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New phases of N_2O_4 at high pressures and high temperatures

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Abstract

High *P–T* studies of molecular N_2O_4 using Raman, synchrotron infrared, and X-ray diffraction measurements reveal several new phenomena. Significant changes in the vibrational spectra indicate a phase transition at about 12 GPa. The X-ray diffraction measurements show that the material remains cubic through the transition. We ascribe the transition to a change in the molecular geometry of N_2O_4 within the cubic unit cell. Further vibrational spectra of heated samples enabled observation of another phase, the ionic isomer $NO^+NO_3^-$ produced at high pressures and temperatures. These studies provide new information on the phase diagram and stability of N_2O_4 at high *P–T* conditions.
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1. Introduction

Pressure-induced phase transitions and chemical reactions have now been documented in a growing number of molecular systems [1,2]. In contrast to ambient-pressure conditions where relatively strong intramolecular interactions dictate the molecular structure and chemical stability, elevated pressure significantly reduces intermolecular distances for highly compressible molecular solids, increasing intermolecular interactions to produce new domains of reactivity. The profound changes in chemical bonding induced by high pressure are often associated with phase transitions, chemical reactions, or changes in molecular geometry [3].

Molecular N_2O_4 has been extensively investigated in condensed phase at ambient pressure and low temperatures by means of Raman and IR spectroscopy over the past two decades [4,5]. Of particular interest is the exceptionally reactive behavior of solid N_2O_4 induced either by heating or photons. N_2O_4 crystallizes in a cubic structure (space group *Im3*) at ambient pressure and −11.2 °C; laser irradiation induces a transition at 1.16 GPa from the α-phase (with the same structure as at ambient pressure) to a phase designated β-N_2O_4 with an unknown lower symmetry structure. The latter phase subsequently undergoes a

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reversible autoionization to form $NO^+NO_3^-$ at 1.5–3.0 GPa [6,7].

This Letter describes an integrated study of N_2O_4 using Raman, sychrotron infrared and synchrotron X-ray diffraction to address three questions: (1) What is the higher-pressure behavior of this compound? Up to now there has been just one high-pressure study on this molecular solid, extending up to only 7.6 GPa [6]. (2) What is the corresponding high-temperature behavior? Previous studies focused chiefly on the low-temperature region (<300 K) [4,5]. (3) What are the crystal structures of the materials under pressure? As yet no X-ray diffraction measurements at high pressures have been reported. In addressing these questions, we document a new transition associated with pressure-induced change in molecular geometry. Further experiments using Raman spectroscopy combined with CO_2 laser heating identified the ionic phase of N_2O_4 in the high P–T region.

2. Experimental procedures

Pure N_2O_4 (99.5%) gas was purchased from Aldrich and used without further purification. The gas is mainly NO_2 monomer but solidifies as a dimer into a diamond anvil cell pre-cooled in a liquid nitrogen bath. The cells were then sealed and pressurized before being warmed to room temperature. The pressure was determined from the pressure shift of the R_1 ruby fluorescence line with an accuracy of ± 0.05 GPa under quasi-hydrostatic conditions [8].

For Raman measurements, the 488.0 and 514.5 nm lines of an Argon ion laser (Coherent Innova 90) were used as the excitation source, with average power of 0.4 W. The resolution achieved using a 460 mm focal length $f/5.3$ imaging spectrograph (ISA HR460) with an 1800 grooves/mm grating and CCD detector (Princeton Instruments) was ± 0.1 cm^{-1}. The wavelength calibration was done using Ne lines with an uncertainty of ± 1 cm^{-1}. Infrared absorption measurements were performed at beamline U2A at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory (BNL). The optical layout of the setup has been described in detail previously [9]. Spectra were taken in the mid-IR region, from 500 to 3000 cm^{-1}, with resolution of 4 cm^{-1}. High P–T conditions were created by heating the pressurized N_2O_4 sample using a CO_2 infrared laser (10.6 μm) operated at about 50 W. The sample was then quenched to room temperature at high pressure for Raman measurements.

