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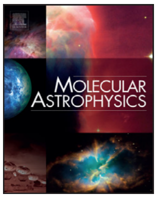

An optical spectrum of a large isolated gas-phase PAH cation: $C_{78}H_{26}^{+}$

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ABSTRACT

A gas-phase optical spectrum of a large polycyclic aromatic hydrocarbon (PAH) cation - $C_{78}H_{26}^{+}$– in the 410–610 nm range is presented. This large all-benzenoid PAH should be large enough to be stable with respect to photodissociation in the harsh conditions prevailing in the interstellar medium (ISM). The spectrum is obtained via multi-photon dissociation (MPD) spectroscopy of cationic $C_{78}H_{26}$ stored in the Fourier Transform Ion Cyclotron Resonance (FT-ICR) cell of the PIRENEA setup using the radiation from a mid-band optical parametric oscillator (OPO) laser.

The experimental spectrum shows two main absorption peaks at 431 nm and 516 nm, in good agreement with a theoretical spectrum computed via time-dependent density functional theory (TD-DFT). DFT calculations indicate that the equilibrium geometry, with the absolute minimum energy, is of lowered, nonplanar C_2 symmetry instead of the more symmetric planar D_{2h} symmetry that is usually the minimum for similar PAHs of smaller size. This kind of slightly broken symmetry could produce some of the fine structure observed in some diffuse interstellar bands (DIBs). It can also favor the folding of $C_{78}H_{26}^{+}$ fragments and ultimately the formation of fullerenes.

This study opens up the possibility to identify the most promising candidates for DIBs amongst large cationic PAHs.

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1. Introduction

The aromatic infrared bands (AIBs), strong emission features at 3.3, 6.2, 7.7, 8.6, 11.2 μm, dominating the near and mid infrared (IR) spectrum of many interstellar sources, are generally attributed to IR fluorescence of large (~50 C atom) PAH molecules pumped by UV photons (Allamandola et al., 1989; Genzel, 1998; Puget and Léger, 1989; Sellgren, 1984; Tielens, 2013). These PAH species are found to be ubiquitous and abundant, containing ~10% of the elemental carbon. They are expected to play an important role in the ionization and energy balance of the ISM of galaxies (Tielens, 2008 and references therein). They have also been proposed as an important catalyst for the formation of molecular H_2 in photodissociation regions (Boschman et al., 2015). In addition, PAHs are also considered as potential carriers for the DIBs (Crawford et al., 1985; Léger and d'Hendecourt, 1985; Salama et al., 1999). The leading idea in this proposal is that if PAHs are as abundant as they need to be to produce the observed AIBs, and since PAHs have prominent bands in the visible when either ionized or large enough, such bands must contribute to DIBs. The main arguments for PAHs as likely DIB carriers were reviewed relatively recently by Cox (2011), and a critical review of the current status of research in this direction is available by Salama and Ehrenfreund (2013).

Over the years, many experimental, theoretical and observational studies have investigated the spectroscopic properties of PAHs in relation with DIBs, ranging from the smallest species (Salama and Allamandola, 1992) to relatively large ones (see e.g. Weisman et al., 2003; Huisken et al., 2013) and to PAH derivatives (see e.g. Hammonds et al., 2009; Rouillé et al., 2013). Some effort was spent in trying to study large numbers of PAHs systematically, attempting to single out general trends that would hopefully allow to choose the most promising candidate DIB carriers in the vast population of this chemical family (see e.g. Ruiterkamp et al., 2005; Weisman et al., 2003; Tan, 2009). It is thus now understood that the onset of absorption due to electronic transitions tends to shift redwards with the increasing size of PAHs, and that very fast non–radiative transitions severely affect the spectral shape of PAH bands, due to lifetime broadening effects (Pino et al., 2011). This latter lifetime broadening effect tends to be

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much stronger for ions than for neutrals, with the former thereby exhibiting shallow, featureless bands, whereas the latter produce bands with some recognisable rotational envelopes. Notably there are DIBs qualitatively matching both kinds of spectral behaviors (see e.g. Sarre, 2013)

Recently four DIBs were identified as due to the fullerene cation C_{60}^+ (Campbell et al., 2015; Walker et al., 2015), which confirms that large carbonaceous molecules are good carrier candidates for the DIBs. However so far no DIBs could be identified as arising from electronic transitions in PAHs. The reason might be that spectroscopic measurements on PAH cations have concerned relatively small species, whereas chemical models predict that only large PAHs can survive the UV radiation field even in the diffuse ISM where this field is quite diluted (Le Page et al., 2001; Montillaud et al., 2013). Berné and Tielens (2012) have shown that closer to stars even large PAHs are expected to be efficiently photodissociated and this photoprocessing could be at the origin of the formation of C_{60} in these regions (Berné et al., 2015).

The very large PAH, $C_{78}H_{26}$ cation, has been studied by Zhen et al. (2014) as a possible precursor of fullerenes. It was selected because its armchair edges give it greater stability than PAHs with zigzag edges (Koskinen et al., 2008; Poater et al., 2007), thereby favoring its presence in space (Candian et al., 2014). But due to the limitations of their experimental set-up, Zhen et al. (2014) had difficulties to observe its photo-fragmentation behavior, especially the dehydrogenation.

We here describe our new study of the photo-fragmentation behavior, and a gas-phase spectrum of cationic $C_{78}H_{26}$ that we obtained in the range of 410–610 nm. The spectrum of this large PAH cation is compared with TD-DFT calculations to investigate its electronic structure. The experimental methods and results are described in Section 2, the computational methods and results are shown in Section 3. Section 4 compares the experimental and theoretical results, and finally Section 5 summarizes the main results.

