

Dehydrogenated coronene cations and interstellar extinction

G. Mallocci¹, G. Mulas¹, C. Cecchi–Pestellini¹,
F. Useli–Bacchitta², A. Bonnamy², and C. Joblin²

¹Istituto Nazionale di Astrofisica–Osservatorio Astronomico di Cagliari,
Strada n.54, Loc. Poggio dei Pini, I–09012 Capoterra (CA) (Italy)
email: [gmulas, gmallocci, ccp]@ca.astro.it

²Centre d'Etude Spatiale des Rayonnements, CNRS et Université Paul Sabatier Toulouse 3,
Observatoire Midi-Pyrénées, 9 Avenue du Colonel Roche, 31028 Toulouse cedex 04 (France)
email: [francesca.useli, anthony.bonnamy, christine.joblin]@cesr.fr

Abstract. Dehydrogenated coronene molecules have been proposed as the carrier of the interstellar UV extinction bump and of some diffuse interstellar bands. To test this hypothesis, we have undertaken a combined a) theoretical and b) experimental work on the subject. a) We use the (time–dependent) density functional theory to study the effect of hydrogenation on the UV absorption cross–section of neutral and ionised coronene molecules. b) For the visible and near–UV, these calculations provide useful guidelines to analyse and interpret the electronic spectra obtained with the PIRENEA experimental set-up dedicated to astrochemistry.

Keywords. Astrochemistry, (ISM:) dust, extinction, ultraviolet: ISM, molecular data

1. Introduction

The carrier of the interstellar extinction bump at 2175 Å seems to require a free–flying form of carbon, either as size–restricted graphite pieces (Draine 1985) or as single or stacked PAHs (Duley & Seahra 1998). Duley (2006a) tentatively assigned this feature to a $\pi \rightarrow \pi^*$ plasmon resonance in dehydrogenated neutral and ionised coronene molecules ($C_{24}H_n$, with $n \leq 3$). The same molecules have been proposed to explain also some of the diffuse interstellar bands (Duley 2006b).

2. Methods

The effect of dehydrogenation on the electronic absorption spectra of gas–phase PAHs is poorly characterized. We have undertaken a combined theoretical and experimental work to assess both the contribution of dehydrogenated coronene molecules and their cations to the UV bump and the DIBs spectrum.

We used state–of–the–art quantum–chemical techniques (Mallocci *et al.* 2007) to obtain the required molecular parameters. The optimised geometries are obtained with density functional theory (DFT) as implemented in the NWChem code. Electronic spectra are computed with time–dependent DFT using two different implementations: (i) the real–time scheme of the Octopus program; (ii) the frequency–space method of NWChem.

In the PIRENEA experiment, coronene cations are produced by laser ablation/ionisation of a solid target. The ions are trapped in the ion cyclotron resonance cell under the combined action of a superconducting magnet and electrostatic potentials. Direct spectroscopy is not feasible due to the low density of trapped species (about 10^6 ions). A tunable laser (broad band OPO from Continuum) is used to perform photo–fragmentation of the isolated cations in the region 420–500 nm (typical energy per pulse is 5 mJ at 420 nm and 12 mJ at 500 nm). The fragment ion signal versus the laser wavelength provides the

fragmentation yield of the species, which depends on the product of the absorption cross section of the cation times the laser intensity.

3. Results

We show in Figure 1 the computed UV absorption spectra (TD-DFT in real time) of neutral and cationic coronene and their completely dehydrogenated counterparts. The photofragmentation spectrum of $C_{24}H_{12}^+$ is shown in Figure 2.

