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Pressure-induced transitions in solid nitrogen: Role of dispersive interactions

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We have investigated the transition from molecular to fully covalent phases of solid nitrogen with an advanced *ab initio* quantum-mechanical method for crystals that rigorously describes weak dispersive interactions. It is demonstrated that the thermodynamic domain of stability of the *cubic gauche* phase (a promising high-energy-density material) extends down to pressures of about 60 GPa and that the high experimental transition pressure of 110 GPa is largely due to kinetic barriers which prevent the dissociation of triply bonded N_2 molecules. The role of temperature is complex: it helps the kinetics of the transition to fully covalent phases while it stabilizes the molecular phases through the entropic term.

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Nitrogen is the only element of the fifth group of the periodic table that crystallizes into molecular instead of fully covalent phases at standard conditions. So far, the existence of 10 different molecular phases of nitrogen can be inferred from the experiment, even if a reliable structural refinement is available just for 5 of them: α, β, γ, δ, and ϵ.[1] Such phases consist of triply bonded N_2 monomers, held together by weak van der Waals interactions. The pressure-induced dissociation of N_2 molecules into "polymerized" fully covalent phases of solid nitrogen was suggested to occur at relatively low pressures by means of *ab initio* simulations;[2,3] in particular, the *cubic gauche* (*cg*) structure was predicted to become more stable than the ϵ one at ~30 GPa within the simplest formulation (local density approximation) of density functional theory (DFT) at the zero-temperature limit.[4] Nitrogen is commonly considered to be an inert element because of the extraordinary stability of the triple bond of its diatomic molecules. Precisely because of the large difference in energy between a single N−N and a third of a triple N≡N bond, the fully covalent *cg* phase has been proposed as a high-energy-density material (HEDM) for applications such as propellant and explosive.[5] The potentialities of *cg* nitrogen as a practical HEDM were early supported by simulations that proved its metastability at ambient pressures[6] and have been recently confirmed by a study that highlights its exceptional mechanical properties.[7]

These predictions have stimulated a lot of experimental work aimed at the synthesis of polymeric nitrogen[8,9] and in 2004, Eremets and *et al.* finally succeeded in synthesizing the *cg* structure at high pressure, 110 GPa.[10] Simulations have predicted a much lower value of the transition pressure from the molecular phases to the *cg* fully covalent one. In particular, two independent studies,[11,12] where a more sophisticated formulation of the DFT (generalized gradient approximation) is adopted, report a transition pressure of ~55 GPa in the low-temperature region of the phase diagram.

Before drawing any conclusion concerning the large discrepancy between the observed and the predicted transition pressures, three aspects have to be critically discussed:[12] (i) Is standard DFT a reliable technique for the investigation of such a transition? (ii) Is ϵ the proper molecular phase to be adopted in the simulations? (iii) Can the effect of temperature be considered purely kinetic? These questions arise from three facts: (i) standard DFT is known to describe incorrectly the dispersive (i.e., van der Waals) interactions that play a clearly crucial role here; (ii) there is evidence of the existence of at least another molecular phase (ζ) that is more stable than ϵ at high pressures;[13] (iii) in principle, temperature could play a relevant thermodynamic role as well.

In this Brief Report, we study theoretically the transition from molecular to fully covalent phases of solid nitrogen by analyzing all the above-mentioned open points with two quantum-mechanical methods for crystals, which are capable of a correct description of weak dispersive interactions.

To achieve accurate dispersion energies, correlated *ab initio* methods are required. The Hartree-Fock (HF) method correctly describes the Fermi correlation among electrons with the same spin while it does not take into account the instantaneous Coulomb correlation of the electronic motions, that is the source of dispersive interactions. The standard DFT formalism, which is commonly adopted in solid state physics to get rid of the limitations of the HF approximation, includes an approximate treatment of electron correlation but not dispersion, due to the short-ranged nature of the functionals.

Wave-function-based techniques can recover a significant portion of the missing Coulomb correlation: this is the case, for instance, of many-body-perturbation-theory, truncated at order *n* (i.e., Møller-Plesset method, MP*n*), or coupled cluster techniques. At variance with DFT, these techniques provide a good description of weak dispersive interactions,[14–17] also when transitions between chemically different phases are considered (see, for instance, the case of cubic and hexagonal boron nitride).[18] While this strategy is quite routinely used in molecular quantum chemistry, only recently, it has become feasible also for solid-state applications.

