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CORRELATIONS BETWEEN FUNDAMENTAL FREQUENCIES AND PHYSICAL PARAMETERS OF SOME R_3SbX_2 COMPOUNDS

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Summary

For molecules of the type R_3SbX_2, where R is methyl or phenyl, and X is a halogen, certain correlations involving the fundamental frequencies of vibration have been established. These frequencies were found to be dependent on the atomic mass and electronegativity of the halogen and the molecular weight and moment of inertia of the molecule.

Introduction

Recently Chremos and Zingaro [1] have shown that the Teller—Redlich product rule [2] can be applied to molecules in the series R_3MY containing similar R (alkyl) substituents, bonded to a central main Group V atom M. For two molecules, R_3MY and R_3MY', in the series the main Group VI atoms Y and Y′ were treated as isotopes. These authors have established a correlation between the fundamental stretching frequency ω(M=X) and the masses and electronegativities of the atoms M and Y. We wish to report that the molecules R_3SbX_2 and $R_3SbX'_2$ can be treated in a similar way. Chremos and Zingaro confined their correlation to the A'_1 species of the point group C_{3v}. We have considered all the species of the D_{3h} point group to which the R_3SbX_2 molecules belong.

Results and discussion

When the Teller—Redlich product rule is applied to two molecules R_3SbX_2 and $R_3SbX'_2$, with similar R groups, the following equation for the A'_1 species is obtained,

$$\frac{\omega_1 \cdot \omega_2}{\omega'_1 \cdot \omega'_2} = \left[\frac{m_{X'}}{m_X}\right]^{1/2} \quad (1)$$

TABLE 1

FUNDAMENTAL FREQUENCIES OF THE $(CH_3)_3SbX_2$ MOLECULES (cm^{-1})

Species	ω_i	X: F	Cl	Br	I
A_1'	ω_1	546	538	526	508
A_1'	ω_2	465	272	168	122
A_2''	ω_3	484	282	215	144
A_2''	ω_4	215	188	172	173
E'	ω_5	591	577	569	559
E'	ω_6	210	166	160	163
E'	ω_7	146	119	91	80
E''	ω_8	245	208	200	196

where ω_1 and ω_2 are the first and second fundamental frequencies, respectively of R_3SbX_2 and m_X is the atomic mass of the halogen; while ω_1', ω_2' and $m_{X'}$ are the corresponding parameters associated with the molecule R_3SbX_2'. Eqn. 1 can be rearranged to give eqn. 2, which represents an equality between two prod

$$\omega_1 \cdot \omega_2 \cdot m_X^{1/2} = \omega_1' \cdot \omega_2' \cdot m_{X'}^{1/2} \tag{2}$$

ucts, each being a function of one type of molecule only. Thus, each side can be set equal to a constant, so we obtain eqn. 3.

$$\omega_1 \cdot \omega_2 = K_1 \cdot m_X^{-1/2} \equiv K_1 \cdot X_1 \tag{3}$$

In a similar manner the respective equations for the A_2'', E' and E'' species can be derived (eqns. 4—6).

$$\omega_3 \cdot \omega_4 = K_2 \cdot M^{1/2} \cdot m_X^{-1/2} \equiv K_2 \cdot X_2 \tag{4}$$

$$\omega_5 \cdot \omega_6 \cdot \omega_7 = K_3 \cdot M^{1/2} \cdot m_X^{-1/2} \equiv K_3 X_3 \tag{5}$$

$$\omega_8 = K_4 \cdot I^{1/2} \cdot m_X^{-1/2} \equiv K_4 \cdot X_4 \tag{6}$$

Here, ω_i ($i = 3$—8) is the i-th fundamental frequency of R_3SbX_2, while M and I are the molecular weight and moment of inertia, respectively, of the same compound.

When eqns. 3—6 are applied to the fundamental frequencies of the trimethy antimony dihalides [3] (Table 1) the correlations given in Table 2 are obtained. It can be seen that the correlation coefficients are poor and that the average standard deviations vary from 18 to 118 cm^{-1}.

TABLE 2

VIBRATIONAL CORRELATIONS FOR R_3SbX_2 MOLECULES WITH SIMILAR R GROUPS

Species	Regression equation [a]	Corr. coeff.	Stand. dev. (cm^{-1})
A_1'	$y_1 = (13.44\,X_1 - 0.63) \times 10^5$	0.9914	0.14×10^5
A_2''	$y_2 = (0.52\,X_2 - 0.72) \times 10^5$	0.9806	0.84×10^4
E'	$y_3 = (73.62\,X_3 - 66.09) \times 10^5$	0.9883	0.91×10^6
E''	$y_4 = (-0.998\,X_4 + 6.05) \times 10^2$	−0.7544	0.18×10^2

[a] y_i Denotes the product of the vibrational frequencies of the species in question.

TABLE 3

MODIFIED VIBRATIONAL CORRELATIONS FOR R_3SbX_2 MOLECULES

Species	Regression equation [a]	Corr. coeff.	Stand. dev. (cm^{-1})
A'_1	$y_1 = (27.54\,Z_1 + 0.29) \times 10^4$	0.9993	0.39×10^4
A''_2	$y_2 = (0.91\,Z_2 - 1.63) \times 10^4$	0.9993	0.17×10^4
E'	$y_3 = (12.82\,Z_3 + 13.04) \times 10^5$	0.9992	0.24×10^6
E''	$y_4 = (10.65\,Z_4 + 84.13) \times 10^0$	0.9994	0.97

[a] For y_i see Table 2.

