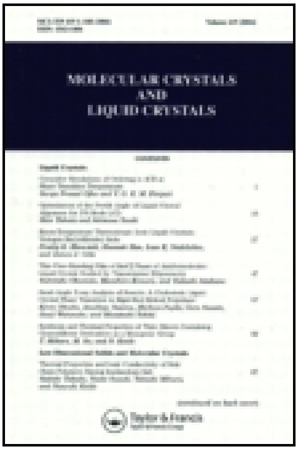

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Temperature Dependence of Raman Spectrum in Solid Carbon Tetrabromide

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Version of record first published: 19 Oct 2010.

To cite this article: Takako Shinoda (1978): Temperature Dependence of Raman Spectrum in Solid Carbon Tetrabromide, Molecular Crystals and Liquid Crystals, 44:3-4, 277-285

To link to this article: http://dx.doi.org/10.1080/00268947808084985

Mol. Cryst. Liq. Cryst., 1978, Vol. 44, pp. 277–286
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Printed in Holland

Temperature Dependence of Raman Spectrum in Solid Carbon Tetrabromide

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(*Received August 22, 1977*)

Laser Raman spectra of carbon tetrabromide have been observed for the lattice and intramolecular vibrational regions over a temperature range of 80–370 K. Many bands were observed in the lattice region and the spectrum at the lower temperature in the monoclinic phase is similar to that of γ-$Si(CH_3)_4$. The temperature dependence of each band has been studied. The ν_3 fundamental indicates a distinct variation corresponding to the phase transition.

INTRODUCTION

Solid carbon tetrabromide (CBr_4) has been shown by a calorimetric study[1] to undergo phase transition at 320.1 K and to melt at 363.3 K. According to the X-ray analysis by Finbak and Hassel[2] the low- and high-temperature phases are monoclinic with 32 molecules per unit cell and face centered cubic, the space group Pa3 with eight molecules per unit cell, respectively. The Raman spectrum of the liquid was obtained in benzene solution[3] or with small amount of allyl alcohol[4] to prevent the liberation of free bromine by photochemical decomposition.

In this report we present a study of the changes in the Raman spectrum of solid CBr_4 with temperature for the entire spectral region including lattice and intramolecular vibrations.

EXPERIMENTAL

CBr_4 obtained from Tokyo Kasei Kogyo Co., Ltd. was purified by being twice sublimed in vacuum. The Raman spectra were obtained with a Raman spectrometer, Kawaguchi Electric Works Ltd. model RL-62 by using

488.0 nm or 514.5 nm line of an Ar^+ laser, NEC model GLG2003 as an exciting light. The cryostat was the same as described previously.[5] The crystal was grown from the liquid state by careful cooling in the sample vessel for laser-Raman measurements. In order to gather information on molecular motions as realistically as possible, no additional material was used. The power of the exciting light was weakened to prevent photochemical decomposition. The liberation of free bromine was not observed during the experiment below room temperature. However, a small amount of photochemical decomposition was inevitable above room temperature.

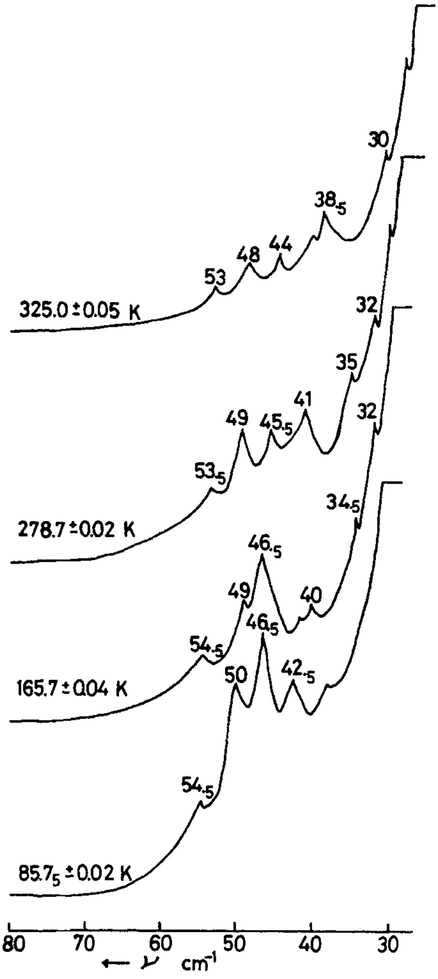


FIGURE 1 The Raman spectra of solid CBr_4 in the lattice region at several temperatures.

