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Constraints on the phase diagram of nonmolecular CO_2 imposed by infrared spectroscopy

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The investigation of the high-pressure phase diagram of CO_2, specifically in the nonmolecular forms, is a challenging experimental issue, due to the large metastability of this material. Here we report on the determination of the pressure threshold for forming nonmolecular CO_2 from the molecular crystal, in the *P-T* range of 10–53 GPa and 296–715 K, respectively. The study is based on a large set of IR spectroscopy measurements, which allows to detect, with a high sensitivity, the onset of the formation of nonmolecular, amorphous carbonia. This metastable form is first formed in the attempts to obtain nonmolecular, crystalline CO_2, upon increasing pressure, for kinetic reasons. Therefore, it is identified an upper pressure bound for the real-phase boundary between the molecular solid and the nonmolecular, thermodynamically stable crystal, which results to be remarkably lower than those detected by other techniques. Also, it is shown how the hysteresis of the molecular-to-nonmolecular transformation is reduced upon increasing the temperature. The study adds constraints on the high-pressure, thermodynamic phase diagram of nonmolecular CO_2.

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I. INTRODUCTION

The high-pressure thermodynamic/kinetic phase diagram of solid CO_2 (kinetic phase diagrams include metastable phases and kinetic borders), despite the simplicity of the molecule, does exhibit a great complexity in terms of different stable and metastable phases and amorphous forms. Indeed, the phase diagram is parted into five molecular crystalline phases (I, II, III, IV, and VII), two nonmolecular crystalline phases (V and VI) and one nonmolecular, rather complex amorphous form (a-carbonia), as discussed in Ref. 1 and summarized in Fig. 1. The solid-solid phase transitions are affected by extremely large metastabilities, which prevented to identify the true phase boundaries above 10–15 GPa. In fact, above this pressure strikingly different kinetic boundaries have been found in the various studies, depending on the different *P-T* paths and analysis techniques. Experimental and *ab initio* computational studies have been showing that all the phases below 25–30 GPa are molecular crystals.[1] Above these pressures the reversible transformation to nonmolecular, extended solids with covalent character have been observed while the thermodynamic phase boundaries are severely confused. This confusion is most likely due to the energetic competition of many extended, metastable structures, as can be inferred from the results of *ab initio* calculations. The determination of the high-pressure thermodynamic phase diagram of CO_2, at *P-T* conditions where the molecular structure is altered, is thereby an extremely challenging issue from the experimental point of view. Nevertheless, several constraints can be imposed which, hopefully, will be supporting a possible, combined experimental and theoretical determination of the phase diagram, in the future. It is worthwhile in this context to briefly recall the main findings concerning nonmolecular CO_2.

The discovery of nonmolecular, crystalline CO_2, CO_2-V, was achieved by laser heating molecular phase III to 1800 K at about 40 GPa.[7] The Raman spectrum of the room temperature (room T) quenched, transformed material was then measured and phase V was identified as an extended solid with carbon in a tetrahedral coordination by oxygen, which in turn was subsequently confirmed by another experimental investigation.[5] An x-ray diffraction study has then shown that phase V is indeed made of CO_4 tetrahedral units arranged in an orthorhombic, trydimite-like structure.[8] *Ab initio* calculation studies have been predicting that CO_2 transforms into tetrahedral structures at high pressures[9–12] while a tetragonal β-cristobalite arrangement of the CO_4 units has been suggested to be the thermodynamic stable structure.[10–12] Recently, the nonmolecular, extended, glassy form of CO_2 was experimentally discovered[6] and its local structure was resolved.[13] Indeed, this material, named a-CO_2 or a-carbonia, is an extended, three-dimensional network of interconnected CO_4 and CO_3 units. Enthalpic considerations suggested that a-carbonia is a metastable intermediate state of the transformation of molecular CO_2 into fully tetrahedral phases. The formation of a-carbonia was first found to start above 48 GPa, at room T as indicated by strong peaks in the IR spectrum, lying between 650 and 1800 cm^{-1}.[6] Another nonmolecular, crystalline phase, CO_2-VI, was then found in coexistence with a disordered phase that to our opinion should be associated to a-CO_2 (Ref. 2) (Fig. 1), as indicated by the Raman spectrum. A*b initio* calculations suggested hypothetical, metastable layered structures for phase VI, composed of two-dimensional networks of corner-sharing CO_4 tetrahedra.[14–16]

