



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Extended CO Solid: A New Class of High Energy Density Material

Magnus J. Lipp, William J. Evans, Bruce J. Baer,
Choong-Shik Yoo

October 20, 2004

Nature Materials

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Extended CO Solid: A New Class of High Energy Density Material

MAGNUS J. LIPP, WILLIAM J. EVANS, BRUCE J. BAER AND CHOONG-SHIK YOO*

Lawrence Livermore National Laboratory, Livermore, California 94551

* e-mail: Yoo1@llnl.gov

Covalently bonded extended phases of molecular solids made of first- and second-row elements at high pressures are a new class of materials with advanced optical, mechanical and energetic properties. The existence of such extended solids has recently been demonstrated using diamond anvil cells in several systems, including N₂¹, CO₂² and CO³. However, the microscopic quantities produced at the formidable high-pressure/temperature conditions have limited the characterization of their predicted novel properties including high-energy content. In this paper, we present the first experimental evidence that these extended low-Z solids are indeed high energy density materials *via* milligram-scale high-pressure synthesis, recovery and characterization of polymeric CO (p-CO). Our spectroscopic data reveal that p-CO is a random polymer made of lactonic entities and conjugated C=C with an energy content rivaling or exceeding that of HMX. Solid p-CO explosively decomposes to CO₂ and glassy carbon and thus might be used as an advanced energetic material.

The application of high-pressure often transforms the configuration of a molecular solid into a crystal structure with more itinerant electrons since the kinetic energy of the electrons dominates the total (potential + kinetic) energy at high pressures. As a result, the intermolecular potential becomes highly repulsive and molecular solids with electrons localized within intramolecular bonds become unstable. Examples of this behavior are the

insulator-to-metal transition resulting from pressure-induced electron delocalization, and the molecular-to-non-molecular phase transition, which has recently been discovered in nitrogen¹, carbon dioxide² and carbon monoxide³. On the other hand, competing with the pressure-induced electron delocalization, molecular solids can also soften their repulsive potential by either ionization or charge transfer especially at high temperatures and moderate high pressures. Examples of this pressure-induced ionization (or charge transfer) include the formation of novel ionic dimers of CO₂ (CO²⁺CO₃²⁻)⁴ and N₂O (NO⁺NO₃⁻).^{5,6}

These types of extended solids, particularly when generated from low-*Z* elements, constitute an entirely new class of materials that may exhibit novel properties including super hardness,⁷ optical nonlinearity,² superconductivity,⁸ and high energy density.^{9,10} For example, previous theoretical calculations⁹ have predicted that nitrogen should transform into polymeric nitrogen at high pressures, with dramatically large energy densities (E/V) of about 3 times that of HMX. Furthermore, the formation/decomposition pathways are typically hindered by large activation energy barriers. Thus, there is a strong possibility that one can metastably recover these novel compounds to ambient conditions. Recent diamond anvil cell (DAC) studies have indeed shown that molecular nitrogen transforms to nonmolecular *cubic gauche*-N above 110 GPa and 2000 K.¹ Previously, the most extended form of nitrogen was that of N₅⁺ in the N₅⁺AsF₆⁻ compound recently synthesized.^{11,12} Unfortunately, attempts to recover the polymeric nitrogen at ambient conditions have been unsuccessful to date, and its properties are largely unknown including the predicted high energy content. The experimental constraints of DAC experiments (typical sample chamber dimensions of less than 100 μm) dictate that the sample quantity could not be more than several nanoliters or a few micrograms. While sufficient for X-ray and optical spectroscopies, this is insufficient for most conventional analytical techniques, which generally require at least mg quantities. This limitation of DAC samples excludes crucial diagnostics such as chemical analysis, mass spectroscopy, and calorimetry, which could definitively confirm the exceptional high energetic content prediction.

In this report, we demonstrate that these low- Z extended solids are indeed good candidates for high energy density materials *via* synthesis of macroscopic quantities of extended carbon monoxide solid and characterization of its structure and energetic behavior. Carbon monoxide (CO) has been chosen for several reasons: It is isoelectronic to nitrogen, exhibiting similar crystal structures, phase diagram¹³ and transformations to nonmolecular phases^{1,3,14}. In addition, the molecular bond in CO (as in N₂) is the strongest bond of any diatomic heteronuclear molecule (N₂, homonuclear), making it a good candidate for storing large amounts of energy. However, CO transforms into a noncrystalline “polymeric” CO material (denoted as p-CO) at 5 GPa and 300K, which can be recovered to ambient conditions. Therefore, in comparison to polymeric nitrogen, synthesis of p-CO requires less demanding pressure/temperature conditions, enhancing the possibility of production of larger quantities and technological applications.

