

Infrared absorption of solid nitrogen at high pressures

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We have observed infrared absorption peaks in solid nitrogen at hydrostatic pressures as high as 7 GPa at liquid-helium temperatures. The shift in the AlSb: $^{12}\text{C}_{\text{Sb}}$ local vibrational mode is used to precisely calibrate the pressure. For all measured pressures we also observe the ν_3 vibrational mode of CO_2 impurities. For pressures greater than 1.9 GPa, a peak appears which we attribute to a N-N stretch mode of nitrogen in the ϵ phase. The single peak is consistent with previous x-ray and Raman studies which suggest that $\epsilon\text{-N}_2$ has a structure which belongs to the rhombohedral space group $R\bar{3}C$. [S0163-1829(96)07138-X]

The development of high-pressure diamond-anvil cells has led to extensive experimental research on the properties of high-density molecular solids.¹ N_2 is in many respects a model molecular system because its triple bond is very stable and its low atomic number simplifies theoretical calculations.² It is commonly used as an ambient for studying solids under hydrostatic pressure.³ At low temperatures and pressures (Fig. 1), N_2 crystallizes into the cubic α phase (space group $Pa\bar{3}$).⁴ At pressures between 0.4 and 1.9 GPa, N_2 is in the tetragonal γ ($P4_2/mnm$) phase.^{5,6} For pressures higher than 1.9 GPa, x-ray diffraction⁷ and Raman⁸ studies have provided evidence that $\epsilon\text{-N}_2$ has a structure which belongs to the rhombohedral space group $R\bar{3}C$. Theoretical studies predict that $\epsilon\text{-N}_2$ has a tetragonal structure with 32 molecules per unit cell, but that the structure is very similar to $R\bar{3}C$.⁹ In this paper we present the results of infrared absorption studies that lend further support to the $R\bar{3}C$ model.

The infrared absorption spectrum of solid nitrogen at normal vapor pressure has been measured in $\alpha\text{-N}_2$ (Ref. 10) and $\beta\text{-N}_2$.¹¹ The α and β phases have infrared absorption features near the fundamental N-N stretch frequency which are attributed to nonlinear coupling between the N-N vibrons and lower-frequency phonons.¹² Recently the profile of the N-N stretch overtone has been used to determine the temperature of solid nitrogen on the surface of Pluto.¹³ In this study, we report the observation of an infrared active peak in nitrogen in the high-pressure ϵ phase. In addition, for all measured pressures, we observe the ν_3 vibrational mode of CO_2 impurities. The pressure dependence of these peaks may serve as a useful *in situ* pressure calibration.

To generate pressures up to 7 GPa, we used a modified Merrill-Basset diamond-anvil cell.^{14,15} The liquid-immersion technique¹⁶ was used to load the cell with liquid nitrogen. To determine the pressure at liquid-helium temperatures, a few grains of ruby were placed in the cell and on the outside face of one of the diamonds. The cell was then placed in a liquid-helium cryostat and the rubies were excited by an argon-ion laser. The ruby fluorescence was dispersed by a double monochromator and detected by a photomultiplier tube. The atmospheric and high-pressure fluorescence lines were recorded by computer, and pressures were determined with the relation¹⁷

$$P = 380.8\{[\lambda_p(T)/\lambda_0(T)]^5 - 1\}, \quad (1)$$

where P is the pressure in GPa, λ_p is the wavelength of the ruby R_1 line at pressure P and temperature T , and λ_0 is the corresponding wavelength at the same temperature and atmospheric pressure.

Following the fluorescence measurements, each sample was warmed to room temperature and then placed in the infrared spectrometer liquid-helium cryostat. Mid-infrared absorption spectra were obtained with a Digilab FTS-80E vacuum Fourier transform spectrometer with a KBr beam-splitter, with a spectral range of 450 to 3400 cm^{-1} . Spectra were taken at a temperature of 7 K with an instrumental resolution of 0.5 cm^{-1} . A light concentrating cone focused the light through the diamonds and sample and onto a Ge:Cu photoconductor mounted directly behind the sample.

To obtain a more precise measurement of the pressure, we loaded some diamond-anvil cells with AlSb:Se,C samples which were cut into disks 300 μm in diameter and polished to a thickness of 50 μm . As observed previously,¹⁸ the $^{12}\text{C}_{\text{Sb}}$ acceptor has a local vibrational mode (LVM) peak at 591.0 cm^{-1} at a temperature of 10 K and atmospheric pressure (Fig. 2). Our samples are co-doped with Se so that they are n type. Since Se is a deep donor,¹⁹ the free carriers freeze out at low temperatures, and the samples are transparent even for high ($\sim 10^{17} \text{cm}^{-3}$) concentrations of C_{Sb} . We assume that the position of the C_{Sb} LVM varies linearly with pressure, as is observed in the case of GaAs: Si_{Ga} .²⁰ The observation that the pressure-induced shift of the C_{Sb} LVM varies linearly with the shifts of the CO_2 and N_2 vibrational modes (Fig. 4) supports this assumption. We therefore use the position of the C_{Sb} LVM peak as a precise pressure calibration.

