

I. INTRODUCTION

In many respects, N$_2$ is a model molecular system because its triple bond is very stable and its low atomic number simplifies theoretical calculations.$^1$ In spite of its apparent simplicity, however, N$_2$ has a complex phase diagram that has presented a formidable challenge to theoretical models. Theoretical studies have predicted the polymerization of nitrogen at high pressures, suggesting that nitrogen could be used as an energetic material.$^2$--$^4$ Optical and electrical studies have provided evidence that solid nitrogen becomes a nonmolecular semiconductor at pressures above 150 GPa.$^5$,6

In this paper, we present the results of infrared (IR) spectroscopy measurements on N$_2$ under hydrostatic pressure. These studies contribute to the knowledge of the N$_2$ phase diagram and the nature of guest-host interactions in dense solids.

The structure of solid N$_2$ under hydrostatic pressure has been studied extensively by Raman spectroscopy,$^7$--$^{15}$ x-ray diffraction,$^{16}$ and theoretical calculations$^{17}$,$^{18}$ making it an ideal system for a study of guest–host interactions. A schematic phase diagram for N$_2$ is shown in Fig. 1. IR spectroscopy at low temperatures and high pressures has yielded interesting results. For pressures greater than 2 GPa, an IR active N–N stretch mode, or vibron, was observed by McCluskey et al.$^{19}$ The IR activity of this mode is due to the low symmetry of the high-pressure $\varepsilon$ phase.$^{11}$ Subsequent investigations have measured IR-active N$_2$ vibrons at higher pressures.$^5$,$^{20}$

There is controversy regarding the structure of the $\varepsilon$ phase. As summarized by Bini et al.$^{20}$ theoretical studies have predicted several different structures that appear to be at odds with experiment. An early theoretical study proposed a rhombohedral ($R\bar{3}C$) structure with eight molecules per unit cell,$^{21}$ a model that was apparently confirmed by x-ray diffraction results.$^{16}$ Subsequent calculations predicted a more complicated, tetragonal structure ($P4_32_12$) with 32 molecules per unit cell.$^{22}$ The positions of the molecules in the latter structure are similar to those in the former, but their different orientations result in a lower symmetry. In this study, the results of IR spectroscopy provide evidence in favor of the tetragonal structure.

II. EXPERIMENTAL METHODS

To generate pressures up to 6 GPa, we used a piston-cylinder diamond-anvil cell.$^{23}$ Type-I diamonds with a culet diameter of 700 $\mu$m were used. After a 250 $\mu$m thick stainless steel gasket was indented to a thickness of 100 $\mu$m, a 340 $\mu$m hole was drilled in the center of the indentation. Nitrogen was used as a pressure medium and was loaded into the gasket hole by liquid immersion.$^{24}$ CO$_2$ molecules were present in the N$_2$ as an “unintentional” contaminant (unless indicated otherwise, the masses of C and O are 12 and 16 amu, respectively). To determine the pressure at liquid-heinem temperature, we measured the IR absorption peak of the $\nu_3$ vibrational mode of isolated CO$_2$ impurities in the solid N$_2$ matrix. The $\nu_3$-mode frequency is sensitive to hydrostatic pressure$^{25}$ and provides a precise in situ pressure calibration. From the calibrated intensity of the $\nu_3$ IR peak in solid CO$_2$,$^{26}$ the thickness of the gasket, and the intensity of the $\nu_3$-CO$_2$ peak in our measurements, the concentration of CO$_2$ was estimated to be 0.1% in the most heavily doped samples.
Mid-IR absorption spectra were obtained with a Bomem DA8 vacuum Fourier transform spectrometer with a KBr beamsplitter. The samples were kept at a temperature of 6 to 9 K in a Janis STVP continuous-flow liquid-helium cryostat with wedged ZnSe windows. The spectral range was 500 to 5000 cm$^{-1}$ and the instrumental resolution was 1 to 2 cm$^{-1}$.

An off-axis parabolic mirror and light-concentrating cone focused the light through the first diamond and onto the sample. The light then passed through the second diamond and onto a Ge:Cu photoconductor detector. After a spectrum was measured, the sample was warmed to room temperature, the pressure was adjusted, and the sample was placed back in the liquid-helium cryostat.

