Mixed Threefold and Fourfold Carbon Coordination in Compressed CO_2

Javier A. Montoya,[1,2] Roger Rousseau,[1] Mario Santoro,[3,4] Federico Gorelli,[3,4] and Sandro Scandolo[2,5]

[1]*International School for Advanced Studies (SISSA), Trieste, Italy*
[2]*CNR-INFM Democritos National Simulation Centre, Trieste, Italy*
[3]*European Laboratory for Non-linear Spectroscopy (LENS) and INFM, Florence, Italy*
[4]*CNR-INFM CRS-SOFT, c/o Università di Roma "La Sapienza," I-00185, Rome, Italy*
[5]*The Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste, Italy*
(Received 30 July 2007; published 23 April 2008)

Carbon dioxide (CO_2) has been recently reported to possess an amorphous form, named "carbonia," structurally similar to other group-IV oxide glasses. By combining *ab initio* constant pressure molecular dynamics, density-functional perturbation theory, and experimental IR spectra, we show that carbonia, and possibly also phase VI, is not SiO_2-like, and that instead it is partially tetrahedral containing also a sizable amount of carbon in threefold coordination, but no sixfold octahedral coordination. Enthalpic considerations suggest that carbonia is a metastable intermediate state of the transformation of molecular CO_2 into fully tetrahedral phases.

DOI: 10.1103/PhysRevLett.100.163002 PACS numbers: 33.15.Dj, 61.43.Fs, 62.50.−p

The carbon-oxygen double bond in CO_2 is one of the strongest molecular bonds in nature at ambient conditions, but it undergoes important reorganization and weakening under pressure. In the half-megabar (50 GPa) pressure range, solid molecular CO_2 transforms into extended, single-bonded phases presumably similar to the ambient-pressure phases of silica (SiO_2) and germania (GeO_2) [1,2]. Vibrational spectra and diffraction patterns of CO_2-V, the first reported nonmolecular crystalline phase of CO_2, suggest structural similarities with the cristobalite and trydimite phases of silica [2–11]. *Ab initio* calculations find a β-cristobalite-like crystal as the most stable phase of CO_2 at 50 GPa among a number of silica-like isomorphs [8,9]. The analogy with silica has been recently extended to include an amorphous, nonmolecular form (a-CO_2 or carbonia) [12], and a second crystalline form, phase VI [13]. Similarities between the infrared (IR), Raman, and x-ray diffraction data of a-CO_2 with those of other group-IV dioxide glasses have been taken as evidence that carbonia is structurally similar to SiO_2 and GeO_2 glasses at high pressure, and thus characterized by a mixed tetrahedral and octahedral coordination for carbon [12]. Octahedral coordination has also been proposed to characterize phase VI, which, according to diffraction data, may be isostructural to stishovite [13]. However this picture is not supported by first-principles calculations [5,6,8,9,14], which predicted a transition pressure from fourfold to sixfold coordination at around 400 GPa [6]. First-principles molecular dynamics (MD) simulations up to 120 GPa and at two different temperatures (1000 K and 2000 K) also do not yield any evidence of octahedral coordination [5]. In this work, we resolve this controversy by combining first-principles calculations and novel experimental IR spectra of a-CO_2. We show that a-CO_2, containing carbon in threefold and fourfold (tetrahedral) coordination, is fully compatible with reported and new measurements making this glass unique among group-IV dioxide glasses. We also show that octahedral coordination as proposed by Refs. [12,13] is not locally stable at the conditions of the experiments.

Calculations were performed with the Quantum Espresso package [15], employing density-functional theory and the Perdew-Burke-Ernzerhoff exchange-correlation functional [16]. A norm-conserving pseudopotential description of the ion-electron interaction was used, together with a plane-wave basis set with a kinetic energy cutoff of 80 Ry. Brillouin-zone integration was found to be converged with a uniform grid of $2 \times 2 \times 2$ points for the 24-molecule supercell and with $7 \times 7 \times 7$ points for smaller systems. Phonon frequencies and IR/Raman intensities were calculated using density-functional perturbation theory [17]. Structural optimizations were performed on lattice parameters and atomic coordinates, at a pressure of 60 GPa. This was done, in order to connect our analysis of carbonia to the recent report of phase VI. In addition, new experimental data are reported for carbonia close to that pressure.

