High-pressure stability, transformations, and vibrational dynamics of nitrosonium nitrate from synchrotron infrared and Raman spectroscopy

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The properties of nitrosonium nitrate ($NO^+NO_3^-$) were investigated following synthesis by laser heating of N_2O and N_2O_4 under high pressures in a diamond anvil cell. Synchrotron infrared absorption spectra of $NO^+NO_3^-$ were measured at pressures up to 32 GPa at room temperature. Raman spectra were obtained at pressures up to 40 GPa at room temperature and up to 14 GPa at temperatures down to 80 K. For both lattice and intramolecular vibrational modes, a smooth evolution of spectral bands with pressure indicates that $NO^+NO_3^-$ forms a single phase over a broad range above 10 GPa, whereas marked changes, particularly evident in the Raman spectra at low temperature, indicate a phase transition occurs near 5 GPa. $NO^+NO_3^-$ could be recovered at atmospheric pressure and low temperature, persisting to 180 K. The Raman and IR spectroscopic data suggest that the $NO^+NO_3^-$ produced by laser heating of N_2O followed by decompression may differ in structure or orientational order–disorder from that produced by autoionization of N_2O_4. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1586695]

I. INTRODUCTION

Recent developments in diamond anvil cell techniques have opened new avenues for exploring the behavior of simple molecules at high densities.[1] At high pressures, many molecular systems exhibit extraordinary properties, phase transitions, or chemical reactions. Of these systems, nitrogen oxides have received particular attention as important species involved in combustion and in the storage of chemical energy. Moreover, instead of the simple pressure-induced polymerization observed in numerous systems, these compounds undergo intriguing and still poorly understood chemical transformations in condensed phase.[2] For instance, solid nitric oxide (NO) disproportionates into nitrous oxide (N_2O) and dinitrogen tetraoxide (N_2O_4) at 176 K and 1.5 GPa.[3] The latter readily undergoes a subsequent transformation to a remarkable stable ionic isomer, nitrosonium nitrate ($NO^+NO_3^-$). This ionic species and its molecular precursor, N_2O_4, have been the subject of several previous studies.[4–9] However, the mechanism governing the transformation between the two forms remain unclear. The formation of $NO^+NO_3^-$ was first detected by Parts and Miller[4] in IR spectra of oxidized NO. Subsequent experiments on N_2O_4 by Bolduan and Jodl[5] established that the ionic form could be spontaneously produced when N_2O_4 is trapped in a Ne matrix. Later, the same group obtained Raman spectra of solid N_2O_4 and observed the formation of ionic $NO^+NO_3^-$ by temperature-induced autoionization of N_2O_4.[6] In these ambient pressure studies, the formation of the ionic nitrosonium nitrate species was observed only in the amorphous solid and only at temperatures below 180 K; its formation was attributed to an intermediate asymmetric $ONONO_2$ isomer (designated D′ in Ref. 6) or to photolysis of NO_2 monomers.

The transformation of molecular N_2O_4 to ionic $NO^+NO_3^-$ under high pressures was first observed by Jones and co-workers.[7,8] They discovered that laser irradiation of cubic *Im*3 α-N_2O_4 results in the formation of β-N_2O_4 with unknown noncubic structure at 1.16 GPa at room temperature. Under pressures of 1.5–3.0 GPa at room temperature, β-N_2O_4 exhibits a reversible phase transition to the ionic form of $NO^+NO_3^-$ with a large hysteresis. Recently, Somayazulu *et al.*[9] found a different way to synthesize $NO^+NO_3^-$ under pressure. At 10–30 GPa laser heating to 1000–2000 K transforms N_2O via the reaction $4N_2O \rightarrow NO^+NO_3^- + 3N_2$. Angular dispersive x-ray diffraction patterns of the products indicated an orthorhombic structure for $NO^+NO_3^-$ at high pressures. Subsequent x-ray diffraction measurements[10] have provided further information about $NO^+NO_3^-$, including the pressure-volume equation of state.

Complete characterization of $NO^+NO_3^-$ requires detailed study by IR and Raman spectroscopy under a variety of conditions. Here we report such data for both the far and mid-IR regions for $NO^+NO_3^-$ at pressures up to 32 GPa. The far-IR measurements appear to be the first absorption data at low wave numbers at any pressure for this compound. Ra-

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TABLE I. Observed IR and Raman frequencies for $NO^+NO_3^-$ (and transformed species) and assignments at various pressures and temperatures.

IR (cm^{-1})[a]			Raman (cm^{-1})[b]				
32 GPa	0.6 GPa	Ref.[c]	80 K	190 K	Ref.[d]	Ref.[e]	Assignment
	167		50,87,117,	71	62(s),		Lattice modes
372			132,150,	118	124(w)		Lattice modes
659	431,532,589		173,221,258				Lattice modes
				278		282.8	ν_3 (A_g) N–N str
				495		498.2	ν_6 (B_{1g}) NO_2 rock
				639		639	ν_6 (A') O═N–O bend
				678		676.8	ν_8 (B_{1g}) NO_2 wag
	743	747					ν_{12} (B_{3u}, NO_2 def)
762			716		714(w)		ν_4 (E', NO_3^- in-plane def)
				814		811.7	ν_2 (A_g) NO_2 sym bend
836		813	823				ν_2 (A_2'', NO_3^- out-plane bend)
1034							lattice combinations
1133		1014	1049		1045(s)		ν_1 (A_1', NO_3^- sym str)
	1250	1248					ν_{11} (B_{3u}, NO_2 sym str)
				1382		1382.3	ν_1 (A_g, NO_2 sym str)
1404	1385	1385			1330,1400(w)		ν_3 (E', NO_3^- antisym str)
			1640				$2\nu_2$ (NO_3^-)
	1723	1722					ν_9 (B_{2u}, NO_2 antisym str)
				1724		1723.5	ν_5 (B_{1g}, NO_2 antisym str)
1738							ν_1+lattice (NO_3^-)
1840							$\nu_1+\nu_4$
2265		2292	2243	2237	2267(vs)		ν_{NO+}
2340	2232						?
2439	2353						ν_3+lattice modes

[a]Infrared bands measured at room temperature.
[b]Raman active modes measured at ambient pressure and 80 and 190 K.
[c]Reference 13, for atmospheric pressure and 20 K.
[d]Reference 15, for atmospheric pressure and low temperature.
[e]Reference 6, for atmospheric pressure and low temperature.

man spectra of $NO^+NO_3^-$ were obtained at room temperature as well as temperatures down to 80 K and pressures up to 40 GPa. These optical spectra, especially the low-temperature Raman data, elucidate important aspects of the transformation, thermodynamic properties, and structure of $NO^+NO_3^-$.

