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The E–e Vibronic Interaction in Octahedral Complexes

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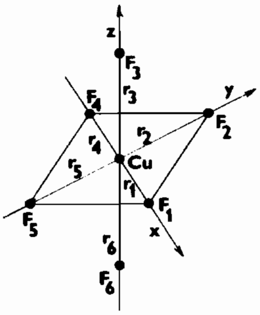

Fig. 1. Coordinate system for CuF_6^{4-}.

The E–e vibronic interaction in octahedral complexes represents the widely studied part of the Jahn–Teller effect demonstration in coordination chemistry (see, *e.g.* the review articles [1–3]). The main aim of our work was to determine the numerical values of particular vibronic constants using the energy hypersurface obtained from the MO calculations. This points out the necessity of investigating the importance of including:

i) the cubic terms in normal vibrations (*e.g.* the anharmonicity of normal vibrations);

ii) the a_{1g} normal vibration into vibronic Hamiltonian in our investigations.

The inclusion of these contributions (quadratic and cubic terms in normal vibrations a_{1g}, e_g and vibronic interactions E_g–$(a_{1g} + e_g)$ up to the quadratic terms in Taylor expansion of vibronic interaction operator) leads to the following total energy expression:

$$\Delta E = E - E_O = W - \sqrt{D} \qquad (1)$$

where E_O is the total energy of optimal O_h configuration;

$$W = \tfrac{1}{2} K_a Q_1^2 + \tfrac{1}{2} K_e(Q_2^2 + Q_3^2) + T_a Q_1^3 + T_{ae} Q_1(Q_2^2 + Q_3^2) + T_e(-Q_2^3 + 3Q_2Q_3^2); \qquad (2)$$

and

$$D = (A - ZQ_1)^2(Q_2^2 + Q_3^2) + B^2(Q_2^2 + Q_3^2)^2 + 2B(A - ZQ_1) \times (Q_2^3 - 3Q_2Q_3^2); \qquad (3)$$

Q_1, Q_2, Q_3 are the normal coordinates of the a_{1g} and e_g normal vibrations (see Fig. 1 and Table I); K_a, K_e (T_a, T_{ae}, T_e) are quadratic (cubic) constants of the particular normal vibrations; A (B) is linear (quadratic) e_g vibronic constant; Z is the e_g–a_{1g} coupling vibronic constant. These terms were only partially included in the previous works [4–9].

Using eqn. (1) the CNDO UHF [10, 11] energy hypersurface was approximated. The particular constants were obtained by the non-linear least squares fit using the Fletcher–Powell minimization of function

$$F = \sum_i w_i (\Delta E_i - \Delta E_i^{CNDO})^2 \qquad (4)$$

TABLE I. Normal Coordinates for a_{1g} and e_g Vibrations in Octahedral Complexes.

Symbol	Symmetry	Normal Coordinate
Q_1	a_{1g}	$\frac{1}{\sqrt{6}}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5 + \Delta r_6)$
Q_2	e_g	$\frac{1}{\sqrt{12}}(\Delta r_1 + \Delta r_2 - 2\Delta r_3 + \Delta r_4 + \Delta r_5 - 2\Delta r_6)$
Q_3	e_g	$\tfrac{1}{2}(\Delta r_2 - \Delta r_1 + \Delta r_5 - \Delta r_4)$
$\rho = \sqrt{Q_2^2 + Q_3^2}$	$\phi = \mathrm{arctg}\,\frac{Q_3}{Q_2}$	

TABLE II. Characteristics of the Energy Hypersurface for System CuF_6^{4-}.

