Vibrational Spectra and Force Constants of Symmetric Tops, XXXVII [1]. High Resolution Infrared Investigation of Unstable H_3SnCl in the ν_1/ν_4 Region Near 1900 cm^{-1}

Martina Betzel, Hans Bürger, and Petra Schulz
FB 9 – Anorganische Chemie, Universität-Gesamthochschule, Wuppertal

Z. Naturforsch. **39 a,** 155–161 (1984); received November 2, 1983

The infrared spectra in the ν_1/ν_4 region near 1900 cm^{-1} of natural H_3SnCl and monoisotopic $H_3{}^{116}Sn^{35}Cl$ have been recorded with a resolution of 0.04 cm^{-1}. Isotopic and rotational fine structure has been resolved, and a rotational analysis based on 472 lines, $\sigma(J, K) \sim 4.3 \times 10^{-3}\,cm^{-1}$, has been performed. ν_1 and ν_4 ($\nu^0 = 1917.1932(7)$ and $1924.6790(4)\,cm^{-1}$ respectively in $H_3{}^{116}Sn^{35}Cl$) interact weakly by Coriolis x, y resonance, $|\zeta^y_{1,4}| \sim 0.019$. No further perturbations of ν_1 and ν_4 were observed. The tin isotopic shift of ν_4 is significant, $\Delta\nu_4$ relative to ^{116}Sn being $-0.170(6)$ and $-0.326(6)\,cm^{-1}$ respectively for ^{118}Sn and ^{120}Sn. The hot band $(\nu_3 + \nu_4) - \nu_3$ has been observed, $x_{34} = +0.423(5)\,cm^{-1}$.

1. Introduction

Of the heavier homologues of methyl halides CH_3X, only the silyl and germyl compounds H_3SiX and H_3GeX which are nearly infinitely stable in the gas phase at room temperature have been characterized by vibrational and, more recently, rovibrational spectroscopy. In contrast, there is no information of that kind available for stannyl halides H_3SnX, and this is clearly due to their instability even below 0 °C.

In context with rovibrational investigations of H_3SiCl, H_3GeCl and the "isobaric" species H_3GeBr and H_3SiI performed with a resolution between 1.5 and $50 \times 10^{-3}\,cm^{-1}$ the vibrational and rovibrational spectrum of H_3SnCl became of interest to us. More sensitive and fast FT spectrometers now available promised some success despite previous reports dealing with the properties of stannyl halides which were in part ambiguous and contradictory.

The synthesis of H_3SnCl from SnH_4 and HCl was first reported in 1960 [2]. It was characterized by its vapor pressure, but because of its fast decomposition these data are at least dubious [3]. In later investigations, low temperature NMR and MS data [3, 4] more conclusively established the existence of H_3SnCl though the purity of the sample remained questionable.

Convincing evidence for the detection of H_3SnCl comes from a mw investigation in which the $J = 3 \rightarrow 4$ transition was observed for the most abundant species, hyperfine components being resolved for the 120-35, 118-35, 120-37 and 118-37 isotopic combinations [5]. A life-time of H_3SnCl at low pressure and −30 °C has been reported to be 60 to 90 s but the sample might well have contained SnH_4 and HCl which do not interfere in the mw spectrum.

Both low temperature solid state IR spectra [4], low temperature Raman spectra [3] and gas phase IR spectra [3] have been reported, but the two different investigations are inconsistent and do not allow a determine of any of the vibrational fundamentals. Therefore we have reinvestigated the synthesis of H_3SnCl and studied its vibrational spectrum in the 400 to 2500 cm^{-1} region under conditions which enabled us to unambiguously determine for the most abundant isotopic species the vibrational frequencies of all fundamentals except ν_3 which is located $< 400\,cm^{-1}$. In addition, we also were able to resolve rotational J and K structure for the monoisotopic species $H_3{}^{116}Sn^{35}Cl$.

In the following we report on the Fourier transform infrared spectra in the region near 1900 cm^{-1} of H_3SnCl recorded with a resolution of 0.12 and 0.04 cm^{-1} and the rovibrational analysis of the fundamentals ν_1 and ν_4. These belong to symmetry classes $\mathbf{a}_1$ and $\mathbf{e}$ respectively and are expected to exhibit parallel and perpendicular rotational structure. The rotational analysis is greatly eased by the analogy to ν_1/ν_4 of the lighter homologues H_3SiCl and H_3GeCl which were recently studied in our

---

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

0340-4811 / 84 / 0200-0155 $ 01.3 0/0. – Please order a reprint rather than making your own copy.

laboratory [6, 7]. An independent forthcoming contribution will deal with the other fundamentals of H_3SnCl though we shall refer to the results as far as required for the present study.

