# Efficiency of Collisional Activation of Gaseous Organic Ions[1]

**Myung S. Kim and Fred W. McLafferty***

*Contribution from the Spencer T. Olin Laboratory, Department of Chemistry,
Cornell University, Ithaca, New York 14853. Received September 6, 1977*

**Abstract:** An approximate energy transfer function $P_c(E)$ for collisional activation (CA) of gaseous ions has been estimated using Massey's adiabatic criterion and experimental charge transfer reaction data. Despite a number of simplifying assumptions, useful agreement is found between CA spectral abundances predicted from $P_c(E)$ and experimental results for $CH_4^+$ and $C_7H_8^+$ precursor ions. The calculated $P_c(E)$ functions also rationalize the unique insensitivity of CA spectra to precursor ion internal energy, and emphasize the importance of using higher translational energies for high mass precursor ions. A surprising correlation is observed between the CA efficiency and the ionization potential of the target gas. Consistent with this, but in contrast to previous conclusions, metal surfaces appear to be poor CA targets.

"Double resonance" techniques have greatly extended the utility of basic spectroscopic tools for both fundamental research and analytical applications. In mass spectrometry (MS), collisional activation (CA) can be viewed as such a technique, as it makes possible the measurement of a mass spectrum of each peak in the normal mass spectrum.[2,3] For example, using a reverse-geometry double-focusing mass spectrometer, a peak in the normal mass spectrum can be separated by the magnetic field and caused to dissociate in a special collision chamber; separation of the resulting fragment ions by the electrostatic analyzer yields the CA mass spectrum of that particular ion. Because this spectrum is characteristic of the ion's structure, CA/MS has been applied extensively in fundamental studies of unimolecular ion and ion–molecule reactions and in the separation and identification of mixture components.[2-4] A key aspect of CA/MS is the collision process itself, which converts part of the ion's translational energy into the internal energy necessary for dissociation.[2,5-7] We report here a study of this process to elucidate further its fundamental aspects and to define conditions for optimization of parameters such as energy transfer and sensitivity. These are of critical importance for several applications of CA, such as the study of larger molecules.[8] The insensitivity to precursor ion internal energy is a unique advantage of CA spectra for ion structure characterization;[2,3] a better understanding of the energy transfer function should help to define the limits of this insensitivity. Further, by analogy to the field ion kinetics technique for molecular ions,[9] it should be possible to study the kinetics of fast unimolecular decompositions of fragment as well as molecular ions if measurable collisional activation can be effected in a sufficiently short ion flight distance ($\pm 0.1$ mm is approximately equivalent to $\pm 1$ ns);[10,11] we originally undertook this problem to see if metal surface activation[7] with a fine ($\sim 5$ $\mu$m diameter) metal mesh could be used for this.

Durup points out[5] that the processes involved in collisional activation can be categorized as (1) vibrational and/or rotational excitation or (2) electronic excitation; (1) are adiabatic processes favored using ion incident energies ($V_0$) below 1 keV and large targets such as Xe atoms,[12] while (2) involve vertical (Franck–Condon) transitions predominant at energies >1 keV (which are those used for CA spectra) with small targets such as He. The cross section for process (2) should reach a maximum at the ion velocity $v$ according to the maximum rule[14]

$$v \approx aE^*/h \qquad (1)$$

derived from Massey's "adiabatic criterion" where $a$ is the adiabatic parameter, $E^*$ is the excitation energy, and $h$ is Planck's constant; for $a = 7$ Å and $m/e$ 25 ions this corresponds to $V_0 = 4$–100 keV for $E^* = 1$–5 eV.[5] This equation predicts

that smaller target atoms or molecules, which will have smaller $a$ values, will reach their maximum cross section at lower values of $V_0$,[5] making such targets more effective at the ion accelerating potentials normally used to determine CA spectra.[2-4]

