

High Pressure Photoinduced Ring Opening of Benzene

Lucia Ciabini,¹ Mario Santoro,² Roberto Bini,^{1,2,*} and Vincenzo Schettino^{1,2}

¹*Dipartimento di Chimica dell'Università di Firenze, Polo Scientifico, Via della Lastruccia 3, I-50019 Sesto Fiorentino, Firenze, Italy*

²*LENS, European Laboratory for Non-linear Spectroscopy and INFN, Polo Scientifico, Via Carrara 1, I-50019 Sesto Fiorentino, Firenze, Italy*

(Received 14 September 2001; published 7 February 2002)

The chemical transformation of crystalline benzene into an amorphous solid (*a*-C:H) was induced at high pressure by employing laser light of suitable wavelengths. The reaction was forced to occur at 16 GPa, well below the pressure value (23 GPa) where the reaction normally occurs. Different laser sources were used to tune the pumping wavelength into the red wing of the first excited singlet state $S_1(^1B_{2u})$ absorption edge. Here the benzene ring is distorted, presenting a greater flexibility which makes the molecule unstable at high pressure. The selective pumping of the S_1 level, in addition to structural considerations, was of paramount importance to clarify the mechanism of the reaction.

DOI: 10.1103/PhysRevLett.88.085505

PACS numbers: 62.50.+p, 82.50.-m

Molecular crystals are very soft materials, and the application of high external pressures forces the molecules to short distances making intermolecular and intramolecular interactions comparable. In this situation, the excess energy can be minimized by the complete modification of the arrangement of the chemical bonds. All unsaturated compounds, such as organic molecules with double and triple bonds, can be transformed to different materials by the application of a suitable pressure [1]. These transformations, which occur as bulk solid state reactions, are not reversible and the reaction products can be recovered. These phenomena have attracted great interest in the past two decades, and simple systems have been investigated in order to characterize the processes on which this new chemistry is based. A transfer to the materials science field could be expected in the future, due to new opportunities in the synthesis of conductive polymers and hard amorphous solids.

The reactivity of very simple molecules containing one or two reactive centers, represented by double or triple bonds, has been reported and investigated by optical techniques [2–8]. All these transformations occur at relatively low pressure, 1–6 GPa, and the formation of ordered polymeric compounds has generally been claimed. The stability of aromatic compounds requires higher reaction pressures while the high molecular symmetry, i.e., the high electronic delocalization, hinders the identification of preferential reactive centers. Benzene, a prototype of aromatic compounds, is, for its simplicity, an appealing system in both fundamental physics and chemistry and has been extensively investigated at high pressures. Different reaction products, hence different reaction paths, are reported in high pressure shock wave [9–11] and static experiments [1,12–18]. This result is reasonable since the temperature and the compression time scale are very different in the two cases. The attempt to give a uniform description of the benzene reactivity at high pressure led to different theoretical interpretation. The formation of diamond-

like carbon and molecular hydrogen was suggested by Ree [19]. Alternatively, the formation of dibenzene dimers was proposed by Engelke *et al.* [20], while new materials, where the C-H bonds are preserved and new carbon-carbon bonds among distinct benzene molecules are formed, were hypothesized by Pucci *et al.* [21]. The last interpretation followed from the idea of Drickamer [1] who suggested a progressive overlap of the π densities of neighbor molecules with increasing pressure. Recently, static experiments, where the final pressure was pushed above 20 GPa, have been reported [14–16,18]. Clear evidences of the formation of disordered reticulated materials constituted by highly branched polymeric units were obtained.

At 4 GPa and 870 K, benzene transforms into a black graphitic compound [12,13,17]. As the temperature is lowered, the required reaction pressure increases and friable compounds of different colors, depending on the P - T conditions, are obtained. The characteristics of these compounds have not been carefully investigated and generically attributed to disordered polymers. At room temperature the chemical transformation of benzene was reported by Pruzan *et al.* after the crystal was pressurized up to 30 GPa [14]. These authors monitored the reaction by means of the infrared absorption in the C-H stretching spectral region, where a broadband assigned to Csp^3 centers appears, indicating that a saturated product is formed. The disordered nature of this compound is confirmed by the vanishing Raman spectrum with releasing pressure [14]. This pure pressure-induced reaction was recently carefully investigated by studying the pressure evolution of the infrared spectrum, at different temperatures, up to 50 GPa [18]. The pressure increase strengthens the interaction of the benzene molecules and new bonds between carbon atoms of different molecules form above 23 GPa. No indication of a chemical reaction was found below this threshold pressure. On releasing the pressure, the distorted benzene molecules rearrange through the opening of the rings and the reaction rapidly propagates by