Despite the relatively modest synthesis conditions, the properties of p-CO remain largely unknown, owing to the microscopic amount of sample generated in DAC experiments. To remedy this situation, we have synthesized mg-quantities of p-CO at high pressures using a large volume press system, specifically a modified Paris-Edinburgh cell (mPEC).^{15,16} High purity CO (99.99+%) was loaded into the mPEC sample chamber in the liquid phase at ~ 10 bar and liquid nitrogen temperature. After capturing the CO sample, the system was warmed up to room temperature, and then the load was increased to the final desired pressure for synthesis. For a successful recovery we found that it was 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 catastrophic failure. It has been recognized in the past that the decompression phase of the experiment is the potentially most destructive step.¹⁷

Figure 1 shows typical p-CO samples synthesized at 7.1 and 5.6 GPa and recovered to ambient conditions, in comparison to a microscopic sample in a DAC at 5.0 GPa. Recovered p-CO shows a great variation in appearance and properties. It was found to be very hygroscopic and photosensitive; its color ranged from yellow to brownish-orange as recovered, but gradually darkened with time and exposure to light. Simple

mass and volume measurements yielded density values as high as 1.65 g/cm^3 , more than twice the value for liquid CO. This value, however, should be considered a lower bound because the sample does not completely fill the gasket hole (see Fig. 1) after recovery due to the different elastic properties of sample and gasket material. The texture of p-CO became gluey when exposed to air for several days. Because of its extremely high photosensitivity, it was not possible to obtain the Raman spectrum of recovered p-CO using visible or IR laser radiation without damaging and degrading the material. Yet, it was possible to obtain the Raman spectrum of p-CO products at high pressures in a DAC. This difference is probably a result of the DAC confining the sample and very efficiently heat-sinking it. The spectrum shows three characteristic bands at 650, 1600 and 1850 cm^{-1} . The latter two are apparently from the symmetric stretching of C=C and C=O bonds, respectively. The interesting vibrational band at 650 cm^{-1} corresponds, on the other hand, to the bending mode ν_b (O=C=O) of CO_2 molecules that are either disproportionated from CO or captured (physisorbed/chemisorbed) in a matrix of p-CO, or both. The latter explanation may be viewed as p-CO supersaturated with CO_2 , consistent with an apparent high conversion of CO to solid p-CO, up to 95 %, observed in the present recovery experiments.

The recovered p-CO was also found to be metastable, slowly releasing gaseous CO_2 after recovery at ambient conditions. 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. This metastability of p-CO made its detailed analysis challenging. For example, our Differential Scanning Calorimetry (DSC) results show a rather large sample-to-sample variation in the measured energy release, 1-8 KJ/g, and location of the exotherm, 100-450 °C. We interpret these variations to be caused by samples with differences in the extent of the time-dependent degradation. However, these values are sufficient to confirm that p-CO is indeed a high energy density material. For example, the DSC measures only thermal energy release. The total energy content is the sum of the thermal and mechanical (PAV) work. Typical high explosives such as TATB, RDX and HMX have thermal energy contents of 1-3 kJ/g, similar to p-CO.¹⁸

Recovered p-CO is explosive, further supporting the claim of high energy content. The sequence of images obtained following Nd:YAG laser initiation (Fig. 2) clearly demonstrates that p-CO behaves explosively when triggered appropriately. p-CO can readily be ignited even at a relatively weak laser power (<100 mW of Nd:YAG at $\lambda = 1064$ nm) and form a self-propagating burn front. For comparison, at similar laser power we found no effect on conventional energetic materials including PETN, NaN_3 , and TATB. This is of course a function of the coupling between the laser wavelength and the material, but it establishes that we are not simply observing combustion with the laser providing the thermal energy for burning. Based on the intense incandescent emission in Fig. 2, the temperature was estimated to be well above 2500 K. The energetic decomposition of p-CO produces a large quantity of gaseous products, determined by mass spectroscopy of the product gases to be primarily CO_2 . The final residue after the explosion was characterized by Raman spectroscopy and determined to be glassy carbon¹⁹ exhibiting strong bands at 1350, 1600 and their overtones at 2700 cm^{-1} . The strong presence of the characteristic D-band at 1350 cm^{-1} and its overtone at 2700 cm^{-1} indicate a substantial amount of sp^3 and sp disorder in sp^2 carbon species, similar to those produced after strong shock compression of hydrocarbons.²⁰

