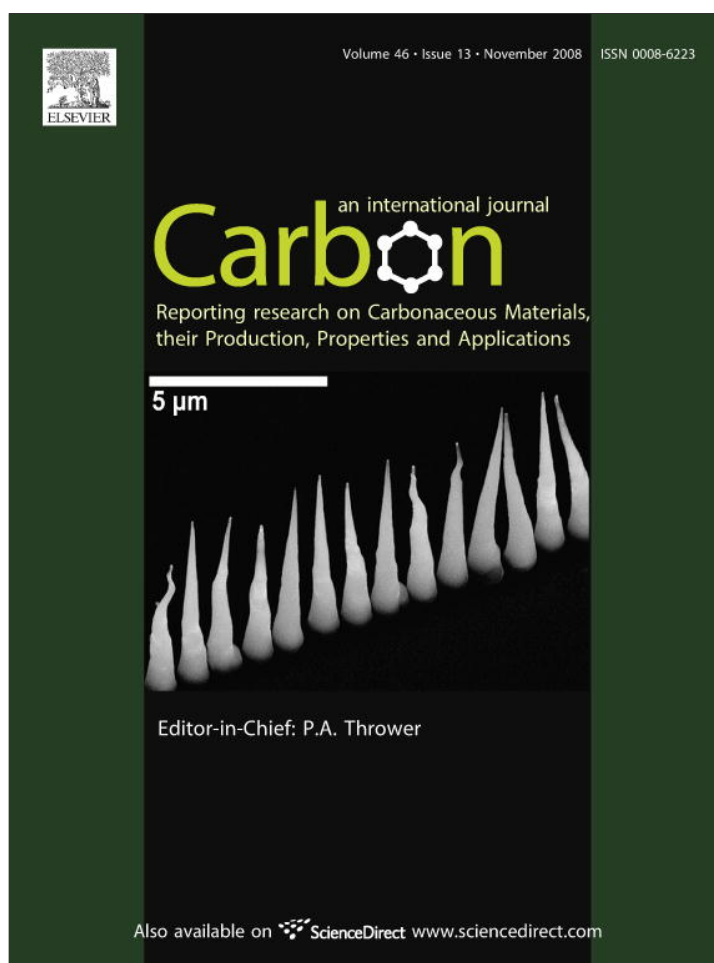


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# Direct synthesis of polyynes in acetone by dissociation using femtosecond laser irradiation

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## ABSTRACT

Hydrogen-capped polyynes have been synthesized by 800 nm femtosecond photolysis of acetone molecules. Four bands appearing in the 1800–2200 cm<sup>-1</sup> range of surface enhanced Raman spectra show a mixture of polyynes with variable chain lengths in the irradiated acetone. The shortest hydrogen-terminated chain is found to be C<sub>6</sub>H<sub>2</sub>. The presence of charged carbon dimer, monomer C<sub>2</sub><sup>+</sup>, C<sup>+</sup> and double charged C<sub>2</sub><sup>2+</sup> has been confirmed by time-of-flight mass spectroscopy. These ions are generated as irradiation products of step-wise dissociation of acetone and further act as building blocks in the synthesis of polyynes.

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Polyynes, linear carbon chains with alternating triple and single sp-hybridized C–C bonds terminated by atoms or groups (conventionally polyynes represent the class of molecules H(C≡C)<sub>m</sub>H, with integer *m*), have attracted considerable interest in astrophysics and nanoscience [1–3]. These compounds have been detected in interstellar materials [1], and are important precursor molecular components in the formation of fullerenes and carbon nanotubes [2]. They have been investigated as prototypes of carbyne, a novel sp-bonded allotrope of carbon [2,4]. Recently, hybrid nano-materials have been developed in which polyynes have been inserted into single wall carbon nanotubes [3] or bonded to silver nanoparticles [4]. Conventional synthesis of polyynes involves reactions of acetylenic coupling [5]. However, due to the complex nature of these chemical reaction sequences, the generation of polyynes via laser ablation of suspended carbon solids [6–11] or by arc discharge [1] using carbon electrodes in organic solvents may constitute a more practical synthetic route.

Polyynes have been generated by the laser ablation of suspended graphite [6–9], C<sub>60</sub> [10] and nanodiamond [11] particles in solution. In these experiments, polyyne molecules do not originate from decomposition of the solvent but by ablation of suspended particles. This is also true for the submerged arc, where the graphite electrode provides the precursor molecules required for the formation of polyynes [1]. It has also been shown that there is no direct formation of polyynes by pyrolysis at the focus of nanosecond laser pulses in hydrocarbon liquids even at pulse energies in excess of 300 mJ [6,10]. It

is expected, however, that pyrolysis would occur at the focus of femtosecond pulses because the high electric intensity generated leads to ionization and bond breaking [12,13]. In our previous work, we have shown that fs irradiation of the surface of graphite produces liquid carbon as part of a non-equilibrium metastable high temperature phase containing polyynes [4]. In this letter, we report the preparation of polyynes in solution by direct dissociation of acetone molecules with fs laser radiation followed by growth of polyynes from the dissociation products. Acetone was chosen because diamond-like carbon films have been successfully deposited using femtosecond laser ablation of frozen acetone [14]. It is found that a variety of carbon species are created by femtosecond laser ablation of hydrocarbons, however, since acetone contains a C=O bond the laser induced dissociation of this molecule is more complex than for alkane molecules [12,13]. It is therefore of interest to elucidate the femtosecond laser induced dissociation of acetone.

