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Nitrogen oxides under pressure: stability, ionization, polymerization, and superconductivity

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Nitrogen oxides are textbook class of molecular compounds, with extensive industrial applications. Nitrogen and oxygen are also among the most abundant elements in the universe. We explore the N-O system at 0K and up to 500GPa through ab initio evolutionary simulations. Results show that two phase transformations of stable molecular NO₂ occur at 7 and 64GPa, and followed by decomposition of NO₂ at 91GPa. All of the NO⁺NO₃⁻ structures are found to be metastable at T = 0K, so experimentally reported ionic NO⁺NO₃⁻ is either metastable or stabilized by temperature. N₂O₅ becomes stable at 9 GPa, and transforms from P-1 to C2/c structure at 51GPa. NO becomes thermodynamically stable at 198GPa. This polymeric phase is superconducting (T_c = 2.0K) and contains a -N-N- backbone.

Both nitrogen and oxygen have been extensively investigated in experiments and theoretical simulations. Generally, nitrogen is an insulator or a semiconductor. Cubic gauche phase of nitrogen¹ is stable in a wide range of pressure². Other nitrogen structures, such as chain and rings³⁻⁵, have also been reported. All known phases of oxygen are molecular^{6,7}. Experiments and first-principles calculations for oxygen under high pressure revealed the complex evolution of insulator->semiconductor->metal->semiconductor⁸. The superconductivity of solid oxygen (T_c = 0.6K) was observed at pressure above 96GPa in experiment⁹. The known nitrogen oxides are semiconducting (for example, the band gap of Im-3 NO₂ calculated is approximately 2.8eV).

At ambient pressure, nitrogen oxides exist as molecular crystals with many applications in chemical industry and important biological roles. The volumetric behavior of nitrous oxide under pressure has been investigated since 1961¹⁰. The synthesis and phase transformations of N₂O have been analyzed in experimental and theoretical studies¹¹⁻¹⁶. Different from normal phases containing N₂O₄ molecules, the ionic NO⁺NO₃⁻ was reported in the range of 1.5 to 3.0GPa¹⁷. The typical N-O stretching frequency of NO⁺ was characterized at 2234cm⁻¹, consistent with previous reports^{17,18}. In 2001, Somayazulu *et al.*¹⁹ synthesized the ionic NO⁺NO₃⁻ (nitrosonium nitrate) phase from N₂O at above 20GPa and 1000K, and performed first structural characterization of NO⁺NO₃⁻. Somayazulu *et al.*¹⁹ proposed an ionic NO⁺NO₃⁻ model based on aragonite with space group of P2₁cn. Other P2₁/m²⁰ and Pna2₁¹⁶ models of

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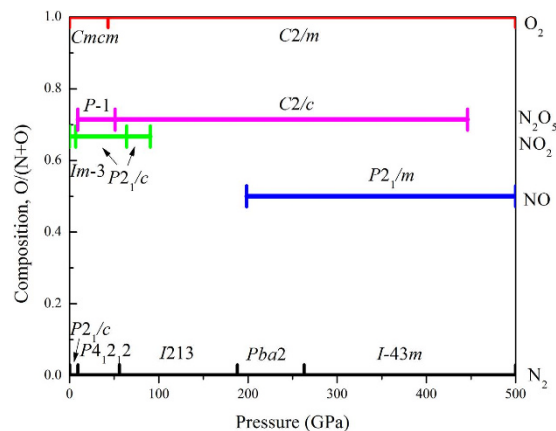


Figure 1. Phase diagram of the N–O system.

