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# Fourier transform infrared study of the pressure and laser induced polymerization of solid acetylene

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The polymerization of solid acetylene under pressure has been studied by Fourier transform infrared (FTIR) spectroscopy. Controlled laser irradiation cycles and the employment of infrared sensors to measure the sample pressure, allowed to separate the photochemical and the pressure effect on the injection and on the evolution of the reaction. The careful assignment of all the spectral features and analysis of their relative intensities and frequencies gave evidence to the specific effect of pressure and laser irradiation on the reaction products. Pressure induces an ordered growth of *trans*-polyenic species, while irradiation produces the opening of the double bonds and a consequent branching of the chains. Constant pressure measurements allowed to obtain precise information on the kinetics of the reaction. A monodimensional growth geometry, involving the molecules on the *bc* plane, agrees with the parameters extracted by the kinetic curves. Comparison between experiments at different temperatures suggests an activation of the reaction essentially due to the translational lattice modes.

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## I. INTRODUCTION

The high pressure techniques, developed in the last few decades, have shown how the thermodynamic and the microscopic properties of condensed matter can be strongly affected by a large variation of the density. The consequences of the variation of applied pressure over three order of magnitude (0.1–100 GPa) are much more impressive than those relative to the effect of temperature. High pressure can modify the structure of molecular crystals by changing the relative position and the orientation of the molecules; it can affect the electronic structure of the molecules, induce charge transfer processes and possibly change the chemical bonds. In this last case, polymerization is one of the most exciting phenomena and it has been investigated in several systems like cyanogen,<sup>1</sup> acetylene,<sup>2,3</sup> benzene,<sup>4</sup> CO.<sup>5</sup> Static experiments with the diamond anvil cell (DAC) are actually performed well above 100 GPa, making possible the investigation of such processes in a wide class of materials.

Because of the simple structure, acetylene can be regarded, both from experimental and computational point of view, as a model system for high pressure chemistry. Due to the high reactivity of the triple bond, polymerization of acetylene occurs in the orthorhombic phase at a moderate

pressure (3–4 GPa). The process is associated with a color change of the sample from transparent to deep red, and with the appearance of new characteristic vibrational bands.<sup>2,3</sup> In principle, the development of this reaction under pressure could represent a method to obtain polyacetylene chains, avoiding stabilizing groups and without solvents and catalysts. The importance of polyacetylenes lies in the electrical conductivity induced by the conjugated bonds. Combining the use of doping and photoexcitation, values of electrical conductivity as high as  $10^5 \Omega^{-1} \text{cm}^{-1}$  have been achieved.<sup>6</sup> At the present state of the art, the main interest in the pressure induced polymerization of acetylene is related to the selectivity of this process concerning the products of the reaction, the length of the polymeric chains and the optimization of the experimental parameters for obtaining long polymers.

The first experimental investigation of the solid state pressure induced polymerization of acetylene was reported by Aoki *et al.*,<sup>2</sup> by means of Raman spectroscopy. The experiment was performed at room temperature and the lowest polymerization pressure resulted to be 3.5 GPa. The probes of this measurement were the C≡C stretching mode of the monomer and the C=C stretching mode of the conjugated polymer. The results of this experiment indicated an essentially *trans* conformation of the obtained polymer and no saturated species were detected. Later, Sakashita *et al.*<sup>3</sup> stud-

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ied the polymerization of acetylene by infrared spectroscopy. In this case the polymerization occurred at 4.2 GPa, at room temperature, and the spectra showed the appearance of vibrational bands due to either saturated and unsaturated species. An *ab initio* simulation performed by Bernasconi *et al.*<sup>7</sup> found the polymerization to occur around 25 GPa, therefore at a much higher pressure than the experimental value. Nevertheless, the transformation pressure felt down to 9 GPa by inserting in the cell a molecule of acetylene in the first triplet state ( $\approx 30\,500\text{ cm}^{-1}$ ; Ref.8) where the molecule has a *cis* bent conformation. This result suggests that the injection mechanism, as well as the propagation of the reaction, can be strongly affected by the laser irradiation. The first singlet excited states of acetylene occur in the spectral region between  $40\,000$  and  $50\,000\text{ cm}^{-1}$  at zero pressure,<sup>9</sup> therefore two-photon absorption processes induced by the  $\text{Ar}^+$  laser radiation are possible. Both the experiments mentioned above used laser light, at least to measure the local pressure by the ruby fluorescence method, making questionable the conclusions drawn about the real pressure effects on the evolution of the reaction. The importance of the laser irradiation results also from the disagreement about the product species obtained in the two experiments. The observation of mainly *trans* conjugated species in the Raman experiment<sup>2</sup> was due to the use of a  $\text{Kr}^+$  laser (647 nm) which produces a strong resonance effect enhancing the vibrational peaks of the conjugated species respect to those of the saturated ones, whose electronic transitions are much higher in energy. Moreover, the resonance effect at the used wavelengths is much stronger for *trans* conjugated species than for the *cis* ones,<sup>10</sup> making the Raman experiment inadequate to discuss the products of the reaction. Finally, in both experiments constant pressure studies were precluded by the strong decrease in pressure, due to the volume contraction of the sample during the reaction, preventing any thermodynamic or kinetic consideration about the reaction.

In this paper we present an experimental investigation of the solid state high pressure induced polymerization of acetylene by using infrared spectroscopy. The main purpose of this work has been to separately investigate the role of pressure and laser irradiation on the polymerization process, to understand if the reaction was pressure, laser or both pressure-laser induced. We have developed a local pressure measurement method by using, as a gauge, an infrared vibrational band of an internal sensor. In this way we can avoid the presence of the laser source which is used in the ruby fluorescence technique. Furthermore, controlled laser irradiation cycles allowed to identify their specific effect on the evolution of the reaction. Second, we took care to keep the pressure on the sample constant during the whole process to investigate the kinetic of the reaction. This was allowed by the use of a membrane diamond anvil cell which allows to compensate any internal pressure drop, occurring during the polymerization, by varying the gas pressure in the membrane. We also paid a particular attention to the assignment of the observed bands to give a precise identification of the reaction products. Finally, we have investigated the effect of temperature on the reaction process by extending our study down to 200 K.

## II. EXPERIMENT

The membrane diamond anvil cell (MDAC) used for the high pressure infrared absorption measurements was equipped with type IIa diamonds. The typical sample dimensions were  $150\text{ }\mu\text{m}$  in diameter and  $40\text{--}50\text{ }\mu\text{m}$  in thickness. Acetylene gas (99.6%), obtained from Rivoira, was further purified from acetone impurities by bubbling through a  $\text{NaHSO}_3$  aqueous solution and then dried over fine granular calcium chloride. The infrared spectrum did not show any trace of impurities in the sample. Due to the instability of acetylene, the standard loading techniques (gas-loading and cryo-loading) could not be used because the large amount of condensed sample makes them unsafe. Therefore the minimum amount of acetylene necessary to fill the gasket hole was condensed directly on the diamond faces at about 190 K. In fact the triple point of acetylene is at  $P=1.282\text{ bar}$  and  $T=192.6\text{ K}$ , while at 1 bar the sublimation temperature is equal to 184.6 K.

