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CORRELATION OF METAL–CHALCOGEN STRETCHING FREQUENCIES OF SOME TRIALKYL GROUP Va CHALCOGENIDES*

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SUMMARY

A correlation has been observed which relates the fundamental stretching frequency, $\nu(M{=}X)$, of compounds having the general formula R_3MX, where R represents an alkyl group, M a group Va atom and X a group VIa atom. It has been shown that the location of these frequencies depends on the total mass of the molecule and the masses and electronegativities of the respective atoms, M and X.

INTRODUCTION

A number of papers which correlate the infrared absorption bands for different homologues of the R_3MX series, with specific structural parameters, have appeared in the literature. Those published prior to 1958 have been reviewed by Bellamy[1]. Thomas and Chittenden[2] have critically discussed correlations for over 900 organophosphorus compounds. Substituent effects for the case of phosphine oxides have been investigated by Griffin[3] and Zingaro and Hedges[4]. Hooge and Christen[5] and Zingaro[6] have published correlations which involve a number of phosphine sulfides.

Since the locations of $\nu(M{=}X)$ frequencies have now appeared in the literature for the R_3PS[6,7], R_3PSe[6,7], R_3AsO[8], R_3AsS[9], R_3AsSe[10], R_3SbO[11], R_3SbS[11], R_3SbSe[11], and R_3PTe[11] molecules, an attempt has been made to provide a theoretical basis for correlating all these frequencies. In order to minimize resonance effects, only alkyl derivatives have been considered.

RESULTS AND DISCUSSION

The R_3MX molecules belong to the C_{3v} point group if R is a single atom. Applying the Teller–Redlich[12] product rule to two molecules R_3MX and R_3MY with similar R substituents on the central atom M and treating X and Y as isotopes, the following formula for the three vibrations of species A_1 can be derived[13].

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$$\frac{\nu_1^i \cdot \nu_2^i \cdot \nu_3^i}{\nu_1 \cdot \nu_2 \cdot \nu_3} = \frac{(m_M \cdot m_X \cdot \Sigma M^i)^{1/2}}{(m_M \cdot m_Y \cdot \Sigma M)^{1/2}} \tag{1}$$

The ν_1, ν_2, ν_3 refer to the $\nu(M{=}X)$ stretching, $\nu(MR_3)$ stretching and $\nu(MR_3)$ bending vibrations, respectively, of the R_3MX molecule, while the ν_1^i, ν_2^i, ν_3^i denote the same vibrations for the R_3MY molecule. ΣM and ΣM^i are the total masses of the two molecules and m_X, m_M and m_Y are the masses of the individual components of R_3MX and R_3MY. The vibrations ν_2, ν_3 and ν_2^i, ν_3^i have been observed experimentally to remain essentially unchanged throughout a series of R_3MX molecules. For example, in the spectra of the trialkylstibine sulfides and selenides, these bands are located in the regions of 500 cm^{-1} and 700 cm^{-1} as they have been observed by Oswald[14] in the trialkylstibines. It is then possible to modify the expression (1) as follows

$$\frac{\nu(M{=}Y)}{\nu(M{=}X)} = \frac{(m_M \cdot m_X \cdot \Sigma M^i)^{1/2}}{(m_M \cdot m_Y \cdot \Sigma M)^{1/2}} \tag{2}$$

and by rearranging

$$\frac{\nu(M{=}X)}{[\Sigma M/(m_M \cdot m_X)]^{1/2}} = \frac{\nu(M{=}Y)}{[\Sigma M^i/(m_M \cdot m_Y)]^{1/2}} \tag{3}$$

The left hand side of equation (3) is a function of the properties of the molecule R_3MX only, while the right hand side is only a function of properties of R_3MY. Hence this function must be a constant, independent of the substituent X. Relation (3) can then be written in the form

$$\frac{\nu(M{=}X)}{[\Sigma M/(m_M \cdot m_X)]^{1/2}} = k' \tag{4}$$

or

$$\nu(M{=}X) = k' \cdot [\Sigma M/(m_M \cdot m_X)]^{1/2} \tag{5}$$

This relationship reflects only the effect of the change in mass of the X substituent on the $\nu(M{=}X)$ frequency since the force constant has been assumed to remain unchanged in its derivation. However, it has been long known that the electronic effects of the substituents influence the location of the $\nu(M{=}X)$ vibration. In order to take into consideration this influence, it was found empirically that eqn. (5) would give a better correlation if it was modified to include the Pauling electronegativities E_M, E_X of the atoms M and X, explicitly in the form:

$$\nu(M{=}X) = k \cdot [\Sigma M/(m_M \cdot m_X)]^{1/2} \cdot E_M \cdot E_X \equiv k \cdot Z \tag{6}$$

