

PHONON RAMAN SPECTRA, MOLECULAR MOTIONS, AND PHASE TRANSITIONS OF DIMETHYLACETYLENE CRYSTAL*

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The phonon Raman spectra of crystals of dimethylacetylene, perdeutero-dimethylacetylene and their mixtures have been investigated down to 20°K. The high temperature phase shows only one line and the low temperature phase only two. Neither of these is related to the R_2 (methyl) rotation, which seems to remain practically free. However, the latter motion is found to be restricted in a newly discovered metastable phase, which is reported here first, displaying 5–6 phonon bands. The well-known λ -point transition appears little related to methyl rotations. The internal rotation of dimethylacetylene seems to stay practically free down to 20°K in the stable phases.

1. Introduction

In view of the fact that the phonon states are entirely due to solid state interactions and since their transitions are very sensitive to the unit cell symmetry, one would expect the phase transition to manifest itself as a change in the phonon spectra. The phonon spectra, however, have not been widely used to investigate the phase transition phenomena in molecular solids. On the other hand, a temperature dependent study of the heat capacity has conventionally been used to detect and investigate phase transitions including that of dimethylacetylene [1]. In this paper we present a Raman phonon study of the phase transition in dimethylacetylene (DMA) crystal which, in our opinion, provides a clear example of how sensitive the phonon spectrum is to the phase transition. Also, with the help of the phonon spectra we have discovered a new metastable phase of the DMA crystal which has been missed before by all other methods, including a very recent NMR study [2]. The reason is that this phase does not appear if the crystal is cooled slowly. The Raman phonon spectra provide us with some insight into the nature of the phase transition at the molecular level, though the investigation at this

stage is only fragmentary. A complete investigation of the phase transition in DMA will be reported later.

2. Experimental

DMA- h_6 , DMA- d_6 and their various concentration mixtures were sealed in a capillary under vacuum. The flow of nitrogen vapor over the capillary provided a temperature bath from room temperature to 100°K. To get a lower temperature (down to 20°K) helium vapor was used. The Raman spectra were taken on a Ramalog Spex double spectrometer model 1401 at a resolution of 1 cm^{-1} . The excitation line was the 4880 Å laser emission from a Coherent Radiation Laboratory argon ion laser.

3. Results and discussion

Fig. 1 shows the Raman phonon spectra of DMA- h_6 in the three different crystalline phases. Phase I is a stable phase which persists down to 155°K when cooled slowly. When cooled fast with nitrogen vapor, this phase can very often be supercooled [3]. In this phase we see one band at 71 cm^{-1} (200°K value) which shifts to 80 cm^{-1} in the supercooled state at

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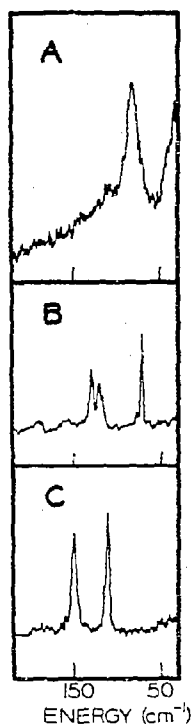


Fig. 1. The spectra of three different crystalline phases of DMA- h_6 . A is the spectrum of phase I supercooled to 100°K. B and C are, respectively, the spectra of phases II and III at 20°K. The spectral resolution is $\approx 1 \text{ cm}^{-1}$. In spectrum A (taken at 100°K), the noise level is high and except for the broad band at 80 cm^{-1} none of the other features are reproducible.

100°K. A metastable phase (we call it phase II) appears when the sample is cooled fast with helium vapor. This phase also appears sometimes when cooled fast with nitrogen vapor. The 20°K spectrum of this phase shows many bands: 69.5, 76, 114, 118, 125 cm^{-1} and a broad band at 152 cm^{-1} . When cooled slowly, phase I starts changing into the low temperature stable phase (phase III) at 155°K. The phase transition is complete if the temperature is kept near 155°K or if the sample is cooled slowly. The phase III spectrum consists of two bands at 108 and 146 cm^{-1} (20°K values). When the sample consisting of a mixture of phase I and phase III (which appears near the phase transition) is cooled fast to 20°K a mixture of phase II and phase III is obtained and the spectrum can be described as a superposition of the spectra of these two phases. We were not able to get

phase III from phase II even if we left it at the low temperature for hours.

DMA- d_6 shows a behavior similar to DMA- h_6 . The DMA- h_6 and the corresponding DMA- d_6 bands for the three phases are listed in table 1. The correspondence between the DMA- h_6 and the DMA- d_6 bands was established by the isotopic mixed crystal studies. In the isotopic mixed crystals all these phonon bands are in the amalgamation limit [4] and their frequencies shift linearly with the concentration of the isotopic component. Table 1 also lists the ratio of the per-proto frequency and the corresponding per-deutero frequency.

