

Vibronic constants for octahedral complexes with triple degenerate electron terms

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$\mathcal{T}_{ig} - (a_{1g} + e_g)$ vibronic coupling ($i = 1, 2$) in octahedral systems is analyzed. The necessary potential constants of analytic formula (including both quadratic vibronic term and anharmonicity of normal vibrations) are evaluated from the numerical maps of the adiabatic potential surfaces by applying a linear regression analysis. Numerical values are obtained for 29 hexahalo complexes using the CNDO—UHF method. Some trends in characteristics of these Jahn—Teller active systems are found.

Анализируется $\mathcal{T}_{ig} - (a_{1g} + e_g)$ взаимодействие колебаний ($i = 1, 2$) в октаэдрических системах. Необходимые константы потенциалов из аналитической формулы (включающей как квадратичный колебательный терм, так и ангармоничность нормальных колебаний) вычислены исходя из числовых карт адиабатических поверхностей потенциальной энергии с применением линейного регрессионного анализа. Числовые значения получены для 29 гексагалоккомплексов с помощью метода CNDO—UHF. Обнаружены некоторые закономерности в характеристиках этих Ян—Теллеровских активных систем.

The Jahn—Teller effect plays an important role in various areas of physics and chemistry. It is connected with the existence of electron degeneracy as a consequence of the electron-vibration (vibronic) interactions. The generally accepted formulation of the Jahn—Teller theorem [1] consists of the assertion that a nonlinear nuclear configuration in the degenerate electron state is energetically unstable. This theorem implies the existence of, at least, one stable nuclear configuration in which the electron degeneracy is removed so that the system relaxes to an energetically more advantageous nondegenerate state. The stable configurations of nuclei correspond to the minima of the adiabatic potential surface (APS).

The theory of vibronic coupling is able to predict an analytic form of the APS in the presence of electron degeneracy. The usual procedure is to consider the

APS in a parametric form where some constants, specifying its shape, occur. They may be obtained from experimental data. Another approach lies in the direct quantum-chemical calculations of the total molecular energy for fixed positions of nuclei thus yielding a continuous parametric function of nuclear configurations [2]. In our previous paper [3] the analytic form of the APS was derived for a three-mode $\mathcal{T}_{ij} - (a_{1g} + e_g + t_{2g})$ coupling scheme ($i = 1, 2$; $j = u, g$). The vibronic coupling constants as well as the quadratic and cubic force constants have been calculated for some hexahalo complexes by a purely theoretical and nonempirical way. They resulted from a nonlinear regression analysis applied to a numerical map of the APS calculated by the CNDO—UHF version of the MO—LCAO—SCF method. As the nonlinear regression is very time-consuming method, some restrictions are needed. Moreover, the obtained results may depend on starting parameters and we usually cannot be sure about their correctness.

Method

The octahedral ML_6 system has 15 normal modes of vibration belonging to the a_{1g} (coordinate Q_1), e_g (Q_2 and Q_3), t_{2g} (Q_4, Q_5, Q_6), t_{2u} , and two sets of t_{1u} irreducible representations. For a symmetrized direct product of t -type irreducible representations of wave functions ($t = \mathcal{T}_{1g}, \mathcal{T}_{2g}, \mathcal{T}_{1u}$ or $\mathcal{T}_{2u}$) the following relation holds

$$[t \cdot t] = a_{1g} + e_g + t_{2g} \quad (1)$$

Consequently, only the coordinates Q_1 — Q_6 are vibronically active in the linear coupling. In our previous paper [3] the following analytic form of the APS was derived

$$\begin{aligned} W(Q_1, Q_2, Q_3, Q_4, Q_5, Q_6) = & E^\circ + K_a Q_1 + \frac{1}{2} K_{aa} Q_1^2 + \frac{1}{2} K_{ee} (Q_2^2 + Q_3^2) + \\ & + \frac{1}{2} K_{tt} (Q_4^2 + Q_5^2 + Q_6^2) + T_{aaa} Q_1^3 + T_{aee} Q_1 (Q_2^2 + Q_3^2) + \\ & + T_{att} Q_1 (Q_4^2 + Q_5^2 + Q_6^2) + T_{eee} Q_3 (3Q_2^2 - Q_3^2) + T_{ett} Q_4 Q_5 Q_6 + \\ & + T_{eet} [Q_4^2 (Q_3 - \sqrt{3}Q_2) + Q_5^2 (Q_3 + \sqrt{3}Q_2) - 2Q_6^2 Q_3] + \varepsilon_i \end{aligned} \quad (2)$$

