Fourier Transform IR Spectra and Rovibrational Investigation of Monoisotopic $H_3{}^{116}Sn^{35}Cl$, $H_3{}^{116}Sn^{79}Br$ and $H_3{}^{116}SnI$ in the ν_6 Region

M. Betzel, H. Bürger, and A. Rahner

FB 9 – Anorganische Chemie, Universität – Gesamthochschule, Wuppertal, West Germany

Z. Naturforsch. **41 a**, 1009–1014 (1986); received April 1, 1986

Fourier transform infrared spectra in the ν_6 region of the unstable monoisotopic species $H_3{}^{116}Sn^{35}Cl$, $H_3{}^{116}Sn^{79}Br$ and $H_3{}^{116}SnI$ have been recorded with a solution of 0.04 cm^{-1} (0.12 cm^{-1} for H_3SnI). Rotational J and K structure of the ν_6 fundamental has been resolved for H_3SnCl and H_3SnBr, while Q branches were measured for H_3SnI. The hot bands $(\nu_3 + \nu_6) - \nu_3$ and $2\nu_6^{\pm 2} - \nu_6^{\pm 1}$ have been identified. A rovibrational analysis has been performed, and the following band centers (for given A_0 values) have been determined: $H_3{}^{116}Sn^{35}Cl$ 488.786(2), $H_3{}^{116}Sn^{79}Br$ 473.493(2) and $H_3{}^{116}SnI$ 453.680(9) cm^{-1}.

1. Introduction

In previous contributions from our laboratory we have reported the first unambiguous detection by infrared spectroscopy of the unstable stannyl halides H_3SnCl, H_3SnBr and H_3SnI [1, 2]. Employing monoisotopic species, J structure of the ν_3 band has been resolved, and a rotational analysis has been performed [2]. Furthermore, the ν_1/ν_4 pair of $H_3{}^{116}Sn^{35}Cl$ near 1900 cm^{-1} involved in Coriolis x, y resonance has been identified in spite of the difficulties encountered by the overlap with strong SnH_4 absorptions unevitably present in this region of the spectrum.

The rotational analysis of the fundamentals ν_1/ν_4 near 1900 cm^{-1} and ν_2/ν_5 near 700 cm^{-1} requires a secure knowledge of the low-lying fundamentals ν_3 and ν_6 because multiply excited states involving ν_3 and ν_6 quanta may interact with ν_1/ν_4 and ν_2/ν_5 by different coupling mechanisms as has been shown for the lighter methyl, silyl and germyl homologues. In proceeding with the rotational analysis of the fundamental vibrations of the stannyl halides, we therefore deal in the present study with the lowest-lying perpendicular fundamental ν_6 which is associated with the SnH_3 rocking mode.

The stannyl halides are short-lived species decomposing in the gas phase at 0 °C within minutes. A major complication is the fact that tin is the element with the greatest number of naturally occurring isotopes. Thus the use of rigorously monoisotopic samples is compulsory if a measurement of lines is intended. We have chosen for this purpose as pilot isotope ^{116}Sn, natural abundance 14.24%, as well as ^{35}Cl and ^{79}Br, natural abundances 75.5 and 50.5% respectively. The low quantity of isotopically enriched samples available and the rapid decomposition of the stannyl halides upon condensation prohibited the use of continuous flow techniques and employment of large cells with great path lengths. Considering the limited measuring time available, the relatively low intensity of the ν_6 fundamental lowered the quality of the spectra, and a further limit was given by the available resolution (4×10^{-2} cm^{-1}). In spite of these difficulties we were able to detect for the first time the ν_6 fundamental of the stannyl halides and to unambiguously assign rotational features. In the present contribution (part LIII, for part LII of this series cf. [3]) we report on our results.

2. Exprimental

The synthesis of the monoisotopic species has been described previously [2]. A double-jacketed 17 cm stainless steel cell equipped with KBr windows was employed, cold N_2 being used to adjust the temperature between – 5 and 0 °C. The total pressure in the cell was of the order of 10 mbar. A Nicolet Series 8000 vacuum interferometer achiev-

Reprint requests to Prof. Dr. H. Bürger, Universität – Gesamthochschule, Gaußstraße 20, D-5600 Wuppertal 1.

