Dissociation of the benzene molecule by ultraviolet and soft X-rays in circumstellar environment

H. M. Boechat-Roberty,1⋆ R. Neves,1 S. Pilling,2 A. F. Lago3 and G. G. B. de Souza4

1Observatório do Valongo, Universidade Federal do Rio de Janeiro - UFRJ, Ladeira Pedro Antônio 43, CEP 20080-090, Rio de Janeiro, RJ, Brazil
2Pontifícia Universidade Católica do Rio de Janeiro, Marquês de S. Vicente 255 CEP22254-970, Rio de Janeiro, Brazil
3Universidade Federal do ABC, Rua Santa Adélia, 166, Santo André, São Paulo, Brazil
4Instituto de Química, Universidade Federal do Rio de Janeiro - UFRJ, Ilha do Fundão, CEP 21949-900, Rio de Janeiro, RJ, Brazil

Accepted 2008 November 27. Received 2008 November 21; in original form 2008 September 1

ABSTRACT
Benzene molecules, present in the proto-planetary nebula CRL 618, are ionized and dissociated by ultraviolet (UV) and X-ray photons originated from the hot central star and by its fast wind. Ionic species and free radicals produced by these processes can lead to the formation of new organic molecules. The aim of this work is to study the photoionization and photodissociation processes of the benzene molecule, using synchrotron radiation and time-of-flight mass spectrometry. Mass spectra were recorded at different energies corresponding to the vacuum UV (21.21 eV) and soft X-ray (282–310 eV) spectral regions. The production of ions from the benzene dissociative photoionization is here quantified, indicating that C6H6 is more efficiently fragmented by soft X-ray than UV radiation, where 50 per cent of the ionized benzene molecules survive to UV dissociation while only about 4 per cent resist to X-rays. Partial ion yields of H+ and small hydrocarbons, such as C2H3+, C3H4+, C4H5+, are determined as a function of photon energy. Absolute photoionization and dissociative photoionization cross-sections have also been determined. From these values, half-life of benzene molecule due to UV and X-ray photon fluxes in CRL 618 was obtained.

Key words: astrochemistry – molecular data – methods: laboratory – ISM: molecules – X-rays: stars.

1 INTRODUCTION
Benzene, C6H6, may be taken as the basic unit for the polycyclic aromatic hydrocarbons (PAHs), which are believed to play an important role in the chemistry of the interstellar medium (Woods et al. 2003). It may also serve as a precursor molecule to more complex organic compounds, such as amino acids like phenylalanine and tyrosine.

It is known that PAHs are mainly formed in the dust shells of late stages of asymptotic giant branch type carbon-rich stars (Chercnneff, Barker & Tielens 1992). Subsequent to the ejection of its C-rich envelope into the interstellar medium, these stars become a proto-planetary nebula (PPN), which evolve to planetary nebulae (PN).

The PAHs are highly efficient absorbers of ultraviolet (UV) radiation, which means they contribute considerably to interstellar UV opacity (Draine 1978; Bakes & Tielens 1994). The UV radiation absorbed by PAHs is converted from electronic to vibrational energy resulting in infrared photon emission. The infrared spectra of PN show these strong emission features at 3.3, 6.2, 7.7 and 11.3 μm which have been attributed to aromatic hydrocarbons and the features at 3.4 and 6.9 μm which might be due to aliphatic hydrocarbons (Kwok 2004). Shan, Suto & Lee (1991) showed experimentally that the 3.4–3.6 μm band, observed in some astronomical objects, may be assigned to stretching vibrational excitation of CH in methylated PAHs, or PAHs with a hydrogen atom substituted by a methyl group. Vijh, Witt & Gordon (2004) evidenced the presence of the anthracene molecule (three benzenic rings) through fluorescence spectra analysis in the PPN Red Rectangle.

The detection of benzene, C6H6, methyl acetylene (CH3C2H) and methyl diacetylene (CH3C2H) in the direction of the PPN CRL 618 was reported by Cernicharo et al. (2001a,b). All the infrared bands arose from a region with kinetic temperatures between 200 and 250 K, probably the photodissociation region (PDR) associated with the material surrounding the central star. Small hydrocarbons have also been detected in another similar object CRL 2688.

PAHs have also been observed within protostellar discs around both low-mass T Tauri and intermediate-mass Herbig Ae/Be stars (Acke & van den Ancker 2004; Geers et al. 2006). T Tauri stars have strong X-ray fields (Feigelson & Montmerle 1999) that ionize the

⋆E-mail: heloisa@ov.ufrj.br
molecular material at various distances around the protostellar discs producing a complicated sequence of chemical reactions, mainly by ion–molecule reactions.

The chemistry in circumstellar regions is strongly modified by the UV photons emitted from the hot central star and by the X-rays associated with its high-velocity winds. The soft X-rays are more effective ionizing agents as compared to UV radiation because they penetrate more deeply in the envelope and heat up the gas more efficiently than UV (Deguchi et al. 1990). These authors have suggested that the observed abundance of the HCO⁺ species can be explained by soft X-ray ionization rather than by UV ionization. Using the Chandra X-ray observatory, Kastner et al. (2003) have reported the discovery of X-ray emission from bipolar PN.

The knowledge of photoabsorption, photoionization and photofragmentation processes in the UV and X-ray regions for knowing PN is consequently extremely important. Le Page, Snow & Bierbaum (2001) have pointed out the important processes that may affect the PAH distribution in the interstellar medium, such as photofragmentation with carbon loss, double ionization and chemistry between PAH cations and minor species presented in diffuse clouds.

