotational energies of a symmetrical top, and A and B are the appropriate rotational constants.

The averaged dipolar moment of a totality of such molecules in an electric field $\mathbf{E}$ can be determined by the expression

$$\mathrm{p} = -\frac{\partial E}{\delta \mathbf{E}} = \frac{\sum\limits_n \left(\dfrac{\partial E_n}{\delta \mathbf{E}}\right) \exp\left(-\dfrac{E_n}{kT}\right)}{\sum\limits_n \exp\left(-\dfrac{E_n}{kT}\right)} \qquad (88)$$

where E_n is the energy of the nth state under the electric field $\mathbf{E}$.

Inserting in eqn. (88) the values given in eqn. (87) and assuming that

$p_0 \mathrm{E} \ll |\delta - mB|$ where m is an integer, one can obtain[100]

$$\bar{p} = \frac{p_0^2 \mathrm{E}}{3Z} \sum_{J,K} \left\{ \frac{[(J+1)^2 - K^2]\,[\delta \tanh(\delta/kT) - B(J+1)]}{(J+1)\,[\delta^2 - B^2(J+1)^2]} \right. \tag{89}$$

$$\left. + \frac{(J^2 - K^2)[\delta \tanh(\delta/kT) + BJ]}{J(\delta^2 - B^2 J^2)} + \frac{(2J+1)\,K^2 \,\mathrm{than}\,(\delta/kT)}{\delta\, J(J+1)} \right\} \exp(-E_{JK}/kT)$$

$$Z = \sum_{J,K} (2J+1) \exp(-E_{JK}/kT)$$

If, as in the Langevin polarization theory, the molecular rotations in the electric field are taken into account in a classical way, then this expression may be essentially simplified to

$$\bar{p} = \frac{p_0^2 \mathrm{E}}{3\delta} \tanh \frac{\delta}{kT} \tag{90}$$

The numerical calculations show that the differences between these two formulas (especially when the temperature is not very low) are negligible.

For a system with four dipolar-type minima, a formula similar to eqn. (90) can be obtained.

$$\bar{p} = \frac{p_0^2 \mathrm{E}}{3kT} \frac{\exp(-\delta/kT) + (kT/\delta)\sinh(\delta/kT)}{\exp(-\delta/kT) + \cosh(\delta/kT)} \tag{91}$$

The temperature dependence of the polarizabilities (in conventional units) $\bar{p}/p_0^2\mathrm{E}$ are illustrated in Fig. 26. As one can see, there are two limiting ranges: (1) for high temperatures, the polarizability is linearly dependent on T^{-1} and coincides with that expected for rigid dipole molecules; (2) for low temperatures, the polarizability becomes independent of T, i.e. it behaves as for highly symmetrical molecules which have no dipole moments. The position of the intermediate range (between the limits) depends on the tunneling splitting value δ: the smaller is δ, the further to the low-temperature ranges (great T^{-1}) is the intermediate behaviour displaced.

Thus the same molecules may behave in an electrical field both as rigid dipole and as high-symmetry non-dipolar molecules dependent on the temperature range at which the measurements are performed (cf. the relativity rule concerning the means of measurement, discussed in Section D). Thereby the fundamental distinction between the two types of molecular polarizability vanishes: they are just two limiting cases for small and large δ values, respectively.

