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W. J. Evans, M. J. Lipp, C.-S. Yoo, J. L. Herberg,  
R. S. Maxwell, M. F. Nicol

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**Pressure-induced polymerization of carbon monoxide: disproportionation and synthesis of an energetic lactonic polymer**

W. J. Evans, M. J. Lipp, C.-S. Yoo, H. Cynn, J. L. Herberg, R. S. Maxwell

*Lawrence Livermore National Laboratory, Livermore, California 94551*

M. F. Nicol

*University of Nevada Las Vegas, Las Vegas, Nevada 89154-4002*

**Abstract**

We have studied pressure-induced chemical reactions in carbon monoxide using both a diamond-anvil cell and a modified large volume press. Our spectroscopic data reveal that carbon monoxide disproportionates into molecular CO<sub>2</sub> and a solid lactone-type polymer; photochemically above 3.2 GPa, thermochemically above 5 GPa at 300K, or at 3 GPa and ~2000K as achieved by laser heating. The solid product can be recovered at ambient conditions with a high degree of conversion, measured to be up to 95% of the original CO. Its fundamental chemical structure includes β-lactone and conjugated C=C, which can be considered a severely modified polymeric carbon suboxide with open ladders and smaller five-membered rings. The polymer is metastable at ambient conditions, spontaneously liberating CO<sub>2</sub> gases exothermically. We find that the recovered polymer has a high energy density, 1-8 KJ/g, and is very combustible. We estimate the density of recovered CO polymer to be at least 1.65 g/cm<sup>3</sup>.

## Introduction

Condensed carbon monoxide (CO) has received a great deal of attention for many reasons, including comparisons to iso-electronic nitrogen ( $N_2$ ), with strong analogies at low pressures and marked differences at high pressures,<sup>1,2</sup> and their similar behavior under shock compression,<sup>3,4</sup> and in particular its pressure-induced transformations to non-molecular phases.<sup>5,6</sup> At low pressures, CO and  $N_2$  crystallize into the same disordered hexagonal solid ( $\beta$ -phase,  $P6_3/mmc$ ) and then transform into ordered cubic structures ( $\alpha$ -phase,  $P2_13$  in CO and  $Pa3$  in  $N_2$ ) on further cooling. At ambient temperatures, CO and  $N_2$  crystallize into the  $\beta$ -phase at around 2 GPa and then into an ordered cubic structure ( $\delta$ -phase,  $Pm3n$ ) near 4.0 GPa. The high-pressure behavior of the  $\delta$ -phase, however, diverges greatly between CO and  $N_2$ .  $\delta$ -CO is not stable above 5 GPa and transforms irreversibly to a colored, non-molecular phase.<sup>5</sup> In contrast, molecular  $N_2$  is stable over a wide range of pressures, undergoing a series of phase transitions from  $\delta$ - $N_2$  to  $\epsilon$ - $N_2$  at 20 GPa, to  $\zeta$ - at 60 GPa, and finally to the non-molecular, probably amorphous,  $\eta$ -phase above 160 GPa.<sup>6,7,8</sup> Recently, it has also been reported that laser-heated  $N_2$  transforms to yet another non-molecular *cubic gauche* (*cg*)-N phase ( $I2_13$ ) above 110 GPa and 2000 K.<sup>9</sup> It is not known, however, whether there is any relationship between the non-molecular  $\tilde{\eta}$  and *cg*-N phases, nor is there any data regarding their predicted novel properties such as the high energy content.<sup>10</sup>

The subtle difference in chemical bonding between CO and  $N_2$  leads to a dramatic divergence in their behaviors at high pressures, which provides fundamental and systematic data for condensed matter theory and solid state chemistry under extreme

conditions. Despite such a pivotal role, substantially less attention has been devoted to understanding the pressure-induced physical and chemical changes of CO.

Katz et al.<sup>5</sup> were the first to report the pressure-polymerized product of CO (which we shall refer to as p-CO) in a diamond anvil cell (DAC). Shortly after the initial discovery, they found that the recovered product was highly photosensitive, very sensitive to atmospheric moisture<sup>11</sup> and continuously changed its color and texture, hampering further characterization.<sup>5</sup> They were unable to observe features in the Raman spectra of the product and speculated – based on some similarities of the infrared spectra with those of polymerized carbon suboxide (poly-(C<sub>3</sub>O<sub>2</sub>)), specifically a sharp absorption edge at 3700 cm<sup>-1</sup> and a maximum in transmission at 2200 cm<sup>-1</sup> - that CO stoichiometrically disproportionates and polymerizes into poly-(C<sub>3</sub>O<sub>2</sub>), leaving behind some residual oxygen. Mills et al. observed that CO loses its x-ray diffraction peaks as the chemical reaction occurs at 5 GPa at room temperature.<sup>12</sup> They also found that the pressure threshold of the chemical instability and associated polymerization increased to ~12 GPa at 15 K. Lipp et al. were the first to actually show Raman, FTIR and absorption spectra of a sample that was converted by laser irradiation in the visible.<sup>13</sup> Based on their observations they concluded that the synthesized material was not a mixture of poly-carbon suboxide and oxalic anhydride as suggested previously,<sup>14</sup> but was composed of graphitic-like carbon, carbon dioxide, and a polymerized network containing vinyl-ester like groups like -(C=O)-O-(C-)=C<. They suggested that the photo-chemical product was different from the one synthesized by compression alone and speculated that the solid CO disproportionated in this fashion:  $6 \text{ CO} \rightarrow 2 \text{ CO}_2 + \text{C} + (\text{C}_3\text{O}_2)$  with the last entity representing the aforementioned vinyl-ester like group.

*Ab initio* molecular dynamics calculations indicated that the transformation might evolve in two steps on a picosecond time scale.<sup>15</sup> The polymerization was suggested to proceed without CO bond breaking when the individual molecules approached each other to closer than  $\sim 2.1 \text{ \AA}$  and, in contrast to the experiments, no formation of CO<sub>2</sub> molecules was observed. In the calculations, CO remained a molecular crystal at 200 K and 9.8 GPa, i.e. well above the experimentally observed chemical instability. At 15 GPa the computer modeling predicted that the crystal initially changed chemical bonding to form (0.25 ps) a simple poly-carbonyl polymer, followed by more extended carbonyl polymers such as five-fold lactonic rings containing four carbon atoms (two carbonyl groups) and one ester bridge as well as linear segments that were partially interconnected. While these calculations seem to capture some detailed features of the CO pressure-induced reaction products, experimental challenges including the high reactivity, metastability and the minute amount of samples synthesized in DACs have hampered further chemical analyses and thus validation of the theoretical results.

The present study was undertaken to address the pressure-induced chemical reaction of carbon monoxide; that is, to characterize the pressure-synthesized products and to improve our understanding of the chemical reactions. Because of the experimental challenges mentioned above, no single experimental technique provides a complete characterization. Therefore, in this study we used several approaches and techniques including (i) *in-situ* investigation of CO reaction in DAC, (ii) synthesis of the reaction products at the macroscopic scale of large volume presses, (iii) characterizing chemical structures of the products by vibrational Raman and FT-IR spectroscopy, mass spectroscopy, magic angle spinning (MAS) solid state <sup>13</sup>C-NMR, solution state <sup>13</sup>C NMR,

and thermal analysis (differential scanning calorimetry - DSC). Details of some aspects of this work – such as the large volume synthesis of p-CO and its energetic properties - were recently published elsewhere.<sup>16</sup> In this paper we review and expand on previous results, presenting new data to construct a more complete understanding of the properties of CO and its transformations at high pressures.

### **Experiment**

The method for filling the sample chamber of a pressure cell with a highly toxic liquefied gas like carbon monoxide involves construction of a leak-tight shield around the anvils enclosing the containment gasket. Careful consideration must to be given to several factors:

- (i) ease of operation
- (ii) utilization of non-reactive materials
- (iii) good thermal conductivity for cryogenic cooling
- (iv) good gasket and loading system performance at the low temperatures necessary for loading liquid CO
- (v) thermal isolation of the sample load chamber from ambient conditions
- (vi) small dead volume to reduce stored energy and quantity of CO needed for loading
- (vii) for large volume presses, protection from shrapnel in case of failure of an anvil or gasket

In this study, we used a stainless steel metal bellows for the diamond anvil cell (DAC) and a brass or aluminum ring as shield for the large volume press. A detailed discussion of these large volume press system is presented elsewhere.<sup>17</sup>

High purity CO (99.99+% from Matheson) was loaded into the sample chamber of a DAC. We used a Livermore-designed diamond anvil cell of the LLL-type, a modified version of Mao-Bell cell without a lever clamp, with 0.5 mm flat diamond anvils and a rhenium gasket. A small stainless steel metal bellows (~5 mm in diameter) was mounted around the diamond anvils and gasket to provide a vacuum-tight sample environment. To load liquid CO samples, the LLL cell was immersed into liquid N<sub>2</sub>, the metal bellows enclosed sample area was evacuated to less than 50 millitorr, and CO gas was introduced at a pressure of about 2-3 atmospheres through a small capillary tube. A sudden drop in of pressure in the the CO supply line was taken to indicate condensation of the CO. After several minutes the diamonds anvils were advanced to capture the liquid CO in the gasket hole. The excess amount of CO gas was diluted with a large amount of N<sub>2</sub> gas and released through a fume hood. All sample loading was performed inside a fume hood and several CO warning detectors continuously monitored the air for any accidental release.

