PHYSICAL CHEMISTRY

N. A. CHUMAEVSKII

1961

SovietRxiv

Fig. 1. Absorption spectra of triethylstannane (a), tetramethylstannane (b), trimethylvinylstannane (v), and trimethylallylstannane (g). Each spectrum is divided into three regions: left, KBr; middle, NaCl; right, LiF. All spectra are plotted on a uniform frequency scale.

Figure 1: Fig. 1. Absorption spectra of triethylstannane (a), tetramethylstannane (b), trimethylvinylstannane (v), and trimethylallylstannane (g). Each spectrum is divided into three regions: left, KBr; middle, NaCl; right, LiF. All spectra are plotted on a uniform frequency scale.

Abstract

Full Text

PHYSICAL CHEMISTRY

N. A. CHUMAEVSKII

VIBRATIONAL SPECTRA OF SOME ALKYL- AND ALKYLALKENYLTINNANES (SnIV)

(Presented by Academician I. V. Obreimov, June 1, 1961)

The present work is devoted to the vibrational spectra of a series of alkyl and alkylalkenyl derivatives of tin.

The infrared absorption spectra were recorded as follows. In the region of 3000 cm−1, on an IR spectrophotometer VIKS M-3 with a LiF prism ($\Delta\nu = 6$ cm−1). In the region 700-2000 cm−1, on an IR spectrophotometer VIKS

Fig. 1. Absorption spectra of triethylstannane (*a*), tetramethylstannane (*b*), trimethylvinylstannane (*v*), and trimethylallylstannane (*g*). Each spectrum is divided into three regions: left, KBr; middle, NaCl; right, LiF. All spectra are reduced to a uniform frequency scale.

M-3 with a NaCl prism ($\Delta\nu$ in the region of 1000 cm−1 was ~10 cm−1). In the region 400-700 cm−1, on an IR spectrophotometer IKS-14 with a KBr prism ($\Delta\nu = 4$ cm−1). The recording of substances in the regions of the LiF and NaCl prisms was carried out in a cuvette of constant thickness 0.050 mm with NaCl windows; some substances were also recorded in a thin layer of indeterminate thickness (between tightly pressed salt windows). In the region of the KBr prism, recording was carried out in a cuvette with an insert and KBr windows (the layer thickness was 0.020 mm).

The Raman spectra were recorded on a three-prism glass spectrograph ISP-51, with registration on the photoelectric attachment FEP-1. The mercury line Hg 4358.3 Å with a blue filter was used as the source of the exciting light.

It has already been noted that the absorption bands of the stretching vibrations of Si–H and Ge–H bonds lie, respectively, at 2125 cm^{-1} and 2010 cm^{-1} (using $(C_2H_5)_3SiH$ and $(C_2H_5)_3GeH$ as examples ([1],[2])). In the case of triethylstannane $(C_2H_5)_3SnH$, the absorption band of the Sn–H bond lies at 1820 cm^{-1} (Fig. 1). Thus, it can be seen that for the M–H bond in the series M = C, Si, Ge, Sn, the frequency of the stretching vibrations decreases from 2900 cm^{-1} (for the frequency of the

$$-C-H$$

bond one may take precisely this value) to 1820 cm^{-1}. The force constant of the M–H bond decreases on going from C to Sn (the influence of the mass of the atom M should be practically small). Thus, for example, for CH_4 the force constant (expressed in the usual units ([3],[4])) is $K_{q(C-H)} = 8.34 \cdot 10^6$ cm^{-2} ([3]), while for SiH_4, $K_{q(Si-H)} = 4.67 \cdot 10^6$ cm^{-2} ([4]), i.e., in silane K_q is almost two times smaller. Using the known formulas ([3]) and assuming that the angular coefficients and interaction coefficients for Ge–H and Sn–H bonds, as compared with Si–H, change little, one can find that $K_{q(Ge-H)}$ is close to $4.3 \cdot 10^6$ cm^{-2}, and $K_{q(Sn-H)}$ to $3.8 \cdot 10^6$ cm^{-2} (for MH_4).

As for the absorption and light-scattering frequencies associated with the Sn—Alk groupings (vibrations with a change in the H—C—Sn angle), they are equal to 1190-1195 cm^{-1} (IR and Raman) in the case of Sn—CH_3 (Fig. 1) and 1183-1190 cm^{-1} for Sn—C_2H_5 (Fig. 2). In the case of $Pb(C_2H_5)_4$, for the Pb—C_2H_5 grouping the absorption band has a frequency of 1158 cm^{-1} (Fig. 4); in $Pb(CH_3)_4$, for Pb—CH_3, 1170 cm^{-1} ([5]).

For vinyl and allyl derivatives, the absorption bands of the C = C bonds have frequencies of 1580 cm^{-1} (using $(C_2H_5)_2Sn(CH=CH_2)_2$ as an example) and 1628 cm^{-1} (using $(CH_3)_3SnCH_2—CH=CH_2$, $(C_2H_5)_3SnCH_2—CH=CH_2$ as examples) (Figs. 1 and 2).

The absorption bands associated with the stretching vibrations of the terminal methylene groups $=CH_2$ have frequencies ν_{as} = 3045–3050 cm^{-1} for the vinyl group and ν_{as} = 3080 cm^{-1} for the allyl group (Figs. 1 and 2).

