

Laser-Assisted High-Pressure Chemical Reactions

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ABSTRACT

The growing need for production methods with a reduced environmental impact drives the search for new synthetic approaches in chemistry. Here we report the state of the art of a recently developed branch of ultra-high-pressure chemistry, employing high pressure to create the necessary reaction conditions to transform simple hydrocarbons and monochromatic light to trigger and direct, according to selective paths, the chemical reaction. For the available systems studied up to now, we will provide an overview of the different effects that can be obtained by the combined use of pressure and laser light.

1. Introduction

Very different pressure conditions are found in the universe, from the intergalactic vacua to the center of neutron stars, covering more than 60 orders of magnitude, so that an incredible variety of aggregation states of matter are produced. This picture makes evident the great capability of pressure, far exceeding that of temperature, to modify the properties of matter, thus revealing its fundamental role in space and geochemistry. Molecular systems are highly compressible, and volume compression greater than 1 order of magnitude with respect to atmospheric pressure can be realized. Under these conditions, the relative weights of the strong intramolecular interactions responsible for molecular bonding, and of the weaker intermolecular forces defining the aggregation state, are completely altered, and the repulsive side of the intermolecular potential is explored. The consequent increase in free energy can be large enough to exceed the strength of the molecular bonds, making the system thermodynamically unstable. This behavior opens wide possibilities in the chemistry of molecular systems because it offers a synthetic route to produce new materials starting from compounds that are extremely stable under normal pressure and temperature conditions.^{1,2} Furthermore, more conventional chemical reactions, such as

oligo- and polymerization, have also been demonstrated to be successfully induced in pure systems in the condensed phase by the application of a suitable external pressure.³

The progress in this new synthetic approach is due, to a significant extent, to recent advances in the techniques employed to generate high pressure. Static pressures up to several megabar can be generated by using diamond anvil cells (DACs), while higher pressures can be generated dynamically by using shock-wave techniques.⁴ The static approach is of interest because it allows continuous tuning of the pressure, control of the temperature from 4 to 1000 K, and the possibility to employ a large number of probing techniques that allow in situ measurements. All the spectroscopic techniques have been successfully adapted to the studies of micrometric samples contained in the DAC, taking advantage of the diamond transparency from the X-ray to the infrared region, and of laser or synchrotron beams that can be focused on the samples inside the DAC. For these reasons, the DAC, despite the small sample volume (50–300 μm diameter and 10–50 μm thickness), is the most reliable tool to study the matter under pressure. The principle of the DAC operation is very simple: two opposing diamond anvils press the sample that is laterally contained by a metal gasket. The pressure applied on the large face of the diamond, and the ratio between the area of this face and that of the smaller flat tip in contact with the sample, determine the pressure to which the sample undergoes (see Figure 1).

The great interest in studying the chemical reactivity of pure molecular species by using DACs lies in the possibility to entirely transform these materials in the condensed phases without employing additional chemicals. Furthermore, pressures as high as 10–15 GPa are routinely obtained on samples of centimeter size by using large-volume presses, offering a rapid extension of the studies in the DAC to synthetic methods of applicative interest. The interest in condensed-phase reactions has been well established for some decades, and the recent extension to the field of ultra-high pressures has shown the possibility to induce both reversible (O_2 ,⁵ CO_2 ,⁶ N_2)⁷ and irreversible transformations, even in the smallest unsaturated molecules.⁸

In this Account, attention is focused on reactions involving simple hydrocarbons, giving products that can be recovered at ambient conditions. The reactivity of these molecules in the gas phase or in solution is known, but in the solid phase the reaction can follow a completely different path, since the molecular arrangement is defined by the crystal structure and the relative orientations and distances are determined accordingly. Furthermore, the molecule of interest is at the same time reactant and solvent, and no catalysts or radical initiators are present in the reaction environment, thus offering opportunities for green chemistry. Relevant recent progress in this synthetic approach is represented by the combination of high-pressure and selective laser irradiation of the sample.

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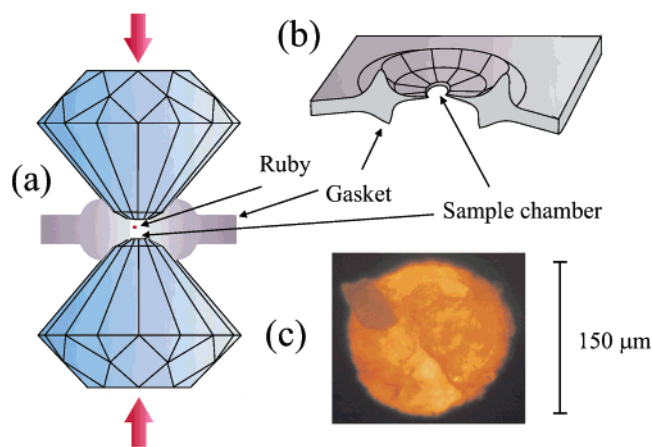


FIGURE 1. The diamond anvil cell. (a) The high pressure is generated on the small sample contained by the two diamonds and the metallic gasket. A ruby chip is placed together with the sample for the local pressure calibration by the ruby fluorescence method. (b) The crater left by the diamonds on the gasket. (c) Photo of a sample recovered by the high-pressure reaction of benzene.