2. Experimental

The synthesis of H_3SnCl from SnH_4 and HCl at $-78\ °C$ following [2] and [3] was accomplished in a low-temperature IR cell because, as observed previously [3], attempts to distill H_3SnCl were always accompanied by considerable decomposition. Typically, 1 mmol SnH_4 and 5 mmol HCl were reacted for 1.5 h at $-60\ °C$ and volatile material (SnH_4, HCl, H_2) pumped off. SnH_4 and $^{116}SnH_4$ (98.0% ^{116}Sn) were prepared as described elsewhere [8]. The isotopic purity of $H^{35}Cl$ was 99.32%. Both $^{116}SnH_4$ and $H_3{}^{116}Sn^{35}Cl$ contained small quantities of N_2O and CO_2 which were not removed but served to calibrate the spectra. Upon warming the H_3SnCl to a temperature at which the vapor pressure was sufficient for the infrared measurement, ~ -20 to $0\ °C$, SnH_4 was evolved, thus we were unable to obtain spectra of H_3SnCl without SnH_4 and HCl being present. Since ν_1/ν_4 and ν_2/ν_5 of H_3SnCl overlap with ν_1/ν_3 and ν_2/ν_4 of SnH_4 respectively, we have subtracted the spectra of natural or monoisotopic $^{116}SnH_4$, which were recorded independently under the same conditions, but at a higher signal: noise ratio prior to the investigation of the H_3SnCl/SnH_4 mixture. A double jacketed 17 cm stainless steel cell equipped with KBr windows was employed, precooled N_2 being used to adjust the temperature close to $-5\ °C$. The total pressure was approximately 10 mbar. A Nicolet type 7199 interferometer equipped with a KBr/Ge beam splitter and a MCT type B detector was used to record spectra with an experimental resolution of 0.12 and $0.04\ cm^{-1}$. The rapid decomposition of H_3SnCl limited the time available for the measurements to 30 min at most. For the high resolution spectra we have therefore successively collected blocks of 16 interferograms and coadded the Fourier transforms after careful inspection. The spectrum illustrated in Fig. 1 was obtained with a measuring time of 1600 s. Calibration was performed with the lines of ν_3 [9] and ν_1 [10] of N_2O. The absolute wavenumber accuracy of peak-finder evaluated lines is better than $4 \times 10^{-3}\ cm^{-1}$.

3. Description of the spectrum

A spectrum of natural H_3SnCl recorded in the region of 1820 to $2000\ cm^{-1}$ with a resolution of $0.12\ cm^{-1}$ is illustrated in Figure 1. The pattern of ν_4 with characteristic Q branches is clearly recognized, and the P and R branches of ν_1 are discernible. The Q branches of ν_4 are apparently equally spaced and of regular intensity. Additional positive and negative spikes marking strong SnH_4 lines are inevitably caused by the subtraction procedure.

With a resolution of $0.04\ cm^{-1}$, the Q branches are split by the isotopic effect of Sn, Figure 2. The isotopic effects of chlorine (75.5% ^{35}Cl, 24.5% ^{37}Cl) and 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) provoke congested isotopic patterns which are usually dominated by the most abundant ^{116}Sn, ^{118}Sn and ^{120}Sn species. The harmonic force field predicts ν_1/ν_4 tin isotopic shifts of $0.016/0.085\ cm^{-1}$ per mass unit, while the chlorine isotopic shifts should be $< 0.001\ cm^{-1}$. In agreement with this prediction, the components of the ν_4 Q branches if resolved are therefore assigned to the species $H_3{}^{116}SnCl$, $H_3{}^{117}SnCl$, $H_3{}^{118}SnCl$, $H_3{}^{119}SnCl$, $H_3{}^{120}SnCl$, $H_3{}^{122}SnCl$ and $H_3{}^{124}SnCl$. From a cubic least squares fit of the Q peaks of the ^{116}Sn, ^{118}Sn and ^{120}Sn species listed in Table 1 isotopic shifts relative to $H_3{}^{116}SnCl$ of $-0.170(6)$ and $-0.326(6)\ cm^{-1}$ respectively were determined. The quality of the

