

**VIBRONIC CONSTANTS FOR TETRAHEDRAL COMPLEXES  
WITH TRIPLE DEGENERATE ELECTRON TERMS**Martin BREZA<sup>a</sup> and Peter PELIKÁN<sup>b</sup><sup>a</sup> *Department of Inorganic Chemistry,  
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$T_i - (a_1 + e + t_2)$  vibronic coupling ( $i = 1, 2$ ) in tetrahedral systems is analysed. Using a non-linear regression analysis the potential (vibration and vibronic) constants in derived analytic formula of adiabatic potential surface are evaluated from numerical maps calculated by CNDO-UHF method for transition metals. The obtained results are in agreement with the correct understanding of the Jahn-Teller theorem: not the degeneracy of molecular orbitals, but the orbital degeneracy of electronic state is of deciding importance.

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Jahn-Teller effect plays an important role for the most part in physics and chemistry of complex compounds of transition metals. According to the Jahn-Teller theorem<sup>1,2</sup>, every nonlinear configuration of nuclei in electronically degenerate state (except Kramers degeneracy) is energetically unstable. Thus, at least, one stable configuration of nuclei in electronically nondegenerate state must exist, that corresponds to a minimum of the adiabatic potential surface (APS). The orbital degeneracy of electronic states and the degeneracy of molecular orbitals is to be distinguished in this case. The complexes studied in this paper (Table I) are characterised by triple degeneracy of molecular orbitals of  $t_2$  type but their electronic states differ one from another. The approach chosen should be able to find out the decisive role of orbital degeneracy of electronic states.

On the basis of the perturbation theory for degenerate electron terms an analytic formula for the APS may be derived in the parametric form; this includes potential constants specifying the APS shape. In our previous papers<sup>3,4</sup> the analytic formula for  $T_{ij} - (a_{1g} + e_g + t_{2g})$  vibronic interaction ( $i = 1, 2; j = u, g$ ) in octahedral  $MX_6$  complexes was derived; it is formally suitable also for tetrahedral  $MX_4$  complexes (as  $O$  and  $T$  symmetry point groups are isomorphous<sup>5</sup>). Because of practical reasons we do not consider the spin-orbit interaction and interactions with crystal lattice that play an important role under magnetic ordering temperature of Jahn-Teller ions with triple electron degeneracy. The above mentioned interactions are not considered<sup>6,7</sup> in the CNDO-UHF version of MO-LCAO-SCF method used for the APS mapping, too.

## THEORETICAL

The geometry of tetrahedral systems is completely defined by nine symmetrized coordinates<sup>8</sup> listed in Table II. The known analytic formula for  $T_{ij} - (a_{1g} + e_g + t_{2g})$  vibronic interaction ( $i = 1, 2; j = u, g$ ) in octahedral  $\text{MX}_6$  complexes may be simply modified to include the both sets of  $t_2$  coordinates for  $\text{MX}_4$  complexes in  $T_d$  group. Thus we obtain

