

# A Resonant Electron Capture Time-of-Flight MS with Trochoidal Electron Monochromator

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**A prototype electron monochromator (EM) reflectron time-of-flight (TOF) mass spectrometer has been constructed and demonstrated to record resonant electron capture (REC) mass spectra of electron-capturing compounds. The electron energy is ramped from  $-1.7$  to  $+25$  eV at a preset frequency, and the energy spread of the electron beam at 15 nA is 100 meV or better. Ions are orthogonally extracted into the analyzer at a frequency of up to 80 kHz while maintaining an upper  $m/z$ -limit of at least 300 and a mass resolving power of  $\sim 1000$ . A complete REC mass spectrum, which includes an effective yield versus electron energy curve for each negative ion formed from the compound being analyzed, typically takes several days to produce with a quadrupole or magnetic sector mass spectrometer. With the EM TOF described in this work, three-dimensional negative ion electron capture spectra are recorded in an interval on the order of only 1 s and displayed in real time. This new analytical capability could make it possible to perform GC REC mass spectrometry as well as easier (a) to measure the temperature dependence of REC cross sections, (b) to determine enthalpies of negative ion formation (accurate determination of the enthalpy of ion formation requires knowledge of the translational energy released during a dissociative capture event), and (c) to provide complete thermochemical descriptions of dissociative electron attachment by measuring ion lifetimes.**

Interactions between low-energy electrons and molecules result in the formation of transient negative ions, which are also known as compound states, resonant states, or simply resonances.<sup>1,2</sup> Resonances normally decay by autodetachment of the extra electron or by dissociation into smaller, negatively charged fragments and their neutral counterparts. If the lifetime of the resonant states with respect to the electron autodetachment exceeds several microseconds, direct mass spectrometric detec-

tion of the resonances becomes possible. Mass spectrometry can also be used to investigate dissociative electron capture by molecules provided that (a) the mean rate constant for dissociation of the negative parent ion is larger than the mean rate constant for electron autodetachment, (b) the dissociation is not forbidden by symmetry selection rules, and (c) there is sufficient energy to induce decay. Whichever the case, the negative ions observed are formed from an intermediate resonant state bearing information about the precursor. In contrast to positive ions, negative ions have a formation cross section that is essentially resonant in nature and, thus, produce a set of signals on an electron energy scale.

Resonant electron capture (REC) mass spectrometry (MS) was developed during the 1950s and 1960s<sup>1,3–5</sup> when the application of mass spectrometry to the analysis of organic molecules was nascent. Although modern mass spectrometric techniques, such as fast atom bombardment, matrix-assisted laser desorption/ionization, and electrospray ionization, successfully produce ions of both charges, understanding the mechanisms by which these methods produce ions is for the most part still an open question. The situation in REC MS is much clearer because it involves an electron beam of precisely known energy and small energy spread. In principle, information on the electronic structure of the compound under investigation can be deduced from a set of these discrete ionizing energies since each of them is directly associated with a specific electronic state. In this respect, REC MS is related and complementary to spectroscopic methods such as photoelectron spectroscopy, electron energy loss spectroscopy, and absorption spectroscopy.

Until now, REC MS has been performed primarily on magnetic sector<sup>4,6–8</sup> and quadrupole mass spectrometers.<sup>9–17</sup> The main disadvantage of these instruments is that they acquire mass

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spectra differentially by scanning at relatively slow speeds. A complete REC mass spectrum includes an effective yield versus electron energy curve for every negative ion formed from the compound being analyzed. Depending on the compound's complexity, it normally takes up to several days with a quadrupole or magnetic sector mass spectrometer to record such a spectrum. This is because every ion yield curve has to be recorded separately with the mass analyzer fixed at a particular ionic mass. This tediously slow acquisition process is almost certainly one of the main reasons modern mass spectrometrists, who often must deal with the analysis of 100 or more compounds daily, have been discouraged from adopting this powerful technique for routine analyses.

