

Novel Broken Symmetry Phase from N₂O at High Pressures and High Temperatures

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Simple molecular solids become unstable at high pressures, typically transforming to dense framework and/or metallic structures. We report formation of an unusual ionic solid NO⁺NO₃⁻ (nitrosonium nitrate) from N₂O at pressures above 20 GPa and temperatures above 1000 K. Synchrotron x-ray diffraction indicates that the compound crystallizes with a structure related to the aragonite form of CaCO₃ and NaNO₃. Raman and infrared spectroscopic data indicate that the structure is noncentrosymmetric and exhibits a strong pressure dependent charge transfer and orientational order.

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The light elements of the first row of the periodic table form simple molecular compounds (e.g., N₂, CO, CO₂, NO₂, CH₄) characterized by strong covalent bonding between the atoms. In the condensed phase, these systems typically form high symmetry structures having weak van der Waals' interactions. At the highest pressures, all solids are expected to lower their free energy by delocalization of electrons and transform to metallic states [1]. In intermediate pressure-temperature ranges, these materials may transform to extended covalent networks to form framework or polymeric solids. This behavior was observed, for example, in CO₂, N₂ and C₂N₂ [2–4]. Recent experiments on CO₂ have shown the existence of a polymeric network solid analogous to the cristobalite or tridymite polymorphs of SiO₂ [2,5–10]. N₂O is an isoelectronic but asymmetric equivalent of linear CO₂, which might also be expected to form a framework or polymeric structure at high pressure, with the N or O atoms forming tetrahedrally coordinated centers. In this sense, N₂O could take on the structure of PON, the isoelectronic equivalent of SiO₂ [11,12], the cristobalite form of which persists to above 70 GPa [13]. We have therefore explored the polymorphism of N₂O at high pressures and temperatures. In contrast to the above systems, we find that N₂O breaks down at high pressures and temperatures to an ionic broken symmetry phase.

N₂O samples were loaded into a symmetric piston-cylinder diamond anvil cell at temperatures below 150 K. To ensure no contamination from H₂O [14], the loading was done in a glove bag with dry N₂ atmosphere. Ruby fluorescence was used to determine the pressure. Samples were heated by laser heating with a 60 W CO₂ laser. Temperature was estimated from spectroradiometric measurements of the heated area to an accuracy of ±100 K. We found that the absorbance of N₂O at 10 μm was sufficient to achieve high temperatures of >2000 K at high pressure. Raman spectra before and after laser heating were recorded at room temperature using the 514.5 and 488.0 nm excitation lines of an Ar-ion laser. Synchrotron

IR spectra were measured at the U2A beam line of the National Synchrotron Light Source (NSLS). Details of the experimental setup are reported elsewhere [15]. X-ray diffraction measurements were carried out at the ID13 beam line of GSECARS at the Advanced Photon Source, using a focused monochromatic beam (with a nominal beam size of 10 μm) from the undulator at 0.4246 Å.

Raman spectra at room temperature measured as a function of pressure revealed shifts consistent with previous studies [16]. However, when heated to temperatures above 1000 K at pressures above 10 GPa, entirely different behavior was observed. Raman spectra reveal the formation of a new phase. The changes were explored at high pressures and temperatures in the range 10–40 GPa and 1000–3000 K. At pressures lower than 10 GPa, or at pressures above 40 GPa, the dissociation of N₂O into N₂ and O₂ was a dominant reaction. Similar dissociation was observed when the sample was heated above 2000 K in the pressure interval 10–30 GPa. Dissociation was evident from the direct observation of N₂ and O₂ Raman vibrons and complete loss of the N₂O Raman spectrum. When the sample was heated to temperatures below 2000 K in the pressure range of 10–30 GPa, the formation of a new phase could be clearly observed.

In Fig. 1, we have shown the Raman spectra before and after laser heating the N₂O sample at 20 GPa. The results of our IR studies on the new phase are shown in Fig. 2. The prominent features of the Raman spectra of this phase is the rich low frequency spectrum and the intense band at 2250 cm⁻¹. These observations are similar to previous spectroscopic studies which suggested the formation of NO⁺NO₃⁻ from N₂O₄ both at ambient and moderate pressures up to 7 GPa. The formation reaction was attributed to a photochemical transformation of N₂O₄ → NO⁺NO₃⁻. The ionic nature was inferred from the proximity of the NO⁺ stretching Raman mode (2224 cm⁻¹) in the nitrate phase to that of isolated NO⁺ (2345.2 cm⁻¹) [17–20], but no structural data were