We note that the pressure threshold reported in Refs. 2 and 17 for the formation of a-carbonia is significantly higher than in the original study on a-carbonia,[6] by about 10–20 GPa, and it is not clear whether this threshold has been accurately and systematically determined at different temperatures or it was only roughly estimated. The higher threshold presented in Refs. 2 and 17 is most likely to be ascribed to the fact that in those studies the formation of nonmolecular CO_2 has been detected by means of the Raman spectrum which, at variance with the IR spectrum, is very weak and thereby less sensitive to the onset of the transformation. Here we investigate this onset by means of the IR spectroscopy and assess a kinetic boundary for the high-pressure transformation from molecular-to-nonmolecular CO_2. We remark that a-carbonia is an amorphous, metastable form, which is

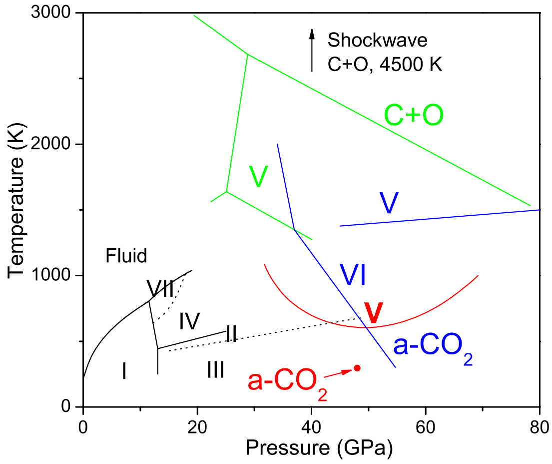

FIG. 1. (Color online) High pressure, phase/kinetic diagram of CO_2 (Refs. 1–3). Continuous lines below 25 GPa and 1000 K: phase boundaries. Dotted lines: kinetic boundaries for forming phase IV from VII and II from III. Continuous, colored lines: kinetic boundaries for forming the nonmolecular phases V and VI, the form a-CO_2, and the dissociated material, C+O, from molecular CO_2 [blue (Ref. 2), green (Ref. 4), and red (Ref. 5) lines correspond to different studies]. The red dot indicates the threshold pressure for forming a-CO_2 from molecular CO_2 at room T, as inferred from Ref. 6.

obtained, for kinetic reasons, instead of the stable, crystalline nonmolecular phase. Therefore, the kinetic boundary has to be considered as an upper pressure limit for the true, thermodynamic phase boundary between molecular and nonmolecular CO_2. We also report on how the metastability of the transformation is reduced upon increasing the temperature.