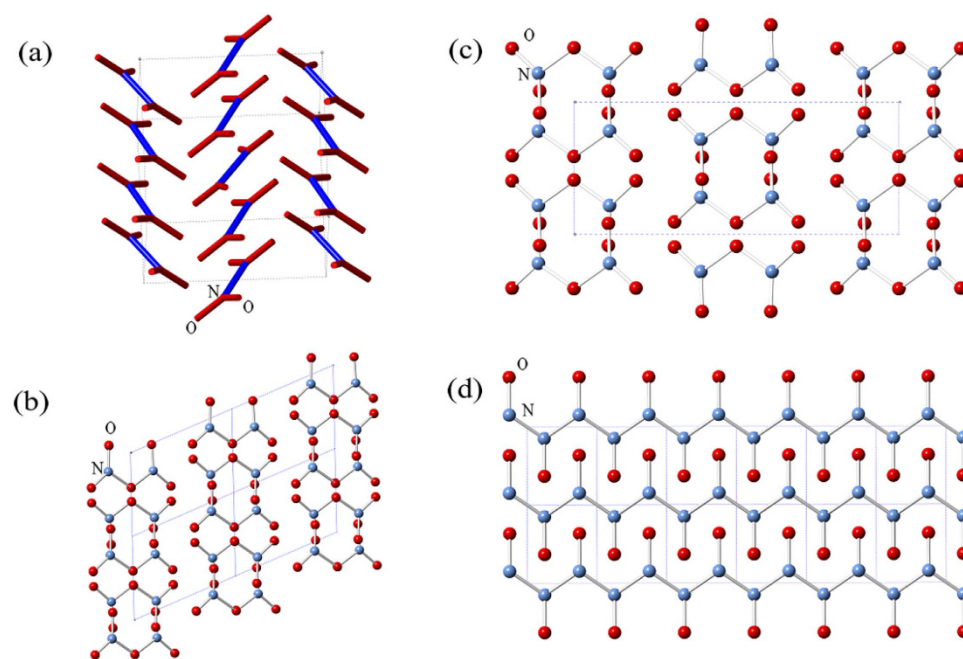


Figure 2. Structures of (a) $P2_1/c$ NO_2 , (b) $P-1$ and (c) $C2/c$ N_2O_5 , (d) $P2_1/m$ NO .

NO^+NO_3^- were also suggested, and the later one is more stable. However, the simulated XRD data of the $Pna2_1$ structure is quite different from that in experiments, indicating that other undiscovered stable NO^+NO_3^- structures might exist.

Results and Discussions

We employed the evolutionary algorithm USPEX^{21–24} to predict stable N–O compounds and structures under high pressures. Up to 500 GPa, only three stable N–O compounds were found (NO_2 , N_2O_5 and NO), as seen in Fig. 1. Most of them retain their molecular structures even under high pressure. Experimentally known “laughing gas” N_2O is metastable. The stable phases are discussed as follows.

- (1) NO_2 : Besides the known cubic ($Im-3$) and monoclinic ($P2_1/c$) NO_2 structures are stable in pressure ranges of 0–7 and 7–64 GPa respectively, another $P2_1/c$ structure was found to be stable from 64 to 91 GPa (Fig. 2a). Similar to the known phases, this novel NO_2 structure also contains N_2O_4 molecules. Different from known $P2_1/c$ NO_2 , the proposed $P2_1/c$ NO_2 is denser and has 8 formula units in the unit cell. NO_2 decomposes at 91 GPa.
- (2) N_2O_5 : Molecular N_2O_5 phases are stable in a wide pressure range (9–446 GPa). At 51 GPa, N_2O_5 transforms from $P-1$ (Fig. 2b) to $C2/c$ (Fig. 2c) structure. The N_2O_5 molecules remain planar. At 446 GPa, N_2O_5 becomes unstable and decomposes into NO and O . At 0 GPa, the $P-1$ N_2O_5 is 0.04 eV/

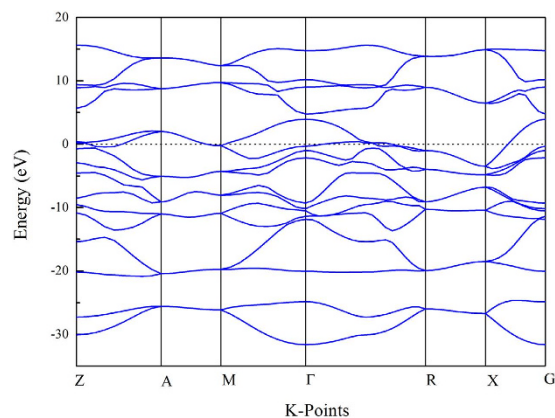


Figure 3. Band structure of $P2_1/m$ NO at 198 GPa. Z(0,0,0.5), A(0.5,0.5,0.5), M(0.5,0.5,0), Γ (0,0,0), R(0,0.5,0.5) and X(0,0.5,0).