The destruction of benzene isolated in two different matrices has been measured for both UV photolysis and proton bombardment by Ruiterkamp et al. (2005). They derived the destruction cross-sections for benzene and found that proton bombardment is more efficient than the UV photolysis.

Using electron energy-loss spectroscopy, we have studied the excitation and photoabsorption processes at the UV region (3–50 eV) of benzene (Boechat-Roberty et al. 2004), naphthalene (de Souza et al. 2002) and anthracene (Boechat-Roberty et al. 1997).

The present work is concerned with the experimental investigation of the photoionization and dissociative photoionization of the benzene molecule upon interaction with UV and soft X-ray (in the vicinity of the carbon K shell), using synchrotron radiation and time-of-flight mass spectrometry. In Section 2, we brieﬂy present the experimental set-up and techniques. The production of ions following the benzene molecule dissociation by UV and soft X-ray photons and the determination of the absolute cross-sections and half-lives as a function of photon fluxes are presented and discussed in Section 3. Finally, in Section 4, ﬁnal remarks and conclusions are given.

2 EXPERIMENTAL

The experiment was performed at the Brazilian Synchrotron Light Laboratory (LNLS), São Paulo, Brazil. UV and soft X-ray photons from a toroidal grating monochromator (TGM) beamline (12–310 eV) perpendicularly intersect the gas sample inside a high-vacuum chamber. The gas needle was kept at ground potential. The emergent photon beam flux (∼10¹² photons s⁻¹) was recorded by a light-sensitive diode. Conventional time-of-flight mass spectra (TOF-MS) were obtained using the correlation between one photoelectron and a photoion (Photoelectron Photoion Coincidence (PEPICO)). The ionized recoil fragments produced by the interaction with the photon beam were accelerated by a two-stage electric field and detected by two micro-channel plate detectors in a chevron configuration, after mass-to-charge (m/q) analysis by a time-of-flight mass spectrometer (297-mm long). They produced the stop signals to a time-to-digital converter (TDC). Photoelectrons, accelerated in an opposite direction with respect to the positive ions, are recorded without energy analysis by two micro-channel plate detectors and provide the start signal to the TDC. The first stage of the electric field (708 V cm⁻¹) consists of a plate-grid system crossed at the centre by the photon beam. The TOF-MS was designed to have a maximized efficiency for ions with kinetic energies up to 30 eV. Negative ions may also be produced and detected, but the corresponding cross-sections are negligible.

A schematic diagram of the time-of-flight spectrometer inside the experimental vacuum chamber and the associated electronics. See details in text.

Figure 1. Schematic diagram of the time-of-flight mass spectrometer (TOF-MS) inside the experimental vacuum chamber and the associated electronics. See details in text.

The destruction of benzene isolated in two different matrices has been measured for both UV photolysis and proton bombardment by Ruiterkamp et al. (2005). They derived the destruction cross-sections for benzene and found that proton bombardment is more efficient than the UV photolysis.

Using electron energy-loss spectroscopy, we have studied the excitation and photoabsorption processes at the UV region (3–50 eV) of benzene (Boechat-Roberty et al. 2004), naphthalene (de Souza et al. 2002) and anthracene (Boechat-Roberty et al. 1997).

The present work is concerned with the experimental investigation of the photoionization and dissociative photoionization of the benzene molecule upon interaction with UV and soft X-ray (in the vicinity of the carbon K shell), using synchrotron radiation and time-of-flight mass spectrometry. In Section 2, we brieﬂy present the experimental set-up and techniques. The production of ions following the benzene molecule dissociation by UV and soft X-ray photons and the determination of the absolute cross-sections and half-lives as a function of photon fluxes are presented and discussed in Section 3. Finally, in Section 4, ﬁnal remarks and conclusions are given.

2 EXPERIMENTAL

The experiment was performed at the Brazilian Synchrotron Light Laboratory (LNLS), São Paulo, Brazil. UV and soft X-ray photons from a toroidal grating monochromator (TGM) beamline (12–310 eV) perpendicularly intersect the gas sample inside a high-vacuum chamber. The gas needle was kept at ground potential. The emergent photon beam flux (∼10¹² photons s⁻¹) was recorded by a light-sensitive diode. Conventional time-of-flight mass spectra (TOF-MS) were obtained using the correlation between one photoelectron and a photoion (Photoelectron Photoion Coincidence (PEPICO)). The ionized recoil fragments produced by the interaction with the photon beam were accelerated by a two-stage electric field and detected by two micro-channel plate detectors in a chevron configuration, after mass-to-charge (m/q) analysis by a time-of-flight mass spectrometer (297-mm long). They produced the stop signals to a time-to-digital converter (TDC). Photoelectrons, accelerated in an opposite direction with respect to the positive ions, are recorded without energy analysis by two micro-channel plate detectors and provide the start signal to the TDC. The first stage of the electric field (708 V cm⁻¹) consists of a plate-grid system crossed at the centre by the photon beam. The TOF-MS was designed to have a maximized efficiency for ions with kinetic energies up to 30 eV. Negative ions may also be produced and detected, but the corresponding cross-sections are negligible.

