

Protonated water and protonated methanol cluster decompositions in a quadrupole ion trap*

Scott A. McLuckey¹, Gary L. Glish and Keiji G. Asano

Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6365 (USA)

John E. Bartmess¹

Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 (USA)

(Received 11 March 1991)

ABSTRACT

Electrospray mass spectra of water and methanol have been studied with a quadrupole ion trap operated with background gas pressures of 2×10^{-5} – 2×10^{-3} Torr. In each case, the most abundant ions observed consist of protonated clusters of varying size, e.g. $(\text{H}_2\text{O})_n\text{H}^+$ in which n ranges up into the twenties. For clusters of $n > 6$ or so, rapid desolvation is observed. For intermediate values of n , the desolvation rate constants can be readily measured in the typical time frame of a quadrupole ion trap experiment. The internal temperatures of the cluster ions can be estimated from the known thermochemical parameters and the measured decomposition rate constants. In all cases, the temperature exceeds that of the bath gas but is significantly less than 1000 K. It is also noted that the ion temperature is inversely proportional to the logarithm of the bath gas pressure.

INTRODUCTION

Use of the quadrupole ion trap has undergone remarkable growth in the past decade due largely to new developments in ion trap technology and the subsequent commercial introduction of analytical instruments based on the three-dimensional quadrupole. Indeed, the development of the ion trap as a versatile tool for mass spectrometry continues to evolve at a rapid pace. Many of these developments are chronicled in recent reviews [1,2]. Although much of the interest in the ion trap is focused on its capabilities as a mass analyzer, the commercial availability of the instrument and its recognized versatility has refocused attention on its use as a device for studying ion/molecule reactions. One of the original chemical applications of the ion trap was the study of bimolecular ion/molecule reactions [3–6] but most of this work was limited to the relatively few laboratories involved in quadrupole ion trap research. However, as commercial ion traps, particularly those capable of multiple stages of mass spectrometry, become more widely available, the quadrupole ion trap

* Dedicated to Professor Paul Kebarle on the occasion of his 65th birthday.

¹ Authors to whom correspondence should be addressed.

can be expected to be increasingly applied to the study of ion/molecule reactions. Several studies have already appeared involving ion/molecule reactions carried out in commercial versions of the three-dimensional quadrupole [7–10].

A variety of factors can affect the rates and relative reaction channels of ion/molecule reactions. Results are, therefore, often highly dependent upon the conditions that prevail within the instrument used to study the reaction. These factors include the internal states of the ion and neutral (total internal energies and their distribution among states), relative collision energies, and the number densities of third bodies. These conditions frequently differ in the instruments ordinarily used to study ion/molecule reactions, such as the pulsed high pressure ion source [11], the flowing afterglow and its variants [12], and the ion cyclotron resonance instrument [13]. It is therefore important to recognize how conditions differ between these instruments in order to reconcile data acquired with them. For this reason, attention has been directed towards the “effective” temperatures of ions in the quadrupole ion trap [4], particularly when a buffer gas is used to kinetically “cool” ions [14,15], as is usually done with the commercial ion trap [16]. The buffer gas clearly moderates the kinetic temperature of the ions, such that they eventually relax to the center of the ion trap. This may be accompanied, however, by conversion of some of the ion kinetic energy into ion internal energy during the initial moderating collisions. At sufficiently long trapping times, after the ions have relaxed to the center of the ion trap, collision with the bath gas at low kinetic energies is expected to force the ions into thermal equilibrium at the bath gas temperature, in the absence of power absorption from the trapping field. It is therefore unclear what the ions’ internal temperature is at any given point during the experiment, particularly when ions are injected into the ion trap from an external ion source. The present study was motivated by the observation that extensive desolvation occurs from highly solvated ions injected into a quadrupole ion trap operated with helium at a pressure of several millitorr [17]. These observations indicated that significant internal heating can accompany kinetic cooling within the ion trap. We therefore chose to study the desolvation of cluster ions well-characterized in the seminal work of Grimsrud and Kebarle [18] to characterize conditions ions experience within the quadrupole ion trap operated with helium as a buffer gas.

EXPERIMENTAL

Ion trap experiments were carried out with a Finnigan ion trap mass spectrometer (ITMS) which has been modified for the injection of ions formed in an external ion source [19]. This system has recently been adapted for injecting ions formed via electrospray, as described in recent publications [17,20]. The interface between the atmosphere and the ion trap is comprised of two in-line

apertures of 100 μm and 800 μm diameters. The 100 μm aperture admits gases at atmospheric pressure into a region which is pumped to a pressure of 0.3 Torr. The inter-aperture distance is 1.9 cm. The 800 μm aperture couples the region at 0.3 Torr into the ion trap vacuum chamber. The base pressure of the system is 2×10^{-5} Torr when both apertures are open. Helium is added directly into the vacuum system through a gas fitting in a side flange via a gas metering valve. Pressure measurements were made with a Bayard–Alpert ionization gauge attached to a side flange which is 3 cm from the ion trap itself. Teflon sleeves, which are often placed between the ion trap electrodes in the commercial ion trap to “enclose” the trapping volume for GC–MS applications, were not used in this work. The difference in the pressure reading between the base pressure and when helium was admitted into the system was corrected for the ionization efficiency of the ion gauge [21]. Uncertainty of the pressure of the background gases leads to the largest source of error in determining rate constants. The rate constants are expected to be accurate to within $\pm 20\%$.