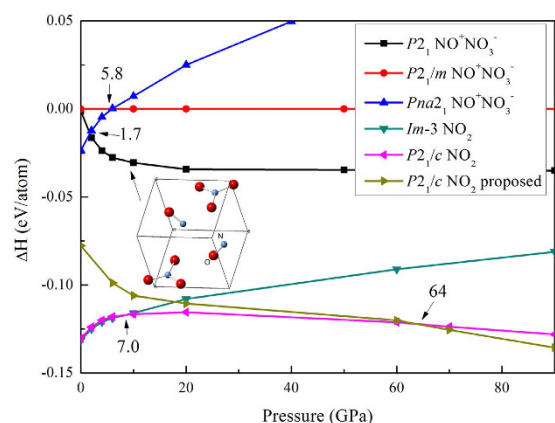


Figure 4. Enthalpies of NO_2 phases as a function of pressures.

atom more stable than known hexagonal NO_2NO_3 , however, both of them are calculated to be above the convex hull, and therefore metastable.

- (3) NO: NO is a metastable compound at low pressures. A polymeric NO structure (Fig. 2d, $P2_1/m$) becomes stable at 198 GPa. Nitrogen atoms form a strong covalent backbone (N-N = 1.34 Å) in the shape of a zigzag chain. Indeed, that is right between the typical values of single (1.45 Å) and double (1.25 Å) nitrogen-nitrogen bonds. Each nitrogen atom is also bonded to one oxygen atom (N-O bond length is 1.20 Å). A similar backbone has also been reported for the N-H system²⁵. Distance between neighboring quasi-one-dimensional structures is 1.86 Å. Phonon dispersion curves of this remarkable polymeric phase were calculated (shown in Fig. S6). No imaginary frequencies were observed, implying its dynamical stability.

While most of the stable N-O phases are semiconducting, polymeric NO is metallic. The band structure of NO is shown in Fig. 3. Using the Allen-Dynes modified McMillan equation^{26,27} with value of the Coulomb pseudopotential $\mu^* = 0.13$, polymeric NO is superconducting with $T_c = 2.0$ K at 200 GPa, which is close to that of oxygen^{8,9}.

As mentioned above, ionic NO^+NO_3^- has been observed in several high-pressure experiments^{19,20,28}. However, no stable NO^+NO_3^- structure was found in our variable-composition searches. To find the lowest-enthalpy ionic NO^+NO_3^- structure, we performed $(\text{NO})_n(\text{NO}_3)_n$ ($n = 6$ or 8) calculations at 0–50 GPa, assembling structures from ready-made NO and NO_3 units in variable proportion. A novel metastable monoclinic NO^+NO_3^- ($P2_1$, Fig. 4) was found to be more stable than orthorhombic phase¹⁶ and monoclinic $P2_1/m$ NO^+NO_3^- ²⁰ at pressures above 1.7 GPa. The main difference between novel $P2_1$ and $P2_1/m$ NO^+NO_3^- models²⁰ is the orientation of the NO^+ molecules. Importantly, at all pressures structures made of N_2O_4 molecules are more stable than ionic NO^+NO_3^- structures (Fig. 4)

In experiments, the typical Raman frequencies of NO^+NO_3^- are 2234 cm^{-1} for the N-O stretch in NO^+ , together with 1345, 1056 and 721 cm^{-1} for anti-symmetric stretch, symmetric stretch and in-plane deformation for NO_3^- respectively^{17,19,28–30}. The Raman frequencies and intensities of NO^+NO_3^- and NO_2 structures were calculated at 20 GPa. Here, Raman frequencies of NO^+ and NO_3^- were used for