A schematic diagram of the time-of-flight spectrometer inside the experimental vacuum chamber is shown in Fig. 1, where A1 and A2 are the pre-amplifiers and D1 and D2 are the discriminators. The connection to the TDC is also shown. Besides PEPICO spectra, other two kinds of coincidence mass spectra were obtained simultaneously: PE2PICO spectra (PhotoElectron Photoion Photoion Coincidence) and PE3PICO spectra (PhotoElectron Photoion Photoion Photoion Coincidence). These spectra involve the detection of ions coming from double- and triple-ionization processes, respectively, that arrive coincidentally with photoelectrons. We have presented results on multi-ionization followed dissociation of acetic acid and alcohols in Pilling et al. (2007a,b). Of all signals received by the detectors, only about 10 per cent come from PE2PICO and 1 per cent from PE3PICO spectra, reflecting that the major contribution is indeed due to single-event coincidence. None the less, PEPICO, PE2PICO and PE3PICO signals were taken into account for normalization purposes. Recoil ion and ejected electron detection efficiencies of 0.23 and 0.04, respectively, were assumed. In addition, we took 0.54 and 0.78 as the efficiencies to detect at least one of the photoelectrons from double- and triple-ionization events, respectively (Cardoso 2001). Benzene was commercially obtained with high purity (99.7 per cent). No further purification was performed other than degassing the liquid sample by multiple freeze-pump-thaw cycles before admitting the vapour into the chamber. Details on the time-of-flight spectrometer are available elsewhere (Lago, Santos & de Souza 2004; Marinho et al. 2006).

The base pressure in the vacuum chamber was in the 10⁻⁸ Torr range. During the experiment, the chamber pressure was maintained below 10⁻⁵ Torr. The pressure at the interaction region (volume defined by the gas beam and the photon beam intersection) was estimated to be ∼1 Torr (10⁶ mols cm⁻³). The measurements were made at room temperature.

© 2009 The Authors. Journal compilation © 2009 RAS, MNRAS 394, 810–817
Downloaded from https://academic.oup.com/mnras/article-abstract/394/2/810/1070488
by guest
on 28 July 2018
3 RESULTS AND DISCUSSION

3.1 Production of ions

Mass spectra of benzene were obtained at the UV energy of 21.21 eV that corresponds to the photon energy emitted by helium atom (Hei) and at energies 282, 285, 289 and 301 eV, around the C1s → π* resonance at 285.2 eV (Hitchcock et al. 1987). The mass spectra obtained at 21.21 and 289 eV are shown in Fig. 2. Clearly, X-rays produce much more types of ions than UV photons. The most abundant ion at 21.21 eV corresponds to the parent ion C6H6, confirming the relatively high stability of the benzene molecule at the UV energy range, whereas at 289 eV the molecule is highly destroyed giving rise to several fragments like C6H5 (diacetylene) and to an enhancement of the H+ proton production.

The following ionic groups are due to carbon loss: C group (12 to 15 amu), C2 group (24 to 27 amu), C3 group (36 to 39 amu), C4 group (48 to 52 amu), C5 group (60 to 64 amu) and C6 group (72 to 79 amu).

In Fig. 3, we present the fragmentation pattern due to multiple hydrogen loss from C6H6 as a function of the photon energy. The phenyl radical, C6H5, derived from benzene by the removal of one hydrogen atom is a possible progenitor of other aromatic species. Kaiser, Asvanya & Leea (2000) pointed out that reactions of the phenyl radical with methylacetylene are relevant to the chemistry of PAHs in extraterrestrial environments. They showed that the reaction of C6H5 radicals with methylacetylene to form phenyl-methy lacetylene is expected to play a role in PAH synthesis only in high-temperature interstellar environments, such as circumstellar outflow of carbon star. The radical C6H5 is the second most abundant ionic species in this mass range formed by hydrogen loss due to X-ray interaction and its yield increases with the photon energy, particularly near the C1s resonance. Our data show that UV photons do not produce this radical from benzene (or PAHs) dissociation, and as the C6H6 was observed in the CRL 618 (Cernicharo et al. 2001a), its abundance in this environment might have a part due to the PAH fragmentation by X-rays.

The partial ion yields (PIY) as a function of the photon energy are shown in Table 1 and Figs 4(a) and (b), for the most significant fragments with intensity >0.1 per cent were tabulated. The estimated experimental error was below 10 per cent.

![Figure 2. TOF-MS of benzene molecule recorded at (a) UV photons (21.21 eV) and (b) soft X-ray photons (289 eV).](https://example.com/fig2)

![Figure 3. Behaviour of C6H5 group in the fragmentation of benzene at energies closer to the C1s resonance (~285 eV) as a function of the energy.](https://example.com/fig3)

