Analysis of the hot band of stannane $^{116}$SnH$_4$ in the 600–850 cm$^{-1}$ range

A. Tabuyaoui$^{1,2,a}$, G. Pierre$^3$, and H. Bürger$^4$

1 FST Settat, Km 3, B.P. 577, 26000 Settat, Morocco
2 LETS, Faculté des sciences, avenue Ibn Batouta, B.P. 1014, Rabat, Morocco
3 LPUB, CNRS UMR 5027, Faculté des sciences Mirande, 9 rue Alain Savary, B.P. 47870, 21078 Dijon, France
4 Anorganische Chemie, FB 9, Universität-GH, Gauss-Str. 20, 5600 Wuppertal 1, Germany

Received 16 July 2003 / Received in final form 7 August 2003
Published online 8 October (2003) – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2004

Abstract. The FTIR spectrum of monoisotopic stannane $^{116}$SnH$_4$ has been recorded in the 600–850 cm$^{-1}$ range, with the Bruker 120 HR interferometer at Giessen, Germany. The resolution was 2.1 × 10$^{-3}$ cm$^{-1}$. The analysis of infrared transitions in this region enabled Brunet et al. [1] to assign many lines to the bending dyad $\nu_2/\nu_4$. However, several lines in this spectrum were found to be unassigned. In a recent work [2], we have analysed the infrared spectrum of stannane in the bending triad region at 1400 cm$^{-1}$. The results obtained enabled us to assign directly, for the spectrum in the region 600–850 cm$^{-1}$, 163 of the observed transitions to the hot band $\{\text{bending triad}\}$ minus $\{\text{bending dyad}\}$ up to $J = 9$. These transitions were combined to the infrared data corresponding to the bending triad (2$\nu_2$, 2$\nu_2 + \nu_4$, 2$\nu_4$), to refine a set of Hamiltonian parameters for the two bands 2$\nu_2$ and (2$\nu_2 + \nu_4$) [2].

PACS. 33.20.Vq Vibration-rotation analysis – 33.20.Ea Infrared spectra

1 Introduction

Many experimental and theoretical studies were devoted to tetrahedral molecules generally and to the stannane molecule SnH$_4$ particularly, using Raman, infrared and microwave spectroscopy. The first work on stannane was done by Levin and Ziffer [3] who determined some molecular constants and showed that the stannane was done by Levin and Ziffer [3] who determined some molecular constants and showed that the stannane molecule SnH$_4$ was tetrahedral in its equilibrium configuration, develop a small induced dipole moment by excitation of a triply degenerate vibration [8,9]. Pure rotational transitions resulting from this induced dipole moment have been observed for several tetrahedral molecules [10–16].

Jörissen et al. [17] have recorded and analysed the infrared spectrum of the ($\nu_1/\nu_3$) dyad of stannane in natural isotopic abundance. Their technique used infrared-microwave double resonance employing a tunable diode laser. They have determined for each of the five most abundant isotopic species of stannane seventeen constants by fitting simultaneously the infrared and microwave data using for the ground state and the $\nu_1 = 1$ state the Hamiltonian of Kirschner and Watson [18] and for the $\nu_3 = 1$ state that of Robiette et al. [19]. Only one coupling term between $\nu_1$ and $\nu_3$ given by Cabana et al. [6] and expressed by Susskind [20] in a tensorial form as $H(\nu_1/\nu_3) = d_{13} T_{123}$ was used. The ground state parameters used in their fit were those determined by Ohshima et al. [21,22].

Krivtsou et al. [23] recorded and analysed the FTIR spectrum of monoisotopic stannane $^{120}$SnH$_4$ in the 1903–1960 cm$^{-1}$ region. More than 230 transitions of the $^{120}$SnH$_4$ isotopic specie were used for simultaneous analysis of the $\nu_1$, $\nu_3$ resonance states. They have determined 21 spectroscopic parameters of the upper states using a model Hamiltonian developed to the forth order
of approximation, which explicitly takes into account the resonance interaction.

The \((\nu_1/\nu_3)\) stretching dyad of stannane was reinvestigated by Tabyaoui et al. [24,25] near 1900 cm\(^{-1}\), employing a monoisotopic sample, \(^{116}\text{SnH}_4\), by which ambiguities caused by mutual blending of lines, belonging to different isotopic species could be circumvented. They have recorded and analysed the FTIR and high-resolution Stimulated Raman spectra. A simultaneous analysis of the Raman, infrared and microwave data using a Hamiltonian developed to the sixth order for the \((\nu_1/\nu_3)\) dyad enabled them to determine 4 parameters for the \(\nu_1\) band, 17 parameters for the \(\nu_3\) band and 6 interaction parameters. The line transitions were assigned up to \(J = 14\). They have shown that for high \(J\) values \((J > 14)\), a perturbation appears due to an interaction between the stretching dyad \((\nu_1/\nu_3)\) and the second overtone of bending modes \((3\nu_2, 2\nu_2 + \nu_4, \nu_2 + 2\nu_4, 3\nu_4)\). In the fit of the Hamiltonian parameters, the ground state parameters were fixed to the values determined by Brunet et al. [1], where the tensorial ones are close to the values determined by Ohshima et al. [21,22].

