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The effects of liquid environments on the optical properties of linear carbon chains prepared by laser ablation generated plasmas

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ABSTRACT

Linear carbon chains (LCCs) were successfully produced by laser generated plasmas in different solvents starting from graphite rods. An identification of the prepared carbon structures was carried out from the analysis of the UV–vis spectra. Moreover, a systematic analysis of the DFT computed structural and electronic response of both polyynic and cumulenic model molecules, as a function of the solvents with different polarity, was carried out. The comparison between the calculated UV–vis spectra of polyynes series with the experimental ones clearly indicates that polyynes are the dominant species produced by the ablation process. The optical limiting properties were investigated by the Z-scan method, using a nanosecond pulsed laser. Both the different solvents and the carbon chain length distribution have a driving role in the nonlinear optical response. Hence, the effect of the solvent polarity and acidity was taken into account to explain the nature of the optical limiting behaviour.

1. Introduction

In the last decade optical limiting phenomena have attracted much research interest for their promising applications such as the production of nonlinear transmission materials able to minimize the potential hazard to eyes and optical sensitive devices in the visible spectra region and in the nanosecond time scale. Among different optical limiting materials, carbon nanostructures such as carbon nanotube and colloids of carbon-based nanomaterials exhibit strong optical limiting properties [1,2]. The advantage of using carbon colloids with respect to those in solid phase is their ability to self-repair and reshape. However, the prepared solutions are not chemically and morphological stable [3]. The one-dimensional structures represent excellent candidates in molecular electronics field applications, thanks to their high electrons density. In this frame, the nonlinear optical properties of linear carbon chains (LCCs) have been widely theoretically explored. These systems are characterized by a high π conjugation and, therefore, they are promising one dimensional conducting materials [4–7]. Polyynes are also the precursors in carbon nanotubes and fullerenes formation. At present, polyynes are successfully synthesized and their long-term stability was checked [8]. However, the results in terms of photo-stability of the produced carbon mixture are not yet fully satisfactory for the study of their third-order nonlinear optical properties.

Moreover, as already reported in literature [8,9], pulsed laser ablation in a confining liquid is a chemically simple and clean synthesis to obtain size controlled carbon based materials dispersed in different solvents, usually in a one step top–down procedure. The intrinsic ability to produce stable species without the a priori need for any aggressive chemicals, like reducing or capping agents, makes laser ablation in liquids particularly attractive as an eco-compatible technique.

The role of solvents on the formation of sp-hybridized molecules produced by plasma ignition techniques was deeply discussed by Cataldo. Electronic absorption spectra and HPLC analysis clearly show that polyynes are the unique products [10].

In this frame, here we discuss about the formation of sp-hybridized molecules produced by laser ablation in solvents with different polarity, starting from graphite rods.

In order to identify the species which contribute to the linear optical properties, DFT calculations were performed to both polyynic series ($HC_{2n}H$, $3 \le n \le 6$) and cumulenic series ($H_2C_{2n}H_2$, $3 \le n \le 6$) in the different solvents, and monocyano $HC_{2n+1}N$ ($3 \le n \le 5$) and dycyano $NC_{2n}N$ ($4 \le n \le 5$) series in acetonitrile. To the best of our knowledge, no systematic studies on the correlation between linear and nonlinear optical properties of LCC prepared in different solvents has been performed. Therefore, Ultraviolet–visible (UV–vis) results were correlated with the nonlinear optical response of produced carbon species. Moreover, the

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effect of the solvent polarity and acidity was taken into account to explain the nature of the optical limiting behaviour.

2. Material and methods

Pulsed laser ablation of a graphite target (99.9% of purity) has been carried out in different solvents (i.e. water, acetonitrile, methanol and cyclohexane) using pulses from the second harmonic (532 nm, 5 ns) of a Nd:YAG laser operating at 10 Hz repetition rate. The target was irradiated, at room temperature, with a power density of 0.5 J/cm^2 for typical irradiation times of 20 min. More details about the preparation procedure are reported in Ref. [8]. The UV–vis spectral characterizations allowed the identifications of the linear carbon chains. The optical absorbance measurements were carried out by a PerkinElmer LAMBDA 2 spectrophotometer, in the 190–900 nm range. The nonlinear optical properties have been determined by the Z-scan method [11] using a pulsed Nd:YAG laser (wavelength 532 nm, 5 ns pulse duration, 10 Hz repetition rate). The incident laser beam was divided by a beamsplitter: the reflected part was taken as reference beam, the transmitted one was focused, with a 300 mm focusing lens, into a 1 cm length quartz cuvette. The sample and the reference beam intensities were detected simultaneously with a dual channel energy meter. The optical limiting efficiency of all the produced samples was investigated by means of nonlinear transmittance measurements as a function of the input fluence. After the nonlinear optical limiting measurements, the optical absorbance of the samples was again carried out in order to test the degree of the LCC photo-stability.

