

Physical and chemical transformations of iron pentacarbonyl under pressure*

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Abstract: We have studied the physical and chemical transformations of iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) in externally-heated diamond anvil cells using *in-situ* confocal micro-Raman spectroscopy. Raman spectroscopy of $\text{Fe}(\text{CO})_5$ were used to identify three different solid polymorphs and a polymeric solid found at high pressures, yielding the phase/chemical transformation diagram to 20 GPa. The pressure-induced Raman spectral changes suggest that liquid $\text{Fe}(\text{CO})_5$ undergoes several phase transformations at room temperature to phase I at 0.3 GPa, phase II at 1.5 GPa, and phase III at 4.9 GPa that polymerizes above 15.2 GPa.

1. Introduction

Over the past decade, new materials and novel phenomena have been discovered and predicted at high pressures and temperatures. Many of these phenomena are fundamental chemistry problems, reflecting how chemical bonds break and form, how atoms and molecules organize over short- and long-ranges, and how kinetics and thermodynamics govern material stability. It is common to observe the transformation of molecular solids into more compact structures with itinerant electrons (such as metallic and nonmetallic extended phases). Such non-molecular extended solids, particularly those composed of low-Z molecules, constitute a new class of high-energy-density solids. These new solids store a large amount of chemical bond energy in their three-dimensional network structure (~ several eV/bond). The large cohesive energy of singly bonded or sp^3 hybridized electrons gives rise to an extremely stiff lattice and novel electronic and optical properties [1,2]. Importantly, nonmolecular solids with monolithic network structures, held together by strong covalent bonds, have high kinetic barriers against reversal, offering opportunities to recover these novel materials at ambient conditions [3].

Examples of the pressure-induced molecular to non-molecular phase transformations are ubiquitous including nitrogen and carbon monoxide, which represent two of the strongest chemical bonds. This highlights the instability of unsaturated chemical bonds at high pressures. Carbon monoxide, for example, forms polymeric CO (p-CO) above 5 GPa [4], which can be recovered at ambient conditions. While containing high-energy density, the recovered p-CO is metastable and slowly decomposes in air,

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posing challenges for further material development and application. Presumably, the instability of p-CO is structural, arising from incomplete nature of chemical bonds especially on the surfaces and interfaces. Therefore, it is hoped that the presence of transition metal may stabilize a polymeric CO at ambient conditions when they are coordinated to central metals.

In this study, we have chosen an organometallic compound – $\text{Fe}(\text{CO})_5$ – to make iron-doped polymeric CO at high pressures. This is because the relatively weak metal (Fe)-ligand (CO) bond can thermally or photochemically decompose to metallic Fe ions (or even stable Fe radicals) and unsaturated ligands, the CO molecules. These ligand molecules of CO, on the other hand, can easily polymerize by themselves into network structures at moderate pressure (1-10 GPa); yet, the metal species can serve as catalysts for the reaction as well as stabilizers for the product. This can result in a homogeneous distribution of metals in low-Z extended solids. Such incorporation of metal species on an atomistic scale differs from conventional reactive metal-polymer mixtures, in its monolithic structure without grain boundaries, interfaces, and metal oxide layers – offering an opportunity to develop novel atomistic composites of Fe and p-CO. Furthermore, $\text{Fe}(\text{CO})_5$ is an important organometallic compound, which has been studied [5-9] extensively at ambient pressure, but not at high pressures. Therefore, our efforts have been focused on investigating the pressure-induced phase and chemical transformations as described in this paper.

2. Experimental Method

Liquid $\text{Fe}(\text{CO})_5$ was obtained from Sigma Alderich Co. (purity >99%) and was used without further purification. The type Ia diamonds with flat culet anvils of 300, 500 and 800 μm were used depending on the pressure required by the experiment. The pressure was increased using a membrane controller to provide uniform pressure to the sample. A rhenium gasket 200 μm in thickness was preindented to a thickness of 60 μm and a 192 μm diameter hole were perforated in the preindented region to contain the sample between the two opposing anvils. We placed several ruby chips to determine the pressure [10]. The 514.5nm line of an Ar^+ laser was used as the excitation source for Raman spectroscopy. The Raman signals were collected in a back-scattering geometry using a liquid-nitrogen cooled CCD (figure 1). The laser intensity and exposure times have been carefully chosen to avoid any photochemical damage to the sample, particularly of its liquid phase and solid phase I.

