Vibrational Spectra and Force Constants of Symmetric Tops, IL [1]

The ν_3 Fundamental of Unstable H_3SnCl, H_3SnBr and H_3SnI Studied by High Resolution FT Spectroscopy of Monoisotopic Species

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Fourier Transform far infrared spectra of unstable stannyl chloride, bromide and iodide have been measured in the gas phase with a resolution of 0.04 cm^{-1}. At pressures below 10 mbar, their lifetimes at 0 °C in preconditioned cells were found to be 10–30 min. The ν_3 fundamentals and hot bands of the series $(n+1)\,\nu_3 - n\,\nu_3$ have been observed. Rotational J structure has been resolved for monoisotopic samples, and band origins ν_3^0, anharmonicity constants x_{33}, α_3^B and D_J^0 values have been determined from the rovibrational analyses. The following ν_3^0 values were obtained: $H_3{}^{116}Sn^{35}Cl$ 375.470 (5), $H_3{}^{116}Sn^{37}Cl$ 367.689 (6), $H_3{}^{116}Sn^{79}Br$ 263.566 (5) and $H_3{}^{116}SnI$ 209.759 (6) cm^{-1}.

1. Introduction

Only very few reports concern the synthesis and characterization of the unstable stannyl halide species H_3SnCl, H_3SnBr and H_3SnI [2–4]. These species were prepared at low temperature from SnH_4 and the respective hydrogen halides, but due to their pronounced instability even at low temperature and in the gas phase at low pressure, vibrational spectra unambiguously attributable to these species could not be obtained. Convincing evidence for their existence comes from the ^1H NMR [4] and mass spectra [3], and some ground state constants were determined by microwave spectroscopy [5–7]. It was reported that the mw experiments performed at low temperature required continuous resampling, and lifetimes of a few minutes were noted.

The increase in sensitivity and precision of infrared spectroscopy by FT techniques and diode lasers since the early seventies makes an investigation of the gas phase IR spectra of these molecules seem promising. As these investigations were aimed at resolving rovibrational structure, the use of monoisotopic samples was compulsory because both tin (0.95% ^{112}Sn, 0.65% ^{114}Sn, 0.34% ^{115}Sn, 14.24% ^{116}Sn, 7.57% ^{117}Sn, 24.01% ^{118}Sn, 8.58% ^{119}Sn, 32.97% ^{120}Sn, 4.71% ^{122}Sn, 5.98% ^{124}Sn) and the halogens (75.5% ^{35}Cl, 24.5% ^{37}Cl; 50.5% ^{79}Br, 49.5% ^{81}Br) are composed of several isotopes which would cause inextricable congestion with eventually complete loss of rotational structure for the resolution (4×10^{-2} cm^{-1}) available to us. This requirement, however, excluded a continuous flow of stannyl halides through the cell, and we were forced to look for possibilities to record extended high resolution spectra of single batches.

This technique has been applied recently to the ν_1/ν_4 band of $H_3{}^{116}Sn^{35}Cl$ appearing in a region, ~ 1900 cm^{-1}, where additional blending by strong absorptions of SnH_4 occurred [8]. Such interference with SnH_4 absorptions does not affect the two lowest-lying fundamentals ν_3 and ν_6 of stannyl halides, but these vibrations, which are less intense in the IR than ν_1/ν_4 and ν_2/ν_5, fall into spectral regions (200–400 cm^{-1} and 400–500 cm^{-1} respectively) which are more difficult to study.

In spite of the great experimental difficulties we decided to study first the ν_3 fundamental which is associated with the tin-halogen stretching motion and which is not expected to be perturbed. The molecular parameters of the $v_3 = 1$ state reflect tin-halogen bonding and may be compared with those of the corresponding trimethyl tin halides [9] and the series of silyl [10–12] and germyl halides [13] recently studied in our laboratory.