All ion trap experiments began with an ion injection period during which time ions are gated into the ion trap via an electrostatic lens for a period of 10–50 ms. The amplitude of the 1.1 MHz sine wave applied to the ring electrode during the ion injection period established a low mass cut-off of 25–35. Mass spectra were acquired following a variable time delay by scanning the amplitude of the ring electrode while applying a supplementary r.f. to the end caps (i.e. the mass-selective instability mode of operation [16] in conjunction with “axial modulation” [22]). Kinetics experiments involving the decomposition of a particular cluster involved a mass selection step, using the combined r.f./d.c. approach for ion isolation [23], directly after ion injection and prior to the variable delay period. Rate constants proved to be insensitive to the value of the q_z parameter [24] during the delay period over the range $q_z = 0.1$ – 0.3 . All data reported herein were acquired at a ring-electrode r.f. amplitude of 576 V (p–p) during the variable delay period.

Protonated water clusters were formed from electrospray of distilled water and protonated methanol clusters were formed from electrospray of HPLC grade methanol each at a flow rate of $1 \mu\text{l min}^{-1}$. Electrospray mass spectra for each solvent were also acquired with a quadrupole mass filter using an identical atmosphere/vacuum interface and identical electrospray conditions to determine the relative cluster ion abundances as the ions exit the interface (see below).

RESULTS AND DISCUSSION

Reaction conditions

Reaction conditions are unique for each type of instrument used to study ion/molecule reactions. Ion trap conditions are briefly discussed below,

therefore, to compare and contrast phenomena that occur within the ion trap with those that might be expected in a high pressure ion source or an ion cyclotron resonance instrument, for example.

Ions within a quadrupole ion trap are continuously under the influence of a rapidly changing electric field. For certain initial positions and velocities, under the appropriate trapping voltages and frequencies, ions describe stable, although somewhat complex, trajectories within the ion trap [24]. The term "stable" referring here to ion trajectories that remain within the ion trap electrodes for the duration of the experiment (e.g. up to several seconds). When a buffer gas is added to the system, collisions with the ions reduce the ion kinetic energy (if it is initially at higher kinetic energy than the buffer gas). A relatively light buffer gas minimizes momentum transfer to the ion that might deflect it into an unstable trajectory. As the ions lose kinetic energy, the amplitudes of their excursions from the center of the trap decrease and they become more concentrated at the center of the ion trap. This effect has been used to advantage to improve sensitivity and resolution in the ion trap [16]. The ions do not necessarily come into thermal equilibrium with the buffer gas due to power absorption from the trapping field. Studies to date to determine the "ion temperatures" in a quadrupole ion trap have indicated values of 500–2000 K in the presence of a buffer gas at 300–400 K [14,15,25]. The point here is that, although the distribution of ion kinetic energies is expected to be such that an "effective" ion temperature is meaningful, the ions are not in thermal equilibrium with either the buffer gas or any neutral reactant present in the vacuum system.

The ion trap is typically operated at pressures intermediate between those of the high pressure ion source and flowing afterglow, on the one hand, and the ion cyclotron resonance mass spectrometer, on the other. For an ion of m/z 100 with an effective temperature of 500 K and a collision cross-section of 100 \AA^2 , there are roughly $20 \mu\text{s}$ between collisions in the ion trap when helium is present at 1 mTorr. Three-body reactions, such as clustering reactions that proceed via stabilization by a third body, are observed to proceed at appreciable rates only when the lifetime of the initially formed complex is significantly longer than $20 \mu\text{s}$ or so. Complex lifetimes are generally maximized when the well-depth is large relative to all possible dissociation channels (i.e. when the complex is strongly bound), when there are many degrees of freedom in the complex, and at low temperatures. Rapid clustering has been observed in the ion trap for some relatively large, multiply protonated peptides and proteins with strong gas-phase bases [26]. However, clustering of smaller ions and molecules in the ion trap, such as the formation of the proton-bound dimer of water, is typically not observed under ion trap conditions even in the presence of 10^{-5} Torr of water vapor. In measuring the decomposition kinetics of protonated water and protonated methanol clusters, we can ignore the reverse reaction which involves third-body stabilization. Experimental results described below support the

expectation that the lifetimes of complexes formed by the condensation of a water or methanol molecule on a protonated cluster are too short for collisional stabilization to occur to a significant extent in these studies.

The typical time frame for an ion trap experiment ranges from 50 ms to several seconds. Ions are injected over a period of 10–50 ms and an ion isolation step, if one precedes a kinetics experiment, typically consumes 5–10 ms. With a period of 20 μ s between collisions, at least 750 collisions with helium occur prior to the beginning of the experiment. We expect that under these conditions, the ions have reached their “effective” temperatures prior to the kinetics experiments. Only at short injection times (10 ms), low pressure (2×10^{-5} Torr), and very little delay periods prior to scanning the ion trap do we expect to observe ions that have undergone less than 20 collisions with background gas in the system. Kinetic measurements at low pressures were made using 50 ms injection times and a delay time of an additional 50 ms prior to the mass-selection step.