radical species to give an amorphous hydrogenated carbon. Based on the pressure behavior of most of the internal modes, it was argued that pressure induces a distortion of the benzene ring to a geometry closely resembling that of the molecule in the first electronic S_1 excited state. This change of the molecular geometry was ascribed to an efficient mixing of this excited state with the S_0 ground state. A similar hypothesis, but suggesting a S_0 - T_1 mixing, was already formulated by Thiery *et al.* [22].

The benzene ring destabilization is sensitive to photochemical effects. So far, the photo-induced reactivity and isomerization of the benzene molecule using low-power laser sources have been reported only at room pressure [23,24]. The aim of this work was to verify the role of the electronic excited states, and in particular of the S_1 level, in the high pressure transformation of benzene. If the distortion of the molecule at high pressure, which is responsible for the reaction, matches the S_1 configuration, we could, in principle, induce or speed up the chemical transformation by selectively pumping the system in the S_1 state. This kind of analysis is of prime importance to clarify the high pressure reaction mechanism and to anticipate a lowering of the reaction pressure in these pure systems in the presence of appropriate irradiation, opening wide perspectives for a new high pressure photochemistry.

High quality crystals (40–50 μm thick and 150 μm in diameter) were grown from the liquid, and then pressurized, by means of a membrane diamond anvil cell (MDAC) equipped with IIa diamonds. The transformation of benzene was monitored by measuring the infrared absorption spectra in the C-H stretching spectral region. The apparatus used to perform infrared experiments under pressure, including the optical beam condenser, has been described in previous reports [25,26]. The selective excitation of the sample was performed by tuning the pumping wavelength into the red wing of the electronic absorption edge. This procedure was made possible through the use of different *cw* laser sources (Kr^+ , Ar^+ , and a dye laser pumped by a 5 W Ar^+ laser) maintained at a fixed incident power of 70 mW and focused on the sample with a spot size of about 80 μm in diameter. In Fig. 1 we report some ultraviolet-visible (UV-VIS) absorption spectra measured along a typical compression-decompression cycle (0–44–0 GPa). The sample was found by visual observation to turn pale yellow around 22 GPa and to progressively darken as the pressure was further increased. The absorption spectra measured below 1 GPa are almost identical with those of a 1 mm thick pure liquid sample. The steep edge of the strong absorption moves very slowly below 3 GPa and then rapidly shifts to lower energy on further compression. This behavior is shown in the inset of Fig. 1 where the wavelength λ_0 corresponding to an absorbance of 0.5 is reported as a function of pressure. The slope change occurring at about 25 GPa in the λ_0 vs P diagram closely matches the observed onset of the chemical reaction [18]. Above 28 GPa, the redshift of the absorption edge is very small,

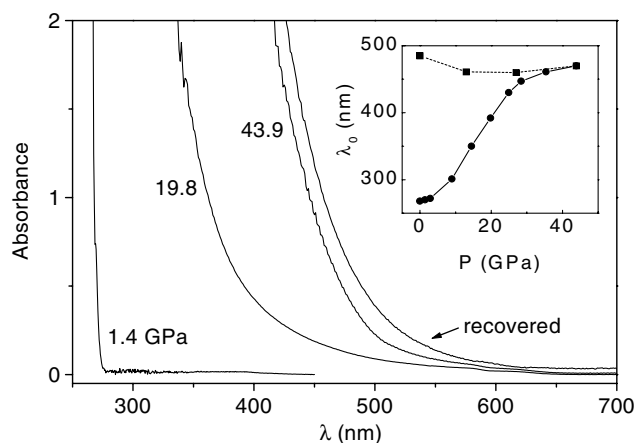


FIG. 1. Absorption edge in the UV-VIS spectral range, measured during sample pressurization. In the inset, the pressure evolution of a typical point of the spectrum, λ_0 (see text), is reported along the full compression (dots)-decompression (squares) cycle.