Despite the relatively modest synthesis conditions, the properties of p-CO remain largely unknown, owing to the microscopic amount of sample generated in the DAC experiments. To remedy this situation, we synthesized milligram-quantities of p-CO at high pressures using a large volume press system, specifically a modified Paris-Edinburgh cell (mPEC).<sup>17,18,19</sup> High purity CO (99.99+%) was loaded into the mPEC sample chamber in the liquid phase at ~10 bar and 80 K (liquid nitrogen). After capturing the CO sample, the system was warmed to room temperature; then the load on the sample was increased to



the desired pressure for synthesis. For successful recovery we found it important to decompress the sample/gasket assembly *very* slowly. This requirement probably arises from the high mechanical energy built up on the sample chamber during loading and the high energy content of p-CO, both of which could result in a premature explosive failure.<sup>20</sup> Figure 1 shows the typical remains of a gasket after such a failure and the Raman spectrum of the residue (dark spot at center of anvil). The Raman spectrum of the residue is typical of glassy carbon produced after an explosion of hydrocarbon materials exhibiting strong carbon D and G bands at around 1354 and 1594  $\text{cm}^{-1}$  and their overtones / combination bands.

We have carried out angle-resolved x-ray diffraction experiments of the DAC produced CO products at a third generation synchrotron source, optimized for DAC research (HPCAT, Advanced Photon Source, Argonne National Laboratory). The x-ray diffraction pattern of p-CO, however, consisted only of a very broad diffuse ring, analogous to that of amorphous or disordered phases. These results imply a lack of long-range order. The nature of the p-CO, such as metastability and amorphous structure, makes its characterization extremely challenging. A collection of analytical tools will be necessary to construct a coherent and thorough description of this material. Therefore, in the present study, we used several approaches; for example, vibrational spectroscopy for the *in-situ* investigation in DAC and conventional analytical methods such as mass spectroscopy, NMR, and DSC.

A chamber was constructed to capture the gaseous products evolved from a p-CO sample synthesized in DAC. This chamber was easily coupled to a mass spectrometer (AEI MS 902) to analyze the emitted gases. The operating conditions were: ion mass range

14-160, electron energy 16 and 70 eV, scan rate of 16 second/decade for low resolution and 34 for high resolution, and a source temperature of 24 °C for the gas samples and 200-300 °C for solid products.

Solid products derived from isotopically enriched  $^{13}\text{C}$  were synthesized and analyzed using MAS  $^{13}\text{C}$ -NMR, which were performed on a Bruker Avance 500MHz spectrometer with a magnetic field of 11.7T. This gives a resonance frequency of 125.77 MHz for  $^{13}\text{C}$  (spin=1/2). The samples were packed in a Doty scientific insert, in order to center the sample, and placed in a 4mm rotor. Spinning rates of 12kHz were used. The Free Induction Decay (FID) spectra were taken with a single excitation pulse. The  $^{13}\text{C}$ -NMR data were taken with a 90° pulse width of 8 $\mu\text{s}$ . The  $^{13}\text{C}$  NMR data were referenced to glycine at 32ppm and 176.5ppm.

We also measured infrared spectra of p-CO both *in-situ* and as recovered using a commercial FT-IR spectrometer (Nicolet Magna 760). The spectrometer had been modified to incorporate a continuous and thorough nitrogen purge and a reflective condenser optical system (6:1) to accommodate the relatively small DAC sample size (~300 microns in diameter). We used liquid nitrogen cooled MCT detector.

Raman scattering was excited using an argon ion laser, focused to a spot size of ~15  $\mu\text{m}$  with an incident power level of less than 20 mW at the sample. The Raman scattered light was collected at an angle of ~30° with respect to the incident laser beam. The Raman signal was spatially filtered and analyzed using a holographic notch filter (Kaiser Optical Systems), a 0.3 meter spectrograph (Instruments SA), and a liquid-

nitrogen-cooled CCD detector (Princeton Instruments). Typical exposure times were 5 minutes.

Because the CO-products might be a highly energetic material, we also performed DSC measurements. The DSC system was a commercial system (TA Instruments Diamond DSC). We used hermetically sealed gold pans that were carefully prepared to remove any contaminants. The DSC was operated to a maximum temperature of 600 °C with typical heating rates of 10 °C/min. The quantity of sample was typically 2-5 milligrams.

## **Results**

Carbon monoxide undergoes irreversible pressure-induced transformations to highly colored solid polymeric products. These transformation can be induced using pressure or alone or with added photochemical and thermochemical stimuli (Figs. 2-4). Using pressure alone, large milligram quantities of solid products (Fig. 5) can be synthesized at 5 to 8 GPa at 300K in a mPEC and then quenched to ambient conditions. At ambient conditions the products are metastable. IR, <sup>13</sup>C-NMR and mass spectroscopic analyses (Fig. 6) indicate that these products are primarily composed of 5 or 6-membered lactone-type rings and conjugated C=C bonds with a high energy content rivaling or exceeding that of HMX (Fig. 7). We discuss these results in further detail in the following sections.

### **A. Thermochemical “dark” reaction**

At ambient temperature, the  $\delta$ -phase of CO transforms to highly colored polymer-like products above  $\sim 5.2$  GPa. The transformed sample is a translucent yellow color, becoming increasingly red and dark as the thickness, and thus optical density, increases. Figure 2 shows such a sample while still at high pressure together with its vibrational Raman (collected at different locations) and FT-IR spectra (collected for the entire sample) over a range of pressures. The key features in the Raman spectra are at 650, 1600 and 1815  $\text{cm}^{-1}$ , which we identify as the symmetric bending mode of  $\text{CO}_2$ , graphitic C=C stretching mode, and C=O stretching mode. Note that there is no indication of unreacted CO. The spectrum of unreacted CO would appear as a narrow band at  $\sim 2140$   $\text{cm}^{-1}$  (see Fig. 3, for example) which is totally absent in spectra of the transformed product.

The infrared spectra of the CO samples are not well resolved because of the rather large sample thickness and strong absorptions bands of the products. As mentioned above, the transformed CO is highly absorptive, easily saturating absorption bands for samples thicker than a few microns. While no features are obvious at 4.2 GPa, broad peaks centered around 1000  $\text{cm}^{-1}$  and 1800  $\text{cm}^{-1}$  are apparent from thick solid products at higher pressures, generated by C-O and C=O stretching modes, respectively. Further infrared absorptions at 3550 and 3800  $\text{cm}^{-1}$ , particularly strong at 8.5 GPa, are believed to be overtones or combination bands involving carbonyl (C=O) stretches. If this is true, the absorption maxima of their fundamental bands should be at  $\sim 1900$  and 1775  $\text{cm}^{-1}$ , far removed from the region ordinarily expected for carbonyl stretches 1720-1760  $\text{cm}^{-1}$ .<sup>21</sup> Nevertheless, it is important to note that the carbonyl vibrations for which two and/or three oxygen atoms are bonded directly to the carbonyl carbons occur precisely in the regions of

1750 and 1900  $\text{cm}^{-1}$ .<sup>21</sup> Examples of this include carbonyls of anhydrides, 5- or 6-membered lactones, or cyclic carbonates.

As stated above the polymerized p-CO is metastable and can be pressure quenched and recovered to ambient conditions. However, not all of the transformed substance can be recovered to ambient conditions. During careful microscopic observation of a sample in a DAC we noted that a significant portion of the solid product converted to a liquid and evaporated during and immediately following a complete release of pressure. From the presence of  $\text{CO}_2$  in the Raman spectra in Fig. 2 (band at 2340  $\text{cm}^{-1}$ ), we attribute a decomposition mode of the metastable synthesized material to  $\text{CO}_2$  molecules evolving from the solid product. In fact, our mass spectroscopic analysis of the gas products evolved from a sample synthesized in DAC confirms the release of  $\text{CO}_2$  and CO immediately after releasing the pressure and opening of the DAC. After complete relaxation of the pressure, we recovered a small piece of the highly colored polymeric solid p-CO in the gasket.

## **B. Photochemical reaction**

Intense visible laser light (e.g. 488 and 514 nm from Ar-ion lasers) causes a similar chemical change in  $\beta$ -CO above 3.2 GPa, well below the 5.2 GPa threshold of the “dark” reaction. Figure 3 shows an image and the associated Raman and FTIR spectra of a CO sample in a DAC after exposure to laser light in the range of 3 to 5 GPa. The Raman spectra were recorded from a sample at 3.6 GPa using 488 nm radiation at 1.5 mW for 300 sec exposure (bottom trace) and at 3 mW power for 300 sec (top trace) to achieve conversion. The Raman spectrum of the top trace again contains the three characteristic bands at 650, 1600 and 1815  $\text{cm}^{-1}$ . The features are very similar to those of the “dark”

products above 5.2 GPa, suggesting that the photochemical product is very similar to the dark (pressure only) product. The vibrational stretching mode  $\nu_1$  of unreacted CO is also apparent at  $2140\text{ cm}^{-1}$ , particularly strong in the lighter yellow regions of the sample (inset in the top of Fig. 3). The relative intensity of the unreacted CO peak is clearly less in the spectrum taken from the dark sample area, where the more intense laser was focused and thus the reaction had progressed further (see top of Fig. 3).

