

Theoretical study of the static Jahn—Teller effect

IV. Simple models of the solid state influences on the vibronic constants

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Dedicated to Professor L. Valko, DrSc., in honour of his 60th birthday

$E_g - (a_{1g} + e_g)$ vibronic coupling in simple models of solid state is analyzed. The model systems consist of CuCl_6^{4-} octahedron symmetrically surrounded by 6 or 8 Na^+ cations or point charges. Using linear regression analysis the potential constants of analytic formula are evaluated from the numerical map of adiabatic potential surface obtained by the CNDO—UHF method. The results for various models of rigid and fully-elastic lattice are compared.

Octahedral copper(II) complexes are typical Jahn—Teller systems with double degenerate electronic ground state. The shape of their adiabatic potential surface (APS) implies the instability of ideal octahedral configuration and the system relaxes to an energetically more advantageous tetragonal bipyramid which removes the electron degeneracy [1]. The theory of vibronic coupling is able to predict an analytic form of the APS in the presence of electron degeneracy as a function of nuclear coordinates. Its shape is characterized by potential (vibration and vibronic) constant values. In our previous papers [2—4] these constants for some isolated MX_6 systems were evaluated. However, the calculated values of Jahn—Teller stabilization energies and the degree of tetragonal distortion are much lower than in real solid state systems. Thus, the solid state influences are responsible for the amplification of these quantities. The aim of this study is to investigate the environmental influence on the values of vibronic constants.

The crystal lattice of lower than octahedral symmetry causes the external distortion of octahedral Jahn—Teller centre and/or may remove its electron degeneracy. Therefore the model systems must be restricted to the cubic or octahedral environment.

There are two extreme forms of the crystal lattice: The rigid one is of fixed geometry regardless of the distortion of the Jahn—Teller centre. The fully-elastic one (realized *e.g.* by fixed ligands—environment distances) is controlled by the geometry of the Jahn—Teller centre. Each of them acts on the APS of the Jahn—Teller centre in different way. Real systems are somewhere between these two limiting cases.

Because of numerical problems it is impossible to take into account the whole crystal. Thus the study must be restricted to some simple model systems. The simplest models of the solid state influence include the second coordination sphere of the central atom M realized by real atoms and/or point charges. Despite this crude approximation it is possible to study the environmental influence on the values of individual vibronic constants at least qualitatively. This knowledge may be useful in understanding the Jahn—Teller effect in real solid state systems.

Method

In our previous papers [2, 4—6] the analytic form of the APS of octahedral MX_6 systems was derived for $E_g - (a_{1g} + e_g)$ vibronic coupling. This may be simplified for the case of centrosymmetrical deformations of the ideal octahedron, defined by changes in two axial (r_a) and/or four equatorial (r_e) M—X distances, as follows

$$W(Q_a, Q_e) = s(A_e - Z_{ae}Q_a)Q_e + sB_{ee}Q_e^2 + K_aQ_a + \frac{1}{2}K_{aa}Q_a^2 + \frac{1}{2}K_{ee}Q_e^2 + T_{aaa}Q_a^3 + T_{aee}Q_aQ_e^2 - T_{eee}Q_e^3 + W_0 \quad (1)$$

where Q_a and Q_e are symmetrized a_{1g} and e_g type coordinates, respectively;

$$Q_a = \sqrt{\frac{2}{3}}(r_a + 2r_e - 3r_0) \quad (2)$$

$$Q_e = \sqrt{\frac{4}{3}}(r_a - r_e) \quad (3)$$

A_e, Z_{ae}, B_{ee} are vibronic constants; $K_a, K_{aa}, K_{ee}, T_{aaa}, T_{aee}, T_{eee}$ are vibrational constants; a and e subscripts denote the type of corresponding normal coor-

dinate; W_0 is the energy of the system in the reference geometrical configuration of an ideal octahedron ($r_a = r_e = r_0$); $s = +1$ for $r_a > r_e$ and $s = -1$ for $r_a < r_e$ (the reverse convention, however, can be also adopted).

