Ab initio determination of the phase diagram of CO$_2$ at high pressures and temperatures

Beatriz H. Cogollo-Olivo,$^1$ Sananda Biswas,$^2$ Sandro Scandolo,$^3$ and Javier A. Montoya$^4$

$^1$Universidad de Cartagena, Doctorado en Ciencias Físicas
Cartagena de Indias, 130001, Colombia

$^2$Institut für Theoretische Physik, Goethe-Universität Frankfurt, 60438 Frankfurt am Main, Germany

$^3$The Abdus Salam International Centre for Theoretical Physics (ICTP)
Trieste, Strada Costiera 11, 34151, Italy

$^4$Universidad de Cartagena, Instituto de Matemáticas Aplicadas
Cartagena de Indias, 130001, Colombia

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The experimental study of the CO$_2$ phase diagram is hampered by strong kinetic effects leading to wide regions of metastability and to large uncertainties in the location of phase boundaries. Here we determine the CO$_2$ phase boundaries by means of ab initio calculations of the Gibbs free energy of several molecular and non-molecular solid phases of CO$_2$. Temperature effects are included in the quasi-harmonic approximation. Contrary to previous results, we find that the boundary between non-molecular phases and phase V has a positive slope and starts at 21.5 GPa at $T = 0$ K. A triple point between phase IV, V, and the liquid phase is found at 35 GPa and 1600 K, indicating a broader region of stability for the non-molecular phases than previously thought. The experimentally determined boundary line between CO$_2$-II and CO$_2$-IV phases is reproduced by our calculations, indicating that kinetic effects are not relevant in that transition.

Widely studied during the past years, carbon dioxide (CO$_2$) is a fascinating system that, despite its simple molecular form at ambient conditions, exhibits a rich polymorphism, with up to seven crystalline structures reported experimentally, in addition to an amorphous form (see Fig. 1). At room temperature the molecular gas transforms into a liquid at 7.5 MPa which then solidifies at 0.5 GPa into CO$_2$-I, a molecular crystal with space group $P6_3$ [1,2]. By further increasing pressure at ambient temperature, CO$_2$-II transforms to the orthorhombic phase III (Cmca space group) above 10 GPa, with a minimal volume change [3]. A recent theoretical study has provided insights into the microscopic mechanism of the $P6_3$-to-Cmca transition [4]. Heating CO$_2$-III above 16 GPa and $\sim 500$ K [3,4] leads to the transformation into phase II. However the transition is not reversible: CO$_2$-II can be recovered at ambient temperature (at high pressure), suggesting that CO$_2$-III is a metastable structure and not a stable phase [5,7]. Initially described as a structure with carbon in an unconventional six-fold coordination, phase II was interpreted as an intermediate state between the molecular and the extended solid form of CO$_2$ [5]. However, subsequent studies disproved the existence of an intermediate bonding state and identified the structure of phase II as composed of undistorted molecules, with space group $P4_2/mnm$ [9]. When CO$_2$-II is heated in the $500 – 720$ K range, depending on pressure [5,7], it transforms into CO$_2$-IV. Similarly to phase II, phase IV was also initially interpreted as an intermediate bonding state [10]. However, it was later shown experimentally that CO$_2$-IV is still composed of well defined linear molecules and that its crystalline structure is rhombohedral with space group $R3c$ [11]. At higher temperatures, an intermediate phase between CO$_2$-I and CO$_2$-IV was observed by heating and compressing CO$_2$-I up to 20 GPa at 950 K. The crystal structure of this molecular high-temperature stable phase (CO$_2$-VII) belongs to space group $Cmca$. [12]. Despite the fact that CO$_2$-VII and CO$_2$-III have the same space group, differences in their Raman spectra and in their lattice parameters suggest that their structures might be qualitatively different [12]. However, a recent theoretical study has shown that CO$_2$-III and CO$_2$-VII belong to the same configurational energy minimum and that CO$_2$-III is a metastable manifestation of CO$_2$-VII at low temperature [13].

