The Raman Spectra of Solid and Liquid Tetramethylsilane

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Laser Raman spectra of tetramethylsilane in its three crystalline forms and in the liquid state have been observed for the lattice and intramolecular vibrational regions. The bands due to lattice vibrations increase as the transitions from α to β and to γ occur. The spectra of the β and γ forms exhibit crystal-field splittings of intramolecular bands. The observed spectra suggest that the β and γ forms are isomorphous with each other and the α form has a higher symmetry.

Solid $Si(CH_3)_4$ has been shown by calorimetric studies[1] to have three crystalline forms designated by α, β, and γ, their triple point temperatures being 165.91, 170.98, and 174.05 K, respectively. The transitions α-to-β-to-γ seem to be irreversible. The infrared and Raman spectra of the liquid state were measured and band assignments made by several authors,[2] but the crystal structures of the three forms have not been studied.

In the present investigation, the Raman spectra of $Si(CH_3)_4$ in its three crystalline phases and liquid state have been measured for the entire spectral region including lattice and intramolecular vibrations in order to obtain information on the crystal structure and molecular motions of the three forms.

Experimental

The sample of $Si(CH_3)_4$ was the same as that used in a previous calorimetric measurement,[1] the purity of which was determined to be 99.995_4 mol% by the measurement of melting point. The Raman spectra were obtained with a Raman spectrometer, Kawaguchi Electric Works Ltd. model RL-62. The exciting light was 488.0 or 514.5 nm line of the Ar^+ laser, NEC model GLG2003. The cryostat, experimental techniques and temperature measurements have been reported.[3] The crystals were grown from the liquid by careful cooling. The result of total thermal analysis obtained by using the apparatus for laser Raman measurements is shown in Fig. 1. After each measurement, the crystalline form was checked by observing its melting point.

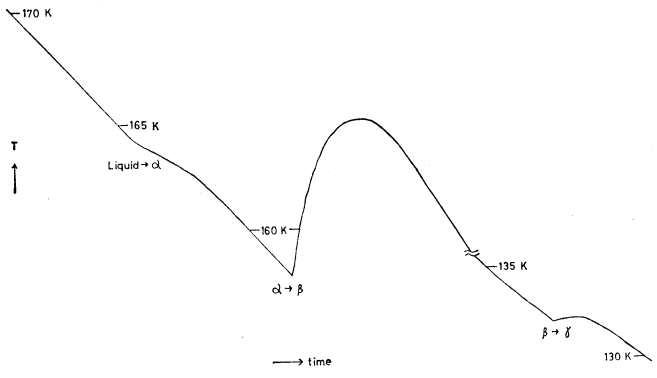

Fig. 1. Cooling curve (total thermal analysis) of $Si(CH_3)_4$.

Results and Discussion

Raman Spectrum in the Lattice Region. The observed spectrum in the lattice region consists of very weak and broad ghost bands. The lattice bands became very weak in the β and γ forms because a transparent crystal could not be obtained. The slitwidths of 3.1—3.6 cm^{-1} were used for reasonable intensities without too much background noise. The spectrum of the α-form in the lattice region is compared with corresponding spectrum of the γ-form in Fig. 2. The temperature measured was 163.9 K, which is about 2 K below the melting point of the α-form. The spectrum in the lattice vibrational region for the β-form at 152.7 K, about 18 K below its melting point, is shown in Fig. 3 together with the corresponding spectrum of the γ-form.

The Raman spectra of the β and γ forms have a pattern similar to each other with a large number of bands (Fig. 3). A similar spectral pattern suggests the two forms to be isomorphous with each other. Many bands in the lattice region suggest that the crystal contains many molecules of non-identical spatial position or orientation in a crystallographic unit cell with a low symmetry, as solid-CCl_4[4] and solid-CBr_4[5] in the low-temperature phases. In the Raman spectrum of the

