One-centre-coordinate approach to the investigation of the Jahn–Teller effect in two-centre vibronic systems with common atoms

L.F. Chibotaru

Institute of Chemistry, Academy of Sciences of Moldavia, Academiei Street 3, 277028 Kishinev, Moldavia

Received 11 May 1991; in final form 8 May 1992

The adiabatic potential of a two-centre vibronic system with common atoms is investigated using one-centre symmetrized nuclear coordinates. In the framework of this approach the energy of the Jahn–Teller stabilization at the extrema points consists of the energies of stabilization of the Jahn–Teller distortions of individual centres and the energy of intercentre correlation of these distortions. This correlation is determined by the intercentre elastic interaction and, implicitly, by the coupling conditions imposed on the one-centre nuclear coordinates as a result of the presence of common atoms in the two-centre systems. Due to intercentre correlation, non-Jahn–Teller distortions of individual centres arise along with Jahn–Teller ones.

1. Introduction

The adiabatic potential of multicentre vibronic systems has been investigated within various approximations (see, for example, refs. [1–3]). To describe the vibronic coupling in these systems the most straightforward approach seems to be to employ multicentre electronic states and the normal nuclear coordinates of the vibrational Hamiltonian [3]. However, such an approach meets with difficulties due to the relatively large number of electronic states and vibrational modes involved in vibronic mixing, which require knowledge of the corresponding vibronic and force constants. The investigation of the adiabatic potential is complicated also by the great number of vibrations active in vibronic coupling. On the other hand, it was shown [4] that in the case when the electronic one-centre states can be considered localized, the adiabatic wavefunction of the multicentre system is the product of one-centre adiabatic wavefunctions. Each of these functions depends on the corresponding one-centre nuclear co-

ordinates only and therefore the vibronic contribution to the adiabatic potential of the multicentre system is a sum of the contributions of different centres.

Thus there are many reasons for the application of one-centre nuclear coordinates to the problems at hand. However, the use of the one-centre-coordinate approach has some characteristic features. First, the existence of the atoms belonging simultaneously to several centres (the common ones) means that one-centre nuclear coordinates of different centres are interdependent. Second, the vibrational Hamiltonian of the multicentre system contains terms which mix one-centre displacements of different centres due to the fact that these displacements are not normal coordinates. These terms can be considered as an intercentre elastic interaction.

In the present paper, the adiabatic potential of some two-centre vibronic systems with common atoms is investigated within the one-centre-coordinate approach.

2. Calculations of the adiabatic potential

Consider a system with two equivalent molecular

Correspondence to: L.F. Chibotaru, Institute of Chemistry, Academy of Sciences of Moldavia, Academiei Street 3, 277028 Kishinev, Moldavia.

groups (centres) with n common atoms. The symmetrized mass-weighted nuclear displacements $q_{\mu\Gamma\gamma}^{(i)}$ (i numerates the centres) transforming as the representation Γ of the corresponding symmetry group are now introduced for each centre. Evidently the number of these one-centre coordinates exceeds the number of independent nuclear degrees of freedom by $3n$. Thus $3n+6$ coupling equations appear for the coordinates $q_{\mu\Gamma\gamma}^{(i)}$ in the absence of centre-of-mass displacements and rotational motions of the two-centre system. Passing to the combinations of the coordinates

$$\begin{aligned} q_{\mu\Gamma\gamma}^+ &= q_{\mu\Gamma\gamma}^{(1)} + q_{\mu\Gamma\gamma}^{(2)}, \\ q_{\mu\Gamma\gamma}^- &= q_{\mu\Gamma\gamma}^{(1)} - q_{\mu\Gamma\gamma}^{(2)}, \end{aligned} \quad (1)$$

the resulting system of coupling equations is divided into a system with $n+3$ equations for $\{q_{\mu\Gamma\gamma}^+\}$ and a system with $2n+3$ equations for $\{q_{\mu\Gamma\gamma}^-\}$.