The tin-halogen stretching vibrations are expected to occur close to 400, 250 and 200 cm^{-1} for chloride, bromide, and iodide, respectively. While a

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pair of bands at 383 and 370 cm^{-1} in the gas phase spectrum of H_3SnCl was assigned to ν_3 [3], an absorption at 283 cm^{-1} observed in the solid state has been attributed to ν SnCl [2]. On the other hand, a frequency $\nu_3 \cong 80$ cm^{-1} has been deduced for H_3SnI from the vibrational satellites of the rotational lines [7].

In the following we report on our attempts to measure and to analyze the IR spectrum with a resolution of $\sim 4 \times 10^{-2}$ cm^{-1} of gaseous $H_3{}^{116}Sn^{35}Cl$, $H_3{}^{116}Sn^{37}Cl$, $H_3{}^{116}Sn^{79}Br$ and $H_3{}^{116}SnI$ in the region of the ν_3 fundamental.

2. Experimental

The synthesis of H_3SnCl, H_3SnBr and H_3SnI was achieved from $^{116}SnH_4$ (98% ^{116}Sn) and the respective hydrogen halides $H^{35}Cl$ (99.3% ^{35}Cl), $H^{37}Cl$ (98.2% ^{37}Cl), $H^{79}Br$ (98.6% ^{79}Br) and HI as previously described [8]. H_3SnCl and H_3SnBr were prepared in a small trap connected to the absorption cell which was held at − 78 °. Typically, 1 mmol SnH_4 and 1 mmol HCl and HBr were reacted for 30 and 10 min, respectively, volatile material pumped off and the halides evaporated into the absorption cell which was held at 0 °C. H_3SnI which is even less stable than the chloride and bromide was directly prepared in the absorption cell by reacting 1 mmol SnH_4 and 2 mmol HI at − 80 ° for 5 min. After removal of volatile material the cell was brought to ~ 0 °C within 10 min, and blocks of interferograms were measured during warm-up. After 10 min at 0 °, all H_3SnI had decomposed.

A double jacketed 17 cm stainless steel cell equipped with polythene windows was employed, precooled N_2 being used to adjust the temperature between − 5 and 0 °. The total pressure in the cell was of the order of 10 mbar. A Nicolet Series 8000 vacuum interferometer operating with an unapodized resolution of 0.035 cm^{-1} was used. It was equipped with a 6 μ mylar beam splitter for the investigation of H_3SnCl and H_3SnBr while a 25 μ mylar beam splitter was employed for H_3SnI. A Cu:Ge detector was used for the spectral region > 340 cm^{-1}, while a bolometer was used in the region < 350 cm^{-1}. Both detectors were operated at 4.2 K. Due to the instability of the molecules in question, the maximum measuring time was 5, 15 and 10 min for chloride, bromide and iodide, respectively.

Calibration was with H_2O rotational lines [14], the absolute wave number accuracy of peakfinder-evaluated lines is better than $\pm 2 \times 10^{-3}$ cm^{-1}.

3. Results

In analogy to the related molecules H_3GeX [13] the ν_3 fundamental of the prolate symmetric top molecules H_3SnX, $A_0 \sim 2.1$ cm^{-1}, $B_0 \sim 0.11$, 0.056 and 0.038 cm^{-1}, X = Cl, Br, and I respectively, should exhibit PQR structure. Due to small α_3^A values ($< 2 \times 10^{-3}$ cm^{-1}) the P and R branches are expected to consist of J clusters which cannot be further resolved into K lines with the available resolution.

The ν_3 transitions are accompanied by hot bands, of which those belonging to the series $(n+1)\nu_3 - n\nu_3$ are most intense. At 270 K, the following Boltzmann factors relative to $\nu_3 = 1$ are calculated:

	$n = 1$	$n = 2$
$H_3{}^{116}Sn^{35}Cl$	0.27	0.06
$H_3{}^{116}Sn^{37}Cl$	0.28	0.06
$H_3{}^{116}Sn^{79}Br$	0.49	0.18
$H_3{}^{116}Sn^{127}I$	0.66	0.32

Both Q branches and J clusters in the P and R branches of the $2\nu_3 - \nu_3$ hot bands are clearly evident in all spectra, Figs. 1−3, and these hot bands have also been included in the band contour simulation. The hot band $3\nu_3 - 2\nu_3$ has been observed only in the best spectrum, Figure 2.

