

MOLECULAR PARAMETERS OF DIHALIDES OF IIB GROUP ELEMENTS

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Received May 15th, 1984

The molecular parameters, *i.e.* force constants, mean amplitudes of vibrations, bond polarizability derivatives and mean molecular polarizabilities have been studied for MX₂ and MXZ (M = Zn, Cd, Hg; X or Z = F, Cl, Br, I but X ≠ Z) type halides of zinc group elements on the basis of current available spectroscopic and structural data. The analysis of the result for CdFBr demands a reinvestigation of the spectroscopic study in detail. The results of the present investigations will be helpful in the interpretation of the Raman intensity and refractometry data whenever available.

The infrared and Raman spectra of matrix isolated binary halides of the elements of group IIB have been studied in detail by Loewenschuss and his coworkers¹⁻³. Recently the vibrational spectra of the species of the type MF₂ and MFX (M = Zn, Cd, Hg; X = Cl, Br) have been investigated by them⁴ and the existence of the MFX molecular species have been pointed out for the first time. They have also reported the valence force constants for the systems which involve ignorance of the interaction force constant. The present work has been undertaken with the purpose of obtaining additional information on the molecular parameters *viz.* force constants, mean amplitudes of vibration, bond polarizability derivatives and mean molecular polarizabilities in the light of current available data.

Details of Computations

Wilson's **FG** matrix method has been followed for the computation of force constants under model force fields⁵⁻⁷. The second order secular equation has been solved using *L-F* approximation method⁸.

The mean amplitudes of vibrations have been studied using Cyvin's secular equation^{6,9} | $\sum \mathbf{G}^{-1} - \Delta E$ | = 0. Here the symbols have their usual meanings⁶.

The bond polarizability derivatives have been evaluated using the expression of Lippincott and Nagarajan¹⁰. It is given by the relation

$$\frac{\partial \bar{\alpha}}{\partial R} = \frac{1}{3} \left(\frac{n}{2} \right) A_{12} \frac{\sigma}{a_0} R^3 ,$$

where $(n/2)$ is the bond order, A_{12} the root mean square of delta function strength of atoms involved in bonding¹¹, σ the polarity correction — the Pauling covalent character of the bond, determined by

$$\exp \left[-\frac{1}{4}(x_1 - x_2)^2 \right],$$

where x is the electronegativity of the atom on Pauling scale and R the interatomic distance, a_0 is the first Bohr's radius.

TABLE I

GVFF and *OVFF* force constants (in 10^2 Nm^{-1}) of MX_2 type molecules^a

Molecule	$f_r(K)$	$f_{rr}(F)$	$f_\Phi(D - 2F')$	Lit.
ZnF_2	3.99 (4.17)	-0.18 (-0.18)	0.083 (0.17)	P.W.
	4.001	-0.0338	0.07961	4
CdF_2	3.55 (3.66)	-0.11 (-0.11)	0.061 (0.12)	P.W.
	3.554	-0.1374	0.06122	4
HgF_2	3.74 (3.87)	-0.14 (-0.14)	0.14 (0.27)	P.W.
	3.739	-0.1334	0.1359	4
ZnCl_2	2.69 (2.667)	0.027 (0.027)	0.439 (0.879)	P.W.
	2.66 (2.668)	(0.027)	(0.872)	7
CdCl_2	2.25 (2.26)	-0.013 (-0.013)	0.050 (0.103)	P.W.
	(2.142)	—	—	7
HgCl_2	2.61 (2.63)	0.037 (0.037)	0.04 (0.08)	P.W.
	(2.63)	(0.022)	(0.076)	7
ZnBr_2	2.34 (2.186)	0.152 (0.152)	0.346 (0.692)	P.W.
	(2.186)	(0.152)	(0.692)	7
CdBr_2	1.96 (1.98)	0.00017	0.037 (0.075)	P.W.
	(1.93)	(0.00017)	—	7
HgBr_2	2.24 (2.249)	-0.006 (-0.006)	0.022 (0.044)	P.W.
	(2.249)	(-0.006)	(0.044)	7
ZnI_2	1.99 (1.83)	0.16 (0.16)	0.03 (0.06)	P.W.
	(1.77)	(0.17)	—	7
CdI_2	1.67 (1.66)	0.008 (0.008)	0.185 (0.37)	P.W.
	(1.611)	—	—	7
HgI_2	1.83 (1.854)	-0.029 (-0.028)	0.018 (0.036)	P.W.
	(1.854)	(-0.028)	(0.036)	7

^a P.W. Present work; values in parentheses are *OVFF* constants, $f_r(K)$ bond stretching force constants, f_{rr} bond-bond interaction force constants, F and F' nonbonded interaction force constants, $f_\Phi(D)$ angle bending force constant.

