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Raman Spectra and Calculations of the Normal Vibrations of Some Organotin Compounds

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Low frequency Raman spectra of a series of tin compounds; tetramethyltin Me_4Sn, hexamethyldistannane Me_6Sn_2, bis (trimethylstannyl) dimethyltin $(Me_3Sn)_2$-$SnMe_2$, tris (trimethylstannyl) organotin $(Me_3Sn)_3$ SnR (R = Me, Et, Bu, i–Bu, *n*-pentyl and phenyl) and tetrakis (trimethylstannyl) tin $(Me_3Sn)_4Sn$, were recorded and assigned in the region 0–600 cm^{-1}. The normal vibrations of these compounds have been calculated and discussed in relation to the observed spectra. It was evident from the data that on going from $Me_8Sn_3 \rightarrow Me_{10}Sn_4 \rightarrow Me_{12}Sn_5$, the change in the vibration frequencies was very small and no shifts are observed for the C–Sn–Sn–stretching vibrations. On the other hand the symmetric and asymmetric stretching vibrations of Sn–Sn display a systematic decrease in the frequencies, which is in harmony with the calculated data. The decrease in vibration frequencies correlate well with published data of ^1J(Sn–Sn) coupling constant.

INTRODUCTION

The so-called GF-martix method should be used to calculate the normal vibtrations[1]. The calculation was carried out with a special computer-programm[2]. Since the present work is mainly interested in the vibrations including the tin atoms, the CH_3–, C_2H_5–, C_3H_7–, C_4H_9– and C_6H_5– groups in the compounds under investigation are treated as mass points with m = 15.03, 29.06, 43.08, 56.12 and 67.11 respectively. For such calculations the following bond lengths are taken[3] into consideration: Sn–Sn = 2.8, Sn–C = 2.18, C–C = 1.45, C–H = 1.09 Å, with the assumption that all the angles exist at Sn and C atoms are those of the tetrahedron. The stretching and the bending force constants are used without consideration of the interactions. The value of f_{Sn-Sn} = 1.15 mdyn/Å, which was calculated by the help of Siebert's rule[4], is used for the Sn–Sn stretching force constant or the C–Sn–C–, Sn–Sn–C– and Sn–Sn–Sn bending force constants[5], the values 2.2 mydn/Å, 0.28, 0.2 and 0.15 mydn Å/radian^2, respectively, were applied.

RESULTS AND DISCUSSION

Tetramethyltin (*Me_4Sn*): The Raman spectrum of Me_4Sn shows strong band at 150 cm^{-1}, which is assigned to the bending vibration of the C–Sn–C. The symmetric and asymmetric stretching vibrations of the Sn–C bond are observed at 510 and 520 cm^{-1} (Fig. 1(a)), respectively.

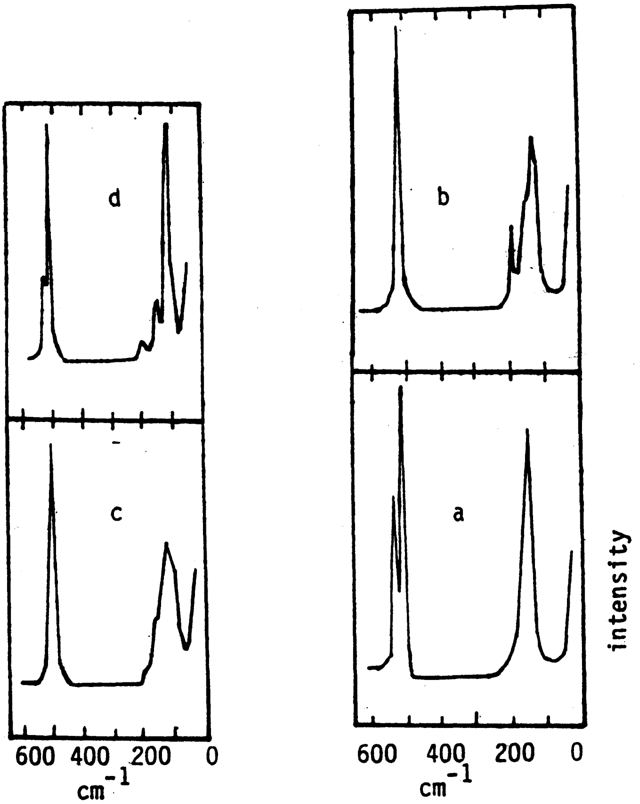

Fig. 1 The recorded Raman spectra of: (a) Me_4Sn, (b) Me_6Sn_2, $(Me_3Sn)_2Sn{-}Me_2$ and $Me_{12}Sn_5$.

