Single Crystal Temperature Dependent Raman Study of Carbamide

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Summary: The Raman study of oriented single crystals of hydrogenated and deuterated carbamide have been investigated in detail. The polarization measurement at ambient temperature and at liquid nitrogen temperature have been used for the assignment of the lattice modes of carbamide crystal. No evidence of any phase transition in the temperature range 373-77K have been observed.

Introduction

Carbamide is an interesting organic compound and its various properties such as crystal structure [1], dielectric dispersion [2], pressure induced phase transitions [3-4], normal coordinate analysis and vibrational spectra [5-9] have been studied in the past. The interest in this material has now grown due to its interesting non-harmonic properties [10]. Although the lattice mode Raman spectra of carbamide single crystals have been investigated by several workers [6-9], a satisfactory assignment of the lowest frequency Raman band has only been reported by Lefebvre et al. [9].

In the present paper the polarized and variable temperature Raman data are reported.

Experimental

Single crystals of hydrogenated carbamide were grown by the controlled evaporation of the saturated solution of $CO(NH_2)_2$ and deuterated samples were prepared by cooling a saturated solution of $CO(ND_2)_2$ in heavy water. The Raman spectra were recorded on a Spex Ramalog 5M system using 488 nm radiation from Spectra Physics 165 ionized argon laser, while the far-infrared spectra of pressed disc samples were recorded on a Grubb parsons cube interferometer fitted with a helium cooled bolometer. The data were analysed on a microcomputer coupled to the interferometer.

Carbamide crystals of relatively large size 2x3x8mm, which can easily be handled, were mounted on a goniometer for orientation purposes. Both right angle and back scattering geometries, with vertical X and Z crystal axes were employed in the polarization measurements. Standard optical cells were used for both low temperature and high temperature experiments.

Results

Raman spectra of carbamide crystals at room temperature and liquid nitrogen temperature in various crystal orientations have been obtained. These orientations correspond to the polarizability tensors α_{xx}, α_{yy}, α_{zz}, α_{xy}, α_{xz}, α_{yz}. The

rotation of the crystal along the optic axis from 0-90° in the polarization measurements allowed us to observe longitudinal optic-transverse optic (LO-TO) splittings for the three polar lattice modes. Several of these spectra were recorded during the experiments, and some of them are shown in figures 1-4. The temperature dependence of the first order vibrational modes of carbamide phase-I has been studied and some of these data are plotted in figure-5.

Discussion

There are three modifications of carbamide [3], but the detailed investigation presented here is only concerned with the ambient temperature and pressure phase of this material. This has been due to:

a) the crystal structure of the other two phases are not known, and
b) polarization measurements on microcrystalline samples do not produce very useful results.

However, it will be less confusing and easier to understand, if the results are discussed under separate sub-headings, such as polarization measurements, effect of temperature etc.

Polarization Measurements:

The carbamide molecule belongs to C_{2v} point group and there are 8 atoms in one formula unit of $CO(NH_2)_2$. Hence 24 degrees of freedom for the free molecule becomes,

$$\Gamma = 8A_1 + 3A_2 + 5B_1 + 8B_2$$

The carbamide crystal has a tetragonal structure and has two molecules or 16 atoms in the primitive unit cell. The 48 degrees of freedom for the crystal can be represented by the irreducible representation of the factor group D_{2d} as follows:

$$\Gamma(\text{total}) = 8A_1 + 3A_2 + 3B_1 + 8B_2 + 13E$$

The normal modes of free molecule can be correlated with those of the crystal, as shown in table I. Of these 48 degrees of freedom, there are only twelve vibrations, which involve rigid translation or rotation of the carbamide molecules, which are,

$$\Gamma_{(\text{optic})} = A_1 + A_2 + B_1 + 3E$$

$$\Gamma(\text{Acoustic}) = B_2 + E$$

Thus group theory predicts that three bands are expected (assuming one band due to a doubly degenerate mode E) in the far-infrared spectrum and five bands ($A_1 + B_1 + 3E$) in the Raman spectrum. These modes are schematically sown in figure 6.

The polarized Raman spectra of lattice modes of hydrogenated carbamide at 293K and 77K are shown in figures 1 and 2, while far-infrared spectra of hydrogenated, and Raman spectra of deuterated samples at room temperature and liquid nitrogen temperature are shown in figures 3 and 4 respectively. There are three bands observed in the far-infrared spectra. These spectra suggest that the strong absorption near 180 cm^{-1} should show strong LO-TO splitting in the polarized Raman or infrared spectra. There are seven bands observed in the low temperature Raman spectrum at frequencies 61, 107, 118, 138, 153, 198, and 214 cm^{-1}, whereas only five bands are predicted by group theory.