Energy-dispersive X-ray diffraction was carried out at beamline X17C of NSLS. The beamline instrumentation and diffraction geometry have been described previously [10]. The N_2O_4 sample was examined at pressures of 6.2 and 13.8 GPa. For each pressure, X-ray diffraction patterns were collected at several 2θ angles, in order to examine the crystal structure of the different phases indicated by the Raman spectra. The diffraction pattern was calibrated using diffraction lines of gold [10].

3. Results

3.1. Raman spectra

Fig. 1 shows the Raman spectrum of molecular N_2O_4 at 8.8 GPa and 300 K, with assignments of the active modes. At this pressure, the spectrum is consistent with the previously reported α-N_2O_4 phase with D_{2h} symmetry. Fig. 1 also compares Raman spectra of molecular N_2O_4 at selected pressures. Significantly different Raman features are observed when the pressure is increased from 8.8 to 12.3 GPa. These features, indicating a new phase of N_2O_4, include enhanced structure in the lattice mode region 210–370 cm^{-1}, splitting and broadening of the peak at 730 cm^{-1} ($\nu_8 B_{1g}$, NO_2 wagging mode) and the appearance of new peaks at 1104 and 2208 cm^{-1}. We designate the new phase as γ (β-N_2O_4 was first observed [6] by laser irradiation of α-N_2O_4 at 1.2 GPa). To probe the high-temperature regime, we performed heating experiments at several high pressures using the CO_2 infrared laser. Fig. 1 includes the Raman spectrum of a typical heated sample at 15.3 GPa. This spectrum exhibits vibrational modes and a lattice profile characteristic of the ionic species $NO^+NO_3^-$ [11–13]. Previously, the transformation

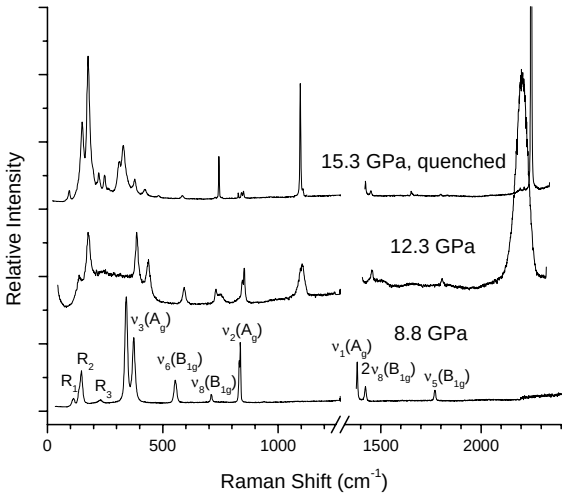

Fig. 1. Raman spectra of N_2O_4 measured at 8.8 GPa, 12.3 GPa at room temperature, and at 15.3 GPa for a sample subjected to heating by a CO_2 laser, then quenched to room temperature. The assignments of molecular vibrational modes are labeled for the Raman spectrum of N_2O_4 measured at 8.8 GPa. Librational lattice modes are designated by R_1, R_2 and R_3. The secondary peak at 374 cm^{-1} is due to crystal field splitting. The region of 1250–1350 is obscured by the T_{2g} mode of the IA type diamond anvils.