In particular, the cell was placed in an inert nitrogen atmosphere and cooled down to 77 K by thermal contact with a liquid nitrogen bath. Only the lower part of the cell is in contact with the bath and there is no possibility for the sample chamber to be filled by liquid nitrogen. During the cooling, acetylene was always flown (0.1 bar) through a capillary directly into the sample region. The two diamonds were placed at a relative distance of  $100\text{--}200\text{ }\mu\text{m}$  and, to increase the efficiency of the condensation, a small indium dam was clamped to the gasket to force the gas coming from the capillary in the sample region. Solidification of acetylene inside the capillary was prevented by warming the final part of the gas line. When the temperature of the cell reached the value of 192 K, the gas started to solidify inside and around the sample region. As the solid sample was formed, the high pressure was applied between diamonds, blowing the helium gas inside the membrane. Finally the DAC was removed from the nitrogen bath, having a final internal pressure of 2–3 GPa at room temperature. In this condition the solid is in the orthorhombic phase, below the polymerization pressure. The whole loading procedure was carefully controlled by means of a microscope and the temperature measured by a sensor diode placed very close to the diamonds.

To separate the effects of pressure and laser irradiation, a vibrational gauge first proposed by Klug and Walley<sup>11</sup> was used to measure the internal pressure of the sample. It consists of a solid solution of  $\text{NaNO}_2$  in  $\text{NaBr}$ . The  $\text{NO}_2^-$  group has three infrared active vibrational modes with the strongly absorbing antisymmetric stretching ( $\nu_3$ ), at  $1279\text{ cm}^{-1}$ , having a quite narrow linewidth ( $10\text{--}20\text{ cm}^{-1}$ ) even at high pressure, and a position strongly dependent on pressure. Furthermore this line falls far away from the absorption bands of the acetylene. The other infrared active internal bands of the nitrite ion are very weak and do not perturb the spectrum of the host. Finally,  $\text{NaBr}$  is transparent to the infrared radiation and it has a phase transition at 29.0 GPa, well above our pressure range of interest. Klug and Walley performed a calibration of the sensor up to 18.6 GPa by means of the ruby fluorescence technique for two different composition of  $\text{NaNO}_2$  corresponding to 0.3% and 0.5% in weight of

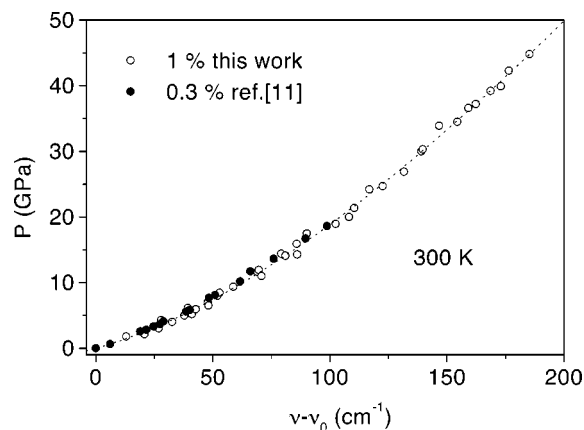


FIG. 1. Evolution with pressure of the frequency variation of the antisymmetric stretching mode ( $\nu_3$ ) of the  $\text{NO}_2^-$  ion in NaBr. The dotted line is the best fit according to Eq. (1).

$\text{NaNO}_2$ , respectively. In the present experiment only a small amount of salt was used in order to have enough acetylene to follow the reaction. Therefore, the  $\text{NaNO}_2$  concentration was increased to 1%. The influence of the  $\text{NaBr}/\text{NaNO}_2$  solid solution on the polymerization was checked by leaving for 32 h a sample of solid acetylene on the 1% saline mixture at 2.4 GPa, i.e. just below the lowest measured polymerization pressure. Neither detectable signatures of the polymer in the infrared spectrum nor color change (red) of the sample were observed. This led us to conclude that a catalytic effect of the salt mixture on the reaction could be ruled out. A calibration up to 44.8 GPa was performed using different samples. In Fig. 1 the pressure, measured by the ruby fluorescence method (nonlinear hydrostatic), versus the frequency shift of the  $\text{NO}_2^-$  vibron line relative to the  $P=0$  value ( $\nu_0 = 1278.67 \text{ cm}^{-1}$ ) is reported. In the figure data from literature are also reported showing a very good agreement with the present measurements. The data can be fitted with the function:

$$P = a_1 \Delta\nu - a_2 \Delta\nu e^{-(\Delta\nu/a_3)}, \quad (1)$$

where  $\Delta\nu = \nu - \nu_0$  and the fitting values are:  $a_1 = 0.376 \text{ GPa cm}$ ,  $a_2 = 0.277 \text{ GPa cm}$  and  $a_3 = 255 \text{ cm}^{-1}$ . It is interesting to note that the phase transition of NaBr at 29.0 GPa does not affect the intrinsic parameters of the  $\text{NO}_2^-$  band ( $\nu$ ,  $\Gamma$  and  $I$ ) making this method reliable up to 50 GPa. Furthermore, the  $\nu_3$  frequency changes at ambient pressure by only  $0.01 \text{ cm}^{-1}/\text{K}$  between 2 and 300 K, therefore the room temperature calibration curve can be confidently used also in the experiment at 200 K.

Infrared spectra were taken in a FTIR spectrometer (Bruker IFS-120HR) equipped with a MCT detector, a glow-bar lamp and a KBr beam splitter. An optical condensing system composed of two ellipsoidal aluminum coated mirrors was used to focus the infrared beam on the small gasket hole. A cold finger was also coupled to the interferometer as described elsewhere.<sup>12</sup> The instrumental resolution was  $1.0 \text{ cm}^{-1}$  and each spectrum resulted from a sum over 500 scans. Three different types of experiment were realized in the present study and denoted in the following as: (A) room temperature experiment using the ruby fluorescence tech-

nique for the pressure measurement; (B) also at room temperature, with the local pressure measurement using the  $\text{NO}_2^-$  vibrational sensors; (C) 200 K experiment using the  $\text{NO}_2^-$  sensors.

### III. RESULTS

The full spectral region between 500 and  $4500 \text{ cm}^{-1}$  was investigated by measuring the infrared spectra at constant pressure and monitoring the polymerization process as a function of time. In this region the spectrum of solid acetylene is dominated by the infrared allowed  $\nu_3$  (antisymmetric C–H stretching) and  $\nu_5$  (antisymmetric C–H bending) modes at  $3200$  and  $750 \text{ cm}^{-1}$ , respectively, and by the  $\nu_4 + \nu_5$  combination mode at about  $1420 \text{ cm}^{-1}$  ( $\nu_4$  being the C–H symmetric bending). Acetylene crystallizes at room temperature in the cubic  $\text{Pa}3$  ( $T_h^6$ ) structure at 0.7 GPa and transforms at  $1.0 \text{ GPa}^{2,3}$  into an orthorhombic phase with structure  $\text{Cmca}$  ( $D_{2h}^{18}$ ) with  $Z=2$ .<sup>13,14</sup> In this phase two and three infrared active components are expected for the  $\nu_3$  and the  $\nu_5$  modes, respectively.<sup>15</sup> Due to the strong absorption none of these Davydov components is resolved in our spectra. The progressive weakening of all the acetylene bands and the appearing of new absorption bands ascribed to the polymer were considered as evidences of the reaction.

