UV Raman Analysis of the C:H Network Formed by Compression of Benzene

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A continuing challenge in understanding the linkage of unsaturated molecules to produce novel networks has been the analysis of the reaction products. Here we report a UV Raman spectroscopic analysis of the amorphous C:H (a-C:H) network formed by compression of benzene. The network contains both sp^2- and sp^3-bonded carbon, indicating that the aromaticity of some of the benzene rings must have been destroyed during the formation of the network. The Raman spectrum of the network resembles that of hydrogen-rich polymeric a-C:H. Analysis by means of UV Raman spectroscopy of a wide range of novel networks produced by compression of unsaturated molecules should be possible.

Introduction

The synthesis of new networks with extended, covalent bonding in two or three dimensions is an interdisciplinary challenge that has attracted considerable attention.[1−4] Covalently bonded networks composed of carbon and hydrogen, in particular, are of especially large scientific and technological interest, as evidenced by the large body of literature concerning them. Much effort has been expended to synthesize hydrocarbon molecules that have high levels of unsaturation that could be linked together to form new networks.[5−7] Pressure is an effective means to link such unsaturated molecules together to synthesize networks. These networks could have unprecedented structural features or incorporate functional groups in a novel manner and exhibit extraordinary physical properties.[8] However, although pi electron systems have been studied under pressure for some time,[9] relatively little is known about the details of the linkage of most unsaturated molecules under pressure, in part because of analytical challenges associated with determining the structure and bonding of the networks formed. Analysis of the reaction products is necessary to understand the formation reaction of a network.

Thus far most of the networks formed by compression of hydrocarbons have been amorphous, although polymeric species with long-range order have been produced.[10,11] The amorphous networks can be compared with the wide range of amorphous carbon/hydrogen materials that have been synthesized by various deposition techniques. A ternary, triangular “phase diagram” can be constructed for these materials that has vertexes of pure sp^2 carbon, pure sp^3 carbon, and pure hydrogen.[12−17] They can also be classified by their different structural features, such as the presence of disordered rings or linear chains of sp^2 carbon, tetrahedral carbon bonded only to other carbons, or tetrahedral carbon bonded to other carbons and hydrogen. It is the possibility of varying the composition and the local bonding environment for the carbons that allows such a wide range of useful and interesting amorphous carbon materials to be synthesized, ranging from hard tetrahedral amorphous carbon (ta-C), to much softer polymer-like, hydrogen-rich amorphous carbon (a-C:H), and amorphous sp^2-bonded carbon (a-C).

Raman spectroscopy is a convenient analytical tool for investigating the structure and bonding of covalently bonded networks. It can often give more direct information about carbon bonding in network solids than infrared spectroscopy, for example. It is not a destructive technique, like electron energy loss spectroscopy (EELS),

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for which changes in sample composition and bonding during analysis, caused by the intense electron beam used for EELS, can also be a concern, especially for samples containing hydrogen.[18] Unfortunately, many covalently bonded networks synthesized under pressure fluoresce when illuminated with visible light, making it difficult to obtain Raman spectra with an adequate signal-to-noise ratio.

Deep UV Raman spectroscopy is emerging as an especially powerful technique for characterizing both amorphous and crystalline carbon and carbon−hydrogen networks that has numerous advantages.[15,19−22] Although many carbon samples still fluoresce upon illumination with UV laser light with wavelengths from 206 to 257 nm, the resulting broad background occurs primarily at longer wavelengths, making it possible to collect Raman spectra with a good signal-to-noise ratio in the region near the excitation frequency. An additional advantage of UV Raman spectroscopy is that the spectral signal due to sp^3-bonded carbon can be directly observed in the presence of sp^2-bonded carbon.[22] This is because the resonance enhancement of the sp^2 carbon scattering that causes it to be much larger in the visible region is not present with deep UV excitation. UV Raman can also differentiate between sp^3 carbon that is part of an all carbon network and sp^3 carbon that has hydrogen bonded to it. Furthermore, UV Raman can give information about whether the sp^2 carbon in a network is organized into chains or rings and whether hydrogen is bonded to the network.[15]

Here we report an analysis by means of deep ultraviolet (257 nm) Raman spectroscopy of the network formed by compression of benzene, which reacts over several hours to form a white, semi-transparent, extended network composed of carbon and hydrogen. To our knowledge benzene cannot be polymerized or linked into extended networks by ordinary chemical means. It can be carbonized by heating under vacuum to form a sp^2-bonded network that is very different from the material characterized here. The primary structural characterization tool thus far for the network formed by compression of benzene has been infrared spectroscopy.[23−25] Visible Raman spectra are featureless due to fluorescence.

