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High Pressure Structural Changes in Amorphous Polymeric Carbon Monoxide by Combined Infrared Spectroscopy and X-ray Diffraction

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ABSTRACT: The high pressure transformation of carbon monoxide into an amorphous polymeric material (a-pCO) is known since decades, yet the determination of its local structure is made difficult by the strong photoreactivity of this material along with the high hygroscopicity of the recovered samples. While accurate, nondestructive IR spectroscopy measurements at a few GPa show that a-pCO is a complex solid dominated by the sp^2 hybridization for C and with oxygen forming both single and double bonds with carbon, the potential evolution of this chemical structure at higher pressures is hitherto terra incognita. Here we report a high pressure investigation of pCO up to 56 GPa, at room temperature, based on in situ IR spectroscopy and synchrotron X-ray diffraction (XRD) measurements in diamond anvil cells (DACs). Our study shows that this material remains amorphous up to the maximum investigated pressure, with sp^2 C substantially converting to sp^3 C upon increasing pressure above 12−13 GPa. This occurrence indicates that unsaturated a-pCO modifies with pressure toward an entirely single bonded amorphous material similarly to its theoretically predicted crystalline counterpart.
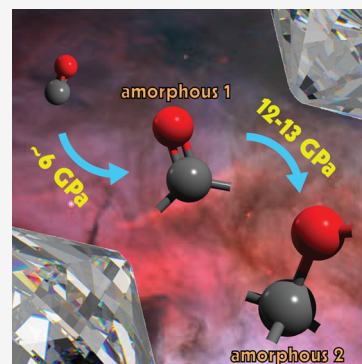
■ INTRODUCTION

As a general trend, strongly compressed molecular materials with multiple chemical bonds undergo bond reconstruction which can lead to the formation of extended, often exotic, solids, both amorphous and crystalline. This notion is largely based on the investigation of the simplest and most widespread molecular systems in nature.[1−13] However, the relevant transformation paths and mechanisms along with the structure of those extended solids are subject of ongoing debate. In this respect, the case of CO, an archetypal triple bonded molecule of paramount importance for industrial and environmental processes, and the second-most abundant diatomic molecule in the interstellar medium, after H_2, is particularly interesting and still somewhat obscure.

The first experimental hints of the high pressure polymerization of CO in the few GPa range were reported in the eighties.[14−16] After that, this phenomenon was extensively investigated by optical spectroscopy[17−20] and XRD,[20] and also visual observations and standard chemical analysis techniques on the solid recovered samples,[18,19] still at reaction pressures in the GPa range and then extended to above 100 GPa.[21] In this last work, polymorphism of polymeric CO was inferred from collections of sample images and Raman spectra. The general notion from these studies is that pressures in the GPa range lead to the chemical transformation of CO into an extended disordered C/O product with C mainly in sp^2 hybridization, graphitic-like carbon, and CO_2. XRD measurements were not able to discriminate among potentially distinct chemical bonds

of the extended product.[20] The ambient recovered solid samples have also been shown to be metastable with a high energy content and to further decompose into carbon and CO_2 exothermically.[18,19] Importantly, all these studies involve laser or X-ray irradiation of the samples, and both molecular and extended CO were found to be strongly photosensitive. Indeed, the reported high pressure partial decomposition into carbon and CO_2 at room temperature is mainly a photo-induced effect,[22] which makes the investigation of the polymerization of CO difficult. Also, the ambient recovered C/O products were shown to readily react with air moisture,[22] which in turn implies that characterizations of recovered samples do not deal with stoichiometrically pure C/O but instead with C/O/H materials of undefined stoichiometry. Therefore, all studies conducted on recovered samples cannot be trivially linked to the high pressure C/O forms. A study on the reactivity of CO in the GPa range was also conducted by our group by avoiding any potential radiation contribution from visible or higher frequency light and instead entirely based on medium IR absorption spectroscopy.[22] This study has been showing that, below room temperature, compressed