The coordinates $q_{\mu\Gamma\gamma}^{\pm}$ may be of vibrational type when the corresponding expression (1) contains vibrational one-centre coordinates and of non-vibrational type when the expression (1) includes either centre-of-mass ($q_{c\gamma}^{(i)}$) or rotational ($q_{r\gamma}^{(i)}$) coordinates of individual centres ($\gamma=x, y, z$). It is convenient to present the system of coupling equations as a set of expressions of nonvibrational coordinates (1) in terms of vibrational ones together with the coupling equations imposed on the vibrational coordinates $q_{\mu\Gamma\gamma}^{\pm}$. The latter are of the form:

$$\begin{aligned} \sum' \alpha_{\mu\Gamma\gamma}^{+j} q_{\mu\Gamma\gamma}^+ &= 0, \quad j=1, \dots, k_+, \\ \sum' \alpha_{\mu\Gamma\gamma}^{-j} q_{\mu\Gamma\gamma}^- &= 0, \quad j=1, \dots, k_-, \end{aligned} \quad (2)$$

where the symbol $\sum'$ stands for the summation over one-centre vibrational coordinates only. The coupling coefficients $\alpha_{\mu\Gamma\gamma}^{\pm j}$ result from the expansion of the Cartesian displacements of common atoms in terms of symmetrized one-centre coordinates. The numbers k_+ and k_- can be obtained from the whole number of coupling equations for the coordinates $q_{\mu\Gamma\gamma}^+$ or $q_{\mu\Gamma\gamma}^-$ by excluding the number of non-vibrational coordinates (1) of corresponding type except those which preserve the centres undistorted. After simple calculations we obtain:

$$\begin{aligned} k_+ &= 0, \quad n \leq 3, \\ &= n-3, \quad n > 3, \end{aligned}$$

$$\begin{aligned} k_- &= 0, \quad n=1, \\ &= 2n-3, \quad n > 1. \end{aligned} \quad (3)$$

The potential energy operator for the two-centre system includes one-centre elastic energies, inter-centre elastic interaction U_{int} and the terms of vibronic mixing of localized electronic states at each centre by the corresponding one-centre nuclear displacements. All these contributions depend on one-centre nuclear coordinates of vibrational type except U_{int} which may contain the non-vibrational ones. Within the approximation of nearest-neighbour interaction, U_{int} depends on the coordinates $q_{\mu\Gamma\gamma}^{\pm}$ only.

Consider further the case of two-centre systems with octahedral centres ML_6 each of them being in a twofold degenerate orbital state E_g . Hence the vibronic $E_g \otimes e_g$ problem in the space of corresponding E_g vibrations is realized at each centre [5]. Using the approach proposed in ref. [4], the following expression for the sheets of adiabatic potential of these systems is obtained:

$$\begin{aligned} U_{m_1 m_2} &= \frac{1}{4} \sum_{\Gamma \neq E_g} K_{\mu\Gamma} [(q_{\mu\Gamma\gamma}^+)^2 + (q_{\mu\Gamma\gamma}^-)^2] \\ &+ \frac{1}{2} \sum_{j=1}^n (K_\gamma \gamma_j^2 + K_\beta \beta_j^2) + \sum_{i=1}^2 (\frac{1}{2} K_{E_g} \rho_i^2 \\ &+ m_i \sqrt{V_{E_g}^2 \rho_i^2 + 2 V_{E_g} W_{E_g} \rho_i^3 \cos 3\varphi_i + W_{E_g}^2 \rho_i^4}), \end{aligned} \quad (4)$$

where $m_i = \pm 1$ are two proper values of the electronic quantum number of the i th centre, $K_{\mu\Gamma}$ are one-centre force constants and V_{E_g} and W_{E_g} are one-centre linear and quadratic vibronic constants. The polar coordinates for E_g vibrations

$$q_{E_g\theta}^{(i)} = \rho_i \cos \varphi_i, \quad q_{E_g\epsilon}^{(i)} = \rho_i \sin \varphi_i \quad (5)$$

are used in (4). The angular coordinates β_j and γ_j (j relates to the common atoms) in the expression for U_{int} describe the bending of the bridge $M-L_j-M'$ in the plane of this bridge and in the perpendicular plane, respectively. The operator of intercentre elastic interaction of the biocuboctahedron with one ligand L in common contains also the contribution from counterphase rotations of octahedra q_{rx}^- with respect to the x axis which connects the centres. However, this contribution does not affect the shape of the adiabatic potential because q_{rx}^- does not mix with other vibrations. In the cases of edge- and face-shared

bioctahedra there is a linear contribution in the coordinates β_j in U_{int} which does not affect the shape of the adiabatic potential and is not taken into account here.

