High pressure solid state chemistry of carbon dioxide†

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A review of experimental and theoretical studies performed over the past three decades on high pressure chemistry of solid CO_2, at 0–80 GPa and 40–3000 K, is presented. Emphasis is placed on the recently discovered non-molecular covalent crystalline phase V, and its glassy counterpart a-CO_2, along with other molecular phases, whose interpretation is crucial for determining the reaction path to non-molecular CO_2. The matter is still under debate, and many open issues are outlined, such as the true reaction mechanism for forming phase V. Finally, we propose arguments to stimulate possible future research in a more extended *P*–*T* range. This work is a *tutorial review* and should be of general interest both for solid state chemistry and condensed matter physics communities.

I. Introduction

High pressure techniques provide the leading tool for widely tuning the interatomic/intermolecular interactions in fluid and solid materials. These interactions become highly repulsive at high densities, mainly due to the average kinetic energy of electrons, which adds to the effective potential energy of nuclei. Strong changes in structural, thermal and mechanical properties of condensed matter occur to minimize the overall energy of the system; therefore, broad interest naturally arises in different contexts such as fundamental physics, chemistry, terrestrial and planetary sciences and material science. Even in simple molecular systems a plethora of new phenomena can be attained, ranging from solid–solid phase transitions to more complex transformations where the molecular framework itself is profoundly perturbed and new extended materials are obtained. This last case usually occurs when the intermolecular and intramolecular distances converge, so that the initial molecular identity is completely altered and chemical bonds are reconstructed. Polymeric compounds have been irreversibly synthesized by compressing small hydrocarbons, both in

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Mario Santoro is a physicist, who studies high pressure condensed matter physics and chemistry of simple systems, trying to investigate the unusual phenomena which occur in these fields. His research interests include: solid–solid (liquid) phase transitions, structural and dynamical properties of fluid and amorphous systems, and chemical reactivity in simple molecular systems such as hydrocarbons. Raman and infrared spectroscopy, along with X-ray scattering, coupled to diamond anvil cells, are the most commonly employed experimental techniques. He was awarded his PhD at the Universtiy of Florence (Italy) in 1998, and has been working as a research scientist at the European Laboratory for Non Linear Spectroscopy of the University of Florence since 1997. He was visiting scientist at the Geophysical Laboratory of the Carnegie Institution of Washington, in Washington DC (USA) in 2003–2004.

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† The HTML version of this article has been enhanced with a colour image of Fig. 3.

the liquid and solid state, in a greatly simplified reaction environment, where neither catalysts nor solvents are present.[1,2] Among paradigmatic molecular solids, intriguing reversible transformations were recently discovered in CO_2[3,4] and N_2 (Eremets *et al.*[5] and references therein) into non molecular extended covalent structures, and in N_2O into an unusual ionic solid $NO^+NO_3^-$ (nitrosonium nitrate).[6]

At least two fundamental issues have to be considered in the investigation of high pressure solid state reactions. The first is that molecular arrangement in the lattice represents a very relevant piece of information for understanding the reaction path, and reacting materials are usually characterized by structures that are often unknown. The second is that large kinetic barriers can prevent the achievement of thermodynamic stable phases in compressed materials, due to reduced molecular mobility. In principle, these barriers can be overcome at high temperatures; nevertheless, a variety of metastable solid phases, including amorphous structures, are commonly obtained in solid–solid phase transitions and/or chemical transformations.

In this work we review the subject of high pressure–high temperature transformations of CO_2 into several molecular solid phases, commonly investigated by means of the diamond anvil cell, and ultimately into extended non molecular covalent structures that are presently thought to be similar to SiO_2 polymorphs. Among simple molecules, carbon dioxide is of vital importance because it is broadly present in nature and is a model system involving the π bond and the hybridization properties of the carbon atom, which are severely affected by pressure. Carbon dioxide is one of the most common volatile systems; it is the dominant component of the atmospheres of terrestrial planets such as Mars and Venus, is commonly found in ice form in planets and asteroids, along with other simple species like NH_3 and CH_4, is important in volcanic and seismic activity,[7] and is employed as supercritical solvent in chemical reactions.[8] Although CO_2 is a simple molecule, its high pressure phase diagram is rather complex, exhibiting up to six different solid phases (Fig. 1). The unambiguous determination of the respective thermodynamic (opposed to kinetic) *P–T* domains is difficult because of strong mestabilities. At room temperature CO_2 solidifies into cubic phase I, commonly known as dry ice. This is a van der Waals crystal with strong (weak) intramolecular (intermolecular) interactions.[9–11] When compressed between 12 and 22 GPa at room temperature phase I undergoes a sluggish transition into the orthorhombic phase III,[4,11–18] which is a molecular crystal too. Actually, the view of a molecular solid for CO_2-III would seem to be challenged by a recent structural investigation,[4] where it was suggested that phase III is a high strength and hard material with increased intermolecular bonds. Finally, the observed CO_2-III was suggested to be metastable, since it was only obtained *via* moderate temperature compression of phase I.[4]

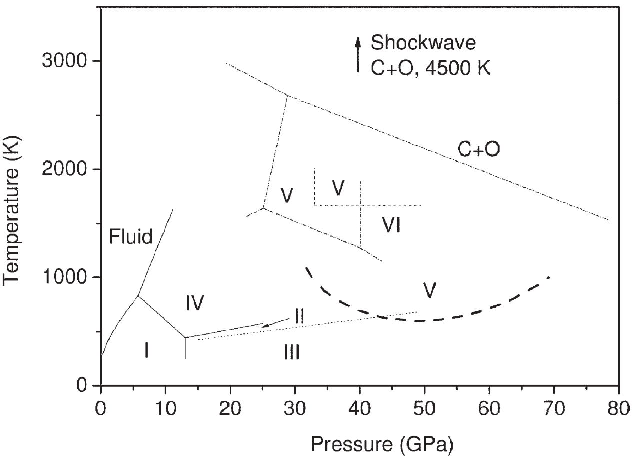

Fig. 1 Thermodynamic and kinetic phase diagram of solid carbon dioxide: continuous lines, phase boundaries delimiting CO_2-I, II, III, and IV;[28,32] dotted line, kinetic transformation boundary from CO_2-III to CO_2-II;[28,32] thick dashed line, kinetic transformation boundary from molecular to non molecular CO_2;[19] dashed[4] and dot-dashed[25] lines, approximate kinetic transformation boundaries from molecular CO_2 to the extended covalent phases V and VI, and to dissociation. We note that the quadruple point which seems to connect phases I, IV, II, and III would imply a thermodynamic paradox, *e.g.* the violation of the Gibbs' phase rule (see the discussion on this point in section VI "Phase II"). Melting line of CO_2-IV is only schematic.

A very interesting material with unconventional structure and properties, the non molecular phase V of carbon dioxide, was discovered by heating CO_2-III above 40 GPa and 1800 K.[3] This phase was temperature quenched and pressure recovered down to a few gigapascals, where it transforms back to molecular CO_2. The strongest signature of non molecular character consisted of a new peak in the Raman spectrum lying in the range of 680–820 cm^{-1}, assigned to the symmetric stretching of the C–O–C bonds, which testifies to the extended covalent nature of this material, involving only single bonds. X-ray diffraction led to the assignment of phase V to a tridymite structure, similar to polymorphs of SiO_2.[4] According to this study, each carbon atom is tetrahedrally bonded with four oxygen atoms, and the CO_4 tetrahedral units share their corner oxygens to form layers of distorted hexagonal rings. Also, phase V was found to be "superhard", *e.g.* as hard as cubic BN that is the second hardest known material. In a subsequent study the temperature threshold for transforming molecular CO_2 into phase V was accurately measured,[19] and it was found to be much lower than that roughly estimated by Iota *et al.*[3] The stable (as opposite to kinetic) high pressure phase diagram in the region of the transformation was also estimated, on the basis of thermodynamic arguments. The high pressure formation of non-molecular structures made of CO_4 tetrahedra was also theoretically predicted and reproduced by different authors, using *ab initio* computer simulations.[20–23] Nevertheless, there is no consensus among these studies in determining the actual crystalline structure, and none of them succeeded in reproducing the large measured incompressibility, on the basis of the calculated equation of state (EOS).

In a recent study made by our group, an amorphous, non-molecular, silica-like carbon dioxide material, christened "a-carbonia" (a-CO_2), was discovered by compressing of CO_2-III above 40–48 GPa.[24] The transformation was expedited by a mild temperature annealing to 570–680 K. The structure of the new glassy form has been determined on the basis of infrared and Raman spectroscopy, synchrotron X-ray diffraction and comparison to *ab initio* computer simulation data. It was then concluded that a-CO_2 is the disordered counterpart of crystalline phase V; a-carbonia was also estimated to be a very hard glassy material as compared to a-SiO_2.