$$\begin{aligned}
 W = & W_0 + K_a Q_1 + \frac{1}{2} K_{aa} Q_1^2 + \frac{1}{2} K_{ee} (Q_2^2 + Q_3^2) + \frac{1}{2} K_{11} (Q_4^2 + Q_5^2 + Q_6^2) + \\
 & + \frac{1}{2} K_{22} (Q_7^2 + Q_8^2 + Q_9^2) + K_{12} (Q_4 Q_7 + Q_5 Q_8 + Q_6 Q_9) + \\
 & + T_{aaa} Q_1^3 + T_{aee} Q_1 (Q_2^2 + Q_3^2) + T_{a11} Q_1 (Q_4^2 + Q_5^2 + Q_6^2) + \\
 & + T_{a22} Q_1 (Q_7^2 + Q_8^2 + Q_9^2) + T_{a12} Q_1 (Q_4 Q_7 + Q_5 Q_8 + Q_6 Q_9) + \\
 & + T_{eee} (3Q_2^2 Q_3 - Q_3^3) + T_{e11} [(Q_3 - \sqrt{3}Q_2) Q_4^2 + (Q_3 + \sqrt{3}Q_2) Q_5^2 - \\
 & - 2Q_3 Q_6^2] + T_{e22} [(Q_3 - \sqrt{3}Q_2) Q_7^2 + (Q_3 + \sqrt{3}Q_2) Q_8^2 - 2Q_3 Q_9^2] + \\
 & + T_{e12} [(Q_3 - \sqrt{3}Q_2) Q_4 Q_7 + (Q_3 + \sqrt{3}Q_2) Q_5 Q_8 - 2Q_3 Q_6 Q_9] + \\
 & + T_{111} Q_4 Q_5 Q_6 + T_{222} Q_7 Q_8 Q_9 + T_{112} (Q_4 Q_5 Q_9 + Q_4 Q_6 Q_8 + Q_5 Q_6 Q_7) + \\
 & T_{122} (Q_5 Q_7 Q_9 + Q_6 Q_7 Q_8 + Q_4 Q_8 Q_9) + \varepsilon, \tag{1}
 \end{aligned}$$

where  $\varepsilon$  is the lowest eigenvalue of the symmetric matrix,  $\mathbf{V}$ , defined by the following matrix elements

$$\begin{aligned}
 V_{11} = & \frac{1}{2} (A_e + Z_{ae} Q_1) (Q_3 - \sqrt{3}Q_2) + B_{ee} (Q_2^2 - Q_3^2 - 2\sqrt{3}Q_2 Q_3) + \\
 & + \sqrt{\frac{1}{6}} B_{11} (-2Q_4^2 + Q_5^2 + Q_6^2) + \sqrt{\frac{1}{6}} B_{22} (-2Q_7^2 + Q_8^2 + Q_9^2) + \\
 & + 2\sqrt{\frac{1}{6}} B_{12} (-2Q_4 Q_7 + Q_5 Q_8 + Q_6 Q_9) \\
 V_{12} = & (A_1 + Z_{a1} Q_1) Q_6 + (A_2 + Z_{a2} Q_1) Q_9 + B_{11} Q_4 Q_5 + B_{22} Q_7 Q_8 + \\
 & + B_{12} (Q_4 Q_8 + Q_5 Q_7) - (Z_{e1} Q_6 + Z_{e2} Q_9) Q_3 \\
 V_{13} = & (A_1 + Z_{a1} Q_1) Q_5 + (A_2 + Z_{a2} Q_1) Q_8 + B_{11} Q_4 Q_6 + B_{22} Q_7 Q_9 + \\
 & + B_{12} (Q_4 Q_9 + Q_6 Q_7) + \frac{1}{2} (Z_{e1} Q_5 + Z_{e2} Q_8) (Q_3 + \sqrt{3}Q_2) \\
 V_{22} = & \frac{1}{2} (A_e + Z_{ae} Q_1) (Q_3 + \sqrt{3}Q_2) + B_{ee} (Q_2^2 - Q_3^2 + 2\sqrt{3}Q_2 Q_3) + \\
 & + \sqrt{\frac{1}{6}} B_{11} (Q_4^2 - 2Q_5^2 + Q_6^2) + \sqrt{\frac{1}{6}} B_{22} (Q_7^2 - 2Q_8^2 + Q_9^2) + \\
 & + 2\sqrt{\frac{1}{6}} B_{12} (Q_4 Q_7 - 2Q_5 Q_8 + Q_6 Q_9) \\
 V_{23} = & (A_1 + Z_{a1} Q_1) Q_4 + (A_2 + Z_{a2} Q_1) Q_7 + B_{11} Q_5 Q_6 + B_{22} Q_8 Q_9 + \\
 & + B_{12} (Q_5 Q_9 + Q_6 Q_8) + \frac{1}{2} (Z_{e1} Q_4 + Z_{e2} Q_7) (Q_3 - \sqrt{3}Q_2) \\
 V_{33} = & -V_{11} - V_{22}. \tag{2}
 \end{aligned}$$