The mean molecular polarizability has been computed employing delta function model due to Lippincott and Stutman¹². It is given by the relation

$$\alpha_M = \frac{1}{3} \left[\sum_i \sigma_i \alpha_{\parallel bi} + \sum_j f_j \alpha_j + n_{df} \sum_j x_j^2 \alpha_j \sum_j x_j^2 \right],$$

where the first term includes the contribution of bond region electrons, the second term takes into account the contribution of non-bond region electrons and the last term represents the contribution of bond perpendicular components. $\alpha_{\parallel bi}$ is the bond parallel component of the polarizability, f_j is the fraction of the electrons of the atom which are not in the bond region and α_j is the atomic polarizability. n_{df} is the number of residual degrees of freedom which is in present case six for ZnF_2 (non-linear) and five for others.

RESULTS AND DISCUSSION

The spectral and structural data for the molecules under present investigation are taken from lit.^{1,4,7,13,14}. The results of the general valence force field (*GVFF*) and orbital valence force field (*OVFF*) for MX_2 -type molecules are collected in Table I. Their values are compared with the Table I results available in lit^{4,7}. Except zinc difluoride other molecules are linear.

A survey of the Table I shows that the bond stretching force constant, f_r , varies in the order: $f_{ZnX} > f_{CdX} < f_{HgX}$ ($X = F, C, Br, I$). This trend is not exhibited

TABLE II
Stretching and bond-bond interaction force constants (in 10^2 Nm^{-1}) of MFX type molecules

Molecule	$f_{(M-X)}$	$f_{(M-F)}$	$f_{MX, MF}$	Lit. ^a
$ZnFCl$	2.50	4.22	0.196	P.W.
	2.615	3.965	—	4
$ZnFBr$	2.28	4.03	0.46	P.W.
	2.341	3.805	—	4
$CdFCl$	2.19	3.61	— 0.28	P.W.
	2.237	3.497	—	4
$CdFBr$	2.69	3.29	0.35	P.W.
	2.764	3.151	—	4
$HgFCl$	2.72	3.60	0.196	P.W.
	2.691	2.554	—	4
$HgFBr$	2.44	3.45	0.197	P.W.
	2.454	3.451	—	4

^a P.W. present work.

by the corresponding force constant in *OVFF* model for the dibromides and diiodides of zinc and mercury. This anomaly can be understood in term of non-bonded interaction. The larger value of the non-bonded interaction force constant (*F*) for the dibromide and diiodide of zinc as compared to the corresponding halides of mercury is responsible for diminishing the magnitude of the stretching force constant. The relative strength of the chemical bonds also follows the same trend as the stretching force constants in the dihalides of the elements of IIB group. Further it is noted that the stretching force constant decreases with the increase of the mass and decrease of the electronegativity of the ligand atom.

There are only two vibrational wavenumbers available for *XYZ* type linear molecules. The stretching and interaction force constants for these molecules are summarized in Table II. The results are also compared with the values given in lit.⁴. A slight difference between force constants is on account of the ignorance of inter-

TABLE III
Mean amplitudes of vibration (in 10^{-10} m)

System	X—Y			Y—Y		
	0 K	298·15 K	500 K	0 K	298·15 K	500 K
ZnF ₂	0·033	0·043	0·047	0·047	0·080	0·097
CdF ₂	0·041	0·043	0·047	0·057	0·061	0·069
HgF ₂	0·040	0·042	0·047	0·056	0·060	0·068
ZnCl ₂	0·032	0·044	0·051	0·047	0·053	0·064
CdCl ₂	0·041	0·048	0·058	0·054	0·067	0·081
HgCl ₂	0·038	0·044	0·053	0·051	0·061	0·074
ZnBr ₂	0·035	0·041	0·049	0·036	0·044	0·069
CdBr ₂	0·038	0·048	0·060	0·045	0·067	0·085
HgBr ₂	0·033	0·043	0·054	0·040	0·054	0·067
ZnI ₂	0·036	0·049	0·060	0·040	0·063	0·081
CdI ₂	0·035	0·052	0·065	0·042	0·072	0·092
HgI ₂	0·031	0·043	0·054	0·035	0·050	0·063
ZnFCl	0·042	0·048	0·057	0·042	0·044	0·049
ZnFBr	0·039	0·049	0·061	0·044	0·048	0·056
CdFCl	0·0414	0·049	0·059	0·0416	0·044	0·050
CdFBr	0·034	0·044	0·054	0·043	0·047	0·054
HgFCl	0·038	0·044	0·052	0·036	0·037	0·043
HgFBr	0·033	0·041	0·055	0·056	0·060	0·069
HgClBr	0·034	0·046	0·058	0·039	0·046	0·056
HgClI	0·033	0·049	0·062	0·038	0·047	0·057
HgBrI	0·034	0·050	0·069	0·034	0·040	0·057