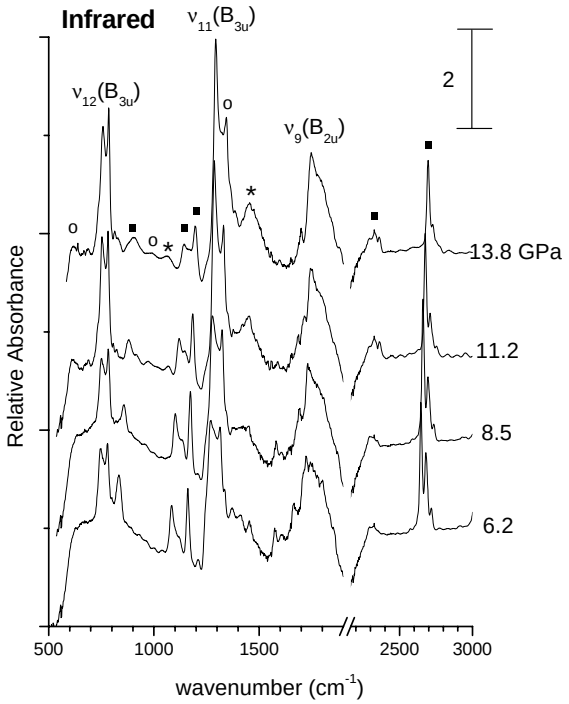

Fig. 2. IR spectra of N_2O_4 obtained at 6.2, 8.5, 11.2 and 13.8 GPa (room temperature). The region of 1900–2200 cm^{-1} is obscured by the absorption of the type II diamond anvils. Assignments of fundamentals are labeled as well as the combinations (■). Vibrational modes with possible origins of D (or D′) isomer of N_2O_4 are denoted by (○), and of ionic isomer $NONO_3$ by (★).

from molecular N_2O_4 to ionic $NO^+NO_3^-$ had been observed only at ambient pressure when induced by heating or at pressures below 3 GPa by laser irradiation [4–7]. The present study seems to be the first to observe such a transformation at high pressure and high temperature.

3.2. IR spectra

Fig. 2 shows the IR spectra of N_2O_4 at four pressures and room temperature. Although the overall absorbance profiles evolve smoothly on compression, some pressure-induced differences are still discernible. For example, several new peaks appear at 610, 976 and 1068 cm^{-1} when the pressure is increased from 8.5 to 11.2 GPa. The doublet at 770 cm^{-1} is significantly enhanced in the two higher-pressure spectra, as is the peak at 1272 cm^{-1}. The two peaks at 837 and 1084 cm^{-1} exhibit broadening and weakening on increasing pressure. The peak(s) around 1453 cm^{-1} appeared vague at 8.5 GPa and below, but at higher pressures become prominent. The peak at about 2360 cm^{-1} is resolved into a doublet at 11.2 GPa and above, whereas the strong IR absorbance peaks near 2650 cm^{-1} merge as the pressure is increased. These pressure-induced changes in the IR spectra are consistent with a phase transition between 8 and 11 GPa, although the changes are much less pronounced than those seen in the Raman spectra. The assignments of the IR bands provide important insight in the characterization of the phase transition as discussed below.

3.3. X-ray diffraction

Fig. 3 displays X-ray diffraction patterns collected at 6.2 and 13.8 GPa. The 2θ angles used were 9.00° and 13.00°, respectively, as calibrated

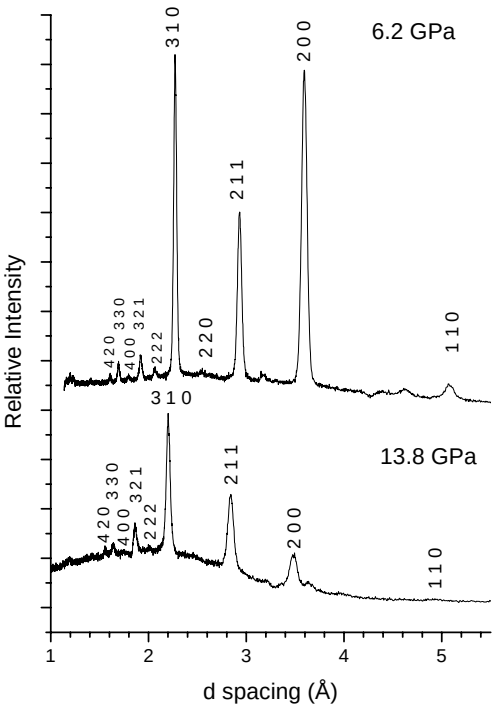

Fig. 3. X-ray diffraction patterns obtained at 6.2 and 13.8 GPa. The respective 2θ angles used were 9.00° and 13.00°. The weak peaks are most likely associated with diffraction from gasket and possible minor species.