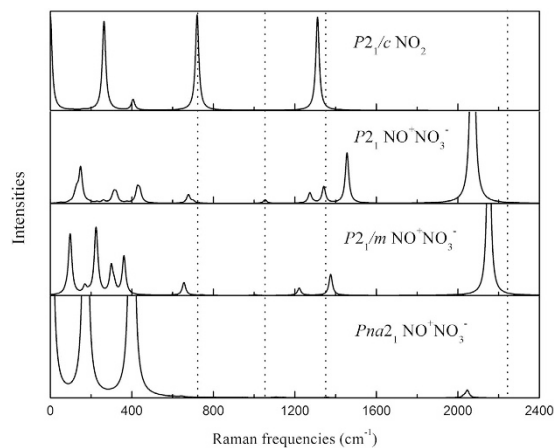


Figure 5. Simulated Raman spectra of $P2_1/c$ NO_2 , and $P2_1$, $P2_1/m^{20}$ and $Pna2_1^{16}$ NO^+NO_3^- at 20 GPa. Typical Raman frequencies of NO^+ and NO_3^- in experiment¹⁷ were drawn by dotted lines.

comparison. As shown in Fig. 5, the computed Raman spectra of $P2_1/c$ NO_2 and $Pna2_1$ NO^+NO_3^- are significantly different from experimental ones¹⁷. The typical Raman frequencies of N-O stretch are 2071 cm^{-1} of $P2_1$ and 2151 cm^{-1} of $P2_1/m$ structures. Both of them basically match the experimental data¹⁹, but that of $P2_1$ NO^+NO_3^- obtains better match in terms of relative intensity. Similar comparison for Raman and XRD data could also be observed under other pressures^{20,31}.

In summary, stable NO_2 , N_2O_5 and NO phases were found in N-O system up to 500 GPa. The $P2_1/c$ NO_2 becomes stable at 64 GPa and decomposes at 91 GPa. N_2O_5 with $P-1$ becomes stable at 9 GPa, transforms to $C2/c$ at 51 GPa and decomposes at 446 GPa. The only metallic structure ($P2_1/m$ NO) has -N-N- zigzag backbone and possesses superconductivity with $T_c = 2.0\text{ K}$. Our results show that ionic NO^+NO_3^- is metastable, and we identify a novel $P2_1$ structure that matches experimental data better and has lower enthalpy than previously proposed structures.

Methods

An evolutionary algorithm, as implemented in the USPEX code^{21–24}, were utilized to search for the stable compounds and structures. This method has already been successfully applied to study numerous systems, including nitrogen and oxygen under pressure^{5,7}. Structure relaxations were done using density functional theory (DFT)^{32,33} within the generalized gradient approximation (GGA)³⁴ using the all-electron projector augmented wave (PAW)^{35,36} method as implemented in the VASP code³⁷. The plane-wave kinetic energy cutoff was set to 600 eV and Brillouin zone was sampled at a resolution of $2\pi \times 0.06\text{ \AA}^{-1}$. At first, variable-composition were carried out at 0, 10, 20, 30, 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 GPa. Stability of compounds was judged using the convex hull construction: those compounds which are on the convex hull (i.e. which are more favorable than any isochemical mixture of other phases) are thermodynamically stable at given conditions. The PHONOPY code³⁸ was employed to calculate phonon dispersions for all promising structures, and all the discussed structures were found to be dynamically stable. All Raman frequencies and intensities were calculated according to the method of Porezag and Pederson³⁹. The electron–phonon coupling calculations in Quantum Espresso⁴⁰ with 180 Ry plane-wave cutoff energy were used to calculate the critical temperature of superconductivity (T_c).

