

MOLECULAR FORCE FIELD FOR SOME X_2Y_2 MOLECULES OF C_2 SYMMETRY

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(Received March 19, 1971)

A normal coordinate analysis was carried out for the six sulphur and selenium monohalides S_2F_2 , S_2Cl_2 , S_2Br_2 , S_2H_2 , Se_2Cl_2 and Se_2Br_2 using the Urey Bradley type of force field. The mean vibrational amplitudes were evaluated. Thermodynamic properties for each molecule were calculated at 100° intervals from 298.16° to $1000^\circ K$.

1. Introduction

The molecular force field investigations of Sulphur and Selenium halides [1], [2] has been of great interest in attempting to explain the influence of the lone pair of electrons in these systems. Yet another important class of these halides are those of the type X_2Y_2 with C_2 symmetry. Their importance lies in the presence of internal rotation and the nature of the $X-X$ bond in those molecules.

The most recent work on the infrared spectra of S_2Cl_2 , S_2Br_2 , Se_2Cl_2 and Se_2Br_2 was done by Forneris and Hennies [3]. They have summarized all the earlier work in their paper. Mean amplitudes of vibration for S_2Cl_2 , S_2Br_2 and S_2H_2 were obtained by Elvebredd and Cyvin [4]. Electron diffraction measurements were made by Hirota [5] and Winnewisser and Haase [6]. Brown and Pez [7] have recently given the vibrational assignments for S_2F_2 . They have also carried out a normal coordinate analysis using the Urey Bradley force field.

However in all the earlier normal coordinate analysis using the Urey Bradley force field the nonbonded $Y \cdots Y$ interaction constant was not taken into account. The present paper deals with a complete normal coordinate analysis of S_2H_2 , S_2F_2 , S_2Cl_2 , S_2Br_2 , Se_2Cl_2 and Se_2Br_2 with a view to study the bond properties of these molecules. Incidentally the mean vibrational amplitudes were also calculated and compared with electron diffraction results.

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2. Calculation of potential energy constants

Using the latest vibrational assignments and the molecular parameters (summarized in Table I) and using essentially the same set of symmetry coordinates given by Forneris and Hennies [3] the complete expressions for the potential functions were written down and the

TABLE I

Molecular parameters and observed vibrational wavenumbers

Molecule	R (Å°)	r (Å°)	β	τ	Vibrational wavenumbers
S_2F_2	1.888 ^a	1.635	108.3°	87.9°	717 ^f , 614.6, 319.8 and 182.5 680 and 301
S_2Cl_2	1.931 ^b	2.07	108.2°	84.8°	540 ^g , 446, 205 and 102 434 and 238
S_2Br_2	1.98 ^c	2.24	106°	83°	534 ^g , 357, 170 and 67 356 and 202
S_2H_2	2.055 ^d	1.352	91.65°	90.6°	2509 ^b , 883, 509, and 416 2577 and 886
Se_2Cl_2	2.32 ^e	2.1	106°	84°	360 ^g , 292, 132 and 87 353 and 147
Se_2Br_2	2.32 ^e	2.24	106°	84°	286 ^g , 260, 107 and 55 260 and 118

^aRef. [17]; ^bRef. [12]; ^cRef. [5]; ^dRef. [6]; ^eTaken from other molecules; ^fRef. [7];
^gRef. [18]; ^hRef. [19] and [20].

relations connecting the valence force constants and the UBBF constants were obtained in the usual way. They are:

$$f_R = K_R + 2S_{XY}^2 F_{XY}^2 + 2t_{XY}^2 F'_{XY} + A^2 F_{YY}$$

$$f_r = K_r + S_{YX}^2 F_{XY} + t_{YX}^2 F'_{XY} + B^2 F_{YY}$$

$$f_\beta = H_\beta + t_{XY} t_{YX} F_{XY} - S_{XY} S_{YX} F'_{XY} + C^2 F_{YY}$$

