Fragmentation dynamics of excited ionized polycyclic aromatic hydrocarbons

To cite this article: C Paris *et al* 2014 *J. Phys.: Conf. Ser.* **488** 102027

Fragmentation dynamics of excited ionized polycyclic aromatic hydrocarbons

C. Paris*, H. Silva Jr.*, S. Díaz-Tendero*, M. Rapacioli†, F. Spiegelman†, F. Martín*‖ and M. Alcamí*[1]

**Departamento de Química, Módulo 13, Universidad Autónoma de Madrid, 28049, Madrid, Spain*
†Lab. de Chimie et Physique Quantiques, IRSAMC, CNRS/Université de Toulouse-UPS, 31062 Toulouse, France
‖*Instituto Madrileño de Estudios Avanzados en Nanociencias (IMDEA-Nanociencia),Cantoblanco 28049 Madrid, Spain*

Synopsis We have theoretically evaluated the fragmentation of excited and ionized polycyclic aromatic hydrocarbons (PAH) and clusters of PAHs. In particular the stability of neutral and positively charged coronene has been studied as a prototype of PAH. We present in this communication vertical and adiabatic ionization potentials with charge up to 6 and dissociation energies and fragmentation paths of several channels: H/H, H_2, H^+/H and H^+/H^+ loss. We present as well results corresponding to the fragmentation dynamics of singly-ionized clusters of pyrene.

Polycyclic aromatic hydrocarbons (PAHs) consist of fused carbon aromatic rings; they are most often benzenic compounds and present a flat structure with delocalized π electrons. These molecules present an important interest in the fields of astrophysics and astrochemistry [1,2] since they are considered as a significant component of interstellar dust and gas. They are indeed responsible for the emission features detected in interstellar IR spectra of many galactic and extragalactic sources [2,3]. In the interstellar medium, PAH molecules are exposed to a variety of ionizing processes due to the presence of keV ions in solar and stellar winds. Therefore it is interesting to study the interaction of PAHs with low-energy ions [4-7]. More precisely, the fragmentation patterns of these molecules after interaction with low energy multiply ions will provide information on their relative stability, which depends on the energy and charge transferred during the collision.

Furthermore, the PAHs molecules seem to be formed in the dense and hot envelopes of evolved carbon stars from the pyrolysis of hydrocarbons [8]. Under these conditions, formation of clusters of PAHs is possible. Previous works [10] showed that interstellar observations do not come from single PAHs molecules, but from photo dissociations of larger grains, which strongly evidences the existence of PAHs clusters [11]. The interaction of multiply charged ions with clusters of PAHs has been recently reported [7]. It was shown that these clusters have much higher tendencies to undergo fragmentation than other weakly bound clusters.

In this communication we present theoretical results obtained using the density functional theory. In particular we have studied the structure and stability of neutral and positively charged coronene ($C_{24}H_{12}$) as a prototype of PAH. We have first computed vertical and adiabatic ionization potentials with charges up to 6, which have been experimentally observed [6]. Dissociation energies for different channels involving hydrogen loss have been also computed: H, H^+, H_2 and H_2^+ loss channels have been considered. Finally, we have explored the potential energy surface of these fragmentation channels. We have analysed the competition between direct H_2 fragmentation and sequential loss of two atomic hydrogen atoms and also between the loss of charged vs neutral hydrogen:

$C_{24}H_{12}^{q+} \rightarrow C_{24}H_{10}^{q+} + H_2$
$C_{24}H_{12}^{q+} \rightarrow C_{24}H_{11}^{q+} + H \rightarrow C_{24}H_{10}^{q+} + 2H$
$C_{24}H_{12}^{q+} \rightarrow C_{24}H_{10}^{(q-1)+} + H_2^+$
$C_{24}H_{12}^{q+} \rightarrow C_{24}H_{11}^{q+} + H \rightarrow C_{24}H_{10}^{(q-1)+} + H + H^+$
$C_{24}H_{12}^{q+} \rightarrow C_{24}H_{11}^{(q-1)+} + H^+ \rightarrow C_{24}H_{10}^{(q-1)+} + H^+ + H$
$C_{24}H_{12}^{q+} \rightarrow C_{24}H_{11}^{(q-1)+} + H^+ \rightarrow C_{24}H_{10}^{(q-2)+} + H^+ + H^+$

We present also in this communication our recent results concerning the fragmentation dynamics of singly charged clusters of pyrene. By means of molecular dynamics simulations at different levels of theory (DFT-TB, ADMP, CPMD and BOMD) we evaluate the stability of these clusters as a function of the internal excitation energy. We also compute the energy and charge redistribution inside the clusters and how the internal degrees of freedom may storage an excess of excitation energy.

References

[1] HW Jochims *et al* 1994 *Astrophys. J.* **420** 307
[2] A Tielens 2008 *Ann. Rev. Astron. Astrop.* **46** 289
[3] AG Li *et al* 2001 *Astrophys. J.* **554** 778
[4] ER Micelotta *et al* 2010 *Astron. Astrophys.* **510** A36 and A37
[5] H Johansson *et al* 2011 *Phys. Rev. A* **84** 043201
[6] A Lawicki *et al* 2011 *Phys. Rev. A* **83** 022704
[7] AIS Holm *et al* 2010 *Phys. Rev. Lett.* **105** 213401
[8] J Cernicharo *et al* 2001 *Astrophys J* **546** L127
[9] F Boulanger *et al* 1990 *Astrophys J* **346** 136
[10] J Bernard *et al* 1993 *Astron Astrophys* **277** 609
[11] M. Rapacioli *et al* 2005 *J Phys Chem A* **109** 2487

[1]E-mail: manuel.alcami @uam.es