CO transforms into an extended amorphous material formed by polycarbonyl linear chains containing a large amount of anhydride groups. In this material, a major amount of C is in sp^2 hybridization while oxygen forms single and double bonds with carbon. For $T > 300$ K, a decomposition of the solid product also occurs, which progressively increases with temperature, as shown by the formation of CO_2. After this study, the fate of the carbon and oxygen coordination at tens of GPa is still an entirely open question. Noteworthy, pure 1D stoichiometric $[-(C=O)-]_n$ polycarbonyl chains were indeed obtained by reacting dense CO strongly confined in the microchannels of host zeolites, at GPa pressures.[23,24]

On the side of computer simulations, pionieering ab initio molecular dynamics simulations found that molecular CO transforms, at 15 GPa, into an extended product that consists of a disordered network of small polycarbonyl chains connecting 5-fold C_4O cycles.[25] This random polymer is made of sp^2 and sp^3 carbon and oxygen in 1- and 2-fold coordination by carbon. More recently, studies based on crystal structure prediction methods and first-principle calculations have been used to explore the lowest energy structures of CO.[26,27] Surprisingly, the most stable structure of CO at ambient pressure resulted to be a crystalline polymeric structure rather than a molecular solid.[27] This phase consists entirely of sp^2 carbon and oxygen bound to carbon by single and double bonds. On the other hand, on compression above 12 GPa, it is energetically favorable for CO to polymerize into purely single bonded crystalline phases with sp^2 carbon fully replaced by sp^3 carbon.[27] Although these phases have never been experimentally observed so far, most likely for kinetic reasons, they appear reasonably to be the ordered parents of undecomposed, amorphous polymeric CO indeed synthesized at high pressures.[22] The a-pCO is therefore a valid experimental proxy of those ordered phases, as far as the local structure is concerned. Our study aims precisely to investigate potential pressure induced changes in the local structure of a-pCO and to compare these changes with those predicted for crystalline pCO. The focus is therefore on the pressure dependence of carbon and oxygen coordination.

In the following paragraphs, we will report a combined XRD and IR absorption investigation of CO at pressures up to 56 GPa, and at room temperature, in DACs. Strong attenuation of the synchrotron X-ray beam ensured to avoid any radiation damage of the samples, while Raman spectroscopy was not exploited for avoiding laser irradiation. Our main outcome is that undecomposed a-pCO, synthesized at ~6 GPa, undergoes substantial structural changes at 12−13 GPa from a network of both double and single bonds toward an entirely single bonded amorphous extended material, similarly to what was predicted for crystalline pCO.

■ EXPERIMENTAL METHODS

Carbon monoxide (Sapio, purity ≥ 99.99%) was cryo-loaded into our DACs[28] at several GPa, using liquid nitrogen. The cells were equipped with type IIa synthetic diamonds and the stainless steel gaskets had holes with an initial diameter and thickness of about 100 and 30 μm, respectively. For the XRD measurements, we loaded pure CO samples (see Figure 1). Instead, for the IR measurements, we pelleted a well-dried KCl powder into the gasket hole, using the DAC, and then evenly scratched one side of the pellet to obtain an empty sample region a few microns thick, which was subsequently loaded with CO. This procedure allowed to avoid the saturation of the
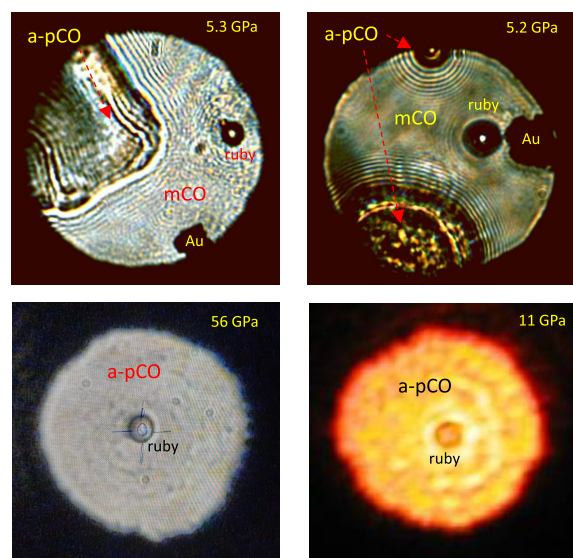

