

## AN ALTERNATIVE MODEL OF THE VIBRONIC COUPLING IN OCTAHEDRAL COMPLEXES

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*Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.*

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It is suggested that for some transition metal hexahalo complexes, the  $E_g-(a_{1g} + e_g)$  vibronic coupling model is better suited than the classical  $T_{2g}-(a_{1g} + e_g)$  model. For the former, alternative model, the potential constants in the analytical formula are evaluated from the numerical map of the adiabatic potential surface by using the linear regression method. The numerical values for 29 hexahalo complexes of the 1st row transition metals are obtained by the CNDO/2 method. Some interesting trends of parameters of such Jahn–Teller-active systems are disclosed.

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The Jahn–Teller effect plays an important role in numerous branches of physics and chemistry. The commonly adopted formulation of the Jahn–Teller theorem<sup>1</sup> states that the nonlinear geometrical configuration of nuclei in an electronically degenerate state (except for the Kramers' and accidental degeneracy) is energetically unstable. From this it follows that at least one geometric configuration of nuclei in the electronically non-degenerate state exists that is energetically stable. This corresponds to the minimum on the adiabatic potential surface (APS). The shape of APS can be described by an analytical function of the total energy of the system, with coordinates of nuclei as parameters. The actual form of this function for complexes in which the Jahn–Teller effect appears may be predicted on the basis of the vibronic coupling theory.

For octahedral  $MX_6$  complexes, vibronic coupling in the  $O_h$  symmetry group for the double or triple electron degeneracy is usually assumed. A systematic study of the octahedral hexahalo complexes of the 1st row transition metals has been the object of our preceding papers<sup>2–5</sup>. Based on the theory of successive splitting of the electron terms associated with the gradual decrease in the entire system symmetry<sup>6,7</sup> due to the Jahn–Teller effect, it has been suggested that the vibronic coupling can be described in a lower symmetry group that still preserves the electron degeneracy<sup>4</sup>.

It has been known for a long time that only three types of vibronic coupling exist<sup>4,8</sup> (apart from the icosahedral and linear symmetry groups), viz.:

- 1)  $T-(a_1 + e + t_2)$  vibronic coupling with the triply degenerate electron term -  $O_h$  type,
- 2)  $E-(a_1 + b_1 + b_2)$  vibronic coupling with the doubly degenerate electron term -  $D_{4h}$  type,
- 3)  $E-(a_1 + e)$  vibronic coupling with the doubly degenerate electron term -  $D_{3d}$  type.

Confining oneself to centrosymmetrical deformations of the initial octahedron, described by changes in two axial ( $r_a$ ) and/or four equatorial ( $r_e$ ) M—X distances, all the above-mentioned types of vibronic coupling can be described by the formula<sup>4</sup>

$$W(Q_1, Q_x) = s(A_x - Z_{ax}Q_1)Q_x + sB_{xx}Q_x^2 + K_aQ_1 + \frac{1}{2}K_{aa}Q_1^2 + \frac{1}{2}K_{xx}Q_x^2 + T_{aaa}Q_1^3 + T_{axx}Q_1Q_x^2 - T_{xxx}Q_x^3 + W^0, \quad (1)$$

where  $A_x$ ,  $Z_{ax}$ ,  $B_{xx}$  are vibronic constants,  $K_a$ ,  $K_{aa}$ ,  $K_{xx}$ ,  $T_{aaa}$ ,  $T_{axx}$ ,  $T_{xxx}$  are vibrational constants,  $Q_1$  and  $Q_x$  are  $a_1$  and  $x$  type coordinates, respectively, the subscript  $x$  stands for  $e$  for the  $O_h$  and  $D_{3d}$  types and  $b_1$  or  $b_2$  for the  $D_{4h}$  type;  $W^0$  is the energy of the system in the reference geometrical configuration of an ideal octahedron,  $s = +1$  or  $-0.5$  for the  $O_h$  type,  $s = +1$  or  $-1$  for the  $D_{3d}$  type and  $s = +1$  or  $-1$ ,  $T_{xxx} = 0$ ,  $B_{xx} = 0$  for the  $D_{4h}$  type. The positive values of the  $s$  parameter refer to  $r_a > r_e$ , the negative values to  $r_a < r_e$ ; the reverse convention, however, can be also adopted.