The non-molecular CO$_2$-V phase was first synthesized by laser heating CO$_2$-III above 40 GPa and 1800 K [14], and its crystal structure is a partially collapsed cristobalite-like structure, with space group $I42d$ [15,16]. By compressing CO$_2$-II to 50 GPa at 530 and 650 K, another non-molecular form of carbon dioxide (CO$_2$-VI) was obtained [10]. Its vibrational spectra are consistent with those of layered tetrahedral structures [17]. In addition to the molecular and non-molecular phases, an amorphous form of carbon dioxide (a-CO$_2$) was observed upon compressing CO$_2$-III in the pressure range 40 – 48 GPa at room temperature [17]. The microscopic structure of a-CO$_2$ has been shown to consist of a mixture of 3- and 4-fold coordinated carbon atoms [18]. Finally, at pressures between 30 and 80 GPa, and temperatures above 1700 K, CO$_2$-V has been reported to dissociate into elemental carbon (diamond) and oxygen ($\epsilon$-O$_2$) [19,20]. However, a recent experimental study [21] showed that not only there is not dissociation of carbon dioxide, but they also suggest that CO$_2$-V is the stable phase of the
FIG. 1: High-pressure CO$_2$ phase diagram adapted from Ref. 22. Yellow, green, blue, and purple areas correspond to the molecular, non-molecular, fluid, and amorphous forms of CO$_2$, respectively. Solid lines correspond to thermodynamic phase boundaries, while dashed lines are kinetic boundaries. A shaded area on top of the molecular phases spans the experimentally restricted region where the true molecular-to-non-molecular boundary should be present. Names in italic indicate metastable phases.

non-molecular forms of carbon dioxide. The currently accepted phase diagram including all the mentioned forms of solid CO$_2$ along with the region where it becomes a fluid is shown in Fig. 1.

Unfortunately strong kinetic effects hinder the experimental determination of the CO$_2$ phase boundaries, and the small size of the samples makes structure determinations difficult. As a consequence, several open questions remain regarding the nature of the phase boundaries and the stability of the phases reported in Fig. 1. In the molecular portion of the phase diagram open questions include the relative stability of CO$_2$-II and CO$_2$-III at low temperature, and the nature of CO$_2$-VII, in particular its structural relationship with CO$_2$-III. At higher pressures one of the fundamental questions is the location of the phase boundary between molecular and non-molecular phases. The molecular-to-non-molecular transition is observed experimentally only above 40-50 GPa, but non-molecular CO$_2$-V has been recovered down to ambient pressure 23, suggesting that the actual location of the boundary could be anywhere between these two extremes (shaded area in Fig. 1). Santoro et al. for example, propose a phase diagram where the boundary between molecular and non-molecular phases at room temperature is located roughly half-way, at 20 GPa 24. Moreover, the kinetic boundary between CO$_2$-III and non-molecular structures, i.e. the P-T region where the transformation occurs upon compression, has a negative slope at low temperature 25, while basic thermodynamic considerations suggest that the slope of the true phase boundary should be positive 23. Theoretical determinations of the molecular/non-molecular boundary at low temperatures, based on ab initio electronic structure methods, predict transition pressures in the range between 18 and 21 GPa when going from CO$_2$-II and CO$_2$-III to the non-molecular forms 23 26 27.

In this paper, we extend the theoretical determination of the phase diagram of CO$_2$ to finite temperatures. Phase boundaries between the molecular phases II, III, and IV, and the non-molecular phase V are calculated based on an ab initio approach for the determination of free energies where vibrational free energies are treated in the quasi-harmonic approximation.

Ab initio electronic structure calculations were carried out using density functional theory (DFT) and the projector augmented wave (PAW) method, as implemented in the Quantum ESPRESSO suite 29 30 with a kinetic energy cutoff of 200 Ry for the plane-wave basis set. The generalized gradient approximation (GGA) for the exchange-correlation energy was implemented using the Perdew-Burke-Ernzerhof functional 31. The Monkhorst-Pack method 32 was used to generate the k-points grids for sampling the Brillouin zone. Variable-cell optimization of all structural parameters was performed for the four phases in the range of pressures between 10 and 70 GPa. Density functional perturbation theory (DFPT) within the linear response scheme 33 was used to calculate phonon frequencies at zero temperature. The