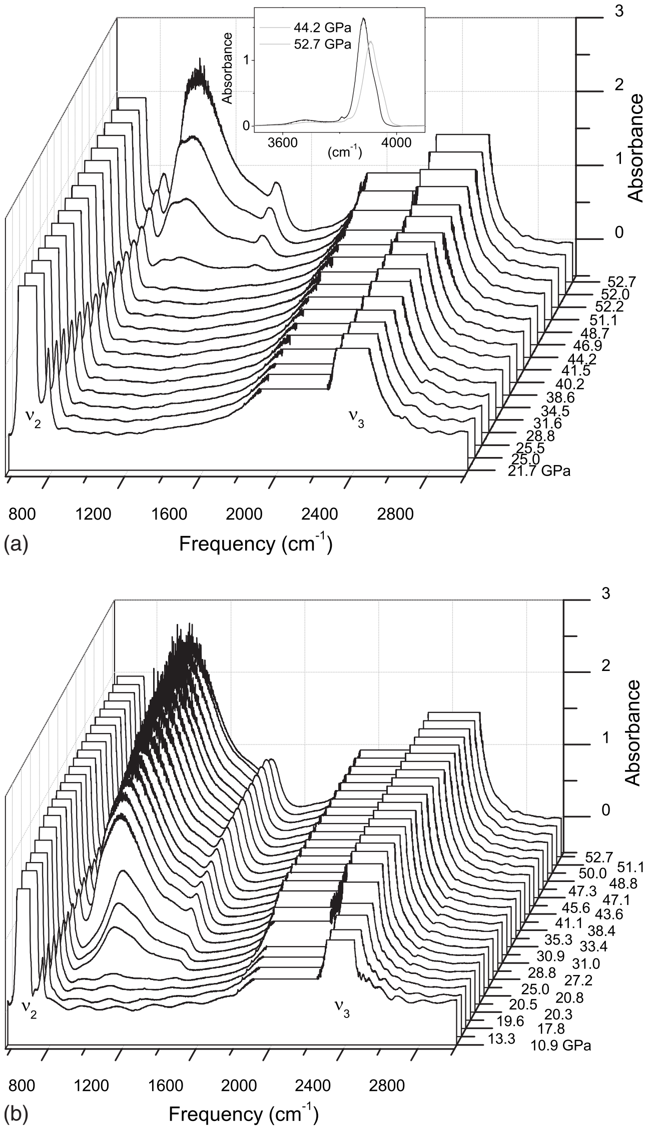

FIG. 2. IR spectra, measured along the 472 K isotherm, showing the reversible formation of a-carbonia. (a): pressure increase and (b): pressure decrease. The symbols ν_2 and ν_3 label the peaks assigned to the bending and the asymmetric stretching mode of molecular CO_2, respectively, whose absorption is saturated. Diamond absorption peaks also partially saturate the absorption close to 2000 cm^{-1}. Inset: $\nu_3+\nu_1$ and $\nu_3+2\nu_2$ combination bands of molecular CO_2 at the initial and final pressure steps along the formation of a-carbonia, upon pressure increase.

II. EXPERIMENTAL RESULTS AND DISCUSSION

The experimental setup which was used in this work includes a resistively heated diamond-anvil cell, and a custom modified Fourier transform Michelson interferometer, and has been described elsewhere.[6,13,18,19] The onset of the formation of a-carbonia at room T, observed by means of IR spectroscopy, has been exhaustively reported in Ref. 6, where it was put forward that the pressure threshold for the transformation to occur is at about 48 GPa. This value has been found and confirmed in many other pressure runs. In Fig. 2 it is reported selected IR spectra of CO_2 measured along an isothermal pressure scan at 472 K upon increasing (panel a) and decreasing (panel b) pressure, between 10 and 53 GPa. A small selection of these spectra were already presented in Ref. 13 where, for space reasons, the details of the pressure-induced transformation were not discussed. The indicated pressure range was scanned by 2–3 GPa pressure steps. The time elapsed between pressure increases and IR measurements was equal to about 30 min. The spectra were found not to change within 12 h, at fixed *P*-*T* conditions. The onset for the transformation from molecular-to-nonmolecular CO_2, upon increasing *P*, has been identified at about 44 GPa. This is indicated by the broad absorption peaks lying between 870 and 1600 cm^{-1}, which were shown to be mainly contributed by stretching modes of the CO_4 units forming a-carbonia.[13] The onset of a-carbonia is assessed as soon as these peaks emerges from the background with an intensity stronger than the signal noise. The absorbance is also seen to increase at around 2000 cm^{-1}, where new peaks are partially superimposed to the two-phonon peaks of diamonds. These peaks are due to the C=O stretching modes of the CO_3 units forming the new network material.[13] The transformation proceeds rather steeply, upon increasing pressure above 45–48 GPa. The absorption of the main band at around 1000 cm^{-1} starts to be saturated at about 53 GPa, where the complete transformation is far to be achieved. In fact, the peaks of molecular CO_2, in the frequency regions of the fundamental