The idea to combine these two physical tools to drive chemical reactions derives from basic considerations concerning the effects of pressure on the electronic states. Besides an increased overlapping among adjacent electronic orbitals that scales up the electronic delocalization, the pressure growth also causes a relative displacement of the molecular orbitals, such as the commonly observed approach of empty π^* (LUMO) to occupied π orbitals (HOMO). Furthermore, horizontal displacement along the configuration coordinate can originate from the different compressibility of the ground and the excited states along that coordinate.⁹ The total effect of these processes can be such that, while the optical absorption energy (vertical transition) is not much affected by the pressure increase, the thermal barrier can be significantly lowered, and a mixing of the ground and the excited states takes place. These changes in the electronic distribution and in the molecular geometry can possibly trigger reaction with neighboring molecules, as has been reported for large aromatic hydrocarbons such as pentacene, whose reactivity was explained on the basis of a thermal occupation of a low-energy π^* state.¹⁰ According to this scheme, the change of the molecular geometry, occurring at high pressure and preliminary to the chemical transformation, can possibly be induced by the optical excitation of the molecule to a suitable electronic state, so that the reaction can be activated or speeded up. This procedure has a two-fold importance. Once the molecular geometry is properly changed by electronic excitation, a lower pressure (lower density) could be sufficient to realize the intermolecular distance required for the chemical reaction to occur. Second, the specific molecular deformation can reduce the number of competitive reaction channels, leading to a greater selectivity in the reaction products.

2. High-Pressure Photoinduced Reactions

Increasing chemical instability following laser irradiation has been reported for several unsaturated molecules

under high external loading. Among simple molecules, it is worth mentioning the observations reported for CO ,^{11,12} N_2O_4 ,¹³ and S_8 .¹⁴ The spectroscopic investigation at high pressure through laser spectroscopy caused, for these substances, a chemical reaction different from that induced by pressure alone. These results represent nice examples showing how light absorption strongly affects the reactivity at very high pressures, but in none of these studies was a careful characterization of the photochemical reaction pursued. In the following, we will focus our attention on small hydrocarbons where the role of electronic excitation in the activation and propagation of the reaction has been clarified. Most of the experimental information is gained from vibrational spectroscopy.⁸ IR absorption spectroscopy is preferable to Raman spectroscopy, since laser irradiation is limited to the pressure calibration by the ruby fluorescence method¹⁵ or completely avoided when alternative pressure sensors are employed, allowing a complete separation of pressure and light absorption effects.¹⁶ Another advantage of IR spectroscopy concerns the possibility to obtain precise kinetic information from the measurement of the product band absorption that, in constant pressure experiments where the sample thickness is fixed, gives a precise measure of the amount of material transformed.

2.1. Polymerization Reactions. Polymerization reactions represent a relevant section of the transformations of interest in the high-pressure field. Polymeric materials are commonly prepared in solution through the employment of catalysts and radical initiators to obtain highly stereoregular materials. At high pressure we have, in principle, the unique chance to induce polymerization reactions by using the geometrical constraints posed by the crystal structure or, more generally, by the high density. Furthermore, the fixed crystalline arrangement offers the possibility to prepare, through the employment of specific chemical groups, tailor-made materials with the desired properties. Unfortunately, crystal defects and competition among different reaction paths make the reactions in real systems less selective than expected. In this section, we will review the role played by laser light in assisting polymerization reactions of simple model hydrocarbons.

2.1.1. Acetylene. Acetylene was found to react in the high-pressure orthorhombic crystal phase when pressurized above 3.5 GPa.¹⁷ The color change from transparent to deep red indicated that the reaction had occurred. Raman spectra showed the reaction product to be mainly *trans*-polyacetylene with a small amount of the *cis* isomer, even though the evaluation of the relative abundance of the two isomers could be altered by resonance effects.¹⁷ The amount of *cis* isomer seems to increase when the reaction is performed at 77 K and 12.5 GPa, but a *cis*-*trans* isomerization is observed when the temperature is raised to ambient.¹⁸ The polymerization reaction develops along a precise crystal direction, namely the diagonal of the *bc* plane,¹⁶ in agreement with the topochemical principle because in this direction the molecules are almost aligned and only a small reorientation is required

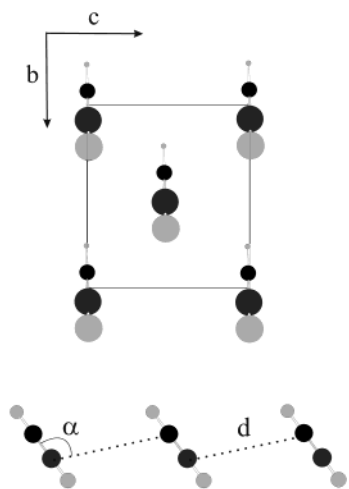


FIGURE 2. (Top) Molecular arrangement on the *bc* face of the orthorhombic cell of acetylene. (Bottom) The molecules involved in the polymerization reaction lying on the plane containing the diagonal of the *bc* face and forming a 39.5° angle with the *b* axis ($\alpha = 109.1^\circ$, $d = 3.05 \text{ \AA}$).