Use of a time-of-flight (TOF) mass spectrometer, which acquires mass spectra without scanning, could in principle solve the problem of acquisition speed in REC MS. Some groups have already used TOF mass analyzers with different types of electron monochromators<sup>18–20</sup> to study REC processes, but none of these groups appear to have addressed the question of recording negative ion mass spectra at fast rates. In fact, the various TOF instruments used in these prior investigations possessed neither the mass resolution, electronic speed, nor computer memory necessary to record REC mass spectra at high rates.

This paper describes the design and construction of a novel mass spectrometer that can be used to monitor the resonant formation of negative ions in the gas phase at spectral recording speeds approaching or exceeding those of spectroscopic methods. The instrument's electron capture ion source incorporates a trochoidal electron monochromator (TEM)<sup>21</sup> capable of generating an electron beam with a narrow distribution of energies (<100 meV). The ion source is coupled orthogonally to a compact reflectron-TOF mass spectrometer that can extract packets of ions into the drift tube at a rate up to 80 kHz. This instrument makes unique use of a list mode to transfer both timing and ion signals from a time-to-digital converter to a computer at slightly more than 4 MB s<sup>-1</sup>. At this rate of data transfer, large numbers of mass spectra can be acquired while the energy of the ionizing electrons  $E_e$  is ramped over a set range of energies ( $-1.7 \leq E_e \leq 25$  eV). This capability makes it possible to obtain the effective-yield versus electron energy curves for all negative ions in an interval on the order of only 1 s.

## EXPERIMENTAL SECTION

**Materials.** Colloidal graphite was purchased from Aquadag, Ted Pella Inc. (Redding, CA). The hexafluorobenzene (99.5+%), carbon tetrachloride (99.9+%), chloroform (99.9+%), and nitrobenzene (99+%) used as test compounds in this study were obtained from Aldrich Chemical Co. (Milwaukee, WI).

**Instrument Design and Fabrication.** The EM TOF mass spectrometer was built on the platform of a JEOL JMS-DX300 mass spectrometer by modifying its ion source to operate in the REC mode and replacing its BE analyzer with a compact orthogonal TOF analyzer (Figure 1).

**REC Ion Source.** The original filament assembly in the JEOL ion source was replaced with a commercial TEM recently introduced by JEOL.<sup>8</sup> The TEM characteristics has an electron beam drift distance of 4.5 mm, a deflection field length of 20 mm, a deflector spacing of 3.5 mm, and electrode apertures of 3.0 mm (Pierce electrode), 1.0 (first anode), 1.0 (second anode), 1.0 (first exit electrode), and 0.8 mm (second exit electrode). The TEM is enclosed along its axis between two permanent magnets that provide an 800-G magnetic field in the deflection space. A provision for fine  $x$ - $y$  movement of one of the magnets makes it possible to precisely align the magnetic field lines relative to the axis of the TEM. As far as the authors know, JEOL's TEM is the only one that utilizes permanent magnets instead of electromagnets. Although the magnetic field in this arrangement is rather strong and cannot be varied, the large dimensions of the TEM's dispersion volume and the application of a low potential difference between the deflector plates (1.0 or  $\pm 0.5$  V with respect to the midpoint of the filament) make it possible to achieve an energy resolution of better than 100 meV (full width at half-maximum, fwhm) at an electron current of 15 nA. To minimize the influence of stray external electric fields, the monochromator assembly was shielded by surrounding it with a foil screen and connecting the shield to the midpoint of the filament so that it is held at the same potential as the plane midway between the deflectors. To prevent formation of secondary electrons, all inner surfaces of both the monochromator and the ion chamber were covered with colloidal graphite. The TEM controller is designed so that the unit can be operated either in a static mode whereby the electron energy is kept constant at some selected value or in a dynamic mode whereby the electron energy is linearly ramped at a frequency  $f_s$  within some preset range between the limits  $-1.70$  and 25 eV.

