Linear Carbon Dioxide in the High-Pressure High-Temperature Crystalline Phase IV

Federico A. Gorelli,[1,2] Valentina M. Giordano,[1] Pier R. Salvi,[1,3] and Roberto Bini[1,3]
[1]*LENS, European Laboratory for Non-linear Spectroscopy and INFM, Via Carrara 1, I-50019 Sesto Fiorentino, Firenze, Italy*
[2]*INFM CRS-SOFT, c/o Universita di Roma La Sapienza, I-00185, Roma, Italy and INFM UdR-FI,*
c/o Dipartimento di Fisica, Universita di Firenze, Firenze, Italy
[3]*Dipartimento di Chimica dell'Università di Firenze, Via della Lastruccia 3, I-50019 Sesto Fiorentino, Firenze, Italy*
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High-temperature IR absorption spectra of solid CO_2 in phases II and IV were measured in a resistive heated diamond anvil cell up to 30 GPa. The spectral structures of the bending mode, observed in high quality thin crystalline samples, and of the IR lattice phonons, measured for the first time between 80 and 640 K, are discussed using group theory arguments. According to this analysis the claimed bent molecular geometry of CO_2 in phase IV can be unambiguously ruled out. Furthermore, the structures of both phases II and IV have been identified, among those so far proposed, as orthorhombic.

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Pressure tuning of intermolecular interactions causes dramatic structural modifications in molecular solids inducing transitions between crystal structures and favoring chemical reactions leading to materials of technological interest [1,2]. Reversible insulator-to-metal [3,4] and molecular-to-nonmolecular transformations [5–8] have been reported to occur in the simplest molecular systems while polymeric compounds have been synthesized compressing small hydrocarbons [9–11]. To this purpose, it is often important to realize high-pressure and high-temperature conditions by coupling to the diamond anvil cell (DAC) technique resistive or laser heating methods. In this way, wide metastability *P-T* regions and large kinetic barriers precluding the transformations to new denser polymeric phases at room temperature have been identified [5,7,12]. Once these barriers are overcome, the new phases are often quenched to much less drastic temperature and pressure conditions becoming available for technological processing. From a theoretical point of view these studies are a strong motivation to develop models able to clarify the role of the intermolecular potential in condensed matter under extreme conditions [12,13].

In this framework carbon dioxide can be considered as a textbook example because it presents several high-pressure polymorphs, including a quartzlike structure (phase V) with a fourfold coordination of the carbon atoms [8], with important implications ranging from astrophysics to the synthesis of new ultrahard materials. Crystal phases from II to V are quenchable to room temperature in a wide pressure range and can be observed at 300 K between 10 and 20 GPa depending on the sample history [14]. The ambient pressure phase I ($Pa\overline{3}$) transforms at 300 K above 10 GPa to III, orthorhombic *Cmca* [15], with a sluggish transition extending up to 30–40 GPa. On heating III between 15 and 20 GPa phase II is obtained above 500 K, while further heating above 750 K makes phase IV to occur [14]. The polymeric phase V is produced above 30 GPa and 800 K [16] and a bulk modulus comparable to that of cubic-BN has been reported [8]. Phases II and IV have been described as associated, the former, tetragonal $P4_2/mnm$ (D_{4h}^{14}, $Z = 2$) or orthorhombic *Pnnm* (D_{2h}^{12}, $Z = 2$) [14,17], with strong pairwise interactions, while the second, tetragonal $P4_12_12$ (D_4^4, $Z = 4$) or orthorhombic *Pbcn* (D_{2h}^{14}, $Z = 4$), is claimed to be composed of bent molecular units [18,19]. Both phases II and IV have been considered as intermediate between the molecular I and the extended, covalently bound, phase V. However, recent calculations challenge this conclusion, emphasizing the strict molecular nature of their structure and suggesting that the geometry of CO_2 in phase IV is linear [20].