The simulated sample used for comparison with the experimental data on carbonia was generated starting from an amorphous structure obtained in a previous *ab initio* MD simulation at 100 GPa [5]. The static structure factor calculated for this sample was shown in Ref. [12], but the sample contained a small number of unsaturated bonds, indicating incomplete polymerization. We tested the stability of the simulated sample by quenching it by MD [18] to zero pressure and 0 K, followed by annealing it for 5 ps at 200 K, and finally by bringing the sample to 60 GPa at 0 K. All bonds were saturated by this process, and a phonon calculation on the sample confirms its mechanical stability at 60 GPa. The annealed sample [19] contains 13 out of 24 carbon atoms in fourfold coordination, whereas the remaining 11 are threefold coordinated to oxygen [Fig. 1(a)]. Annealing did not affect the x-ray structure factor of the amorphous form, which is indistinguishable from that in Fig. 4 of Ref. [12], and

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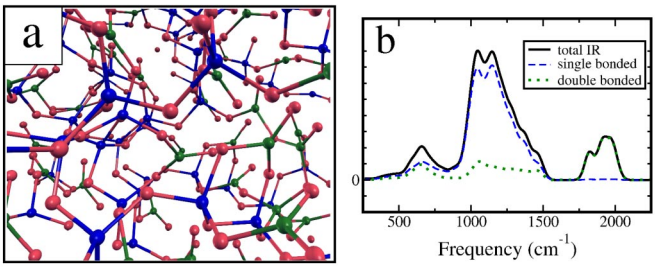

FIG. 1 (color online). Simulated structure and IR spectrum of carbonia. (a) Annealed nonmolecular a-CO_2 simulated sample at 60 GPa, showing fourfold coordinated carbon atoms (blue), threefold coordinated (green), and oxygen (red). (b) Theoretical IR absorbance (solid line) and its local projection on atoms linked exclusively by single bonds (dashed blue line) and on atoms with a double bond (dotted green line).

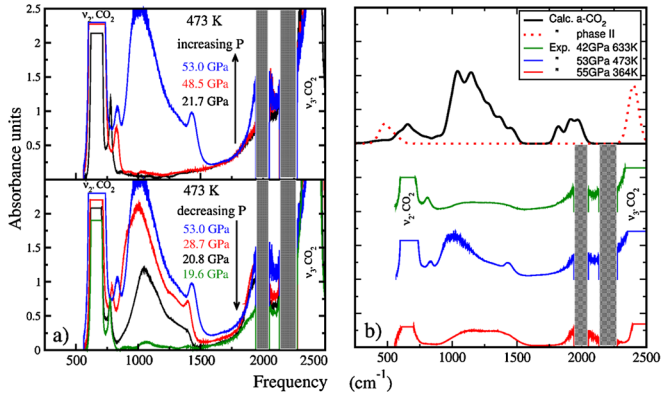

FIG. 2 (color online). IR spectra. (a) Experimental IR spectra along the 473 K isotherm showing the onset of carbonylic signatures around 2000 cm^{-1}. Grey areas mark regions dominated by diamond absorption. (b) Calculated (up) and experimental (lower three) spectra. Calculated spectra are at 60 GPa and are expressed in arbitrary units. Experimental samples were obtained through different P-T paths; in particular, the one at 55 GPa and 364 K has been already reported in [12].

reproduces the main features of the experiment. As already shown in Ref. [12] however, a hypothetical octahedral coordination of carbonia would yield a very similar structure factor, so the analysis of this quantity cannot be used to distinguish between different carbon coordinations.

Vibrational spectroscopy, on the other hand, can be very informative about local coordination. We thus conducted a new series of experiments to monitor the transition to carbonia along carefully controlled P-T paths. Pressurized CO_2 (6 bar, purity $\geq 99.99\%$) was cryoloaded, in the liquid phase, in a diamond anvil cell equipped with type IIa diamonds. The sample diameter and thickness were typically equal to 100–150 μm and 25–40 μm, respectively. The local pressure was measured by the $R1$ ruby fluorescence band shift [20]. Several pressure-temperature scans of the phase diagram were performed up to 53 GPa and 710 K, by means of uniform resistive heating of the cell. Two isothermal pressure scans were performed at temperatures equal to 473 and 633 K, respectively, in the pressure range of 20–52 GPa, in order to monitor the formation of a-CO_2 from the molecular solid phase II. Temperatures were measured by a J-type thermocouple, placed 1 mm away from the diamonds. Details of our IR spectroscopy apparatus are reported elsewhere [21,22].

