Ionisation and fragmentation of polycyclic aromatic hydrocarbons by femtosecond laser pulses at wavelengths resonant with cation transitions

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Abstract

When femtosecond (fs) laser pulses irradiate hydrocarbon molecules, then many fragmentation channels evident in nanosecond irradiation are bypassed, providing a strong analytically useful parent ion. However a number of molecules show only a very small or indeed no parent ions and recent papers suggest that those that do not produce parent peaks have cation transitions in resonance with the femtosecond laser wavelength. This Letter shows that this resonance effect is not universal and some aromatic molecules not only show strong parent peaks but also doubly and triply ionised entities when their cation absorption spectrum is strongly resonant at either the 800 or 400 nm or indeed both. © 2002 Published by Elsevier Science B.V.

1. Introduction

In the 1990s it was noticed that when a number of small as well as organic molecules were irradiated with femtosecond (fs) laser light in the intensity regime 10^{13-16} W cm^{-2}, the strong fragmentation observed with nanosecond irradiation was largely bypassed [1–4] leading to enhanced parent ion production desirable for analytical purposes and led to the development of femtosecond laser mass spectrometry (FLMS) [5–7]. Femtosecond laser irradiation of molecules has been extensively reviewed recently [8,9].

It has however been noticed that strong parent ionic mass production is not universally evident and whenever the parent mass is not visible, extensive lower mass fragmentation invariably takes place [10,11]. Markevitch et al. [12] have discussed the relative ionisation/fragmentation yield as a

function of molecular size. They observed an exponential increase in dissociation rate with increasing number of atoms in the molecule and have attributed this to, e.g., lower bond dissociation energies, higher rate of energy transfer from electronic to nuclear co-ordinates and weaker vibrational force constants. However another possible explanation for increased fragmentation has been forwarded in three recent papers [11,13,14]. These studies have pointed out that in the femtosecond irradiation regime, whenever parent mass peaks are small or not visible, accompanied with extensive fragmentation, then the excitation wavelength is resonant with the electronic absorption of the parent cations. Furthermore, Harada et al. [11] emphasise that if the excitation wavelength is off-resonant then FLMS is a promising analytical technique.

Whenever large parent mass peaks are visible, multiply charged parent ions are also invariably observed after femtosecond irradiation of organic molecules. Although this has been observed in the intensity regime 10^{13-15} W cm^{-2}, most instances occur for intensities greater then 10^{15} W cm^{-2}, leading to so called 'atomlike' behaviour of the molecules [15,16].

The purpose of this Letter is to investigate the femtosecond irradiation of a number of polycyclic aromatic molecules which are known to have cation absorption spectra resonant with either the 400 or 800 nm or both wavelengths available in the present experiment.

2. Experimental

The four polycyclic aromatics molecules anthracene ($C_{14}H_{10}$, mass = 178.23), pyrene ($C_{16}H_{10}$, mass = 202.25), tetracene ($C_{18}H_{12}$, mass = 228.29) and chrysene ($C_{18}H_{12}$, mass = 228.29) were obtained from Sigma Aldrich.

The TOPS femtosecond laser [17] and the reflectron time-of-flight (ToF) mass spectrometer used in the present experiment have been described in detail elsewhere [18,19]. Briefly, the TOPS femtosecond laser system is used for ionisation of the nanosecond laser desorbed gas-phase molecules. The Ti:Sapphire laser produces pulses of 800

and 400 nm wavelength with a duration of 80 fs. The laser was linearly polarised with the E vector direction parallel to the ToF axis. Attenuation of the beam was achieved by using neutral density filters and the pulse duration was measured using a second-order autocorrelator.

In order to quantify any non-linear effects in the laser beam, a value for the B integral (described later) was calculated:

$$B = \frac{2\pi n_2}{\lambda} \int_0^z I(t,z)\,\mathrm{d}z, \tag{1}$$

where n_2 is the non-linear refractive index of a material, λ is the wavelength and $I(t,z)$ is the intensity of the laser pulse in the medium under consideration. All optical components as well as air paths were included in this integral. It is thought that significant distortion of the beam can occur when B is greater than 5. The value $B \approx 3$ in this experiment suggests that beam is not dramatically distorted. A cross-correlation of the laser pulse at 800 nm is shown in Fig. 1 revealing a small pre-pulse and with an intensity contrast ratio of about $1:10^3$.