FIG. 2: Pressure-volume relation of phases (a) II, (b) III, (c) IV, and (d) V of CO$_2$ at room temperature are shown in black solid lines. For each case, reported values from experimental (red circles) and theoretical (blue squares, purple diamonds and yellow crosses) studies for the different phases are displayed as well.
zero-point energy and the finite-temperature contributions to the Helmholtz free energy were computed in the quasi-harmonic approximation (QHA) \[34, 35\]. For the construction of the pressure-temperature phase diagram, the Helmholtz free energy at different temperatures was fitted to a 3rd order Birch-Murnaghan equation of state. Finally, the Gibbs free energy was calculated as:

$$ G(P, T) = F[V(P, T), T] + PV(P, T), $$

Room-temperature equations of state obtained with the above approximations are compared with experimental data for phases CO\(_2\)-II, CO\(_2\)-III, CO\(_2\)-IV, and CO\(_2\)-V in Fig. 2. The agreement is excellent and confirms the validity of the approach. Phase boundaries constructed based on the calculated Gibbs free energies are shown in Fig. 3.

We begin our discussion with an analysis of the solid molecular portion of the phase diagram. This portion is indicated in yellow in Fig. 1, it contains the molecular phases I, II, III, and IV, and its upper bound in pressure coincides with the transition to the non-molecular phase. Because phase I as well as its boundaries with the other phases are well known and constrained, we focus specifically on phases II, III, and IV, at pressures higher than 12 GPa. According to the enthalpy-pressure relations, with and without the zero-point energy contribution, at \( T = 0 \) K CO\(_2\)-II is the most stable molecular phase in the pressure range considered, until the transition to CO\(_2\)-V. This indicates that the orthorhombic \( Cmca \) structure (phase III) obtained experimentally from the compression of phase I is indeed only metastable. Notice that this remains true even after the inclusion of zero-point contributions, in agreement with previous reports \[5, 28\]. However, CO\(_2\)-III becomes more stable than CO\(_2\)-II at finite temperatures (solid green line with stars in Fig. 3(a)). The transition temperature between CO\(_2\)-III and CO\(_2\)-II has a strong pressure dependence and reaches values in excess of 1000 K close to the boundary with the non-molecular phase. Comparing the free energies of CO\(_2\)-II and CO\(_2\)-IV we find that the boundary between phases II and IV (solid brown line with down triangles in Fig. 3(a))

| TABLE I: Thermodynamic properties of carbon dioxide from the molecular phases \( P_{42/mmm} \) (CO\(_2\)-II) and \( R\bar{3}c \) (CO\(_2\)-IV) to the non-molecular phase \( I\bar{4}2d \) (CO\(_2\)-V). |
|---|---|---|---|---|---|---|
| \( P_{42/mmm} \) | \( T \) | \( V \) | \( \Delta V_{CO_2-V} \) | \( S \) | \( \Delta S_{CO_2-V} \) | \( dP/dT \) |
| GPa | K | a.u. \(^3\)/atom | | J/mol/K | | GPa/K |
| 21.95 | 200 | 4.0610 | 0.9538 | -5.7145 | -5.6997 | 0.0159 |
| 22.57 | 300 | 4.0513 | 0.9508 | -7.0807 | -7.0598 | 0.0243 |
| 23.50 | 400 | 4.0296 | 0.9394 | -10.7455 | -10.7160 | 0.0334 |
| 24.41 | 500 | 4.0094 | 0.9284 | -15.3715 | -15.3345 | 0.0389 |
| 25.33 | 600 | 3.9896 | 0.9172 | -20.3605 | -20.3167 | 0.0427 |
| 25.06 | 600 | 3.3852 | 0.3090 | -20.3605 | -20.3462 | 0.1265 |
| 25.39 | 800 | 3.3714 | 0.2990 | -20.7385 | -20.6944 | 0.1302 |
| 26.45 | 1000 | 3.3520 | 0.2941 | -21.2663 | -21.2211 | 0.1355 |
| 31.27 | 1200 | 3.3436 | 0.2922 | -22.0693 | -22.0127 | 0.1460 |
| 33.10 | 1400 | 3.3285 | 0.2904 | -22.5765 | -22.5265 | 0.1572 |