| m/q   | Attribution | 21.21 eV | 282 eV | 285 eV | 289 eV | 301 eV |
|-------|-------------|---------|--------|--------|--------|--------|
| 1     | H+          | 0.4     | 6.6    | 6.2    | 8.1    | 8.3    |
| 2     | H2          | –       | 0.1    | 0.1    | 0.1    | 0.1    |
| 12    | C+          | –       | 1.8    | 1.5    | 2.1    | 2.1    |
| 13    | CH+         | –       | 1.5    | 1.2    | 1.6    | 1.7    |
| 14    | CH2+        | –       | 1.3    | 0.7    | 1.1    | 0.8    |
| 15    | CH3+        | –       | 1.9    | 2.1    | 2.2    | 2.8    |
| 16    | CH4+        | –       | 1.1    | 0.6    | 1.0    | 0.4    |
| 24    | C2+         | –       | 1.4    | 1.3    | 1.7    | 1.6    |
| 25    | C3H+        | –       | 3.2    | 3.1    | 3.8    | 3.8    |
| 26    | C3H2+       | 0.7     | 8.5    | 8.2    | 9.2    | 11     |
| 27    | C3H3+       | 0.3     | 1.9    | 3.3    | 3.4    | 3.6    |
| 28    | C3H4+       | 2.0     | 0.3    | 0.3    | 0.8    | 0.1    |
| 36    | C4+         | –       | 2.9    | 2.1    | 2.9    | 2.9    |
| 37    | C5H+        | 0.3     | 8.4    | 7.6    | 8.6    | 11     |
| 38    | C5H2+       | 0.7     | 11     | 6.3    | 11     | 15     |
| 39    | C5H3+ (C6H4+) | 5.0 | 5.4 | 4.4 | 3.6 | 2.4 |
| 40    | C6H+        | –       | 0.8    | 0.3    | 0.3    | 0.3    |
| 48    | C7+         | –       | 0.9    | 0.9    | 1.2    | 1.2    |
| 49    | C6H2+       | 0.2     | 2.6    | 4.1    | 3.5    | 2.8    |
| 50    | C6H3+       | 2.7     | 8.3    | 10     | 10     | 8.0    |
| 51    | C6H4+       | 5.9     | 7.6    | 8.5    | 4.6    | 3.2    |
| 52    | C6H5+       | 12      | 2.4    | 2.8    | 1.4    | 1.0    |
| 53    | C6H6+       | 2.0     | 0.8    | 0.7    | 0.5    | 0.4    |
| 60    | C7+         | –       | 0.5    | 0.5    | 0.6    | 0.5    |
| 61    | C7H+        | –       | 0.9    | 0.9    | 1.0    | 1.0    |
| 62    | C7H2+       | –       | 0.8    | 0.8    | 0.7    | 0.5    |
| 63    | C7H3+       | 1.5     | 1.9    | 1.8    | 1.7    | 2.2    |
| 72    | C8+         | –       | 0.1    | 0.2    | 0.2    | 0.1    |
| 73    | C8H+        | –       | 0.8    | 1.0    | 1.1    | 0.5    |
| 74    | C8H2+       | –       | 1.6    | 2.5    | 2.2    | 0.7    |
| 75    | C8H3+       | –       | 0.7    | 0.9    | 0.7    | 0.2    |
| 76    | C8H4+       | 3.3     | 0.5    | 0.6    | 0.3    | 0.4    |
| 77    | C8H5+       | 9.7     | 1.4    | 1.2    | 0.7    | 0.3    |
| 78    | C8H6+       | 50      | 5.4    | 4.3    | 2.6    | 1.5    |
| 79    | C13C6H4+    | 3.5     | 0.5    | 0.2    | 0.2    | 0.1    |

© 2009 The Authors. Journal compilation © 2009 RAS, MNRAS 394, 810–817
Photodestruction of the benzene molecule

Figure 4. PIY for some fragments of C₆H₆ molecule as a function of the photon energy. (a) PIY > 5 per cent and (b) PIY < 5 per cent.

outcomes (H⁺, C₄H₊, C₃H₊, C₂H₊, C₁H₊, C₊, C₊₊) and for other minor outcomes, respectively. The production of some ions like C₄H₊, C₂H₊, and C₊ shows an inverse behaviour. The statistical uncertainties are below 10 per cent.

The peak at m/q = 39 amu may be assigned to C₃H₊ with probably a contribution from C₂H₊. Braitbart et al. (1992) have obtained mass spectra for benzene in the 25–70 eV region. They provided information on the relative yields of C₆H₊/C₃H₊ and C₄H₊/C₂H₊ at 35 and 70 eV. The photoionization mass spectrum of benzene at 21.21 eV was also discussed by Berkowitz (1979), where he presented relative intensity values for ionic fragments taken from three different measurements. As an example, the obtained average value of the ratio C₆H₊/C₃H₊ is 9.13, in reasonable agreement with our result, 10.0, taking into account the present experimental error which is about 10 per cent. A comparison between our results and Berkowitz (1979) and Braitbart et al. (1992) data is presented in Fig. 5(a). The ratio C₆H₊/C₃H₊ is seen to decrease with increasing energy in the UV and soft X-Ray ranges. The C₆H₊/C₃H₊ yield ratio is shown in Fig. 5(b). A value of about 0.17 was estimated at 21.21 eV by linear fitting. It should, however, be taken into consideration that the peak intensity at m/q = 39 amu contains a 17 per cent contribution from benzene dications. The formation process of benzene dications at energies below the double-ionization potential (IP₊₊ = 26.1 eV) proceeds by two stages (Leach 1995), such as

\[ C₆H₊ + h\nu₁ \rightarrow C₆H₊ + e⁻ \] and \[ C₆H₊ + h\nu₂ \rightarrow C₆H₊₊ + e⁻ \].

The fragmentation pathways of C₆H₊ were calculated using density functional theory by Rosi, Bauschlicher & Bakes (2004). They suggest that the Coulomb explosion is not a significant channel under most astrophysical conditions and therefore the dications are long-lived and should be considered in the modelling of the interstellar medium. The behaviour of PAH dications in H I and H II regions has been discussed by Leach (1995) based on experimental results. It was concluded that in H I regions, dication fragmentation will proceed mainly by the covalent channel (A₊₊ → B₊₊ + C) giving rise to small neutral products such as H, H₂, C₂H, C₃H, C₃H₂.