II. EXPERIMENTAL PROCEDURES

Pure N_2O (99%) and N_2O_4 (99.5%) gas was purchased from Aldrich and used without further purification. Loading was done by precooling a diamond anvil cell in liquid nitrogen. The melting point for N_2O is $-90\,°C$ so gaseous N_2O solidifies on the cooled rhenium gasket of the cell in a liquid nitrogen bath. The cells were then sealed and the solid N_2O pressurized before warming up to room temperature. The pressure was determined from the pressure shift of the R_1 ruby fluorescence line, according to the relationship[11]

$$P(\mathrm{GPa}) = A/B[\{1+\Delta\lambda(T)/\lambda_0(T)\}^B - 1], \quad (1)$$

where $A=1904$ GPa, $B=7.665$, $\lambda_0(T)=694.28$ nm at 298 K and $\Delta\lambda(T)$ is the difference between the wavelength of the R_1 line at pressure P and that at atmospheric pressure. The accuracy of the pressure measurement was ± 0.05 GPa under quasihydrostatic conditions.

Samples were heated by a CO_2 infrared laser (10.6 μm lines) operated at about 50 W typically at 15 GPa. The laser beam was focused to less than 30 μm to achieve an estimated temperature of 1000–2000 K. The transformation of N_2O to $NO^+NO_3^-$ was instantaneous at high temperature and irreversible when the sample was quenched to room temperature at high pressures (>10 GPa). The completion of transformation was confirmed by Raman spectroscopy.

Infrared absorption measurements were performed at beamline U2A at the National Synchrotron Light Source of Brookhaven National Laboratory. The optical layout of the setup has been described in detail previously.[12] Briefly, the synchrotron light is collected from a source in a 40 $\times$40 mrad solid angle and collimated to a 1.5-in.-diam beam before entering a Bruker IFS 66V vacuum FT spectrometer. The spectrometer is equipped with a number of beam splitters and detectors including a silicon bolometer and MCT. In addition, a grating spectrograph with a CCD array detector is used in the visible, giving complete coverage of the spectral range from 50 to 2000 cm^{-1}. The resolution used in the present study is 4 cm^{-1}.

Raman spectroscopy was performed at the Geophysical Laboratory. Both the 488.0 and 514.5 nm lines of a Coherent Innova Ar^+ laser were used as the excitation source, with average power of 0.4 W for the spectral measurements. The collimated laser beam was typically focused on the sample in a backscattering geometry with an estimated power of less than 100 mW. The resolution achieved using a 460 mm focal length $f/5.3$ imaging spectrograph (ISA HR460) equipped with an 1800 grooves/mm grating was ± 0.1 cm^{-1}. The calibration of the Raman scattering was done using Ne lines with an uncertainty of ± 1 cm^{-1}. For the low-temperature Raman measurements, an optical cryostat was used; the tem-

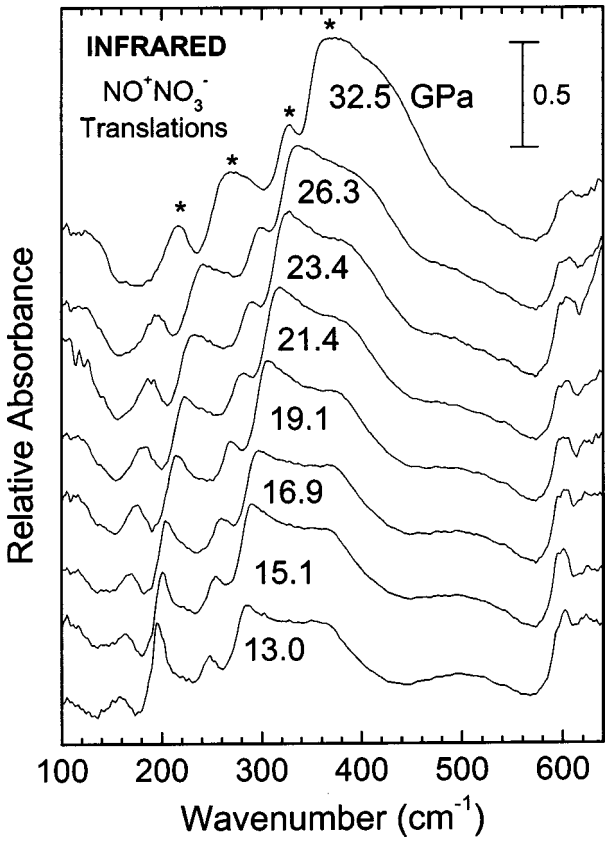

FIG. 1. Far-IR spectra of $NO^+NO_3^-$ in the range 100–600 cm^{-1} measured at room temperature for eight pressures (labeled in GPa). At each pressure, the absorbance has been normalized to adjust for changes in the beam current of the synchrotron light source. The asterisks (*) denote the translational modes (see the text).

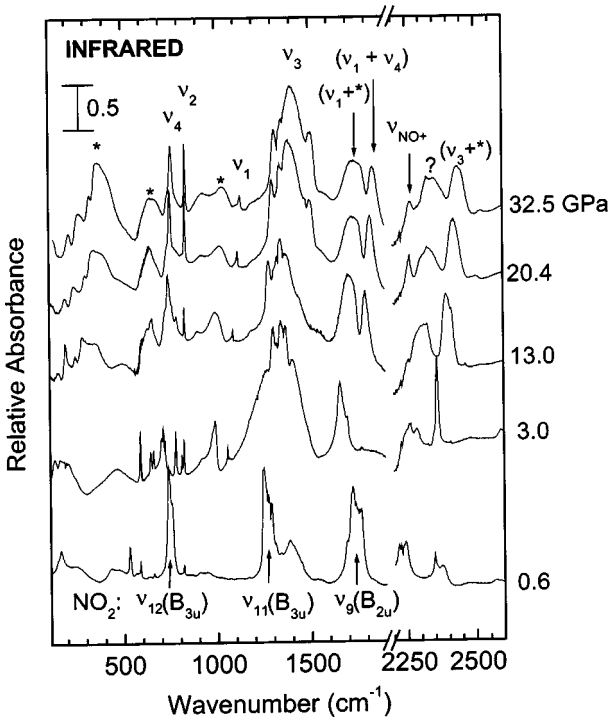

FIG. 2. IR spectra of $NO^+NO_3^-$ in the range 100–2500 cm^{-1} measured at room temperature for five pressures (indicated in GPa on the right-hand ordinate). The absorbance has been normalized with respect to the beam current of the synchrotron light source. The sample thickness was about 23 μm. The region 1900–2200 cm^{-1} is omitted because of interfering absorptions from the type II diamonds used as anvils. Asterisks (*) indicate lattice modes or combinations.

perature range from 80 to 300 K was explored using liquid nitrogen as the cryogen.

