Dimerization of CO_2 at High Pressure and Temperature

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Dedicated to Professor Michele Parrinello on the occasion of his 60th birthday.

Understanding the behavior of simple molecular systems under the combined effect of high pressure (*P*) and temperature (*T*) has important implications in the modeling of planetary interiors, in the chemistry of detonation, and in the synthesis of new materials. Extreme conditions of *P* and *T* can be partially accessed in the laboratory either in heated diamond-anvil cells or in shock wave experiments, where dramatic changes in the chemical and physical properties of simple molecules have been reported.[1] Depending on the detailed situation, compression may result in the formation of intermolecular bonds, or in disproportionation, or even in full dissociation into the constituent elements. In such a context, the theoretical prediction of stable or metastable structures and of their properties is highly desirable. However, this requires an accurate quantum description, capable of discriminating the often subtle changes in the nature of chemical bonds. First-principles molecular dynamics methods with variable-cell, constant-pressure dynamics[2]—a natural derivation of the two revolutionary methods introduced more than 20 years ago by Michele Parrinello together with Roberto Car[3] and Anees Rahman[4]—offer a unique tool for this kind of exploration.

Molecular CO_2 was independently observed[5] and predicted[6] to transform into extended quartz-like covalent solids at moderately high pressures (about 50 GPa). The actual structure of this high-pressure phase, as well as its *P–T* range of thermodynamic stability, are still widely debated.[7–11] High temperatures (thousands of Kelvin) were crucially required in the synthesis of an extended covalent network, both in experiments[5] and in theoretical simulations,[6] which indicated that large reaction barriers are overcome in the synthesis. One possible explanation is that these barriers are associated with the rehybridization of carbon atomic orbitals, from linear (sp) in the molecule, to tetrahedral (sp^3) in all candidates for the extended solid proposed so far. Carbon is well-known to change its hybridization state with pressure. For example, carbon's hybridi-

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zation changes from sp² to sp³ across the graphite–diamond transition, and varies all the way from sp to sp² and finally to sp³ in the polymerization of acetylene.[12] Because of this, it is also conceivable that in CO_2 new, as yet undiscovered, molecular or extended species with carbon in an intermediate sp² hybridization state may act as precursors to the sp³ covalent extended phase. Indeed, recent experiments suggest that the transition from molecular CO_2 to the extended phases could be more complex than initially thought.[10–15]

Herein, we examine liquid CO_2 by performing first-principles, constant-pressure molecular dynamics simulations up to 50 GPa and 4000 K. This approach allows us to look at the various species that may exist within the liquid at conditions similar to those at which polymerization into a condensed-phase material occurs. As such, we are able to gain insight into the nature of possible precursors or reaction side products which may play an important role in the formation of the extended CO_2 solid under extreme conditions.

Simulation Method

Constant-pressure molecular dynamics simulation was implemented with the first-principles variable-cell method of Focher et al.[2] Here, a density functional theory (DFT) approach to electronic states allows the accurate and predictive description of a changing chemical environment. Pressure-induced structural transformations are dealt with using the variable-cell constant-pressure method.[4] The combination of DFT with the variable-cell approach provides an effective and unbiased method to explore the large phase space of the molecular systems at extreme conditions. Timescale and size limitations intrinsic of DFT-based simulations lead in some cases to the need for overpressurizing the system to induce the transitions.[16] However, such problems are more severe at low temperatures and in solid systems, while experience with liquids at high temperatures indicates that transitions occur without significant hysteresis at extreme conditions.[17] The approach was successfully proved in the description of pressure-induced phase transformations in a variety of molecular systems, including the polymerization of carbon monoxide[18] and the molecular to nonmolecular transformation of carbon dioxide.[6] Herein, we used the Becke–Lee–Yang–Parr generalized-gradient density functional (BLYP),[19,20] and employed nonlocal[21] pseudopotentials for ion cores,[22] thus expanding valence electron wave functions in a plane-wave basis set. The basis set was truncated at a kinetic energy cutoff of 80 Ry, referred to the simulation cell of the first configuration of the ab initio run. Plane-wave momenta were then rescaled dynamically during the simulation following the changes of the simulation cell.[2] The simulation cell contained 32 molecules, with Γ-point sampling of the Brillouin zone, suitable for the simulation of a liquid. Validity of these approximations for the carbon-based molecular system was thoroughly tested in previous investigations,[6,18] with excellent results in every respect.

