Plasmon excitation in valence shell photoelectron spectroscopy for PAHs

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Abstract. The photon energy dependence of photoelectron spectra (PES) for two members of the polycyclic aromatic hydrocarbon (PAH) family namely pyrene and fluorene is studied in FUV regime (15 - 40 eV) using high-resolution synchrotron photoelectron spectrometer. The difference in outer (π dominated) and inner (σ dominated) valence relative photoelectron emission cross sections as a function of photon energy identifies the region of plasmon excitation (∼15 - 27 eV). This excitation mode is present in the same region for both the molecule irrespective of the difference in their structure and symmetry. The feature is observed to be independent of the details of the molecular orbital associated with the outgoing electron. The results are in contradiction to the observed in benzene for inner valence bands. With the help of OVGF/cc-pVDZ calculations, the experimental bands are assigned as per their binding energy and symmetry. The first ionization potentials are estimated to be 7.436 ± 0.015 and 7.944 ± 0.055 eV for pyrene and fluorene, respectively.

1. Introduction

The photon collision with PAHs are significant to study because of their role in interstellar physics and chemistry [1] as well as on earth [2]. PAHs are efficient absorber of UV radiation coupling the electronic energy to vibrational excitation and emit in IR. The unidentified IR bands emitted from different galactic sources have resemblance with the spectroscopic signature of PAHs. The IR emission spectrum at 3.3, 6.2, 7.7, and 11.3 µm are attributed to PAHs [3]. A large fraction of interstellar carbon is locked in the form of PAHs and their cations, hydrogenated derivatives are considered as the possible carrier of diffuse interstellar bands [4, 5]. At the same time on earth they are considered as the mutagenic and carcinogenic [2, 6] element formed upon incomplete combustion of carbon (C) rich compounds like fuel, coal, crude oil.

PAHs are a family of hydrocarbons consisting of molecules where C atoms are arranged in a honeycomb lattice type structure of fused six-member aromatic rings with H atoms located at the periphery of the ring. The smallest member of this family is benzene and the family expands by attaching more number of benzene rings linearly or otherwise. The inherent stability for PAHs and aromatic character is due to the existence of delocalized electrons above and below the plane of molecule due to the sp² hybridized C atoms.
PAHs are associated with a multiparticle excitation mode upon interaction with external radiation known as plasmon excitation. This mode of excitation is already established for two dimensional graphite (at $\sim 25$ eV) to three dimensional $C_{60}$ (at $\sim 21$ eV) [7, 8]. For PAHs it was observed to be at $\sim 17$ eV in electron energy loss spectroscopy studies of PAH films and photo ion yield studies in the gas phase [7, 9]. For other PAHs like, phenanthrene, anthracene, fluoranthene, pyrene, triphenylene, plasmon resonance is observed in the range of 7 - 21.2 eV for gas phase VUV photoionization mass spectrometry studies [10] and it was found that plasmon excitation leads to autoionization [9]. Hence this common mode of excitation at $\sim 17$ eV for PAHs [10, 7] is attributed to the collective or plasmon excitation as well as to a mixture of various inner shell transition like $\pi \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$ transitions. This mode of excitation is shown to play a major role in PAHs in studies like photon impact [10, 7] and ion impact [11].

So far the PES experiments for PAHs are done using He - I and II discharge sources [12, 13, 14] and the theoretical measurements also rely on it. In the present study, synchrotron radiation has been used to investigate the systematic variation of the state selective PE cross sections over a wide range of photon energies. This state selective photoemission intensities have never been measured for PAHs except benzene [15]. In addition to this a detail study of photon energy dependence of PES for a wide range of photon energy in UV regime is performed for the first time for PAHs.

2. Experimental details
The experiment was performed at the GASPHASE photoemission beamline at the Elettra-Sincrotrone Trieste laboratory (Trieste, Italy). The details about the beamline (resolving power 2000 at the energies used here) can be found elsewhere [16, 17]. Pyrene and fluorene were obtained from Sigma-Aldrich at $>99\%$ purity. The photon beam crosses the target placed in a copper container having a 3.3 cm length nozzle with a 3 mm opening. The container for pyrene was heated resistively to $\sim 74$°C (for obtaining the vapor pressure), which was kept constant with the help of a temperature controller. For fluorene, the vapor pressure was sufficiently high to avoid any heating. PES for a wide range of photon energies from 15 to 40 eV were measured using a hemispherical electron energy analyzer with six channel electron multiplier (CEM) detectors with a resolution down to 50 meV. The spectrometer acceptance angle is a cone of $\pm 4\°$ with the axis of the cone oriented at the magic angle with respect to the direction of polarization.

