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Calculation to determine the mass of daughter ions in metastable decay

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Abstract

A new method is presented for determining the mass of products resulting from metastable decay in a reflectron time-of-flight mass-spectrometer. The validity of the calculation was confirmed through comparison to experimental values obtained while studying a water cluster and a methanol cluster system. (Int J Mass Spectrom 213 (2002) 81–89) © 2002 Elsevier Science B.V.

Keywords: Metastable decay; Clusters; Reflectron; Time-of-flight mass-spectrometer; Daughter; Mass

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1. Introduction

The study of clusters has become a flourishing field providing new information between the realms of the gas and condensed phases. A plethora of new phenomena has been uncovered over the recent years as those interested look deeper into this medium with an increasing number and variety of methods. Cluster science continues to grow as a vehicle of study providing insight into the molecular world of nanoscale dimensions.

Previous studies of clusters, focusing on the study of unimolecular reactions in the form of metastable decay (MSD) during cluster fragmentation in the first field free region (FFR) of a reflectron time-of-flight mass spectrometer (R-TOFMS) (see Fig. 1), have provided information about the binding energy of clusters [1–3] and the kinetic energy released (KER) [1,4,5]. The metastable decay processes, which are observable in the time windows accessible by this technique, are ones which occur after neutral clusters are ionized in a Wiley–McLaren TOF lens assembly and thereafter accelerated into the first FFR. Ions possessing sufficient internal energy from the ionization process can undergo cluster rearrangement and/or a cluster fragmentation analogous to evaporation. These “hot” ion clusters, referred to as parent ions, which have a sufficient amount of energy to undergo fragmentation, lose neutral *n*-monomer units, where n is an integer, to become daughter ions. Rearrangement of the excited ion clusters can occur without fragmentation; however, daughter ions are not produced in this situation and therefore these are not included in the study of MSD.

Some examples of cluster systems that undergo the process of metastable decay are protonated water clusters, ($H^+(H_2O)_n$) [6], protonated methanol clus-

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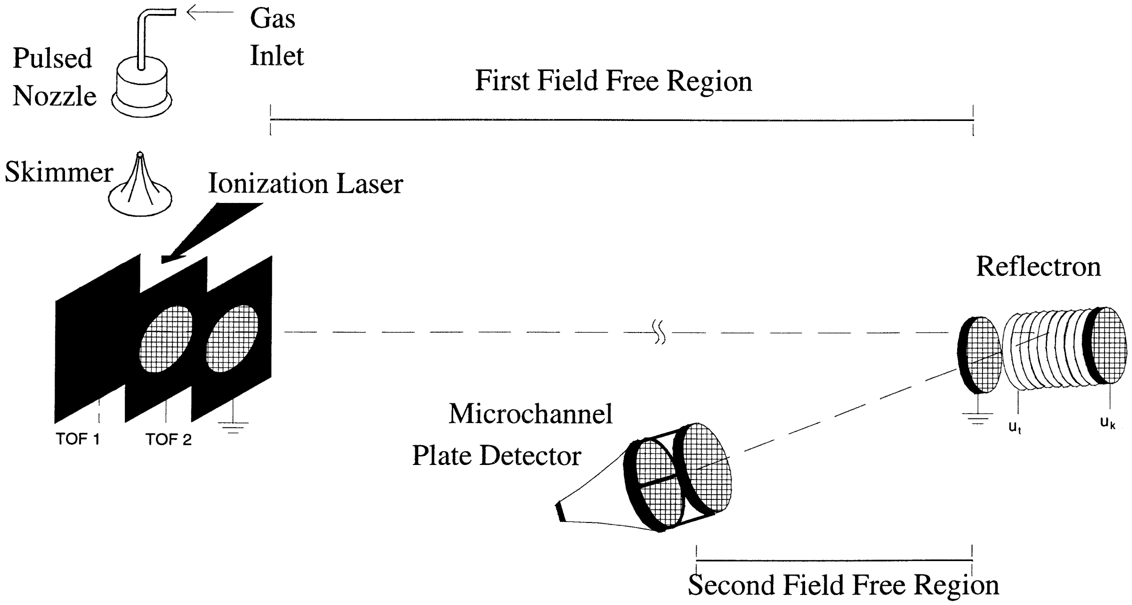

Fig. 1. Schematic diagram of the R-TOFMS displaying the source/acceleration region, the first field free region, the reflectron, the second field free region, and the MCP detector. Note the first field free region where metastable decay occurs.

