International Journal of Mass Spectrometry 185/186/187 (1999) 207–219

Thermal dissociation in the quadrupole ion trap: ions derived from leucine enkephalin

Keiji G. Asano, Douglas E. Goeringer, Scott A. McLuckey*

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6365, USA

Received 25 May 1998; accepted 22 July 1998

Abstract

Rates of dissociation of protonated leucine enkephalin and the b_4^+ fragment ion derived from protonated leucine enkephalin have been measured as a function of helium bath gas temperature in a quadrupole ion trap. Dissociation rates were observed to be insensitive to the amplitude of the trapping voltage over the range of values studied. This observation, along with theoretical arguments based on predicted levels of "rf heating," indicates that any internal excitation of the ions due to ion trap storage is minimal. The bath gas temperature can therefore be used to characterize the internal temperatures of the ions. This approximation is expected to be most valid for high mass ions and low mass bath gases, such as helium. Activation parameters were obtained from Arrhenius plots of the rate data, and master equation modeling of the activation, deactivation, and dissociation processes was performed to provide an indication as to how closely these ions approached high-pressure limit behavior. Protonated leucine enkephalin more closely approached the high-pressure limit than the b_4^+ ion due to its larger size and the fact that the activation parameters were derived from somewhat lower dissociation rates. These studies suggest that the quadrupole ion trap operated in the presence of a light, heated bath gas can be used to obtain Arrhenius activation parameters from the dissociation kinetics of relatively high mass ions. (Int J Mass Spectrom 185/186/187 (1999) 207–219) © 1999 Elsevier Science B.V.

Keywords: Thermal dissociation; Quadrupole ion trap; Leucine enkephalin; Ion temperatures

1. Introduction

The array of products resulting from the unimolecular dissociation of gaseous polyatomic ions has long been used to draw conclusions regarding the structures of ions. For example, most studies employing mass spectrometry/mass spectrometry (MS/MS) have tended to base their conclusions upon the abundances and mass-to-charge ratios of the product ions [1,2]. In recent years, however, ion trapping instruments capable of MS^n experiments have made possible the precise measurement of absolute rates of unimolecular dissociation using "slow heating" methods [3], such as continuous wave infrared multiphoton dissociation (cwIRMPD) [4–10], dissociation induced by blackbody radiation [11–20], and collisional activation in a quadrupole ion trap [21]. Slow heating methods in conjunction with ion storage devices allow for the acquisition of dissociation rates as a function of ion temperature, thus making accessible information regarding dissociation energetics and, in favorable cases, dissociation dynamics.

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* Corresponding author. E-mail: mcluckeysa@ornl.gov

Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

PII S1387-3806(98)14116-7

As has been illustrated by Williams et al. by use of blackbody infrared radiative dissociation of ions derived from relatively large biomolecules [17–20], the Arrhenius activation parameters E_a and A factor can be obtained via measurement of dissociation kinetics, provided the parent ion approaches the so-called "rapid energy exchange" or high-pressure limit. We and others have noted that the rates of collision-induced dissociation in the quadrupole ion trap correlate with the critical energies for dissociation of various ions [22,23]. That is, for a fixed set of ion activation conditions, ions of lower critical energy fragment at higher rates than do ions of higher critical energy. (The parent ions in the studies just alluded to were probably not close to the high pressure limit but such a correlation is still expected.) In principle, it should be possible to use collision-induced dissociation in a quadrupole ion trap to determine Arrhenius activation energies and A factors for ions that approach the high-pressure limit, or to determine critical energies for ions that do not (with the help of master equation modeling).

A number of issues must first be addressed before quantitative values of activation parameters derived from ion trap collision-induced dissociation can be regarded with confidence. Of primary importance is the establishment of the internal energy of the parent ion population as a function of experimental conditions. The minimum internal energy of an ion under steady-state storage conditions is the temperature of the bath gas. The internal energy of the ion can be increased over the temperature of the bath gas if the ion is accelerated to increase the average energy of the ion/bath gas collisions. A variety of approaches to ion acceleration that are effective in inducing dissociation in an ion trap have been demonstrated [24–28]. However, for the purpose of determining quantitative activation parameters, any approach that increases the ion kinetic energy by accelerating the ion with an externally applied electric field must be amenable to the determination of the ion internal temperature under steady-state ion acceleration conditions. For example, we have used a simple model to predict ion internal energies under ion trap single-frequency collisional activation conditions in a pure quadrupolar electric field [29,30]. However, it is not currently known the extent to which the ion internal temperatures derived from this simple model deviate from those that result from the normal situation in which ions are accelerated in an ion trap with intentionally imposed higher order fields [31–33]. The accurate prediction of ion internal temperature resulting from the application of a supplementary oscillating electric field is a challenging problem that we are currently considering. However, it must first be established if it is necessary to apply a correction as a result of power absorption by the ion from the radio-frequency (rf) potential applied to ring electrode of the ion trap necessary for ion storage (i.e. the trapping voltage). This effect, sometimes referred to as "rf heating" [34–37], must be examined before the issue of ion acceleration with a supplementary oscillating electric field can be addressed. The phenomenon of rf heating underlies many of the wide range of studies directed towards the determination of "ion temperatures" in the quadrupole ion trap [34–48]. Some confusion, however, can arise from what is meant by ion temperature (e.g. internal energy distribution, translational energy distribution, or average translational energy). Within the context of this work, the important quantity of interest is the internal energy distribution of relatively high mass ions stored in a quadrupole ion trap in the presence of helium bath gas under normal ion storage conditions (e.g. $a_z = 0$, $q_z = 0.1 - 0.3$, where a and q are dimensionless storage parameters and the subscript z represents the axial coordinate z [49]). Therefore, we discuss here the ion *internal* temperature under normal ion storage conditions.