where E^0 is the total energy of system for reference nuclear configuration [Q^0] which corresponds to unperturbed octahedral geometry; K_a is the linear force constant vanishing for the optimal reference geometry; K_{aa} , $K_{\ell\ell}$, and $K_{\ell\ell\ell}$ are the harmonic force constants; T_{aaa} , $T_{a\ell\ell}$, $T_{\ell\ell\ell}$, $T_{\ell\ell}$, $T_{\ell\ell\ell}$, and $T_{\ell\ell\ell}$ are the anharmonicity constants; ε_i is the vibronic correction term which may be obtained as the lowest eigenvalue of the symmetric matrix $\mathbf{V}$ defined by the following elements

$$\begin{aligned}
 V_{11} &= \frac{1}{2}A_{\ell}(Q_3 - \sqrt{3}Q_2) + \frac{1}{2}B_{\ell\ell}(Q_2^2 - Q_3^2 - 2\sqrt{3}Q_2Q_3) + \\
 &\quad + \frac{1}{2}Z_{a\ell}Q_1(Q_3 - \sqrt{3}Q_2) + \frac{1}{\sqrt{6}}B_{\ell\ell\ell}(-2Q_4^2 + Q_5^2 + Q_6^2) \\
 V_{12} &= V_{21} = A_{\ell}Q_6 - Z_{\ell\ell}Q_3Q_6 + Z_{a\ell}Q_1Q_6 + B_{\ell\ell}Q_4Q_5 \\
 V_{13} &= V_{31} = A_{\ell}Q_5 + \frac{1}{2}Z_{\ell\ell}Q_5(Q_3 + \sqrt{3}Q_2) + Z_{a\ell}Q_1Q_5 + B_{\ell\ell}Q_4Q_6 \\
 V_{22} &= \frac{1}{2}A_{\ell}(Q_3 + \sqrt{3}Q_2) + \frac{1}{2}B_{\ell\ell}(Q_2^2 - Q_3^2 + 2\sqrt{3}Q_2Q_3) + \\
 &\quad + \frac{1}{2}Z_{a\ell}Q_1(Q_3 + \sqrt{3}Q_2) + \frac{1}{\sqrt{6}}B_{\ell\ell\ell}(Q_4^2 - 2Q_5^2 + Q_6^2) \\
 V_{23} &= V_{32} = A_{\ell}Q_4 + \frac{1}{2}Z_{\ell\ell}Q_4(Q_3 - \sqrt{3}Q_2) + Z_{a\ell}Q_1Q_4 + B_{\ell\ell}Q_5Q_6 \\
 V_{33} &= -V_{11} - V_{22}
 \end{aligned} \tag{3}$$

where A_{ℓ} and A_{ℓ} are the linear vibronic constants; $B_{a\ell}$, $B_{\ell\ell}$, $Z_{a\ell}$, $Z_{a\ell}$, and $Z_{\ell\ell}$ are the quadratic vibronic constants. For the sake of simplicity we may restrict to the deformations of the D_{4h} symmetry only. These ones are fully described by

Table 1

Some characteristics of the studied systems

System	Electron configuration	Electron term
CrX_6^{4-} , MnX_6^{3-}	t_{2g}^4	${}^1(\mathcal{A}_1 + \mathcal{E}_g + \mathcal{T}_{2g})$
MnX_6^{4-} , FeX_6^{3-}	t_{2g}^4	${}^3\mathcal{T}_{1g}$
FeX_6^{4-} , CoX_6^{3-}	t_{2g}^5	${}^2\mathcal{T}_{2g}$
CoX_6^{4-} , NiX_6^{3-}	$t_{2g}^4 e_g^2$	${}^5\mathcal{T}_{2g}$
	$t_{2g}^5 e_g^2$	${}^4\mathcal{T}_{1g}$

Table 2

The calculated values of potential constants of the 1st row transition metal hexahalo complexes with triple degenerate electron terms