ters, ($H^+(CH_3OH)_n$) [7], protonated ammonia clusters ($H^+(NH_3)_n$) [8], and rare gas clusters such as Ar_n^+ [9]. A number of properties of clusters can be determined from studying the unimolecular reaction processes such as the binding energy and KER as mentioned previously, and the rates of the unimolecular reaction [10]. However, according to theoretical predictions made by Klots considering metastable decay as an evaporative ensemble model [11] and experimental verifications [1,8,12–14], no cluster ion ensemble may be assigned a unique lifetime due to the fact that the reaction rates are not inherent to the ions, but are caused by a particular range of internal energies (temperatures) after the ionization event. In the experiments of Märk et al. [12–14], the voltage of the acceleration region was scanned. As the voltage of TOF_1 was decreased, the rates of reaction of the metastable decay also decreased as large as a factor of 10, proving that the MSD did indeed occur over a statistical range as Klots predicted.

However, no theoretical treatment has been derived to determine the loss of mass due to the fragmentation of the parent ion clusters into daughter ion clusters. Previously, the only effective method of determining the mass of the daughter ions (m_d) was to perform a time intensive cutoff study using the reflectron as an energy analyzer. Presented herein is a method to determine m_d using the difference in time (Δt) between the arrival of the parent and daughter ions at the detector without the tedious process of performing a reflectron cutoff study.

2. Experimental

Water clusters were generated via supersonic expansion of room-temperature water vapor seeded in helium at a pressure between 1.7 and 2.4 bar. The molecular beam produced in this fashion was skimmed and then ionized between the TOF grids with femtosecond laser pulses. The methanol clusters were generated in a similar fashion.

Under typical operating conditions, a potential of 4600 V was applied to TOF_1 whereas the potential applied to TOF_2 was 2980 V. In the studies presented here, the reflectron was operated in an even gradient/

soft reflection mode with a potential of 530 V applied to U_t and a potential of 4600 V applied to U_k. The potentials applied to the grids of the reflectron necessary to attain an even gradient, depend on the characteristics of the reflectron. The process used in order to determine the correct voltages is described in more detail below. The ions are turned around in the reflectron and accelerated towards the detector, which employs a pair of microchannel plates coupled to an oscilloscope (Agilent Technologies 54820A) for detection.

The ionization laser is an amplified colliding pulse mode-locked ring dye laser. In this arrangement, a gain jet containing rhodamine 590 tetrafluoroborate is pumped by a continuous wave argon ion laser (Coherent Innova 305). Continuous wave lasing from the gain jet is interrupted by a saturable absorber jet containing DODCI. Laser pulses on the order of 100 fs are generated at 90 MHz with pulse energies of ~200 pJ. Amplification of the laser pulses is achieved in four stages using a six-pass bowtie amplifier and three successive Bethune cells where the beam is progressively expanded from a 2 mm initial diameter to a final beam diameter of 12 mm. All amplification is achieved by transverse pumping of sulphorhodamine 640 by the second harmonic of a 10 Hz Nd:YAG laser (Spectra Physics GCR-4). Recompression is performed using a prism pair to compensate for group velocity dispersion. The amplified laser pulse is 120–150 fs in duration, possesses ~1.5 mJ of energy and has a wavelength centered at 620 nm. The laser is focused into the mass spectrometer with a 40 cm optical lens to yield a final focused beam diameter of ~6.6 μm, which was calculated according to [15]

$$\omega_{0,2} = \frac{\lambda f}{\pi\omega_{0,1}\left[1 + \left(\frac{\lambda f}{\pi\omega_{0,1}^2}\right)^2\right]^{1/2}} \qquad (1)$$

where $\omega_{0,2}$ is the beam diameter at the focal point, λ is the wavelength (620 nm), f is the focal length of the focusing lens (40 cm), and $\omega_{0,1}$ is the initial beam diameter (12 mm). With a focused beam diameter of this size the peak power was $\sim 10^{16}$ W/cm^2.

3. Results and discussion

The majority of detected ions are created in the ~6.6 μm focal point of the laser positioned between the repeller plate (TOF_1) and the accelerating plate (TOF_2). The potential on these two plates is applied in order to accelerate the parent ions toward the FFR. Since all clusters are ionized in a very confined region within the potential, the charged clusters have a very narrow kinetic energy distribution (±1.1 V). Therefore, the velocity of each parent ion, once it is accelerated into the FFR, is proportional to the inverse square of the ions mass

$$v_0 = \sqrt{\frac{2V_0 q}{m_p}} \qquad (2)$$

where V_0 is the ion birth potential (BP), q is the charge of an electron, and m_p is the mass of the parent ion.