III. RESULTS

A. $N_2$ vibrons

Evidence for an additional IR-active vibron is shown in Fig. 2. In this figure, an infrared absorption spectrum is shown for two different pressures that lie within the $\varepsilon$ phase. On the high-frequency side of the main $N_2$ vibron, a weaker peak is observed, which we attribute to a second IR-active vibron. The spectra shown in Fig. 2 were obtained with a spectral resolution of 2 cm$^{-1}$. For resolutions $\leq 1$ cm$^{-1}$, the noise in the spectrum was high enough so that such a weak peak would not be detected. The integrated absorbance of the weak peak is approximately 7% that of the strong peak.

The $N_2$ vibron frequencies are plotted in Fig. 3 as a function of pressure. In this figure, IR-active vibrons observed in this work are shown by the circles. The solid lines are linear fits to the data:

$$\nu = A + BP,$$

where the frequency $\nu$ is in cm$^{-1}$ and the pressure $P$ is in GPa. The coefficients $A$ and $B$ are listed in Table I for the modes measured in this work. For these $N_2$ vibron measurements, a sample with no detectable CO$_2$ was used. The pressure dependence of the main $N_2$ vibron was used to calibrate the pressure; i.e., the lower branch in Fig. 3 determines the pressure. Pieces of GaN were also in the DAC, and the pressure dependence of their two-phonon modes agreed with published data. The solid squares are IR-active vibrons measured by Bini et al., and show good agreement with our results. The diamonds are Raman-active vibrons measured by Schiferl et al.

In the rhombohedral $R\bar{3}C$ structure, there are two inequivalent sites, only one of which ($6e$) gives rise to an IR-active vibron. Our observation of two IR-active vibrons would appear to exclude the $R\bar{3}C$ structure. In the tetragonal $P4_212_1$ structure predicted by Nosé and Klein, nitrogen molecules reside on two inequivalent $8b$ sites ($C_1$ symmetry) and four inequivalent $4a$ sites ($C_2$ symmetry). In principle, six IR- and Raman-active vibrons should be observed, but many of these modes may be nearly degenerate or very weak. In addition, the orientations of the $N_2$ crystals were not well controlled. Theoretical calculations performed by Belak et al. predicted a tetragonal structure at low tempera-
tions and a pressure of 7 GPa, with two vibron frequencies. These frequencies were calculated to be 2351 and 2362 cm$^{-1}$, in reasonable agreement with Raman spectroscopy experiments. In our work, if one extrapolates to a pressure of 7 GPa, the IR-active vibrons lie within 2 cm$^{-1}$ of the Raman modes, which is on the order of the uncertainty of the calculations. Hence, the experimental results are consistent with the theoretical predictions for the tetragonal model.

### B. CO$_2$ transverse ($\nu_2$) modes

As in previous work, we observed the antisymmetric stretching ($\nu_3$) mode of CO$_2$ impurities in solid N$_2$ under pressure (not shown). In the present study, the higher concentration of CO$_2$ molecules allowed us to observe the $\nu_2$-mode frequencies of CO$_2$ impurities (Fig. 4). In the gas phase, the linear CO$_2$ molecule has two degenerate $\nu_2$ modes that give rise to a single peak at 667 cm$^{-1}$. These modes involve the transverse motion of the carbon atom, out of phase with the oxygen atoms. For the low-pressure $\alpha$ phase, only one $\nu_2$ mode was observed. For the high-pressure phases, the interaction with the N$_2$ matrix lifts the degeneracy, resulting in two distinct peaks. The peaks shift discontinuously at the critical pressures for phase transitions in solid nitrogen (Fig. 5). As pressure is increased, the $\nu_2$ modes decrease in frequency and their splitting increases.