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ing an unapodized resolution of 0.04 cm^{-1} was used. It was equipped with a 3 μ mylar beam splitter, and a Cu:Ge detector operating at 4.2 K was used. Measuring times on the order of 5 to 15 min were available before complete decomposition of the samples was noted, and blocks of interferograms were collected consecutively and examined later. Calibration was with H_2O rotational lines [4]; the absolute wavenumber accuracy of peakfinder-evaluated lines is better than $\pm 2 \times 10^{-3}$ cm^{-1}.

3. General

The ν_6 fundamental of the stannyl halides is similar to that of the silyl and, in particular, germyl halides H_3GeCl [5], H_3GeBr [6] and H_3GeI [7], all of which are prolate symmetric tops with a large $A:B$ ratio. For details the reader is referred to [5–7].

The spectra comprise unresolved, strong Q branches with alternating intensity, which are accompanied by hot bands, and rotational lines. The intensities of the most prominent hat bands at 270 K relative to the cold bands are as follows:

	$(\nu_3+\nu_6)-\nu_3$	$2\nu_6^{\pm 2}-\nu_6^{\pm 1}$	$2\nu_6^0-\nu_6^{\pm 1}$
$H_3{}^{116}Sn^{35}Cl$	0.14	0.16	0.08
$H_3{}^{116}Sn^{79}Br$	0.24	0.17	0.08
$H_3{}^{116}SnI$	0.33	0.19	0.09

The intensity alternation due to hydrogen nuclear spin gives double intensity to transitions of ν_6 and $(\nu_3+\nu_6)-\nu_6$ with $K''=3p$, $p=0, 1, 2, 3, \ldots$, while double intensity for $K''=3p\pm 1$ is associated with $\Delta K=\pm 1$ transitions of $2\nu_6^{\pm 2}-\nu_6^{\pm 1}$ and $\Delta K=\mp 1$ transitions of $2\nu_6^0-\nu_6^{\pm 1}$.

Since no lines due to the hot bands could be assigned with certainty, relative displacements of Q branch edges of $(\nu_3+\nu_6)-\nu_3$ and $2\nu_6^{\pm 2}-\nu_6^{\pm 1}$ from ν_6 were determined by polynomial methods, Table 3. From these displacements x_{36} and $(x_{66}+g_{66})$ were determined using the appropriate formulae. Since the hot band $(2\nu_6^0-\nu_6^{\pm 1})$ appeared to be buried under the Q branches of ν_6, as was also observed for the germyl halides [5–7], the quantity $(x_{66}-g_{66})$ and hence x_{66} and g_{66} could not be determined.

Excited state parameters of ν_6 of $H_3{}^{116}Sn^{35}Cl$ and $H_3{}^{116}Sn^{79}Br$ were determined from individual rotational lines which, for a fixed ground state

$$E_0(J,K)=(A_0-B_0)\,K^2+B_0\,J(J+1) - D_J^0\,J^2(J+1)^2-D_{JK}^0\,J(J+1)\,K^2-D_K^0\,K^4 \quad (1)$$

were fitted to excited state energies

$$E_6(v_6,l_6,J,k)=\nu_6^0+(A_6-B_6)\,k^2+B_6\,J(J+1) - D_J^6\,J^2(J+1)^2-D_{JK}^6\,J(J+1)\,k^2-D_K^6\,k^4 - [2A\,\zeta_6^z-\eta_{6J}\,J(J+1)-\eta_{6K}\,k^2]\,k\,l_6. \quad (2)$$

Perturbations due to $\Delta l=\Delta k=\pm 2$ interactions affecting the $k\,l=1$ sublevels were accounted for by an off-diagonal element:

$$\langle v_6=1, l_6=+1, J, k+1 \mid H \mid v_6=1, l_6=-1, J, k-1\rangle = -2F_6[J(J+1)-k(k+1)]^{1/2} \cdot [J(J+1)-k(k-1)]^{1/2} \quad (3)$$

with the sign convention of [8], $q_6^+=4F_6$.