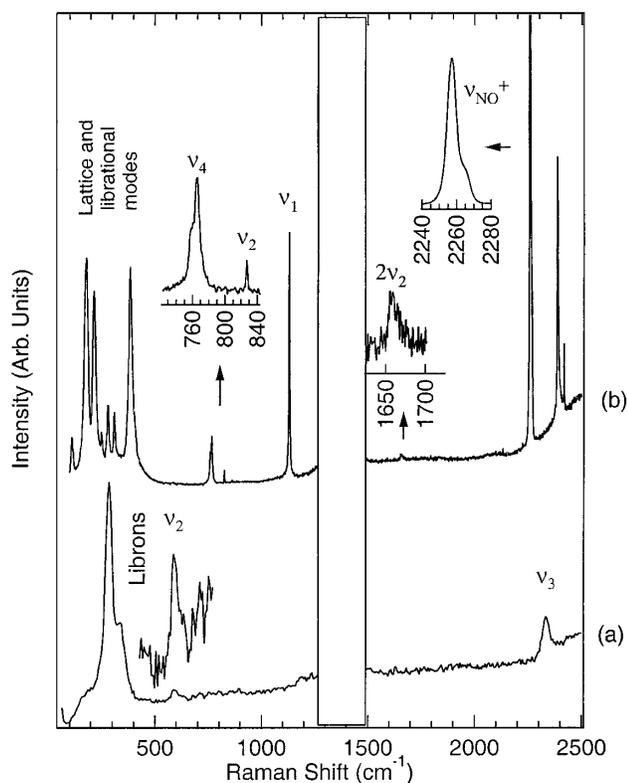


FIG. 1. (a) Raman spectrum of N_2O at 21 GPa before laser heating. (b) Raman spectrum of $NONO_3$ obtained after laser heating the sample to approximately 1200 K. The vibrational modes of N_2 are observed but those of O_2 are absent, indicative of insignificant amounts of dissociation into $N_2 + O_2$. The region of the first order diamond peak has been blanked out for clarity. The insets show the vibrational modes characteristic of NO^+ and NO_3^- . The vibrational splitting in ν_4 and ν_{NO^+} is clearly evident.

presented in these reports. Based on the observation of the vibrational modes of N_2 and $NONO_3$, we propose that the following reaction takes place, $4N_2O \rightarrow NONO_3 + 3N_2$.

We can assign the spectra based on the observed intensities and proximity of those observed in $NONO_3$ both at ambient [17] and moderate pressures [18]. Our Raman measurements reveal ν_1 , ν_2 , and ν_4 fundamentals of NO_3^- (Fig. 1), while ν_2 , ν_3 , and ν_4 are observed in the IR (Fig. 2). Similarly, the strong, high frequency Raman and IR modes can be assigned to the NO fundamental (symmetric stretch). The ν_2 and ν_4 fundamentals of the NO_3 group and the NO stretching mode show several components both in the Raman and in the IR spectra. The splitting of ν_4 can be ascribed to the distortion of the NO_3 group [21], while the splitting in ν_2 and the NO stretch is induced by intermolecular interactions. In addition, several weak bands are observed in both the Raman and IR spectra (Fig. 1) which can be assigned as the combination bands (lattice modes and the fundamentals). A rich spectrum of lattice modes is observed in the low frequency.

Despite the similarities in spectral features of the phase observed here and those reported in earlier studies

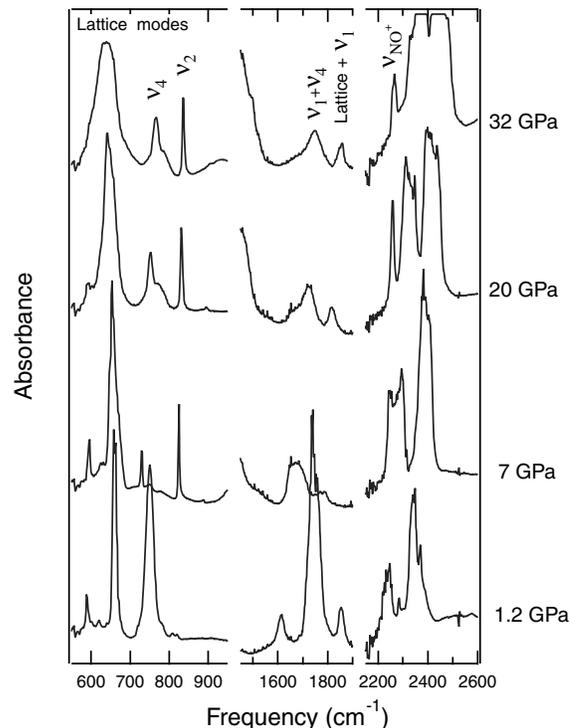


FIG. 2. Representative IR absorption spectra obtained during decompression. The decrease in the IR activity of the NO^+ modes with decreasing pressure can be clearly seen. The spectra have been offset vertically for the sake of clarity. All the spectra have been normalized for diamond absorption and are on the same scale.

