



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF. Once completed, the original report should be sent, together with 5 reduced (A4) copies, to the User Office.

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Reports accompanying requests for additional beam time

If your report is to support a **new proposal**, the original report form should be sent with the new proposal form, and a copy of your report should be attached to each copy of your proposal. The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
 - type your report, in English.
 - include the reference number of the proposal to which the report refers.
 - make sure that the text, tables and figures fit into the space available.
 - if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.
 - bear in mind that the report will be reduced to 71% of its original size. A type-face such as "Times", 14 points, with a 1.5 line spacing between lines for the text, produces a report which can be read easily.
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	Experiment title: Crystal Structures of Carbon Dioxide at High Pressures and Temperatures	Experiment number: HS-1388
Beamline: ID 30	Date of experiment: from: Oct. 4, 2000 to: Oct. 9, 2000	Date of report: Feb. 26, 2000
Shifts: 15	Local contact(s): Tristan Le Bihan and Mohamed Mezouar	<i>Received at ESK</i>
Names and affiliations of applicants (* indicates experimentalists): Choong-Shik Yoo*, Lawrence Livermore National Laboratory, Livermore, CA94550 Hyunchae Cynn, Lawrence Livermore National Laboratory, Livermore, CA94550 Malcolm F. Nicol, University of Nevada, Las Vegas, Nevada		

Report:

PRESSURE-INDUCED DISPROPORTION OF N₂O:

Nitrous oxide (N₂O) is a good molecular analog to carbon dioxide (CO₂). Those are isoelectronic and have similar melting temperatures and crystal structures at high pressures. At ambient temperature N₂O crystallizes into an orientation-disordered cubic (Pa3) -phase at 1 GPa and transforms into an ordered orthorhombic (Cmca) -phase at 4 GPa [1]. The crystal structures of - and -N₂O are similar to those of CO₂-I and III, respectively. All these phases are considered to be molecular below 10-20 GPa, again, stabilized mainly by quadrupole-quadrupole interactions. The properties of N₂O, however, are not known at higher pressures where CO₂-III develops highly unusual lattice strain and strength (above 20 GPa) and transforms

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into the non-molecular phase V like SiO_2 (above 35 GPa and 1800 K) [2]. Therefore, during the past run, we have studied the phase transitions in N_2O at high pressures and temperatures [3] in order to obtain a systematic understanding of those simple linear triatomic molecular solids.

Our main findings in this study is that, unlike to CO_2 , the laser-heated nitrous oxide ($\beta\text{-N}_2\text{O}$, Cmca) disproportionates into an ionic form of dimeric nitrogen dioxide, nitrosonium nitrate or NO^+NO_3^- , and nitrogen at 10-55 GPa and 2000-3400 K (middle in Fig.1). Raman spectra of the quenched products suggest that the ionic phase is stable to 50 GPa but, upon subsequent heating (or heating at lower pressures below 30 GPa), further dissociates into nitrogen, oxygen and other nitrogen-oxygen compounds (top in Fig. 1).