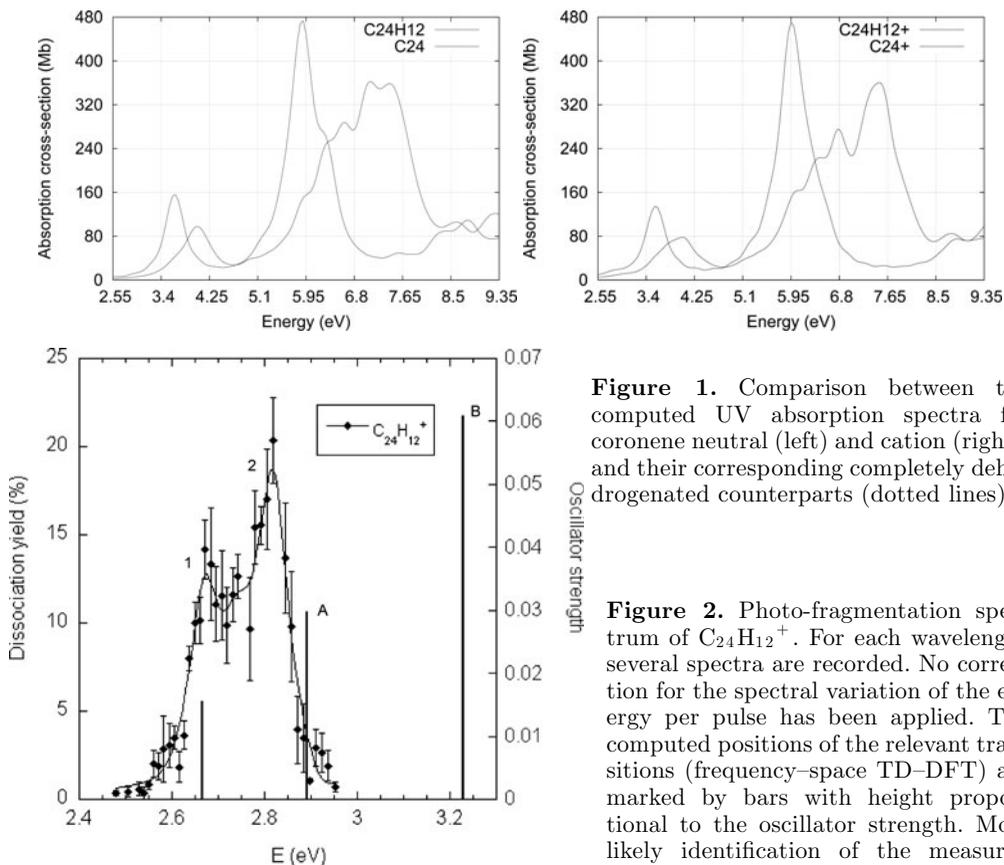


Figure 1. Comparison between the computed UV absorption spectra for coronene neutral (left) and cation (right), and their corresponding completely dehydrogenated counterparts (dotted lines).

Figure 2. Photo-fragmentation spectrum of $C_{24}H_{12}^+$. For each wavelength several spectra are recorded. No correction for the spectral variation of the energy per pulse has been applied. The computed positions of the relevant transitions (frequency-space TD-DFT) are marked by bars with height proportional to the oscillator strength. Most likely identification of the measured bands is 1-A, 2-B.

4. Discussion and future work

Progressive dehydrogenation translates into a blue shift of the main electronic transitions. The $\pi \rightarrow \pi^*$ collective resonance gets broader and bluer upon dehydrogenation. Its calculated energy position becomes incompatible with the observed position of the 220 nm extinction bump. The PIRENEA facility is being used to explore the visible spectra of coronene cations in various hydrogenation states (Useli-Bacchitta *et al.* 2008). NWChem TD-DFT calculations are used to identify the measured spectra. In the case of C_{24}^+ , in particular, different isomers (ring, cage, bicyclic ring, ...) are taken into account.

References

- Draine B. T. 1985, *ApJS*, 57, 587
 Duley, W. W. 2006a, *ApJ* (Letters), 639, L59
 Duley, W. W. 2006b, *ApJ* (Letters), 643, L21
 Duley, W. W. & Seahra, S. 1998, *ApJ*, 507, 874
 Mallocci, G., Joblin, C., & Mulas, G. 2007, *Chem. Phys.*, 332, 353
 Useli-Bacchitta, F. *et al.* 2008, in preparation