Determining the structure of p-CO is especially challenging because of the lack of long-range order resulting from a random polymer network. Nevertheless, with a mg-quantity of p-CO recovered it was possible to determine elements of the chemical structure using solid-state Magic Angle Spinning (MAS) ^{13}C -NMR, FT-IR and Mass Spectrometry (MS). These spectroscopic results show that p-CO is made of lactone-like carbonyls and conjugated $\text{C}=\text{C}$ bonds in chemical configurations that can easily liberate CO_2 and convert to oxygen deficient graphitic $\text{C}=\text{C}$ layers. This liberation of CO_2 is also consistent with our observations of the metastability. The MAS- ^{13}C -NMR spectra (Fig. 3a), for example, show two very sharp features at 223 and 151 ppm, characteristic of carbon atoms in ester- or lactone-like carbonyl groups, $-\text{O}-(\text{C}=\text{O})-$, and $>\text{C}=\text{C}<$ double bonds, respectively.²¹ After several days, the intensity of the 223 peak substantially reduces, while that of the 151 peak enhances. Two broad features at ~ 189 and 109 ppm are probably from carbon atoms attached to the ester bridge of the $-\text{O}-(\text{C}=\text{O})-$ group and

single-bonded carbon atoms attached to an oxygen bridge or just singly bonded carbons, both of which enhance and develop side bands with time.

The presence of lactone rings (containing -C-O-(C=O)-C-), is also evident in the FT-IR spectra of p-CO (Fig. 3b). Three dominant overlapping features centered at 1776 cm^{-1} indicate the presence of carbonyl (C=O) and (C=C) groups (sideband at 1645 cm^{-1}). The bands at 1199 and 1266 cm^{-1} can be assigned to the stretching motion of -C-(C=O)-C- and -C-(C=O)-O- groups, respectively.²¹ Upon heating the sample to $200\text{ }^\circ\text{C}$, the bands at 1200 cm^{-1} have nearly disappeared while the 1645 cm^{-1} band due to C=C bonds remains, again an indication for the conversion of -C-(C=O)-O- to C=C by liberating CO_2 . A broad band at $\sim 3400\text{ cm}^{-1}$ possibly represents the asymmetric stretch of -OH or more likely the second harmonic or combinational bands of the C=O and C=C stretching modes. However, we can rule out -OH since similar broad bands are observed for *in-situ* CO products in the DAC, where the samples remain pristine without any contamination of H_2O , and recovered p-CO exhibits this band even at high temperatures of $200\text{ }^\circ\text{C}$.

The mass spectrum (MS) of p-CO (Fig. 3c) exhibits three main fragments: 44 amu for CO_2 , 28 amu for CO and 16 amu for O, the secondary fragments of CO_2 and CO. After the MS run, we found a black residue, left on the probe which is probably graphitic carbon or simply carbon “soot”. It is worth mentioning that the mass spectrum of polymeric C_3O_2 also yields CO_2 and CO without any parent molecule, C_3O_2 .²²

Although pressure-induced disproportionation of CO is a plausible mechanism to yield CO_2 and C_3O_2 , it is not apparent when the material actually disproportionates, *i.e.*, prior to or after the polymerization. Clearly, the former yields stoichiometrically balanced products of CO_2 and $(\text{C}_3\text{O}_2)_p$ while the latter is unconstrained. The present results suggest the latter case, leading to more irregular and disturbed structures than $(\text{C}_3\text{O}_2)_p$ and a lesser amount of CO_2 . For example, the structure of p-CO is similar to that of $(\text{C}_3\text{O}_2)_p$: (i) the strong presence of -C-(C=O)-O- and possibly C=C-C species (ii) a chemical configuration that can easily liberate CO_2 , (iii) a hygroscopic nature that can easily produce C-H and O-H bonds, and (iv) mass spectrometric fragments of CO_2 and CO consistent with those of C_3O_2 . However, there are also important differences between p-CO and $(\text{C}_3\text{O}_2)_p$: (i) Several IR bands are missing in p-CO, including the strong

