Optical Evidence for a Nonmolecular Phase of Nitrogen above 150 GPa

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Optical spectroscopy techniques, including visible and near infrared (IR) Raman and synchrotron IR methods have been applied to study solid nitrogen at megabar pressures. We find that nitrogen becomes totally opaque above 150 GPa, accompanied by the disappearance of Raman and IR vibrational excitations, while new broad IR and Raman bands become visible. Optical absorption measurements reveal that the semiconducting absorption edge responsible for the change of color is characterized by the presence of a wide Urbach-like tail and a high-energy (Tauc) region. These data are consistent with the dissociation of molecular nitrogen into a nonmolecular (possibly amorphous) phase.

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A number of molecular solids are known to undergo a transition to a nonmolecular (NM) phase under high compression (e.g., iodine [1], hydrogen halides [2], and ice [3]), which could be accompanied by an insulator-to-metal transition. In this regard, nitrogen is considered a model system, as it is the most strongly bonded simple molecule and is expected to undergo the NM transition (destabilization of its triple bond) in the pressure range accessible by modern experimental techniques. This prediction is based on the results of shock-wave experiments, which provided evidence for the NM transition in the liquid phase at 30 GPa and 6000 K [4], as well as theoretical calculations for the solid [5–7]. The latter predictions involved transitions to various threefold coordinated phases below 100 GPa. It has been suggested that the observed transition pressure can be substantially higher because of a large potential barrier to dissociation (e.g., Refs. [6,7]).

Nitrogen is known to have a variety of extensively studied disordered and ordered molecular phases at moderate pressures [8–11]. According to x-ray studies [10], the high-pressure ϵ phase is stable from 16 GPa to at least 44 GPa at room temperature. Raman measurements at low temperatures [12] and higher pressures [13] report transformations to other as yet unknown phases that are characterized by increased numbers of Raman vibrons. Recent Raman studies [14] suggest that the high-pressure phases are closely related in structure. Further increase in pressure leads to a turnover and softening of some of the intramolecular vibrations [13,15], which could either be related to the weakening of intramolecular bonding or to increased vibrational coupling [14].

Raman measurements of nitrogen have been carried out to 130 [13] and 180 GPa [15]. The lowest-frequency vibron has been observed in both studies to the highest pressure reached, and the persistence of this vibron was interpreted as the existence of molecular phase to those pressures. Also, visual observations [13,15] and visible transmission measurements in Ref. [13] reveal color changes at 130–180 GPa but no quantitative characterization has been done. Here we report the results of a combined study of the optical and vibrational properties of N_2 by visible and infrared (IR) spectroscopy and Raman scattering done with new techniques [16], including synchrotron IR spectroscopy and Raman spectroscopy with near IR excitation. We present evidence for the NM transformation in the 140–160 GPa range to a disordered, single-bonded, threefold-coordinated structure.

Two separate high-pressure experiments with a Mao-Bell diamond anvil cell have been performed at low temperature (15 K up to 41 GPa) and room temperature (up to 170 GPa). Details of our synchrotron infrared/Raman technique are presented in Ref. [16]. Beyond the pressure of 130 GPa, excitations in the 693–750 nm range from a Ti:sapphire laser were used for both Raman and ruby luminescence measurements to avoid strong sample and diamond fluorescence as well as premature diamond failure.

Raman spectra to 140 GPa (Fig. 1a) reveal an abundance of vibrational modes, in agreement with previously reported results [12–14,17]. At moderate pressures, our data are in agreement with those reported in Refs. [12, 13,17]. We find a monotonic increase in frequency (Fig. 2) of all lattice modes and redistribution of their intensities with pressure, so that high-frequency bands dominate at the highest pressures. As in Refs. [13,14,17], we observe branching of the Raman-active vibrons at about 90 GPa followed by an increase in their frequency separation. Intensity redistribution is also observed as the lowest-frequency vibron ν_2 gathers most of the intensity at the highest pressures.