FT-IR spectra taken at 4.2 GPa (see the lower panel in Fig. 2) after weak laser exposure (20 mW at 514 nm for 5 min) exhibit two sharp peaks at  $2375$  and  $675\text{ cm}^{-1}$  - slightly higher than the above-mentioned 3.2 GPa where 488-nm laser exposure initiates the reaction. We identify these features as the stretching and bending modes of  $\text{CO}_2$ ,<sup>22</sup> noting that they are not present without the exposure to the laser light at pressures below 5.0 GPa. At 5.0 GPa, a relatively opaque dark brown solid is produced at the location where the laser is focused and strong broad features centered near  $1150$  and  $1900\text{ cm}^{-1}$  appear in the infrared spectrum. These features are again similar to those of the dark (pressure only) reaction products. Untransformed carbon monoxide should have an infrared-active fundamental asymmetric stretching mode,  $\nu_a$ , at around  $2150\text{ cm}^{-1}$ , which is obscured by the strong diamond absorption.

The photo-assisted transformation products are also metastable, although there is some variation in stability with some products decomposing faster than others, again presumably by evolving  $\text{CO}_2$ , when quenched to ambient conditions. There are no apparent differences in either visual appearance or vibrational spectra between the dark pressure-only and the photo-assisted reaction products. The *in-situ* spectroscopic Raman and FTIR studies demonstrate that the photo-assisted reaction produces a type of

polymeric CO very similar to the one produced dark pressure only synthesis conditions. Both sets of conditions yield a product that evolves molecular CO<sub>2</sub>, with the exception that the photo-assisted product appears to contain more CO<sub>2</sub> at an equivalent pressure. Our work also indicates that the amount of CO<sub>2</sub> produced also increases with synthesis pressure. A plausible explanation is that the photo-assisted process and higher pressures may overdrive the transformation beyond the solid poly-CO product resulting in production of excess CO<sub>2</sub>. Furthermore, the photo-assisted process requires uniform exposure of the sample to the laser stimulus, which if incomplete would lead to a sample that is only partially converted with more dangling bonds and thus inherently more unstable. Although the photochemical reaction is localized to places exposed to laser light, no obvious differences between the photo and dark products were found during further compression up to 40 GPa.

### **C. Thermochemical reactions of laser-heated CO**

A chemical transformation to the polymerized CO solid phase also occurs from different phases of carbon monoxide; for example,  $\epsilon$ -CO transforms to the polymerized products at 10.0 GPa at 20 K and laser-heated CO transforms at pressures as low as 3 GPa, as shown in Fig. 4. In this laser-heating experiment, the  $\beta$ -phase of solid CO (instead of the  $\delta$ -phase) was heated at 3.0 GPa using a YLF laser (1053 nm). CO does not have an absorption band at this wavelength and thus does not absorb the 1053 nm light directly. To address this problem tiny ruby particles (appearing as black dots in the image of the CO sample) were used as radiation couplers, absorbing the 1053 nm light and converting it to heat. After heating, a part of the sample in the vicinity of the ruby particles nearly

instantaneously transformed to an opaque material (see Fig. 5b inset). Because this change occurs rapidly, we are unable to determine whether the reaction started from solid  $\beta$ -CO or the solid first melted and then proceeded to polymerize from supercritical fluid CO. The transient temperature was estimated from pyrometry to have an upper bound of  $\sim 2000$  K. It is important to note that this reaction occurred at  $\sim 3.0$  GPa, again substantially lower than the  $\sim 5.2$  GPa threshold of the dark pressure only synthesis. After laser heating and reaction, we also observed a relatively large pressure drop, of  $\sim 1.0$  GPa. Since the sample chamber is approximately isochoric, this result suggests that the reaction products are more dense than the starting material. From basic mass and volume measurements, densities of solid p-CO product recovered from mPEC large volume press experiments were evaluated to be  $1.65 \text{ g/cm}^3$ , which is indeed substantially higher than that of  $\beta$ -CO at 3 GPa,  $\sim 1.4 \text{ g/cm}^3$  and more than twice the density of liquid CO. These measurements do not account for the porosity in the sample; thus this value is a lower bound on the density.<sup>23</sup> In addition to the formation of the opaque region, parts of the transparent region of the sample turned into a mixture of two materials, as evident is from the grain boundaries in the inset of Fig. 4b.

Figure 4a displays an image and Raman spectra of unreacted CO (top panel) and Fig. 4b shows the spectra of the transparent (lower panel) and opaque product (upper panel) after laser heating. The vibrational features of the opaque product are similar to those of the “dark” and “photo-assisted” products described above. The Raman spectrum of the transparent area consists of CO<sub>2</sub> crystals (bands near  $1273$  and  $1383 \text{ cm}^{-1}$ ), fluid CO (band at  $2141 \text{ cm}^{-1}$ ) and nearby solid p-CO products (bands at  $1607$  and  $1801 \text{ cm}^{-1}$ ). While the presence of CO<sub>2</sub> is apparent from its characteristic Fermi-resonance bands, note that



the CO<sub>2</sub> bending mode  $\nu_b$  at 650 cm<sup>-1</sup> is nearly absent in the Raman spectrum of transparent products (primarily CO<sub>2</sub> and a small amount of unreacted CO). This contrasts with the relatively strong  $\nu_b$  intensity of the dark and photo products in Figs. 2 and 3, clearly indicating a perturbation of the local inversion symmetry in CO<sub>2</sub> molecules in the dark and photo-assisted products. There is some residual intensity in the CO<sub>2</sub> bending mode, albeit very weak, in the Raman spectrum of the opaque product (marked by an arrow) in Fig. 4b, consistent with those of the dark and photo-assisted products in Figs. 2 and 3.

#### **D. Synthesis of mg-quantities of solid CO products**

We performed over thirty successful syntheses of p-CO using the mPEC. Recovered p-CO products had a variety of appearances, ranging over translucent orange, orange-brown, red-brown, and grey-red to name a few. We propose that these variations are the result of differing sample thicknesses and precise details of the synthesis conditions. Figure 5 shows two images of solid p-CO recovered after synthesis at 6.7 GPa (5a) and 7.0 GPa (5b) in a mPEC. These images provide examples of the wide variation in the optical characteristics of the samples. We find that we can achieve a product yield, i.e., conversion from molecular CO, of up to 95% with the mPEC. The yield does not appear to correlate with either the color of the sample or details of synthesis in any discernable way. This may be due to uncertainties in the applied pressure, which was calculated from the applied load. An *in-situ* pressure monitoring technique would be a better diagnostic of the pressure than the post mortem evaluation technique we have used.<sup>24</sup> Improved accuracy in our pressure measurement might elucidate a correlation between pressure and

the nature of the product and yield. The recovered p-CO solid product was hygroscopic and photosensitive; its color ranged from milky white to brownish-orange as recovered and gradually darkened with time and exposure to light. The degree of metastability and rate of decomposition varied, with recovered product persisting from hours to weeks. Regardless of the decomposition rate, the product would continuously evolve CO<sub>2</sub> until simply carbon remained. As discussed above, the recovered product has a density of at least 1.65 g/cm<sup>3</sup>. Thus it appears possible to “lock” the high density of the molecular solid at the transformation pressure into the recovered p-CO product. The texture of p-CO became gooey when exposed to air for several days or when immersed in organic solvents, including methanol or acetone. The solid product can be dissolved in deuterated dimethylsulfonyl oxide (DMSO-d<sub>6</sub>). Raman spectra of recovered p-CO could not be obtained using visible argon ion laser radiation, which damaged and degraded the material because of its extremely high photosensitivity.

#### **E. Characterization of the chemical structure of p-CO**

*In-situ* determination of the structure of p-CO is especially challenging because of the lack of long-range order resulting from the random polymer network. Nevertheless, a mg-quantity of recovered p-CO permits the determination of the chemical structure using solid-state Magic Angle Spinning (MAS) <sup>13</sup>C-NMR, FT-IR and Mass Spectrometry (MS). These spectroscopic results (summarized in Fig. 6 and Table I) suggest that p-CO is built from lactone-like carbonyls and conjugated C=C bonds in chemical configurations that can easily liberate CO<sub>2</sub> and convert to oxygen deficient graphitic C=C layers. The liberation of CO<sub>2</sub> is also consistent with our observations regarding the metastability and decomposition. The MAS-<sup>13</sup>C-NMR spectra of solid samples (Fig. 6a) show two very

sharp features at 223 and 151 ppm, characteristic of carbon atoms in ester- or lactone-like carbonyl groups,  $-O-(C=O)-$ , and  $>C=C<$  double bonds, respectively.<sup>21</sup> After several days, the relative intensity of the 223 peak substantially decreases, while that of the 151 peak grows (see Fig. 6b). Two broad features at  $\sim 189$  and 109 ppm are identified as carbon atoms attached to the ester bridge of the  $-O-(C=O)-$  group and single-bonded carbon atoms coupled to an oxygen bridge or alternatively just singly bonded carbons. Both of these features gain intensity and develop side bands over timescales of several hours to days. We identified similar sharp features at around 202 and 149 ppm when the product was dissolved into DMSO- $d_6$ , as shown in the third panel of Fig. 6a.

