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## High Pressure and Equation of State of Nitrosonium Nitrate from Synchrotron X-ray Diffraction

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Beamline(s): X17C

**Introduction:** Remarkably, several nitrogen oxides transform to nitrosonium nitrate ( $\text{NO}^+\text{NO}_3^-$ ) under high pressures. In this study,  $\text{NO}^+\text{NO}_3^-$  was synthesized by laser heating of  $\text{N}_2\text{O}$  in a diamond anvil cell and characterized by *in situ* x-ray diffraction as a function of pressure. The unit cell parameters are refined up to 32.2 GPa and are compared with previous results. These cell parameters were fitted to both Birch and Vinet equation of state for the  $\text{NO}^+\text{NO}_3^-$ . The analysis indicates that  $\text{NO}^+\text{NO}_3^-$  is denser than other nitrogen-oxygen assemblages, consistent with the conclusion that formation of the ionic species is driven by density rather than entropic effects.

**Methods and Materials:** Pure  $\text{N}_2\text{O}$  was loaded cryogenically into Mao-Bell diamond anvil cells with large optical openings on both sides. Ruby chips were added to the sample chamber to enable pressures to be determined by the shift of the  $R_1$  ruby fluorescence line. The pressurized  $\text{N}_2\text{O}$  sample (above 10 GPa) was heated by means of a  $\text{CO}_2$  infrared laser (10.6  $\mu\text{m}$ ) to drive the reaction to form  $\text{NO}^+\text{NO}_3^-$ . The transformation of  $\text{N}_2\text{O}$  to  $\text{NO}^+\text{NO}_3^-$  was confirmed by Raman spectroscopy. The samples were taken to beamline X17C for x-ray diffraction measurements. For each measurement, the cell was oscillated along  $\omega$  and  $\chi$  to overcome the preferred orientation and  $2\theta$  was fixed at  $8.99^\circ$ . The diffraction pattern was calibrated with diffraction lines of gold.

**Results:** Figure 1 shows typical diffraction patterns for pressures of 9.9, 21.4 and 32.2 GPa. By tracing the major peaks, the diffraction patterns can be consistently assigned at all pressures. There are some substantial differences in both the intensity distribution and peak positions between the previous angle-dispersive and our energy-dispersive diffraction patterns. The combination of the two patterns gives a new set of cell parameters for both the angle-dispersive and energy-dispersive experiments.

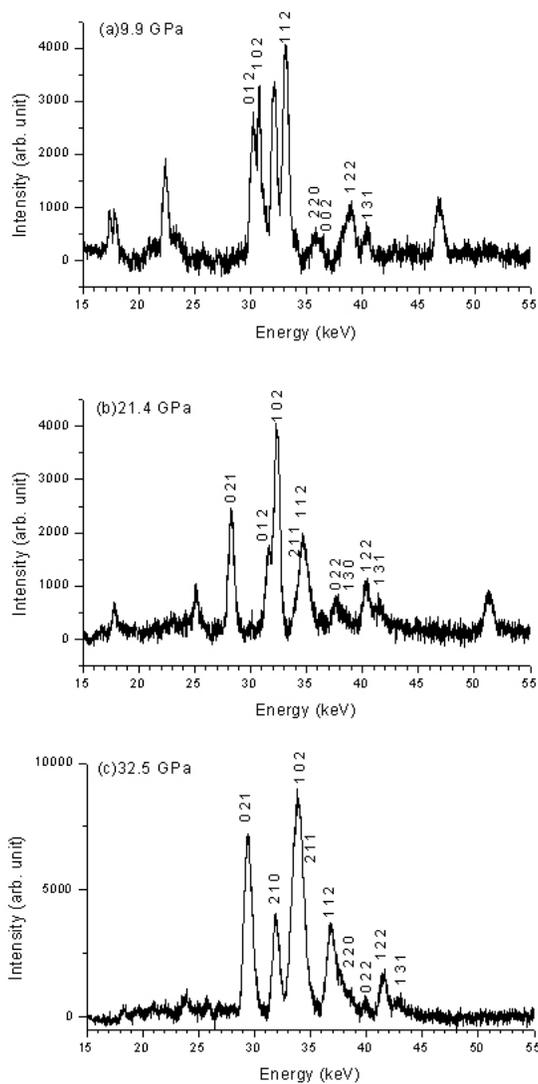
The compression data for  $\text{NO}^+\text{NO}_3^-$  have been fitted to a third-order Birch and Vinet equation of state. This procedure gives the  $V_0$  as  $265.0 \pm 2.0 \text{ \AA}^3/\text{cell}$ , with  $K_0 = 45.2 \pm 0.9 \text{ GPa}$  and  $K_0' = 3.18 \pm 0.90$  by least square simulation. Using the Vinet formula and the  $V_0$  used in the Birch equation, the bulk modulus and its first derivative are determined to be  $K_0 = 42.3 \pm 1.0 \text{ GPa}$  and  $K_0' = 3.52 \pm 0.60$ , very close to those fitted to the Birch equation. In Figure 2, we plot the P-V equations of state for  $\text{O}_2$ ,  $\text{N}_2$  and  $\text{N}_2\text{O}$  to compare the densities of these species. As can be seen from the P-V curve,  $\text{NO}^+\text{NO}_3^-$  is denser than the assemblage at all pressures in the present study. The density of  $\text{NO}^+\text{NO}_3^-$  established by the equation of state gives important insight into the stability, thermodynamics, and the reaction mechanism related to  $\text{NO}^+\text{NO}_3^-$ .