System	$A_{..}$ $10^{10} \text{ eV m}^{-1}$	$B_{..}$ $10^{20} \text{ eV m}^{-2}$	$Z_{..}$ $10^{20} \text{ eV m}^{-2}$	$K_{..}$ $10^{10} \text{ eV m}^{-1}$	$K_{...}$ $10^{20} \text{ eV m}^{-2}$
$^1\text{CrF}_6^{4-}$	-0.07233	-0.0556	-0.1540	0.001250	16.0363
$^1\text{CrCl}_6^{4-}$	-0.07176	-0.1033	-0.1497	-0.00313	14.9068
$^1\text{CrBr}_6^{4-}$	-0.10598	-0.0567	-0.1571	-0.000675	18.8566
$^1\text{MnF}_6^{3-}$	-0.40515	-0.2690	-0.893	0.0113	29.115
$^1\text{MnCl}_6^{3-}$	-0.26454	-0.033	-0.102	0.01188	26.110
$^1\text{MnBr}_6^{3-}$	-0.27908	-0.2539	-0.2513	0.0170	30.3507
$^3\text{CrF}_6^{4-}$	-0.03211	-1.997	-0.003	0.00013	15.885
$^3\text{CrCl}_6^{4-}$	-0.02936	-1.965	-0.010	0.00165	14.881
$^3\text{CrBr}_6^{4-}$	-0.04941	-3.120	0.216	0.001582	18.707
$^3\text{MnF}_6^{3-}$	-0.1914	-8.81	0.67	0.0230	29.00
$^3\text{MnCl}_6^{3-}$	-0.1203	-7.52	0.24	0.0879	25.570
$^3\text{MnBr}_6^{3-}$	-0.1238	-8.18	-0.76	0.0128	30.255
$^2\text{MnF}_6^{4-}$	-0.0350	-2.33	3.02	-0.0222	17.95
$^2\text{MnCl}_6^{4-}$	-0.04768	-1.132	0.611	0.01693	20.813
$^2\text{MnBr}_6^{4-}$	-0.07358	-1.199	0.249	0.00320	25.040
$^2\text{FeF}_6^{3-}$	-0.21168	-0.4467	-0.5663	0.00923	32.9818
$^2\text{FeCl}_6^{3-}$	-0.14987	-0.374	-0.295	0.10352	30.0153
$^2\text{FeBr}_6^{3-}$	-0.13509	-0.1320	-0.110	0.00250	34.7628
$^5\text{FeF}_6^{4-}$	-0.04412	-3.040	-0.26	0.00574	26.627
$^5\text{FeCl}_6^{4-}$	-0.04532	-2.539	-0.309	-0.01643	24.453
$^5\text{FeBr}_6^{4-}$	-0.05675	-4.010	-0.213	-0.00164	28.644
$^5\text{CoF}_6^{3-}$	-0.3479	-14.82	0.66	0.0284	43.40
$^5\text{CoCl}_6^{3-}$	-0.2633	-14.86	-4.55	-0.0117	34.489
$^5\text{CoBr}_6^{3-}$	-0.1302	-9.90	-2.56	-0.0086	40.33
$^4\text{CoF}_6^{4-}$	-0.0929	1.62	-4.35	-0.0203	33.666
$^4\text{CoCl}_6^{4-}$	-0.06501	-0.078	-0.024	-0.01177	30.047
$^4\text{CoBr}_6^{4-}$	-0.0792	0.77	2.0	0.0154	33.92
$^4\text{NiF}_6^{3-}$	-0.30749	-0.334	-0.565	0.01562	49.4560
$^4\text{NiCl}_6^{3-}$	-0.15720	-0.432	0.295	0.01266	41.551

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

axial (r_a) and equatorial (r_e) metal—ligand distances. So we have

$$Q_1 = \sqrt{\frac{2}{3}}(r_a + 2r_e - 3r^0)$$

$$Q_2 = 0$$

$$Q_3 = \frac{2}{\sqrt{3}}(r_a - r_e)$$

Table 2 (Continued)