**TOF Analyzer.** The TOF analyzer was custom-made by Ionwerks. The external dimensions of its aluminum housing are 211 mm  $\times$  142 mm  $\times$  64 mm. A two-stage ion reflector with a rectangular cross section is integral to the analyzer's design and gives the ions an effective flight path of  $\sim 0.45$  m. At a frequency of 80 kHz, which is close to the maximum extraction frequency for ions up to the  $m/z$ -limit of 300 (flight time of  $\sim 12.5$   $\mu$ s), ions can be orthogonally extracted into the analyzer while a mass resolving power  $m/\Delta m$  of  $\sim 1000$  is maintained. The analyzer's detector is fitted with two anodes to increase dynamic range by a factor of  $\sim 20$ .<sup>22</sup>

**Timing Control.** In the ramping mode, the TEM's controller issues a trigger signal to the TOF timing controller (Figure 1) at the beginning of each ramping cycle, and the TOF timing

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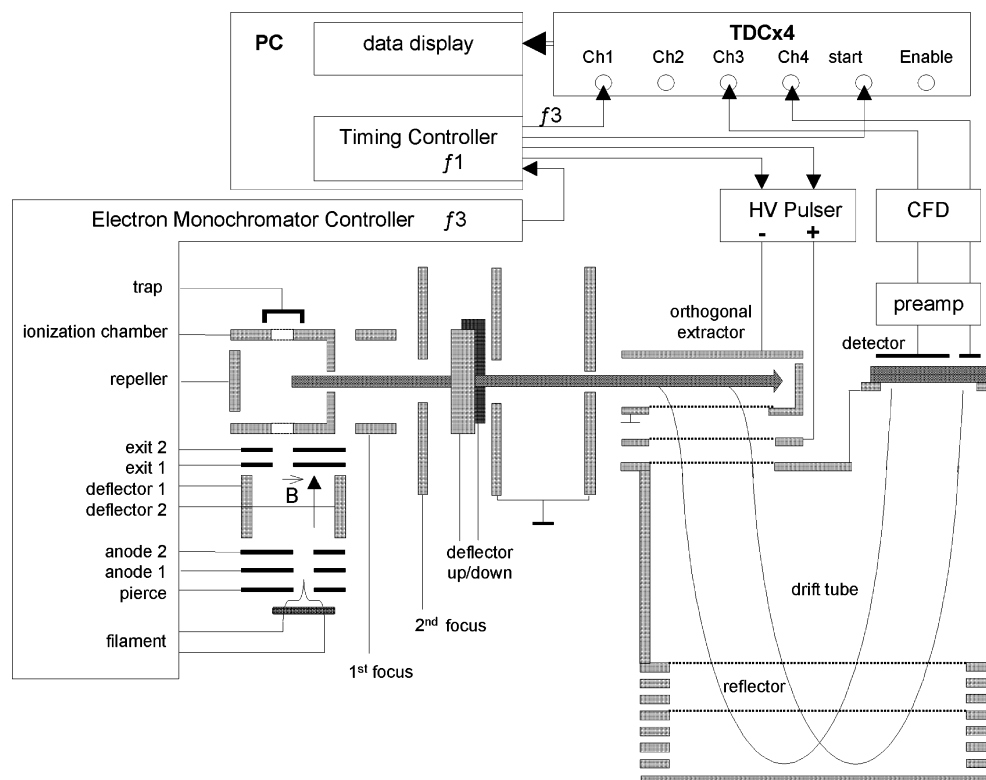


Figure 1. Schematic diagram of the TEM/TOF mass spectrometer, including TOF electronics.

controller passes this trigger signal to channel 1 of the time-to-digital converter (TDC). The TDC used at present (Ionwerks TDCx4) has a timing resolution of 625 ps and is capable of transferring more than 1 mega events  $s^{-1}$  (i.e., 4 MB  $s^{-1}$  at 4 bytes/event) to the PC. The timing controller also triggers the high-voltage pulser connected to the orthogonal ion extraction electrodes so that ions are extracted into the TOF analyzer at a frequency  $f_1$ . All trigger events are routed to the TDC so that it can write them into a chronological list together with the ion signals received from the TOF detector's two anodes. This list is transferred to a dual-processor Intel P-III 1 GHz/1 GHz computer operating under OS Windows 2000 Pro. The PC both stores the list on disks and displays the data in real time as it is acquired.