The intensities of the focused laser beam were determined from the measured pulse energy and width and with a calculated spot size and verified using the known threshold laser intensities of the different charged states of Xe^{n+}.

Laser desorption of the solid samples was achieved using the fourth harmonic output (266
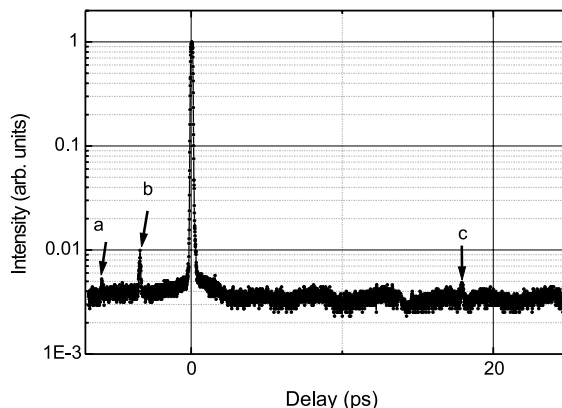

Fig. 1. Cross-correlation of the 800 nm laser pulse containing the following features: (a) pre-pulse at −6 ps; (b) reflection from the SHG crystal at −3.4 ps; (c) post-pulse at 18 ps.

nm, 5 ns) from a Nd:YAG laser focussed onto the sample stub. The energy of the desorption laser beam was controlled using an optical attenuator and monitored using a joulemeter. Focussing the ~7 mm diameter beam using a 27 cm focal length lens generated intensities up to 1×10^{10} W cm^{-2}. The timing between the desorption and ionisation laser pulses was accurately controlled using a pulse/delay generator.

The reflectron ToF mass spectrometer used in this experiment comprised a sample load-lock (sample transfer system), source chamber and flight tube. The source chamber and flight tube were pumped to a base pressure of ~10^{-9} Torr using turbomolecular pumps. The powder samples were dissolved in methanol, deposited onto the sample stub and allowed to dry. Following evaporation of the solvent, the stub is admitted to the chamber via a rotary-pumped load-lock and transfer arm. Ion extraction and acceleration is achieved using the sample stage and a two elec-

trode ion optic designed for this instrument [20]. An electrostatic potential of +2.7 kV is applied to the sample stage with +2 kV and +520 V s being applied to the first and second plates, respectively. The ions are detected by a multi-channel plate detector maintained at −2 kV. Signal output from the detector is coupled to a Lecroy digital oscilloscope (9344C) for single-shot and averaged data collection. A PC installed with GRAMS/32 software, connected to the oscilloscope through a GPIB interface, is used for data acquisition, mass calibration and analysis.

3. Results and discussion

Femtosecond laser ionisation mass spectra for the four molecules; anthracene, pyrene, tetracene and chrysene are shown in Figs. 2–4. These were taken with typical laser ablation intensities of ~3×10^9 W cm^{-2} (apart from anthracene which
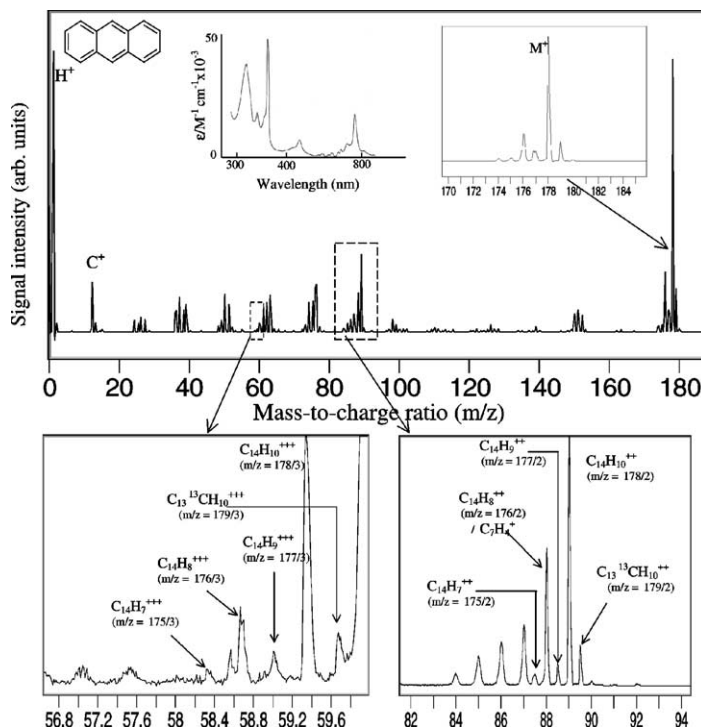