## Experimental Section

Electron ionization (EI) and collisional activation (CA) spectra were measured with a reversed-geometry Hitachi RMU-7 double-focusing mass spectrometer described previously[15] using a 100-$\mu$A ionizing electron beam of 70 eV energy and ion accelerating potentials of 2.1, 4.8, and 7.8 kV. With the magnetic field set to select the precursor ion, the metastable ion (MI) spectrum is measured by scanning the electrostatic analyzer potential. The pressure in the special collision chamber near the $\beta$-focal point is increased with the target gas until the precursor ion intensity is reduced to 33% of its value (67% was used for the Figure 4 data), and a similar scan is used to determine the CA product abundances. These are based on peak areas and are corrected for the MI contributions as described previously.[2a] The EI mass spectrum of toluene was scanned at 15, 21, and 28 eV electron energies to determine which fragment ions had appearance potentials less than these values. To obtain collisional activation with metal surfaces a number of fine meshes, dendrites, and porous membranes of a variety of materials were tried without producing measurable amounts (<0.1% of that with the collision chamber) of CA decomposition. As a more sensitive method, the precursor ions were caused to undergo grazing collisions with a 1 × 2 cm stainless steel plate positioned as shown in Figure 1 with its long axis in the direction of ion travel. A variety of collision angles up to 3° from normal were tried by moving the magnet toward the ion source (while keeping the pole face orthogonal to the ion beam) and away from the electrostatic analyzer. However, *no CA decomposition products could be detected* for a variety of reactions with high CA cross sections such as $m/e$ 84$^+$ → 55$^+$ of cyclopentanone and $CH_3^+$ → $CH_2^+$ of methane; detection limits were <0.05% of the ion abundances observed with helium as the target gas under the conditions described above. Placing a variety of potentials on the collision plate was also of no avail. The experimental configuration is similar to that used in the original study[7] which reported apparent surface-induced dissociations. It should be noted that the target plates yielding no CA products were carefully baked under vacuum prior to the experiment; without baking CA decompositions were occasionally observable ($\sim 1$% of the abundance found with the collision chamber), apparently to gases desorbing from the target surface under ion bombardment.

**Calculation of Collisional Energy Transfer Probability, $P_c(E)$.** Calculation of $P_c(E)$ functions appears to have been done only for diatomic ions,[13] and the quantum mechanical methods used for this are not practical for large ions. $P_c(E)$ should be determined by the densities of excited ionic states accessible (vibrational as well as electronic) and the transition probabilities for each; however, useful experimental data on the excited states of large ions are not generally available. $P(E)$ functions for ions formed by electron ionization can be estimated from the corresponding photoelectron spectra (PES),[16]
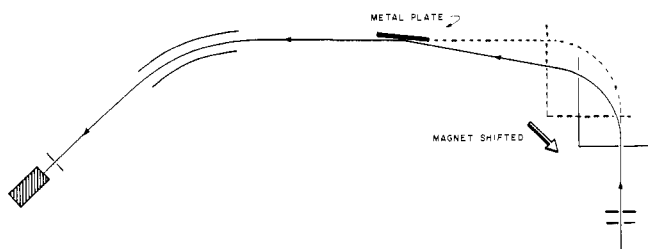
**Figure 1.** Measurement of collisional activation at a metal surface. The ion beam is moved off-axis by shifting the magnet in the direction of the arrow.



**Figure 2.** Collisional energy transfer probability functions $P_c(E)$ calculated assuming an adiabatic parameter of 4 Å.

but these only show energy levels accessible by electron removal; ion excitation (such as by collision) can also involve promotion of electrons to unoccupied orbitals. For example, for $CH_4^+$· there is a large energy gap between the highest vibrational levels of the ground electronic state ($\sim$3 eV) and the first excited electronic state ($\sim$10 eV);[17] yet peak shift measurements show[18] that the formation of $CH_2^+$ ions by collisional activation of $CH_4^+$· ions involves an average excitation of $\sim$5 eV, consistent with a more continuous state density function than indicated by PES. Although the approach taken here could lead only to very approximate $P_c(E)$ functions, their predictive value can be checked experimentally.