A detailed investigation of the reactivity and ring-opening reaction of benzene under pressure by means of infrared spectroscopy has been reported by Ciabini et al., who also provide a thorough summary of prior work.[24,25] They find that the high-pressure chemical transformation is driven by the S_1 singlet electronic excited state of benzene, which becomes more accessible under pressure. In this state the ring is deformed and becomes more reactive. The threshold pressure for ring opening can be reduced by selective pumping of the S_1 level by suitable laser light (although this does not appear to affect the final reaction product). Thus, photochemical control of high-pressure reactions provides the potential for desirable products to be made under less extreme pressure conditions. The reaction is hindered by steric effects at high pressure, but once the pressure is released free radicals formed from the opened rings can propagate to form an amorphous carbon hydrogen network. Three broad bands are present above 1000 cm^{-1} in the infrared spectrum of the resulting material at ambient pressure. Similar bands are observed in the infrared spectrum of tetrahedral amorphous carbon prepared by means of plasma-enhanced deposition from benzene vapor[26] that contains 35% hydrogen, but with the modes 50 to 100 cm^{-1} lower, with the exception of the C−H stretch band, which is at the same frequency for both samples. This blue-shift of the compressed benzene sample is attributed to residual internal strain or the presence of shorter olefinic chains. The infrared band in the C−H stretching region of the compressed benzene sample is considerably more intense than that of the chemical vapor deposition (CVD) sample, indicating that the hydrogen content of the compressed benzene sample is likely larger than 35%. Ciabini et al. concluded that no hydrogen is lost during the reaction. The relative intensities of the C−H stretching bands associated with sp^2- and sp^3-bonded carbon give evidence that the sp^3-bonded carbon content is approximately 76%. Thus there can be little doubt that the sp^3-bonded carbon content of compressed benzene is substantial. Ciabini et al. also found that compressed benzene can support an internal stress corresponding to 1.3 GPa. This provides further evidence that compressed benzene is an extended network because a molecular crystal bound by weak intermolecular forces could not support such a large internal stress.

By comparison with the a-C:H sample containing 35% hydrogen, Ciabini et al. proposed that the amorphous C−H network formed by compression of benzene is different from materials prepared by conventional CVD or plasma-enhanced CVD in view of the high hydrogen content and the lack of clusters of sp^2 carbon.[24,25] However, polymer-like a-C:H (PLHC) can be deposited by means of plasma-enhanced CVD with a hydrogen content as high as 50%,[12,15,16,27] which may be a more appropriate material for comparison with the compressed benzene reaction product, hereafter referred to as compressed benzene. PLHC is relatively soft compared with other hard carbons and contains in excess of 60% sp^3-bonded carbon. Similar to the compressed benzene sample,[25] polymeric a-C:H also has a wider band gap than that of a-C:H with only 35% hydrogen, which is considerably darker than either of the other two materials. Furthermore, unlike a-C:H with only 35% hydrogen, polymeric a-C:H exhibits strong luminescence upon illumination with visible laser light. Compressed benzene samples are also luminescent,

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which allows us to place a lower bound on their hydrogen content. We find that the UV Raman spectrum of the network formed from benzene most closely resembles that of polymeric a-C:H.