IR absorption spectra reveal a multiplet of modes in the vibron spectral range and also a newly discovered mode of lattice vibrations (Fig. 1b). The pressure dependencies of IR vibron frequencies match well the extrapolation of the lower pressure data (Fig. 2) reported in Refs. [18,19]. The pressure dependence of the lattice mode frequency is very close to that of the highest frequency Raman lattice mode (Fig. 2). As in the case of Raman vibrons, the IR vibrons show branching with pressure, so that up to five vibrons can be observed at high pressure, all of which originate from the ν_2 multiplet. The Raman and IR vibrons probe

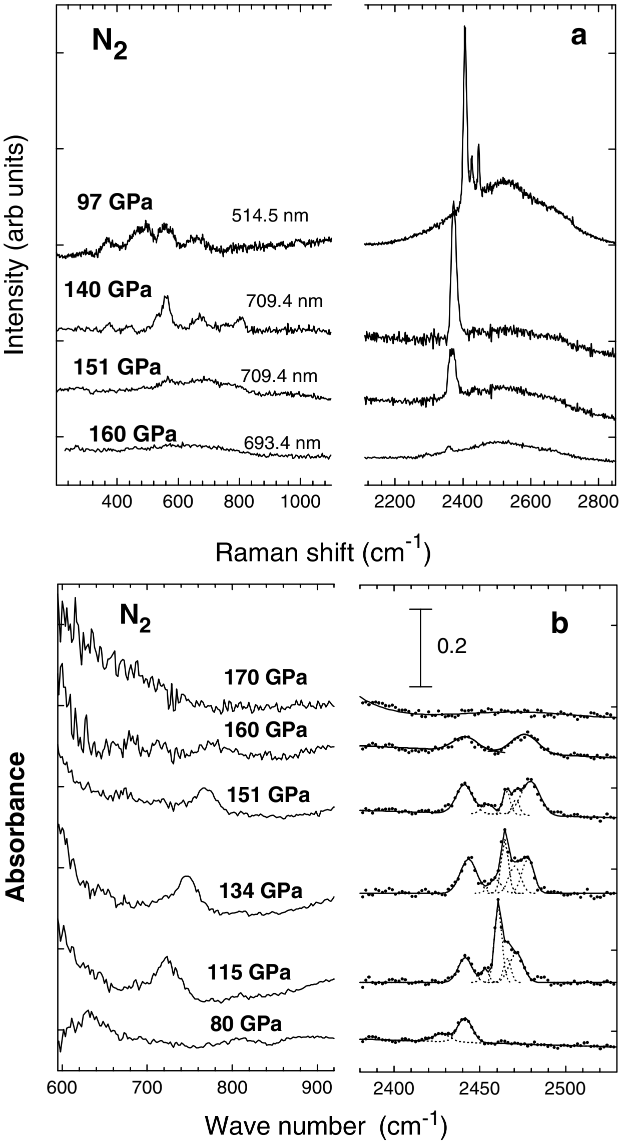

FIG. 1. (a) Representative Raman spectra between 97 and 160 GPa and room temperature. Left panel: lattice vibrations region. Right panel: vibron region. A broad band at 2550 cm^{-1} corresponds to the second order Raman spectrum of diamond. Numbers in nm represent the excitation wavelength. (b) IR absorption spectra in the 80–170 GPa range and room temperature. Left panel: lattice vibrations. Right panel: vibrons (points: experiment; solid lines: phenomenological fit; dotted lines: individual bands) spectra in the two panels have different baseline offsets.

different points of the large Brillouin zone and become accessible because of its folding. The lowest-frequency Raman vibron corresponds to the lowest frequency of the Brillouin zone and represents the case where all molecules on the faces of the unit cell (e.g., Ref. [17]) vibrate in phase [20]. The other vibrons (Raman and IR) involve different out-of-phase vibrations and form a compact group close to the frequency of the uncoupled *N*-*N* stretch. The splitting between the highest- and lowest-frequency vibrons approximately quantifies the Brillouin zone bandwidth, which increases dramatically with pressure [20]. The frequency of the uncoupled *N*-*N* stretch tentatively determined near the position of the density maximum of the observed vibrons (Fig. 2) levels off in the 100–150 GPa pressure range. Thus, the turnover and softening with pressure of the lower-frequency Raman vibron is naturally explained by an increase in the vibrational splitting, which in turn is caused by an increase in the intermolecular interactions. The observed redistribution of intensities between lattice and vibron modes can be considered a consequence of mixing of vibrational states arising from the difference in crystallographic positions at the unit cell face and origin. This means that nitrogen molecules are sitting in quasihomogeneous sites prior to the NM transition unlike another possible scenario involving formation of heterostructures [23].