The function $P_c(E)$ was estimated here using experimental data for charge transfer reactions, correcting for differences in adiabatic parameters according to eq 1.[14] Charge transfer studies describe the cross section $\sigma$ for the transfer of a fixed amount of energy $E^*$ as a function of the ion velocity $v$, while the desired $P_c(E)$ function relates $\sigma$ values at a particular value of $v$ (or accelerating potential $V_0$) to the $E^*$ transferred; because $\sigma$ depends on $E^*/v$, it should thus be possible simply to transform the first function into the desired one. Calculation of estimated $P_c(E)$ functions was done in this way using a number of simplifying assumptions; for a particular molecule the results could represent only a rough approximation. It is assumed that only electronic excitations are important for the ion translational energies used, that the density of states of the precursor ion is constant over the accessible energy range, and that other differences in transition moments between energy levels can be neglected. The general shape of the function was taken from the experimental cross section data for the $He^+$–$Ne$ charge transfer reaction.[19] $E^*$ values corresponding to maximum $\sigma$ values at a particular $V_0$ [the peak in the $P_c(E)$ function] were calculated from eq 1 for target helium atoms assuming $a = 4$ and 7 Å. To relate the maximum value of $\sigma(\sigma_{max})$ at a particular $V_0$ to $\sigma_{max}$ at another ion accelerating potential $V_0'$ (i.e., the effect of $E^*$ on $\sigma_{max}$), the results of theoretical calculations concerning the effect of $E^*$ on $\sigma_{max}$ vs. $v$ for the $Xe^+$–$Xe$ charge transfer reaction were used,[20] as the ionization potentials of most organic ions are comparable to that of xenon. Calculated $P_c(E)$ functions for several values of $V_0$ and ion mass are shown in Figure 2; $P_c(E)$ functions for $m/e$ 16 and 92 ions were also derived to calculate the data of Tables I and II.

## Results

Relative cross sections $\sigma$ for collisional activation with the various target gases were determined for the $CH_4^+$ ions from methane and the $C_7H_8^+$ ions from toluene based on the measured yields of product ions requiring the transfer of known amounts of internal energy. For methane the average translational energy converted into internal energy on collision of $CH_4^+$ ions has been determined by Wachs;[18] these energies are 2, 5, 10, and 15 eV for $CH_4^+$ ions dissociating to form $CH_3^+$, $CH_2^+$, $CH^+$, and $C^+$ ions, respectively (the difference in appearance potential and ionization potential values for these ions are 1.7, 2.6, 9.6, and 12.4 eV, respectively). The product ion $H^+$ was not determined; its abundance in the EI mass spectrum of $CH_4$ is comparable to that of $C^+$.[21] Measured abundances are shown in Table I and Figures 3 and 4.

Measurements of the CA cross sections of toluene molecular ions utilized the CA abundances of 21 fragment ions separated into three groups representing particular ranges of appearance potential values: <15 eV, $C_7H_7^+$; 15–21 eV (group II), $C_2H_3^+$, $C_3H_4^+$, $C_3H_5^+$, $C_4H_4^+$, $C_4H_5^+$, $C_5H_5^+$, $C_5H_6^+$, $C_6H_4^+$,
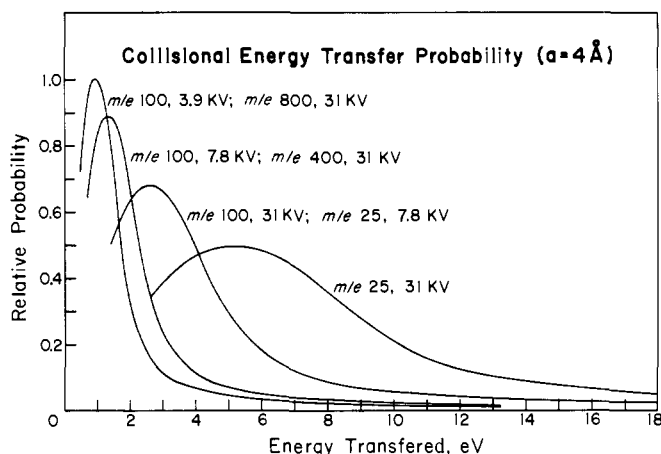
$C_6H_5^+$, $C_6H_6^+$, $C_7H_5^+$, and $C_7H_6^+$; and 21–27 eV (group III), $C_3H_2^+$, $C_3H_3^+$, $C_4H_2^+$, $C_4H_3^+$, $C_5H_3^+$, $C_5H_4^+$, $C_6H_2^+$, and $C_6H_3^+$. The relative total abundances of ions in each of the three groups is shown in Table II.