3. Theory/calculation

The equilibrium geometry of cumulene $H_2C_{2n}H_2$ ($3 \leq n \leq 6$) and polyyne $HC_{2n}H$ ($3 < n < 6$), monocyano $HC_{2n+1}N$ ($3 \leq n \leq 5$) and dycyano $NC_{2n}N$ ($4 \leq n \leq 5$) chains were calculated, in different solvents, e.g., water, methanol, acetonitrile and cyclohexane, using the Becke's three parameters exchange functional supplemented with the Lee–Yang–Parr correlation functional, B3LYP [12–14]. The conductor-like Polarizable Continuum Model (CPCM) [15–17] was adopted for calculating the solvent effect. In this approach the solute molecule is embedded into a cavity surrounded by a dielectric continuum of a given permittivity and interacts with the solvent represented by a dielectric continuum model.

UV–vis spectra were investigated by using the single excitation configuration interactions (CIS) [18] whose results are in good agreement with experimental data. The simulation of the UV–vis spectra was conducted via configuration interaction that involves 20 excited states starting from the optimized geometries.

Eventually, geometry optimization and UV–vis spectra were performed by using the 6-311+** basis set [19–23], while D95 (d) basis set [24] was adopted to evaluate atomic charges.

4. Results and discussion

4.1. Linear optical properties

In Fig. 1a–d absorption spectra of as prepared LCCs in cyclohexane, methanol, water and acetonitrile are reported together with those recorded after every Z-scan analysis. Features of sp-hybridized carbon chains dominate in the ultraviolet region because of electronic transitions peaking between 190 and 300 nm, with increasing wavelengths as the chain length increases. As reported in a previous work [25] when a carbon target is laser ablated in water (see Fig. 1a), carbon chains $C_{2n}H_2$ with mainly $n = 3$–4 are produced. Carbon species with $n = 6$ have been identified by a prominent absorption feature at 200 nm (with a shoulder at 207 nm), while carbon chains with $n = 8$ produce two weak signals at 216 and 226 nm. Both features (C_6H_2 and C_8H_2) are clearly visible in Fig. 1a. Otherwise, longer polyynes from C_6H_2 to $C_{12}H_2$ have been found to be the dominant species in methanol and cyclohexane solution with a similar chain distribution (see Fig. 1b, c). During the nonlinear optical measurements (see the following paragraph), samples are subjected to prolonged 532 nm irradiations, as a consequence the UV–vis LCC features gradually disappear. Moreover, depending on the ablation liquid medium, a different degradation behaviour was detected. While a gradual decreasing in intensity of the overall polyyne peaks together with a light red shift was detected in water, in cyclohexane and methanol, the C_6H_2 chain was the main polyyne molecule that continued to exist. The detected red-shift can be ascribed to the degradation products resulting from chain interactions that tend to evolve toward sp^2-like structures [8]. Moreover, when laser ablation is carried out in acetonitrile in addition to H-terminated polyynes, monocyano and dicyano carbon chains are also present in solution as already reported by Cataldo [10,26]. In this case electronic transitions of $NC_{2n+1}H$ and $NC_{2n}N$ were also considered for peak assignments and for the relative concentration calculation. In particular, additionally to hydrogenated polyynes with 6–14 carbon atoms/chain, HC_7N, HC_9N, $HC_{11}N$, C_6N_2 and C_8N_2 were also detected. Regarding the LCC behaviour in acetonitrile after repeated Z-scan measures, we observed that the absorbance features of shorter chain molecules disappeared and only $C_{12}H_2$ and $C_{14}H_2$ were detected in solution. For all the produced systems, the complete LCC photodegradation was observed after 4–5 cycles of Z-scan measures.

As reported in the next section, a simulation of the UV–vis spectra was conducted via DFT calculations in order to confirm the previous absorbance assignments and to clarify the effects of the different solvents, in terms of polarity and acidity, on the LCC optical properties.

In Table 1 the amount (in terms of relative abundance expressed in %) of the different species, estimated on the basis of the simulated and the experimental data, are shown. We outline that the calculations were made by fitting the most intense observed peaks and assuming the same extinction coefficient for the calculated and experimental spectra. The resulting percentage, reported in Table 1, is in good agreement with the literature data [10,27]. It is necessary to point out an uncertainness in the identification of the NC_6N and NC_8N absorption wavelengths, being the experimental positions in agreement with data reported by Caltaldo [10] but partially different from our DFT calculated values.

4.2. DFT calculations

All the calculations were carried out respectively in water, methanol, acetonitrile and cyclohexane but no significant difference is observed among the polar solvents. Therefore, henceforth we will report the data in methanol (M, polar solvent, 1.70 debye) and cyclohexane (C, apolar solvent) in order to evidence the effect of polarity solvents on LCCs electronic transitions.

Atomic charges, evaluated by means of B3LYP/D95(d), are symmetrically distributed in all the analyzed systems. It was found that the polar solvent increases the negative charge along the chain leaving a more marked positive charge onto hydrogen atoms, see Tables A.1 and A.2 reported in the Appendix. The net charge tends to become neutral in the central region of the molecules with increasing of the chain length. In cumulenes the net positive charge of hydrogen atoms is mainly balanced by the next carbon atom while in polyynes the two carbon atoms next to hydrogen are principally involved in the charge balance.

Calculated values for the main electronic transitions of $D_{\infty h}$ polyynes ($1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$) and D_{2h} cumulenes ($^1B_{1u} \leftarrow X^1A_{1g}$) are reported in Table 2 together with the oscillator strength.