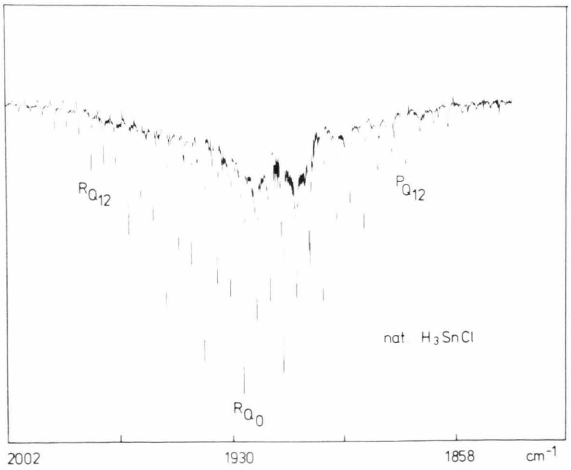

Fig. 1. Survey spectrum of natural H_3SnCl, resolution $0.12\ cm^{-1}$.

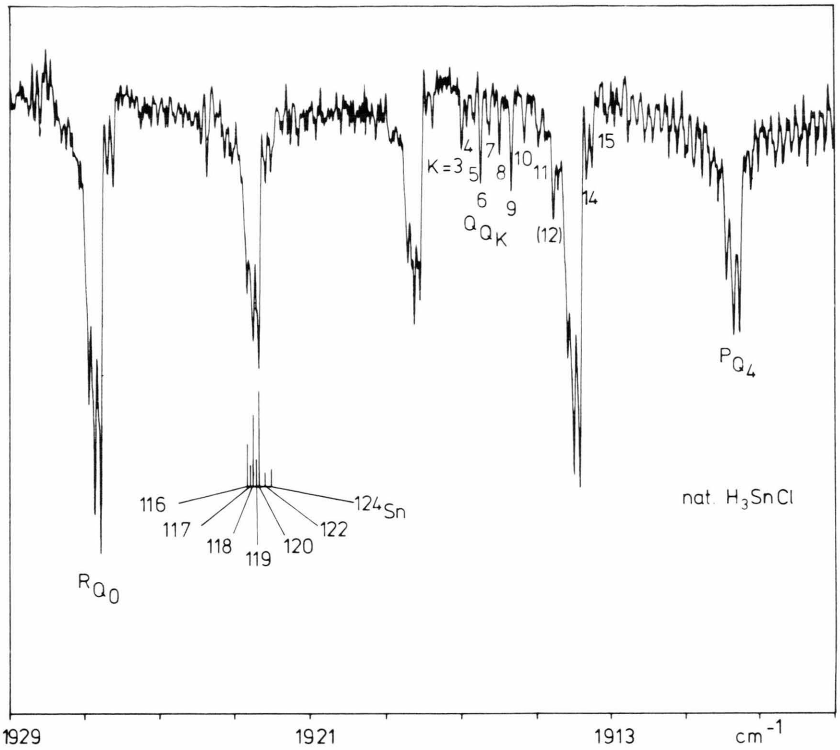

Fig. 2. Detail of the spectrum of natural H_3SnCl near $1920\ cm^{-1}$, resolution $0.04\ cm^{-1}$, with illustration of isotopic splitting.

fits, $\sigma(K) \sim 0.006\ cm^{-1}$, suggests that for the K values in question, the Q branches of these three species are not significantly displaced.

In order to resolve individual rotational lines, further investigations were made on monoisotopic $H_3{}^{116}Sn^{35}Cl$. Figure 3, lower trace, shows the experimental spectrum of $H_3{}^{116}Sn^{35}Cl$ recorded with a resolution of $0.04\ cm^{-1}$ in which many details are visible. First, rotational lines of ν_4 are resolved both for $\Delta K = +1$ and -1 subbands, and the K assignment follows unambiguously from missing ^PP and ^RR lines. Second, all Q branches of ν_4 are equally spaced and consistently exhibit sharp, blue-degraded, unsplit contours with regular intensity patterns. This suggests the absence of perturbations at the actual level of precision. Third, the ^QQ_K branches of ν_1 near $1917\ cm^{-1}$ are well pronounced and can be followed up to $K = 18$. Their location between $^PQ_2$ and $^PQ_3$ and their appearance which is consistent with a small $(B_1 - B_0)$ value and a fairly large, negative $(A_1 - A_0)$ value exactly resemble the behaviour observed in H_3SiCl [6] and H_3GeCl [7].