Experimental Section

Benzene was loaded into a Mao−Bell type diamond anvil cell with a 165-μm gasket hole by freezing it with liquid nitrogen. Visible Raman spectra collected at 1 GPa confirmed the purity of the sample. UV Raman spectra were collected with a single stage of a model 1400 SPEX spectrometer equipped with a Princeton Instruments model 1340-PB back-thinned CCD detector. A Coherent FRED frequency-doubled argon ion laser was used for excitation at 257 nm. After passing through a Pellin−Broca prism and spatial filter, the laser light was focused at an angle of 35° onto the sample with a spot size of approximately 10 μm. The scattered light was collected with a Coherent Ealing 0.5 NA 15× reflecting objective. The Rayleigh scattered light was rejected by a pair of Omega Optical dielectric edge filters.[28] The Raman spectra were collected for 300 s at a laser power of 0.5 mW. At excitation powers above 1 mW, the sample began to degrade, gradually turning brown and eventually black, likely as a result of degradation to a primarily sp^2-bonded material. No change in sample appearance or the Raman spectra was observed if the laser power was kept below 0.5 mW. Visible Raman spectra were collected with a DILOR XY spectrometer and 514 nm excitation.

The sample was compressed slowly to 30 GPa and left at that pressure for about 20 h. Visible Raman spectroscopy of the C−C ring-breathing Raman mode of benzene at 1000 cm^{-1} was used to track the progress of the reaction.[29] As the reaction neared completion, this mode could no longer be observed because of the presence of a large background fluorescence. The pressure was then released and the sample was taken out of the diamond anvil cell. In contrast to prior reports, no liquid was observed on the top of sample after taking it out of the diamond anvil cell.[23] The product did not dissolve in common solvents, such as acetone, methanol, benzene, and ethyl acetate, indicating that it had a substantial molecular weight. Transmission electron microscopy analyses were performed on the reaction product placed on lacey carbon grids. EELS spectra were collected with a Gatan PEELS spectrometer in a Hitachi HF-2000 TEM.

Results and Discussion

The reaction product is white and semi-transparent in appearance, in agreement with previous observations,[23] and brittle. The sample does not evaporate or visibly degrade under illumination from a 100 keV electron beam in the TEM, consistent with the formation of an extended network (although damage from the electron beam in this hydrogen-containing material cannot be ruled out). Raman spectra collected at 514 nm on the quenched sample are featureless because of background fluorescence.

In contrast, UV Raman spectra (Figure 1) exhibit excellent signal-to-noise ratios. The most important features are two broad peaks centered at ~1400 cm^{-1} and 1614 cm^{-1}, which we attribute to the "D" (disorder) and "G" peaks, respectively, of sp^2-bonded carbon. These two peaks are common to the Raman spectra collected with excitation from the IR to the deep UV of many different forms of disordered, nanocrystalline, and amorphous carbons. Their widths, intensities, and dispersion with excitation wavelength are different for different carbons, providing a powerful means for identifying a given form of carbon.[15] Although the details of the origin of the "D" peak remain under debate,[30,31] it can be associated with the breathing modes of sp^2-bonded carbon rings.[15] It disappears in the UV Raman spectra of nanocrystalline and disordered graphite, but not in the UV Raman spectra of amorphous carbons. The "G" peak is due to bond stretching of sp^2 carbon atoms in rings and chains. It is at 1582 cm^{-1} in crystalline graphite, but shifts to higher frequencies in disordered carbons that have sp^2-bonded chains in addition to rings.[15] Thus, the UV Raman spectrum shows that compressed benzene must have both sp^2-bonded chains and rings.

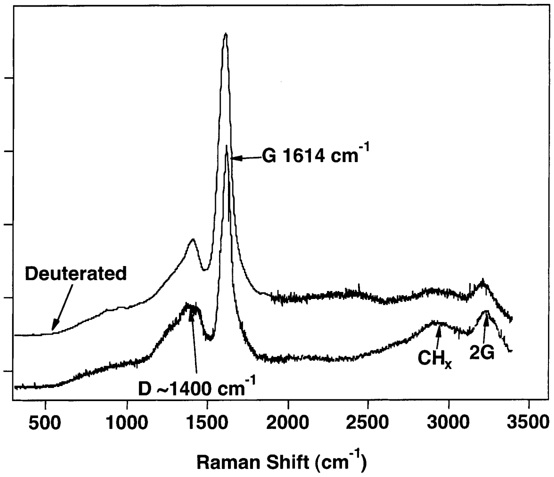

Figure 1. UV Raman spectra of networks formed by compression of benzene and deuterated benzene.