$$f_\tau = H_\tau + D^2 F_{YY}$$

$$f_{Rr} = S_{XY} S_{YX} F_{XY} - t_{XY} t_{YX} F'_{XY} + A B F_{YY}$$

$$f_{R\beta} = S_{XY} (t_{YX} t_{YX})^{1/2} F_{XY} + t_{YX} S_{XY} F'_{XY} + B C F_{YY}$$

$$f_{r\tau} = B D F_{YY}$$

$$f_{R\tau} = A D F_{YY}$$

$$f_{rr} = B^2 F_{YY}$$

where $X = S, Se$; $Y = F, Cl, Br, H$

$$A = \frac{R - 2r \cos \beta}{q_{YY}}$$

$$B = \frac{2r \cos^2 \beta + r \sin^2 \beta - R \cos \beta - r \sin^2 \beta \cos \tau}{q_{YY}}$$

$$C = \frac{Rr^{1/2} \sin \beta - r^{3/2} \sin \beta \cos \beta - r^{3/2} \sin \beta \cos \beta \cos \tau}{R^{1/2} q_{YY}}$$

$$D = \frac{r \sin^2 \beta \sin \tau}{q_{YY}}$$

$F'_{XY} = -0.1 F_{XY}$, F'_{YY} is assumed to be zero and S_{ij} and t_{ij} have the usual meaning.

TABLE II

UBFF constants of X_2Y_2 molecules

Molecules UBFF constants ^a	S ₂ F ₂	S ₂ Cl ₂	S ₂ Br ₂	S ₂ H ₂	Se ₂ Cl ₂	Se ₂ Br ₂
K_R	3.8547 ^b	2.3934	2.4634	2.3120	1.8845	1.7638
K_r	2.9026	1.6843	1.4220	3.6873	1.6332	1.4137
H_β	1.0538	0.9363	1.1823	0.7325	0.8036	0.7543
H_τ	0.2555	0.1820	0.1230	0.0900	0.1892	0.1684
F_{XY}	0.1132	0.1954	0.1547	0.1438	0.1345	0.1037
F_{YY}	0.0086	0.0120	0.0210	0.0150	0.0115	0.0185

^a Stretching constants are in mdyn/A⁰, angle-angle constants are in mdyn A⁰/rad² and bond angle interaction constants are in mdyn/rad.

^b This number of significant digits is retained to secure internal consistency in the calculations.

TABLE III

Valence force constants of X_2Y_2 molecules

Molecules Valence constants ^a	S ₂ F ₂	S ₂ Cl ₂	S ₂ Br ₂	S ₂ H ₂	Se ₂ Cl ₂	Se ₂ Br ₂
f_R	4.0139 ^b	2.6313	2.6430	2.5148	2.0621	1.9007
f_r	2.9708	1.8127	1.5418	3.7200	1.7251	1.5029
f_β	1.1030	1.0223	1.2573	0.8088	0.8654	0.8055
f_τ	0.2570	0.2088	0.1604	0.0911	0.2149	0.1721
f_{Rr}	0.0828	0.1391	0.1139	0.0803	0.1005	0.0867
$f_{R\beta}$	0.0552	0.0878	0.0734	0.0867	0.0657	0.0538
$f_{r\beta}$	0.0491	0.0904	0.0797	0.0489	0.0641	0.0581
$f_{r\tau}$	0.0024	0.0094	0.0197	0.0034	0.0061	0.0103
$f_{R\tau}$	0.0031	0.0107	0.0211	0.0052	0.0038	0.0062
f_{rr}	0.0040	0.0053	0.0104	0.0087	0.0173	0.0290

^{a,b} As in table II.

Using these expressions and the set of symmetry coordinates the F matrix elements can be written in terms of the six Urey Bradley constants (K_R , K_r , H_β , H_r , F_{XY} and F_{YY}). Vibrational frequencies were calculated by solving the secular equation

$$|GF - EA| = 0.$$

The values of the six Urey Bradley constants were varied until a set was obtained which gave the best agreement between the observed and calculated frequencies. The scheme of calculations was essentially the same as that of Shimanouchi and Suzuki [8]. The Z matrices were constructed following the procedure given by Overend and Scherer [9]. All the calculations were carried out using an I.B.M. 1130 Computer. The final sets of Urey Bradley constants, and the corresponding valence constants are presented in Tables II and III.