RESULTS AND DISCUSSION

Raman spectra in the lattice region

Figure 1 shows the Raman spectra of the crystals in the lattice region at several temperatures. Many bands in the lattice region are consistent with the result of the X-ray analysis[2] that many molecules of non-identical spatial positions or orientations are contained in a crystallographic unit cell. In Figure 1 the spectrum observed at 278.7 K is more similar to that obtained in the high-temperature phase (at 325.0 K) than those observed in the low-temperature phase. This suggests that the transition begins cooperatively from far below the transition temperature. The number of bands did not decrease as the transition took place. From this feature, it can be assumed that the spatial positions of the molecules in the unit cell are identical but the spatial orientations are not identical with each other in the high-temperature phase by comparing with the result of the X-ray analysis.[2]

The Raman spectrum observed at 85.7_5 K is similar to that of the γ-form of $Si(CH_3)_4$.[6] This suggests that the crystals are isomorphous with each other. The ratios of the squared frequencies, the moments of inertia and the transition (or melting) temperatures of CBr_4 to those of γ-$Si(CH_3)_4$ are about $(46.5/47.5)^2 = 0.96$, $(156/27.2) = 5.7$ and $(320.1/174.05) = 1.84$, respectively. According to Kirkwood's theory of the transition in a crystal arising from molecular rotation, the transition temperature to disordering of two equilibrium orientations is three times that to free rotation. If this theory is applied, the result may be reasonably explained by assuming a transition to a free rotational model for CBr_4 and an order-disordered orientational one for γ-$Si(CH_3)_4$.

Raman spectra of intramolecular vibrations

In the free molecules (T_d symmetry), all four fundamentals $\nu_1(a_1)$, $\nu_2(e)$, $\nu_3(f_2)$, $\nu_4(f_2)$ are active in Raman scattering. In the monoclinic phase a splitting of the degenerate fundamental is expected to occur. The observed spectra of solid or liquid CBr_4 at several temperatures are shown in Figures 2 and 3.

The region of the ν_3 fundamental shows the expected three lines (Figure 2). In the high-temperature phase these lines became a broad band centered at 662 cm^{-1}, although a ghost splitting to two peaks was observed just above the transition temperature (323.7_5 K). The peak of the band moved to 665 cm^{-1} in the liquid (368.0 K). We attempted to separate the three overlapping bands by using the Du Pont 310 Curve Resolver, assuming a Lorentzian band shape, and to estimate the ratio of the areas. The separated

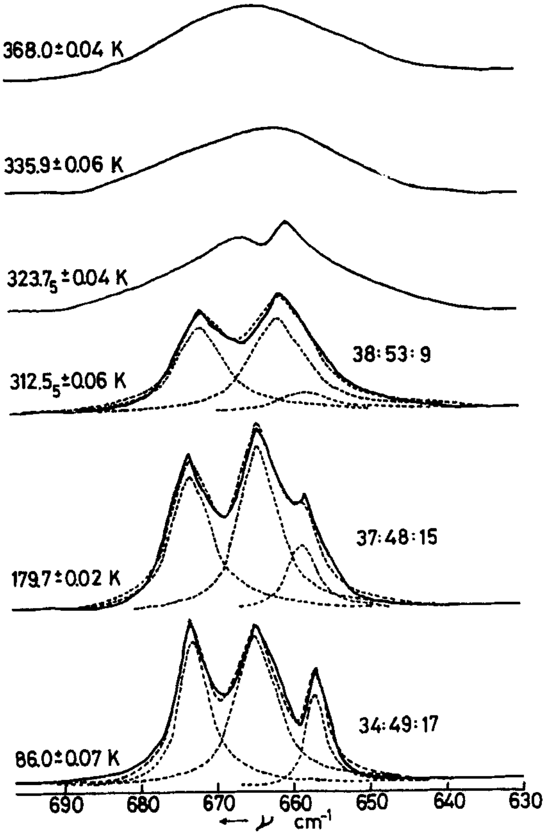


FIGURE 2 The Raman spectra of the ν_3 region of CBr_4 at several temperatures. Solid line; experimental spectrum, broken line; Lorentzian decomposition.

bands are illustrated by broken lines and the experimental spectra by solid lines in Figure 2. The frequencies of the band center are plotted against temperature, as shown in Figure 4. Open circles indicate the observed values and black circles the values obtained from Lorentzian decompositions of the experimental spectra.

