High Energy Density Mixed Polymeric Phase from Carbon Monoxide and Nitrogen

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Carbon monoxide and nitrogen are among the potentially interesting high-energy density materials. However, in spite of the physical similarities of the molecules, they behave very differently at high pressures. Using density functional theory and structural prediction methods, we examine the ability of these systems to combine their respective properties and form novel mixed crystalline phases under pressures of up to 100 GPa. Interestingly, we find that CO catalyzes the molecular dissociation of N_2, which means mixed structures are favored at a relatively low pressure (below 18 GPa), and that a three-dimensional framework with *Pbam* symmetry becomes the most stable phase above 52 GPa, i.e., at much milder conditions than in pure solid nitrogen. This structure is dynamically stable at ambient pressure and has an energy density of approximately 2.2 kJ g^{-1}, making it a candidate for a high-energy density material, and one that could be achieved at less prohibitive experimental conditions.

Both carbon monoxide and nitrogen form molecular crystals that irreversibly polymerize at high pressures to form dense single-bonded frameworks with high-energy densities. It has been shown that CO undergoes the transition from a molecular crystal to a polymeric phase at much lower pressures than nitrogen [1,2]. While both high-pressure CO and N are potential high-energy density materials (HEDM), polymeric CO has been found to decompose under ambient conditions, and polymeric N can only be formed at prohibitively high pressures and has not been recovered to ambient pressure [3]. In this Letter, we present calculations demonstrating that a mixture of CO and N_2 will undergo a transition to a van der Waals-bound polymeric phase at modest pressures compared with nitrogen. This material will undergo a further transition as the pressure is increased further, to a high-energy density three-dimensional framework, which is expected to be metastable at ambient pressure.

Our interest in the CNO system is also motivated by recent success in the experimental synthesis of such condensed molecular materials [4], some of which are HEDM [1,5]. This class of low-Z materials formed at high pressures is also of interest for reasons beyond HEDM; they may have other useful properties such as superhardness in the case of polymeric CO_2 [6,7], superconductivity and optical nonlinearity [1]. They are crucial in our understanding of high-pressure carbon chemistry, which in turn is vital for projects such as the Deep Carbon Observatory (DCO), concerned with carbon capture and sequestration. Bonds involving carbon, nitrogen and oxygen form the backbone of organic biochemistry, and this work will help improve our understanding of their chemistry.

CO and N_2 molecules are very similar. CO has the strongest known chemical bond and N_2 has the strongest

homonuclear bond [8]. They are isoelectronic, have the same total mass number, have moments of inertia that are within 3% [9], and have qualitatively similar phase diagrams [10]. Although they are similar at low and ambient pressures, differences in chemical bonding leads to a divergence at high pressures, a regime in which CO remains poorly experimentally characterized. They also differ in symmetry and charge distribution; CO has a small dipole moment, but its quadrupole moment is significant, with consequences in its phase diagram [11]. For example, quadrupole considerations forbid the formation of a CO phase analogous to γ-N_2 [12].

In spite of these similarities, the literature contains only a small amount of work on CO/N_2 mixtures, limited to Raman studies on low temperature and ambient pressure CO/N_2 and experimental work on orientation and substitutional disorder in molecular CO/N_2 crystals [13]. *Ab initio* molecular dynamics simulations of a liquid CO/N_2 mixture suggest that molecular dissociate happens at much lower temperatures and pressures (3500 K, 20 GPa) than for pure liquid nitrogen [14].

At low temperatures and pressures, nitrogen forms molecular crystals weakly bound by van der Waals interactions. As the pressure is increased, the molecules dissociate, resulting in single-bonded covalent solids with three-coordinated atoms. The cubic gauche (cg-N) nonmolecular phase was predicted by Mailhiot *et al.* via distortions of a simple cubic lattice [15], and first synthesized over ten years later in diamond anvil cell experiments at high pressure and temperature (110 GPa, 2000 K) [2]. There is striking disagreement in the stability regime of cg-N between theory (50 GPa [15] to under 100 GPa [16]) and experiment (above 94 GPa [17]); it has been suggested that this is a result of approximate density functional theory

(DFT), incorrect nitrogen structures in calculations and high kinetic barriers to molecular dissociation [18]. Indeed, phonon calculations indicate the cg-N structure is dynamically stable across a large pressure range, and that there is a 0.86 eV barrier separating cg-N from the β-O_2 phase of nitrogen at ambient pressure (compared with approximately 0.3 eV between diamond and graphite) [19].