3. Experimental data analysis
The relative photoelectron cross sections were obtained by including photon flux normalization and spectrometer efficiency correction (assuming a constant target density). These relative cross sections are directly proportional to the absolute cross sections, by a constant factor unique to each target molecule. Xenon ionization cross section from the same set up (with identical experimental set up parameters) were used to obtain the normalization to the photon flux after comparing with the previously published absolute cross sections for Xe 5p photoionization [18, 19]. This procedure is followed because of the change in photodiode efficiency with photon energy which makes the photon beam intensity measurement with this photodiode unreliable for normalization. For the spectrometer efficiency correction, Xe Auger electron spectra at 95.1 ev photon energy (figure 1) with present set up is compared with the Auger intensity distribution reported in previous investigations [20]. The efficiency curve was obtained by fitting a polynomial to the measured factors for each individual CEM (figure 2).

4. Experimental results
The HOMO of PES is associated with vibrational structure resolved up to $3 \leftarrow 0$ progression in the case of pyrene due to symmetry as compare to fluorene. The first ionization potential
agrees very well with the highly accurate results of studies like REMPI-ZEKE and TPEPICO. The inner valence band onwards in PES are broadened due to the breakdown of MO picture as described by Deleuze [21] which involves the strong electron-electron correlation leading to redistribution of intensity around the main peak.

The relative photoelectron cross sections are plotted as a function of photoelectron kinetic energy and photon energy in figure 3. Despite the fundamental differences in the structure of the two molecules, such as symmetry, the presence of sp³-hybridized carbon and cyclopentane ring, etc., the photon energy dependences are markedly similar. This figure shows the enhanced intensity for the inner valence band in the photon energy region < 27 eV which is attributed to the plasmon excitation. The cross section again follows an almost uniform variation for the photon energy > 27 eV for the studied range. The trend in outer valence band (pure π MOs) and inner bands (mixture of π and σ as well as pure σ bands) are almost same for all photon energy for the case of pyrene. Whereas for fluorene the PE cross section for entire band differs except the outer valence band. Hence it is concluded that the inner valence band couples to plasmon excitation more efficiently. The most distinct characteristic we observe is the peak of
cross sections at \( \sim 17 \) eV particularly for the outer valence bands of pyrene (a plateau in the case of fluorene).

![Graph](image)

**Figure 4.** Comparison of HOMO photoelectron cross section with that of benzene study.

This study for the first time reports the quantitative intensity variation showing the parallel trend for \( \pi \) orbital photoelectron cross section for different photon energy which is theoretically studied by Carravetta et al.\cite{22} for large polyenes. However for the benzene case\cite{23}, particularly at a lower photon energy the individual \( \pi \) MO cross sections show a different trend which is possibly due to the role of autoionization in large PAHs. Another contradictory measurement with benzene is the increasing evolution of inner bands for benzene as a function of photon energy\cite{23,15}. Figure 4 shows no difference in behavior of PE cross section from HOMO for benzene, pyrene, fluorene for the studied range of photon energy. The detail discussion can be found elsewhere\cite{24}.

5. **Computational results and analysis**

The outer valence Green’s function calculations were performed using the nonlocal hybrid Becke three parameter Lee-Yang-Parr functional (B3LYP) and Dunning’s correlation consistent polarized valence basis set of double-\( \zeta \) quality (cc-pVDZ) incorporated in GAUSSIAN09\cite{25} to estimate molecular orbital ionization energies with respective pole strengths. The ground-state geometry optimization was done within the constraint of \( D_{2h} \) and \( C_{2v} \) symmetry point groups for pyrene and fluorene respectively, using density functional theory (DFT).

The convoluted spectrum obtained from OVGF/cc-pVDZ calculations using Lorentzian and Gaussian function reproduced the experimental PES binding energy positions as well as their intensity to a reasonably good accuracy for the valence MOs. Orbital symmetry assignments are made by comparing the binding energies of experimental and theoretical peaks obtained by OVGF calculations.

6. **Conclusions**

PAHs due to their significance in nature form a very intriguing system to investigate. Taking Pyrene and fluorene as two examples of this family, a two dimensional photoionization measurement was performed with binding energy and photon energy as variable. The binding energy structure was well reproduced with the help of OVGF calculations particularly in the outer valence region where the shakeup and shakeoff processes are less dominant. The evolution of PES as a function of photon energy demonstrated clearly that at the lower photon energies the inner valence bands contribute substantially compared to the outer valence bands. But beyond 27 eV photon energy the outer valence bands dominate. Over all, the cross sections for
both inner and outer valence orbital are found to peak at around 17 eV photon energy. This observation along with the previously studied photoion yield studies and EELS studies indicate the plasmon like excitation which appears to be independent of individual valence bands. The observations are explained in terms of this plasmon excitation process which couples with various ionization channels after photoexcitation.

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