Finally, the comparison with the simulated spectrum (upper trace) reveals the presence of additional Q branches shifted $\sim +0.4\ cm^{-1}$ from the Q branches of ν_4. These are assigned to the hot band $(\nu_3 + \nu_4) - \nu_3$, the assignment following from the expected relative intensity, 14% for an assumed frequency $\nu_3 = 380\ cm^{-1}$, and the analogy to silyl and germyl halides which generally show the hot band $(\nu_3 + \nu_4) - \nu_3$ to higher frequencies from the cold band ν_4. In a few cases, indication for Q branches of $(2\nu_3 + \nu_4) - 2\nu_3$ is found.

The Q branch maxima of ν_4 and $(\nu_3 + \nu_4) - \nu_3$ listed in Table 2 were subjected to a quadratic polynomial analysis in $K\Delta K$. The standard deviation $\sigma(K)$ and the consistency of the coefficients unambiguously confirm the absence of significant K-dependent perturbations also for the hot band. The deduced anharmonicity constant, $x_{34} = 0.423(5)\ cm^{-1}$, may be compared with that of related molecules $H_3{}^{74}Ge^{35}Cl$, $x_{34} = 0.633(1)\ cm^{-1}$ [7], and $H_3{}^{28}Si^{35}Cl$, $x_{34} = 0.801(3)\ cm^{-1}$ [6]. No features attributable to other hot bands were observed. The relative weakness of ν_1 has similarly precluded the detection of hot bands of ν_1 in H_3SiCl and H_3GeCl though spectra with much higher sensitivity were available.