There is a great deal of interest in high-pressure nitrogen phases due to the large difference between the energy of a single bond and a third of the energy of a triple bond. This is predicted to result in a large energy release when cg-N decomposes to molecular nitrogen at ambient pressure, corresponding to an energy density of approximately 9.7 kJ g^{-1} [20] (including a zero-point energy correction), around three times higher than the most powerful conventional explosives [21]. Its decomposition to harmless and undetectable nitrogen gas makes it is an excellent candidate for a rocket propellant; however, DFT predicts that it is metastable at ambient pressure, while experiments have only succeeded in recovering it to around 50 GPa to date [3]. Recent MP2 and dispersion corrected hybrid DFT calculations indicate that the domain of thermodynamic stability extends only as low as 62 GPa at low temperatures [22].

Carbon monoxide transforms to a polymerized, noncrystalline form at 5 GPa and 300 K [1], undemanding conditions compared with nitrogen. It has since been suggested that this polymeric form of CO is in fact not a high-pressure phase, even though it was synthesized at pressure [23]. The positions of the stability lines on the CO phase diagram are at much lower pressures and temperatures compared with other simple molecular solids such as N_2, N_2O, and CO_2 [11]. In fact, CO is predicted to polymerize to polycarbonyl chains even at ambient pressure and low temperatures [8]. Polymeric CO decomposes to molecular CO_2 and graphitic carbon, releasing a large amount of energy, in excess of the explosive HMX. It has been recovered to ambient conditions, at which point it is metastable [24].

Thus far, only amorphous CO has been synthesized in experiments at high pressure; however, nonmolecular crystalline phases have been predicted, in particular, the $I2_12_12_1$ single-bonded three-dimensional framework is stable in the 2 to 55 GPa range, and the layered $Cmcm$ configuration is favored above 55 GPa [8]. The $Cmcm$ structure is particularly interesting because the interlayer separation and band gap can be modified by varying the pressure, such that it becomes a semiconductor with a 0.1 eV band gap at approximately 150 GPa [8].

We used the AIRSS method to find candidates for the most stable structures containing carbon monoxide and nitrogen molecules. AIRSS employs random structure searching by generating a large ensemble of random ''sensible structures,'' which may involve the application of biases such as symmetry, structural units or experimentally derived lattice parameters [25]. At the most basic

level, we construct unit cells with random lattice vectors and place atoms in the chosen stoichiometry at random positions. This lattice vectors and atomic positions of these cells are fully relaxed to the local minimum using DFT, and the enthalpies compared to in principle find the global minimum. The method is described in detail in Ref. [26]. It has been applied successfully in the determination of, among others, high-pressure structures of silane [25], nitrogen [18], carbon monoxide [8], and recently a unique cagelike diamondoid nitrogen phase [27].

In the first instance, we generated at least 1000 structures for 1, 2, 3, and 4 formula units of CON_2 at pressures of 20, 60, and 100 GPa, since these pressures are easily experimentally accessible and are most likely to yield high-energy density materials in the form of a three-dimensional framework. Additional searches with larger unit cells were biased towards high-symmetry structures by construction using either two or four symmetry operations. Later, structures were generated using 1–4 formula units of $2(CO)N_2$. All structures were optimized using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional; after ranking by enthalpy, the best structures were reoptimized at a higher precision [28].

We first note that the appearance of a mixed carbon monoxide and nitrogen phase occurs at low pressures compared with pure nitrogen, which forms molecular crystals up to 56 GPa. Carbon monoxide is a much more reactive molecule, and appears to facilitate polymerizations even at low pressures.