2. Experimental methods and results

We have studied the $C_{78}H_{26}$ cation using PIRENEA (*Piège à Ions pour la Recherche et l'Etude de Nouvelles Espèces Astrochimiques*), which is an original home-built experimental set-up conceived to perform photo-physical and chemical studies on large molecules and nano-sized particles of astrophysical interest in isolation conditions approaching those of interstellar space in terms of collisions and interactions (Joblin et al., 2002). One of its advantages is that it can be used to study individual photofragments (which can be extremely reactive radicals), and very effectively isolate them by expelling everything else from the trap (Kokkin et al., 2013; Useli-Bacchitta et al., 2010; West et al., 2014). PIRENEA can be used to study electronic transitions via multi-photon dissociation (MPD) action spectroscopy. Strengths and drawbacks of this technique are described in detail by Useli-Bacchitta et al. (2010).

Desorption and ionization of PAH molecules result from laser irradiation of a solid sample of $C_{78}H_{26}$ by the fourth harmonic (266 nm) of a Nd:YAG laser (Minilite II, Continuum). The sample was produced by the Müllen group following the synthesis method described by Müller et al. (1997), which ensures that only one isomer is produced. Trapping of ionized species is achieved through the conjugated action of an axial magnetic field of 5 T, generated by a superconducting magnet, and an electrostatic field. The magnetic field confines the ions in the radial direction while the static electric field traps them in the axial direction. The ion trap (ICR cell) can be operated at very low temperature (~35K) and in ultra-high vacuum ($<10^{-10}$ mbar), to approach the isolation conditions of the ISM. The ions of interest can then be selected and isolated in the ICR cell by ejection of all the other species that could be produced. This is achieved by generating a suitable RF oscillating field containing an appropriately defined spectrum of frequencies, excluding frequencies that can excite the species one wants to retain.

A mid-band tunable OPO laser system (Panther EX, Continuum; 5 cm^{-1} bandwidth, 5 ns pulse duration) operating at a pulse frequency of 10 Hz is used to irradiate the trapped ions. *In-situ* non-destructive Fourier Transform ICR mass spectroscopy is used to analyse the effects of irradiation. Scanning the laser over a grid of wavelengths an action photo–absorption spectrum is obtained (Useli-Bacchitta et al., 2010).

In the conditions of the experiment, the photo-processing of PAH cations is heavily biased towards dissociation through the lowest energy channel. Each fragmentation event is initiated by absorption of multiple photons, the exact number depending on the wavelength of the OPO laser and the dissociation thresholds. The absorption of a photon in an electronic transition, followed by fast Internal Conversion (IC), leaves the molecule in a highly excited vibrational state in the ground electronic state, typically on a timescale of the order of 50 fs (Marciniak et al., 2015). Intramolecular vibrational redistribution (IVR) then quickly spreads the excess energy among all available vibrational modes, leaving the cation amenable to further excitation through the same sequence of electronic excitation and radiationless relaxation. Whenever the laser wavelength is in resonance with an electronic transition of the cation, the sequential absorption of multiple photons can take place and the dissociation can proceed. For reasons discussed later in Section 4, the width of these resonances is very broad due to the experimental technique.

Fig. 1 summarizes the photo-fragmentation results of $C_{78}H_{26}$ cation irradiation at 440 nm. The mass spectrum before irradiation of $C_{78}H_{26}$ cation reveals some residual fragmentation (peaks due to H loss) as a byproduct of the UV laser desorption and ionization process as well as the presence of the isotopic species containing one to three ^{13}C at higher mass. Fig. 1(A) shows the resulting mass spectra of trapped $C_{78}H_{26}$ cations upon 440 nm irradiation at different laser intensities; all experiments are performed under the same conditions with an irradiation time of 2.0 s. A wide range of dehydrogenated fragment ions are evident in these mass spectra that are attributed to multiple, sequential photon absorption and resulting photo-fragmentation events. The photo-dissociation of the $C_{78}H_{26}$ cation mainly follows sequential 2H (or H_2) separations until full dehydrogentaion, leading to the predominance of even-mass fragments $C_{78}H_{2n}^+$ with $n = [0-12]$. Fig. 1(B) shows the resulting mass spectra of $C_{78}H_{26}$ cation upon 440 nm irradiation with different irradiation times from 1.0 s to 6.0 s, at a fixed energy of 11.2 mJ per pulse. This shows the dehydrogenation photo-products as well as further fragmentation of the bare carbon cluster C_{78}^+ leading to C_{78-2n}^+ with $n = [1-4]$, similarly to what was observed by Zhen et al. (2014).

In Fig. 2, the MPD spectrum of $C_{78}H_{26}$ cation is shown. The resulting spectrum was obtained with laser intensity fixed at (7.0 ± 1.0) mJ per pulse and 2.0 s laser irradiation. Laser wavelengths were scanned in steps of 3 nm. The strongest transitions in the region studied were found to lie at 431 nm and 516 nm (FWHM ~ 20 nm in the MPD spectrum). The large bandwidth could be related to the lifetime broadening but is more likely related to the high rotational and vibrational temperatures. Sequential transitions after the first one arise from more and more highly excited ro-vibrational levels of the electronic ground state, populated by IC-IVR that redistributes the electronic excitation energy of the previously absorbed photons.

3. Computational methods and results

Our theoretical calculations were carried out in the framework of the DFT, in its stationary formulation for molecular properties in the electronic ground state, and in its time-dependent formulation (TD-DFT) to study excited states. In particular, we used the B-LYP gradient-corrected exchange-correlation functional (Lee et al., 1988) in combination with the def2-TZVP Gaussian basis set (Schafer et al., 1993),

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