In H II regions, where more energetic photons are available, the PAHs could be destroyed by charge separation processes (A₊₊ → B + C⁺) producing more ions like C₂H₊ and C₃H₊. These ionic...
species could participate in the formation of new molecules. Photodestruction of PAHs has been proposed to explain the abundance enhancement of C$_8$H$_3$ or the presence of small hydrocarbons in PDRs (Fuente et al. 2003; Pety et al. 2005).

PIY or relative intensities for the ionic fragments observed in the C$_8$H$_6$ mass spectra recorded with 70 eV electrons [National Institute of Standard and Technology (NIST) data base], UV (21.21 eV) and soft X-ray (289 eV) photons are compared in Figs 6(a)–(c), respectively. A comparison between the mass spectra recorded with 70 eV electrons and 21.21 eV photons reveals a similar fragmentation pattern despite the different dissociation mechanisms. This corroborates the idea that 70 eV electrons produce, as a first approximation, the same ionic dissociation as created by UV photons, as suggested before (Lago et al. 2004; Boechat-Roberty et al. 2005; Pilling, Santos & Boechat-Roberty 2006). The molecular ion C$_8$H$_6^+$ is clearly more destroyed by soft X-rays than by UV photons, or only 3 per cent survive to X-rays while 50 per cent resist to UV, as expected.

The major dissociative photoionization pathways (PIY > 5 per cent) of benzene due to UV (21.21 eV) and soft X-rays (282–301 eV) photons are presented in Tables 2 and 3, respectively. We show that 12 per cent of C$_8$H$_6$ are UV dissociated via acetylene loss C$_8$H$_3^+$ while 9 per cent are X-rays dissociated by releasing the ionized acetylene. The dissociation channel with the liberation of the C$_8$H$_3^+$ + neutrals represents about 5.9 per cent on both radiation regimens.

The abundance of benzene depends on both the production and destruction rates. Therefore, the knowledge of the photodissociation processes and its ion yields plays an essential role in interstellar chemistry. This work point out to the importance of the ionic species to the increase of molecular complexity. In PDRs, many ions can be produced by the photodissociation of large molecules. We have previously suggested that the production of H$^+$ via the dissociative photoionization of methylated organic molecules (Pilling et al. 2007c). In this work, we are quantifying the production of ions by benzene fragmentation.

The formation mechanism of complex molecules, such as benzene, is considered to involve additions of C$_2$H$_2$ or C$_2$H and subsequent closure to form a ring (Cherchneff et al. 1992). These mechanisms use a neutral–neutral chemistry and need very high densities and temperatures in the vicinity of 1000 K to be efficient. Woods et al. (2002) have found that the enhanced ionizing radiation results in abundance of complex molecules. The benzene molecule can be formed efficiently near regions with intense ionizing sources such as high X-ray photons. The authors have also shown that the physical conditions in CRL 618 may efficiently contribute to the formation of C$_8$H$_6$. In addition, the formation mechanism of benzene depends on the environment with different pathways in PN and interstellar medium (Woods & Willacy 2007).

### 3.2 Half-lives of benzene and UV and X-ray photon fluxes

Absolute cross-section values for both photoionization and photodissociation processes of organic molecules are extremely important as inputs for molecular abundance models (Sorrell 2001). In these theoretical models, molecules are formed inside the bulk of icy grain mantles photoprocessed by starlight (UV and soft X-ray photons). The main chemistry route is based on radical–radical reactions followed by chemical explosion of the processed mantle that ejects organic dust into the ambient gaseous medium. The destruction of a given molecule subjected to a radiation field in the energy range $E_2 - E_1$ inside a gaseous dusty cloud can be written as (Cottin, Moore & Benilana 2003)

$$\frac{dN}{dt} = N k_{ph}.$$  (1)

### Table 2. Main dissociation pathways from single ionization due to UV photons (21.21 eV).

| Reaction | Product |
|----------|---------|
| C$_8$H$_6$ + h$\nu$ | C$_8$H$_6^+$ + e$^-$ |
| C$_8$H$_6^+$ | 12 per cent |
| C$_8$H$_5^+$ + C$_2$H$_2$ |
| 9.7 per cent |
| C$_8$H$_4^+$ + H |
| 5.9 per cent |
| C$_8$H$_3^+$ + C$_2$H$_2$ + H |
| 5.0 per cent |
| C$_7$H$_5^+$ + neutrals |

### Table 3. Main dissociation pathways from single ionization due to soft X-rays (282–301 eV).

| Reaction | Product |
|----------|---------|
| C$_8$H$_6$ + h$\nu$ | C$_8$H$_6^+$ + e$^-$ |
| C$_8$H$_6^+$ | 11 per cent |
| C$_8$H$_5^+$ + neutrals |
| 9.2 per cent |
| C$_8$H$_4^+$ + neutrals |
| 9.1 per cent |
| C$_8$H$_3^+$ + neutrals |
| 8.9 per cent |
| C$_7$H$_5^+$ + neutrals |
| 7.3 per cent |
| H$^+$ + neutrals |
| 5.9 per cent |
| C$_4$H$_3^+$ + neutrals |

---

Figure 6. Comparison between PIY of C$_8$H$_6$ molecule obtained and (a) 70 eV electrons from NIST, (b) 21.21 eV photons and (c) 289 eV photons.
where \( N \) is the column density (molecules cm\(^{-2}\)) and \( k_{ph} \) is the photodissociation rate (s\(^{-1}\)) given by

\[
k_{ph} = \int_{E_1}^{E_2} \sigma_{ph-d}(E) f(E) \, dE,
\]

(2)

where \( \sigma_{ph-d}(E) \) (cm\(^2\)) is the photodissociation cross-section and \( f(E) \) is the photon flux both as a function of energy (photons cm\(^{-2}\) eV\(^{-1}\) s\(^{-1}\)). The photoionization rate is also given by

\[
\zeta_i = \int_{E_1}^{E_2} \sigma_{ph-i}(E) f(E) \, dE,
\]

(3)

where \( \sigma_{ph-i}(E) \) (cm\(^2\)) is the photoionization cross-section.