Mass spectra and desolvation kinetics of $(H_2O)_nH^+$ and $(CH_3OH)_nH^+$ ions

The long time frame of the ion trap experiment relative to the collision frequency tends to minimize the effect of any differences in the initial internal energies of the trapped ions. A time period sufficient to allow for at least several hundred collisions was used prior to the beginning of a kinetics experiment for this reason. Nevertheless, we were concerned about the possibility of exciting the ions during the injection part of the experiment. Fragmentation of ions upon injection into an ion trap has been observed both in the present system [19] and by others [27,28] and tends to be maximized at low pressures. We therefore compared electrospray mass spectra obtained with the ion trap with spectra obtained using an identical interface mated to a quadrupole mass filter. Essentially no collisions occur after the ions exit the interface in the quadrupole mass filter. For this comparison the ion trap system was operated under conditions in which the number of collisions after exit from the interface is minimized in order to determine the extent to which ions are excited during ion injection. The comparisons are given in Figs. 1 and 2 which show protonated water cluster mass spectra and protonated methanol cluster mass spectra respectively. The ion trap mass spectra were acquired using a 10 ms injection period without helium added to the system and the spectrum was scanned immediately thereafter. Even under these circumstances, the ions probably undergo roughly 10 collisions with the background air in the system. The comparisons show that the ion trap discriminates against the lowest mass ions, which is a result of operating the ion trap at a low mass/charge cut-off of 30 during injection. The higher mass clusters also have reduced relative intensities. Nevertheless, essentially all of the clusters observed using the quadrupole mass filter are also observed in the ion trap

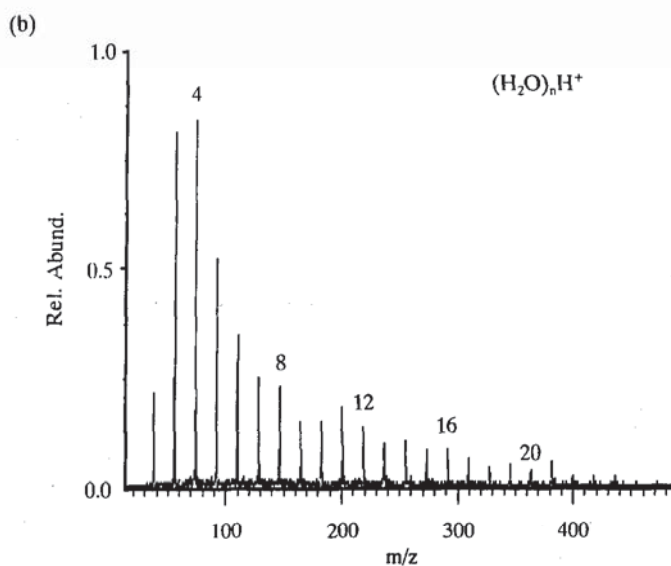
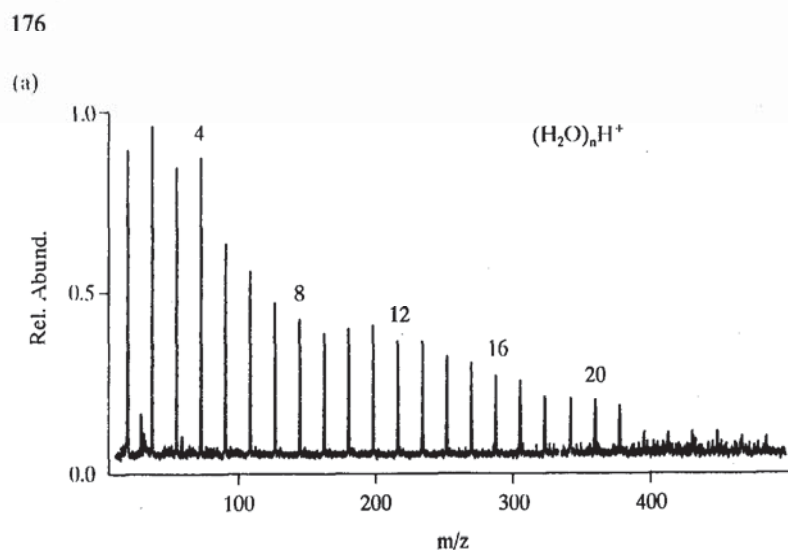


Fig. 1. Electrospray mass spectra of water acquired (a) with a quadrupole mass filter and (b) with a quadrupole ion trap. (See text for ion trap conditions.)

under these conditions. Furthermore, as a delay time is added prior to scanning the ion trap the high mass clusters are seen to rapidly diminish and disappear, presumably due to collisions with the background gas. The reduced intensities of the high mass clusters in the ion trap mass spectra of Figs. 1 and 2 can be attributed, at least in part, to the collisions that occur after the ions are trapped but before they are detected. These data strongly suggest that the ions studied here are not significantly excited internally during injection and