To explore the possible contributions of rf heating to the internal energies of moderately large polyatomic ions undergoing collision-induced dissociation, we have measured the dissociation kinetics of ions as a function of bath gas temperature. In so doing, we avoid the issue of determining quantitatively the relationship between ion acceleration using a supplementary oscillating electric field to activate the ions and ion internal temperature. We simply measure the rates of collision-induced dissociation resulting from collisions with the bath gas at temperatures sufficiently high to yield readily measurable rates. We have chosen for study ions derived from leucine enkephalin because this system has already been studied via blackbody infrared radiative dissociation [50] and via heated capillary dissociation in an electrospray ionization source [51]. We report here rates of dissociation, the activation parameters derived therefrom, the implications of these results on the extent to which rf heating might contribute to the measurement of dissociation kinetics of high mass polyatomic ions in the quadrupole ion trap, and the results of modeling studies intended to indicate the extent to which the ions approach the high pressure limit.

2. Experimental

Leucine enkephalin (tyr-gly-gly-phe-leu or YGGFL) obtained commercially (Sigma, St. Louis, MO) was dissolved in a solution of 50:50 methanol:water to a concentration of roughly 2160 μm with 1% acetic acid. Working solutions (~50 μm) were prepared by diluting the stock solution with 99% methanol/1% acetic acid. The solution was infused at a rate of 1.0 μL/min through a 100 μm inner diameter (i.d.) stainless steel capillary held at +3.5–4.0 kV.

All experiments were performed with a Finnigan ion trap mass spectrometer (ITMS, Finnigan, San Jose, CA), modified for electrospray ionization. An electrospray interface/ion injection lens/ion trap assembly, which has been described previously [52], was attached to the vacuum system of the ITMS. The ITMS vacuum system is equipped with infrared heaters and a closed-loop temperature control system. A constant bath gas temperature was achieved by suspending the platinum resistance thermometer of the temperature control system in the vacuum system (i.e. it was disconnected from its normal attachment to the surface of the vacuum system). The location of the platinum resistance thermometer is somewhat remote from the ion trap itself. The temperature indicated by the platinum resistance thermometer was therefore calibrated against a temperature measurement made by suspending a temperature probe (Omega Engineering, Stamford, CT) adjacent to the ion trap (in the absence of any applied voltage) and systematically altering the temperature set point of the temperature feedback system. Essentially identical temperatures were also measured when the probe was physically touching a mounting bracket of the ion trap electrodes. In all cases, helium was introduced into the vacuum chamber to a total pressure (uncorrected) of 1.1×10^{-4} Torr, as measured on the ion gauge.

Following an ion accumulation period of 100–300 ms, protonated leucine enkephalin ions were isolated using a single resonance ejection ramp. That is, isolation of the parent ion of interest was effected using a single scan of the rf-voltage amplitude applied to the ring electrode while simultaneously applying a single frequency in either monopolar or dipolar fashion chosen to sweep out ions of mass-to-charge ratio greater than that of the ion of interest. Lower mass-to-charge ratio ions were swept out by passing the ions through the $q_z = 0.908$ exclusion limit. A relatively broad ion isolation window (i.e. several mass-to-charge ratio units) was employed to avoid collisional activation of the parent ion by off-resonance power absorption because of the isolation step. In the case of the b_4^+ ion, protonated leucine enkephalin was first isolated and subjected to ion trap collisional activation [21] to produce the b_4^+ product ion. Collisional activation conditions could be readily achieved that yielded the b_4^+ ion as the most abundant product ion. A second ion isolation period, once again using a single resonance ejection ramp, was then used to isolate the b_4^+ ion.

The rates of dissociation of the parent ions were measured by recording the product ion mass spectra as a function of reaction time and as a function of bath gas temperature. At each temperature, product ion spectra were obtained over reaction periods extending to as long as 15 s. The spectrum used for each reaction time was the average of 100 repetitions of the experimental sequence described above.

3. Results and discussion

Spectra derived from thermal dissociation of protonated leucine enkephalin and the b_4^+ ion (derived