In principle the symmetries of the modes in a Raman spectrum can be unambiguously assigned by recording

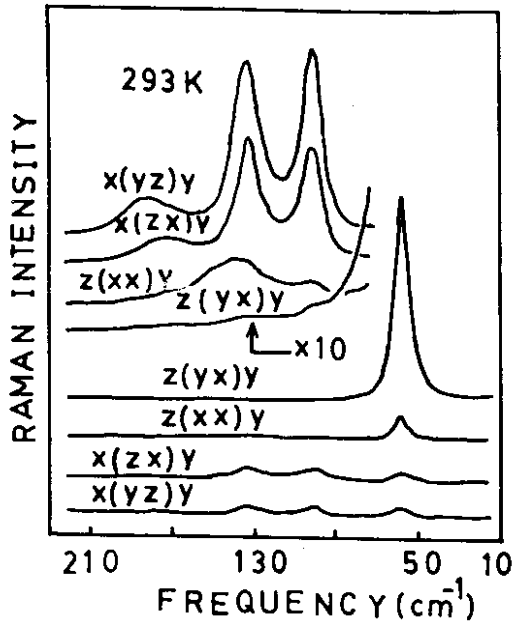


Fig.1: Polarized Raman spectra of the low frequency modes of carbamide crystal at 293K.

the spectra under different polarization geometries. In practice, for carbamide it has not been possible to match the theoretical predictions completely. Our polarized Raman spectra show that the 59 cm^{-1} band is most intense, in Y(XY)Z polarization. Figure 1 shows that the component seen in the Y(XX)Z and X(YY)Z polarization are weak compared with Y(XY)Z band. However, Raman selection rules suggest that this band should appear only in Y(XX)Z and X(YY)Z polarizations. These facts were not highlighted in the previous papers [6-9]. In one of these papers the assignment of the low frequency band disagrees with the basic group theoretical rule [6], while in a recent paper they have associated this band with polarization due to the interference effects in convergent polarized light. The author has performed polarization measurements in both 90° and back scattering geometries on thin crystals (thickness≈ 0.5mm) of carbamide in conjunction with small-angle collection optics, and has also tried by masking the collection optics (perpendicular or parallel to the spectrometer slit) to stop the unwanted polarized Raman signal. It has been observed that regardless of the method employed this band (59cm^{-1}) is always strong in Y(XY)Z polarization.

However, this band is active in Y(XX)Z and has been observed at 55cm^{-1} in the Raman spectrum of deuterated carbamide. The phonon dispersion curves of deuterated carbamide have been measured by Lefebure et al. (6). They have assigned a band at 51cm^{-1} to the B_1 torsional mode. We have therefore assigned the 59cm^{-1} band to the B_1^1 mode. The strength of the feature in the Y(XY)Z polarization remains unexplained. Two strong bands at 102cm^{-1} and 134cm^{-1} and a weak band at 177.5cm^{-1} have been found active in X(ZX)Y and X(YZ)Y polarizations and assigned to polar modes of symmetry E. The high frequency polar mode (E^4) appears at different frequencies in X(ZX)Y and X(YZ)Y polarizations. This mode (E^4) appears at different frequencies in X(ZX)Y and X(YZ)Y polarizations. This occurs only due to the use of a favourable scattering geometry for observing LO-TO modes. Our results of angular phonon dispersion in carbamide crystal will be discussed later under separate sub-heading.

We have employed the back scattering geometry for observing low temperature polarized Raman spectra, figure 2. On cooling the sample some new bands are seen in the frequency region 100 - 150cm^{-1}, in Y(XX)$\bar{Y}$,

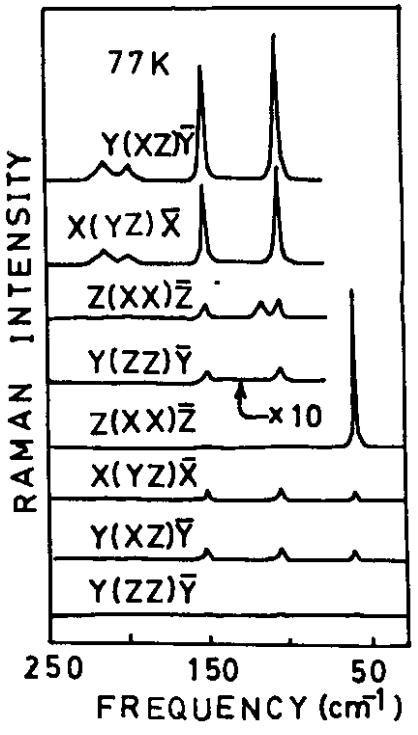


Fig.2: Polarized Raman spectra of the low frequency modes of carbamide crystal at 77K.