In the absence of resolvable K structure, the observed spectra can be analyzed with polynomial least squares methods. Observed P and R branch peaks were fitted to the equation

$$\nu^{P,R} = a + bm + cm^2 + dm^3$$

with

$m = J'' + 1$ in the R and $m = -J''$ in the P branch .

The coefficients a to d are related to molecular parameters according to

$$\begin{aligned} a &= \nu_0 + [(A' - A'') - (B' - B'')]K^2 , \\ b &= B' + B'' - 2D_{JK}K^2 , \\ c &= B' - B'' - (D'_J - D''_J) \cong -\alpha^B , \\ d &= -2(D'_J + D''_J) . \end{aligned}$$

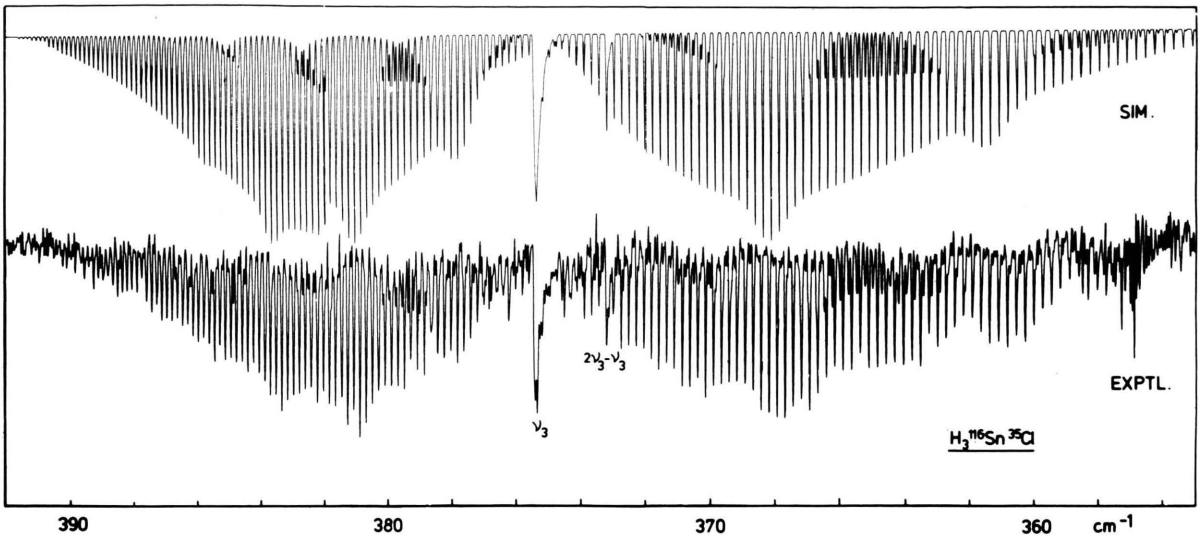

Fig. 1. Experimental (lower trace) and simulated spectrum (upper trace) of $H_3{}^{116}Sn^{35}Cl$ in the ν_3 region.

Table 1. Coefficients of the polynomials $\nu^{P,R} = a + bm + cm^2 + dm^3$ and standard deviations (cm^{-1}) of stannyl halides.

		a	b	$c \times 10^4$	$d \times 10^8$	$\sigma \times 10^3$
$H_3{}^{116}Sn^{35}Cl$	ν_3	375.465(1)	0.22035(2)	−4.778 (2)	−14.2(4)	3.3
	$2\nu_3-\nu_3$	373.232(2)	0.21930(3)	−4.689 (5)	−	5.4
$H_3{}^{116}Sn^{37}Cl$	ν_3	367.684(2)	0.21143(3)	−4.474 (4)	−12.5(6)	5.0
	$2\nu_3-\nu_3$	365.553(5)	0.21013(6)	−4.455(10)	−	12.9
$H_3{}^{116}Sn^{79}Br$	ν_3	263.561(1)	0.11332(2)	−1.756 (2)	− 4.1(2)	4.0
	$2\nu_3-\nu_3$	262.377(3)	0.11308(5)	−1.702 (8)	−	6.0
$H_3{}^{116}Sn^{127}I$	ν_3	209.754(2)	0.07524(4)	−0.965 (4)	− 3.0(5)	5.5
	ν_3	209.756(3)	0.07509(3)	−0.973 (4)	−	6.7