to realize the polymer geometry (see Figure 2). Analysis of the reaction at different temperatures allows zone boundary translational modes to be identified that are responsible for both the nucleation and the propagation steps of the reaction.¹⁶

The sudden branching of the polymeric chain is caused by irradiation with a few milliwatts of the 514.5-nm line of an Ar⁺ laser. Visual inspection reveals that the sample turns from deep red to colorless, while the relative intensities of specific bands in the IR spectrum change continuously along the irradiation period. Specifically, absorptions due to vibrational motions involving saturated carbon atoms increase during irradiation while the bands involving sp² carbon atoms weaken, thus providing a sharp indication of the conjugation loss and of the branching of the polymer chain. This process is interpreted straightforwardly on the basis of efficient one-photon absorption processes to π^* antibonding states.¹⁹ In the excited state, the torsional barrier around the C–C bonds of the chain is lowered, thus favoring the interaction with carbon atoms belonging to other polyenic chains or with acetylene molecules lying out of the *bc* plane diagonal, thus inducing the polymer ramification. The same effect was also found when compression was pursued above 4 GPa.²⁰ This result has a two-fold importance, showing that, in principle, by joining light absorption to pressure effects, i.e., changing the molecular geometry at high density, on one side we can open new reaction paths or, alternatively, we can considerably lower the reaction threshold pressure.

2.1.2. Butadiene. The study of the high-pressure reactivity of butadiene, the simplest linear conjugated hydrocarbon, was motivated by the competition existing in the chemistry of the isolated molecule between dimerization and polymerization. Unless appropriate catalysts and radical initiators are employed to produce polybutadiene,²¹ dimerization prevails, giving different products, among which vinylcyclohexene is the most abundant.²²

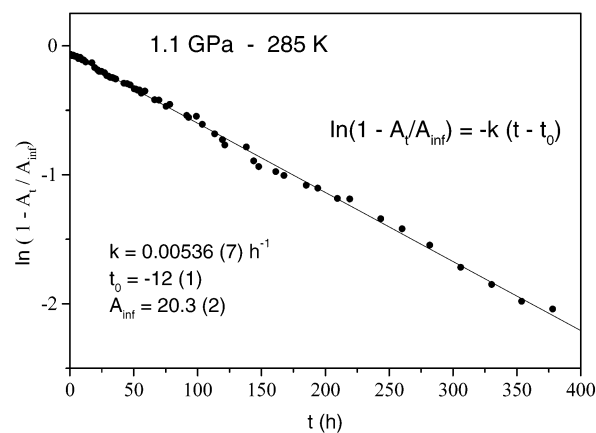


FIGURE 3. Logarithmic plot reporting the time evolution of $\ln(1 - A_t/A_{\text{inf}})$ during the dimerization reaction in liquid butadiene at 285 K and 1.1 GPa. A_t and A_{inf} are the integrated absorptions of the band at 1643 cm^{-1} (C=C stretch) of vinylcyclohexene at time t and at the end of the reaction, respectively. A linear evolution of the data agrees with the first-order kinetics reported in the figure. The full line is the best linear fit from which the rate constant k and the initial time t_0 of the reaction are obtained.

Dimerization is also the main reaction when liquid butadiene is compressed at room temperature.²³ At 0.6–0.7 GPa, the monomer transforms after several days in a transparent liquid, yielding 4-vinylcyclohexene, which can be recovered after the pressure is released and the cell opened. Although the same product is obtained by both ambient and high-pressure reactions, the analysis shows a first-order kinetics at high pressure (see Figure 3), while the ambient pressure dimerization is a second-order concerted (Diels–Alder) reaction. Even though both dimerization processes are bimolecular, their mechanisms are different. As a matter of fact, the process cannot be concerted at high pressure, as it can also be derived from the missed observation of *cis* monomers, and a multistep process, characterized by a rate-limiting step consisting of an internal rearrangement, must be taken into account.

When butadiene is compressed to 0.6–0.7 GPa and is simultaneously irradiated with less than 20 mW at 488 or 458 nm, the complete transformation of the monomer to *trans*-polybutadiene occurs in less than 50 h.²³ Laser irradiation is necessary only in the early stages of the reaction, which proceeds also when the laser light is switched off. The activation of the reaction sharply depends on the incident wavelength, revealing a threshold for the reaction; in fact, the green line at 514.5 nm does not activate the polymerization reaction and the usual dimerization to vinylcyclohexene takes place. The photochemical nature of the reaction appears evident from these results, but, unfortunately, the analysis of the process must be based on the ambient-pressure structure of the electronic states since no high-pressure data are available. There is some debate about the symmetry of the S_1 state (1^1B_u or 2^1A_g) and about the location of the 2^1A_g state (from 5.5 to 7.4 eV).^{24,25} Since the lowest-energy photons that are useful to induce the high-pressure polymerization possess an energy of 2.54 eV, it is clear that we are exciting the butadiene molecules through a

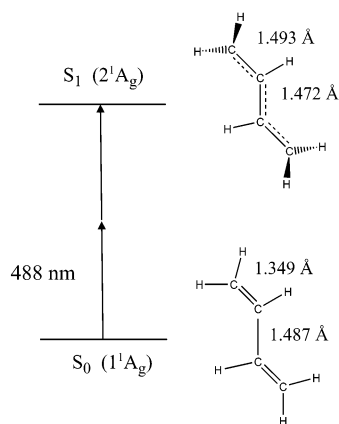


FIGURE 4. Two-photon excitation to the S_1 (2^1A_g) state and the corresponding change of the butadiene molecular geometry.