In accordance with Newton’s second law, velocity is conserved when a parent ion fragments in the FFR. The daughter ion that is formed after a parent ion loses n-neutral monomer units has the same velocity as the parent ion; however, it has less mass and therefore less kinetic energy. The daughter ions, therefore, have less momentum and do not penetrate the reflectron as deeply as the parent ions that did not fragment. The daughter ions reach the detector at a time (Δt) before their respective parent ions. Since the loss of mass occurred in the FFR, the mass of the daughter peak cannot be assigned in the typical manner used in R-TOFMS and typically a reflectron cutoff study is performed.

As a means of comparison to the method developed here, a reflectron cutoff study was performed. The reflectron was set in soft reflection mode and the potential of U_k (see Fig. 1) was lowered until the parent ions were no longer detected. The potential at which the parent ion peaks disappear is the BP of the ions (see Fig. 2). After the parent ions were no longer detected, U_k was continually lowered until the daughter ion peaks were no longer detected. The potential at which the daughter and parent ions disappear is

$$U_i = V_i q \qquad (3)$$

where U_i is the energy of the ion in Joules and V_i is the potential at which the ion was no longer detected.

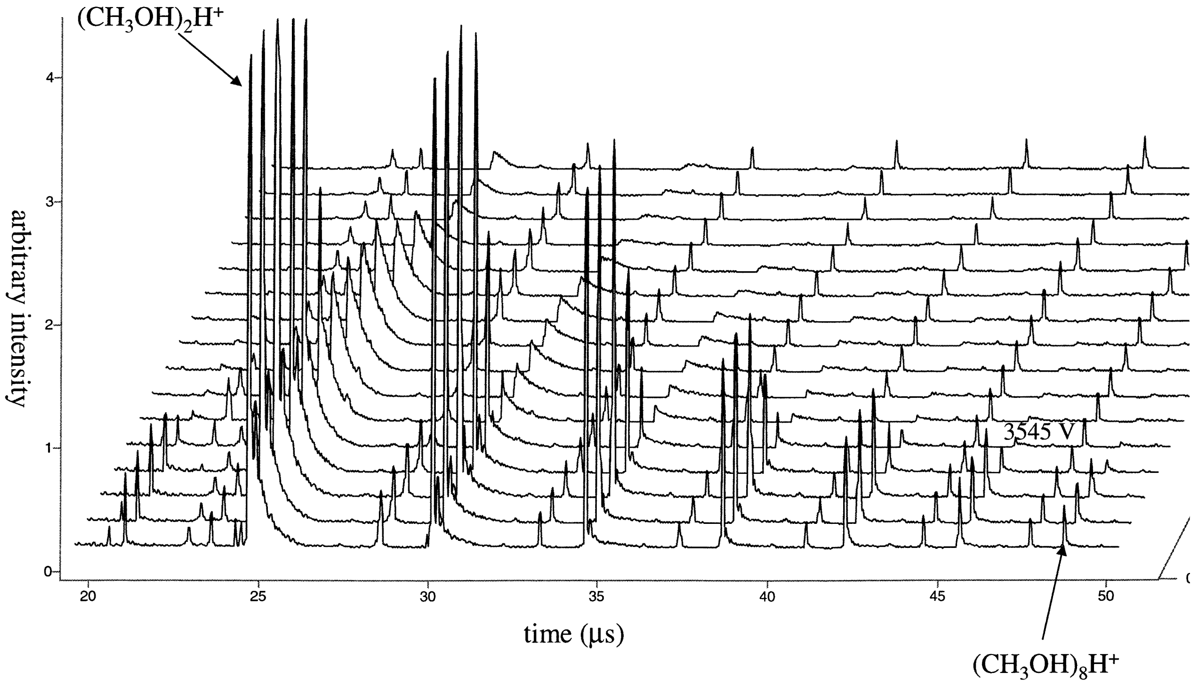

Fig. 2. The reflectron study on methanol used to determine the BP of the parent ions. The potentials on U_k range from 3 580 V (the front spectrum) to 3 200 V (the back spectrum). The parent ion peaks (dimer to octamer) all disappear at ~3 545 V whereas the daughter ions continue to be detected. The broad peaks that continue after the parent ions disappear are parent ions that underwent fragmentation in the acceleration region.