by gold diffraction patterns. The patterns conform well with indices for a cubic unit cell. The space group *Im3* is assumed as a starting point, as indicated by the previous ambient pressure and low-temperature X-ray diffraction of single-crystal N_2O_4 [14], although in the present study N_2O_4 is in a high-pressure phase. The Miller indices are given above each peak. Table 1 lists the observed and calculated *d*-spacings, together with cell parameters. The small deviations indicate excellent agreement between the observed and calculated *d*-spacings, which in turn yield precise cell parameters and volumes, evidence that the analysis is reliable.

4. Discussion

A primary goal of this study was to obtain structural information on N_2O_4 at high pressures; such data are important for establishing the equation of state. Previous X-ray diffraction at ambient pressure and −40 °C found that solid N_2O_4 has a cubic unit cell structure with space group *Im3* (T_h^5) and six molecules per unit cell [14]. The cell parameter $a = 7.77$ Å yields a cell volume of 469.1 Å^3 and a molecular volume of 78.2 Å^3. On the basis of Raman measurements, Agnew et al. [6] suggested that high-pressure N_2O_4 is identical to the low-temperature cubic *Im3* phase. Since the X-ray diffraction pattern we obtained at 6.2 GPa can be indexed by the same structure, our study supports their argument and provides experimental evidence that N_2O_4 can persist from ambient pressure up to at least 12 GPa.

As our Raman spectra indicate pressure-induced phase transitions above 12 GPa, we expected to find X-ray patterns differing from that at ambient pressure. However, the pattern we obtained at 13.8 GPa showed only smooth *d*-spacing shifts with pressure, with the ambient pressure *d*-spacings preserved, and thus indexed by the same space group. The analysis assumes that the each unit cell contains six molecules. To check the plausibility of that assumption, we compared in Fig. 4 the *P–V* equations of state for oxygen and nitrogen with that estimated from the unit cell volumes. The molecular volume of N_2O_4 is seen to be bounded by that of $NONO_3$ and the assemblage $N_2 + 2O_2$, in excellent agreement with the previous observation that $NONO_3$ is denser than molecular N_2O_4 [12].

As the X-ray diffraction patterns do not reveal uneven evolution with pressure indicative of phase transitions, the main evidence for a transition near 12 GPa stems from the appearance of new peaks and altered lattice profiles in our Raman spectra. In our heating experiment, the two strong peaks at 1097 and 2250 cm^{-1} at 15.3 GPa (Fig. 1) can be assigned to characteristic stretching modes of NO_3^- and NO^+, respectively. Accordingly, at 12.3 GPa, the prominent peaks with similar inferences were noted in previous Raman studies at ambient pressure and low temperature [4,5] wherein spectral features induced by radiation indicated formation of isomeric forms of N_2O_4. The Raman spectrum we observed at 8.8 GPa indicates the molecular geometry at this pressure has D_{2h}

Table 1
Observed and calculated d-spacings of N_2O_4 at 6.2 and 13.8 GPa

h k l	6.2 Gpa			13.8 GPa		
	d_{obs} (Å)	d_{calc} (Å)	Δd (Å)	d_{obs} (Å)	d_{calc} (Å)	Δd (Å)
1 1 0	5.073	5.075	0.002	4.925	4.925	0.000
2 0 0	3.593	3.589	−0.004	3.486	3.483	−0.003
2 1 1	2.930	2.930	0.000	2.841	2.843	0.002
2 2 0	2.539	2.538	−0.001	2.464	2.462	−0.002
3 1 0	2.272	2.270	−0.002	2.201	2.202	0.001
2 2 2	2.065	2.071	0.006	2.010	2.011	0.001
3 2 1	1.919	1.919	0.000	1.863	1.862	−0.001
4 0 0	1.795	1.794	−0.001	1.746	1.741	−0.005
3 3 0	1.694	1.692	−0.002	1.641	1.642	0.001
4 2 0	1.606	1.605	−0.001	1.558	1.557	−0.001
Lattice parameter	$a = 7.178 \pm 0.002$ Å			$a = 6.965 \pm 0.001$ Å		
Volume	$V = 369.84 \pm 0.40$ Å^3			$V = 337.94 \pm 0.22$ Å^3		