III. RESULTS

Table I lists vibrational frequencies assigned to $NO^+NO_3^-$ and related species; the IR data pertain to room temperature and pressures of 32 and 0.6 GPa, the Raman spectra to atmospheric pressure and temperatures of 80 or 190 K. Most of the data were obtained from laser heating N_2O under pressure, although the results for laser heated N_2O_4 are also included. Where available, results from previous spectroscopic studies, at atmospheric pressure and low temperature, are included for comparison.

A. Far-IR spectra

Figure 1 shows far-infrared absorption spectra of $NO^+NO_3^-$ in the region 100–600 cm^{-1} collected at room temperature and eight selected pressures. Due to the small sample size (diameter about 150 μm) the diffraction limit was near 100 cm^{-1} and thus absorption bands below that could not be observed unambiguously. The major feature in the far-IR is a broad band, peaking at 372 cm^{-1} at 32.5 GPa, with several shoulders at lower frequencies. This peak and the shoulders can be assigned to lattice modes of NO^+NO_3. The absorption intensity of the major lattice mode decreases with decreasing pressure. This trend resembles the IR activity previously seen in the mid-IR region,[9] indicating that the ionic character of $NO^+NO_3^-$ increases with compression. However, the far-IR lattice mode had not been observed previously, either in IR spectra of N_2O_4 at atmospheric pressure[13–15] or in $NO^+NO_3^-$ at high pressure.[9] As the pressure was decreased from 32.5 to 9.5 GPa, the positions of the lattice modes shift smoothly and gradually downwards. This indicates the existence of only one phase in this pressure region, consistent with our x-ray diffraction measurements.[10]

B. Mid-IR spectra

Figure 2 shows the mid-IR spectra of $NO^+NO_3^-$ obtained at room temperature and pressures ranging from 32.5 to 0.6 GPa. The region 1900–2200 cm^{-1} is omitted because of interference by strong absorption from the type II diamonds used in the pressure cell. Above 2500 cm^{-1}, no prominent absorption peaks were observed. At the highest pressure, 32.5 GPa, 12 IR bands are clearly resolved, as listed in Table I. Like the peak at 372 cm^{-1} observed in the far-IR region, that centered at 659 cm^{-1} is attributed to a lattice mode. The peaks observed at 761, 836, and 1133 cm^{-1} are assigned to vibrational modes of the NO_3^- anion, respectively ν_4 (E', in plane bend), ν_2 (A_2'', out of plane bend) and ν_1 (A_1', symmetric stretch). The assignment of ν_4 and ν_2 and their intensity enhancement at high pressure are consistent with our previous study of $NO^+NO_3^-$ at high pressure,[9] but in that study the ν_1 mode was not observed. In previous atmospheric pressure studies[13–16] of $NO^+NO_3^-$, the

ν_4, ν_2, and ν_1 modes were all found to be very weak. The low intensity of the ν_1 band at all pressures indicates that the relatively small transition dipole moment of this symmetric stretch vibrational mode changes little with compression. Our observation of the ν_4, ν_2, and ν_1 modes at all pressures above 1 GPa at room temperature provides a definitive identification of the NO_3^- anion; as described later, we also saw these three modes in the Raman spectra.

The peak centered at 1034 cm^{-1} in Fig. 2 was not observed in the previous IR spectra of $NO^+NO_3^-$, either at high pressure[9] or atmospheric pressure.[13–16] As the pressure is reduced, it behaves much like the 659 cm^{-1} band, as both become sharper and stronger. This suggests that the 1034 cm^{-1} band is a combination of the two lattice modes at 372 and 659 cm^{-1}. The intense and broad peak centered near 1400 cm^{-1} is the most prominent feature in our IR spectra above 3 GPa. It could not be observed in the previous high pressure IR study[9] due to absorption by the type I diamonds used in that work.[12] This peak is assigned to ν_3, the NO_3^- asymmetric stretching mode. Its high intensity is in accord with IR spectra of $NO^+NO_3^-$ at atmospheric pressure,[13–16] and attributable to the large transition dipole associated with the antisymmetric stretching mode (in contrast to the symmetric ν_1 mode). Another diagnostic frequency for $NO^+NO_3^-$ is the stretching mode of NO^+; in Fig. 2, this appears near 2265 cm^{-1} but could only be unambiguously observed at high pressures (32 and 20 GPa) because at lower pressures it is engulfed by a more intense absorption band (not yet assigned, as discussed in the following).

Four other strong peaks seen near 1740, 1840, 2340, 2440 cm^{-1} at 32.5 GPa also appear consistently at lower pressures. The 1840 cm^{-1} peak can be assigned to the ($\nu_1 + \nu_4$) combination of $NO^+NO_3^-$. Accordingly, the 1740 cm^{-1} band (suggested previously as $\nu_1 + \nu_4$)[9] could be associated with the combination of a far-IR lattice mode (372 cm^{-1}) and the strong ν_3 band at 1402 cm^{-1}. The peaks at 2340 and 2440 cm^{-1}, which saturate due to strong absorption with thick samples,[9] are clearly resolved in Fig. 2, since a thinner ($\sim$23 μm) sample was employed here. These peaks seem likely to be combination bands but other possibilities are discussed in the following as well.