Two quantum-mechanical methods are used here that explicitly embody the description of dispersive interactions: (i) a fully periodic MP2 method;[19–22] (ii) the hybrid DFT technique in its B3LYP formulation, augmented with a recently proposed empirical dispersion term (D),[23] reparametrized for molecular crystals (to be referred to in the following as DFT-D).[24,25] The latter method can serve as an independent check of the results obtained with the *ab initio* MP2 scheme and it allows for the solution of the nuclear motion equation in a harmonic approximation and for the evaluation of the corresponding temperature-dependent thermodynamic properties.

We have recently applied both methods to the study of the experimentally well-characterized low-temperature low-pressure region of the phase diagram of nitrogen (i.e., where molecular phases are stable), in order to investigate their merits and limitations in describing dispersive interactions.[26] Reference is made to that work for computational details; in particular, the role of the quality of the basis set of Gaussian functions has been extensively discussed. Three molecular phases have been considered which are stable at zero temperature: the cubic α, the tetragonal γ, and the rhombohedral ϵ with 4, 2, and 8 molecules per cell, respectively. The computed equilibrium geometries, cohesive energies (corrected for zero-point motion), bulk moduli, Grüneisen's parameters, pressure-volume curves, and volume losses at the transition have been found in a good agreement with the experiment. Of particular relevance to our discussion are the MP2 simulated transition pressures between such purely dispersively bonded crystals: 0.42 GPa for the $\alpha \rightarrow \gamma$ and 2.25 GPa for the $\gamma \rightarrow \epsilon$ transition with experimental values of 0.36 and 2.00 GPa, respectively.[27,28]

The thermodynamic state function which dictates phase transitions is the Gibbs free energy. Its estimate in the present work can be expressed as follows:

$$G^X(V,T;\phi) = E_{\text{el}}^X(V;\phi) + E_{\text{vib}}(V,T;\phi) + PV - TS_{\text{vib}}(V,T;\phi). \tag{1}$$

Here X is the technique adopted (MP2 or DFT-D) for computing the electronic energy $E_{\text{el}}^X(V;\phi)$ of a given phase (ϕ) for a given volume (V);[29] $E_{\text{vib}}(V,T;\phi)$ and $S_{\text{vib}}(V,T;\phi)$ are the vibrational contributions to the internal energy and entropy at the temperature T, respectively, estimated using the harmonic model and the vibrational spectrum resulting from the DFT-D calculations; finally, pressure (P) and volume are related to each other through the relationship:

$$P = -\frac{\partial}{\partial V}\left[E_{\text{el}}^X(V;\phi) + E_{\text{vib}}(V,T;\phi)\right]_S. \tag{2}$$

The derivative is analytically evaluated after fitting the energy-versus-volume data with the Murnaghan's equation of state.[30]

Figure 1 is indicative of the kind of calculations performed in the present work. Ten configurations, corresponding to different volumes, have been considered for both the ϵ and *cg* phases; for each configuration, $E_{\text{el}}^{\text{MP2}}(V;\phi)$ has been computed with a correlation-consistent triple-ζ basis set, as discussed in Ref. 26. After fitting both experimental and computed data to Murnaghan's equation of state, our theoretical determination of the bulk modulus B_0 and the zero-pressure atomic volume V_0 of the *cg* phase (327 GPa and 6.61 Å^3) can be compared with their experimental counterparts (298 GPa and 6.59 Å^3);[10] the agreement is noteworthy. As is clear from Fig. 1 and from Eqs. (1) and (2), the $\epsilon \rightarrow cg$ transition pressure at zero temperature can be graphically represented by the slope of the tangent to the two curves, by neglecting the difference in the zero-point energy between the two phases.[31] The MP2 estimated value is 62 GPa that is, ~10–30 GPa higher than that predicted by standard DFT in several formulations.[32]