G. CONCLUDING REMARKS

The aim of this short review is to draw the attention of chemists and

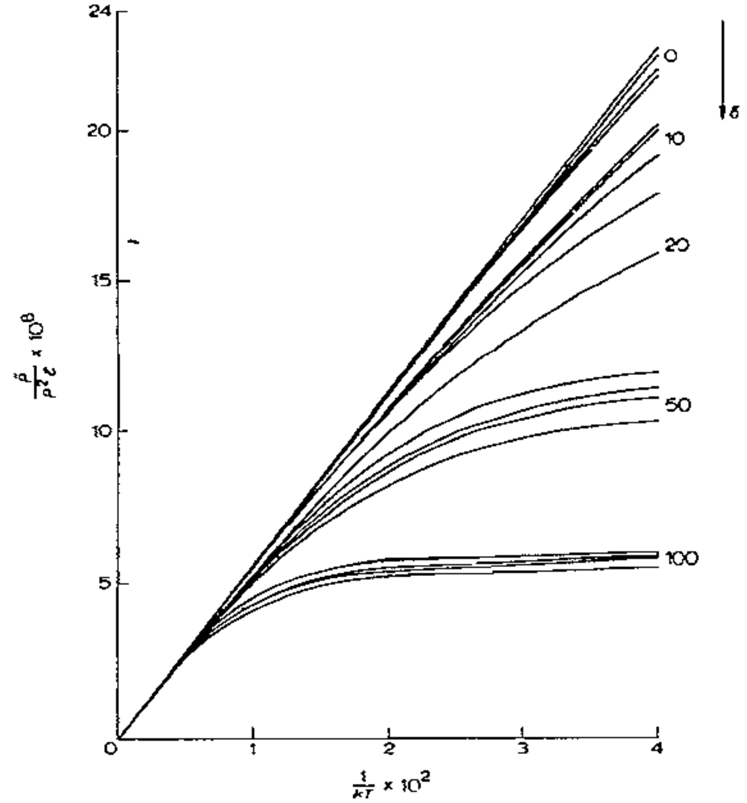


Fig. 26. Averaged polarizabilities (in conventional units) as a function of temperature, tunneling splitting δ shown right (in cm^{-1}) and rotational constant B ($0 \leqslant B \leqslant 9.3$ cm^{-1}). For details see ref. 100.

physicists engaged in the investigation of coordination compounds to a wide range of new effects, inherent in these compounds, which may be of great importance for their work.

From the theoretical point of view, the novelty of these effects is mainly due to their origin from a specific nuclear motion determined by the electronic structure, whereas in most other cases of theoretical chemistry, the electronic structure for a definite nuclear configuration is considered.

One significant aspect of the problem was not discussed above, namely, the Jahn—Teller and pseudo-Jahn—Teller effects in reactions of coordination compounds. It is obvious from general considerations that the Jahn—Teller instabilities may be of great importance in the area of determining the reaction mechanisms. Indeed, as is shown in Section C, a mixing of the ground and excited states by nuclear displacements leads to an instability of the ground state nuclear configuration with regard to some definite nuclear displacements. This statement, applied to chemical reaction intermediate states, may lead to definite conclusions about the direction of its nuclear configuration instability and hence about the direction (mechanism) of the chemical reaction. This approach to the problem can be found in refs. 102—104.

On the other hand, in a distorted configuration, identical ligands are differently bonded and therefore differently subjected to chemical substitution. This is the reason why, for instance, octahedral complexes of Cu^{II} with different ligands are mainly *trans*-substituted[5,105]. The importance of these and related problems for chemical reaction mechanisms calls for particular attention and discussion.

The Jahn—Teller problem in coordination compound chemistry is at present far from being exhausted; further contributions seem to be of great significance.