The A type experiment was carried at room temperature and at a constant pressure of  $4.0 \pm 0.1 \text{ GPa}$ . The local pressure was measured by the ruby fluorescence technique using an  $\text{Ar}^+$  multi-line laser as excitation source. The sample was irradiated for a few seconds ( $\leq 10 \text{ s}$ ) every 15–20 min with a power, measured just before the MDAC, of  $\approx 0.4 \text{ mW}$ . Immediately after loading the cell, the internal pressure of the sample was 3.8 GPa, the polycrystalline sample was transparent and only the acetylene spectral features were detected in the infrared spectrum. Then, the pressure was quickly reduced to a value (3.0 GPa) lower than the reported polymerization threshold.<sup>2,3</sup> Nevertheless, after about 60 h the sample assumed a bright red color and the pressure dropped to 2.6 GPa, clear evidences of the polymerization process. Since, however, the presence of polymeric species was hardly detectable in the infrared spectrum, we raised the pressure up to 4.0 GPa. Spectra were taken every 0.5 h at the beginning of the kinetics, and later at larger time steps. In Fig. 2(a) four representative spectra of the C–H bending region recorded at the beginning (0.0 h), at intermediate stages (3.9 h, 9.1 h) and at the end of the reaction (42.2 h) are shown. In this region of the spectrum, characterized by the strong  $\nu_5$  mode of acetylene, the onset of the reaction is easily detectable because the product bands do not overlap with the acetylene bands. On the high frequency side of the acetylene ( $\nu_5$ ) band two weak peaks at  $923$  and  $987 \text{ cm}^{-1}$  appear, whose intensity increases as the reaction evolves. Also a weak broadband, at about  $860 \text{ cm}^{-1}$ , is observed in the last spectrum. The spectra change very slowly after about 20 h indicating that an equilibrium has been reached. However, the intensity of the strong ( $\nu_5$ ) acetylene mode decreases during the reaction, but it always remains out of scale indicating that a significant amount of unreacted monomer is still present.



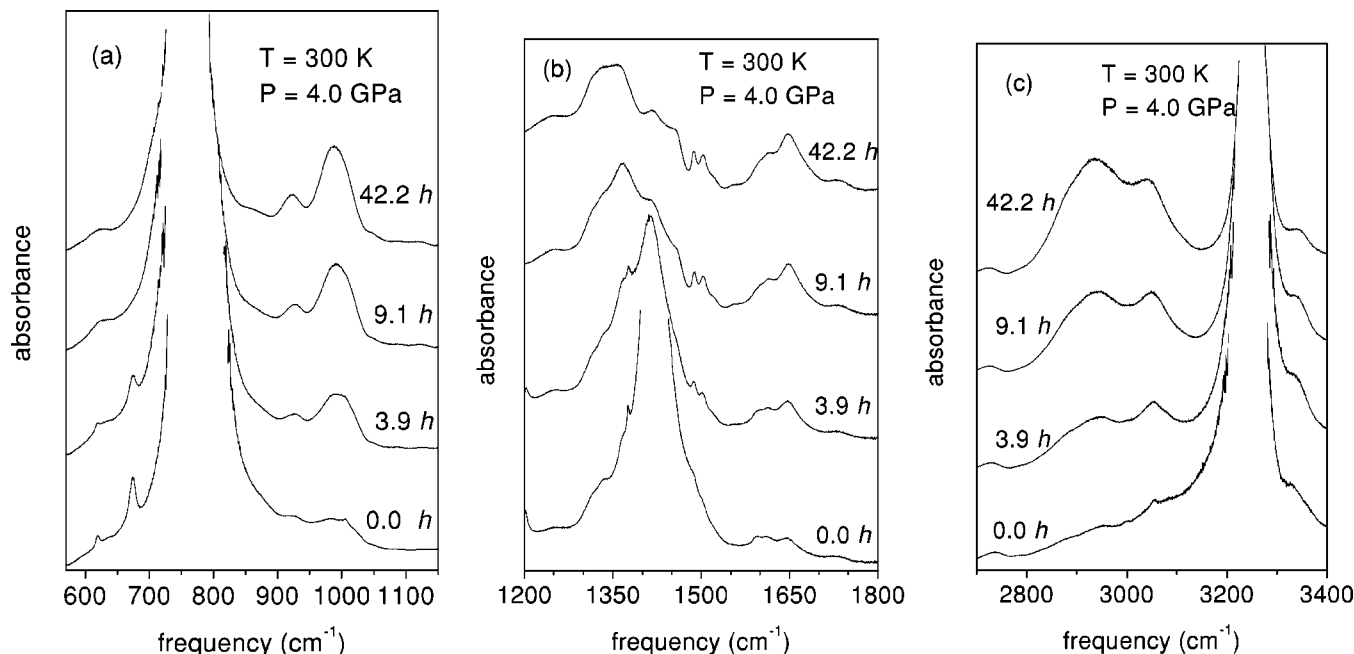


FIG. 2. Time evolution of the spectra in: (a) C=C-H antisymmetric bending ( $\nu_5$ ) region of acetylene; (b) region of the  $\nu_4 + \nu_5$  combination mode of acetylene and of the C=C stretching modes of polyacetylene; (c) C-H stretching modes region.

The spectral region where the C=C stretching modes of the polymeric species are expected is shown in Fig. 2(b). In the acetylene spectrum the region is dominated by the  $\nu_4 + \nu_5$  combination band at about  $1420\text{ cm}^{-1}$ . The intensity of this band decreases rapidly disappearing at the end of the kinetics. A complex structure is observed between  $1550$  and  $1700\text{ cm}^{-1}$ , where three components can be distinguished at  $1596$ ,  $1612$  and  $1647\text{ cm}^{-1}$ . The first band is probably due to an impurity since its intensity does not change as the reaction proceeds, while an increasing absorption is observed for the  $1612$  and  $1617\text{ cm}^{-1}$  peaks. At  $1487$  and  $1503\text{ cm}^{-1}$  two narrow peaks, with a weak shoulder at  $1522\text{ cm}^{-1}$ , are visible after a few hours from the beginning of the reaction. On the high frequency side of the acetylene combination band a weak and broad peak appears at  $1453\text{ cm}^{-1}$ .

The C-H stretching region is shown in Fig. 2(c). The intensity of the strong acetylene absorption bands decreases during the reaction, but it remains always out of scale. On the low frequency side a broad feature develops with two overlapped peaks centered at  $2938\text{ cm}^{-1}$  and at  $3042\text{ cm}^{-1}$  and a clear shoulder at  $2880\text{ cm}^{-1}$ .