C. Room-temperature Raman spectra

The Raman spectrum of $NO^+NO_3^-$ was typically measured immediately after laser heating of N_2O to check the degree of completion of reaction and transformation. We found that from about 10 to 40 GPa, heating of N_2O results in an inhomogeneous mass within the cell that appears fabriclike to the eye. The presence of $NO^+NO_3^-$ and N_2 is confirmed by characteristic peaks (e.g., at 13 GPa) at 740 cm^{-1} (ν_4), 827 cm^{-1} (ν_2), 1096 cm^{-1} (ν_1), 2253 cm^{-1} (ν_{NO^+}), 2362 cm^{-1}, and 2383 cm^{-1} (N_2) as well as abundant lattice modes below 400 cm^{-1}. Figure 3 shows sample Raman spectra of $NO^+NO_3^-$ obtained at five pressures ranging from 40.0 to 0.8 GPa. The major characteristic modes, (e.g., ν_4, ν_2, ν_1, and ν_{NO^+}) are seen to shift to lower frequencies on decreasing pressure. The Raman profiles of these internal vibrational modes typically change less with pressure than in the lattice region. Upon decompression, the number of resolvable Raman peaks is reduced as a result of peak broadening. This trend is consistent with the proposal[9] that $NO^+NO_3^-$ becomes more disordered on decompression. When the pressure drops below 1 GPa, the Raman spectrum shows significant changes, in particular a broad peak near 280 cm^{-1} is enhanced and the strong NO^+ peak disappears. This accords with our low temperature results (discussed in the following), which suggest a phase transformation of $NO^+NO_3^-$ occurs at low pressure.

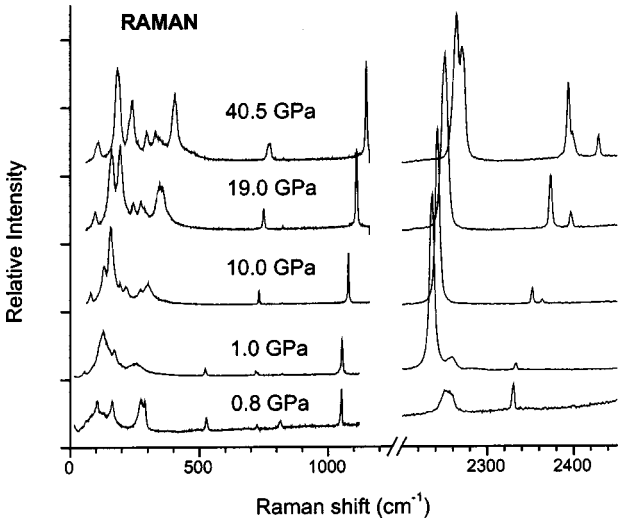

FIG. 3. Raman spectra of $NO^+NO_3^-$ in the range 50–2500 cm^{-1} measured at room temperature for five pressures (indicated in GPa).

On decompression from 40 to 1 GPa, changes in the room temperature Raman spectra appear to be steady and continuous. Accordingly, unlike the IR spectra, which exhibit changes in both the lattice and intramolecular modes indicative of a possible phase transition, the room-temperature Raman spectra show no major changes above 1 GPa. Moreover, the evolution of the peak positions with pressure is linear for ν_4, ν_2, ν_1, ν_{NO^+} as well as the major lattice modes. Therefore, we undertook to obtain low-temperature Raman spectra in the expectation that peaks would be better resolved and thereby respond more sensitively to pressure.

D. Raman spectra at low temperatures

Figure 4 displays the temperature dependence of the Raman shifts of $NO^+NO_3^-$ at a nominal pressure near 14 GPa. During cooling from room temperature to 80 K, the pressure of the sample inside the cell increased slightly, causing the peaks to move to higher frequencies. With the temperature held constant at 80 K, the Raman spectra were measured as a function of pressure between 14 GPa and ambient. Selected spectra are plotted in Fig. 5. At such a low temperature, both the lattice and internal modes exhibit significant pressure shifts. For example, the peak centered at 337 cm^{-1} at 14 GPa appears as a doublet at atmospheric pressure, with a separation of 38 cm^{-1}. In addition, the two almost equally strong peaks centered at 142 and 180 cm^{-1} evolve into a fairly weak peak at 87 cm^{-1} and a much stronger peak at 118 cm^{-1}, respectively. For the ν_4 mode near 716 cm^{-1} a more

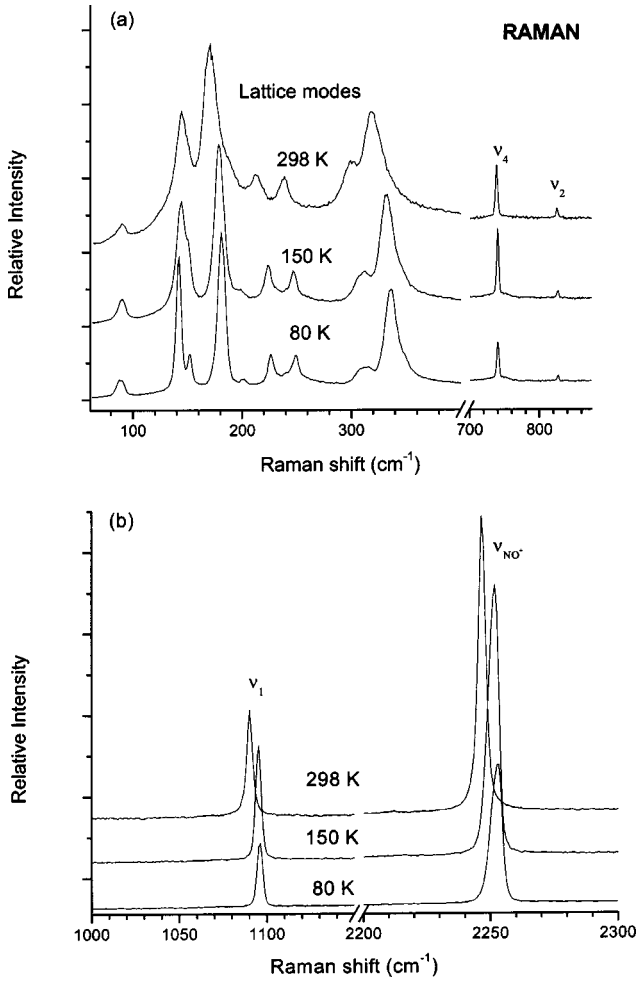

FIG. 4. Raman spectra of $NO^+NO_3^-$ in the ranges (a) 60–900 cm^{-1} and (b) 1000–2300 cm^{-1} measured at constant nominal pressure of about 14 GPa at 298, 150, and 80 K.

