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THE VIBRATIONAL SPECTRA OF TRIMETHYL(METHYLTHIO)-STANNANE AND -GERMANE

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SUMMARY

The IR and Raman spectra of trimethyl(methylthio)germane and -stannane have been measured. Vibrational assignments are proposed, based on characteristic group frequencies and Raman polarization data.

INTRODUCTION

The vibrational spectra of the molecules $(CH_3)_3XSCH_3$ (X=Ge or Sn) are investigated as part of a study of the physico-chemical properties of compounds of the type $(CH_3)_nX(SCH_3)_{4-n}$ ($0 \leqslant n \leqslant 3$). In compounds of this type d_π–p_π bonding between the atoms X and S is possible. The presence of partial double bonding of the above type would result in hindering of the rotation about the X–S axis and consequently in molecules with more than one SCH_3 group there could exist different rotational conformations. The existence of the latter is indicated by the dipole moment of $Ge(SCH_3)_4$ and $Sn(SCH_3)_4$ which have a value of respectively 1.69 D and 1.99 D*. Free rotation in these molecules would result in zero dipole moment. An approach to the identification of the most propable conformation, using the dipole moments, was carried out by Cumper and coworkers[1] for silicon, germanium and carbon methoxy and silicon and carbon methylthio compounds. However, a more straightforward means of characterizing them is by IR and Raman spectroscopy, as one expects different symmetry and consequently different spectra for the various conformations. In the present communication we report the results for the compounds with one SCH_3 group in order to obtain a better insight into the fundamental vibrations, and their frequencies.

EXPERIMENTAL

The preparation and purification of the compounds have been published elsewhere[2].

The Raman spectra were recorded with a Coderg PH_1 double grating mono-

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* Unpublished results.

chromator using an O.I.P. He–Ne laser with an output of 200 mW for the excitation. The depolarisation ratio's were measured by two successive recordings with the polarisation vector of the incident beam turned over 90° with a half-wave plate.

The IR Spectra were recorded in the range 4000 to 200 cm^{-1} with a Perkin–Elmer model 225 spectrophotometer using CsI cells for the low frequency region. The frequencies observed and their tentative assignment to the fundamentals (discussed in the following section) are given in Table 1.

TABLE 1

IR AND RAMAN SPECTRA OF TRIMETHYL(METHYLTHIO)GERMANE AND -STANNANE

$(CH_3)_3GeSCH_3$					Assignment	$(CH_3)_3Sn\ SCH_3$				
IR		Raman				IR		Raman		
(cm^{-1})	Int.	(cm^{-1})	Rel. Int.	ρ_n		(cm^{-1})	Int.	(cm^{-1})	Rel. Int.	ρ_n
2980	s	2983		0.8	ν_{as}(C–H)(Me, SMe)	2980	s	2984		0.65
2921	s	2924	1	0.05	ν_s(C–H)(SMe)	2919	s	1919	1	0.04
2906 (sh)	s	2908	1	0.05	ν_s(C–H)(Me)					
2842	m	2844			$2\delta_{as}$(C–H)(SMe)	2843	m	2845		
2793	w	2797			$2\delta_{as}$(C–H)(Me)					
2455	vw				$2\delta_s$(C–H)(Me)					
1841	vw				ν_{as}(X–C) + δ_s(C–H)(Me)	1715	vw			
1802	vw				ν_s(X–C) + δ_s(C–H)(Me)	1695	vw			
1436	m	1436		0.81	δ_{as}(C–H)(SMe)	1435	m	1435		
1407	m	1407		0.84	δ_{as}(C–H)(Me)					
1315	m	1319			δ_s(C–H)(SMe)	1313	m	1320		
1235	s	1247	0.5	0.35	δ_s(C–H)(Me)	1186	m	1197	2	0.27
956	m	962			$\rho(CH_3)$(SMe)	957	m	961		
824	vs	829			$\rho(CH_3)$(Me)	771	vs	773		
753	m	757			$\rho(CH_3)$(Me)	718	w			
700	m	703	2	0.15	ν(S–C)	699	m	699	2	0.2
602	vs	605	2	0.68	ν_{as}(X–C)	531	vs	533	3	0.60
564	s	570	10	0.04	ν_s(X–C)	509	s	512	15	0.04
385	vs	385	5	0.11	ν(X–S)	341	s	339	5	0.13
222	w	226	2	0.51	Bending X–S–C			192	2	0.38
		191	4	0.75	$\delta(C_3$–X) en $\rho(C_3$–X)			146	5	0.65
		174 (sh)	2		Bending C_3–X–S					
		135			Twisting X–S–C					

DISCUSSION

Skeletal vibrations

Taking into account the mutual repulsion forces of the H atoms, one would expect the C atom of the S–C bond to be located in one of the planes of symmetry of the XC_3 group, so that the molecule would have only one plane of symmetry (the X–S–C plane). Accordingly, these molecules belong to the C_s point group and there should be eight vibrations symmetric to the plane (class a') and four anti-symmetric (class a'').

Four of the symmetric vibrations should be close to the four anti-symmetric vibrations, since if the X–S–C groups were linear they would coïncide and form the four double degenerate vibrations of the point group C_{3v}. The splitting would be expected to be smaller, if detectable at all, for the X–C_3 vibrations, but it should be larger for the deformations of the C_3–X–S–C chain. All the fundamentals were Raman and IR active. In the Raman effect the *a'* vibrations should be polarised.

The considerations mentioned above, together with the data for Me_3GeCl[3] and Me_3SnCl[4] allow the assignment of the fundamentals in a straightforward manner. However, in the region below 250 cm^{-1} an unambiguous assignment is difficult. By analogy with the location of the GeC_3 symmetrical deformation and the two rockings in $GeMe_4$ and Me_3GeCl the strong band at 191 cm^{-1} is ascribed to these fundamentals. A shoulder at a somewhat lower frequency (174 cm^{-1}) is attributed to the C–Ge–S bending, which is in accordance with the absorption region of the C_3–Ge–Cl bending in Me_3GeCl. In the Sn compound these two bands overlap each other and yield a broad band at 146 cm^{-1}; this shift and the accidental coïncidence may be due to the higher mass of the central atom.

A band at 226 cm^{-1} is polarised, and we therefore ascribe it to the Ge–S–C in plane bending. The S–C twisting is then represented by the remaining band at 136 cm^{-1}. In the spectrum of $Me_3Sn(SCH_3)$ the Sn–S–C in plane bending is also present at 192 cm^{-1}. Probably the S–C twisting is overlapped by the C_3–Sn and C_3–Sn–S vibrations, the frequencies of which are more dependent on mass than that of the S–C twisting.

CH_3 vibrations

A comparison of the spectra of Me_3XSCH_3 with those of Me_4X[3], $X(SMe)_4$* and Me_3GeCl[3,5] enables us to make an unambiguous assignment for the CH_3 fundamentals bonded directly to the X atom as well as for those bonded to the sulfur atom.

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