Vibronic constants		A	B	C
K_a	$[10^{20}\ eV\ m^{-2}]$	44.146 ± 0.004	45.655 ± 0.001	41.302 ± 0.004
K_e	$[10^{20}\ eV\ m^{-2}]$	32.613 ± 0.002	32.861 ± 0.001	31.970 ± 0.004
A	$[10^{20}\ eV\ m^{-2}]$	1.04125 ± 0.00005	1.05301 ± 0.00003	1.0192 ± 0.0001
B	$[10^{20}\ eV\ m^{-2}]$	0.52286 ± 0.00003	0.739 ± 0.002	–0.306 ± 0.005
Z	$[10^{20}\ eV\ m^{-2}]$	4.4053 ± 0.0003	3.9648 ± 0.0002	–
T_a	$[10^{30}\ eV\ m^{-2}]$	0.19432 ± 0.00002	–	–
T_{ae}	$[10^{30}\ eV\ m^{-2}]$	–0.6252 ± 0.0001	–	–
T_e	$[10^{30}\ eV\ m^{-2}]$	1.5291 ± 0.0006	–	–
Coordinates of minimal points:				
Q_1	$[10^{-10}\ m]$	–0.003457 ± 0.000001	–0.0029704 ± 0.0000008	–
ρ	$[10^{-10}\ m]$	0.034285 ± 0.000004	0.033929 0.000006	0.03250 ± 0.00002
ϕ	[rad]	0, 2/3π, 4/3 π	0, 2/3π, 4/3π	1/3π, π, 5/3π
ΔE	[eV]	–0.017816 ± 0.000003	–0.017862 ± 0.000004	–0.01656 ± 0.00001
Coordinates of saddle points:		A	B	C
Q_1	$[10^{-10}\ m]$	–0.0031096 ± 0.0000008	–0.0026689 ± 0.0000007	–
ρ	$[10^{-10}\ m]$	0.031769 ± 0.000003	0.030973 ± 0.000005	0.03128 ± 0.00002
ϕ	[rad]	1/3 π, π, 5/3 π	1/3 π, π, 5/3 π	0, 2/3 π, 4/3 π
ΔE	[eV]	–0.016568 ± 0.000003	–0.016308 ± 0.000004	–0.01594 ± 0.00001
F		0.109385	0.166727	0.523567
Correlation coefficients		0.999946	0.999671	0.997551

where ΔE_i^{CNDO} values were obtained by the CNDO mapping of the energy hypersurface near the optimal O_h geometry. The weighting factors w_i were defined as

$$w_i = (\Delta E_i^{CNDO})^{-2} \qquad (5)$$

so that the relative weight of the nearest surroundings of optimal O_h geometry were preferred.

The described method is illustrated by the results obtained for the CuF_6^{4-} complex (Table II):

A) using the complete equations (1–3);

B) neglecting the anharmonic part of normal vibrations ($T_a = 0, T_{ae} = 0, T_e = 0$);

C) as B plus neglecting of coupling term between a_{1g} and e_g normal vibrations (Z = 0).

The values of particular constants with their standard deviations are presented together with the geometries and energies of extremal points of energy hypersurface. It is obvious that for practical use of the proposed method only the first two or three significant digits of obtained values may be considered. In the presented results more significant digits are included in order to compare the reliability of individual approaches (A, B, C).

The comparison of the F-values and the standard deviations of individual constants for all the considered cases shows that the best fit is obtained in case A). It must be pointed out that the omission of a_{1g}–e_g coupling term (case C), frequently employed so far, causes the qualitative change of the energy hypersurface shape (the interchange between minimal and saddle points) as illustrated in Table 2.

It can be summarized that the up to now employed simplifications of equations [1–3] frequently failed already in a qualitative description of the energy hypersurface (the mutual interchange between the minimum and saddle points including the a_{1g} vibration). About 30 coordination compounds are presently under calculation in our laboratory, and results obtained (which will be published later) support this conclusion. The presented method well describes not only qualitatively but also quantitatively, the vibronic interactions. It must be stated here that the method proposed may be of course used with another more sofisticated MO method. The type of MO method used is not so important for numerical tests of suitability of the developed method (done in the present work).

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