The $\nu(M{=}X)$ vibrational frequencies for different R_3MX molecules have been reported in the literature, and are listed in Table 1. In Table 2 are listed the regression equations for a number of different substituents and central atoms correlated by means of eqn. (6). Since many $\nu(M{=}X)$ absorptions are doublets, the calculations with eqn. (6) were carried with the use of both sets of frequencies for the same parameter. The lower frequency observed in the case of the trialkylstibine oxides was not included since it was considered to be too low to represent a $\nu(Sb{=}O)$ vibration. The frequency values observed in solution were used whenever possible. It can be seen that the correlation coefficients are good while the standard deviations vary from 5 to 70

TABLE 1

ν(M=X) STRETCHING FREQUENCIES OF CHALCOGENIDES (cm^{-1}), R_3MX

R	ν(P=X) (cm^{-1})				ν(As=X) (cm^{-1})			ν(Sb=X) (cm^{-1})		
	X=O	X=S	X=Se	X=Te	X=O	X=S	X=Se	X=O	X=S	X=Se
CH_3	1176[a]	570[d]	441[e]		903[f]	473[g]	337[h]			
C_2H_5	1166[b]	552[d]	442[e]		885[f]	476[g]	332[h] 358[h]	678[i]	439[i]	272[i]
n-C_3H_7	1172[a]	596[d] 583[d]	496[e]	445[i] 400[i]	888[f]	487[g] 485[g]	349[h] 357[h]	650[i]	439[i]	300[i]
n-C_4H_9	1169[c]	596[d]	511[e]	462[i] 400[i]	892[f]	487[g]	338[h] 347[h]	650[i]	440[i]	294[i]
n-C_5H_{11}		599[d] 588[d]	507[e]	467[i] 404[i]		484[g]		650[i]	438[i]	296[i]
cyclo-C_6H_{11}	1143[c]	619[d]	543[e]	518[i]	871[f]	476[g]	360[h]		440[i]	290[i]
n-C_8H_{17}	1169[c]			455[i] 405[i]	900[f]		331[h] 356[h]			

[a] Ref. 15. [b] Ref. 5. [c] Ref. 4. [d] Ref. 7. [e] Ref. 6. [f] Ref. 8. [g] Ref. 9. [h] Ref. 10. [i] Ref. 11.

TABLE 2

CORRELATIONS OF ν(M=X) VIBRATIONS FOR R_3MX MOLECULES WITH THE SAME R_3M GROUP

No. of observations	R	M	Regression equation[a]	Corr. coeff.	Stand. dev. (cm^{-1})	Slope
3	CH_3	P	$\nu(M{=}X) = -81.97+394.25\,Z$	0.997	38.9	394.25
3	C_2H_5	P	$\nu(M{=}X) = -60.75+318.33\,Z$	0.996	47.0	318.33
6	n-C_3H_7	P	$\nu(M{=}X) = 114.09+232.09\,Z$	0.984	56.0	232.09
5	n-C_4H_9	P	$\nu(M{=}X) = 152.82+203.15\,Z$	0.988	54.8	203.15
5	n-C_5H_{11}	P	$\nu(M{=}X) = 290.75+110.20\,Z$	0.956	27.7	110.20
3	n-C_8H_{17}	P	$\nu(M{=}X) = -245.99+216.52\,Z$	0.998	35.3	216.52
4	cyclo-C_6H_{11}	P	$\nu(M{=}X) = 250.89+151.93\,Z$	0.981	69.9	151.93
3	CH_3	As	$\nu(M{=}X) = -5.44+384.81\,Z$	0.998	7.1	384.81
4	C_2H_5	As	$\nu(M{=}X) = 38.82+313.18\,Z$	0.998	14.6	313.18
4	n-C_3H_7	As	$\nu(M{=}X) = 62.64+274.67\,Z$	0.999	6.3	274.67
4	n-C_4H_9	As	$\nu(M{=}X) = 53.81+255.91\,Z$	0.999	4.8	255.91
3	n-C_8H_{17}	As	$\nu(M{=}X) = 68.91+198.11\,Z$	0.999	17.6	198.11
3	cyclo-C_6H_{11}	As	$\nu(M{=}X) = 87.71+209.01\,Z$	0.998	18.0	209.01
3	C_2H_5	Sb	$\nu(M{=}X) = 90.66+264.31\,Z$	0.986	46.5	264.31
3	n-C_3H_7	Sb	$\nu(M{=}X) = 144.60+208.41\,Z$	0.989	35.5	208.41
3	n-C_4H_9	Sb	$\nu(M{=}X) = 141.63+195.14\,Z$	0.988	39.1	195.14
3	n-C_5H_{11}	Sb	$\nu(M{=}X) = 144.82+181.76\,Z$	0.989	36.1	181.76

[a] $Z=[\Sigma M/(m_M\cdot m_X)]^{\frac{1}{2}}\cdot E_M\cdot E_X$.

cm^{-1}. The discrepancies in the magnitudes of the standard deviations appear reasonable, since only three or four observations were used for each type of R_3MX molecule, and X is the only variable.