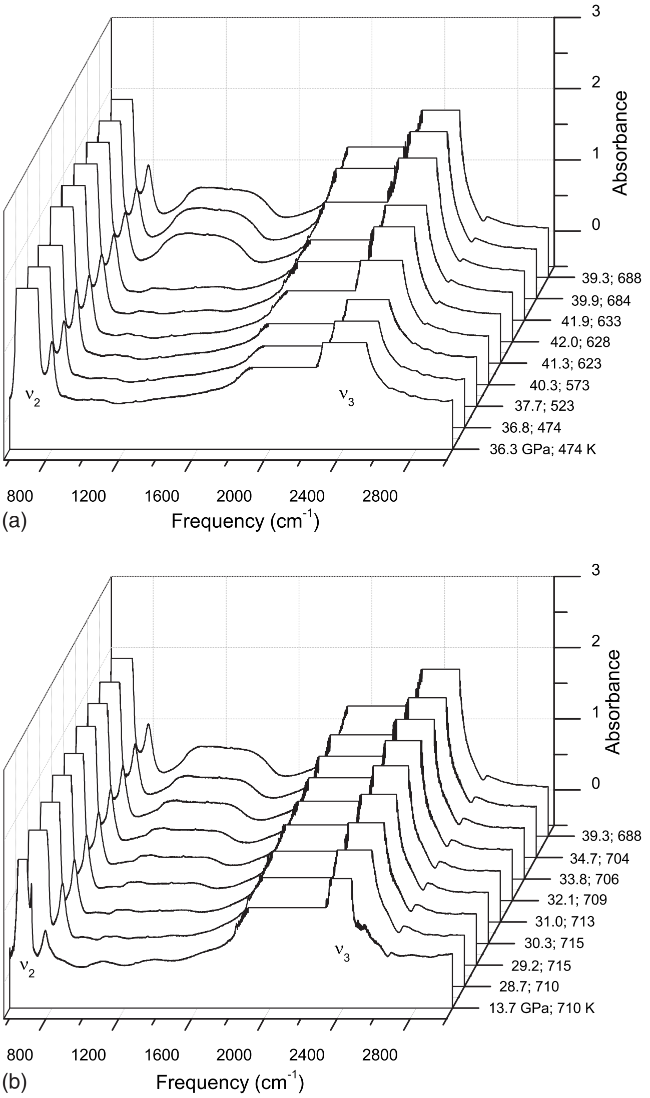

FIG. 3. IR spectra, measured along combined *P*-*T* paths, at 470–715 K, showing the reversible formation of a-carbonia. (a): pressure and temperature increase (the pressure slightly decreases in the last three *P*-*T* steps) and (b): pressure decrease and slight temperature increase. The symbols ν_2 and ν_3 label the peaks assigned to the bending and the asymmetric stretching mode of molecular CO_2, respectively, whose absorption is saturated. Diamond absorption peaks also partially saturate the absorption close to 2000 cm^{-1}.

modes, still saturate the absorption. In the inset of the Fig. 2, panel a, it is shown the IR spectra in the region of the overtone/combination bands. The amount of the transformed CO_2 is evaluated as the variation in the integrated absorbance of these peaks and it results to be equal to about 16% of the starting molecular material, as the transformation proceeded between 44 and 53 GPa. In Fig. 2, panel b, it is then evident how a-carbonia reverts to molecular CO_2 upon decreasing pressure. The back transformation is complete at 19–20 GPa.

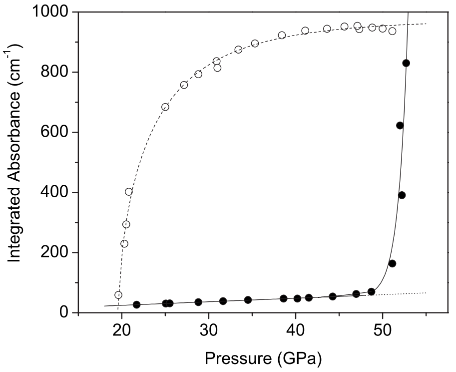

FIG. 4. Integrated, IR absorbance of the main a-CO_2 band, between 870 and 1600 cm^{-1}, vs *P*, along the isotherm at 472 K. Full dots: pressure increase and open dots: pressure decrease.