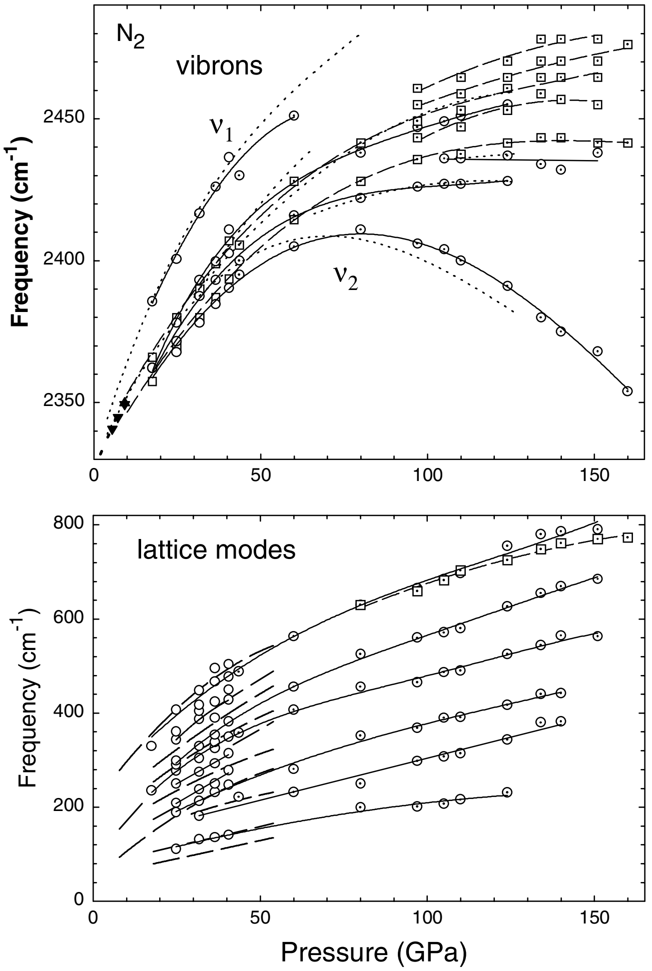

FIG. 2. Raman and IR frequencies of N_2 in the molecular state up to 160 GPa. Solid and dashed thin lines (guides to the eye) show observed Raman and IR frequency shifts, respectively; dotted and open circles: room and low temperature Raman frequencies, respectively; dotted and open squares: room and low temperature IR frequencies, respectively; thin dotted lines are from Ref. [13] (discrepancies are due to the use of different pressure scales); thick dotted lines and solid triangles are low-pressure data on the IR vibron from Refs. [18,19], respectively; thick dashed lines are Raman lattice mode data from Ref. [17].

The Raman and IR vibrons lose their intensities in the 140–160 GPa pressure range and completely disappear at higher pressures. No substantial change in linewidth has been observed prior to the disappearance of the vibrational features, so this effect cannot be due to pressure gradients. This is also observed for the Raman and IR lattice modes. It may be argued that the disappearance of the Raman modes is attributed to the presence of a luminescence background (quite moderate with red excitation) and an increase of the visible sample absorption (see below). However, IR intensities are totally independent of these factors because the sample remained transparent in the mid-IR spectral range.