Although the Raman spectrum of the ν_4 region is expected to split into three peaks, the observed result is not so distinct as that of the ν_3 region as seen from Figure 3. From a plot of the observed frequencies of the band centers against temperature, it seems that the ν_4 fundamental splits into three bands at 183, 184 and 187 cm^{-1} in the low-temperature phase and becomes one band centered at 182.5 cm^{-1} and 182 cm^{-1} in the high-temperature phase and in the liquid, respectively (see Figure 3). The experimental spectrum was separated as shown in Figure 3, assuming three Lorentzian bands,

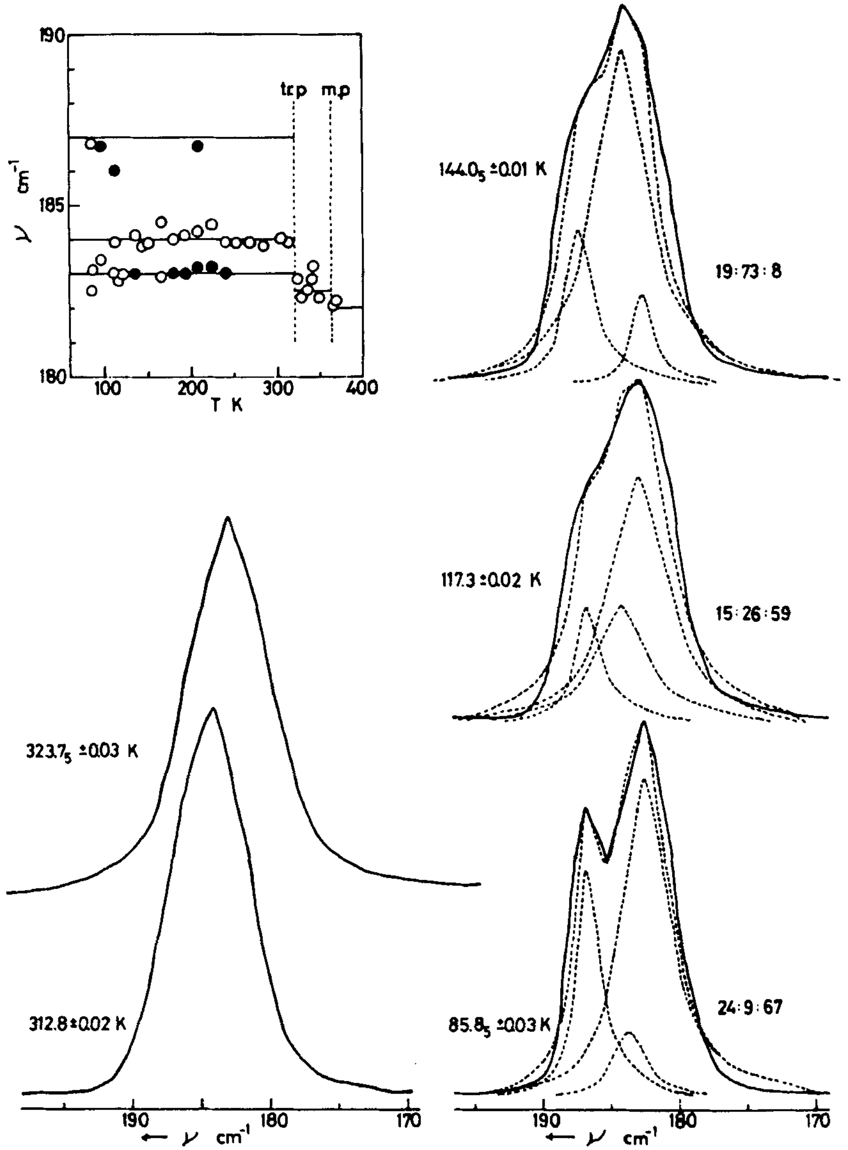


FIGURE 3 The Raman spectra of the ν_4 region of solid CBr_4 at several temperatures (solid line; experimental spectrum, broken line; Lorentzian decomposition), and plots of observed band centers of the ν_4 region against the temperature of CBr_4 (black circle; very weak or shoulder).