**Operating Conditions.** The ionization chamber's temperature was set at 65 °C, and its pressure was maintained at less than  $1 \times 10^{-6}$  Torr as measured by an ion gauge close to the ionization chamber. Samples in amounts of 2–3  $\mu L$  were injected from a syringe into a reference inlet system heated to the same temperature as the ionization chamber. When the TEM was operated in the ramping mode, the ionizing electron beam's energy was swept linearly over the range 0–12 eV at a frequency  $f_3$  of 10 Hz (100 ms/sweep). For each experiment, the TEM was tuned to set the width of the electron beam's energy distribution at some fixed value between about 100 and 330 meV. The repeller potential was set at  $-0.3$  V with respect to the ionization chamber, and the chamber potential itself was set at  $-24$  V.

Ions from the 24-eV primary beam were orthogonally extracted into the TOF drift tube with 0.250- $\mu s$ , 600-V pulses. At an extraction frequency (pulse rate)  $f_1$  of 80 kHz and acceleration voltage of 2 kV, the upper limit of the TOF analyzer's  $m/z$  range is 300. The resolution of the TDC was set at 625 ps.

**Data Acquisition.** Since REC spectra are three-dimensional (ion intensity versus  $m/z$  and electron energy), the amount of data acquired placed stringent demands on the data acquisition system. An example helps illustrate the magnitude of the problem. Consider a REC experiment in which the energy is ramped from 0 to 10 eV in 100 steps (i.e., 0.1 eV/step). If the ramping repetition rate  $f_3$  is 25 Hz, (which would be the minimum rate necessary to quantitatively record a capillary GC peak of  $\sim 0.5$ -s duration,<sup>23</sup> the energy stepping frequency will be 2.5 kHz (or 400  $\mu s$ /step) (Figure 2). If the TOF analyzer is operated at 80 kHz (12.5  $\mu s$ /ion acquisition), ions would be extracted 32 times into the drift tube per energy step. Since the software has to produce one mass spectrum from these 32 ion acquisitions, each time the energy is stepped (i.e., every 400  $\mu s$ ), 2500 mass spectra must be produced per second!

If one were using a transient recorder, each TOF spectrum thus would require 20 000 bins when operating the TOF at a time resolution of 625 ps (Figure 2). Assuming 14 bits ( $\sim 2$  bytes)/bin, it would be necessary for the transient recorder to acquire and transfer data at a rate of 100 MB  $s^{-1}$  ( $2500 \times 20\,000 \times 2$  bytes). In as much as this requirement is beyond the capability of any currently available transient recorder, it was necessary to devise a data acquisition scheme based on time-to-digital conversion. This was accomplished by operating the Ionwerks TDC in its list mode, in which it transfers a stream of data events to the PC. An event comprises 4 bytes, 1 byte to identify the TDC channel that recorded it and 3 bytes of timing information. The following actions are recorded as events: (1) energy ramp start, (2) TOF extraction start, and (3) ion arrival. All spectral data can