[17,18,20], our IR and Raman results show that the phase reported earlier is a high symmetry, molecular phase. This is demonstrated first by measurements of the higher frequency IR absorption as a function of pressure (Fig. 2). Two striking features that need to be noted are (a) the intense modes at 2374 and 2446 cm^{-1} and (b) the decrease in IR activity of these modes with decreasing pressure. The earlier IR spectra measured at ambient pressure [17] reveal only one IR-active mode in this frequency range, whereas, even at the lowest pressures, we observe a total of five IR-active modes in the region 2300–2500 cm^{-1} . The band at 2226 cm^{-1} matches the NO mode observed by Raman. However, the band at 2334 cm^{-1} and the relatively strong multiplet centered around 2348 cm^{-1} were not reported in the low-pressure studies. The frequency difference between these bands and that of the Raman active NO stretching matches with observed low frequency lattice modes observed by Raman has an identical pressure dependence, suggesting they are combination bands [22]. The large increase in IR activity of these modes with pressure implies an increasing degree of ionic character of the solid. By using a classical damped oscillator model [23], the effective charge associated with the intense IR absorption peaks at 2374 and 2446 cm^{-1} is estimated to be $0.3e$ at the highest pressures (Fig. 2). The effective charge estimated from the pure NO^+ stretching mode

at 2226 cm^{-1} is $0.05e$, which is an order of magnitude higher than the value for the free ion [24].

Confirmation of the ionic nature of the phase requires direct structural data which allow us to delineate the bonding topology. X-ray diffraction was therefore measured using a synchrotron source and a Bruker CCD(2k) and calibrated using a CeO_2 standard. To overcome the high degree of crystallinity in the solid, the sample was rocked over $\pm 10^\circ$ in the xray beam. The diffraction peaks of $\epsilon\text{-N}_2$ could be identified and extracted from the pattern in accordance with the reported cell parameters at this pressure [25]. The diffraction peaks of NONO_3 were best indexed by an orthorhombic unit cell with cell constants $a = 5.658(6)$, $b = 7.324(5)$, $c = 6.202(7)$ Å, and $V = 257.0(7)$ Å³. The diffraction data and the indexing of the two phases are shown in Fig. 3. Comparing the pressure-volume relations for $\epsilon\text{-N}_2$ and $\epsilon\text{-O}_2$ [25,26], we estimated NONO_3 to be 6% denser than $\text{N}_2 + 2\text{O}_2$ at this pressure. This indicates that the formation of NONO_3 has a lower free energy even at room temperature. However, the formation of this phase from N_2O at elevated temperatures is indicative of an activation barrier that is substantially higher than the one present in the photochemical transformation in N_2O_4 reported earlier [18]. The systematic absences in the observed diffraction pattern point to space group $Pm\bar{c}n$ or $P2_1cn$. The cell constants and the axial ratios are very similar to those reported for the aragonite phase of CaCO_3 and KNO_3 at ambient conditions.

In contrast to the centrosymmetric aragonite structures, ν_2 , ν_4 (of NO_3^-), and ν_{NO^+} are observed to be both IR and Raman active (Figs. 1 and 2). This implies the noncentrosymmetric space group $P2_1cn$. Although a full structural refinement was not possible because of preferred orientation (texture) effects, we consider a range of struc-