Figure 3 presents the results of visible and IR absorption measurements of nitrogen at elevated pressures. Below 140 GPa nitrogen is transparent in the entire (except the absorption on relatively weak vibrational excitations) measured spectral range (600–20 000 cm^{-1}). At 150 GPa a wide absorption edge appears in the visible part of the spectra, at which point the sample becomes yellow, and then totally opaque (Fig. 3) at 160 GPa. This transformation substantially affected the measurement of IR spectra because of increased absorption in the near IR range. Nevertheless, we measured IR absorption spectra to the highest pressure reached in the experiment (about 170 GPa). By inspecting the spectra at different pressures above 150 GPa, one can easily infer that, to a first approximation, they can be obtained by simple scaling, indicating an increase of the abundance of the new phase with increasing pressure. This matches closely the vibrational spectroscopic observations of a gradual disappearance of all excitations in the molecular phase (see above) between 140 and 170 GPa. The Raman and IR spectra of the new phase show a rather broad, weak Raman band at 640 cm^{-1} as well as a broader IR band at 1450 cm^{-1} (Figs. 1 and 4). Their intensities seem to increase gradually with pressure, concomitant with a decrease in the intensity of molecular excitations, implying the coexistence of two phases between 140 and 170 GPa.

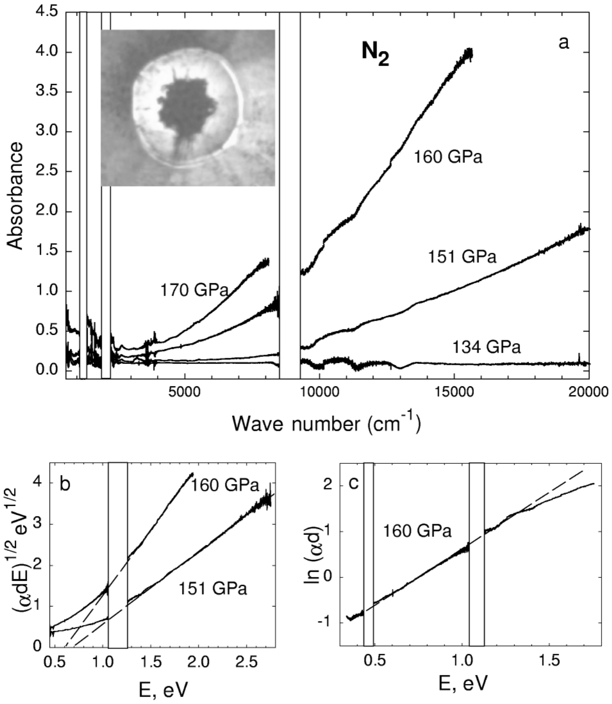

FIG. 3. (a) Optical absorption spectra in a wide spectral range at different pressures [Inset: the microphotography of the opaque sample at 160 GPa (reflected and transmitted light)]. (b) Absorption data at 151 and 160 GPa plotted in photon energy (E) versus $(\alpha dE)^{1/2}$ (α-absorption coefficient, d-sample thickness) coordinates illustrating a direct allowed gap absorption law at high energies. Extrapolations of those dependencies to zero absorption gives an estimate of the direct gap value. (c) Absorption data at 160 GPa plotted in E versus $\ln(\alpha d)$coordinates illustrating an Urbach-like absorption law at low energies. The frequency ranges of strong diamond absorption are shown by empty boxes. Absorbance A and absorption coefficient α are related by the expression $\alpha d = A \ln 10$.

The complete change in vibrational excitations and the appearance of the low-energy band gap provide evidence for the transformation from the molecular phase to a nonmolecular phase with a narrow gap. Theoretical calculations predict a transformation to threefold-coordinated cubic or distorted cubic structures [5–7] associated with a substantial volume discontinuity (25%–33%). We can rule out with a high probability the simple cubic high-pressure phase [5], which must be metallic. Other calculations indicated semiconducting phases [5–7], which agree with the experiment [24].