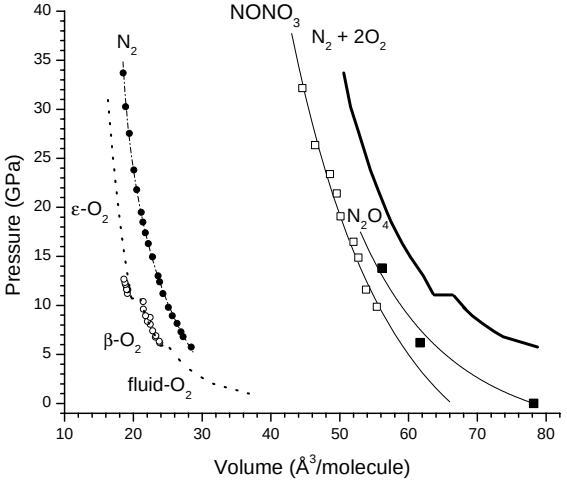

Fig. 4. P–V relations for O_2 (○ and ···), N_2 (● and -·-) and $NO^+NO_3^-$ (□ and –) from previous study [ref] compared with that of N_2O_4 (■) in present study. The curve (–) for N_2O_4 is a tentative fit of the Birch–Murnaghan equation of state [12]. Also shown are corresponding volumes of the stoichometrically equivalent assemblages of $N_2 + 2O_2$ (▬).

symmetry since the spectrum exhibits the corresponding active Raman modes, as seen in the N_2O_4 spectrum at low temperature and ambient pressure. On compression, the appearance of new peaks associated with the principal NO^+ and NO_3^- modes indicates that the molecular symmetry is no longer D_{2h}. This conclusion is reinforced by the broad structure that emerges in the lattice region. Formation of the ionic $NONO_3$ species implies a totally broken symmetry as established in previous studies [11–13]. The high-pressure phase (designated as γ-N_2O_4) thus could be interpreted as intermediate between the α-phase of molecular N_2O_4 with D_{2h} symmetry and the ionic $NONO_3$ with an orthorhombic structure [11]. The molecular units within the γ phase could be close to the D or D′ type isomers of N_2O_4 known at ambient pressure [4,5]. Fig. 5 summarizes the pressure-induced transitions between phases with different molecular geometries.

The Raman data indicate that γ-N_2O_4 has a molecular structure closer to α-N_2O_4 than to $NO^+NO_3^-$, with some but less pronounced ionic character and lower symmetry than D_{2h}. Even when the pressure was increased up to 18 GPa, the prominent peak at 2208 cm^{-1} did not shift noticeably. This peak, the most distinctive for γ-N_2O_4, is appreciably lower in frequency but correlates with the stretching mode of the NO^+ moiety seen in the ionic isomer $NONO_3$.

In addition, although less prominent changes were observed in IR spectra than Raman, the fine features observed in IR spectroscopy also support the existence of such an intermediate new phase. In Fig. 2, the three major IR peaks at 770, 1294 and