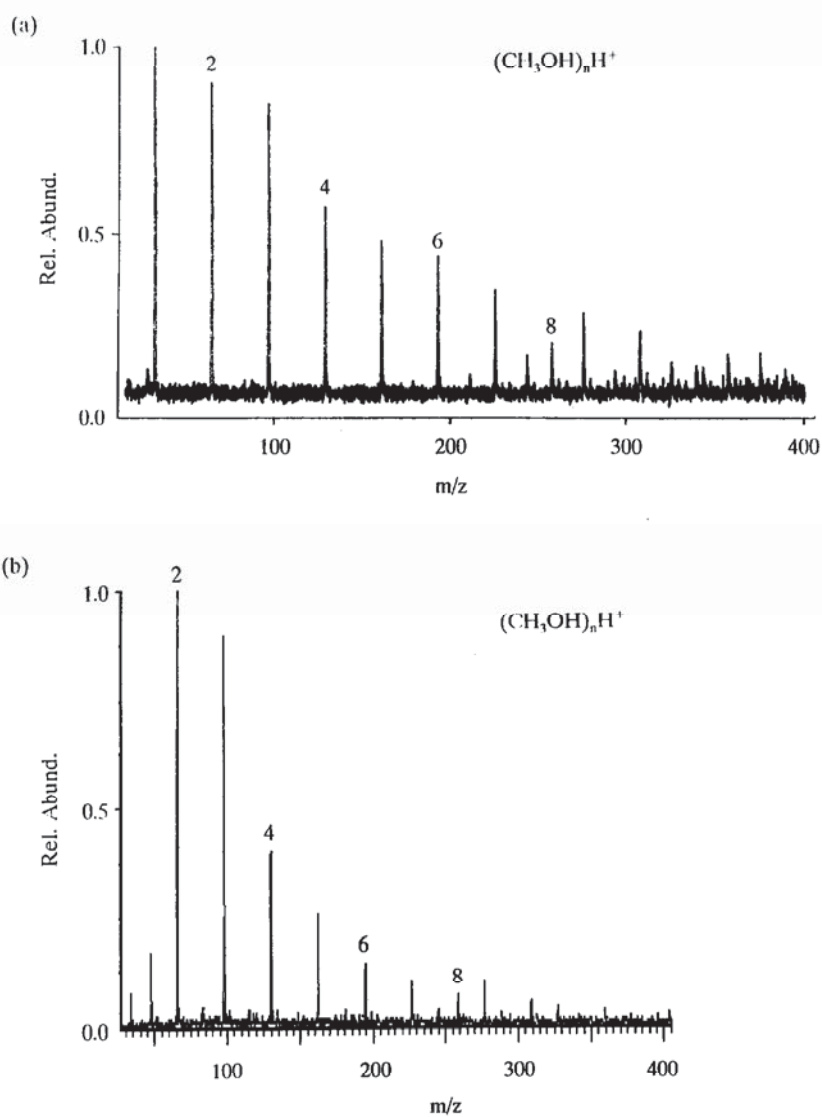


Fig. 2. Electrospray mass spectra of methanol acquired (a) with a quadrupole mass filter and (b) with a quadrupole ion trap. (See text for ion trap conditions.)

that the energy that they acquire to cause dissociation (desolvation) is obtained after they are trapped.

It was observed that by far the most important variables in determining the appearance of the mass spectra of the protonated water and methanol clusters were the pressure in the system and the time delay before scanning the mass spectrum. These observations are illustrated in Fig. 3 which summarizes mass spectra of protonated methanol clusters at 1 mTorr helium and no added

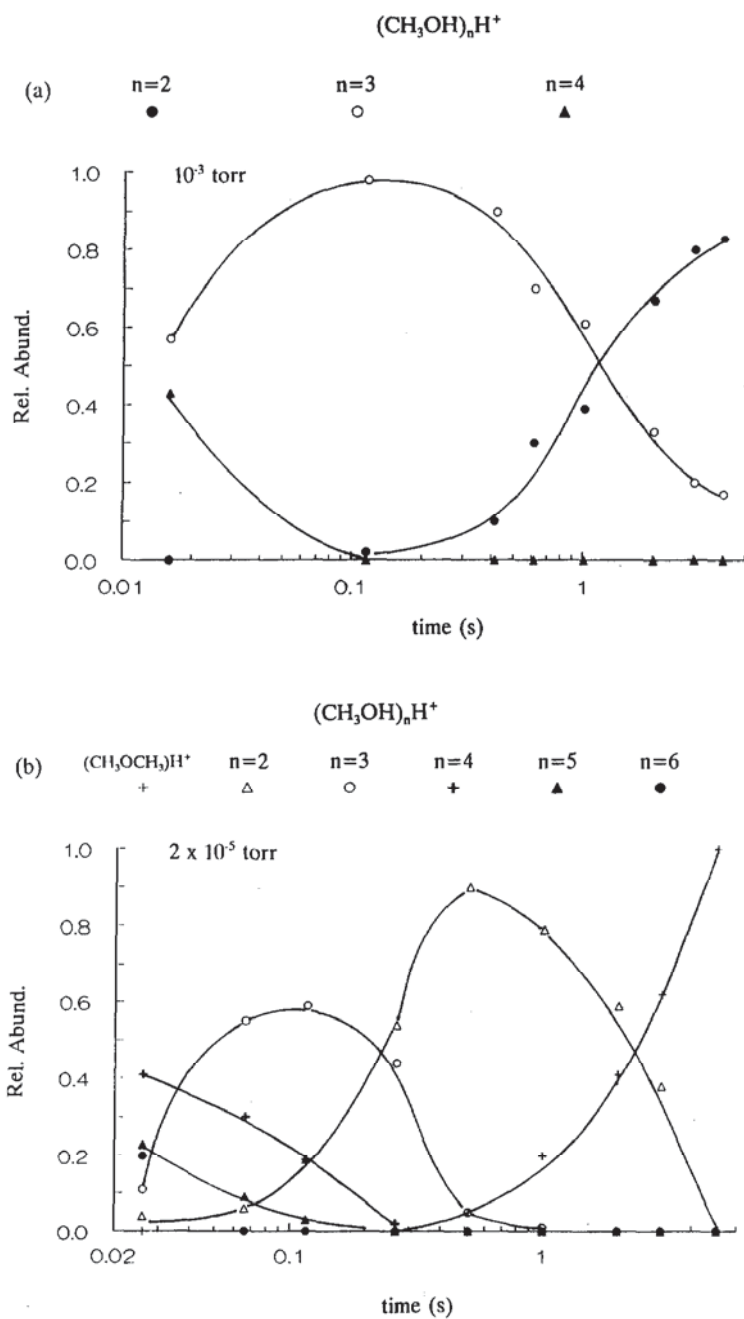


Fig. 3. Summary of methanol electrospray mass spectra acquired as a function of delay time with a helium bath gas pressure of 1 mTorr (a) and with a background pressure of air of 2×10^{-5} Torr (b) (no helium present).

