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High Pressure Single-Crystal X-Ray Diffraction Investigation of Nitrosonium Nitrate: Solving a 55 Years Old Enigma

The study of the behavior of matter at extreme pressure conditions is essential to deepen our understanding of the pressure dependence of interatomic interactions and to benchmark theoretical models. Simple molecular systems at high densities are well known to exhibit a transformation towards polymeric (*e.g.* N₂,^[1,2] CO,^[3] CO₂,^[4,5] C₂H₂<sup>[6]</s
or metallic (*e.g.* O₂,^[7] H₂^[8,9]) states as a mechanism to redistribute their electron density. In contrast, nitrogen-oxygen systems (N₂O, N₂O₄, N₂-O₂ mixtures) are hypothesized to instead exploit a third avenue, ionization, and are presumed to form nitrosonium nitrate (NO⁺NO₃⁻).^[10,11] Despite its first solid state synthesis in 1965^[12] and an impressive number of subsequent in-situ high pressure powder X-ray diffraction studies as well as theoretical calculations,^[10,11,13–19] the crystal structure of nitrosonium nitrate remains controversial.

Here, we present experimental investigations on nitrosonium nitrate between 3 and 55 GPa employing synchrotron single-crystal X-ray diffraction applied to polycrystalline samples (sc-XRDp)—a novel technique developed by our group. Through these measurements, a full structural solution of NO⁺NO₃⁻ was obtained. Its structure is shown in Fig. 1. Chemical peculiarities of this compound were unveiled, namely the striking presence of a positively charged oxygen atom in the NO⁺ ion deduced from crystal-chemical principles. Accompanying theoretical calculations validated the positively charged nature of the oxygen atom in the NO⁺ ion and established the experimentally determined structure as the most thermodynamically stable among those previously proposed.

This study unambiguously authenticates the unorthodox preference of nitrogen and oxygen to form an ionic compound to redistribute its pressure-induced increase in electron density. Moreover, it highlights the importance of a high accuracy characterization techniques, such as sc-XRDp, as an essential method that is key to expose the crystal chemical and physico-chemical singularities indigenous to high pressure research.

Figure caption:
Figure 1: a) Monoclinic unit cell of NO⁺NO₃⁻ at 37 GPa. b) Representation of the trigonal planar nitrate (top) and linear nitrosonium (bottom) ions. c-d) Environment of the O2 and N2 atoms forming the NO⁺ cation: both N2 and O2 atoms are five-fold coordinated by negatively-charged oxygen atoms from the NO⁺NO₃⁻ anions. When shown, bond lengths and bond angles are given in Angstroms (Å) and degrees (°), respectively.

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