Calculation of Vibrational Wavenumbers of Octahedral Closed-Shell Complexes Using Semiempirical Methods of Quantum Chemistry

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The equilibrium geometries and the wavenumbers of all vibration modes were computed for closed-shell systems MX_6^{2-} (M = Ti, Zr, Hf, X = F, Cl). Quasi-relativistic parametrization of INDO/1 method was used for all studied systems. Complexes containing Ti were studied by both the nonrelativistic CNDO/2 and INDO/2 method, too. The results show reasonable agreement with the experimental data. The quasi-relativistic INDO/1 method provides substantially better reproduction of experimental data than the nonrelativistic parametrizations.

Quantum-chemical computations for systems containing heavier atoms meet troubles of two kinds at least. The first one concerns the systems containing transition metal atoms. In such cases, one needs to use extraordinary extensive basis sets for obtaining reliable results. Therefore, at present one cannot expect a common use of *ab initio* computations in the area of solving of object-oriented problems in which transition metal atoms occur. The second trouble follows from the requirement to include relativistic effects in the case of heavier atoms. The use of a semiempirical quasirelativistic method consistently parametrized for a wide range of elements offers an acceptable solution of these troubles. Quasi-relativistic INDO/1 (QR-INDO/1) method [1] meets these requirements. With regard to the known drawbacks of the ZDO-type methods this paper is devoted to the testing of the ability of QR-INDO/1 to provide a correct description of curvature of energy hypersurface in the vicinity of its minima. Usually, the ZDO-type methods are not very successful at this task. For obtaining of reliable frequencies, the scaling of the force constants computed using ZDO methods very often must be applied. The next motivation and future application of this work follows from the need to identify some complexes generated by electrochemical processes in molten salts [2].

METHOD

The quasi-relativistic INDO/1 method [1] was used for calculation of the total energy of closed-shell systems MX_6^{2-} (M = Ti, Zr, Hf, X = F, Cl). The nonrelativistic methods CNDO/2 [3] and INDO/2 [4—6] were used for TiF_6^{2-} and $TiCl_6^{2-}$. The abovementioned methods are not parametrized for Zr and Hf. Therefore, the comparison of individual ZDO methods was done only for titanium-containing systems.

The geometry optimization was carried out in a way which preserves the octahedral symmetry. Thus, the optimization turned out to be a single-parameter one, the optimized parameter being the M—X bond length only. In the case of closed-shell systems the Jahn—Teller effect does not take place and the geometry of total energy minimum should preserve the maximum possible symmetry. The fulfilling of this requirement was tested by optimization of all internal degrees of freedom starting with the geometry found by the preceding one-parameter optimization. All the computations were carried out using the program MOSEM7 [7].

The energy hypersurface needed for the computation of force constants was computed after the minimum was found and verified. The geometry of minimum was shifted two steps in positive and also in negative direction of all symmetry-adapted vibration coordinates of an octahedron. In the case of triple degenerated irreducible representation t_{1u}, all combinations of bond and deformation coordinates belonging to this representation were generated. The step for the shift of the bond length and the angle change was chosen to be 0.05 nm and 5°, respectively. Molecular orbital calculation of the total energy was performed for all generated geometries. The force constants were obtained using the least-squares fitting of this energy surface. The expression used for the energy surface is as follows

$$
\begin{aligned}
2V = {} & F(A_{1g})\,S^2(A_{1g}) + F(E_g) \times [S_a^2(E_g) + S_b^2(E_g)] + \\
& + F(T_{2g}) \times [S_a^2(T_{2g}) + S_b^2(T_{2g}) + S_c^2(T_{2g})] + \\
& + F_1(T_{1u}) \times [S_{1a}^2(T_{1u}) + S_{1b}^2(T_{1u}) + S_{1c}^2(T_{1u})] + \\
& + F_2(T_{1u}) \times [S_{2a}^2(T_{1u}) + S_{2b}^2(T_{1u}) + S_{2c}^2(T_{1u})] + \\
& + 2\,F_{1,2}(T_{1u}) \times [S_{1a}(T_{1u})\,S_{2a}(T_{1u}) + \\
& + S_{1b}(T_{1u})\,S_{2b}(T_{1u}) + S_{1c}(T_{1u})\,S_{2c}(T_{1u})] + \\
& + F(T_{2u}) \times [S_a^2(T_{2u}) + S_b^2(T_{2u}) + S_c^2(T_{2u})] \qquad (1)
\end{aligned}
$$

Table 1. Computed and Experimental Bond Lengths for Octahedral Anions $[MX_6]^{2-}$

System	Method	Full optimization $R_{M-X}/10^{-10}$ m	Symmetrical optimization $R_{M-X}/10^{-10}$ m	Experiment $R_{M-X}/10^{-10}$ m
$[TiF_6]^{2-}$	CNDO	2.27	2.27	1.91 [13]
	INDO	2.27	2.27	
	QR-INDO	2.43	2.43	
$[TiCl_6]^{2-}$	CNDO	2.58	2.58	2.35 [14]
	INDO	2.58	2.58	
	QR-INDO	2.76	2.76	
$[ZrF_6]^{2-}$	QR-INDO	2.56	2.57	2.26 [15]
$[ZrCl_6]^{2-}$	QR-INDO	2.96	2.97	2.44 [16]
$[HfF_6]^{2-}$	QR-INDO	2.34	2.34	2.26 [17]
$[HfCl_6]^{2-}$	QR-INDO	2.77	2.78	

Note: The scaling factor for off-diagonal matrix elements of the one-electron Hamiltonian $K_{off} = 1.0$.

All the symbols are used in accordance with the work of *Cyvin* [8]. The reader will find there the definition of the symmetry-adapted coordinates of vibrations of the octahedron as well.