$K_a, K_{aa}, K_{ee}, K_{11}, K_{22}, K_{12}, T_{aaa}, T_{aee}, T_{a11}, T_{a22}, T_{a12}, T_{eee}, T_{e11}, T_{e22}, T_{e12}, T_{111}, T_{222}, T_{112}$  and  $T_{122}$  are vibration constants;  $A_e, A_1, A_2, B_{ee}, B_{11}, B_{22}, B_{12}, Z_{ae}, Z_{a1}, Z_{a2}, Z_{e1}$  and  $Z_{e2}$  are vibronic constants;  $W_0$  is the system energy in the reference geometrical configuration of an ideal tetrahedron.

If an ideal tetrahedron of minimal energy is chosen as the reference system then  $K_a$  is identically equal to zero because

$$\left(\frac{\partial W}{\partial Q_1}\right)_{\text{ref}} = 0. \quad (3)$$

TABLE I  
The systems under study

System	Electron configuration	Multiplicity	Electron term
$\text{CuX}_4^{2-}$	$e^4 t_2^5$	2	$T_2$
$\text{NiX}_4^{2-}$	$e^4 t_2^4$	1	$A_1 + E + T_2$
		3	$T_1$
$\text{CoX}_4^{2-}$	$e^4 t_2^3$	2	$E + T_1 + T_2$
$\text{FeX}_4^{2-}$	$e^4 t_2^2$	1	$A_1 + E + T_2$
$\text{MnX}_4^{2-}$	$e^4 t_2^1$	2	$T_2$

TABLE II  
Symmetrized normal coordinates for tetrahedral  $\text{MX}_4$  systems of  $T_d$  symmetry group ( $r_i$  is the bond length between the central atom, M, and the  $i$ -th ligand,  $L_i$ ;  $r_0$  is the reference M-L bond length;  $\alpha_{ij}$  is the angle of M- $L_i$  and M- $L_j$  bonds)

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

For the known analytic APS form the values of potential (vibration and vibronic) constants may be evaluated from the points of numerical map,  $W_i^c$ , obtained by quantum-chemical calculation of the total energy of the system for fixed nuclear coordinates. For this purpose a non-linear regression method is to be used with the optimization of the functional in the form of weighted sum of deviations squares

$$F = \sum_i (W_i^c - W_i^a)^2 w_i^2 = \min, \quad (4)$$

where  $W_i^a$  are approximate energies calculated for a trial set of potential constants according to Eq. (1) and  $w_i$  are metric statistical weights analogously as in our previous papers<sup>3,4</sup>.

TABLE III

Calculated values of potential constants for  $^2[\text{CuX}_4]^{2-}$  systems. The  $R$ -factor is defined as  $R = [\sum_i (W_i^a - W_i^c)^2 / \sum_i (W_i^c)^2]^{1/2}$