REFERENCES

1 H.A. Jahn and E. Teller, *Proc. Roy. Soc. London*, 161 (1937) 220.
2 R. Englman, *The Jahn—Teller Effect in Molecules and Crystals*, Wiley—Interscience, London, 1972.
3 E. Ruch and A. Schonhofer, *Theor. Chim. Acta*, 3 (1965) 291.
E.I. Blount, *J. Math. Phys.*, 12 (1971) 1890.
4 I.B. Bersuker, *Teor. Exp. Khim.*, 2 (1966) 518.
5 I.B. Bersuker, *Stroenie i svoistva coordinationich soedinenii. Vvedenie v teoriu* (Structure and Properties of Coordination Compounds. Introduction to the Theory), Chimia, Leningrad, 1971.
6 H.C. Longuet-Higgins, *Advances in Spectroscopy*, Vol. 2, New York, 1961, p. 429.
7 R. Renner, *Z. Phys.*, 92 (1934) 172; H. Sponer and E. Teller, *Rev. Mod. Phys.*, 13 (1941) 75.
8 A.D. Liehr and C.J. Ballhausen, *Ann. Phys. (New York)*, 3 (1958) 304.
9 I.B. Bersuker, *D. Sc. Thesis*, Leningrad University, 1964.
10 R.E. Coffman, *J. Chem. Phys.*, 44 (1966) 2305.
11 I.B. Bersuker, in *Physics of Impurity Centers in Crystals*, Tallin, 1972, p. 479; *Teor. Exp. Khim.*, to be published.
12 U. Opik and M.H.L. Pryce, *Proc. Roy. Soc. London, Ser. A*, 238 (1957) 425.
13 A.D. Liehr, *J. Phys. Chem.*, 67 (1963) 389, 471.
14 M.C.M. O'Brien, *Phys. Rev.*, 187 (1969) 407.
15 I.B. Bersuker and V.Z. Polinger, *Phys, Lett.*, 44A (1973) 495; *Zh. Eksp. Teor. Fiz.*, 66 (1974) 2078.
16 I.B. Bersuker, *Phys. Lett.*, 20 (1966) 589.
17 I.B. Bersuker, B.G. Vechter, G.S. Danil'chuk, L.S. Kremenchugskii, A.A. Muzalevskii and M.L. Rafalovich, *Fiz. Tverd. Tela*, 11 (1969) 2452.
18 I.B. Bersuker, *Teor. Exp. Khim.*, 5 (1969) 293; *IUPAC Congress, 22nd, Sydney, 1969*, Abstracts, p. 16.
19 I.B. Bersuker, Proc. Conf. Coord. Chem., 2nd, Smolenice-Bratislava, 1969, p. 24.
20 I.B. Bersuker, The Jahn—Teller effect, its real meaning and applications, *Section Lectures*, XIII ICCC, Cracow-Zakopane, 1970, p. 9.
21 I.B. Bersuker and B.G. Vekhter, *Proc. Symp. Crystal Chem. 2nd Smolenice-Bratislava*, 1973, p. 132.
22 M.C.M. O'Brien, *Proc. Roy. Soc. London, Ser. A*, 281 (1964) 323.
23 P.T. Miller, P.G. Lenhert and M.D. Joesten, *Inorg. Chem.*, 12 (1973) 218.
24 P.J. Wojtowitz, *Phys. Rev.*, 116 (1957) 32.
25 J. Kanamori, *J. Appl. Phys.*, 31 (1960) 14.
S.M. Kataoka and J. Kanamori, *J. Phys. Soc. Jap.*, 32 (1972) 113.
26 I.B. Bersuker and B.G. Vechter, *Fiz. Tverd. Tela*, 9 (1967) 2652; *Izv. Akad. Nauk, SSSR, Ser. Fiz.*, 33 (1969) 199; I.B. Bersuker, B.G. Vechter and A.A. Muzalevski, *J Phys.*, 33 (1972) C2-139; *Ferroelectrics*, 6 (1974) 197.

