

Theoretical study of the static Jahn—Teller effect

V. Vibronic constants for tetrahedral complexes with double degenerate electron terms

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Vibronic coupling in tetrahedral complexes with double degenerate electron E term is analyzed. Including all the vibration modes of a_1 , e , and t_2 symmetries the necessary potential constants of analytic formula are evaluated from the numerical map of the adiabatic potential surface by nonlinear regression analysis. Numerical values are obtained for $^5[\text{FeX}_4]^{2-}$ complexes ($X = \text{F}, \text{Cl}, \text{Br}$) using the CNDO—UHF method.

The role of Jahn—Teller effect in various areas of physics and chemistry is well known. As a consequence of electron degeneracy (except Kramers degeneracy) and electron-vibration (vibronic) interactions the nonlinear configuration of nuclei is energetically unstable. This Jahn—Teller theorem [1, 2] implies the existence of at least one stable nuclear configuration with removed electron degeneracy (the system relaxes to an energetically more advantageous nondegenerate electron state). The stable configurations of nuclei correspond to the minima of the adiabatic potential surface (APS).

The vibronic coupling theory predicts an analytic form of the APS in the presence of electron degeneracy using perturbation method. The values of potential constants for this analytic formula may be obtained from experiment (in very simple cases) or by quantum-chemical calculations [3]. In our previous papers [4, 5] the method of direct evaluation of these constants was developed and applied to some octahedral complexes. These values resulted from a nonlinear regression analysis applied to a numerical map of the APS calculated by the CNDO—UHF version of MO—LCAO—SCF method.

Method

The tetrahedral MX_4 systems have nine normal modes of vibration belonging to a_1 (Q_1 coordinate), e (Q_2 and Q_3), and two sets of t_2 (Q_4 — Q_6 and Q_7 — Q_9) irreducible representations [6] (Table 1).

For a symmetrized direct product of E -type irreducible representations of electron wave functions in T_d symmetry group the following relation holds

$$[E \times E] = A_1 + E \quad (1)$$

Consequently, only the Q_1 , Q_2 , and Q_3 coordinates of a_1 and e symmetries are vibronically active in the linear coupling. Including the quadratic vibronic and vibration terms also the t_2 coordinates are to be accounted because the reducible representation of their direct product contains irreducible representations of a_1 and e symmetry

Table 1

Symmetrized normal coordinates for tetrahedral MX_4 systems of T_d symmetry group^a

Coordinate	Symmetry	Definition
Q_1	a_1	$\frac{1}{2}(r_1 + r_2 + r_3 + r_4 - 4r_0)$
Q_2	$e(x^2 - y^2)$	$\frac{1}{\sqrt{12}}(2\alpha_{23} - \alpha_{12} - \alpha_{13} + 2\alpha_{14} - \alpha_{34} - \alpha_{24})$
Q_3	$e(z^2)$	$\frac{1}{2}(\alpha_{13} - \alpha_{12} + \alpha_{24} - \alpha_{34})$
Q_4	$t_2(yz)$	$\frac{1}{2}(r_1 - r_2 + r_3 - r_4)$
Q_5	$t_2(xz)$	$\frac{1}{2}(r_1 + r_2 - r_3 - r_4)$
Q_6	$t_2(xy)$	$\frac{1}{2}(-r_1 + r_2 + r_3 - r_4)$
Q_7	$t_2(yz)$	$\frac{1}{\sqrt{2}}(\alpha_{24} - \alpha_{13})$
Q_8	$t_2(xz)$	$\frac{1}{\sqrt{2}}(\alpha_{34} - \alpha_{12})$
Q_9	$t_2(xy)$	$\frac{1}{\sqrt{2}}(\alpha_{14} - \alpha_{23})$

^a r_i — the bond length between the central atom M and the i -th ligand L_i ; r_0 — the reference M—L bond length; α_{ij} — the angle of M— L_i and M— L_j bonds.

$$[t_2 \times t_2] = a_1 + e + t_2 \quad (2)$$

Octahedral O and tetrahedral T_d groups are isomorphous and their coupling schemes are the same [7]. Thus we may modify the $E_g - (a_{1g} + e_g)$ coupling formula for octahedral systems by including two sets of t_2 coordinates. Analogously as in our previous papers [3, 4] we obtain the formula as follows

$$\begin{aligned} W = & W_0 + K_a Q_1 + \frac{1}{2} K_{aa} Q_1^2 + \frac{1}{2} K_{ee} (Q_2^2 + Q_3^2) + \\ & + \frac{1}{2} K_{11} (Q_4^2 + Q_5^2 + Q_6^2) + \frac{1}{2} K_{22} (Q_7^2 + Q_8^2 + Q_9^2) + \\ & + K_{12} (Q_4 Q_7 + Q_5 Q_8 + Q_6 Q_9) - \sqrt{V_1^2 + V_2^2} \end{aligned} \quad (3)$$

where

$$\begin{aligned} V_1 = & (A_e + Z_{ae} Q_1) Q_3 + B_{ee} (Q_2^2 - Q_3^2) + \\ & + \sqrt{\frac{1}{6}} B_{11} (Q_4^2 + Q_5^2 - 2Q_6^2) + \sqrt{\frac{1}{6}} B_{22} (Q_7^2 + Q_8^2 - 2Q_9^2) + \\ & + \sqrt{\frac{1}{6}} B_{12} (Q_4 Q_7 + Q_5 Q_8 - 2Q_6 Q_9) \\ V_2 = & (A_e + Z_{ae} Q_1) Q_2 + 2B_{ee} Q_2 Q_3 + \sqrt{\frac{1}{2}} B_{11} (-Q_4^2 + Q_5^2) + \\ & + \sqrt{\frac{1}{2}} B_{22} (-Q_7^2 + Q_8^2) + \sqrt{\frac{1}{2}} B_{12} (-Q_4 Q_7 + Q_5 Q_8) \end{aligned}$$