3. Calculation of mean vibrational amplitudes

Using the F and G matrices the matrix L was calculated by the method given by Toman and Pliva [10]. The mean square vibrational amplitude matrices Σ were evaluated for all the six molecules by the well known method of Cyvin [11]. The mean amplitude quantities both for bonded and nonbonded distances were evaluated and are presented in Table IV along with the available electron diffraction results.

Mean vibrational amplitudes of X_2Y_2 molecules in Å° at 298.16°K

TABLE IV

Distances Molecules	$X-X$	$X-Y$	$X---Y$	$Y---Y$	Ref.
S_2F_2	0.0417	0.0496	0.0815	0.1376	a
S_2Cl_2	0.0490	0.0549	0.0887	0.1864	a
	0.0496	0.0546	0.0919	0.1665	[4]
	0.05 ± 0.03	0.05 ± 0.01	0.087 ± 0.0	0.14 ± 0.07	[5]
S_2Br_2	0.0484	0.0574	0.0894	0.2119	a
	0.0489	0.0577	0.0966	0.1835	[4]
	0.05	0.053 ± 0.015	0.098 ± 0.02	0.31	[5]
S_2H_2	0.0491	0.0823	0.1294	0.2208	a
	0.0487	0.0824	0.1318	0.2232	[4]
	0.067	0.077	0.079	—	[6]
Se_2Cl_2	0.0482	0.0547	0.0882	0.2033	a
Se_2Br_2	0.0527	0.0556	0.1071	0.2297	a

^a Present work.

4. Calculation of thermodynamic properties

Using the vibrational wavenumbers, the heat content, free energy, entropy and heat capacity were computed by the usual statistical methods for all the six molecules. The calculations were made for one atmosphere pressure for a rigid rotor, harmonic oscillator approximation. The values obtained are given in Table V.

5. Discussion

The force constant values presented in Tables II and III are comparable with the corresponding values of sulphuryl and seleninyl halides. The increase in the sulphur and selenium halogen stretching force constants (S—Br 1.4220 md/A°, S—Cl 1.6843 md/A°, S—F 2.9026 md/A° and Se—Br 1.4137 md/A°, Se—Cl 1.6332 md/A°) is in correspondence with the increase in the electronegativity of the halogen atoms.

TABLE V
Heat capacity C_p , heat content H , free energy F and entropy S in cal deg⁻¹ mole⁻¹ for X_2Y_2 molecules

Molecule	$T(^{\circ}\text{K})$	C_p°	$\frac{(H^{\circ} - E_0^{\circ})}{T}$	$-\frac{(F^{\circ} - E_0^{\circ})}{T}$	S°
S_2F_2	298.16	15.79	11.70	59.92	71.63
	400	17.21	12.95	63.56	76.51
	500	18.03	13.89	66.55	80.45
	600	18.53	14.62	69.13	83.76
	700	18.86	15.21	71.45	86.65
	800	19.08	15.68	73.50	89.18
	900	19.24	16.07	75.38	91.46
	1000	19.35	16.39	76.10	93.49
S_2Cl_2	298.16	17.44	13.27	64.85	78.12
	400	18.38	14.46	68.90	83.36
	500	18.88	15.31	72.27	87.59
	600	19.16	15.93	75.13	91.06
	700	19.34	16.40	77.58	93.98
	800	19.46	16.78	79.82	96.00
	900	19.55	17.10	81.88	98.98
	1000	19.61	17.34	83.63	100.97
S_2Br_2	298.16	17.93	14.00	69.68	83.68
	400	18.70	15.12	73.96	89.08
	500	19.09	15.88	77.43	93.31
	600	19.32	16.44	80.36	96.80
	700	19.46	16.86	82.90	99.77
	800	19.55	17.19	85.19	102.43
	900	19.62	17.45	87.19	104.65
	1000	19.67	17.69	89.26	106.95

