High-pressure molecular phases of solid carbon dioxide

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We present a theoretical study of solid carbon dioxide (CO$_2$) up to 50 GPa and 1500 K using first-principles calculations. In this pressure-temperature range, interpretations of recent experiments have suggested the existence of CO$_2$ phases which are intermediate between molecular and covalent-bonded solids. We reexamine the concept of intermediate phases in the CO$_2$ phase diagram and propose instead molecular structures, which provide an excellent agreement with measurements.

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Understanding the evolution of the bonding properties of molecular crystals as a function of pressure is a fundamental question in condensed matter physics. Recently, this question has received a widespread attention due to key progress in experimental techniques and hence, the availability of new data for a number of molecular solids [3, 4, 5, 6, 7]. In the case of CO$_2$, the interest has been further intensified due to its importance for planetary science and technical applications. However, despite several experimental investigations of the CO$_2$ high-pressure phases, the changes of intra- and inter-molecular bonds, as well as of electronic and vibrational properties, as a function of pressure are not yet well understood. In addition, large portions of the CO$_2$ phase diagram are unexplored from a theoretical standpoint.

At low pressure ($P$) and temperature ($T$), CO$_2$ condenses as a molecular solid in the cubic $P$-a$_3$ structure (known as dry ice, phase I), which is characterized by strong double bonds (C=O distance of 1.16 Å) and rather weak inter-molecular interactions $\sigma$. Recently, a high-$P$ and high-$T$ phase of CO$_2$ (phase V) has been discovered [2] and is completely different from the molecular solid. It has a polymeric quartz-like structure, and a very low compressibility (the experimentally derived bulk modulus, $B_0$, is 365 GPa). Following this exciting discovery, two additional new phases have been reported [3, 4, 5, 6, 7] experimentally (II and IV in Fig. 1), both of which were credited with unusual properties; their structures were described as intermediate between that of molecular and covalently bonded crystals.

In this Letter, we present a study of the CO$_2$ phase diagram based on first-principles density functional theory (DFT) calculations. Our results challenge the interpretation of CO$_2$-II, III, and IV as exhibiting dramatic differences in the nature of the molecular bonding with respect to the low-pressure molecular crystal. In place of the previously proposed structures for CO$_2$-II and IV, we suggest new, molecular ones. We demonstrate that in addition to being stable, our newly proposed structures give results in excellent agreement with measurements and provide a consistent explanation of experimental observations.

At ambient $T$, CO$_2$-I undergoes a pressure-induced transformation to the orthorhombic $Cmca$ symmetry (phase III) between 12 and 22 GPa [3, 11, 12, 13, 14, 15, 16]. The exact nature of this transition and the structure of phase III are still unsettled; experimental studies have suggested a region of co-existence between CO$_2$-I and III [14], and also an intermediate distorted low-$T$ phase [10]. Furthermore, it was reported [3] that the I to III transition is strongly temperature dependent, becoming abrupt above 400 K, and that CO$_2$-III may actually be metastable. The two newly discovered phases II and IV are believed to be thermodynamically stable and quenchable. It was proposed that CO$_2$-II has the $P4_2/mnm$ symmetry with elongated C=O bonds, 1.33 Å, reduced inter-molecular distances below 2.38 Å (hence named associated or dimeric phase), and $B_0 = 131$ GPa [2, 10]. CO$_2$-IV was described as Phcn, with C=O bonds as long as 1.53 Å, and bent (O=C=O angle of 160°) and strongly (dipole) interacting molecules $\sigma$. Such remarkable properties would imply that CO$_2$ is losing its molecular character in a “gradual” way, a concept promoted as a key for understanding its phase diagram in analogy with solids like N$_2$O and SiO$_2$. In addition, CO$_2$-III, despite having a stable C=O bond, was also assigned a $B_0$ as high as 87 GPa $\sigma$. The stability of the proposed bent and associated phases, and the unusual bulk properties of CO$_2$-II, III, and IV have not been investigated theoretically up to date.