Dissociation of solid CO_2 into diamond and molecular oxygen was found by heating this material at 30–80 GPa and 1500–3000 K.[25] Above 40 GPa the dissociation was preceded by the formation of a new non molecular phase, CO_2-VI, which was thought to be precursor of the dissociation itself. Also in this study temperatures were only roughly estimated. On the other hand, the investigation of Santoro *et al.*[19] included, in principle, the phase domain of CO_2-VI, whose existence was not confirmed. Decomposition of carbon dioxide was also found in the hot dense fluid state in shock wave experiments.[26]

After the discovery of crystalline non-molecular CO_2, two new solid phases, named IV and II, where reported to exist, close to the pressure–temperature range of CO_2-V.[27–30] Both phases were produced at high temperatures, and found to be temperature quenchable. According to the authors, the CO_2-IV and II would seem to show intermediate character between molecular solids and covalent bonded solids, thus playing the role of precursors to forming phase V. In CO_2-IV the molecules were suggested to be highly nonlinear (bent), which corresponds to the broken inversion symmetry, on account of Raman and X-ray diffraction data. Also, the intramolecular C–O bond length would be increased to the typical distance of a C–O single bond, while the intermolecular C···O distance would be reduced to less than the free molecule length. Also in phase II, but at a lower degree than in CO_2-IV, it was suggested that the C=O distance is highly elongated while the intermolecular separation is collapsed. Surprisingly, phase II have been reported to be largely incompressible, on the basis of the measured EOS, as compared to normal molecular solids.

The notion of intermediate phases between molecular and covalent-bonded solids, belonging to CO_2-II, IV and in a way also to phase III, was strongly challenged in a recent study by Bonev *et al.*,[31] using first-principles calculations. The authors re-examined the relative stability field of CO_2-I, II, III and IV and proposed that all these phases are normal molecular solids formed by linear CO_2 molecules. Specifically, the C=O bond length was found to be comparable to that of the free CO_2 molecule. The theoretical structures provide good agreement with most of experimental data, although the experimentally reported unusual large incompressibility of phases III and II was not reproduced by the calculated EOS. Such a discrepancy was indeed ascribed to an incorrect analysis of the measured equation of state. In a subsequent study by Gorelli *et al.*[32] the structures of CO_2-II and IV were investigated by means of accurate IR absorption and Raman measurements. These phases were confirmed to have normal molecular character, since none of the relevant spectral changes which could be expected on the basis of possible pseudo-extended structures, specifically in the IR spectrum, have been found. Instead, it was given the picture of slightly bent molecules, with C=O bond distance similar to that of the free molecule, whose bending is mainly induced by the weak crystal field interaction. By comparing the above-mentioned findings, the entire subject of high pressure solid state physics and chemistry of carbon dioxide appears still very controversial and even obscure, including different points such as: (i) the correct interpretation of the high pressure structures, along with (ii) their actual physical and chemical properties, (iii) the determination of the thermodynamic (as opposite to kinetic) high *P–T* phase diagram, (iv) the reaction mechanism for transforming molecular CO_2 to the non-molecular material. In the following we present and discuss in some detail the relevant experimental and theoretical results concerning each one of the mentioned solid phases, by proceeding, when possible, on a chronological basis. We place particular emphasis on the important controversies, trying to offer the view of a still rapidly developing field. Finally, we propose some points aimed to stimulating possible future research, in a much more extended *P–T* range than the one investigated so far.

II. Molecular phase I (dry ice)

Carbon dioxide solidifies into phase I at 0.5 GPa, at room temperature. The phase has face centred cubic structure, whose symmetry space group is *Pa*3. Four molecules are contained in the primitive cell, with molecular axis pointing in the body-diagonal directions (Fig. 2). The compression of CO_2-I at room temperature between 1 and 10 GPa was first investigated by Olinger,[9] by means of X-ray diffraction, who reported the cell parameter, the volume and the compressibility, *e.g.* the EOS (Fig. 3). The bulk modulus (inverse of the compressibility) was below 10 GPa while, most recently, Yoo *et al.*[4] reported a value of 12.4 GPa. These values are typical of a molecular solid, where molecules interact only by means of weak van der Waals forces.

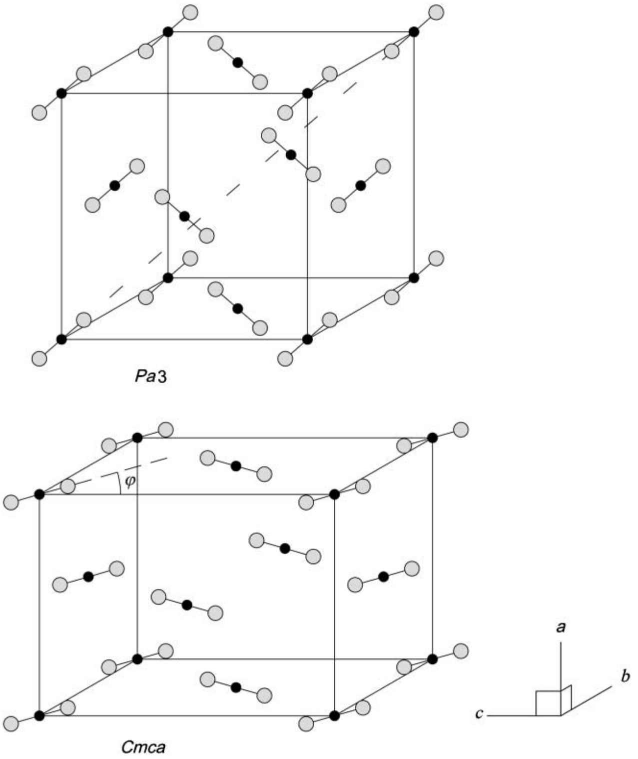

Fig. 2 The cubic *Pa*3 and orthorhombic *Cmca* structures, assigned to phase I and III, respectively.

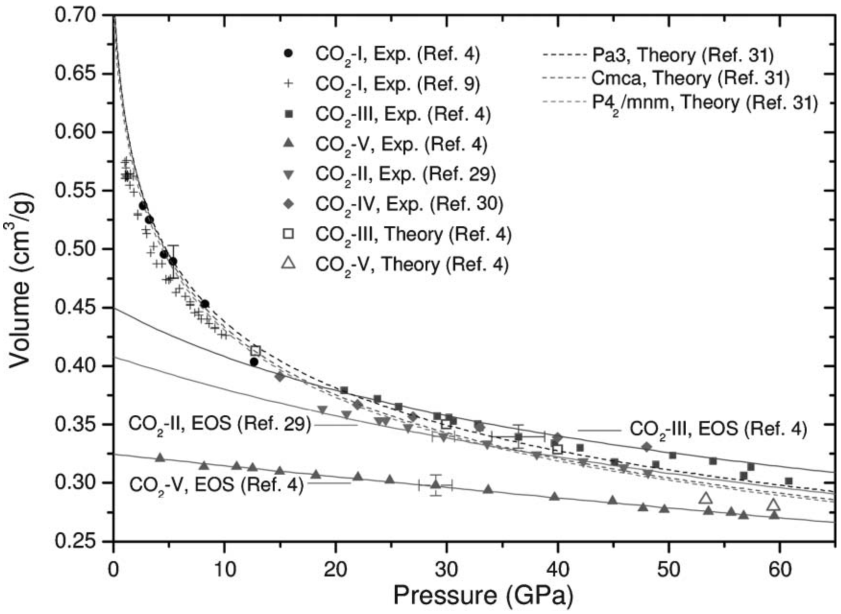

Fig. 3 Pressure–volume relations of solid phases of CO$_2$ (see legend and text). Dots: experimental (error bars are indicated for selected points) and theoretical data; continuous lines: Birch–Murnaghan fits to experimental data; dashed lines: theoretical equations of state.

Raman and infrared vibrational spectroscopies are a powerful tool for investigating the intra(inter)-molecular interactions, and they have been employed by several authors for studying phase I under pressure.[12,13,15,17,18,32] The spectral range assigned to vibrational frequencies of external (phonons) and internal (vibrons) molecular modes are well separated, which corroborates the notion of weakly interacting molecules. In the Raman spectrum three librational (hindered rotations in the solid state) phonon lines are observed, lying in the range of 50–350 cm^{-1}, along with two peaks, named ν_- and ν_+, that are positioned in the 1260–1280 cm^{-1} and 1380–1420 cm^{-1} intervals, respectively.[12,13,18] The ν_- and ν_+ peaks are originated by the Fermi resonance of the overtone (double excitation) of the CO$_2$ bending mode, $2\nu_2$, with the symmetric stretching mode ν_1. This phenomenon occurs when two vibrational modes having the same symmetry and comparable energy are coupled by the anharmonic part of the potential. The energy levels of both vibrations shift and are observed at different frequencies, as compared to the unperturbed case. The Fermi resonance tends to vanish with increasing pressure, due to detuning of $2\nu_2$ and ν_1, and only the ν_+ peak is observed, which corresponds, in these conditions, to the unperturbed ν_1 mode.[13,18] In the infrared spectrum bands are observed and assigned to translational phonons at 100–350 cm^{-1}, to the bending mode ν_2 at 550–750 cm^{-1}, to the anti-symmetric stretching mode ν_3 at 2300–2550 cm^{-1}, and to overtone modes at 3550–3850 cm^{-1} and 4950–5250 cm^{-1}.[15,17,32] Vibrational frequencies were found to harden with increasing pressure, as commonly observed, with the exception of ν_2 and ν_- as well, whose behaviour mostly reflects that of ν_2. The pressure dependence of phonon frequencies is much stronger than that of internal modes, which once again points to weak intermolecular interactions as compared to intramolecular ones.