TABLE V (continued)

Molecule	$T(^{\circ}\text{K})$	C_p°	$\frac{(H^{\circ} - E_0^{\circ})}{T}$	$\frac{(F^{\circ} - E_0^{\circ})}{T}$	S°
S_2H_2	298.16	11.66	9.27	52.91	61.66
	400	12.97	10.06	55.23	65.29
	500	13.91	10.74	57.55	68.31
	600	14.64	11.33	59.56	70.89
	700	15.27	11.85	61.35	73.21
	800	15.81	12.31	62.96	75.27
	900	16.30	12.74	64.44	77.18
	1000	16.71	13.11	65.81	78.93
S_2Cl_2	298.16	18.55	14.73	69.84	84.58
	400	19.10	15.79	74.35	90.14
	500	19.37	16.48	77.94	94.43
	600	19.52	16.97	80.96	97.94
	700	19.61	17.34	83.53	100.87
	800	19.67	17.65	86.08	103.72
	900	19.71	17.87	88.08	105.95
	1000	19.74	18.04	90.00	108.05
Se_2Br_2	298.16	18.99	15.59	74.59	90.19
	400	19.37	16.52	79.31	95.83
	500	19.54	17.09	82.99	100.09
	600	19.64	17.53	86.31	103.84
	700	19.70	17.83	89.00	106.83
	800	19.74	18.06	91.32	109.39
	900	19.77	18.25	93.43	111.69
	1000	19.79	18.41	95.44	113.86

We see that in the case of S_2F_2 it exhibits rather unusual force field as reported by Brown and Pez [7]. The S—S stretching force constant in S_2F_2 (3.8547 md/A $^{\circ}$) is small when compared with the constants for SSF_2 , SSO and S_2 which range from approximately 4.7 to 5.0 md/A $^{\circ}$, even though the S—S bond lengths in S_2F_2 and S_2 are one and the same [12]. Further the torsion force constant in S_2F_2 is larger than those in S_2Cl_2 and S_2Br_2 . This may be due to a higher barrier against internal rotation, in this molecule. We expect a higher barrier in S_2F_2 since the ν_{tors} is high in this molecule. The relation [13] connecting the torsional frequency ν_{tors} and barrier to internal rotation V_0 is given by

$$\nu_{\text{tors}} = (n/2\pi) \sqrt{V_0/2I_r}$$

where n is the symmetry number, and I_r is the reduced moment of inertia. These novel molecular features of S_2F_2 can be explained as arising from contributions of ionic resonance structures such as $\text{FS}^+ = -\text{SF}$ and the utilization of 2 and 3 centre molecular orbitals [14].

In the case of selenium monohalides our calculated Se—Se stretching force constant values are slightly higher than those obtained by Forneris and Hennies. The other Se—Se

stretching force constants available for comparison are those for the $^{80}\text{Se}_2$ molecule ($k = 3.498 \text{ md/\AA}^\circ$, $r_e = 2.1661 \text{ \AA}$) [15] and for dimethyl diselenide. For $(\text{CH}_3)_2\text{Se}_2$ the value of $k = 1.674 \text{ md/\AA}^\circ$ has been estimated on the basis of a modified valence force field calculation. Gillespie and Pez [16] reported a value of 2.2 md/\AA° in the case of Se_4^{2+} ion and according to them this value is high. Our calculated value is nearly 1.8 md/\AA° which is nearly the same as that of $(\text{CH}_3)_2\text{Se}_2$.

The calculated mean amplitude values for sulphur monohalides agree well with the electron diffraction results within experimental errors. No electron diffraction data are available for Se_2Cl_2 and Se_2Br_2 . The reported values here are believed to be very helpful for future electron diffraction investigations.

One of the authors (S.J.) is grateful to the Council of Scientific and Industrial Research, New Delhi for financial assistance by the award of a Junior Research Fellowship. The cooperation extended by the staff of the Computer Installation at the Centre of Advanced Study in Physics, Madras (I.B.M. 1130) is gratefully acknowledged.

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