Decomposition and Polymerization of Solid Carbon Monoxide under Pressure

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By performing constant-pressure deformable-cell *ab initio* molecular dynamics simulations we have studied the pressure-induced chemical instability of CO above 5 GPa. The simulation shows that, contrary to previous speculations, polymerization proceeds without CO bond dissociation. The resulting polymer consists of a disordered network of small polycarbonyl $(CO)_n$ chains connecting fivefold C_4O cycles. The computed vibrational spectra and electronic gap agree very well with (and shed light on) very recent experimental data. [S0031-9007(98)07059-8]

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The high pressure behavior of simple molecular solids such as CO is presently under intense scrutiny, and is intriguing. Unlike its isoelectronic partner N_2 which is a stable molecular crystal up to at least 180 GPa [1], solid carbon monoxide (CO) becomes chemically unstable already at about 5 GPa at room temperature [2,3], due to polymerization of the initial molecular crystal [2]. Pressure-induced polymerization of molecular crystals has recently attracted considerable interest. Irreversible polymerization in the solid phase has been obtained experimentally under shock waves or hydrostatic pressure conditions in several systems such as CS_2 [4], C_2N_5 [5], and a number of unsaturated hydrocarbons [6–8]. The microscopic mechanisms of such processes have also been investigated, for the case of acetylene, with first-principles theoretical methods [9]. The possible pressure-induced polymerization of CO is particularly intriguing, both because of the high abundance of this molecule in nature, and because a polymer entirely composed of carbon and oxygen has never been investigated in detail so far, while it might open the way to the synthesis of a new class of materials.

Molecular CO crystallizes, above 4 GPa, into a rhombohedral ϵ phase at low temperature, and into a cubic, rotationally disordered δ phase at temperatures higher than ~100 K [10]. When compressed above 5 GPa δ-CO transforms, in equilibrium at room temperature, to a polymerlike colorless or yellow solid [3]. A similar reaction can be induced at slightly lower pressures by laser irradiating δ-CO [2,11]. IR spectra on the recovered samples revealed a strong similarity with those of poly(C_3O_2) [12]. On the basis of these findings, one proposed mechanism for the pressure-induced reaction was the following: above ~5 GPa, CO begins to disproportionate chemically, forming carbon suboxide C_3O_2 and oxalic anhydride C_2O_3; C_3O_2 would then polymerize, and C_2O_3 only dimerize [11].

Recently, Lipp *et al.* [13] carried out a more detailed IR and Raman analysis of light-exposed and pressurized solid CO. Surprisingly, their data did not reveal any evidence of poly(C_3O_2), and could instead be interpreted with the presence, among other products, of a polymer with hypothetical vinyl esterlike repeat unit: —(C=O)—O—(C—)=C<.

In this paper we study theoretically the pressure-induced decomposition of CO using a recently developed method for constant-pressure deformable-cell first-principles molecular dynamics [14,15]. In our calculations, we have adopted the generalized gradient approximation [16] to the local density approximation. A Car–Von Barth-type pseudopotential [17] was used for carbon and a numerical Troullier-Martins [18] for oxygen, both in Kleinman-Bylander factorized form [19]. The integration time step was fixed to 1.2×10^{-16} s. The electronic wave functions, assumed to have the same periodicity of the (deformable) simulation cell, were expanded on a plane wave basis set, up to a kinetic energy cutoff of 80 Ry. We reproduce quite satisfactorily the properties of an isolated CO molecule, namely, its bond length $d_{\text{C-O}}^{\text{calc}} = 1.126$ Å ($d_{\text{C-O}}^{\text{expt}} = 1.1283$ Å), its vibration frequency $\omega_e^{\text{calc}} = 2150\ \text{cm}^{-1}$ ($\omega_e^{\text{expt}} = 2169.8\ \text{cm}^{-1}$), the orientation and absolute value of its dipole moment $\|\mu^{\text{calc}}\| = 0.18D$ ($\|\mu^{\text{expt}}\| = 0.12D$), and its singlet excitation gap $E^{\text{calc}} = 7.0$ eV ($E^{\text{expt}} = 8.1$ eV). The dipole moment, in particular, is known to represent a very delicate test for calculations on this molecule, its sign being inverted with respect to what is expected from a conventional ionic model.