Figure 1. Pictures of pure CO samples under pressure recorded in transmitted light. Top left and top right panels: coexistence of yellowish domains of a-pCO and colorless monomeric solid CO (mCO) for two typical samples. The monomeric samples were compressed to the polymerization pressure, 5.9 GPa at room temperature, and an uncompensated pressure drop occurred while transformation to the denser polymeric form was taking place, therefore the reaction was not complete. Bottom panels: another a-pCO sample compressed to 56 GPa (left) and then decompressed down to 11 GPa (right). Hole diameters: 90 μm (top) and 80 μm (bottom). Gold and ruby chips were inserted in the sample chamber as the pressure sensors.

IR absorption due to the strong IR peaks of a-pCO. A ruby or a gold chip were added for pressure measurements, which we performed using the ruby fluorescence method[29] or the gold equation of state,[30] respectively. The ruby fluorescence was measured using a very efficient micro-Raman setup,[31] with laser ($\lambda = 660$ nm) intensity as low as a few hundred W/cm^2 and acquisition time of a few seconds. We verified, by IR spectroscopy and visual observations, that these values for the laser irradiation parameters where low enough to avoid any spurious photochemical effects. We also verified that the KCl pellet did not affect the high pressure beaviour of CO by comparing the IR spectra of CO/KCl samples with those of pure CO samples. Synchrotron angle-dispersive, powder XRD measurements in DACs ($\lambda = 0.410693$ Å) were performed at the ESRF (beamline ID15B), using a MAR555 flat panel detector. We attenuated the incident photon flux down to 4×10^{10} photons/s and used a relatively large spot with diameter of 20 μm; the acquisition time was typically equal to 10 s. Under these conditions, we were able to avoid radiation damage, which was checked by visually observing the absence of potentially darkened regions in the irradiated samples. The diffractometer was calibrated using a silicon powder standard, and the 2D diffraction patterns were analyzed and integrated using Dioptas.[32] IR absorption spectra were measured by a Fourier transform IR spectrometer (Bruker IFS-120 HR) equipped with a globar lamp, KBr beam splitter, MCT detector, and optical beam condenser based on ellipsoidal mirrors which provided a natural beam spot size of several hundred microns.[33] The frequency resolution was set to 1 cm^{-1}.

■ RESULTS AND DISCUSSION

XRD Characterization. We performed the in situ XRD investigation on already polymerized samples, as we found that only these samples were not damaged by the radiation, in contrast to the molecular solid. In Figure 2, we report two
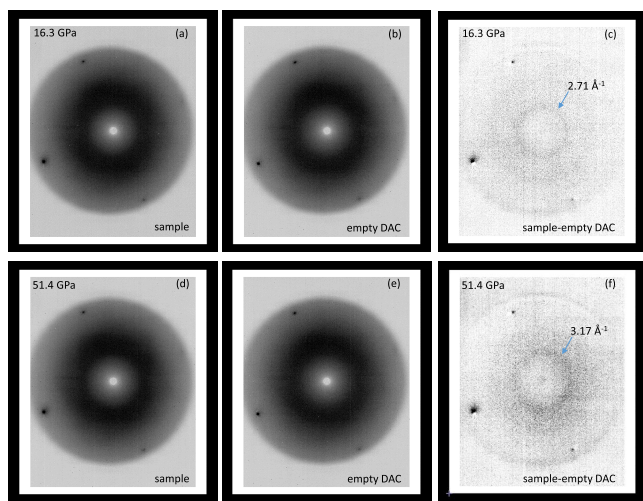
Figure 2. 2D XRD patterns of a-pCO measured upon increasing pressure, at two selected pressures. The gray scale for the intensities ranges from zero, in white, to high values in black. Images (a) and (d): sample patterns at 16.3 and 51.4 GPa, respectively; (b) and (e): empty DAC patterns to subtract from sample patterns (a) and (d); (c) and (f): sample patterns after subtraction of the empty DAC backgrounds. Patterns (a), (b), (d), and (e) are dominated by the Compton scattering background from diamonds. Three strong diamond Bragg peaks are also observed at the highest angles. Blue arrows in (c) and (f) highlight the lowest-Q, diffuse scattering halo of a-pCO.