The determination of \( \sigma_{ph-d} \) of molecules is very important to estimate the molecular abundance in the interstellar environments. Moreover, knowing the photon dose and \( \sigma_{ph-d} \) values, it is possible to determine the half-life of a given molecule.

The half-life may be obtained from equation (2) by writing

\[
t_{1/2} = \frac{\ln 2}{k_{ph}},
\]

(4)

which does not depend on the molecular number density.

Assuming a negligible fluorescence yield due to the low-carbon atomic number (Chen, Crasemann & Mark 1981) and discarding anionic fragments in the present X-ray photon energy range, we assumed that all absorbed X-rays photons lead to cationic ionizing process. Therefore, the precise determination of non-dissociative single-ionization cross-section (\( \sigma_{ph-i} \)) and the dissociative single-ionization (photodissociation) cross-section (\( \sigma_{ph-d} \)) of benzene can be determined by

\[
\sigma_{ph-i} = \sigma^+ \frac{\text{PIY}_{C_6H_6} \chi^+}{100},
\]

(5)

and

\[
\sigma_{ph-d} = \sigma^+ \left( 1 - \frac{\text{PIY}_{C_6H_6} \chi^+}{100} \right),
\]

(6)

where \( \sigma^+ \) is the cross-section for single-ionized fragments (see description in Boechat-Roberty et al. 2005; Pilling et al. 2006).

In order to put our data on an absolute scale after subtraction of the linear background and false coincidences coming from aborted double and triple ionization (see Simon et al. 1991), we have summed the contributions of all cationic fragments, and the sum has been normalized to the photoabsorption cross-sections measured by Hitchcock et al. (1987).

Absolute dissociative photoionization and photoionization cross-sections as a function of the X-ray photon energy can be seen in Fig. 7. The absolute absorption cross-section of benzene (Hitchcock et al. 1987) is also shown (solid line). These values are also shown in Table 4. The \( \sigma_{ph-d} \) is about 0.93 of \( \sigma_{ph-abs} \) and \( \sigma_{ph-i} \) is about 0.033 of \( \sigma_{ph-abs} \).

In the UV interstellar radiation field (ISRF), a benzene molecule is destroyed by acetylene loss at a rate of \( 1.5 \times 10^{-10} \) s\(^{-1}\) (Woods & Wilcay 2007), which corresponds to a survival time of around 200 years. Taken into account that the diffuse interstellar UV flux, integrated from 6 to 13.6 eV, is \( 10^6 \) photons cm\(^{-2}\) s\(^{-1}\), the integrated cross-sections are \( \sigma_{UV} = 1.5 \times 10^{-18} \) cm\(^2\). However, Ruiterkamp et al. (2005) reported that the half-life of gas phase benzene due to photolysis in diffuse clouds is 27 yr that corresponds to \( \sigma_{UV} = 8.1 \times 10^{-18} \) cm\(^2\). Therefore, this latter cross-section is 5.4 times higher than the dissociation by acetylene loss only.

As mentioned before, employing electron energy-loss spectroscopy, we have determined photoabsorption cross-sections (\( \sigma_{ph-abs} \)) at the UV region (3–45 eV) for the benzene molecule.

The half-life may be obtained from equation (2) by writing

\[
\frac{\ln 2}{k_{ph}} =
\]

(4)

which does not depend on the molecular number density.

Assuming a negligible fluorescence yield due to the low-carbon atomic number (Chen, Crasemann & Mark 1981) and discarding anionic fragments in the present X-ray photon energy range, we assumed that all absorbed X-rays photons lead to cationic ionizing process. Therefore, the precise determination of non-dissociative single-ionization cross-section (\( \sigma_{ph-i} \)) and the dissociative single-ionization (photodissociation) cross-section (\( \sigma_{ph-d} \)) of benzene can be determined by

\[
\sigma_{ph-i} = \sigma^+ \frac{\text{PIY}_{C_6H_6} \chi^+}{100},
\]

(5)

and

\[
\sigma_{ph-d} = \sigma^+ \left( 1 - \frac{\text{PIY}_{C_6H_6} \chi^+}{100} \right),
\]

(6)

where \( \sigma^+ \) is the cross-section for single-ionized fragments (see description in Boechat-Roberty et al. 2005; Pilling et al. 2006).

In order to put our data on an absolute scale after subtraction of the linear background and false coincidences coming from aborted double and triple ionization (see Simon et al. 1991), we have summed the contributions of all cationic fragments, and the sum has been normalized to the photoabsorption cross-sections measured by Hitchcock et al. (1987).

Absolute dissociative photoionization and photoionization cross-sections as a function of the X-ray photon energy can be seen in Fig. 7. The absolute absorption cross-section of benzene (Hitchcock et al. 1987) is also shown (solid line). These values are also shown in Table 4. The \( \sigma_{ph-d} \) is about 0.93 of \( \sigma_{ph-abs} \) and \( \sigma_{ph-i} \) is about 0.033 of \( \sigma_{ph-abs} \).