We started our calculations with a CO molecular solid in the disordered-cubic δ phase. This phase has $Pm3n$ symmetry and the unit cell contains eight molecules. Among the eight sites, six are disk-orientationally disordered, while the other two are spherically orientationally disordered. However, the time scale of our simulations (a few picoseconds), is too short for the equilibration of the (slow) molecular rotation degrees of freedom: molecules do not have enough time to rotate, as they would do on a nanosecond time scale. Aiming for an unbiased result, we therefore started from initial random orientations of the molecules, performing many different compression runs with different initial conditions. Three different supercells have been used, containing 8, 16, and 32 molecules, respectively. We set the initial conditions of the simulation to a temperature of 200 K and a pressure of 9.8 GPa (i.e., above the pressure at which the chemical instabilty sets in experimentally). The equilibrium volume was $14.6\ \mathrm{cm}^3/\mathrm{mol}$, in good agreement with the extrapolated experimental equation of state [3]. At these conditions we found that the simulated CO remains in the randomly oriented δ phases, with no evidence of molecular decomposition within ~ 1 ps [20]. There are clearly large energy barriers which hamper the transformation process which may be lowered by further raising the pressure.

We then compressed directly up to 15 GPa. In all simulations the system quickly transformed, within 0.25–0.5 ps, into a new stable state which then remained unchanged, and apparently in equilibrium, at least for several ps. Annealing and heating up to a few thousand Kelvin caused no further change. The transformation was accompanied by a 30% drop in the specific volume. The energy released by the transformation process was similar in all the simulations (about 0.65 eV/mol), and was absorbed by a Nosè thermostat coupled to the ionic degrees of freedom [21].

When analyzed in detail the transformation consists of two separate steps. The early stage of the transformation process (e.g., before 0.25 ps) consists in the sudden formation of small pieces of a very simple polycarbonyl polymer, built with —(C═O)— units. The polymer forms because as soon as two carbon atoms from neighboring molecules come close enough to each other due to compression (≤ 2.1 Å), they attach, forming a C—C bond of length $d_{\text{C-C}} \simeq 1.53$ Å. The C═O bond length is $d_{\text{C-O}} \simeq 1.20$ Å and the C-C-C angle is 110°. In a second step (i.e., roughly between 0.25 and 0.5 ps), some C═O bonds open up, and oxygens get into bridge positions between carbons, forming C—O—C units ($d_{\text{C-O}}^{\text{bridge}} \simeq 1.38$ Å, with an average C—O—C bending angle of 115°). Because of the formation of these bridges, the bits of polymer formed earlier tend to bend, leading to the formation of very characteristic fivefold cycles which are present in all our final products (Fig. 1). The remaining carbonyl units have a C═O bond length of about 1.19 Å, very close to that of the initial carbonyl polymer.

We never observed any C—O bond breaking, and we can therefore rule out the polymerization mechanism involving formation of poly(C_3O_2) proposed in early experimental works [2]. The final polymers are indeed very different from poly(C_3O_2), being formed of chains combining fivefold cycles and simpler linear tracts. The chains, formed by cycles and polycarbonyl tracts, are partially interconnected, the resulting product looking like a quasi-2D structure.

These rough features are present in all the simulations. However the length of the interconnecting chains, their spatial arrangement, and the density of the fivefold cycles, depend on simulation cell size and/or initial conditions. In particular small cells show an artificial quasicrystalline order which disappears in larger cells. There appears to be a real tendency of the polymerization to develop disordered structures (see Fig. 1) rather than long-range crystalline order, as expected from the high level of energetic degeneracy of the products of our simulations. In fact, a simple total energy estimate based on bond energies [22] yields very close values for all these different structures, in nice agreement with the simulation results.

In order to address existing experimental observations—mostly spectroscopical—we used our real-time dynamical simulations to characterize the resulting products. To obtain Raman and IR spectra, we computed the Fourier transform of the velocity autocorrelation function.

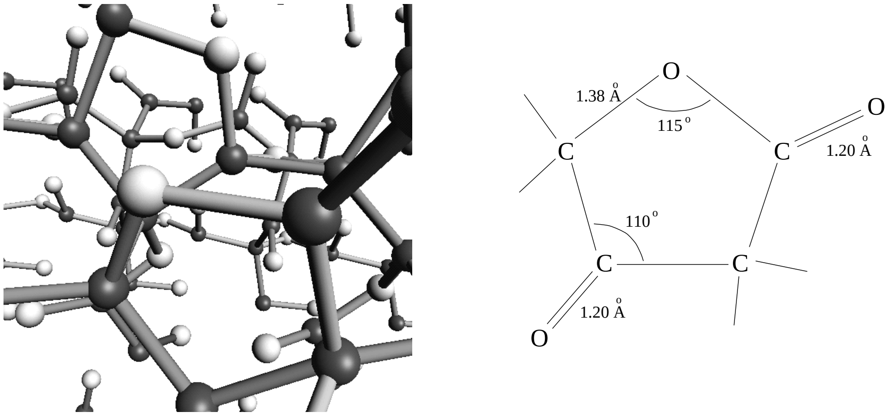

FIG. 1. Left: Snapshot of the simulation endpoint showing the decomposition products. The simulation cell initially contained 32 molecules. Grey balls are carbon atoms; white balls are oxygen atoms. Right: Sketch of the fivefold-cycle unit. Bond angles and bond lengths refer to average values calculated along a 1 ps molecular dynamics run. These cycles are interconnected through linear polycarbonyl pieces.