Fig. 2. A mass spectrum of anthracene ($C_{14}H_{10}$, $m = 178$) post-ionised with 800 nm, 80 fs laser light at an intensity of ~2×10^{15} W cm^{-2}. The parent mass is the base peak and doubly and triply ionised entities are clearly seen. The cation absorption spectrum is shown indicating the wavelength is resonant to some degree.
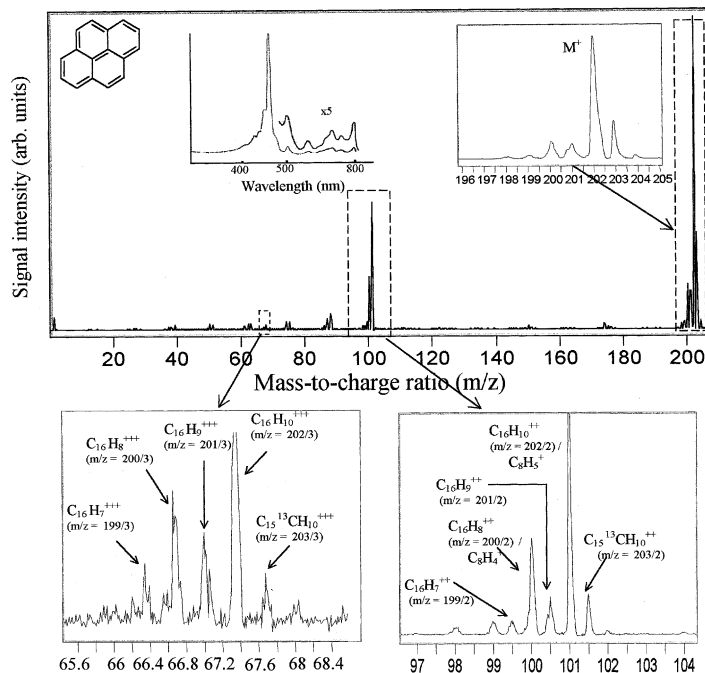
Fig. 3. A mass spectrum of pyrene ($C_{16}H_{10}$, $m = 202$) with the molecules laser desorbed with 5 ns, 266 nm at an intensity of 3×10^9 W cm^{-2} and post-ionised with 800 nm, 80 fs laser light at an intensity of about 2×10^{15} W cm^{-2}. The parent mass is the base peak and doubly and triply ionised entities are clearly seen. The cation absorption is again resonant.

was sublimed in to the vacuum) and with ionisation laser intensities of about 2–3×10^{15} W cm^{-2}. The spectra were averaged over ~ 1000 sweeps. It can be seen that in all four spectra the parent is the principal peak and that doubly ionised parent peak envelopes are also visible. Moreover for anthracene and pyrene, triply ionised parent peak envelopes can also be clearly seen. In each of the figures the cation absorption spectrum is also presented [21]. It can be clearly seen that considerable absorption strength exists at both 800 and 400 nm for all molecules and in particular for tetracene the two ionisation wavelengths are resonant with absorption peaks. For these four molecules, parent and multiply ionised parent entities are the base peaks. This is contrary to the findings in Refs. [11,13,14] which suggest that when the ionisation laser wavelength is resonant with cation absorption features the parent peak is small and heavy fragmentation results. Detailed descriptions of the fragmentation of these and other PAHs and nitro-PAHs will be presented later [22,23].

Fig. 5 shows the mass spectra for the four molecules at 400 nm with typical intensities of between 5×10^{14} and 9×10^{14} W cm^{-2} and again the parent masses are the base peaks with doubly ionised parents also visible. The absorption spectra are also shown with considerable strength at 400 nm.