action force constant by Givan and Loewenschuss⁴. The stretching force constants f_{MF} show the expected trend as given in the case of MX_2 but the trend in f_{MCl} and f_{MBr} is not in good agreement with each other. These vary in the sequence: $f_{Zn-Cl} > f_{Cd-Cl} < f_{Hg-Cl} > f_{Zn-Cl}$ and $f_{Zn-Br} < f_{Cd-Br} > f_{Hg-Br} > f_{Zn-Br}$. The abrupt change in the value of f_{Cd-Br} is unexpected. As no side effect has been reported for CdFBr, therefore on the basis of our present results we propose two possibilities: a) either CdFBr does not possess $C_{\infty v}$ point group or b) reported frequency data are not reasonable. On the basis of the above possibilities we understand that this species should be reexamined spectroscopically.

The mean amplitudes of vibrations calculated for the bonded and nonbonded distances at temperatures $T = 0, 298.15, 500$ K are tabulated in Table III. The values show expected trend with temperature. In general larger magnitude of bonded mean amplitude of vibration at room temperature for the dihalides of cadmium as compared to the other dihalides of zinc and mercury also supports the trend in stretching force constants (Table I). This implies that the Cd-halogen bond is more flexible as compared to the metal-halogen bond in the dihalides of zinc and mercury.

The bond polarizability derivatives and mean molecular polarizabilities for the molecules under study are collected in Table IV and Table V, respectively. These two parameters exhibit very regular trend and increase with the growing total mass of the molecule. These results will be helpful in the interpretation of Raman intensity and refractometry data.

TABLE IV
Bond polarizability derivatives (in 10^{-22} m^2) of M—X bonds in MX_2 and MXZ type molecules

Bond	$\partial\bar{\alpha}/\partial R$
Zn—F	0.52
Zn—Cl	1.79
Zn—Br	2.38
Zn—I	3.33
Cd—F	0.79
Cd—Cl	2.38
Cd—Br	3.07
Cd—I	4.23
Hg—F	1.12
Hg—Cl	3.09
Hg—Br	3.69
Hg—I	4.91

TABLE V
Molecular polarizabilities (in 10^{-31} m^3) of MX_2 and MXZ type molecules^a

Molecule	$\sum \alpha_{\parallel b\parallel}$	$\sum \alpha_{\parallel n\parallel}$	$\sum 2\alpha_{\perp}$	α_M
ZnF_2	15.62	11.73	64.52	30.62
CdF_2	24.15	11.73	84.12	39.99
HgF_2	34.88	11.73	83.15	43.25
ZnCl_2	57.20	29.14	150.23	78.86
CdCl_2	81.13	29.14	161.13	90.47
HgCl_2	108.51	29.14	157.19	98.29
ZnBr_2	81.28	43.43	201.90	108.87
CdBr_2	111.91	43.43	215.39	123.58
HgBr_2	136.23	43.43	205.84	128.50
ZnI_2	121.98	56.28	252.42	118.95
CdI_2	165.01	56.28	265.02	162.11
HgI_2	194.16	56.28	255.10	168.16
ZnFCl	36.41	20.433	104.16	53.67
$\text{ZnFB}\ddot{\text{r}}$	48.44	27.58	120.74	65.59
ZnFI	68.79	34.00	130.07	77.43
CdFCl	52.64	20.43	112.87	61.48
$\text{CdFB}\ddot{\text{r}}$	68.03	27.58	129.62	75.08
CdFI	94.58	34.00	139.39	89.33
HgFCl	71.69	20.43	111.11	67.75
$\text{HgFB}\ddot{\text{r}}$	85.55	27.58	127.35	80.75
HgFI	114.52	34.00	136.71	95.08

^a For symbols see text and lit.¹².

One of the authors (A.N.P.) is thankful to the University Grants Commission, New Delhi for sponsoring his visit to Czechoslovakia under Indo-Czech Cultural Exchange Programme. He would like to thank the Ministry of Education of ČSR for hospitality at the Department of Inorganic Chemistry Faculty of Science, Charles University, Prague.

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