IR spectra were collected to study the effect of temperature and to gain insights into the stability and decomposition modes of the recovered p-CO. The infrared spectra of the recovered p-CO solid product, mullied with NaCl and heated to two different temperatures for 24 hours, are presented in Fig. 6b, with the energies of the peak positions summarized in Table II. Mulling was necessary to reduce the concentration of the p-CO, which would otherwise have simply yielded spectra with saturated absorption bands. Several vibrational bands overlap producing the broad feature centered at  $1780\text{ cm}^{-1}$ . Two of them, at  $1780$  and  $1800\text{ cm}^{-1}$ , are the carbonyl vibrations corresponding to the broad features centered in the *in-situ* spectra of p-CO at 8.5 GPa in Fig. 2. However the energies are lower than expected when one interprets the peak at  $3815\text{ cm}^{-1}$  as an overtone, whereas the band at  $3533\text{ cm}^{-1}$  might well be one. However, the large pressure dependence of the stretching mode as well as further chemical changes due to loss of  $\text{CO}_2$  and CO should also be reflected in a shift of the carbonyl vibration to lower energies. During heating to  $100\text{ }^\circ\text{C}$  the high energy carbonyl vibration disappears first, while the energy of the other

shifts down to  $1720\text{ cm}^{-1}$ , and it disappears on further heating to  $200\text{ }^{\circ}\text{C}$ . The bands at  $1275$  and  $1200\text{ cm}^{-1}$  and the shoulders at  $1650$  and  $1400\text{ cm}^{-1}$  are consistent with the vibrations of C-(C=O)-O and O-C-C and C=C in cyclic systems.<sup>21</sup> Therefore incorporating these observations into a unified interpretation, we propose that the structure of the solid product involves an unsaturated lactonic ring with 5 or/and 6 members at ambient temperature with the C=C bond adjacent to the -O- bridge. As the temperature increases, the absorption band of the lactone shifts to lower energy until it disappears, while the absorption strength of the C=C stretch is enhanced. This is related to the chemical changes that result from the liberation of  $\text{CO}_2$  and CO molecular units, which are further reflected in color changes of the product during decomposition.

The mass spectrum (MS) of p-CO (Fig. 6c) exhibits three main fragments: 44 amu for  $\text{CO}_2$ , 28 amu for CO and 16 amu for O; O and CO are the secondary fragments of  $\text{CO}_2$  and CO. Larger molecular fragments were not observed suggesting the p-CO is indeed unstable and prone to decompose into simple  $\text{CO}_2$  and CO units under MS conditions. After the MS run we noted a black residue left on the source probe. This residue appeared to be graphitic carbon or simply carbon “soot”. We found that similar gaseous products evaporated when the product was dissolved into  $\text{DMSO-d}_6$ .<sup>25</sup> We concede that the MS does not definitively identify the composition of p-CO and polymeric carbon suboxide (p- $(\text{C}_3\text{O}_2)$ ) also evolves  $\text{CO}_2$  and CO without evidence of the parent molecule,  $\text{C}_3\text{O}_2$ .<sup>26</sup>

#### **F. Characterization of energy content of p-CO**

Recovery of macroscopic quantities of p-CO makes it possible to evaluate the material's energy content. A key question is whether this material is indeed a high energy

density material similar to the theoretical predictions for nonmolecular *cg-N*.<sup>10</sup> There are some inherent difficulties in this measurement since p-CO is metastable, slowly releasing gaseous products such as CO<sub>2</sub> after recovery to ambient conditions. Nevertheless, our measurements represent a lower bound on the energy content. Though most conventional energetic materials are indefinitely stable, we emphasize that any energetic material is metastable by definition, *i.e.*, the system is kinetically impeded from releasing its energy and reconfiguring itself into a lower energy configuration. Because of this metastability of p-CO, our Differential Scanning Calorimetry (DSC) results exhibit rather large sample-to-sample variations in the measured energy release of 1-8 KJ/g, and location of the exotherm at 100-450 °C. We interpret these variations to be caused by the variations of the samples after recovery and/or the differences in the extent of their time-dependent degradation. However, these values are sufficient to establish that p-CO is indeed a high energy density material. Typical modern high explosives, such as TATB, RDX and HMX, have thermal energy contents of 1-3 kJ/g.<sup>27</sup> An important qualifier for these measurements is that the DSC measures only thermal energy release. The total energy content, the sum of thermal energy and mechanical (pdV) work released, will be even larger given the CO<sub>2</sub> and CO gases produced by the decomposition.

The sequence of images obtained following laser initiation of the sample decomposition (Fig. 7) further demonstrates that p-CO has a high energy content and behaves explosively when appropriately triggered. p-CO is rather sensitive and can readily be initiated even at a relatively weak laser power (< 100 mW of Nd:YAG at  $\lambda = 1064$  nm) and form a self-propagating front. To verify that the laser was not simply burning the sample, a subsequent exposure to the laser at the same spot – now

energetically spent – does not lead to another ignition. For comparison, at similar laser powers we found no effect on conventional energetic materials including PETN,  $\text{NaN}_3$ , and TATB. The ignition of these materials is a function of the absorption of the laser wavelength by the material, but it establishes that we are not simply observing combustion with the laser providing the thermal energy to ignite and burn the sample. Based on the intense incandescent emission from the initiated sample shown in Fig. 7, the temperature was estimated to be well above 2500 K. The energetic decomposition of p-CO produces a large quantity of gaseous products. Using mass spectroscopy we determined the product gases to be primarily  $\text{CO}_2$ . The final residue after the rapid decomposition (see inset of Fig. 8) was characterized by Raman spectroscopy and determined to be glassy carbon<sup>28</sup> exhibiting the typical bands at 1350, 1600 and their overtones at 2700-3200  $\text{cm}^{-1}$ . very similar to the characteristic bands of the residue of a premature explosive failure during recovery unloading of a sample synthesized in the mPEC as shown in Fig. 1. The strong presence of the characteristic D-band at 1350  $\text{cm}^{-1}$  and its overtone at 2700  $\text{cm}^{-1}$  indicate a substantial amount of  $\text{sp}^3$  and  $\text{sp}$  disorder in  $\text{sp}^2$  carbon species, similar to those produced after strong shock compression of hydrocarbons.<sup>29</sup>

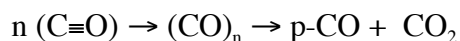
## Discussion

### A. Pressure-induced disproportionation of CO

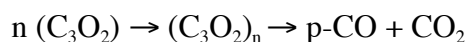
Our results clearly demonstrate that at room temperature CO undergoes an irreversible reaction that takes place photochemically at  $> 3.2$  GPa and thermochemically at  $> 5.2$  GPa. Based on the pressure-temperature data we have collected, we propose the chemical/phase diagram of CO in Fig. 9. Based on the *in-situ* IR and Raman spectroscopy of the converted CO in a DAC, we can confidently state that the reaction products include

a polymeric solid, p-CO, and CO<sub>2</sub>. It is important to note that when we refer to the polymeric solid, p-CO, it is derived from CO, but is not stoichiometrically CO. Our spectroscopic work also demonstrates that the relative proportions of p-CO and CO<sub>2</sub> vary depending on the details of the reaction conditions. Nevertheless the spectroscopic evidence that establishes the presence of these two components in the products of the pressure-induced transformation, regardless of conditions, demonstrates the disproportionation of CO at high pressures.

Several reaction pathways have been suggested in the past.<sup>13,14</sup> Pressure reduces the intermolecular distance eventually destabilizing the CO molecule, and initiating a reconfiguration of the bonds. A simple reaction would be a direct polymerization of CO forming a carbon backbone with oxygen groups bonded to the chain, -(C=O)-(C=O)-(C=O)-. However, the presence of CO<sub>2</sub> and the complexity of the NMR and IR spectra eliminate this as a possibility, and decomposition of this chain structure to p-CO is necessary to adequately account for the observed spectral signatures. Thus we arrive at a two-step process,



Another possible reaction pathway, consistent with the data, could be disproportionation of the CO into carbon dioxide and carbon suboxide, followed by polymerization of the carbon suboxide forming p-CO and some residual carbon dioxide,



A key feature distinguishing these two proposed reaction pathways is the disproportionation of CO, i.e. prior to or following polymerization. If, as proposed by the first pathway, the disproportionation occurs following formation of an oxygen terminated carbon chain, a broad unconstrained range of daughter products can be achieved depending on the degree of disproportionation. Alternatively, the second reaction pathway has a stoichiometrically fixed amount of disproportionation. Measurement of the amount of CO<sub>2</sub> produced in the reaction might possibly be a tool to validate one of these proposals while eliminating the other. Unfortunately this approach to identifying the reaction pathway is difficult because the p-CO material is itself unstable, releasing CO<sub>2</sub> and complicating a measurement of the amount of CO<sub>2</sub> produced by the transformation.

By having recognized the above-mentioned difference, we can evaluate our measurements relative to a molecular structure of a quasi-random poly-carbon suboxide (C<sub>3</sub>O<sub>2</sub>)<sub>n</sub>, as illustrated in Fig. 10. Then, our results supporting this model include:

- (i) the strong presence of O-C=O and C=C-C species observed in both NMR and FT-IR
- (ii) a chemical configuration that can easily liberate CO<sub>2</sub>
- (iii) a hygroscopic nature that can easily produce C-H and O-H bonds as observed in both NMR and FT-IR
- (iv) mass spectrometric fragments of CO<sub>2</sub> and CO consistent with those of C<sub>3</sub>O<sub>2</sub>.

