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Lifetime Measurements using PIKE Analysis

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Lifetime Measurements using Pre-dissociation Imparted Kinetic Energy (PIKE) Analysis
Michaela L. Rich, Ira M. Simet, Curtiss D. Hanson

Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometry has long been recognized for its flexibility for studying unimolecular and ion-molecule reactions. One of the inherent strengths of the technique is its ability to obtain information on the reaction kinetics and ion lifetimes that occur in the millisecond timescale. These studies are performed by direct observation of changes in the intensity of the reactants and products in the mass spectra. Often, reactions proceed through intermediates that dissociate prior to detection and therefore are not directly observed in the mass spectra. Although these are not compatible with direct ion detection, ion excitation can occur on the microsecond timescale and therefore can be used as a probe of short lived intermediates.

The ability to study the translational kinetic energy of ions caused by rf ion excitation has been accomplished using the conductance limit orifice in a two-section cell as a kinetic energy filter. This same approach can be employed to measure the kinetic energy imparted to product ions following rf excitation of a short lived intermediate precursor. If an intermediate is formed in the presence of a continuously applied rf excitation field that is resonant with its cyclotron frequency, it will gain translational energy at a rate given by the amplitude of the applied field, increasing the radius of its cyclotron orbit. Any product ions formed following dissociation will maintain their mass fraction of the kinetic energy and therefore maintain an increased cyclotron orbit. Because the rf excitation is mass specific, the product ions formed following dissociation of the intermediate will no longer gain kinetic energy, because the applied rf frequency will no longer be resonant with its cyclotron frequency. The amount of energy gained by the intermediate and imparted to any resulting product ions will be limited to the lifetime of the intermediate in the excitation field prior to dissociation. Therefore, the translational kinetic energy of the product ion is directly related to the lifetime of the precursor intermediate. Successively increasing the amplitude of the applied rf excitation field will result in increased radii of the product ions. The radius of the product ion can then be monitored using the conductance limit orifice. Using this technique, the lifetimes of intermediates that cannot be directly observed in the FT-ICR mass spectrometer can be monitored.

Preliminary results monitoring the reactions of unimolecular and bimolecular reactions will be discussed.

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