Results and Discussion

We prepared an initial configuration of liquid CO_2 at 2000 K and 10 GPa starting with atomic positions generated under these conditions in a classical molecular dynamics simulation (based on empirical interaction forces proposed and tested in the literature[23,24]), and then running the configuration by first-principles molecular dynamics for about 1 ps. Subsequently, T and P were rapidly raised to 4000 K and 20 GPa within another picosecond, after which first-principles molecular dynamics was continued at constant P–T conditions for another picosecond. A temperature of 4000 K is higher than any temperature reached so far in static experiments on CO_2, and may even be above the dissociation limit.[10] The short duration of our simulations does not allow for full dissociation, therefore here we take advantage of very high temperatures only to speed up reactions within molecular species. In this simulation, a large number of intermolecular collisions took place in the picosecond of dynamics at 4000 K and 20 GPa. Among these, one resulted in the formation of a metastable dimer, which lasted about 40 fs. Figure 1 shows a snapshot of the dimer taken during its short lifetime, after which the dimer broke up into the two original molecules.
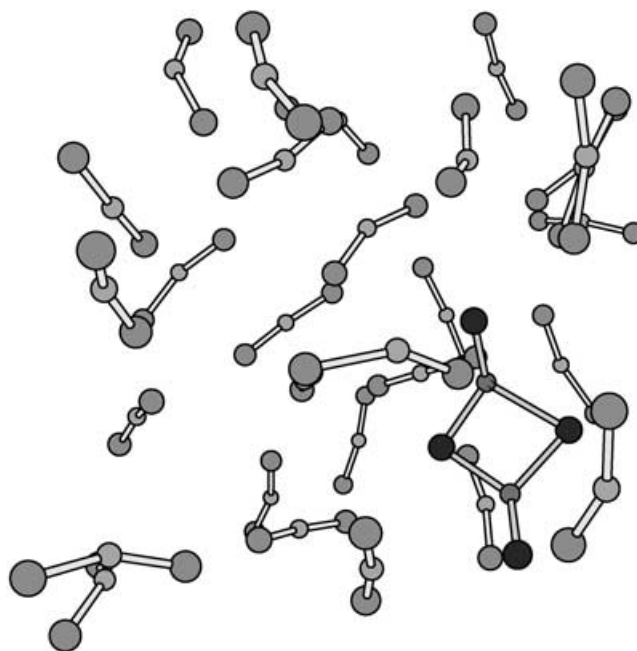

Figure 1. The dimer in liquid CO_2 at 4000 K and 20 GPa. Oxygen atoms are the larger spheres, and the dimer atoms are in a darker shade.

To increase the binding tendencies and to check whether more extended polymerization could require some degree of overpressurization in our simulations, we increased the pressure to 50 GPa. At this pressure extended covalent structures could be energetically favored.[5,10,11] However, transformation to this phase did not occur during the subsequent 2 ps of simulation. Indeed, in the simulation of Serra et al.,[6] a spontaneous transition to quartz-like structures within such short simulation times was only observed above 100 GPa, probably as a consequence of the overpressurization problem mentioned above. During the present high-pressure, high-temperature liquid dynamics, two additional collision events resulted in the formation of the same CO_2 dimer seen at lower pressure. The dimer was quasiplanar, with only slight deviations from planarity resulting presumably from the anisotropic environment of the liquid, which thus suggests sp² hybridization of carbon. The dimer molecule contains a central square motif with alter-

nating oxygen and carbon atoms. The two outer oxygen atoms possess a shorter bond distance, and are aligned with the carbon atoms along a diagonal of the square (see Figures 1 and 2). Plots of the valence electron density (not shown) clear-
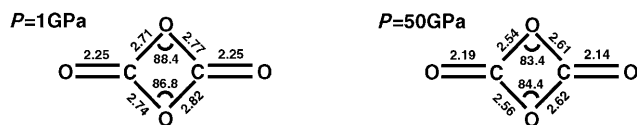
Figure 2. The structure of the dimer at 1 and 50 GPa. Distances in a.u.