Having derived this analytic form of the APS the values of potential (vibronic and vibration) constants can be determined from the points of the numerical map $W^c(Q_{ai}, Q_{ei})$ obtained by quantum-chemical calculations of the total energy of the system with fixed nuclear coordinates. The simple regression method can be used for this purpose. Fitting may be accomplished by using the weighted least-squares method

$$F = \sum [W^c(Q_{ai}, Q_{ei}) - W^a(Q_{ai}, Q_{ei})]^2 p_i^2 = \min \quad (4)$$

where $W^a(Q_{ai}, Q_{ei})$ are the energies calculated according to eqn (1) for Q_{ai} and Q_{ei} local coordinates of the i -th point of APS. The statistical metric weighting is defined by

$$p_i = (Q_{ai} + Q_{ei})^{-1/2} \quad (5)$$

Results and discussion

The values of potential constants ($A_e, Z_{ae}, B_{ce}, K_a, K_{aa}, K_{ce}, T_{aaa}, T_{ace}, T_{cee}$) were evaluated for ${}^2[\text{CuCl}_6^{4-} \quad n\text{Na}^+]$ ($n = 0$ for A, $n = 6$ for B and $n = 8$ for C models) and ${}^2[\text{CuCl}_6^{4-} \quad 8q]$ (q — point charge, C models) complexes (Fig. 1). Both the fully-elastic and rigid (inelastic) model of the lattice have been considered. In the former approach the Cl—L distances (L = Na^+ or point charge q) have been fixed during the geometry variation. The constant Cu—L distances are typical for the latter approach with fixed positions of Na^+ or point charges. All the models under study are listed in Table 1.

Two-dimensional numerical maps $W^c(Q_{ai}, Q_{ei})$ were obtained by the semiempirical CNDO—UHF version [7—10] of the MO—LCAO—SCF method. The energy cut-off was 10^{-5} eV. From the obtained values of potential constants ($A_e, Z_{ae}, B_{ce}, K_a, K_{aa}, K_{ce}, T_{aaa}, T_{ace}, T_{cee}$) the extreme points Q_a^* and Q_e^* were determined. Consequently, the Jahn—Teller stabilization energies were obtained as follows

$$E_{\text{JT}} = W(Q_a^0, 0) - W(Q_a^*, Q_e^*) \quad (6)$$

where $Q_a^0 = -K_a/K_{aa}$ is the Q_a value corresponding to the ideal octahedron of

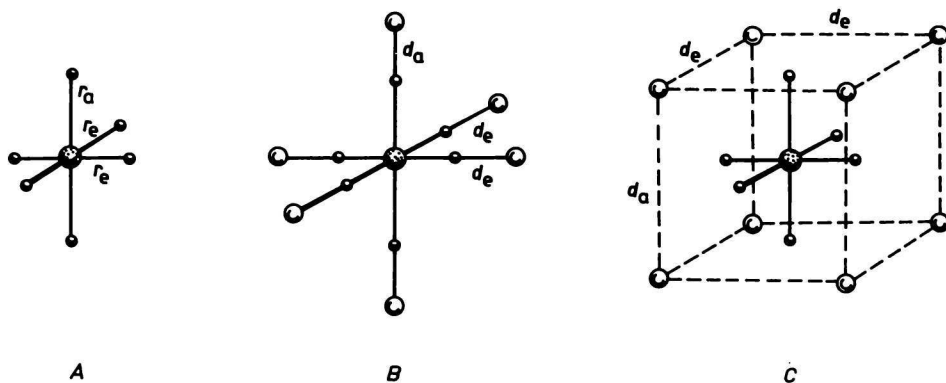


Fig. 1. Model systems of ${}^2[\text{CuCl}_6^{4-} + n\text{L}]$. $\text{L} = \text{Na}^+$ or point charges; $n = 0$ (A model), 6 (B model) or 8 (C model); r_a (r_e) denotes axial (equatorial) Cu—Cl distance; d_a (d_e) denotes the axial (equatorial) Cl—Na distance in B model and L—L distance in C model.

Table 1

Some characteristics of the systems under study^a

System	Model	Fixed parameters
No lattice effect: ${}^2[\text{CuCl}_6^{4-}]$	A	—
Inelastic lattice: ${}^2[\text{CuCl}_6^{4-} + 6\text{Na}^+]$	B1	$r_a + d_a = r_e + d_e = 5 \times 10^{-10} \text{ m}$
${}^2[\text{CuCl}_6^{4-} + 8\text{L}]$	C1	$d_a = d_e = 10 \times 10^{-10} \text{ m}$
Fully-elastic lattice: ${}^2[\text{CuCl}_6^{4-} + 6\text{Na}^+]$	B2	$d_a = d_e = 2.8 \times 10^{-10} \text{ m}$
${}^2[\text{CuCl}_6^{4-} + 8\text{L}]$	C2	$d_a = 2r_a \quad d_e = 2r_e$

^a $\text{L} = \text{Na}^+$ or point charge; d_a (d_e) denotes the axial (equatorial) Cl—Na distance in B models and L—L distance in C models (see Fig. 1).

minimal energy. The reliability of the results obtained was assessed *via* statistical characteristics such as the standard deviations of the individual constants, the correlation coefficient, and the discrepancy *R*-factor.