## Discussion

**Effect of Collision Gas.** The relative efficiencies for collisional activation of helium and deuterium as target gases are shown in Figure 3. $D_2$ is actually more efficient for the transfer of $\sim$2 eV at lower ion accelerating potentials, but He is more efficient at 7.8 kV, and dramatically superior at this potential for the transfer of $\sim$15 eV. Following Durup's conclusions,[5] at low $V_0$ values vibrational energy transfer (process 1) appears to be much more important for $D_2$ than He, while He is much more proficient for electronic excitation (process 2) leading to much higher efficiencies for CA at $V_0 = 7.8$ kV. The probability that $\sim$15 eV of energy is transferred by a vibrational process should be negligible, consistent with the much larger $He/D_2$ differences observed for the $CH_4^+ \rightarrow C^+$ reaction. However, these differences imply a very large difference in the adiabatic parameter $a$ (eq 1) for He and $D_2$; to elucidate this further, the relative CA efficiencies[22] for a number of target gases of various sizes and molecular weights were studied, using $V_0 = 7.8$ kV and the $CH_4^+ \rightarrow C^+$ reaction to minimize the vibrational energy transfer contribution. Surprisingly, as shown in Figure 4, the target gas property found to correlate best with CA efficiency is its ionization potential (IP). Including the negligible cross section found for metal surfaces, the six targets show a fortuitously close correlation between CA efficiency and IP. Possibly this is due to the increasingly favorable enthalpy for charge transfer reactions as the IP of the target gas is lowered; the similar values found for $D_2$ and Ar indicate that differences in scattering efficiencies are relatively unimportant. The consistency of the results provides confirmation for our inability to observe CA spectra using metal targets, and suggests that these will not be useful for CA experiments. (The contrasting results of previous experiments[7] could have been due to desorbing gases or a different surface, such as an oxide film.) On the other hand, helium is unique in its high ionization potential as well as its small atomic size, and these results confirm that it is the preferred target gas for electronic excitation.

**Comparison of Calculated and Experimental $P_c(E)$ Functions.** The peak abundances expected in the CA spectra of $CH_4^+$ ions based on the calculated $P_c(E)$ curve for $a = 4$ and 7 Å were determined using two assumptions: the $CH_3^+$, $CH_2^+$, $CH^+$, and $C^+$ ions are formed from ground-state $CH_4^+$ ions which have received 2–5, 5–10, 10–15, and 15–20 eV, respectively, or have received 2–4, 4–9, 9–13, and 13–17 eV,

**Table I.** Experimental and Calculated CA Spectra of $CH_4^+$ from Methane

| | | $V_0 = 4.8$ kV | | | 7.8 kV | |
| | | Calcd[a] | | | Calcd | |
| Product ion | Exptl | $a = 4$ Å | 7 Å | Exptl | 4 Å | 7 Å |
| --- | --- | --- | --- | --- | --- | --- |
| $CH_3^+$ | 100 | 100 | 100 | 100 | 100 | 100 |
| $CH_2^+$ | 51 | 39 (74) | 26 (40) | 58 | 59 (120) | 28 (47) |
| $CH^+$ | 13 | 11 (15) | 12 (13) | 20 | 16 (24) | 13 (14) |
| $C^+$ [b] | 4.6 | 6.2 (8) | 8.0 (10) | 6.1 | 8.8 (13) | 8.6 (11) |

[a] Assuming that the fragment ions shown are formed from $CH_4^+$ ions which have received 2-5, 5-10, 10-15, and 15-20 eV, respectively; values in parentheses assuming 2-4, 4-9, 9-13, and 13-17 eV, respectively. [b] See ref 23.

**Table II.** Experimental and Calculated CA Spectra of $C_7H_8^+$ from Toluene

| | | $V_0 = 4.8$ kV | | 7.8 kV | |
| Product ion | $E^*$, eV[a] | Exptl | Calcd | Exptl | Calcd |
| --- | --- | --- | --- | --- | --- |
| $C_7H_7^+$ | 3-6 | 100 | 100 | 100 | 100 |
| Group II | 6-12 | 35 | 35 (63)[b] | 45 | 34 (55) |
| Group III | 12-18 | 20 | 14 (25) | 30 | 16 (26) |