Calculations of mode frequencies and of the EOS of CO$_2$-I have been performed with semi-empirical potentials.[10,11] In these studies the intramolecular potential is described as an expansion in powers up to the cubic term of the atomic displacement from the equilibrium, and the intermolecular potential is added as a perturbation. The perturbing term is given by the sum of all pairwise interactions between atoms on different molecules. These last exhibit the typical structure of a van der Waals potential, involving: a repulsive overlap short range term, an attractive long range (dispersion) term, and a long range quadrupole–quadrupole interaction term, which is expected to have a large effect in molecular condensation of CO$_2$. The resulting potential wells have typical depth of several milli-electronvolts, while the binding energy of the double C=O bond amounts to 7.7 eV. The calculated frequencies and the EOS agree fairly well with the experimental data, thereby demonstrating the entirely molecular character of phase I. Specifically, the softening of the ν_2 and ν_- modes, observed with increasing pressure, is quantitatively reproduced, which rules out the hypothesis of a possible pressure-induced instability of the molecule.

III. Molecular phase III

Phase II of solid CO$_2$ in the 0.5–2.3 GPa pressure range was reported by Liu[33] on the basis of X-ray powder diffraction studies, but never confirmed by subsequent studies. On the other hand, a transition from CO$_2$-I to a new phase, CO$_2$-III, was observed by Hanson[12] by Raman investigation and, after that, largely confirmed. He reported three new phonon peaks between 14.9 and 18 GPa, at room temperature, replacing those of phase I. The transition pressure was not accurately determined, likely because of the limited signal to noise ratio. Also, large pressure gradients were observed in the new phase. These findings were confirmed by Olijnyk *et al.*,[13] using Raman data at room and low temperatures. The correct determination of the I–III phase boundary was obscured by a very large hysteresis, and the overall results were found to be strongly affected by the sample history. Additional Raman and infrared studies through the years confirmed the I–III phase transition.[15,17,18] Also, an intermediate phase, named IV, which may involve minor modifications of phase I, was suggested to form prior to the transformation to phase III,[13,18] which has also some theoretical support.[31] An orthorhombic structure with four molecules per conventional unit cell (space group is *Cmca*) was assigned to phase III by Aoki *et al.*[16] (Fig. 2), based on synchrotron X-ray powder diffraction. The I–III phase transition was observed to be sluggish, starting at about 10 GPa at room temperature, and to have a volume change close to zero. Indeed, the *Pa*3 (I) and *Cmca* (III) structures are closely related to each other. As in the cubic structure, the molecular centres are on the face-centred positions in the orthorhombic crystal, while they are differently oriented: all the molecules are aligned in the same plane parallel to the *bc* plane, and they form an angle φ of 52° with the *c* axis, as theoretically predicted[11] (see below). The *Pa*3–*Cmca* transition can occur ideally by a simple transformation: starting from the cubic structure all the molecules rotate until they become parallel to one of the base planes and the unit cell is deformed from a cube to a rectangular parallelepiped. Similar pressure-induced *Pa*3–*Cmca* transitions have been found for other simple linear molecules with large quadrupole moments [*e.g.* acetylene at 0.9 GPa and nitrous oxide at 4.8 GPa (see references in Aoki *et al.*[16])]. Before this X-ray diffraction study, Kuchta and Etters predicted the *Pa*3–*Cmca* phase transition[11] at 4.3 GPa and zero temperature by modelling solid CO_2 as a van der Waals crystal (see above, for CO_2-I). They also found that a large hysteresis associated with the transition may be the result of big energy barriers, combined with small energy difference between the phases. These authors also predicted that the transition pressure should be rather temperature independent, in the whole range between 0 and 300 K.[14]

More recently CO_2-III was investigated up to 60 GPa by synchrotron X-ray diffraction and Raman spectroscopy.[4,28] The I–III phase transition was confirmed to be sluggish at ambient temperature, occurring with no apparent volume discontinuity. On the other hand, it was found that at around 400 K the transition occurs abruptly, at 12–13 GPa; this result also rules out the presence of the stable (as opposed to metastable) intermediate, distorted cubic phase (IV), proposed by Olijnyk *et al.*[13,18] The *Cmca* structure of phase III was confirmed up to 60 GPa. Large pressure gradients equal to 100–200 GPa mm^{-1} were reported above 30 GPa. The EOS was measured (Fig. 3), and an unusually high bulk modulus amounting to 87 GPa was found by extrapolating volume data down to ambient pressure. It was also suggested that the layered crystal structure of CO_2-III should likely support electron charge transfer from intramolecular to intermolecular linkages, which could imply a tendency to dimeric association. Indeed, collapsed intermolecular distances have been found: the nearest C···O distances are reduced down to about 2.6 Å, to be compared to 3.144 Å in phase I.[28] It was then concluded that CO_2-III is a high strength material with increased intermolecular bonds, implying that such a solid is not entirely molecular. This view was refuted in a recent *ab initio* study of Bonev *et al.*[31] where the orthorhombic *Cmca* structure was found to be a strictly molecular solid. The zero temperature EOS, along with vibrational frequencies were calculated and compared to the experimental results, and a reasonable agreement was found within the experimental errors (Fig. 3 and 4), though the theoretical volumes are smaller than the measured ones by about 2%–3%. On the other hand, the computed bulk modulus is much lower than the measured one (3.53 GPa), a typical value for a van der Waals solid; the large difference was suggested to come from an incorrect extrapolation of experimental data, spread out above 20 GPa, down to ambient pressure.

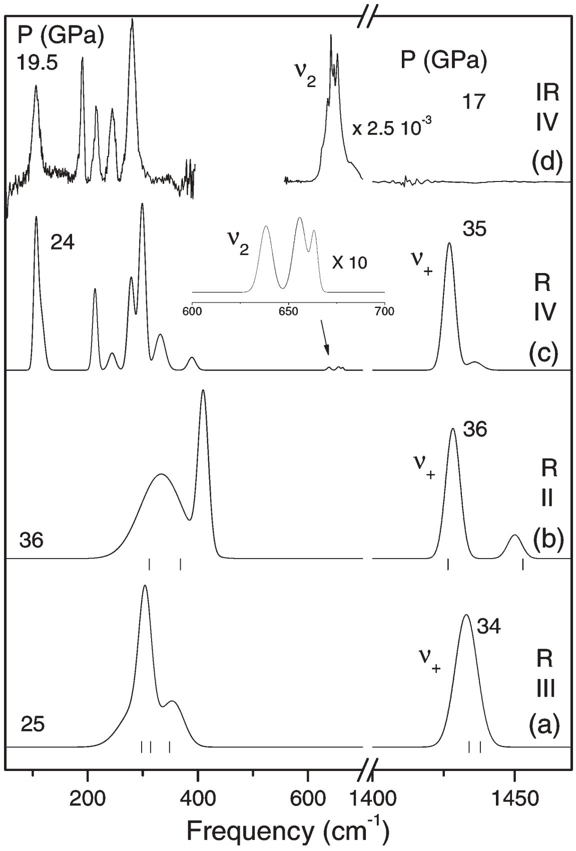

Fig. 4 Typical room temperature Raman spectra of phases III (a), II (b), and IV (c).[27–29] (d): Typical room temperature infrared spectrum of phase IV.[32] Vertical bars indicate theoretical Raman frequencies.[31] Frequencies below 500 cm^{-1} (above 600 cm^{-1}) are assigned to external (internal) modes. Raman spectra have been analytically reproduced.

IV. Non molecular solid carbon dioxide: crystalline phase V, and amorphous carbonia

The discovery of non molecular crystalline carbon dioxide,[3] named phase V, synthesized from CO_2-III at high pressures and temperatures, brought broad attention to high pressure chemistry of this important substance. Phase V was soon identified as an extended covalent solid with carbon–oxygen single bonds, since based on Raman spectra of the temperature-quenched material it was found to be similar to the quartz polymorph of SiO_2. The main point supporting this analogy consisted of a sharp peak in the range of 680–820 cm^{-1}, which

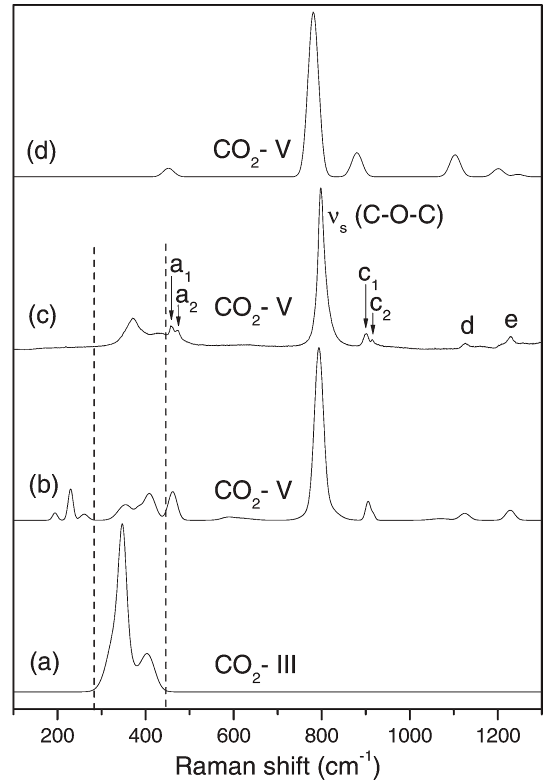

Fig. 5 Raman spectra of solid CO_2 at 40 GPa and room temperature. (a): spectrum of molecular phase III;[3] (b), (c), and (d): spectra of non molecular phase V measured by Iota *et al.*,[3] (b), Santoro *et al.*,[19] (c), and theoretically evaluated by Dong *et al.*,[21] (d). The strong peak at 780–800 cm^{-1} is assigned to the symmetric stretch of the C–O–C bonds, and suggests that CO_2-V is made of C–O single bonds. Peaks between the vertical dashed lines are assigned to the molecular crystal. Spectra (a) and (b) have been analytically reproduced.