RESULTS AND DISCUSSION

Table 1 contains the computed and experimental bond lengths of the studied complexes. The calculated bond lengths are systematically longer than the experimental ones, obtained by X-ray diffractography for crystals. Analyzing this fact, one should keep in mind that the computations were carried out for isolated ions MX_6^{2-} *in vacuo*. The comparison of geometry *in vacuo* and geometry of crystal can be only a preliminary criterion. Experimental geometries more similar to the *in vacuo* state (*e.g.* solutions) are for these complexes not known. It is well known that the computations provide longer bond lengths of transition metal complexes *in vacuo* than are the experimental values for the solid state [1, 9—11]. The obtained results describe correctly the observed trends in the series of studied complexes. The bond lengths obtained by complete optimization of geometry differ from those obtained by one-parameter search within the numerical accuracy of the used procedure only. The values obtained for titanium complexes using CNDO/2 and INDO/2 methods are closer to the experimental values than the bond lengths provided by QR-INDO/1. These results were obtained using the value 1.0 for the scaling factor for off-diagonal matrix elements of the one-electron Hamiltonian (K_{off}). Better agreement between the calculated equilibrium bond lengths and the experimental solid phase data was obtained using the value $K_{off} = 1.4$ (according to the recommendation of the author of the QR-INDO method [1]). The problem of K_{off} value optimization respecting both the geometry and vibrational characteristics will be treated separately [22]. Table 2 shows the calculated and observed wavenumbers of individual vibration modes. The comparison of reproduction of experimental wavelengths using QR-INDO/1 with the reproduction obtained by CNDO/2 and INDO/2 for the titanium complexes does not lead to unambiguous preference of some of these parametrizations. The bonding vibrations are reproduced significantly better by the nonrelativistic ZDO methods. For the vibrations which include changes of the valence angle, the wavenumbers are reproduced substantially better by QR-INDO/1. Individual vibration modes are reproduced by QR-INDO/1 method with errors of approximately equal magnitude for all vibration modes. Errors of reproduction of different vibration modes in the case of CNDO/2 and INDO/2 vary within one order of magnitude. This fact can serve as an argument for preference of the QR-INDO/1 method also in the case of the first transition series.

The reproduction of the experimental wavenumbers by QR-INDO/1 is surprisingly good. The computations correctly follow the trends existing in the studied series.

The trend of differences between the computed and experimental wavenumbers shows a slow increase of these differences with the growing atomic number of the metal atom. This fact demonstrates the necessity of including the relativistic effects in quantum-chemical computations for heavy atoms. For elements heavier than hafnium the fully relativistic computation will likely be required for obtaining such properties as the vibrational frequencies.

CONCLUSION

The obtained results unambiguously demonstrate the usability of QR-INDO/1 method for computation of vibrational frequencies of transition metal complexes up to the atomic number 72. The interpretation of vibrational spectra of such systems using theoretical computations by this method is possible. The method is capable of providing at least qualitatively correct predictions. The method satisfactorily

Table 2. Vibrational Wavenumbers for Octahedral Anions $[MX_6]^{2-}$

System	Vibration mode	$\tilde{v}$/cm⁻¹ Methods used			Exp. conditions		Difference (QR-INDO – EXP)/cm⁻¹	
		QR-INDO	INDO	CNDO	Solution	Solid	Solution	Solid
TiF_6^{2-}	$v_1(A_{1g})$	414	509	521				
	$v_2(E_g)$	379	448	445				
	$v_3(T_{1u})$	479	575	669		560 [18]		– 81
	$v_4(T_{1u})$	138	159	206				
	$v_5(T_{2g})$	124	113	285				
	$v_6(T_{2u})$	58	59	114				
$TiCl_6^{2-}$	$v_1(A_{1g})$	281	343	338	320 [19]	331 [20]	– 39	– 50
	$v_2(E_g)$	246	290	294	271 [19]	284 [20]	– 25	– 38
	$v_3(T_{1u})$	289	423	464	316 [19]	330 [20]	– 27	– 41
	$v_4(T_{1u})$	173	123	136	183 [19]	193 [20]	– 10	– 20
	$v_5(T_{2g})$	161	207	114	173 [19]	194 [20]	– 12	– 33
	$v_6(T_{2u})$	66	77	69				
ZrF_6^{2-}	$v_1(A_{1g})$	446						
	$v_2(E_g)$	393						
	$v_3(T_{1u})$	451						
	$v_4(T_{1u})$	112						
	$v_5(T_{2g})$	134						
	$v_6(T_{2u})$	102						
$ZrCl_6^{2-}$	$v_1(A_{1g})$	262				327 [20]		– 65
	$v_2(E_g)$	241				237 [20]		4
	$v_3(T_{1u})$	313			293 [21]	330 [20]	20	– 17
	$v_4(T_{1u})$	87				150 [20]		– 63
	$v_5(T_{2g})$	75				153 [20]		– 78
	$v_6(T_{2u})$	38						
HfF_6^{2-}	$v_1(A_{1g})$	601						
	$v_2(E_g)$	531						
	$v_3(T_{1u})$	576						
	$v_4(T_{1u})$	125						
	$v_5(T_{2g})$	200						
	$v_6(T_{2u})$	35						
$HfCl_6^{2-}$	$v_1(A_{1g})$	322				333 [20]		– 11
	$v_2(E_g)$	294				237 [20]		57
	$v_3(T_{1u})$	335				288 [20]		47
	$v_4(T_{1u})$	100				145 [20]		– 45
	$v_5(T_{2g})$	95				157 [20]		– 62
	$v_6(T_{2u})$	47						

reproduces the wavenumbers of vibrations of the studied octahedral systems and correctly describes the trends in the studied series of complexes.

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