fundamental bands near 806, 1365 and 1511 cm^{-1} that are observed in $(\text{C}_3\text{O}_2)_p$ whereas the broad feature at $\sim 3400 \text{ cm}^{-1}$ observed in p-CO is missing in $(\text{C}_3\text{O}_2)_p$, (ii) the estimated yield of p-CO, $\sim 95\%$ is substantially higher than that expected from the formation of $(\text{C}_3\text{O}_2)_p$, suggesting that a smaller amount of CO_2 was being produced. Therefore, p-CO may be considered as highly perturbed $(\text{C}_3\text{O}_2)_p$ “supersaturated” with CO_2 at high pressures, which make it highly metastable upon pressure release. Recent *ab initio* molecular dynamics calculations²³, however, suggest an entirely different transformation, neither disproportionation (CO_2 and $(\text{C}_3\text{O}_2)_p$) nor total polymerization. Despite this difference, the suggested final structure, a partially interconnected poly-carbonyl polymer with fivefold lactone-like units, exhibits characteristics similar to those measured in the present study.

In summary, we presented the first experimental evidence that an extended solid derived from low-Z elements, p-CO, is a high energy density material. It is synthesized from CO above 5 GPa at ambient temperature. The chemical structure of p-CO contains doubly and singly bonded carbon atoms and segments of $-\text{C}-(\text{C}=\text{O})-\text{O}-$ and $-\text{C}-(\text{C}=\text{O})-\text{C}$, resembling that of poly-carbon suboxide but with severe modifications to smaller 5- or 6-membered rings of lactonic nature. The p-CO solid exothermically decomposes to CO_2 and glassy carbon and, thus, could be used as an advanced energetic material. The high metastability of p-CO, however, may pose some challenges towards technological applications. Nevertheless, it is important to note that the metastability of p-CO is mainly due to structural sensitivity which can be modified by various physical and chemical means such as chemical passivation and/or doping with metallic impurities. Furthermore, p-CO could be synthesized in carbon foam to reduce its sensitivity, similarly to the way how highly sensitive TNT was developed into dynamite.

References

1. Eremets, M.I., Gavriluk, A.G., Trojan, I.A., Dzivenko, D.A., & Boehler, R. Single bonded cubic form of nitrogen. *Nature Mater.* **3**, 558-563 (2004).
2. Iota, V., Yoo, C.S. & Cynn, H. Quartz-like carbon dioxide: an optically nonlinear extended solid at high pressures and temperatures. *Science* **283**, 1510-1513 (1999).
3. Katz, A.I., Schiferl, D. & Mills, R.L. New phases and chemical reactions in solid CO under pressure. *J. Phys. Chem.* **88**, 3176-3179 (1984).
4. Yoo, C.S. in *Science & Technology of High Pressure* (ed. by M.H. Manghnani, W.J. Nellis, and M. Nicol) 86-89 (University Press, AIRAPT, India, 2000).
5. Iota, V., Park, J-H. & Yoo, C.S. Phase diagram of nitrous oxide: analogy with carbon dioxide. *Phys. Rev. B* **69**, 64106-64112 (2004).
6. Somayazulu, M., Madduri, A., Goncharov, A.F., Tschauer, O., McMillan, P.F., Mao, H-K. & Hemley, R.J. Novel broken symmetry phase from N₂O at high pressures and temperatures. *Phys. Rev. Lett.* **87**, 135504-135507 (2001).
7. Yoo, C.S., Cynn, H., Gygi, F., Galli, G., Iota, V., Nicol, M., Carlson, S., Häusermann, D. & Mailhot, C. Crystal structure of carbon dioxide at high pressure: "Superhard" polymeric carbon dioxide. *Phys. Rev. Lett.* **83**, 5527-5530 (1999).
8. Ashcroft, N.W. Hydrogen dominant metallic alloys: High temperature superconductors?. *Phys. Rev. Lett.* **92**, 187002-187005 (2004).
9. Mailhot, C., Yang, L.H. & McMahan, A. Polymeric nitrogen. *Phys. Rev. B* **46**, 14419-14435 (1992).
10. Barbee, III., T.W., McMahan, A.K., Klepeis, J.E. & van Schilfgaarde, M. High-pressure boron hydride phases. *Phys. Rev. B* **56**, 5148-5155 (1997).
11. Christe, K.O., Wilson, W.W., Sheehy, J.A. & Boatz, J.A. N₅⁺: A novel homolepic polynitrogen ion as a high energy density material. *Angew. Chem. Int. Ed. Engl.* **38**, 2002-2009 (1999).