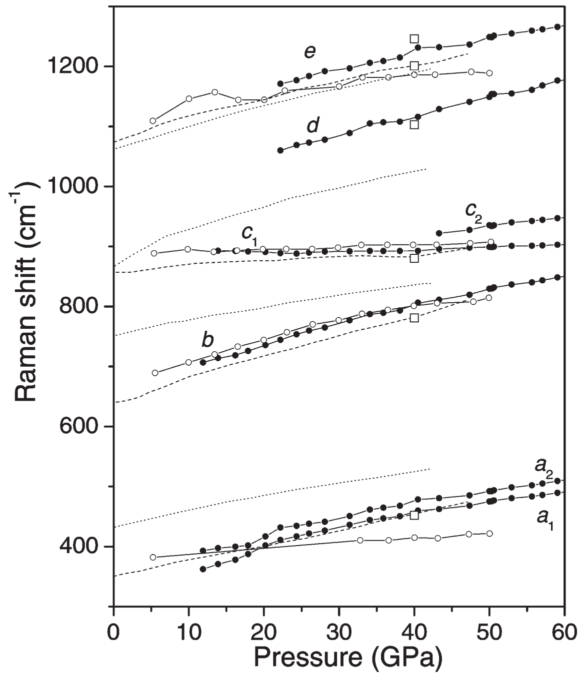

Fig. 6 Pressure shift of Raman frequencies of phase V. Open[3] and filled[19] circles: experimental data; dashed and dotted lines: theoretical behaviours for non molecular CO_2 in β-cristobalite (also, open squares) and α-quartz-like structures, respectively.[21]

was assigned to the symmetric stretching of C–O–C single bonds (Fig. 5). The position of this peak, when extrapolated down to ambient pressure (Fig. 6) and rescaled on account of the different masses, is close to the corresponding peak of quartz. We point out that the assignment of the Raman peaks below 450 cm^{-1} is not entirely convincing. The two modes observed at 353 and 410 cm^{-1} were assigned to CO_2-V, while they are rather from the unconverted molecular solid CO_2, since they are positioned very close to phonon peaks of the starting phase III. On the other hand, the three peaks at 200, 230, and 260 seem to be entirely new features, while the two of them at the lowest Raman shift were assigned to CO_2-III in the original study.

Phase V was also found to be optically non linear, generating second harmonic signal from a near infrared laser. This result poses constraints on the structure of CO_2-V. As a matter of fact, the second harmonic of light is only generated in noncentrosymmetric crystals as, for instance, quartz.

The crystal structure of phase V was subsequently investigated by synchrotron X-ray powder diffraction in the 2–60 GPa pressure range at room temperature.[4] The diffraction pattern of CO_2-V (Fig. 7) was fitted in terms of an orthorhombic structure (space group $P2_12_12_1$) belonging to the class of tridymite structures, which includes a crystalline phase of silica. We note that the intensity data and evidence for preferred orientation did not allow precise refinement of the actual structure, *e.g.* of the atomic positions. Multiple assignment of the Miller's indices (*h*,*k*,*l*) was proposed for some of the peaks (see Table I of ref. 4), while only one term for each peak seems to have been definitely selected (see Fig. 2 of ref. 4), according to a procedure that was not entirely clarified. According to the authors, phase V is formed by CO_4 tetrahedral units (Fig. 8) sharing "their corner oxygens to form sixfold distorted holohedral rings with alternating tetrahedral apices pointing up and down the *ab* plane. The apices of tetrahedral are then connected through oxygen atoms along the *c* axis". This is an interconnected layer structure of tetrahedra. The carbon oxygen bond distance was found to be equal to 1.34 (1.40) Å at 60 (10) GPa, and the intra (inter)-tetrahedral O–C–O (C–O–C) angles were estimated to be about 110° (130°). It was noted that the intertetrahedral angle is smaller than in SiO_2 polymorphs, where it amounts to 174–180° and 145° in tridymites and quartz, respectively. The small C–O–C angle, as compared to silica, implies higher rigidity, which in turn was argued to reflect a higher covalence. Large volume changes were reported, associated to the III to V transition, equal to 15.3% (12.6%) at 40 (60) GPa, and the equation of state (Fig. 3) of CO_2-V points to surprising mechanical properties. Phase V has very small compressibility, and the EOS data, when extrapolated to ambient pressure, provide a bulk modulus as high as 365 GPa, which is higher than that of silica quartz (37 GPa) or even stishovite (310 GPa) and is comparable to that of cubic BN (369 GPa). On account of this result CO_2-V was proposed to be "superhard", which in principle is a very relevant point also for the material science

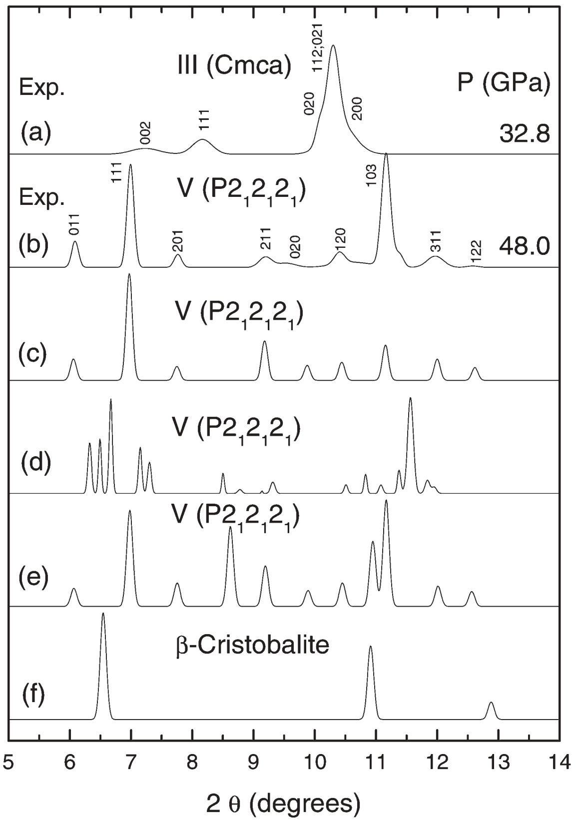

Fig. 7 X-ray diffraction patterns of solid CO_2 at high pressures and room temperature ($\lambda = 0.3738$ Å). (a): pattern of molecular phase III;[4] (b), (c): measured and calculated (fitted to the measured peaks) patterns of non-molecular phase V, respectively;[4] (d) theoretical pattern of non-molecular CO_2, evaluated by Dong *et al.*[22] on the fully refined tridymite $P2_12_12_1$ structure; (e), (f): theoretically patterns of non-molecular CO_2 in tridymite $P2_12_12_1$ and in β-cristobalite, respectively, evaluated by Holm *et al.*.[23] Patterns have been analytically reproduced. Miller indices (*hkl*) are indicated for phases III and V.

and engineering community. In the same study volumes of phase III and V were also theoretically evaluated at selected pressure values, by *ab initio* techniques, and a reasonable agreement with the experimental data was obtained.

The formation of phase V was investigated and confirmed by other authors, using Raman spectroscopy.[19,25] Tschauner *et al.*[25] studied the temperature quenched material, as the earlier study. A lower transformation temperature from the molecular solid to phase V was estimated (Fig. 1), decreasing with increasing pressure down to 1000–1200 K at 45 GPa. Subsequently Santoro *et al.* investigated this transformation by means of Raman spectra measured *in situ*, *e.g.* at simultaneous high temperatures and pressures.[19] The transformation temperatures were accurately determined at different pressures by considering the temperature dependent asymmetry of the anti-Stokes/Stokes sides of the vibrational spectrum. The observed transformation boundary was found to be much lower than those previously estimated, by more than 1000 K; it exhibits a minimum at about 50 GPa (about 600 K; Fig. 1), indicating that the previous result represented a kinetic barrier rather than a phase boundary. Since the molecular-to-non-molecular transformation does involve a reconstruction of chemical bonds, this should be considered a true chemical reaction. On the other hand, reactions may proceed when intermolecular distances reach a minimum; this condition can be achieved statically by increasing pressure or dynamically (lattice phonons) by increasing temperature. Viewed in this way, the negative slope of the transformation boundary can be explained. A similar behaviour was also found in other simple molecular systems such as acetylene, butadiene, benzene and nitrogen (see references in Gorelli *et al.*[32]) which transform under pressure into extended covalent phases. At higher pressures the reduced molecular mobility most likely tends to hinder the chemical reactivity in CO_2, and a higher temperature is required for promoting the reaction.