When the adiabatic potential of the systems under consideration is investigated, it is necessary to note that the coordinates contained in (4) are not independent. Therefore to search the extrema points in this case the method of Lagrange multipliers [6] must be used, i.e. the extrema of the following functional must be obtained:

$$F_{m_1 m_2} = U_{m_1 m_2} + \sum_{j=1}^{k-} \lambda_j^- \sum' \alpha_{\mu\gamma}^{-j} q_{\mu\gamma}^-, \quad (6)$$

where λ_j^- are Lagrange multipliers. It is taken into account in (6) that, in the case of bioctahedra ($n \leq 3$) according to (3), the coupling conditions are imposed on the vibrational coordinates of $q_{\mu\gamma}^-$ type only.

3. Results and discussion

Now the minima of the lowest sheet of adiabatic potential of bioctahedral systems are investigated.

3.1. Bioctahedron with one shared ligand

There are no coupling equations for vibrational one-centre coordinates in this case. The expressions for angular vibrations γ_1 and β_1 do not contain E_g coordinates. Therefore the coordinates $q_{E_g}^{(i)}$ of different centres are not mixed with one each other or with other coordinates. This means that the adiabatic potential of this bioctahedron is a superposition of the adiabatic potentials of individual octahedral centres in the space of corresponding E_g coordinates. Using well known results for the $E_g \otimes e_g$ problem we may conclude that in the case of linear vibronic coupling at the centres ($W_{E_g} = 0$) a two-dimensional trough in the space of polar coordinates ϕ_1 and ϕ_2 arises near the bottom of the lowest sheet^{#1}. The equilibrium values of the coordinates ρ_1 and ρ_2 and the energy of stabilization are as follows:

$$\rho_1^{(0)} = \rho_2^{(0)} = |V_{E_g}| / K_{E_g},$$

$$E_{JT} = V_{E_g}^2 / K_{E_g}. \quad (7)$$

In the case $W_{E_g} \neq 0$ the trough becomes warped and nine absolute minima with the same energy appear. They correspond to the combinations of minima of the one-centre adiabatic potential of different centres and have the following coordinates ρ_1 and ρ_2 and energy of stabilization:

$$\rho_1^{(0)} = \rho_2^{(0)} = |V_{E_g}| / (K_{E_g} - 2|W_{E_g}|),$$

$$E_{JT} = V_{E_g}^2 / (K_{E_g} - 2|W_{E_g}|). \quad (8)$$

The equilibrium values of all coordinates of non- E_g type are zero except the coordinates $q_{\text{ex}}^{(i)}$:

$$\begin{aligned} q_{\text{ex}}^{(1,2)} = & \frac{1}{4} \sqrt{(m_0 + 6m_1)/m_1} \{ (1 \mp m_1/M) \rho_1^{(0)} \\ & \times [- (1/\sqrt{3}) \cos \phi_1 + \sin \phi_1] \\ & + \frac{1}{4} (1 \pm m_1/M) \rho_2^{(0)} \\ & \times [- (1/\sqrt{3}) \cos \phi_2 + \sin \phi_2] \}, \end{aligned} \quad (9)$$

where m_0 and m_1 are the mass of the central atom and of the ligand in the octahedra, M is the whole mass of the bioctahedron. The axes of local Cartesian coordinate systems at the centres transform one into another by the symmetry transformation σ_h of the bioctahedron.

It should be noted that the conclusion made in section 3.6.1 of ref. [5] that one-centre nuclear coordinates become interdependent (hence the two-dimensional trough vanishes in the case of linear vibronic coupling) when $m_0/m_1 \rightarrow \infty$ seems to be doubtful. Indeed, the adiabatic potential, being the electronic energy as a function of nuclear displacements, cannot depend on the mass of the nuclei. The dependence on the latter arises in the expressions for equilibrium nuclear displacements and in the coupling equations due to the fact that in ref. [5] and in the present work mass-weighted nuclear displacements are employed.