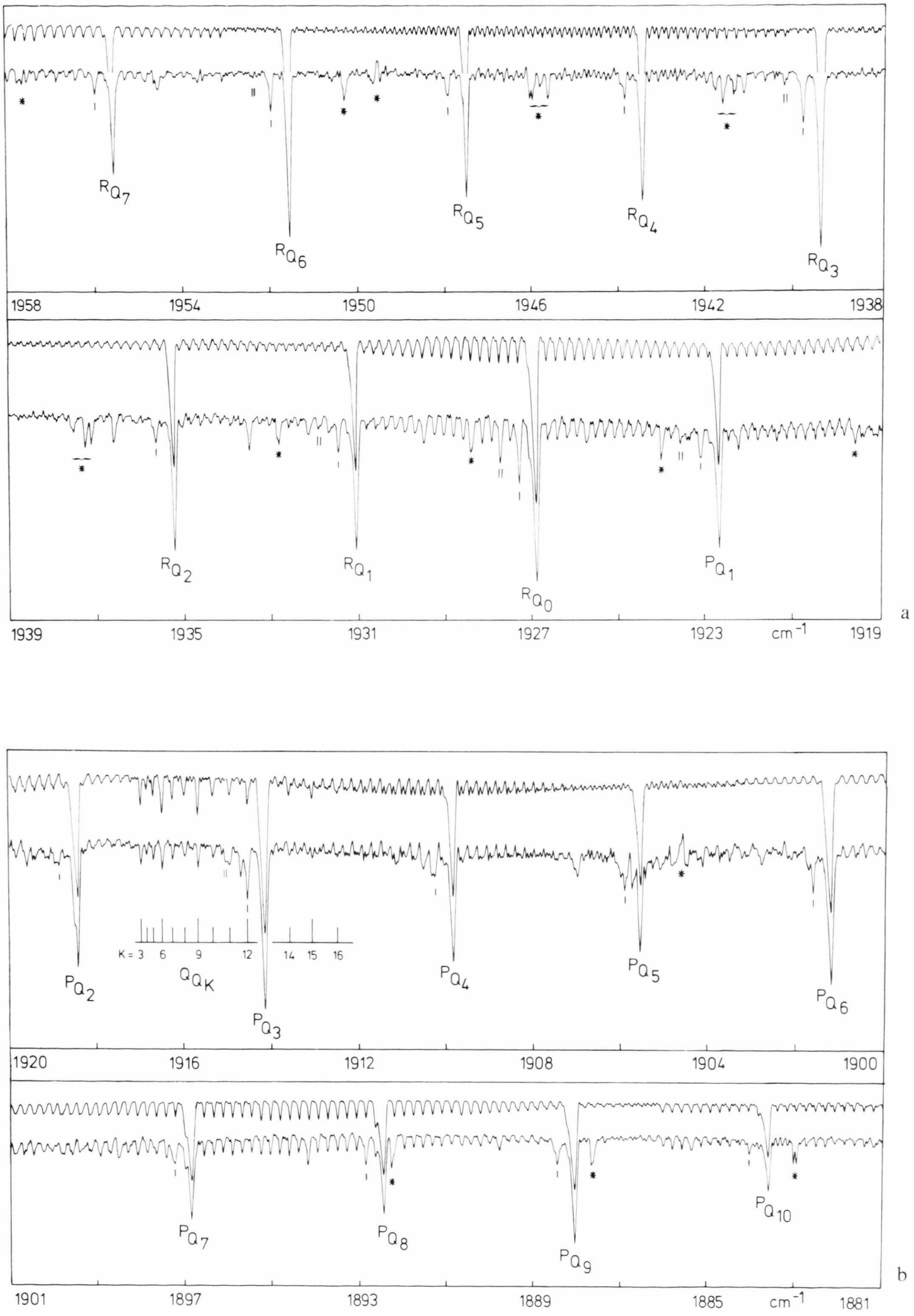

Fig. 3. Computed (upper trace) and observed spectrum (lower trace) of $H_3{}^{116}Sn^{35}Cl$ between 1881 and 1958 cm^{-1}, resolution 0.04 cm^{-1}. Peaks due to imperfectly compensated SnH_4 absorptions are marked by an asterisk. Q branches of the hot bands $(\nu_3 + \nu_4) - \nu_3$ and $(2\nu_3 + \nu_4) - 2\nu_3$ are marked singly and doubly respectively.

Table 1. ν_4 Q branch maxima of $H_3{}^{116}SnCl$, $H_3{}^{118}SnCl$ and $H_3{}^{120}SnCl$ and differences $\Delta = \nu_{obs} - \nu_{calc}$ (cm^{-1}).

$K\Delta K$	$H_3{}^{116}SnCl$		$H_3{}^{118}SnCl$		$H_3{}^{ß120}SnCl$	
	ν_{max}	$10^3\Delta$	ν_{max}	$10^3\Delta$	ν_{max}	$10^3\Delta$
−12	–		1874.460	−8	–	
−11	–		–		–	
−10	–		83.429	8	1883.251	−1
−9	1888.052	−1	87.873	10	87.690	−5
−8	92.468	−2	92.284	2	92.126	11
−7	–		96.669	−7	96.508	−3
−6	1901.235	4	1901.051	4	1900.885	2
−5	05.579	4	05.388	−5	–	
−4	09.905	11	09.707	−7	09.549	−3
−3	14.178	−8	14.008	−1	13.845	−4
−2	18.448	−4	18.274	−3	18.122	3
−1	22.684	−8	22.511	−9	22.362	0
0	26.900	−4	26.740	5	26.578	−1
1	31.094	5	30.926	4	30.765	−3
2	35.248	2	35.087	5	34.928	−1
3	39.382	9	39.216	3	39.064	3
4	43.474	2	43.325	10	43.166	1
5	47.529	−13	47.385	−3	47.247	8
6	51.584	3	51.428	−3	51.285	1
7	55.589	−1	55.441	−2	55.293	−5
8	59.548	−20	59.419	−6	–	
9	63.527	13	63.373	−2	63.231	−3
10	–		67.293	−1	67.153	−2
11	–		71.185	5	71.043	−1
12	–		75.029	−5	74.904	4

Coefficients of polynomial fit
$\nu = a_0 + a_1\, K\Delta K + a_2\,(K\Delta K)^2 + a_3\,(K\Delta K)^3$

a_0	1926.905(5)	1926.735(3)	1926.579(4)
a_1	4.199(3)	4.201(2)	4.203(1)
$a_2 \times 10^2$	−1.384(8)	−1.378(4)	−1.376(3)
$a_3 \times 10^5$	−7.7(4)	−7.8(2)	−7.6(1)
$\sigma(K) \times 10^3$	7.9	5.6	4.0