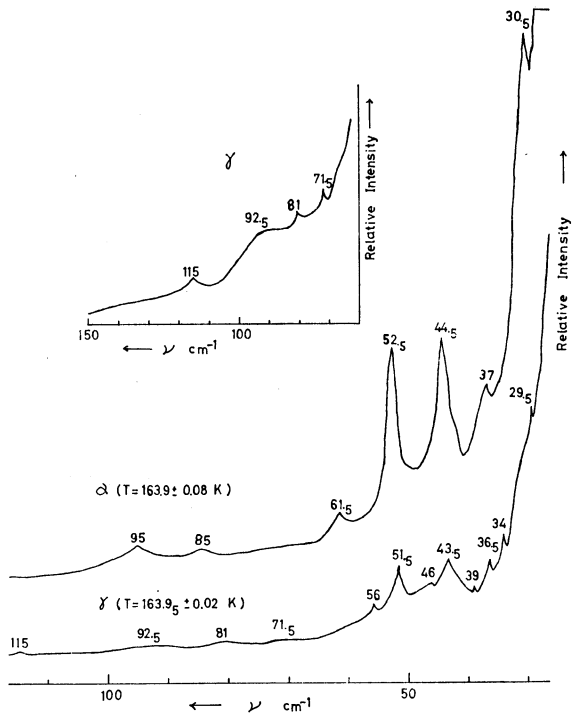

Fig. 2. Raman spectra in the lattice region of the α and γ forms at 163.9 K.

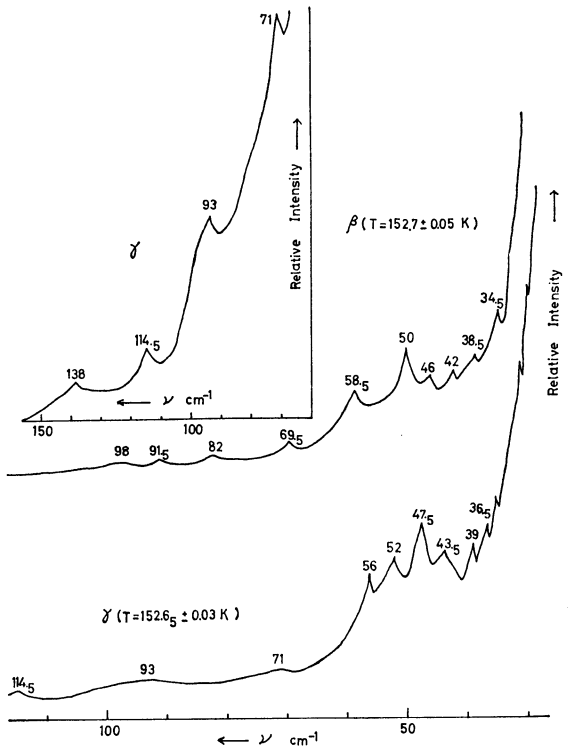

Fig. 3. Raman spectra in the lattice region of the β and γ forms at 152.7 K.

α-form the number of bands is smaller than that for the β and γ forms, probably owing to the high symmetry of the unit cell. We find no values in literature to compare with the ν values of lattice vibrations observed. The activation energies for the molecular reorientation or tumbling motion for γ-$Si(CH_3)_4$ were found to be 7.23 ± 0.40 and 8.7 ± 0.5 kcal mol^{-1} (above $\approx$140 K) by Smith[6] and Albert and Ripmeester[7] from their NMR studies. If molecules are assumed to be rigid rotators in a potential field of the type

$$V = (1/2)V_0(1-\cos n\theta), \quad (1)$$

the corresponding frequencies of librational lattice vibrations can be estimated from the above activation energies. The value of the moment of inertia of the molecule was calculated to be 27.20×10^{-39} g cm^2 by assuming the bond angle to be $\angle HCH=109°$ and interatomic distances $r_{CH}=1.10$ and $r_{CSi}=1.888$ Å.[8] The calculated results for $n=2$ and $n=3$ give values of frequencies of 32—35 and 48—53 cm^{-1}, respectively. Thus, the present values of lattice vibrations are reasonable.