$Z(YY)\bar{Z}$ and $Y(ZZ)\bar{Y}$ polarizations. A weak band at about $102cm^{-1}$ (which was covered under the E^2 mode envelope at room temperature in figure 1) is now separated and appears at about $117cm^{-1}$ at 77K. It is strong in the $Y(ZZ)\bar{Y}$ polarization, and $98cm^{-1}$ is the frequency proposed in the neutron scattering measurements [6]. We have therefore assigned it to A_1^1 mode. Another weak band at about $138cm^{-1}$ has been found active $Y(XX)\bar{Y}$ and $X(YY)\bar{X}$ polarizations only. The low temperature spectra shown in figure 2 suggest that its intensity decreases rapidly when the sample is cooled to 77K. Also it does not show a significant frequency shift with variation of temperature. We suggest that this band involves destruction of phonons, therefore assigned to a hot band.

There are three bands expected in the far-infrared spectrum, as predicted by group theory. The Raman spectrum (figure 1) suggests that the high frequency band near $180cm^{-1}$ should show very strong infrared absorption. Far-infrared spectra of carbamide pressed disc (with polyethylene) have been recorded at several temperatures in the range 293K - 80K. Some of these spectra are shown in figure 3. There are three bands at $103cm^{-1}$, $135cm^{-1}$ and $180cm^{-1}$. These frequencies are similar to the three bands observed in the Raman spectrum at $102cm^{-1}$, $134cm^{-1}$ and near $180cm^{-1}$. On the basis of polarized Raman data of carbamide-H_4 and temperature dependent Raman data of carbamide-D_4 we have

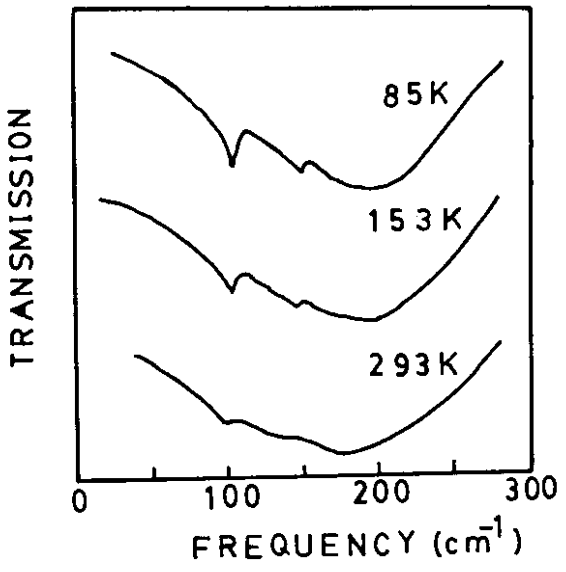
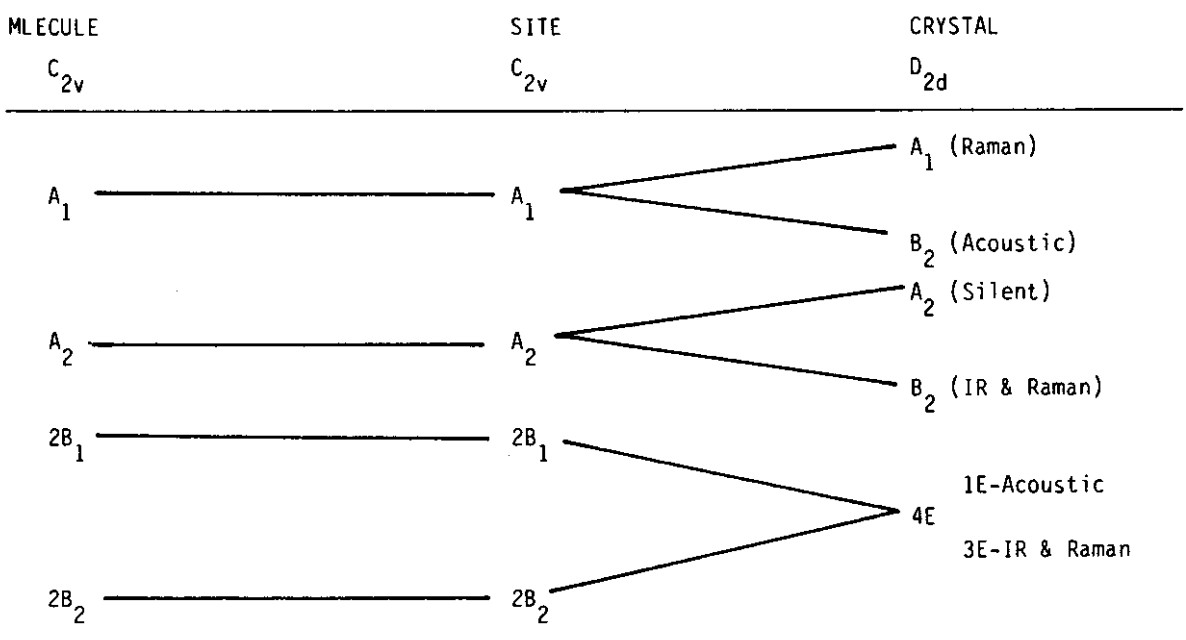