Tables 2 and 3 summarize the calculated potential constants values, given to the full number of valid digits (the order of the last digit is equal to the order of the standard deviation) and the characteristics of the extreme points (minima and saddle points) of the APS. The obtained results lead to the following conclusions:

Table 2

Calculated potential constants values and extreme coordinates for ${}^2[\text{CuCl}_6^{4-} + n \text{Na}^+]$ systems

Model	C2	B1	B2	A
n	8	6	6	0
$r_0/10^{-10}$ m	2.28	2.21	2.21	2.289
Number of points	24	23	24	52
Correlation coefficient	1.0000	1.0000	0.9987	1.0000
R -factor ^a	0.0001	0.0002	0.0375	0.0027
$K_{aa}/(10^{20} \text{ eV m}^{-2})$	81.9987	57.2558	48.35	39.157
$K_{ee}/(10^{20} \text{ eV m}^{-2})$	31.3912	42.1771	34.81	24.891
$K_z/(10^{10} \text{ eV m}^{-1})$	0.09815	– 0.121552	– 0.0058	0
$A_e/(10^{10} \text{ eV m}^{-1})$	– 0.515816	– 0.545048	– 0.5328	– 0.4497
$B_{ee}/(10^{20} \text{ eV m}^{-2})$	0.0661	0.0900	0.18	– 0.06
$Z_{ae}/(10^{20} \text{ eV m}^{-2})$	– 0.7125	– 0.6605	0.87	– 1.649
$T_{aaa}/(10^{30} \text{ eV m}^{-3})$	– 18.904	– 10.209	– 11.6	– 8.67
$T_{acc}/(10^{30} \text{ eV m}^{-3})$	– 28.55	– 28.125	42	– 33.11
$T_{ccc}/(10^{30} \text{ eV m}^{-3})$	– 2.452	– 4.847	26.4	– 5.843
Minimum:				
E_{JT}/eV	– 0.00453	– 0.004406	– 0.00413	– 0.00408
$Q_a/10^{-10}$ m	– 0.001244	0.00206	0.00019	– 0.0005
$Q_e/10^{-10}$ m	– 0.0166	– 0.01304	0.0157	– 0.018
$r_a/10^{-10}$ m	2.2986	2.2259	2.1919	2.2993
$r_e/10^{-10}$ m	2.2699	2.2033	2.2191	2.2835
Saddle point:				
E_{JT}/eV	– 0.00447	– 0.004004	– 0.00403	– 0.00405
$Q_a/10^{-10}$ m	– 0.001245	0.002058	0.00019	– 0.00045
$Q_e/10^{-10}$ m	0.01632	0.01281	– 0.01495	0.018
$r_a/10^{-10}$ m	2.2606	2.1960	2.2273	2.2784
$r_e/10^{-10}$ m	2.2889	2.2182	2.2014	2.2939

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

i) All the vibration and vibronic constants are modified by the environment. A_e value is modified in the lowest extent.

ii) The ratio of the individual constants values may be modified by environment (e.g. A_e/Z_{ae} or K_{aa}/K_{ee}).

iii) The fully-elastic lattice modifies the constants values in higher extent than the inelastic (rigid) lattice.

iv) K_{aa} and K_{ee} values for cubic C model (8 Na^+) are higher than for octahedral B model (6 Na^+).

v) K_{aa} , K_{ee} , and A_e values increase with environmental charge. The values of other constants exhibit an extreme at some environmental charge value. So do E_{JT} and coordinates of minima or saddle points of the APS.

Table 3

Calculated potential constants values and extreme coordinates for $^2[\text{CuCl}_6^{4-} + 8q]$ systems of Cl model (inelastic lattice)