Characteristics	X		
	F	Cl	Br
Number of points	71	60	51
$r_0$ [ $10^{-10}$ m]	1.87333	2.16228	2.31948
$A_e$ [eV rad $^{-1}$ ]	-0.119	-0.13	-0.6763
$A_1$ [ $10^{10}$ eV m $^{-1}$ ]	0.710	-0.088	-0.248
$A_2$ [eV rad $^{-1}$ ]	0.243	-0.139	-0.04
$B_{ee}$ [eV rad $^{-2}$ ]	-0.26	0.22	1.48
$B_{11}$ [ $10^{20}$ eV m $^{-2}$ ]	0.4	0.46	1.7
$B_{22}$ [eV rad $^{-2}$ ]	-0.52	0.015	0.4
$B_{12}$ [ $10^{10}$ eV m $^{-1}$ rad $^{-1}$ ]	—	0.03	—
$Z_{ae}$ [ $10^{10}$ eV m $^{-1}$ rad $^{-1}$ ]	—	0.5	—
$Z_{a1}$ [ $10^{20}$ eV m $^{-2}$ ]	—	-0.24	—
$Z_{a2}$ [ $10^{10}$ eV m $^{-1}$ rad $^{-1}$ ]	—	-0.03	—
$Z_{e1}$ [ $10^{10}$ eV m $^{-1}$ rad $^{-1}$ ]	—	41.	—
$Z_{e2}$ [eV rad $^{-2}$ ]	—	-42.	—
$K_{aa}$ [ $10^{20}$ eV m $^{-2}$ ]	61.62	49.10	61.3
$K_{ee}$ [eV rad $^{-2}$ ]	5.01	8.3	323.2
$K_{11}$ [ $10^{20}$ eV m $^{-2}$ ]	53.6	37.9	52.1
$K_{22}$ [eV rad $^{-2}$ ]	2.33	1.448	13.7
$K_{12}$ [ $10^{10}$ eV m $^{-1}$ rad $^{-1}$ ]	9.67	5.8	0.8708
Correlation coefficient	0.9951	0.9994	0.9942
$R$ -factor	0.0743	0.0314	0.0959

## RESULTS AND DISCUSSION

The values of potential constants ( $K_{aa}$ ,  $K_{ee}$ ,  $K_{11}$ ,  $K_{22}$ ,  $K_{12}$ ,  $T_{aaa}$ ,  $T_{acc}$ ,  $T_{a11}$ ,  $T_{a22}$ ,  $T_{a12}$ ,  $T_{ccc}$ ,  $T_{c11}$ ,  $T_{c22}$ ,  $T_{e12}$ ,  $T_{111}$ ,  $T_{222}$ ,  $T_{112}$ ,  $T_{122}$ ,  $A_e$ ,  $A_1$ ,  $A_2$ ,  $B_{ee}$ ,  $B_{11}$ ,  $B_{22}$ ,  $B_{12}$ ,  $Z_{ae}$ ,  $Z_{a1}$ ,  $Z_{a2}$ ,  $Z_{e1}$  a  $Z_{e2}$ ) were calculated for 18  $[MX_4]^{2-}$  complexes ( $X = F, Cl, Br$ ) shown in Table I. The total energy values of individual APS points were obtained by the CNDO/2 method in the UHF version for transition metals<sup>6,7,9</sup> with energy cut-off of  $10^{-5}$  eV. An ideal tetrahedron of minimal energy (i.e.  $K_a = 0$ ) was chosen for the reference system. From the known values of potential constants the coordinates of the APS minima and Jahn–Teller stabilisation energies,  $E_{JT}$ , were calculated. The reliability of results was tested by statistical characteristics such as standard deviations of individual constants, correlation coefficient and discrepancy  $R$ -factor.

Because of some reasons discussed below an attempt to obtain the values of all potential constants of Eq. (1) was not successful, and moreover, rational values of constants could not be obtained for some complexes at all (e.g. negative  $K_{aa}$  and  $K_{ee}$  values, extremally high  $T_{ijk}$  values). Tables III and IV summarize the calculated

TABLE IV

Calculated values of potential constants for  $NiX_4^{2-}$  and  $MnCl_4^{2-}$  systems. The  $R$ -factor is defined as  $R = [\sum_i (W_i^a - W_i^c)^2 / \sum_i (W_i^c)^2]^{1/2}$