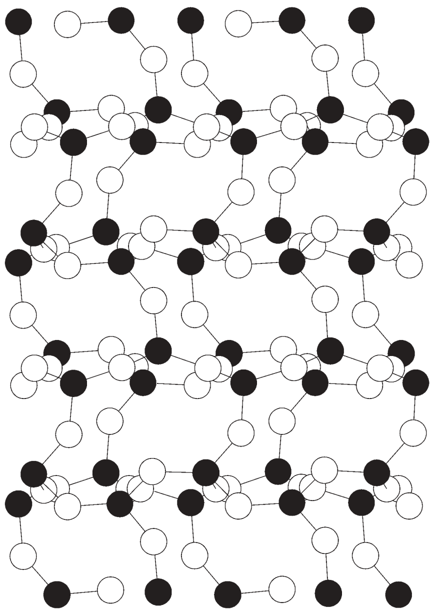

Fig. 8 Non molecular CO_2-V in an ideal crystal structure $P2_12_12_1$ with 8 carbon (●) and 16 oxygen (○) atoms per unit cells.[4]

The Raman spectrum of temperature quenched phase V, Fig. 5(c), exhibits substantial agreement with that measured by Iota *et al.*,[3] Fig. 5(b), with exception of the three peaks below 300 cm^{-1} that are not observed in spectrum (c). These extra peaks may be related to the presence of additional materials put in the cell for enhancing the laser heating process, employed for synthesizing non molecular CO_2. Peaks lying in the 280–450 cm^{-1} range were definitely assigned to untransformed molecular solid.[19] The two doublets labelled as a_1, a_2 and c_1, c_2, that are resolved in spectrum (c), form two asymmetric peaks in spectrum (b) where, on the other hand, they were suggested to be doubly degenerate. Up to three very weak peaks are observed in (c), close to lines *d* and *e*, which are not evident in spectrum (b), and tend to vanish at higher pressures.

In Fig. 6 we collect the pressure shift of Raman peaks of CO_2-V reported by Iota *et al.*[3] and Santoro *et al.*,[19] respectively. The two set of data are only qualitatively in agreement with each other, *e.g.* shifted frequency positions and different slopes are found. This discrepancy is likely to be ascribed to the fact that the samples in the two studies were synthesized at different *P*–*T* conditions and decompressed starting from different pressures. Also, Iota *et al.*[3] reported the pressure shift of only one of the two bands observed above 1000 cm^{-1}, and a unique frequency is reported for each one of the two manifolds (a_1, a_2) and (c_1, c_2), respectively. We note a large difference in the slopes of different modes: strong and weak pressure dependencies are observed, for instance, for the *b* and the c_1 peak, respectively. Tschauner *et al.* found different behaviour by decompressing non molecular CO_2: peaks corresponding to lines *a* and *b* exhibited a discontinuous change at about 40 GPa, and an additional peak was reported between these bands, which disappears below 40 GPa. These findings suggested the existence of a new non molecular crystalline phase of CO_2, named phase VI, which on the other was not easily observed in subsequent studies.[19] Interestingly, the dissociation of CO_2 into its constituent elements C (diamond) + O_2 (molecular), between 28 and 75 GPa, and temperatures as high as 2000–3000 K, was observed. The kinetic barrier for dissociation decreases with increasing pressure, and free energy estimates indicated that compression of non molecular CO_2 will ultimately end in dissociation at moderate temperatures and very high pressures. This point was also theoretically examined by Serra *et al.*,[20] but a study of Holm *et al.*[23] provided a contrasting view (see below).

The high pressure synthesis of non molecular carbon dioxide was theoretically investigated by several authors, with *ab initio* molecular dynamics computer simulations based on density functional theory. In a study almost simultaneous with the experimental report on the discovery of phase V[4], Serra *et al.*[20] predicted that above 100 GPa at 2000 K CO_2-III transforms into a silica-like three-dimensional amorphous solid. This material has carbon atoms at the fourfold centre of oxygen tetrahedra, and oxygen atoms twofold coordinated, in bridge positions between two carbons. Also, some of the tetrahedra were organized in a crystalline structure. The authors then performed refinement calculations, for identifying the most stable crystal structure among those suggested by the simulations. The set of candidate structures included silica-like crystals such as α-quartz, cristobalite, coesite, stishovite along with other carbonates, involving special arrangements of CO_4 tetrahedra. All these non molecular structures are characterized by tetrahedral carbon coordination, with exception of stishovite, where the carbon coordination is six. Thermodynamically, the most stable phase was found to be α-quartz, at zero temperature and above 35 GPa, up to at least 500 GPa. Stishovite resulted to be disfavoured over all the fourfold selected structures and over the full dissociation into C (diamond) + O_2 (molecular), which would make it possible that CO_2 will finally dissociate into its constituent elements, at very high pressures, directly from the quartz-type phase. The appearance of an amorphous quartz-like structure in the high-temperature simulations led the authors to suggest that a high energy barrier has to be overcome for transforming molecular CO_2 into α-quartz CO_2. This point implies that heating to high temperatures may be a crucial factor in the synthesis of non molecular crystalline CO_2, as indeed experimentally reported (see above).

The theoretical bulk modulus for quartz-type CO_2 was equal to 183 GPa,[20] which is much lower than that subsequently measured by Yoo *et al.*[4] This material is insulating, with an estimated energy gap of 10 eV at ambient pressure, and it was argued to be more covalent than silica. In a subsequent theoretical study of non-molecular crystalline CO_2 it was predicted that phase V should be a cristobalite-like rather than a quartz-like solid.[21] The authors refined several structures containing corner sharing CO_4 tetrahedra analogous to SiO_4, and found that tetragonal β-cristobalite is the lowest energy crystal by at least 0.2 eV per CO_2 (binding energy), corresponding to about 2400 K. This structure is very similar to tridymite. Tetrahedral carbon atoms form a hexagonal network in tridymite and a diamond network in β-cristobalite. The stability of β-cristobalite was shown to be due to the rigidity of the C–O–C inter-tetrahedral angles, amounting to 120–125°, as compared to the soft Si–O–Si angles in silica (145–150°). This difference led the authors to predict that non molecular CO_2 would not form a rich variety of polymorphs, as observed in SiO_2. The Raman spectrum of β-cristobalite CO_2 was also calculated (Fig. 5); it reproduces the most relevant experimental features, with the exception of the peaks below 300 cm^{-1} in spectrum (b), which on the other hand are not observed in spectrum (c). We note that only one doubly degenerate mode in the calculated spectrum does correspond to each one of the two doublets a_1, a_2 and c_1, c_2, respectively. This point suggests that, even though β-cristobalite resembles the main properties of phase V, the actual structure of this phase may have a lower symmetry. In Fig. 6 the theoretical pressure shift of Raman peaks for the β-cristobalite structure, and the α-quartz as well, are compared to the experimental behaviours.[3,19] Much better general agreement is indeed observed for β-cristobalite than for the α-quartz.

In a second theoretical study Dong *et al.*[22] re-examined the experimental assignment of the tridymite $P2_12_12_1$ structure to phase V and the notion that this phase is "superhard".[4] The authors investigated the stability and compressibility of a variety of tetrahedrally bonded non-molecular CO_2 structures analogous to silica, including different tridymite and cristobalite structures, along with quartz. Again β-cristobalite was found to be the most stable structure, at least between 0 and 80 GPa at zero temperature, whereas all the tridymite-type crystals exhibited much higher minimum binding energy values, by about 0.19–1.83 eV per CO_2. The bulk modulus for the selected phases ranges between 1/2 and 1/3 of the measured one (365 GPa), in agreement with the theoretical value of Serra *et al.*,[20] challenging the notion of "superhard" material. Discrepancies are also found between theoretical and experimental X-ray diffraction patterns. The diffraction pattern of a $P2_12_12_1$ structure, whose lattice parameters were assumed to be equal to the measured ones at 48 GPa while only the internal coordinates were theoretically refined, bears similarity with the experimental pattern, whereas the fully theoretically refined $P2_12_12_1$ crystal exhibits rather different diffraction peaks[22] (Fig. 7). Theoretical diffraction patterns of quartz and cristobalite phases are even less compatible with the experimental data. Finally, the question arose whether density functional theory can describe non molecular CO_2 correctly, or the framework of this material contains only CO_4 tetrahedra.

An additional contribution to this debate was provided by the theoretical study of Holm *et al.*.[23] Here, on account of energy calculations at zero temperature, the *Cmca* molecular phase was found to undergo a transition to non molecular CO_2 in the β-cristobalite phase at 15 GPa, which in turn resulted more stable than the $P2_12_12_1$ structure. These findings corroborate the theoretical results of Dong *et al.*.[21,22] On the other hand, the calculated pattern of Holm *et al.*[23] for the refined $P2_12_12_1$ structure (see Table I of ref. 23) matches the experimental one reasonably well (Fig. 7), apart for the theoretical extra-peaks at 8.62° and 10.95°, respectively, while the β-cristobalite is too symmetric to generate the rather rich pattern of phase V (details of the refining procedure were not given in this study). It was therefore suggested that, while all theoretical structural refinements mentioned above were performed at zero temperature, finite temperature could indeed play an important role in stabilizing the structure of phase V in the actual experimental conditions. Calculations of the electronic density of states show that the β-cristobalite and $P2_12_12_1$ tridymite crystals have rather different optical properties: the first is a typical covalent solid, highly insulating with a large band gap of 7 eV,[23] while the second has a relatively small band gap of 2.2. eV. The stability of non molecular CO_2 in the stishovite phase, the octahedrally coordinated structure, was also investigated.[23] This crystal was predicted to be a very ionic material and to become stable around 400 GPa, with a bulk modulus of 310 GPa, which is about twice that of β-cristobalite (154 GPa). This point is in striking contrast with results of Serra *et al.*,[20] where stishovite was indicated to be disfavoured over a variety of silica-like structures and over the full dissociation into the constituent elements, C + O_2, which could finally prevail at very high pressures.