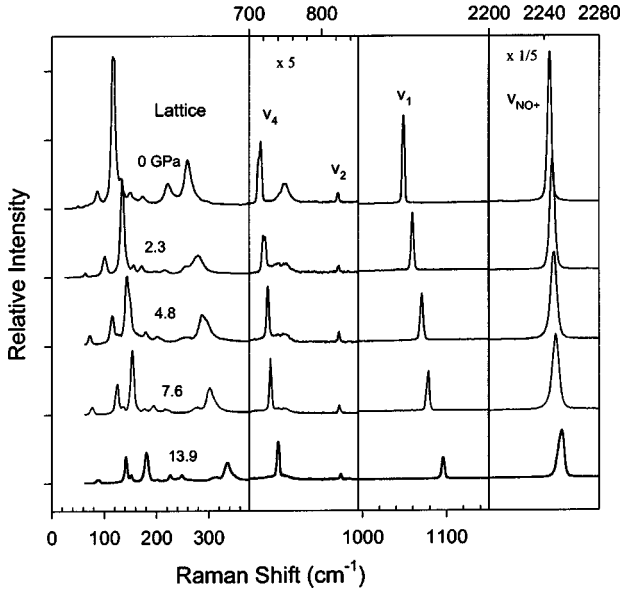

FIG. 5. Raman spectra of $NO^+NO_3^-$ in the regions 50–380; 700–860; 1000–1150; and 2200–2280 cm^{-1} measured near 80 K and five pressures. The measurements were performed at successive steps of decompression, starting from 13.9 GPa. Due to the low intensity of ν_4 and ν_2 and high intensity of ν_{NO^+}, the spectra in the 700–850 and 2200–2280 cm^{-1} regions are scaled by 5 and 1/5, respectively.

striking change occurs; at high pressures, it is a singlet but as the pressure drops to 4.8 GPa and below, it develops into a doublet with a separation of 34 cm^{-1}. We interpret these changes in the Raman spectrum as evidence for a phase transition in $NO^+NO_3^-$.

Figure 6 shows the variation of the peak positions of Raman modes in the lattice mode region observed at 80 K as a function of pressure. These bands exhibit a distinct change in $(d\nu/dP)_T$ at about 5 GPa, indicating a transition occurs near that pressure. The behavior of the second highest frequency mode changes most markedly at 5 GPa. In addition, nine modes can be identified at high pressures while at low pressures (<5 GPa), only seven are discernible. The pressure dependence of higher frequency intramolecular modes (not shown) shows changes at 5 GPa, but this is much less pronounced. We note that the low-pressure phase remains at least partially ordered as indicated by the Raman features discussed in the following. The evolution of these Raman bands in the lattice-mode region was also examined on compression in a separate run. There are slight differences in slopes for several modes between compression and decompression (most likely due to different stress conditions), but a distinct change at 5 GPa on compression is still prominent, indicating the transition is reversible and has very little hysteresis.

Despite the presence of a transition, these low-temperature measurements also established that $NO^+NO_3^-$ can be recovered at ambient pressure. We find that all the principal low- and high-frequency modes associated with $NO^+NO_3^-$ persist down to ambient pressure. The accompanying N_2 formed by the laser heating of N_2O has escaped, as

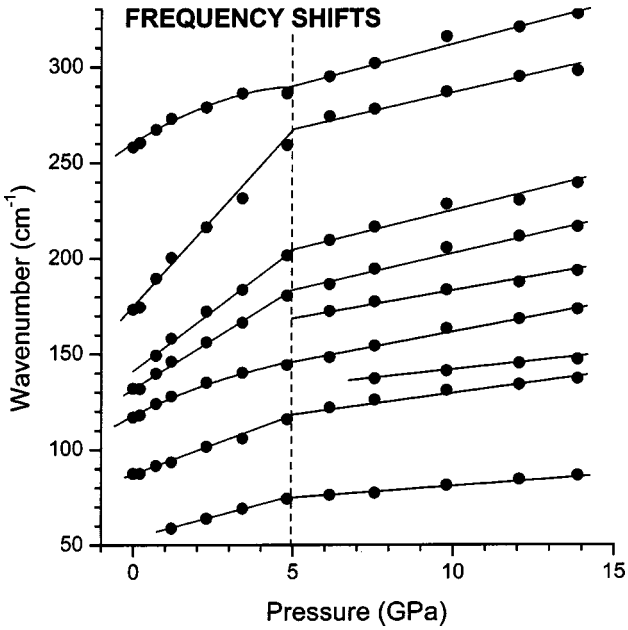

FIG. 6. Variation with pressure of Raman shifts in the lattice region (50–350 cm^{-1}) up to 15 GPa at 80 K. The lines are guides to the eye. The vertical dashed line at about 5 GPa indicates the approximate phase boundary.

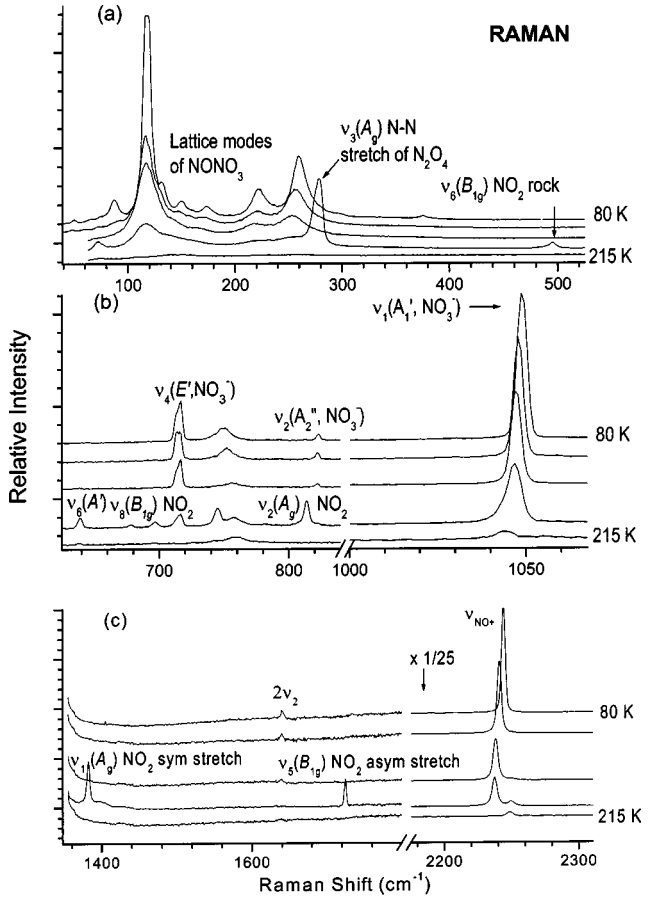

FIG. 7. Raman spectra of $NO^+NO_3^-$ in the ranges of (a) 40–530 cm^{-1}, (b) 630–1070 cm^{-1} and (c) 1350–2300 cm^{-1} measured at ambient pressure and five temperatures: 80, 135, 180, 190, and 215 K.