Characteristics	System			
	$NiBr_4^{2-}$	$NiF_4^{2-}$	$NiBr_4^{2-}$	$MnCl_4^{2-}$
Multiplicity	1	3	3	2
Number of points	29	29	26	44
$r_0$ [ $10^{-10}$ m]	2.3383	1.8294	2.3383	2.3466
$A_e$ [eV rad <sup>-1</sup> ]	-0.587	0.331	0.0031	-0.298
$A_1$ [ $10^{10}$ eV m <sup>-1</sup> ]	-0.183	0.615	0.0308	-0.125
$A_2$ [eV rad <sup>-1</sup> ]	-0.300	0.208	0.116	0.155
$B_{ee}$ [eV rad <sup>-2</sup> ]	10.4	3.01	-0.0072	-0.06
$B_{11}$ [ $10^{20}$ eV m <sup>-2</sup> ]	0.41	5.03	0.15	-0.46
$B_{22}$ [eV rad <sup>-2</sup> ]	-0.049	0.04	0.19	0.66
$K_{aa}$ [ $10^{20}$ eV m <sup>-2</sup> ]	53.09	54.86	40.12	27.97
$K_{ee}$ [eV rad <sup>-2</sup> ]	27.41	8.55	18.19	11.52
$K_{11}$ [ $10^{20}$ eV m <sup>-2</sup> ]	41.08	41.04	40.91	18.1
$K_{22}$ [eV rad <sup>-2</sup> ]	3.11	1.00	2.30	0.58
$K_{12}$ [ $10^{10}$ eV m <sup>-1</sup> rad <sup>-1</sup> ]	8.43	6.47	4.856	3.8
Correlation coefficient	0.9999	0.9993	0.9995	0.9969
$R$ -factor	0.0125	0.0313	0.0236	0.066

values of potential constants, given to the full number of valid digits (the order of the last digit is equal to the order of the standard deviation). In a similar way, the characteristics of APS extremal points are presented in Tables V a VI.

TABLE V  
Calculated extreme coordinates of  $^2[\text{CuX}_4]^{2-}$  systems

Characteristics	X		
	F	Cl	Br
Tetragonal extrema:			
$Q_1 [10^{-10} \text{ m}]$	0.000	-0.0002	0.000
$Q_3 [\text{rad}]$	-0.286	-0.0161	-0.00225
$E_{\text{JT}} [10^{-13} \text{ eV}]$	-1.58	-0.97	-0.70
$r [10^{-10} \text{ m}]$	1.87333	2.1623	2.3195
$\Delta\alpha_{12} = \Delta\alpha_{34} [\text{deg}]$	0.760	0.427	0.059
$\Delta\alpha_{13} = \Delta\alpha_{24} [\text{deg}]$	-0.758	-0.426	-0.059
$\Delta\alpha_{14} = \Delta\alpha_{23} [\text{deg}]$	0.119	0.000	0.000
Trigonal extrema I.:			
$Q_1 [10^{-10} \text{ m}]$	0.000	0.000	0.000
$Q_4 = Q_5 = Q_6 [10^{-10} \text{ m}]$	-0.0990	0.0375	0.0001
$E_{\text{JT}} [10^{-3} \text{ eV}]$	-6.21	-0.13	-0.75
$r_1 = r_2 = r_3 [10^{-10} \text{ m}]$	1.8690	2.16304	2.3210
$r_4 [10^{-10} \text{ m}]$	1.8864	2.16000	2.3149
Trigonal extrema II.:			
$Q_1 [10^{-10} \text{ m}]$	0.000	0.000	0.000
$Q_7 = Q_8 = Q_9 [\text{rad}]$	-0.0990	0.0375	0.0001
$E_{\text{JT}} [10^{-3} \text{ eV}]$	-24.1	-5.22	-0.0
$r [10^{-10} \text{ m}]$	1.87333	2.1623	2.31948
$\Delta\alpha_{12} = \Delta\alpha_{13} = \Delta\alpha_{23} [\text{deg}]$	0.384	-1.542	0.004
$\Delta\alpha_{14} = \Delta\alpha_{22} = \Delta\alpha_{34} [\text{deg}]$	-4.18	1.501	-0.004
Trigonal extrema III.:			
$Q_1 [10^{-10} \text{ m}]$	—	0.001	—
$Q_4 = Q_5 = Q_6 [10^{-10} \text{ m}]$	—	-0.00650	—
$Q_7 = Q_8 = Q_9 [\text{rad}]$	—	0.05290	—
$E_{\text{JT}} [10^{-3} \text{ eV}]$	—	-6.8	—
$r_1 = r_2 = r_3 [10^{-10} \text{ m}]$	—	2.1591	—
$r_4 [10^{-10} \text{ m}]$	—	2.1721	—
$\Delta\alpha_{12} = \Delta\alpha_{13} = \Delta\alpha_{23} [\text{deg}]$	—	-2.185	—
$\Delta\alpha_{14} = \Delta\alpha_{24} = \Delta\alpha_{34} [\text{deg}]$	—	2.105	—