two-photon absorption process. Furthermore, due to the very low laser power necessary to induce the transition, the final state should be the 2^1A_g since the two-photon transition to this state is symmetry-allowed and an elevated cross section has been calculated.²⁶

The 2^1A_g is considered to be the central state in the photochemistry of butadiene,²⁷ because from this state the molecule relaxes to the ground state through nonradiative processes, likely in the form of funnels connecting the two energy surfaces.²⁸ Different accessible trajectories in the ground state give rise to a distribution of possible products, making the photochemical reaction in the isolated molecule not selective. The peculiarity of the high-pressure reaction is that the molecule reacts directly in the excited state, the interaction time with the nearest-neighbor molecules being at least comparable with the S_1 lifetime. In the S_1 state, corresponding to the excitation to an antibonding π^* MO, the molecule is stretched ($\sim 7\%$) and the rotational barrier around the double bonds is lowered.^{29,30} Two consequences result from these geometrical changes, shown in Figure 4. First, there is a significant reduction of overlapping of the π -bonding electron densities of nearest-neighbor molecules, which is the primary requirement for the dimerization process. Second, the CH_2 terminal groups rearrange to minimize the steric repulsion between the same groups of nearest-neighbor molecules, therefore favoring the head-to-tail interaction, a mandatory step for the polymerization.

The reaction of butadiene at high pressure has also been studied at different pressures (2–6.6 GPa) in the ordered crystal phase I (C_{2h}^5 , $Z = 2$).³¹ Below 4 GPa, vinylcyclohexene is the only product of the reaction.³² By studying the reaction evolution with time, the order and the activation volume have been determined, and a three-step mechanism has been proposed for the dimerization. In this scheme, the dimer is formed by the two molecules of the primitive cell (full molecules in Figure 5). Above 4 GPa, an increase of the dimerization rate is found as the pressure is raised, while the formation of the polymer is also detected. These results are explained by the reduction of the intermolecular distances due to the volume contraction of the crystal cell. The polymer growth involves different pairs of molecules in the unit cell, other than

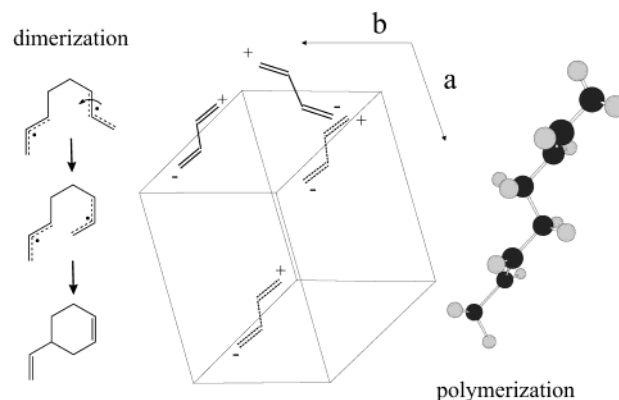


FIGURE 5. Schematic arrangement of the molecules in the monoclinic unit cell of butadiene. Only the molecules of interest for the discussion are shown, while the orientation and position of the other units can be found by translating the molecules reported in the figure along the cell axes. Dimerization occurs in the bc plane between the full molecules according to the mechanism sketched on the left side. Polymerization involves the molecules lying in the ab (dashed lines) or in the ac planes. Plus and minus signs indicate the position of the $\text{C}=\text{C}$ bonds with respect to the bc plane.

those responsible for the dimer formation, in such a way that only an out-of-phase translational motion is required to bring the molecules into a suitable configuration for a head-to-tail interaction (dashed molecules in Figure 5). The polymeric chains formed according to this scheme produce vacancies in the lattice that favor the rate-determining step of the dimerization reaction (the internal rearrangement), accelerating the formation of the dimer.³¹

When laser irradiation is employed to trigger the reactivity of the crystal, different effects are observed. The polymerization reaction is induced also below 4 GPa, and the amount of polymer produced increases with the irradiation time, being, in any case, much higher than that in the purely pressure-induced reaction. Nevertheless, in contrast to the results obtained in the liquid phase, the dimerization always prevails over the polymerization reaction. This result can be explained by considering that the laser light is absorbed through a two-photon process, like in the liquid phase, and the molecules excited to the S_1 (2^1A_g) state are stretched ($\sim 7\%$), making the intermolecular distances shorter. The effect is therefore analogous to that obtained by raising the pressure (higher density) or the temperature (larger amplitude of the lattice motions); nevertheless, the decrease in the intermolecular distances is less isotropic in the laser-assisted reaction, being directed along the molecular backbone so that the selective head-to-tail attack, and then the polymerization process, is favored. Also in this case, the polymer formation speeds up the dimerization process, favoring the internal rearrangement step.