evidenced by the disappearance of the peaks at about 2350 cm^{-1}, and $NO^+NO_3^-$ appears to be the sole product. The sample was warmed at ambient pressure and Raman spectra of $NO^+NO_3^-$ measured at five temperatures ranging from 80 to 215 K. Figure 7 gives a panoramic view of these spectra, for three regions. In the lattice mode region (a), peaks at 118, 222, and 260 cm^{-1}, which are rather sharp at 80 K, become weaker and broader as the temperature increases from 80 to 180 K. While the peak at 118 cm^{-1} has no obvious shift, the latter two exhibit noticeable shifts of -3 and -6 cm^{-1}, respectively. In addition, the small peak at 87 cm^{-1} disappears near 135 K. Other bands at 132, 150, and 174 cm^{-1} also disappear when the temperature reaches 135 K. In the internal mode region (b) and (c), the frequencies of ν_4 and ν_2 are found to remain nearly constant with temperature, while ν_1 and ν_{NO^+} modes exhibit a consistent shift to lower energy.

The highest temperature at which the $NO^+NO_3^-$ retains its identity is found to be about 180 K. When the sample was heated to 190 K at ambient pressure, significant changes in the Raman spectrum were observed. The lattice mode region is reduced to two weak, broad peaks at 71 and 118 cm^{-1}. In addition, a sharp and strong peak occurs at 278 cm^{-1} that coincides with the $\nu_3(A_g)$ N–N stretching mode of molecular N_2O_4. Other changes include the appearance of numerous Raman modes at 450–1800 cm^{-1}, most of which can be assigned as internal modes associated with molecular N_2O_4, such as the $\nu_6(B_{1g})$ NO_2 rocking mode at 495 cm^{-1}, the $\nu_6(A')$ O═N–O bend at 639 cm^{-1}, the $\nu_8(B_{1g})$ NO_2 wagging mode at 678 cm^{-1}, the $\nu_2(A_g)$ NO_2 symmetric bend at 814 cm^{-1}, the $\nu_1(A_g)$ NO_2 symmetric stretch at 1382 cm^{-1} and the $\nu_5(B_{1g})$ NO_2 antisymmetric stretch at 1724 cm^{-1}.[6,8,16] However, the ν_4, ν_1, and ν_{NO^+} modes of $NO^+NO_3^-$ still have discernible intensities. We conclude that at 190 K, ionic $NO^+NO_3^-$ has mostly converted to molecular N_2O_4 in bulk, so the Raman spectrum arises from a mixture of the two phases. Further heating of the sample to 215 K results in loss of sample due to evaporation and disappearance of the Raman features.

IV. DISCUSSION

The present work provides the first far-IR data at any pressure on this material, as well as a more complete study of the mid-IR and Raman spectra as a function of both pressure and temperature. Accurate assignments of the spectra require factor group-analysis[17] based on detailed information on the crystal structures involved. X-ray diffraction studies[9,10] have provided determination of the unit-cell symmetry and constraints on possible space group, but no information on the atom coordinates needed for detailed symmetry assignments. Alternatively, we can compare the spectra with those of materials that appear related, such as KNO_3, whose IR and Raman spectra have been studied both experimentally and theoretically.[18–20] The legitimacy of this comparison relies on two facts: (a) the calculated topology of $NONO_3$ exhibits a similar symmetry to the predicted stable bidentate geometry of KNO_3,[18] both close to point group C_{2v}; and (b) the stable phase of KNO_3 at room temperature, phase II, also has an aragonite structure with four ion pairs per cell as does $NONO_3$.[19,20] The predicted ambient pressure IR-active modes involving the vibrations between the ion pairs of KNO_3 ($NaNO_3$) are $\nu_4(A1)$: 234 (322) cm^{-1}, $\nu_9(B2)$: 187(255) cm^{-1} and $\nu_6(B1)$: 73 (108) cm^{-1}.[18] There are 18 predicted active Raman modes in the lattice region of phase II KNO_3, as compared with fewer experimentally observed and reported in the region of 53–165 cm^{-1}. Of these Raman modes, those below 100 cm^{-1} are believed to be rotational (or librational) modes of the nitrate ion while those above 100 cm^{-1} are due to translational modes.[19,20] Considering the above, we believe all peaks observed at 180–360 cm^{-1} in the far-IR spectra of $NONO_3$ are most likely due to the vibrations between the NO^+ and NO_3^- ion pair, while rotational modes may occur at lower frequencies (not resolved in the present study). This assignment is based on the assumption that NO^+ is similar to K^+ as a rigid and fully charged ion (with a molar mass between Na^+ and K^+), since the vibrational correlation between the NO^+ group and NO_3^- will double the number of possible optical modes. Other differences could arise from differences in space group (see Ref. 10). Further x-ray and spectroscopic studies are required to address these issues.

One of the interesting questions regarding nitrosonium nitrate is the degree of ionicity, or symmetry breaking charge transfer in the material, and how this changes with pressure. Our previous work suggested evidence for an increase in

charge transfer with increasing pressure based on the behavior of the high frequency mid-IR bands.[9] The far-IR contains much more definitive information, in part because of some uncertainty in the assignment of the higher frequency bands, but this region was not explored in the previous study. Clearly, the overall intensity of the bands in the far-IR region increases with pressure, indicating that the ionicity of $NO^+NO_3^-$ is enhanced by pressure. An empirical estimate of the ionicity can be obtained from the classical damped oscillator model, in terms of the dynamic effective charge associated with a particular vibrational mode. The dynamic effective charges give a measure of the static charges in the system. The model expresses the electronic polarization of a molecule as[21]

$$\varepsilon - n^2 = \left(\frac{n^2+2}{3}\right)^2 N \frac{(sze)^2}{\pi m \nu_t^2}, \tag{2}$$

where ε is the static dielectric constant, n the optical refractive index, ν_t the frequency of the mode and m the reduced mass of the ion pair, N the number oscillators per unit volume, z the valency of the ions, and e the electron charge. From this, one can derive s, the reduced form of the dynamic effective charge,

$$s = \frac{\nu_t}{e} \frac{3}{n^2+2} \sqrt{\frac{\pi m f}{N}}, \tag{3}$$

where $f = \varepsilon - n^2$ is the oscillator strength. For example, the effective charge associated with the strong lattice mode at 372 cm^{-1} obtained using the parameters assumed previously ($n=1.75$, $m=20.2$ g/mol, $N=1.9-2.2\times10^{22}/cm^3$)[9,10] ranged from $0.11e$ to $0.17e$ in the pressure interval of 13–32 GPa. This corresponds to the observed intensity change by a factor of 2.4. The pressure dependence of IR absorption was found to be more prominent for the lattice modes than for the intramolecular modes, indicating that intermolecular electronic polarization responds more strongly to pressure than does intramolecular polarization. The value of the dynamic effective charges implies a value of the static effective charge to be less than for ionic compounds such as NaCl or KBr, whose effective charges are $0.74e$ and $0.76e$, respectively (i.e., much closer to unity).[21]