In the UV interstellar radiation field (ISRF), a benzene molecule is destroyed by acetylene loss at a rate of \( 1.5 \times 10^{-10} \) s\(^{-1}\) (Woods & Wilcay 2007), which corresponds to a survival time of around 200 years. Taken into account that the diffuse interstellar UV flux, integrated from 6 to 13.6 eV, is \( 10^6 \) photons cm\(^{-2}\) s\(^{-1}\), the integrated cross-sections are \( \sigma_{UV} = 1.5 \times 10^{-18} \) cm\(^2\). However, Ruiterkamp et al. (2005) reported that the half-life of gas phase benzene due to photolysis in diffuse clouds is 27 yr that corresponds to \( \sigma_{UV} = 8.1 \times 10^{-18} \) cm\(^2\). Therefore, this latter cross-section is 5.4 times higher than the dissociation by acetylene loss only.

As mentioned before, employing electron energy-loss spectroscopy, we have determined photoabsorption cross-sections (\( \sigma_{ph-abs} \)) at the UV region (3–45 eV) for the benzene molecule.

The half-life may be obtained from equation (2) by writing

\[
\frac{\ln 2}{k_{ph}} =
\]

(4)
the Earth (Fig. 8). The integrated photon flux from 280 to 310 eV,

\[ F_X = \int_{280 \text{ eV}}^{310 \text{ eV}} f(E) \, dE, \]  

is equal to \( 7.6 \times 10^4 \) (photons cm\(^{-2}\) s\(^{-1}\)), which corresponds to a half-life of the benzene of \( 7.6 \times 10^3 \) yr. As the X-ray extinction was not taken into account in this calculation, the actual photon flux will be consequently smaller than the presented value. For comparison, approximately the same flux is present at the dense molecular cloud AFGL 2591 (Stauber et al. 2005). The photon flux (280–310 eV) from the Sun at 1 au is about \( 8 \times 10^3 \) photons cm\(^{-2}\) s\(^{-1}\) (Gueymard 2004) whose half-life is only 7.2 yr.

The half-life of the benzene molecule as a function of UV and X-ray photon fluxes is shown in Fig. 9. The cross-section \( \sigma_{UV} \) for the benzene molecule, it was possible to obtain the half-life as a function of photon fluxes that can be used to know about the survival of this molecule in circumstellar and interstellar environments where the PAHs are present.

**ACKNOWLEDGMENTS**

The authors would like to thank the staff of the Brazilian Synchrotron Light Laboratory (LNLS) for their valuable help during the experiments. We are particularly grateful to Professor A. Naves de Brito for the use of the Time-of-Flight Mass Spectrometer. This work was supported by LNLS, CNPq, CAPES, FAPESP and FAPERJ.

**REFERENCES**

Acke B., van den Ancker M. E., 2004, A&A, 426, 151
Bakes E. L. O., Tielens A. G. G. M., 1994, ApJ, 427, 822
Berkowitz J., 1979, Photoabsorption, Photoionization and Photoelectron Spectroscopy. Academic Press Inc., New York
Boechat-Roberty H. M., Rocco M. L., Lucas C. A., de Souza G. G. B., 2004, J. Phys. B: At. Mol. Opt. Phys., 37, 1467
Boechat-Roberty H. M., Rocco M. L., Lucas C. A., de Souza G. G. B., 1997, J. Phys. B: At. Mol. Opt. Phys., 30, 3369
Boechat-Roberty H. M., Rocco M. L., Lucas C. A., de Souza G. G. B., 2004, J. Phys. B: At. Mol. Opt. Phys., 37, 1467
Boechat-Roberty H. M., Pilling S., Santos A. C. F., 2005, A&A, 438, 915
Braitbart O., Tobita S., Leach S., Roy P., Nenner I., 1992, AIP Conf. Proc. Vol. 258, Synchrotron Radiation and Dynamic Phenomena. Am. Inst. Phys., New York, p. 42
Cardoso E. S., 2001, MSc thesis, IF/UNICAMP, Sao Paulo, Brazil
Cernicharo J., Heras A. M., Tielens A. G. G. M., Pardo J. R., Herpin F., Guélín M., Waters L. B. F. M., 2001a, ApJ, 546, L123
Cernicharo J., Heras A. M., Pardo J. R., Tielens A. G. G. M., Guélín D. E., Neri R., Waters L. B. F. M., 2001b, ApJ, 546, L130
Chen M. H., Crasemann B., Mark H., 1981, Phys. Rev. A, 24, 177
Cherchneff I., Barker J. R., Tielens G. G. M., 1992, ApJ, 401, 269

& Cernicharo 2000), leading to a half-life of about 2 h. The molecular dissociation due to X-rays becomes more important than due to UV mainly in X-ray-dominant regions, XDR, where UV radiation is almost totally attenuated.

**4 CONCLUSIONS**

We have performed an experimental study of the photoionization and dissociative photoionization processes of the benzene molecule using synchrotron radiation and time-of-flight mass spectrometry in the electron–ion coincidence mode.

It was observed that the benzene molecules are more efficiently fragmented by soft X-rays, producing many more ions, than UV photons. per cent of the \( \text{C}_6\text{H}_6^+ \) molecules survive to UV dissociation while only about 4 per cent resist to X-ray destruction. PIY of \( \text{H}^+ \) and small hydrocarbons such as \( \text{C}_2\text{H}_3^+, \text{C}_2\text{H}_4^+, \text{C}_3\text{H}_4^+ \) are determined as a function of photon energy.

