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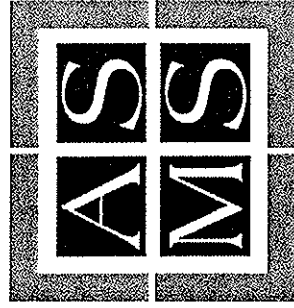
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PROCEEDINGS



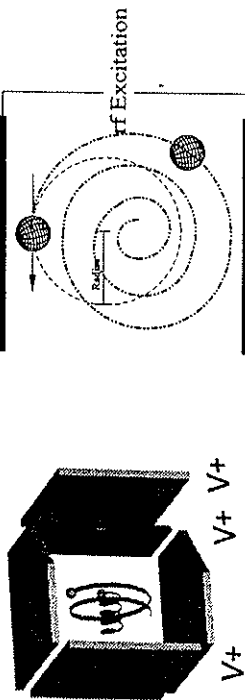
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Lifetime Measurements using Pre-dissociation Imparted Kinetic Energy Analysis

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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.

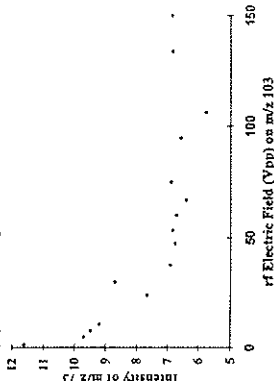


The ability to study the translational kinetic energy of ions caused by rf ion excitation has been accomplished using the conductance limit orifice in a two-section cell as a kinetic energy filter. This same approach can be employed to measure the kinetic energy imparted to product ions following rf 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.

All gas-phase reactions were performed on an Ion Spec OMEGA 50 FT-ICR mass spectrometer. Background pressure of 7.0×10^{-10} torr was maintained in the vacuum system analyzing chamber by a Balzers 300 liter/second turbo molecular pump backed by an Alcatel direct drive roughing pump. Gaseous reagents were set and maintained using a Varian leak valve. Experimental pressures in

the range of $2 \times 10^{-7} - 3 \times 10^{-7}$ torr in the 5 cubic centimeter analyzer cell were maintained using a Bayard-Alpert type ionization pressure gauge. To perform the ion skimming experiment a second trapping plate was added to the single section cell. This trap plate contained a 3 mm radius hole which was used as the skimming orifice. During normal operation of the cell a standard trapping potential was applied to this trapping plate. To accomplish the mass and energy selective elimination of ions, the skimmer was pulsed to ground and the ions were partitioned through the orifice and repelled by the rear trapping plate.

The ability of the technique to determine the lifetime of short lived intermediates was evaluated by studying the methyl cation transfer reaction of methoxymethyl cation ($\text{CH}_3\text{-O-CH}_2^+$; m/z 45) with acetone. This reaction proceeds by an intermediate proton bound adduct ion (m/z 103) which dissociates to form a methylated acetone product ion ($\text{(CH}_3\text{)CO-CH}_3^+$; m/z 73). The methoxymethyl cation was formed by electron impact of chloromethoxyethane and isolated in a background of acetone neutrals. Following isolation of the methoxymethyl cation, a continuous rf excitation was applied at the cyclotron frequency corresponding to m/z 103. As soon as the methoxymethyl cation reacted with the neutral acetone, the adduct ion gained energy. The radius of the adduct ion continued to increase until it dissociated to form the methylated acetone product ion at m/z 73. The product ion maintained its mass percentage of the intermediate's kinetic energy at the time of the dissociation resulting in an increased radius and shift in the orbit center. It is important to note that all product ions formed from dissociation of the intermediate will be formed at the corresponding increased radii. Following a reaction delay of 1500 ms, the ion skimmer was pulsed to ground and any ions having a radius greater than the skimmer orifice were quenched. If the lifetime of the intermediate was short, the product ions would maintain a small orbit radius and pass through the orifice. By sequentially increasing the electric field strength of the applied rf excitation field, the rate that the intermediate gains energy increases. Therefore, for the same intermediate lifetime the product ion is formed at a larger radius and no longer efficiently passes through the skimmer orifice.



Shown in figure 2 is a plot of the intensity of the product ion (m/z 73) as a function of the electric field strength of the rf excitation of the intermediate (m/z 103). From the intercept it can be seen that the product ion is eliminated at an electric field strength of 50 V_{pp} . This excitation power corresponds to an average lifetime of the intermediate of 200 ns.

This approach permits measuring the lifetimes of short lived intermediates that occur in the microsecond timescale. Because the ions do not need to be ejected, the time required to eliminate the intermediate is greatly reduced. Furthermore, because only ions that are located near the center of the cell are detected, the efficiency of ion detection is unaffected by the excitation. In combination with a two section cell and low background pressures, this approach will provide an effective method of determining the lifetimes of short lived intermediates.