Raman Spectrum of Intramolecular Vibrations. The Raman spectra of the liquid state and the three crystalline forms of $Si(CH_3)_4$ are shown in Fig. 4 for the intramolecular vibrational regions. The observed frequencies are given in Table 1 together with those reported.[2] The lines of the β and γ forms show a splitting of the degenerate fundamental of 7—26 cm^{-1}. In the crystal, the presence of some molecules of non-identical spatial position or orientation in the unit cell induces a splitting of the vibrational levels. In recent studies of other similar tetrahedral molecular crystals (CF_4[9] and CCl_4[10]) under high resolution, crystal splittings of the degenerate fundamentals were observed. The splittings observed for the degenerate fundamentals in the β and γ forms may be due to crystal effects.

The relative intensities of the lines obtained by integration are given in Table 1. We see that the relative intensities of the lines belonging to species e are large in α and those in β and γ are similar to each other. If only skeletal modes are taken into account, the vibrations $\nu_1(a_1)$, $\nu_2(e)$, $\nu_3(f_2)$, $\nu_4(f_2)$ are active in Raman scattering in the free molecule (T_d symmetry), The ratios of the intensity to that of the totally symmetric vibration, ν_1, for the liquid state, α, β and γ forms were estimated. The results are as follows, $I(\nu_2)/I(\nu_1)$: 1.3,

Table 1. Observed Raman active molecular vibrations of $Si(CH_3)_4$

Liquid[a]		Liquid			Solid(α)			Solid(β)			Solid(γ)			Sym. species
ν (cm^{-1})	Int	ν (cm^{-1})	Int	T(K)	ν (cm^{-1})	Int	T(K)	ν (cm^{-1})	Int	T(K)	ν (cm^{-1})	Int	T(K)	
199	80	199.$_5$	36(53)	176.6$_5$(295.2)	201.$_5$	98	163.9	205	45	152.6$_5$	181 207.$_5$	35	102.2	e
245	46	245	22(27)	176.5 (295.2)	243	58	163.9	232 248	29	152.7	235.5 248.5 249.5	19	102.2	f_2
593	40	594	24(30)	176.2 (295.1)	595	44	163.9	593	61	152.6	592	48	102.2	a_1
694	33	694	21(19)	176.2$_5$(295.0$_5$)	694.$_5$	37	163.9	694	21	152.6$_5$	694.$_5$	18	102.2	f_2
862	—	861.$_5$	7.7(4.9)	176.4 (295.1$_5$)	860.$_5$	18	164.0	853 862 866	10	152.6	854.5 864.5	9	102.1$_5$	f_2
1250	8	1250	2.7(1.5)	176.2 (295.2)	1251	5	163.9	1248	3.3	152.6	1247.$_5$	2.3	102.1	f_2
1263	8	1263	1.1(0.9)	176.2 (295.2)	1264	0.7	163.9	1257	2.5	152.6	1256.$_5$	1.9	102.1	a_1
1418	40	1418	14(11)	176.0 (295.0)	1418.$_5$	27	163.8$_5$	1418 1425	18	152.6	1418.5 1429.5	16	102.1$_5$	e
2900	100	2900	100(100)	176.2 (294.9)	2902	69	164.0	2901	100	152.6$_5$	2901	100	107.4$_5$	a_1
2957	88	2957.$_5$	88(76)	176.2 (294.9)	2958.$_5$	100	163.9$_5$	2961	77	152.6	2957 2959.5 2963	90	107.6	f_2

a) Ref. 2. The relative intensities are integrated intensities referred to the maximum intensity of 100. Correction in sensitivity dependent upon the exciting light is made.