The abundance of the hydrocarbons \( \text{C}_2\text{H}_2, \text{C}_3\text{H}_2, \text{C}_4\text{H}_4, \text{CH}_2\text{C}_3\text{H}, \text{CH}_3\text{C}_2\text{H} \) detected in the CRL 618 could also be associated with the photodissociation of benzene, PAHs and their methyl derivatives that might undergo the radiative recombination.

The X-ray dissociative photoionization cross-section \( \sigma_{X} \) (integrated in the 280–310 eV range) is 4.7 times higher than the UV photodissociation cross-section \( \sigma_{UV} \) (integrated from 6 to 13.6 eV). As the stellar UV photon flux is more intense than X-ray one, UV destruction rate is larger than X-ray destruction rate, despite the fact that X-rays produce many more types of ionic fragments.

From the absolute UV and X-ray photodissociation cross-sections, \( \sigma_{UV} \) and \( \sigma_{X} \), for the benzene molecule, it was possible to obtain the half-life of benzene as a function of photon fluxes that can be used to know about the survival of this molecule in circumstellar and interstellar environments where the PAHs are present.
Photodestruction of the benzene molecule

Cottin H., Moore M. H., Benilan Y., 2003, ApJ, 590, 874
Deguchi S., Izumiura H., Kaifu N., Mao X., Nguyen-Q-Rieu U. N., 1990, ApJ, 351, 522
de Souza G. G. B., Rocco M. L. M., Boechat-Roberty H. M., Lucas C. A., Borges I. Jr, Hollauer E., 2002, J. Electr. Spectr. Rel. Phen., 123, 315
Draine B. T., 1978, ApJSS, 36, 595
Feigelson E. D., Montmerle T., 1999, ARA&A, 37, 363
Fuente A., Rodriguez-Franco A., Garcia-Burillo S., Martin-Pintado J., Black J. H., 2003, A&A, 406, 899
Geers V. C. et al., 2006, A&A, 459, 545
Guerrero M. A., Chu Y. H., Gruendl R. A., 2000, ApJS, 129, 295
Guerrero M. A. et al., 2006, in Barlow M. J., Mendez R. H., eds, IAU Symp. No. 234, Planetary Nebulae in our Galaxy and Beyond Proceedings
Guemyard C. A., 2004, Sol. Energy, 76, 423
Herpin F., Cernicharo J., 2000, ApJ, 530, L129
Hitchcock A. P., Fisher P., Gedanken A., Robin M. B., 1987, J. Phys. Chem., 91, 531
Kaiser R. I., Asvanya O., Leea Y. T., 2000, Plan. Space Sci., 48, 5
Kastner J. H., Balick B., Blackman E. G., Frank A., Soker N., Vrtilek S. D., Li J., 2003, ApJ, 591, L37
Kwok S., 2004, Nat, 430, 985
Lago A. F., Santos A. C. F., de Souza G. G. B., 2004, J. Chem. Phys., 120, 9547
Le Page V., Snow T. P., Bierbaum V. M., 2001, ApJSS, 132, 233
Leach S., 1995, Planet. Space Sci., 43, 1153
Lee C-F., Sahai R., 2003, ApJ, 586, 319
Marinho R. R. T., Lago A. F., Homem M. G. P., Coutinho L. H., de Souza G. G. B., Naves de Brito A., 2006, Chem. Phys., 324, 420
Pety J., Teysier D., Posso D., Gerin M., Roueff E., Abergel A., Habart E., Cernicharo J., 2005, A&A, 435, 885
Pilling S., Santos A. C. F., Boechat-Roberty H. M., 2006, A&A, 449, 1296
Pilling S., Boechat-Roberty H. M., Santos A. C. F., de Souza G. G. B., Naves de Brito A., 2007a, J. Elec. Spec. Relat. Phenom., 155, 70
Pilling S., Boechat-Roberty H. M., Santos A. C. F., de Souza G. G. B., 2007b, J. Elec. Spec. Relat. Phenom., 156–158, 139
Pilling S., Andrade D. P. P., Neves R., Ferreira-Rodrigues A. M., Santos A. C. F., Boechat-Roberty H. M., 2007c, MNRAS, 375, 1488
Rosi M., Bauschlicher C. W. Jr, Bakes E. L. O., 2003, ApJ, 609, 1192
Ruiterkamp R., Peeters Z., Moore M. H., Hudson R. L., Ehrenfreund P., 2005, A&A, 440, 391
Shan J., Suto M., Lee L. C., 1991, ApJ, 383, 459
Simon M., LeBrun T., Morin P., Lavolée M., Maréchal J. L., 1991, Nucl. Instrum. Meth. B, 62, 167
Sorrell W. H., 2001, ApJ, 555, L129
Stauber P., Doty S. D., van Dishoeck E. F., Benz A. O., 2005, A&A, 440, 949
Vijh U. P., Witt A. N., Gordon K. D., 2004, ApJ, 606, L65
Woods P. M., Willacy K., 2007, ApJ, 655, L49
Woods P. M., Millar T. J., Zijlstra A., Herbst E. A., 2002, ApJ, 574, L167
Woods P. M., Millar T. J., Herbst E., Zijlstra A. A., 2003, A&A, 402, 189

This paper has been typeset from a \TeX/\LaTeX file prepared by the author.