selected 2D XRD patterns of a-pCO measured upon increasing pressure at 16.3 and 51.4 GPa, respectively, along a 4.0−51.4−7.0 GPa pressure cycle for a typical polymer sample, after polymerization has occurred at around 6 GPa, followed by an uncompensated pressure drop to 4.0 GPa. The rough, as-measured patterns are dominated by the Compton scattering background from diamonds. Empty DAC patterns were measured at the end of the compression cycle and after having removed the recovered a-pCO sample from the gasket hole. The empty DAC backgrounds were then subtracted to the sample patterns measured at high pressures and the results show typical diffuse scattering haloes, the intensity of which is lower than the background intensity by more than a factor of 10. The Compton background-free sample patterns where finally azimuth averaged, at all the investigated pressures, for obtaining the 1D diffraction patterns shown in Figure 3 (left panel). The $I(Q)$ patterns reported in this figure show, at all pressures, a diffuse, liquid-like peak, located at 2.4−3.2 Å^{-1} along with a weaker peak at 5.4−5.5 Å^{-1}. The full width at half-maximum (fwhm) of the first peak provides an estimation of the spatial correlation length l ($l \sim 2\pi/\text{fwhm}$), that results to be equal to 8.7 Å at 4.0 GPa and decreases down to 5.3 Å at 51.4 GPa. These values show that the spatial order of the sample is limited to just a few atomic coordination shells, which immediately qualifies the sample as an amorphous material. Accordingly, we find appropriate to label this type of polymeric CO as a-pCO. The pressure behavior for the Q position of the lowest-Q diffuse peak (Q_{max}) is reported in the
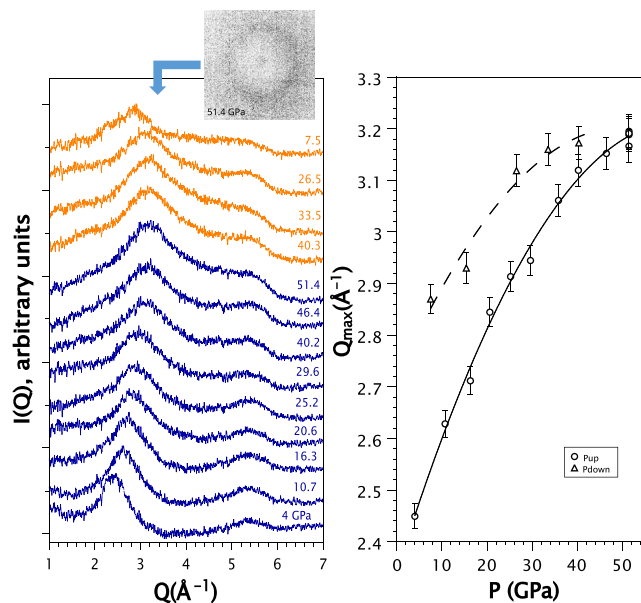
Figure 3. XRD characterization of a typical a-pCO sample. Left panel: selected XRD patterns measured upon increasing (blue) and subsequently decreasing (orange) pressure, after subtraction of the empty DAC signal from the total intensity. The pattern at 4 GPa has been measured after polymerization at around 6 GPa, followed by a pressure drop. The patterns have been vertically shifted for the sake of clarity. Inset: 2D XRD pattern at 51.4 GPa, zoomed around the diffuse scattering halo corresponding to the peak at 3.17 Å^{-1}. Right panel: pressure shift for the lowest-Q diffuse scattering peak. Circles and triangles correspond to measurements performed upon increasing and decreasing pressure, respectively. Guides for the eye have been fitted through the points.

right panel of Figure 3, where we see that this peak undergoes a continuous and positive pressure shift with also some hysteresis effect upon decreasing pressure. This compression curve is referred to a material with a pressure-dependent chemical structure (see below) and, consequently, it is expected to inextricably entangle two driving factors: the pure physical compressibility for a fixed chemical structure and the pressure-induced modifications of this structure. While the limited Q range for the present XRD investigation prevented us to extract the pair distribution function from our measurements, the local, chemical structure of a-pCO is clearly revealed by IR spectroscopy.