12. Knapp, C. & Passmore, J. On the way to "Solid Nitrogen" at normal temperature and pressure? Binary azides of heavier group 15 and 16 elements. *Angew. Chem. Int. Ed. Engl.* **43**, 4834-4836 (2004).
13. Mills, R.L., Olinger, B. & Cromer, D.T. Structures and phase diagrams of N₂ and CO to 13 GPa by x-ray diffraction. *J. Chem. Phys.* **84**, 2837-2845 (1986).
14. M.I. Eremets, R.J.Hemley, H-K. Mao & E. Gregoryanz. Semiconducting non-molecular nitrogen up to 240 GPa and its low-pressure stability. *Nature* **411**, 170-174 (2001).
15. Besson, J.M., Nelmes, R.J., Hamel, G., Loveday, J.S., Weill, G. & Hull, S. Neutron powder diffraction above 10 GPa. *Physica B* **180&181**, 907-910 (1992).
16. Klotz, S., Gauthier, M., Besson, J.M., Hamel, G., Nelmes, R.J., Loveday, J.S., Wilson, R.M. & Marshall, W.G. Techniques for neutron diffraction on solidified gases to 10 GPa and above: applications to ND₃ phase IV. *Appl. Phys. Lett.* **67**, 1188-1190 (1995).
17. F.P. Bundy. Ultra-high pressure apparatus. *Phys. Rep.* **167**, 133-176 (1988).
18. Dobratz, B.M. *LLNL Explosive Handbook: Properties of Chemical Explosives and Explosive Simulants*. UCRL-52977, NTIS (1985).
19. Knight, D.S. & White, W.B. Characterization of diamond films by Raman spectroscopy. *J. Mater. Res.* **4**, 385-393 (1989).
20. Yoo, C.S. & Nellis, W.J. Phase transformations in carbon fullerenes at high shock pressures. *Science* **254**, 1489-1491 (1991).
21. Silverstein, R. & Webster, F. *Spectrometric Identification of Organic Compounds*, 6th ed., chs. 3 and 5 (John Wiley & Sons, New York , 1997).
22. Yang, N.L., Snow, A. & Haubensstock, H. Poly(carbon suboxide): a photosensitive paramagnetic ladder polymer. *J. Polym. Sci.* **16**. 1909-1927 (1978).
23. Bernard, S., Chiarotti, G.L., Scandolo, S., & Tosatti, E. Decomposition and polymerization of solid carbon monoxide under pressure. *Phys. Rev. Lett.* **81**, 2092-2095 (1998).

Acknowledgments

We thank Dr. Julie Herberg for running the MAS-NMR experiment and Ken Visbeck for help with the large volume press. Work performed at Lawrence Livermore National Laboratory under the auspices of the U.S. Department of Energy under contract number W-7405-Eng-48.

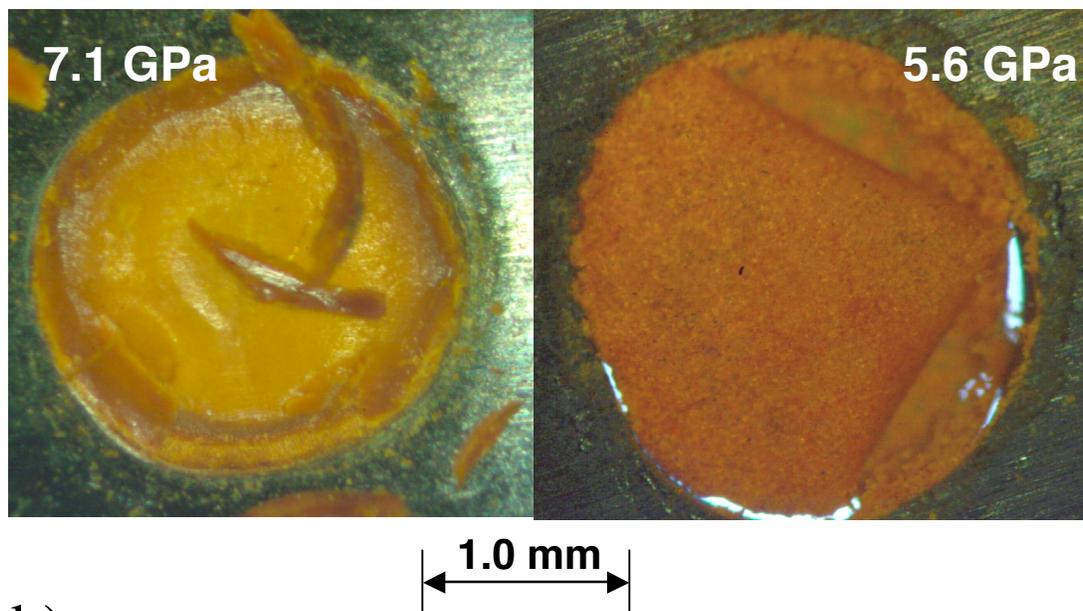
Correspondence and requests for materials should be addressed to C.S.Y. (yoo1@llnl.gov).

