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Lifetime Measurements using pre-dissociation imparted kinetic energy (PIKE) analysis: Iowa Academy of Science

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were calculated at the UHF/3-21G level of theory. MP4/6-31G* calculations for thermodynamic data is in progress. Zero point vibrational energies were also calculated for the molecules in question at the UHF/3-21G leve lof theory. It has been found that zero point energy corrections are negligible and therefore will not need to be calculated at the MP4/6-31 G* level

58. Kinetic energy analysis of metastables using a two section electrostatic particle guide in a time-of-flight mass spectrometer

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The continued growth in biomolecular analysis has led to the need for efficient instrumentation. Most biomolecules are difficult to obtain and laborious to isolate, and this results in very small available sample sizes. The ability to obtain as much information from as little of sample is desired. To address this problem, work on a new technique in the area of time-of-flight mass spectrometry has been performed at the University of Northern Iowa. By the addition of a two section electrostatic particle guide, it has been shown that ion isolation and kinetic energy analysis can be accomplished in a single time-of-flight instrument. This advancement has allowed for tandem MS to be done in one time-of-flight mass spectrometer. By the use of this technique, structural information and ion isolation of trace samples can be obtained.

59. Ammonia and glutamate levels in hippocampal synaptic vesicles

S.L. PATTERSON, S.K. SPEAR, & M.A. ARNOLD

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Increases in glutamate and ammonia levels in extracellular fluid surrounding toad eye cup and retinal tissue preparations have previously suggested that depolarization of these tissues results in simultaneous release of glutamate and ammonia. We hypothesized that the ammonia is stored within synaptic vesicles as a counterion for the neurotransmitter, glutamate, and that the two molecules are coreleased. Slices of rat hippocampus, which are known to contain high levels of glutamatergic neurons, were depolarized and release of glutamate and ammonia was observed. Additionally, synaptosomes were isolated from rat hippocampi, ruptured, and the synaptic vesicles collected. Glutamate and ammonia levels were determined in the synaptic vesicle containing buffers before and after the synaptic vesicles were dissolved with trichloroacetic acid. From these analyses and the determination of vesicular protein concentrations, glutamate concentrations within the isolated synaptic vesicles were calculated to be 99.1 ± 36.3 mM (n=7) in HEPES buffer and 297 ± 77.6 mM (n=7) in ATP buffer. Intravesicular ammonia was not detected, however, upon rupturing of the synaptic vesicles. These experiments verify that glutamate is found within hippocampal synaptic vesicles at high concentrations. Moreover, these results demonstrate that no significant amount of ammonia is located within these same vesicles. The source of ammonia released into the extracellular fluid is yet to be determined.

60. Lifetime measurements using pre-dissociation imparted kinetic energy (PIKE) Analysis

97-108

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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

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