It is important to note that all of the parent ions disappear at approximately the same voltage, the birth potential, but daughter peaks disappear over a range of potentials with the heavier daughter ions disappearing at the higher potentials (see Fig. 3). Because the ions were all born at the same potential (±1.1 V) the parent ions are all turned around at approximately the same point in the reflectron. The differences in times-of-arrival of the parent ions are due to the differences in velocity according to Eq. (2). Once the potential at which the ions disappear is determined the mass of the daughter ions are then calculated as

$$m_d = \left(\frac{U_d}{U_0}\right) m_p \tag{4}$$

and are reported in Table 1.

A new method is presented below to calculate the mass of the daughter ions using the difference in time-of-arrival (Δt) between the daughter and parent ions. Since the difference in time is a result of the daughter ion being turned around in the reflectron earlier than the parent ion, the Δt is directly related to the loss of mass. In order to obtain the Δt in a manner that facilitates the calculation of the m_d, the reflectron was set in a soft reflection mode where the reflecting electric field is an even gradient. That is, the potential on the second grid in the reflectron, U_t (see Fig. 1), is set according to

$$U_t = \left(\frac{U_k}{l_{ref}}\right) * l_{U_t} \tag{5}$$

where l_{ref} is the length of the reflectron and l_{Ut} is the distance between the grounded grid of the reflectron and U_t (see Fig. 1).

Once the even gradient is established, the electric field of the reflectron is represented as

$$E = \frac{U_k}{l_{ref}} C_r \tag{6}$$

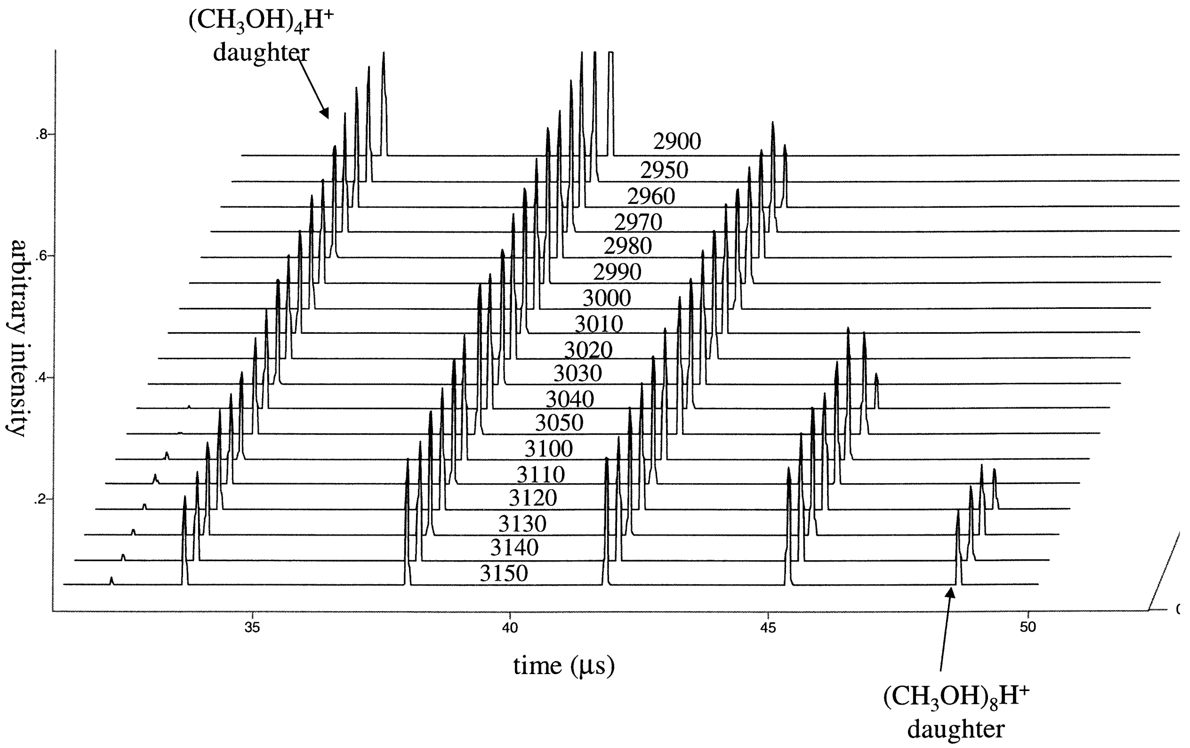

Fig. 3. A portion of the reflectron study used to determine the daughter masses showing the result of the decrease in potential on U$_k$ from 3 150 V to 2 900 V. The peaks represent the daughter ions from the methanol tetramer up to the methanol octamer. Notice that the heavier daughter ions pass through the reflectron at higher potentials.

where l_{ref} is the length of the reflectron and C_r is a reflectron constant specific to the reflectron that is used to fit the data.

