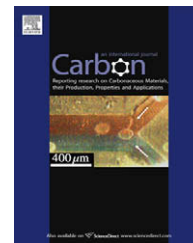


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Time of flight mass spectrometry of polyynes formation in the irradiation of liquid alkanes with femtosecond laser pulses

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ABSTRACT

The production of polyyne molecules arising from the irradiation of liquid octane with femtosecond (fs) laser pulses has been studied using time of flight mass spectrometry (TOFMS). We attribute the primary formation mechanism for polyynes in solution to the creation of small polyyne and cumulene molecules formed in molecular dissociative ionization, that subsequently increase in length through addition reactions with other products C, C₂, C₂H, the ions of which are detected in the TOFMS of octane. Polyynes up to C₁₄H₂ have been identified and we propose that photo-dissociation limits the length of polyynes produced in solution.

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1. Introduction

Recently polyynes, which are linear chain carbon molecules containing alternating single and triple bonds and capped at each end by one hydrogen atom, have been the subject of several studies. This is because of their importance as precursors in the formation of nano-structures [1] including nano-wires with controllable conductivity [2], and it is therefore of great interest to investigate novel methods for the tailored formation of these compounds. Studies have concentrated on production mechanisms such as nanosecond laser ablation of suspended graphite particles in water [3,4], and in the laser ablation of graphite [5]. Very recently a method has been discovered for producing polyynes from pure liquid solvents acetone [6] and hexane [7] simply by femtosecond laser irradiation. Here we study liquid octane as a source of polyyne chain production, after irradiation by femtosecond laser pulses. We investigate the length of the polyynes produced

using Surface Enhanced Raman Spectroscopy (SERS) and we identify the precursor species using time of flight (TOF) mass spectrometry which allows us to comment on the mechanism for polyyne formation.

2. Experimental system

Liquid octane (99% purity) was irradiated by 800 nm, 100 fs pulses of 300 μJ from a regeneratively amplified Ti:Sapphire tabletop laser with a repetition rate of 1 kHz. Octane was placed in a 20 ml rectangular quartz container and irradiated for 2 h. The incident laser beam was focused with a 4 cm focal length lens to produce a visible white filament within the liquid; of a few millimeters in length, this has the effect of increasing the interaction volume by three orders of magnitude while capping the intensity at around 4×10^{13} W/cm² [8]. After irradiation, the liquid remained transparent with no evidence of suspended particles.

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3. SERS of pure and irradiated octane

In order to study the composition of the irradiated liquid we use the SERS technique employing a 488 nm laser (0.3 mW) and a solution of 0.1 M nano-silver particles in water added to the irradiated octane in a ratio of 1:5. In order to optimize the signal the laser was focused on the interface between the Ag solution and the irradiated octane. Fig. 1 shows the SERS spectra of pure and irradiated octane, C_8H_{18} . SERS spectra of unirradiated octane show no evidence for the presence of polyynes in the fingerprint region $1800\text{--}2200\text{ cm}^{-1}$. However, the spectrum of irradiated octane shows a complex of spectral features in this range that can be associated with the polyynes C_8H_2 , $C_{10}H_2$, $C_{12}H_2$ and $C_{14}H_2$ [9]. Fig. 2 shows a plot of the energy of the alpha mode in these polyynes versus

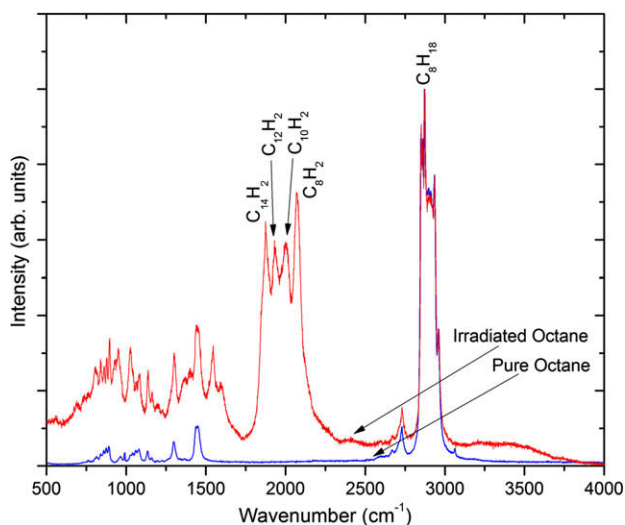


Fig. 1 – SERS spectra of octane before and after irradiation. The notable difference in these spectra is the appearance of features arising from polyyne molecules between 1800 and 2200 cm^{-1} after irradiation.