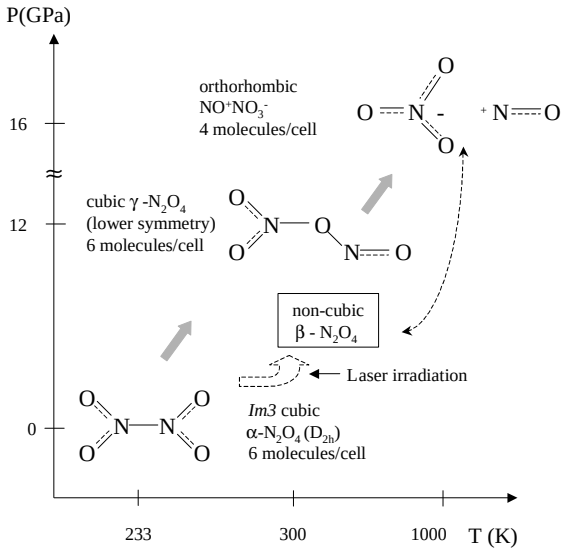

Fig. 5. Schematic diagram of phase transitions of N_2O_4 in the P–T region of the present study. Gray arrows indicate phase transitions induced by P–T. The arrow with dashed edge indicates the photon-induced transition. The long dashed line with both ends of arrows indicates a reversible transformation between β and ionic phases.

1746 cm^{-1} at 13.8 GPa are labeled as ν_{13} (B_{3u}) NO_2 deformation, ν_{11} (B_{3u}) NO_2 symmetric stretch and ν_9 (B_{2u}) NO_2 asymmetric stretch modes associated with D_{2h} N_2O_4, consistent with previous observations [5]. The peaks labeled with solid squares are tentatively assigned as combinations of fundamentals of lattice or/and internal vibrational modes. The low-frequency modes, such as 904, 1144 and 1197 cm^{-1} are most likely associated with combinations of lattice modes in the far-IR region, while the high-frequency modes (e.g., 2335 and 2698 cm^{-1}) could result from the combination of 904 + 1454 cm^{-1} and overtone of the peak at 1343 cm^{-1}, respectively. In addition to the intensity changes on compression, new peaks develop noticeably as well. The peaks labeled with open circles are found to coincide with certain vibrational modes of D or D′ isomer of N_2O_4 [4,5]. Especially the lower frequency modes of 625 and 989 cm^{-1} are only observable above 11.2 GPa, indicating a pressure induced symmetry lowering, in excellent accord with the Raman measurements. Similar to the observation of two prominent peaks at 1104 and 2208 cm^{-1} with close origins to the ionic isomer in the Raman spectra, the peaks labeled by asterisks in Fig. 2, i.e., at 1060 and 1454 cm^{-1} observed only above 11.2 GPa, are also in the close vicinity of ν_1 (A_1') and ν_3 (E') of NO_3^-, again convincingly coincident with the Raman spectra.

The pressure and temperature-induced phase transitions reported here are strongly associated with kinetic factors and path dependent. When the N_2O_4 was loaded cryogenically to high pressure (>6 GPa) before warming, γ-N_2O_4 is readily accessible as described above. However, when the initial loading pressure is not sufficiently high, for example, only raised to 2 GPa before warming, the γ-N_2O_4 is suppressed even when very high pressure is subsequently applied. In the Raman spectrum obtained under the latter conditions, even for a final pressure of 13.0 GPa, the two most characteristic vibrational modes for the γ-phase (i.e., 1104 and 2208 cm^{-1}) are not observed (despite similar laser power and exposure time). It is also found that at different pressures, the extent of transformation induced by heating varies. For example, at 8.3 GPa the conversion to γ-N_2O_4 is incomplete, as judged from the intensity of Raman active modes associated with residual α-N_2O_4. On the other hand, pure compression on the γ-N_2O_4 to higher pressures (>20 GPa) without heating results in only enhanced intensity of the characteristic peak at 2208 cm^{-1} without the typical pressure-induced frequency shift, indicating that pressure is insufficient to induce the complete transformation to the ionic phase.

5. Conclusions

Using Raman and IR spectroscopy as well as X-ray diffraction, we have documented and characterized new high-pressure phases of molecular N_2O_4. Both Raman and IR spectra indicate a phase transition at about 12 GPa. X-ray diffraction showed that both low and high-pressure phases have cubic unit cells, but the high-pressure phase has lower symmetry, likely corresponding to a molecular geometry intermediate between that of N_2O_4 and the ionic isomer. Laser heating of the

molecular phase at high pressures completes formation of the ionic isomer, $NO^+NO_3^-$.

Acknowledgements

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