IR Spectroscopy Characterization. Vibrational IR absorption spectroscopy provided direct information on the high pressure chemical modifications of carbon monoxide. In Figure 4, we report selected IR spectra for a few micron thick sample loaded on a KCl pellet, measured upon increasing and subsequently decreasing pressure over the 4−51−4 GPa pressure range. The reduced sample thickness with respect to pure, typically tens of micron thick CO samples indeed allowed to avoid saturation of the absorption for the polymeric form (see Figure S1). Below the polymerization pressure, at 4.5 GPa, we observed no IR features other than the molecular C≡O stretching peak at about 2150 cm^{-1}, that strongly interferes with the two-phonon absorption band of diamond and its overtone at around 4270 cm^{-1} (see Figure S2 for the overtone). Upon surpassing the ∼6 GPa threshold by no more than 1 GPa, the spectrum suddenly transformed into an entirely different one which, at 7.2 GPa, shows a fair agreement with the spectrum previously observed for a-pCO[22] at similar
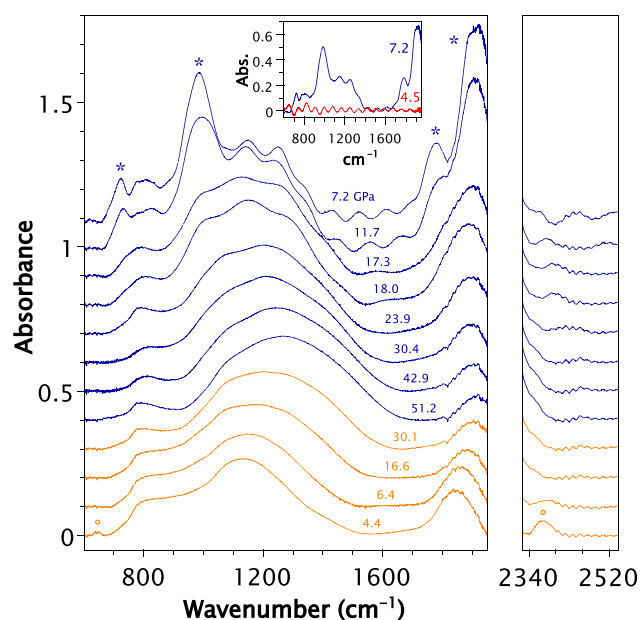
Figure 4. Selected IR absorption spectra of a few microns thick a-pCO sample, formed on a thicker and completely transparent KCl pellet, measured upon increasing (blue) and subsequently decreasing (orange) pressure. The spectra have been vertically shifted for the sake of clarity. The top two-three spectra are slightly modulated by interference fringes, which vanish with increasing pressure. Stars: peaks involving the carbonyl group. Open circles: peaks of CO_2. The not shown $1950-2320$ cm^{-1} frequency interval is affected by the strong, two-phonon diamond peak. Inset: comparison between spectra of molecular (red) and polymeric (blue) CO, measured below and above the polymerization pressure ($\sim$6 GPa), respectively.

