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Structural, dynamical and spectroscopic properties of atomic carbon clusters and clusters of polycyclic aromatic hydrocarbons

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Abstract. We give an overview of a few recent developments and applications of the Density Functional Tight Binding approach for quantum modelling of relatively large atomic and molecular clusters of astrophysical interest. New results on the structural, energetic and spectral properties of carbon clusters and PAH clusters are highlighted, such as the possible contribution of the C₆₀ "cage" isomers' family to interstellar IR emission and UV-bump absorption features. We also show that spectra of PAH clusters present some characteristic signatures (electronic charge excitation bands) in the near IR and slight perturbations of the vibrational mid-IR isolated PAH spectra. Finally, we evidence that fast (i.e. non statistical) dissociation can be an efficient process in photo- or collision induced dissociation of PAH clusters.

Keywords: Carbon clusters, Polycyclic Aromatic Hydrocarbons, PAH clusters, Infrared spectra, Dissociation, UV-visible spectra

1 Introduction

A large fraction of interstellar carbon is contained in large molecules or dust grains. Due to its allotropy, carbon has been observed in space under various forms *ie* (nano-)diamonds, fullerenes, polyaromatic structures, amorphous carbon and their hydrogenated forms[1]. The ubiquitous carbonaceous material (large molecules and very small grains) plays a crucial role in determining the interstellar medium (ISM) physical conditions [2], for instance heating the gas through photoelectron ejection when irradiated from nearby stars. These carbonaceous species are also interesting from the chemical point of view as they could contain a large variety of chemical functions and could play a catalytic role favouring interstellar chemical richness, from H₂ to more complex molecules synthesis.

The suspected significant role of large carbon molecules in the physics and chemistry of the ISM has motivated experimental and theoretical studies in the last decades, most of them devoted to the physical chemistry and spectroscopic signatures of polycyclic aromatic hydrocarbons (PAHs, see A.G.G. Tielens in this volume). Atomic carbon clusters have also received interest since they could be

intermediate species in the formation of the detected buckminsterfullerene C_{60} [3, 4], the mechanism of which is still debated, both "top-down" and "bottom-up" processes being considered [5, 6]. PAH clusters have been proposed to be at the origin of spectral features mixing molecular and small grains patterns [7, 8]. It was suggested that they could survive in dense UV-protected molecular clouds and be destroyed in the vicinity of stars giving birth to free-flying PAHs. In order to characterize the role of atomic and molecular clusters in the ISM, astrophysical observations must be complemented by laboratory experiments and molecular simulations. Theoretical modeling of atomic and molecular with tens to hundreds of atoms is still out of reach for purely first principle schemes, especially when global structural exploration or extensive dynamical simulations are intended. Force fields schemes may offer an alternative, but proper description of chemical reactivity is challenging, while ionization effects or electronic spectroscopy are out of the scope of these methods. In this report, we give an overview of the theoretical tools developed by our group to address these systems in the framework of the Density Functional Theory based Tight Binding (DFTB) scheme [9], an efficient approximation of DFT retaining a quantum description for the electronic system. We illustrate some of its applications to compute astrophysically relevant properties of atomic carbon and molecular PAH clusters.

2 Atomic carbon clusters: structural diversity and spectroscopy

The identification of buckminsterfullerene C_{60} motivated us to investigate the structural and spectroscopic properties of its isomers, that could be intermediates in its formation. We explored the structural diversity and the infrared (IR) and UV-visible spectra of hundreds of thousands of isomers of large carbon clusters C_n ($n=24,42,60$), and recently of hydrogenated carbon clusters $C_{24}H_n$ ($n=6,12,18,24$).

The potential energy surface (PES) of C_n ($n=24,42,60$) were first investigated using Molecular Dynamics Parallel Tempering simulations, while interactions were described using the REBO reactive force field [10, 11]. This approach allowed for an efficient exploration of the PES. Alternatively, we explored the PES of $C_{24}H_n$ ($n=6,12,18,24$) using a procedure based on the genetic algorithm with electronic energy determined with DFTB scheme. With such a procedure, we explored the lowest energy part of the PES [12] followed by local DFTB optimisation. Up to hundreds of thousands of isomers were treated. For each of them, the harmonic IR spectrum was computed while the optical spectra were computed for a reduced sample of isomers (tens of thousands) using linear response time-dependent (TD)-DFTB.