At the onset of the transformation the amount of a-CO_2 increased upon increasing pressure, as shown by the strong, nonmolecular IR absorption band between 800 and 1500 cm^{-1} [Fig. 2(a)]. The pressure rise was stopped when about 10% of the sample had transformed [53 GPa for the sample in Fig. 2(a)], in order to avoid saturation of the IR absorption. Comparison with the data in Ref. [12] and with data along the two isotherms shows that the shape of the infrared bands at the early stages of formation depends on the sample history [see Fig. 2(b)] as expected for amorphous materials. A previously unnoticed peak can be distinguished in the experimental spectra on the two sides of the diamond absorption band, slightly below 2000 cm^{-1}, whose frequency differs clearly from the frequency of the molecular stretching mode (~ 2400 cm^{-1}). The intensity of the new peak changes by about 100% concomitantly with changes in the other a-CO_2 signatures at 800–1500 cm^{-1} [Fig. 2(a)], demonstrating that this feature belongs to the vibrational spectrum of the new material. The IR spectrum calculated at 60 GPa [Figs. 1(b) and 2(b)] shows remarkable agreement with the experimental data. Projecting the displacement components of the calculated modes on the different atoms [Fig. 1(b)] shows that the broad peak around 2000 cm^{-1} is localized on the carbonyl (C = O) units of the threefold coordinated carbon atoms [23]. The main peak between 800 and 1500 cm^{-1} is primarily localized on single C-O bonds (tetrahedral units) and can therefore be interpreted as the analogue of the peak centered at 1050 cm^{-1} in the IR spectrum of SiO_2 glass at ambient conditions [24]. Previous interpretations of the Raman and IR spectra [12], suggesting octahedral coordination, were based on a naive mass rescaling of the frequencies, whose predictive power is far more limited than the current *ab initio* approach. To summarize, both diffraction patterns and IR spectra on carbonia point unambiguously to a local structure consisting of a mixture of threefold and fourfold coordinated carbon atoms.

Even though mixed threefold and fourfold coordination explains the experimental data, we performed an extensive theoretical search for octahedral structures that might also be compatible with the experimental results. Our search was done by using crystalline samples. Because of the recent report of a new sixfold coordinated crystalline phase of CO_2 [13], we started by considering the octahedral structure proposed therein. We used a supercell with four CO_2 units, fixed its lattice parameters to the experimental values, and mimicked disorder by placing the four carbon atoms in positions chosen randomly among the equivalent possibilities given in Ref. [13]. Structural relaxation led this configuration to decompose back into molecular

phase II. Similar behavior was observed starting from stishovite, α-PbO_2, and $CaCl_2$-like structures. Starting atomic internal parameters for these phases were taken from their silica counterparts [25], and lattice parameters were scaled to match CO_2 volumes. Thus, at least up to 60 GPa, octahedral coordination for carbon is not likely to be stable or energetically favored [14], and hence is not able to explain the observed vibrational spectra of carbonia or phase VI.

Raman spectrum of phase VI [13] can be interpreted as composed of narrow crystalline peaks emerging from broad amorphous components similar to those reported for carbonia [Fig. 3(a)]. A strong peak around 2000 cm^{-1}, coinciding with the carbonia, is also reported in the Raman spectra of phase VI [13] and was assigned to a carbonyl stretching mode of the C_2O_4 dimer as reported in Ref. [23], which, however, was proposed to exist only at higher temperatures in the liquid phase [23]. This assignment suggests that crystalline phases with mixed threefold/fourfold coordination or with just tetrahedral coordination may exist, having carbonia as a precursor. To clarify this issue, and provide a theoretical framework for the interpretation of the observed vibrational spectra of carbonia, IR and Raman spectra were calculated for $I\bar{4}2d$ β-cristobalite and for three hypothetical model crystals containing pure threefold coordinated (poly-carbonyl) and mixed, threefold and fourfold coordination of the carbon atoms (Fig. 4). The two mixed structures (mix a and mix b) were chosen as representatives of different relative amounts of σ and π bonded oxygen atoms, with different structural packings. In mix a, tetrahedral and carbonyl units are arranged in a periodic alternate fashion along one direction. In mix b each carbonyl group is separated by a pair of tetrahedral units. Table I reports the relative percentages of single- and double-bonded atoms present in these samples. In Fig. 3, we compare the Raman spectra reported for carbonia and phase VI, with those calculated for the four theoretical structures, and the simulated carbonia sample. Our calculated β-cristobalite Raman spectrum matches perfectly the observed spectrum for phase V [3,4,11] at 60 GPa [arrows in Fig. 3(b)]. As expected, the peak around 2000 cm^{-1} only appears in structures containing carbonyl (C = O) units. Therefore carbonia, and possibly phase VI, must contain sizable amounts of carbon in threefold coordination. The series of peaks with frequencies between 600 and 1200 cm^{-1} are related, as in the IR decomposition of Fig. 1(b), to tetrahedral carbon coordination and display a large variation among the four crystalline candidates. The main peaks in carbonia and phase VI [Fig. 3(a)] lie at a frequency 13% and 24% higher than the main peak of phase V, respectively (Table I), whereas the hypothetical