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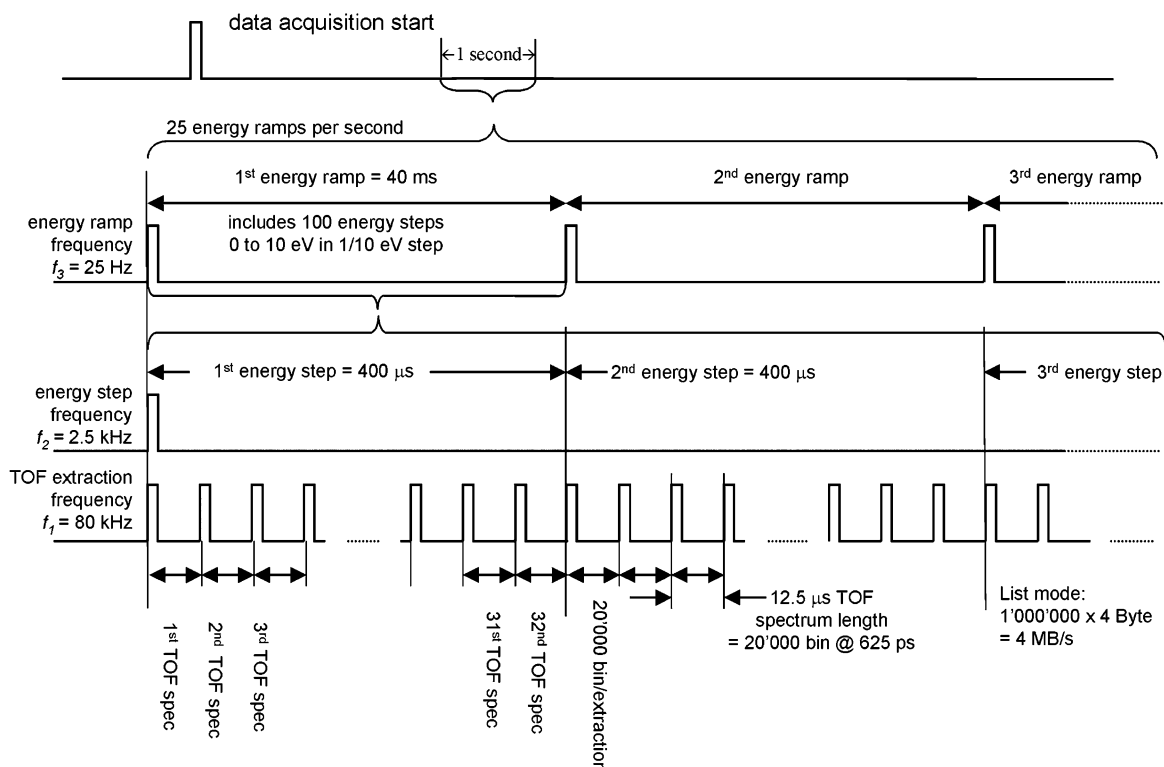


Figure 2. Timing diagram for REC TOF mass spectrometry.

be rapidly reconstructed from this list. The list is stored in binary format on two fast hard drives configured in a redundant array of independent disks, level 0 (RAID-0). Later the data can be converted to ASCII files for treatment by data processing software (Transform<sup>24</sup> and Microcal Origin<sup>25</sup> were used in the present work). Examples of REC spectra reconstructed from experimental data as 3D contour plots and 3D graphs are shown in Figure 3.

## RESULTS AND DISCUSSION

The compounds used in this investigation to evaluate the performance and test the reliability of the new instrument were chosen because their REC spectra are well documented in the literature and because they exhibit electron attachment cross sections over several orders of magnitude and form resonant negative ions over wide ranges of energy (0–15 eV) and mass (up to 300 u).

**Hexafluorobenzene.** Low-energy interactions between electrons and hexafluorobenzene molecules have been reported by two laboratories.<sup>26,27</sup> Figure 4 shows the effective yield curves of the negative ions formed from  $C_6F_6$  that were obtained in the present work. The appearance energies and resonant maximums of the negative ions in these recordings are in excellent agreement with those observed in the spectrum published by Fenzlaf and Illenberger,<sup>26</sup> but the relative cross sections for the formation of the negative fragment ions are not in good agreement with those reported by these researchers. The spectrum obtained in this