The least squares program MILLI [9] was used for the numerical treatment of the data. For $H_3{}^{116}SnI$ we proceeded in a different way. Due to the smallness of B_0, 0.038 cm^{-1}, the extensive population of vibrationally excited levels at 270 K and the overlap of J systems belonging to different K values, the interferometer available to us did not permit resolution of rotational J structure. Therefore this structure was fully suppressed by measuring the spectra with a resolution of 0.12 cm^{-1}. Q branch edges were treated as first Q branch lines $[{}^RQ_K(J=K+1), {}^PQ_K(J=K)]$ with (B_6-B_0) determined by band contour simulation. Clearly a larger uncertainty has to be ascribed to the excited state parameters, in particular ν_6^0, of H_3SnI.

4. Rovibrational Analysis

4.1 Ground State

Some ground state constants, Table 1, are available from mw measurements [10–12]. Further data come from the ν_3 analysis [2], while parameters not otherwise accessible were computed by a harmonic force field (D^0's) or deduced from the predicted geometry (A_0). The quantities not directly measured and the values to which they are related (ν_0, $A\zeta^z$, η_J, η_K) should be considered with great caution.

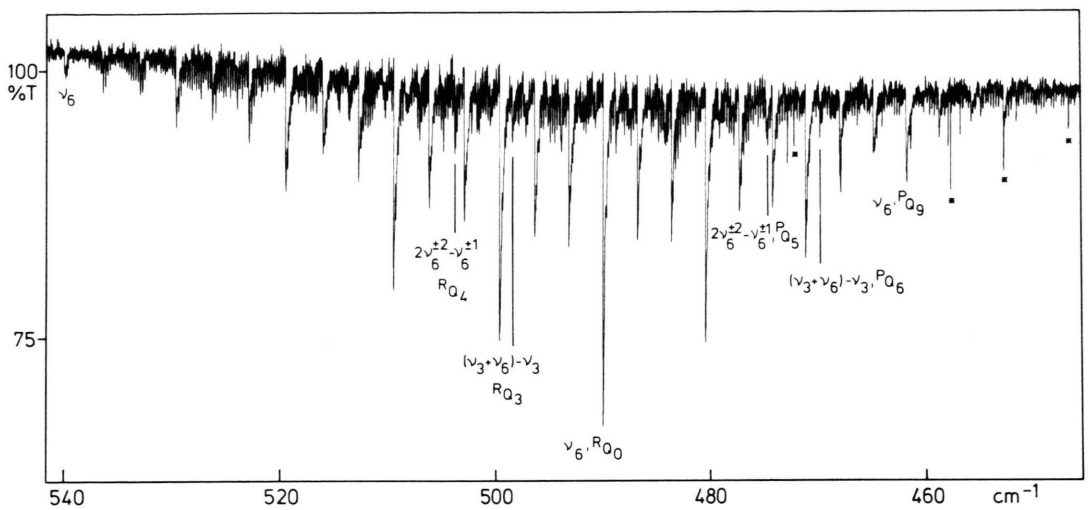

Fig. 1. Survey spectrum of $H_3{}^{116}Sn^{35}Cl$ in the ν_6 region. Resolution 0.04 cm^{-1}. Some Q branches of ν_6, $(\nu_3+\nu_6)-\nu_3$ and $2\nu_6^{\pm2}-\nu_6^{\pm1}$ are assigned. Lines marked with an asterisk are due to H_2O.

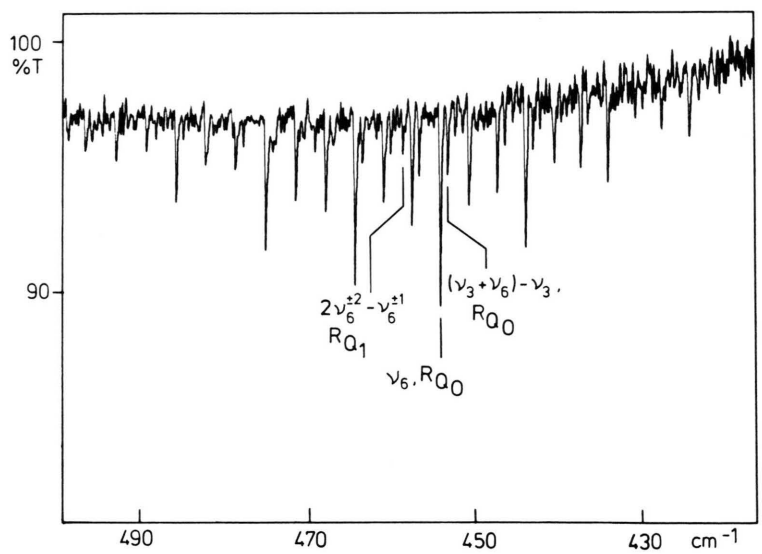

Fig. 2. Survey spectrum of $H_3{}^{116}SnI$ in the ν_6 region. Resolution 0.12 cm^{-1}. Some assignments are given.

