

ION TRAP CID – IT'S NOT JUST FOR SEQUENCING ANYMORE

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A primary goal of our ongoing work is investigation of the ion processes occurring in the unique environment of quadrupole ion traps. Because the underlying principles for many of the phenomena are not yet fully understood, in-depth study of them will likely indicate directions for improving mass spectrometric approaches to solving molecular measurement problems, and conceivably, altogether new analytical measurements. For example, collision-induced dissociation (CID) is generally used to obtain macro-ion sequence information from the spectrum of charged products arising from unimolecular decomposition. Yet, the multiple collision nature of ion trap collisional activation also makes it possible to use the measurement of CID kinetics to derive the Arrhenius activation energy and the entropy change leading to the transition state. There is considerable interest in developing and refining methods to derive still other fundamental information for such species. Thus, we will discuss the possibility of using ion trap CID rate data to make a new kind of measurement, namely the determination of cross-sections for activated ions.

Although it is still uncertain as to how closely gas-phase conformations are related to those in solution, accurate measurements of collision cross-sections can improve the understanding of the specific conformations of peptides and proteins. Among the most popular techniques for making collision cross-section determinations is ion mobility spectrometry, a technique based on measuring the transport velocity of gas-phase ions through a buffer gas while under the influence of a DC electric field. Ion velocity in an electric field depends on charge state, z , collision cross-section, and ion-neutral reduced mass, which is independent of ion mass for macro-ions. The ion trap CID method generally involves the use of an AC electric field in resonance with ion secular motion to increase the velocity of stored ions. The corresponding effective temperature for ions undergoing dissociation can be established using Arrhenius parameters. With the effective temperature in hand, the expression below can then be used to determine ion velocity, and subsequently, the collision cross-section.

$$T_{\text{eff}} = T_{\text{buffer}} + \frac{m_{\text{buffer}}}{3k} v_{\text{ion}}^2$$

In this case, the relevant cross-section is that for the activated ion. The charge dependence can become complex if macro-ions adopt an enlarged conformation with higher charge state to reduce the increasing coulomb repulsion energy. In addition, a complex dependence on effective temperature could result if variation in ion internal energy disrupts the relatively weak intramolecular interactions that contribute to ion conformation, thereby affecting the cross-section.

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