helium both as a function of delay time prior to scanning the ion trap. Note that at 1 mTorr of helium even in as little time as 15 ms after ion injection the higher mass clusters apparent in Fig. 2 have fragmented to the point where the tetramer is the largest cluster observed (see Fig. 3a). After a delay of 4 s the tetramer has disappeared and the dimer is the dominant ion. At lower pressures the higher mass clusters persist somewhat longer due to the lower collision frequency (see Fig. 3b), but the spectra ultimately show more extensive desolvation. In the case of the methanol clusters, essentially 100% of the ions after 4 s arise from the well-known loss of water from the methanol dimer [29,30]. The protonated water clusters behaved very similarly. That is, the high mass clusters disappeared very quickly and the size of the clusters continued to decrease with time both at 1 mTorr He and without He added. At low pressures the higher mass water clusters persisted somewhat longer than at higher pressures but more extensive desolvation was noted at long times. The smallest water-containing ion observed at long times and at all pressures was the proton-bound dimer. The longest delay period was 5 s and in all cases the protonated water trimer gave rise to the base peak with the relative abundance of the dimer ion most nearly equal to that of the protonated trimer at the lowest pressure.

The observations just described stand in contrast to those made when covalently bound ions, ones that do not decompose during storage, are admitted into the ion trap. Trapping efficiency decreases with helium pressure for all ions but this decrease in trapping efficiency is not strongly mass-dependent for the range of masses and trapping conditions relevant to this study. The trapping efficiencies for ions over the range m/z 40–100 relative to one another, for example, change less than 10% over the pressure range in this work. Mass discrimination effects, therefore, cannot account for the behavior of the protonated clusters with changes in pressure and trapping time and are expected to have little effect on the kinetic measurements.

The kinetics for desolvation for a variety of clusters of various size were examined by isolating the cluster ion of interest and monitoring its normalized intensity as a function of time after ion isolation. Figure 4 shows a plot of the negative logarithm of the relative water tetramer $((\text{H}_2\text{O})_4\text{H}^+)$ signal as a function of delay time at 1.2 mTorr total pressure indicating a linear decay expected from pseudo first-order kinetics. (The average interval between collisions in these experiments is at least $10 \mu\text{s}$. It is therefore expected that the rate of energy transfer via collision is rate-determining rather than the rate for unimolecular decay of the cluster. Hence, the overall decomposition reaction is second order and the bimolecular rate constant is determined by dividing the slope of the line in Fig. 4 by the neutral number density.) All kinetics plots showed comparable linearity. This observation is consistent with the contention that the ions have reached their eventual effective temperature by the

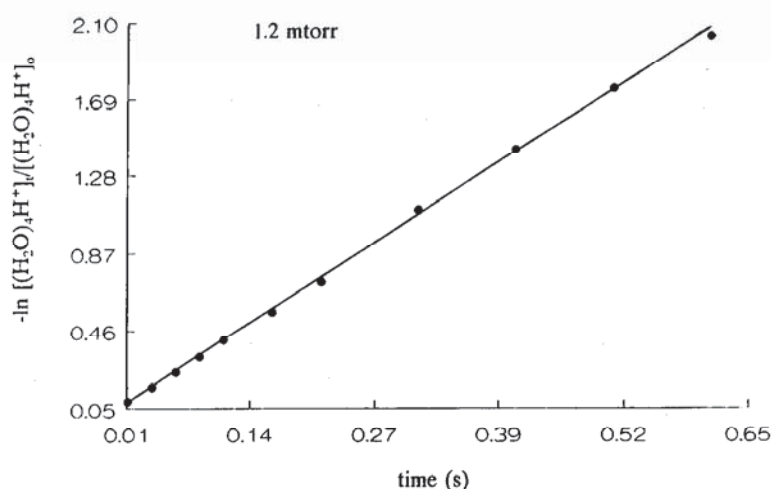


Fig. 4. A plot of the negative logarithm of the relative abundance of the protonated water tetramer $(\text{H}_2\text{O})_4\text{H}^+$ as a function of delay time at a total bath gas pressure of 1.2 mTorr.

onset of the kinetics experiment. Some non-linearity would be expected at short times had this not been the case. Furthermore, linearity at long times indicates that the reverse reaction, i.e. clustering, does not occur to a measurable extent in these experiments.

The most important experimental variable noted to affect the bimolecular rate constants, k_{bi} , for the decompositions of protonated water clusters and protonated methanol clusters was the pressure of the background gas. Table 1 lists the bimolecular rate constants measured for several water and methanol clusters at four background gas pressures (one reflecting the pressure of the background air in the system and the others reflecting the addition of various amounts of helium). Rate constant measurements were made only in those cases where reaction rates were neither too fast nor too slow to obtain a

TABLE 1

Bimolecular rate constants, k_{bi} , ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for several water and methanol clusters at four background gas pressures