Despite this support, there are important differences between p-CO and (C<sub>3</sub>O<sub>2</sub>)



- (i) Hydrolysis of  $C_3O_2$  typically yields  $CO_2$  and CO with a 4:1 ratio at 250 °C, whereas our Mass Spec results shows a substantially higher amount of CO evolving from p-CO
- (ii) Several strong IR bands are missing in p-CO, including the strong fundamental bands near 1365 and 1511  $cm^{-1}$  that are characteristic of  $(C_3O_2)_n$  whereas the broad feature at 3400  $cm^{-1}$  observed in p-CO is missing in  $(C_3O_2)_n$
- (iii) the estimated yield of p-CO, ~95%, is substantially higher than that expected from the formation of  $(C_3O_2)_n$ <sup>30</sup>
- (iv) some of our experiments show only minute amounts of  $CO_2$  following the polymerization, suggesting that much of the  $CO_2$  is evolved in decomposition after the polymerization

Therefore, we conclude that our measurements favor the latter model; that is, the pressure-induced polymerization followed by disproportionation. This model will certainly lead to more irregular structures than the  $(C_3O_2)_n$  intermediate and produce a smaller amount of  $CO_2$ , as observed in the present study. Viewed from the perspective of polymeric carbon suboxide, p-CO can be thought of as an oxidized form of  $(C_3O_2)_n$ , i.e., higher oxygen content.

In contrast to our experimental deductions, recent *ab initio* molecular dynamics calculations<sup>15</sup> suggest an entirely different transformation; neither disproportionation ( $CO_2$  and  $(C_3O_2)_n$ ) nor total polymerization. Despite differing reaction pathways, the theoretically predicted final structure of a partially interconnected poly-carbonyl polymer with fivefold lactone-like units exhibits characteristics similar to those measured in the

present study. One possible explanation of this discrepancy is that the theoretical simulation may be too tightly constrained to permit formation of multiple phases or the time scale of the simulation is insufficient to capture the disproportionation process if it proceeds relatively slowly.

## **B. Metastability**

The solid p-CO product is metastable at ambient conditions. We remind the reader that the inversion symmetry of CO<sub>2</sub> is strongly perturbed in the dark pressure only and photo-assisted products at high pressures, e.g. in Figs. 2-4. A plausible interpretation of this is that CO<sub>2</sub> molecules are strongly associated with those solid products *via* chemisorption or physisorption. This conjecture is certainly consistent with the observed high yield of recovered p-CO which contains has an oxygen content similar to that of a highly oxidized state of (C<sub>3</sub>O<sub>2</sub>)<sub>n</sub>. In this regard, p-CO can also be considered as a polymer, a severely perturbed analog to (C<sub>3</sub>O<sub>2</sub>)<sub>n</sub>, “supersaturated” with CO<sub>2</sub> at high pressures. One would expect this unique configuration to result in a material that is highly metastable upon pressure release or even a simple pressure-temperature change. The broad range of “oxidation” and CO<sub>2</sub> contents possible also provides an explanation for the wide range of variation in the color and properties of p-CO.

The recovered p-CO product is not indefinitely stable at ambient conditions and continuously decomposes by releasing CO<sub>2</sub> and CO molecules, while the color of the product darkens and gradually turns to black. Time sequences of vibrational spectra taken from the recovered p-CO (see Fig. 6a or Table II) showed the following changes: shifts of the carbonyl stretching to lower wavenumbers, increase in the intensities of the carbon

double bond stretching mode, and disappearance of the carbonyl vibrational bands. Consistent with our observations, a degrading p-CO sample that contains fewer oxygen atoms near carbons will have carbonyl stretches that are less intense and centered at lower wavenumbers. Furthermore, in the spectrum at 200 °C in Fig. 6b only the vibrational bands of the conjugated carbon double bond in the graphite-like molecules are present, with no evidence of any oxygen bonds. Loss of oxygen is also evident in the NMR spectrum, showing a remarkable enhancement of the C=C feature at 151 ppm with time (see Fig. 6a). The color of conjugated polyene can be intensified by increasing the number of double bonds<sup>31</sup> as seen in the color changes in organic dyes and cyclic dienes, for example.<sup>32</sup> Therefore, it is likely that the metastability of recovered p-CO arises from relatively weak binding of CO<sub>2</sub> and weak carbonyl bonds which break liberating CO<sub>2</sub> and CO, increasing the number of conjugated carbon double bonds, and eventually forming a substance composed primarily of graphitic and glassy carbon phases.

### **C. Novel energetic content of p-CO**

It has been suggested that the extended phases of low-Z molecular solids made of interconnecting strong covalent bonds are an entirely new class of materials that may exhibit novel properties including super hardness,<sup>33</sup> optical nonlinearity,<sup>34</sup> superconductivity,<sup>35</sup> and high energy density.<sup>36</sup> The present study clearly demonstrates for the first time that such novel materials can be synthesized at high pressures and recovered to ambient conditions; that is, the high energy content of p-CO, rivaling or exceeding that of HMX.

The energetic nature of p-CO is, in retrospect, not at all surprising. We note that the polymerization of carbon suboxide  $(C_3O_2)_n$  has been observed to result in explosive energy release, as has already been reported previously.<sup>37</sup> Therefore, the high energy content of p-CO, similar in many respects to  $(C_3O_2)_n$ , should not be unexpected. We speculate that the energy release process would result in



the same decomposition process that makes p-CO metastable at ambient conditions. In this regard, considering that p-CO is a polymer saturated with  $\text{CO}_2$  and a highly oxidized state of  $(C_3O_2)_n$ , one expects the energy content of p-CO to be substantially greater than that of  $(C_3O_2)_n$ . The quantitative measurement of the energy content, however, remains a challenge at the present time, again because of its metastability and environmental sensitivity. Therefore, control of the metastability appears to be the key issue in the further development of recovered p-CO as a new high explosive or energy source. The very moderate transition pressure, which is a viable for industrial production, enhances the possibility of p-CO being developed for modern technological applications.

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**Table I.** MAS  $^{13}\text{C}$  NMR of solid  $\text{p-}^{13}\text{CO}$  products versus age and in comparison with solution  $^{13}\text{C}$  NMR taken in  $\text{DMSO-d}_6$ .

Solid - new		Solid - old		in $\text{DMSO-d}_6$		Assignments
Ppm	intensity-width	ppm	intensity-width	ppm	intensity-width	
223	vs-sh	224	w-sh	202	4.7-sh	$-\text{O}-(\text{C}^*=\text{O})-$ or $>\text{C}^*=\text{O}$
189	w-br	203	s-br			$-\text{C}-(\text{C}^*=\text{O})-\text{C}-$
		194	s-br			
151	w-sh	151	vs-sh	149	w-sh	$>\text{C}^*=\text{C}<$
109	w-sh	100	s-br	103	2.9-sh	$-(\text{C}=\text{O})-\text{O}-\text{C}=\text{C}^*$
85	w-br	80	s-br	94	1.4-sh	$-\text{C}^*-\text{O}-(\text{C}=\text{O})$

vs=very strong, s=strong, w=weak, sh=sharp, br=broad

**Table II. Vibrational bands. Photo-assisted, thermally-treated, and recovered.**

8.7 GPa 25°C	Frequency (cm <sup>-1</sup> )			Spectr. Type	Vibrational Mode Assignments	Std Ref Value
	Ambient pressure					
	25 °C	100 °C	200 °C			
3815				IR	2*[C-(C=O)-O]	
3533				IR	2*[C-(C=O)-O]	
2365				IR	CO <sub>2</sub> stretch	
1900	1800			IR	C-(C=O)-O in 5-lactone ring	1750- 1800
1815				Raman	C-(C=O)-O	
	1780	1720		IR	C-(C=O)-O in 6-lactone ring	1720- 1760
	1650	1630	1640	IR	C=C in unsaturated lactone	1660- 1685
			1600	Raman	C=C	1600
1600	1400	1380	1400	IR	?	
			1360	IR	?	
	1200	1190		IR	-C-(C=O)-C- stretch	1150- 1280
1180				IR	C-O-C in lactone	
	1000	1000		IR	C-O of unconjugated linear chain anhydride	
					?	
	710	690		IR	-C=C-	<720
677				IR	CO <sub>2</sub> bending	
650				Raman	CO <sub>2</sub> bending	

## Figure captions

**FIG. 1** Raman spectrum of the black residue left at the center of a Bridgman anvil after a catastrophic failure during decompression. The inset shows the microphotographs of the Bridgman anvil and gasket remains recovered after the failure.

**FIG. 2** Micro-photograph of “dark” reaction products of CO at 5.2 GPa and its associated Raman and FT-IR spectra. The Raman spectra were recorded from two different areas at the top of the sample (appearing as faint yellow stripes), and the FT-IR spectra were taken at different pressures.

**FIG. 3** Micro-photograph of “photo” reaction products of CO at 3.6 GPa and associated Raman and FT-IR spectra. The Raman spectra were obtained from a sample at 3.6 GPa by using weak 488 nm laser light: (bottom trace) at 1.5 mW for 300 sec exposure and (top trace) at 3 mW power for 300 sec to achieve conversion. The FTIR spectra were obtained after sample exposure to weak 514 nm laser light at 4.2 GPa and after further compression to 5.0 GPa.

**FIG. 4** Micro-photographs of unreacted CO before laser-heating at 3.0 GPa and reaction products after the laser heating decreased the pressure to 2.0 GPa. The Raman spectra were taken from the transparent and opaque areas of the sample.

**FIG. 5** Micro-photographs of mg-quantity CO products, synthesized at  $\sim 6.7$  and 7.0 GPa using a modified PEC and quenched to ambient conditions, taken (a) under a microscope in reflection and (b) taken by a video camera.

**FIG. 6** (a) Magic Angle Spinning  $^{13}\text{C}$  NMR spectra of p- $^{13}\text{C}$ CO recovered from 5.6 GPa (left), a 10 day old sample (middle), and of p-CO in DMSO- $d_6$  solution (right). (b) FTIR spectra of recovered p-CO mulled in NaCl taken at different temperatures. (c) Mass



spectrum of recovered solid p-CO, showing main fragments of CO<sub>2</sub> and CO and their secondary fragment O.