223 pressures. The spectra of a-pCO exhibit several intense peaks
224 in the $600-1950$ cm^{-1} frequency interval, whose large
225 bandwidth parallels the main information gained from the
226 XRD measurements about our polymer being an amorphous
227 material. Importantly, we checked for the presence of CO_2 in
228 a-pCO by looking at the CO_2 asymmetric stretching peak, at
229 $2330-2520$ cm^{-1}, and we found this peak to be very weak over
230 the entire investigated pressure range, with just a slight increase
231 at GPa pressures along the downstroke run. By roughly
232 evaluating the integrated intensity of this peak and by following
233 a procedure described elsewhere,[34] we estimated the relative
234 concentration of CO_2 being close to 0.3%. Hence, we can
235 safely assess that our study deals with undecomposed a-pCO
236 samples, except for very low pressures upon reducing
237 pressures.
238   When we look at the spectrum at 7.2 GPa with a few more
239 details, we can easily identify peaks for the carbonyl $[-(C=$
240 $O)-]$ groups, which are the building blocks of the
241 polycarbonyl structures found in a-pCO. We labeled these
242 peaks by stars, following the assignment given previously.[22]
243 Particularly, the peak at about 720 cm^{-1} corresponds to the
244 carbonyl bending, while the two strong peaks at 1780 and 1908
245 cm^{-1} stem from the in-phase and out-of-phase C=O
246 stretching modes of the two carbonyl moieties forming
247 noncyclic $[-(C=O)-O-(C=O)-]$ anhydride groups. The
248 peak at 990 cm^{-1} also belongs to these groups while involving
249 single bond C−C−O and C−O−C stretching modes. All other
250 features in the $750-1390$ cm^{-1} interval were assigned to
251 additional stretching and deformation modes of the extended
252 network involving only single bonds and not including the

253 internal motion of carbonyl groups. It is therefore immediately
254 clear that carbon in threfold−fold coordination (Csp^2) and
255 oxygen in one-fold coordination are major components of a-
256 pCO in the GPa pressure range.
257   The spectra change remarkably with increasing pressure
258 above $\sim$12 GPa. All peaks assigned to the carbonyl groups
259 decrease, particularly those at 720 and 990 cm^{-1} that vanish
260 entirely while the two C=O stretching peaks converge into a
261 much weaker single peak, whose intensity decreases further but
262 slightly upon increasing pressure to 51.2 GPa. In parallel, all
263 bands other than those of the carbonyl groups barely change
264 upon increasing pressure, except for a general positive shift of
265 the band located at $900-1670$ cm^{-1}, at 51.2 GPa, which in
266 turn looks featureless and rather symmetric. All these changes
267 straightforwardly suggest that the local, chemical structure of a-
268 pCO modifies significantly upon increasing pressure above
269 $\sim$12 GPa. The main modification clearly consists of a major
270 coordination increase for both carbon and oxygen, which
271 transform to 4-fold (Csp^3) and 2-fold coordinated, respec-
272 tively, with just a residual amount of the pristine, lower
273 coordination at the maximum investigated pressures. Then, the
274 spectrum remains substantially unchanged upon reducing
275 pressure down to about 6 GPa, except for the pressure shift,
276 while instead we observed that the sample began to decompose
277 slightly below this pressure as indicated by the appearance of
278 the peaks of CO_2, the amount of which was estimated to have
279 increased to approximately 1% at 4.4 GPa. Furthermore, akin
280 to a-pCO formed at much lower pressures,[22] our recovered
281 solid material reacted with the air moisture by incorporating
282 OH groups (Figure S3), which strongly altered its chemical
283 composition. This result makes it very clear once again that the
284 recovered samples can hardly be used to study the properties
285 of the high pressure a-pCO form.
286   In Figure 5, we report a description of the high pressure
287 variations of a-pCO in terms of the ratio $\eta = A_{C=O}/A_{tot}$, where
288 $A_{C=O}$ is the integrated IR intensity of all bands assigned to
289 carbonyl groups, labeled by stars in Figure 4, and A_{tot} is the
290 total integrated IR intensity in the $600-2100$ cm^{-1} interval.
291 These intensities were obtained through a fitting procedure
292 which, for the C=O stretching peaks, also involved a slight
293 extrapolation to frequencies higher than 1950 cm^{-1}, where
294 there is a strong interference with the two-phonon peak of
295 diamond. Details on the fitting procedure are reported in the
296 Supporting Information (see SI text and Figure S4). The
297 quantity η reflects the concentration of carbon and oxygen sites
298 with 3- and 1-fold coordinations, respectively, and can be a
299 useful probe of pressure-induced changes in the local
300 coordination. The η decreases almost irreversibly by about a
301 factor of 17 upon compression of a-pCO in the $7-51$ GPa
302 pressure range, thus signaling the substantial transformation of
303 a-pCO from a material with both single and double bonds to a
304 pure single-bonded polymer network with increased coordi-
305 nation for both C and O. Most notably, the η ratio drops
306 remarkably with increasing pressure just above $12-13$ GPa,
307 which is very close to the pressure value at which the transition
308 from a double- and single-bonded crystalline pCO phase to a
309 pure single-bonded crystalline pCO phase was predicted
310 through ab initio computer simulations.[27] Therefore, our
311 experimental results corroborate the simulations in the key
312 physical property studied here: the pressure dependence of the
313 local structure, which in turn amorphous materials and their
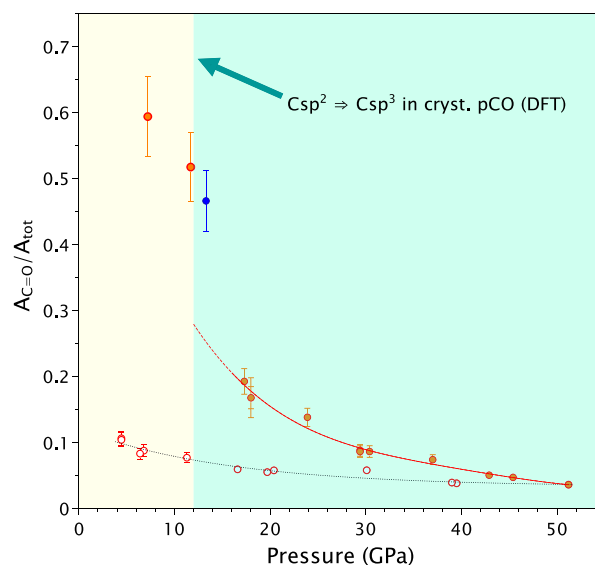314 crystalline counterparts generally have in common.