After the reaction reached its equilibrium and the spectra did not show further changes with time, the sample was continuously irradiated for two periods of  $7.5\text{ h}$  with the output of an  $\text{Ar}^+$  laser using a  $8\text{ mW}$  incident power. Upon laser irradiation the reaction started again as it is monitored by the remarkable intensity decrease of the monomer absorption bands and the growth of new peaks. The effect of laser irradiation can be seen from Fig. 3. In Fig. 3(a) the significant increase of the  $1453\text{ cm}^{-1}$  peak can be appreciated. In Fig. 3(b) the C-H stretching region is shown and it can be seen that, while the monomer absorption considerably decreases upon irradiation, the  $2938\text{ cm}^{-1}$  peak increases while the  $3042\text{ cm}^{-1}$  peak does not seem to be much affected. As it

will be clearly shown in the following, as soon as the laser is turned off, the reaction immediately stops.

The B type experiment was carried out at the same pressure and temperature of the A type one. The only difference was the pressure measurement which was made using the  $\text{NO}_2^-$  vibrational sensors therefore avoiding any interaction with the laser beam. The spectral evolution with pressure was essentially identical as in the A type experiment. Some minor differences in the kinetics will be discussed in the next sections together with the detailed analysis of the data. These results confirm the intrinsic role of the pressure in the solid state polymerization of acetylene. The equilibrium of the reaction was reached in about  $20\text{ h}$ . After  $73.3\text{ h}$  the pressure was increased up to  $7.7\text{ GPa}$  and the reaction started again. When the new equilibrium was reached, the sample was irradiated with the  $\text{Ar}^+$  laser observing a further evolution of the reaction as already described above.

Type C experiment was carried at  $200\text{ K}$  in order to investigate the role of the temperature on the pressure induced polymerization. The local pressure was measured with the  $\text{NO}_2^-$  sensors. Once the orthorhombic crystal was obtained at room temperature and  $2.5\text{ GPa}$ , the sample was cooled isobarically at  $200\text{ K}$  and then the pressure increased in steps of  $1\text{ GPa}$ . After each step the infrared spectra were monitored for  $36\text{ h}$  to check the appearance of polymer bands. Such bands were observed only around  $9\text{ GPa}$ , so that the kinetic evolution of the polymerization process was studied at  $9.4 \pm 0.1\text{ GPa}$ . The higher pressure required to observe the reaction at such a low temperature causes a very strong broadening of most of the spectral features. In these conditions the process is very slow and the reaction takes about  $80\text{ h}$  to achieve the equilibrium. The only spectral region where

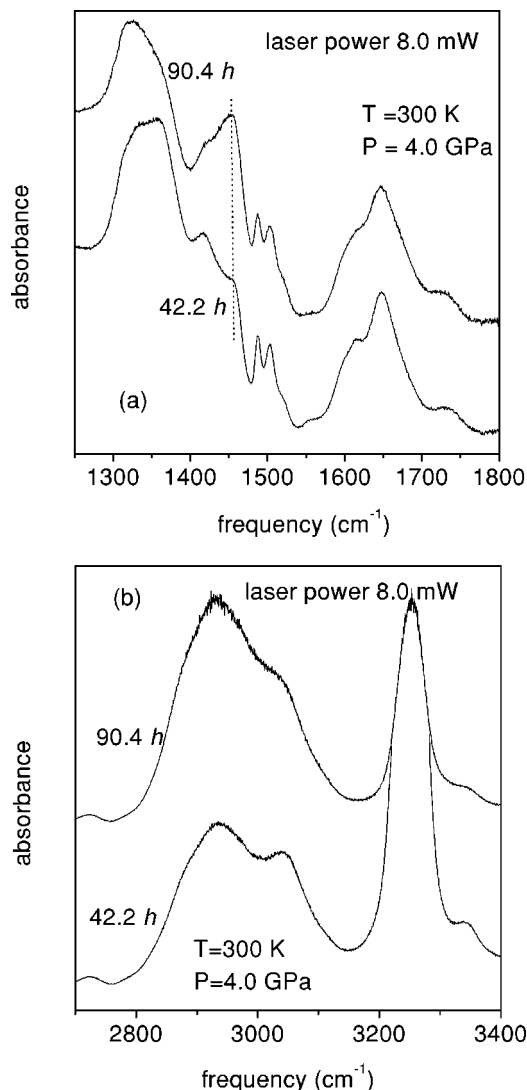


FIG. 3. Spectral regions where the effects of the laser irradiation are more evident: (a) region of the  $\nu_4 + \nu_5$  combination mode of acetylene; the dotted line identifies the band strongly intensified under irradiation; (b) the C–H stretching region. In both cases the last spectrum measured before to irradiate the sample (42.2 h), and the last after the two irradiation cycles (90.4 h) are reported.

the polymeric peaks can be clearly distinguished is that of the C–H bending of acetylene.

#### IV. ASSIGNMENT OF THE SPECTRA

All the spectral features described in the previous paragraph, which appear and grow during the process, can be easily assigned to polymeric species. First, the characteristic bands of saturated and unsaturated species must be identified and then the different conformers (*trans*-, *cis*-) of the latters must be distinguished.

The absorptions relative to unsaturated species were mainly identified by comparison with the experimental data on the longest unsubstituted polyenes available, octatetraene and decapentaene, either in *trans* and in *cis* conformation.<sup>16–18</sup> Even though these data were obtained at zero

pressure, they can be used with confidence because the frequencies are weakly dependent on pressure for these systems.<sup>3</sup>

It is worth to first discuss the low frequency region of the spectrum [see Fig. 2(a)] where a doublet (923 and 987  $\text{cm}^{-1}$ ) develops, as the pressure induced reaction proceeds, with an intensity ratio of the high ( $I_H$ ) to the low ( $I_L$ ) frequency band  $I_H/I_L=4$ . This doublet, assigned to out of plane C–H bending motions, is also present in both *trans,trans*-1,3,5,7-octatetraene and in *cis,cis*-1,3,5,7-octatetraene (see Table I) accompanied by an additional weak intermediate component. While in the *trans* isomer the intensity ratio  $I_H/I_L$  is slightly larger than 1, in the *cis* isomer it is smaller than 0.1. From this, one can conclude that the polyene chains formed during the reaction should be in the *trans* conformation. This analysis can be farther pursued considering the results recently reported by Schettino *et al.*<sup>19</sup> on DFT calculations of the vibrational frequencies and intensities of linear polyenes with a number of C atoms up to 24. It is found by calculations and confirmed by comparison with experiments that the intensity ratio  $I_H/I_L$  for the doublet in discussion rapidly increases with the chain length and that only the higher frequency component finally survives in an infinite polyacetylene chain.<sup>6</sup> From the results of Schettino *et al.*,<sup>19</sup> and considering the  $I_H/I_L$  ratio observed experimentally, it can be guessed that chains with at least nine conjugated double bonds should be formed during the pressure reaction. Furthermore, from analysis of this spectral region there is no evidence of the formation of saturated polymers. In fact, in the spectra of alkanes measured at zero pressure one or two intense absorption bands, assigned to the rocking-twisting modes of the methylene group, are observed between 720 and 750  $\text{cm}^{-1}$  depending on the length of the paraffinic chain, and a medium intensity peak around 900  $\text{cm}^{-1}$  due to the rocking of the  $-\text{CH}_2$  group is expected.<sup>20</sup> None of these bands were detected in our spectrum.