The spectra for anthracene and tetracene shown here differ considerably from the data present by Markevitch et al. [12]. The femtosecond laser intensities in the present work at both 400 and 800 nm are somewhat higher but despite this the fragmentation is very much reduced. It should be pointed out however that Markevitch et al. heated their tetracene sample to augment the ion signal whereas laser ablation was used in the present case. Similarly for recent work with nitro-aromatic samples Hankin et al. [24] noticed that laser ablated samples followed by femtosecond ionisation considerably reduced fragmentation over heating followed by femtosecond laser ionisation.

Why the Markevitch data is so different from the present spectra when the femtosecond lasers
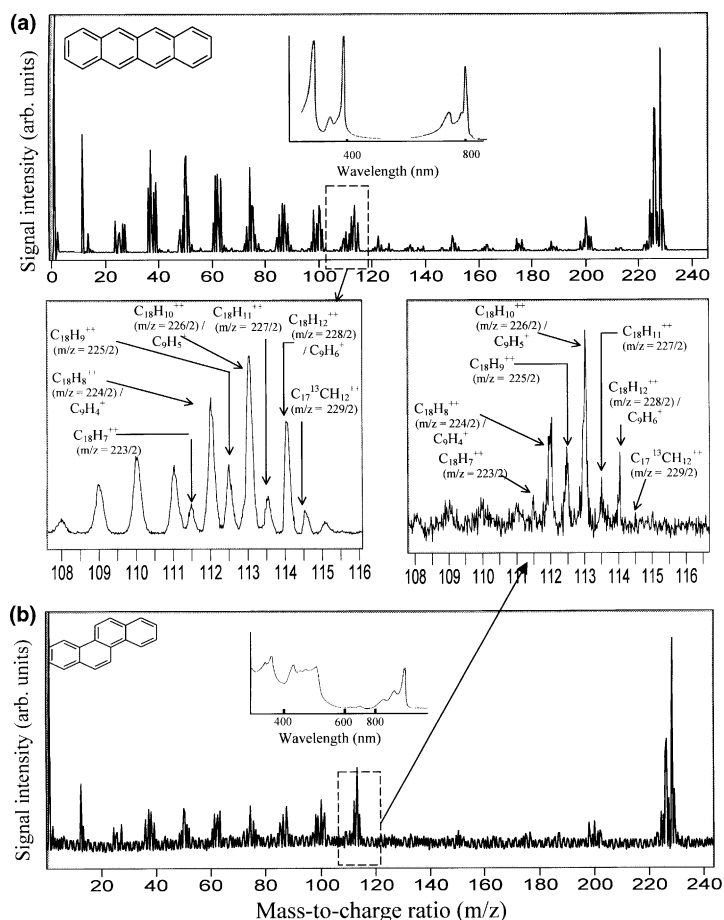
Fig. 4. A mass spectrum of (a) tetracene and (b) chrysene ($C_{18}H_{12}$, $m = 228$) under the same conditions as in Fig. 3. The parent mass is the base peak for both molecules and the doubly ionised entities are clearly seen. The cation absorption is again resonant.

have rather similar wavelengths and pulse widths is difficult to explain. It has been known for some time that although the fragmentation and ionisation for the same molecules presented by different groups using similar femtosecond lasers is qualitatively the same, quantitative differences exist. Several possible explanations for this behaviour exist. Muller et al. [25] attempted to explain these discrepancies in terms of unwanted contributions from non-linear effects in the laser beam as expressed by the B integral [26]. This is a deleterious effect when a high intensity laser beam propagates through a medium, e.g., optics and windows where the index of refraction changes non-linearly with the intensity. Significant distortion occurs when B

is of the order of 5. Muller et al. had a laser system that had a B value of 1.7 but most authors do not quote these values.