Once the field of the reflectron has been modeled, the acceleration of the parent ion in the reflectron can be determined. Since the force of the electric field is

$$F = Eq = ma. \tag{7}$$

Table 1
Mass of methanol daughter ions (loss of one monomer unit) determined experimentally through a reflectron study compared to masses of daughter ions determined via this new technique

	m$_d$ (amu)	
m$_p$ (amu)	refl. study	calc.
97	65.7	66.6
129	97.0	97.6
161	128.8	129.3
193	160.7	160.9
225	192.9	192.8
257	225.9	224.3

Equation (7) can be solved for the acceleration of the parent ion, a_p. After substitution of Eq. (6), Eq. (7) becomes

$$a_p = C_r \left(\frac{U_k\, q}{l_{ref}\, m_p} \right), \tag{8}$$

where m_p is the mass of the parent.

Using the kinematic equation for motion in a straight line under constant acceleration, the velocity as a function of time is

$$v = v_0 - at \tag{9}$$

However, the final velocity, v, at the turning point in the reflectron is equal to zero. Taking this into account and solving for time gives

$$t_{ir} = \frac{2v_0}{a_i} \tag{10}$$

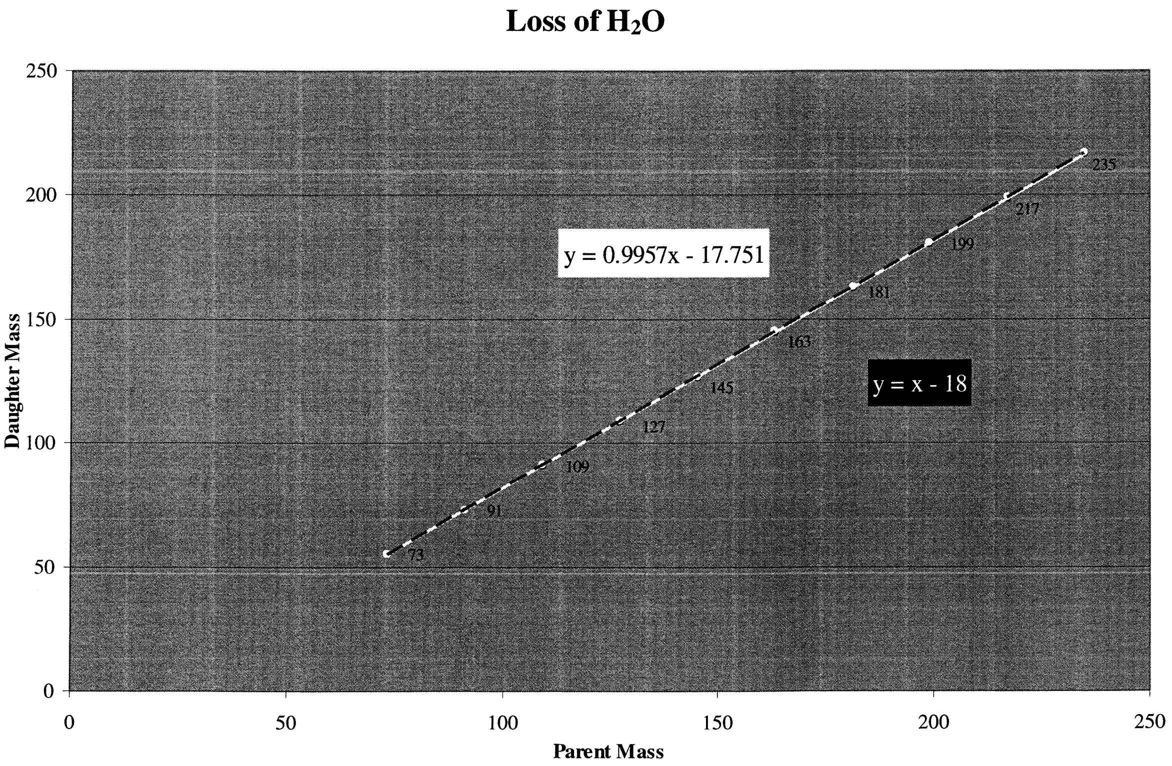

Fig. 4. Mass of daughter ions plotted vs. mass of parent ions for loss of one H_2O monomer. The dark line represents ideal masses of the daughter ions confirmed experimentally (reflectron study) whereas the light line represents masses determined with the technique presented herein.

where t_{ir} is the total time an ion spends in the reflectron, a_i is the acceleration of that ion, and v_0 is from Eq.(2).