$K_{\epsilon\epsilon}$ $10^{20} \text{ eV m}^{-2}$	T_{aaa} $10^{30} \text{ eV m}^{-3}$	T_{aee} $10^{30} \text{ eV m}^{-3}$	T_{eee} $10^{30} \text{ eV m}^{-3}$	Correlation coefficient	R-factor
10.5245	-3.585	-9.517	-2.147	1.000000	0.00049
9.0491	-3.2892	-8.747	-2.469	1.000000	0.00066
10.9532	-4.011	-9.679	-1.722	1.000000	0.00041
20.232	-6.547	-18.20	-3.41	0.999999	0.00097
17.729	-6.241	-14.85	-2.00	1.000000	0.00044
19.4792	-7.265	-15.78	-4.41	1.000000	0.00047
9.353	-1.48	-7.4	-28.02	0.999926	0.00883
7.742	-2.04	-10.9	-28.28	0.999884	0.01066
9.280	-1.94	-2.0	-44.3	0.999882	0.01152
15.26	-6.3	0.4	-79.0	0.999695	0.01983
13.528	-0.3	-7.9	-100.9	0.999427	0.02357
14.637	-7.34	-39.3	-115.6	0.999944	0.00973
14.07	46.6	27	-36.3	0.997517	0.10009
14.174	-5.119	-14.7	-16.4	0.999981	0.00564
16.645	-6.93	2.05	-16.96	0.999994	0.00271
24.0392	-7.422	-23.44	-10.42	0.999998	0.00160
21.069	-6.891	-20.01	-5.29	0.999999	0.00123
22.4145	-7.641	-18.77	-4.291	1.000000	0.00045
15.437	-6.88	-22.5	-34.06	0.999973	0.00660
13.774	-5.453	-19.3	-32.40	0.999994	0.00343
14.492	-2.34	-19.5	-59.6	0.999799	0.01547
27.66	6.7	102.1	135.8	0.999897	0.12349
21.050	4.35	-22.6	-195.8	0.999959	0.00806
17.58	6.5	-48.0	-124.5	0.999929	0.01103
25.70	-1.56	-126.8	42.2	0.999801	0.01797
20.567	-6.80	-7.1	8.9	0.999992	0.00349
23.05	-8.7	14.1	32.7	0.999954	0.00852
37.1262	-12.744	-31.89	-8.07	1.000000	0.00049
28.018	-9.872	-12.6	-12.42	0.999993	0.00321

$$Q_4 = Q_5 = Q_6 = 0 \quad (4)$$

and the APS becomes

$$\begin{aligned}
 W(Q_1, Q_3) = E^o + K_a Q_1 + \frac{1}{2} K_{aa} Q_1^2 + \frac{1}{2} K_{ee} Q_3^2 + T_{aaa} Q_1^3 + T_{aee} Q_1 Q_3^2 - \\
 - T_{eee} Q_3^3 + s(A_e + Z_{ae} Q_1) Q_3 + s B_{ee} Q_3^2
 \end{aligned} \quad (5)$$

where we may assign $s = 1$ for the elongated octahedron and $s = -1/2$ for the compressed one.

Table 3

The calculated characteristics of APS extreme points for hexahalo complexes of the 1st row transition metals with triple degenerate electron terms

System	r^o 10^{-12} m	Minimum				
		Q_1^e 10^{-12} m	Q_3^e 10^{-12} m	r_a^e 10^{-12} m	r_e^e 10^{-12} m	E_{JT} 10^{-3} eV
$^1\text{CrF}_6^{4-}$	234.60	-0.0116	-0.6829	235.384	234.201	0.25
$^1\text{CrCl}_6^{4-}$	262.320	0.0167	-0.7801	263.228	261.876	0.28
$^1\text{CrBr}_6^{4-}$	272.590	0.0003	-0.9620	273.701	272.035	0.51
$^1\text{MnF}_6^{3-}$	207.949	-0.075	-1.961	210.183	206.786	3.97
$^1\text{MnCl}_6^{3-}$	239.542	-0.039	-1.493	241.251	238.664	1.97
$^1\text{MnBr}_6^{3-}$	254.308	-0.0573	-1.409	255.911	253.471	1.96
$^3\text{CrF}_6^{4-}$	234.60	-0.0006	-0.244	234.882	234.459	0.04
$^3\text{CrCl}_6^{4-}$	262.335	-0.0108	-0.2563	262.627	262.183	0.04
$^3\text{CrBr}_6^{4-}$	272.590	0.0123	-0.3278	272.974	272.406	0.08
$^3\text{MnF}_6^{3-}$	207.955	-0.058	-0.065	208.630	207.578	0.58
$^3\text{MnCl}_6^{3-}$	239.668	-0.339	-0.438	240.035	239.277	0.41
$^3\text{MnBr}_6^{3-}$	254.306	-0.026	-0.051	254.77	254.04	0.26
$^2\text{MnF}_6^{4-}$	219.643	0.157	-0.214	219.954	219.583	0.05
$^2\text{MnCl}_6^{4-}$	249.397	-0.0722	-0.2895	249.702	249.200	0.07
$^2\text{MnBr}_6^{4-}$	262.472	-0.0090	-0.390	262.919	262.243	0.14
$^2\text{FeF}_6^{3-}$	204.355	-0.0375	-0.8585	205.331	203.844	0.91
$^2\text{FeCl}_6^{3-}$	235.702	-0.348	-0.691	236.358	235.161	0.52
$^2\text{FeBr}_6^{3-}$	251.035	-0.00716	-0.5977	251.722	250.687	0.40
$^5\text{FeF}_6^{4-}$	217.635	-0.0232	-0.207	217.865	217.506	0.05
$^5\text{FeCl}_6^{4-}$	245.821	0.0646	-0.243	246.127	245.707	0.06
$^5\text{FeBr}_6^{4-}$	259.742	0.0043	-0.257	260.041	259.595	0.07
$^5\text{CoF}_6^{3-}$	199.352	-0.0463	-0.634	200.065	198.967	1.09
$^5\text{CoCl}_6^{3-}$	230.798	-0.0290	1.063	229.559	231.400	0.82
$^5\text{CoBr}_6^{3-}$	247.505	-0.001	-0.361	247.922	247.296	0.23
$^4\text{CoF}_6^{4-}$	207.3676	0.0143	-0.402	207.838	207.141	0.19
$^4\text{CoCl}_6^{4-}$	237.759	0.0392	-0.312	238.136	237.595	0.10
$^4\text{CoBr}_6^{4-}$	253.4837	-0.0244	-0.360	253.889	253.266	0.14
$^4\text{NiF}_6^{3-}$	191.882	0.0266	-0.8178	192.777	191.361	1.26
$^4\text{NiCl}_6^{3-}$	224.901	-0.0257	-0.5478	225.523	224.574	0.43