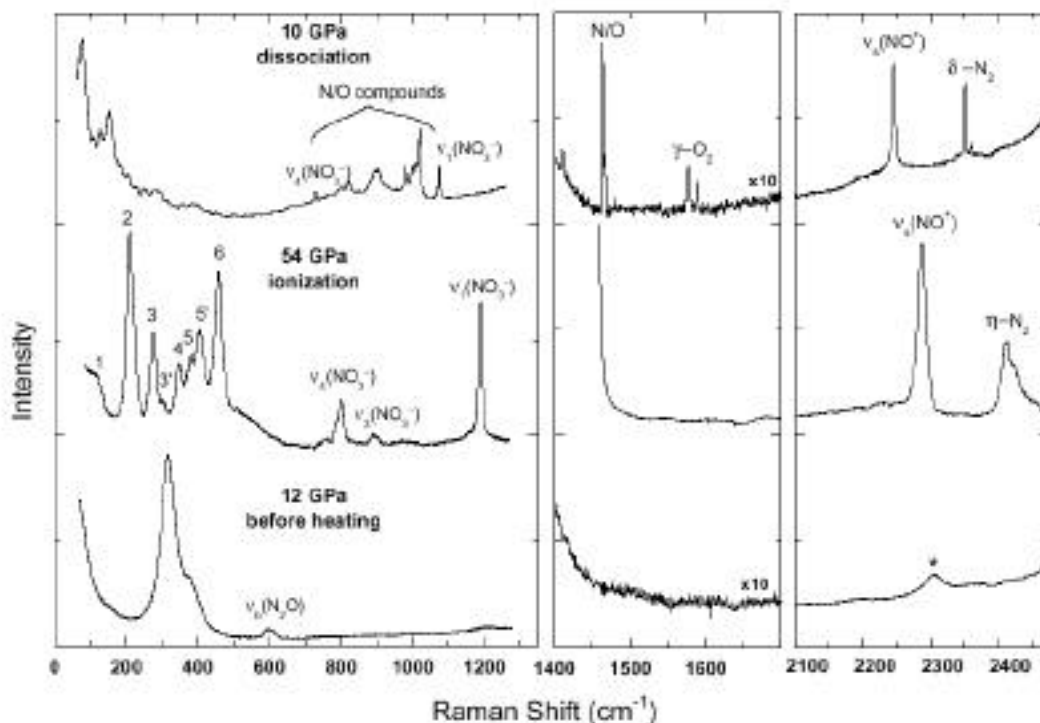


Figure 1. Raman spectra of $\beta\text{-N}_2\text{O}$ (a) before and (b, c) after laser-heating, showing the pressure-induced reactions to (b) the ionization products of NO^+NO_3^- and $\beta\text{-N}_2$ at 54 GPa and (c) the dissociative products of $\beta\text{-N}_2$, $\gamma\text{-O}_2$, N/O-compounds, and NO^+NO_3^- at 10 GPa. The broad feature with asterisk indicates the second order Raman of diamond.

The crystal structures of $\beta\text{-N}_2\text{O}$ and NO^+NO_3^- have been characterized to 55 GPa at ambient temperature (Fig. 2). The diffraction pattern of $\beta\text{-N}_2\text{O}$ before heating can easily fit to the known structure: the orthorhombic Cmca cell with $Z=4$. The x-ray diffraction pattern of the quenched ionic product, on the other hand, is composed of the reflections from $\beta\text{-N}_2$ (Pm3n), $\beta\text{-N}_2\text{O}$ (Cmca), and NO^+NO_3^- . The x-ray intensity data with highly preferred orientation, however, do not allow rigorous refinement of crystal structures for all products. Nevertheless, we have

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found a reasonable description for the structure of the ionic phase NO^+NO_3^- in terms of an orthorhombic structure such as Pbcm or Pnma with lattice parameters, $a = 5.923 \text{ \AA}$, $b = 7.255 \text{ \AA}$, $c = 4.717 \text{ \AA}$ with 4 molecules per unit cell. Note that this structure is analogous to the aragonite structure of CaCO_3 .