A "T" peak near 930 cm^{-1}, associated with sp^3-bonded carbon that is not bonded to hydrogen may be present as well (Figures 1 and 2).[15] However, this peak is quite weak and very broad, and it tails off in a region of the spectrum where the absorbance of the dielectric edge filters gradually begins to increase, indicating that the peak may be partially or entirely an artifact of the filters. Angle tuning of the dielectric edge filters[28] merely increased the background level due to Rayleigh scattered light, making the low-frequency peak difficult to observe. A substantial sp^3-bonded pure carbon network with no hydrogen bonded to it would not be expected in compressed benzene in view of the large hydrogen content. This is consistent with the observation that the "T" peak of compressed benzene is weak or nonexistent.

It is important to consider whether various C−H deformation and twisting modes, which can appear in the spectral region from ~1270 to ~1370 cm^{-1}, may contribute to the peak centered at ~1370 cm^{-1} that we attribute to sp^2 bonding. UV Raman spectra of a sample prepared by compression of deuterated benzene (Figure 1) are similar to the spectra of the sample prepared from normal benzene in this spectral region. Because no isotope effect is observed, it can be concluded that C−H modes make little contribution to this peak. Deuteration

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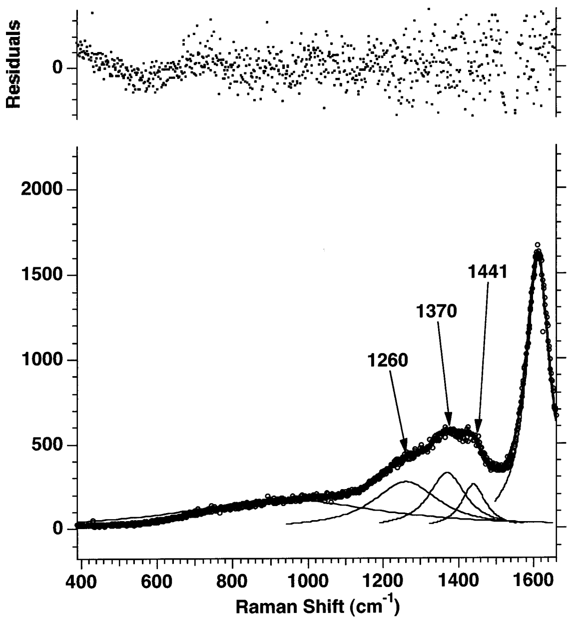

Figure 2. UV Raman spectrum showing triplet in the "D" region.

does shift the position of the "G" peak down by about 10 cm^{-1} because there is a small contribution from C−H bending to the carbon−carbon stretching modes of the sp^2 chains.[15]

The "D" peak can actually be fit by three peaks (Figure 2). Different polycyclic aromatic hydrocarbons (PAHs), which can be viewed as molecular subunits of a graphene plane,[32] exhibit different UV Raman peaks in the spectral region where the "D" peak is found.[33] We conclude that a mixture of different, partially resolved bonding environments for the sp^2 rings is present. During the high-pressure reaction it must be possible for PAH-like assemblages of rings to form from isolated benzene rings. The three "D" peaks persisted even after the sample was illuminated with 10 mw of 257-nm light, which was sufficient to darken the sample because of the formation of additional sp^2 bonds (Figure 3). The persistence of the three resolved peaks even after so much sample damage and the formation of many additional sp^2 bonds is somewhat surprising and suggests that the PAH-like assemblages may be isolated from each other.

The low-loss EELS spectrum exhibited a plasmon peak at 25 eV, consistent with the formation of an sp^3-bonded amorphous phase containing substantial amounts of hydrogen.[34] Hydrogen rich samples, however, are susceptible to damage from the electron beam.[18] The EELS core loss region was characteristic of a primarily sp^2-bonded material. Unlike UV Raman, EELS cannot distinguish between sp^3-bonded carbon that has hydrogen bonded to it and sp^3 carbon bonded only to other carbon, so EELS should detect the sp^3 bonding in an undamaged sample. We conclude that the sample was damaged by the electron beam. The hydrogen content, infrared[25] and UV Raman spectra, and band gap of the sample[25] are not consistent with a primarily sp^2-bonded material. To avoid sample damage it probably would be necessary to work at very low incident beam currents on samples at low temperatures.