The time of the parent ion in a reflectron, set to hard reflection, has been determined previously by Wei, et al. [1] as

$$t_{pr} = C\left[\frac{U_0}{m_p}\right]^{1/2}\frac{m_p}{U_t} \tag{11}$$

where U_0 is the birth potential, C is a proportionality constant equal to $2.88L/\surd q$ and L is the length (1.5 cm) between the ground plate of the reflectron and U_t. Substituting Eq. (2), and Eq. (8), into Eq. (10) gives

$$t_{pr} = C_s\left[\frac{U_0}{m_p}\right]^{1/2}\frac{m_p}{U_k} \tag{12}$$

where $C_s = 1.63\mathrm{l}_{\mathrm{ref}}/\surd\mathrm{q}$ and l_{ref} is the length of the reflectron (13.0 cm). The difference in the proportionality constants (C and C_s) is due to the fact that the equation derived by Wei et al. is for hard reflection whereas the one derived in this paper is for soft reflection.

Since the Δt between parent and daughter ions occurs in the reflectron,

$$\Delta t = t_{pr} - t_{dr}. \tag{13}$$

After substitution of Eq. (10),

$$\Delta t = 2v_0\left(\frac{1}{a_p} - \frac{1}{a_d}\right) \tag{14}$$

Solving for the acceleration of the daughter ion, a_d, gives

$$a_d = \frac{2a_p v_0}{2v_0 - a_p\,\Delta t}. \tag{15}$$

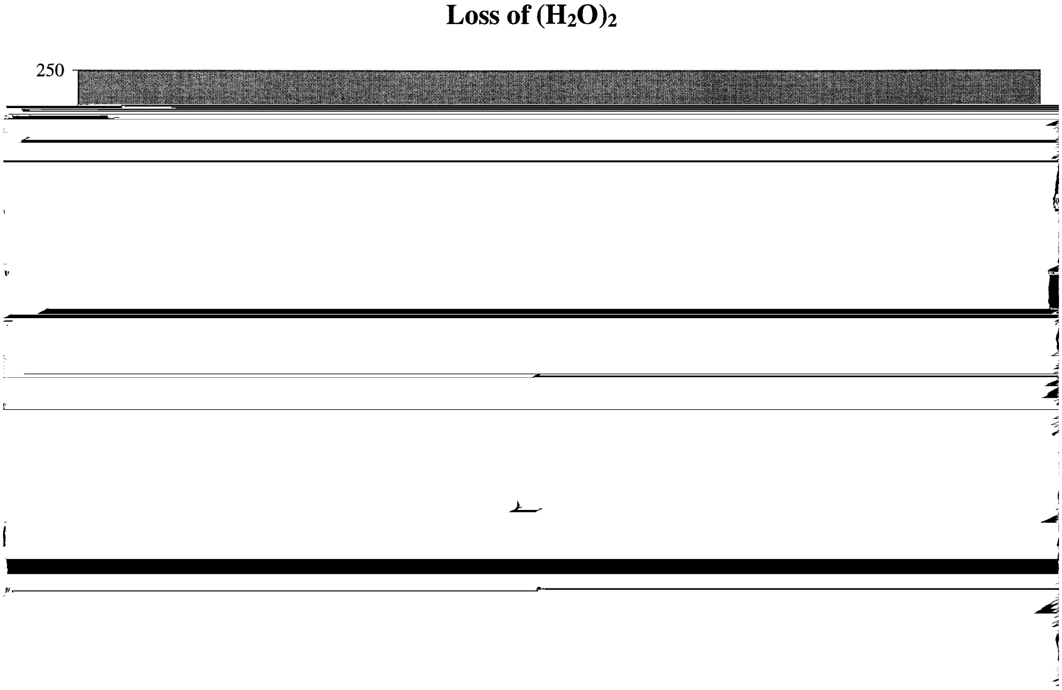

Fig. 5. Mass of daughter ions plotted vs. mass of parent ions for loss of two H_2O monomer units. The dark line represents ideal masses confirmed experimentally (reflectron study) whereas the light line represents masses determined with the technique presented herein.

