Computational Study of Photochemistry and Spectroscopy of Polycyclic Aromatic Hydrocarbons (PAHs) in Model Interstellar Ices.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a particularly important class of aromatic molecule which account for up to 20 % of the galactic carbon and are likely to exist in the presence of water ice as either a part of the carbonaceous component of dust grain itself or as a component of icy mantles.

Studies of the chemical evolution of bulk ices during irradiation by UV light have been studied extensively. It has been observed that UV irradiation of water ice containing PAHs may play an important role in the formation of complex organic species such as alcohols, quinones and ethers.

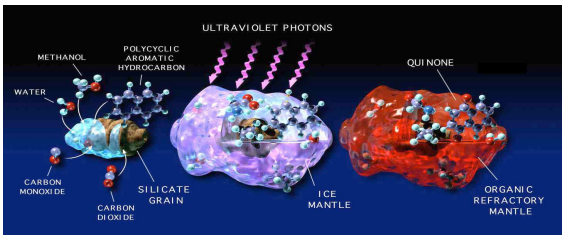


Fig I : UV irradiation of ices involving both simple and more complex molecule including PAHs. [From Bernstein *et al.*, in *Sci.Am*, 1999, 26]

Benzene may be thought of as a prototypical PAH compound and is amongst the list of known interstellar molecules and water ice is a good representation of icy mantles on grains. Therefore , the study of the ground and excited states of the complexes of the benzene with water clusters (W_n, n =variable integer) is environmentally relevant.

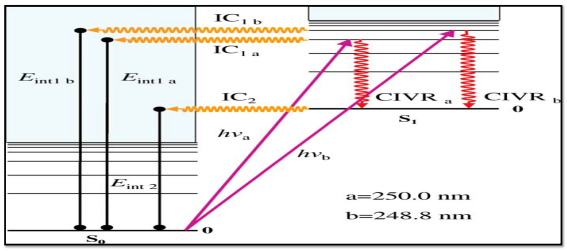


Fig II : Jablonski diagram showing the possible photophysical pathway for energy redistribution within the $C_6H_6\cdots(H_2O)_n$ complex following absorption of (a) 250.0 nm and (b) 248.8 nm photons. [From Thrower *et al.*, *J. Vac. Sci. Techno*. A 28(4), 2010]

Literature cited

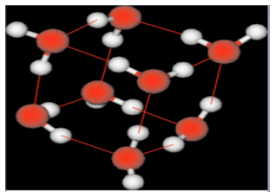
•Zwier and their co-workers (1994) have experimentally determined the binding energies of $C_6H_6\cdots(H_2O)_n$ complexes.
•Experimental studies by Thrower *et al.* (2008) on photo-processes in benzene-water (Bz-W_n) complexes has identified three distinct photodesorption mechanisms.
(i) Direct adsorbate-mediated desorption of benzene
(ii) Indirect adsorbate-mediated desorption of water
(iii) Substrate-mediated desorption of both benzene and water
•Recent experimental work by Thrower *et al.* (2010) on photon- and electron-induced desorption from laboratory models of interstellar ice grains has obtained desorption cross sections and first order rate coefficients for the desorption processes..
•Ma *et al.* (2009) have calculated the interaction energy of Bz with W clusters using different electronic structure methods including HF, MP2, CCSD, and DFT with exchange correlational functions.
•Detailed computational study on geometries, binding energies and infrared (IR) spectra of Bz-W_n(n=1-10) clusters has been carried out on Bz-W clusters using hybrid meta DFT based M05-2X method by Prakash *et al.* (2009) .
•Computational studies on low lying excited states of Bz-W_n(n=1-6) has been done by Upadhyay *et al.* (2002) using configuration interaction method involving all the singly excited configurations (CIS).

Objectives of the computational study

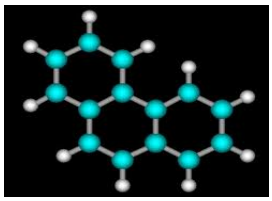
Our project aims to perform computational studies on the qualitative changes in the structures and the properties of different Benzene-Water complexes that would take place following their electronic excitation to excited states. The excited states of the complex systems are difficult to treat computationally. Therefore, the photochemistry and spectroscopy of both water clusters and benzene-water clusters following photon absorption will be studied using high level quantum chemical computational methods.

The following model systems will be studied computationally :

(i) Water $(H_2O)_n$ clusters

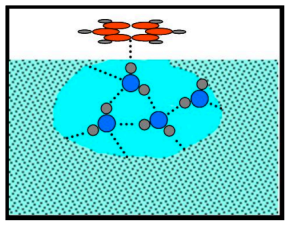


(ii) Isolated PAHs



(iii) Benzene– smaller $(H_2O)_n$ clusters

(iv) Benzene–larger$(H_2O)_n$ clusters



- **Water interacts with the benzene via $OH\cdots\pi$ *H*-bond.**

➢ Following molecular properties will be obtained computationally :

- **Potential energy surfaces**
- **Geometry Optimizations**
- **Energy levels and spectroscopy**
- **Intermolecular interactions**
- **Temperature dependence**
- **Entropy and internal energies**

Methods

Density Functional Theory (DFT)

DFT is the most promising approach to compute the great variety of molecular properties: molecular structures, vibrational frequencies, ionization energies, reaction paths, *etc.* DFT method inclusive of ***long range corrected functionals*** *will be* used for calculating ground state properties of the complex systems with more accuracy.

Time-Dependent Density Functional Theory (TDDFT)

This method of theory investigate the properties and dynamics of many-body systems in the presence of time-dependent potentials, such as electric or magnetic fields. TDDFT will be used to extract features like excitation energies, frequency-dependent response properties, and photo-absorption spectra of complex systems under study .

Complete Active Space Self-Consistent field (CASSCF) Method

This CASSCF method incorporates a full Configuration interaction (CI) involving a subset of orbitals. This method is extremely flexible and can be used across the potential energy surface for any kind of chemical bonding and regions of non-adiabatic coupling.

Hybrid Quantum mechanics/ Molecular Mechanics (QM/MM)

QM/MM is a molecular simulation methodology that couple both Quantum Mechanics and Molecular Mechanics approaches. It involves QM treatment of the active site and classical MM treatment of environment. The larger Benzene-water clusters will be studied by using this computational approach.

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