ROLE OF COLLECTIVE EXCITATION IN HIGH ENERGY RADIATION INTERACTION WITH POLYCYCLIC AROMATIC HYDROCARBONS

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by

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ABSTRACT

The work here is primarily associated with the understanding of structural and dynamical properties of few members of polycyclic aromatic hydrocarbons (PAHs), theoretically and experimentally under energetic radiation interaction. Influence of collective electronic excitations in this class of molecules while interacting with UV and FUV radiation as well as charged particle radiation is explored in this research work.

Ion-PAH collision using Electron Cyclotron Resonance source: Using Electron Cyclotron Resonance source at Tata Institute of Fundamental Research, Mumbai and Inter University Accelerator Center, New Delhi, the ion-PAH collision experiments were performed for the targets like naphthalene, fluorene with low energy (keV) projectiles (proton, helium, argon) of different charge state in coincidence. For 50 - 240 keV proton-naphthalene collision the mass spectra are obtained in two mode of detection using linear two field time-of-flight mass spectrometer for ion detection in coincidence with outgoing electrons and neutral projectile. Evaporation process like H loss, C_2H_2 loss and different fragments including up to triply charged parent intact molecular ion are visible in mass spectrum. Resonant capture process explained the independent nature of fragmentation yield in electron capture mode. The neutral evaporation process is used as the measure of internal energy. The detailed energetics of the ion-PAH collisions in the intermediate velocity regime and the importance of the collective excitation in this interaction is revealed. This is of great significance in the thermodynamics of interstellar medium in specific circumstances like supernova reverse shock region. We also observe a unique resilience toward fragmentation in such PAHs compared to other

type of organic molecules with structural similarity. Ions detected in multihit mode are used to obtain the kinetic energy released during the fragmentation process and infers about different dissociation pathways. The multifragmentation yields for electron emission mode is found to be decreasing with increase in projectile velocity. To reproduce this trend, *Monte Carlo* simulation within local density approximation were done and the electronic stopping is calculated. The theoretical cross sections obtained from this simulation matched well with the experimental results.

Photon-PAH collision by photoelectron spectroscopy using synchrotron source: The photoelectron spectroscopy studies as a function of photon energy were planned and performed for two PAH molecules namely, pyrene and fluorene. The aim is to investigate different coupling mechanisms between photoionization and electronic states of the molecule using synchrotron source facility at Elettra, Trieste, Italy. The multihit mode mass spectra and photoelectron spectra (PES) for a wide range of photon energy were recorded. The photoionization cross section is found to peak at collective excitation region around 17 eV for the outer valence band. The inner valance bands are found to be coupled with collective excitation feature more efficiently. The observed vibrational progressions were following the same trend for the whole photon energy range, indicating photon energy independent structural alteration post ionization. In addition to this to identify the correlation between photoelectron emission from a particular molecular orbital and the state of the residual ion, the photoelectron-photoion coincidence (PEPICO) measurement is performed. Near edge X-ray absorption fine structure (NEXAFS) data is taken at photon energy close to the *1s* edge of carbon atom to explore the inner shell molecular orbital structure.

For the present work, the Outer valence Green's function (OVGF) technique implemented in GAUSSIAN09 is used to reproduce the measured PES binding energies. The prominent peaks in the PES are identified according to their binding energy and symmetry using OVGF calculations with a reasonable success. The PES is broadened due to Franck-Condon (FC) overlap of vibrational states. Using Hartree-Fock (HF) and Density functional theory (DFT), the Franck-Condon factors for vibrational progression in $D_0 \leftarrow S_0$ transition were calculated. The simulated results compare well with the experimental results.

Electron affinity calculation and its correlation to HOMA index: Adiabatic electron affinity (AEA) calculations are done using GAUSSIAN09 to understand the stability of PAH anions as well as the property of accommodating charges with the help of delocalization, geometry based aromatic index and structural character. Different levels of HF and DFT calculations are performed on few examples of PAHs and their anions. The calculated AEA matched well with the existing experimental values and also provide the AEA values for some PAHs which are not available in the literature. Presence of a cyclopenta ring is observed to enhance the AEA whereas sp^3 hybridized carbon atom decreases it. The electron density distribution over the anionic molecular volume is analyzed with the help of electrostatic potential maps and electron spin distribution. A geometry based aromatic index known as Harmonic oscillator model of aromaticity (HOMA) index is used to quantify the aromatic character.

Experimental setup developmental work: In order to study the molecules as well as its ions with kinematical correlations in the fragmentation process, an in house mass spectrometer setup is developed. The setup includes an electrospray ion source to produce molecular ions ranging from monomers to complex clusters by soft ionization method followed by an octupole ion guide to bring the ions from atmosphere to high vacuum region, multipole ion trap to thermalize the ions to a specific temperature by collisional cooling, and then an accelerating tube with a provision of pulsing the ion beam. The pulsed ion beam thus produced is made to collide with inert gas target

or irradiated with high intensity pulsed laser beam (UV to IR) of nanosecond width. The resulting fragmentation process is investigated using a parallel plate analyzer with a provision to detect neutral and ionic fragments in coincidence using position sensitive micro channel plate detectors. The ion-optics simulation is extensively done to obtain the optimized parameters and effect of electric field distortion due to mechanical defects for Wiley McLaren type time-of-flight mass spectrometer and parallel plate analyzer using SIMION 8.0. The mechanical drawings and fabrications are done for vacuum chambers, octupole ion guide, gauss tube for pulsed extraction of ion beam, parallel plate analyzer, detector mounting and other accessories using SOLIDWORKS. Position data is obtained from the detector and various calibrations and testing were performed using imaging mask to obtain detector resolution. The ultra high vacuum testing for chambers, electrical testing for power supplies and the testing for functionality of individual components, calibration and resolution measurement for detector are done. Using a penning ionization source, the functionality of parallel plate analyzer is tested. A fast multihit data acquisition time-to-digital converter (TDC) system of 50 picoseconds time resolution is established using NIM modules. The interfacing is done between the position sensitive detectors and the TDC using a MATLAB program. The full set up is tested and successfully gives mass spectrum at present for biomolecules.