Pressurized (6 bars) CO_2 (purity $\geq 99.99\%$) was loaded in a DAC in the liquid phase by means of cryoloading equipment. The local sample pressure was measured by the R_1 ruby fluorescence band shift [21]. Temperatures up to 700 K were reached by means of the resistive heating of the cell and measured by a J-type thermocouple. The setup employed to measure high-pressure IR spectra has been described in previous reports [22,23]. Thick pure CO_2 samples (~30–40 μm) were employed for far infrared (FIR) measurements. Thin crystals, ~1–3 μm thick, were produced above a KBr pellet and used to measure the strongly absorbing internal phonons avoiding absorption saturation. Raman spectra were measured with the 647.1 nm line of a Kr^+ laser.

The room temperature IR spectra of the ν_2 and $\nu_1 + \nu_3$; $2\nu_2 + \nu_3$ CO_2 phonons (Fig. 1) provide three basic pieces of information: (i) all the components of the ν_2 mode in phase I [24] are observed by virtue of the high quality of the thin crystal slabs; (ii) the ν_2 spectrum of phase IV shows, at 15 GPa, three well resolved TO bands (633, 639, 654 cm^{-1}) that are crucial in revealing the linear molecular structure in this phase, and one LO mode at higher energy (690 cm^{-1}) reminiscent of the phase I LO mode; (iii) the sharp doublet (3750–3800 cm^{-1}) measured in phase IV in the $\nu_1 + \nu_3; 2\nu_2 + \nu_3$ combination region represents the spectral signature of this phase.

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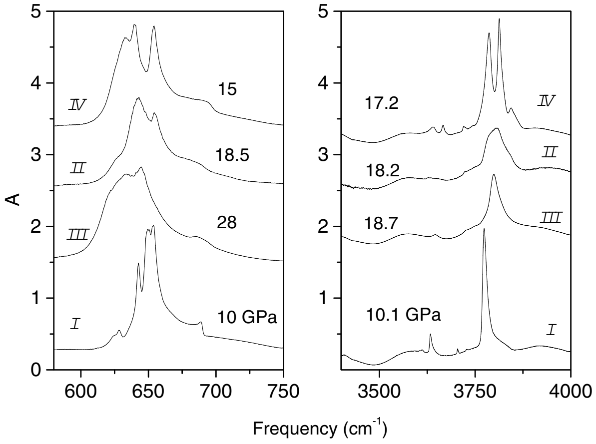

FIG. 1. Room temperature mid-IR absorption spectra for the I, III, II, and IV crystal phases of CO_2 (from bottom to top). Left: ν_2 bending region (thin slabs 1–3 μm); right: $\nu_1 + \nu_3; 2\nu_2 + \nu_3$ combination regions (thick sample 30–40 μm).

The FIR spectrum of phase I is observed on compression up to above 20 GPa without detecting any spectral change indicating the formation of phase III. The lattice phonon spectrum of phase III appears only after the sample is annealed above 400 K (Fig. 2) showing two bands, in agreement with expectations based on the *Cmca* structure, at 230 and 296 cm^{-1}. By further heating above 465 K, the FIR spectrum changes and consists of one broad intense band at 203 cm^{-1} and a second weak absorption at 238 cm^{-1}. This spectrum is assigned to phase II. These frequency values are lower than those measured for the Raman modes ($\sim$263 and 324 cm^{-1}) at the same pressure [14], thus ruling out their activation due to stress or crystal defects. The transition is also visually detected for the formation of the polycrystalline morphology characteristic of this phase [14]. The FIR data allow us to choose between the two proposed structures for phase II, $P4_2/mnm$ and $Pnnm$ [17], in favor of the latter because one IR active phonon mode is expected for the $P4_2/mnm$ structure, while two are expected in the $Pnnm$ case.