Reaction	Pressure (Torr)			
	1.2×10^{-3}	7.4×10^{-4}	8.7×10^{-5}	2.0×10^{-5}
$(\text{H}_2\text{O})_5\text{H}^+ \rightarrow$		4.8×10^{-12}	2.2×10^{-11}	
$(\text{H}_2\text{O})_4\text{H}^+ \rightarrow$	8.4×10^{-14}	1.6×10^{-13}	3.5×10^{-12}	2.0×10^{-11}
$(\text{H}_2\text{O})_3\text{H}^+ \rightarrow$		3.4×10^{-15}	1.8×10^{-13}	5.4×10^{-12}
$(\text{CH}_3\text{OH})_4\text{H}^+ \rightarrow$		1.9×10^{-12}	1.3×10^{-11}	5.8×10^{-11}
$(\text{CH}_3\text{OH})_3\text{H}^+ \rightarrow$	1.1×10^{-14}	1.4×10^{-14}	4.6×10^{-13}	9.3×10^{-12}
$(\text{CH}_3\text{OH})_2\text{H}^+ \rightarrow$	$\leq 1 \times 10^{-14}$	$\leq 2 \times 10^{-14}$	$\leq 1 \times 10^{-13}$	6.2×10^{-13}

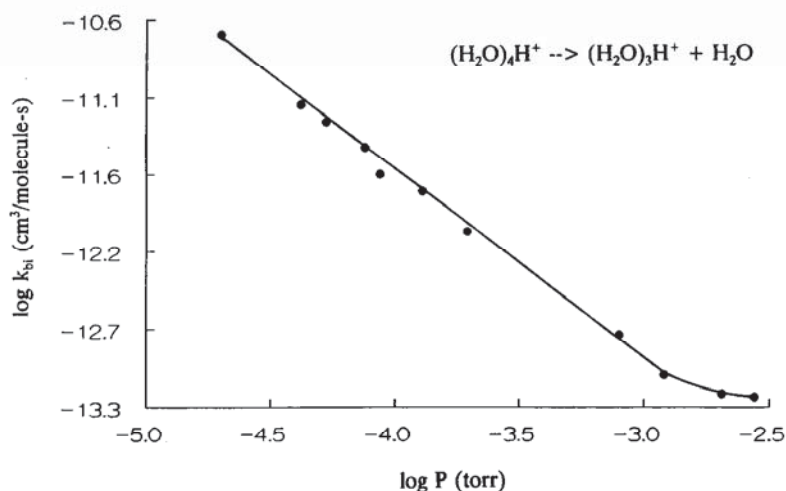


Fig. 5. A plot of the logarithm of the decomposition rate constant, k_{bi} , for the protonated water tetramer vs. the logarithm of the bath gas pressure.

reliable measurement. For example, measurements were not made on clusters with $n > 5$ for water clusters nor with $n > 4$ for methanol clusters because those ions were typically already dissociated by the time ion injection and a mass-selection step could be completed. For the methanol dimer, only an upper limit is given at some number densities because the rate of change of the dimer signal was too slow to make a reliable measurement over a delay period of up to 10 s.

For every cluster ion investigated it is apparent that the decomposition rate constant decreases as the pressure of the bath gas increases. This behavior is further illustrated in Fig. 5 which shows a plot of the logarithm of the decomposition rate constant for the water tetramer as a function of the logarithm of the pressure of the background gas. A linear relationship with a slope of -1.3 is observed from 2×10^{-5} Torr up to 1.2 mTorr. Deviation from linearity is apparent at pressures in excess of 1.2 mTorr. The inverse relationship between decomposition rate constant and pressure over the range 2×10^{-3} – 1.2×10^{-3} Torr is interpreted as being due to a pressure effect on the ion internal temperature, the decomposition rate constant increasing with temperature. If there is no temperature effect, the bimolecular rate constant should be independent of pressure. The leveling observed at higher pressure may be due to a leveling of the ion temperature, but transition from second-order to first-order kinetics cannot be ruled out. In any event, instrument performance begins to degrade at pressures in excess of one mTorr (i.e. ion signals decrease, background noise increases, etc.). We therefore cannot draw firm conclusions regarding the behavior at high pressure.

TABLE 2

Thermochemical parameters for dissociation^a

n	$\Delta H_{n,n-1}$	$\Delta S_{n,n-1}$	T_d^b
$(\text{H}_2\text{O})_n\text{H}^+ \rightarrow (\text{H}_2\text{O})_{n-1}\text{H}^+ + \text{H}_2\text{O}^c$			
2	31.6	24.3	1300
3	19.5	21.9	890
4	17.5	27.3	641
5	15.3	32.6	469
6	13.0	30.3	429
7	11.7	29.6	395
8	10.3	27.0	381
$(\text{MeOH})_n\text{H}^+ \rightarrow (\text{MeOH})_{n-1}\text{H}^+ + \text{MeOH}^c$			
2	33.1	30.5	1085
3	21.3	28.2	755
4	16.1	28.9	557
5	13.5	28.7	470
6	12.5	31.1	402
7	11.9	32.9	362
8	12.0	35.7	336

^a Enthalpies in kcal mol⁻¹, entropies in e.u., temperatures in K.^b From eqn. 1.^c Ref. 18.

Can an internal temperature be assigned to these ions, based on their chemical behaviors? Because the thermochemical parameters for these desolvation reactions have been determined by Grimsrud and Kebarle [18], as well as by others [31], certain limits on temperature can be calculated. For any solvated species, entropy favors dissociation, while enthalpy opposes such a reaction. There is a dissociation temperature, T_d , where these balance and the free energy for dissociation is zero. At any internal temperature above T_d , all ionic complexes rapidly dissociate. This assumes that there is no barrier to such a process save for the endoergicity; for such cluster complexes where fragmentation involves breaking of a hydrogen bond only, this is a reasonable assumption. At temperatures lower than T_d , some of the complexes in a population may fragment, but most will exist on the time frame of this experiment. The T_d values, calculated as

$$T_d = \Delta H_{n-1,n} / \Delta S_{n-1,n} \quad (1)$$

are given in Table 2. Large clusters are seen to have lower T_d values than smaller clusters reflecting the decrease in solvation energies as cluster size increases [18,31].