The splitting of the $\nu_2$ peak is consistent with the structures of the different phases. The $\alpha$ phase has a $P\bar{4}a\bar{3}$ space group, with nitrogen molecules residing on equivalent 4$a$ sites that have $S_6$ symmetry. Assuming the CO$_2$ molecules occupy substitutional sites, then the $\nu_2$ modes are doubly degenerate. The $\gamma$ phase has a $P4_2/mnm$ space group, with nitrogen molecules residing on equivalent 2$a$ sites that have $D_{2h}$ symmetry. In this symmetry, the degeneracy of the $\nu_2$ modes is lifted. In the tetragonal $\epsilon$ phase discussed previously, there are six inequivalent sites, all of which have a low symmetry such that the $\nu_2$ modes would be split. The fact that only two modes are observed in the $\epsilon$ phase suggests that the CO$_2$ molecules reside on one energetically preferred site.

For the highest CO$_2$ concentration samples, a weak peak is observed on the high-frequency side of the main $\nu_2$ peaks, possibly a result of CO$_2$ dimers. For pressures less than 1 GPa, two peaks appear on the low-frequency side of the main $\nu_2$ peaks, as indicated by the arrows in Fig. 6(a). These peaks are ascribed to $\nu_2$ modes from solid CO$_2$ precipitates.

### Table I. Coefficients for the linear frequency shifts [Eq. (1)] of vibrational modes in solid N$_2$. The linear fits are valid for the pressure ranges indicated. The units for $A$ and $B$ are cm$^{-1}$ and GPa$^{-1}$, respectively.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\alpha$ phase ($0$–$0.45$ GPa)</th>
<th>$\gamma$ phase ($0.45$–$1.9$ GPa)</th>
<th>$\epsilon$ phase ($1.9$–$6$ GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$</td>
<td>$B$</td>
<td>$A$</td>
</tr>
<tr>
<td>N$_2$ vibrons</td>
<td>$\ldots$</td>
<td>$\ldots$</td>
<td>$\ldots$</td>
</tr>
<tr>
<td>$\nu_3$(CO$_2$)</td>
<td>$662.2\pm0.1$</td>
<td>$-2.6\pm0.3$</td>
<td>$662.3\pm0.1$</td>
</tr>
<tr>
<td>$\nu_2$(CO$_2$)</td>
<td>$2349.3^a$</td>
<td>$12.3^a$</td>
<td>$2348.2^{ab}$</td>
</tr>
<tr>
<td>$\nu_1$(CO$_2$)</td>
<td>$2283.4\pm0.4$</td>
<td>$11.7\pm0.9$</td>
<td>$2282.2\pm0.1$</td>
</tr>
<tr>
<td>$\nu_1+2\nu_2$(CO$_2$)</td>
<td>$3609.6\pm0.1$</td>
<td>$9.7\pm0.3$</td>
<td>$3608.9\pm0.3$</td>
</tr>
<tr>
<td>$\nu_3+\nu_1$(CO$_2$)</td>
<td>$3714.0\pm0.3$</td>
<td>$13.7\pm0.7$</td>
<td>$3712.7\pm0.5$</td>
</tr>
</tbody>
</table>

$^a$From McCluskey et al. (Ref. 19).
$b$A somewhat more precise fit is given in Ref. 19.

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**FIG. 4.** Low-temperature IR absorption spectra of isolated CO$_2$ molecules in solid N$_2$, for pressures of 0.34, 1.7, and 2.9 GPa. The pressures correspond to the $\alpha$, $\gamma$, and $\epsilon$ phases of solid N$_2$, respectively. The peaks are attributed to $\nu_2$ modes of the CO$_2$ molecules.

**FIG. 5.** $\nu_2$ frequencies of isolated CO$_2$ molecules in solid N$_2$, as a function of pressure, at low temperatures. Discontinuous shifts of the frequencies occur at the critical pressures for phase transitions in solid N$_2$. Solid lines are fits to the data (Table I).
By extrapolating the frequencies, zero-pressure values of 655 and 660 cm\(^{-1}\) are obtained, in good agreement with low-temperature IR spectra of solid CO\(_2\) at ambient pressure.\(^{26}\)