ly indicate bonding density between the two CO_2 molecules in the dimer, which confirms that covalent bonding does occur within the square motif. The bridging oxygen atoms were exchanged between the CO_2 molecules after the dimers broke, further indicating that covalent bonds were indeed formed between the two molecules. Vibrations could be observed and their frequencies estimated during the 40-fs lifetime of the dimer, at both 20 and 50 GPa. In both cases, we observed in the dimer a sizable red shift (of about 200 cm^{-1}) of the infrared active peak of the CO_2 molecule (see below for further discussion).

The finite dimer lifetime at 4000 K suggests metastability at lower temperatures. To test this suggestion, we quenched the dimer-containing configuration below 1000 K at 50 GPa. In a subsequent 1-ps dynamics under these conditions, the dimer did not break. This finding is a stronger indication of metastability than previously found at higher temperature and confirms the existence of a high energy barrier against dissociation, which is reasonable for covalent bonding and for the need of carbon to change its hybridization state to break the dimer. However, as only relatively short simulation times are accessible in first-principles simulations, we could not extract the height of this energy barrier. When we finally reduced the pressure to below 10 GPa, at the same temperature, the dimer remained stable for the whole run (of about 1 ps). This is consistent with recent first-principles calculations by Frapper,[25] which showed that even an isolated planar dimer is locally stable. Figure 2 shows a schematic structure of the dimer at 50 GPa and at low pressures, the latter of which compares well with the isolated dimer calculations.[25]

Figure 3a shows the Fourier transform of the velocity–velocity autocorrelation function for both the dimer and the single CO_2 molecules at 50 GPa. Due to an unphysical dragging force exerted by the electronic cloud, the dynamics of nuclei during a high-temperature Car–Parrinello simulation is known to show a spurious additional atomic inertia that red-shifts the frequency position of peaks in the vibrational density of states.[26] We remedied that in the following way. Room-temperature frequencies of solid CO_2 at 50 GPa can be easily extrapolated from existing experimental data.[27,28] We calculated the corrected carbon and oxygen masses by comparing the experimental frequencies with our results (dashed line in Figure 3a), and subsequently using these masses to appropriately correct the simulated dimer frequencies (solid line in Figure 3a).[26] Using the corrected data, we analyzed the dimer vibration spectra, and found that the CO_2 Raman-active mode at
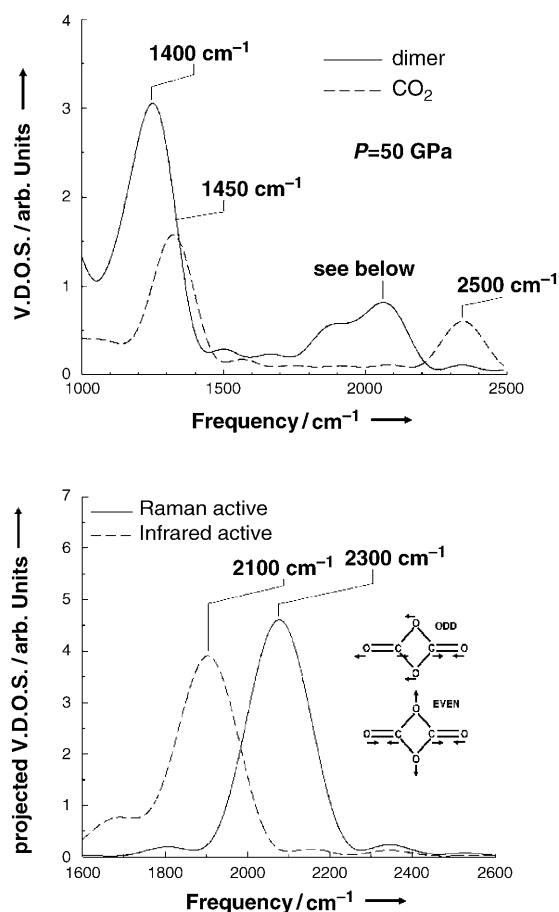
Figure 3. a) Vibrational density of states (VDOS) as obtained from the Fourier transform of the velocity–velocity autocorrelation function for CO_2 and CO_2 dimer at 50 GPa. b) Fourier transform of the projected velocity–velocity autocorrelation function for the dimer onto the even (Raman active) and odd (infrared active) modes. These two modes are also schematically shown as insets. Peak frequencies corrected for electronic dragging are labeled in both figures.