Fig.3: Far-infrared transmission spectra of carbamide-H_4 pressed disc in the temperature range 293 - 85K.

Table-I: Correlation between the free molecular modes and lattice modes of carbamide.



assigned these frequencies corresponding to E^2, E^3 and E^4 modes respectively. The band assignments together with those of Besnainou et al. [7] and Lefebvre et al. [9] have been summarized in Table II.

Polar Modes in Carbamide:

Although near-forward scattering geometry is ideal for observing the dispersion that is due to the modulus of the wave-vector of polar phonons in uniaxial crystals, in the present study 90° scattering geometry (at ambient temperature) was employed in order to study the effects of phonon propagation in this material. In these experiments the polarization directions of the incident and scattered beams were fixed and the crystal was rotated about its optic axis. A 90° rotation about the optic axis brought the crystal into the Y(ZY)X orientation from X(ZX)Y.

For room temperature measurements the carbamide crystals was mounted on a goniometer. The method outlines above was used in a 90° scattering arrangement. At liquid nitrogen temperature, the standard cold cell was used in a back scattering arrangement. The carbamide crystal was mounted on a sample block by using an indium seal. At one end of the cold finger the sample block was attached, and at the other (top) end a graduated scale in degrees from 0° - 90° was attached. This allowed the rotation of the crystal to any desired angle about the vertical axis from the top--end. The Z-axis of the crystal was mounted parallel to the axis of rotation. Thus, a 90° rotation about the Z-axis brought the crystal into the $Y(XZ)\bar{Y}$ orientation from $X(YZ)\bar{X}$.

The carbamide crystal (parallelopiped) has made it possible to measure ν_θ for θ=0° to 180°, and

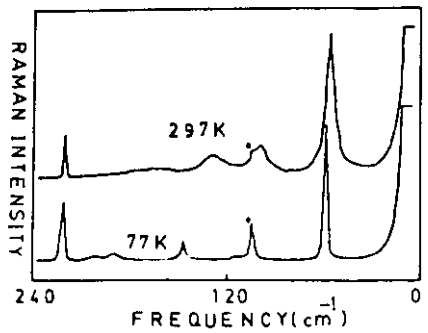


Fig.4: Raman spectra of carbamide-D_4 crystal at 297K. Asterisks show peaks due to laser emission.

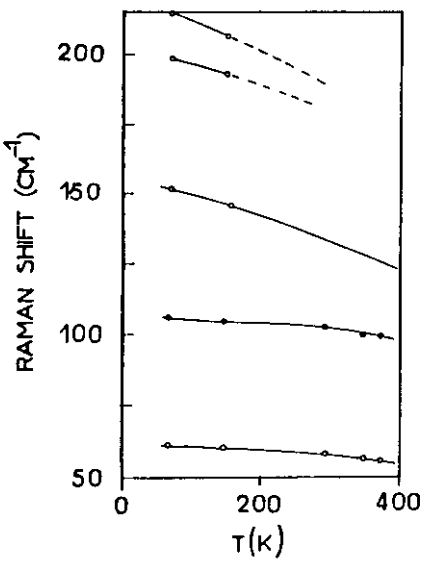


Fig.5: Temperature dependence of the Raman active lattice modes of carbamide-H_4 crystal.