Because the central atoms, M, of the R_3MX molecules belong to the same group of the periodic system, it would perhaps be expected that their spectra should show certain additional regularities. When the slopes of various regression equations of $\nu(M{=}X)$ *versus* $[\Sigma M/(m_M \cdot m_X)]^{1/2} \cdot E_M \cdot E_X$ are compared, it becomes obvious that additional regularities do exist. For the tripropyl derivatives of antimony, arsenic and phosphorus, for example, the values of the slopes are quite close, 208.4, 274.7 and 232.1 cm^{-1}, and the same is true for comparisons among the other substituents (Table 2). This observation suggests the use of eqn. (6) for the correlation of the

TABLE 3

CORRELATIONS OF $\nu(M{=}X)$ VIBRATIONS FOR R_3MX MOLECULES

R	No. of observations	Corr. coeff.	Stand. deviation (cm^{-1})	Regression equation[a]
CH_3	6	0.994	40.0	$\nu(M{=}X) = -19.62 + 376.72\,Z$
C_2H_5	10	0.988	45.7	$\nu(M{=}X) = 50.16 + 288.96\,Z$
$n\text{-}C_3H_7$	13	0.985	43.0	$\nu(M{=}X) = 107.34 + 237.98\,Z$
$n\text{-}C_4H_9$	12	0.987	42.8	$\nu(M{=}X) = 121.62 + 215.09\,Z$
$n\text{-}C_5H_{11}$	9	0.952	35.6	$\nu(M{=}X) = 214.92 + 145.88\,Z$
cyclo-C_6H_{11}	9	0.979	57.2	$\nu(M{=}X) = 173.82 + 172.82\,Z$
$n\text{-}C_8H_{17}$	6	0.936	135.5	$\nu(M{=}X) = 52.20 + 167.81\,Z$

[a] For Z see Table 2.

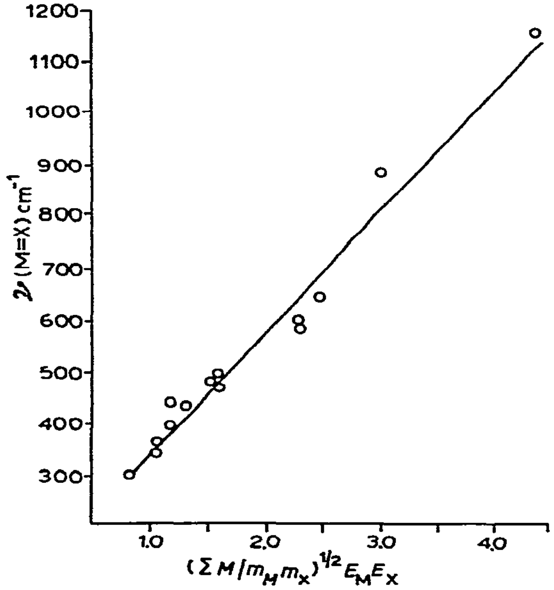

Fig. 1. Linear correlation of $\nu(M{=}X)$ in cm^{-1} *versus* $[\Sigma M/(m_M \cdot m_X)]^{\frac{1}{2}} \cdot E_M \cdot E_X$ $(=Z)$ for R_3MX compounds (R = propyl).

ν(M=X) vibration when the central atom, M, of the R_3MX molecule is varied as well as X.

The regression equations obtained are listed in Table 3 and a typical plot is shown in Figure 1. In general, the correlation coefficients are good and the standard deviations are reasonable, especially for the lower members of the alkyl derivatives. It is possible that in the case of the higher alkyl group substituents the large increase in mass is not adequately accounted for by eqn. (6).

The successful application of eqn. (6) in the case of all the R_3MX molecules indicates that the ν(M=X) vibrations are influenced mainly by two factors when R is kept constant, the mass of the molecule and the electronegativities of the atoms, M and X, and that their effects may be correlated in a relatively simple manner.

EXPERIMENTAL

The regression equations were computed with the use of a standard least-squares computer program processed at the Data Processing Center of Texas A & M University.

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