1450 cm^{-1} [14] is basically unchanged (1400±50 cm^{-1}) in the dimer. However, the higher-frequency IR mode of molecular CO_2 near 2500 cm^{-1} is considerably red-shifted by about 400 cm^{-1} and shows a clear bimodal structure.

Detailed analysis of the origin of such a double-peak structure showed that the high-frequency infrared-active mode of the CO_2 molecule can be combined into two high-frequency modes of the dimer (see Figure 3b), one of which is odd and IR active, with the other even and Raman active. The structure at 2000 cm^{-1} shown in Figure 3a is in fact composed of these two overlapping peaks. We projected the motion of the ions in the dimer onto the even and odd symmetries, and resolved the double-peak structure (Figure 3b). The Raman-active mode has the largest frequency, as confirmed by a heuristic analysis based on spring constants between the ions. Using the frequency correction described above, at 50 GPa we obtain a frequency of 2100±100 cm^{-1} for the IR-active mode and of 2300±100 cm^{-1} for the Raman-active mode. If we assume that these frequencies scale with pressure similarly to the high-frequency IR mode of the monomer, then the Raman-active mode should drop to about 2200±100 cm^{-1} at 10 GPa.

Indeed, just such a peak at 2240 cm^{-1} has been observed in the $P = 9$ GPa Raman spectrum of a sample obtained from the high-temperature (> 2000 K) combustion of carbon and oxygen.[15] The lack of Raman activity for the single molecule, and the proximity of the experimental peak frequency to our estimate for the Raman-active peak of the dimer at the same pressure, suggests that the observed peak may be attributed to the high-temperature formation of C_2O_4 entities and their metastable quenching at ambient temperature. A gas-phase calculation of the harmonic normal modes of C_2O_4 also finds the IR- and Raman-active bands at 1960 and 2110 cm^{-1}, respectively. For comparison, we also investigated larger cyclic oligoacid anhydrides, such as $(CO_2)_n$, as suggested by Frapper et al.[25] The $n = 3$ species is also planar with a central six-membered ring; however, now all O—C—O bond angles have increased from the $\approx 95°$ of the dimer to 116°—that is, closer to the value expected for perfect sp^2 hybridization at the carbon atom. This result has a consequence for the C—O stretching modes in the 1800–2200 cm^{-1} range, in that all three modes are now significantly lower in frequency than that of the dimer: a doubly degenerate IR-active band at 1860 cm^{-1} and a Raman-active band at 1940 cm^{-1}. Similarly, the $n = 4$ and 5 species (and by inference the larger n species) also contain larger O—C—O bond angles and no longer display C—O stretching modes as high as 2000 cm^{-1}, which indicates that this feature is unique to the dimer due to the strain induced by the four-membered ring. This analysis further strengthens the hypothesis that the observed Raman-active band at 9 GPa may indeed result from the dimer.