**C. CO\(_2\) combination modes**

In addition to the \(\nu_2\) and \(\nu_3\) fundamental modes, combination modes were also observed near 3600 and 3700 cm\(^{-1}\) [Fig. 6(b)]. By comparison with gas-phase data, these modes are identified as the \(\nu_3 + 2\nu_2\) and \(\nu_3 + \nu_1\) combination modes, where \(\nu_1\) is the Raman-active, symmetric stretch mode. The combination modes are in Fermi resonance. In the \(\varepsilon\) phase, two IR peaks are observed. In the \(\alpha\) and \(\gamma\) phases, a sideband is observed on the low-frequency side of each of the main peaks. The intensity of the sideband grows as pressure is decreased. The reason for this behavior may be related to the formation of CO\(_2\) dimers. The combination-mode frequencies are plotted as a function of pressure in Fig. 7.

![Combination-mode frequencies of isolated CO\(_2\) molecules in solid N\(_2\), as a function of pressure, at low temperatures. Discontinuous shifts of the frequencies occur at the critical pressures for phase transitions in solid N\(_2\). Solid lines are fits to the data (Table I).](image1)

For clarity, the low-frequency sidebands are excluded from this figure.

Along with the appearance of the solid-CO\(_2\) \(\nu_2\) modes, solid-CO\(_2\) peaks also appear on the low-frequency side of the combination modes, indicated by arrows in Fig. 6(b). These modes match the \(\nu_3 + 2\nu_2\) and \(\nu_3 + \nu_1\) combination modes of solid CO\(_2\), which have frequencies of 3600 and 3708 cm\(^{-1}\), respectively.\(^{30}\) Since the spectroscopic signatures for solid CO\(_2\) only occur for pressures less than 1 GPa, we conclude that phase separation of CO\(_2\) in solid N\(_2\) is suppressed by the application of pressure. This observation suggests that phase separation results in an increase in the total volume of the CO\(_2\)–N\(_2\) mixture.

**D. Isotope effects**

The high CO\(_2\) concentration samples allowed us to observe the \(\nu_3\) mode of \(^{13}\)CO\(_2\) molecules in solid nitrogen. This mode is plotted as a function of pressure in Fig. 8. The mode frequency increases with pressure, and decreases discontinuously at the critical pressures for solid-nitrogen phase transitions. It is apparent that \(^{13}\)CO\(_2\) molecules provide a sensitive probe of the surrounding nitrogen atoms. The isotopic frequency ratio is defined as \(r = \nu_3({\rm ^1\!CO}_2)/\nu_3({\rm ^{13}\!CO}_2)\), and is plotted as a function of pressure in the inset of Fig. 8. A linear fit yields a zero-pressure value of \(r = 1.02883 \pm 0.00003\) and a slope of \((3.5 \pm 1.1) \times 10^{-5}\) GPa\(^{-1}\). Given the standard error, it can be stated that the slope is greater than zero with 99.9% confidence.\(^{31}\)

For a linear CO\(_2\) molecule, in the harmonic approximation, the \(\nu_3\)-mode frequency is given by

\[ \nu_3 = \sqrt{k(2/M_C+1/M_O)} \]

where \(k\) is the linear force constant, \(M_C\) is the carbon mass (12 or 13 amu), and \(M_O\) is the oxygen mass (16 amu). In this model, the isotopic frequency ratio is given by \(r = 1.02920\). Various anharmonic terms reduce the value of \(r\).\(^{32}\) The application of pressure brings N\(_2\) molecules closer to the CO\(_2\)

![Combination-mode frequencies of isolated CO\(_2\) molecules in solid N\(_2\), as a function of pressure, at low temperatures. Discontinuous shifts of the frequencies occur at the critical pressures for phase transitions in solid N\(_2\). Solid lines are fits to the data (Table I).](image2)

For clarity, the low-frequency sidebands are excluded from this figure.
molecule, which may result in a reduction in such anharmonic terms, bringing the value of \( r \) closer to the harmonic value.

