

X-ray interactions with condensed chlorobenzene: formation of PAHs on dust grains surfaces

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Abstract. Polycyclic aromatic hydrocarbons (PAHs), a class of organic molecules, are detected in several galactic and extragalactic objects and can play an important role in physical and chemical processes of interstellar and circumstellar environments. Although their aromatic rings are constituted mainly by C and H atoms, other atoms such as Chlorine (Cl), or functional groups, can substitute the H atoms depending on the astronomical environment conditions. In this work, we study the interaction of soft X-rays at 2.8 keV with condensed phase chlorobenzene (90 K), a unity of chlorinated PAHs, using Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS). The results show that the presence of a chlorine atom in the aromatic ring favors the reaction of association of benzenic rings on icy surfaces of dust grains, forming larger molecules, including PAHs and chlorinated aromatic species, such as Polychlorierte Bi- and Terphenyles (PCBs and PCTs).

Resumo. Os hidrocarbonetos aromáticos policíclicos (PAHs), uma classe de moléculas orgânicas, são encontradas em objetos galácticos e extragalácticos, e podem desempenhar um papel importante nos processos físicos e químicos de meios circustelares e interestelares das galáxias. Apesar das estruturas de anéis aromáticos serem constituídas principalmente por átomos de C e H, outros átomos como o Cl, ou grupos funcionais, podem substituir átomos do H dependendo das condições do ambiente astronômico. Neste trabalho, estudamos a interação de raios-X moles de 2.8 keV com clorobenzeno na fase condensada (90 K), uma unidade de PAH clorado, usando a espectroscopia de estrutura fina de absorção de raios-X (NEXAFS). Os resultados mostram que a presença de um átomo de cloro no anel aromático favorece a reação de associação de anéis de benzeno na superfície congelada de grãos de poeira, formando moléculas maiores, incluindo PAHs e espécies aromáticas cloradas, como os bi- and trifenilos policlorados

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1. Introduction

Among the larger molecular species present in the Interstellar Medium (ISM), polycyclic aromatic hydrocarbons (PAHs) arose increasing interest as some species have been detected in recent years. PAHs contribute to many key physical processes that affect the basic structure and evolution of the ISM of galaxies and are also the most abundant class of organic molecules in space (Tielens 2011).

PAHs are essentially constituted by carbon and hydrogen atoms arranged in structures of aromatic rings. However, the substitution of a hydrogen atom by other functional groups or the exchange of a ring carbon by another atom, such as nitrogen or oxygen, modifies the bonding length, charge distribution and symmetry of the aromatic network. Consequently, new vibrational bands are observed in infrared (IR) spectra. In other words, the study of PAHs with substituted atoms or groups may explain some spectral signatures of ISM.

One way to provide a better understanding of how the substitution of C or H for other atoms modifies the ring properties of PAHs is to study the smaller units of these structures. Besides, some of these precursor molecules of PAHs have been found in a large variety of astronomical environments. Benzene (C₆H₆) was detected in the pre-planetary nebula CRL 618 (Cernicharo et al. 2001), benzonitrile (C₆H₅CN) in the molecular cloud TMC-1 (McGuire et al. 2018) and chlorobenzene (C₆H₅Cl) in meteorites samples and in Mars craters (Studier, Hayatsu & Anders 1965; Freissinet et al. 2015). The search for chlorinated compounds has been highly emphasized. Recently, the de-

tection of the first chlorinated organic compound in the ISM, chloromethane (CH₃Cl), was reported in the coma of comet 67P/Churyumov-Gerasimenko and in the hot corino of the low-mass protostar IRAS 16293-2422 (Fayolle et al. 2017).

2. Methodology

We studied experimentally the degradation of the chlorobenzene ice by photons delivered at the soft X-ray spectroscopy beamline (SXS) of the Brazilian Synchrotron Light Laboratory (LNLS). The major elements of experimental setup consists in a high vacuum chamber ($P < 10^{-8}$ mbar), target holder, where the condensed sample deposited onto an aluminum substrate was kept at the temperatures of 90 K by a closed-cycle cryostat and temperature controller, aiming to simulate the conditions of dust grain mantles around circumstellar environments, picoammeters, that collect the incident photon beam current and the draining current on the target, respectively, and a residual gas analyser to monitor the sample injection and deposition procedure. After exposure times to X-rays at the energy of Cl 1s resonance (2822 eV), absorption spectra were collected using near-edge X-ray absorption spectroscopy (NEXAFS).