4. Rotational analysis

While rotational lines of ν_4 are well resolved for $K'' \leqq 15$ and $J'' \leqq 58$, ν_1 ${}^QP$ and ${}^QR$ lines are much weaker, appear in clusters and are often blended by lines of ν_4. In order to give more significance to the analysis of ν_1, we have used the Q branch peaks as hypothetical ${}^QQ_K(K+3)$ lines in the least squares refinement. This is based on a total of 61 and 411 pieces of data on ν_1 and ν_4 respectively. The model chosen is essentially the same as used for H_3SiCl, simultaneously accounting for $l(\pm 2, \pm 2)$ resonance within ν_4 and $l(\pm 1, \pm 1)$ interactions between ν_1 and ν_4 [6]. This Coriolis $x-y$ resonance is expected to be weak, mostly affecting the $K = 2$ and 3 levels of ν_1 and the $k\,l = -1$ and -2 levels of ν_4. Since however or data were not good enough to determine the parameter of the $l(\pm 2, \pm 2)$ resonance with significance, the interaction constant was constrained to zero.

Transition frequencies were fitted to upper state parameters for a fixed ground state. Unperturbed upper state energies are given as

$$\begin{aligned} E(v, l, J, K) = {} & \nu_0 + (A - B)\,K^2 + BJ\,(J+1) \\ & - D_J J^2 (J+1)^2 - D_{JK} J\,(J+1)\,K^2 \\ & - D_K K^4 \\ & - [2\,(A\zeta) - \eta_J J\,(J+1) - \eta_K K^2]\,K\,l\,. \end{aligned}$$

The off-diagonal element of the matrix accounting for the $l(\pm 1, \pm 1)$ interaction

$$\langle v_1 = 0, v_4 = 1, l_4 = \pm 1, JK \pm 1 \,|\, \mathbf{H} \,|\, v_1 = 1, v_4 = 0, JK \rangle$$

is

$$\pm \sqrt{2}/2\,[(\nu_1/\nu_4)^{1/2} + (\nu_4/\nu_1)^{1/2}] \cdot B\zeta^y_{1,4}[J\,(J+1) - K\,(K \pm 1)]^{1/2}\,.$$

Table 2. Q branch maxima of ν_4 and $(\nu_3 + \nu_4) - \nu_3$ and differences $\Delta = \nu_{obs} - \nu_{calc}$ in monoisotopic $H_3{}^{116}Sn{}^{35}Cl$ (cm^{-1}).

$K\Delta K$	ν_4		$(\nu_3 + \nu_4) - \nu_3$	
	ν_{max}	$10^3\Delta$	ν_{max}	$10^3\Delta$
−15	1861.057	7	–	
−14	–		–	
−13	70.137	−5	1870.578	6
−12	74.654	0	–	
−11	79.142	−2	–	
−10	83.611	1	84.058	20
−9	88.050	−2	88.472	−7
−8	92.465	−5	92.888	−10
−7	96.866	2	–	
−6	1901.233	0	1901.656	−4
−5	–		–	
−4	09.894	−1	10.334	13
−3	14.187	0	14.605	−8
−2	18.453	0	18.885	7
−1	22.689	−3	23.122	6
0	26.910	5	27.327	−1
1	31.093	4	31.516	5
2	35.247	1	35.671	4
3	39.383	8	39.797	2
4	43.476	1	43.890	−4
5	47.547	1	47.950	−13
6	51.590	3	52.008	4
7	55.600	1	56.007	−7
8	59.568	−13	59.990	−4
9	63.533	1	63.953	10
10	–		–	
11	71.336	−6	71.742	−7
12	75.194	−5	75.611	−7
13	–		–	
14	–		–	
15	86.586	8	86.975	0

Table 3. Molecular Parameters of $H_3{}^{116}Sn^{35}Cl$ (cm^{-1}).

Ground State		
A_0	2.12	
B_0	0.110 435	
$D_J^0 \times 10^8$	3.51	
$D_{JK}^0 \times 10^7$	8.98	
$D_K^0 \times 10^5$	1.6	
Excited States	**Set 1**	**Set 2**
ν_1^0	1917.193 2(7)	1917.192 7(8)
$(A_1 - A_0) \times 10^2$	−1.803 7(12)	−1.803 1(12)
ν_4^0	1924.679 0(4)	1924.678 7(4)
$(A_4 - A_0) \times 10^2$	−1.367 8(5)	−1.367 5(5)
$(B_4 - B_0) \times 10^5$	3.427(32)	3.501(32)
$(A\zeta)_4$	−0.103 809(25)	−0.103 910(18)
$\eta_{4J} \times 10^7$	2.5(5)	0
$\lvert\sqrt{2}\, B\, \Omega_{14}\, \zeta_{1,4}^{y}\rvert \times 10^3$	2.93(30)	0
$\sigma(J, K) \times 10^3$	4.27	4.51
No. of fitted lines	472	472

$\eta_{4K} = (B_1 - B_0) = 0$, $D'_J = D_J^0$, $D'_{JK} = D_{JK}^0$, $D'_K = D_K^0$.