It is evident from these data that in our case the  $D_{3d}$  and  $D_{4h}$  types differ only in the values of the  $T_{xxx}$  and  $B_{xx}$  constants. For practical purposes (i.e., for assessing whether they can be neglected or not) it is sufficient to investigate the  $D_{3d}$  type coupling model.

## CALCULATIONS

In accordance with our previous studies<sup>2-5</sup>, the symmetrized coordinates to be inserted in Eq. (1) can be defined as follows:

$$\begin{aligned} Q_1 &= \sqrt{\frac{2}{3}}(r_a + 2r_e - 3r^0) \\ Q_x &= Q_3 = \sqrt{\frac{4}{3}}(r_a - r_e), \end{aligned} \quad (2)$$

where  $r_a$  are (two) axial and  $r_e$  (four) equatorial distances between the central atom and the ligand and  $r^0$  is this distance in the reference geometrical configuration of the ideal octahedron.

If the analytical form (1) of the APS is known, the potential constant values can be determined from the points of the numerical map,  $W_i^s(Q_1, Q_3)$ , 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

$$F = \sum_i [W_i^c(Q_1, Q_3) - W_i^a(Q_1, Q_3)]^2 w_i^2 = \min, \quad (3)$$

where  $W_i^a(Q_1, Q_3)$  are the approximate energies calculated for a trial set of potential constants of the analytical form of the APS (Eq. (1)). The statistical metric weighing is defined by

$$w_i = (Q_1^2 + Q_3^2)^{-1/2}, \quad (4)$$

where  $Q_1$  and  $Q_3$  are the local coordinates of the  $i$ -th point of APS.

### RESULTS AND DISCUSSION

The values of the potential constants ( $K_a, K_{aa}, K_{xx}, T_{aaa}, T_{axx}, T_{xxx}, A_x, B_{xx}, Z_{ax}$ ) were evaluated for 29 complexes of the  $^m[\text{MX}_6]^a$  type ( $X = \text{F}, \text{Cl}, \text{Br}$ ), listed in Table I. The two-dimensional maps,  $W^c(Q_1, Q_3)$ , (33 to 42 points for each system) were obtained by the semiempirical CNDO/2 method in the UHF version for transition metals<sup>9-11</sup>. The energy was calculated with an accuracy of  $10^{-5}$  eV. The points of APS extremes ( $Q_1^c, Q_3^c$ ) and the Jahn-Teller stabilization energies

$$E_{\text{JT}} = W(-K_a/K_{aa}, 0) - W(Q_1^c, Q_3^c) \quad (5)$$

were determined from the calculated potential constants values. 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 scattering  $R$ -factor.

TABLE I

Some characteristics of the  $\text{MX}_6$  systems under study ( $X = \text{F}, \text{Cl}, \text{Br}$ )

Electron configuration	Symmetry descent <sup>4</sup>	
	Yes	No
$t_{2g}^4$	$^3[\text{CrX}_6]^{4-}, ^3[\text{MnX}_6]^{3-}$	$^1[\text{CrX}_6]^{4-}, ^1[\text{MnX}_6]^{3-}$
$t_{2g}^5$	$^2[\text{MnF}_6]^{4-}, ^2[\text{MnCl}_6]^{4-}$	$^2[\text{MnBr}_6]^{4-}, ^2[\text{FeX}_6]^{3-}$
$t_{2g}^4 e_g^2$	$^5[\text{FeX}_6]^{4-}, ^5[\text{CoX}_6]^{3-}$	—
$t_{2g}^5 e_g^2$	$^4[\text{CoX}_6]^{4-}$	$^4[\text{NiF}_6]^{3-}, ^4[\text{NiCl}_6]^{3-}$

Table II summarizes the calculated potential constant values, given to the full number of valid digits (the order of the last digit is equal to the order of the standard deviation). The characteristics of the extreme points of the APS are similarly given in Table III.