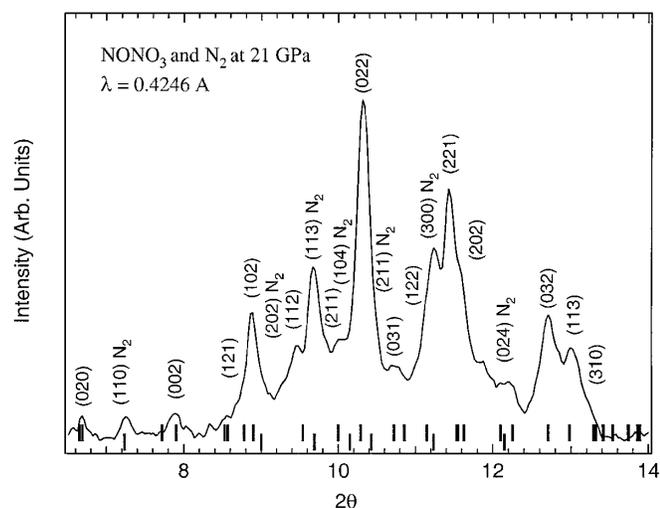


FIG. 3. Powder x-ray diffraction pattern at 21 GPa. The indices are based on a fit to the orthorhombic unit cell of NONO_3 and the hexagonal unit cell of $\epsilon\text{-N}_2$. The Raman spectrum of this phase is shown in Fig. 1(b).

tural models based on placing the NO_3 ions on the corresponding CO_3 positions in the aragonite structure (in the case of $P2_1cn$, these would all be the $4a$ sites). We place the NO ions on $4a$ positions close to those of the Ca ions giving rise to a molecular arrangement, $\text{ON}\cdots\text{O}_2\text{NO}$, which is close to one of the N_2O_4 conformations [20]. The proposed structure is shown in Fig. 4. A LeBail extraction of the observed powder pattern based on this model yields a fairly good fit (weighted R -factor of the order of 11%) [27].

An interesting consequence of such a proposed structural model is the possibility of rotational disorder of the NO groups at lower densities. Indeed, this would imply that the solid NONO_3 is a high symmetry structure at very low pressures, where both the NO and the NO_3 groups are orientationally disordered (as in the cubic forms of TlNO_3 [28]). With increasing pressure, the disorder would be hindered and could result in a structural transition. Indeed, our IR and low frequency Raman data provide evidence for a structural transition associated with rotational order and disorder. Changes are observed in the IR at the low pressures (Fig. 2). Moreover, we observe a reduction in the number of lattice modes at about 4 GPa in low frequency Raman data. The smaller number of lattice modes observed in the earlier reports [17,18] is also consistent with this interpretation. The behavior is indicative of a decreasing charge transfer between neighboring NO and O_2NO groups.

In conclusion, we report the formation of NONO_3 from N_2O at high pressures and temperatures. Based on the analysis of powder x-ray diffraction together with the Raman and IR spectroscopy data, we infer that the structure of NONO_3 is an aragonite-type and possibly noncentrosymmetric. In contrast to the earlier reports on this compound, our results indicate that, at low pressure, the material is largely molecular, consisting of polarized

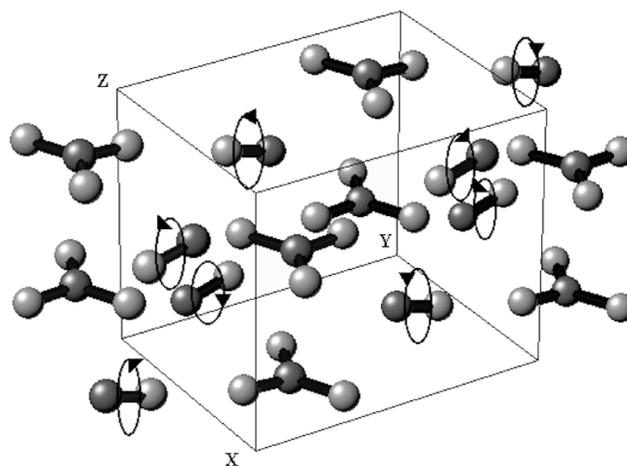


FIG. 4. The proposed structure of NONO_3 in the $P2_1cn$ phase with four molecules per unit cell at high pressures and temperatures. The NO molecules are rotationally disordered at low pressures as shown.

N_2O_4 species. With increasing pressure the compound transforms to an ionic solid via a strongly pressure dependent charge transfer interaction, possibly coupled with orientational ordering. The structure is similar to a conventional classical ionic crystal (e.g., aragonite-type), but the pressure dependence of the effect also suggests parallels to other, rather different, molecular systems. These include the symmetry breaking increase of IR activity in phase III of solid molecular H_2 [29] and the neutral-to-ionic transition in tetrathiafulvalene chloranil [30,31], where strong pressure dependent charge transfer interactions have been proposed [32]. Such a transition opens the possibility of new pathways to the formation of high-pressure–high-temperature ionic phases and low-dimensional inorganic materials, possibly with intriguing dielectric or electronic properties.

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