27 R. Englman, B. Halperin, *Phys. Rev.*, B2 (1970) 75; B3 (1971) 1668.
28 R. Brout, K.A. Müller and H. Thomas, *Solid State Commun.*, 4 (1966) 507; H. Thomas and K.A. Müller, *Phys. Rev. Lett.*, 28 (1972) 820.
29 R.J. Elliot, R.T. Harley, W. Haves and S.R.P. Smith, *Proc. Roy. Soc. London. Ser. A*, 328 (1972) 217.
30 N.N. Kristoffel and P. Konsin, *Phys. Status. Solidi*, 21, K39 (1967).
N.N. Kristoffel, in *Titanat Baria* (Russian), Nauka, Moscow, 1973, p.11.
31 I.B. Bersuker and V.Z. Polinger, *Zh. Eksp. Teor. Fiz.*, 66 (1974) 2078; B.G. Vekhter, *Fiz. Tverd. Tela*, 15 (1973) 509; B.G. Vekhter and M.D. Kaplan, *Phys. Lett. A*, 43 (1973) 389.
32 S. Sugano, Y. Tanabe and H. Kamimura, *Multiplets in Transition - Metal Ions in Crystals*, Academic Press, New York, London, 1970.
33 V.P. Chlopin, B.S. Tsukerblat, Iu. B. Rosenfeld, and I.B. Bersuker, *Fiz. Tverd. Tela*, 14 (1972) 1060.
34 M.C.M. O'Brien, *Proc. Phys. Soc.*, 86 (1965) 847.
35 P.R. Moran, *Phys. Rev.*, 137 (1965) A1016.
36 Y. Toyozawa and M. Inoue, *J. Phys. Soc. Jap.*, 21 (1966) 1663.
37 K. Cho, *J. Phys. Soc. Jap.*, 25 (1968) 1372.
38 M. Wagner, *Phys. Lett. A*, 29 (1969) 472; *Z. Phys.*, 230 (1970) 460; 244 (1971) 275.
39 B.G. Vekhter, Iu. E. Perlin, V.Z. Polinger, Iu. B. Rosenfeld and B.S. Tsukerblat, *Crystal Lattice Defects*, 3 (1972) 61, 69.
40 Iu.E. Perlin and B.S. Tsukerblat, *Vibronic Interaction Effects on Optical Spectra of Paramagnetic Impurity Ions* (Russian), Shtiintza, Kishinev, 1974.
41 I.B. Bersuker V.P. Chlopin, Yu. E. Perlin, V.Z. Polinger, Yu. B. Rozenfeld, B.S. Tsukerblat and B.G. Vechter, *Proc. Int. Conf. Coord. Chem., 16th*, Toronto, 1972, p. 357.
42 M.H. Perrin and M. Gouterman, *J. Chem. Phys.*, 46 (1967) 1019.
43 B.S. Tsukerblat, B.G. Vekhter, I.B. Bersuker and A.V. Ablov, *Zh. Strukt. Khim.*, 11 (1970) 102.
44 I.B. Bersuker and V.Z. Polinger, in *Crystal Spectroscopy* (Russian), Nauka, Moscow, Vol. 4, 1974, to be published.
45 H.C. Longuet-Higgins, U. Öpik, M.H.L. Pryce and R.A. Sack, *Proc. Roy. Soc. London, Ser. A*, 244 (1958) 1.
46 M. Caner and R. Englman, *J. Chem. Phys.*, 44 (1966) 4054.
47 R. Englman, M. Caner and S. Toaff, *J. Phys. Soc. Jap.*, 29 (1970) 306.
48 W. Moffitt and W. Thorson, *Phys. Rev.*, 108 (1957) 1251.
49 M.S. Child, *J. Mol. Spectrosc.*, 108 (1957) 357.
50 M.C.M. O'Brien, *J. Phys. C. (Solid State Phys.)*, 4 (1971) 2524.
51 R. Romestain and Merle D'Aubigne, *Phys. Rev.*, 4B (1971) 4611.
52 I.B. Bersuker and V.Z. Polinger, *Phys. Status Solidi* (b), 60 (1973) 85.
53 J.R. Fletcher, *Solid State Commun.*, 11 (1972) 601.
54 I.B. Bersuker, *Alunional Conference on Chemistry of Co and Ni*, Kishinev, 1960, Abstracts (Russian), p. 22; *Opt. Spectrosk.*, 11 (1961) 319.
55 I.B. Bersuker, *Zh. Eksp. Teor. Fiz.*, 43 (1962) 1315; *Sov. Phys. — JETP, Engl. Tranl.*, 16 (1963) 933.
56 I.B. Bersuker and B.G. Vekhter, *Fiz. Tverd. Tela*, 5 (1963) 2432.
57 F.S. Ham, *Phys. Rev.*, 138 (1965) A1727; 166 (1968) 307.
58 M.S. Child and H.C. Longuet-Higgins, *Phil. Trans. Roy. Soc. London, Ser. A*, 254 (1962) 259.
59 F.S. Ham, in S. Geschwind (Ed.), *Electron Paramagnetic Resonance*, Plenum Press, New York, 1972, p.1.
60. M.D. Sturge, *Phys. Rev.*, 140 (1965) A880.
61 B.S. Tsukerblat and B.G. Vekhter, *Fiz. Tverd. Tela*, 9 (1972) 2544.
62 B.G. Vekhter, *Phys. Lett.*, 45A (1973) 133.
63 M.C.M. O'Brien, *J. Phys. C. (Solid State Phys.)*, 5 (1972) 2045.
64 I.B. Bersuker, *Zh. Eksp. Teor. Fiz.*, 44 (1963) 1239; *Soviet Phys. — JETP, Engl. Transl.*, 17 (1963) 836.