Recently, the non-molecular, silica-like, three-dimensional, carbon dioxide amorphous solid which was predicted to exist by Serra *et al.*[20] was indeed experimentally discovered.[24] The synthesis of the new material (a-carbonia, or a-CO_2) was initiated by compressing CO_2-III between 40 and 48 GPa at room temperature, and almost completed (a few percents of residual molecular CO_2 was observed) by increasing the temperature to 570–680 K. In Fig. 9 we report the infrared spectrum of temperature quenched a-CO_2, showing the prominent bands A_{IR} and B_{IR}, whose large width is related to the disorder. By analogy to the IR spectra a-SiO_2, the two bands of a-carbonia have been assigned to different modes of the carbon–oxygen network made of single C–O bonds. We also report (Fig. 9) the Raman spectrum of a-carbonia, also exhibiting broad bands, compared to that of phase V, which in turn has much narrower lines. The Raman lines of CO_2-V are close to the a-CO_2 band edges, thereby it was speculated that bands of a-CO_2 reflect vibrational density-of-state features of CO_2-V. This also supported the notion that a-CO_2 is the glassy counterpart of phase V, which was then definitely assessed by the X-ray diffraction analysis once it had been compared to the computer simulated diffraction pattern. We recall here that even amorphous along with liquid materials exhibit features in the X-ray diffraction pattern, reflecting the local (microscopic) order of these systems.

Just a few years after the discovery of phase V, another two high pressure molecular solid phases of carbon dioxide were found, named CO_2-IV[27] and II.[28] The new phases were initially thought to be not entirely molecular, exhibiting precursor character for the formation of CO_2-V. By strict analogy with CO_2, Iota *et al.*[34] assigned intermediate character to high pressure solid phases of N_2O, that would anticipate the transformation into the ionic $NO^+NO_3^-$ compound and N_2. This view recently stimulated a debate about the true reaction path related to the molecular-to-non-molecular transformation of this important substance.

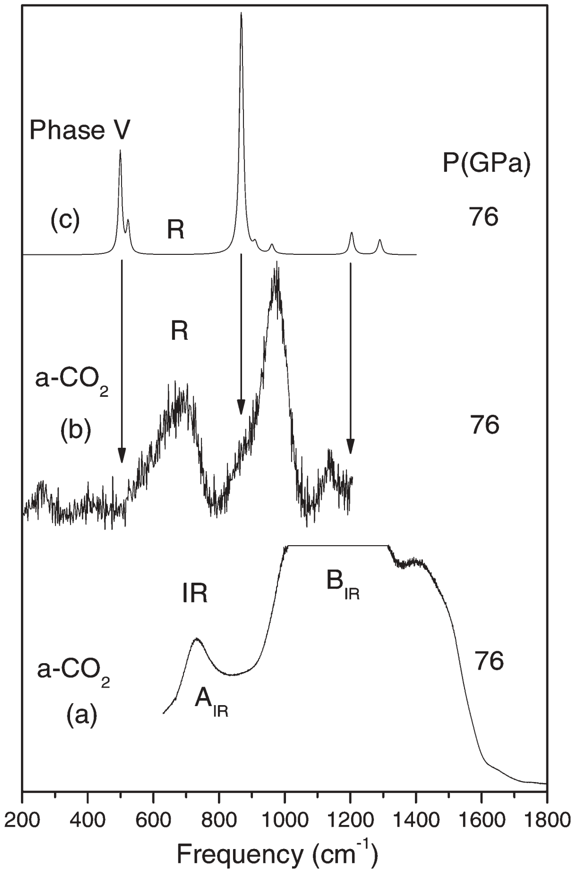

Fig. 9 Vibrational spectra of non-molecular CO_2:[24] (a) IR spectrum of a-carbonia, showing two prominent bands labelled as A_{IR} and B_{IR} (the absorption of B_{IR} is partially saturated); (b) and (c) Raman spectra of a-carbonia and phase V, respectively. Arrows point out the correspondence of phase V Raman lines to band edges of a-carbonia.

V. Phase IV

Phase IV was found in heating experiments on the molecular solid above 500 K, at 10–30 GPa,[27,28] using *in situ* Raman spectroscopy as the probe tool. Though CO_2-IV was found to be stable only at a high temperatures (Fig. 1 and 10), it was temperature quenched, and persisted over the whole pressure range of CO_2-III, up to 80 GPa, while it transformed to phase I below 8 GPa. Also, CO_2-IV transformed to CO_2-V above 30 GPa upon heating, and the reverse transition was observed by heating CO_2-V below 30 GPa. The Raman spectrum of phase IV exhibited a weak triplet feature around 650 cm^{-1} (Fig. 4), which is close to the frequency range of the IR active bending mode ν_2 of CO_2. Since this mode is Raman silent,

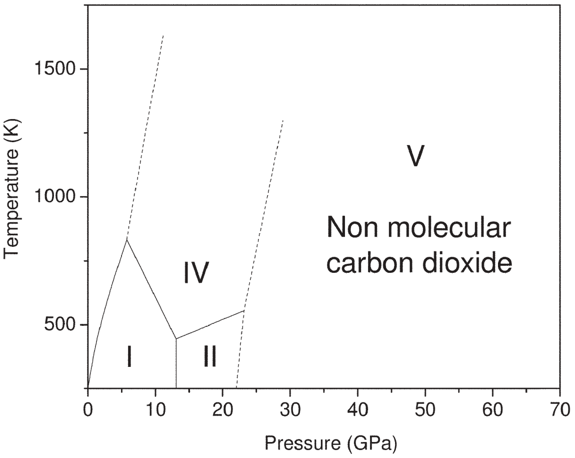

Fig. 10 Schematic thermodynamic phase diagram of solid CO_2[19] (see in Gorelli *et al.*[32] for the II–IV phase boundary). Dashed lines are approximate phase boundaries (see text).

evidence of its characteristic frequencies in the Raman spectrum led the authors to suggest a loss of inversion symmetry of the linear molecule because of bending. The new phase was thus labelled "non-linear carbon dioxide phase IV". CO_2-IV exhibited a rich phonon spectrum below 500 cm^{-1} (Fig. 4), as compared to both CO_2-III and I, consisting of at least 8 peaks, which indicates a reduced symmetry structure. Above 40 GPa a relevant broadening of the phonon peaks was observed. Above 60 GPa, the blue shifting phonon bands tend to merge to the red shifting bending mode peaks, indicating that intermolecular and intramolecular bonds strengths become comparable. The whole Raman spectrum became progressively weaker with increasing pressure, and it disappeared above 80 GPa. Therefore, phase IV was claimed to transform into an extended glassy material, whose structure was speculatively argued to be based on a mixture of fourfold similar to CO_2-V, and threefold carbon atoms. Indeed, concrete evidence of such a structure was lacking, since no features at all were observed neither in vibrational spectra nor in X-ray diffraction patterns. Nevertheless, all this matter led the authors to conclude that phase IV has such a nature to link twofold coordinated linear molecular phases I and III to the fourfold coordinated extended covalent phase V. This view was enforced by a subsequent synchrotron powder X-ray diffraction study.[30] The authors indexed the diffraction patterns either by a tetragonal or an orthorhombic unit cell, whose symmetry space groups are $P4_12_12$ and Pbcn, respectively (Fig. 11). The atomic positions were obtained by means of a fitting procedure, Rietveld refinement (see original references for details), to the experimental diffraction patterns. Both proposed structures contain four bent molecules per unit cell, where carbon atoms were considered as pseudo six fold, e.g. intermediate four- and six-fold coordinating oxygen atoms, standing at the apices of highly distorted octahedra. The bending intramolecular O–C–O angle was equal to 171° and 160° in $P4_12_12$ and Pbcn, respectively. The intramolecular bond was reported to be highly elongated to 1.5 Å, which is in the range of C–O single bonds, as opposed to C=O double bonds ($\sim$1.2 Å). Surprisingly, the bond length is even larger than that reported in phase V ($\leqslant$1.4 Å) in the same range of pressures.[4] Also, the intermolecular C···O distance was found to be substantially shorter than twice the C–O intramolecular distance. According to the authors, these distances show that phase IV consists of strongly (dipole) interacting molecules, pointing to an intermediate state between a molecular crystal and an extended covalent solid. The value of bulk modulus would be very useful for supporting this picture, but has not been reported. We note that specific volume values of phase IV are rather close to those of molecular CO_2-III, which in turn could be fitted together with CO_2-I values to a unique EOS (Fig. 3). This argument challenges the description of CO_2-IV in terms of a not entirely molecular structure. It should also be considered that the measured X-ray diffraction patterns show only four to five intense Bragg peaks, whereas the Rietveld