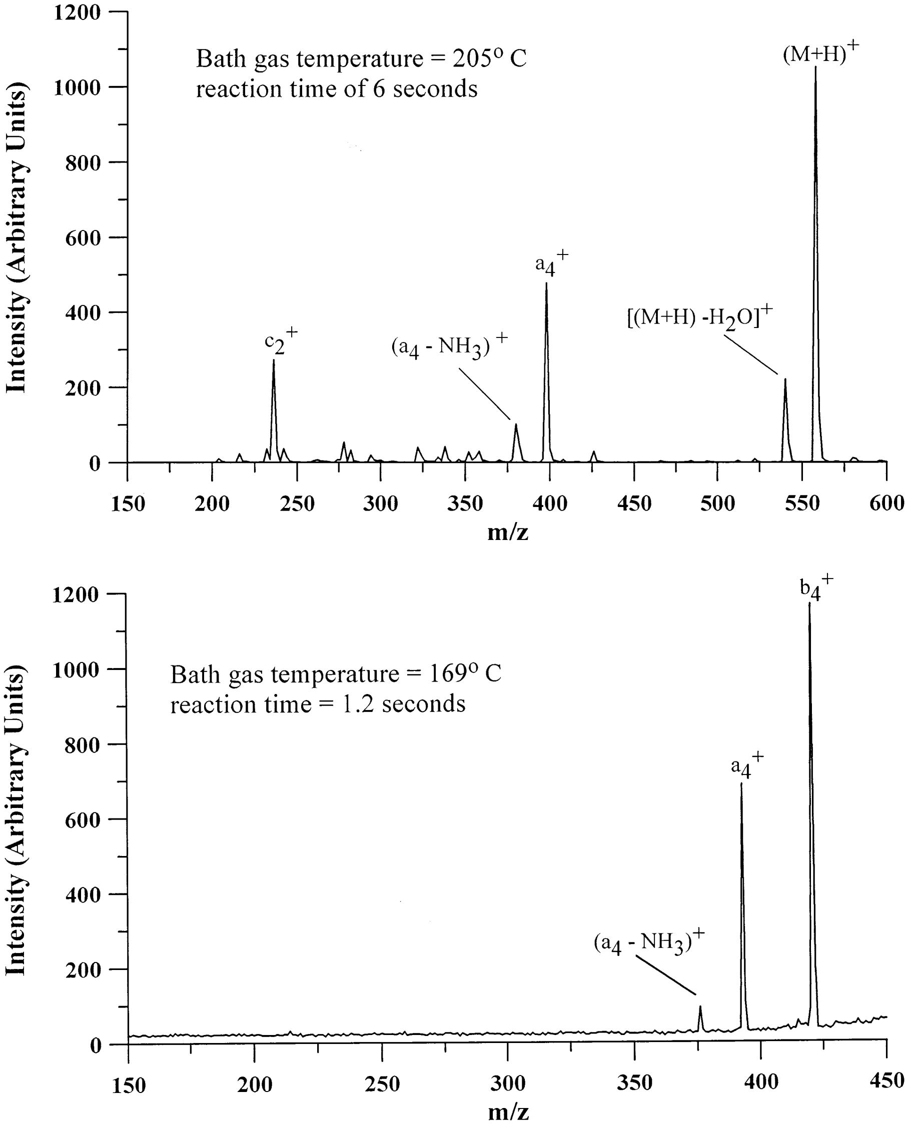

Fig. 1. (a) Spectrum of protonated leucine enkephalin at a bath gas temperature of 205°C after a delay period following ion isolation of 6 s. (b) Spectrum derived from the thermal dissociation of the b_4^+ ion at a temperature of 169°C following a delay period of 1.2 s.

from protonated leucine enkephalin via ion trap collisional activation) are shown in Fig. 1. Fig. 1(a) shows the spectrum derived from protonated leucine enkephalin at a bath gas temperature of 205°C after a delay period of 6 s following ion isolation. Note that these products are identical to those reported as arising from blackbody infrared dissociation [50], and with relative abundances very similar to those reported at a similar temperature. Figure 1(b) shows the spectrum derived from the thermal dissociation of the b_4^+ ion at a temperature of 169°C following a delay period of 1.2 s. Once again, these results are qualitatively very similar to those reported in the blackbody infrared radiative dissociation study.

For each of the ions dissociation rates at a fixed temperature could be derived from data such as those shown in Fig. 2. This figure shows the relative abundances of the b_4^+ parent ion, and a_4^+ and $(a_4 -$

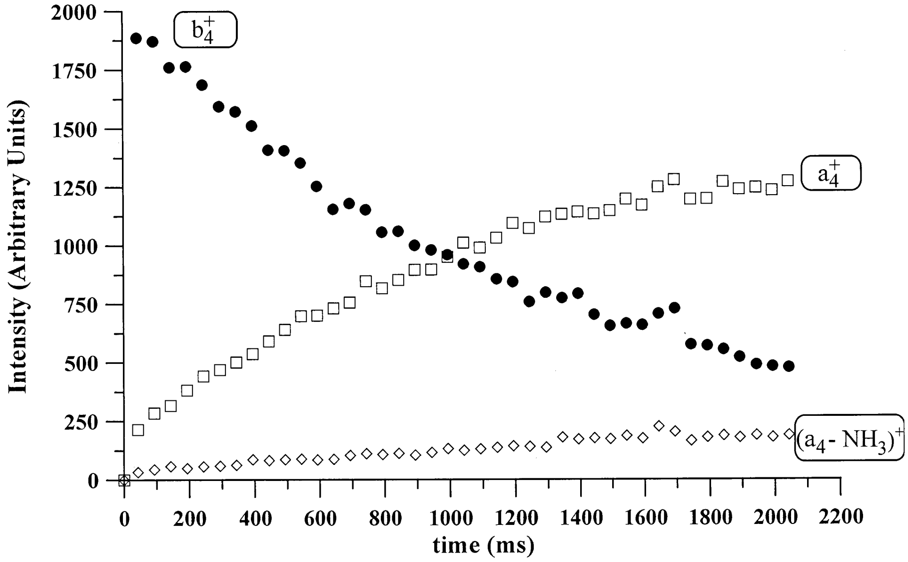

Fig. 2. Relative abundances of the b_4^+ parent ion, and a_4^+ and $(a_4 - NH_3)^+$ product ions as a function of time at a bath gas temperature of 185°C.

$NH_3)^+$ product ions as a function of time at a bath gas temperature of 185°C. Note that the trapping efficiency exceeds 90% over a 2 s time frame. High trapping efficiencies were noted for all of these studies. In any case, to normalize for ion losses, dissociation rates were determined by the slope of the plot of ln[parent ion]$_t$/([parent ion]$_t$ + Σ[product ions]$_t$) versus time. Fig. 3 shows the plots indicating parent ion dissociation as a function of time from which temperature-dependent dissociation rates can be derived. Fig. 3(a) shows data collected for protonated leucine enkephalin with the parent ion stored at a q_z value of 0.163. Fig. 3(b) shows data collected for the b_4^+ ion with the parent ion stored at a q_z value of 0.214.