Our results indicate some trends, applying to the classical  $T_{2g} - (a_{1g} + e_g)$  vibronic coupling model<sup>3,5</sup> as well as to systems with double electron degeneracy<sup>2</sup>:

- 1) For the harmonic potential constants we have  $K_{aa} > K_{xx}$ , so that the non-symmetrical  $Q_3$  vibration can be considered as a „soft” mode, energetically more favourable than the symmetric stretching.
- 2) The two-mode quadratic vibronic constant  $Z_{ax}$  attains a significantly high value as compared to the single-mode  $B_{xx}$  constant, which documents its importance. The anharmonic effects also cannot be neglected, as demonstrated by the values of the  $T_{aaa}$ ,  $T_{aax}$ , and  $T_{xxx}$  constants.
- 3) The values of the  $K_{aa}$  and  $K_{xx}$  constants are higher for the M(III) complexes than for the M(II) complexes; the linear vibronic constant  $A_x$  also attains more negative values for the higher oxidation state of M than for the lower oxidation state. From this it also follows that the  $E_{JT}$  values will be higher for the M(III) complexes than for the M(II) complexes.
- 4) The value of the  $K_{aa}$  constant increases with increasing proton number of the central atom.

Some other trends observed are only partly analogous to our previous results<sup>2-5</sup>:

- 5) In the case of the Cr(II) and Mn(III) complexes the effect of spin multiplicity can be observed: the higher number of unpaired electrons is associated with a decrease in the  $A_x$  values and with more negative values of the  $B_{xx}$  constants. For  $K_{xx}$ ,  $Z_{ax}$  and  $E_{JT}$ , however, such trends are not observed.
- 6) Except for the cobalt complexes, the  $E_{JT}$  values depend on the metal–ligand bond polarity: for the M(II) complexes these values increase in the ligand order F – Cl – Br, whereas for the M(III) complexes they increase in the reverse order.

The results obtained in this study also reveal some new facts:

- 7) For all ligands, the type of distortion (elongation or compression of the octahedron) depends on the oxidation and spin state of the central atom.
- 8) The values of the  $K_{aa}$ ,  $K_{xx}$ , and  $A_x$  constants, the  $E_{JT}$  values and the magnitude of the distortion differ only slightly for the two (classical and alternative) vibronic coupling models.

In conclusion it should be stressed that the differences between the measurable quantities in the two models are small and are not amenable to observation in real systems. The CNDO/2 method also has intrinsic quantitative limitations bringing about over- or underestimation of some constants and thereby, of the distortions and stabilization energies. Nevertheless, our experience warrants the assumption

TABLE II

Calculated potential constant values of the systems under study. Units used:  $A_x$  and  $K_a$  are in  $10^{10}$  eV m $^{-1}$ ;  $B_{xx}$ ,  $Z_{ax}$ ,  $K_{aa}$ , and  $K_{xx}$  are in  $10^{20}$  eV m $^{-2}$ ;  $T_{aaa}$ ,  $T_{axx}$ , and  $T_{xxx}$  are in  $10^{30}$  eV m $^{-3}$ ;  $1$  eV =  $1.6022 \cdot 10^{-19}$  J. The  $R$ -factor is defined as  $R = \left[ \frac{\sum_i (W_i^a - W_i^c)^2}{\sum_i (W_i^c)^2} \right]^{1/2}$