![FIG. 1: Phase diagram of CO$_2$ according to Ref. 9, where CO$_2$-III ($Cmca$) is reported to be metastable.](image-url)
We performed a series of first-principles calculations, including full structural optimizations, phonon spectra, and free energies, in order to study the stability and properties of the phases proposed experimentally up to 50 GPa and 1500 K. The DFT calculations were carried out within the Perdew-Burke-Ernzerhof (PBE) \(^{17}\) generalized gradient approximation (GGA) using the ABINIT code \(^{18}\), which implements plane-wave basis sets \(^{19}\).

First, we have examined the stability of the bent and dimeric structures for phases II and IV. Starting from the previously proposed \(P4_2/mnm\) and \(Pbcn\) with elongated molecular bonds, we carried full structural optimizations at various pressures up to 50 GPa. In all cases, upon relaxing the atomic coordinates the C=O bond lengths decreased by about 15% and 30% for \(P4_2/mnm\) and \(Pbcn\) respectively, to become comparable to the free CO\(_2\) molecule \(^{20}\). In the case of \(Pbcn\), the O=C=O angle also straightened to 180°. The energy differences between the theoretically stable molecular structures and the associated and bent phases are respectively more than 3 and 6 eV per molecule. These are energy scales corresponding to the breaking of a covalent bond. They are beyond the errors of the GGA and present a strong evidence that the previously proposed bent and dimeric structures are not stable. In order to further investigate this issue, we examine below published experimental data for CO\(_2\)-II, III, and IV, and demonstrate that they can be explained in terms of two stable structures, \(Cmca\) and \(P4_2/mnm\), which are strictly molecular.

Computed equation of state (EOS) at \(T = 0\) for the three molecular structures \(Pa3\), \(Cmca\), and \(P4_2/mnm\) are reported in Fig. 2 along with the available experimental data. In all three cases, the calculated EOS agrees very well with the measured one; the computed \(PV\) curves fall within the experimental uncertainties. We find about 2% relative volume reduction from \(Pa3\) to \(Cmca\) \(^{21}\) above 30 GPa and another 0.5% from \(Cmca\) to \(P4_2/mnm\) (see insert in Fig. 2). Yoo et al. reported a \(\sim 5-7\)% volume decrease associated with the III to II transition; however, they also observed lattice strain in their phase III samples \(^{5}\), which may explain the difference between their results and ours. Furthermore, the \(PV\) curve of \(Cmca\) comes close to and eventually merges with that of \(Pa3\) below 20 GPa in agreement with Aoki et al. \(^{14}\). Thus, the measured EOS data are reproduced well despite the lack of molecular association in our optimized \(P4_2/mnm\). The computed EOS parameters are summarized in Table I together with values derived form experiment \(^{22}\). The agreement is good for \(Pa3\), but there is an order of magnitude difference for the values of \(B_0\) of \(Cmca\) and \(P4_2/mnm\). Since we are using the same EOS fit as Ref. \(^{14}\) and we in fact agree very well with the direct \(PV\) measurements, the large difference likely comes from extrapolating the experimental data, spread above 20 GPa, down to ambient pressure.

The published experimental evidence invoked to propose that CO\(_2\)-II exhibits the properties of a dimeric polymorph consists of: (i) a large splitting of the internal symmetric stretching mode, \(\nu_1\) \(^{8}\), (ii) a broad librational mode identified as \(B_{1g}\) \(^{9, 10}\), and (iii) powder x-ray diffraction measurements \(^{10}\). We carried out calculations of the vibron spectrum \(^{23}\) of \(molecular\) \(P4_2/mnm\) and \(Cmca\) as a function of \(P\). A plot of \(\nu_1\) in Fig. 3 shows that the measured splitting, as well as the relative values for \(P4_2/mnm\) and \(Cmca\), are reproduced remarkably well by the theoretical structures. Yoo et al. assumed that the large vibron splitting observed in CO\(_2\)-II is an evidence for decreased inter-molecular distances; our results indicate that the crystal field in the molecular \(P4_2/mnm\) is sufficient to explain the splitting. One should note that phonons are calculated as a second derivative of the energy; therefore the agreement with experimental frequencies within meV, as found here, is a strong indication that computed total energies and forces are extremely accurate.