Hexamethyldistannane (Me_6Sn_2): The Raman spectrum of Me_6Sn_2 shows the bands at 140 and 510 cm^{-1}, which are assigned to the C–Sn–C bending and Sn–C stretching vibrations. In addition the spectrum shows Raman bands at 125 and 190 cm^{-1}; which are not observed in the spectrum of tetramethyltin hence can be assigned to the C–Sn–Sn bending and the Sn–Sn–stretching vibrations (Fig. 1(b)). Brown[6] has given a similar assignment for the same compound. Spiro[7] postulated for the compound $(C_6H_5)_6Sn_2$, that the total symmetric vibrations of Sn–Sn would appear at 136–140 cm^{-1}, while Gager's[8] assigned the band at 207 cm^{-1} to the symmetric Sn–Sn– vibrations of $(C_6H_5)_6Sn_2$.

Bis (trimethylstannyl) dimethyltin ($(Me_3Sn)_2SnMe_2$): Fig. 1(c) shows the Raman spectrum of this compound. The calculated and the observed vibration frequencies and their assignements are given in Table 1, where the observed and the calculated frequencies are in agreement to each other.

TABLE 1
THE OBSEVED AND THE CALCULATED VIBRATION FREQUENCIES (cm^{-1}) AND THEIR ASSIGNMENTS OF $(Me_3Sn)_2SnMe_2$.

Observed	Calculated	Assignement
110	109	δ C–Sn–Sn
138	136	δ C–Sn–C
170	175	ν_s Sn–Sn
200	204	ν_{as} Sn–Sn
513	509	ν_s Sn–C

Tris (trimethylstannyl) organoltin: $(Me_3Sn)_3Sn{-}R$ (R = Me,Et, Bu, *i*-Bu, *n*-pentyl and phenyl). The Raman spectra of these compounds are recorded in the pure liquid state. These compounds as expected, would yield spectra that are similar to each other, which donate that the alkyl (aryl) group had a small influence on the normal vibrations, and hence, no much change would appear in the vibration frequencies. Table 2 contains the observed and the calculated frequencies and their assignments whereas Fig. 2 shows the recorded spectra.

TABLE 2
THE OBSERVED AND THE CALCULATED VIBRATION FREQUENCIES (in cm^{-1}) AND THEIR ASSIGNMENTS OF $(Me_3Sn)_3Sn{-}R$.

R = Me		R = Et		R = *n* Bu		R = *i* Bu		R = *n* pentyl		R = phenyl		assignments
obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	
112	118	112	118	113	115	112	115	112	115	—	—	δ C–Sn–Sn
138	135	140	138	141	140	140	140	139	140	139	142	δ C–Sn–C
161	166	162	168	161	168	161	168	162	168	165	169	ν_s Sn–Sn
200	205	198	207	207	208	200	209	200	207	202	209	ν_{as} Sn–Sn
511	510	511	509	513	507	511	507	512	508	508	513	ν_s Sn–C
423	530	524	523	523	531	522	531	524	532	525	533	ν_{as} Sn–C

Tetrakis (trimethylstannyl) tin $(Me_3Sn)_4Sn$: The Raman spectrum of the high symmetric compound was recorded in cyclohexane solution (0.25 mole/l). Fig. 1d shows the recorded spectum while the observed and the calculated frequencies with their assignment are collected in Table 3, where the observed and the calculated frequencies are in agreement to each other. These results contradict with the postulated assignements previously made by some authors[7,8] on the compound $(C_6H_5)_3Sn_4Sn$.

