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Excitation process of a polycyclic aromatic hydrocarbons (PAH)

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Abstract. In recent years, thanks to significant and parallel advances in experimental, theoretical and observational techniques, great advances have been made in our understanding of the role that aromatic materials play in the interstellar medium (ISM). It is noteworthy that, in the terrestrial ecosystem, PAHs (polycyclic aromatic hydrocarbons) are produced by burning fossil fuels, while in the interstellar medium, which is the focus of this work, PAHs are associated with emissions in the middle infrared, and have already been detected by space telescopes. This work aims to address the basic concepts of microcononics of the system applied to a vibrationally excited PAH, at a molecule temperature that may vary from 2000 K to 10 K, with data obtained from the database of the NASA Ames PAH IR SPECTRAL, over which we presented an quantum computing study using Density-functional theory (DFT) computational modeling in order to study the excitation process of the microcononics view fo the PAH molecules.

Resumo. Nos últimos anos, graças a avanços significativos e paralelos em técnicas experimentais, teórica e observacionais, grande avanços foram feitos em nossa compreensão, do papel que os materiais aromáticos desempenham no meio interestelar (ISM). Vale ressaltar que, no ecossistema terrestre os PAHs são produzidos pela queima de combustíveis fósseis, já no meio interestelar, que é o foco desse trabalho, os hidrocarbonetos aromáticos policíclicos estão associados com emissões no infravermelho médio, e já foram detectadas por telescópios espaciais. O presente trabalho tem como objetivo abordar os conceitos básicos de microcônonicos do sistema aplicados a um hidrocarboneto aromático policíclico (PAH) vibracionalmente excitado, a uma temperatura da molécula podendo variar de 2000 K para 10 K, tais dados obtidos a partir do banco de dados da NASA Ames PAH IR SPECTRAL, no qual nós apresentamos um estudo computacional quântico usando modelagem computacional da Teoria do Funcional de Densidade (DFT) para estudar o processo de excitação no regime microcanônico das moléculas de PAHs.

Keywords. Statistical Mechanics - Microcanonical – Polycyclic Aromatic Hydrocarbon.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a family of planar molecules, in which, their structures have been mainly composed of multiple benzene rings (Woods et al. 2003) composed by alternated double aromatic bonds. Therefore, PAHs are "semiconductors" and their optical properties in the UV range are dominated by electronic transitions and at IR wavelengths by vibrational transitions (Tielens 2008). Dust clouds in galaxies absorb energy from starlight reemiting it in the infrared (IR) wavelengths (Draine 2010). In particular, IR emission from PAHs seens to be an IR fluorescence process in which the absorption of a single UV photon leads to electronic excitation, hence, this electronic energy is then transferred to the vibrational collector of the molecule and is eventually radiated through the vibrational modes of the species (Tielens 2008). Microcanonical and canonical ensembles are a way of exposing problems in statistical physics, which include fixing the number, volume and temperature of particles in a macroscopic system. This is a statistical ensemble that describes the microstate of the system, in which the number, volume and the temperature is fixed. In contrast, Statistical Mechanics is a probabilistic theory that establishes the connection between the two levels of description, the microscopic (Mechanics) and the macroscopic (Thermodynamics), and the central concept of thermodynamics is entropy. The focus of this work aims to address the basic concepts of microcanonics of the system applied to a vibrationally excited PAHs, at a temperature of the molecule that can vary from 2000 K to 10 K, with data obtained from the database from NASA Ames PAH IR SPECTRAL.

2. Materials and methods

In the present work, data obtained through computational modeling was used. The structure of the molecule was drawn in Gabedit which is a graphical user interface for computational chemistry packages. The ORCA software, besides to be free, is quite versatile and easy to learn, in which a calculation based on the Density Functional Theory (DFT) was used with hybrid B3LYP approach.

3. Result and Discussion

PAHs are composed by carbon atoms molecules with several aromatic rings geometry, and they belong to the family of planar molecules. PAHs can have different types of molecular structures (see Figure 1).

The structure of a PAH is closely linked to its stability, with centrally condensed PAHs being among the most stable PAHs. The MIR region is the most used in chemical analysis and the best known mid-infrared bands related to PAHs are: 3.3, 6.2, 7.7. 8.6 e 11.3 μm Sales et al. (2010). The molecular vibration of the PAH's atoms is a results of the motion of the molecules after recive a avalable UV fotons. It is worth mentioning that the main vibrational modes are: axial deformation (elongation) and angular deformation (curvature), as shown in figure 2.