65 I.B. Bersuker and B.G. Vekhter, *Izv. Akad. Nauk MSSR*, No. 11 (1965) 3.
66 L.L. Chase, *Phys. Rev.*, 168 (1968) 341.
67 I.B. Bersuker (to be published).
68 I.B. Bersuker and B.G. Vekhter, *Proc. Alunional Conf. on Spectroscopy, 15th*, (Russian) Vol. 3, VINITI, Moscow, 1965, p. 520.
69 A.I. Burshtein and Yu.I. Naberukhin, *Zh. Eksp. Teor. Fiz.*, 52 (1967) 1202.
70 E.M. Gyorgy, R.C. Le Craw and M.D. Sturge, *J. Appl. Phys.*, 37 (1966) 1303.
71 I.B. Bersuker, 44 (1963) 1577 (*Soviet Phys. — JETP, Engl. Transl.*, 17 (1963) 1060).
72 I.B. Bersuker, *Fiz. Tverd. Tela*, 6 (1964) 436.
73 S.A. Altshuller, B.I. Kochelaev and A.M. Leushin, *Usp. Fiz. Nauk*, 75 (1961) 459.
74 M.D. Sturge, J.T. Krause, E.M. Gyorgy, R.C. Le Craw and F.R. Merritt, *Phys. Rev.*, 155 (1967) 218.
75 M.D. Sturge, *Solid State Phys.*, 20 (1968) 91.
76 I.S. Cicarello, R. Arzt, K. Dransfeld, *Phys. Rev.*, 138 (1965) A934.
77 K.A. Müller, Jahn—Teller effects in magnetic resonance, in *Magnetic Resonance and Relaxation, Proc. Colloque Ampere, 14th*, R. Blinc (Ed.), Ljubljana, 1966, North-Holland, Amsterdam, 1967, p. 192.
78 A. Abraham and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 1970.
79 R.E. Coffman, *Phys. Lett.*, 19 (1965) 475.
80 A. Abraham and M.H.L. Pryce, *Proc. Phys. Soc. London, Ser. A*, 63 (1950) 409.
81 R.E. Coffman, *Phys. Lett.*, 21 (1966) 381; *J. Chem. Phys.*, 48 (1968) 609.
82 B. Bleaney and D.J. E. Ingram, *Proc. Phys. Soc. London, Ser. A*, 63 (1950) 408.
83 B. Bleaney and K.D. Bowers, *Proc. Phys. Soc. London, Ser. A*, 65 (1952) 667.
84 B. Bleaney, K.D. Bowers and R.S. Trenam, *Proc. Roy. Soc. London, Ser. A*, 228 (1955) 157.
85 D. Bijl and A.C. Rose-Innes, *Proc. Phys. Soc. London, Ser. A*, 66 (1953) 954.
86 I.B. Bersuker, S.S. Budnikov, B.G. Vekhter and B.I. Chinik, *Fiz. Tverd. Tela*, 6 (1964) 2583.
87 I.B. Bersuker and B.G. Vekhter, *Fiz. Tverd. Tela*, 7 (1965) 1231.
88 F.I.B. Williams, D.C. Krupka and D.P. Breen, *Phys. Rev.*, 179 (1969) 241, 255.
89 K.P. Lee and D. Walsh, *Can. J. Phys.*, 49 (1971) 1620.
90 A.A. Maradudin, *Solid State Phys.*, 18 (1966) 273; 19 (1967) 1.
91 A.A. Caplianskii and A.C. Przevuskii, *Opt. Spectrosk.*, 19 (1965) 597; 20 (1966) 1045.
92 L.L. Chase, *Phys. Rev. Lett.*, 23 (1969) 275; *Phys. Rev.*, B2 (1970) 2308.
93 I.B. Bersuker, S.A. Borshch and I.Ya. Ogurtzov, *Phys. Status Solidi* (b), 59 (1973) 707.
94 T.C. Gibb and N.H. Greenwood, *Tech. Rept. I.A.E.A.*, 50 (1966) 143.
95 M. Tanaka, T. Tokoro and Y. Aijama, *J. Phys. Soc. Jap.*, 21 (1966) 262.
96 I.B. Bersuker and I.Ya. Ogurtsov, *Fiz. Tverd. Tela*, 10 (1969) 3651.
97 I.B. Bersuker, I.Ya. Ogurtsov and E.I. Polinkovskii, *Izv. Akad. Mauk MSSR*, No. 4 (1969) 72.
98 F.S. Ham, W.H. Schwarz and M.C.M. O'Brien, *Phys. Rev.*, 185 (1969) 548.
99 I.B. Bersuker, I.Ya. Ogurtsov and Yu.V. Shaparev, *Opt. Spectrosk.*, 36 (1974) 315.
100 I.B. Bersuker, I.Ya. Ogurtsov, Yu.V. Shaparev, *Toer. Exp. Khim.*, 9 (1973) 451.
101 K. Fox, *Phys. Rev. Lett.*, 27 (1971) 233; *Phys. Rev.*, A6 (1972) 907.
102 R.F.W. Bader, *Can. J..Chem.*, 40 (1962) 1164.
103 R.G. Pearson, *J. Amer. Chem. Soc.*, 91 (1969) 4947; *Theor. Chim. Acta*, 16 (1970) 107; *J. Chem. Phys.*, 52 (1970) 2167.
104 T.F. George, J. Ross, *J. Chem. Phys.*, 55 (1971) 3851.
105 I.B. Bersuker, *Teor. Exp. Khim.*, 1 (1965) 5.