The q_z value at which an ion is stored is noted here because it is related to the amplitude of the trapping voltage. If there is a significant degree of rf power absorption by the ion that might be coupled into internal energy, a dependence of the dissociation rate on the q_z value at which the parent ion is stored might be expected. Indeed, it is well-known that placing an ion near to the edge of a stability boundary can lead to ion dissociation [26,53–56]. This is sometimes referred to as boundary-activated dissociation and is an example of rf heating whereby acceleration of the ion by the trapping voltage is coupled via collisions into internal modes. However, boundary-activated dissociation requires close approach to a stability boundary and the conditions under which these experiments were conducted keep the parent ions far from any stability boundary. Nevertheless, in recognition of a possible rf heating effect on the dissociation rates under heated bath gas conditions we conducted experiments over a range of q_z values. Over a q_z range of roughly 0.075–0.3 within experimental error we observed no difference in dissociation rates. Fig. 4, for example, shows the dissociation rate measured for protonated leucine enkephalin as a function of q_z at 205°C illustrating the independence of dissociation rate on q_z at relatively low values.

Our observations for protonated leucine enkephalin and the b_4^+ ion indicate that the dissociation rates of the ions resulting from collisions with the helium bath gas are insensitive to the range of ion storage conditions examined here. There is theoretical support that rf heating of internal modes should be minimal under these conditions. For example, Blatt et al. [37] have published a model for ion confinement in quadrupole ion traps that allows for the derivation of the

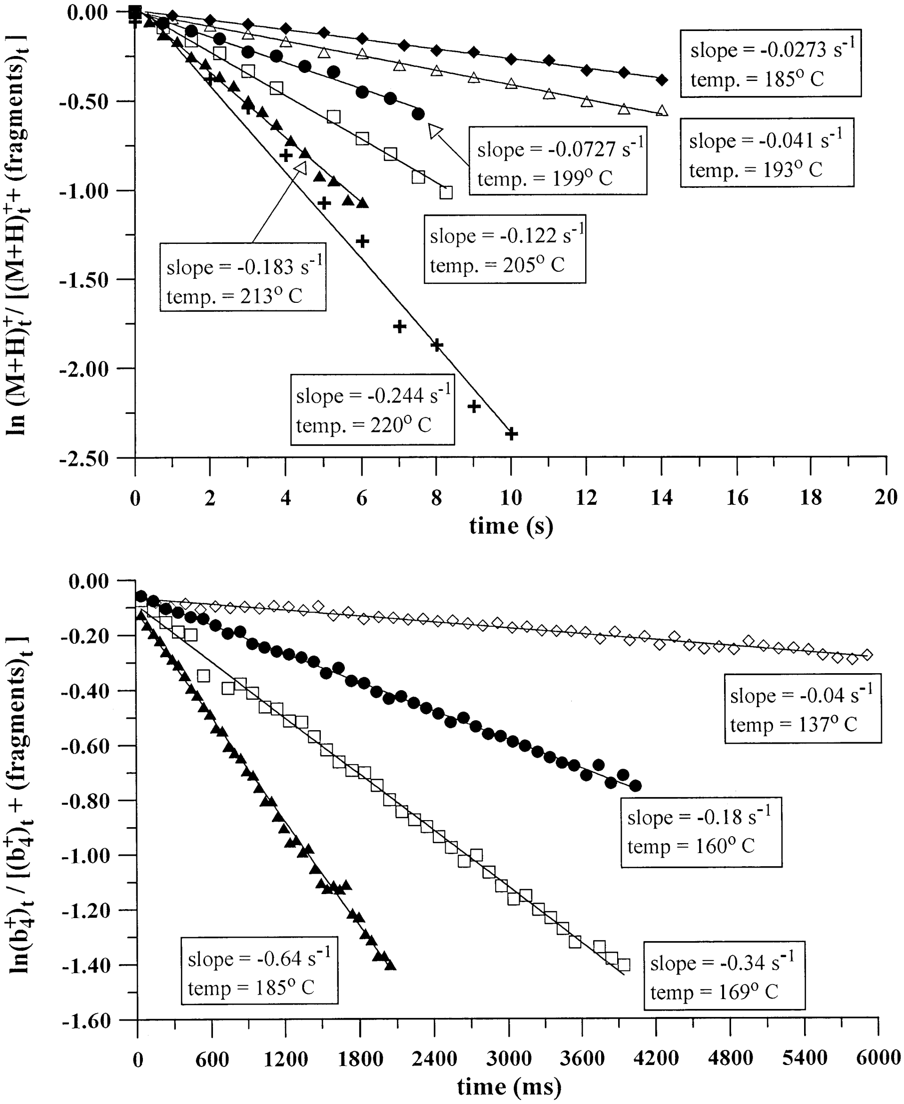

Fig. 3. (a) Kinetic data collected for protonated leucine enkephalin with the parent ion stored at a q_z value of 0.163. (b) Kinetic data collected for the b_4^+ ion with the parent ion stored at a q_z value of 0.214.