study shows intensities for the fragment ions relative to  $C_6F_6^{*-}$  near 0 eV that are roughly five ( $F^-$ ) and fifteen ( $C_5F_3^-$  and  $C_6F_5^-$ ) times less than those recorded by Fenzlaf and Illenberger. Although the energy resolution used by the latter group ( $\sim 100$  meV)<sup>26</sup> was roughly half that used to obtain the spectrum in the present study (180 meV, fwhm), it is unlikely that the difference in relative intensities is due to the different energy resolutions. Since the spectral widths of the  $C_6F_6^{*-}$  resonant peak near 0 eV in both these experiments reflect the widths of the respective electron energy distributions, one would expect the peak corresponding to this ion to be less intense in the spectrum with the poorer energy resolution than in the spectrum with the better resolution. In fact, the reverse is observed. It is more probable that the difference in relative intensities in the two REC spectra reflect significantly different transmission efficiencies through the two instrument geometries involved. The stability of  $C_6F_6^{*-}$  is well established (refs 4 and 17 in ref 26). Nevertheless, the fragment anions under discussion, which are formed from shorter lifetime, high-energy resonances of  $C_6F_6^{*-}$ , will in principle possess large translational energies, and the relative intensities of these fast-moving fragments through any given instrument would be expected to depend on the geometry of that particular instrument. Unfortunately, previous attempts to measure excess translational energies of hexafluorobenzene's negative fragment ions were unsuccessful,<sup>26</sup> so this particular question cannot be resolved at the moment. It is clear, nonetheless, from the experiments conducted in this study that, despite the very rapid electron energy scanning it uses to acquire spectra, the EM TOF instrument does not discriminate (beyond the presence of external stray and withdrawing electric fields, which are typical for any instrument) between 0 eV and higher energy electrons.

(24) Transform Version 3.4; Fortner Software LLC, 100 Carpenter Drive Sterling, VA, 20164.

(25) Microcal Origin Version 5.0; Microcal Software, Inc.: One Roundhouse Plaza, Northampton, MA, 01060.

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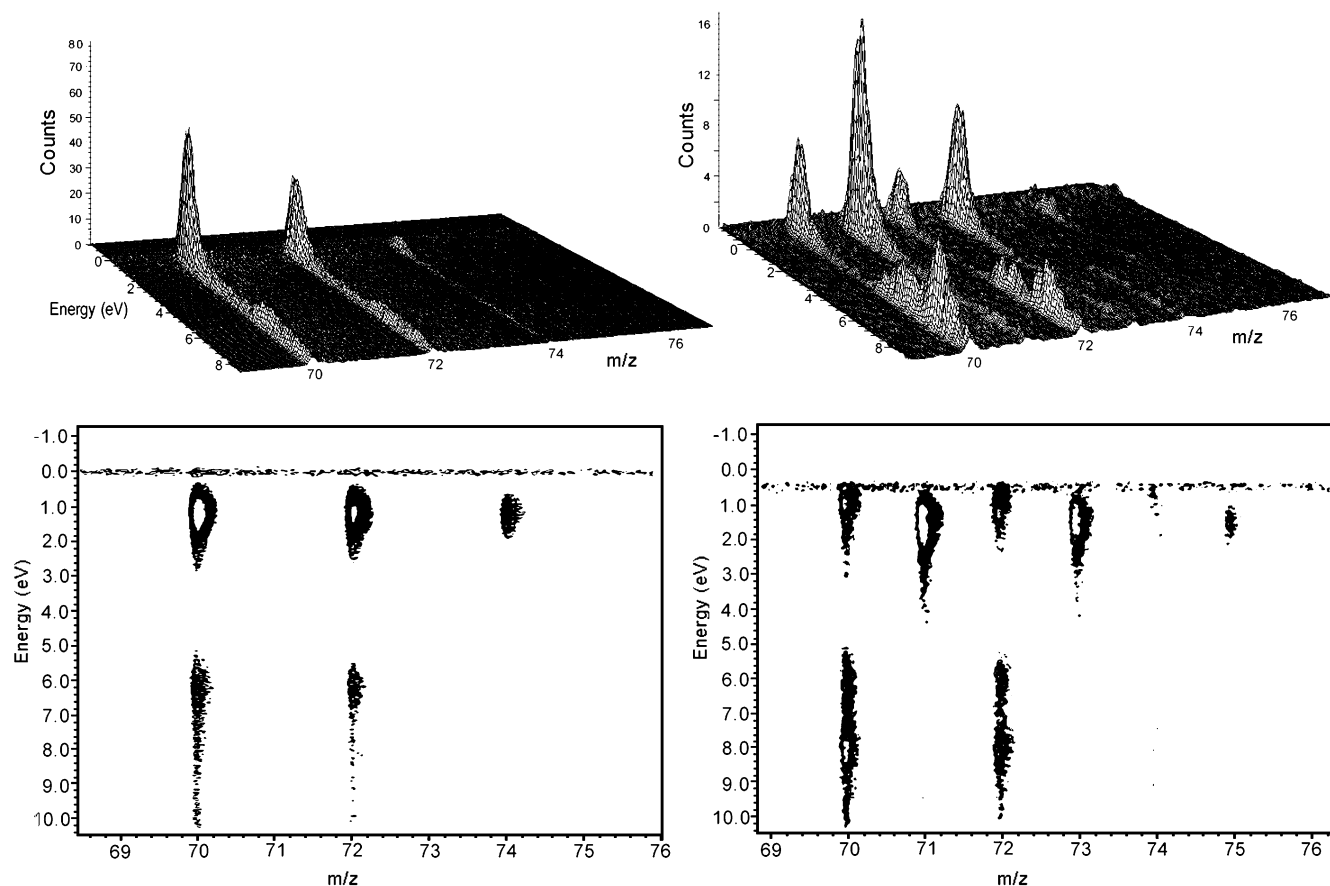