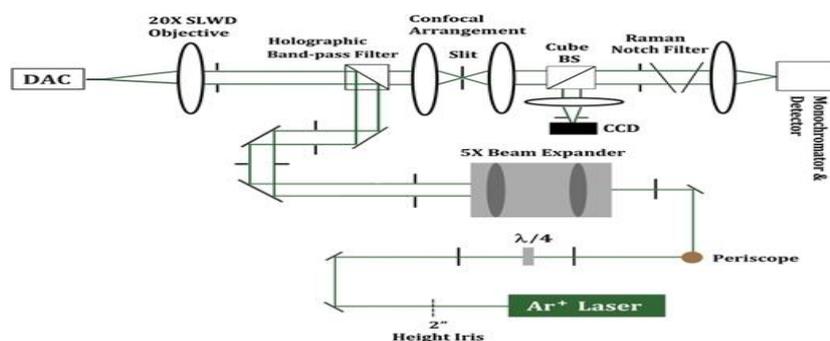


Figure 1. Experimental arrangement used for *in-situ* micro-Raman spectroscopy.

3. Results

$\text{Fe}(\text{CO})_5$ is in a bipyramidal structure with an Fe atom at the center and five carbonyls attached to the central Fe, three on the equatorial plane and two on the axial direction. Each of the carbon atoms is bonded to oxygen to form a carbonyl group. Therefore, the molecule belongs to the D_{3h} point group, and has fundamental stretching vibrational modes of symmetries $2A_1' + A_2'' + E'$ for both Fe-C and C=O bonds. Of these, the selection rules yield that the A_2'' and E' modes are IR active for a transition dipole moment in the Z-direction and doubly degenerate (E') for X and Y direction and three are Raman active ($2A_1' + E'$). $\text{Fe}(\text{CO})_5$ dissociates under ultraviolet light and loses one or more CO ligands. This results in five different products of $\text{Fe}(\text{CO})_x$ where $x=4, 3, 2, 1,$ and 0 depending on the excitation

wavelength. These products can then be recombined to form $\text{Fe}(\text{CO})_5$ as well as the dimer $\text{Fe}_2(\text{CO})_9$ and trimer $\text{Fe}_3(\text{CO})_{12}$ which has strong modes at $1700\text{--}1900\text{ cm}^{-1}$ [11-13].

$\text{Fe}(\text{CO})_5$ undergoes several pressure-induced transformations as can be seen in figures 2 and 3. All of the phases can be identified by their characteristic Raman features. At low pressures, it is a liquid consistent with the observed features of the Raman spectrum (the broad band centered 108 cm^{-1} and the broad C-O stretching modes $\sim 2000\text{ cm}^{-1}$ region). These broad features arise from the collisions of the molecules.

