

Role of excited electronic states in the high-pressure amorphization of benzene

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High-pressure methods are increasingly used to produce new dense materials with unusual properties. Increasing efforts to understand the reaction mechanisms at the microscopic level, to set up and optimize synthetic approaches, are currently directed at carbon-based solids. A fundamental, but still unsolved, question concerns how the electronic excited states are involved in the high-pressure reactivity of molecular systems. Technical difficulties in such experiments include small sample dimensions and possible damage to the sample as a result of the absorption of intense laser fields. These experimental challenges make the direct characterization of the electronic properties as a function of pressure by linear and nonlinear optical spectroscopies up to several GPa a hard task. We report here the measurement of two-photon excitation spectra in a molecular crystal under pressure, up to 12 GPa in benzene, the archetypal aromatic system. Comparison between the pressure shift of the exciton line and the monomer fluorescence provides evidence for different compressibilities of the ground and first excited states. The formation of structural excimers occurs with increasing pressure involving molecules on equivalent crystal sites that are favorably arranged in a parallel configuration. These species represent the nucleation sites for the transformation of benzene into amorphous hydrogenated carbon. The present results provide a unified picture of the chemical reactivity of benzene at high pressure.

benzene crystal | electronic transitions | high-pressure chemistry | two-photon spectroscopy

Both technological and fundamental research interests highlighted in recent years a remarkable growing focus on high-pressure studies. The discovery of new transformations, including insulator-to-metal transitions, and the search for superhard materials have stimulated great interest in the high-pressure behavior of molecules consisting of light elements, which has subsequently resulted in the merging of different disciplines such as chemistry, physics, geoscience, and material science. The formation of extended covalently bonded solids has been observed through pressurizing simple molecular systems (1). High-quality polymeric materials have been recovered at ambient conditions by high-pressure processing of small hydrocarbon molecules (2–5), demonstrating the potential of this approach for synthesis. In addition, attractive amorphous materials have been obtained by compressing model compounds. Because these processes are often reversible, a fundamental question concerns the way to quench at ambient conditions products existing in a metastable form that will allow them to be used, for example, as energetic materials in the case of nitrogen (6), or as an ultrahard glass for carbon dioxide (7).

The design and optimization of solid-state chemical reactions require knowledge of transformation mechanisms at the microscopic level. A comprehensive picture of these mechanisms is still lacking; studies as a function of pressure are a powerful tool to complement the concepts developed so far (8–12). Pressure is indeed the most efficient tool to reduce the intermolecular distances, allowing precise and continuous tuning of the corre-

sponding interactions. The response of the system to density increases is a complex interplay between relative molecular arrangements and internal structural changes, and the energy excess generated can give access to new minima on the potential surfaces. An important step in understanding the mechanisms that regulate the solid-state reactivity is represented by recent high-pressure studies, which have revealed the role of lattice phonons in the activation and propagation of the chemical reaction that transforms crystalline benzene into a completely different material, specifically an amorphous hydrogenated carbon, which is recoverable at ambient conditions (13). During this process the long-range order that characterizes a crystalline structure is lost, and we observe a complete reconstruction of the molecular bonds, giving rise to a complex network made by both sp^2 (having a planar trigonal bonding geometry) and sp^3 (tetrahedrally coordinated) carbon atoms.

Another fundamental issue that remains far from being fully understood concerns the role of electronic excited states in high-pressure reactivity (14–16). Increasing overlap of molecular orbitals of adjacent molecules, leading to electronic delocalization, is produced by compression. In terms of electronic states, this generally corresponds to a reduction of the energy gap between the ground and excited electronic states (vertical contribution). These observations directly apply to systems containing conjugated π bonds. π orbitals are indeed more pressure sensitive than σ orbitals because of the smaller overlap occurring at atmospheric conditions. As a direct consequence of this, the $\pi \rightarrow \pi^*$ transitions, generally the lowest in energy, are strongly affected by compression. However, it is not easy to quantify the extent to which the energy gap reduces with increasing pressure, because the energy surfaces of the different states also undergo various displacements along suitable configuration coordinates because of their different compressibility (horizontal contribution) (14). The combination of the two contributions in this regard can result in a significant lowering of the thermal barrier, which gives rise to a mixing of the ground and excited states. This mixing, tuned by pressure, has been invoked to explain the reaction occurring among neighboring molecules in some large aromatic hydrocarbon crystals (15), but it has also been suggested that the same process can be activated or increased at milder density through the optical excitation of the molecule to a suitable electronic state, as successfully demonstrated for several unsaturated hydrocarbons (16). In addition, a remarkably high selectivity in reaction products can also be achieved in the photoinduced high-pressure polymerization of butadiene (2), ethylene (4), and isoprene (17).