Figure 3. REC mass spectra for  $\text{CCl}_4$  and  $\text{CHCl}_3$  in the mass range 66–79 u depicted as 3D graphs (upper pane) and 3D contour plots (lower pane).

**Chloromethanes:  $\text{CCl}_4$  and  $\text{CHCl}_3$ .** The formation of negative ions from these two molecules has been intensively studied, but just a few articles relevant to the present work are cited here.<sup>28–32</sup> Mass analysis of negative ions from chloromethanes was performed in three of these studies.<sup>28,30,31</sup> It is of particular interest to compare the results of the current study with those of Scheunemann et al.<sup>31</sup>

The effective yield curves of all negative ions formed by dissociative electron attachment to carbon tetrachloride are shown in Figure 5. Both the positions of the resonant peaks and the relative intensities of the negative ions in all of these curves are in very good agreement with the corresponding published results.<sup>31</sup> The cross sections for formation of  $\text{Cl}^-$  from  $\text{CCl}_4$  (absolute units) were recorded for three different energy spreads of the electron beam (Figure 6). It is clear from this graph that the relative intensity of the second resonant peak, which appears at  $\sim 0.8$  eV, with respect to the one near 0 eV is a function of energy resolution. This observation is in accordance with recent, more thorough investigations of dissociative electron attachment

to  $\text{CCl}_4$ .<sup>33,34</sup> Thus, there is no evidence in the  $\text{CCl}_4$  results that fast ramping of the electron energy in the EM TOF has any significant influence on the electron beam's ionizing characteristics.

The effective yield curves for the negative ions resulting from dissociative electron attachment to chloroform (Figure 7) show that the positions of resonant peaks for  $\text{CHCl}_3$  are in excellent agreement with earlier published results from two sources.<sup>28,31</sup> Again, as in the case of  $\text{CCl}_4$  (Figure 6), the shape of the  $\text{Cl}^-$  effective yield curve depends on the energy resolution used (see inset to Figure 7a). The same is not true for all the relative intensities. While the relative intensities of all the negative ions from  $\text{CHCl}_3$  registered in the present experiments are very close to those determined by Dorman,<sup>28</sup> those found in the current study for  $\text{CCl}_2^-$  and  $\text{Cl}_2\text{H}^-$  are different from those reported by Scheunemann et al.<sup>31</sup>

In an early study, Johnson et al. claimed on the basis of TOF mass spectrometric measurements that  $\text{Cl}_2^-$  ions are formed from  $\text{CHCl}_3$ .<sup>30</sup> In a subsequent study, Scheunemann et al.<sup>31</sup> used a quadrupole mass spectrometer, which had higher mass resolution than that of Johnson and co-workers' TOF instrument to detect the formation of  $\text{Cl}_2\text{H}^-$  from  $\text{CHCl}_3$ , but they were not able to