There are two main pressure regimes of interest below 100 GPa. At approximately 20 GPa and below, for both stoichiometries, one-dimensional planar polymers based on an unsaturated carbon or nitrogen six-ring are favored. At pressures above 20 GPa, fully covalent three-dimensional frameworks are preferred. In a 1:1 mixture of CO and N_2, the aforementioned polymers are intermixed with nitrogen molecules, suggesting a degree of phase separation that can be removed by reducing the proportion of nitrogen.
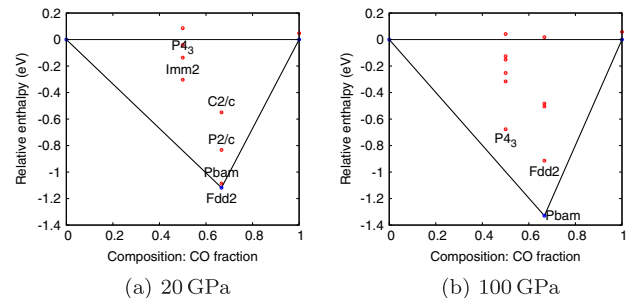

FIG. 1 (color online). Binary hulls for CO/N_2. Enthalpies relative to the most stable separate phases of carbon monoxide and nitrogen at the respective pressures. At 20 GPa, these are molecular $P4_12_12$ N and three-dimensional framework $I2_12_12_1$ CO structures, and at 100 GPa, cg-N and layered $Cmcm$ CO.

The binary hulls (Fig. 1) show that the best structures for a 2:1 mixture of CO:N_2 are more stable than the 1:1 mixture with respect to the separate CO and N_2 phases by up to 0.5 eV, and that the best structures found for a 1:1 mixture are unstable because they are not on the convex hull. Searches using another potentially interesting stoichiometry, CO_2/N_2 (the carbon dioxide or nitrogen system), yielded no stable structures.

A search at 20 GPa with the CNO stoichiometry (i.e., a 2:1 mixture) yielded the polymeric *Pbam* structure [Fig. 2(a)]. This phase is the ground state at pressures up to 18 GPa according to Fig. 3(b) and is more stable than its CN_2O counterpart (*Imm*2) because it does not exhibit signs of phase separation.

The *Fdd*2 structure [Fig. 2(c)] is the most stable in the 18 to 52 GPa range; notably, it contains C=O double bonds which degrade barrierlessly as the pressure increases beyond 50 GPa. As a result, it transforms into an energetically unfavorable, unsaturated structure at pressures above 52 GPa, and the *Pbam* three-dimensional framework
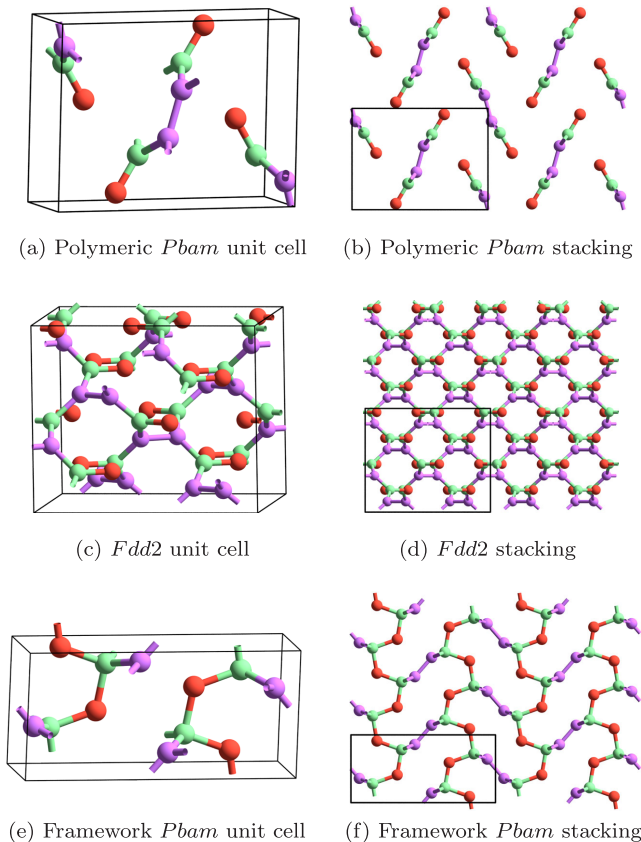

(a) Polymeric *Pbam* unit cell

(b) Polymeric *Pbam* stacking

(c) *Fdd*2 unit cell

(d) *Fdd*2 stacking

(e) Framework *Pbam* unit cell

(f) Framework *Pbam* stacking

FIG. 2 (color online).   Ground state structures for the CNO system (a 2:1 mixture of CO:N_2). Carbon atoms are green, nitrogen pink, and oxygen red. Polymeric *Pbam* is stable below 18 GPa, *Fdd*2 between 18 and 52 GPa, and framework *Pbam* above 52 GPa (see Supplemental Material [29]). The unit cells are on the left, and two-dimensional projections showing stacking on the right. Note the similarity in stacking between the two *Pbam* phases in (b) and (f).