2.1.3. Other Systems. Preliminary results concerning the optical catalysis of high-pressure polymerization reactions have also been obtained in other two model systems: ethylene and propylene. Polyethylene is obtained in syntheses activated by both radical initiators and catalysts, while polypropylene is generally prepared from the monomer by only catalytic methods. In both cases,

the preparation method determines the characteristics of the final product. Linear polyethylene is by far more interesting than the branched one, and when linear chains having a molecular weight larger than $(3-5) \times 10^6$ are produced, we are looking at one of the most resistant materials. On the other hand, the position of the methyl group with respect to the polymer backbone is the feature that determines the properties of polypropylene (tacticity).

Compressed ethylene reacts in the solid phase at 2.5 GPa,³³ whereas propylene starts to transform at 3.1 GPa when it is likely still liquid. Both reactions, characterized by IR absorption spectroscopy, show a slow evolution with time, and in the case of propylene the reaction does not proceed further after only a small amount of monomer is transformed. Polyethylene and a mixture of propylene oligomers are obtained in the two reactions. Even though a full characterization of the laser-assisted reaction is not yet available, we obtained two important results when an optical catalysis was employed. First, the reaction threshold pressure is lower under irradiation, and thus the transformations are observed in both cases below 1 GPa. The wavelength dependence is currently under investigation; therefore, a precise picture of the electronic states responsible for the reaction activation cannot be obtained, but in both cases the molecules are likely excited to the lowest singlet excited state, corresponding to a π^* -antibonding configuration. The second effect is that both reactions are greatly speeded up, allowing the amount of propylene transformed to be substantially increased, while all the monomer converts to the polymer in the case of ethylene. Therefore, in these cases the catalytic role of the laser light is also two-fold: to increase the reaction yield and to define less drastic pressure conditions for the reaction to occur.

2.2. Reactivity of Aromatic Molecules. Aromatic molecules are, in general, characterized by a different high-pressure reactivity with respect to linear unsaturated hydrocarbons, because the stability of the aromatic ring makes the pressure threshold for the reaction much higher. A reactivity scale analogous to that of the isolated molecule is found for the simplest aromatic and heteroaromatic systems; in fact, in order of increasing molecular instability, benzene, thiophene, and furan react at 21–23,^{34,35} 16,³⁶ and 10 GPa,³⁷ respectively. In more complex molecules containing other reactive centers, such as phenylacetylene ($C\equiv C$) and styrene ($C=C$), the reaction occurs at lower pressure, driven by the greater reactivity of these groups, and does not involve the aromatic ring.^{38,39} Another important difference with respect to the linear hydrocarbons is that the reaction kinetics are too fast to be detected by a frequency-resolved technique and evolve only upon increasing the temperature or the pressure. The mechanism of the reaction has been identified in the case of benzene³⁵ and later confirmed in furan.³⁷ With increasing pressure, there is a progressively growing interaction among nearest-neighbor carbon atoms belonging to different molecules, but only part of the monomer transforms when pressures 3–4 times larger than the threshold value of the reaction are applied. The reaction occurs

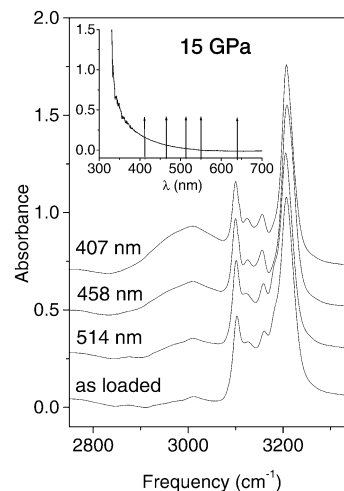


FIGURE 6. Photoinduced reaction in benzene at 15 GPa. The laser wavelength is tuned through the red absorption edge (see inset), and the effect of a 5-h irradiation cycle is revealed by the growth of the broad C–H absorption band due to saturated carbon atoms, which indicates the bonding among nearest-neighbor benzene molecules.

mainly when the pressure is released through opening the aromatic ring. This behavior is due to the large rearrangement the molecules must undergo to realize a four-fold coordination of the carbon atoms (saturated species characterize the recovered product); such rearrangement is inhibited at high pressure by the high density of the crystal. This scheme implies a lack of selectivity of the process since no preferential paths are identified on the basis of the crystal arrangement. The unselective ring opening and also the hydrogen migration are particularly clear in the case of furan, where the oxygen atom behaves as a marker of the reaction evolution.³⁷ The products recovered in these reactions are amorphous hydrogenated carbons (a:C–H) presenting interesting peculiar properties with respect to analogous samples prepared by CVD techniques.³⁵