r_a^e — extreme axial metal—ligand distance, r_e^e — extreme equatorial metal—ligand distance, r^o — optimum metal—ligand distance for ideal octahedron.

Having derived this analytic form of APS the values of potential constants may be evaluated from the points of numerical map $W_i^e(Q_1, Q_3)$, obtained by a quantum-chemical calculation of the total molecular energy for fixed nuclear coordinates. For this purpose the simple linear regression method may be used. The fitting is realized by the weighted least-squares method

$$F = \sum_i [W_i^e(Q_1, Q_3) - W_i^a(Q_1, Q_3)]^2 w_i^2 = \min \quad (6)$$

Table 3 (Continued)

Saddle point				
Q_1^c	Q_3^c	r_a^c	r_c^c	E_{JT}
10^{-12} m	10^{-12} m	10^{-12} m	10^{-12} m	10^{-3} eV
-0.0087	0.3447	234.198	234.795	0.06
-0.0072	0.0200	261.867	262.559	0.07
0.0028	0.4852	272.031	272.872	0.13
-0.0478	1.005	206.769	208.510	1.02
-0.0438	0.745	238.664	239.954	0.50
-0.0563	0.7219	253.451	254.702	0.51
-0.0006	0.213	234.354	234.723	0.02
-0.0107	0.245	262.047	262.472	0.02
0.0107	0.3715	272.165	272.809	0.05
-0.067	1.065	206.698	208.542	0.56
-0.339	0.724	238.694	239.948	0.39
-0.045	0.697	253.483	254.690	0.24
0.135	0.163	219.510	219.792	0.03
-0.078	0.179	249.158	249.469	0.03
-0.0117	0.236	262.194	262.604	0.04
-0.0238	0.4461	203.828	204.600	0.24
-0.3146	0.361	235.144	235.770	0.13
-0.00717	0.3026	250.683	251.207	0.10
-0.0222	0.175	217.423	217.727	0.02
0.0663	0.198	245.620	245.962	0.03
0.0052	0.259	259.445	259.894	0.04
-0.0333	1.019	198.162	199.927	0.96
-0.0715	-0.5577	231.427	230.460	0.72
0.0057	0.645	246.762	247.880	0.23
0.0504	0.168	207.194	207.485	0.04
0.0392	0.1590	237.591	237.867	0.03
-0.0405	0.1657	253.267	253.563	0.04
0.0303	0.4167	191.353	192.075	0.32
-0.0292	0.2836	224.562	225.053	0.11

where $W_i^a(Q_1, Q_3)$ are the approximate energies calculated for a trial set of potential constants from the analytic form of APS. The statistical weights w_i were chosen in accordance with the metric weighting concept

$$w_i = (Q_1^2 + Q_3^2)^{-1/2} \quad (7)$$

where Q_1 and Q_3 are displacement coordinates for a given point of the APS.