H_3SnCl

The spectrum of $H_3{}^{116}Sn^{35}Cl$ is illustrated in Fig. 1 and may be compared with a contour simulation including ν_3 and $2\nu_3-\nu_3$ obtained with the parameters listed in Table 2. An essentially identical spectrum was obtained for the ^{37}Cl species, though due to the energy cut-off by the Cu:Ge detector the low-frequency end was even more noisy than for $H_3{}^{116}Sn^{35}Cl$. $^QP/^QR$ (J'') clusters were assigned up to $J''=73/78$ and 77/72 for ν_3 of $H_3{}^{116}Sn^{35}Cl$ and $H_3{}^{116}Sn^{37}Cl$ respectively; for $2\nu_3-\nu_3$, J''_{max} was 79/76 and 69/75 respectively. In the polynomial fit, some peaks which were broad or apparently blended were given lower weight.

For the hot bands, the number of data was considerably smaller than for ν_3 because of the lower intensity. Therefore it was physically not meaningful to expand the polynomial beyond the quadratic term. The coefficients of the polynomial fits are set out in Table 1. Lists of observed and calculated frequencies of peaks have been deposited as supplementary material [15].

H_3SnBr

The spectrum of $H_3{}^{116}Sn^{79}Br$ and its simulation including ν_3 and $2\nu_3-\nu_3$ are shown in Figure 2. Peaks of ν_3 and $2\nu_3-\nu_3$ were assigned and subjected to a polynomial fit for $J'' \leqq 99/130$ and 69/28 ($^QP/^QR$) respectively. As for H_3SnCl, the cubic coefficient was not determined significantly for $2\nu_3-\nu_3$. The coefficients of the polynomials are listed in Table 1.