The output beam of a regenerative amplified Ti:sapphire laser operating at 800 nm producing 90 fs pulses at a repetition frequency of 1 kHz was focused into an optical cell containing 20 ml of acetone with a 4 cm focal length lens. As the diameter at the beam focus was ≈10 μm, the resulting laser intensity was ~10<sup>15</sup> W/cm<sup>2</sup> at a pulse energy of 300 μJ. The molecular composition of the solution after irradiation for one hour was obtained from surface enhanced Raman spectra (SERS) after mixing at a ratio of 5:1 with a 0.1 M solution of nanosilver particles. SERS spectra were recorded by focus-

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ing a 632 nm laser beam into the resulting solution with a  $\times 50$  objective at an excitation power of 0.3 mW.

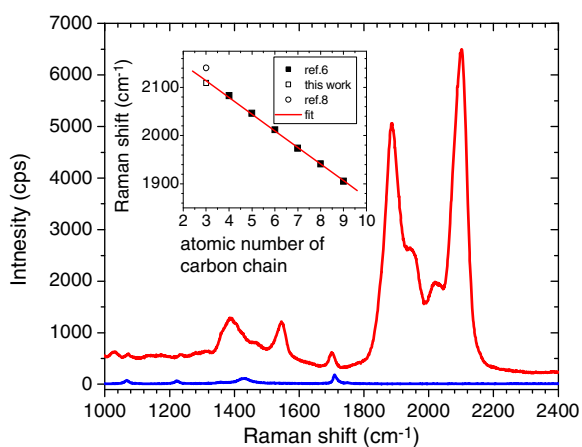
Fig. 1 shows SERS spectra of irradiated and unirradiated acetone. It can be seen that four Raman bands appear in the 1800–2200  $\text{cm}^{-1}$  range after irradiation. These features can be attributed to polyynes with different chain lengths [4,7,8]. An estimate of chain length can be obtained as the two primary SERS bands in polyynes have been characterized by Tabata et al. [7] using size-separated polyynes  $\text{C}_n\text{H}_2$  in the range  $n = 8$ –16. They found that the high vibration frequency of the  $\alpha$  mode is linearly dependent on chain length, with a lower frequency corresponding to an increase in chain length. Compagnini et al. [8] have used this correlation to show that  $\text{C}_6\text{H}_2$  is produced as a result of the laser ablation of graphite in water. The inset to Fig. 1 shows the correlation derived by Tabata et al. [7] together with the high frequency band observed in fs-irradiated acetone. It is evident that the frequency of the present SERS mode lies on this curve indicating that the shortest chain produced after fs irradiation is also  $\text{C}_6\text{H}_2$ . The possible presence of longer chains cannot be detected as the frequency of the  $\beta$  mode in SERS spectra of  $\text{C}_8\text{H}_2$ – $\text{C}_{14}\text{H}_2$  is not strongly correlated with chain length. In addition, there is considerable overlap between the  $\beta$  modes of short chains and the  $\alpha$  mode of longer chains [7]. Further experiments using high performance liquid chromatography will be used to determine if longer polyynes are also present in the irradiated solution.

During irradiation of liquid acetone with fs pulses, bubbles were observed to evolve from the focal volume. This gas was collected and analyzed using gas-phase chromatography combined with ion trap mass spectroscopy (GC-MS). Irradiated acetone was colorless clear transparent liquid without solid suspension. Molecular fragments due to fs irradiation were characterized by a Wiley–McLaren time-of-flight (TOF) mass spectroscopy equipped with a double multichannel plate detector, which enables more than  $10^7$  gain. The pristine acetone was fed into the chamber through a high vacuum leak valve and the work pressure of the TOF mass spectroscopy was kept as  $2 \times 10^{-7}$  Torr. The laser was focused by a

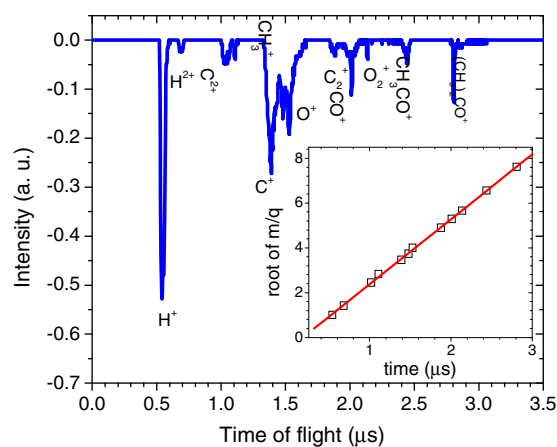
5 cm focal length spherical mirror. Positive charged ions were first extracted by a 20000 V/m electric field and then accelerated by 1.2 kV voltage prior to flying into a free drift chamber. The free drift length was about 30 cm.