**E. Ab initio calculations**

To estimate the pressure dependence of vibrational frequencies of \( \text{CO}_2 \) molecules in solid \( \text{N}_2 \), ab initio calculations were performed, using Gaussian 98W.\(^{33} \) The restricted Hartree–Fock method was used, with the 3-21G basis set. In the \( \alpha \) phase, \( \text{N}_2 \) molecules occupy fcc lattice sites and are oriented along the various [111] directions.\(^{34} \) For the calculations, one \( \text{CO}_2 \) molecule was placed on a site, surrounded by twelve \( \text{N}_2 \) nearest neighbors. The position of each N atom was determined by the lattice constant \( a \) and the calculated N–N distance for an isolated \( \text{N}_2 \) molecule. While the N atoms were held fixed, the C–O bond length was optimized, to minimize the total energy. To mimic the application of pressure, lattice constants of \( a = 5.6, 5.4, 5.2, \) and 5.0 Å were chosen (experimentally, \( a = 5.644 \) Å).\(^{35} \) A lattice constant of \( a = 5.4 \) Å corresponds to a pressure of approximately 0.4 GPa.\(^{36} \) However, since our calculations do not allow relaxation of the \( \text{N}_2 \) molecules, a direct correspondence between \( a \) and pressure cannot be made. For \( a = 5.6 \) Å, \( \text{CO}_2 \) frequencies of \( \nu_2 = 661.4 \text{ cm}^{-1} \) (doubly degenerate) and \( \nu_3 = 2471.3 \text{ cm}^{-1} \) were calculated, in good agreement with experiment. The equilibrium C–O bond length was determined to be 1.155 Å.

As the lattice constant is decreased, the equilibrium C–O bond length decreases. The compression of the bond leads to an increase in the \( \nu_2 \)-mode frequency and a decrease in the \( \nu_3 \)-mode frequency. Specifically,

\[
\delta \nu_2 = (1300 \pm 100) \Delta a, \\
\delta \nu_3 = -(10150 \pm 30) \Delta a,
\]

where \( \delta \nu_2 \) and \( \delta \nu_3 \) are the frequency shifts (cm\(^{-1} \)) and \( \Delta a \) is the change in C–O bond length (Å). The standard errors were obtained by linear fits to the calculated data. The ratio of the shifts is \( \delta \nu_3/\delta \nu_2 = -8 \). Experimentally, in the \( \alpha \) phase, \( \delta \nu_3/\delta \nu_2 = -5 \), in reasonable agreement with the calculations. For the \( \nu_3 \)-mode, the calculated isotopic frequency ratio is \( r = 1.029 \pm 0.025 \) and does not vary significantly with \( a \). Since frequencies are calculated using the harmonic approximation, this result is consistent with the hypothesis that changes in anharmonic terms are responsible for the experimentally observed increase in \( r \) with pressure.

**IV. CONCLUSIONS**

In conclusion, vibrational spectroscopy of \( \text{N}_2 \) and \( \text{CO}_2 \) in solid nitrogen under pressure has yielded information about the phase diagram of \( \text{N}_2 \) and interactions between isolated \( \text{CO}_2 \) molecules with their host environment. The presence of two IR-active \( \text{N}_2 \) vibrors in the \( \alpha \) phase is consistent with a tetragonal structure (P4\(_1\)2\(_1\)2\(_1\)) and is inconsistent with an earlier proposed rhombohedral (R3\(_C\)) structure. The transverse (\( \nu_2 \)) vibrational modes of \( \text{CO}_2 \) molecules showed a splitting consistent with the structures of the different \( \text{N}_2 \) phases. All the vibrational-mode frequencies shifted discontinuously at the critical pressures for \( \text{N}_2 \) phase transitions, demonstrating that matrix-isolated molecules are sensitive probes of the host crystal. For \( \text{CO}_2 \) concentrations of 0.1%, phase separation is present at low pressures, but is suppressed for pressures greater than 1 GPa. Future studies will address the phase-separation issue in more detail and at higher pressures.

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\(^27\) The Gruneisen parameters for the two-photon modes were \( \gamma \approx 1.4 \), in agreement with single-photon results. See A. R. Göbi, H. Siegle, K. Syassen, C. Thomsen, and J.-M. Wagner, Phys. Rev. B 64, 035205 (2001), and references therein.