The pressure of the reaction can be lowered considerably when laser light of suitable frequency is focused on the sample. Only qualitative information is available for thiophene, where the reaction pressure threshold drops to less than 10 GPa,³⁶ while a more carefully analysis has been performed for both benzene⁴⁰ and furan.⁴¹ Characterization of the pressure evolution of the electronic absorption edge of benzene allowed precise tuning of the exciting wavelength through this edge, revealing that the high-pressure reaction is activated in less drastic pressure conditions by exciting the molecules to the S_1 state⁴⁰ (Figure 6). This result opens different possibilities to explain the high-pressure reactivity of benzene. According to the picture provided by Drickamer for pentacene,¹⁰ the pressure increase can favor a large relative displacement of the ground and S_1 states, considerably reducing the thermal activation energy for this transition. Unfortunately, calculation of this thermal barrier from the optical transition energy requires the knowledge of specific parameters, such as the transition bandwidth,⁹ which are, in general, unknown at high pressure. From the estimation

of the thermal barrier on the basis of the available spectroscopic data, it is found that a huge pressure broadening is required in order to have a non-negligible thermal population on S_1 . Another possible interpretation is based on the change of the molecular geometry in the first singlet excited state, where a symmetric expansion of the ring occurs and all the C–C bond lengths increase by 3.7 pm.⁴² As a consequence, the distance between nearest-neighbor carbon atoms of two coplanar molecules, assuming the crystal structure given in ref 43, is reduced by 6.4 pm. According to our X-ray diffraction data, this reduction is very close to the distance decrease between nearest-neighbor C atoms of parallel molecules on going from 15 to 21 GPa, thus indicating that the distance between nearest-neighbor C atoms of different molecules is the same in the room-temperature pressure-induced reaction and in the laser-assisted reaction at 15 GPa. Recent IR and X-ray diffraction studies as a function of temperature show that the reaction threshold pressure is strongly temperature dependent, varying from 28 GPa at 100 K³⁵ to 13.5 GPa at 540 K. This result is readily interpreted as being due to the increased amplitude of the lattice motion on raising the temperature.¹⁶ By calculating the nearest-neighbor distances between C atoms at different reaction pressures, including also the displacement due to out-of-phase (zone boundary) translational motions, we obtain for all the different P – T points where the reaction occurs values ranging between 2.5 and 2.6 Å. This result indicates that the high-pressure reaction in benzene is driven by the relative distance of the molecules, which can be modified both thermally and photochemically.

In the photoinduced reaction of furan, the reaction pressure is lowered to 3 GPa when the 458-nm laser line is employed, and a precise threshold wavelength, red-shifting with increasing pressure,⁴⁴ is identified.⁴¹ This information, in combination with the knowledge of the electronic states at ambient pressure, points to a photochemical activation of the reaction through a two-photon absorption process. In contrast to the case with benzene, the products obtained in the pressure-induced and in the laser-assisted reactions present remarkable differences (see Figure 7). Comparison between the IR spectra of the recovered samples obtained in the two cases shows the presence of a considerable amount of carbon dioxide and an increase of the carbonyl absorption in the laser-assisted reaction, suggesting a preferential dissociation involving breakage of the C–O bonds. The two-photon energy employed in the high-pressure photoinduced reaction is very close to the onset of the absorption to the lowest excited states, all having Rydberg character in the isolated molecule with the exception of the 1^1B_2 and 2^1A_1 states, which have a mixed $\pi \rightarrow \pi^*$ valence-Rydberg and a pure $\pi \rightarrow \pi^*$ nature, respectively. Even though the Rydberg states have been found to be responsible for the photochemical dissociation of the isolated molecule through selective C–O bond cleavage,⁴⁵ their role at high pressure should be not relevant since only the electronic states having valence character should undergo a red shift with

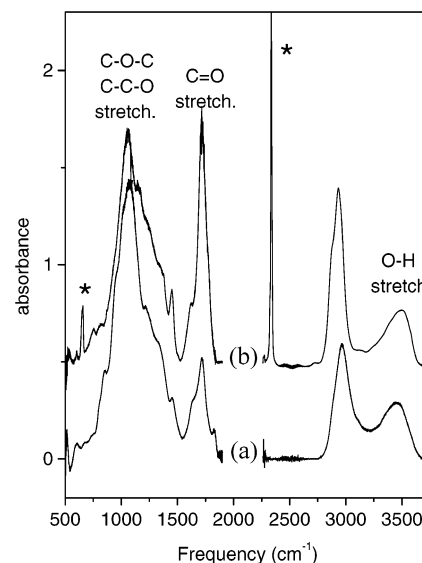


FIGURE 7. Comparison of the IR spectra of the compounds recovered by the purely pressure-induced (a) and by the laser-assisted reaction (b) of furan. Asterisks indicate the CO_2 absorption bands. Also remarkable is the intensification of the C=O stretching band in the laser-assisted reaction.

increasing pressure. As the pressure is increased, the products of the photoinduced reaction are progressively more similar to those of the purely pressure-induced reaction, demonstrating the importance of the molecular arrangement in the crystal. On going from the orientationally disordered phase IV to the ordered phase III ($4 \leq P \leq 6.5$ GPa),³⁷ CO_2 formation is gradually inhibited, probably due to molecular localization in positions that do not allow the simultaneous interaction of a carbon with two oxygen atoms.