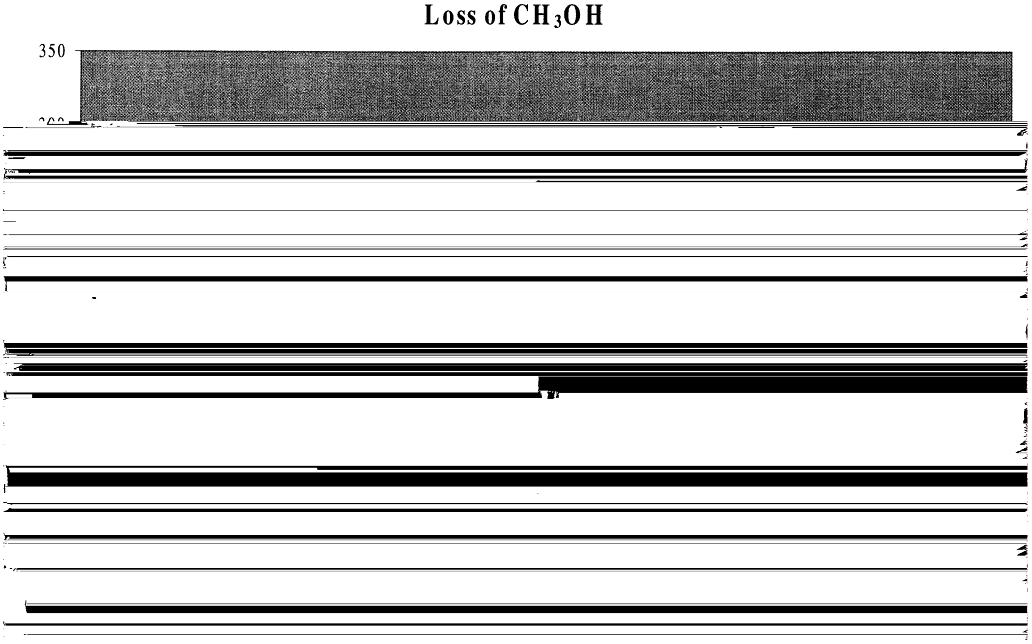

Fig. 6. Mass of daughter ions plotted vs. mass of parent ions for loss of one CH_3OH monomer. The dark line represents ideal masses confirmed experimentally (reflectron study) whereas the light line represents masses determined with the technique presented herein.