References

- Mailhot, C., Yang, L. H. & McMahan, A. K. Polymeric Nitrogen. *Physical Review B* **46**, 14419–14435 (1992).
- Dong, H., Oganov, A. R., Zhu, Q. & Qian, G. R. The phase diagram and hardness of carbon nitrides. *Sci Rep* **5**, 9870 (2015).
- Mattson, W. D., Sanchez-Portal, D., Chiesa, S. & Martin, R. M. Prediction of new phases of nitrogen at high pressure from first-principles simulations. *Physical Review Letters* **93**, 125501 (2004).
- Yao, Y., John, S. T. & Tanaka, K. Metastable high-pressure single-bonded phases of nitrogen predicted via genetic algorithm. *Physical Review B* **77**, 052103 (2008).
- Ma, Y., Oganov, A. R., Li, Z., Xie, Y. & Kotakoski, J. Novel high pressure structures of polymeric nitrogen. *Physical Review Letters* **102**, 065501 (2009).
- Akahama, Y., Kawamura, H., Häusermann, D., Hanfland, M. & Shimomura, O. New High-Pressure Structural Transition of Oxygen at 96 GPa Associated with Metallization in a Molecular Solid. *Physical Review Letters* **74**, 4690–4693 (1995).
- Ma, Y., Oganov, A. R. & Glass, C. W. Structure of the metallic ζ -phase of oxygen and isosymmetric nature of the ϵ - ζ phase transition: Ab initio simulations. *Physical Review B* **76**, 064101 (2007).
- Sun, J., Martinez-Canales, M., Klug, D. D., Pickard, C. J. & Needs, R. J. Persistence and eventual demise of oxygen molecules at terapascal pressures. *Physical review letters* **108**, 045503 (2012).
- Shimizu, K., Suhara, K., Ikumo, M., Eremets, M. & Amaya, K. Superconductivity in oxygen. *Nature* **393**, 767–769 (1998).
- Couch, E. J., Kobe, Kenneth. A. Volumetric Behavior of Nitrous Oxide. Pressure-Volume Isotherms at High Pressures. *J Chem Eng Data* **6**, 229–233 (1961).