Table 1. Ground state constants of stannyl halides (cm^{-1}).

	$H_3{}^{116}Sn^{35}Cl$	$H_3{}^{116}Sn^{79}Br$	$H_3{}^{116}SnI$
A_0	2.12 [a]	2.11 [a]	2.10 [a]
B_0	0.110 431 [10]	0.056 746 9 [11]	0.037 614 7 [12]
$D_J^0 \times 10^8$	3.51 [b]	1.02 [2]	0.477 [2] [c]
$D_{JK}^0 \times 10^7$	8.98 [b]	2.30 [11]	1.37 [12]
$D_K^0 \times 10^5$	1.60 [b]	1.615 [b]	1.60 [b]

[a] From estimated structure. – [b] From harmonic force field. – [c] $4B^3/(\nu_3)^2$.

4.2 Excited States

The spectra of $H_3{}^{116}Sn^{35}Cl$ and $H_3{}^{116}SnI$ are illustrated in Figs. 1 and 2, while a detail of the spectrum of $H_3{}^{116}Sn^{79}Br$ together with a band contour simulation neglecting hot bands is shown in Figure 3. The assignment follows from the intensity alternation in connection with the significantly sharper $^RQ_0$ branch (and hence negative F_6) and first lines which are clearly discernible in many cases. Though there are hardly any pure lines, peaks

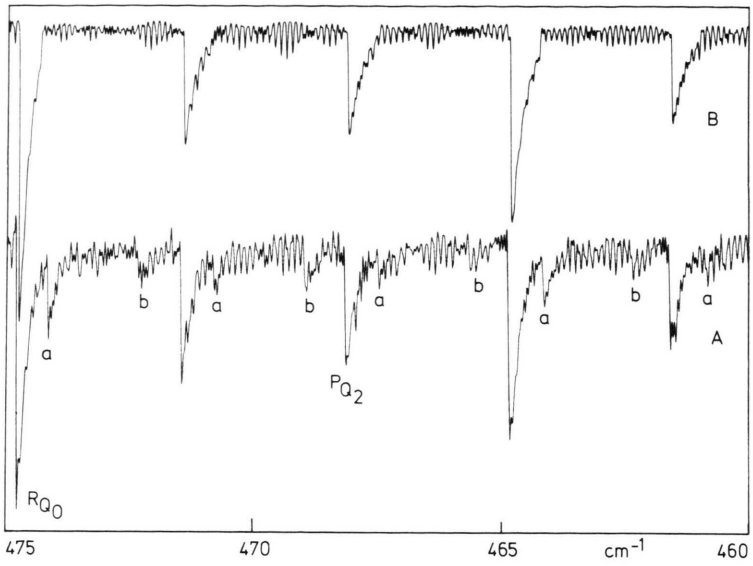

Fig. 3. Detail of the spectrum of $H_3{}^{116}Sn^{79}Br$ in the ν_6 region. A) Experimental spectrum, resolution 0.04 cm^{-1}.
a) Q branches of $(\nu_3 + \nu_6) - \nu_3$;
b) Q branches of $2\nu_6^{\pm 2} - \nu_6^{\pm 1}$.
B) Band contour simulation, hot bands omitted.

Table 2. Excited state molecular parameters of stannyl halides (cm^{-1}).