In Fig. 3 we report selected IR spectra of CO_2 measured along a mixed *P*-*T* path. Here (panel a) the pressure was increased from 20 to 42 GPa (and slightly decreased down to 39.3 GPa, in the last three pressure steps), by pressure steps of 0.5–2 GPa, while the temperature was increasing from 470 and 690 K, by steps of 4–50 K. The onset of the transformation was found at about 41 GPa and 600 K. The peaks of a-carbonia exhibit different band shape than those observed along the isothermal run at 472 K although lying at the same frequency positions, which is likely to be due to the different *P*-*T* path. As a matter of fact, the details of the microscopic structure of a-carbonia are not well defined since this is a metastable, glassy material moving among different local minima in the energy landscape, and this behavior is likely to produce some minor variation in the vibrational spectra. In panel *b* of Fig. 3 it is reported the IR spectra measured upon decreasing pressure while the temperature was slightly rising up to 715 K. Here it is seen the back transformation of a-carbonia to molecular CO_2, which is complete at about 25 GPa.

In Fig. 4 we report the integrated absorbance in the region of the nonmolecular peaks, between 870 and 1600 cm^{-1}, as a function of pressure, as measured in the isothermal run at 472 K. Here it is clear that the overall absorption emerges from the background, which is slightly pressure dependent, above 44 GPa, and steeply increases with pressure. It is also clear from Figs. 2 (panel b) and Fig. 4 that the nonmolecular material is either more stable than molecular CO_2 or it is metastable with strong confinement in the energy landscape, between 35 and 53 GPa. As a matter of fact, the amount of a-carbonia does not change significantly in this range, upon decreasing pressure. Then, below 35 GPa, the amount of a-CO_2 decreases from the plateau value exhibiting a smooth knee, which in turn changes into a very steep decrease between 20 and 25 GPa. At about 20 GPa a-carbonia is completely reverted into the molecular solid. It is thereby clear that at pressures lower than the "smooth knee" range, molecular CO_2 is more stable than the amorphous, nonmolecular material. It seems then a natural conclusion to interpret the knee pressure range as the low-pressure limit for the phase boundary between molecular and nonmolecular CO_2, although one should be aware that in this case things are complicated by the fact that some nonmolecular crystal of CO_2 could be more stable than the nonmolecular amorphous form. Interestingly, we note that at temperatures as high as 690–715 K (Fig. 3) the pressure range in which the amount of nonmolecular material did not significantly change upon

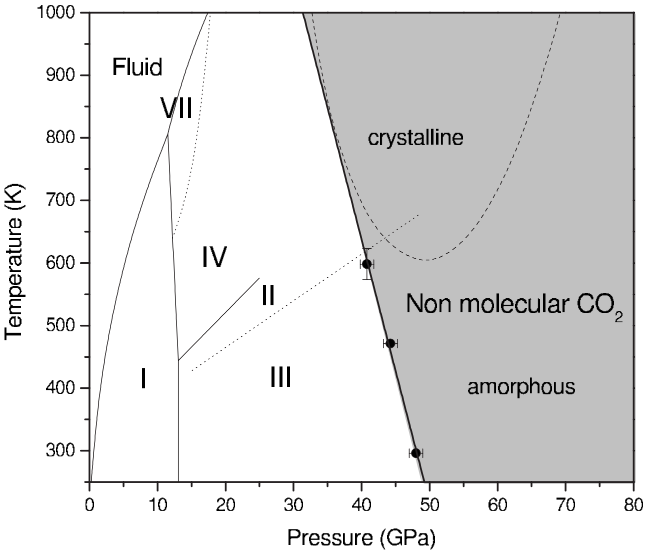

FIG. 5. Thermodynamic/kinetic phase diagram of molecular CO_2 (as in Fig. 1) and kinetic phase diagram of nonmolecular CO_2 based on this work. Dots and thick straight line: kinetic border for forming nonmolecular CO_2 from the molecular material (the line is extrapolated above 600 K). Gray pattern: P-T region pertaining to the thermodynamic stability domain of nonmolecular CO_2. The kinetic boundary (dashed line) for forming phase V from molecular CO_2 (Ref. 5) is also reported.

