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Indian J. Phys. **43**, 361—364 (1969)

Normal coordinate analysis of tungsten hexachloride (WCl_6)

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(*Received* 8 *March* 1969)

On the basis of available molecular dimensions and spectroscopic data, several molecules and ions of octahedral symmetry (O_h) have been subjected to normal coordinate analysis using various types of potential functions, enabling the evaluation of molecular constants like force constans, thermodynamic function, mean amplitudes of vibration etc. In continuation of the same type of work Nagarajan (1964) calculated the valence force field constants and mean amplitudes of vibration of tungsten hexachloride (WCl_6) from the estimated frequencies used in the calculation of thermodynamic functions by Stull and his associates (1962). Recently Evans & Lo (1968) have reported the assignments of all the six fundamentals frequencies of tungsten hexachloride with the help of two infrared active fundamental modes and six combination bonds. The fundamental frequencies differ appreciably from the estimated frequencies used by Nagarajan (1964) in his calculations. Since we have been interested in similar work on octahedral molecules and ions (Pandey, Singh & Sanyal 1969), it was considered worthwhile to recalculate the molecular constants like force constants mean amplitudes of vibration and shrinkage effect for this molecule with the recent spectroscopic data (Evans & Lo 1968)

Valence force constants were calculated using Wilson's F-G matrix method. The general valence force field has been used and the elements of F and G matrices are taken from Kimura & Kimura (1963)' The 2×2 determinant of f_{1u} species consisting of three unknown quantities was solved by a method proposed by Müller & Peacock (1968) for XY_m type molecules where $m_x > m_y$. The results of valence force field constants are presented in table 1 where the symbols have their usual significance.

TABLE 1. FORCE CONSTANTS OF TUNGSTEN HEXACHLORIDE

G. Q. P. F.	mdyne/A°	Observed frequencies cm−1	Calculated from G. Q. P. F. cm−1
$A=f_r$	2.2999	$\nu_1=408$	408
$B=f_{rr}$	0.2405	$\nu_1=312$	312
$C=f_{r\alpha}-f_{r\alpha}''$	0.0508	$\nu_1=367$	367
$D=f_{\alpha}-f_{\alpha\alpha}'''$	0.2020	$\nu_1=165$	164.9
$E=f_{\alpha\alpha}-f_{\alpha\alpha}''$	−0.0097	$\nu_1=206$	206
$F=f_{\alpha\alpha}'-f_{\alpha\alpha}'''$	0.0519	$\nu_1=97$	97
$G=f_{rr}'$	0.2137		

TABLE 2. SHRINKAGE EFFECT IN THE CASE OF TUNGSTEN HEXACHLORIDE (IN 10^{-2} A° UNITS)

Distance	T=0°K	T=298°K	T=500°K
Cl........Cl (nonlinear)	−0.0275	0.0465	0.0987
Cl.. .....Cl (linear)	0.2550	0.8929	1.4720

Linear as well nonlinear Bastiansen-Marino shrinkages have been computed at temperatures $T=0$°K, $T=298$°K, and $T=500$°K using expression given by Cyvin & Meisingseth (1963). The results are presented in table 2.

The generalized mean square amplitude quantities and mean amplitude of vibration were evaluated at three temperatures $T=0$°K, $T=298$°K and $T=500$°K using the the method of Bye & Cyvin (1963), given in terms of symmetrized mean square amplitude matrices (Σ). The results are presented in table 3. From the results it is concluded that the mean amplitudes of vibrations for bonded as well as non-bonded distances increase with the increase in temperature.

TABLE 3. GENERALIZED MEAN-SQUARE AND MEAN AMPLITUDE QUANTITIES IN TUNGSTEN HEXACHLORIDE.

Distance	Mean-square amplitude quantites, $10^{-4} \times A^2$				Mean amplitudes of vibration, $10^{-2} \times A$		
	Symbol	0°K	298°K	500°K	0°K	298°K	500°K
W—Cl	$\langle z^2 \rangle$	16.805	26.159	39.256	4.099	5.115	6.265
	$\langle x^2 \rangle$	44.115	134.305	219.742			
	$\langle y^2 \rangle$	44.115	134.305	219.742			
Cl......Cl (linear)	$\langle z^2 \rangle$	28.075	42.164	62.958	5.299	6.493	7.935
	$\langle x^2 \rangle$	23.070	50.164	80.102			
	$\langle y^2 \rangle$	23.070	50.154	80.102			
Cl..... Cl (nonlinear)	$\langle z^2 \rangle$	52.415	124.380	197.789	7.240	11.153	14.064
	$\langle x^2 \rangle$	42.075	102.132	170.240			
	$\langle y^2 \rangle$	60.530	328.089	393.294			

The authors are grateful to C.S.I.R., New Delhi and State C.S.I.R., U.P. for financial assistance to two of them (A.N.P and H.S.S).

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