For all pressures, we observe an infrared absorption peak which we attribute to the ν_3 vibrational mode of CO_2 impurities in the N_2 matrix (Fig. 3). In Fig. 4, the open and filled circles refer to CO_2 vibrational frequencies measured by the C_{Sb} LVM's and ruby fluorescence lines, respectively. By matching the two sets of points, we obtain the relation

$$P = 0.073[\nu(\text{C}_{\text{Sb}}) - 591.0], \quad (2)$$

where P is the pressure in GPa and $\nu(\text{C}_{\text{Sb}})$ is the position of the C_{Sb} LVM peak in cm^{-1} at liquid-helium temperatures. This pressure calibration is used in the subsequent analysis.

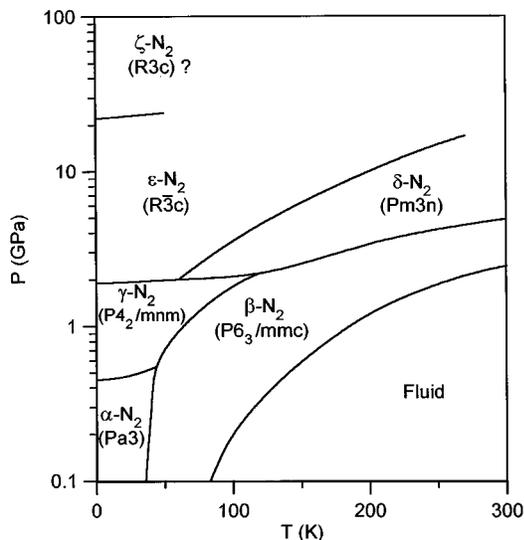


FIG. 1. Phase diagram of nitrogen (Ref. 9).

The pressure-induced phase transitions of solid N_2 can be inferred from discontinuities in the positions of the CO_2 and N_2 peaks (Fig. 4). For low pressures, N_2 is in the α phase, and the CO_2 peak shifts linearly:

$$\nu_3(CO_2) = 2349.3 + 12.3P, \quad 0 \leq P \leq 0.45, \quad (3)$$

where $\nu_3(CO_2)$ is the frequency in cm^{-1} and P is the pressure in GPa. At 0.45 GPa, two CO_2 peaks are observed, indicating a coexistence of the α and γ phases. This transition pressure differs from the value obtained by Thiéry *et al.*,⁶ who found a transition pressure of 0.35 GPa at a temperature of 4.2 K.

In the γ phase, the position of the CO_2 peak is best described by two piecewise linear fits:

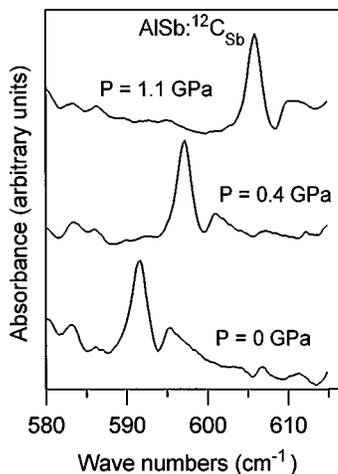


FIG. 2. Pressure dependence of the AISb: $^{12}C_{Sb}$ local vibrational mode (LVM) at a temperature of 10 K. The position of the LVM is used as an *in situ* pressure calibration.

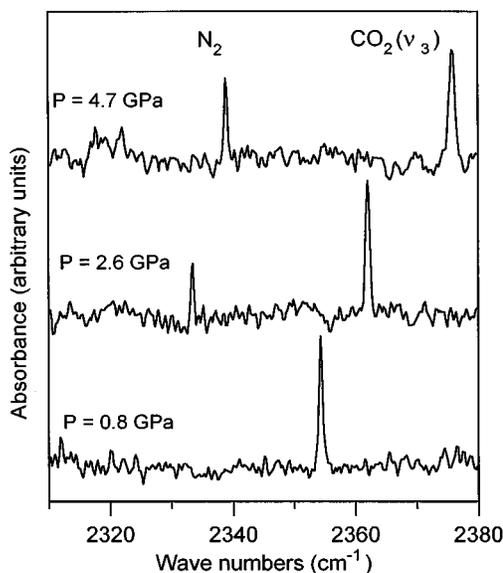


FIG. 3. Infrared absorption spectra of solid nitrogen under pressure. For all measured pressures, the ν_3 vibrational mode of CO_2 impurities is observed. For pressures above 1.9 GPa, the N-N stretch mode becomes infrared active.

$$\nu_3(CO_2) = \begin{cases} 2347.6 + 8.4P, & 0.45 \leq P \leq 1.3 \\ 2349.5 + 6.9P, & 1.3 \leq P \leq 1.9. \end{cases} \quad (4)$$