Fig. 2 shows time-of-flight mass spectra of acetone vapor dissociated by fs pulses. The relationship between drift time and mass/charge ratio is given by  $t \approx k\sqrt{m/q}$ , where  $k$  is a constant which depends on experimental configurations,  $t$  is the total drift time,  $m$  and  $q$  are the ion mass and charge. This relation is derived on the basis of the following assumptions: 1. that the initial ion velocity corresponds to that at 300 K (corresponding kinetic energy of 0.25 eV); 2. all ions experience the same extraction and acceleration voltages. All charged species in the TOF spectrum can be identified on the assumption that the first peak at 0.542  $\mu\text{s}$  is that of  $\text{H}^+$  while the last strong peak at 2.81  $\mu\text{s}$  corresponds to singly-charged acetone. From fast species to low ones the analysis shows that these ions are  $\text{H}^+$ ,  $\text{H}^{2+}$ ,  $\text{C}^{2+}$ ,  $\text{C}^+$ ,  $\text{CH}_3^+$ ,  $\text{O}^+$ ,  $\text{C}_2^+$ ,  $\text{CO}^+$ ,  $\text{O}_2^+$ ,  $\text{CH}_3\text{CO}^+$  and  $(\text{CH}_3)_2\text{CO}^+$ . The inset to Fig. 2 shows all TOF peaks plotted vs. the root of  $m/q$ . The perfect linear correlation confirms that individual species have been correctly identified. Furthermore, the presence of CO and  $\text{CH}_4$  molecules in the gas extracted during irradiation has been detected by GC-MS as expected from the assignment of ionic species shown in Fig. 2. It is apparent that carbon radicals and radical ions like  $\text{C}_2^+$ ,  $\text{C}^+$  and  $\text{C}^{2+}$ , are created in the dissociation of acetone molecules. These species are likely the primary building blocks in the growth of polyyne molecules.

The growth of polyynes proceeds by the addition of C,  $\text{C}_2$  and H to acetylenic groups [6]. Hydrogen atoms required in the terminal or capping bonds can be extracted from the solvent. While C atoms require the breaking of all C–C and CH bonds the formation of polyyne molecules cannot proceed in the absence of this species. Previous experimental and theoretical work has shown that the dissociation of acetone with fs pulses is a stepwise procedure that occurs sequentially in increasing energy as C–C, C=O, C–H bonds are each dissociated [12,13]. At intensities  $< 10^{14}$  W/cm $^2$ , the C–H bond does not break so that C atoms are not available for the growth



**Fig. 1** – Surface enhanced Raman spectra of unirradiated (dashed line) and acetone after irradiation with fs pulses. Inset: Raman shift of the  $\alpha$  mode of polyynes as a function of the number of carbon atoms in a polyyne chain [15].



**Fig. 2** – Time-of-flight mass spectra of molecular acetone after irradiation with 120 fs pulses from a 800 nm laser at a pulse energy of 300  $\mu\text{J}$ . Inset: drift time of identified atomic and molecular species plotted vs. mass/charge ratio.

of polyynes molecules. This result is consistent with the effects observed after irradiation with ns laser pulses where the intensity is in  $10^8$ – $10^{12}$  W/cm<sup>2</sup> range [2]. In the present experiment, the laser intensity at the focus of the spherical mirror is  $\approx 10^{15}$  W/cm<sup>2</sup>, which is close to the threshold value for the production of a Coulomb explosion. At this intensity, all bonds in acetone can be easily broken resulting in the generation of C and C<sup>+</sup>. The presence of the C<sup>2+</sup> ion may indicate that dissociation occurs via Coulomb explosion. A similar picture can also explain the femtosecond laser ablation of acetone solid, where the presence of C<sup>+</sup>, C<sup>2+</sup> and C<sub>2</sub> are evident from emission spectra [14]. However, it is necessary to point out that the use of acetone is not critical to the production of polyynes via fs laser irradiation of hydrocarbons. Recently we have also successfully synthesized polyynes using different alkane molecules as precursors. It is worth noting that polyynes are not stable at high temperature [15]. At temperatures in the range between 50 °C and 100 °C, polyynes form graphene-like species by crosslinking. This process cannot however occur during fs irradiation as the timescale for thermal heating is much longer than that of the pulse width. This is a manifestation of the highly non-equilibrium nature of fs laser processing and indicates that the local thermal effect (occurring over a nanoscale dimension) by fs irradiation can enhance the stability of the resulting polyyne composition [4].

In summary, polyynes have been successfully synthesized in a single-step process involving the dissociation of acetone molecules in a liquid. Time-of-flight mass spectroscopy confirms that the dissociation of acetone generates simple carbon species such as C and C<sub>2</sub> and their ions that act as the molecular building blocks of polyynes.

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