q/e	1.0	0.6	0.2
$r_0/10^{-10}$ m	2.27	2.27	2.28
Number of points	24	28	26
Correlation coefficient	1.0000	1.0000	1.0000
R -factor	0.0024	0.0001	0.0001
$K_{aa}/(10^{20}$ eV m $^{-2}$)	43.8071	43.44491	41.67122
$K_{ee}/(10^{20}$ eV m $^{-2}$)	28.719	27.8374	25.9789
$K_e/(10^{10}$ eV m $^{-1}$)	0.28684	- 0.349012	0.044148
$A_e/(10^{10}$ eV m $^{-1}$)	- 0.47682	- 0.468100	- 0.450127
$B_{ee}/(10^{20}$ eV m $^{-2}$)	0.205	0.0105	0.0176
$Z_{ae}/(10^{20}$ eV m $^{-2}$)	- 0.428	- 0.6058	- 0.5862
$T_{aaa}/(10^{30}$ eV m $^{-3}$)	- 8.84	- 9.8168	- 9.7706
$T_{acc}/(10^{30}$ eV m $^{-3}$)	- 17.8	- 25.751	- 25.246
$T_{ccc}/(10^{30}$ eV m $^{-3}$)	0.56	- 5.303	- 5.016
Minimum:			
E_{JT}/eV	- 0.00780	- 0.009507	- 0.004028
$Q_a/10^{-10}$ m	- 0.00657	0.008012	- 0.001119
$Q_e/10^{-10}$ m	- 0.01679	- 0.017074	- 0.017515
$r_a/10^{-10}$ m	2.28670	2.29299	2.29977
$r_e/10^{-10}$ m	2.25763	2.26341	2.26943
Saddle point:			
E_{JT}/eV	- 0.00770	- 0.009450	- 0.003965
$Q_a/10^{-10}$ m	- 0.00675	0.008009	- 0.0011218
$Q_e/10^{-10}$ m	0.01635	0.016717	0.0171217
$r_a/10^{-10}$ m	2.24844	2.253967	2.259772
$r_e/10^{-10}$ m	2.27676	2.282921	2.289427

vi) Na^+ cations and point charges modify the potential constants values in different ratios (C2 model — Tables 2 and 4).

Finally, it must be mentioned that the CNDO/2 version of the MO—LCAO—SCF method used has its quantitative limitations. For example, the stretching force constants K_{aa} are overestimated by a factor of two [2—6]. Similarly, the obtained results may be influenced by the chosen set of APS points. Nevertheless, in spite of very simple models of solid state used it is shown that the high-symmetrical environment modifies the values of individual vibronic constants in different extent. Thus the more realistic models of crystal lattice may lead to the distortions comparable with real systems. Our simplified model could give such distortions for unrealistic large point charges only.

Table 4

Calculated potential constants values and exteme coordinates for ${}^2[\text{CuCl}_6^{4-} + 8q]$ systems of C2 model (fully-elastic lattice)

q/e	1.0	0.6	0.2
$r_0/10^{-10}$ m	2.11	2.17	2.24
Number of points	22	23	23
Correlation coefficient	1.0000	1.0000	1.0000
R -factor	0.0002	0.0001	0.0001
$K_{aa}/(10^{20}$ eV m $^{-2}$)	63.68653	54.90956	46.01389
$K_{ee}/(10^{20}$ eV m $^{-2}$)	52.3705	41.4112	30.8278
$K_e/(10^{10}$ eV m $^{-1}$)	0.175298	− 0.35297	− 0.425125
$A_e/(10^{10}$ eV m $^{-1}$)	− 0.810081	− 0.659530	− 0.516752
$B_{ee}/(10^{20}$ eV m $^{-2}$)	0.0812	0.05913	0.03719
$Z_{ae}/(10^{20}$ eV m $^{-2}$)	− 0.9123	− 0.7792	− 0.6380
$T_{aaa}/(10^{30}$ eV m $^{-3}$)	− 14.875	− 12.745	− 10.6373
$T_{aee}/(10^{30}$ eV m $^{-3}$)	− 41.363	− 34.371	− 27.687
$T_{eee}/(10^{30}$ eV m $^{-3}$)	− 9.100	− 7.094	− 5.393
Minimum:			
E_{JT}/eV	− 0.007299	− 0.009083	− 0.012128
$Q_a/10^{-10}$ m	− 0.002812	0.006391	0.009237
$Q_e/10^{-10}$ m	− 0.015624	− 0.016158	− 0.017048
$r_a/10^{-10}$ m	2.12689	2.19127	2.26346
$r_e/10^{-10}$ m	2.09988	2.16328	2.23393
Saddle point:			
E_{JT}/eV	− 0.007193	− 0.009695	− 0.012056
$Q_a/10^{-10}$ m	− 0.002814	0.006389	0.009234
$Q_e/10^{-10}$ m	0.015280	0.015800	0.016662
$r_a/10^{-10}$ m	2.09121	2.15436	2.22453
$r_e/10^{-10}$ m	2.11767	2.18173	2.25339

The cooperative Jahn—Teller effect causes the asymmetry of the environmental influence due to mutual interactions of individual Jahn—Teller centres. Thus the distortion is magnified and it is very difficult or impossible to distinguish between the pure Jahn—Teller and solid state effects. The portion of Jahn—Teller effect by full inclusion of the environment may be deduced from the isolated complex. However, our model is too simple for quantitative conclusions.

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