Ion Internal Temperature Determination in the Quadrupole Ion Trap

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The parent ion internal energy distribution that results from ion activation is an important factor underlying the appearance of the MS/MS spectrum. Under normal collisional activation conditions in the ion trap, where ion activation, ion deactivation, and unimolecular dissociation occur in parallel, parent ions obtain either a near-Boltzmann distribution of internal energies or a truncated Boltzmann distribution. The shape of this distribution is determined by relative rates of ion activation, deactivation, and dissociation. For cases where a near-Boltzmann distribution exists, the parent ion internal energy distribution can be characterized by a temperature.

We have been studying the dissociation kinetics in the quadrupole ion trap to determine parent ion internal temperatures (T_{int}) using leucine enkephalin as a model system. Leucine enkephalin was chosen as a model system because the dissociation kinetics have already been studied using BIRD (1) and heated capillary dissociation in an electrospray ionization source (2). Previously, we have determined that for thermal dissociation conditions, T_{int} is equivalent to the bath gas temperature (3). Master equation modeling suggests that rapid energy exchange (REX) conditions do not apply for leucine enkephalin at rates above 1 s^{-1}, which is the case for most MS/MS experiments in the quadrupole ion trap, so T_{int} cannot be directly calculated using the Arrhenius equation. Therefore we used an empirical calibration that relates k_{diss} to effective T_{int} which is described below.

In this work, parent ion dissociation rates under collisional activation conditions were measured to draw conclusions about effective parent ion internal temperatures achievable under ion trap collisional activation conditions, specifically resonance excitation and boundary activated dissociation (BAD). Effective internal temperature is defined here as the bath gas temperature necessary to achieve the observed parent ion dissociation rate in the absence of ion acceleration via an external electric field.

We have determined an empirical relationship between leucine enkephalin dissociation rates and effective T_{int} that applies to any continuous activation method in the quadrupole ion trap. The plot in Figure 1 shows this relationship between k_{diss} and effective T_{int}. This relationship was used to determine effective ion internal temperatures under resonance excitation and boundary activated dissociation conditions. Figure 2 shows the plot of effective T_{int} versus resonance excitation amplitude (dashed line) using the Arrhenius equation and activation parameters found from thermal dissociation experiments (1). The non-linear increase in temperature with increasing amplitude arises from the parent ion not being in the rapid energy exchange (REX) limit. However, when corrected values for effective T_{int} for the measured rates are plotted (solid line), we obtain a linear relationship between resonance excitation voltage and effective T_{int}. An effective internal temperature 357 K over the bath gas temperature was determined using monopolar resonance excitation of 540 mV. The k_{diss} vs effective T_{int} relationship in Figure 1 was also used to determine effective T_{int} under boundary activated conditions. Figure 3 shows effective T_{int} vs dc voltage (and corresponding a_z) for boundary activated conditions. For rates below 1 s^{-1}, the Arrhenius equation was used to calculate effective T_{int} and for rates greater than 1 s^{-1}, the equation describing the plot in Figure 1 was used to calculate effective T_{int}. An effective T_{int} 170 K over the bath gas temperature was determined using 112 V (a_z = -0.029).

The temperature of the bath gas can also affect mass spectral appearance by either controlling the rate of ion cooling for product ions or by thermally activating first generation (or higher) product ions to fragment further. Figure 4a and 4b illustrate how the environment (i.e. bath gas temperature) in

which the product ion is formed affects the mass spectrum. The spectrum in Figure 4a is obtained at room temperature with an effective T_{int} of 522 K. The spectrum in Figure 4b is obtained with an effective T_{int} of 434 K which is equivalent to the bath gas temperature. The spectrum in Figure 4b shows many sequential fragments despite having a lower parent ion temperature than the parent ion of Figure 4a. This difference arises because the b_4^+ ion has a fast dissociation rate of 2.8 s^{-1} at 434 K while the dissociation rate for b_4^+ at 298 K is only 1 x 10^{-6}.

FIGURE 1

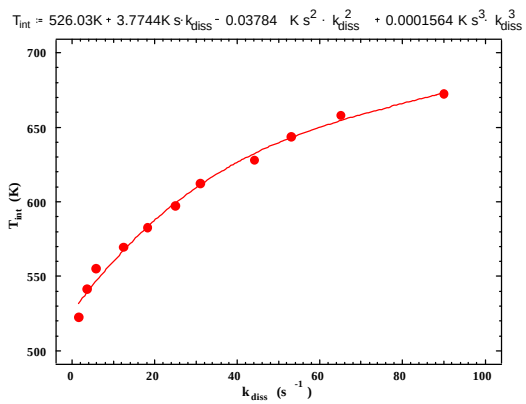


FIGURE 2

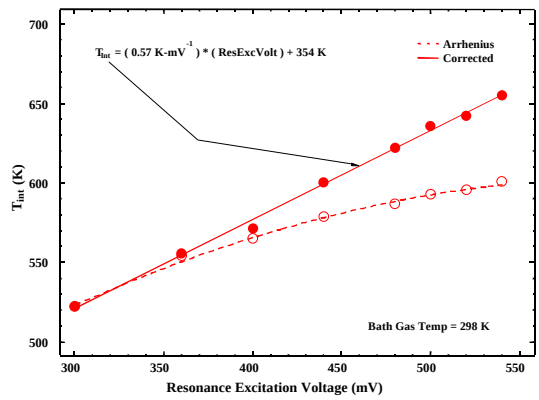


FIGURE 3

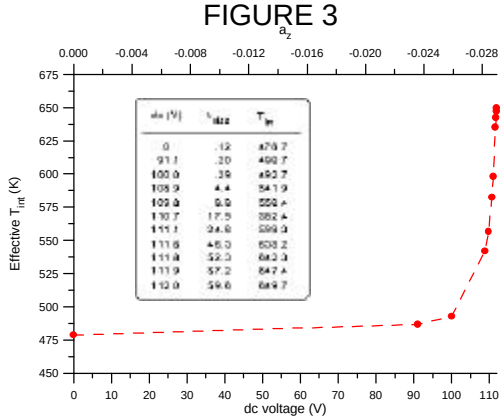


FIGURE 4a

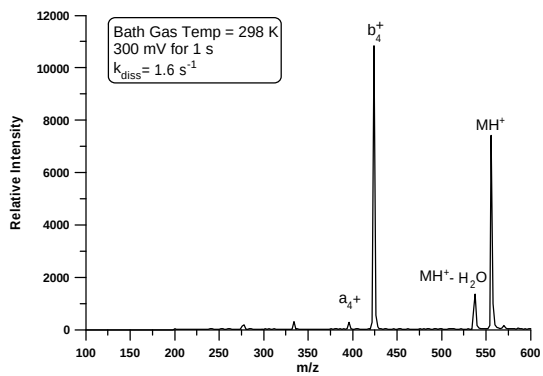
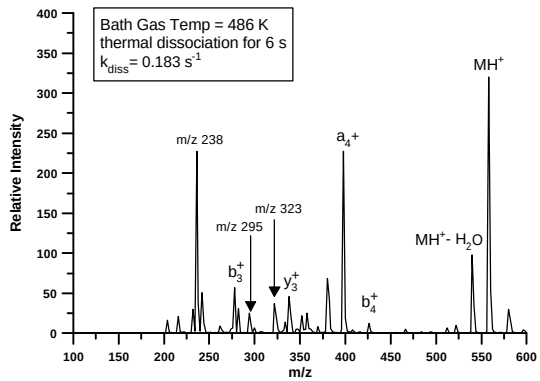


FIGURE 4b



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