Theoretical calculations [6,25] predict at least a twofold decrease in the frequency of the N-N stretch as a result of the transformation from a triple- to a single-bonded molecule. Our IR measurements reveal a broad band in this spectral range (Fig. 4). A Raman band at 640 cm^{-1}

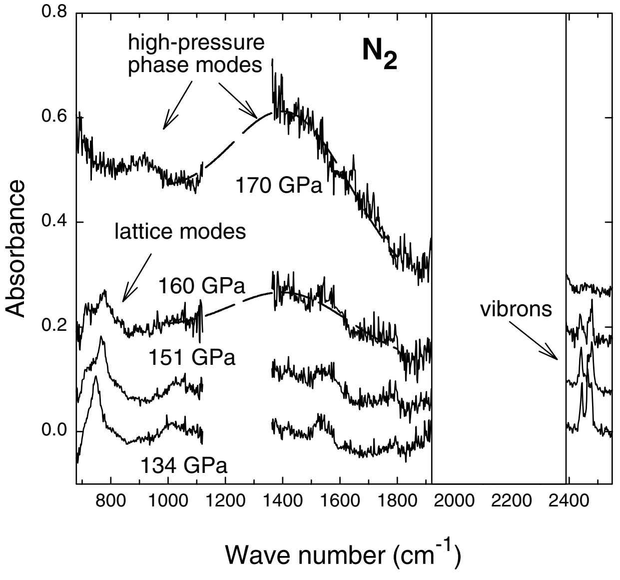

FIG. 4. IR absorption spectra in the vibrational spectral range through the transition. Dashed lines are guides to the eye. No data could be obtained in the 1120–1370 cm^{-1} and 1920–2380 cm^{-1} spectral ranges because of strong absorption by the diamonds.

was also observed, which can be a bending mode based on its frequency. Comparison of our data with the calculations of Barbee (Ref. [25]) shows even more striking correspondence between experiment and theory assuming the "cubic gauche" [7] high-pressure structure (i.e., possible appearance of the second weak IR peak at 900 cm^{-1}, Fig. 4). A variety of IR and Raman modes are predicted for this phase, and most of them are degenerate. Those modes can split under nonhydrostatic conditions or further lowering of the symmetry (Ref. [25]), which can explain the observed large linewidth of Raman and IR excitations. Alternatively, the high-pressure phase could be a fine-mixture of different three-coordinate structures with very close total energies (e.g., arsenic, black phosphorus, cubic gauche) and the chainlike structure [7] with a high concentration of stacking faults and open bonds which would make it appear amorphous by vibrational spectroscopy. The analysis of the shape of the absorption edge of the high-pressure phase (Fig. 3) shows the existence of two spectral ranges with different types of energy dependence on the absorption coefficient. At high values of absorption it follows the empirical Tauc relation [26] in the case of parabolic band edges (Fig. 3b), while at smaller absorption a so-called Urbach or exponential absorption tail [27,28] is observed (Fig. 3c). The existence of this type of absorption edge is normally related to amorphous semiconductors. The optical absorption gap determined from our experiment is 0.6–0.7 eV and seems to decrease with pressure. The slope of the Urbach tail, which can be considered as a measure of a random microfield [28], is found to be $\Gamma = 2.6\ \text{eV}^{-1}$ at 160 GPa. This is very close to what one would expect for an amorphous phase with a coordination of 2.5(3) [28].

In conclusion, we present optical evidence for a transition of molecular nitrogen to a nonmolecular state. The transition occurs on compression when the ratio of intermolecular-to-intramolecular force constants reaches 0.1 [20]. This is small compared to the highest ratio reached for hydrogen $(1900/4100)^{1/2} = 0.21$ [16] in its molecular phase. It suggests that the destabilization of the triple-bonded nitrogen molecule is the driving force of the NM transition. Vibrational and optical spectroscopic data indicate that the high-pressure phase is a narrow-gap, disordered, and single-bonded phase.

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[1] K. Takemura, S. Minomura, O. Shimomura, and Y. Fujii, Phys. Rev. Lett. **45**, 1881 (1980).

[2] E. Katoh *et al.,* Phys. Rev. B **61**, 119 (2000); E. Katoh *et al.,* Phys. Rev. B **59**, 11 244 (1999).

[3] A. F. Goncharov *et al.,* Science **272**, 149 (1996); K. Aoki, H. Yamawaki, M. Sakashita, and H. Fujihisa, Phys. Rev. B **54**, 15 673 (1996); A. F. Goncharov, V. V. Struzhkin, H. K. Mao, and R. J. Hemley, Phys. Rev. Lett. **83**, 1998 (1999).