Next, we try to explain the result in light of the known crystal structures [5, 6] of phase I and phase III. The crystal structure of phase I is tetragonal with two molecules per unit cell. It shows that the molecules are arranged in linear chains along their long axis. The resulting chains are packed in parallel to form layers in which each chain is translated with respect to its neighbors on either side (in the direction of the chain and through one half of the unit repetition). These layers are stacked one upon another with successive rotations through 90° and with systematic translations such that the center of a molecule in one layer lies directly above the center between colinearly adjacent molecules. For this crystal structure, the observation of one phonon band will be consistent with a model of (1) free methyl motion or rather free R_z libration along the molecular three-fold axis and (2) small site and factor group splittings. Small site splitting implies that the R_x and R_y librations are degenerate. This model of small site and factor group splittings is also supported by the coincidence of the observed ratio of the per-proto frequency and the corresponding per-deutero frequency with that calculated on the assumption that the principal axes of the moment of inertia are along the molecular axes. In view of these considerations it appears that in phase I the important C-H and H-H interactions are along the linear chain (pairs of methyl groups belonging to colinearly adjacent molecules, may be rotating "in gear" [7]).

In phase III, the crystal data [5] show that molecules are tilted with respect to each other along the chain. This results in an increase from 2 to 4 molecules per primitive unit cell. Kopelman [7] suggested that such tilt increases significantly the barrier for the

Table 1

Phase studied	Observed DMA- h_6 bands, ν_h in cm^{-1}	Observed DMA- d_6 bands, ν_d in cm^{-1}	Isotope shift (the ratio ^{a)} ν_h/ν_d)
stable phase I supercooled to 100°K	80	70	1.14
metastable phase II (20°K)	69.5 76 114 118 125 152 (broad)	60 ? 90 104 115 140 (broad)	1.16 ? 1.27 1.13 1.09 1.09
stable phase III (20°K)	108 146	98 134	1.10 1.09

a) Assuming that the principal axes of the moment of inertia are along the molecular axes the calculated isotope ratios for R_x and R_y librational frequency is 1.14, while for the R_z librational frequency the ratio is 1.41.

methyl motion resulting in a 110 cm^{-1} lattice mode. We see two phonon bands in this phase (108 and 146 cm^{-1} in DMA). However, the isotope ratios for these two bands are ≈ 1.10 and are, thus, too low (compared with 1.41) to be a methyl motion (or R_z libration). Our result, thus, does not provide any evidence for the earlier suggestion [7] that the phase transition involves a change from a free methyl rotation to a hindered methyl rotation. Several possibilities exist: (i) the methyl rotation is still free in the low temperature phase; (ii) the barrier is lower than it was thought and as a result the R_z libration frequency is of the order of 10 cm^{-1} instead of 110 cm^{-1} ; (iii) the R_z librational transition is at least 50 times weaker than the observed phonon transitions. We seem to prefer the second possibility.

The observed two phonon bands may be due to increased site splitting, as the R_x and R_y librations are now more different because of the tilting of the molecules, or they may be due to increased factor group splitting (compared to phase I). In absence of any polarization study our present result cannot distinguish between the two possibilities, though in view of a rather large splitting ($\approx 30 \text{ cm}^{-1}$), one would be tempted to assign it as a site splitting.

In the absence of any X-ray crystal structure data of the metastable phase, it is difficult to interpret our results. However, considering that there are 6 observed

phonon bands, and assuming an effective center of inversion, the primitive unit cell in this phase must have at least two molecules. The observed isotope ratio for the band at 114 cm^{-1} (DMA- h_6 frequency at 20°K) is 1.27. This is much larger than the calculated isotope ratio for the R_x and R_y librations which is 1.14. As a matter of fact, all other bands show isotope ratios of 1.09–1.16. This makes the 114 cm^{-1} band of DMA- h_6 (and the corresponding 90 cm^{-1} band of DMA- d_6) a better choice for the R_z libration. In view of the fact that this ratio is substantially different from 1.41 we think that the principal axis of the moment of inertia for this motion may be different from the molecular long axis.

We would like to point out that in the region of the intramolecular vibrations the phase transition involves no drastic spectral changes. As a matter of fact, the spectra of the intramolecular region are almost identical for phases II and III. We would also like to point out that this investigation is consistent with previous conclusions [7, 8] about practically free internal rotation of DMA in the high temperature phase, as well as in the free molecule [7–11].

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