time-averaged velocity and spatial distributions of ions stored in the presence of a random damping force, such as that provided by a bath gas. Attractive aspects of the model are that it applies to a parametric oscillator potential (i.e. it does not rely on an harmonic oscillator approximation) and it allows for an exact solution of average ion velocity in the long time limit, which is the condition of interest here, for virtually any location within the stability diagram of the ion trap. Fig. 5(a) shows a plot of the kinetic temperature, T_{kin} (solid line), of an ion of the mass of protonated leucine enkephalin (m/z 556) in 1 mTorr helium ($T = 300$ K) as a function of q_z ($a_z = 0$) determined using the model of Blatt et al. [37]. The damping factor, γ, used in the model of Blatt et al. was determined using a collision cross section of 397 Å^2 and the ion trap parameters applied to those of the ITMS (viz. $r_0 = 1$ cm, $\Omega/2\pi = 1.1$ MHz). The

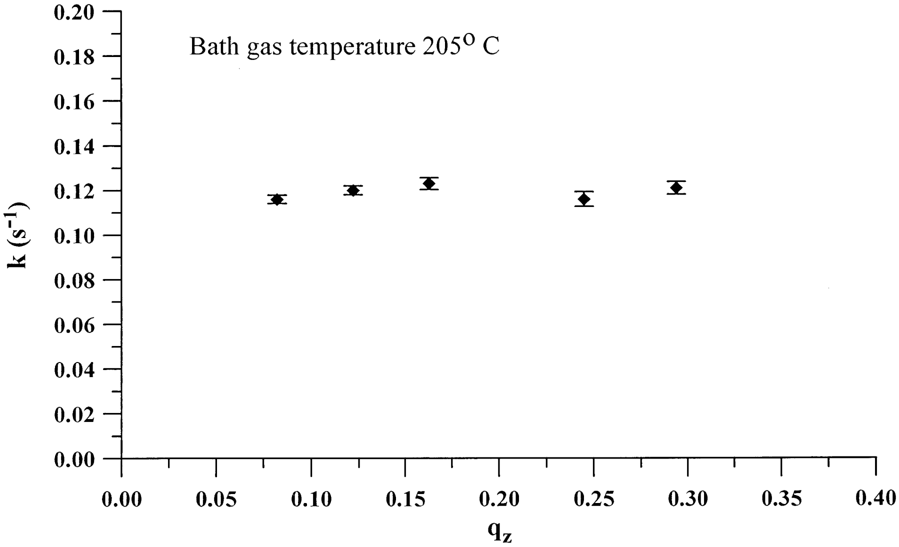

Fig. 4. Dissociation rate measured for protonated leucine enkephalin at 205°C as a function of q_z. Error bars represent $\pm 1\sigma$ of the slopes from which the rate data were derived.

kinetic energy is plotted in terms of a kinetic "temperature" by converting the average kinetic energy to an equivalent temperature. The model indicates that the average kinetic energy of the ion stored under these conditions increases with q_z relatively slowly up to about a q_z of 0.5 and increases somewhat faster as q_z increases beyond 0.5. The model predicts the kinetic temperature to approach infinity as q_z approaches the exclusion limit (stability boundary) at $q_z = 0.908$, reflecting the transition from stable to unstable trajectories.

Although the absolute values of the kinetic temperatures predicted by this model have not been evaluated against experimental data, the qualitative shape of the kinetic energy versus q_z plot is consistent with observation in that dissociation of polyatomic ions can be induced when they are placed close to a stability boundary. Of particular relevance to this work is the degree to which the ion kinetic energy resulting from storage at relatively low q_z values in the ion trap is converted into internal energy via collisions with helium. From the theory of ion transport in gases, the extent of internal heating predicted by two-temperature theory [57] is

$$T_{\mathrm{int}} = (mT + MT_{\mathrm{kin}})/(m + M) \qquad (1)$$

where T_{int} is the temperature that describes the distribution of internal energies of the ion, T is the temperature of the bath gas, T_{kin} is the kinetic temperature of the ion, m is the mass of the ion, and M is the mass of the bath gas. The dashed line of Fig. 5(a) shows a plot of T_{int} as a function of q_z based on the values of T_{kin} obtained from the model of Blatt et al. (Fig. 5(a) solid line). The vertical scale is expanded in Fig. 5(b) to show more clearly the predicted dependence of T_{int} on q_z over the range of $q_z = 0 - 0.8$. This plot shows behavior that is similar to the predicted kinetic temperature in that changes in the internal temperature as a function of q_z are minimal at q_z values less than about 0.5 and that significant internal excitation is expected only as q_z exceeds about 0.75. The absolute elevation of the ion internal temperature over the bath gas temperature is only a very small fraction of the kinetic temperature of the ions due to the large ion/target mass ratio.

The lack of a dependence of dissociation rates on q_z and the expectation of negligible internal excitation of the ions by the models just alluded to above (under the storage conditions used here) suggest that the internal temperature of the ions under study can be considered to be essentially equal to the temperature