TABLE 4

CORRELATIONS OF (Sb—X) STRETCHING VIBRATIONS OF R_3SbX_2 MOLECULES

No. of points	Species	Regression equation [a]	Corr. coeff.	Stand. dev. (cm^{-1})
4	A'_1	$y = 492.93\,Z + 15.62$	0.9994	6.57
8	A'_1	$y = 514.87\,Z + 5.77$	0.9987	8.12
4	A''_2	$y = 38.30\,Z - 16.67$	0.9968	14.38

[a] For y see Table 2.

TABLE 5

CORRELATIONS BETWEEN SYMMETRIC AND ASYMMETRIC STRETCHINGS FOR R_3SbX_2 MOLECULES

No. of points	Type	Regression equation [a]	Corr. coeff.	Stand. dev. (cm^{-1})
8	(Sb—R)	$y = 1.02\,Z + 32.73$	0.9994	5.73
8	(Sb—X)	$y = 0.96\,Z + 32.59$	0.9969	12.10

[a] For y see Table 2.

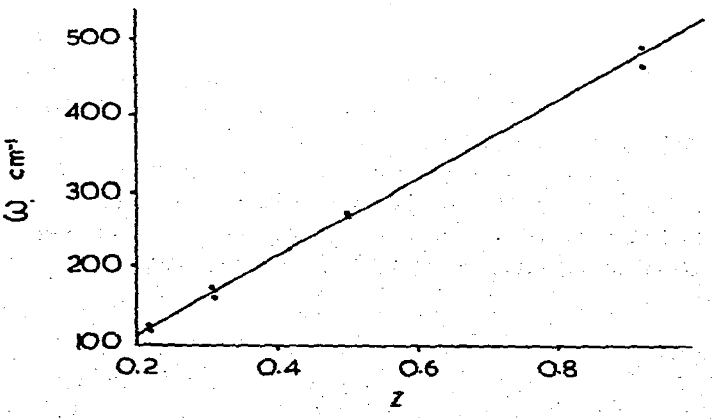

Fig. 1. Linear correlation of $(m_X^{-1/2} \cdot E_X)$ versus (Sb—X) stretching mode for R_3SbX_2 compounds.

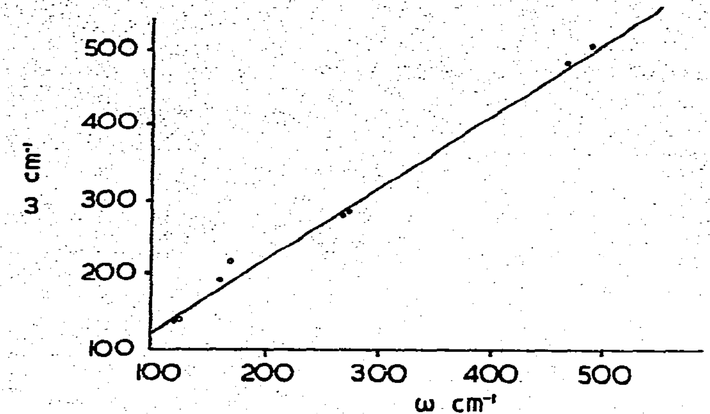

Fig. 2. Linear correlation between symmetric and asymmetric stretching modes of (Sb—X) for R_3SbX_2 compounds.

Chremos and Zingaro found empirically that better results could be obtained by modifying the correlation equations to include the Pauling electronegativity values [4] (E_X) of the halogens. Eqns. 3—6 are now written in the form given in eqns. 7—10.

$$\omega_1 \cdot \omega_2 = K_1 \cdot X_1 \cdot E_X \equiv K_1 \cdot Z_1 \tag{7}$$

$$\omega_3 \cdot \omega_4 = K_2 \cdot X_2 \cdot E_X \equiv K_2 \cdot Z_2 \tag{8}$$

$$\omega_5 \cdot \omega_6 \cdot \omega_7 = K_3 \cdot X_3 \cdot E_X \equiv K_3 \cdot Z_3 \tag{9}$$

$$\omega_8 = K_4 \cdot X_4 \cdot E_X \equiv K_4 \cdot Z_4 \tag{10}$$

The modified vibrational correlations together with their average standard deviations are listed in Table 3. They indicate a significant improvement over those given in Table 2.

It can be noted from Table 1 that the frequencies of ω_1, the (Sb—C)-symmetric stretching, and ω_4, the (Sb—C)-out of plane deformation mode, are essentially independent of the nature of the halogen. If, then, ω_1 and ω_4 are assumed to be constant, the (Sb—X) stretching mode can be given as:

$$\omega(\text{Sb—X}) = K \cdot Z \tag{11}$$

Eqn. 11 was applied initially to the four trimethylantimony dihalides and then (considering only the A_1' species) it was applied to both these four compounds and the four analogous triphenyl [3] derivatives. The results are given in Table 4. The linear correlation for the eight points of species A_1' is illustrated in Fig. 1.

We have also found that the frequencies of the symmetric (Sb—C) and (Sb—X) stretching modes are related to their respective asymmetric vibrations. The linear regression equations obtained are listed in Table 5 and a typical plot is shown in Fig. 2.

References

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