3.2. Edge-shared bioctahedron

According to (3) there is one coupling equation for the coordinates $q_{\mu\gamma}^-$. These coordinates and the coordinates $q_{\mu\gamma}^+$ contained in the expression for angular vibrations β_j are mixed with E_g coordinates. In

^{#1} The same result was obtained in ref. [7] and in a more complicated manner in ref. [5].

consequence, the energy of stabilization in the extrema points depends on additional parameters B and ξ besides one-centre vibronic constants:

$$\xi = \sum_{\Gamma \neq E_g} (\alpha_{\mu\Gamma\gamma})^2 / K_{\mu\Gamma},$$

$$B = \frac{K_\beta}{4m_1 a^2} \left(1 + \sum' (\beta_{\mu\Gamma\gamma}^1 - \beta_{\mu\Gamma\gamma}^2)^2 \frac{K_\beta}{K_{\mu\Gamma}} \right), \quad (10)$$

where $\beta_{\mu\Gamma\gamma}$ are the coefficients of the expansion of β_j in the coordinates $q_{\mu\Gamma\gamma}^+$, a is the M-L distance. The parameters ξ^{-1} and B are force constants which describe an additional elasticity. The first one (ξ^{-1}) appears due to the fact that any distortion of E_g type of one centre leads to distortions in the other (non- E_g) coordinates on the second centre. The parameter B describes the elasticity arising as a result of the changes of angular coordinates β_j when the centres are distorted.

In the case of linear vibronic coupling a trough arises at the bottom of the lowest sheet along the coordinate

$$\varphi = \frac{1}{2}(\varphi_1 - \varphi_2), \quad (11)$$

which describes counterphase motion of the deformations of E_g type at the centres. In the case $K_\beta = 0$ an additional trough arises at the bottom of the lowest sheet along the coordinate

$$\chi = \frac{1}{2}(\varphi_1 + \varphi_2), \quad (12)$$

which describes in-phase motion of one-centre deformations of E_g type. The equilibrium values of ρ_1 and ρ_2 and the energy of stabilization are given in eq. (7).

If $W_{E_g} \neq 0$ two types of minima arise near the bottom of the lowest sheet.

(1) There are three absolute minima which appear along the line of the trough in φ as a result of its warping with the radial coordinates and the energy of stabilization (8). The corresponding equilibrium nuclear configurations are depicted in figs. 1a-1c.

(2) There are two minima which appear along the line of the trough in χ as a result of its warping. The energies of stabilization are of the form

$$E_{JT} = V_{E_g}^2 / [K_{E_g} + B(\frac{3}{2} - \frac{4}{3}\delta^2) - 2|W_{E_g}|(1 + 4\delta^2)^{3/2}],$$

Fig. 1. Equilibrium nuclear configurations of an edge-shared bi-octahedron corresponding to its localization near an absolute minimum. Continuous lines correspond to elongated, and the dashed ones to shortened M-L bonds.

$$\delta = B / 12 |W_{E_g}|. \quad (13)$$

If $B = 0$ these minima become absolute ones with the energy of stabilization (8). The corresponding equilibrium nuclear configurations are shown in figs. 1d and 1e. The distortions of E_g type in these minima are accompanied by the distortions in coordinates $q_{\mu\Gamma\gamma}^+$ contained in the expansion of β_j vibrations:

$$q_{\mu\Gamma\gamma}^{+(0)} = -\frac{B}{K_{\mu\Gamma}} (\beta_{\mu\Gamma\gamma}^1 - \beta_{\mu\Gamma\gamma}^2) [\rho_1^{(0)} \cos(\varphi_1^{(0)} + \pi/6) + \rho_2^{(0)} \cos(\varphi_2^{(0)} + \pi/6)], \quad (14)$$

where $\mu\Gamma\gamma$ include two vibrational modes of T_{1u} type.

The equilibrium nuclear configurations in the extrema points can be distorted also in the coordinates $q_{\mu\Gamma\gamma}^-$ contained in the coupling equation (2):

$$q_{\mu\Gamma\gamma}^{-(0)} = -\frac{\xi^{-1} \alpha_{\mu\Gamma\gamma}}{K_{\mu\Gamma}} - [\rho_1^{(0)} \sin(\varphi_1^{(0)} + \pi/6) + \rho_2^{(0)} \sin(\varphi_2^{(0)} + \pi/6)], \quad (15)$$

where $\mu\Gamma\gamma \in A_{1g}, 1T_{1u}\gamma$ ($\gamma = x, y, z$), $T_{2g}\gamma$ ($\gamma = \xi, \eta, \zeta$).