3. Results

Figure 1 shows the absorption X-ray spectrum of condensed phase chlorobenzene at Cl K-edge before irradiation. The structural feature changes of the absorption cross section on the pho-

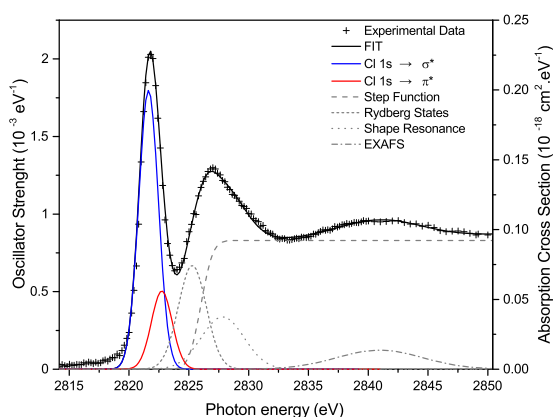


FIGURE 1. Absorption X-ray spectrum of condensed chlorobenzene at Cl K-edge (2822 eV), measured before irradiation (Tenorio et al. in prep).

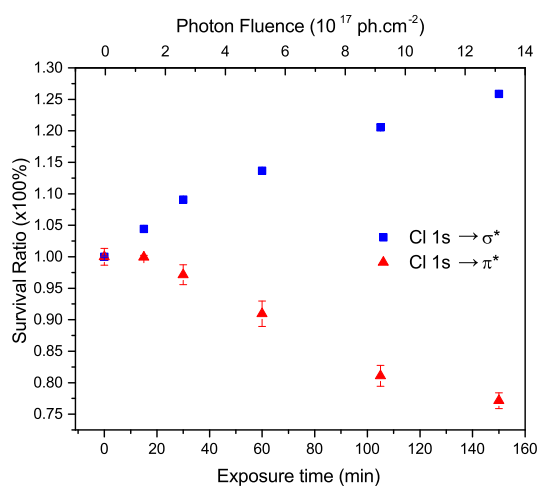
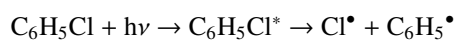


FIGURE 2. Time evolution of the areas of the transitions from Cl 1s to σ^* and π^* .

ton energy indicate the excitation of core electrons (Cl 1s) to unoccupied molecular orbitals (σ^* and π^*), Rydberg states and to the continuum. Based on the theoretical calculations of the energies and the oscillator strengths of the transitions, Gaussian functions and a step function, above the ionization potential, were fitted to the spectrum.

The experimental results of the irradiation of the sample using a monochromatic X-ray beam with energy of 2822 eV, coinciding with the electronic transition Cl 1s \rightarrow σ^* , are summarized in Fig 2.

The changes in the peak areas of Cl 1s \rightarrow σ^* and π^* states as a function of the photon fluences suggest chemical transformations of the sample. The experimental data indicated by blue squares are explained by chlorobenzene dissociation into radicals after the excitation to Cl 1s \rightarrow σ^* state (Tenorio et al. in prep):



Chlorobenzene molecule and atomic chlorine both exhibit state transitions with energies very close to 2822 eV (Tab. 1). The dissociative behavior of the Cl 1s \rightarrow σ^* state of chlorobenzene produces radicals, such as chlorine atoms, deposited on the condensed surface, leading to an increase in the absorption

TABLE 1. Values of energies and oscillator strengths for chlorobenzene and atomic chlorine transitions near 2822 eV region (Tenorio et al. in prep.).

State	Energy (eV)	Oscillator Strength
Chlorobenzene		
1s \rightarrow σ^*	2821.6	3.7×10^{-3}
1s \rightarrow π^*	2822.8	1.1×10^{-3}
Chlorine atom		
1s \rightarrow 3d	2822.3	0.6×10^{-2}

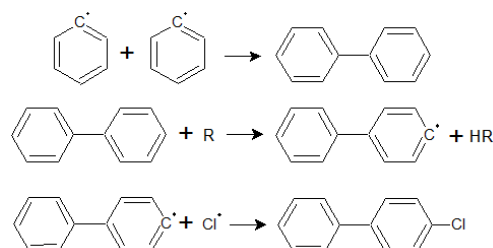


FIGURE 3. Formation of chlorobiphenyl after the dissociation of chlorobenzene, where R represents a general radical. Other isomers of chlorobiphenyl and chloroterphenyl may also form following a similar route.

at 2822 eV. In addition, the oscillator strength of the Cl 1s \rightarrow 3p transition of the chlorine atom is greater than the oscillator strength of the chlorobenzene Cl 1s \rightarrow σ^* transition, which also accounts in an absorption increase.

With the dissociation of chlorobenzene molecule, the free chlorine and phenyl ($\text{C}_6\text{H}_5^\bullet$) radicals react to generate larger molecules on the frozen surface. The chemical equations below (Fig. 3) show, as an example, the route of chlorobiphenyl formation ($\text{C}_6\text{H}_5 - \text{C}_6\text{H}_4\text{Cl}$):

4. Conclusion

These results suggest that the presence of the chlorine atom favors the reaction of association of benzene rings that may form PAHs and chlorinated aromatic species on the frozen dust grain surface. As chlorobenzene has been found in meteorites samples, probably it was frozen on circumstellar grains and may have contributed for the formation of PAHs in our interplanetary environment.

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