A vibrationally excited interstellar PAH is a system with constant energy and, therefore — in terms of statistical mechanics —, forms a microcanonical, according to Figure 3 of a small molecule that presents the emission spectrum calculated using a fixed temperature emission model (1000k) and each transition co-involved with a Gaussian emission profile in agreement with the bibliography. After the calculations performed by the computer simulations, one can see in figure 4 the characteristic

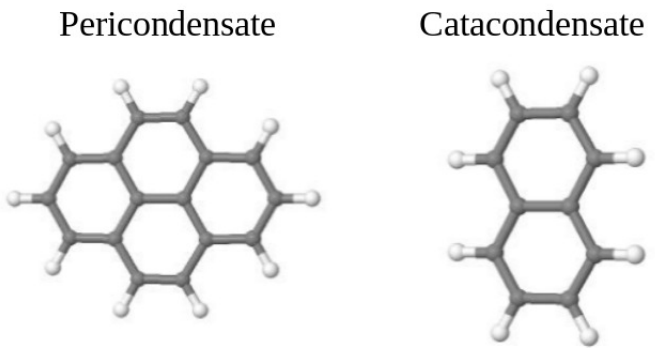

Figure 1. The molecular structure of some representative polycyclic aromatic hydrocarbon molecules. Pericondensate PAHs are on the left and Catacondensate PAHs are on the right. Source: Tielens, 2005

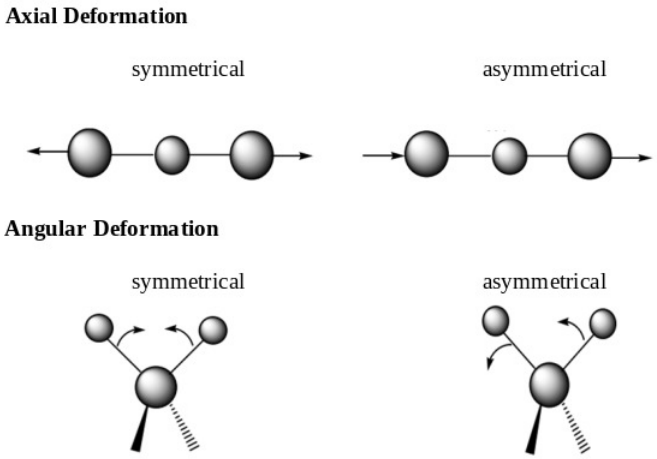

Figure 2. Molecular vibration modes. Source: the author, 2022

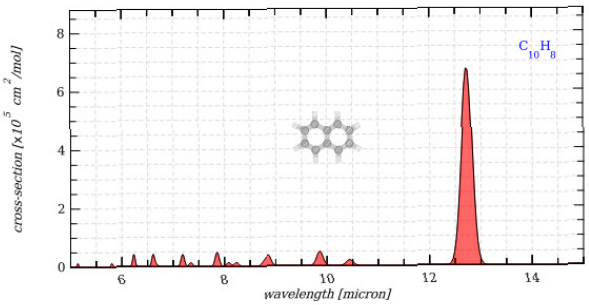

Figure 3. Molecular emission spectrum of the PAH $C_{10}H_8$ molecule. Source: NASA Ames PAH

vibrational modes of the naphthalene molecule and its electromagnetic spectrum. We can infer between the data from NASA Ames PAH and the modeled data a great similarity with the closer emission bands, reinforces our agreement with the bibliography.

4. Conclusions

This work carried out a brief description of the system's microcanonical assembly formalism applied to a vibrationally excited polycyclic aromatic hydrocarbon (PAH). We also analyzed the electronic excitation by UV photons of a small molecule. We find that the whole theory of statistical ensembles applies very well to these systems. We also demonstrate that PAH molecules can be described by means of ensemble equations and, in order to evaluate the temperature related to the vibratory excitation of the PAH, it is necessary to resort to the canonical and microcanonical system, since in statistical mechanics the temperature is connected to the average energy of a system and it was possible to analyze the emission energy in the middle infrared (MIR) by a PAH molecule. In conclusion, the application of probabilistic calculations in the context of statistical mechanics proved to be very convenient to address the microcanonical concepts of the system applied to a vibrationally excited polycyclic aromatic hydrocarbon (PAH).

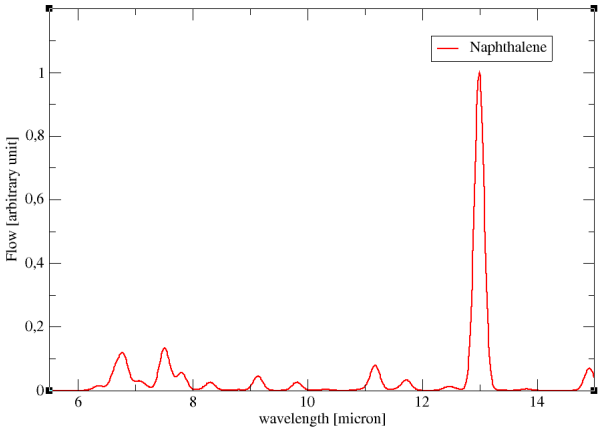

Figure 4. Infrared spectrum of the naphthalene molecule. Source: the author 2022.

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