Other very important quality indicators for a femtosecond laser system that could explain the discrepancies are whether there are pre-pulses or considerable amplified stimulated emission (ASE) [27] associated with the ionisation pulse. If either of these is present, an initial plasma could be set up in the gas target affecting the interaction of the main pulse. This has been shown to be crucial for experiments [28] carried out at higher laser intensities above 10^{18} W cm^{-2}. Also it has been shown by a number of authors, e.g., Assion et al. [29] that tailoring femtosecond pulses using a computer
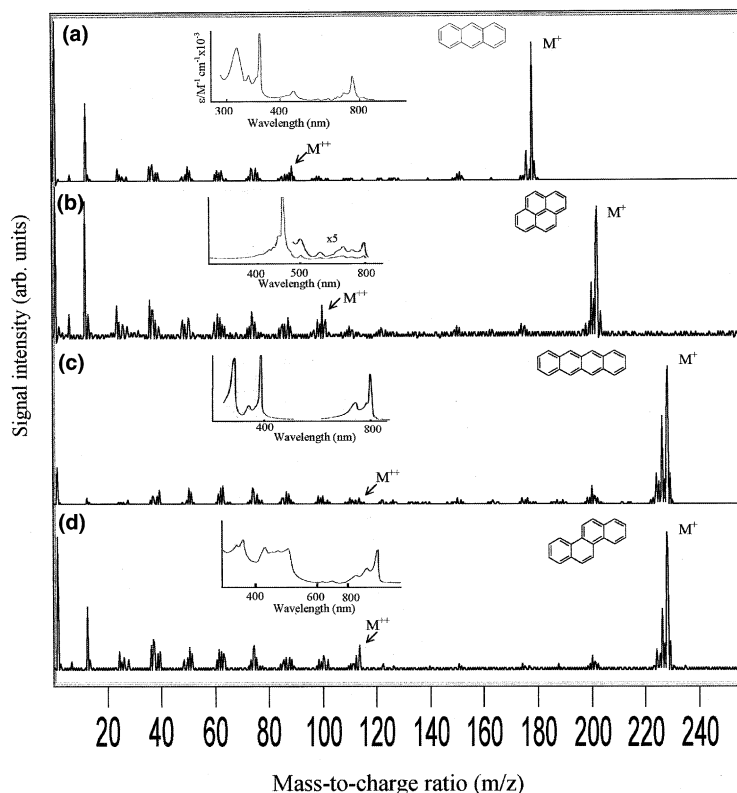
Fig. 5. The combined mass spectra of the four molecules showing how similar the degree of fragmentation is at 400 nm and an intensity of about 8×10^{14} W cm^{-2}. The degree of resonance with the cation absorption spectrum varies without greatly affecting the degree of fragmentation.

controlled pulse shaper can radically alter photodissociation branching ratios. All femtosecond laser systems have considerably different pulse shapes as well as pulse lengths resulting in quantitatively different ionisation/fragmentation results. Finally the question as to how the variation of the ion signal as a function of intensity within a focused high intensity laser spot has been dealt with in detail by El-Zein et al. [30] using a scanned apertured detector. Depending on the size and position of this aperture relative to the minimum waist of the laser focus, the detection or lack of detection of multiply charged species was observed. Although this work was carried out using xenon ions, similar results have been obtained with multiply charged and fragmentation patterns of CO_2 [31]. In addition, recent work carried out by the Glasgow group on nitro-aromatics [32] and

benzene [33] involved scanning the beam waist over 3 cm in the beam direction perpendicular to the ToF axis. The ion yield of the cations and high mass fragments exhibited distributions which depended critically on the position of the focal spot in relation to the extraction aperture and were symmetric for each 'wing' of the laser pulse. Any one or a combination of the above could explain the quantitative differences observed by research groups for femtosecond fragmentation and ionisation of organic molecules.

4. Conclusions

Femtosecond reflectron ToF mass spectra of solid phase samples of anthracene, pyrene, tetracene and chrysene have been recorded using the 5

ns fourth harmonic output from a Nd:YAG laser for desorption and 800 and 400 nm 80 fs pulse duration for photoionisation. This was expressly carried out to investigate whether the fact that the cation absorption spectrum of these molecules being resonant with the femtosecond laser wavelengths caused excessive fragmentation. It was shown that for these four molecules at the two wavelengths, the parent mass was the base peak and that doubly ionised (for all) and triply ionised (for anthracene and pyrene) were evident. This is contrary to the findings of the authors [11,13,14] who suggested that when resonance exists, little or no parent ions accompanied by extensive fragmentation result. It was also shown for anthracene and tetracene that the present spectra differ to some degree with the data presented by Markevitch et al. [12] for very similar laser systems. A number of possible explanations for this behaviour were suggested, differing *B* integrals, pre-pulse and ASE differences, pulse shape and length differences as well as the magnitude of the ion extraction volume of the mass spectrometer.

Acknowledgements

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