Optical Studies of Nitrogen to 130 GPa

Robin Reichlin,(1) David Schiferl,(2) Sue Martin,(1) Craig Vanderborgh,(2) and Robert L. Mills(2)
(1) *University of California, Lawrence Livermore National Laboratory, Livermore, California 94550*
(2) *University of California, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

(Received 7 August 1985)

Nitrogen is observed to remain a molecular solid up to 130 GPa, contrary to recent theoretical predictions of metallization below 100 GPa. Raman scattering reveals three new phases at 20, 66, and 100 GPa, which are distinguished by branching of existing vibronic modes. One mode increases in frequency to a broad maximum at 66 GPa and then decreases, similar to the case of H_2. In H_2, such behavior was attributed to a weakening of the H-H bond. In N_2, three other vibronic frequencies continue to increase, showing the situation to be more complicated than just a weakening of the N-N bond.

PACS numbers: 62.50.+p, 78.30.Gt

There has been a great deal of recent interest in insulator-metal transitions, particularly in diatomic molecules such as N_2, H_2, and I_2.[1] Recent experimental and theoretical results for nitrogen indicate that N_2 might transform to a monatomic metallic state at pressures below 100 GPa (1 Mbar). The results of experimental studies by Nellis and co-workers[2,3] of single- and double-shocked nitrogen appear to show a continuous dissociation of molecular nitrogen to a monatomic state starting at 30 GPa and 6000 K. Theoretical calculations by McMahan and LeSar[4] indicate that crystal structures composed of N_2 molecules may be less stable than a monatomic simple cubic structure at 0 K and 77 to 94 GPa. They suggested that structures observed in other group-V elements might have even lower cohesive energies than the simple cubic structure at high pressures. Martin[5] has subsequently made calculations which show that nitrogen would have a lower cohesive energy in the arsenic ($A7$) rhombohedral structure at pressures around 100 GPa.

Our work was intended to investigate the prediction that molecular nitrogen would transform to a monatomic structure, possibly metallic, at pressure accessible to the diamond-anvil cell. Preliminary experiments which we performed at pressure above 110 GPa showed a color change in nitrogen, but no dramatic transition to a metallic phase. Concurrently, Hemley, Mao, and Bell[6] made preliminary Raman measurements on nitrogen up to pressures of 160 GPa. They showed that the frequency of the ν_2 vibron increases with pressure to a maximum at about 80 GPa and then drops, in a manner similar to the behavior of the vibrational mode of molecular hydrogen at 50 GPa.[7,8]

These experimental developments prompted us to study the optical absorption spectrum of nitrogen and to investigate the N_2 vibron region carefully with high-resolution Raman spectroscopy in order to detect any subtle phase changes in molecular nitrogen at pressure.

Our high-pressure experiments were made with "megabar" diamond-anvil cells.[9] We employed the techniques described by Goettel, Mao, and Bell,[10] and used beveled-diamond anvils for generating pressures above 100 GPa. The anvils used were standard brilliant-cut diamonds with sixteen facets, a central flat of 50 μm, a 5° bevel, and a 300-μm total culet diameter.

The sample chamber was formed by preindenting a 250-μm-thick T-301 stainless-steel gasket to a thickness of 15 to 20 μm, and drilling a 50-μm hole in the center of that area corresponding to the central flat. A small amount of very fine ruby powder was placed in the sample chamber for *in situ* pressure measurements by the ruby-fluorescence technique.[11] Care was taken to ensure that pressurized nitrogen samples would have a volume ratio of ruby to nitrogen not exceeding 20%. We suspected that large amounts of ruby might result in inaccurate pressure determinations because of bridging effects. This is in contrast to the sample preparation technique used by Hemley, Mao, and Bell.[6] Their high-pressure samples had substantially larger concentrations of ruby, which was used as a strengthening filler as well as pressure sensor in their experiments.

Samples were prepared by condensing ultrahigh-purity N_2 gas in the sample chamber and pressurizing at liquid-nitrogen temperatures. Once nitrogen was trapped at pressure in the sample chamber, the cell was warmed to room temperature for the optical experiments. Pressures were determined from the ruby R_1 line position with use of the calibration of Mao *et al.*[12] Both R_1 and R_2 ruby lines were clearly resolved in all of our fluorescence spectra up to the maximum pressure of 130 GPa.

Raman spectra were measured at Los Alamos with a Spex 1403 double-monochromator with a cooled GaAs photomultiplier detector. The spectrometer was equipped with a periscope for viewing the sample image in the entrance slits, so that it was possible to position the laser spot (focused down to about 8 μm) possibly on a small area of the nitrogen sample. We repositioned the laser spot for each measurement at a new pressure on the same spot in the sample. This spot was located in the center of a cluster of easily recognizable ruby grains, yet the spot itself was free of any observable pieces of ruby. Both the Raman emission and ruby fluorescence measurements were made in the exact same sample spot with no repositioning of the sample between measurements. Two laser lines were used on separate runs, the argon laser 20 492-cm^{-1} line with 160–240 mW incident on the sample and the krypton 21 000-cm^{-1} line with 40 mW. With increasing pressure, some of the Raman peaks became progressively weaker and broader. For this reason, and because the assignment of phase transitions depends critically on the observation of changes in the weaker peaks, extra care was taken to obtain good counting statistics at pressure over about 100 GPa.