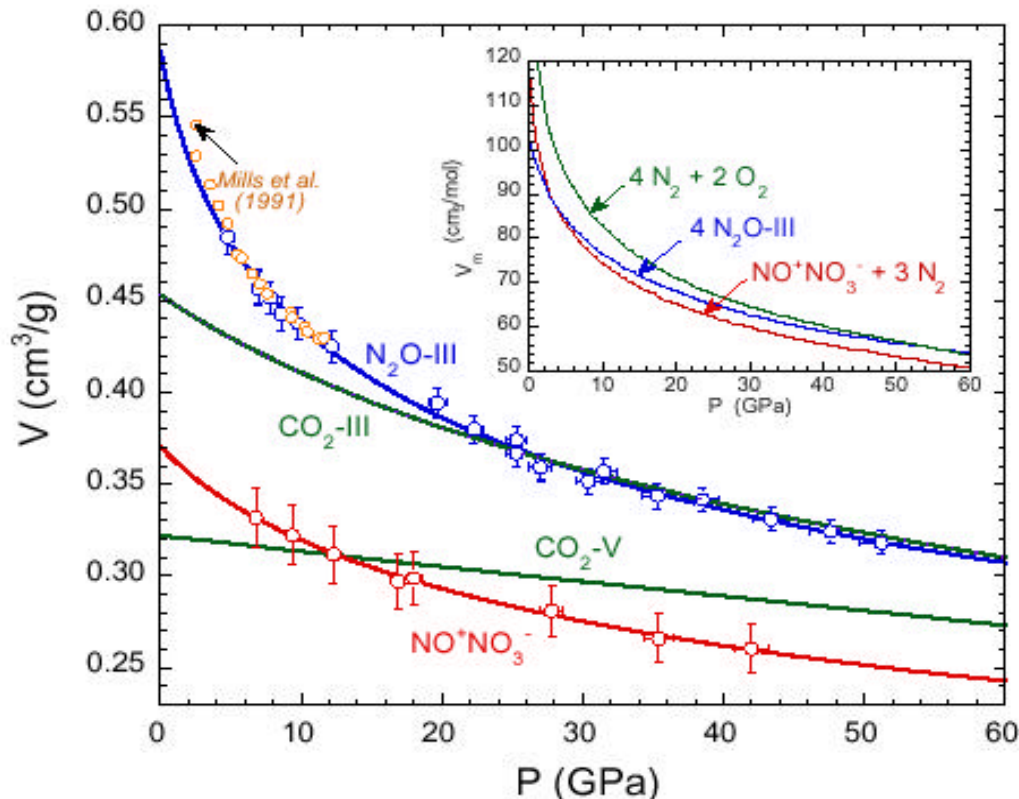


Figure 4. The room-temperature isotherms of N_2O and NO^+NO_3^- , in comparison with those of $\text{CO}_2\text{-III}$, $\text{CO}_2\text{-V}$, and N_2 . The inset compares the molar volumes of $4 \text{ N}_2\text{O}$ and $\text{NO}^+\text{NO}_3^- + 3 \text{ N}_2$, illustrating that the densification is responsible for the ionization of N_2O above 5 GPa

The present data shows that, in contrast to the similarity between N_2O and $\text{CO}_2\text{-III}$, the ionic phase of NO^+NO_3^- behaves quite differently from its non-molecular counter part $\text{CO}_2\text{-V}$. The ionic phase NO^+NO_3^- is substantially softer ($B_0=45.0 \text{ GPa}$) than the polymeric phase $\text{CO}_2\text{-V}$ ($B_0=362 \text{ GPa}$). As a result, NO^+NO_3^- becomes denser than $\text{CO}_2\text{-V}$ above 12 GPa despite its lower density at the ambient. The higher density of NO^+NO_3^- than $\text{CO}_2\text{-V}$ at high pressures probably reflects more efficient packing of the ion pairs in NO^+NO_3^- . It is probably due to relatively strong attractive coulombic interaction of the ion pairs, in contrary to very stiff covalent bonds of $\text{CO}_2\text{-V}$ in an open structural configuration. This result is also consistent with the higher number of

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nearest neighbor in NO^+NO_3^- than $\text{CO}_2\text{-V}$; for example, each nitrosonium (NO^+) ion has eight nearest nitrogen ions [20], whereas each carbon atoms in $\text{CO}_2\text{-V}$ has only four nearest oxygen atoms [8].

The inset of Fig. 2 compares the molar volumes of $\text{-N}_2\text{O}$ with the ionic and dissociative products. Above 5 GPa, the mixture of NO^+NO_3^- and N_2 has smallest molar volume, which favors over both $\text{-N}_2\text{O}$ and the dissociative mixture of N_2 and O_2 [22]. On the other hand, the molar volume of the N_2 and O_2 mixture becomes smaller than that of $\text{-N}_2\text{O}$ above 56 GPa and, based on the extrapolation, of the mixture of NO^+NO_3^- above 130 GPa. Therefore, it appears that the ionization is primarily driven by densification at high pressures, yet the dissociation observed between 10 and 30 GPa is resulted from the combined effect of densification and entropy increase at high pressures and temperatures. The experimental observation that the dissociation requires higher temperature than the ionization also supports this conclusion.

References:

- [1] R. L. Mills, B. Olinger, D. T. Cromer, and R. LeSar, *J. Chem. Phys.* **95**, 5392 (1991).
- [2] C. S. Yoo, H. Cynn, F. Gygi, G. Galli, V. Iota, M. Nicol, S. Carlson, D. Hauserman and C. Mailhot, *Phys. Rev. Lett.* **83**, 5527 (1999).
- [3] C. S. Yoo, H. Cynn, V. Iota, M. Nicol, T. Le Bihan, M. Mezouar, *Phys. Rev. Lett.*, in review (2001).

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