The computed pressure dependence of the Raman-

![FIG. 2: Pressure-volume dependence of selected CO\(_2\) structures: \(Pa3\) (black), \(Cmca\) (blue), and \(P4_2/mnm\) (red). The solid lines are ab initio calculations; the points indicate experimental data from Ref. \(^{12}\) (no error bars), Ref. \(^{2}\) (\(Pa3\) and \(Cmca\)), and Ref. \(^{14}\) (\(P4_2/mnm\)). The inset shows calculated reduction in volume of \(P4_2/mnm\) and \(Cmca\) relative to \(Pa3\).]

| Structure | \(V_0\) (cm\(^3\)/g) | \(B_0\) (GPa) | \(B'_0\) | \(Ref.\) |
|-----------|----------------|----------------|--------|---------|
| \(Pa3\)   | 0.714          | 2.93           | 7.8    | 11      |
| \(Pa3\)   | 0.726          | 3.21           | 8.10   | this study |
| \(Cmca\)  | 0.450          | 87             | 3.3    | 10      |
| \(Cmca\)  | 0.725          | 3.53           | 7.12   | this study |
| \(P4_2/mnm\) | 0.408       | 131            | 2.1    | 10      |
| \(P4_2/mnm\) | 0.701       | 4.37           | 6.66   | this study |

TABLE I: Equation of state parameters for selected CO\(_2\) phases. The theoretical data is well fitted to a third-order Birch-Murnaghan equation of state.
active external modes of the three theoretical structures is shown in Fig. 3b. The agreement with experiment is again good, though our values are consistently slightly lower than the measured ones. The experimental frequencies of the two Raman-active modes of CO$_2$-II at 19 GPa are about 260 and 320 cm$^{-1}$ - the former being a broad peak - and were classified as B$_{1g}$ and E$_g$ respectively. The broad mode was previously associated with dynamical disorder in the lattice. The molecular P4$_2$/mm structure has modes with frequencies 245 and 300 cm$^{-1}$ at this P; however it is the degenerate E$_g$ which has the lower frequency, and therefore corresponds to the experimentally observed broad peak. Its broadening can be explained by invoking a lifting of the E$_g$ degeneracy when the tetragonal cell is deformed into an orthorhombic one (resulting in the Pnam symmetry). Such a distortion is consistent with the x-ray data reported in Ref. 12. We therefore estimate that between 20 and 30 GPa there is a 10 cm$^{-1}$ splitting for every 1% modification of a and b.

We now turn our attention to the x-ray analysis. In P4$_2$/mm, the atomic positions are C(2a) at [0,0,0], and O(4f) at [x,x,0]. The associated phase, according to Ref. 10, corresponds to x = 0.2732, while our stable structure corresponds to x = 0.23075, i.e. x ≈ 0.25 ± 0.02. Among the observed diffraction peaks, only the (101) and (211) reflections depend on the sign of δ; their measured intensities relative to the calculated intensities of the same reflections are in ratios of 2.3 and 0.3 for the associated, and 0.4 and 1.8 for the molecular structures respectively. We therefore conclude that at present the diffraction measurements are insufficient to distinguish between the proposed dimeric and the theoretical molecular P4$_2$/mm structure.