These T_d values could be utilized directly to estimate internal temperature, if the ions were in chemical equilibrium with water in the vacuum system. As

TABLE 3
Calculated internal temperatures for cluster ions

Cluster ion	$P(\text{mTorr})^a$	$T(\text{K})^b$	T_d^c	q_z^d
(MeOH) ₄ H ⁺	0.74	401	557	0.085
	0.087	444		
	0.02	478		
(MeOH) ₃ H ⁺	1.2	429	755	0.115
	0.74	433		
	0.087	504		
	0.02	581		
(MeOH) ₂ H ⁺	1.2	< 634	1085	0.17
	0.74	< 652		
	0.087	< 695		
	0.02	744		
(H ₂ O) ₅ H ⁺	0.74	363	469	0.12
	0.087	391		
(H ₂ O) ₄ H ⁺	1.2	391	641	0.15
	0.74	402		
	0.087	468		
	0.02	506		
(H ₂ O) ₃ H ⁺	0.74	426	890	0.2
	0.087	515		
	0.02	617		

^a Pressure of helium bath gas, or background air (0.02 mTorr).

^b Internal temperature, from eqn. 3.

^c Dissociation threshold temperature, eqn. 1.

^d Mathieu q_z parameter (see ref. 24) during desolvation period.

noted above, this is not the case under the experimental conditions used here. However, if one assumes that the observed rate constants for dissociation are due to collisional activation of the cluster ion involving He or other background gas, then dissociation is based on internal temperature. The rate constant should then be given by the equation:

$$k_{\text{bi}} = k_{\text{coll}} e^{-\Delta G/RT} = k_{\text{coll}} e^{-\Delta H/RT} e^{\Delta S/R} \quad (2)$$

or, rearranging:

$$T = -\Delta H/[R \ln(k_{\text{bi}}/k_{\text{coll}}) - \Delta S] \quad (3)$$

Note that if $k_{\text{bi}} = k_{\text{coll}}$, this is equivalent to eqn. 1.

Using the standard trajectory rate constants for k_{coll} [32], the internal temperatures calculated using eqn. 3 are given in Table 3. For the lowest

pressure of 0.02 mTorr, it was assumed that the collision rate reflected collisions with background air. For the higher pressures, the somewhat smaller rate constant for collision with helium was used. If the literature uncertainties of $\pm 2 \text{ kcal mol}^{-1}$ in $\Delta H_{n-1,n}$ and $\pm 2 \text{ e.u.}$ in $\Delta S_{n-1,n}$ are taken into account, along with the $\pm 20\%$ uncertainty for the rate constants, absolute uncertainties for these temperatures of about $\pm 120 \text{ K}$ are obtained. The relative uncertainties for the thermochemical parameters are undoubtedly smaller, so the relative uncertainties in the internal temperatures are more likely on the order of $\pm 20\text{--}30 \text{ K}$.

In all cases, the ions' internal temperatures are significantly less than T_d , as reflected by the fact that all k_{bi} are significantly less than k_{coll} . Furthermore, for each cluster ion the internal temperature decreases with increasing helium pressure. This is consistent with the picture that the bath gas is increasingly effective at confining the ions to the center of the ion trap, where they are minimally perturbed by the r.f. field, as the pressure increases. Interestingly, at any given pressure each cluster species appears to have a different internal temperature when the temperature is determined using the procedure described herein. (It is, perhaps, noteworthy that the internal temperatures for $(\text{H}_2\text{O})_n\text{H}^+$ and $(\text{MeOH})_n\text{H}^+$ are the same for equal n .) Within the methanol and water series the trend in cluster temperatures correlates with the q_z value during the desolvation period. Ion energies might be expected to increase with q_z [24]. However, k_{bi} for a given cluster was not observed to vary significantly when q_z was varied over 0.1–0.3. Furthermore, the ion temperature of $(\text{H}_2\text{O})_5\text{H}^+$ at 0.74 mTorr ($q_z = 0.12$) was determined to be 363 K whereas that for $(\text{MeOH})_3\text{H}^+$ at the same pressure ($q_z = 0.115$) was determined to be 433 K. The difference in ion internal temperatures cannot, therefore, be accounted for on the basis of the q_z value during the desolvation period.

The difference in ion internal temperatures for each cluster at a given pressure precludes a determination of a general relationship between pressure and ion temperature. However, for each cluster ion the internal temperature is inversely related to log pressure. For example, the water tetramer temperature, as determined from the k_{bi} values used in the plot of Fig. 5, is given by $T = (-65.5)\log P(\text{torr}) + 197 \text{ K}$.

CONCLUSIONS

The results described herein are consistent with the picture that ions injected into the ion trap undergo moderating collisions with the bath gas and reach some steady-state internal energy distribution that, although there is no direct evidence that the distribution is Boltzmann, is expected to be broad and might be characterized by a temperature. Like previous studies of "effective temperatures" in a quadrupole ion trap [14,15,25], these results indicate that ion

internal temperatures, like ion kinetic temperatures, exceed the temperature of the bath gas. In the case of the loosely bound cluster ions, the relatively "warm" environment within the ion trap leads to evaporation. For these particular cluster ions, the back reaction does not occur to a measurable extent under the conditions that prevail in the ion trap. Perhaps the most noteworthy observation in these studies is the inverse relationship between ion temperature and log pressure. The damping effect of the bath gas, which increases with pressure, acts to minimize power absorption by the ions by confining ions in the center of the ion trap where field strengths are smallest. This pressure effect is not particularly dramatic, however, in that pressure changes over two orders of magnitude result in ion temperature changes of 100–200 K, depending upon the cluster ion. This effect is clearly apparent in these studies because the dissociation rate constants for these clusters are highly sensitive to temperature.