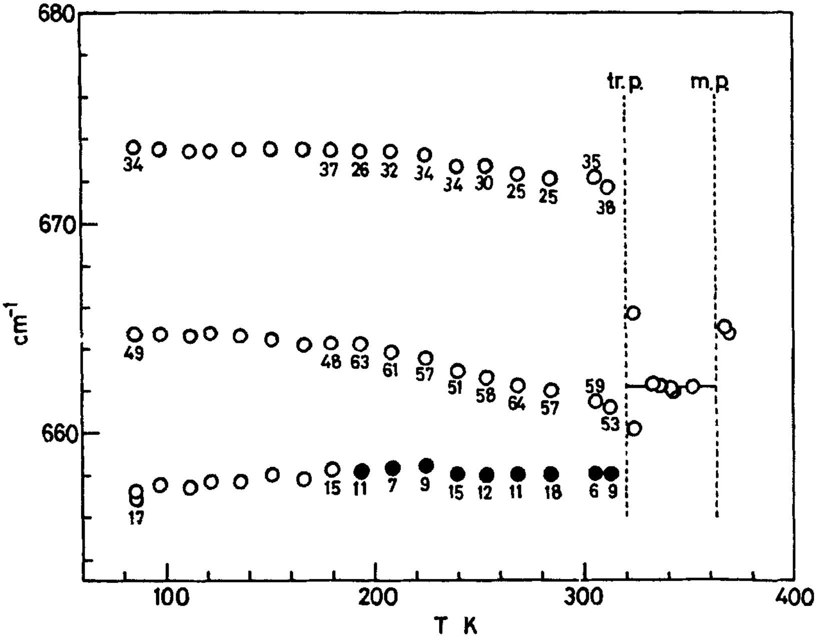


FIGURE 4 Plots of Raman frequencies of the ν_3 region against the temperature of CBr_4. Numbers indicate percentages of areas by Lorentzian decomposition.

and the ratio of the areas was estimated. It is to be noted that the ν_3 fundamental splits into two bands and further the lower-frequency band splits into two, whereas the ν_4 fundamental splits into low- and high-frequency sides with decreasing temperature in the monoclinic phase.

The line of the ν_2 region presents a slight splitting of about 0.7–1.0 cm^{-1} at the lower temperature in the monoclinic phase (125.9 and 126.8 cm^{-1}). The observed frequencies were 125.$_7$ and 125 cm^{-1} in the high-temperature phase and in the liquid, respectively.

The ν_1 fundamental is a totally symmetric vibration and no temperature dependence was observed in each phase. The ν_1 band showed no splitting even at low temperature. This suggests that the observed splittings of the degenerate fundamentals are not due to isotopic molecules. The observed ν_1-frequency is 267.$_5$ cm^{-1} in the low-temperature phase and 267 cm^{-1} in the high-temperature and liquid phases.

It is also interesting to note that the ν_3 fundamental indicates a more distinct temperature dependence corresponding to the phase transition than the lattice vibrations.

Although the observed relative intensities are of questionable accuracy because free bromine is liberated by the exciting laser, we attempted to plot