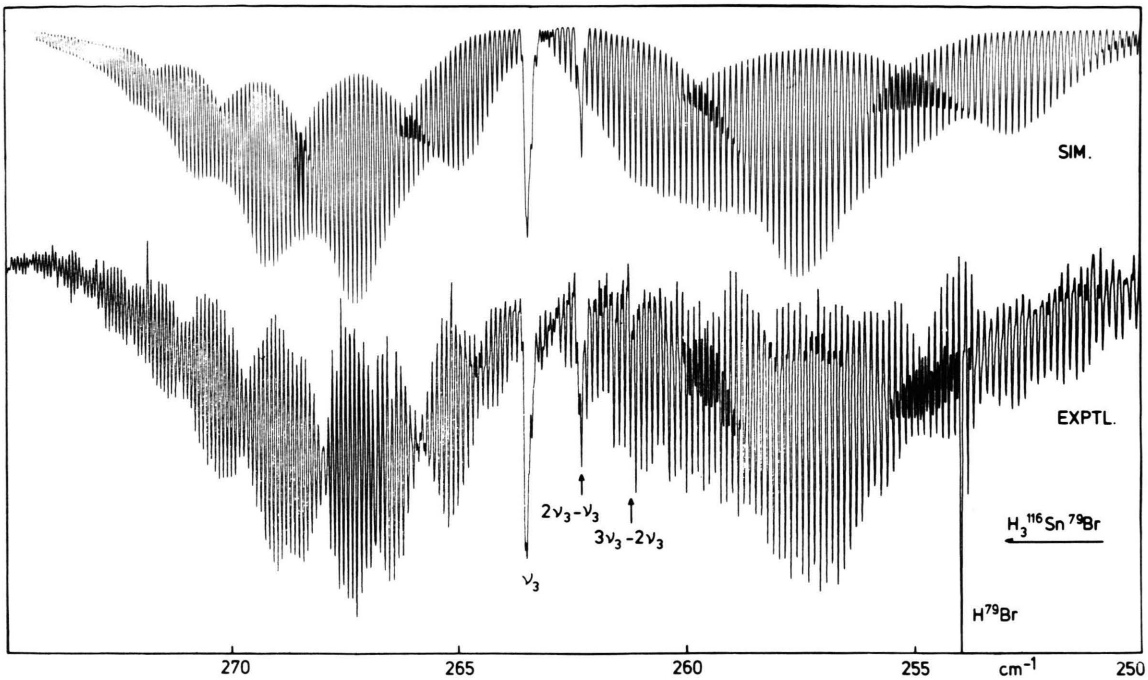

Fig. 2. Experimental (lower trace) and simulated spectrum (upper trace) of $H_3{}^{116}Sn^{79}Br$ in the ν_3 region.

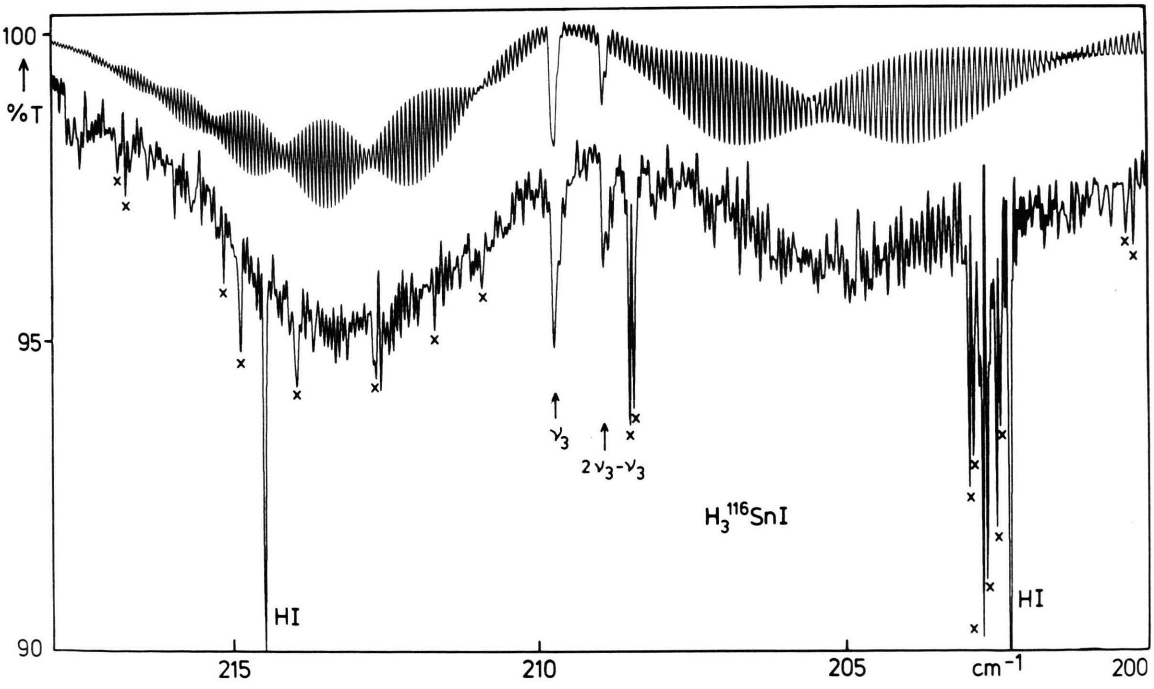

Fig. 3. Experimental (lower trace) and simulated spectrum (upper trace) of $H_3{}^{116}SnI$ in the ν_3 region. Major rotational lines of H_2O are marked.

Table 2. Molecular parameters of stannyl halides (cm^{-1}).