ACKNOWLEDGMENTS

The work at ORNL was sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract DE-AC05-84-OR21400 with Martin Marietta Energy Systems. J.E.B. acknowledges support of the State of Tennessee Science Alliance.

REFERENCES

- 1 J.F.J. Todd, *Mass Spectrom. Rev.*, 10 (1991) 3.
- 2 R.G. Cooks, G.L. Glish, R.E. Kaiser, Jr. and S.A. McLuckey, *Chem. Eng. News*, 69 (1991) 26.
- 3 R.F. Bonner, G. Lawson and J.F.J. Todd, *Int. J. Mass Spectrom. Ion Phys.*, 10 (1972/73) 197.
- 4 G. Lawson, R.F. Bonner, R.F. Mather, J.F.J. Todd and R.E. March, *J. Chem. Soc., Faraday Trans. 1*, 72 (1976) 545.
- 5 R.F. Bonner, G. Lawson, J.F.J. Todd and R.E. March, in A.R. West (Ed.), *Advances in Mass Spectrometry*, Vol. 6, Institute of Petroleum, London, 1974, p. 377.
- 6 J.F.J. Todd and G. Lawson, in A. Maccoll (Ed.), *International Review of Science, Physical Chemistry, Series 2: Mass Spectrometry*, Butterworth, London, 1975, Vol. 5, p. 289.
- 7 J.S. Brodbelt and R.G. Cooks, *Anal. Chim. Acta*, 206 (1988) 239.
- 8 J.S. Brodbelt-Lustig and R.G. Cooks, *Talanta*, 36 (1989) 255.
- 9 R.A. Flurer, G.L. Glish and S.A. McLuckey, *J. Am. Soc. Mass Spectrom.*, 1 (1990) 217.
- 10 S.A. McLuckey, G.J. Van Berkel and G.L. Glish, *J. Am. Chem. Soc.*, 112 (1990) 5668.
- 11 A.J. Cunningham, J.D. Payzant and P. Kebarle, *J. Am. Chem. Soc.*, 94 (1972) 7627.
- 12 S.T. Graul and R.R. Squires, *Mass Spectrom. Rev.*, 7 (1988) 263.
- 13 B.S. Freiser, in J.M. Farrar and W.H. Saunders, Jr. (Ed.), *Techniques for the Study of Ion-Molecule Reactions*, Wiley, New York, 1988, p. 61.
- 14 B.D. Nourse and H.I. Kenttämä, *J. Phys. Chem.*, 94 (1990) 5809.
- 15 F. Vedel, *Int. J. Mass Spectrom. Ion Processes*, 106 (1991) 33.
- 16 G.C. Stafford, P.E. Kelley, J.E.P. Syka, W.E. Reynolds and J.F.J. Todd, *Int. J. Mass Spectrom. Ion Processes*, 60 (1984) 85.

- 17 G.J. Van Berkel, G.L. Glish and S.A. McLuckey, *Anal. Chem.*, 62 (1990) 1284.
- 18 E.P. Grimsrud and P. Kebarle, *J. Am. Chem. Soc.*, 95 (1973) 7939.
- 19 S.A. McLuckey, G.L. Glish and K.G. Asano, *Anal. Chim. Acta*, 225 (1989) 25.
- 20 S.A. McLuckey, G.J. Van Berkel, G.L. Glish, J.D. Henion and E.C. Huang, *Anal. Chem.*, 63 (1991) 375.
- 21 J.E. Bartmess and R.M. Georgiadis, *Vacuum*, 33 (1983) 149.
- 22 M. Weber-Grabau, P.E. Kelley, S.C. Bradshaw and D.J. Hoekman, *Proc. 36th ASMS Conf. Mass Spectrometry and Allied Topics*, San Francisco, CA, 1988, p. 1106.
- 23 J.N. Louris, J.S. Brodbelt-Lustig, R.G. Cooks, G.L. Glish, G.J. Van Berkel and S.A. McLuckey, *Int. J. Mass Spectrom. Ion Processes*, 96 (1990) 117.
- 24 R.E. March and R.J. Hughes, *Quadrupole Ion Storage Mass Spectrometry*, Wiley, New York, 1989.
- 25 C. Basic, R.A. Yost and J.R. Eyler, *Proc. 38th ASMS Conf. Mass Spectrometry and Applied Topics*, Tucson, AZ, 1990, p. 858.
- 26 S.A. McLuckey, G.L. Glish and G.J. Van Berkel, ORNL unpublished results, 1991.
- 27 J.N. Louris, J.W. Amy, T.Y. Ridley and R.G. Cooks, *Int. J. Mass Spectrom. Ion Processes*, 88 (1989) 97.
- 28 R.E. Pedder, R.A. Yost and M. Weber-Grabau, *Proc. 37th ASMS Conf. Mass Spectrometry and Allied Topics*, Miami Beach, FL, 1989, p. 468.
- 29 D.S. Bomse and J.L. Beauchamp, *J. Am. Chem. Soc.*, 103 (1981) 3292.
- 30 S.T. Graul and R.R. Squires, *Int. J. Mass Spectrom. Ion Processes*, 81 (1987) 183.
- 31 M. Meot-Ner, *J. Am. Chem. Soc.*, 108 (1986) 6189.
- 32 T. Su and W.J. Chesnavich, *J. Chem. Phys.*, 76 (1982) 5182.