[Fig. 2(e)] becomes the ground state. Although the *Fdd*2 structure is the most stable for a significant proportion of the pressure range, we have focussed on the phase transition between the two *Pbam* structures since they are much closer in configuration space, and are likely to be separated by a much smaller kinetic barrier. We expect the transition between the *Pbam* structures to occur at much lower temperatures than any transition involving the *Fdd*2 structure.

The three-dimensional framework *Pbam* phase consists of near-planar three-coordinated nitrogens, tetrahedral four-coordinated carbons, and two-coordinated oxygens, and is a large band gap insulator throughout the pressure regime. The PBE band gap is 2.95 eV at ambient pressure, and 3.35 eV at 100 GPa, although it should be noted that DFT consistently underestimates band gaps. Phonon calculations performed at pressures in the range 0.1 to 100 GPa yield no imaginary frequencies, suggesting that it is dynamically stable throughout the pressure range, and significantly, that the three-dimensional framework phase can be recovered to ambient pressure. The polymeric *Pbam* structure is only dynamically stable above approximately 30 GPa. At 20 GPa and below, it has negative frequencies corresponding to an antiparallel motion of the weakly bound polymer chains. Since it is conceivable that van der Waals interactions may be significant for unsaturated polymeric structures at the low end of the pressure scale, the pressure-enthalpy relationships were recomputed using a semiempirical dispersion correction [32]. Figure 3 demonstrates that this correction results in a uniform shift in energy that is approximately invariant with
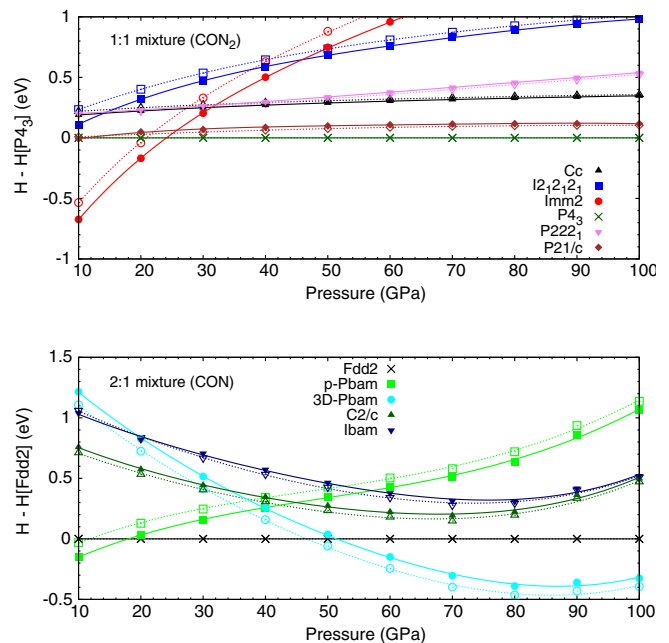

FIG. 3 (color online).   Equation of state plots for CO/N_2 mixture. Enthalpies are relative to the $P4_3$ phase for the 1:1 mixture, and relative to *Fdd*2 for the 2:1 mixture. Broken lines represent calculations performed using a dispersion correction.
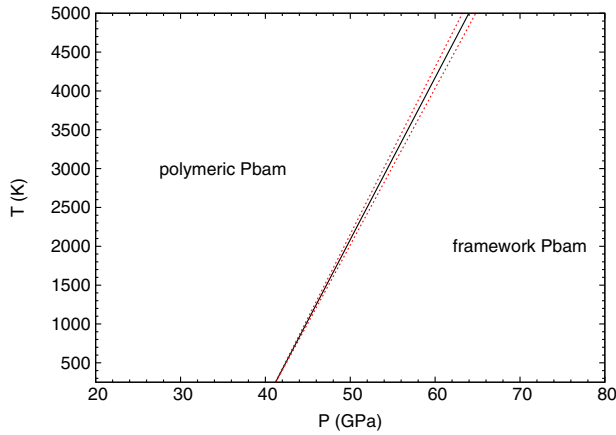
FIG. 4 (color online). Theoretical pressure-temperature phase diagram. The line is calculated using the zero temperature phase transition pressure of 40 GPa and a Clapeyron slope ($dP/dT = \Delta S/\Delta V$) of 4.80 ± 0.16 MPa K^{-1}. The broken lines denote the error in the gradient.

respect to pressure; however, the phase transition pressures are reduced by 5 to 8 GPa.