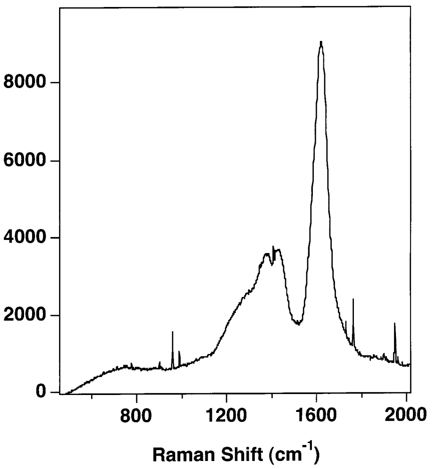

Figure 3. UV Raman spectrum at 10 mw of incident laser power. Triplet in "D" region persists.

There are two broad peaks at 2926 and 3227 cm^{-1} that are due to C−H stretching modes and the second order "2G" mode (Figure 1).[15] The C−H stretching modes decreased in intensity for the deuterated sample and a very weak feature is observed near ~2250 cm^{-1} that we assign to C−D stretching modes (Figure 1). The observation of the C−H stretching modes in the UV Raman is consistent with the observation of such modes in the infrared spectra previously reported, the conclusion that little or no hydrogen evolves during the reaction in the diamond anvil cell, and the presence of substantial amounts of sp^3-bonded carbon that is also bonded to hydrogen.[25]

The UV Raman modes of the compressed benzene sample most closely resemble those of PLHC.[15] Both the "G" and "D" peaks are present in PLHC at ~1620 cm^{-1} and as a broad feature in the range of ~1100 cm^{-1} to ~1450 cm^{-1}, respectively, compared with 1614 cm^{-1} and the triplet in the range of 1200 cm^{-1} to 1500 cm^{-1} for compressed benzene. The full width at half-maximum (fwhm) for the "G" peak in PLHC is about 80 cm^{-1}, compared with 77 cm^{-1} for compressed benzene. Disordered non-hydrogenated carbons have larger fwhms, consistent with the presence of hydrogen in compressed benzene. There is a clear "dip" between the "G" and "D" peaks in the compressed benzene that is also characteristic of PLHC.[15] Deuteration of the PLHC films red shifts the "G" peak slightly by 15 cm^{-1} and the "2G" peak by 30 cm^{-1},[15] slightly more than what is observed in the compressed benzene sample. In PLHC there may be a weak "T" peak, but it is not clearly evident, similar to what is observed for compressed benzene. PLHC also has a C−H stretch mode that decreases in intensity upon deuteration and a "2G" mode, again similar to compressed benzene.

This interpretation from the UV Raman spectrum of compressed benzene as more similar to PLHC than other hydrogenated carbons is also supported by the previously reported data.[24,25] PLHC films photoluminesce,[12] making it difficult to obtain Raman spectra with visible excitation, and are transparent.[17] ta-C:H, in

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contrast, has less hydrogen (35 at. % H or less) and does not luminesce nearly as much upon illumination with visible laser light.[35] The presence of significant sp^3 bonding, the hydrogen content, the luminescence, and the transparency of the samples produced by compression of benzene indicate that they are more similar to PLHC than to ta-C:H. Furthermore, the luminescence of the compressed benzene samples allows us to place a lower bound on their hydrogen content of approximately 40%, although it is likely that the hydrogen content is closer to 50%.[25]

Finally, we note that it should be possible to apply UV Raman to the analysis of other amorphous and crystalline networks produced by compression of unsaturated molecular species to obtain useful information about their structure and bonding. Compression of a variety of precursors containing saturated and/or unsaturated rings and/or chains may provide a means to assemble networks having different, controlled distributions of rings and chains with different "D" features. Raman spectra of these materials may provide valuable additional insights into the origin of the "D" peak, a major issue in the analysis of the Raman spectra of carbon materials.[30−32]

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