NOTIZEN

Molecular Force Fields of Tungsten and Uranium Hexachlorides

M. N. Avasthi and M. L. Mehta

Physics Department, University of Jodhpur, Jodhpur, India

Molecular force field studies of tungsten and uranium hexachloride have been carried out using the Urey-Bradley force field (UBFF) and the orbital valence force field (OVFF). Weighted least square adjustment has been used to fit the observed frequencies. Comments are also made on the suitability of the force fields used. The trends in stretching force constants have been discussed.

1. Introduction

Aldous and Mills [1] have suggested that the potential field expressed in terms of symmetry coordinates has a definite physical meaning. These symmetry coordinates are convenient in the calculation of normal modes. Urey and Bradley [2] have suggested a potential model which includes the repulsions between the nonbonded atoms. Heath and Linnett [3] have improved this potential field (UBFF) and have suggested that the angular part of the potential energy is proportional to the sum of the squares of the angles β_i — the angle, as seen from the metal, between the centre of the i-th orbital and the actual position of the i-th ligand atom where the orbital energy is minimized. They called this potential to be orbital valence force field (OVFF) and have applied it for different XY_n type molecules and ions. Heath and Linnett [3] and Kim et al. [4] have shown the superiority of this type of force field over UBFF for hexafluoride molecules of O_h symmetry.

Recently, the vibrational spectra of hexachlorides — WCl_6 and UCl_6^{-2} — were studied by Evans et al. [5] and by Woodward et al. [6] respectively. Using the vibrational data of hexachlorides, the present investigation was carried out to evaluate the force constants and also to test the applicability of the potentials (UBFF and OVFF) based on different angle treatment.

Spherical top molecules and ions of XY_6 type belonging to O_h symmetry, possess six normal modes of vibration. Out of these six, the three gerade modes — one nondegenerate a_{1g} vibration (ν_1), one doubly degenerate e_g vibration (ν_2) and one triply degenerate f_{2g} vibration (ν_5) — are Raman active; the two triply degenerate f_{1u} vibrations (ν_3 and ν_4) are permitted in the infrared, and the one triply degenerate f_{2u} vibration (ν_6) is inactive in infrared and Raman effect. The ν_1, ν_2, and ν_3 fundamentals are associated with the metal-halogen stretching and ν_4, ν_5, and ν_6 are associated with the skeletal deformation $(Y-X-Y)$.

2. Least Square Adjustment and Force Constant Evaluation

The hexachlorides of O_h symmetry have been subjected to normal coordinate analysis within the frame work of Wilson's GF matrix method [7]. The symmetry coordinates used are the same as those of Pistorius [8]. The kinetic energy matrix elements and potential energy matrix elements for both force fields used here are the same as used earlier [9].

The number of observed fundamentals is bigger than the number of force constants to be evaluated assuming both force fields. Under the circumstances, a least square adjustment has been applied for the best fit of the observed fundamentals. Using the notations due to Mann et al. [10], the refinement in the force constants Δf_m is giving by the expression *

$$\Delta f_m = - (J' \, W \, J)^{-1} J' \, W \, X \, .$$

The refinement Δf_m is added to the corresponding force constant to give an improved set of force con-

Table 1. Observed and calculated frequencies in cm^{-1} and force constants in mdyne/Å.

Hexachloride		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	K	H or D	F	F'	Average percent deviation (ν_1, ν_2, ν_3)	(ν_4, ν_5, ν_6)
WCl_6													
	OBS.	408	312	367	165	206	97						
	UBFF	426	293	379	169	189	99	1.46	−0.15	0.58	−0.08	4.9	4.1
	OVFF	410	302	379	165	204	97	1.63	−0.21	0.47	−0.07	2.3	0.3
UCl_6^{-2}													
	OBS.	299	237	262	114	121	80						
	UBFF	285	232	276	112	126	78	1.00	−0.02	0.18	−0.02	3.9	2.7
	OVFF	295	228	275	114	120	80	0.69	−0.19	0.28	0.04	3.4	0.4

Reprint requests to Dr. M. N. Avasthi, Department of Physics, University of Jodhpur, *Jodhpur*, India.

* D. E. Mann et al. [10] have omitted a minus sign in their published work.

stants. An initial set of the force constants has been calculated from one dimensional secular equations, i. e. for a_{1g}, e_g, f_{2u}, and f_{2g} vibrational species. For each iteration, a new Jacobian is calculated with an improved set of force constants, and this procedure was repeated until all the Δf_m converged to finite values. A computer program for an IBM 1620 was prepared to facilitate the weighted least square adjustment. The observed fundamentals, calculated force constants and fundamentals using both force fields, are give in Table 1.

3. Results and Discussion

For the convergence, the UBFF model takes more iterations than the OVFF model. Comparing the percentage deviation of the stretching fundamentals as well as the bending fundamentals, it is noted that the percentage deviation for the UBFF model is greater than for the OVFF model for these hexachlorides.

The stretching (K) and nonbonded repulsion force constants (F) are lower for the metal hexachloride than the corresponding metal hexafluoride molecule [4]. This may be due to the higher interatomic distance for hexachlorides [11, 12] as compared with hexafluorides [13, 14] as well as due to the decrease in electronegativity as we go from fluorine to chlorine. Comparing the stretching force constants, it is observed that it is lower for uranium than for tungsten irrespective of the internuclear distance involved. This may be due to the difference in their electronic configurations. A similar trend was observed while using general valence force field [15]. Recently, the trends in the stretching force constants of these hexachlorides with respect to the nature of the central metal-atom have been discussed by the present authors [9, 16]. The calculated fundamentals for the hexachlorides are quite close to the observed ones.

[1] J. ALDOUS and I. M. MILLS, Spectrochim. Acta 19, 1567 [1963].

[2] H. C. UREY and C. A. BRADLEY, Phys. Rev. 38, 1969 [1931].

[3] D. C. HEATH and J. W. LINNETT, Trans. Faraday Soc. 44, 873, 878, 884 [1948].

[4] H. KIM, P. A. SOUDER, and H. H. CLAASSEN, J. Mol. Spectry. 26, 46 [1968].

[5] J. C. EVANS and G. Y.-S. LO, J. Mol. Spectry. 26, 147 [1968].

[6] L. A. WOODWARD and M. J. WARE, Spectrochim. Acta 24 A, 921 [1968].

[7] E. B. WILSON, JR., J. Chem. Phys. 7, 1047 [1939]; 9, 76 [1941].

[8] C. W. F. T. PISTORIUS, J. Chem. Phys. 29, 1328 [1958].

[9] M. N. AVASTHI and M. L. MEHTA, Z. Naturforsch. 26 a, 1137 [1971]; J. Quant. Spectry. Radiat. Trans. 11, 1583 [1971].

[10] D. E. MANN, T. SHIMANOUCHI, J. H. MEAL, and L. FANO, J. Chem. Phys. 27, 43 [1957].

[11] R. V. G. EWANS and M. W. LISTER, Trans. Faraday Soc. 34, 1358 [1938].

[12] S. SEIGEL, Acta Cryst. 9, 827 [1956].

[13] M. KIMRA, V. SCHOMAKER, and D. M. SMITH, J. Chem. Phys. 48, 4001 [1968].

[14] H. SIEBERT, Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie, Springer-Verlag, Berlin 1966.

[15] M. N. AVASTHI and M. L. MEHTA, Spectry. Letters 2, 327 [1969].

[16] M. L. MEHTA, J. Mol. Spectry. (in press).