System	$A_x$	$B_{xx}$	$Z_{ax}$	$K_a$	$K_{aa}$	$K_{xx}$	$T_{aaa}$	$T_{axx}$	$T_{xxx}$	Correl. coeff.	$R$
1[CrF <sub>6</sub> ] <sup>4-</sup>	-0.054	1.721	0.201	0.0033	16.067	10.448	-4.47	1.9	32.16	0.999894	0.01128
1[CrCl <sub>6</sub> ] <sup>4-</sup>	-0.0563	1.730	0.128	-0.00012	14.884	9.375	-3.70	-1.2	33.89	0.999929	0.00950
1[CrBr <sub>6</sub> ] <sup>4-</sup>	-0.0787	2.615	0.384	0.00245	18.845	10.756	-5.15	10.7	51.0	0.999796	0.01630
3[CrF <sub>6</sub> ] <sup>4-</sup>	-0.02774	-0.845	-0.213	0.00005	15.996	10.600	-2.81	-15.13	-17.76	0.999980	0.00456
3[CrCl <sub>6</sub> ] <sup>4-</sup>	-0.0250	-0.830	-0.22	0.00138	14.9156	8.893	-2.78	-15.36	-17.08	0.999971	0.00533
3[CrBr <sub>6</sub> ] <sup>4-</sup>	-0.04185	-1.2700	-0.134	-0.00015	18.848	11.157	-3.59	-13.7	-26.33	0.999972	0.00566
1[MnF <sub>6</sub> ] <sup>3-</sup>	-0.3157	8.505	0.74	0.0125	29.314	21.46	-7.90	32.5	162.1	0.999817	0.01650
1[MnCl <sub>6</sub> ] <sup>3-</sup>	-0.2077	7.327	0.49	0.0176	26.145	18.148	-6.652	-11.4	157.5	0.999996	0.00259
1[MnBr <sub>6</sub> ] <sup>3-</sup>	-0.2106	5.884	1.20	0.0263	30.209	19.818	-8.77	27.1	107.0	0.999961	0.00808
3[MnF <sub>6</sub> ] <sup>3-</sup>	-0.1592	-3.567	-0.60	0.0154	29.087	20.89	-6.34	-28.4	-47.8	0.999921	0.01030
3[MnCl <sub>6</sub> ] <sup>3-</sup>	-0.1022	-3.130	-1.07	0.0829	25.932	18.052	-5.87	-43.3	-61.0	0.999859	0.01170
3[MnBr <sub>6</sub> ] <sup>3-</sup>	-0.1041	-3.370	-0.805	0.0113	30.426	19.345	-6.48	-40.9	-66.1	0.999985	0.00492
2[MnF <sub>6</sub> ] <sup>4-</sup>	-0.0302	0.29	7.44	0.0118	19.47	14.53	19.3	171	3.7	0.998931	0.06507
2[MnCl <sub>6</sub> ] <sup>4-</sup>	-0.0387	0.365	1.52	0.0227	20.866	14.826	-5.587	7.2	4.6	0.999983	0.00521
2[MnBr <sub>6</sub> ] <sup>4-</sup>	-0.05381	2.482	1.990	0.00709	25.221	16.998	-6.81	38.98	47.64	0.999994	0.00294
2[FeF <sub>6</sub> ] <sup>3-</sup>	-0.1486	8.383	0.401	0.0179	32.959	23.068	-14.27	7.5	275.4	0.999909	0.01145
2[FeCl <sub>6</sub> ] <sup>3-</sup>	-0.1141	1.749	-0.91	0.10282	29.958	21.58	-6.83	-29.4	10.81	0.999980	0.00589
2[FeBr <sub>6</sub> ] <sup>3-</sup>	-0.1012	1.471	0.137	0.0062	34.765	22.480	-7.27	-16.88	7.11	0.999986	0.00481
5[FeF <sub>6</sub> ] <sup>4-</sup>	-0.0412	-1.281	-0.111	0.00682	26.684	17.942	-6.56	-19.27	19.07	0.999993	0.00331
5[FeCl <sub>6</sub> ] <sup>4-</sup>	-0.0381	-1.098	-0.425	-0.0173	24.4744	15.197	-5.399	-23.30	20.87	0.999998	0.00160
5[FeBr <sub>6</sub> ] <sup>4-</sup>	-0.0480	-1.665	-0.371	-0.00001	28.734	16.830	-5.30	-26.6	35.48	0.999995	0.00807
5[CoF <sub>6</sub> ] <sup>3-</sup>	-0.2508	-4.533	-0.43	0.0190	42.517	36.95	2.53	-124.8	-62.5	0.999966	0.00814
5[CoCl <sub>6</sub> ] <sup>3-</sup>	-0.2293	-4.878	-0.99	0.0259	34.552	31.590	-12.7	23	-87.6	0.999969	0.00724
5[CoBr <sub>6</sub> ] <sup>3-</sup>	-0.1086	-3.622	-0.62	0.00756	39.326	24.159	-4.47	-9.7	-63.7	0.999981	0.00546
4[CoF <sub>6</sub> ] <sup>4-</sup>	-0.0744	3.331	-6.22	-0.0347	33.1055	24.94	2.7	-179.4	89.7	0.999890	0.01387
4[CoCl <sub>6</sub> ] <sup>4-</sup>	-0.0556	1.832	-1.240	-0.0109	29.9781	20.950	-7.279	-33.86	42.25	0.999998	0.00152
4[CoBr <sub>6</sub> ] <sup>4-</sup>	-0.05637	1.218	1.57	0.01370	34.505	22.024	-4.78	8.4	36.2	0.999985	0.00466
4[NiF <sub>6</sub> ] <sup>3-</sup>	-0.2451	5.880	0.74	-0.0110	49.499	37.982	-13.3	2.6	98.3	0.999988	0.00421
4[NiCl <sub>6</sub> ] <sup>3-</sup>	-0.1186	3.821	0.978	0.0159	41.570	28.276	-10.68	16.5	70.6	0.999980	0.00555