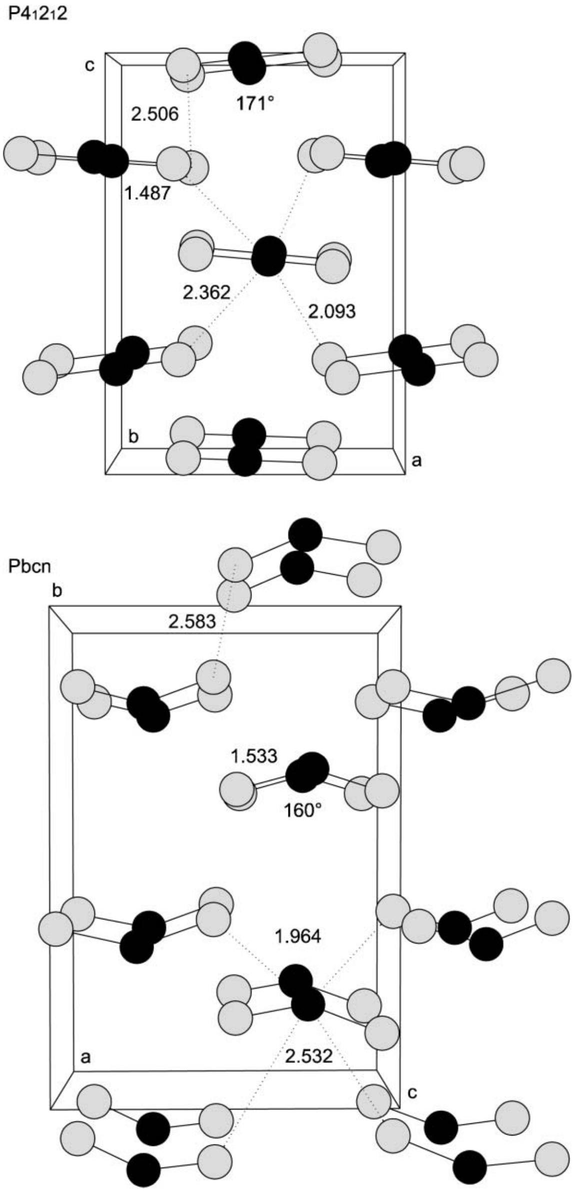

Fig. 11 Crystal structure of phase IV, according to Park *et al.*,[30] refined in the space groups of $P4_12_12$ (tetragonal) and *Pbcn* (orthorhombic), respectively. Intra(inter)-molecular distances are indicated in Å.

refinement procedure indeed included more than ten fitting parameters (see Yoo et al.[29] for details). This point indeed poses some concerns on the actual precision in determining the atomic positions, and ultimately in claiming the intermediate character of phase IV.

Indeed, this view was contested in the recent study of Bonev *et al.*,[31] based on first principles density functional calculations, including predicted structures, vibrational spectra, and free energies up to 50 GPa and 1500 K. This investigation was devoted to phases I, II, III, and IV. It was then found that starting from the experimentally proposed orthorhombic *Pbcn* structure of phase IV, upon energy optimization the C=O bond length decreased by about 30% to a value comparable to that of the free CO_2 molecule, while the O=C=O angle straightened to 180°. The energy difference between the theoretically stable molecular structure and the bent phase is more than 6 eV per CO_2, which corresponds to energy scales for breaking a covalent bond. The authors then refined the orthorhombic *Cmca* structure, where the molecule arrangement would be like the one assessed for phase III (this point was not explicitly stated). Four Raman phonon peaks, between 100 and 450 cm^{-1}, and two crystalline components for the vibron mode v_+ were calculated, along with the zero temperature EOS, and gave reasonable agreement with experimental data for phase III (Fig. 3 and 4). The P–T stability domain of the Cmca structure was also calculated and, surprisingly, it was found to match the measured domain of CO_2-IV, instead of that of CO_2-III. As a result the authors concluded that phase III is metastable in the P–T range where it is was experimentally reported, while its structure should be reassigned to the stable phase IV. We note that this conclusion is not compatible with at least two important experimental facts: (i) the Raman spectrum of phase IV shows up to ten peaks in the 100–450 cm^{-1} frequency range,[32] instead of four as in the selected Cmca structure, and (ii) in this Cmca structure the v_2 bending mode of CO_2 is Raman silent, while it was clearly observed experimentally. The authors suggest that the v_2 mode is most likely induced by crystallographic defects, which may locally lower the crystalline symmetry therefore allowing silent modes to be indeed observed.

Relevant insights to the structure of phase IV were provided in a recent infrared and Raman study.[32] The authors investigated the *P–T* range of molecular phases up to 25 GPa between 80 and 640 K. In CO_2-IV five infrared and ten Raman sharp phonon peaks were observed, in the 70–380 cm^{-1} frequency range, along with three infrared crystalline components for the v_2 bending modes in the 570–750 cm^{-1} interval. All vibrational frequencies of phase IV are well separated into external and internal modes (Fig. 4), as observed for the familiar molecular solid phase I, which really points to model CO_2-IV as a rather conventional CO_2 molecular crystal. On the other hand, the chemical bonds are so altered in the proposed intermediate bent structures[30] that rather different Raman and IR spectra should be observed, involving peaks which cannot be related to molecular modes. The study of Gorelli et al.[32] showed that the Raman activity of the v_2 bending mode originates by the loss of the inversion symmetry at the crystal site level (site symmetry), which commonly occurs in a variety of molecular crystals and does not imply any relevant alteration of the chemical bonds. Also, a group-theoretical analysis interpreted all the observed vibrational peaks on the basis of the orthorhombic Pbcn or Cmca structures, while the tetragonal $P4_12_12$ was ruled out because it predicts coincidences of Raman and IR frequencies that were not observed. We note that the Cmca structure considered in this study has four molecules per primitive cell on non-centrosymmetric crystal sites, instead of two molecules on centrosymmetric sites as in phase III.

VI. Phase II

Phase II was found by heating CO_2-III above 16 GPa and 500 K (Fig. 1), on the basis of *in situ* Raman spectroscopy and visual observations, in the attempt to investigate the thermodynamic stability of CO_2 phases.[28] Once obtained, the new phase was temperature quenched. Therefore, the III-to-II transition was suggested to be irreversible. Phase II was then observed to transform into CO_2-IV upon increasing temperature in the 500–750 K range, depending on pressure, while the reverse transformation was observed by slowly lowering the temperature. Much lower transition temperatures from CO_2-II to IV were subsequently found,[32] by even a few hundreds of degrees, leading to a proper estimate of the II–IV phase boundary (see Fig. 1 and 10). It was noted that phases I, II, IV and V are thermodynamically stable, since they always form at their stability conditions regardless of the *P–T* path followed.[28] Instead, phase III only forms upon compression of CO_2-I, which seems to suggest that CO_2-III is a metastable phase, and that the observed III-to-II transformation boundary is a kinetic barrier rather than a phase boundary. This hypothesis would remove the thermodynamic paradox, *e.g.* the violation of the Gibbs' phase rule, indicated by the apparent quadruple point connecting phases I, IV, II, and III (Fig. 1). On the other hand, a second hypothesis arose, which indicates the III-to-II transformation boundary to be a true phase boundary and assumes the existence of two distinct triple points separated by less than the experimental precision (5 K and 1 GPa).[28] Indeed, additional work is needed to definitely clarify this problematic aspect on an experimental basis. The new CO_2 polymorph was suggested to be characterized by dimeric pairing of molecules, on the basis of splitting of the internal v_+ mode into two components (Fig. 4), whose separation exceeds 25 cm^{-1} at 40 GPa. This value was thought to be substantially larger than that expected for crystal field splitting in conventional molecular solids. The molecular association was then suggested to be due to charge transfer between neighbouring CO_2 units. In this view the observed components in the v_+ manifold would correspond to two different internal modes (in-phase and out-of-phase) of the dimer. Molecular bending of the O=C=O units was also proposed, because of the observation of the v_2 bending mode in the Raman spectrum.

A subsequent synchrotron X-ray powder diffraction study strengthened the notion of strongly interacting molecules.[29] The experimental patterns were indexed either by a tetragonal (*$P4_2/mnm$*), Fig. 12, or an orthorhombic unit cell (*Pnnm*), and the atomic positions were obtained by means of the Rietveld refinement procedure. Both proposed structures contain two molecules per unit cell. As in phase IV, the carbon atoms were

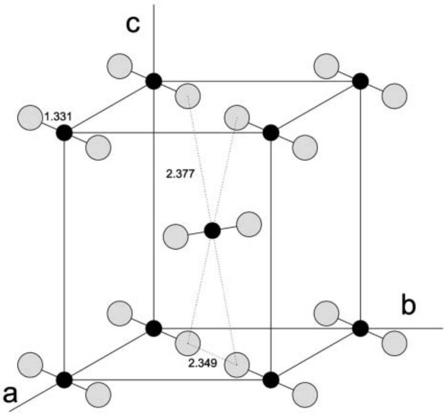

Fig. 12 Crystal structure of phase II, according to Yoo *et al.*,[29] refined in the space group of *P*4$_2$/*mnm* (tetragonal). Intra(inter)-molecular distances are indicated in Å.

considered as pseudo-six-fold coordinated by oxygens similar to SiO$_2$-stishovite. The octahedra include two bonded oxygens at a distance of 1.331 Å and four non bonded ones at 2.377 Å. Therefore, the C–O bond is highly elongated from the typical C=O double bond distance, though less than in phase IV, whereas the nearest intermolecular separation is shorter than twice the C–O bond distance. As in CO$_2$-IV, these distances would indicate strongly interacting molecules, pointing to an intermediate state between a molecular crystal and an extended covalent solid. The EOS was also reported: the density increase is 5–7% with respect to CO$_2$-III, and a very high bulk modulus of 131.5 GPa was obtained. Also in this case, as in phase IV, the high number of fitting parameters involved in the Rietveld refinement, as compared to the limited number of intense diffraction peaks, seems to cast a shadow on the actual precision in the determining the atomic positions and, ultimately, on the model of an associated phase.

