Statistical and Non-Statistical Processes in Polycyclic Aromatic Hydrocarbons and their Derivatives under Charged Particle Interaction

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by

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Abstract

Abundant occurrence of polycyclic aromatic hydrocarbons (PAHs) and their nitrogen derivatives, polycyclic nitrogen heterocycles (PANHs) in nature in general, and in the astrophysical environment in particular, has intrigued researchers in recent decades. The functionality and survivability of these molecules in the ecosystem is entirely governed by their ability to discharge and accumulate smaller molecular subunits to and from their surroundings. The thermodynamics of their internal excitation modes and its correlation with the excitation mechanism is of utmost significance in deciding the role of these molecules. The time scale of internal rotational-vibrational oscillation of these molecules are in picoseconds and the relative magnitude of unimolecular dissociation timescales in comparison with this will decide whether it is a statistical or a nonstatistical which envisage the survivability of these molecules. Thus the excitation of these molecules by high-energy radiation and resulting statistical dissociation processes have been at the center stage of many research campaigns. Particularly of interest are the statistical dissociation processes leading to the formation of molecular hydrogen, acetylene or hydrogen cyanide molecules. The interest in these channels is not only driven by the intriguing molecular dynamics but also due to their pivotal role in deciding the biochemistry in astronomical environments. The correlation of the decay channels and internal energy is very important to completely understand these aspects. The decay constant is governed by the internal energy of the molecule which is strongly dependent on the collision parameters. To this end, electron spectroscopy and mass spectroscopy have been the most commonly used tools to investigate their dynamics, but they are seldom used together in coincidence. Typical linear ToF mass spectrometry measurements are on microsecond time scales. Thus if the effect of thermal velocity is mitigated on the time scale of first few microseconds, it is possible to probe the time evolution of the unimolecular dissociation channels of these molecules which fall in this decay time range. Moreover, electron-ion coincidence measurement can give a correlation of the internal energy and a given dis-

sociation channel. The inherent complexity of the design, implementation, and analysis make such experiment technically very challenging and time-consuming. Moreover, generally, such instruments are used with high energy photon collisions due to very selective excitation energetics, simplifying the selection scheme of coincidence. Charged particle interaction, in spite of being of great significance for PAHs and their derivatives, are rarely studied using such elucidative technique. This work addresses such a challenging task of designing and realizing a full instrumentation to probe the electron impact excitation in PAHs and PANHs in three different modes, namely, electron spectroscopy, mass spectrometry and most significantly, energy selective secondary electron-ion coincidence mode. After realizing the instrument it was used to elucidate the role of molecular structure in statistical dissociation channels, especially C_2H_2 and HCN loss in basic PAH and PANH.

The higher sensitivity of the projectile electron below 250 eV restricted our ability to do measurement below 4 a.u., the velocity of the charged particle. Therefore, to probe the energy loss in this velocity regime where we expect the charged particle to deposit more energy in electronic energy loss model, we perform the experiment with proton beam at lower velocity. But when this is done, the proton beam itself introduces additional complications due to the electron capture (EC) and capture ionization (CI) processes. Using multi-coincidence technique we have isolated as many contributions as possible. Using this data it was possible to identify the extent to which the structural randomisation can happen at a given projectile velocity. This method has also helped to compare the rate of evaporation from mono and di-cation. A detailed comparison of energetics and resulting statistical dissociation of C_2H_2 and HCN loss is done in the two complementary cases of proton and electron impact measurements. This work quantifies the structural randomization process and positional identity of carbon and nitrogen in collision-induced excitation of PAHs and PANHs.