Finally, we examine the relative stability of all considered crystal structures as a function of both P and T. A plot of enthalpies showing that Cmca is never thermodynamically stable at low T is reported in Fig. 4a. This finding confirms a previous observation by Iota and Yoo that the orthorhombic symmetry obtained during ambient T compression of CO$_2$-I is metastable; the reason why the system reverts to it is the low kinetic barrier associated with the rotation of the molecules from their alignment in Pa3 to that in Cmca. In additional support of this conclusion, we have performed structural optimizations starting from the Pbca structure, and relaxing the atomic coordinates. The Pbca lattice is obtained from Pa3 by deforming the cubic cell; further rotations of the molecules in the y-z plane then leads to Cmca. In all such calculations above 15 GPa, the CO$_2$ molecules quickly align in the y-z plane, thus ending up in the Cmca, rather than in the energetically favorable P4$_2$/mm phase. This happens regardless of whether the unit cell is tetragonal or orthorhombic; the deformation of P4$_2$/mm to the orthorhombic Pnam costs only about 1 meV per molecule for 1% distortion of a and b.

The kinetic barrier between Cmca and P4$_2$/mm can be overcome by heating the system above ambient T. Interestingly, we find that upon further heating at constant P there is a thermodynamic phase boundary above which the orthorhombic phase is now stable. The phonon free energies, computed as described in Ref. 23, are plotted in Fig. 4b. The transition to Cmca is entropy driven and is

![FIG. 3: Computed Raman-active modes (solid symbols) of the theoretically stable structures. (a) Symmetric stretching vibron. The dashed lines indicate experimental data from Ref. 8; they are from a Fermi resonance band, and have been shifted by 52 cm$^{-1}$ for comparison. (b) External modes.](image)

![FIG. 4: (a) Enthalpy versus P relative to the Cmca phase at T = 0. (b) Phonon free energy versus T relative to the Cmca structure at 16 GPa; the reported differences do not vary strongly with P. (c) Relative stability of selected CO$_2$ structures from Gibbs free energy comparison; here P includes phonon contributions. The dotted lines indicate the experimental phase diagram constraints from Ref. 8 (see Fig. 1).](image)
mainly due to a soft acoustic phonon mode. Its physical origin is in the specific geometry of \( \text{Cmca} \), allowing for a relatively unobstructed shear-like motion parallel to the \( y \) axis; we have confirmed this by sampling the potential surface with frozen-phonon calculations.

The computed stability regions for \( \text{Pa3}, \text{P4}_2/\text{mmm}, \) and \( \text{Cmca} \) are shown in Fig. 4. Since we are comparing the relative stability of a limited number of structures, we cannot firmly conclude that Fig. 4 represents the actual phase diagram of \( \text{CO}_2 \). However, the almost perfect matching of the stability region of \( \text{Cmca} \) with that of \( \text{CO}_2-\text{IV} \) makes the identification between the two phases rather compelling. We note that a phase \( \text{IV} \) of \( \text{CO}_2 \) was first suggested by Olijnyk and Jephcoat \([16]\) based on the observed multiplicity of external Raman-active modes, although the interpretation of this effect was not straightforward. Their observation of a similar distorted phase with a weak (otherwise forbidden) Raman activity of the bending internal mode, which they related to the presence of pressure inhomogeneities in the sample, is in good agreement with our calculations. This work was performed under the auspices of the U.S. Department of Energy at the University of California/LBNL under contract no. W-7405-Eng-48.

In conclusion, we have presented a new interpretation of experimental data recently obtained for \( \text{CO}_2-\text{II}, \text{III}, \) and \( \text{IV} \). Our ab initio calculations identify \( \text{CO}_2-\text{II} \) as a molecular structure with the \( \text{P4}_2/\text{mmm} \) symmetry. We have also elucidated the high-\( T \) behavior of molecular \( \text{CO}_2 \), and have found the \( \text{Cmca} \) symmetry to be preferable due to its relatively large entropy. Based on our findings, we propose that measurements of the high-\( T \) phase \( \text{IV} \) be interpreted along the lines of an orthorhombic, and possibly distorted, phase. Finally, we note that the external Raman modes of several \( \text{CO}_2 \) molecular structures are very close in frequency (see Fig. 4), and therefore may not be sufficient to discriminate between different phases.

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