Of the ground state parameters, Table 3, B_0 is from the measured $J = 3 \rightarrow 4$ mw transition [5] corrected for D_J^0 and D_{JK}^0 contributions, while D_J^0, D_{JK}^0 and D_K^0 were calculated from a harmonic force field taking into account all experimental data available for H_3SnCl. The adopted values for B_0, D_J^0 and D_{JK}^0 fall into the range computed from ground state combination differences obtained from coresponding $\Delta J = \pm 1$ lines of ν_1, ν_4 and ν_5. The force field data are assumed to be more reliable at the moment. D_K^0 is confirmed by the smallness of η_{4K} ($|\eta_{4K}| \leqq 5 \times 10^{-6}$ cm^{-1}) keeping in mind that η_K absorbs the error $-4\Delta D_K$. No serious information concerning A_0 is at hand. As a guess we have assumed that A_0 of H_3SnCl is slightly smaller than B_0 of SnH_4, 2.1631(2) cm^{-1} [8]. This assumption is fulfilled through the series CH_4/H_3CCl to GeH_4/H_3GeCl, but the value adopted for H_3SnCl, $A_0 = 2.12$ cm^{-1}, may well be in error by 0.05 cm^{-1}. This is of relevance for the A_0-dependent parameters ν_4^0 and $(A\zeta)_4$. Observed and calculated line positions are available as supplementary material [11].

The refinement of excited state centrifugal distortion coefficients was not physically meaningful. Therefore they were constrained to the ground state values. Furthermore, η_{4K} and $(B_0 - B_1)$ were not determined with significance from the available data and therefore fixed to zero, an upper limit, $|B_0 - B_1| \leqq 2 \times 10^{-5}$ cm^{-1}, following from the simulation of the ^{Q}Q branches. The final molecular parameters of $H_3{}^{116}Sn^{35}Cl$ determined in this investigation are set out in Table 3. The standard deviation, $\sigma(J, K) = 4.27 \times 10^{-3}$ cm^{-1}, is comparable to the quality of the data and indicates that the employed model is fully satisfactory. Constraint of η_{4J} and $B\zeta_{1,4}^{y}$ to zero increased $\sigma(J, K)$ to 4.51×10^{-3} cm^{-1}, while the physical meaningfulness of the refined parameters hardly changes, Table 3.

The comparison of the experimental spectrum with a simulation obtained with the parameters of Set 1, Table 3, and shown in Fig. 3 proves the correctness of the rovibrational analysis. Differences of the two traces reflect hot band contributions and weak residual positive and negative peaks due to $^{116}SnH_4$ which are marked with an asterisk. The relation of the transition moments, M_1/M_4, is close to 1. The relative intensities of $^{Q}Q_2$ and $^{Q}Q_3$ of ν_1 strongly favour negative intensity perturbation of the Coriolis resonance [12]. This is in agreement with the prediction of the force field and consistent with the result of H_3SiCl [6].

5. Discussion

The present study provides for the first time unambiguously frequency data of the fundamentals ν_1 and ν_4 of H_3SnCl. Results of the previous mw investigation [5] are confirmed, and a comparison of the major rovibrational parameters within the series of H_3XCl molecules, X = C, Si, Ge and Sn, is now possible (Table 4).