3. Conclusions

The high-pressure chemistry of simple hydrocarbons differs substantially from the chemistry at ambient conditions as far as the products and the reaction mechanisms are concerned. These changes are due to the geometrical constraints posed by the higher density, and to the modification with pressure of the electronic molecular structure. High-pressure chemical reactions occur when specific interaction orientations and distances are realized among the molecules of the compressed fluid or solid. It is easy to understand that, under these conditions, the effect of producing excited molecules through light absorption corresponds to altering the molecular and electronic structure and can result in creating the conditions for the reaction to occur. In this Account, we have reported some examples of laser-assisted high-pressure reactions of very simple model molecules. We have shown that the laser light absorption is extremely powerful for lowering the reaction threshold pressure in almost all the systems studied. This is a very important result, allowing for a possible extension of these synthetic methods to industrial large-volume presses. Furthermore, by modifying the molecular and electronic structure, new reaction channels can be opened or, alternatively, a specific path

can be selected among competitive reactive processes, as clearly demonstrated in the case of butadiene. At the present time, the main limitations to these studies are represented by the missing knowledge of the behavior of the electronic states as a function of pressure, which is mandatory to understand which states are involved in the reaction, and a big effort should be made in this direction. We think that these results reveal the potential of a new field that, although still in its infancy, opens new possibilities for specific synthesis, polymerization for instance, to be entirely realized with physical methods.