	$H_3{}^{116}Sn^{35}Cl$	$H_3{}^{116}Sn^{79}Br$	$H_3{}^{116}SnI$
ν_6^0 [a]	488.785 7(6)	473.492 9(7)	453.680(9)
$(A_6 - A_0) \times 10^3$	9.632(8)	9.849(9)	10.41(13)
$(B_6 - B_0) \times 10^5$	−14.27(3)	− 7.00(4)	− 3.5 fixed [b]
$A\zeta_6^z$	0.415 15(6)	0.393 75(7)	0.399 8(5)
$\eta_{6J} \times 10^6$	1.60(5)	0.66(7)	0 fixed
$\eta_{6K} \times 10^5$	1.68(12)	1.17(13)	0 fixed
$F_6 \times 10^5$	−1.48(3)	− 0.55(4)	0 fixed
No. of data	732	630	34
$\sigma \times 10^3$	8.1	8.4	29.7

[a] See text for dependence on A_0. − [b] By band contour simulation.

were assigned to their major constituents at the expense of a worse rms deviation of observed and calculated wavenumbers. The fits included 723 and 630 unit-weighted lines for H_3SnCl and H_3SnBr, respectively, and 24 Q branch edges for H_3SnI. Lists with observed and calculated transition wavenumbers and the correlation matrices of free parameters have been deposited as supplementary material [13].

The fits readily converged to the excited state parameters set out in Table 2 with $\sigma = 8.1$, 8.4 and 29.5×10^{-3} cm^{-1}, respectively. Refinement of excited state centrifugal distortions was physically not meaningful; therefore they were constrained to their ground state values.

The results of the polynomial analyses of Q branch edges for ν_6, $(\nu_3 + \nu_6) - \nu_3$ and $(2\nu_6^{\pm 2} - \nu_6^{\pm 1})$ are given in Table 3, and the deduced anharmonicity constants are quoted.

5. Discussion

The present study unambiguously provides the major rovibrational parameters associated with the ν_6 fundamental for one isotopic species of stannyl chloride, bromide and iodide. In contrast to the C, Si and Ge homologues, no evidence has yet been found for a monomeric fluoride H_3SnF. The important parameters ν_6^0 and $A\zeta_6^z$ are correlated with A_0, and there is urgent demand for information on that parameter, eventually by application of the ζ sum rule or mw investigations of partly deuterated species. Whether perturbation-allowed IR transitions which supply information on A_0 can be observed seems questionable presently due to the experimental difficulties in obtaining spectra and the weakness of perturbations in such heavy molecules.

Combining the results of the present study with those of the ν_3 analysis [2], some predictions of possible perturbations can be made. These follow from inspection of Table 4. The ν_6 fundamental is

Table 3. Results of polynomial analyses for hot bands. Fit of Q branch edges according to ${}^{(P,R)}Q_K = a_0 + a_1(K\,\Delta K) + a_2(K\,\Delta K)^2$ (cm^{-1}) [a].

		$H_3{}^{116}Sn{}^{35}Cl$	$H_3{}^{116}Sn{}^{79}Br$	$H_3{}^{116}SnI$
ν_6	a_0	489.957(5)	474.775(5)	454.954(10)
	a_1	3.202 9(4)	3.334 2(5)	3.340 1(10)
	$a_2 \times 10^2$	0.934(7)	0.967(8)	1.028(15)
	$\sigma \times 10^2$	1.5	1.7	3.2
$(\nu_3 + \nu_6) - \nu_3$	a_0	488.760(15)	474.113(8)	454.108(12)
	a_1	3.218 0(32)	3.356 7(9)	3.351 3(18)
	$a_2 \times 10^2$	1.023(58)	1.008(13)	0.849(34)
	$\sigma \times 10^2$	3.7	2.4	3.2
$2\nu_6^{\pm 2} - \nu_6^{\pm 1}$	a_0	490.774(12)	475.641(12)	455.788(26)
	a_1	3.232 3(18)	3.369 2(21)	3.383 6(32)
	$a_2 \times 10^2$	0.888(32)	1.016(35)	1.642(70)
	$\sigma \times 10^2$	3.2	3.0	6.2
	x_{36}	− 1.228(16)	− 0.666(10)	− 0.853(15)
	$x_{66} + g_{66}$	0.808(7)	0.819(7)	0.741(14)

[a] In many cases better fits were obtained with inclusion of a cubic term.

Table 4. Rounded vibrational energy levels of stannyl halides (cm^{-1}).