The frequencies and pressure dependences of the mid-IR absorption bands (Fig. 2) are consistent with the previous study.[9] However, the relative intensities of the bands in the two studies show some variability. Indeed, these differences were found from run to run in this study with N_2O and with N_2O_4 as starting materials. These differences are likely to be associated with variability in laser heating temperature in different runs, resulting in slight differences in order/disorder and the presence of ionic defects. These must be particularly IR-sensitive as the Raman profiles from different runs are virtually indistinguishable. Nevertheless, the IR data taken together provide a basis for testing assignments of the bands, which is important for fully characterizing the material and its transformations as a function of pressure and temperatures.

Two IR bands with moderate intensity at the highest frequencies (e.g., 2340 and 2439 cm^{-1} at 32.5 GPa) are observed consistently at all pressures. Previous analysis of these peaks suggested that they are combination bands originating from the NO^+ stretching mode (2265 cm^{-1}) and far-IR lattice modes (at about 75 and 174 cm^{-1}).[9] Our measurement of the far-IR spectrum reveals a strong and broad lattice peak about 300 cm^{-1} (Fig. 1) well above the anticipated region, casting doubt on that assignment. Another explanation for these fairly strong bands would be IR-active N_2 vibrons.[9] The IR active ν_2 mode of N_2 reported by Bini *et al.*[22] occurs at 2330–2380 cm^{-1} from 10 to 27 GPa. In addition, this mode remains a singlet below 18.3 GPa and splits into a doublet above that pressure. The two bands observed in the present study, however, appear at different frequencies (i.e., 2241–2381 cm^{-1} and 2373–2438 cm^{-1}, respectively), and have much higher intensity at all pressures than those of bulk N_2.[22]

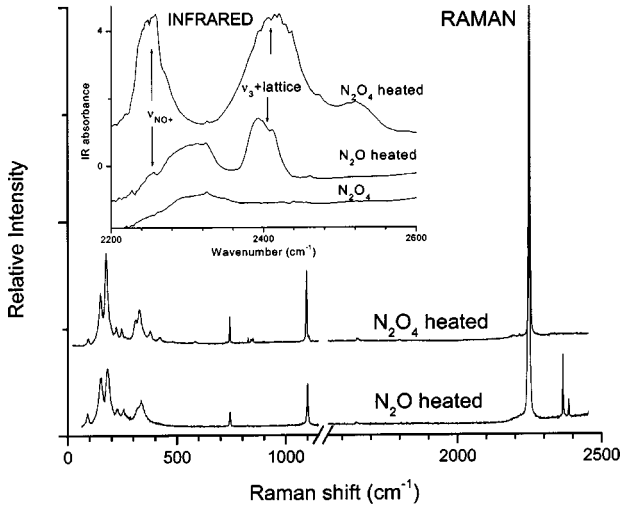

FIG. 8. Raman spectra of heated N_2O_4 and N_2O near 13 GPa. The 1150–1450 cm^{-1} region corresponds to the region of the strong diamond first-order Raman signal and has been omitted. The inset shows IR absorbance of heated N_2O_4, heated N_2O and pure N_2O_4 measured at 13 GPa and room temperature.

Spectra of $NO^+NO_3^-$ formed by heating N_2O_4 at high pressures were used to identify these peaks. Raman and IR spectra are presented in Fig. 8. Heating both N_2O_4 and N_2O produces ionic $NO^+NO_3^-$ as confirmed by almost identical Raman bands. Only minor differences are discernible, such as additional lattice features and the ν_2 multiplet at 830 cm^{-1} in the spectrum of heated N_2O_4, as well as the lack of N_2 vibrons at 2365 and 2386 cm^{-1} observed in the spectrum of heated N_2O. The inset shows IR spectra of N_2O_4 before and after heating in comparison with heated N_2O. A dramatic difference in the IR spectra of unheated and heated N_2O_4 is observed: the two strong peaks at 2250 and 2415 cm^{-1} provide unambiguous evidence for a structural change induced by heating. The former peak is assigned to the NO^+ stretching mode, consistent with previous work.[9] The latter could originate from the combination of ν_3, the NO_3^- asymmetric stretching mode and the peak at 1034 cm^{-1}, which is also a combination from two lattice modes. A combination excitation associated with strong fundamentals is expected to be intense. In the IR spectrum of heated N_2O, however, the NO^+ stretching mode was found weak while the combina-

tion peak appears as strong as the heated N_2O_4. Since the peak at 2310 cm^{-1} was not observed in heated N_2O_4 (i.e., pure $NO^+NO_3^-$), alternatively, the band could be assigned to N_2 molecules alloyed with $NO^+NO_3^-$ (i.e., not a separate phase).[9] The position of this peak occurs at slightly lower frequencies than the pure N_2 vibron at the same pressure ($\sim$13 GPa). If it arises from N_2 trapped in $NO^+NO_3^-$, the absence of the corresponding peak in the Raman spectrum indicates fairly low concentrations, hence the intrinsic cross section (polarization) would have to be very high. A satisfactory interpretation of this mode requires further experimental and theoretical investigation.