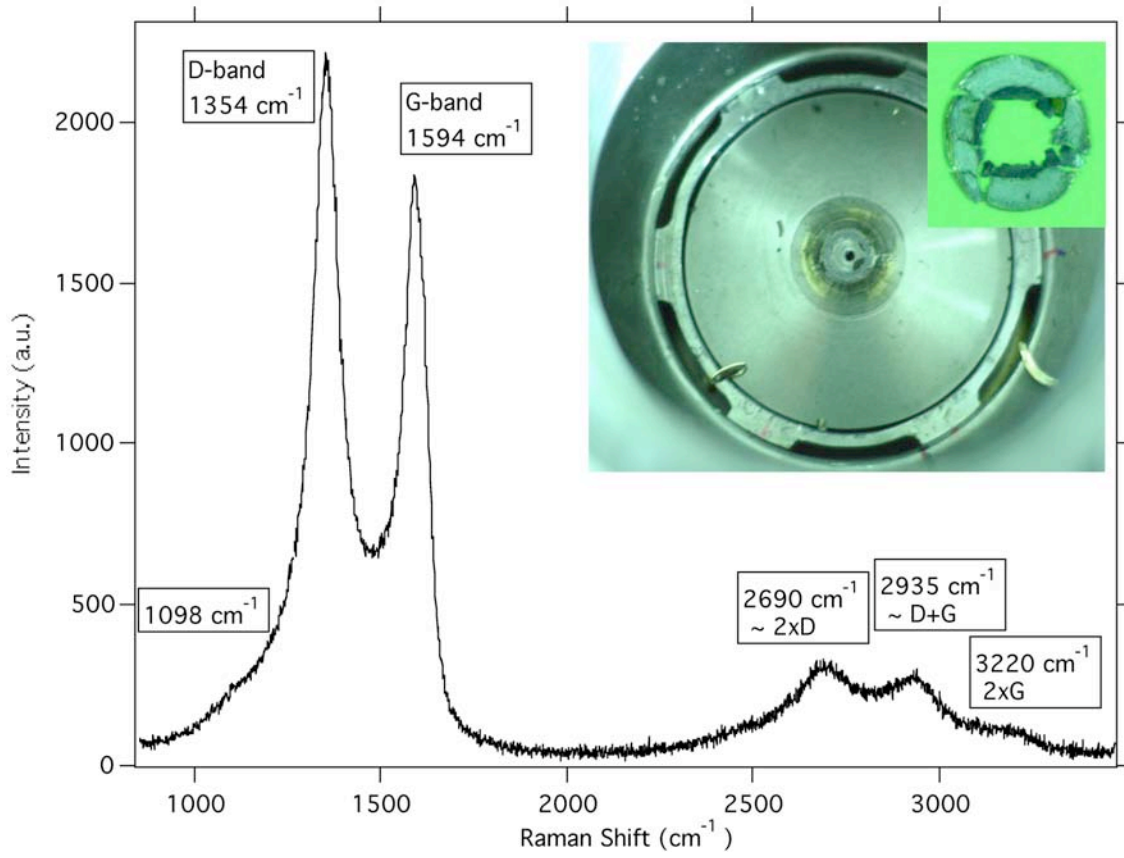
**FIG. 7** Video images of a p-CO sample initiated by a cw-YAG laser ( $\lambda=1064$  nm) with the elapsed time marked (in sec) after the start of the exposure to the laser. The He-Ne laser (visible at the top frame) was used for alignment. The explosive energy release produces a plume of CO<sub>2</sub> gas that scatters the light from both He-Ne and YAG lasers leaving vertical streaks (red initially, but most of the time white). Note that the rate of energy release is highest at around 100-300 msec after the ignition (the second frame), during which period solid particles are violently ejected from the sample. The process continues for the next half second, after which only a small piece of black glassy carbon remains in the gasket (not shown).

**FIG. 8** Raman of the residue after the explosive reaction of p-CO in Fig. 7.

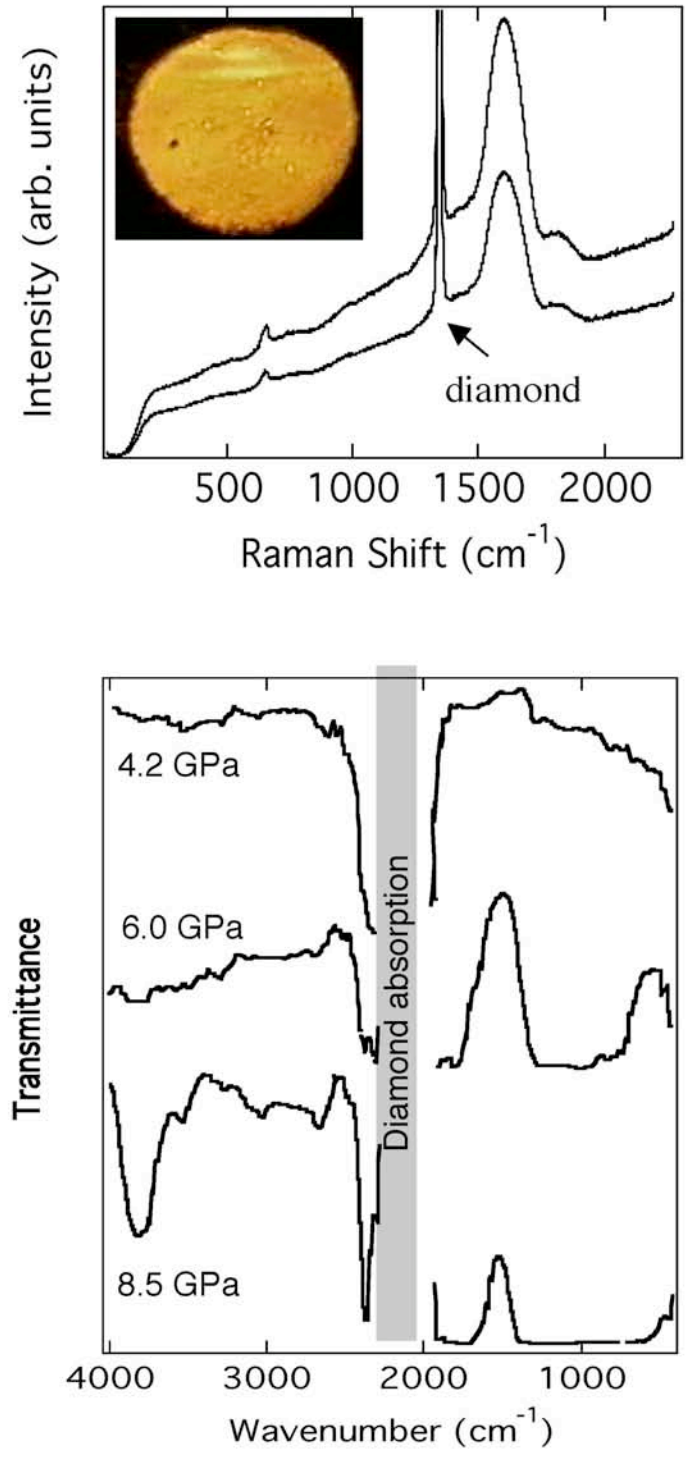
**FIG. 9** Chemical stability/ phase diagram of carbon monoxide at high pressures. Filled and open symbols represent the reacted and unreacted CO samples, respectively.

**FIG. 10** Proposed plausible structures of p-CO (showing associated CO<sub>2</sub>) and possible liberation mechanisms of CO and CO<sub>2</sub> molecules resulting in its (chemical) metastability. Left side path depicts reaction with water, liberating CO<sub>2</sub>. Right side path depicts spontaneous decomposition liberating CO<sub>2</sub>.

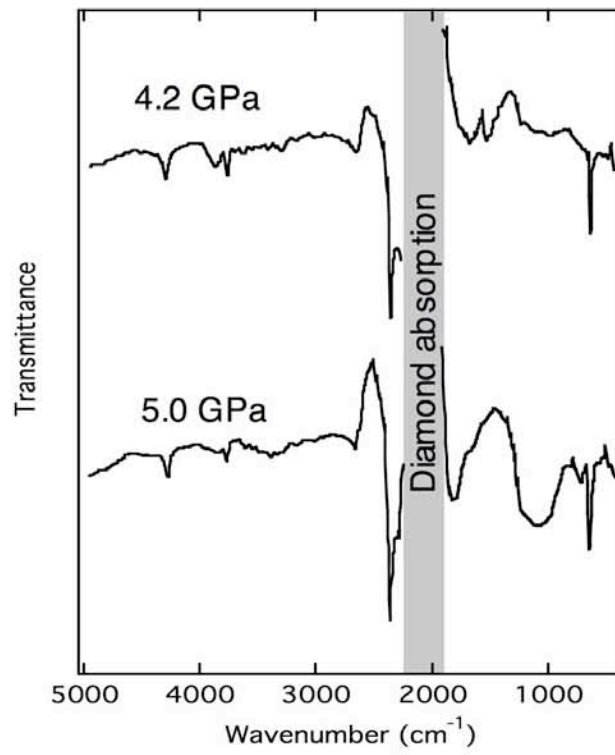
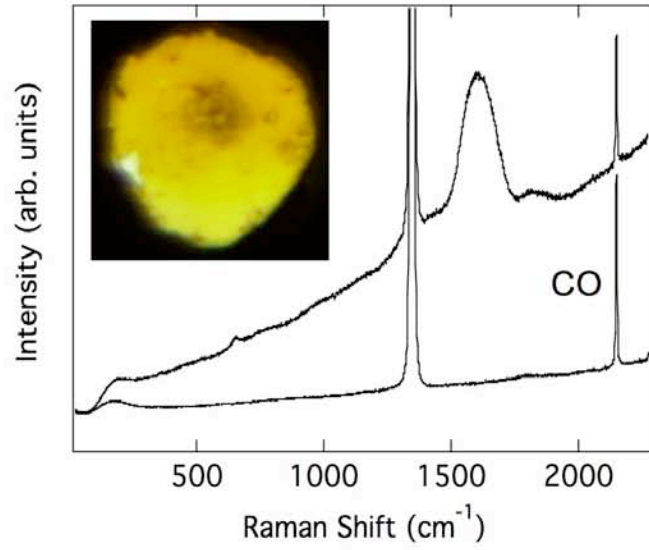
**Figure 1**