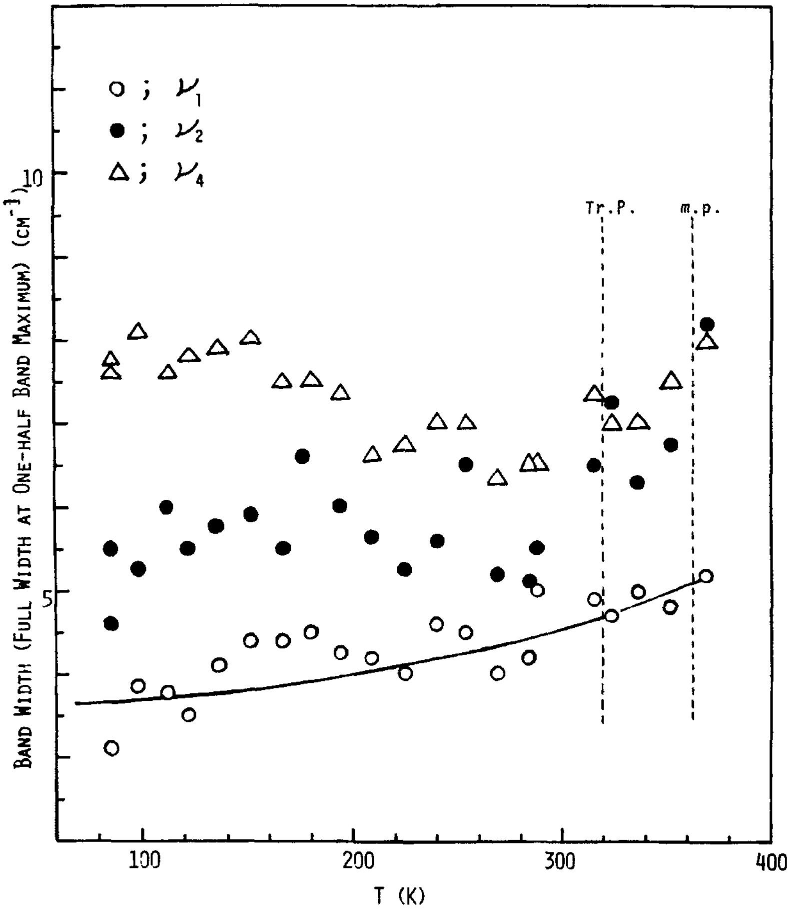
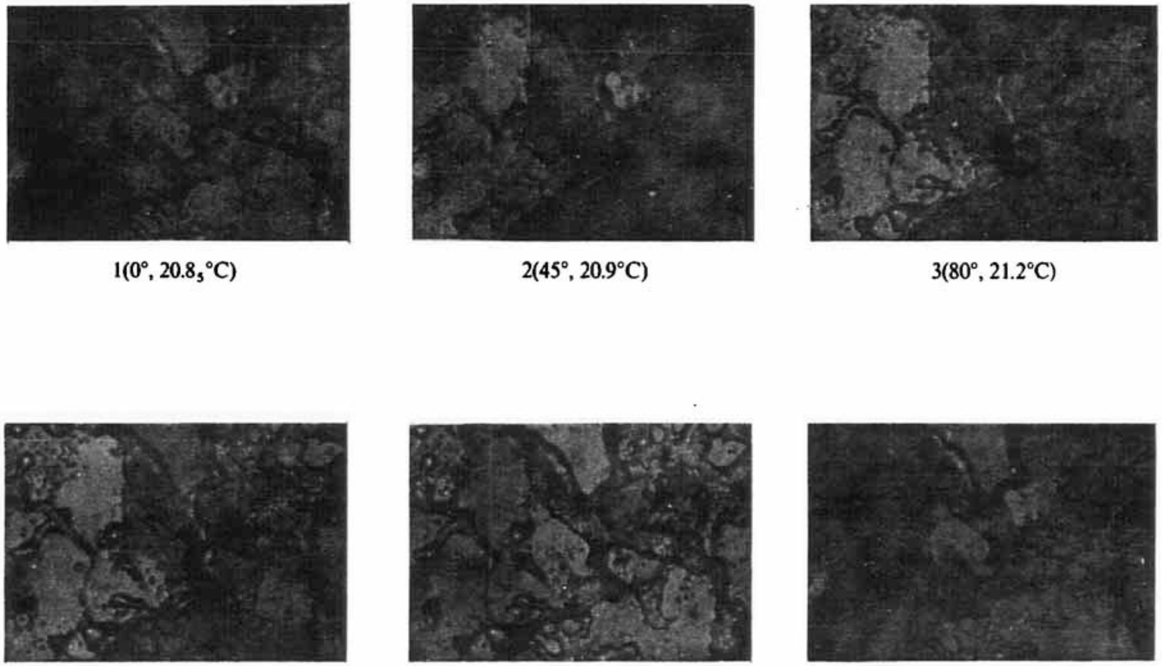


FIGURE 5 Temperature dependences of the line widths of the ν_1, ν_2 and ν_4 bands.

full widths at one-half band maxima of the ν_1, ν_2 and ν_4 lines against temperature (Figure 5). We see that the line widths of the ν_1 increase and those of the ν_2 and ν_4 decrease with increasing temperature in the monoclinic phase. This feature may be evidence of the splittings of the ν_2 and ν_4, and no splitting of the ν_1.

Although it has been reported by a calorimetric study[1] that the transition displays a thermal hysteresis, no hysteresis was observed in our measurement.

We attempted to investigate the crystal states of the sample by using a polarizing microscope. Observations were carried out through crossed nicols and a color-sensitive plate, magnification being 200. A tungsten lamp (30 W) was used as a light source. The result is shown in Figure 6. By rotating



1(0°, 20.8_5°C) 2(45°, 20.9°C) 3(80°, 21.2°C)

4(90°, 20.9°C) 5(125.3°, 20.9_5°C) 6(180°, 21.0°C)

FIGURE 6 Microscopic photographs of monoclinic CBr_4 crystal at room temperature. The rotating angle of crossed nicol and the temperature are noted in parentheses.

the crossed nicol the variation in color was observed at 90° period, and a photograph with homogeneous color was obtained at 125.3° (see Figure 6-5). This corresponds to an extinction or a diagonal position, and the rotating angle is accidentally equal to the β-angle of the monoclinic crystal of CBr_4. It seems that the sample is characteristic of a single crystal on a macroscopic scale. This is consistent with distinct temperature dependence of the ν_3 fundamental.

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