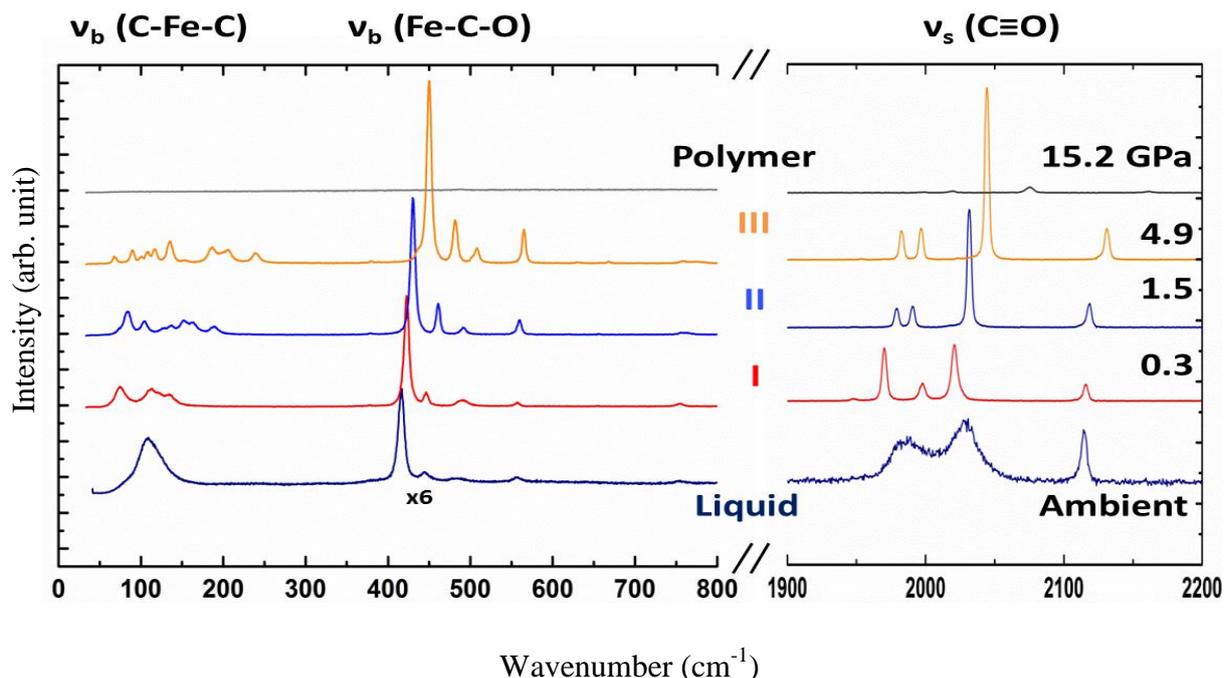


Figure 2. Raman spectrum of $\text{Fe}(\text{CO})_5$, CO stretching, vibrational and lattice modes observed in different pressure. Raman spectra of $\text{Fe}(\text{CO})_5$ are most characteristic to three different solid polymorphs (phase I to III) and a polymeric solid found at high pressure-ambient condition, yielding the phase/chemical transformation diagram to 16GPa. Due to the photosensitivity, exposure times for the spectra were different in liquid phase, thus the spectrum were magnified by six times than the other phase.

Upon increasing the pressure to 0.3 GPa, the changes in the spectra indicate that it has transformed to Phase I, with the appearance of lattice modes in the low-frequency region, and the C-O stretching modes becoming particularly sharp. Additionally, it is the splitting of the doubly-degenerate at 1990 cm^{-1} band suggests a change in symmetry of the molecule. Further, increasing the pressure leads to the transition to Phase II at 1.5 GPa to a lower symmetry phase as evidenced by the increase in the number of lattice modes, and the discontinuities in the C-O stretching modes. In particular, one of the modes redshifts by 7 cm^{-1} , and three of the modes blueshift indicating a softening of one vibrational mode and a shortening of the bond lengths. At 4.9 GPa, a Phase III is formed, evident by the appearance of a new peaks, and in particular the dramatic increase in intensity of the 2044 cm^{-1} band, which suggests a change in the polarizability of the molecule. Finally, above 15 GPa, the sample begins to polymerize and the transformation is complete by 18 GPa. It becomes black and the Raman modes completely disappear. This polymeric phase persists to ambient pressures and can be recovered. At no point during the experiment were the signatures of the dimer or trimer observed, indicating that no decomposition occurred.

Further evidence of phase transformation is provided by pressure-dependent shift of the frequencies of the Raman-active modes (figure 3). The solidification of $\text{Fe}(\text{CO})_5$ is evident by appearance of new peaks and discontinuities at 0.3 GPa and splitting of the degenerated equatorial mode from 1987 cm^{-1} . Similarly for the Phase I to Phase II transition with the discontinuities at 1970 cm^{-1} and 2000 cm^{-1} . Phase III exhibits the appearance of new peaks 2023 cm^{-1} and 68 cm^{-1} . The lattice modes $\sim 200 \text{ cm}^{-1}$ show a strong blueshift indicating a shortening of the bonds and stiffening of the lattice. The modes from the Fe-CO at $350\text{-}800 \text{ cm}^{-1}$, and the C-O modes from $1950\text{-}2150 \text{ cm}^{-1}$ do not show as strong of pressure dependence, nevertheless in any given phase they all blueshift. Note that above 15 GPa all Raman active modes become weak and disappear by 18 GPa, indicating the occurrence of a major chemical change.