**Conclusions:** We have conducted an x-ray diffraction study of  $\text{NO}^+\text{NO}_3^-$  at both room temperature and low temperatures using synchrotron radiation facilities. Based on the orthorhombic structure previously determined by angle dispersive x-ray diffraction, we were able to derive the cell parameters from 9.9 GPa to 32.2 GPa. The molecular volume has been fitted to the Birch equation of state, from which the bulk modulus  $K_0$  and its first derivative  $K_0'$  are determined. We find that the density for  $\text{NO}^+\text{NO}_3^-$  is larger than both the assemblage of  $\text{N}_2 + 2\text{O}_2$  and of  $\text{N}_2\text{O} + 3/2 \text{O}_2$  indicating that the transformation to  $\text{NO}^+\text{NO}_3^-$  is thermodynamically driven by pressure. The room temperature and low temperature *in situ* x-ray diffraction data, together with spectroscopic measurements, provide estimates of phase relations for the system.

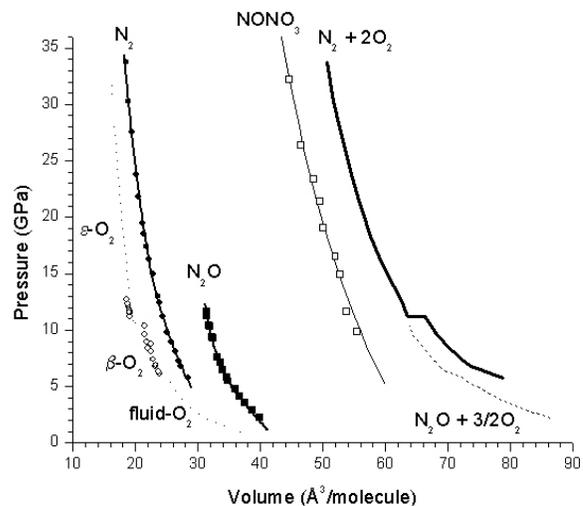
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### References:

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**Fig 1.** Energy dispersive x-ray diffraction pattern of  $\text{NO}^+\text{NO}_3^-$  measured at (a) 9.9 GPa, (b) 21.4 GPa and (c) 32.2 GPa and room temperature. Background has been subtracted. The energy calibration was obtained from a gold external standard diffraction pattern and the pattern has been background subtracted. The  $2\theta$  used was  $8.99^\circ$ . The d-spacings were indexed from a the orthorhombic  $\text{P2}_1\text{cn}$  structure determined by the previous angular dispersive x-ray diffraction measurement.



**Fig 2.** Molecular volume of  $\text{NO}^+\text{NO}_3^-$  ( $\square$ ) in the pressure region of 9-32 GPa, determined by the energy-dispersive x-ray diffraction. The P-V data have been fitted with Birch equation of state (—). The equation of state for  $\text{O}_2$  ( $\cdots$ ) and several experimental data points ( $\circ$ ), and that for  $\text{N}_2$  ( $\bullet$ ) and  $\text{N}_2\text{O}$  ( $\blacksquare$ ) are also plotted based on previous report (see text). The volumes of stoichiometrically equivalent assemblage of  $\text{N}_2 + 2\text{O}_2$  (—) and  $\text{N}_2\text{O} + 3/2 \text{O}_2$  (---) vs. pressure are also plotted for comparison.