



	Experiment title: Structural properties of HNO ₃ at high pressure	Experiment number: HS 1899
Beamline: ID09A	Date of experiment: from: 20/11/02 to: 23/11/02	Date of report: 21/08/03
Shifts: 9	Local contact(s): M. Hanfland	<i>Received at ESRF:</i>
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Report:

The high-pressure behaviour of nitric acid (HNO₃) has been studied by X-ray diffraction up to 37.5 GPa on the ID09A beam line. The aim of the experiment was to determine the structural evolution of HNO₃ at high pressure. Structural data are necessary to confirm the phase transitions and the high-pressure ionisation process inferred from our computer simulations and from Raman measurements.

Experimental method

Pure liquid nitric acid was loaded into a membrane diamond anvil cell (DAC) with large X-ray aperture (equipped with boron seats) [1]. Care was taken to avoid any pollution from atmospheric moisture. The presence of a small amount of water can change the high-pressure behaviour of HNO₃. In order to check the absence of water, Raman measurements were performed in our laboratory, prior to the X-ray diffraction experiment. Nitric acid was crystallised in the DAC at P = 1.4 GPa (pressure measured using the ruby scale). We performed angle-dispersive diffraction with a monochromatic beam ($\lambda = 0.416532 \text{ \AA}$). The X-ray diffraction patterns were collected with an on-line image-plate detector (MAR3450).

Results

Diffraction images of solid HNO₃ were taken at ambient temperature for different pressures between P = 3 GPa and P = 37.5 GPa. The diffraction pattern observed at P = 3 GPa did not show very nice rings,

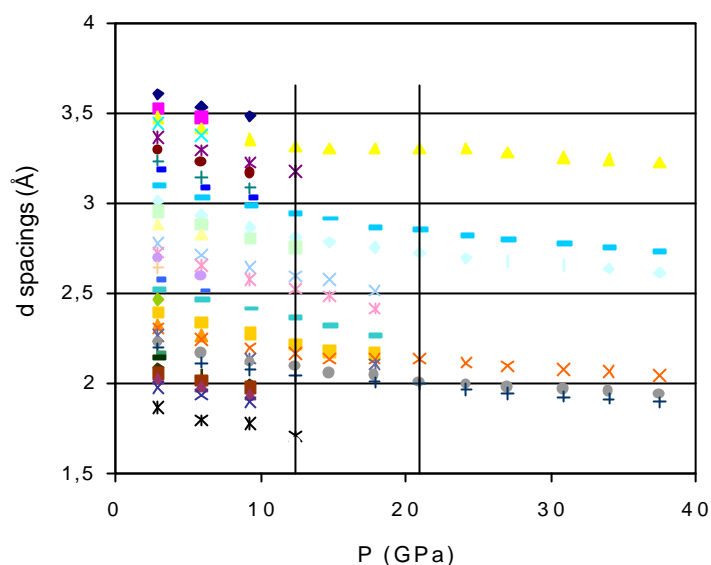
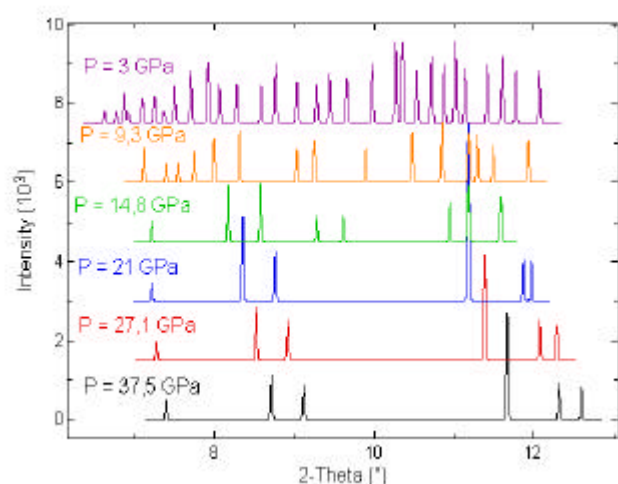


Figure 1 (left) : Diffraction spectra for solid HNO_3 between $P = 3$ GPa and $P = 37.5$ GPa

Figure 2 (right) : d spacings as a function of pressure

indicating that the powder obtained by crystallisation of liquid HNO_3 under pressure is of rather poor quality. This makes it difficult to get an accurate measurement of the diffraction peaks intensities. At high pressure, the diffraction rings tend to disappear, leading to a single-crystal like pattern with only a few diffraction peaks showing hexagonal structure. At $P = 3$ GPa, the structure is monoclinic, which is compatible with the structure proposed previously. The evolution of the diffraction spectra and of the d spacings between $P = 3$ GPa and $P = 37.5$ GPa is shown in Figure 1 and Figure 2 respectively. The number of peaks decreases with pressure, only six peaks remaining at high pressure. A first transition can be seen around 12 GPa with the disappearance of some peaks and with the change in slope in the evolution of the d spacings of the remaining peaks. At 22 GPa, a second change in slope is observed, indicating the presence of a second transition. These results are consistent with previous Raman measurements [2] and with our calculations [3]. In these works, the two transitions were observed around 10 GPa and 25 GPa. The Raman data indicated that the first transition originated from strong H-bonding between neighbour molecules and beginning of ionisation of the HNO_3 molecules. This ionisation was found to be total after 25 GPa. Our calculations showed that only three quarters of the molecules undergo ionisation at $P = 10$ GPa. To account for total ionisation at high pressure, the assumption of a phase transition at $P = 25$ GPa was made. This transition was characterised by the transfer of an H atom between two oxygen atoms, leading to a ribbon-like structure.

The analysis of our diffraction data is still under progress. Our results seem to confirm the presence of two transitions leading to ionisation of HNO_3 at high pressure. The evolution of the structure is not fully determined yet. Single-crystal X-ray diffraction could help in the description of the ionisation process.

References

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- [2] H. Lucas, J.P. Petit, J. Phys. Chem., 103, 8952 (1999).
- [3] R. Méreau et al., *to be published*.