The reason for the two linear regimes is currently not known. In the ϵ phase, the CO_2 peak shifts linearly:

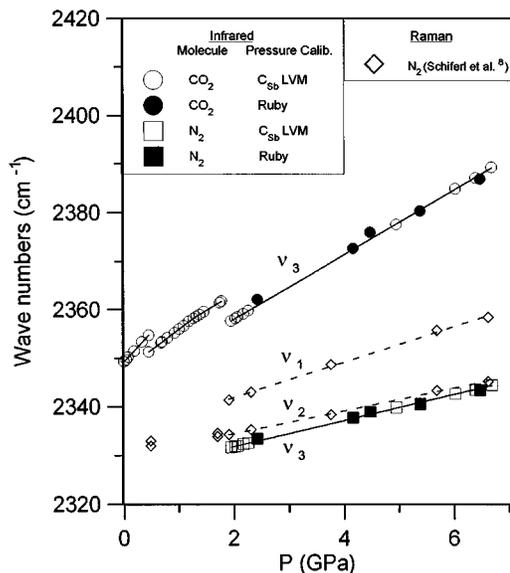


FIG. 4. Positions of the CO_2 and N_2 infrared absorption peaks in nitrogen under pressure at liquid-helium temperatures. For the solid circles and squares, ruby fluorescence was used as a pressure calibration [Eq. (1)]. For the open circles and squares, the position of the AISb: $^{12}C_{Sb}$ local vibrational mode (LVM) was used to calibrate the pressure [Eq. (2)]. The open diamonds are Raman-active modes measured by Shieferl *et al.* (Ref. 8) at a temperature of 15 K. The solid lines are linear fits given in Eqs. (3)–(6) and the dashed lines are guides to the eye. The discontinuities near 0.45 and 1.9 GPa are due to structural phase transitions.

TABLE I. Correlation diagram for the N-N stretch mode of solid nitrogen in the ε ($R\bar{3}C$) phase, at the center of the Brillouin zone.

Site	Molecular symmetry	Site symmetry	Factor group symmetry	Activity	
2b	$D_{\infty h}$ Σ_g^+ (N-N stretch)	$S_6 \equiv C_{3i}$	D_{3d}	Raman	
			A_g		A_{1g} (1) A_{2g} (1)
6e	$D_{\infty h}$ Σ_g^+ (N-N stretch)	C_2	D_{3d}	Raman	
			A_g		A_{1g} (1) E_g (1)
			A_u	A_{1u} (1)	Infrared
			E_u	E_u (1)	

$$\nu_3(\text{CO}_2) = 2345.1 + 6.6P, \quad 1.9 \leq P \leq 7. \quad (5)$$

In addition, a new infrared absorption peak appears (Fig. 3). We attribute this new peak to a N-N stretch mode, since its frequency is similar to that of the Raman-active N-N stretch mode of solid nitrogen under pressure (Fig. 4). In keeping with the notation of Schiferl *et al.*,⁸ we label this mode ν_3 . The pressure dependence of the peak position can be described by a least-squares linear fit:

$$\nu_3(\text{N}_2) = 2326.5 + 2.7P, \quad 1.9 \leq P \leq 7. \quad (6)$$

The infrared activity of this mode is consistent with the rhombohedral space group $R\bar{3}C$ (D_{3d}^6), which has one infrared-active and three Raman-active stretch modes (Table

I). N_2 molecules on the 2b site have one Raman-active stretch mode while those on the 6e site have two Raman-active modes and one infrared-active mode. Previous Raman studies have only revealed two of the three Raman-active peaks,⁸ perhaps because the difference between the A_{1g} and E_g modes is too small to be resolved. The ν_3 infrared-active mode has a frequency very similar to the ν_2 Raman-active mode (Fig. 4), an observation which suggests that they both arise from N_2 molecules on the 6e site. If that is the case, then the factor group splitting is much smaller than the site splitting for the $R\bar{3}C$ structure. The absence of a N-N infrared-active absorption peak for pressures below 1.9 GPa is consistent with the symmetries of the cubic α phase ($Pa\bar{3}$) (Ref. 4) and tetragonal γ phase ($P4_2/mnm$).⁵

In conclusion, we have observed infrared absorption peaks in solid nitrogen under large hydrostatic pressures and liquid-helium temperatures. The ν_3 mode of CO_2 was observed for all measured pressures. For pressures greater than 1.9 GPa, we observe the N-N stretch mode of solid nitrogen in the ε ($R\bar{3}C$) phase. Using the shift of the $\text{AlSb}:^{12}\text{C}_{\text{Sb}}$ LVM as an *in situ* pressure calibration, we measured the pressure-dependent shifts of the CO_2 and N_2 vibrational modes. In the future, these shifts may be used as a precise pressure calibration for infrared absorption experiments.

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