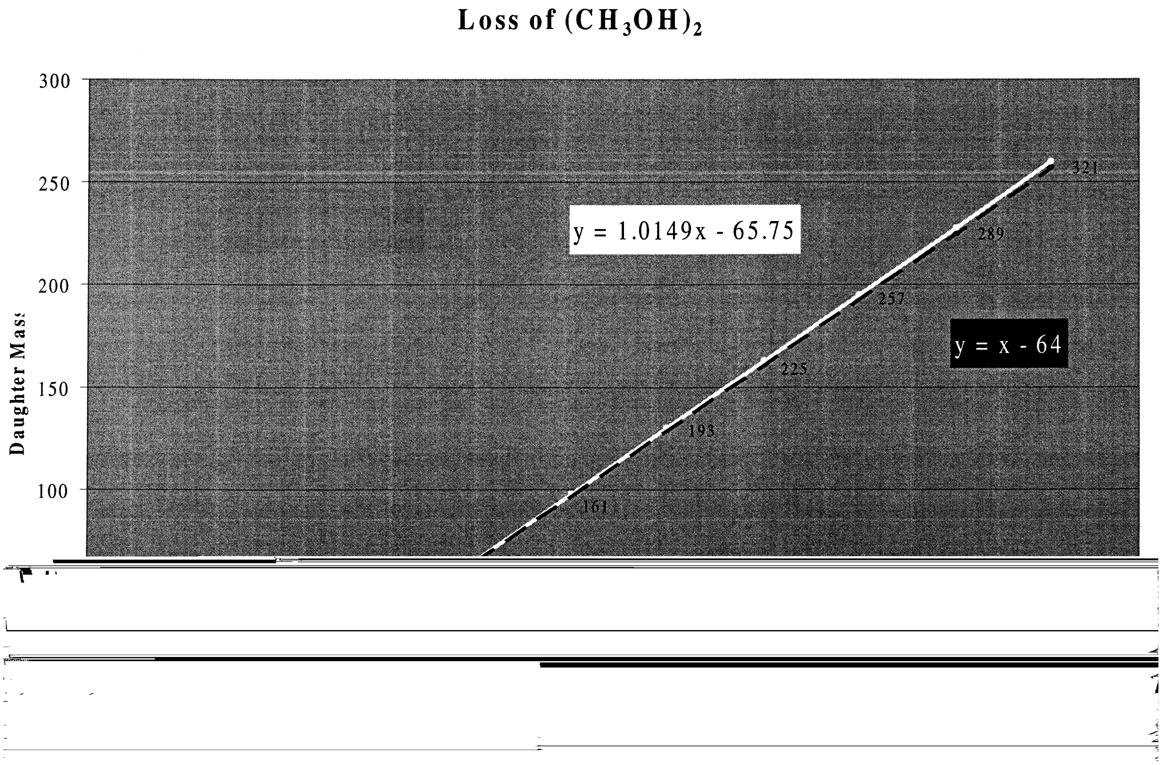

Fig. 7. Mass of daughter ions plotted vs. mass of parent ions for loss of two CH_3OH monomer units. The dark line represents ideal masses confirmed experimentally (reflectron study) whereas the light line represents masses determined with the technique presented herein.

Since the force of the electric field ($F = Eq$) in the reflectron is constant for species of the same charge, q, the accelerations of ions in the reflectron, $a = F/m$, differ only when the mass of the ions are different. The daughter ion has less mass than the parent ion, and hence the daughter ion experiences a larger acceleration that is inversely proportional to the difference in mass such that

$$a_p - a_d = \frac{F}{m_p - m_d}. \tag{16}$$

Therefore, after substitution and rearrangement, the mass of the daughter ion, m_d, is determined to be

$$m_d = m_p - \left[\left(C_r \frac{U_k q}{l_{ref}}\right)\left(\frac{a_d - a_p}{a_p\, a_d}\right)\right], \tag{17}$$

where the term in brackets represents the mass of the neutral fragment (n-monomer units) lost in the metastable decay.

The validity of the calculation was confirmed with water clusters and methanol clusters. As mentioned earlier, a reflectron cutoff study was performed to determine the daughter ion masses (Table 1). Then, with the reflectron set to an even gradient, the masses of the parent ions and the difference in time between the parent and daughter ions were noted and used in the calculation previously to determine the mass of the daughter ions.

Fig. 4 plots the parent masses of water clusters on the x axis and the daughter masses for a loss of one monomer unit ($m = 18$) along the y axis. Also, Fig. 5 plots the daughter masses versus the parent masses for the loss of two monomer units ($m = 36$) from water cluster parents. Figs. 6 and 7 display plots of the methanol cluster results in a similar manner. The dark line represents the ideal daughter masses confirmed experimentally via the reflectron cutoff study, whereas the white line represents the daughter masses

Table 2
Differences between calculated m_d and ideal m_d values for Figs. 5 and 6

	Daughter mass (amu)			
	Loss of H_2O		Loss of $(H_2O)_2$	
Parent mass (amu)	Calculated	Ideal	Calculated	Ideal
73	54.9	55	38.4	37
91	72.9	73	56.2	55
109	90.8	91	73.9	73
127	108.7	109	91.7	91
145	126.6	127	109.5	109
163	144.5	145	127.3	127
181	162.5	163	145.1	145
199	180.4	181	162.8	163
217	198.3	199	180.6	181
235	216.2	217	198.4	199

determined by the calculation derived above. Values for Figs. 4–7 can be seen in Tables 2 and 3. The marked agreement is considered to be indicative of the validity of the calculation.

4. Conclusions

Presented in this paper is a new, less demanding experimental method, to determine the mass of daughter ions that form when parent cluster ions fragment in an evaporative metastable decay process. This process occurs in the first FFR of a R-TOFMS. Previous studies of MSD have provided information concerning binding energy of clusters, kinetic energy released during fragmentation, and rates of decay that are not inherent to the ions, but are caused by a particular range of internal energies (temperatures) after the ionization event as predicted by Klots. However, until now, no theoretical method has been successfully employed to calculate the mass of the daughter ions using the difference in time (Δt) between the parent and daughter ions. As a result, the work presented here provides a useful new tool for the study of metastable decay.

Table 3
Differences between calculated m_d and ideal m_d values for Figs. 7 and 8

	Daughter Mass (amu)			
	Loss of CH_3OH		Loss of $(CH_3OH)_2$	
Parent Mass (amu)	Calculated	Ideal	Calculated	Ideal
97	66.6	65	32.6	33
129	97.6	97	65.1	65
161	129.3	129	97.6	97
193	160.9	161	130.1	129
225	192.8	193	162.6	161
257	224.3	225	195.0	193
289	255.1	257	227.5	225
321	286.8	289	260.0	257
353	318.5	321	292.5	289
385	350.3	353	324.9	321

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