As mentioned above, the high-pressure transformation of benzene to an amorphous hydrogenated carbon is a case study of particular relevance; it has been studied in some considerable

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transient dimers (structural excimers) that represent the seeds of the chemical reaction. The stabilization of benzene dimers at high pressure is demonstrated by the present experiment, in agreement with first-principle simulations (13). This suggests that dimerization is the first stage of benzene amorphization. The formation of these species is driven by lattice motions, and their reproducibility over a wide pressure–temperature range (13) indicates that the process occurs not only at specific points (defects) but also in the bulk crystal. When the crystal is optically excited, the excimers form at lower pressure because of the dipolar interaction between the excited molecule and the nearest neighbor benzene molecule favorably arranged in the slipped parallel configuration. Therefore, the same mechanism characterizes the two reactions, as they mainly occur on releasing pressure and lead to the same product.

Conclusions

Increased gigapascal pressure has been used to induce chemical transformations in the simplest molecular systems. Notwithstanding the synthetic interest, high-pressure studies represent a powerful tool for understanding the mechanisms driving solid-state reactivity. In this study, we investigated how the electronic excited states participate to the pressure-induced benzene amorphization. We measured TP excitation spectra and obtained a precise characterization of the evolution with pressure of the first electronic excited state applied up to 12 GPa, close to the onset of the photoinduced high-pressure reaction. The pressure shift of the $S_0 \rightarrow S_1$ exciton transition is remarkably different, about 1/10 as large as that previously estimated from OP absorption spectra. TP fluorescence spectra present a complex structure changing with pressure because of simultaneous emission of monomeric and excimeric species. The pressure shift of the monomer fluorescence, compared with the frequency and intensity evolution with pressure observed through the absorption data, reveals a different compressibility for the ground and first electronic excited state. The formation of the excimeric species, the amount of which depends on pressure and steeply increases above 5 GPa, also occurs when irradiation of the sample is avoided, thus demonstrating its structural origin. The parallel arrangement of the molecules along the a and b crystal axes allows for dimer formation. These species are identified as the nuclei of the chemical reaction; i.e., they are the same in the purely pressure-induced and photo-assisted reaction. This behavior, which is unusual for the reactivity of hydrocarbons under pressure, can be explained through the emergence of a progressive stabilization of the dimer with rising pressure. Finally, the simultaneous observation of a moderate pressure shift of the lowest electronic transition and the formation of structural dimers is of interest. In general, the progressive coloration observed when compressing several molecular crystals is attrib-

uted to a decrease in the energy gap between the monomer fundamental and excited states. In this analysis, we provide evidence for a more complex phenomenon in which stable excimers are present in the sample and whose formation not only is related to the presence of crystal defects or the absorption of radiation through a suitable wavelength but is intrinsically dependent on the crystal structure. The formation of these structural dimers is, in principle, always possible in π -bonded systems for molecules related by translational symmetry through the assistance of zone boundary acoustic modes. The stability and concentration of these species can strongly modify optical properties and represent a preferential site for chemical transformation.

Methods

Liquid benzene (Merck; purity $\geq 99.9\%$) was loaded in a membrane diamond anvil cell (MDAC) equipped with IIa diamonds. The sample dimensions were typically 40–50 μm thick and 150 μm in diameter. Phase I crystals were produced by slowly compressing the liquid. After the transition to phase II, which occurs at room temperature at ≈ 1.5 GPa, the sample was annealed to 450–500 K to completely remove phase I remnants (20). At each pressure both the TP fluorescence spectrum and the corresponding excitation profile were measured. Before this and immediately after these measurements, IR absorption spectra were measured in the mid-infrared region to identify whether any chemical change took place in the sample and determine its pressure. In fact, we did not use the standard local pressure calibration through R_1 ruby fluorescence band shifting to avoid any possible damage of the sample because of absorption of visible light by the ruby and as a result of local heating. To achieve internal calibration, the pressure shift of the ν_{15} IR active vibrational mode at $\approx 1,150$ cm^{-1} (ambient pressure) was used. The frequency of this mode was carefully calibrated in a separate experiment performed up to 20 GPa on a perfectly annealed phase II crystal by measuring the pressure by the ruby fluorescence band shift. The apparatus used to perform infrared experiments under pressure, including the optical beam condenser, has been described elsewhere (31, 32). A Fourier-transform infrared (FTIR) spectrometer (Bruker IFS-120 HR) was used to measure the IR absorption spectra with an instrumental resolution better than 1 cm^{-1} . For fluorescence measurements we used an optical parametric generator (OPG) as excitation source, pumped by the third harmonic (355 nm) of a mode-locked Nd-YAG laser (from EKSPILA). Tunable light in the 420- to 680-nm spectral range was generated by a lithium triborate crystal. The pulse duration from the OPG was ≈ 25 psec and the repetition rate was 10 Hz. Pulse energies not exceeding 0.5 μJ were applied during the experiment to avoid damage to the diamonds and to reduce the possibility of activating any chemical reaction. The fluorescence from the sample was collected in a 180° geometry, filtered by a single stage monochromator (2,400 grooves per mm), revealed by a photomultiplier (ET-9235QB) and both averaged and integrated by an oscilloscope (LeCroy LC584A). A quadratic dependence of the fluorescence signal on the excitation energy was found in all of the ranges investigated.

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