	$H_3{}^{116}Sn{}^{35}Cl$	$H_3{}^{116}Sn{}^{79}Br$	$H_3{}^{116}SnI$
ν_3	375.5	263.6	209.8
$2\nu_3$	748.7	525.9	418.7
$3\nu_3$	1 119.7	787.1	626.8
ν_6	488.8	473.5	453.7
$2\nu_6$ av.	978	947	907
$\nu_3 + \nu_6$	863.0	736.4	662.6
ν_2 [14]	694.7	686.7	676.1
ν_5 [14]	702.3	702.6	703.9

expected to be unperturbed, the crossing with $2\nu_3$ occurring for larger K values is than relevant in the present study. For $H_3{}^{116}Sn{}^{35}Cl$, it can be predicted that $2\nu_3$ and ν_5 will exhibit a local rotational resonance near K, $(k-l) = 10$, similar to that reported for $H_3C{}^{35}Cl$ [15]. In H_3SnBr, a Fermi resonance between ν_5 and $\nu_3 + \nu_6$ similar to that reported for H_3SiI [16] and H_3GeBr [17] is predicted, which shifts the $\nu_3 + \nu_6$ level to greater wavenumbers and hence increases the effective x_{36} value. Repulsion of $\nu_3 + \nu_6$ by ν_5 in the opposite way is predicted for H_3SnI, and since W_{356} is expected to be large (2−3 cm^{-1}), the discontinuous change of x_{36} going from H_3SnCl to H_3SnI finds a simple explanation.

Finally it should be noted that the excited state parameters of the stannyl halides are semiquantitatively in good agreement with those of the corresponding germyl halides [5−7], and an analogy in the treatment of the higher-lying fundamentals of the stannyl halides may be expected.

Acknowledgement

We wish to thank the Deutsche Forschungsgemeinschaft for financial support through the Sonderforschungsbereich 42. Support by the Fonds der Chemie is gratefully acknowledged.

[1] M. Betzel, H. Bürger, and P. Schulz, Z. Naturforsch. **39a,** 155 (1984).
[2] H. Bürger and M. Betzel, Z. Naturforsch. **40a,** 989 (1985).
[3] H. Bürger, P. Schulz, and J. Kauppinen, J. Mol. Spectrosc., in the press.
[4] J. Kauppinen, T. Kärkkäinen, and E. Kyrö, J. Mol. Spectrosc. **71,** 15 (1978).
[5] H. Bürger, P. Schulz, and S. Cradock, Z. Naturforsch. **40a,** 383 (1985).
[6] H. Bürger, R. Eujen, A. Rahner, and P. Schulz, Z. Naturforsch. **39a,** 871 (1984).
[7] H. Bürger, R. Eujen, A. Rahner, P. Schulz, J. E. Drake, and S. Cradock, Z. Naturforsch. **38a,** 740 (1983).
[8] G. J. Cartwright and I. M. Mills, J. Mol. Spectrosc. **34,** 415 (1970).
[9] C. Betrencourt-Stirnemann, G. Graner, D. E. Jennings, and W. E. Blass, J. Mol. Spectrosc. **69,** 179 (1978).
[10] L. C. Krisher, R. A. Gsell, and J. M. Bellama, J. Chem. Phys. **54,** 2287 (1971).
[11] S. N. Wolf, L. C. Krisher, and R. A. Gsell, J. Chem. Phys. **54,** 4605 (1971).

[12] S. N. Wolf, L. C. Krisher, and R. A. Gsell, J. Chem. Phys. **55,** 2106 (1971).
[13] Lists of observed and calculated transition wavenumbers may be obtained from Fachinformationszentrum Energie – Physik – Mathematik, D-7514 Eggenstein-Leopoldshafen, West Germany, on submission of the name of the authors, the literature reference and the registry Nr. IRD-100 20.
[14] M. Betzel, H. Bürger, and P. Schulz, to be published.
[15] M. Morillon-Chapey, G. Guelachvili, and P. Jensen, Canad. J. Phys. **62,** 247 (1984).
[16] F. Lattanzi, C. di Lauro, H. Bürger, and P. Schulz, Mol. Phys. **48,** 1209 (1983).
[17] F. Lattanzi, C. di Lauro, H. Bürger, R. Eujen, P. Schulz, and S. Cradock, Mol. Phys. **51,** 81 (1984).