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Figure 5. Pressure dependence for the integrated IR absorbance $A_{C=O}$ of all the peaks assigned to the carbonyl groups, labeled by stars in Figure 4, normalized to the total integrated absorbance A_{tot} between 600 and 2100 cm^{-1}. Closed (open) circles: points measured upon increasing (decreasing) pressure. Blue, closed circle: point obtained by re-elaborating data at 100 K from ref 22. Lines: guides for the eye. The panel was divided into a yellow and a cyan sector bordering at 12 GPa, the pressure value at which the transition from a double- and single-bonded crystalline pCO phase to a pure single-bonded crystalline pCO phase was predicted to occur through ab intio computer simulations.[27]

Indeed, our experimental observations are suggestive of some sort of amorphous—amorphous transition that appears to correspond to the predicted low coordination-to-high coordination phase transition for crystalline pCO.

The ab initio predictions also provide a possible explanation for why our polymeric sample is amorphous rather than crystalline. Indeed, the simulations predict that at least five distinct stable crystalline pCO phases, three in low coordination and two in high coordination, are quite close in energy in the pressure range in which polymeric CO was experimentally obtained. The enthalpy difference among these phases amounts to at most a few hundredths of eV/CO. It is therefore natural that the kinetically driven experimental sample simultaneously reflects all the different local structures found for the crystals, thus resulting in a disordered material.

CONCLUSIONS

In summary, we conducted a combined XRD and IR spectroscopy experimental investigation of polymeric CO synthesized at several GPa and subsequently compressed to 56 GPa. Our study shows that this material is amorphous over the entire pressure range investigated and that it undergoes major changes in the local structure above 12–13 GPa, from a double- and single-bonded solid toward a purely single-bonded solid. Consequently, the average atomic coordination increases which, for carbon, corresponds to changing the hybridization from sp^2 to sp^3. This transformation mimics the similar phase transition predicted ab initio in crystalline pCO at 12 GPa,[27] and parallels those observed in other simple group IV oxides (see ref 12 and references therein). On the other hand, the

synthesis of a crystalline version of polymeric CO remains a challenge.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c03204.

Additional IR spectra of a-pCO (PDF)

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Notes

The authors declare no competing financial interest.

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