Fig. 1 Micro-photographs of CO products: (a) Milligram quantities of p-CO products, synthesized at ~ 7.1 GPa (left) and 5.6 GPa (right), using a modified PEC and quenched to ambient conditions. (b) Polymerized CO product in a DAC at 5 GPa and its Raman spectrum showing the $\nu_b(\text{O}=\text{C}=\text{O})$ of CO_2 molecules presented together with p-CO. Up to 1.65 g/cm^3 were measured for the density of recovered p-CO. This value should be considered a lower bound.

Fig. 2: Video images of a p-CO sample initiated by a cw-YAG laser ($\lambda=1064 \text{ nm}$), each frame separated by 33 msec. The He-Ne laser (visible from the second frame on) was used for alignment. The explosive energy release produces a fume of CO_2 gas that scatters the light from a He-Ne laser 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. 3: Spectral analysis of the recovered p-CO reveals that it is a random polymer made of lactonic entities and conjugated $\text{C}=\text{C}$ bonds: (a) Magic Angle Spinning ^{13}C NMR spectra of p- ^{13}C CO recovered from 5.6 GPa (left) and 10 days later (right). (b) FTIR spectra of recovered “fresh” p-CO in KBr taken at room temperature. (c) Mass spectrum of recovered solid p-CO, showing main fragments of CO_2 and CO and their secondary fragment O.

a).



b).