Absorption spectra were measured at Livermore with an optical system similar to that described by Syassen and Sonnenschein.[13] Absorption measurements were made in the spectral region 1.5 to 5 eV with use of a xenon source to illuminate the nitrogen samples.

Pressure measurements taken during the absorption experiments were made with the 21 839-cm^{-1} line of an argon laser operating at about 50 to 75 mW power. The laser beam was focused to a spot size of 2 to 3 μm, so that it was possible to measure pressures at individual spots within the small (50-μm) sample chamber. This enabled us to characterize the pressure distribution within the nitrogen sample quite accurately.

We found no evidence for a metallic phase transition in nitrogen in either the Raman or absorption experiments over the pressure range 2 to 130 GPa. This is in agreement with the results of Hemley, Mao, and Bell.[6] Our data indicate that nitrogen retains its molecular character despite several phase transitions in this region. Whether the diatomic molecular form is actually the stable one above the calculated transition pressure range of 77 to 94 GPa is not certain. McMahan and LeSar[4] pointed out that molecular structures could remain metastable to much higher pressures.

On freezing at 2.4 GPa at room temperature, solid nitrogen was observed to be transparent and colorless. With increasing pressure, samples gradually changed from colorless to pale pinkish brown to much deeper shades of brown at 130 GPa. The color changes appeared to be continuous. This is consistent with a preliminary analysis of absorption measurements which shows the tail of an absorption edge moving from the uv into the visible starting at about 70 GPa.

The pressure dependence of the Raman-active vibron frequencies of nitrogen is shown in Fig. 1. The peaks cannot be labeled according to symmetry character because the space groups are unknown over most of the pressure range. However, they do appear to be derived from closely related structures. The numbering scheme used in Fig. 1 shows the evolution of the peaks as they branch out with increasing pressure.

The low-frequency mode ν_2 ($\nu_2 \rightarrow \nu_{2C} \rightarrow \nu_{2C(2)}$) was the highest-intensity mode observed in the nitrogen Raman spectrum and persisted up to the highest pressures of our experiments. The frequency of this mode increases steadily to a broad maximum at about 66 GPa and then slowly decreases with increasing pressure. This observation was confirmed by Hemley, Mao, and Bell,[6] although they report a maximum at about 80 GPa. This may be attributable to the fact

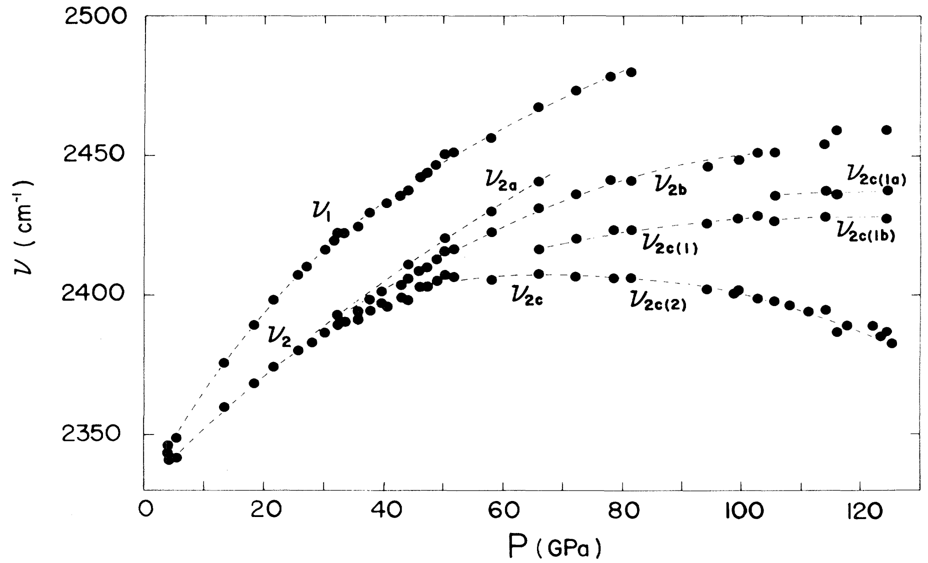

FIG. 1. Pressure dependence of the Raman-active N_2 vibrons up to 125 GPa.

that their samples contain much more ruby.