[a] Internal energy added to the precursor $C_7H_8^+$ ions on collision in addition to the 1 eV assumed to be present originally. [b] In calculating the values in parentheses it was assumed that the $C_7H_8^+$ ions were in their ground state ($E^* = 0$).
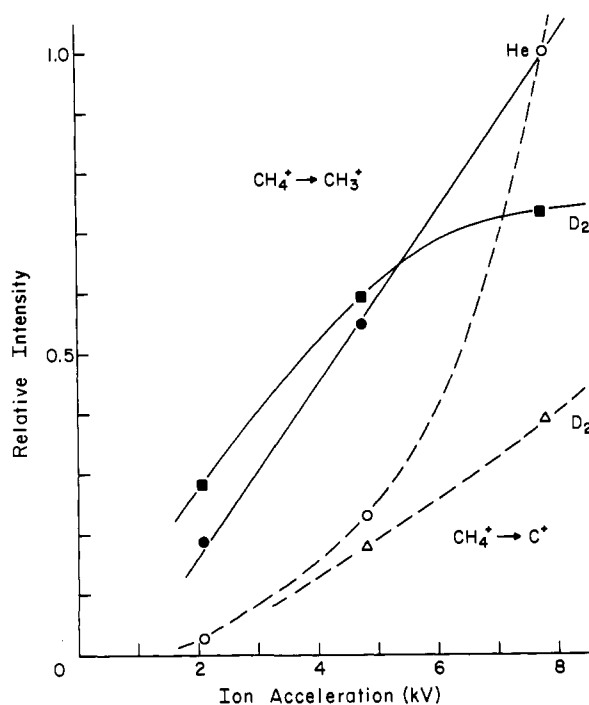


**Figure 3.** Collisional activation efficiencies for $CH_4^+ \rightarrow CH_3^+$ and $CH_4^+ \rightarrow C^+$ using He and $D_2$ as target gases.
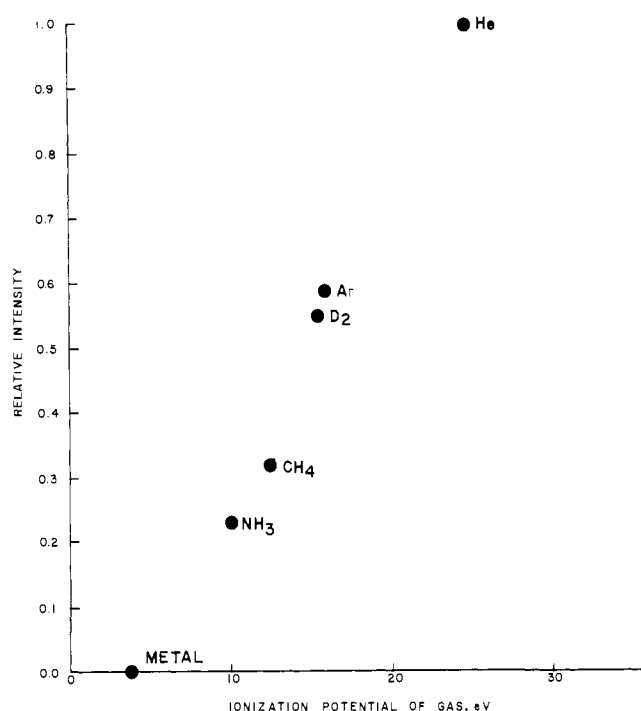


**Figure 4.** Collisional activation efficiencies for 7.8 kV $CH_4^+ \rightarrow C^+$ using different targets as a function of their ionization potentials.

respectively. These values are compared to the experimental CA abundances at $V_0 = 4.8$ and 7.8 kV in Table I. Assigning discrete energy ranges to each product ion is obviously an oversimplification; these ranges will overlap in a manner determined by the position and slope of the $k(E)$ functions of the corresponding decomposition reactions. For example, the reaction $CH_4^+ \rightarrow CH_2^+$ should have a much tighter activated complex than that for $CH_4^+ \rightarrow CH_3^+$, so that $CH_3^+$ formation should be competitive from $CH_4^+$ ions with 5 eV internal energy after collision;[23] the results (Table I) obviously are very sensitive to the assumption of 4 vs. 5 as the upper limit for $CH_3^+$ formation. (Assuming that the $CH_4^+$ ions have 1 eV of internal energy before collision would change the results less than the change caused by the energy range assumptions.) However, within these limitations, the agreement between predicted and experimental values is gratifying;[21] the fair

agreement in the [$CH_2^+$] values indicates that the state density function is more continuous than that indicated by the photoelectron spectrum,[17] as discussed above. The 4 Å value for $a$ appears to give better agreement than the 7 Å value found[14] appropriate in charge transfer reactions, but the uncertainties outlined above do not make this a clear choice. The predicted and experimental values for the relative abundance change in going from 4.8 to 7.8 kV are also in good agreement, especially considering that there may be differential effects of vibrational excitation processes on the experimental values.