	$H_3{}^{116}Sn^{35}Cl$	$H_3{}^{116}Sn^{37}Cl$	$H_3{}^{116}Sn^{79}Br$	$H_3{}^{116}SnI$
From mw spectroscopy	[5]		[6]	[7]
B_0	0.110431(21)	–	0.0567469(3)	0.0376147(3)
$D_{JK}^0 \times 10^7$	–	–	2.30(13)	1.37(10)
$(B_3 - B_0) \times 10^4$	–	–	–	−0.964(10)
From present work				
ν_3^0	375.470(5)	367.689(6)	263.566(5)	209.759(6)
x_{33}	−1.117(2)	−1.066(5)	−0.592(3)	−0.405(10) [a]
B_0	0.11041(1)	0.10594(2)	0.05675(1)	0.03767(2)
$(B_3 - B_0) \times 10^4$	−4.778(2)	−4.474(4)	−1.756(2)	−0.965(4)
$(A_3 - A_0) \times 10^4$ [a]	−8		−8	−6
$D_J^0 \times 10^8$	3.55(10)	3.13(15)	1.02(5)	0.75(13)
$4B^3/(\nu_3)^2 \times 10^8$	3.8	3.5	1.1	0.48

[a] From band contour simulation.

Table 3. Observed/calculated isotopic shifts (cm^{-1}).

from	^{118}Sn	^{120}Sn
$H_3{}^{116}Sn^{35}Cl$	−0.77/−0.706	−1.47/−1.390
$H_3{}^{116}Sn^{79}Br$	−0.91/−0.871	−1.76/−1.716
$H_3{}^{118}Sn^{81}Br$		−0.85/−0.852
$H_3{}^{116}SnI$	0.90/−0.897	−1.80/−1.768
$H_3{}^{116}Sn^{35}Cl$	^{37}Cl −7.782/−7.933	
$H_3{}^{118}Sn^{79}Br$	^{81}Br −1.92/−1.969	
$H_3{}^{120}Sn^{79}Br$	^{81}Br −1.92/−1.975	
Stretching force constants (10^2 Nm^{-1})		
SnCl 2.245	SnBr 1.942	SnI 1.592

H_3SnI

The spectrum of H_3SnI, Fig. 3, was most difficult to measure. Due to the smallness of $2B$, ~0.075 cm^{-1}, with respect to the resolution available, ~0.04 cm^{-1}, the low vapor pressure at 0 °C, the unavoidable presence of residual water in the interferometer and the high relative intensity of hot bands, the spectrum is not as good as those of the lighter species are. Rotational J structure was however clearly evident in favorable regions of the P and R branch, where hot band peaks are "in phase" with those of ν_3. ^QP and ^QR peaks with $J'' \leqq 80$ and 99 were assigned and subjected to the polynomial fit, Table 1. The hot band $2\nu_3 - \nu_3$ was only identified by its Q branch, though it was included in the simulation.

K structure

Though K structure has not been resolved, the shape of the Q branches gives some indication for the size of α^A. By experience, the quantity $\alpha^A - \alpha^B$ is easily overestimated if determined from the shape of the Q branch because its low-frequency wing may well bury weak hot bands. Therefore the α^A values obtained by band contour simulation, though small anyway, should be considered as upper limits. For the K correction of the a values from Table 1 it was assumed that the J peaks correspond to $K = 3$ and the quantity $\alpha^A - \alpha^B$ is $\sim 5 \times 10^{-4}$. Thus, $5(5) \times 10^{-3}$ cm^{-1} were added to the a coefficients to yield the ν_0 values of Table 2.

4. Discussion

The ν_3 fundamentals of the pilot stannyl halide species have been detected and rotationally resolved in their Far Infrared spectra. It turns out that the absorptions previously observed at 383 and 370 cm^{-1} [3] could well be attributable to the ν_3 fundamental of naturally abundant H_3SnCl. We have also made some measurements on natural material. Though no rotational structure could be resolved, some isotope shifts of Q branches which are listed in Table 3 could be measured. It is evident that these can be well reproduced by a model which treats H_3SnX as diatomic molecules. Therefore the quoted "diatomic" SnX force constant should be quite reliable. Similarly the centrifugal distortion constant D_J^0 calculated according to the diatomic approximation $D_J^0 = 4B^3/\omega^2$ agrees within 3σ with the experimental values.