TABLE V  
(Continued)

Characteristics	X		
	F	Cl	Br
Mixed-type extrema I.:			
$Q_1$ [ $10^{-10}$ m]	0.000	—	0.000
$Q_3$ [rad]	0.0113	—	0.00105
$Q_6$ [ $10^{-10}$ m]	0.218	—	0.004
$E_{JT}$ [ $10^{-3}$ eV]	—5.01	—	—0.75
$r_1 = r_4$ [ $10^{-10}$ m]	1.867	—	2.3172
$r_2 = r$ [ $10^{-10}$ m]	1.880	—	2.3 18
$\Delta\alpha_{12} = \Delta\alpha_{34}$ [deg]	—0.323	—	—0.030
$\Delta\alpha_{13} = \Delta\alpha_{24}$ [deg]	0.324	—	0.030
$\Delta\alpha_{14} = \Delta\alpha_{23}$ [deg]	0.0002	—	0.000
Mixed-type extrema II.:			
$Q_1$ [ $10^{-10}$ m]	0.000	—	—
$Q_3$ [rad]	0.0113	—	—
$Q_9$ [rad]	0.128	—	—
$E_{JT}$ [ $10^{-3}$ eV]	—15.8	—	—
$r$ [ $10^{-10}$ m]	1.8733	—	—
$\Delta\alpha_{12} = \Delta\alpha_{34}$ [deg]	—0.406	—	—
$\Delta\alpha_{13} = \Delta\alpha_{24}$ [deg]	0.241	—	—
$\Delta\alpha_{14}$ [deg]	5.08	—	—
$\Delta\alpha_{23}$ [deg]	—5.25	—	—

Despite a little number of systems with successfully enumerated potential constants values some trends may be registered similarly as for octahedral systems<sup>3,4,10,11</sup>: (i) The value of  $K_{aa}$  vibration constant increases with the proton number of the central atom. (ii) Similarly to octahedral systems, the calculated distortions are much lower than for real solid state systems. This is caused by the overestimation of the vibration constants and by the underestimation of the linear vibronic ones in our model. (iii) The changes of M—X bond lengths are very small and they achieve similar values as for octahedral complexes with triple electron degeneracy ( $10^{-13}$  to  $10^{-12}$  m). (iv) The changes of angular coordinates achieve higher values than for the systems with double electron degeneracy<sup>12</sup> similarly to octahedral complexes. (v) The values of Jahn–Teller stabilization energies,  $E_{JT}$ , are comparable with  $E_{JT}$  values of octahedral systems with double electron degeneracy; they are higher than those for triple degenerate octahedral and double degenerate tetrahedral systems.

TABLE VI  
Calculated extreme coordinates of  $\text{NiX}_4^{2-}$  and  $\text{MnCl}_4^{2-}$  systems