The assignment of the C=C stretching modes is more complicated since the infrared frequencies are strongly dependent on the conjugated chain length.<sup>19</sup> For instance, the most intense Raman C=C stretching band decreases regularly in frequency with increasing chain length, ranging from 1663  $\text{cm}^{-1}$  in butadiene to 1453  $\text{cm}^{-1}$  in polyacetylene. In the present experiments two distinct features [see Fig. 2(b)], that can be assigned as C=C stretching modes, have been observed. The first occurs at 1647  $\text{cm}^{-1}$  with some structure and a shoulder at low frequency ( $\approx 1615 \text{ cm}^{-1}$ ). The second feature is a weak and sharp doublet observed at 1487–1503  $\text{cm}^{-1}$  with an overall intensity approximately 1/10 of the 1647  $\text{cm}^{-1}$  peak. Schettino *et al.*<sup>19</sup> calculated the infrared spectrum of polyenes with chain lengths up to 12 double bonds. From the additional results available from Ref. 19, the evolution of the infrared spectrum in the C=C region is calculated as shown in Fig. 4. It can be seen that, at least for moderate chain length, the highest infrared intensity is always in the 1600–1650  $\text{cm}^{-1}$  region, while for longer chain a second much weaker absorption, whose intensity was enhanced in Fig. 4, is observed at frequencies just above 1500  $\text{cm}^{-1}$ . Since the weak doublet is observed just below 1500  $\text{cm}^{-1}$ , it is reasonable to assign it as arising from overlap-

TABLE I. Frequencies and intensities of the infrared C–H bending and C=C stretching modes in *trans,trans*-1,3,5,7-octatetraene (t,t-o) and in *cis,cis*-1,3,5,7-octatetraene (c,c-o).

Mode	t,t-o <sup>a,b</sup>		Mode	c,c-o <sup>a</sup>	
	$\nu$ (cm <sup>-1</sup> )	I (ir)		Freq (cm <sup>-1</sup> )	I (ir)
CH bend	897	96.6	CH bend	947	133.8
	954	19.8		987	13.0
	1007	114.2		1031	11.7
C=C stretching	1584	7.5	C=C stretching	1550	10.6
	1631	21.8		1619	2.1

<sup>a</sup>Reference 16.<sup>b</sup>Reference 19.

ping absorptions of conjugated segments with more than 12 double bonds. This inference is in agreement from what was argued from the analysis of the C–H out of plane bending region discussed above. The 1453 cm<sup>-1</sup> band is a characteristic absorption feature of alkanes to be assigned to saturated C–H bending motions. The quite low intensity of this band in the spectra of Fig. 2(b) implies that only a small amount of saturated species is formed during the pressure induced reaction. The interesting point is that upon laser irradiation the intensity of this band increases considerably, thus indicating that the laser radiation mostly promotes the generation of saturated species. On the other hand, the change of the carbon atoms from an sp<sup>2</sup> to an sp<sup>3</sup> hybridization must be accompanied by a break of the conjugation length, through a branching of the polyacetylene chains. One could argue that this process should mostly affect the bands ascribed to longer polyenic sequences and not much the shorter ones that are likely already connected in branched areas of the sample. As a matter of fact, in the spectral region under discussion the increase of the absorption intensity at 1453 cm<sup>-1</sup> is accompanied by a decrease of the 1487–1503 cm<sup>-1</sup> doublet previously assigned to long sequences, while the shorter polyene feature at 1643 cm<sup>-1</sup> is not much affected (Fig. 3).

A detailed assignment of the peaks in the C–H stretching region is not possible because of the broadening and overlap of the bands. However, it is clear that the feature peaked at 2950 cm<sup>-1</sup>, whose intensity remarkably increases upon laser irradiation, should be assigned to C–H stretching modes of saturated species, while the 3050 cm<sup>-1</sup> band is due to unsaturated polyenic segments (Fig. 3).

## V. KINETICS

In the previous section the assignment of the spectral features to product species developing during the polymerization reaction has been discussed. For a more detailed analysis of the time evolution of the various products the complex spectral patterns observed were fitted with pseudo-Voigt line shape functions. The evolution of the integrated absorption intensity of the various peaks as a function of time was obtained. The results are presented in Figs. 5(a)–5(f). The observed behavior is well reproduced by the Avrami's law:

$$A(t) = A_{\infty} [1 - e^{-(t-t_0)/\tau}]^n \quad (2)$$

originally proposed to model the crystal growth from a liquid phase<sup>21</sup> and later applied by Yoo *et al.*<sup>1</sup> to solid state polymerization processes. In Eq. (2)  $A(t)$  and  $A_{\infty}$  are the band intensities at time  $t$  and at the equilibrium, respectively;  $t_0$  is the initial time related to the nucleation step,  $\tau$  is the rise time constant and  $n$  is a parameter whose value depends on the growth geometry of the process. The value of  $\tau$  and  $n$  are collected in Table II. From Figs. 5(a)–5(f) a nucleation time, particularly in the B type experiments (empty circles), is evident. The nucleation step is not included in the Avrami's model and was not considered in the fitting procedure. It can be seen that in the A type experiment the product bands intensity is larger by approximately a factor of 3. This is due to the use of the NO<sub>2</sub><sup>-</sup> sensors in the B type experiment which reduce the sample volume.

In Fig. 5(a) the time evolution of the intensity of the two polyacetylenic C–H bending peaks at 923–987 cm<sup>-1</sup> is shown. By comparing the two kinetic curves, for  $t \leq 5$  h, it can be seen that in the B type experiment the full nucleation process was observed. In the A type experiment two different irradiation cycles (45–52 h and 68–75 h) were performed,

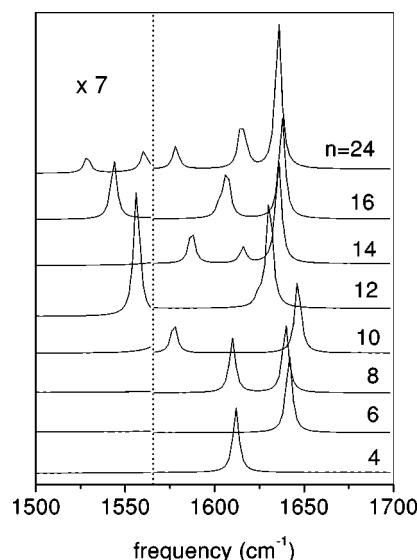


FIG. 4. Calculated infrared spectra, at 300 K and ambient pressure, of the C=C stretching region as a function of the number  $n$  of C atoms (Ref. 19). The intensity of the frequency region on the left of the dashed line was multiplied by a factor 7.