11. Agnew, S. F., Swanson, B., Jones, L. & Mills, R. Disproportionation of nitric oxide at high pressure. *The Journal of Physical Chemistry* **89**, 1678–1682 (1985).
12. Olijnyk, H., Daufer, H., Rubly, M., Jodl, H. J. & Hochheimer, H. D. Effect of Pressure and Temperature on the Raman-Spectra of Solid N₂O. *Journal of Chemical Physics* **93**, 45–54 (1990).
13. Mills, R. L., Olinger, B., Cromer, D. T. & LeSar, R. Crystal structures of N₂O to 12 GPa by x-ray diffraction. *The Journal of Chemical Physics* **95**, 5392 (1991).
14. Yoo, C. S. *et al.* Disproportionation and other transformations of N₂O at high pressures and temperatures to lower energy, denser phases. *J Phys Chem B* **107**, 5922–5925 (2003).
15. Iota, V., Park, J. H. & Yoo, C. S. Phase diagram of nitrous oxide: Analogy with carbon dioxide. *Physical Review B* **69** (2004) doi: 10.1103/Physrevb.69.064106.
16. Xiao, H., An, Q., Goddard, W. A., 3rd, Liu, W. G. & Zybin, S. V. Formation of the -N(NO)N(NO)- polymer at high pressure and stabilization at ambient conditions. *Proc Natl Acad Sci USA* **110**, 5321–5325 (2013).
17. Agnew, S. F., Swanson, S. I., Jones, L. H., Mills, R. L. & Schlerf, D. Chemistry of N₂O₄ at High Pressure: Observation of a Reversible Transformation between Molecular and Ionic Crystalline Forms. *Journal of physical and chemical* **87**, 5065–5068 (1983).
18. Goulden, J. D. S. & Millen, D. J. Vibrational Spectra of Ionic Forms of Oxides and Oxy-Acids of Nitrogen .6. Raman-Spectral Evidence of the Ionisation of Dinitrogen Tetroxide in Nitric Acid - the Nitrosonium Ion, NO⁺, and the Nitrosonium - Nitrogen Dioxide Ion, N₂O₃⁺. *J Chem Soc* 2620–2627 (1950), doi: 10.1039/Jr9500002620
19. Somayazulu, M. *et al.* Novel broken symmetry phase from N₂O at high pressures and high temperatures. *Physical Review Letters* **87**, 135504 (2001).
20. Meng, Y. *et al.* Hard x-ray radiation induced dissociation of N₂ and O₂ molecules and the formation of ionic nitrogen oxide phases under pressure. *Physical Review B* **74** (2006), doi: 10.1103/PhysRevB.74.214107
21. Oganov, A. R. & Glass, C. W. Crystal structure prediction using ab initio evolutionary techniques: Principles and applications. *Journal of Chemical Physics* **124**, 244704 (2006).
22. Oganov, A. R., Ma, Y., Lyakhov, A. O., Valle, M. & Gatti, C. Evolutionary crystal structure prediction as a method for the discovery of minerals and materials. *Reviews in Mineralogy and Geochemistry* **71**, 271–298 (2010).
23. Oganov, A. R., Lyakhov, A. O. & Valle, M. How Evolutionary Crystal Structure Prediction Works • and Why. *Accounts of chemical research* **44**, 227–237 (2011).
24. Zhu, Q. & Oganov, A. R., Glass, C. W. & Stokes, H. T. Constrained evolutionary algorithm for structure prediction of molecular crystals: methodology and applications. *Acta Crystallographica Section B: Structural Science* **68**, 215–226 (2012).
25. Goncharov, A. F. *et al.* Backbone NxH compounds at high pressures. *The Journal of Chemical Physics* **142**, 214308 (2015).
26. McMillan, W. L. Transition Temperature of Strong-Coupled Superconductors. *Physical Review* **167**, 331–344 (1968).
27. Allen, P. B. & Dynes, R. C. Transition temperature of strong-coupled superconductors reanalyzed. *Physical Review B* **12**, 905–922 (1975).
28. Song, Y. *et al.* High-pressure stability, transformations, and vibrational dynamics of nitrosonium nitrate from synchrotron infrared and Raman spectroscopy. *Journal of Chemical Physics* **119**, 2232–2240 (2003).
29. Song, Y., Hemley, R. J., Mao, H. K. A., Liu, Z. X. & Herschbach, D. R. New phases of N₂O₄ at high pressures and high temperatures. *Chemical Physics Letters* **382**, 686–692 (2003).
30. Song, Y., Somayazulu, M., Mao, H. K., Hemley, R. J. & Herschbach, D. R. High-pressure structure and equation of state study of nitrosonium nitrate from synchrotron x-ray diffraction. *Journal of Chemical Physics* **118**, 8350–8356 (2003).
31. Sihachakr, D. & Loubeyre, P. High-pressure transformation of N₂/O₂ mixtures into ionic compounds. *Physical Review B* **74** (2006).doi: 10.1103/Physrevb.74.064113
32. Hohenberg, P. & Kohn, W. Inhomogeneous electron gas. *Physical review* **136**, B864 (1964).
33. Kohn, W. & Sham, L. J. Self-consistent equations including exchange and correlation effects. *Physical Review* **140**, A1133 (1965).
34. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Physical review letters* **77**, 3865 (1996).
35. Blöchl, P. E. Projector augmented-wave method. *Physical Review B* **50**, 17953 (1994).
36. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B* **59**, 1758 (1999).
37. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* **54**, 11169 (1996).
38. Togo, A., Oba, F. & Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and CaCl₂-type SiO₂ at high pressures. *Physical Review B* **78**, 134106 (2008).
39. Porezag, D. & Pederson, M. R. Infrared intensities and Raman-scattering activities within density-functional theory. *Physical Review B* **54**, 7830–7836 (1996).
40. Giannozzi, P. *et al.* QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter* **21**, 395502 (2009).

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Author Contributions

D.X.L., X.D., G.R.Q., Q.Z., H.F.D. and X.F.Z. performed calculations and analyzed the data. D.X.L., A.R.O. and Q.Z. wrote the paper. All authors reviewed the manuscript.

Additional Information

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