Rotational constants B_0 of H_3SnCl and H_3SnBr agree within their standard deviations with those of [5] and [6]. The slight B_0 difference for H_3SnI has an explanation. In the mw investigation of the 13 ← 12 and 14 ← 13 transitions, no distortion due to D_J^0 was observed, and this was fixed to zero. If an averaged correction $+2D_J^0\ (J+1)^2$ with $\bar{J} = 1/2\ (12+13)$ is applied to B_0, assuming $D_J^0 = 0.5 \times 10^{-8}\ \mathrm{cm}^{-1}$, an improved B_0 value, 0.0376165 cm^{-1}, is calculated. If D_J^0 is fixed to this value in the rovibrational analysis of ν_3, a smaller value, 0.037645(15) is obtained, which is now closer than 2σ to the mw value. If the value resulting from the ν_3 fit with D_J^0 constrained to zero, $B_0 = 0.037596(15)$, is compared with the mw value, even closer agreement is observed. Thus, we conclude that the high-J peaks employed in the least squares refinement are systematically blended. Assuming $\Delta D_J^0 = 0.25 \times 10^{-8}$, this systematic shift $\Delta\nu = 4\Delta D_J^0\ (J+1)^3$ is of the order of $5 \times 10^{-3}\ \mathrm{cm}^{-1}$ for $J'' = 80$.

The observed SnX stretching frequencies are at the upper end of the range quoted for methyl tin halides $(CH_3)_{4-n}SnX_n$, 383−331, 264−235 and 207−174 cm^{-1} for X = Cl, Br, and I [16], but substantially higher than in $(CH_3)_3SnX$ compounds (331, 234, and 189 cm^{-1} [9]). The extrapolated ν_3 frequency of H_3SnI, ~ 80 cm^{-1} [7], turns out to be immaterial. An interesting comparison of ν_3 rovibrational parameters for the entire series $H_3E^{IV}X$ with E^{IV} = Si, Ge, and Sn; X = Cl, Br, and I is now possible. This is set out in Table 4.

We were surprised to note how close the respective parameters of isobaric compounds with comparable mass ratios, $E^{IV}:X \cong X:E^{IV}$, are. Thus, H_3SiI and H_3SnCl are very similar, but different from H_3GeBr, though all three molecules are about isobaric. Similarly, H_3SiBr and H_3GeCl as well as H_3GeI and H_3SnBr are closely related pairs. The methyl halides are excluded from this comparison because they would correspond to $H_3E^{IV}F$ species which are not considered here.

Table 4. Comparison of rounded ground and $v_3 = 1$ excited state parameters of $H_3E^{IV}X$ molecules (cm^{-1}; M in amu).

		X = ^{35}Cl	^{79}Br	^{127}I
$H_3{}^{28}SiX$	M	66	110	158
	ν_3^0	550.94	430.76	362.82
	x_{33}	−2.10	−1.41	−1.10
[10−12]	B_0	0.2226	0.1442	0.1073
	$D_J^0 \times 10^7$	1.37	0.63	0.36
	$\alpha_3^B \times 10^3$	1.291	0.658	0.444
$H_3{}^{74}GeX$	M	112	156	204
	ν_3^0	422.93	306.59	248.98
[13]	x_{33}	−1.55	−0.77	−0.56
	B_0	0.1446	0.0793	0.0544
	$D_J^0 \times 10^7$	0.62	0.20	0.12
	$\alpha_3^B \times 10^3$	0.689	0.282	0.167
$H_3{}^{116}SnX$	M	154	198	256
	ν_3^0	375.47	263.57	209.76
This work	x_{33}	−1.12	−0.59	−0.40
	B_0	0.1104	0.0567	0.0376
	$D_J^0 \times 10^7$	0.36	0.10	0.06
	$\alpha_3^B \times 10^3$	0.478	0.176	0.096

The results obtained in the present study give a reliable picture of the $n\nu_3$ vibrational states for $n = 1, 2$ and, in part, 3. The multiply excited $n\nu_3$ states have been shown to perturb rovibrational states involving other fundamentals if levels suited for interactions are close. Therefore the present analysis of the $n\nu_3$ states is of importance for forthcoming rovibrational studies of stannyl halides in other frequency regions.

Acknowledgement

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