K_a , K_{aa} , K_{ee} , K_{11} , K_{22} , and K_{12} are vibration constants; A_e , B_{ee} , B_{11} , B_{22} , B_{12} , and Z_{ae} are vibronic constants; W_0 is the energy of the system in the reference geometrical configuration of an ideal tetrahedron. If W_0 corresponds to the reference ideal tetrahedron of minimum energy then K_a is identically zero because

$$\left[\frac{\partial W}{\partial Q_1} \right]_{\text{ref}} = 0 \quad (4)$$

Having derived this analytic form of APS the values of potential (vibration and vibronic) constants may be evaluated from the points of numerical map W_i^c obtained by a quantum-chemical calculation of the total molecular energy for fixed nuclear coordinates [3—5]. For this purpose the nonlinear regression method must be used. The fitting is realized by the weighted least-squares method

$$F = \sum_i (W_i^c - W_i^a)^2 p_i^2 = \min$$

where W_i^a are the approximate energies calculated for a trial set of potential constants from the analytic form of the APS. The statistical weights p_i were chosen in accordance with the metric weighting concept as in our previous papers [3—5].

Results and discussion

The values of potential constants (K_{aa} , K_{ee} , K_{11} , K_{22} , K_{12} , A_e , B_{ee} , B_{11} , B_{22} , B_{12} , and Z_{ae}) were evaluated for $^5[\text{FeX}_4]^{2-}$ complexes ($X = \text{F}, \text{Cl}, \text{Br}$). The multidimensional maps W_i^c were obtained by the semiempirical CNDO/2 method in the UHF version for transition metals [8—10]. The energy was calculated with an accuracy of 10^{-5} eV. The geometry of an ideal tetrahedron with minimal energy was taken as the reference one. The points of APS minima and corresponding Jahn—Teller stabilization energies E_{JT} were determined from the calculated potential constants values. The reliability of results was assessed *via* statistical characteristics such as the standard deviations of individual constants, the correlation coefficient, and the discrepancy *R*-factor. Table 2 summarizes the calculated potential constant values, given to the full number of valid digits (the order of the last digit being equal to the order of the standard deviation), and the characteristics of the APS minima.

Our results indicate some trends analogous to octahedral systems [4]:

- i) Calculated distortions are very small.
- ii) Jahn—Teller stabilization energy E_{JT} increases with the magnitude of distortion.
- iii) FeF_4^{2-} complex exhibits the largest distortion.
- iv) Relatively large value of Z_{ae} vibronic constant (interaction of a_1 and e vibrations) indicates the necessity of inclusion of totally-symmetric a_1 vibrations.

Finally, it must be mentioned that the CNDO/2 version of MO—LCAO

Table 2

Calculated potential constants values and extreme coordinates for $^5[\text{FeX}_4]^{2-}$ systems

System	$^5[\text{FeF}_4]^{2-}$	$^5[\text{FeCl}_4]^{2-}$	$^5[\text{FeBr}_4]^{2-}$
Number of points	67	43	33
$r_0/10^{-10}$ m	2.0545	2.3178	2.43914
$A_{\text{e}}/(\text{eV rad}^{-1})$	- 0.160	- 0.0002	0.094
$B_{\text{ee}}/(\text{eV rad}^{-2})$	- 1.15	- 0.04	- 0.7
$B_{11}/(10^{20} \text{ eV m}^{-2})$	- 0.35	1.5	2
$B_{22}/(\text{eV rad}^{-2})$	- 1.06	- 7.8	1
$B_{12}/(10^{10} \text{ eV m}^{-1} \text{ rad}^{-1})$	4.02	1.92	- 1.6
$Z_{\text{ae}}/(10^{10} \text{ eV m}^{-1} \text{ rad}^{-1})$	98	- 4.7	- 58
$K_{\text{aa}}/(10^{20} \text{ eV m}^{-2})$	35.515	32.78	38.53
$K_{\text{ee}}/(\text{eV rad}^{-2})$	9.6	9.6	14.6
$K_{11}/(10^{20} \text{ eV m}^{-2})$	32.3	30	33
$K_{22}/(\text{eV rad}^{-2})$	1.4	5.0	2.4
$K_{12}/(10^{10} \text{ eV m}^{-1} \text{ rad}^{-1})$	2.4	- 2.4	- 1.4
Correlation coefficient	0.999962	0.998367	0.999884
R -factor ^a	0.0076	0.0455	0.0123
Minimum:			
$E_{\text{JT}}/10^{-3}$ eV	- 1.71	- 0.0	- 0.27
$Q_1/10^{-10}$ m	0.000	0.000	- 0.000
Q_3/rad	- 0.0214	- 0.00003	0.006
$r/10^{-10}$ m	2.0545	2.3178	2.4391
$\Delta\alpha_{12}/^\circ = \Delta\alpha_{34}/^\circ$	0.61	0.0010	0.00
$\Delta\alpha_{13}/^\circ = \Delta\alpha_{24}/^\circ$	- 0.61	- 0.0010	- 0.16
$\Delta\alpha_{14}/^\circ = \Delta\alpha_{23}/^\circ$	0.0008	0.0000	0.16

a) The R -factor is defined as $R = \left[\frac{\sum (W_i^a - W_i^c)^2 / \sum (W_i^c)^2}{i} \right]^{1/2}$

—SCF method used has its quantitative limitations. For example, the stretching force constants K_{aa} are overestimated by a factor of two [3—5]. Nevertheless, the trends [3—5] in the calculated vibration and vibronic constants seem to be correct. On the other hand, the solid state influences are responsible for the amplification of these quantities in real systems.

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