Results and discussion

The values of vibronic and force constants have been calculated for 29 complexes of ML_6^q type ($L = F^-, Cl^-, Br^-$). These systems are characterized in Table 1. Two-dimensional numerical maps $W_i^e(Q_1, Q_3)$ (33–42 points for each system) were obtained by the semiempirical CNDO—UHF version [4–6] of the MO—LCAO—SCF method. The energy cut-off was 10^{-5} eV. From the obtained values of potential constants ($K_a, K_{aa}, K_{\epsilon}, T_{aaa}, T_{aa\epsilon}, T_{a\epsilon\epsilon}, A_{\epsilon}, B_{\epsilon}, Z_{aa}$) the extreme points of the APS (Q_1^e and Q_3^e) were determined. Consequently, the Jahn—Teller stabilization energies were obtained as follows

$$E_{JT} = W(-K_a/K_{aa}, 0) - W(Q_1^e, Q_3^e) \quad (8)$$

The quality of the regression was measured by statistical characteristics. The standard deviations of individual potential constants, the correlation coefficient, and the discrepancy R -factor belong to them. Table 2 shows the values of calculated potential constants which are presented in significant number of digits (the order of the last digit being higher than the standard deviation). They will be discussed together with calculated characteristics of the APS extreme points as they appear in Table 3.

i) The harmonic force constants fulfil the relation $K_{aa} > K_{\epsilon}$, so the e_g mode may be considered as a “soft” mode. In other words, the tetragonal or orthorhombic distortions are more “profitable” than the symmetric stretching. The same holds for systems with $\mathcal{E}_g$ electron terms [2].

ii) The two-mode quadratic vibronic constant Z_{aa} adopts significant values. It may be of the same order as the quadratic vibronic constant B_{ϵ} . Thus the importance of this term is clearly demonstrated. Also the cubic force constants ($T_{aaa}, T_{aa\epsilon}$, and $T_{a\epsilon\epsilon}$) adopt significant values so that the anharmonicity effects are not negligible. The same conclusion was pointed out for octahedral complexes with $\mathcal{E}_g$ electron term [2].

iii) Higher values of harmonic force constants (K_{aa}, K_{ϵ}) occur in M(III) complexes compared to M(II) systems. The same holds for the vibronic constant A_{ϵ} ; its value is more negative in higher oxidation state also when comparing various central atoms. Consequently, the Jahn—Teller stabilization energies of M(III) complexes are higher than those of the M(II) ones.

iv) The value of harmonic force constant K_{aa} increases with the proton number of central atom (similarly as in the case of double electron degeneracy [2]).

v) The effect of spin multiplicity is demonstrated on Cr(II) and Mn(III) complexes: Increasing number of unpaired electrons implies decreasing values of K_{ϵ} , A_{ϵ} , and Z_{aa} constants. On the other hand, in systems with higher multiplicities the values of B_{ϵ} vibronic constants are much more negative (this

holds also for various central atoms). As a consequence, increasing number of unpaired electrons is connected with decreasing Jahn—Teller stabilization energies. Similar effect in octahedral complexes with double degenerate electron terms is interpreted [2] as a consequence of the asymmetry of the corresponding electron configuration.

vi) The calculated degree of tetragonal distortion Q_3 (10^{-13} — 10^{-12} m) is lower in comparison with analogous complexes having double degenerate electron state [2]. Since Q_3^e is negative for the energy minimum (except $^5\text{CoCl}_6^{3-}$), the elongated form of the tetragonal bipyramid represents the equilibrium geometry of the complexes under study.

vii) The values of Jahn—Teller stabilization energies E_{JT} span the range of 10^{-5} — 10^{-3} eV and are lower than in the case of analogous complexes with double degenerate electron terms (10^{-3} — 10^{-1} eV) [2].

viii) The values of E_{JT} are also functions of the polarity of the metal—ligand bonds: they increase in the ligand series F, Cl, Br for M(II) complexes (except $^4\text{CoF}_6^{4-}$) but decrease for the M(III) ones.

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 are overestimated by a factor of two and the vibronic constants are probably underestimated. Consequently, the Jahn—Teller distortions and stabilization energies may be underestimated. Nevertheless, the trends in the calculated force constants, vibronic constants, coordinates of stationary points, and stabilization energies seem to be correct. On the other hand, the solid state influences are responsible for amplification of these quantities in real systems.

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