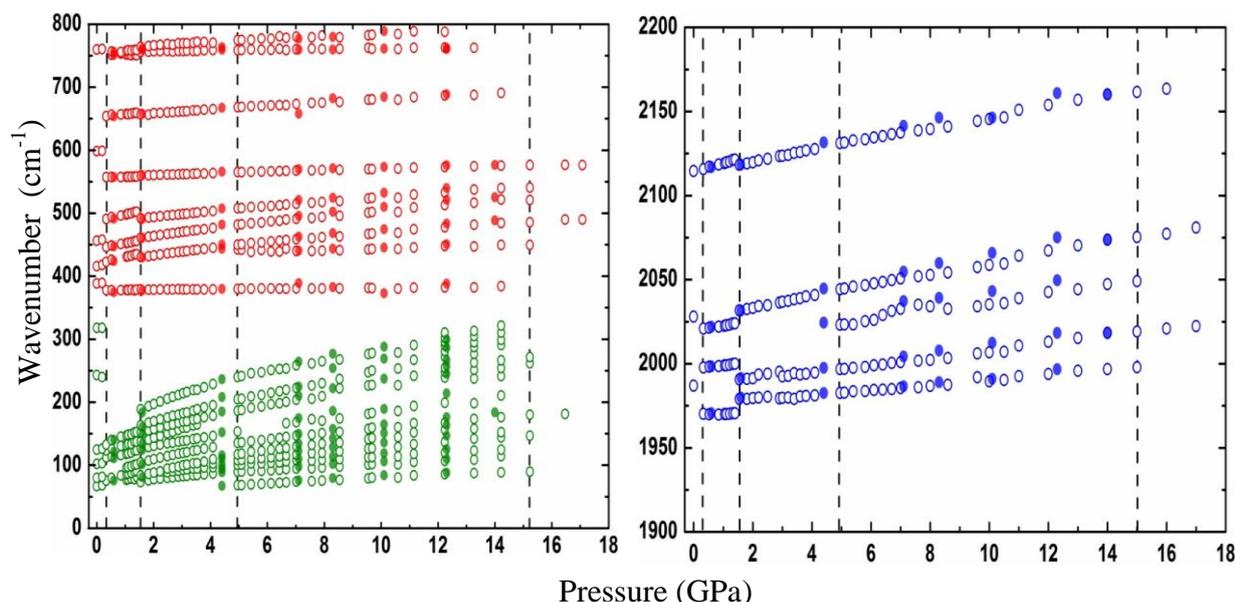


Figure 3. Pressure dependence of Raman shift up to 18 GPa. The vertical dotted lines represent the phase transitions. Open circle indicate the pressurizing and closed circle symbol indicate the depressurizing. (Right) Peak shift of the C-O stretching (1900 cm^{-1} to 2200 cm^{-1}) region. (Left) Peak shift of the lattice mode and the C-Fe-C and Fe-C-O vibrational (50 cm^{-1} to 800 cm^{-1}) region. Liquid to Phase I show appearance of new peaks at C-O stretching mode and Fe-CO bending mode. Transition to Phase II shows discontinuity at 1.5 GPa and to the new peak at 4.9 GPa indicates the appearance of Phase III. Polymerization started at 15.2 GPa and is complete at above 18 GPa.

4. Conclusions

The pressure-induced Raman changes indicated the presence of three polymorphs: liquid $\text{Fe}(\text{CO})_5$ solidifies to phase I at 0.3 GPa, transforms to phase II at 1.5 GPa and phase III at 4.9 GPa, all of which occur reversibly. Upon further compression, phase III polymerizes above 15.2 GPa, which can be recovered at ambient pressure. We are currently extending our studies to high temperatures to complete the phase diagram of $\text{Fe}(\text{CO})_5$ and characterizing the crystal structure of high-pressure polymorphs and polymeric solid.

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