Our sample-loading technique resulted in samples 40 to 60 μm in diameter, generaly centered on the central flat of the diamond anvils. The percentage of finely ground ruby powder in the sample ranged from about 5% to 25%, and in one case was estimated to be as high as 80%. We took six nitrogen samples to pressures greater than 100 GPa. Five of these samples had relatively small percentages of ruby which was well dispersed within the nitrogen. In these runs we observed relatively small pressure gradients within the sample area in the region of the central diamond flats. This variation in pressure within individual samples ranged from 5 GPa in the best case to 15 GPa in the worst case for pressures over 100 GPa. Also noteworthy is the observation that pressures measured in areas with small clusters of ruby powder were generally found to be 10 to 15 GPa higher than those measured on an isolated 1- to 2-μm ruby chip completely surrounded by nitrogen. In the sample which contained over 80% ruby powder, much larger pressure gradients were observed in the area of the sample overlying the central flats. At a peak pressure of 106 GPa, for example, the pressure in this sample varied by as much as 40 GPa. Because of these problems, no data were taken on this sample.

The behavior of the ν_2 mode in N_2 is very similar to that described by Mao, Bell, and Hemley for H_2.[8] They observed an initial increase in frequency followed by a sharp decrease above 50 GPa. In the case of hydrogen the bending over of the molecular vibron at high pressure was attributed to weakening of the H-H bond with pressure, possibly a precursor to a metallic transition. In the case of nitrogen, however, several other Raman-active vibrational modes were measured in our experiments. These are depicted in Fig. 1. The most striking observed is that unlike the low-frequency vibron, ν_2, the five other modes observed in this pressure region were not seen to decrease in frequency at high pressures. It is tempting to draw a parallel with the H_2 experiments and conclude on the basis of the behavior of the ν_2 vibron that N-N bonds may be weakening with pressure. However, the fact that these other vibrons do not behave in a similar manner indicates that the situation may be far more complicated.

Three new high-pressure phase transitions were also detected in nitrogen in our Raman experiments. Their appearance is indicated by the splitting of existing vibrational modes at pressure, as illustrated in Fig. 1. The onset of the phase transitions appear to be at 20, 66, and 100 GPa, and the newly resolved branches of the vibrational peaks at these pressures are labeled. All the new phases appear to involve distortions of the δ-N_2 (Schiferl, Buchsbaum, and Mills[14]) ($Pm3n$) structure, inasmuch as the persistence of lower-pressure modes indicates that the structures are closely related. All three phase transitions are indicated by the appearance of additional branchings of the ν_2 vibron. These new structures probably involve the formation of superlattices from the original $Pm3n$ structure.

The disappearance of the ν_1 peak above 80 GPa and the ν_{2a} peak above 66 GPa seems to be a consequence of their weakening in intensity with pressure until they were lost in the large background, rather than a result of any additional phase transformations.

In summary, nitrogen in the predicted metallic simple cubic or $A7$ rhombohedral structure has not been observed up to 130 GPa. However, three new phases of diatomic N_2 were found at room temperature between 14 and 125 GPa. These appear to be distortions of the $Pm3n$ cubic structure, probably involving the formation of superlattices. It is surprising that the phase diagram of such an apparently simple substance as nitrogen should reveal increasing complexity with pressure.

The authors are very grateful to K. Goettel for many helpful discussions and descriptions of the techniques developed at the geophysical laboratory for routinely reaching pressures in excess of a megabar. We also acknowledge the contributions of N. Holmes and H. Radousky to the absorption measurements mentioned here. R. LeSar, A. K. McMahan, R. M. Martin, W. J. Nellis, A. G. Duba, and B. P. Bonner provided stimulating discussions and unpublished calculations. R. J. Hemley and H. K. Mao generously kept us informed of their progress on similar experiments on nitrogen. This work was performed under the auspices of the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

---

[1] M. Ross and A. K. McMahan, in *Physics of Solids Under Pressure,* edited by J. S. Schilling and R. N. Shelton (North-Holland, New York, 1981), p. 161.

[2] W. J. Nellis and A. C. Mitchell, J. Chem. Phys. **73**, 6137 (1980).

[3] W. J. Nellis, N. C. Holmes, A. C. Mitchell, and M. Van Thiel, Phys. Rev. Lett. **53**, 1661 (1984).

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

[5] R. M. Martin, private communication.

[6] R. J. Hemley, H. K. Mao, and P. M. Bell, private communication.

[7] S. K. Sharma, H. K. Mao, and P. M. Bell, Phys. Rev. Lett. **44**, 886 (1980).

[8] H. K. Mao, P. M. Bell, and R. J. Hemley, Phys. Rev. Lett. **55**, 99 (1985).

[9] H. K. Mao and P. M. Bell, *Carnegie Institution of*

Washington Year Book (Carnegie Institution, Washington, D.C., 1975), p. 300.

[10] K. A. Goettel, H. K. Mao, and P. M. Bell, Rev. Sci. Instrum. (to be published).

[11] J. D. Barnett, S. Block, and G. J. Piermarini, Rev. Sci. Instrum. **44**, 1 (1973).

[12] H. K. Mao, P. M. Bell, J. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[13] K. Syassen and R. Sonnenschein, Rev. Sci. Instrum. **53**, 644 (1982).

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