Contribution ID: **60** Type: **Talk 22min**

Controlling Biomolecular Fragmentation within an Ion Funnel Interface

Wednesday 10 July 2024 11:45 (22 minutes)

Analyzing biomolecular structures and spectra in the gas phase is challenging due to the large mass and intricate structures. Research frequently concentrates on selectively sampling specific biomolecules to gain insights into the broader system's structure. This focused approach, rather than studying the entire system indiscriminately, provides valuable information about the behavior of the larger system in different environments. To conduct spectroscopic studies, an ion-trap-based setup is essential for isolating ions in the gas phase. In such an experimental arrangement, optimizing parent ion count while minimizing fragmentation is crucial.

Our recent experiments, concentrating on the impact of increased DC gradients on ion fragmentation, revealed unexpected outcomes within the ion funnel region—a site anticipated to experience significant fragmentation due to higher pressure compared to other operational regions (0.1 mbar). For this investigation, we selected deprotonated deoxyadenosine monophosphate (d-dAMP), a fundamental building block of DNA. This system has been extensively studied, and reports on collision-induced studies are already available [1]. The analysis of recorded mass spectra included evaluating the relative abundance of each fragment ion at different DC gradients by adjusting gradients across the ion funnel (GradIF) and between the ion transfer capillary (ITC) and ion funnel (GradITC). Unexpectedly, these results diverged from the anticipated correlation between higher gradients and increased fragmentation.

To understand this, we used SIMION simulations, analyzing recorded kinetic energy to determine the center-of-mass energy (E_{cm}). A portion of E_{cm} contributed to the increment in internal energy, expressed as $E_{int} = \eta' E_{cm}$ [2], where η' is the inelasticity parameter. The specific η' value was obtained by fitting the energy dependence of the relative yield of a fragment ion [3]:
\begin{eqnarray}
Y(E)=Y_0\frac{(E-E_0)^n}{E},
\end{eqnarray}
where, Y_0, n, and E_0 serve as fitting parameters.

The simulations predicted a higher fragmentation yield in GradITC than GradIF, contrary to experimental findings. Considering fluid dynamics effects within the ion funnel, we performed Computational Fluid Dynamics (CFD) simulations using COMSOL, along with ion trajectory simulations. This confirmed the expected supersonic jet expansion at the ITC exit leading to the ion funnel. Comparing the increment in internal energy with and without CFD, CFD data aligned well with our experimental observations. While it is recognized that ions undergo collision-induced dissociation during their traversal through this device, the influence of gas flow dynamics on ion fragmentation remains unexplored.

This novel technique holds promise for future endeavors, offering a simplified simulation approach to determine the Collision-Induced Dissociation (CID) threshold of various other molecular ions.

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Authors: Mrs N N, UMA (PhD scholar); Dr S, Sunilkumar (Associate Professor)

Co-authors: Dr DINESAN, Hemanth (Post doctoral fellow); Mrs MOHANDAS, Salvi (PhD scholar)

Presenter: Mrs N N, UMA (PhD scholar)

Session Classification: Molecular Spectroscopy

Track Classification: Molecular Spectroscopy