Bonev *et al.*[31] rejected the view of an associated phase for CO$_2$-II and instead proposed a molecular structure. The authors found that starting from the proposed tetragonal *P*4$_2$/*mnm* structure for CO$_2$-II,[34] the optimized C=O bond length was comparable to the free CO$_2$ molecule. The energy difference between the theoretical stable molecular structure and the associated phase was very high, amounting to more than 3 eV per CO$_2$. The theoretical zero temperature EOS for the optimised *P*4$_2$/*mnm* structure fits reasonably well to the measured EOS. On the other hand, the calculated bulk modulus (4.37 GPa), typical of a molecular solid, differs a lot from the measured one. The large difference was suggested to be due to the possible erroneous extrapolation of experimental data down to ambient pressure. The theoretical vibrational frequencies closely agree with the experimental ones. Specifically, the large splitting of the v_+ band, which was firmly assumed to be a signature of molecular pairing,[28] is rather well reproduced. The thermodynamic P–T phase domain of the simulated P4$_2$/mnm structure was also calculated, and it was found to match the entire measured domain of both phases II and III. On account of this finding it was definitely concluded that phase III is metastable, at the P–T conditions where it was observed, while CO$_2$-II is the stable phase, having indeed P4$_2$/mnm structure.

VII. Thermodynamic phase diagram

A schematic thermodynamic phase diagram of solid CO$_2$ was recently proposed in the *P*–*T* region of transformation from the molecular phases to CO$_2$-V.[19] An updated version of this diagram is shown in Fig. 10, where phase boundaries of CO$_2$-I and IV are traced by taking into account different phase transition data.[28,32] The melting line of CO$_2$-IV has not been measured, and the one reported is only schematic. Phase III was not indicated, since it was suggested to be metastable, as discussed above. The II–V phase boundary was estimated according to the following arguments. The entire region extending below the kinetic barrier to phase V[19] above 30 GPa was assigned to the stable CO$_2$-V (this point was subsequently proved by the discovery of a-carbonia,[24] which was indeed formed below the kinetic barrier to phase V, and is the glassy counterpart of CO$_2$-V). Consequently, the II–V phase boundary, *T*(*P*), cannot intersect this *P*–*T* range, and it was suggested that it may exhibit a positive slope. This last point was based on the Clapeyron equation: $\mathrm{d}T/\mathrm{d}P = \Delta V/\Delta S$, where ΔV and ΔS are the volume and entropy difference, respectively, between two coexisting phases at thermodynamic equilibrium. Indeed, phase V is much denser than molecular phases and, once provided that it is also lower in entropy, this would imply a positive value of $\mathrm{d}T/\mathrm{d}P$. Finally, it was noted that at room temperature phase V can be recovered down to about 12 GPa,[19] where it tends to transform to CO$_2$-I, but it could also start to be metastable at some point below 30 GPa. Therefore, the phase transition point at room temperature was estimated to be in the middle of the 12–30 GPa pressure interval. The IV, II, and V triple point is also expected. The high kinetic barriers make the precise determination of the actual phase boundaries difficult, and additional work is needed to definitively assess the high pressure phase diagram of CO$_2$.

VIII. Discussion and conclusions

It appears that the rich high pressure solid state chemistry of CO$_2$ presents many open issues, despite the variety of experimental and theoretical studies which have been performed on this subject in the recent years. This important substance transforms under pressure from molecular crystalline phases to a non-molecular covalent crystalline (amorphous) solid, phase V (a-carbonia), and this transformation is a true chemical reaction, since chemical bonds are entirely reconstructed. The reaction is reversible: phase V and a-carbonia transform to dry ice upon pressure release. X-ray diffraction data have been reported to indicate CO$_2$-V as a "superhard" material, having tetrahedral coordination of carbon by oxygens in a tridymite structure similar to polymorphs of SiO$_2$.[3,4] Theoretical calculations, based on first principles molecular dynamics, predicted and supported the high pressure stability of crystalline structures made of CO$_4$ tetrahedra, with respect to molecular solid phases.[20–23] On the other hand, these studies are still far from a consensus on the crystalline structure of such a material, and different polymorphs, similar to those of SiO_2 (tridymite-, cristobalite- and quartz-like), have been indeed proposed. Tridymite type structures, which are of the lowest symmetry among the proposed ones, seem to be the best candidates for reproducing the experimental X-ray diffraction patterns of phase V, while they are unstable, at zero temperature, with respect to β-cristobalite. It was suggested that finite temperatures may play a relevant role in stabilizing the observed structure of CO_2-V,[23] but this remains to be verified. Also, all simulation studies report non-molecular CO_2 to be much softer than experimentally observed; the theoretical bulk modulus values range between 1/2 and 1/3 of the measured one, which is puzzling. It cannot be excluded that some amounts of carbon clusters (C clusters form at high temperatures, by dissociation of CO_2 into C + O_2[25]) are contained in the experimentally investigated phase V samples, thereby affecting the actual X-ray diffraction pattern and, ultimately, the determination of the EOS and of the bulk modulus. This remains an open question.

We note that the debate on the structure of phase V is based on comparisons between simulations and a single experimental X-ray diffraction study,[4] other diffraction patterns have not been measured and additional work is clearly needed. Definitive assessment of the true CO_2-V structure is a crucial point for identifying the chemical reaction path which leads to the formation of this material. Also very important for this purpose is the debate on structures of the high-pressure molecular solid phases II, III, and IV, bounding the *P–T* range of CO_2-V. These phases were first described on the basis of Raman and X-ray diffraction to have intermediate character between molecular solids and extended covalent solids, so that they would play the role of precursors for the formation of non-molecular phase V.[27–30] Specifically, strong intermolecular interactions were suggested to occur in phases II and IV. This view was refuted in a recent theoretical study, where entirely molecular structures where proposed for phases II, III and IV, fitting reasonably well to the entire set of experimental data.[31] A subsequent IR and Raman study confirmed this picture.[32] The interpretation of the phenomenology of these phases on the basis of entirely molecular, rather than "intermediate", structures, seems to be plausible, more elegant, and ultimately more convincing.

In this view, the following main injection mechanism for forming phase V was suggested: substantially linear molecules approach to each other statically, by increasing pressure, and/or dynamically (lattice phonons), by increasing temperature, until the minimum intermolecular distances for the reaction to occur are achieved.[19,32] We note that the detailed reaction mechanism is a very important issue that has still to be determined. Another relevant piece of information for assessing the entire reaction path leading to phase V includes the precise knowledge of the thermodynamic phase diagram, even if the reaction path can be distinct from this diagram. This issue is made difficult by strong metastability, even in such a simple system.[19] Additional experimental and theoretical efforts are required to definitely determining the stable phase diagram, and to understand the kinetics.

Finally, we outline two future approaches to resolve current issues. This involves studies of a more extended *P–T* range than that investigated so far. First, melting of phase V should be investigated to determine whether a tetrahedral melted state, similar to fused quartz, exists and is stable or not. This is an important issue from a fundamental point of view, as it could add to the list of tetrahedral network forming group IV oxides such as SiO_2 and GeO_2. We note that a-carbonia should correspond to the temperature quenched state of such a high pressure fluid. The identification of pressure induced amorphous states with temperature quenched states of high pressure fluids is indeed proposed in many tetrahedrally coordinated materials such as silica, water, silicon and germanium. The search for a possible non-molecular extended covalent liquid, would also be a crucial project for investigating the reaction mechanisms leading to the final high *P–T* dissociation of CO_2 into its constituent elements, which was indeed experimentally documented.[25] The proposed studies will require *in situ* measurements on high pressure samples at temperatures in excess of 2000 K; even if difficult, these experiments can indeed be performed, for instance, by combining laser heating techniques, diamond anvil cells, and Raman and X-ray diffraction methods. A second approach would be the search for further possible transformations in the multimegabars pressure range, which also requires challenging experiments. Extreme compressions of solid carbon dioxide, even at moderate temperatures, may either end up in the final dissociation (C + O_2), as suggested by Tschauner *et al.*[25] and theoretically predicted by Serra *et al.*,[20] or into a non molecular stishovite-like phase made of CO_6 octahedra, as theoretically predicted by Holm *et al.*.[23] Metallization could also occur in the non-molecular state.

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