and at the maximum pressure (44 GPa) λ_0 is 472 nm. Upon releasing the pressure, no remarkable changes of λ_0 are observed apart from a further slight redshift below 10 GPa, which brings the absorption edge of the recovered sample very close to 500 nm. The λ_0 parameter was arbitrarily defined as the wavelength where the absorbance equals 0.5. However, it can be seen that this is a good probe to monitor the $S_0 \rightarrow S_1$ electronic transition. As a matter of fact, extrapolation to ambient pressure of the lower curve of the inset gives a λ_0 value equal to 268 nm which, when compared with the transition wavelengths to the T_1 , S_1 , S_2 , and S_3 states at 340, 265, 215, and 180 nm [27], respectively, clearly shows that the pressure evolution reported in the inset of Fig. 1 is related to the $S_0 \rightarrow S_1$ transition. The observed pressure-induced redshift can be easily explained as being due to increasing intermolecular interactions that produce a narrowing of the gap between the π and the π^* manifolds. This result indicates that the mixing of the two states, or the thermal activation of the $S_0 - S_1$ transition, can be the basis of the reaction mechanism as proposed in our previous study [18]. According to this reaction scheme, we should therefore be able to induce the reaction at lower pressure by populating the first electronic excited state by means of laser irradiation at a suitable wavelength.

Freshly prepared benzene samples were slowly pressurized up to 16 GPa. The crystal stability at this pressure was checked by monitoring the infrared spectrum for 30 h. No changes that could be due to a high pressure chemical reaction were observed. Then we irradiated the sample for 5 h with monochromatic laser light. Laser excitation frequencies were selected to probe the low frequency wing of the electronic absorption band in order to demonstrate the high selectivity of the process. Immediately after the irradiation we verified the effect by measuring the infrared spectra in the C-H stretching spectral region as shown in

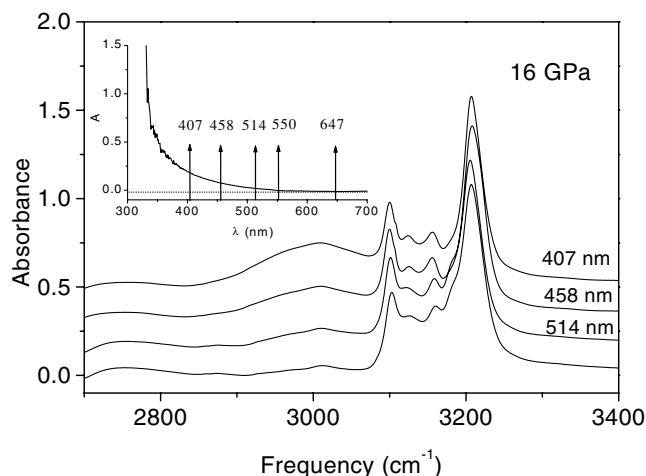


FIG. 2. Infrared spectra in the C-H stretching region corresponding to the chemical transformation occurring at constant pressure (16 GPa), which is indicated by the broad absorption at 3000 cm^{-1} , when the sample is irradiated (5 h) with suitable wavelengths. In the inset, we also report the laser lines employed and their position with respect to the electronic absorption spectrum.