The structural diversity of C_n ($n=24,42,60$) was investigated using two order parameters, the dimensionless shape parameter β describing the oblateness of the cluster, and the number of sp^2 carbon atoms. Using these two parameters, the computed structures were sorted into four families : the cage family (high sp^2 fraction and low asphericity), the flake family (quite high sp^2 frac-

tion but with higher asphericity), the pretzel family (several chains of sp^1 atoms with a low asphericity) and the branched family (containing long carbon chains but mainly aspherical, see Fig.1). In order to analyze the structural diversity of $C_{24}H_n$ ($n=6,12,18,24$), we also used two order parameters, namely the same β parameter and the number of 5 and 6 carbon rings $R_{5/6}$ [12]. Contrary to C_{60} , we were not able to rigorously distinguish between families but these parameters allowed us to characterize the structural diversity of the hydrogenated clusters. We showed that the most abundant and lowest energy population, designated as the flake population (isomers of variable shapes, large $R_{5/6}$ values), was characterized by an increasing number of spherical isomers when n_H/n_C increases [12]. By averaging the individual IR spectra of all isomers for a given family,

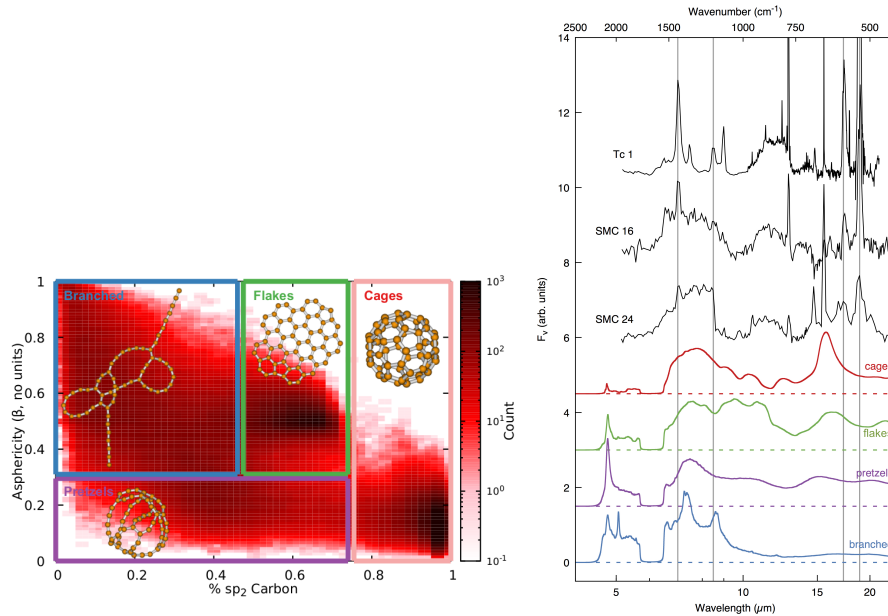


Fig. 1. Adapted from ref [11]. Structures and IR spectra (compared to astronomical spectra) of the C_{60} isomer families.

we showed that the cage population could contribute to the plateau observed in the 6-9 μm region of fullerene-rich planetary nebulae (PNe) [11]. Using the same approach with TD-DFTB spectra, we showed that the cage isomers were the best candidates to contribute to the interstellar UV bump, with flakes to a lesser extent whereas the experimental spectrum of carbonaceous species formed in flame experiments seems dominated by flakes isomers, with a smaller contribution of cages isomers. [13]. The vibrational and optical spectra of hydrogenated carbon clusters have been under investigation and will be published soon.

The DFTB and TD-DFTB data obtained for populations of C_n ($n=24,42,60$) isomers were further used for modeling other aspects of astrophysical relevance. A systematic interpolation scheme for correlating structural and IR spectral features was implemented and trained on these specific cluster sizes [14]. The obtained machine learning algorithm was further validated on the C_{33} and C_{52} systems. In addition, both IR harmonic DFTB data and UV-visible TD-DFTB results were used as input for a kinetic Monte Carlo model describing the radiative relaxation dynamics of populations using appropriate rate constants. The model notably emphasizes the importance of recurrent fluorescence, also known as Poincaré fluorescence, where part of the vibrational energy flows back into the electronic degrees of freedom (reverse internal conversion) and the system relaxes then through electronic fluorescence [15]. This process is found to compete with vibrational emission, especially at high excitation energies [16].