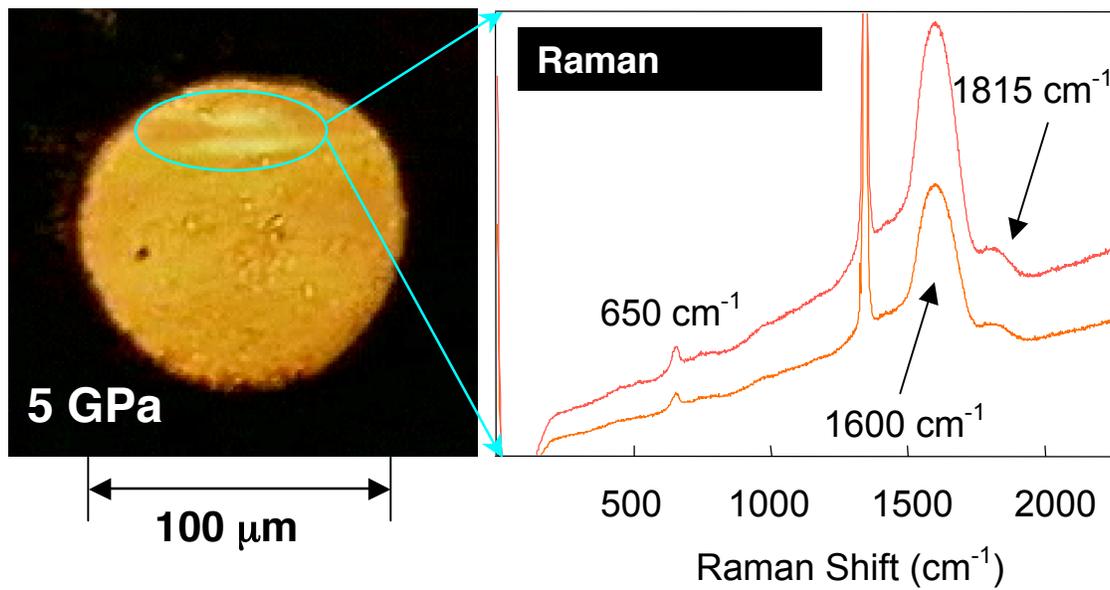


Fig. 1

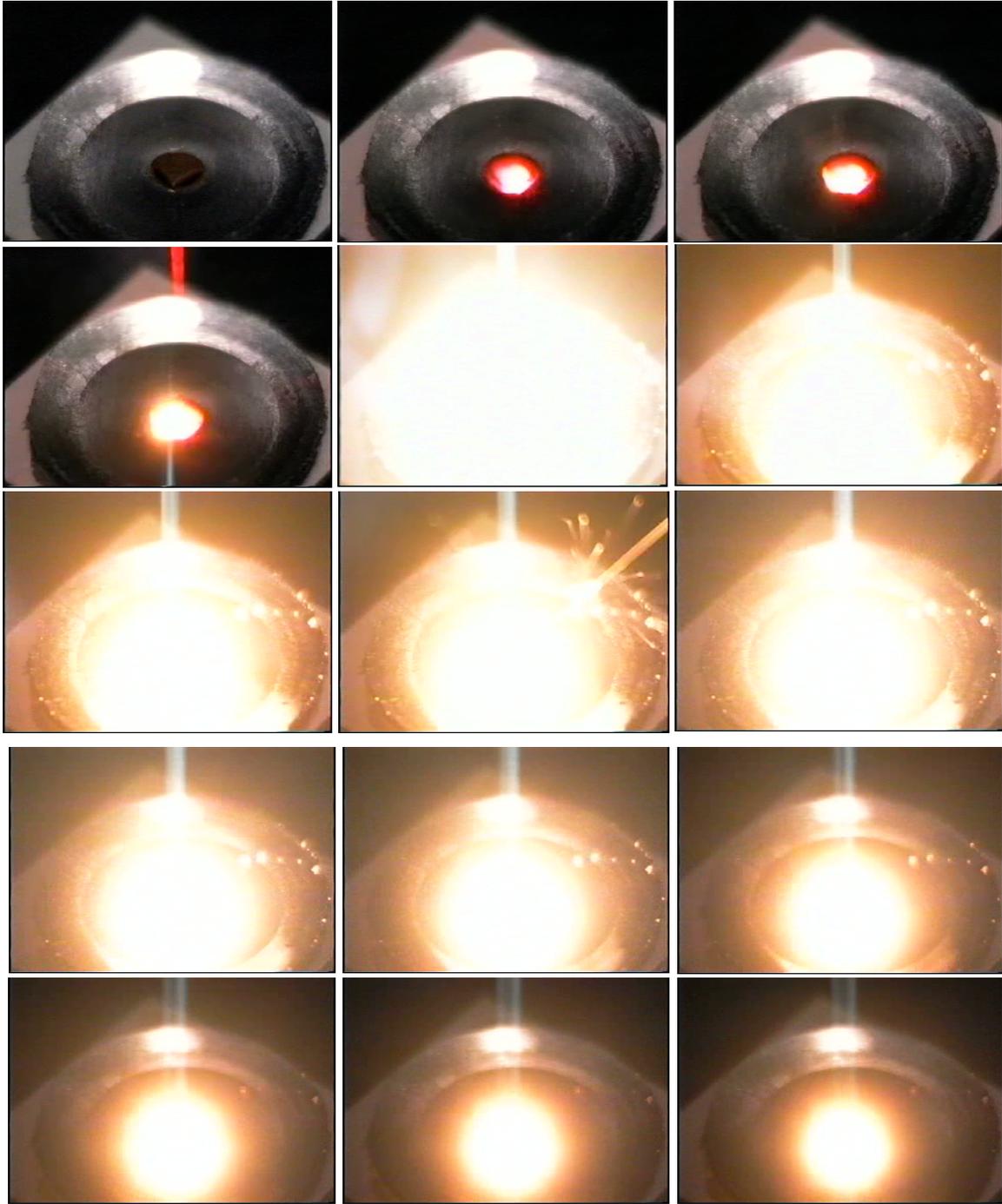
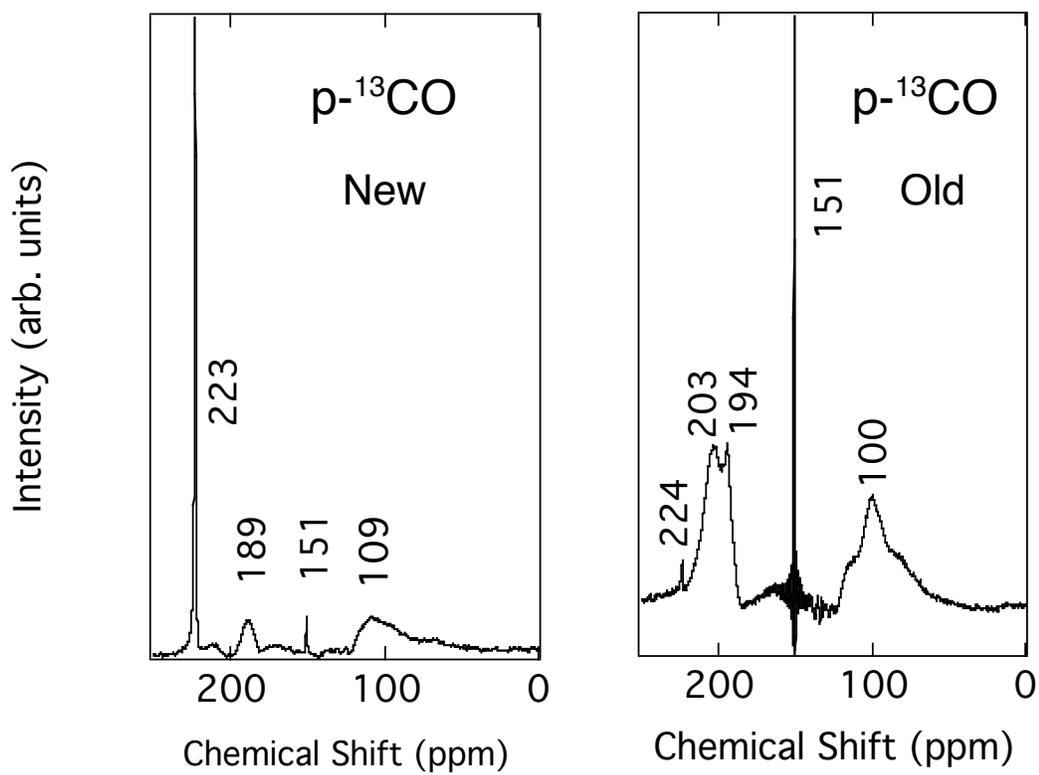
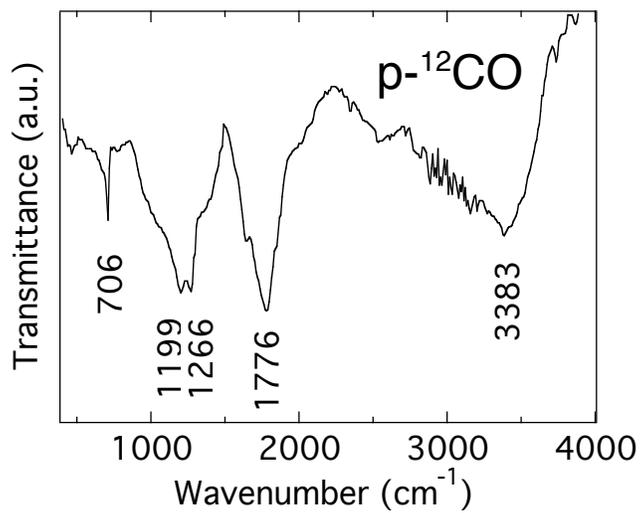