Fig. 2. The lowest spectrum was measured just before irradiation. The strong and sharp structure observed in the $3070\text{--}3300\text{ cm}^{-1}$ interval is due to the crystal components of the ν_{13} (b_{1u}) and the ν_{20} (e_{1u}) modes of the molecule; the combination band $\nu_8 + \nu_{19}$ also contributes to this structure. The other three spectra were measured on different samples after the irradiation cycle with some of the previously mentioned laser sources. The small differences in the thickness of the samples were corrected by normalizing the spectra before the irradiation to the same peak absorption, in order to directly compare the intensities after the laser exposure. In the inset, we report the electronic absorption spectrum measured at 16 GPa together with the excitation lines employed during the irradiation cycles. No effects were detected after irradiation with the 647 nm (Kr^+) and the 550 nm (rhodamine-dye) lines, and the corresponding spectra are not reported. After irradiation with the 514 nm (Ar^+) line a very weak absorption was observed at 3000 cm^{-1} . We recall here that this spectral feature, assigned to C-H stretching modes involving sp^3 carbon atoms, was considered as the main signature of the occurrence of a chemical reaction [14,18]. By tuning the excitation wavelength within the $S_0\text{--}S_1$ absorption edge, the amount of reacted sample rapidly increases as indicated by the spectra which follow the irradiation with the 458 nm (Ar^+) and the 407 nm (Kr^+) lines. This is clear evidence that the ring distortion characteristic of the molecule in the S_1 state is the real driving force which leads to the formation of the saturated carbon atoms triggering the chemical reaction. In Fig. 3 we also present some spectra measured during an irradiation cycle with the 458 nm (Ar^+) line which gives an indication of the kinetics of the reaction. The amount of transformed material

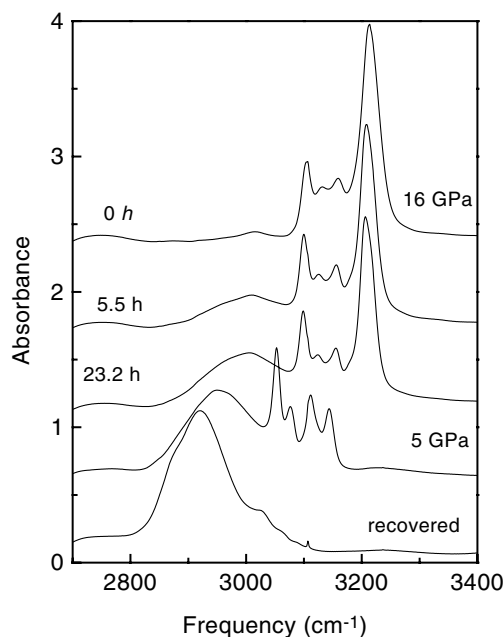


FIG. 3. The upper three infrared spectra have been collected at 16 GPa during an irradiation cycle of about 23 h using the 458 nm (Ar^+) line. The pressure was then released and the two bottom spectra were measured on decompression at 5 GPa and ambient pressure, respectively.

increases with the irradiation time, but a physical interpretation of this behavior cannot be proposed since the absorption by the reaction product decreases the amount of radiation which reaches the unreacted sample, thus reducing the efficiency of the process. By far, more interesting is the behavior, reported in the same figure, observed when the pressure is released. The reaction proceeds very rapidly as can be directly deduced by the strong increase of the intensity ratio between the C-H stretching bands of the product (sp^3 carbon atoms) and those of benzene. The spectrum of the recovered sample, recorded after the cell was opened in atmosphere, is also reported. The main band at 2920 cm^{-1} and a shoulder at 2864 cm^{-1} , both assigned to sp^3 carbon atoms, and three weak components at 3027 , 3064 , and 3085 cm^{-1} , assigned to sp^2 C centers, can be identified.

It is remarkable that the laser-induced and the purely pressure-induced reactions are qualitatively analogous. The transformation proceeds with increasing pressure or with the irradiation time, but, in both cases, decompression greatly accelerates the transformation, and at the end of the entire cycle the same recovered sample is obtained. The ring opening is sterically hindered at high density, but once the molecules are properly distorted by the strong pressure-induced interaction, decompression increases the average molecular volume thus allowing the reconstruction of the chemical bonds. The same behavior in the two cases demonstrates that the reaction is activated by the S_1 excited state. We also note that the laser driven chemical transformation was induced selectively, i.e.,

laser sources were tuned just at the absorption edge where other possible contributions, apart from that assigned to S_0 - S_1 , can confidently be ruled out.

In conclusion, we demonstrated that the high pressure chemical transformation of benzene is driven by the S_1 excited state, in which the ring is deformed and the electronic charge is no longer uniformly distributed on the molecular ring. This effect is induced by the application of very high external pressure (~ 23 GPa). It has been shown in this Letter that the threshold pressure for the ring opening can be strongly reduced by selective pumping of the S_1 electronic level. We emphasize here that laser light represents a powerful tool, which can be applied to initially pressurized samples to reduce the reaction pressure and open a completely new chemistry of pure systems in the condensed phase.