3.3. Face-shared biotetrahedron

In the case $n=3$ there are three coupling equations for the coordinates $q_{\mu\Gamma\gamma}$, as follows from (3). One of these equations transforms according to the irreducible representation A'_1 of the symmetry group D_{3h} . Two other ones transform according to the rows of irreducible representation E' and therefore contain octahedral E_g coordinates. The equilibrium values of the coordinates and the energies of stabilization depend, as in the case of the edge-shared biotetrahedron, on the parameters

$$\xi \equiv \sum_{\Gamma \neq E_g} (\alpha_{\mu\Gamma\gamma}^{-E_g})^2 / K_{\mu\Gamma} = \sum_{\Gamma \neq E_g} (\alpha_{\mu\Gamma\gamma}^{-E_t})^2 / K_{\mu\Gamma},$$

$$B = \left(\frac{K_\beta}{3m_1\alpha^2} \right) \left(1 + \sum' (\beta_{\mu\Gamma\gamma}^1 - \beta_{\mu\Gamma\gamma}^2)^2 \frac{K_\beta}{K_{\mu\Gamma}} \right), \quad (16)$$

which have the same physical meaning as the parameters (10).

In the case of linear vibronic coupling two types of equipotential continua of extrema arise near the bottom of the lowest sheet along the coordinate χ . The first has the following equilibrium values of E_g coordinates and energy of stabilization:

$$\rho_1^{(0)} = \rho_2^{(0)} = |V_{E_g}| / (K_{E_g} + 2B), \quad \varphi^{(0)} = 0,$$

$$E_{JT} = V_{E_g}^2 / (K_{E_g} + 2B). \quad (17)$$

In these extrema the coordinates $q_{\mu\Gamma\gamma}^+$ contained in the expansion of β_j also differ from zero:

$$q_{\mu\Gamma\gamma}^{+(0)} = \sqrt{\frac{8}{3}} \frac{B}{K_{\mu\Gamma}} \left(\frac{\beta_{\mu\Gamma\gamma}^1 - \beta_{\mu\Gamma\gamma}^2}{\sqrt{2}} \right. \\ \times (\rho_1^{(0)} \sin \varphi_1^{(0)} + \rho_2^{(0)} \sin \varphi_2^{(0)}) \\ - \frac{\beta_{\mu\Gamma\gamma}^1 + \beta_{\mu\Gamma\gamma}^2 - 2\beta_{\mu\Gamma\gamma}^3}{\sqrt{6}} \\ \left. \times (\rho_1^{(0)} \cos \varphi_1^{(0)} + \rho_2^{(0)} \cos \varphi_2^{(0)}) \right), \quad (18)$$

where $\mu\Gamma\gamma = 1T_{1u}, 2T_{1u}$. The second type of equipotential continuum of extrema has the following equilibrium values of ρ_1, ρ_2 and φ and the energy of stabilization:

$$\rho_1^{(0)} = \rho_2^{(0)} = |V_{E_g}| / (K_{E_g} + \xi^{-1}), \quad \varphi^{(0)} = \pm \pi/2,$$

$$E_{JT} = V_{E_g}^2 / (K_{E_g} + \xi^{-1}). \quad (19)$$

In these extrema the coordinates $q_{\mu\Gamma\gamma}^-$ contained in the coupling equations of E'_g and E'_t type are nonzero:

$$q_{\mu\Gamma\gamma}^{-(0)} = - \frac{\xi^{-1}}{K_{\mu\Gamma}} \left(\alpha_{\mu\Gamma\gamma}^{-E_g} [\rho_1^{(0)} \sin(\varphi_1^{(0)} + \pi/6) \right. \\ - \rho_2^{(0)} \sin(\varphi_2^{(0)} + \pi/6)] \\ + \alpha_{\mu\Gamma\gamma}^{-E_t} [\rho_1^{(0)} \cos(\varphi_1^{(0)} + \pi/6) \\ \left. - \rho_2^{(0)} \cos(\varphi_2^{(0)} + \pi/6)] \right), \quad (20)$$

where $\mu\Gamma = 1T_{1u}, 2T_{1u}, T_{2g}, T_{2u}$.