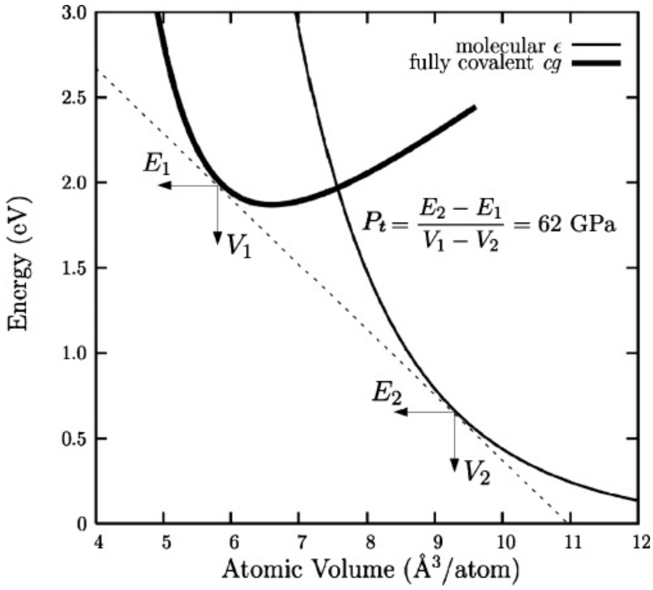

FIG. 1. Energy versus volume curves as obtained by fitting the computed MP2 data to the Murnaghan's equation of state. The reported data for the ϵ molecular phase (thin solid line) and for the *cg* fully covalent phase (thick solid line) are energy differences with respect to the equilibrium energy of the α phase. The values (E_1,V_1) and (E_2,V_2) are those where the two phases have the same Gibbs energy. The transition pressure P_t is graphically represented by the slope of the tangent to the two curves (dashed line). All data are per atom.

For a comprehensive discussion of the various points raised above, reference will now be made to the data in Fig. 2. The various curves report, as a function of pressure, the *difference* ΔG^X in Gibbs free energy with respect to the *cg* phase, estimated using the same method and at the same temperature.

Let us first discuss the influence of the quantum-mechanical method adopted, by comparing the zero-temperature data concerning the ϵ phase, obtained with the two theoretical models. From inspection of Fig. 2, it is clear that the description of the pressure dependence of the enthalpies of the two phases is equal for MP2 (thick solid line) and DFT-D (thin solid line), the only difference between the two being a slight rigid shift in the energy axis. The transition pressure, graphically represented by the crossing with the zero line in the figure, is 62 and 63 GPa in the two cases. The effect of taking into account van der Waals interactions is that of widening the thermodynamic domain of stability of the molecular phases, but not to an extent that could explain the high transition pressure observed experimentally (>110 GPa), thus suggesting that large kinetic barriers could be responsible for such a discrepancy. Nevertheless, as mentioned above, before validating such a conclusion, both the effect of the considered molecular phase and the role of temperature should be rigorously investigated.

We now address the problem of the adopted molecular phase in the simulations. The transition pressure from molecular to fully covalent phases of solid nitrogen is largely dominated by the different typologies of bonding interactions which take place in the structures involved; as

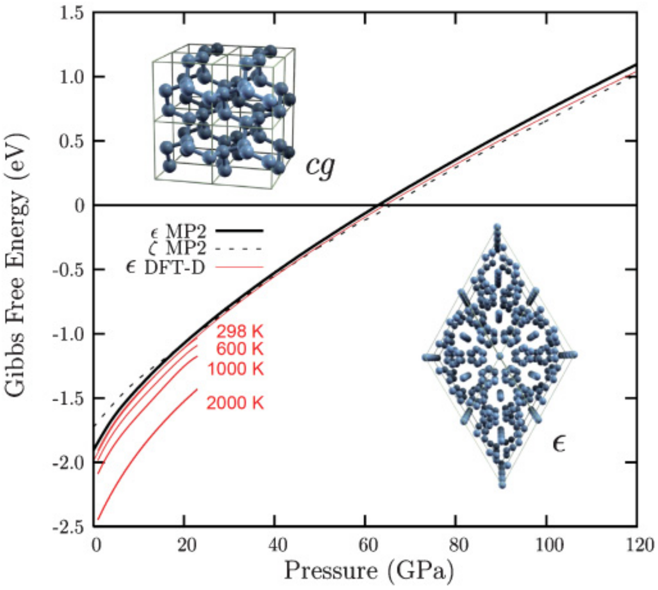

FIG. 2. (Color online) Gibbs free energy per atom as a function of the pressure. The reported data are differences with respect to the cg phase. The MP2 curves for the ϵ and ζ phases are represented by the thick solid and dashed lines, respectively. DFT-D data for the ϵ phase are reported as a red thin solid line. Data are also reported for some finite temperatures as obtained at DFT-D level for the ϵ phase (red thin solid lines in the low-pressure region where they have actually been computed). The two insets show the crystalline structure of the rhombohedral ϵ phase (space group $R\bar{3}c$) and the fully covalent cg phase (space group $I2_13$).