The frequency spectrum obtained from the largest simulation cell (initially containing 32 CO molecules) is reported in Fig. 2. We focused on the 1000–2500 cm^{-1} domain, where we expect to find the characteristic frequencies of CO groups. We find four bands, labeled *A*, *B*, *C*, and *D* in Fig. 2, and centered at 1210, 1440, 1650, and 1760 cm^{-1}, respectively, with an accuracy of about ± 20 cm^{-1}, due to the finite time scale of the simulations.

By filtering out the eigenvector of Fourier components resonating at 1760 cm^{-1} (band *D*) we can unambiguously assign this peak to the vibration of the —O—(C═O)—C— group in the fivefold cycles. This mode is in excellent agreement with the mode at 1770–90 cm^{-1} of the —O—(C═O)—C— group in fivefold cycles of tetronic acids [23]. The presence of this peak (at 1775 cm^{-1}) in the decomposition products of Lipp *et al.* strongly supports our theoretical findings. With the same procedure we also assign the 1650 cm^{-1} peak (*C* in Fig. 2) to the vibration of the —C—(C═O)—C— group in the fivefold ring. Although this frequency is rather low compared to characteristic ketonic modes (1700–1800 cm^{-1}), the latter is known to be quite sensitive to the chemical environment [22]. A peak at 1650 cm^{-1} is also present in the IR spectra of Lipp *et al.* [13]. The two lower vibrational broader bands *A* and *B* are mainly related to vibrations of components in the bridging units between the cycles. They correspond reasonably well to the peaks at 1130, 1210, and 1310 cm^{-1} measured by Lipp *et al.* Additional features observed experimentally above 1775 cm^{-1} are not found in the calculation, strongly supporting their attribution [13] to unreacted CO, to CO_2 molecules, and to overtones.

We also analyzed the electronic spectrum. We find that the transformed material is insulating, with an average gap of about 1.9 eV, in excellent agreement with the yellow color displayed by the products of the diamond-cell reaction.

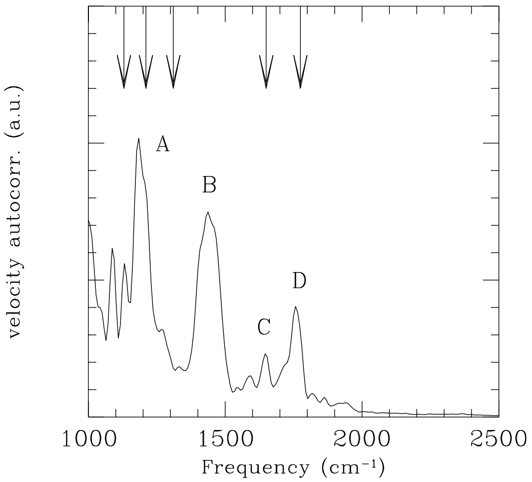

FIG. 2. Frequency spectrum of the velocity-velocity correlation function of our decomposition products. Arrows indicate positions of peaks in the IR absorption spectrum of Ref. [13]

We have therefore found a remarkable agreement of the properties of the experimental material—obtained under combined pressurization and light exposure—and our simulated system subject just to pressure. We speculate that the influence of light on the decomposition process is probably twofold. On the one hand, by promoting CO molecules of the crystal into excited states (we calculate an electronic gap of 2.5 eV for δ-CO at 9 GPa), light is likely to favor and accelerate the polymerization mechanism, as is the case in other systems [9]. On the other hand, laser heating might simply promote the formation of graphite and CO_2 (which are in fact observed by Lipp *et al.*, and possess a larger heat of formation) by simple annealing.

Finally, we find that the polymer is stable upon pressure release, yielding a zero pressure density of about 2.7 g/cm^3. Moreover, we find that the fivefold cycles, once formed, are extremely stable upon heating, surviving at least up to 2500 K at 10 GPa.

In conclusion, we have found in a series of extensive *ab initio* simulations a new mechanism for the decomposition of CO above 5 GPa. The final product is a polymer, characterized by fivefold cycles each involving one C—O—C bridging oxygen and two carbonyl groups, interconnected by a network of polycarbonyl chains consisting of —(C═O)— repeating units. The simulated polymer is stable upon pressure release and heating. The previously hypothesized C_3O_2 polymer and C_2O_3 dimers do not appear. The computed vibrational and electronic properties of the final material appear to agree very well with those seen in experiment.

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