Calculated characteristics of APS extreme points. Units used:  $r^0$ ,  $r_a^e$ ,  $r_c^e$ ,  $Q_3^e$ , and  $E_{JT}$  are in  $10^{-12}$  m;  $E_{JT}$  are in  $10^{-3}$  eV;  $r_a$  is axial ( $2x$ ) metal-ligand distance,  $r_c$  is equatorial ( $4x$ ) metal-ligand distance,  $r^0$  is optimum metal-ligand distance for the ideal octahedron

System	Minimum					Saddle point				
	$r^0$	$Q_3^e$	$r_a^e$	$r_c^e$	$E_{JT}$	$Q_3^e$	$r_a^e$	$r_c^e$	$E_{JT}$	
1[CrF <sub>6</sub> ] <sup>4-</sup>	234.60	-0.013	235.41	234.19	0.20	-0.011	0.016	234.13	234.82	0.11
1[CrCl <sub>6</sub> ] <sup>4-</sup>	262.32	-0.833	263.29	261.85	0.24	0.0125	0.142	261.80	262.59	0.13
1[CrBr <sub>6</sub> ] <sup>4-</sup>	272.59	-1.093	273.85	271.96	0.46	-0.004	0.518	271.99	272.89	0.20
3[CrF <sub>6</sub> ] <sup>4-</sup>	234.60	-0.035	234.25	234.78	0.04	-0.003	-0.228	234.86	234.47	0.03
3[CrCl <sub>6</sub> ] <sup>4-</sup>	262.335	-0.013	261.94	262.52	0.04	-0.012	-0.240	262.61	262.19	0.03
3[CrBr <sub>6</sub> ] <sup>4-</sup>	272.59	0.006	272.05	272.86	0.10	0.006	-0.311	272.95	272.41	0.07
1[MnF <sub>6</sub> ] <sup>3-</sup>	207.949	-0.040	210.39	206.70	4.15	-0.029	0.930	206.86	208.47	1.40
1[MnCl <sub>6</sub> ] <sup>3-</sup>	239.542	-0.021	241.56	238.52	2.26	-0.0522	0.0703	238.81	239.93	0.71
3[MnBr <sub>6</sub> ] <sup>3-</sup>	254.308	-0.047	256.13	253.37	1.89	-0.063	0.717	253.45	254.70	0.73
3[MnF <sub>6</sub> ] <sup>3-</sup>	207.955	-0.066	206.72	208.53	0.86	-0.063	-0.586	208.61	207.59	0.47
3[MnCl <sub>6</sub> ] <sup>3-</sup>	239.668	-0.341	238.63	239.98	0.43	-0.334	-0.444	240.04	239.28	0.23
3[MnBr <sub>6</sub> ] <sup>3-</sup>	254.306	-0.049	253.43	254.71	0.40	-0.046	-0.413	254.76	254.05	0.22
2[MnF <sub>6</sub> ] <sup>4-</sup>	219.643	0.021	219.91	219.52	0.03	0.015	0.207	219.41	219.77	0.03
2[MnCl <sub>6</sub> ] <sup>4-</sup>	249.397	-0.090	249.66	249.21	0.05	-0.092	0.241	249.08	249.50	0.06