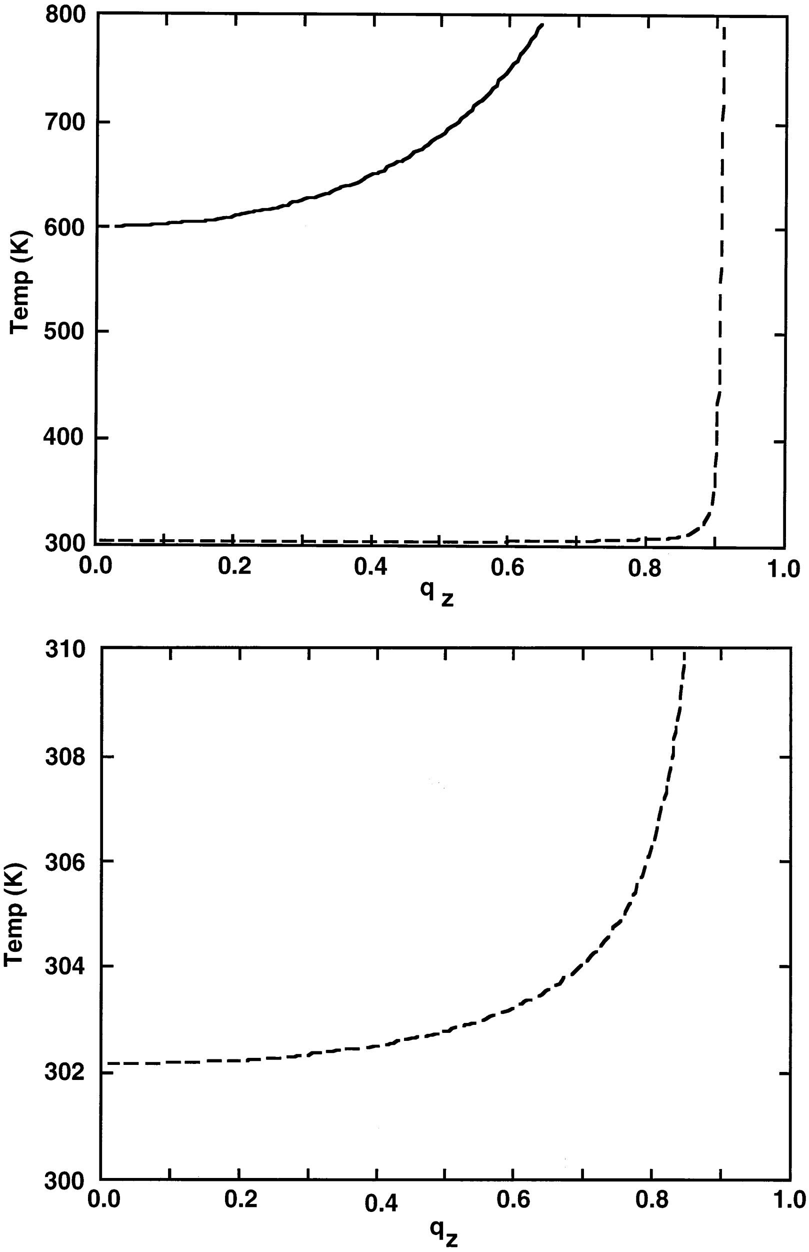

Fig. 5. (a) Plot of the average ion kinetic energy (solid line), plotted in terms of a kinetic temperature (T_{kin}) and ion internal temperature (T_{int}, dashed line) versus q_z as predicted from the model of Blatt et al. [37]. (b) Expansion of the vertical axis of the plot of (a) to highlight the predicted dependence of T_{int} on q_z.

of the bath gas. It is important to recognize that the dissociation rates are determined by the internal temperatures of the ions. The kinetic energies of the ions and the temperature of the bath gas are important only insofar as they influence the ion internal temperature. Many of the studies in the literature that address ion “temperatures” in electrodynamic traps are concerned with ion kinetic energies. Some of the “thermometer" reaction studies have used reactions in which either the relative velocity of the collision partners is the main rate-determining factor or both the internal energies of the reactants and relative velocity are important [43–48]. It is therefore important to recognize that ions are not in complete thermal equilibrium with the bath gas such that a single "temperature" can be used to define the entire system. That is, the internal temperature of an ion and its kinetic "temperature" (quotation marks are used here because the kinetic energy distribution is not necessarily Boltzmann) need not be the same. For this reason, the term "effective temperature" is often used. For the purpose of interpreting dissociation kinetics of a moderately high mass ion in an ion trap under conditions in which dissociation is driven by a heated bath gas, however, a true internal temperature applies and the temperature of the bath gas appears to be a very close approximation to that temperature.

Assuming the bath gas temperature to be a very close approximation to the internal temperature of the ion, Arrhenius plots can be constructed from the temperature-dependent data from which the activation energy and *A* factor can be derived. Fig. 6 shows the Arrhenius plots obtained for protonated leucine enkephalin (6a) and the b_4^+ ion (6b) with the activation energies and *A* factors derived from the slopes and intercepts of the plots, respectively, indicated in the figure. The degrees to which these quantities approximate the true Arrhenius parameters for these ions depends upon how closely the activation conditions approach the high-pressure limit. In analogy with the work of Williams' group with blackbody infrared radiative dissociation [17–20,51], master equation modeling of the activation, deactivation, and dissociation processes can indicate how closely the high-pressure limit is approximated. We have described an approach to modeling collisional energy exchange in the ion trap [29,30] and coupled this model with Rice-Ramsperger-Kassel-Marcus (RRKM) theory to allow for the determination of the ion internal energy distribution for an ion population in which dissociation competes with ion activation/deactivation. Using the critical energies and vibrational frequencies used to model blackbody infrared radiative dissociation of protonated leucine enkephalin and the b_4^+ ion [50], we have determined the internal energy distributions of the ions at several bath gas temperatures and compared them with the expected distributions for nonfragmenting ions. The difference between the two distributions reflects the extent to which the ions deviate from the high-pressure limit. Figs. 7 and 8 show two such comparisons. Fig. 7 shows the comparison for protonated leucine enkephalin at 220°C, the temperature corresponding to the highest dissociation rate indicated in the plot of Fig. 6(a) ($0.244\ \mathrm{s}^{-1}$), and Fig. 8 shows the comparison for the b_4^+ ion at 185°C, the temperature corresponding to the highest dissociation rate indicated in the plot of Fig. 6(b) ($0.64\ \mathrm{s}^{-1}$). Although both simulations show that the internal energy distributions of the fragmenting ions approximate the expected Boltzmann distributions, there is clearly a larger deviation in the case of the b_4^+ ion than in the case of the protonated molecule. The experiment involving protonated leucine enkephalin, therefore, more closely approached the high pressure limit condition than did the experiment involving the b_4^+ ion. In general, the smaller the ion and the higher the observed dissociation rate the greater the expected deviation from the high pressure limit condition.