\(^{116}\text{SnH}_4\) was investigated too by Brunet et al. [1] who analysed the FTIR spectrum of the \((\nu_2/\nu_4)\) dyad using a sixth order Hamiltonian. The analysis of the infrared transitions allowed them to determine 10 ground state parameters, \(\nu_0\) parameters, 17\(\nu_4\) parameters and 18 interaction parameters.

Halonen et al. [26] have analysed the FTIR spectrum of the \((2000, A_1/F_2)\) stretching vibrational band system of \(^{116}\text{SnH}_4\) up to \(J = 20\) and refined 21 Hamiltonian parameters in a local mode model. Also, Halonen et al. [27] have analysed the FTIR spectra of the \((1000, A_1/F_2), (2000, A_1/F_2), (3000, A_1/F_2)\) vibrational band systems for \(^{120}\text{SnD}_4\). They have made a rotational analysis of the spectra. The local mode relations obtained confirm that vibrational energy localization takes place in the second stretching vibrational overtone of deuterated stannane.

Recently, we have made an analysis of the FTIR spectrum of the monoisotopic stannane in the 1400 cm\(^{-1}\) region corresponding to the bending triad [2]. The results obtained enabled us to assign directly most observed transitions to the hot band \{bending triad\} minus \{bending dyad\} near 700 cm\(^{-1}\). We have then included these transitions in the fit of the Hamiltonian parameters. The simultaneous analysis of infrared data corresponding to both hot band and bending triad enabled us to determine 26 Hamiltonian parameters for the \(2\nu_2\) and \((\nu_2 + \nu_4)\) bands [2]. The standard deviation was \(1.5 \times 10^{-3}\) cm\(^{-1}\).

In this work, we present for the hot band \{bending triad\} minus \{bending dyad\}, the assignments realized up to \(J = 9\) and the results obtained for this hot band during the analysis of the bending triad \((2\nu_2, \nu_2 + \nu_4, 2\nu_4)\).

2 Experimental details

Monoisotopic stannane, \(^{116}\text{SnH}_4\), was prepared by reacting a solution containing \(\text{SnCl}_2\)\(^{-2}\) (1 mg Sn/ml), obtained by dissolving \(^{116}\text{Sn}\) (98% \(^{116}\text{Sn}, \text{Oak Ridge}) in an aqueous HCl/HNO\(_3\) mixture, with an aqueous solution of NaBH\(_4\) (3%) in vacuum (50–80 mbar). Gaseous \(^{116}\text{SnH}_4\) evolved was collected at \(-196\) °C and purified by repeated fractional condensation using a standard vacuum line, yield \(\sim 90\%\).

FTIR spectra were recorded at Giessen in the 490–980 cm\(^{-1}\) range with a Bruker 120 HR spectrometer equipped with a Ge/KBr beam splitter and a Cu:Ge detector. The resolution, trapezoidal apodization, was \(2.0 \times 10^{-3}\) cm\(^{-1}\); the Doppler width at 700 cm\(^{-1}\) is approx. 0.7 \(\times 10^{-3}\) cm\(^{-1}\). The actual width of weak lines (FWHM) was \(\sim 2.1 \times 10^{-3}\) cm\(^{-1}\). A cell of 18.7 cm length equipped with KBr windows was employed, and a pressure of 1 mbar chosen. A total of 50 scans were co-added. Calibration was performed with N\(_2\)O lines [28]; relative to these lines it is better than \(1.0 \times 10^{-4}\) cm\(^{-1}\).

The medium-resolution spectrum showed in Figure 1 was recorded with a Nicolet 7199 FTIR spectrometer employing a resolution of 0.05 cm\(^{-1}\).

3 Theory

The transformed vibrational-rotational Hamiltonian for tetrahedral molecules developed by Champion and Pierre [29–31] is especially well adapted for vibrational extrapolation. Vibrational operators are expressed in terms of tensor products of creation and annihilation elementary operators in such a way that each term of the Hamiltonian expansion corresponds to a given vibrational state or set of quasi-degenerate vibrational states. According to this scheme, the completely transformed Hamiltonian for the vibrational states taken into account in this work, can be written as

\[
\mathbf{\hat{H}} = \mathbf{\hat{H}}_{(GS)} + \sum_s \mathbf{\hat{H}}_{(\nu_s)} + \sum_s \mathbf{\hat{H}}_{(2\nu_s)} + \sum_{s < s'} \mathbf{\hat{H}}_{(\nu_s + \nu_{s'})}. \quad (1)
\]