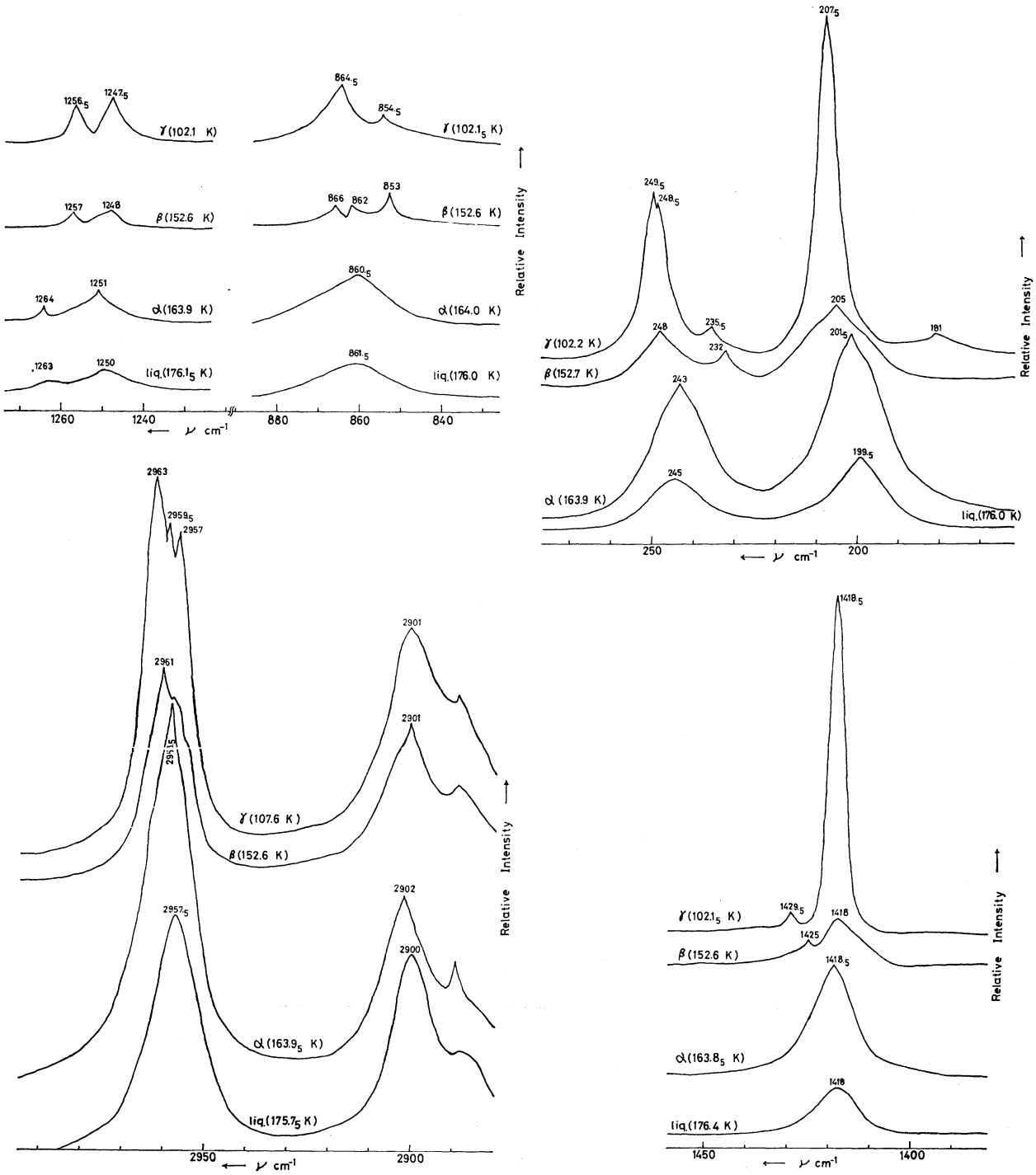

Fig. 4. Raman spectra in the intramolecular vibrational region of liquid and three crystalline forms. The temperatures observed are given in parentheses.

2.0, 0.67, 0.73; $I(\nu_3)/I(\nu_1)$: 0.87, 0.84, 0.35, 0.38; $I(\nu_4)/I(\nu_1)$: 0.81, 1.2, 0.44, 0.40, respectively.* The values for the β and γ forms are close to each other, the values for the α-form being nearer those for liquid than for the β and γ forms. On the assumption of the oriented gas model,[11] the derived polarizability tensor of the crystal related to the Raman intensity is obtained by the elements of the derived polarizability tensor of the free molecule and information on molecular orientation in crystal. It seems that the molecules of the α-form orientate in disorder favoring a high unit-cell symmetry, if we take into account the fact that the spectrum of the α-form exhibits on crystal-field splitting of intramolecular bands.

* The temperature dependence of the intensity is given by $I(T_1)/I(T_2)=[1-\exp(-h\nu/kT_2)]/[1-\exp(-h\nu/kT_1)]$. The present results are estimated at $T=102$ K.

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