already pointed out by other authors,[12] it sounds implausible that another molecular phase could exist with an enthalpy so different from the other molecular phases to justify a transition pressure above 100 GPa. However, through infrared and Raman spectroscopy, there are evidences of the existence of an intermediate molecular phase, ζ, between ϵ and cg in the low-temperature region of the phase diagram.[13] The structure of the ζ phase is still unknown; nevertheless, experimental observations indicate a group-subgroup relation with the ϵ phase and the same number of molecules per primitive cell. A monoclinic $C2/c$ symmetry has recently been proposed for that phase along with a description of the possible structural transition mechanism which links the ϵ to the cg phase, through ζ.[1]

We have calculated the $G^X(V,0;\zeta)$ function using both the MP2 and the DFT-D method. The resulting ΔG^{MP2} data are reported in Fig. 2 as a dashed line. In the low-pressure region of the figure, a crossing between the ϵ and the ζ curves occurs at 19 GPa which represents the $\epsilon \rightarrow \zeta$ transition pressure in the zero-temperature limit (the experimental value is known to be in the range 16.5–19 GPa).[1,13] Beyond this crossing, the two curves run almost parallel, thus confirming the expected similarity between the pressure dependence of the enthalpies of these two molecular phases. The ζ curve crosses the horizontal line at 64 GPa which represents the MP2 $\zeta \rightarrow cg$ transition pressure (the corresponding DFT-D value is 66 GPa). The thermodynamic transition pressures computed for the $\epsilon \rightarrow cg$ and for the $\zeta \rightarrow cg$ transitions are found to be almost identical, thus proving that the structure of the starting molecular phase cannot reliably be considered a significant factor in explaining the high experimental transition pressure from molecular to fully covalent phases of solid nitrogen.

The last factor to be discussed is temperature. From the experiments, its effect is known to be relevant as concerns the kinetics of the *molecular* → *fully covalent* phase transition in solid nitrogen: (i) there is a strong dependence from T of the observed transition pressure (to a fully covalent amorphous phase) in the low-temperature ($T < 700$ K) region of the experimental phase diagram;[33] (ii) the transition to the cg phase occurs only at $T > 2000$ K.[10] In Fig. 2, we report $\Delta G^{\mathrm{DFT\text{-}D}}$ data obtained for the ϵ phase at different temperatures: 300, 600, 1000, and 2000 K in a range of pressures from 0 to 20 GPa where our computed data are maximally reliable. It has been suggested that the entropic term $-TS$ would favor fully covalent with respect to molecular phases of solid nitrogen as they are more “dissociated”.[33] From Fig. 2, however, it clearly emerges that with increasing temperature, the molecular phase is strongly stabilized by the entropic term with respect to the fully covalent phases. The role of temperature is then found to be complex: from the one hand, it helps the transition by favoring its kinetics while from the other hand, it stabilizes the molecular phases through the entropic term. From the relative slope of such curves, we can argue that the entropic gain of the molecular phases reduces while the pressure increases.

In conclusion, this paper shows how the MP2 technique for the *ab initio* description of weak van der Waals interactions provides a reliable insight on the transition from molecular to fully covalent phases of solid nitrogen. The thermodynamic domain of stability of the fully covalent cg phase (a potential HEDM) is found to extend down to 63 GPa in the low-temperature region of the phase diagram. The high transition pressure that is observed in the experiments is reproduced neither by accurately describing dispersive interactions nor by considering a different starting molecular phase. These findings help to strengthen the hypothesis of the kinetic origin of such a high transition pressure, due to the large activation barriers which prevent the dissociation of strongly bonded N_2 molecules. Let us stress that, within the frame of *ab initio* solid-state quantum chemistry, the possibility of directly handling the kinetics of such a transition (i.e., of estimating its activation energy) usually passes through the search of an adequate transition state, following standard techniques described in Ref. 34. From this work, it appears that the values of 110 GPa and 2000 K in the transition from molecular to fully covalent phases can be considered as the result of a balance between two opposite effects: a temperature increase hinders the transition from an entropic point of view while working kinetically in the opposite direction by favoring the dissociation of triply bonded N_2 molecules.

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