FIG. 3: (a) Phase boundaries between CO\(_2\)-II and CO\(_2\)-III (green, stars), CO\(_2\)-II and CO\(_2\)-IV (brown, down triangles), and CO\(_2\)-III and CO\(_2\)-IV (magenta, diamonds). Suggested boundaries reported by Iota et al. \[5\] (experimental) and Bonev et al. \[28\] (theoretical), are shown in orange dot-dashed line and violet dotted line, respectively. (b) Phase boundaries between molecular phases CO\(_2\)-II (red, circles), CO\(_2\)-III (blue, up triangles), and CO\(_2\)-IV (gray, crosses), and the non-molecular phase CO\(_2\)-V. Proposed limits of the kinetic region (shaded area) reported in previous works are also included: Ref. \[24\] (violet, dot-dashed line) and Ref. \[25\] (orange squares).
The weak pressure dependence of the II-IV boundary narrows down the region of stability of phase II, pushing it towards lower temperatures. Finally, we find that the boundary between CO$_2$-III and CO$_2$-IV (solid magenta line with diamonds in Fig. 3(a)) is almost vertical, which restricts the domain of stability of phase III to a narrower window of pressure than the other phases. We summarize the results of the free-energy calculation for the three molecular phases II, III, and IV in Fig. 4. Phase I and II are the only stable molecular phase of CO$_2$ at ambient and lower temperatures. Phase III and IV are both stabilized by temperature, and phases II, III, and IV coexist at a triple point located at 15 GPa and 500 K.

Our findings are in agreement with the simulations of Bonev et al. [28] that suggested the Cmca phase as a temperature stabilized form [28]. Because the structure of phase IV was not known at the time, Bonev et al. proposed a wider region of stability for CO$_2$-III. Interestingly, as can be seen in Fig. 3(a), the $P-T$ region of stability of CO$_2$-III obtained from our calculations has a large overlap with the region of stability reported for the so-called phase VII of CO$_2$ [12]. A recent theoretical work has shown that phase III and VII have, in fact, the same crystal structure (space group Cmca) [13]. We therefore confirm that phase III is stable in the P-T region where phase VII was reported. The observation of phase III outside this region (e.g. at ambient conditions, as a result of the compression of phase I) must be thus attributed to kinetic effects.

We now turn to the boundary between the molecular phases and non-molecular phase-V (Fig. 3(b)). We find that at zero temperature the phase boundary between CO$_2$-II and CO$_2$-V is at 20.8 GPa. The transition between (amorphous) CO$_2$-III and CO$_2$-V would instead take place at 21.5 GPa, in the absence of kinetic effects. This is in good agreement with previous theoretical works [25, 26, 27]. Phase boundaries between molecular phases and CO$_2$-V are rather insensitive to the choice of the molecular structure and they all have a positive slope, as already suggested [24]. Considering that non-molecular phases are denser than molecular ones, a positive slope implies a decrease of entropy in going from molecular to non-molecular. This is not unexpected, given the stiffness of the non-molecular structure, when compared with the molecular ones. Our calculated volume and entropy jumps across the transition confirm this picture, see table 1. Using the experimentally determined melting line, our calculations show a triple point between phases IV and V, and the liquid phase at 35 GPa and 1600 K. The calculations therefore suggest that molecular CO$_2$ could be stable up to pressures as high as 35 GPa, at high temperature.

In summary, we have presented finite-temperature theoretical calculations in the quasi-harmonic approximation for various molecular and non-molecular solid forms of CO$_2$. The calculations aimed at resolving experimental uncertainties and inconsistencies due to kinetic effects and metastability. We find that the boundary between non-molecular phases and phase V has a positive slope and starts at 21.5 GPa at $T = 0$ K. We also find that the phase diagram shows a triple point between phase IV, V, and the liquid phase at 35 GPa and 1600 K. This indicates that the non-molecular phases have a broader region of stability than previously reported. We were able to reproduce the known thermodynamic boundary line between CO$_2$-II and CO$_2$-IV, confirming that kinetic effects are not relevant in that transition. Finally, it was shown that phase II is the most stable molecular phase at low temperatures, extending its region of stability to every $P - T$ condition where phase III has been reported experimentally. However, our results also show that CO$_2$-III is instead stabilized at high temperature and its stability region coincides with the $P - T$ conditions where phase VII was reported experimentally, implying that phase III and phase VII are indeed the same.

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