Characteristics	System			
	$\text{NiBr}_4^{2-}$	$\text{NiF}_4^{2-}$	$\text{NiBr}_4^{2-}$	$\text{MnCl}_4^{2-}$
Multiplicity	1	3	3	2
Tetragonal extrema:				
$Q_1 [10^{-10} \text{ m}]$	0.000	0.000	0.000	0.000
$Q_3 [\text{rad}]$	-0.0131	0.0227	0.00022	-0.0261
$E_{\text{JT}} [10^{-3} \text{ eV}]$	-3.6	-3.8	-0.0	-3.9
$r [10^{-10} \text{ m}]$	2.3383	1.8924	2.3383	2.3466
$\Delta\alpha_{12} = \Delta\alpha_{34} [\text{deg}]$	0.349	-0.650	-0.0063	0.750
$\Delta\alpha_{13} = \Delta\alpha_{24} [\text{deg}]$	-0.349	0.652	0.0063	-0.748
$\Delta\alpha_{14} = \Delta\alpha_{23} [\text{deg}]$	0.000	0.871	0.000	0.115
Trigonal extrema I.:				
$Q_1 [10^{-10} \text{ m}]$	0.000	0.000	0.000	0.000
$Q_4 = Q_5 = Q_6 [10^{-10} \text{ m}]$	0.00293	-0.00859	0.00050	0.00476
$E_{\text{JT}} [10^{-3} \text{ eV}]$	-0.54	-5.28	-0.02	-0.60
$r_1 = r_2 = r_3 [10^{-10} \text{ m}]$	2.3398	1.8881	2.3380	2.3490
$r_4 [10^{-10} \text{ m}]$	2.3339	1.9053	2.3390	2.3395
Trigonal extrema II.:				
$Q_1 [10^{-10} \text{ m}]$	0.000	0.000	—	—
$Q_7 = Q_8 = Q_9 [\text{rad}]$	0.0657	0.132	—	—
$E_{\text{JT}} [10^{-3} \text{ eV}]$	-19.7	-27.4	—	—
$r [10^{-10} \text{ m}]$	2.3383	1.8924	—	—
$\Delta\alpha_{12} = \Delta\alpha_{13} = \Delta\alpha_{23} [\text{deg}]$	-2.72	-5.65	—	—
$\Delta\alpha_{14} = \Delta\alpha_{24} = \Delta\alpha_{34} [\text{deg}]$	2.60	5.01	—	—
Trigonal extrema III.:				
$Q_1 [10^{-10} \text{ m}]$	0.000	—	—	—
$Q_4 = Q_5 = Q_6 [10^{-10} \text{ m}]$	-0.0236	—	—	—
$Q_7 = Q_8 = Q_9 [\text{rad}]$	0.1311	—	—	—
$E_{\text{JT}} [10^{-3} \text{ eV}]$	-35.0	—	—	—
$r_1 = r_2 = r_3 [10^{-10} \text{ m}]$	2.3265	—	—	—
$r_4 [10^{-10} \text{ m}]$	2.3737	—	—	—
$\Delta\alpha_{12} = \Delta\alpha_{13} = \Delta\alpha_{23} [\text{deg}]$	-5.53	—	—	—
$\Delta\alpha_{14} = \Delta\alpha_{24} = \Delta\alpha_{34} [\text{deg}]$	5.09	—	—	—



TABLE VI  
(Continued)