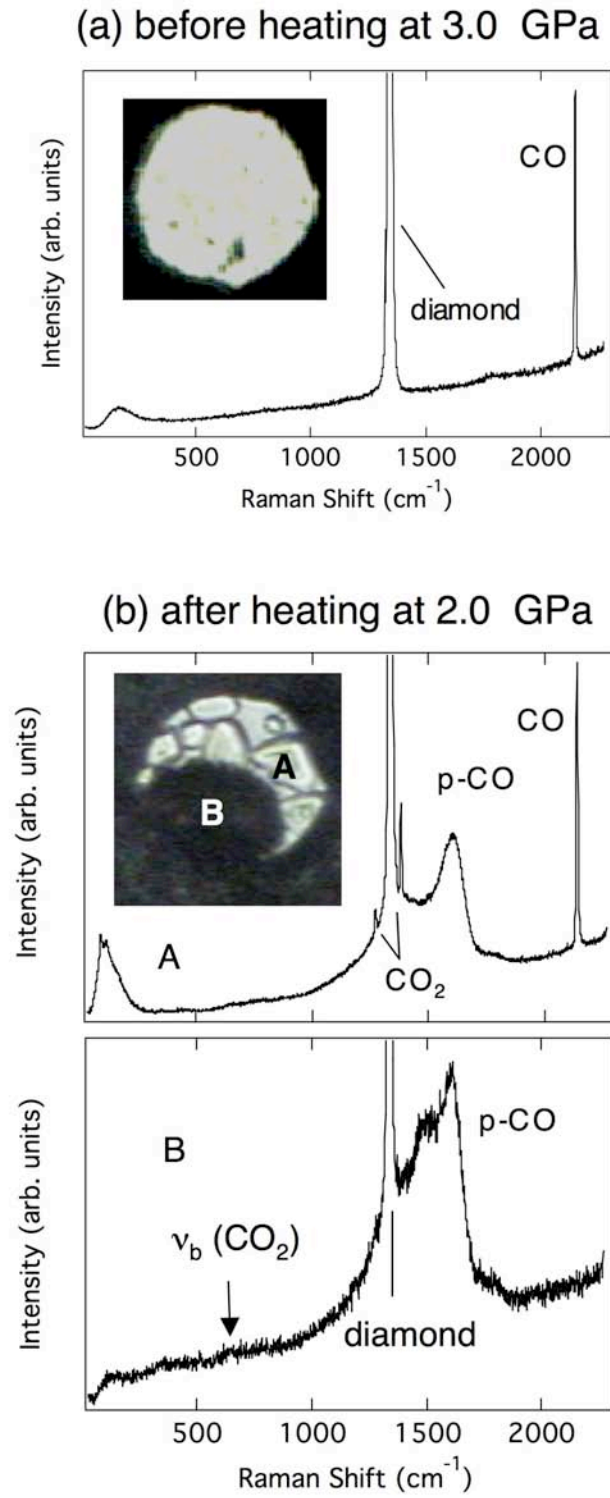
**Figure 2**



**Figure 3**



**Figure 4**



**Figure 5**

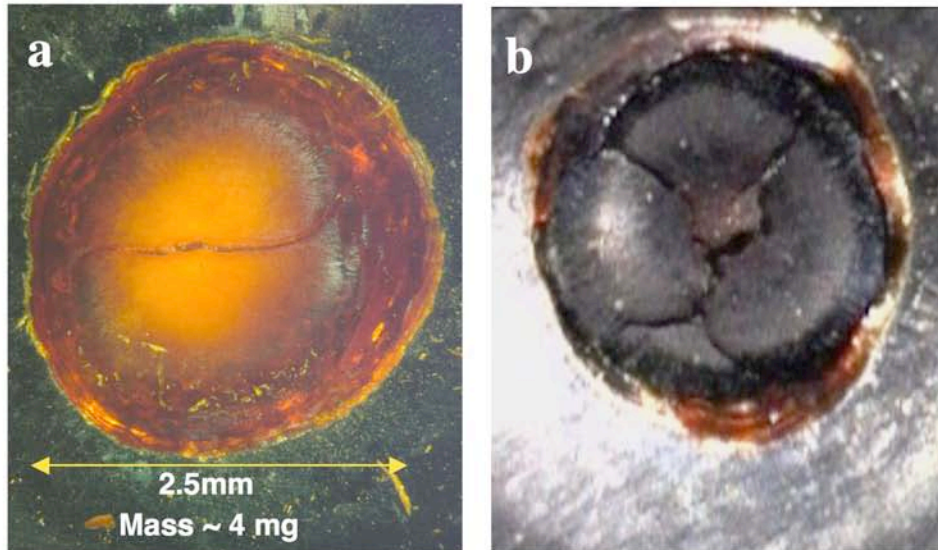
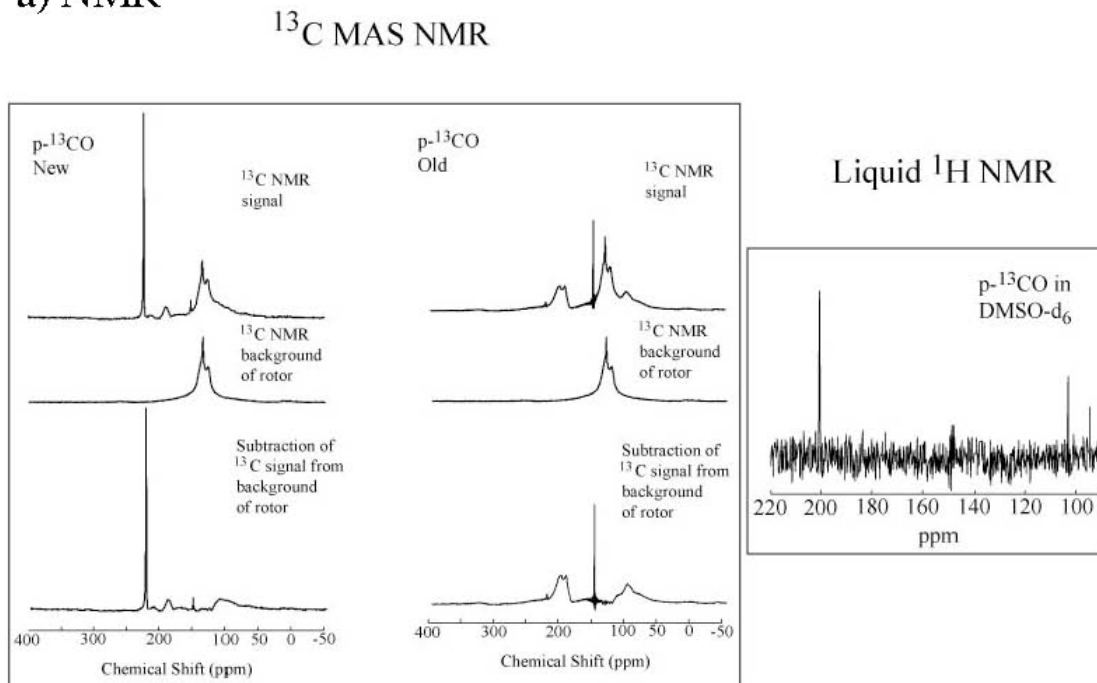
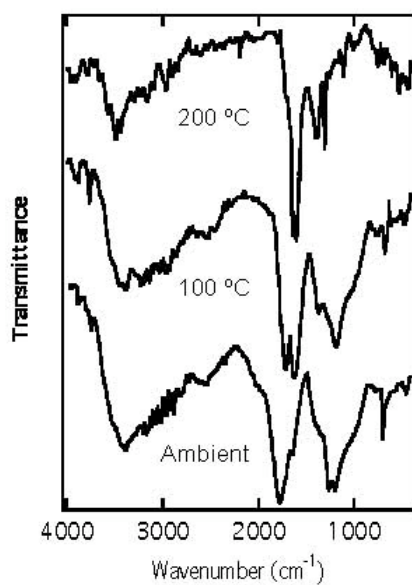