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References

- McMillan, P. F. New materials from high-pressure experiments. *Nature Mater.* **2002**, *1*, 19–25.
- Hemley, R. J. Effects of high pressure on molecules. *Annu. Rev. Phys. Chem.* **2000**, *51*, 763–800.
- Schettino, V.; Bini, R. Molecules under extreme conditions: Chemical reactions at high pressure. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1951–1965.
- High-Pressure Phenomena*; Chiarotti, G. L., Bernasconi, M., Ulivi, L., Hemley, R. J., Eds.; International School of Physics "Enrico Fermi" 147; IOS Press: Amsterdam, 2002.
- Gorelli, F.; Santoro, M.; Ulivi, L.; Bini, R. The epsilon phase of solid oxygen: evidence of an O₄ molecule lattice. *Phys. Rev. Lett.* **1999**, *83*, 4093–4096.
- Iota, V.; Yoo, C. S.; Cynn, H. Quartzlike carbon dioxide: an optically nonlinear extended solid at high pressures and temperatures. *Science* **1999**, *283*, 1510–1513.
- Eremets, M. I.; Hemley, R. J.; Mao, H. K.; Gregoryanz, E. A. Semiconducting non-molecular nitrogen up to 240 GPa and its low-pressure stability. *Nature* **2001**, *411*, 170–174.
- Bini, R. Chemical transformations of molecular crystals at high pressure. In *High-Pressure Phenomena*; Chiarotti, G. L., Bernasconi, M., Ulivi, L., Hemley, R. J., Eds.; International School of Physics "Enrico Fermi" 147; IOS Press: Amsterdam, 2002; p 455.
- Drickamer, H. G.; Frank, C. W.; Slichter, C. P. Optical versus thermal transitions in solids at high pressure. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 933–937.
- Drickamer, H. G.; Frank, C. W. *Electronic transitions and the high pressure chemistry and physics of solids*; Chapman and Hall: London, 1973.
- Katz, A. I.; Shiferl, D.; Mills, R. L. New phases and chemical reactions in solid CO under pressure. *J. Phys. Chem.* **1984**, *88*, 3176–3179.
- Lipp, M.; Evans, W. J.; Garcia-Baonza, V.; Lorenzana, H. E. Carbon monoxide: spectroscopic characterization of the high-pressure polymerized phase. *J. Low Temp. Phys.* **1998**, *111*, 247–256.
- Agnew, S. F.; Swanson, B. I.; Jones, L. H.; Mills, R. L. Disproportionation of nitric oxide at high pressure. *J. Phys. Chem.* **1985**, *89*, 1678–1682.
- Eckert, B.; Schumacher, R.; Jodl, H. J.; Foggi, P. Pressure and photoinduced phase transitions in sulphur investigated by Raman spectroscopy. *High Pressure Res.* **2000**, *17*, 113–146.
- Mao, H. K.; Bell, P. M.; Shaner, J. V.; Steinberg, D. J. Specific volume measurements of Cu, Mo, Pd, and Ag and calibration of the ruby R1 fluorescence pressure gauge from 0.06 to 1 Mbar. *J. Appl. Phys.* **1978**, *49*, 3276–3283.
- Ceppatelli, M.; Santoro, M.; Bini, R.; Schettino, V. Fourier transform infrared study of the pressure and laser induced polymerization of solid acetylene. *J. Chem. Phys.* **2000**, *113*, 5991–6000.
- Aoki, K.; Usuba, S.; Yoshida, M.; Kakudate, Y.; Tanaka, K.; Fujiwara, S. Raman study of the solid-state polymerization of acetylene at high pressure. *J. Chem. Phys.* **1988**, *89*, 529–534.
- Trout, C. C.; Badding, J. V. Solid-state polymerization of acetylene at high pressure and low temperature. *J. Phys. Chem. A* **2000**, *104*, 8142–8145.
- Moses, D.; Feldblum, A.; Ehrenfreund, E.; Heeger, A. J.; Chung, T. C.; MacDiarmid, A. G. Pressure dependence of the photoabsorption of polyacetylene. *Phys. Rev. B* **1982**, *26*, 3361–3369.
- Sakashita, M.; Yamawaki, H.; Aoki, K. FT-IR study of the solid state polymerization of acetylene under pressure. *J. Phys. Chem.* **1996**, *100*, 9943–9947.
- Miller, G. H. Thermal polymerization of butadiene to solid polymer. *J. Polym. Sci.* **1960**, *43*, 517–525.
- Benson, S. W. Mechanism of the Diels–Alder reactions of butadiene. *J. Chem. Phys.* **1967**, *46*, 4920–4926.
- Citroni, M.; Ceppatelli, M.; Bini, R.; Schettino, V. Laser-induced selectivity for dimerization versus polymerization of butadiene under pressure. *Science* **2002**, *295*, 2058–2060.
- Chadwick, R. R.; Zgierski, M. Z.; Hudson, B. S. Resonance Raman scattering of butadiene: Vibronic activity of a *b_u* mode demonstrates the presence of a ¹A_g symmetry excited electronic state at low energy. *J. Chem. Phys.* **1991**, *95*, 7204–7211.
- Doering, J. P.; McDiarmid, R. J. Electron impact study of the energy levels of trans-1,3-butadiene: II. Detailed analysis of valence and Rydberg transitions. *J. Chem. Phys.* **1980**, *73*, 3617–3624.
- Galasso, V. Ab initio study of the two-photon bound electronic transitions of trans-butadiene. *J. Chem. Phys.* **1988**, *89*, 4529–4534.
- Kohler, B. E. Octatetraene photoisomerization. *Chem. Rev.* **1993**, *93*, 41–54.
- Olivucci, M.; Ragazos, I. N.; Bernardi, F.; Robb, M. A. A conical intersection mechanism for the photochemistry of butadiene. *J. Am. Chem. Soc.* **1993**, *115*, 3710–3721.
- Aoyagi, M.; Osamura, Y.; Iwata, S. An MCSCF study of the low-lying states of trans-butadiene. *J. Chem. Phys.* **1985**, *83*, 1140–1148.
- Aoyagi, M.; Osamura, Y. A theoretical study of the potential energy surface of butadiene in the excited states. *J. Am. Chem. Soc.* **1989**, *111*, 470–474.
- Citroni, M.; Ceppatelli, M.; Bini, R.; Schettino, V. Phase-diagram and crystal phases of trans-1,3-butadiene probed by FTIR and Raman spectroscopy. *Chem. Phys. Lett.* **2003**, *367*, 186–192.
- Citroni, M.; Ceppatelli, M.; Bini, R.; Schettino, V. The high-pressure chemistry of butadiene crystal. *J. Chem. Phys.* **2003**, *118*, 1815–1820.
- Wieldraaij, H.; Schouten, J. A.; Trappeniers, N. J. Investigation of the phase diagrams of ethane, ethylene and methane at high pressures. *High Temp.-High Pressure* **1983**, *15*, 87–92.
- Pruzan, Ph.; Chervin, J. C.; Thiery, M. M.; Itie, J. P.; Besson, J. M. Transformation of benzene to a polymer after static pressurization. *J. Chem. Phys.* **1990**, *92*, 6910–6915.
- Ciabini, L.; Santoro, M.; Bini, R.; Schettino, V. High-pressure reactivity of solid benzene probed by infrared spectroscopy. *J. Chem. Phys.* **2002**, *116*, 2928–2935.
- Pruzan, Ph.; Chervin, J. C.; Forgerit, J. P. Chemical and phase transformations of thiophene at high pressures. *J. Chem. Phys.* **1992**, *96*, 761–767.
- Ceppatelli, M.; Santoro, M.; Bini, R.; Schettino, V. High-pressure reactivity of solid furan probed by infrared and Raman spectroscopy. *J. Chem. Phys.* **2003**, *118*, 1499–1506.
- Santoro, M.; Ciabini, L.; Bini, R.; Schettino, V. High-pressure polymerization of phenylacetylene and of the benzene and acetylene moieties. *J. Raman Spectrosc.* **2003**, *34*, 5579–5566.
- Gourdain, D.; Chervin, J. C.; Pruzan, Ph. Transformations of styrene at high pressure. *J. Chem. Phys.* **1996**, *105*, 9040–9045.
- Ciabini, L.; Santoro, M.; Bini, R.; Schettino, V. High-pressure photoinduced ring opening of benzene. *Phys. Rev. Lett.* **2002**, *88*, 085505.
- Santoro, M.; Ceppatelli, M.; Bini, R.; Schettino, V. High-pressure photochemistry of furan crystal. *J. Chem. Phys.* **2003**, *118*, 8321–8325.
- Klessinger, M.; Michl, J. *Excited states and photochemistry of organic molecules*; VCH Publishers: New York, 1995.
- Gauthier, M.; Chervin, J. C.; Pruzan, Ph. Pressure induced polymerization of cyclic molecules: a study of benzene and thiophene. In *Frontiers of High-Pressure Research*; Hochheimer, H. D., Eters, R. D., Eds.; Plenum: New York, 1991; pp 87–95.
- Wan, J.; Meller, J.; Hada, M.; Ehara, M.; Nakatsuji, H. Electronic excitation spectra of furan and pyrrole: Revisited by the symmetry adapted cluster configuration interaction method. *J. Chem. Phys.* **2000**, *113*, 7853–7866.
- Sorkhabi, O.; Qi, F.; Rizvi, A. H.; Suits, A. G. Ultraviolet photodissociation of furan probed by tunable synchrotron radiation. *J. Chem. Phys.* **1999**, *111*, 100–107.

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