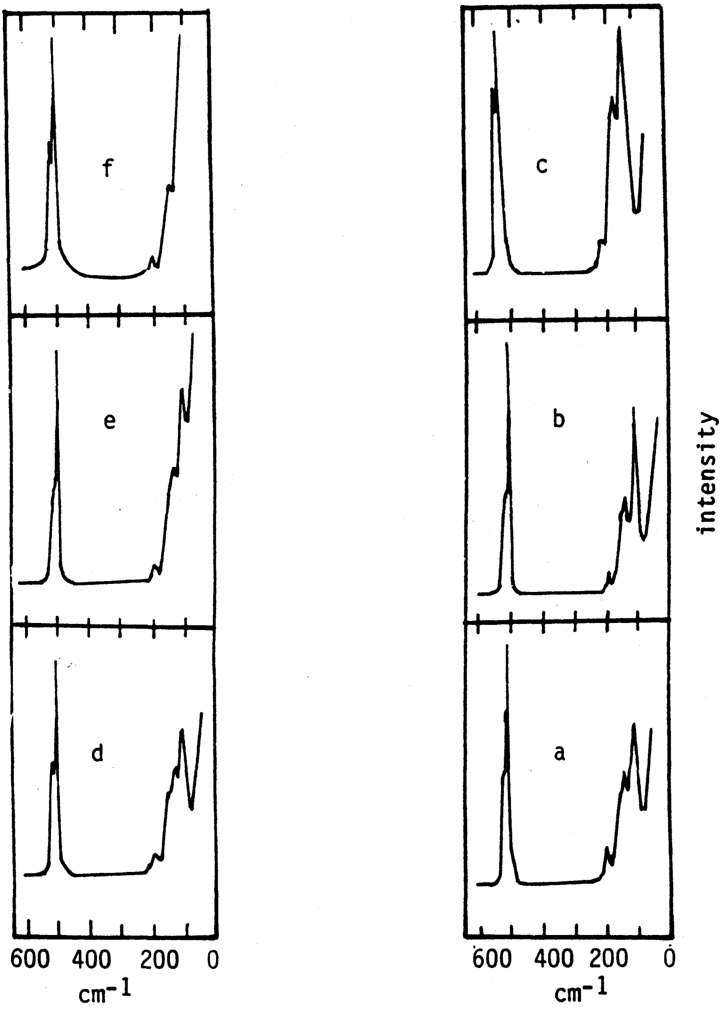

Fig. 2 The recorded Raman spectra of $(Me_3Sn)_3Sn$–R. (a) R = Me, (b) R = Et, (c) R = n *Bu*, (d) R = *i* Bu, (e) R = *n* pentyl and (f) R = phenyl

The characteristic vibration frequencies of this series of tin compounds are collected in Table-4, from this Table it is observed, that the change in the vibration frequencies is very small by the passage from $Me_8Sn_3 \rightarrow Me_{10}Sn_4$ to $Me_{12}Sn_5$. For the C–Sn–Sn– bending vibrations and Sn–C–stretching vibrations, there is no change, which is in harmony with the previous published data of $^1J(Sn^{119}–C_1)$ coupling constants[10], while the symmetric and asymmetric stretching vibrations of Sn–Sn–, decreased in a systematic manner. This results is correlated in a very good way with the decreased $^1J(Sn^{119}-Sn^{119})$ coupling constants in these compounds[10]. It is observed in the same trend that there is a very small increase appear in the C–Sn–C bending vibrations. The vibration forms of the high symmetric molecule $Me^{12}Sn_5$ (T_d symmetry) can be depicted diagramatically, which represent the Sn–Sn– stretching, C–Sn–C– and C–Sn–Sn– deformation vibrations. These calculations were carried out by the aid of a computer-programme[9].

TABLE 3
THE OBSERVED AND THE CALCULATED VIBRATION FREQUENCIES AND THEIR ASSIGNMENTS (cm^{-1}) OF $(Me_3Sn)_4Sn$.

observed*	calculated*	assignment
111	102	δ C–Sn–Sn
142	140	δ C–Sn–C
159	157	ν_s Sn–Sn
198	204	ν_{as} Sn–Sn
508	505	ν_s Sn–C
521	530	ν_{as} Sn–C

TABLE 4
THE CHARACTERISTIC VIBRATION FREQUENCIES cm^{-1}, AND THE COUPLING CONSTANTS IN Hz. OF THE INVESTIGATED COMPOUNDS

Compounds	δ (C–Sn–Sn)	δ (C–Sn–C)	ν_s (Sn–Sn)	ν_{as} (Sn–Sn)	ν_s (Sn–C)	ν_{as} (Sn–C)	$^1J(^{119}Sn-^{119}Sn)^a$
Me_4Sn	—	150	—	—	510	520	—
Me_6Sn_2	125	140	190	—*	510	—*	4404
Me_8Sn_3	110	136	175	204	509	—*	2873
$Me_{10}Sn_4$	112	136	161	200	511	523	1733
$Me_{12}Sn_5$	111	142	160	198	508	521	876

*not observed due to band overlap: a Data from ref. 10.

EXPERIMENTAL

The organotin compounds were prepared as reported previously[10] and their purity was established by elemental analysis. Raman spectra were recorded at room temperature using the T800 Coderg and an Argon-ions Laser Model 171 Spektra Physics.

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