From now on we turn our attention specifically to phase IV. As the occurrence of this phase is readily appreciated from the splitting of the combination band, we have determined the upper temperature limit of phase II as a function of pressure in the range 12–25 GPa. As may be seen from the inset of Fig. 2, phase IV is observed at temperatures appreciably lower than previously reported [14]. Phase IV, typically prepared at 20 GPa and 500 K, is transparent and presents a high crystal quality, as attested by the almost Lorentzian line shape of all the phonon bands. The lattice phonon spectrum of phase IV, consisting of five bands (top of Fig. 2), was studied in a wide temperature range (80–640 K) on releasing pressure. The phonon bands' intensity does not decrease on lowering temperature down to 80 K, thus excluding their assignment as hot band transitions. The IV-I phase transition was studied along three isothermal decompressions at 80, 300, and 640 K (Fig. 3). The transition is observed at 3, 10, and 11.5 GPa, respectively, highlighting a large hysteresis in recovering phase I at low temperature.

Summarizing ours and previous [18] results on phase IV, at least (i) three Raman and three IR ν_2 components and (ii) eight Raman and five IR phonons are observed. The ν_2 Raman triplet was suggested to be activated by crystal stress and/or disorder [20], but we measured the same profile in samples prepared above 500 K and presenting a high quality phonon spectrum ruling out possible metastabilities as those reported in Ref. [25]. The bent shape of carbon dioxide in phase IV was proposed on the basis of the Raman activity of the ν_2 bending mode, attributed to the loss of the molecular inversion symmetry [18]. On the other hand, the activity of *u* modes in the crystal Raman spectrum (or, vice versa, *g* modes in the IR) is not surprising and generally originated by the loss of the inversion symmetry at the crystal

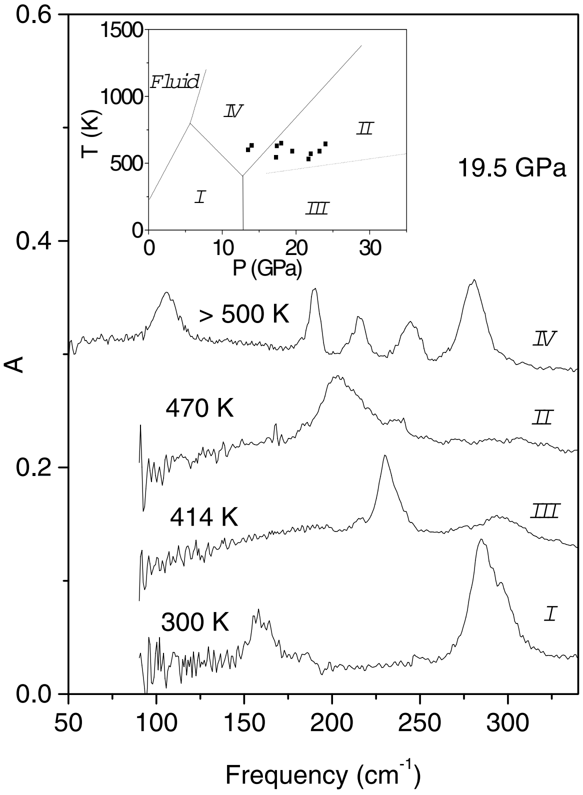

FIG. 2. Room temperature phonon spectra of the four phases of CO_2 measured at 19.5 GPa after the sample has been heated at constant pressure at the temperature values given. The spectrum of phase IV is obtained by merging two spectra measured with different Mylar beam splitters: 23 μm (50–150 cm^{-1}) and 6 μm (100–450 cm^{-1}). Inset: the experimental *P-T* values (full squares) where phase IV is observed are reported in the phase diagram from Ref. [14].

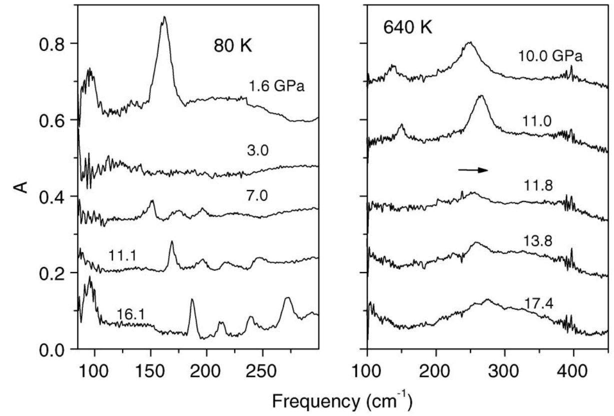

FIG. 3. Phonon spectrum of phase IV measured on decreasing pressure along two isotherms at 80 K (left panel) and 640 K (right panel). The IV-I phase transition is observed below 3 and 12 GPa in the two cases, respectively. During the low temperature decompression, between 6 and 2 GPa, the phonon spectrum is not observed due to the bad crystal quality.