Characteristics	System			
	NiBr <sub>4</sub> <sup>2-</sup>	NiF <sub>4</sub> <sup>2-</sup>	NiBr <sub>4</sub> <sup>2-</sup>	MnCl <sub>4</sub> <sup>2-</sup>
Mixed-type extrema I.:				
$Q_1$ [ $10^{-10}$ m]	0.00	0.000	0.000	0.000
$Q_3$ [rad]	0.0173	-0.0299	-0.00011	0.0129
$Q_6$ [ $10^{-10}$ m]	0.004	0.014	0.00075	0.007
$E_{JT}$ [ $10^{-3}$ eV]	-2.94	-6.7	-0.01	-1.4
$r_1 = r_4$ [ $10^{-10}$ m]	2.3361	1.8856	2.3379	2.3431
$r_2 = r_3$ [ $10^{-10}$ m]	2.3405	1.8992	2.3387	2.3501
$\Delta\alpha_{12} = \Delta\alpha_{34}$ [deg]	-0.494	0.857	0.315	-0.368
$\Delta\alpha_{13} = \Delta\alpha_{24}$ [deg]	0.495	-0.854	-0.315	0.369
$\Delta\alpha_{14} = \Delta\alpha_{23}$ [deg]	0.000	0.0015	0.000	0.0003
Mixed-type extrema II.:				
$Q_1$ [ $10^{-10}$ m]	0.000	0.000	0.000	0.000
$Q_3$ [rad]	0.0172	-0.0299	-0.00011	0.0129
$Q_9$ [rad]	0.098	0.201	0.04725	0.139
$E_{JT}$ [ $10^{-3}$ eV]	-17.2	-23.4	-2.7	-11.7
$r$ [ $10^{-10}$ m]	2.3383	1.8924	2.3383	2.3466
$\Delta\alpha_{12} = \Delta\alpha_{34}$ [deg]	-0.542	0.652	-0.0082	-0.465
$\Delta\alpha_{13} = \Delta\alpha_{24}$ [deg]	0.447	-1.059	-0.0145	0.272
$\Delta\alpha_{14}$ [deg]	3.91	7.96	1.90	5.52
$\Delta\alpha_{23}$ [deg]	-4.01	-8.36	-1.93	-0.571
Mixed-type extrema III.:				
$Q_1$ [ $10^{-10}$ m]	0.000	—	0.000	—
$Q_3$ [rad]	0.0173	—	-0.00011	—
$Q_6$ [ $10^{-10}$ m]	-0.035	—	-0.0063	—
$Q_9$ [rad]	0.194	—	0.060	—
$E_{JT}$ [ $10^{-3}$ eV]	-28.4	—	-3.4	—
$r_1 = r_4$ [ $10^{-10}$ m]	2.3558	—	2.3415	—
$r_2 = r_3$ [ $10^{-10}$ m]	2.3208	—	2.3351	—
$\Delta\alpha_{12} = \Delta\alpha_{34}$ [deg]	-0.684	—	-0.015	—
$\Delta\alpha_{13} = \Delta\alpha_{24}$ [deg]	0.305	—	-0.021	—
$\Delta\alpha_{14}$ [deg]	7.67	—	2.40	—
$\Delta\alpha_{23}$ [deg]	-8.05	—	-2.44	—

Half the studied systems (Table I) cannot be described by a single electronic state and thus the formula (1) represents too rough approximation of their APS, as confined by our study results. However it must be realised that the Jahn–Teller theorem relates not to the molecular orbital degeneracy but to the orbital degeneracy of electronic state.

The values of all constants in formula (1) were not successfully enumerated; this is implied probably by the fact that too many parameters are optimized by the non-linear regression. Simultaneously, this lowers the reliability of the results obtained. Therefore the starting parameters and the statistic weighting methods were varied in order to increase the reliability of results.

The remaining failures may be ascribed to the incorrect choice of APS points, problematic convergency of the SCF procedure or to the parametrisation of the CNDO/2 method used. As a consequence, an overlap of APS corresponding to different electronic states with the same multiplicity may arise. Therefore some numerical map points do not accommodate to Eq. (1).

Ascertaining the APS extremal points we concentrated upon the extrema of  $D_{2d}$  (tetragonal, realised by the change of  $e$  type coordinates),  $C_{3v}$  (trigonal, realised by the change of  $t_2$  type coordinates) and their combinations (mixed type extrema) symmetries. Tables V a VI present only single geometries of every extrema type apiece, the remaining geometries may be obtained by symmetry operations of  $T_d$  symmetry group. These extrema types were forecasted for the interactions including quadratic vibronic constants. The potential constants values determine whether the individual extrema types really come true or not<sup>13</sup>.

Finally it is necessary to mention that the situation in real systems is more complicated. The magnitude and the type of tetrahedron distortions are influenced also by spin-orbit interaction and by solid state effects that were not covered by this paper. The quantum-chemical method used has also its quantitative limitations but it grants the correct trends of the quantities considered in our paper.

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