A very crude estimate of the order of magnitude of the transition rate for dimer formation based on our simulations, where three dimer formation events are observed in a 32-molecule cell in a total time of 3 ps, gives a value of about 10^{-10}–10^{-11} s^{-1} at 4000 K. Moreover, considering that each event lasted for about 40 fs, we predict that the order of magnitude of the concentration of dimers should be a few tenths of a percent. The temperatures in the experiments were very likely lower than 4000 K; on the other hand, the known overestimate of transition barriers typical of DFT suggests that the above transition rate should be taken only as a lower limit. Therefore, it is likely that a detectable concentration of dimers could remain frozen in upon rapid quenching from high temperatures.

The possibility of dimer formation at high temperatures and pressures has intriguing implications for the polymerization of CO_2 at high pressures. It is experimentally known that CS_2 under high pressure spontaneously polymerizes into a chain-like structure, with sp^2-hybridized carbon. It thus seems plausible that CO_2 itself might display, for pressures intermediate between the molecular (sp-hybridized carbon) and the extended covalent phases (sp^3-hybridized carbon), a polyacid anhydride structure. Frapper and Saillard have shown that the dimer is the shortest element of a series of cyclic oligoacid anhydrides.[25] According to their calculations, the energetic stability (per CO_2 unit) in vacuum of the molecules in the series increases with their length, which leads to the conclusion that an infinite one-dimensional CO_2 chain with threefold coordinated

carbon is energetically more stable than the free dimer. To pursue this hypothesis we turned to static (zero temperature) calculations of the enthalpy of two possible polymer structures where the planar chains were lying either perpendicular relative to each other, thus optimizing quadrupolar energy, or parallel, thus optimizing closer packing. The latter configuration coincides with the known structure of polymeric CS_2, with exception made for strong bonding between the sulfur atoms of adjacent chains which is clearly impossible in a CO_2 polymer.[29] We chose to restrict our analysis to structures with straight, unfolded chains, as chain folding in solid phases is generally known to introduce strain fields and local atomic distortions that increase the energy with respect to the ideal unfolded structure.[30] Even after full atomic and cell-shape minimization, however, the small gain in volume (V) with respect to the molecular CO_2 solid was not sufficient to compensate for the loss of internal energy (E), thus leading for both perpendicular and parallel structures to a higher enthalpy ($H = E + PV$) with respect to the molecular phase.

The above analysis suggests the following scenario. Kinetically, the dimer is most likely to form by intermolecular collisions; however, the four-membered ring must be reopened at a later stage in a reaction for it to proceed to completion toward the extended solid. The formation of a polyacid anhydride would require a concerted series of collisions forming molecules of increasing length, but even if this occurs it is not likely to lower the overall enthalpy of the system. Even if other reactions occur leading directly to a condensed phase, it may be inferred from the fact that the four-membered ring is not compatible with the lowest-enthalpy silicate structures[6] that this ring must be reopened. Thus, the dimer is best viewed as an unwanted side reaction leading to oligomerization and not the desired product. As a consequence, dimer formation may significantly alter the kinetics of the polymerization process, which may be the reason for the discrepancies in the reported P–T range of observation of the extended polymeric phase.

Conclusions

Herein, we have shown that the chemistry and physics of simple liquid CO_2 at high pressures and temperatures leads to surprising results. Metastable CO_2 dimers make their appearance, short-lived at high temperatures but longer-lived after quenching. In an experiment, measurable changes in the physical properties of the liquid would follow from the dimerization of a substantial fraction of CO_2 molecules. In particular, the kink in the slope of the shock–compression curves of CO_2 observed at 33 GPa[31] could be related to dimer formation. The dimer displays Raman activity at high frequency—about 2300 cm^{-1} at 50 GPa—whereas neither molecular nor nonmolecular forms of CO_2 show this effect, and therefore its identification should be possible. Recent reports of Raman activity in samples quenched from high temperature[15] can be interpreted as evidence of dimers. Finally, these dimers represent an undesirable intermediate on the way toward the bulk extended solid. Thus, future work will focus on possible doping

schemes to suppress dimer formation, which will hopefully lead to polymerization at lower temperatures and pressures.