site level (site symmetry). For this reason we performed a group-theoretical analysis for the two experimentally proposed structures [19] assuming both a linear and a bent, C_{2v}, molecular geometry. The results, reported in Table I, sharply indicate that independently on the crystal structure only a linear molecule can account for the observed IR and Raman ν_2 components. It is interesting to note that the calculated *Cmca* structure is consistent with IR/Raman data only with four linear molecules in the primitive cell on C_2 (or C_s) sites, as suggested [20].

Once the linearity of the molecule has been established, we can use Table I to choose between the tetragonal $P4_12_12$ and the orthorhombic (*Pbcn* and *Cmca*) space groups. In fact, only in the tetragonal case some external modes, four of E symmetry, show both Raman and IR activity. To this purpose we have measured the lattice phonons of phase IV on the same sample under identical conditions of pressure and temperature. The frequency evolution with pressure of the four IR and the eight Raman peaks is compared in the lower panel of Fig. 4. The fifth IR band around 100 cm^{-1} is not reported because it is not detectable below 17 GPa. It results that only the highest IR phonon is possibly coincident with a Raman peak. Raman spectra were acquired at 11.4 GPa from different regions of the sample (Fig. 4, upper panel) revealing important spectral differences attributed to crystalline domains having different orientations. The spectrum more frequently measured (top of the panel) corresponds to those presented in previous papers [18,19] and indicates the existence of a preferred orientation. The dotted lines identify the positions of the eight bands present in this spectrum and reported in the literature and help in the comparison with the other two spectra which show changes of band intensity and occurrence of new bands. Two new peaks are indeed observed at 95 and 290 cm^{-1} coinciding with none of the observed IR bands, thus allowing us to rule out the tetragonal factor group for phase IV because, in total, only one coincidence is observed. Moreover, according to the orthorhombic structure all the lattice modes are now identified.

The vibrational spectra of phases II and IV have been successfully discussed on a pure molecular basis. On the contrary, the extended association and the huge (25%) increase in the internal bond distance reported in Refs. [17,19] should have sizable effects in the peak frequencies and intensities, and in their evolution with pressure as, for instance, observed in oxygen [23]. Also the transformation to phase V should be regarded as a reaction instead of a phase transition analogous to those reported for several small unsaturated hydrocarbons [10] and occurring in a pure molecular framework. A negative slope ($P < 55$ GPa) has been recently determined for the stability boundary of the molecular CO_2 phases with respect to the covalently bonded phase V [16] in analogy to those observed for the chemical reactions occurring in solid acetylene [26], butadiene [27], and benzene [28]. Here, the increase in the oscillation amplitudes (lattice phonons) of the rigid molecules rising temperature allowed the dynamical realization of nearest neighbor (nn) distances and configurations suitable to induce the chemical reaction. Particularly enlightening is the case of benzene where the high-pressure reaction to an extended amorphous hydrogenated carbon has been studied both in a wide T range (100–540 K) and by using a photochemical activation [29]. In all the different P-T-$h\nu$ conditions the nearest neighbor distances are nearly identical once the structural data are renormalized with respect to the atomic thermal displacement and to the ring deformation following the excitation to the S_1 state [11].

TABLE I. Results of group theory analysis for the lattice phonons and for the ν_2 bending mode relatively to the proposed crystal structures. All the structures have four molecules in the primitive cell. The numbers in parenthesis for the tetragonal $P4_12_12$ structure indicate the modes of E symmetry that are active both in Raman and IR spectra.