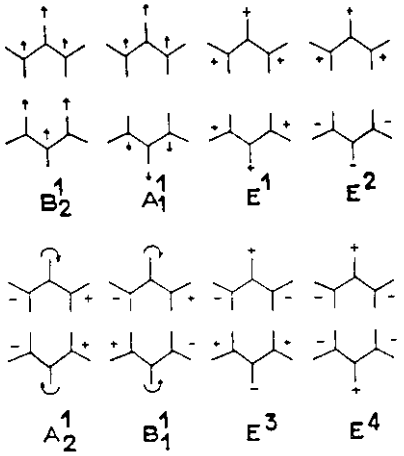


Fig.6: Schematic representation of displacement of atoms during rigid translation or rotation of carbamide single crystal. Note the plancs of the two molecules in the unit cell are perpendicular to one another.

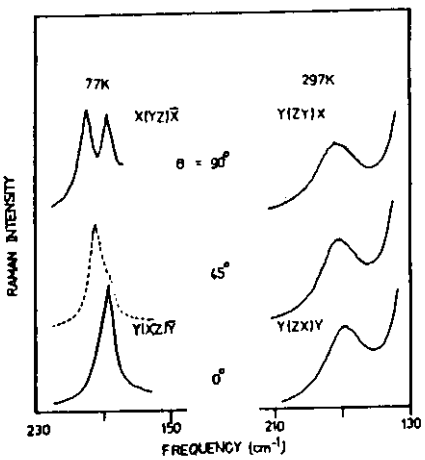


Fig.7: Angular shift of the E^4 mode in carbamide at room temperature and liquid nitrogen temperature.

the frequency variation of the polar modes have been studied both at room temperature and liquid nitrogen temperature, figure 7. Of the three polar lattice modes, only one mode, E^4, has been found to present a strong angular dispersion at liquid nitrogen temperature. At room temperature the measurement of ν_Θ is difficult because of the natural width of this line (about $22cm^{-1}$) and on account of its position in the wing of the E^2 band. For the other two polar modes the splitting is very small, say less than $0.4cm^{-1}$ both at room temperature and liquid nitrogen temperature.

Table-II: Vibrational IR and Raman band assignment.

LEFEBVRE RAMAN			BESNAINOU	THIS WORK						
				INFRARED		RAMAN				
293K	100K	Assign-ments.	Calculated	CARBAMIDE-H_4 RT	CARBAMIDE-H_4 80K	CARBAMIDE-H_4 RT	CARBAMIDE-H_4 77K	CARBAMIDE-D_4 RT	CARBAMIDE-D_4 77K	Assignment
59	61.4	B_1	57	---	---	59	61.5	55.1	58	B_1^1
102	105.8	E^1	101	103	105	102.3	106.8	99.8	103.3	E^2
102.8	113.8	A_1	124	---	---	102.8	117.6	---	---	A_1^1
134.0	148.4	E^2	139	135	151	134	152.3	129.6	148	E^3
						177.5	198.4	---	191	TO
177.0	194.6	E^3	189	180	195			171		E^4
						184	214		203	Lo

Effect of Temperature:

The far-infrared and low frequency Raman spectra of carbamide are shown in figures 3-4. These spectra suggest that on cooling the sample, vibrational bands shift to higher frequencies and become sharp. The Raman shifts in the temperature range 373 - 77K have been shown in figure 5.

Conclusion

Vibrational Raman and infrared study of the lattice modes of both hydrogenated and deuterated carbamide as a function of temperature has been presented. Polarization measurements using various scattering geometries have been used in improving our understanding of angular dispersion of phonons in this material. Spectra of higher quality than previously published are presented and unambiguous assignment of both the Raman and infrared active lattice modes has been carried out.

Our carefully recorded temperature dependent Raman spectra of the single crystals of carbamide in the temperature range 373 - 77K suggest no phase transition, while Lebioda et al. [11] have reported a low temperature phase transition in this material. This discrepancy is probably due to the use of imperfect crystals by Lebioda et al. in their experiments. Their results suggest that carbamide crystals with fewer defects did not undergo any phase transition. This is in agreement with our temperature dependent vibrational study of "Perfect" carbamide single crystal. Our vibrational band assignments together with the previously published data have been summarized in table II.

Acknowledgement

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