A similar CA study of the $C_7H_8^+$ ($m/e$ 92) ions from toluene[16,24] was made to test the applicability of this method to higher mass precursor ions. The peak abundances expected for the CA spectra of $C_7H_8^+$ ions based on the calculated $P_c(E)$ curve for $a = 4$ Å were determined using $C_7H_7^+$ and two sets of other ions grouped according to their appearance potentials

to represent fragment ions formed from $C_7H_8^+$ ions that have received 3–6, 6–12, and 12–18 eV, respectively, of internal energy on collision. An average internal energy of 1 eV was assumed for the $C_7H_8^+$ ions[24] before collision. Again, these are somewhat arbitrary assumptions, but within these limitations the agreement of predicted and experimental values (Table II) is encouraging. Thus this method appears to provide a useful (although curve) estimate of $P_c(E)$; its applications to particular CA experiments will be discussed further.

**Effect of Precursor Ion Internal Energy on the CA Spectrum.** A unique advantage of CA spectra for ion structure determination is their insensitivity to ion internal energy;[2] if the peaks arising from low activation energy fragmentations (those which also appear in the MI spectrum) are ignored, the CA spectra of ions of a particular chemical structure but formed from different precursors or at different ionizing electron energies will show the same relative abundances within an experimental error of a few percent.[15,25] The $P_c(E)$ curve for $m/e$ 100 ions at $V_0 = 7.8$ kV (Figure 2) is consistent with this behavior. The distribution of internal energy values of the precursor ions, $P_{p+}(E)$, after collision should be represented by the convolution of $P_c(E)$ with $P_{p+}(E)$ before collision. The formation of CA peaks not in the MI spectrum will require the transfer of $\gg 1$ eV of energy[16] [irrespective of $P_{p+}(E)$ before collision], a value well above the maximum cross section of $P_c(E)$. Thus $P_{p+}(E)$ after collision should resemble $P_c(E)$ above 1 eV as a function of smoothly decreasing slope; a change in $P_{p+}(E)$ before collision will change the abscissa values of $P_{p+}(E)$ after collision, but its general shape should closely resemble $P_c(E)$, and thus there should be a little effect on the *relative* cross section for producing precursor ions of a particular energy value by CA. This is borne out by the calculations for CA of $C_7H_8^+$ ions from toluene assuming internal energy values of zero and of 1 eV before collision (Table II). Although the abundances of the group II and III ions change relative to $[C_7H_7^+]$, which is the dominant peak in the MI spectrum, the abundances of the group II and III ions *relative to each other* remain the same well within the limits of error (2.50 vs. 2.52 at 4.8 kV, 2.13 vs. 2.12 at 7.8 kV) as found experimentally.[2b,15,25] Following the same reasoning, even an increase of $V_0$ should not have a large effect on the abundances relative to each other of CA ions arising from reactions of high activation energies.

It is important to note that the observed independence of CA spectra to precursor ion internal energy demands that $P_c(E)$ be relatively free of discontinuities, further justifying the assumption of a smooth distribution of energy state densities made for these calculations. However, the data of Figure 2 also indicate that CA spectra taken at higher ion accelerating potentials should show more variation with precursor ion internal energy. For $m/e$ 25 precursor ions using $V_0 = 31$ kV the maximum in $P_c(E)$ corresponds to 3 eV, so that variation in relative abundances with $P_{p+}(E)$ could be detectable for ions produced by reactions with activation energies of several eV.

**Optimized Experimental Parameters for CA Spectra.** Extension of the applications of CA in areas such as structure determination and complex mixture analysis[2-4] is limited in particular by experimental capabilities in sensitivity and precursor ion mass range. The predicted $P_c(E)$ functions of Figure 2 show clearly that higher values of ion accelerating potential should be particularly valuable in this regard. Thus $V_0 = 31.2$ kV will be necessary for $m/e$ 400 precursor ions to achieve the same $P_c(E)$ now obtained for $m/e$ 100 ions at 7.8 kV. Also with $m/e$ 100 precursor ions the sensitivity for CA fragment ions whose formation requires high activation energies would be

substantially improved by using $V_0 = 31$ kV. We are presently constructing an instrument to obtain CA spectra of ~30 kV ions[26] of $m/e$ values up to 2000 to test this further. The $V_0 = 30$ kV should also increase the sensitivity of this instrument for kinetic studies of fast unimolecular ion decompositions induced by CA.[8]

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