Between 32 and 10 GPa, the IR bands in both the lattice mode and internal vibration regions evolve smoothly with pressure. The pressure dependence of the major IR-active modes is close to linear, and fairly gradual. For instance, the lattice mode at 372 cm^{-1} exhibits a pressure shift of 5.33 cm^{-1}/GPa, whereas the ν_4, ν_2, ν_1 internal vibrational modes of NO_3^- have $(d\nu/dP)_T = 1.40$, 0.46, and 2.65 cm^{-1}/GPa for ν_4, ν_2, and ν_1, respectively. The smooth evolution of the major IR modes indicates a single phase of $NO^+NO_3^-$ persists in this broad pressure region, consistent with x-ray diffraction measurements.[10] However, when the pressure is reduced further, a significant change in the absorption is observed. For example, at about 3 GPa, the IR spectrum exhibits a significant redshift of the lattice mode, accompanied by abundant new IR bands at 600–800 cm^{-1}, and the disappearance of the peak at 1800 cm^{-1}, although the major internal modes (ν_4, ν_2, and ν_1) are preserved (Fig. 2). These changes strongly suggest that a new phase of $NO^+NO_3^-$ occurs in the low-pressure region. On further release of pressure to below 1 GPa (Fig. 2), the absorption pattern again changed dramatically, including the loss of characteristic modes of ionic $NO^+NO_3^-$. We conclude that below 1 GPa, $NO^+NO_3^-$ has transformed to molecular N_2O_4, since the major peaks match the active modes of N_2O_4 unambiguously.[13–16,23] The three strongest peaks centered at 740, 1250, and 1722 cm^{-1} can be assigned (Fig. 2 and Table I) as ν_{12} (B_{3u}, NO_2 deformation), ν_{11} (B_{3u}, NO_2 symmetric stretch) and ν_9 (B_{2u}, NO_2 asymmetric stretch) of ordered or disordered N_2O_4.[13–16,19]

The characteristic absorption peaks observed in the present study, such as ν_{NO^+} (2264 cm^{-1}), ν_1 (1130 cm^{-1}, NO_3^- symmetric stretch) and ν_3 (1403 cm^{-1}, NO_3^- asymmetric stretch), are in excellent accord with the previous IR investigations of $NO^+NO_3^-$ conducted at atmospheric pressure and at low temperatures.[13–16] However, we observed additional peaks in both low and high frequency IR spectra that were not observed in the previous atmospheric pressure measurements. As an ionic form of molecular N_2O_4, nitrosonium nitrate had previously been produced by thermal or photolytic autoionization.[3–6] The N_2O_4 molecule is planar with D_{2h} symmetry but has an unstable, asymmetric isomer ONO–NO_2 (denoted D'' in Ref. 6) which is believed to be the precursor of $NO^+NO_3^-$. However, Givan *et al.*[16] reported observing a direct transformation of N_2O_4 to $NO^+NO_3^-$ at atmospheric pressure without precursors or subsequent induction by visible light. Therefore, the nature of this conversion process, speculated as arising from either intra- or intermolecular mechanisms, still poses an interesting question.

The transformation between molecular N_2O_4 and ionic $NO^+NO_3^-$ has been investigated since the early 1980s. Bolduan *et al.*[6] reported observing temperature-induced autoionization of solid N_2O_4 condensed on the surface of a copper mirror. They discovered that when the N_2O_4 was heated to 180 K, autoionization to ionic $NO^+NO_3^-$ occurs and the product remains stable from 15 to 180 K. The transformation temperature in our experiments, which is between 180 and 190 K, is in excellent agreement with their result. However, our experiments correspond to the opposite transformation, from ionic $NO^+NO_3^-$ to molecular N_2O_4. The combination of results of the present study with previous observations[6] provides convincing information about the thermodynamic properties of ionic $NO^+NO_3^-$ and molecular N_2O_4, specifically that (1) $NO^+NO_3^-$ is the more stable phase at low temperatures and ambient pressure; (2) the transformation from either side involves a thermochemical barrier characterized by a temperature of about 180 K at ambient pressure; and (3) the transformation is reversible.

For the Raman profile of the internal mode region (e.g., ν_4, ν_1 and ν_{NO^+}), we find good agreement between the present study and previous work on $NO^+NO_3^-$. However, significant differences appear in the lattice mode region between the material formed from N_2O and from N_2O_4 in our work and previous reports. In previous Raman studies of the transformation of N_2O_4 to $NO^+NO_3^-$, only two weak peaks centered at 60 and 125 cm^{-1} were observed.[3] In contrast, we found a total of eight clearly resolved peaks below 360 cm^{-1}, despite the fact that both studies examined the material at almost identical $P-T$ conditions (ambient pressure and 80 K). This difference suggests that the detailed structure, or the degree of order/disorder of $NO^+NO_3^-$ formed by high pressure N_2O differs from that formed by autoionization of N_2O_4 at atmospheric pressure or under pressure. We conclude that instead of amorphous $NO^+NO_3^-$ produced by autoionization of different forms of N_2O_4, laser heating of N_2O results in the formation of ordered or crystalline $NO^+NO_3^-$ at high pressure, and this ordered structure remains stable and can be recovered at ambient pressure and low temperature (80 K).

The ordered or crystalline structure of the $NO^+NO_3^-$ phase documented in the present study is also consistent with the observation of a pressure-induced reversible transformation between the molecular and ionic forms reported by Angew *et al.*[8] In their Raman measurement of $NO^+NO_3^-$ at room temperature, two sharp and intense peaks occur in the lattice region at 3.1 GPa, consistent with crystalline material. They suggest that this ionic form of $NO^+NO_3^-$ is the thermodynamically favored structure at high density. Our x-ray diffraction investigation supports this argument.[10]

Our Raman measurements at both room and low temperature establish that crystalline $NO^+NO_3^-$ is favored either by high pressure or low temperature or both. In addition, both the pressure-induced and temperature-induced transformation of $NO^+NO_3^-$ to molecular N_2O_4 may proceed via amorphous $NO^+NO_3^-$ as a precursor. This is evident from comparison of the Raman spectrum of $NO^+NO_3^-$ at 0.8

and 1.0 GPa and room temperature (Fig. 3) with that at ambient pressure and 190 K [Fig. 7(a)]. These spectra represent the Raman response measured at threshold pressures of the transformation from $NO^+NO_3^-$ to N_2O_4, in which the lattice region displays weak and broadened peaks that could be associated with amorphous $NO^+NO_3^-$.

V. CONCLUSIONS

Detailed studies indicate a broad range of stability of $NO^+NO_3^-$ formed under a variety of conditions and from different starting materials. Far- and mid-IR measurements of the ionic isomer $NO^+NO_3^-$ up to 32 GP revealed the major IR-active lattice modes and intramolecular vibrational modes as well as their combinations, and the IR pressure dependences. $NO^+NO_3^-$ forms a crystalline phase at high pressure. Moreover, it is quenchable to ambient pressure and low temperature. Our Raman measurements conducted at various temperatures agree with previous studies of the transformation of N_2O_4 to $NO^+NO_3^-$. The low temperature measurements provide evidence of a phase transition near 5 GPa. There are differences in the Raman and IR spectra of $NO^+NO_3^-$ formed from N_2O by laser heating and from N_2O_4 autoionization either at ambient pressure and low temperatures or under pressure. These differences can be attributed to different degrees of order/disorder in that material.

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