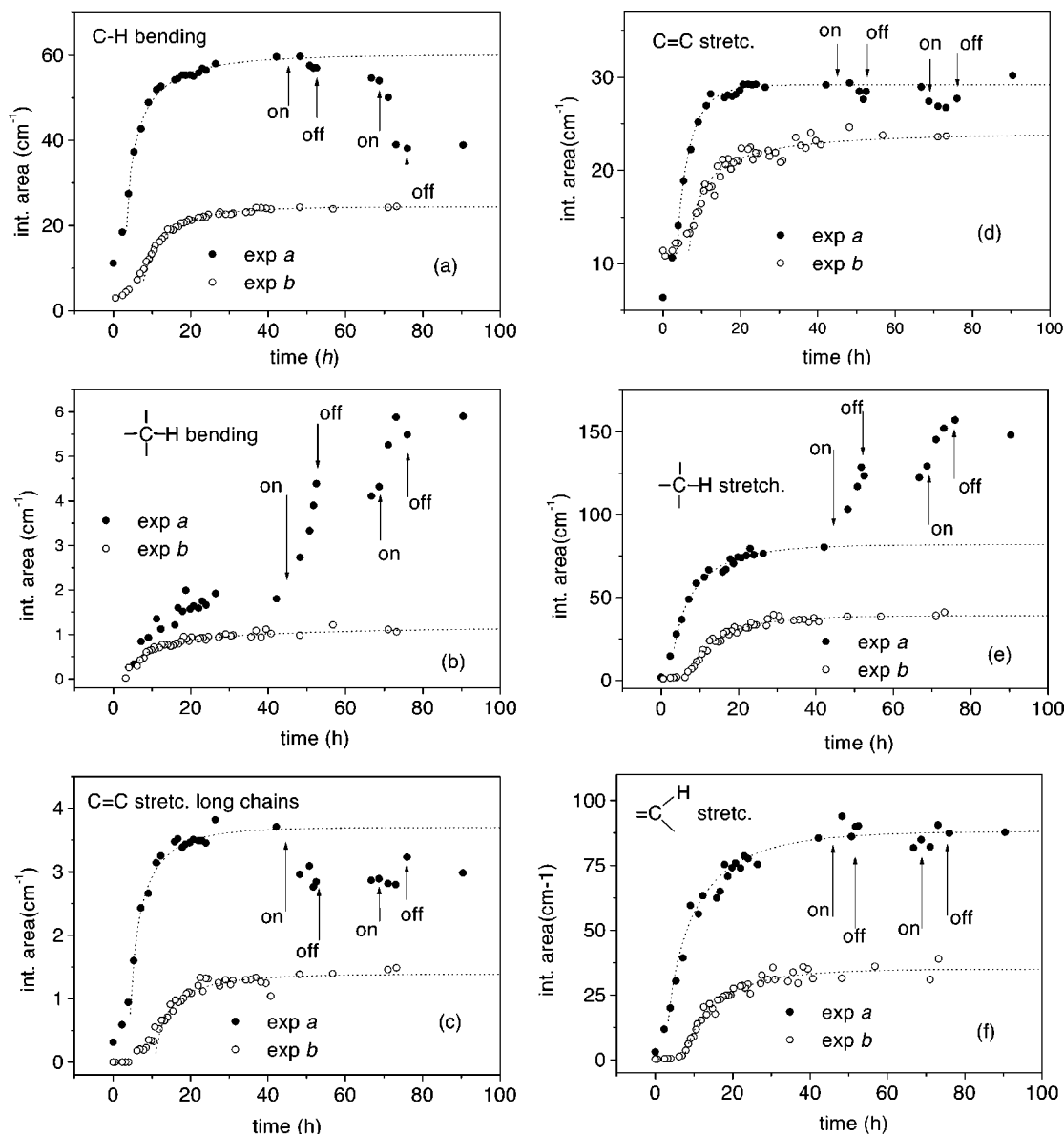


FIG. 5. Time evolution of the integrated absorbances of the bands assigned to the polymeric modes: (a) total area of the two bands (polyacetylenic bending modes) at 923 and 987  $\text{cm}^{-1}$ ; (b) area of the band at 1453  $\text{cm}^{-1}$  assigned to the CH bending of the saturated species; (c) total intensity of the doublet at 1487 and 1503  $\text{cm}^{-1}$  assigned to C=C stretching modes of long polyacetylenic chains; (d) the whole intensity of the bands ranging between 1540 and 1700  $\text{cm}^{-1}$  assigned to C=C stretching modes of the polymer; (e, f) total absorption of the C-H stretching modes of the saturated species (e) and of the polyacetylene (f). The arrows indicate the beginning (on) and the end (off) of the laser irradiation cycles.

which affected the two bands by lowering their absorption intensity. The fit of the data concerning the A type experiment was realized disregarding the values relative to the laser irradiation cycles.

In Fig. 5(b) the absorption of the 1453  $\text{cm}^{-1}$  peak, assigned to the bending of the  $-\text{CH}$  groups of the saturated species is shown. The laser irradiation increases the intensity of this peak (by 100% in the first cycle and by 50% in the second), qualitatively mirroring the decrease in the absorption of the polyacetylenic C-H bending modes described above.

Figure 5(c) shows the total intensity of the sharp doublet at 1487 and 1503  $\text{cm}^{-1}$  to which we have assigned to the C=C stretching modes in longer polyenic chains. The laser irradiation strongly reduces the doublet absorption, specially

during the first cycle. In Fig. 5(d) the whole intensity of the spectral features ranging between 1540 and 1700  $\text{cm}^{-1}$  is reported. These features have all been assigned to the C=C stretching modes of the polyenes with various chain length. In this case the intensity is only weakly affected by the laser. This is in agreement with the assignment of the previous section where it was discussed that the infrared intensity in the 1600–1650  $\text{cm}^{-1}$  region should remain constant when the chain length is shortened. A comment is required by the high initial value of the absorbance in the B run. The presence of impurities in the sample (band at 1596  $\text{cm}^{-1}$ ), probably due to traces of water condensed during the loading of the cell, it is responsible for a constant offset in this kinetic curve.

Finally, in Figs. 5(e) and 5(f) the total intensities of the



TABLE II. Values of the parameters  $\tau$  and  $n$  obtained by the fit of the kinetic curves according to Eq. (2). The conditions of the different experiment types are: (A) 300 K, 4.0 GPa and pressure measured by the ruby fluorescence method; (B) 300 K, 4.0 GPa and pressure measured by the infrared sensors; (C) 200 K, 9.4 GPa and pressure measured by the infrared sensors. In the upper and lower sections the data relative to the polyacetylenic and to the saturated species, respectively, are reported. HF and LF denote, respectively, the high frequency and the low frequency (long chains) C=C stretching modes.