Figure 6

a) NMR



b) FT-IR



c) Mass Spec

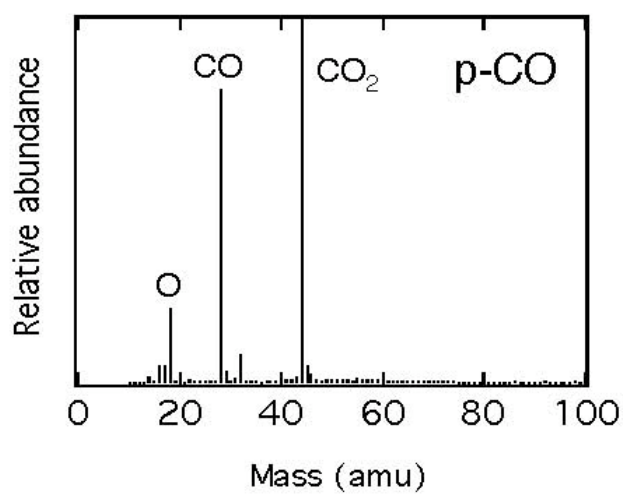


Figure 7





**Figure 8**

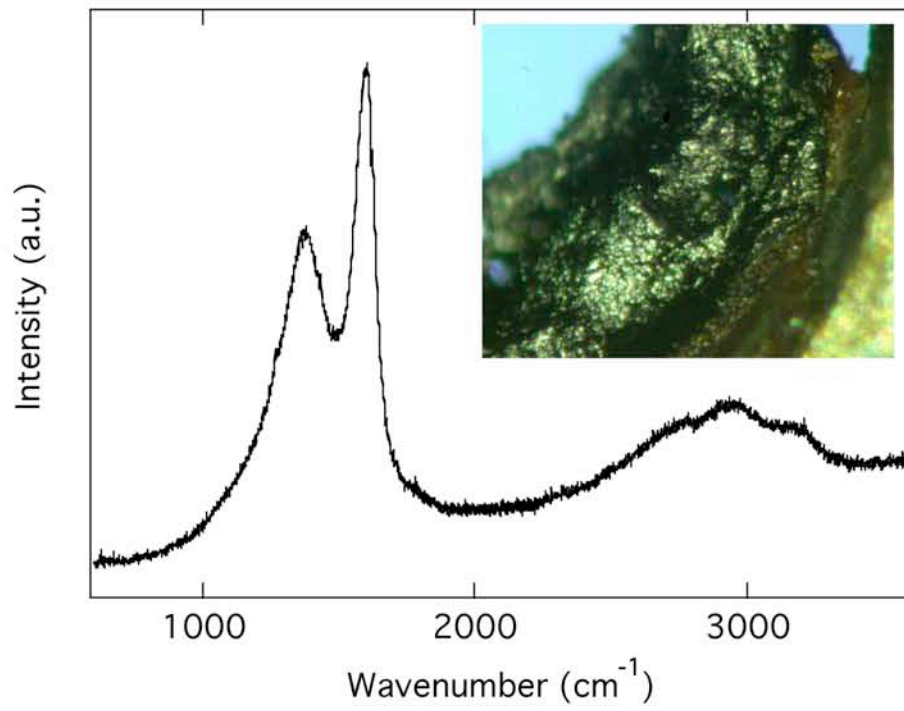


Figure 9

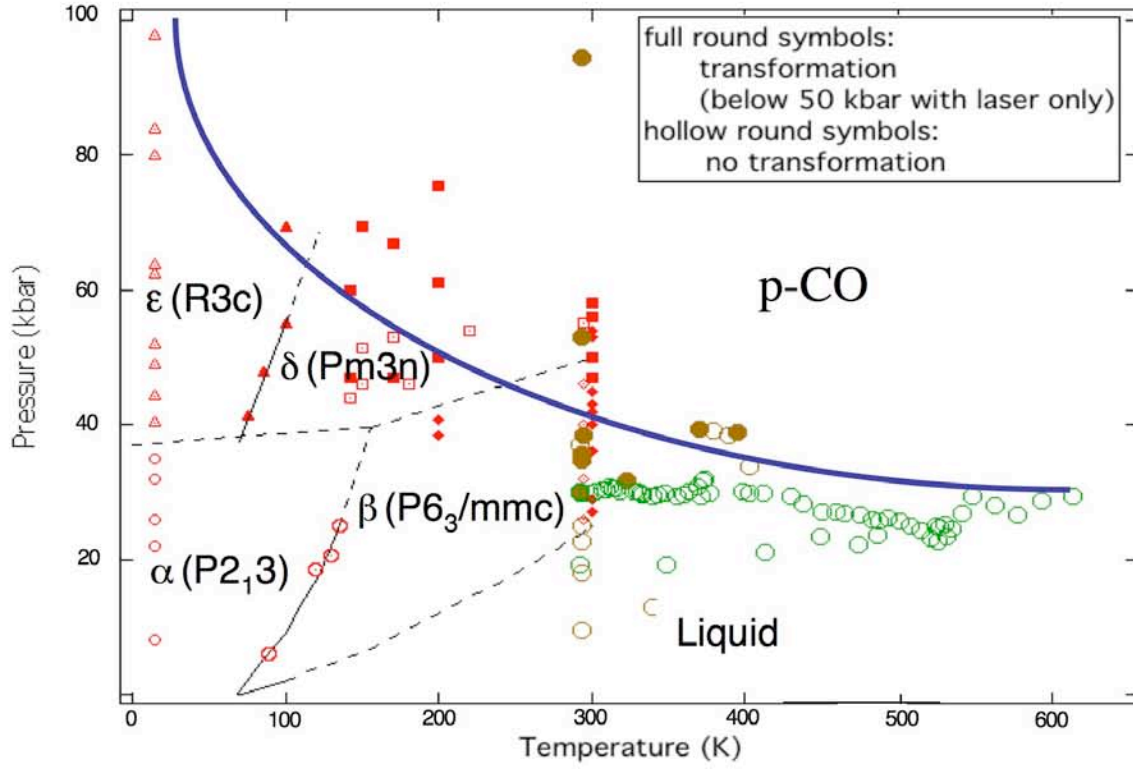
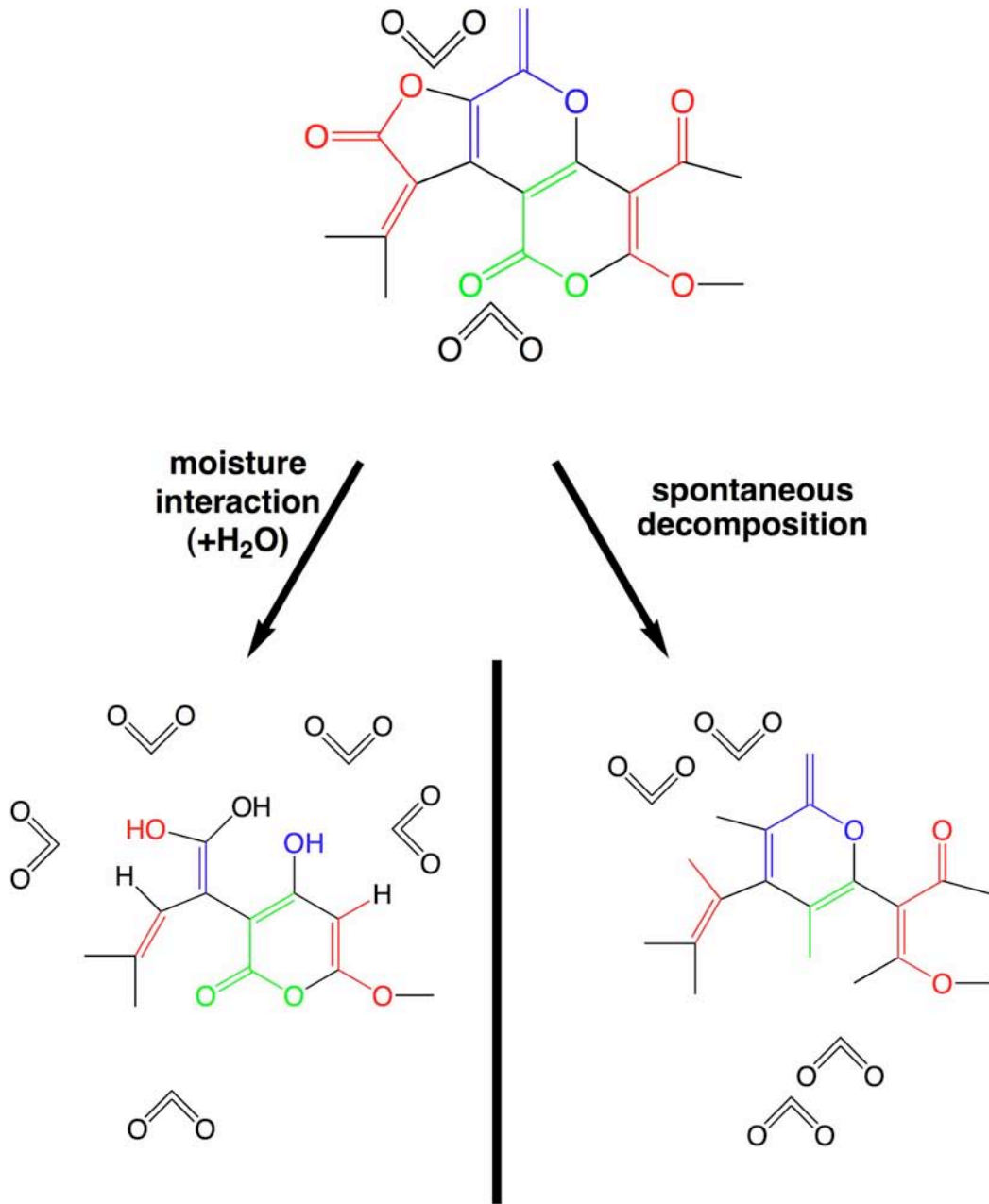


Figure 10





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