3 Molecular PAH clusters : dynamics and spectroscopy

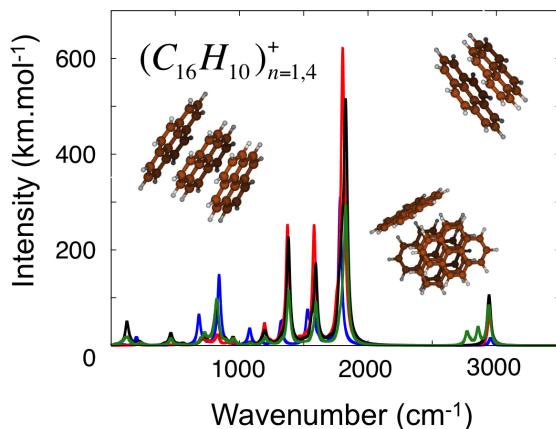


Fig. 2. Structures and IR spectra of cationic pyrene clusters. From reference [17]

In order to model neutral PAH clusters, we have modified the DFTB approach to provide a fair description of the long range van der Waals and accurate Coulomb interactions between the molecular cluster's units [18]. In the case of cationic clusters, an original model mixing DFTB and valence-bond configuration interaction (DFTB-CI) was developed to deal with charge resonance [19], further extended to cover electronic excitations in cations [20]. The most stable structures of pyrene and coronene clusters have been obtained from Parallel Tempering Monte Carlo (PTMC) explorations. For neutral or cationic small clusters, they consist of single stacks up to 4-5 units. Beyond these sizes, the

growing pattern is different for neutrals and cations. In neutrals, the cluster structures can be seen as assemblies of building blocks made of dimer or trimer stacks. In cations, the charge is localized on a dimer or a trimer core and the remaining, almost neutral molecules, organize around this core [21] (Fig. 2). We computed the ionisation potentials (IPs) of PAH clusters which essentially decrease when the number of units increases (IPs for pentamers are about 1 eV below the monomer values, in agreement with experimental results) [22]. The IP decrease may emphasize the role of PAH clusters, similarly to that of large free-flying PAH molecules, in ISM heating through photoelectron emission.

The stability of PAH clusters primarily relies on binding energies, but also on the dissociation mechanisms, energy deposition and redistribution processes. We were able to provide the interpretation of several experiments investigating dissociation. (i) We could reproduce experimental collision-induced dissociation results [23] by combining MD simulations describing energy deposition and fast dissociation (i.e. direct/non-statistical) with a statistical approach to access slow dissociation processes (i.e. indirect/statistical) [24]. At low energy, the dissociation cross sections increase with collision energies, whereas they remain almost constant for collision energies greater than 10-15 eV. (ii) We were able to interpret the experimental photo-ionisation/dissociation of cold neutral pyrene dimers from the analysis of the excited PES of the reached electronic state, which determines if the absorbed energy is likely to be redistributed over non-dissociative vibrational modes or dissociative pathways [25]. (iii) In the case of photodissociation of hot cationic pyrene dimers, we simulated from PTMC the evolution of the absorption spectrum and found that it compares well with the experimental dissociation action spectrum. A broadening and redshift of the charge resonance band with increasing temperature was shown [26].

In addition to electronic spectroscopy, the theoretical vibrational spectra were also simulated for neutral and cationic pyrene clusters [17]. For neutrals, the results were found in agreement with previous DFT calculations [27]. For cations, a depletion of the intensity of the CH stretch modes around 3000 cm^{-1} was observed (Fig. 2). With respect to the monomer cation, the in-plane CC modes in the region $1400\text{--}2000\text{ cm}^{-1}$ are enhanced in the cationic cluster spectra while the CH bending modes in the range $700\text{--}1000\text{ cm}^{-1}$ are significantly weakened. Soft intermolecular modes possibly mixed with monomer folding modes are also observed in the region $70\text{--}120\text{ cm}^{-1}$.

4 Conclusion

We have presented recent developments of the DFTB method which allow to probe the complex PES of atomic and molecular clusters. Their application to clusters of astrophysical interest, here atomic carbon clusters and molecular PAH clusters, allowed to characterize their structural, energetic, dynamical and spectral properties. In particular, it was shown that atomic carbon clusters can be classified in several families, and that the cage family is the most likely one to contribute to both the 6-9 μm plateau IR emission and to the interstellar

UV bump. We have characterized the spectral signatures of PAH clusters which present slight modifications with respect the free flying PAH spectra as well as a characteristic charge resonance absorption band. We showed that the stability of PAH clusters strongly depends on the energy deposition process. For instance, collisions can induce fast or delayed dissociations. We also stressed the importance of the nature of the reached excited states (dissociative or not) in photodissociation processes. Such studies bring some new insight in the dynamics and spectroscopy of PAH-containing compounds and possibly help for the detection of PAH clusters or small carbonaceous grains in interstellar or circumstellar media.

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