2[MnBr <sub>6</sub> ] <sup>4-</sup>	262.472	0.003	262.97	262.23	0.12	-0.010	0.248	262.18	262.61	0.07
2[FeF <sub>6</sub> ] <sup>3-</sup>	204.355	-0.0442	205.51	203.75	0.90	-0.050	0.407	203.86	204.57	0.30
2[FeCl <sub>6</sub> ] <sup>3-</sup>	235.702	-0.358	236.29	235.19	0.37	-0.354	0.467	235.02	235.83	0.27
2[FeBr <sub>6</sub> ] <sup>3-</sup>	251.035	-0.014	251.62	250.73	0.26	-0.015	0.399	250.57	251.26	0.20
5[FeF <sub>6</sub> ] <sup>4-</sup>	217.635	-0.026	217.32	217.78	0.06	-0.026	-0.202	217.86	217.51	0.04
5[FeCl <sub>6</sub> ] <sup>4-</sup>	245.821	0.066	245.52	246.01	0.06	0.067	-0.219	246.10	245.72	0.05
5[FeBr <sub>6</sub> ] <sup>4-</sup>	259.742	-0.003	259.34	259.94	0.08	-0.002	-0.241	260.02	259.60	0.06
5[CoF <sub>6</sub> ] <sup>3-</sup>	199.352	-0.032	198.36	199.83	1.09	-0.041	-0.557	199.98	199.01	0.70
5[CoCl <sub>6</sub> ] <sup>3-</sup>	230.798	-0.108	229.66	231.30	1.14	-0.094	-0.579	231.43	230.43	0.66
5[CoBr <sub>6</sub> ] <sup>3-</sup>	247.505	-0.028	246.80	247.84	0.34	-0.025	-0.354	247.90	247.29	0.19
4[CoF <sub>6</sub> ] <sup>4-</sup>	207.368	0.042	207.82	207.17	0.13	0.065	0.229	207.13	207.53	0.08
4[CoCl <sub>6</sub> ] <sup>4-</sup>	237.759	0.024	238.13	237.59	0.09	0.028	0.277	237.51	237.90	0.06
4[CoBr <sub>6</sub> ] <sup>4-</sup>	253.484	0.027	253.80	253.31	0.08	-0.029	0.231	253.21	253.61	0.07
4[NiF <sub>6</sub> ] <sup>3-</sup>	191.822	0.035	192.82	191.82	1.08	0.030	0.508	191.25	192.13	0.62
4[NiCl <sub>6</sub> ] <sup>3-</sup>	224.901	-0.027	225.52	224.58	0.33	-0.031	0.336	224.50	225.08	0.20

that the trends of the calculated quantities are correct within the framework of the model adopted. It should be, however, borne in mind that the higher distortions and stabilization energies observed in real systems are to a high extent contributed to by solid state effects, which can predominate substantially over the Jahn–Teller effect as would manifest itself in isolated systems.

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