[4] H. B. Radousky *et al.,* Phys. Rev. Lett. **57**, 2419 (1986).

[5] A. K. McMahan and R. LeSar, Phys. Rev. Lett. **54**, 1929 (1985).

[6] R. M. Martin and R. J. Needs, Phys. Rev. B **34**, 5082 (1986).

[7] C. Mailhiot, L. H. Yang, and A. K. McMahan, Phys. Rev. B **46**, 14 419 (1992).

[8] D. T. Cromer, R. L. Mills, D. Schiferl, and L. A. Schwalbe, Acta. Crystallogr. Sect. B **37**, 8 (1981).

[9] R. L. Mills, B. Olinger, and D. T. Cromer, J. Chem. Phys. **84**, 2837 (1986).

[10] H. Olijnyk, J. Chem. Phys. **93**, 8968 (1990).

[11] M. Hanfland, M. Lorenzen, C. Wassilew-Reul, and F. Zontone, Rev. High Pressure Sci. Technol. **7**, 787 (1998).

[12] D. Schiferl, S. Buchsbaum, and R. L. Mills, J. Phys. Chem. **89**, 2324 (1985).

[13] R. Reichlin *et al.,* Phys. Rev. Lett. **55**, 1464 (1985).

[14] H. Olijnyk and A. P. Jephcoat, Phys. Rev. Lett. **83**, 332 (1999).

[15] P. M. Bell, H. K. Mao, and R. J. Hemley, Physica (Amsterdam) **139B–140B**, 16 (1986); R. J. Hemley (unpublished results).

[16] A. F. Goncharov *et al.,* in *Science and Technology of High Pressure,* edited by M. H. Manghnani, W. J. Nellis, and M. F. Nicol (Universities Press, Hyderabad, India, to be published). The IR measurements were carried out at the NSLS.

[17] H. Schneider, W. Hafner, A. Wokaun, and H. Olijnyk, J. Chem. Phys. **96**, 8046 (1992).

[18] M. D. McCluskey, L. Hsu, L. Wang, and E. E. Haller, Phys. Rev. B **54**, 8962 (1996).

[19] R. Bini, M. Jordan, L. Ulivi, and H. J. Jodl, J. Chem. Phys. **106**, 6849 (1998).

[20] The fact that the main Raman vibron is lower in frequency than the IR vibrons clearly indicates a negative vibrational coupling term, as in the case of hydrogen [21]. The frequency of the lattice mode and the frequencies of intramolecular vibrations corresponding to the top and bottom of the vibrational band are related by the approximate formula (linear chain model) $\nu_l^2 = \nu_t^2 - \nu_b^2$ [22], which agrees with the experiment. At the highest pressures of observation of these vibrons (about 150 GPa), the ratio of intermolecular to intramolecular frequencies amounts approximately to $800/2450 \simeq 0.3$, which corresponds to the ratio of 0.1 of the intermolecular to intramolecular force constant.

[21] A. F. Goncharov *et al.,* Phys. Rev. B **54**, R15590 (1996).

[22] R. Zallen, Phys. Rev. B **9**, 4485 (1974).

[23] D. Hohl, V. Natoli, D. M. Ceperley, and R. M. Martin, Phys. Rev. Lett. **71**, 541 (1993).

[24] This is also consistent with recent electrical resistivity measurements of the nonmolecular phase at 193 GPa and 77 K [M. I. Eremets *et al.* (to be published)].

[25] T. W. Barbee III, in *High-Pressure Science and Technology-1993,* edited by S. C. Schmidt *et al.,* AIP Conf. Proc. No. 309 (AIP, New York, 1994), p. 163.

[26] J. Tauc, R. Grigorovici, and A. Vancu, Phys. Status Solidi **15**, 627 (1966).

[27] F. Urbach, Phys Rev. **92**, 1324 (1953).

[28] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon Press, Oxford, 1979), 2nd ed.