Because it is clear that the experiment involving the b_4^+ ion deviates from the high pressure limit condition more so than the experiment involving the protonated molecule, it is not clear at this time what the absolute deviation is in either case. The results of a simulation of the energy distribution of an ion undergoing competitive activation/deactivation/dissociation depends upon several assumptions. These include the vibrational frequencies of the reactant and transition state, the critical energy, and the average energy transfer step-size. The uncertainty in the average collisional energy transfer step-size in our model is analogous to the uncertainty in the transition dipoles associated with master equation modeling of dissociation taking place when infrared absorption and emission are the main energy exchange mechanisms [50]. In the model used to generate the distributions of Figs. 7 and 8, we used an average down-step size, α (which, by microscopic reversibility, also determines the up-step size) of

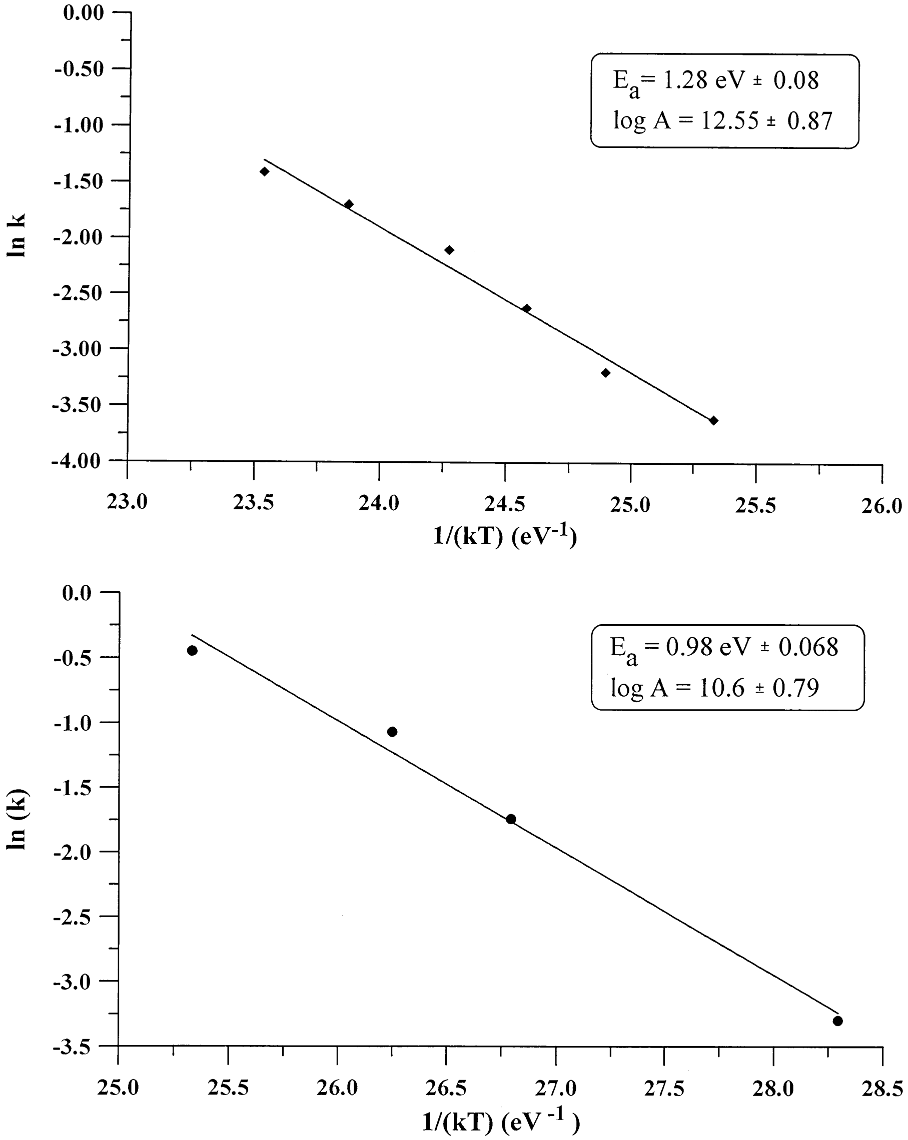

Fig. 6. (a) Arrhenius plot of protonated leucine enkephalin derived from dissociation rate data of Fig. 3(a). (b) Arrhenius plot of the b_4^+ ion derived from dissociation rate data of Fig. 3(b).

$$\alpha = 0.625\ kT + 0.001k(T_{\mathrm{int}} - T) \qquad (2)$$

where T and T_{int} are defined as in Eq. (1). Such a relation for the down-step size is physically reasonable because it increases with the difference between the internal temperature of the ion and the bath gas temperature. However, further comparisons with well-characterized systems are needed to determine if further refinement of this assumption are warranted.