This work has been supported by the European Union under Contract No. HPRICT1999-00111 and by the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST).

*Electronic address: bini@chim.unifi.it

- [1] H. G. Drickamer, *Science* **156**, 3779 (1967).
- [2] C. S. Yoo and M. Nicol, *J. Phys. Chem.* **90**, 6732 (1986).
- [3] K. Aoki, Y. Kakudate, M. Yoshida, S. Usuba, and S. Fujiwara, *J. Chem. Phys.* **91**, 778 (1988).
- [4] K. Aoki, S. Usuba, M. Yoshida, Y. Kakudate, K. Tanaka, and S. Fujiwara, *J. Chem. Phys.* **89**, 529 (1989).
- [5] M. Sakashita, H. Yamawaki, and K. Aoki, *J. Phys. Chem.* **100**, 9943 (1996).
- [6] M. Ceppatelli, M. Santoro, R. Bini, and V. Schettino, *J. Chem. Phys.* **113**, 5991 (2000).
- [7] C. C. Trout and J. V. Badding, *J. Phys. Chem.* **104**, 8142 (2000).
- [8] M. Citroni, M. Ceppatelli, R. Bini, and V. Schettino (to be published).
- [9] R. D. Dick, *J. Chem. Phys.* **52**, 6021 (1970); **71**, 3203 (1979).
- [10] W. J. Nellis, F. H. Ree, R. J. Trainor, A. C. Mitchell, and M. B. Boslough, *J. Chem. Phys.* **80**, 2789 (1984).
- [11] M. Nicol, M. L. Johnson, and N. C. Holmes, *Physica (Amsterdam)* **139B&140B**, 582 (1986).
- [12] G. J. Piermarini, A. D. Mighell, C. E. Weir, and S. Block, *Science* **165**, 1250 (1969).
- [13] S. Block, C. E. Weir, and G. J. Piermarini, *Science* **169**, 586 (1970).
- [14] Ph. Pruzan, J. C. Chervin, M. M. Thiery, J. P. Itie, and J. M. Besson, *J. Chem. Phys.* **92**, 6910 (1990).
- [15] J. M. Besson, M. M. Thiery, and P. Pruzan, *Molecular Systems Under High Pressure*, edited by R. Pucci and G. Piccitto (Elsevier, Amsterdam, 1991), p. 341.
- [16] M. Gauthier, J. C. Chervin, and P. Pruzan, *Frontiers of High Pressure Research*, edited by H. D. Hochheimer and R. D. Etters (Plenum, New York, 1991), p. 87.
- [17] F. Cansell, D. Fabre, and J. P. Petitet, *J. Chem. Phys.* **99**, 7300 (1993).
- [18] L. Ciabini, M. Santoro, R. Bini, and V. Schettino, *J. Chem. Phys.* (to be published).
- [19] F. H. Ree, *J. Chem. Phys.* **70**, 974 (1979).
- [20] R. Engelke, P. J. Hay, D. A. Kleier, and W. R. Wadt, *J. Chem. Phys.* **79**, 4367 (1983).
- [21] R. Pucci and N. H. March, *J. Chem. Phys.* **74**, 1373 (1981).
- [22] M. M. Thiery, J. M. Besson, and J. L. Bribes, *J. Chem. Phys.* **96**, 2633 (1992).
- [23] M. Klessinger and J. Michl, *Excited States and Photochemistry of Organic Molecules* (VCH, New York, 1995).
- [24] V. I. Minkin, M. N. Glukhovtsev, and B. Y. Simkin, *Aromaticity and Antiaromaticity* (Wiley, New York, 1994).
- [25] R. Bini, R. Ballerini, G. Pratesi, and H. J. Jodl, *Rev. Sci. Instrum.* **68**, 3154 (1997).
- [26] F. Gorelli, M. Santoro, L. Ulivi, and R. Bini, *Phys. Rev. Lett.* **83**, 4093 (1999).
- [27] L. D. Ziegler and B. S. Hudson, *The Vibronic Spectroscopy of Benzene: Old Problems and New Techniques*, Excited States (Academic, New York, 1982), Vol. 5.