Acknowledgements

[1] R. J. Hemley, *Annu. Rev. Phys. Chem.* **2000**, *51*, 763.
[2] P. Focher, G. L. Chiarotti, M. Bernasconi, E. Tosatti, M. Parrinello, *Europhys. Lett.* **1994**, *36*, 345.
[3] R. Car, M. Parrinello, *Phys. Rev. Lett.* **1985**, *55*, 2471.
[4] M. Parrinello, A. Rahman, *Phys. Rev. Lett.* **1990**, *65*, 1196.
[5] V. Iota, C. S. Yoo, H. Cynn, *Science* **1999**, *283*, 150.
[6] S. Serra, C. Cavazzoni, G. L. Chiarotti, S. Scandolo, E. Tosatti, *Science* **1999**, *284*, 788.
[7] C. S. Yoo, H. Cynn, F. Gygi, G. Gali, V. Iota, M. Nicol, S. Carlson, D. Haussermann, C. Maiboit, *Phys. Rev. Lett.* **1999**, *83*, 5527.
[8] J. Dong, J. K. Tomfohr, O. Sankey, *Phys. Rev. B* **2000**, *61*, 5967.
[9] B. Holm, R. Ahuja, A. Belonoshko, B. Johansson, *Phys. Rev. Lett.* **2000**, *85*, 1258.
[10] O. Tschauner, H.-k. Mao, R. J. Hemley, *Phys. Rev. Lett.* **2001**, *87*, 075701.
[11] M. Santoro, J. Lin, H.-k. Mao, R. Hemley, *J. Chem. Phys.* **2004**, *121*, 2780.
[12] M. Bernasconi, G. L. Chiarotti, P. Focher, M. Parrinello, E. Tosatti, *Phys. Rev. Lett.* **1997**, *78*, 2008.
[13] C. S. Yoo, V. Iota, H. Cynn, *Phys. Rev. Lett.* **2001**, *86*, 444.
[14] V. Iota, C. S. Yoo, *Phys. Rev. Lett.* **2001**, *86*, 5922.
[15] C. S. Yoo in *Science and Technology of High Pressure* (Eds.: M. H. Manghnani, W. J. Nellis, M. F. Nicol), University Press, Hyderabad, **2000**.
[16] S. Scandolo in *Proc. of the International School of Physics "E. Fermi" on High Pressure Phenomena*, Course CXLVII, IOS, Amsterdam, **2002**, pp. 195–214.
[17] S. Scandolo, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3051.
[18] S. Bernard, G. L. Chiarotti, S. Scandolo, E. Tosatti, *Phys. Rev. Lett.* **1998**, *81*, 2092.
[19] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
[20] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[21] L. Kleinman, D. M. Bylander, *Phys. Rev. Lett.* **1982**, *48*, 1425.
[22] N. Trouiller, J. L. Martins, *Phys. Rev. B* **1991** *43*, 1993.
[23] C. A. English, J. A. Venables, *Proc. R. Soc. London Ser. A* **1974**, *340*, 57.
[24] B. Kuchta, R. D. Etters, *Phys. Rev. B* **1988**, *38*, 6265.
[25] G. Frapper, J.-Y. Saillard, *J. Am. Chem. Soc.* **2000**, *122*, 5367.
[26] P. Tangney, S. Scandolo, *J. Chem. Phys.* **2002**, *116*, 14.
[27] R. Lu, A. M. Hofmeister, *Phys. Rev. B* **1995**, *52*, 3985.
[28] H. Olijnyk, A. P. Jephcoat, *Phys. Rev. B* **1998**, *57*, 879.
[29] J. J. Colman, W. C. Trogler, *J. Am. Chem. Soc.* **1995**, *117*, 11 270.
[30] F. W. Billmeyer, *Textbook of Polymer Science*, Wiley, New York, **1984**.
[31] A. C. Mitchell et al., in *Shock Compression of Condensed Matter* (Eds.: S. C. Schmidt, J. N. Johnson, L. W. Davison), Elsevier, Amsterdam, **1989**, p. 95.