Fig. 2

a) MAS-¹³C NMR



b) FT-IR



c) Mass Spec

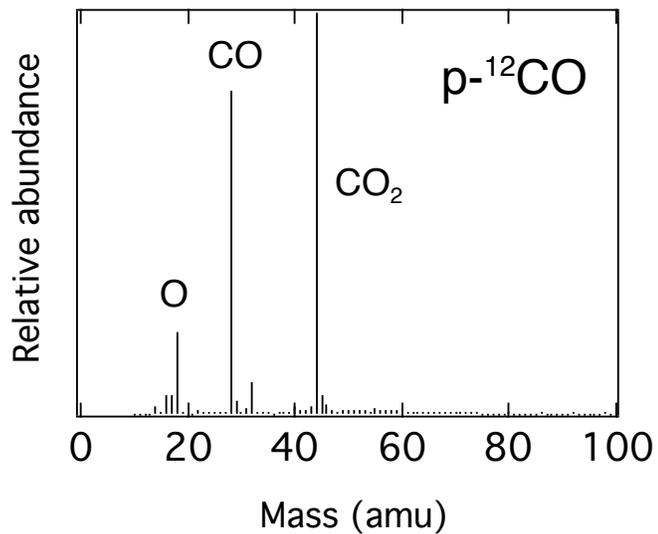


Fig. 3