Table 1

Frequencies of vibrations of Sn–C bonds

Symmetry group	Compound / structural fragment	Frequency, cm^{-1}	Method / symmetry species
T_d	$(CH_3)_4Sn$	528	IR, F
T_d	$(CH_3)_4Sn$	525	Raman, F
T_d	$(CH_3)_4Sn$	500	Raman, A
T_d	$(C_2H_5)_4Sn$	503	IR, F

Fig. 2. Absorption spectra of tetraethylstannane (a), triethylallylstannane (b), diethyldivinylstannane (c), diethylvinylchlorostannane (d). The rest as in Fig. 1.

Figure 2: Fig. 2. Absorption spectra of tetraethylstannane (a), triethylallylstannane (b), diethyldivinylstannane (c), diethylvinylchlorostannane (d). The rest as in Fig. 1.

Symmetry group	Compound / structural fragment	Frequency, cm^{-1}	Method / symmetry species
T_d	$(C_2H_5)_4Sn$	500	Raman, F
T_d	$(C_2H_5)_4Sn$	475	Raman, A
C_{3v}	$(CH_3)_3SnCH = CH_2$	527	E
C_{3v}	$(CH_3)_3SnCH = CH_2$	512?	A
C_{3v}	$(CH_3)_3SnCH = CH_2$	462	A
C_{3v}	$(CH_3)_3SnCH_2CH = CH_2$	527	E
C_{3v}	$(CH_3)_3SnCH_2CH = CH_2$	512	A
C_{3v}	$(CH_3)_3SnCH_2CH = CH_2$	480	A
C_{3v}	$(C_2H_5)_3Sn—CH_2CH = CH_2$	517	E
C_{3v}	$(C_2H_5)_3Sn—CH_2CH = CH_2$	495	A
C_{3v}	$(C_2H_5)_3Sn—CH_2CH = CH_2$	478	A
C_{2v}	$(C_2H_5)_2Sn(CH = CH_2)_2$	518	A
C_{2v}	$(C_2H_5)_2Sn(CH = CH_2)_2$	495	B
C_{2v}	$(C_2H_5)_2Sn(CH = CH_2)_2$	476	A
C_{2v}	$(C_2H_5)_2Sn(CH = CH_2)_2$	462	B

Note: F –triply degenerate frequencies; E –doubly degenerate frequencies; A –symmetric vibrations.

Data on the frequencies in the absorption and light-scattering spectra of vibrations of Sn–C bonds in individual molecules are given in Table 1 (see also the figures).

Fig. 2. Absorption spectra of tetraethylstannane (a), triethylallylstannane (b), diethyldivinylstannane (c), diethylvinylchlorostannane (d). The rest as in Fig. 1.

For diethylvinylchlorostannane, ν_{Sn-C} = 526 cm^{-1} and 495 cm^{-1} for the $Sn(C_2H_5)_2$ grouping and 471 cm^{-1} for $Sn—CH = CH_2$ (Fig. 2).

Fig. 3. Raman spectra (combined light-scattering spectra): 1–tetramethylstannane, 2–tetraethylstannane. The right-hand spectrum (in the region of 3000 cm^{-1}) was recorded with a speed more than five times greater than in the region up to 1460 cm^{-1}.

Fig. 3. Raman spectra (combined light-scattering spectra): 1—tetramethylstannane, 2—tetraethylstannane. The right-hand spectrum (in the region of 3000 cm^{-1}) was recorded with a speed more than five times greater than in the region up to 1460 cm^{-1}.

Figure 3: Fig. 3. Raman spectra (combined light-scattering spectra): 1—tetramethylstannane, 2—tetraethylstannane. The right-hand spectrum (in the region of 3000 cm^{-1}) was recorded with a speed more than five times greater than in the region up to 1460 cm^{-1}.

Fig. 4. Absorption spectrum and scattering spectrum

Figure 4: Fig. 4. Absorption spectrum and scattering spectrum

In the case of tetraethyllead, $\nu_{Pb-C} = 443$ cm^{-1} (type A), 458 cm^{-1} (type F) in the Raman spectrum and 460 cm^{-1} (type F) in the infrared, i.e., the frequencies of the skeletal vibrations are lower than for tetraethylstannane (Figs. 2, 3, 4).

It can be seen that the IR absorption bands and Raman lines associated with stretching vibrations of Sn—C bonds, in the general case, lie in the interval 450-530 cm^{-1}; for organogermanium compounds the frequency interval of stretching vibrations of Ge—C bonds is 500-650 cm^{-1} (^{2}).

Fig. 4. 1 —absorption spectrum of tetraethyllead (explanation as in Fig. 1); 2 — scattering spectrum of $Pb(C_2H_5)_4$. The rise of the curve, indicated in the figure by an arrow, is the moment at which chemical decomposition of the substance began during the recording.

The author expresses gratitude to I. V. Obreimov for his interest in the work and for its discussion, and to V. F. Mironov for kindly providing the substances.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
27 V 1961

REFERENCES CITED

1. N. A. Chumaevskii, *Optics and Spectroscopy*, **10**, 69 (1961).

2. M. V. Vol' kenshtein, M. A. El' yashevich, B. I. Stepanov, *Molecular Vibrations*, **1**, 1949.

3. I. F. Kovalev, *Proceedings of the 10th All-Union Conference on Spectroscopy*, 1957, Lviv, **1**, 1957, p. 304.

4. C. W. Young, J. S. Koehler, D. S. McKinney, *J. Am. Chem. Soc.*, **69**, 1410 (1947).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.