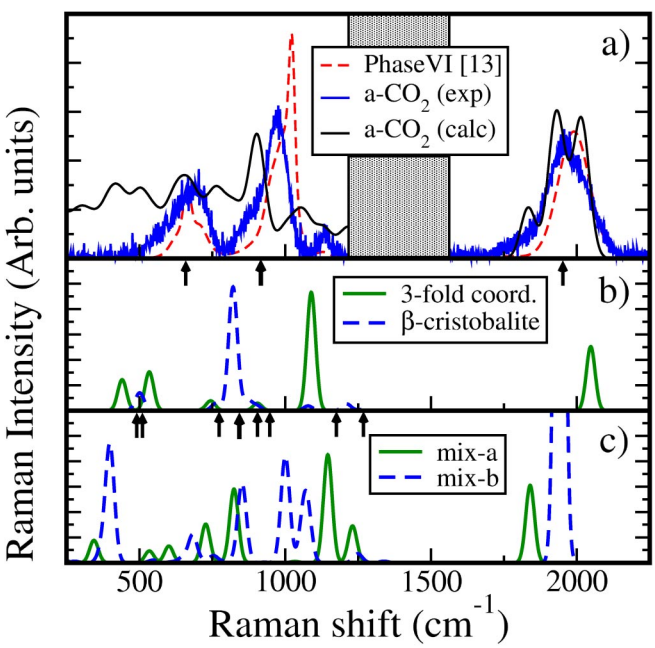

FIG. 3 (color online). Raman spectra. (a) Spectra from experiments on a-CO_2 at 76 GPa [12], phase VI at 62.5 GPa [13], and calculated for the simulated amorphous sample. Arrows indicate interpolated positions of the peaks of carbonia at 60 GPa, based on measurements at 43 GPa and 76 GPa. Grey area marks the region dominated by first order Raman scattering from diamonds. (b) Spectra calculated for the threefold and fourfold coordinated crystals described in the text. Arrows mark the position of peaks in phase V. (c) Spectra calculated for the mixed coordination crystalline structures shown in Fig. 4. All calculated spectra were obtained at 60 GPa.