4. Conclusions

Both experimental and theoretical evidence presented here suggest that, at least for relatively high mass ions, elevation of the ion internal temperature over the temperature of the bath gas due to rf heating is very small. Any correction to the internal temperature of the ion as a result of rf heating under normal

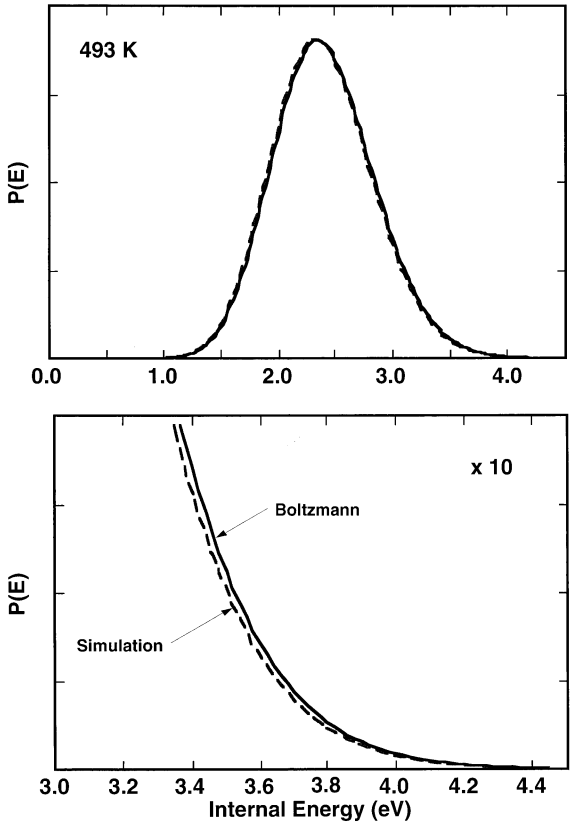

Fig. 7. Internal energy distribution, P(E), comparisons for protonated leucine enkephalin at 220°C (493 K). (Top) full distributions with the solid line indicating the Boltzmann distribution expected for a nonfragmenting ion and the dashed line reflecting the simulated distribution for a fragmenting ion. (Bottom) expansion of both the vertical and horizontal scales to show the deviation between the two distributions in the high energy tail.

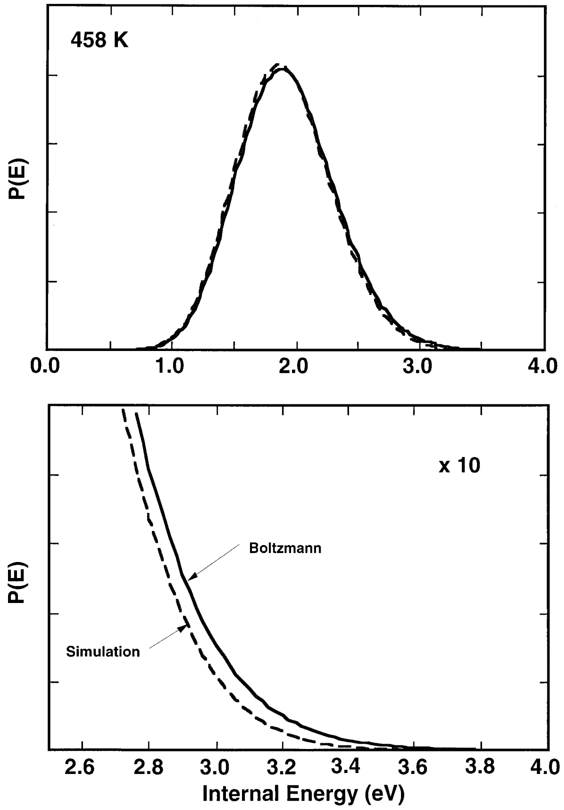

Fig. 8. Internal energy distribution comparison for the b_4^+ ion derived from protonated leucine enkephalin at 185°C (458 K). (Top) full distributions with the solid line indicating the Boltzmann distribution expected for a nonfragmenting ion and the dashed line reflecting the simulated distribution for a fragmenting ion. (Bottom) expansion of both the vertical and horizontal scales to show the deviation between the two distributions in the high energy tail.

ion storage conditions would fall within the experimental error associated with thermal dissociation measurements and is therefore unjustified. Consequently, Arrhenius activation parameters can be derived from ion trap thermal dissociation measurements made as a function of bath gas temperature for systems in which the high-pressure limit is approached. Such dissociation data are described herein for the ions derived from leucine enkephalin. Master equation modeling of the activation/deactivation/dissociation processes suggests that protonated leucine enkephalin more closely approaches the high pressure limit than does the b_4^+ ion. Further comparisons with well-characterized systems are needed, however, to refine the assumptions regarding the magnitudes of collisional energy transfer step-sizes before the master equation model can be used to provide an accurate measure of the deviation from the high pressure limit.

This study suggests that the measurement of ion dissociation kinetics in a quadrupole ion trap operated with a bath gas present at about 1 mTorr is an alternative to similar measurements using infrared dissociation methods [4–20] and to the use of heated capillary electrospray methods [51,58–60]. An important advantage over the latter is the capability for MS^n experiments which allow for confident definition of the parent ion/product ion relationships. Higher rates of collisional energy transfer compared with radiative energy transfer may allow for the derivation of Arrhenius activation parameters at higher observed dissociation rates than with the former methods.

Acknowledgements

Professor Evan Williams and Dr. Paul Schnier of the University of California at Berkeley are gratefully acknowledged for providing the vibrational frequencies they used to model the leucine enkephalin ions in their blackbody infrared radiative dissociation study of these ions. Dr. James L. Stephenson Jr. is acknowledged for his valuable assistance and advice throughout the course of this study. Dr. Gary J. Van Berkel is acknowledged for construction of the electrospray source used in this study. Research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract no. DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

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