Mode	Exp (A) $\tau$ (h)	Exp (B) $\tau$ (h)	Exp (C) $\tau$ (h)	Exp (A) $n$	Exp (B) $n$	Exp (C) $n$
C-H bend.	$2.4 \pm 0.3$	$4.2 \pm 0.4$	$14 \pm 2$	$0.50 \pm 0.06$	$0.63 \pm 0.06$	$0.8 \pm 0.2$
C=C stretch. (HF)	$2.8 \pm 0.6$	$2 \pm 1$		$0.8 \pm 0.1$	$0.4 \pm 0.2$	
C=C stretch. (LF)	$2.8 \pm 0.7$	$4 \pm 2$		$0.6 \pm 0.2$	$0.6 \pm 0.2$	
C-H stretch.	$8 \pm 1$	$8.5 \pm 0.9$		$0.8 \pm 0.1$	$0.8 \pm 0.1$	
C-H stretch.	$5.4 \pm 0.8$	$7.4 \pm 0.7$		$0.7 \pm 0.2$	$0.8 \pm 0.1$	
C-H <sub>2</sub> bend.	$7.1 \pm 2$	$7.5 \pm 7$		$0.8 \pm 0.4$	$0.4 \pm 0.1$	

C-H stretching absorption bands assigned to saturated and to polyacetylenic species, respectively, are reported. As already stated, because of the large overlap, the separation of these two contributions is not well defined. Anyway, the absorption of the saturated species increases enormously during the laser irradiation as in the case of the peak at  $1453 \text{ cm}^{-1}$  [Fig. 5(b)]. The two identical behaviors confirm the assignment of the two bands at  $1453$  and  $2830\text{--}3000 \text{ cm}^{-1}$  to the same chemical species. On the contrary, the absorption due to the C-H stretching modes involving  $sp^2$  carbon atoms does not change with laser irradiation. The interpretation of this behavior can be easily understood by following the schemes of the acetylene monomer addition to the radicalic chain proposed by Sakashita *et al.*<sup>3</sup> A linear ordered growth of the polymer implies an increase of the number of double bonds while, on the contrary, for a branching of the chain only the increase of the single bonds is expected.

The values of  $\tau$  and  $n$  (see Table II) obtained from different vibrational modes should be in agreement, in a given experiment, being relative to the same physical process. Actually we observe that these values are scattered in both experiments A and B. Recalling that the data relative to the C-H stretching can be affected by the overlap occurring in this region, and those concerning the high frequency C=C stretching modes (HF) by the presence of some impurities, we could limit the attention to the C-H bending and to the long chain C=C stretching data (LF). For these modes  $\tau$  and  $n$  are found to be in good agreement in both types of experiment. The values of  $\tau$  are larger in the B experiment, where the laser was not used to measure the pressure. This result can indicate that also a weak and very short laser irradiation, beside branching the chain, weakly accelerates the formation of the polymer. Finally, the  $n$  values for the C-H bending and for the long chain C=C stretching modes are in very good agreement in the two experiments, showing that the growth geometry is not altered by a weak laser irradiation.

The original Avrami's model was only concerned with the growth step since it assumed that the nuclei of the new phase were already present in the sample. According to this model the values of  $n$  are expected to increase with the dimensionality of the process, ranging between 1 and 2 in the linear growth case. In previous studies of solid state reactions involving a first step, where the reactants are transported to

the reaction sites (diffusion step), values of  $n$  close to 0.5 were found.<sup>1</sup> Model calculation found that for diffusion controlled one dimensional growth processes, the value of  $n$  is 0.5.<sup>22</sup> Experimental studies on the same class of reactions found values of  $n$  ranging between 0.53 and 0.58.<sup>23</sup> In the present work,  $n$  values ranging between 0.4 and 0.8 were found. Taking into account only the most reliable spectral data (the C-H bending of the unsaturated species and the C=C stretching of the long chains), the variation of  $n$  reduces between 0.5 and 0.6. This result is an explicit indication that a diffusion step is involved in the polymerization process.

Concerning the results obtained in the low temperature experiment, it should be pointed out that the only region which could be analyzed with confidence is that relative to the C-H bending mode. In this case, the  $n$  value is comparable to the room temperature values, while the  $\tau$  value is three times larger in spite of an almost double polymerization pressure. This suggests that an important role in the reaction is played by the thermal motions of the molecules.

## VI. DISCUSSION

The results of the present work from both the A and B type experiments demonstrate that the polymerization of acetylene is induced by pressure and that the main products of the reaction are *trans*-polyenic chains. No evidences of *cis* species were detected, and only a small amount of saturated species was revealed. Controlled laser irradiation induced branching of the polyenic chains, as it is evident from the large increase of the absorption relative to saturated species and the corresponding decrease of the bands assigned to the polyacetylenic chains. Basing our discussion on the previous assignment of the reaction products we are able to give a remarkable improvement in the understanding of the mechanisms leading to the formation and to the growth of the polyacetylenic chains.

In Fig. 6 the crystal structure of orthorhombic acetylene is shown, while in Table III the cell parameters  $a$ ,  $b$  and  $c$  measured at zero pressure and  $4.2 \text{ K}^{13}$  and calculated at  $4.2 \text{ GPa}$  ( $0 \text{ K}$ )<sup>24</sup> are listed. The molecules lie in the  $ab$  plane in a T shape arrangement forming an angle of  $\pm 39.5^\circ$  with the  $b$  axis. The distance and the relative orientation between

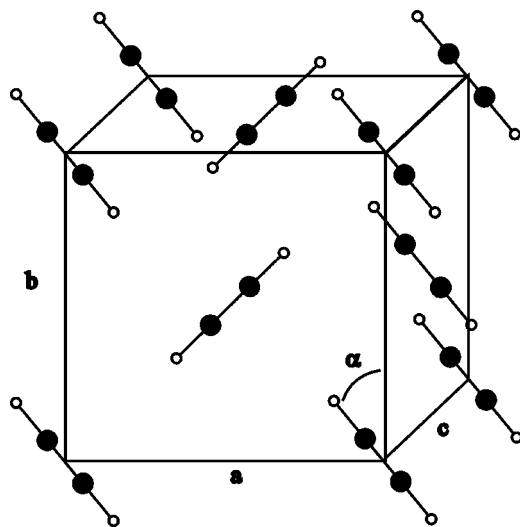


FIG. 6. The orthorhombic  $Cmca$  unit cell of solid acetylene.  $\alpha$  is the angle ( $39.5^\circ$ ) between the molecular and the  $b$  axes.

nearest neighboring molecules are the two key properties to outline the polymerization process. In Table III the distances  $r_1(bc)$ ,  $r_2(ac)$  and  $r_3(ab)$  between nearest neighbor carbon atoms of different molecules in the  $bc$ ,  $ac$  and  $ab$  planes, respectively, are reported. These distances always involve the molecules lying on the center and on the vertex of the face. The minimum distance occurs for molecules in the  $bc$  plane both at high and low pressure. In order to form conjugated double bonds, the arrangement of the molecules must satisfy three obvious requirements: (1) the molecular axes must lie in the same plane; (2) the angle between the molecular axis of a molecule and the line connecting the nearest neighbor C atom of another molecule should be close to  $120^\circ$ ; (3) the molecules must approach each other with the minor steric repulsion.