	Pbcn (D_{2h}); site C_2		$P4_12_12$ (D_4); site C_2		*Cmca* (D_{2h}); sites C_2 and C_s			
					Linear		Bent	
Mode	Linear	Bent	Linear	Bent	C_2	C_s	C_2	C_s
ν_2	4R + 3IR	2R + 1IR	5R + 3IR (2)	3R + 1IR (1)	4R + 3IR	4R + 3IR	2R + 1IR	2R + 2IR
Lattice ph.	10R + 5IR	12R + 7IR	11R + 6IR (4)	13R + 8IR (5)	10R + 5IR	10R + 5IR	12R + 7IR	12R + 5IR

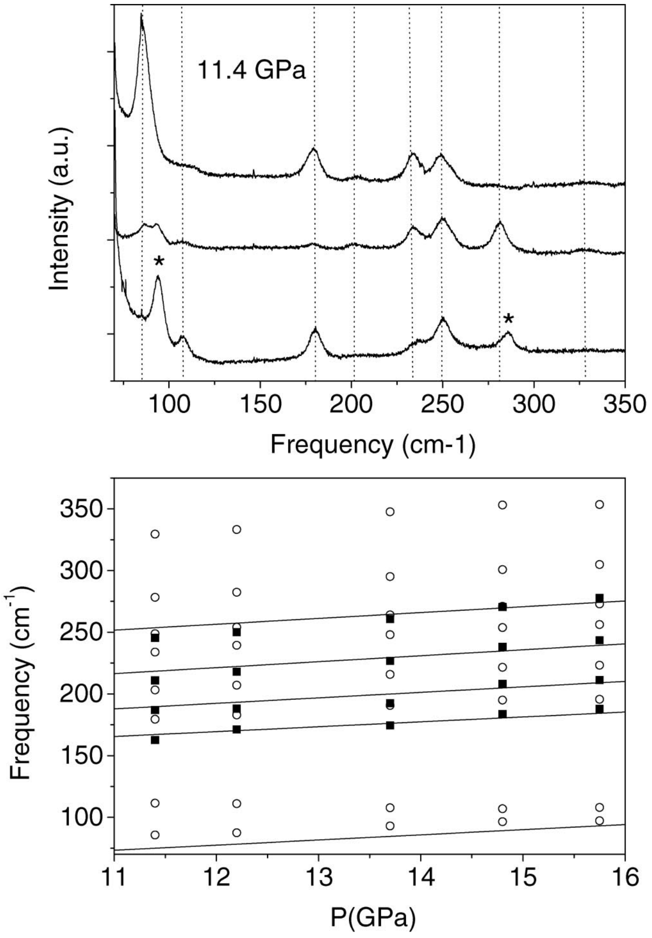

FIG. 4. Lower panel: frequencies of the IR (full squares) and Raman (empty circles) lattice modes measured on the same sample in the same P-T conditions. The full lines indicate the frequency evolution with pressure of the IR phonons measured on other samples and are reported for comparison due to the missed observation of the fifth low frequency peak (see the text). Upper panel: Raman spectra measured probing different regions of the sample at 11.4 GPa. The dotted lines indicate the eight peaks reported in the literature [19]. The two peaks marked by an asterisk have been identified in this study.

Furthermore, the fact that polymeric CO_2 is obtained by different phases (II, III, and IV), claimed to possess very different characteristics (molecular/nonmolecular structures, linear/bent molecules), supports the more general concept of a reaction on molecular basis (nn distances) instead of the existence of an "intermediate phase."

The entire IR spectrum of CO_2 crystal in phases II and IV has been characterized in a wide pressure and temperature range. The slope of the II-IV phase boundary is found much less steep than previously reported, thus reducing the stability field of phase II. Our data are discussed without resorting to the idea of molecular association in phases II and IV and unambiguously indicate the linearity of the molecule also in phase IV. To the hypothesis of a precursor structure to the polymeric phase V is favored a molecular reaction driven by the lattice phonons. The preferred structures have been identified as orthorhombic, *Pnnm* for phase II and *Pbcn* or *Cmca* for phase IV.

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