Depending on the relationship between the parameters ξ^{-1} and B two cases are possible. If $\xi^{-1} > 2B$, a trough is realized along the line of the extrema (17) and an equipotential continuum of saddle points appears along the line of extrema (19). If $\xi^{-1} < 2B$, the contrary is the case.

When $W_{E_g} \neq 0$ three types of minima arise near the bottom of the lowest sheet.

(1) There are three minima which appear along the line of the trough (17) as a result of its warping. The corresponding equilibrium nuclear configurations are shown in figs. 2a and 2b and the energy of stabilization is

$$E_{JT} = V_{E_g}^2 / (K_{E_g} + 2B - 2|W_{E_g}|). \quad (21)$$

Fig. 2. Possible types of equilibrium nuclear configurations corresponding to the localization of a face-shared biotetrahedron near an absolute minimum. Continuous and dashed lines have the same meaning as in fig. 1.

Nonzero distortions (18) are present in these minima.

(2) There are three minima which arise along the line of the trough (19) as a result of its warping, the corresponding equilibrium nuclear configurations being depicted in figs. 2c and 2d. The relation $\rho_1^{(0)} \neq \rho_2^{(0)}$ takes place in these minima and the energy of stabilization is

$$E_{JT} = V_{E_g}^2 / [K_{E_g} + \xi^{-1} - 4W_{E_g}^2 / (K_{E_g} + 2B)] . \quad (22)$$

(3) There are also six minima with the following energies of stabilization:

$$E_{JT} = V_{E_g}^2 / \{ K_{E_g} + \frac{1}{2}B + \frac{3}{4}\xi^{-1} \pm 2W_{E_g} [-40\delta^3 - \sqrt{1+4\delta^2} (20\delta^2 - 1)] \} ,$$

$$\delta = (\xi^{-1} - 2B) / 24 | W_{E_g} | . \quad (23)$$

The corresponding equilibrium nuclear configurations for the case $\delta=0$ are given in figs. 2e and 2f. Both the coordinates (18) and (20) are nonzero in the minima of second and third type.

Depending on the relationship between the parameters ξ^{-1} and B , each type of minima may correspond to absolute minima on the surface of the lowest sheet.

Evidently the one-centre distortions in minima are accompanied by rotations and centre-of-mass displacements of individual octahedra in the systems considered above. To describe this, the coupling equations for one-centre coordinates of non-vibrational type must be used (see the previous section).

To conclude, the Jahn–Teller problem for two-

centre systems with common atoms has some features which distinguish it from the one-centre problem and which become evident in the framework of the one-centre-coordinate approach.

(a) The energy of Jahn–Teller stabilization in the extrema points of the adiabatic potential includes the energies of stabilization of Jahn–Teller distortions of individual centres and the energy of intercentre correlation of these distortions. This correlation is determined by intercentre elastic interaction and by the coupling equations imposed on the one-centre nuclear coordinates. The energy parameters of this correlation for biocahedral systems considered above are ξ^{-1} (coupling equations) and B (intercentre elastic interaction).

(b) The intercentre correlation of Jahn–Teller distortions of different centres results in non-Jahn–Teller distortions in the extrema points as well.

References

- [1] L.L. Lohr, Proc. Natl. Acad. Sci. US 59 (1968) 720.
- [2] P. Novak, J. Phys. Chem. Solids 30 (1969) 2357.
- [3] I.B. Bersuker, B.G. Vekhter and M.L. Rafalovich, Cryst. Lattice Defects 6 (1975) 1.
- [4] L.F. Chibotaru, V.Z. Polinger and I.B. Bersuker, Teor. Eksp. Khim. 23 (1987) 657.
- [5] I.B. Bersuker and V.Z. Polinger, Vibronic interactions in molecules and crystals (Springer, Berlin, 1989).
- [6] G.A. Korn and T.M. Korn, Mathematical handbook for scientists and engineers (McGraw-Hill, New York, 1968).
- [7] L.F. Chibotaru, Abstracts of 10th International Symposium on the Jahn–Teller Effect (Kishinev, Moldavia, 1989) p. 64.