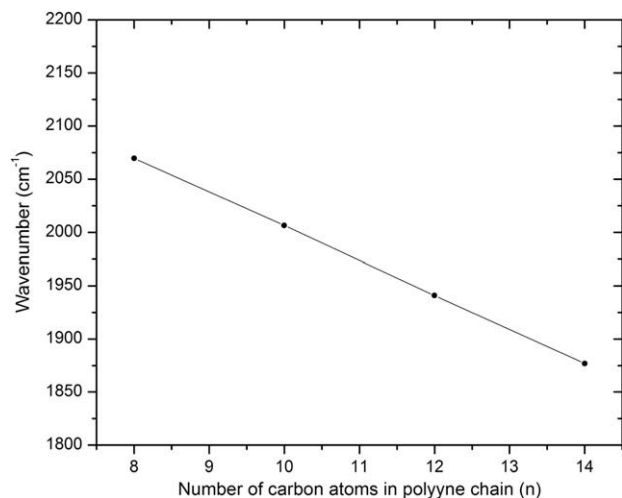


Fig. 2 – Energy of Raman bands of polyynes detected in irradiated liquid octane plotted vs. number of carbon atoms.

the number of carbon atoms in the molecule. This dependence was also observed by Tabata et al. [9,10]. It is apparent from these data, that a range of polyynes having different lengths are generated and are retained in the octane solution after irradiation by the fs pulses.

4. Time of flight mass spectrometry

In order to start to understand the processes which lead to the observed polyynes we have studied the gas phase ionization and dissociation of octane using the same laser system and a time of flight mass spectrometer (TOFMS) of the dual-stage Wiley-McLaren type [11] with a drift region of 0.92 m. Using an on axis spherical mirror of focal length 5 cm, the laser beam in the source region was focused to produce a peak intensity of 10^{15} W/cm^2 and the pressure in the TOFMS during irradiation was maintained at 10^{-7} Torr, in order to prevent space charge effects. Although the peak intensity in the vacuum chamber is much higher than in the liquid, the largest focal volume in gas phase is responsible for producing the lowest intensity processes and so by monitoring the low charge state species produced in the vacuum experiment, we can effectively see the fragment ions which are produced in the liquid.

A TOF spectrum resulting from the irradiation of octane is shown in Fig. 3 while Fig. 4 shows a plot of $(m/q)^{1/2}$ for a selection of detected fragments. Usually for small molecules we would expect to see a large parent ion peak but for larger molecules of this type and pulse length greater than 100 fs, so called ladder switching into a dissociative mode has been found to dominate [12,13], so that for large molecules with many internal vibrational modes break up into smaller ions leading to the loss of all parent ions. Small amounts of C^{2+} , C^{3+} from the high intensity region indicate that the majority of ions are formed in low intensity region of the focus. A variety of molecular ions together with H^+ and C^+ can be identified in this spectrum. Several groups of ions can be identified which include between one and four carbon ions, the C_2 group for instance shows the presence of $C_2H_2^+$, $C_2H_3^+$ and $C_2H_4^+$ which are common ions in the dissociation of alkanes. Most importantly, we see small polyynes from C_2H_2 to C_4H_2 .

5. Discussion

The TOF spectrum shows that the octane decomposition results in the formation of a wide variety of radical ions. When this process occurs in liquid octane, these radicals undergo secondary reactions with neutral octane molecules in the surrounding liquid. Recombination with electrons and negative ionic species is also expected. Despite the inherent complexity of the decomposition products, secondary reactions are likely dominated by reactions involving C , CH , C^+ , CH^+ , CH_2^+ , C_2^+ , C_2H^+ , etc. These species are traditionally the most significant species resulting from multi photon ionization (MPI) and multi photon dissociation (MPD) of hydrocarbon molecules and all will react with octane to form secondary products. The reaction between octane and any of the species listed above will lead to a variety of branched hydrocarbons, with

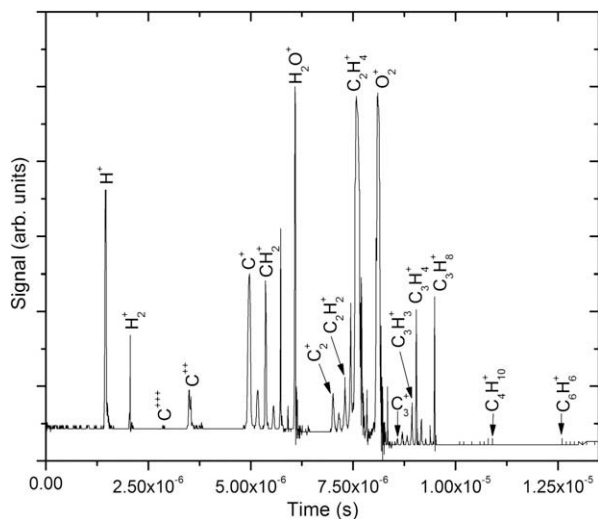


Fig. 3 – Normalized mass spectrum resulting from the irradiation of pure octane in the gas phase by 100 fs pulse at 800 nm and peak intensity of 10^{15} W/cm². Mass peaks are separated by 1 amu. This indicates that the primary interaction involves dissociative ionization.