The stability of framework *Pbam* was tested against decomposition into likely combinations of products from the ternary hull of the C-N-O system at 60 GPa. It was found to exothermically decompose to $\alpha - C_3N_4$, $I\bar{4}2d$ CO_2 and cg-N.

At ambient pressure, the metastable framework *Pbam* phase is expected to decompose exothermically to the same products as solid carbon monoxide (graphitic carbon and molecular CO_2) and cg-N (molecular N_2),

$$4CNO \rightarrow 2CO_2 + 2C + 2N_2 + 4.1 \text{ eV}.$$
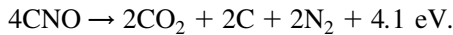
The *chemical* energy released during this reaction is estimated to be 4.1 eV at the PBE level (including a semi-empirical dispersion correction [32]). This corresponds to an energy density of approximately 2.2 kJ g^{-1}, which compares favorably to values in the range 1 to 3 kJ g^{-1} for modern explosives such as TATB, RDX, and HMX [24].

Both the polymeric and framework *Pbam* structures have a six-ring motif containing four 3-coordinated nitrogen and two carbon atoms that are sp^2 hybridized in the former (resulting in a C=O double bond), and sp^3 in the latter (two C-O single bonds). Given the similarities in the stacking of these units, a phase change is conceivable, although the separate lines in Fig. 3(b) suggest that there is an associated energy barrier. This transition is expected to occur at 40 GPa at zero temperature. By deriving the entropy from the phonon spectra, we estimated the Clapeyron slope to obtain the temperature dependence of the transition pressure (Fig. 4).

The Knoop hardness of the framework *Pbam* phase at ambient pressure was calculated to be 18 GPa using the electronegativity method [33,34], which is below the superhardness threshold of 40 GPa. Its bulk modulus, 288 GPa, is lower than that of cubic gauche nitrogen which

has been experimentally determined as over 300 GPa [2]. This, and the low Knoop hardness, can be attributed to the large interstitial voids in this structure.

We find that a mixture of two parts CO to one part N_2 polymerizes to form a one-dimensional polymeric phase with *Pbam* symmetry under undemanding conditions compared with cg-N (below 18 GPa). This low-pressure transition is somewhat surprising considering the physical similarities of CO and N_2 molecules. This phase will transform to a three-dimensional framework with the same symmetry at the relatively low pressure of 40 GPa at zero temperature. This framework represents the best of both worlds; the carbon monoxide allows the mixture to polymerize at a low pressure, and the nitrogen stabilizes the mixture in a fully covalent crystalline form. It has a high-energy density of 2.2 kJ g^{-1} with respect to molecular nitrogen, carbon dioxide and graphitic carbon, making it comparable to conventional explosives, and it is dynamically stable at ambient pressure, fulfilling the crucial requirements of a HEDM.

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[28] All structures were relaxed at the generalized gradient approximation (GGA) level using the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional. Valence electrons were represented in a plane wave basis set with a cutoff of 340 eV, and core electrons were modelled using ultrasoft pseudopotentials which were tested against hard pseudopotetials comparable to all-electron quality. Monkhorst-Pack k-point grids were generated on a per cell basis, using a spacing of $2\pi \times 0.07$ Å^{-1}. All DFT calculations were performed using the CASTEP code [30]. Higher precision calculations were performed using a plane wave cutoff of 500 eV, a k-point grid spacing of $2\pi \times 0.03$ Å^{-1} and tighter convergence tolerances. Phonon calculations were performed using density functional perturbation theory (DFPT) as implemented in CASTEP [31], on a $3 \times 5 \times 9$ Monkhorst-Pack grid, using norm-conserving pseudopotentials and a plane wave cutoff of 900 eV, in order to test the dynamical stability of the very best structures. In order to avoid a core overlap resulting from the short length of the N_2 bond, decomposition enthalpies were computed using a harder pseudopotential.

[29] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.111.235501 for lattice parameters and fractional atomic coordinates for the three pictured configurations.

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