As to the  $ab$  plane, all the molecules are co-planar ( $ab$ ), but the distance between the nearest neighbors is larger than in any other plane. Furthermore, the closest molecules are disposed in a T shape conformation which prevents the formation of a *trans*-polymer. The same conclusion was reached by Le Sar who studied the reaction in this plane favoring a cross-linked product.<sup>24</sup>

In the  $ac$  plane the distance between nearest neighbors is more favorable than in the  $ab$  one but the molecules are not

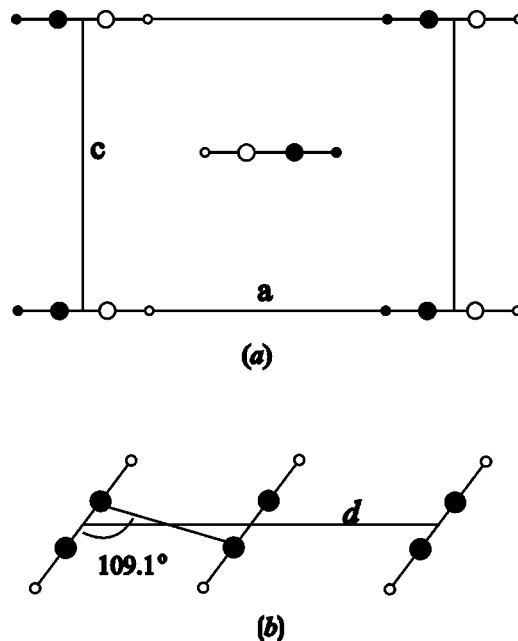


FIG. 7. Molecule arrangement in the orthorhombic acetylene: (a) molecular projections on the  $ac$  plane, black and white atoms lie above and below the  $ac$  plane, respectively, and the molecular axes form an angle of  $\pm 39.5^\circ$  with the  $b$  axis; (b) plane containing the molecules having the center of mass on the diagonal  $d$  of the  $bc$  plane.

coplanar. In Fig. 7(a) the projection of the molecules having the center of mass on this plane is shown. Black and white atoms lie, respectively, above and below the  $ac$  face. Different polymerization paths are possible to obtain either *cis* or *trans* polymers, but all the processes require at least a two-step reorientation mechanism. In the first step all the molecules should rotate to be in the same plane and in the second step the relative orientation should adjust to favor the  $sp^2$  hybridization.

Finally, in the  $bc$  face the molecules having the center of mass along the diagonal are already coplanar, and the nearest neighbors C atoms are at the minimum distance. The plane containing the molecules intersects the  $bc$  face along the diagonal at an angle of  $52.7^\circ$ . The geometry of the molecules lying in this plane is represented in Fig. 7(b), from which it can be appreciated that the angle between the  $C=C$  bond and the nearest neighbor  $C \cdots C$  contact is  $109.1^\circ$ , such that only a small reorientation is needed to match the theoretical arrangement for the formation of a conjugated chain.

The growth of the polyacetylenic chains along the diagonal of the  $bc$  lattice plane leads to the formation of a *trans*-transoid polymer. This result is in agreement with the kinetic data of the previous section and with an unidimensional growth geometry ( $0.5 \leq n \leq 0.6$ ) controlled by the diffusion of the reactants.<sup>1,22,23</sup> It is worth to point out that also Aoky *et al.*<sup>2</sup> proposed the preferential growth of the *trans*-polymer in the  $bc$  face, but the mechanism they invoked, on the basis of a value of  $n$  equal to 1.34, was a one-step diffusionless linear growth.

Concerning the dynamics of the nucleation step of the reaction we notice (see Table III) that the distance between nearest neighbor non bonded carbon atoms in the  $bc$  plane is

TABLE III. Cell parameters and distances among closest neighbors C atoms in the orthorhombic  $Cmca$  structure of acetylene. All values are expressed in Å.

Cell parameters	Exp. data <sup>a</sup>	Calc. data <sup>b</sup>
	T=4.2 K, P=0 GPa	T=0 K, P=4.0 GPa
a	6.193	5.878
b	6.005	5.713
c	5.551	4.611
$r_1(bc)$	3.46	3.05
$r_2(ac)$	3.65	3.22
$r_3(ab)$	3.77	3.45

<sup>a</sup>Reference 13.

<sup>b</sup>Reference 24.

$3.05 \text{ \AA}^{24}$  at 0 K and 4 GPa. In a recent *ab-initio* molecular dynamic simulation Cardini *et al.* found that acetylene molecules in the *bc* plane type arrangement readily react only when the nonbonded  $\text{C} \cdots \text{C}$  distance approaches  $2.6 \text{ \AA}$ .<sup>25</sup> In the present experiment such a close approach can be ensured by the translational phonons. The  $\Gamma$  point translational modes have been measured, at room pressure, at 106 and  $127 \text{ cm}^{-1}$ .<sup>26</sup> Assuming that the translational modes have similar dependence on pressure as the librational modes<sup>27</sup> one finds, in the classical limit, a translational mean square amplitude at 300 K and 4 GPa of the order of  $0.5 \text{ \AA}$ . This should be large enough to ensure the approach of the acetylene molecules leading to the polymerization reaction. The translational amplitude reduces considerably at 200 K and it can be estimated to be of the order  $0.2 \text{ \AA}$  at 9.0 GPa. This explains the drastic reduction of the reaction rate at 200 K, such that for the reaction to occur a higher pressure is needed. The role of the lattice motions in the activation of the reaction was already suggested by Le Sar who, however, only considered the effect of the librational modes.<sup>24</sup> The lattice motions must be involved also in the development of the reaction but with a minor importance, since the presence of radicalic terminations, formed during the nucleation step, would assist the chain propagation mechanism.

As discussed in the previous section the length of the polymer chains formed during the reaction can be estimated to be more than 12 double bonds. A more precise assessment is not possible since the pressure dependence of the vibrational frequencies of the polyenes is not known. Finally, the discussion has been based on comparison with the spectra of isolated and unsubstituted polyenes, but it is known that different end terminations of the conjugated chain<sup>28</sup> can considerably change its properties and, particularly the  $\text{C}=\text{C}$  stretching, frequencies.

It should also be mentioned that the polycrystalline nature of the sample and the presence of grain boundaries is of primary importance in the growth of the polymer units. Chemical impurities and lattice defects can play the same role as the grain boundaries in inducing termination mechanisms. The presence of impurities and defects can also account for the branching of the polymer revealed by the presence of saturated species. This process is enormously enhanced when the sample is irradiated. In fact, the laser frequency is high enough to induce  $\pi \rightarrow \pi^*$  transitions favoring the breaking of the double bonds and the consequent formation of saturated species. The main effect, beside destroying the linear geometry of the polymer, is the reduction of the chain lengths, as shown by the decrease in intensity of the doublet at  $1487$  and  $1503 \text{ cm}^{-1}$  under irradiation.

## VII. CONCLUSIONS

In this study we have demonstrated that the polymerization of solid acetylene is induced by pressure. The reaction is activated by the collective motions of the molecules and it develops in a plane containing the diagonal of the *bc* plane leading to the formation of a *trans*-polyacetylene. Laser irradiation plays a role in the reaction, even at very low incident power, inducing  $\pi \rightarrow \pi^*$  transitions which favor the opening

of the double bonds with a consequent branching of the polymer. The specific effect of controlled laser irradiation cycles on the different vibrational bands allowed to identify the different product species and estimate their relative abundance. Conjugated *trans* chains with more than 12 double bonds form in the reaction. The factors limiting the development of this cooperative reaction are ascribed to the polycrystalline nature of the sample. We expect that in a perfect monocrystal an ordered *trans*-polymer should be obtained with the linear chains extending all along the lattice. It would be therefore a very important experimental task to grow a monocrystal of acetylene and to study the polymerization process in these conditions

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