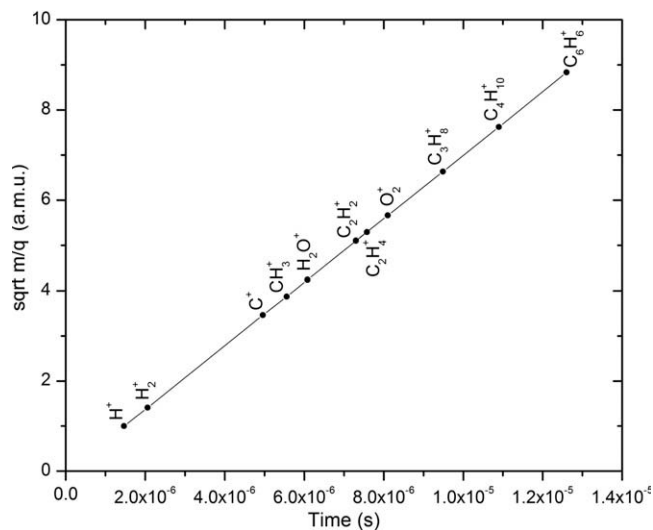
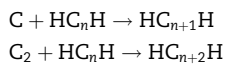


Fig. 4 – TOFMS plot of $(m/q)^{1/2}$ vs. time, t , in seconds. The largest molecule detected, $C_6H_6^+$ fits on this line well, but there is no evidence for polyynes larger than $C_4H_2^+$.

no single species dominating in the overall mixture. In solution then higher order polyynes can be observed since the concentration of each chain can build up by selected secondary reactions. These secondary reactions likely involve the insertion of C, C⁺, C₂, etc. into smaller chains. Such reactions would take the general form.



In this model, small polyynes and cumulenes such as HC₂H, HC₃H, HC₄H, etc. produced by laser-induced dissociation of octane are retained in solution and undergo subsequent insertion reactions with the fragments produced in

the laser interaction. This leads to the formation and retention of longer polyyne molecules as indicated from the SERS measurements. Obviously, this mechanism is not possible when a gas phase octane molecule is dissociated by intense fs radiation since this occurs under collision free conditions.

Since 100 fs pulses result in the decomposition of octane into smaller fragments rather than the retention of the parent molecule, it is clear from our data that the HC₈H polyyne cannot then be produced directly from octane under the conditions of our experiments either in solution or in the gas phase. Furthermore it is clear that the produced polyynes can not survive laser irradiation if it results in ionization, otherwise they would be visible in the TOF spectrum. In the case of octane therefore we can say that an equilibrium in polyyne production and destruction must limit the ultimate concentration. It is of interest to see if this situation changes i.e. (HC₈H can be formed directly from C₈H₁₈) when irradiation occurs with shorter pulses. This effect also gives a clue as to the reason for the observed maximum chain length in solution. In the very lowest intensity part of the focus, ionization will not be possible but multi photon dissociation MPD will be possible in fact a strong electronic absorption band moves to lower energy as the chain length increases [14]. This facilitates the absorption of incident laser radiation and enhances MPD once a critical length has been reached.

6. Conclusions

We have used a combination of TOF mass spectroscopy and SERS measurements to investigate the mechanisms by which polyynes are formed in the irradiation of liquid octane with fs laser pulses. No evidence is found for the direct formation of HC₈H by elimination of H from C₈H₁₈. The primary mechanism for the generation of polyynes in solution appears to involve the laser-induced decomposition of octane to produce small chains including HC₂H, HC₃H, HC₄H, etc. These molecules then subsequently undergo addition reactions with C, C₂, etc., to form longer chains. Under the conditions of our experiments, these reactions result in the formation of polyynes extending from HC₈H to HC₁₄H. The maximum chain length appears to be determined by laser-induced photo-dissociation as a strong absorption band of the polyyne chain moves to longer wavelengths with increasing chain length.

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