decreasing pressure (the plateau) only extends over a few GPa, in contrast to what has been observed at 472 K. The reducing plateau extension, i.e., the reducing hysteresis of the transformation with increasing temperature shows the enhanced capability of the system to overcome the energy barriers which separate the different structures. This result is of crucial relevance here. In fact, since the metastabilities significantly reduce upon increasing T, we think that a true thermodynamic transition point between molecular and nonmolecular CO_2 could be measurable at temperatures higher than those achieved in this work.

In Fig. 5 it is reported an updated thermodynamic/kinetic phase diagram where we summarize the pressure threshold values for forming a-carbonia. The threshold points have been determined at three different temperatures, as discussed above. The error bars include the inaccuracy in the determination of pressure and temperature. These bars also include the minimum P-T step separating the two closest points where CO_2 was observed to be strictly molecular and where it was found the onset a-carbonia, respectively. A straight line has been fitted through the threshold P-T points, identifying the kinetic border for forming a-carbonia from molecular CO_2. Interestingly, this line merges to the kinetic line for forming crystalline phase V from molecular CO_2, as found in the laser heating study by Santoro *et al.*[5] In that work the kinetic border shows a minimum at around 50 GPa while the formation of the amorphous, nonmolecular material, was missed. It was then argued,[5] on the basis of thermodynamic indications, that the entire portion of the phase diagram extending toward low temperatures, below the kinetic line, could pertain to the P-T domain of thermodynamic stability of nonmolecular CO_2. Indeed, the validity of such a hypothesis is concretely supported here. The entire region at higher P-T conditions than marked by the new kinetic border is straightforwardly interpreted as pertaining to the stability field of some nonmolecular crystal. In fact, we have shown that a-carbonia forms between room T and 600 K, beyond the kinetic line. This suggests that some nonmolecular crystal, of which a-carbonia is expected to be an amorphous counterpart, is thermodynamically stable beyond the new kinetic border, at temperatures down to at least room T. We note that the negative slope of the kinetic line seems to be a typical feature of chemical, reconstructive transformations. A kinetic line with negative slope was also found in the high-pressure transformation of model molecular systems such as C_6H_6 and N_2 into nonmolecular materials.[20,21] In fact, reconstructive transformations may proceed when intermolecular distances reach a minimum,[20] which in turn can be achieved statically by increasing P or dynamically by increasing T because of the thermally activated atomic motions. A natural consequence of this study is that the true phase boundary between molecular and nonmolecular CO_2 is expected not to intersect the nonmolecular P-T region delimited by the new kinetic line reported in Fig. 5, within our temperature range. Of course, the thermodynamic phase boundary and the kinetic line should merge above some high temperature where hysteresis effects become ineffective. Also, the phase boundary should intersect the plateau pressure region of the reverse nonmolecular-molecular transformation. As a matter of facts, the plateau is limited between the lower and upper pressure bounds of the phase boundary itself.

III. CONCLUSIONS

The large metastability of CO_2 at high pressures makes the experimental determination of the thermodynamic phase diagram difficult, specifically in the pressure range of the nonmolecular material ($P > 30$ GPa). Nonetheless, we think that the constraints imposed here could pave the way to the determination of the molecular-to-nonmolecular thermodynamic phase boundary. Based on IR spectroscopy we found upper and lower pressure limits for the thermodynamic transition pressures, at different temperatures. Also, we have shown that the metastability of the transformation is greatly reduced upon increasing temperature and that there is hope to measure thermodynamic transition points at temperatures higher than those reported here. On the other hand, in our range of temperatures the metastabilities of solid CO_2 prevent the experimental determination of the thermodynamic phase boundary. We think that, at these conditions, the phase boundary could be only unveiled by the help of *ab initio* computational studies, whose outcomes should then be compared to our experimental results. We hope our work will trigger such an investigation.

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