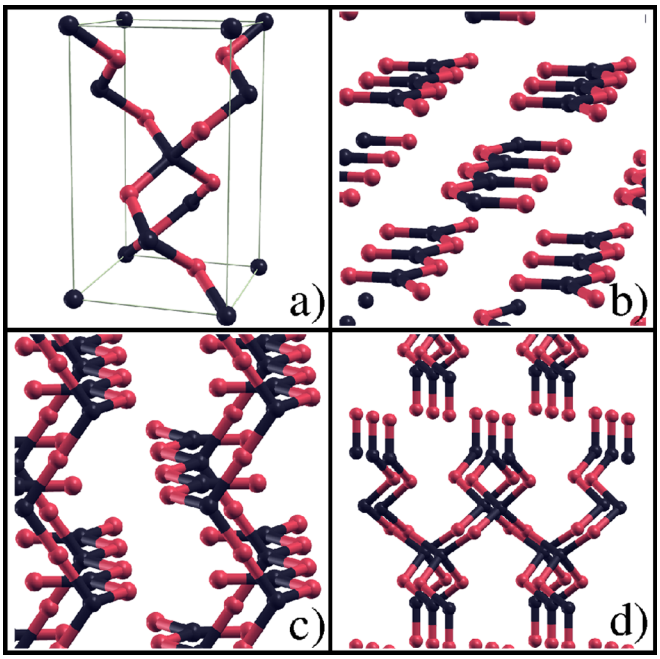

FIG. 4 (color online). Hypothetical structures. (a) CO_2 β-cristobalite (100% fourfold coordinated structure), (b) planar chains with only threefold coordinated carbon atoms, (c) layered structure (mix a) containing single tetrahedral units placed between threefold coordinated carbon atoms along the layers, (d) layered structure (mix b) with two tetrahedral units interconnected along z, placed between carbonyl units.

TABLE I. Dependence of the main (noncarbonylic) Raman peak on the oxygen coordination inside the hypothetical samples. C3 and C4 stand for threefold and fourfold coordinated carbon sites, respectively. Pressure of the samples is 60 GPa.

	Mix *a*	Poly-carbonyl	Mix *b*	Amorphous	*β*-cristobalite
Freq.[a] (cm^{-1})	1150	1090	1010–1060	900	820
C3 = O (%)	50	50	25	22.9	0
C3-O-C4 (%)	25	0	50	29.2	0
C4-O-C4 (%)	25	0	25	39.6	100
C3-O-C3 (%)	0	50	0	8.3	0

[a]Experimental frequency for a-CO_2 at 60 GPa: 925 cm^{-1}.

structures containing threefold coordinated carbon appear to give a closer agreement [Figs. 3(b) and 3(c)]. Table I shows that, in general, the position of the main Raman peak in crystals correlates well with the relative amount of oxygen double bonded to carbon, indicating that, while the origin of this peak can be traced to the C-O single bonds, its precise frequency depends strongly on the local environment. This explains the presence of a small frequency difference between the center of the most intense band of carbonia at 60 GPa [interpolated arrows in Fig. 3(a)] and that of the amorphous shoulder seen in the spectra of phase VI, which may be due to a difference in the single- to double-bond proportion, and also accounts for the shape variation of the measured IR spectra of carbonia [Fig. 2(b)] upon their history and P-T conditions.

We now speculate on the thermodynamics and kinetics of formation of carbonia. The calculated enthalpy for our theoretical carbonia sample, as estimated from equation of state data [19], becomes lower than that of the molecular phase II at about 50 GPa, i.e., close to the pressure where carbonia starts to appear in experiments. Phase V instead forms well within its thermodynamic range of stability [11], which has been calculated to start at around 15 GPa at 0 K [6]. Therefore, carbonia must be a metastable form of CO_2, whose formation is favored by kinetics. This fact is consistent with the formation of carbonia in molecular dynamic simulations [5], a technique that is known to favor kinetically facile transitions. On the other hand, static calculations [6,8,9] have never considered carbonia so far since they have focused only on candidates for the thermodynamically stable crystal structure of CO_2. Disorder and threefold coordination may be intimately connected in CO_2. Disorder in silica glass is, in fact, known to be linked to the flexibility of the tetrahedral SiO_2 network, which permits a large variety of competing configurations and topologies with similar energies. As shown in Ref. [8], CO_2 tetrahedral phases lack such bond flexibility, since the reorientation of the internal tetrahedral subunits implies variation of the very stiff C-O-C angle. Threefold coordination can thus be seen as a mechanism to increase the flexibility of the network and generate a large number of quasidegenerate configurations ultimately leading to disorder.

In summary, we have shown, based on a combined theoretical and experimental analysis, that it is now possible to discriminate between differently coordinated local atomic environments in a-CO_2 and rule out the presence of octahedrally coordinated sites. Our analysis shows that the local atomic structure of a-CO_2 contains carbon in mixed threefold and fourfold coordination, in similar proportions. This is qualitatively different with respect to other group-IV amorphous oxides. Since carbonia is likely to be an intermediate, metastable state of the transformation into crystalline superhard phases, our findings may help with improving strategies to facilitate the synthesis of such phases.

M. S. and F. G. acknowledge the European Union supporting LENS under Contract No. RII3-CT2003-506350, and the Ente Cassa di Risparmio di Firenze supporting research at LENS under the grant "Firenze Hydrolab." J. M., R. R., and S. S. acknowledge support from INFM-CNR through "Progetti di Calcolo Parallelo."

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