Surprisingly both the $v_1 = 1$ and $v_4 = 1$ levels appear to be unperturbed. This contrasts with the behaviour observed for the lighter homologues, and if as pronounced effects as in H_3SiCl and H_3GeCl were present in H_3SnCl, they would be clearly visible in our spectra. In H_3SiCl and H_3GeCl, $\nu_3 + \nu_5 + \nu_6$, $\nu_2 + \nu_3 + \nu_5/3\nu_3 + \nu_5$ and $\nu_5 + 2\nu_6$ were found to perturb ν_4 and, in part, also ν_1. Both local and extended interactions were observed [6, 7]. With the vibrational frequencies of ν_2, 695 cm^{-1}, ν_5, 702 cm^{-1}, ν_6, 488 cm^{-1} and assuming $\nu_3 = 380$ cm^{-1}, it is evident that in H_3SnCl the above-mentioned combination levels lie much below ν_1 and ν_4 and are not suited for significant interactions. Compared to the lighter homologues, the frequencies of the

Table 4. Comparison of molecular parameters (cm^{-1}).

	$H_3{}^{12}C^{35}Cl$ [13, 14]	$H_3{}^{28}Si^{35}Cl$ [6]	$H_3{}^{74}Ge^{35}Cl$ [7]	$H_3{}^{116}Sn^{35}Cl$, this work
Ground State				
A_0	5.20530	2.844	2.6277	2.12
B_0	0.443403	0.222615	0.144546	0.110435
$D_J^0 \times 10^7$	6.030	1.377	0.642	0.351
$D_{JK}^0 \times 10^6$	6.555	2.017	1.086	0.898
$D_K^0 \times 10^5$	8.85	2.6	2.05	1.6
Excited States				
ν_1^0	2967.777	2201.944	2119.977	1917.193
$(A_1 - A_0) \times 10^2$	−5.538	−2.417	−2.350	−1.804
$(B_1 - B_0) \times 10^5$	5.7	−4.1	–	[a]
ν_4^0	3039.286	2209.639	2128.484	1924.679
$(A_4 - A_0) \times 10^2$	−2.696	−1.682	−1.674	−1.368
$(B_4 - B_0) \times 10^4$	2.42	0.274	0.718	0.343
$(A\zeta)_4$	0.3889	0.0326	−0.1468	−0.1038
$\eta_{4J} \times 10^6$	−12.3	0.007	−0.13	0.25
$\eta_{4K} \times 10^5$	–	−0.14	−1.36	[a]
$(\sqrt{2} B \Omega_{14} \zeta_{1,4}^{y}) \times 10^3$	–	± 2.69	± 3.68	± 2.9

[a] See text.

fundamentals ν_2, ν_3, ν_5 and ν_6 relative to ν_1 and ν_4 are considerably lower in H_3SnCl, which requires higher excitation to provoke resonance and consequently weakens the effect of the interactions. It should however be kept in mind that, for H_3SiCl and H_3GeCl, better resolved spectra were available, and furthermore higher J and K values were studied. Nevertheless the (fortunate) absence of local and extended resonances at the actual level of precision is fortuitous.

Acknowledgement

Support by the Deutsche Forschungsgemeinschaft through SFB 42 is gratefully acknowledged.

[1] For Part XXXVI see A. Ruoff, H. Essig, H. Bürger, S. Dobos, and P. Schulz, Mol. Phys., in press.
[2] E. Amberger, Angew. Chem. **72,** 78 (1960).
[3] J. R. Webster, M. M. Millard, and W. L. Jolly, Inorg. Chem. **10,** 879 (1971).
[4] J. M. Bellama and R. A. Gsell, Inorg. Nucl. Chem. Letters **7,** 365 (1971).
[5] L. C. Krisher, R. A. Gsell, and J. M. Bellama, J. Chem. Phys. **54,** 2287 (1971).
[6] H. Bürger and P. Schulz, J. Mol. Spectrosc. **102,** 160 (1983).
[7] F. Lattanzi, C. di Lauro, H. Bürger, R. Eujen, and S. Cradock, to be published.
[8] A. G. Robiette et al., to be published.
[9] C. Amiot and G. Guelachvili, J. Mol. Spectrosc. **59,** 171 (1976).
[10] W. B. Olson, A. G. Maki, and W. J. Lafferty, J. Phys. Chem. Ref. Data **10,** 1065 (1981).
[11] Lists of observed and calculated transition frequencies and the correlation matrix may be obtained from Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, West Germany, on submission of the name of the authors and the literature reference.
[12] C. di Lauro and I. M. Mills, J. Mol. Spectrosc. **21,** 386 (1966).
[13] P. Jensen, S. Brodersen, and G. Guelachvili, J. Mol. Spectrosc. **88,** 378 (1981).
[14] M. Morillon-Chapey and G. Graner, J. Mol. Spectrosc. **31,** 155 (1969).