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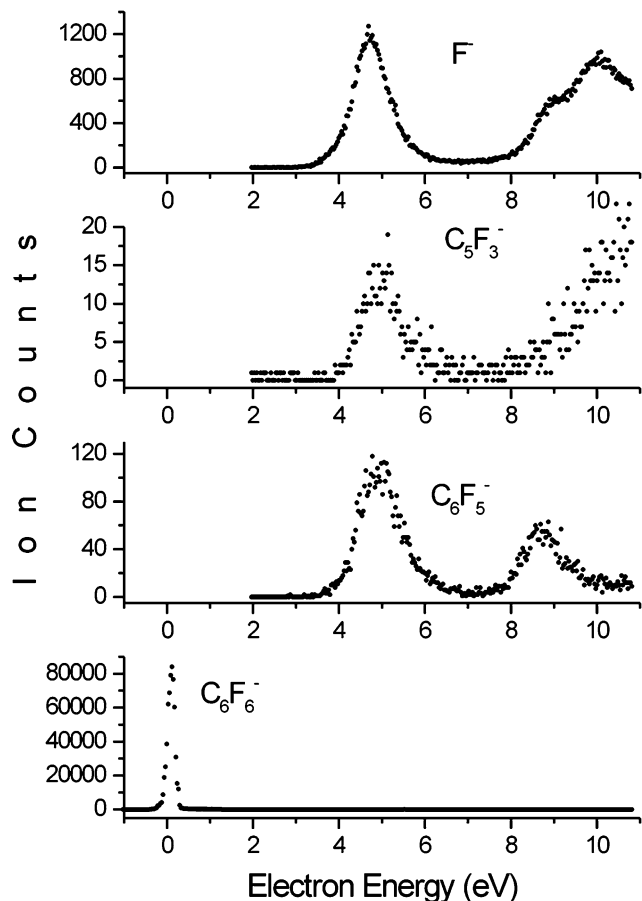


Figure 4. Effective negative ion yield curves from hexafluorobenzene obtained at the energy resolution (fwhm)  $\sim 180$  meV.

detect the formation of  $\text{Cl}_2^-$  reported by Johnson et al.<sup>30</sup> The mass resolution and sensitivity of the instrument used in the present work were sufficient to unambiguously resolve this historical discrepancy. Peaks due to  $\text{Cl}^-$ ,  $\text{Cl}_2^-$ ,  $\text{Cl}_2\text{H}^-$ ,  $\text{CCl}_2^-$ , and  $\text{CCl}_3^-$  were observed with the EM TOF mass spectrometer (Figure 7) when chloroform was introduced into the instrument following introduction of  $\text{CCl}_4$  in an immediately preceding experiment. In the energy range 0–2 eV, the shape and relative intensity of the  $\text{Cl}_2^-$  and  $\text{CCl}_3^-$  peaks were found to be absolutely identical to those produced from  $\text{CCl}_4$ ; however, after the instrument was warmed up for several hours, these two ion signals gradually disappeared from the spectrum. In contrast, the two broad resonant features seen in the effective yield curve for  $\text{Cl}_2^-$  at about 6.3 and 8.5 eV, which the present authors believe are genuine products of chloroform, remained in the spectrum after heating. Burrow and Chu<sup>32</sup> had difficulty determining the true shape of the  $\text{Cl}^-$  curve from  $\text{CH}_3\text{Cl}$  because of the presence of  $\text{CCl}_4$ ; in trying to explain the dissociative electron attachment spectrum of  $\text{CH}_3\text{Cl}$ , these two investigators noted that  $\text{CCl}_4$  is “notoriously difficult to remove once the system has been exposed to it”. The effect of  $\text{CCl}_4$  in the present case should not, however, be as great as it was in the case of Burrow and Chu because (1) the attachment cross section of  $\text{CCl}_4$  is not much larger than that of chloroform whereas it is very much larger than that of  $\text{CH}_3\text{Cl}$  and (2) the relative abundance of  $\text{CCl}_4$  in the sample that produced Figure 7 is estimated to be only 3.5%, which is not enough to dramatically influence the effective yield curve of  $\text{Cl}^-$  from  $\text{CH}_3\text{Cl}$ . This case

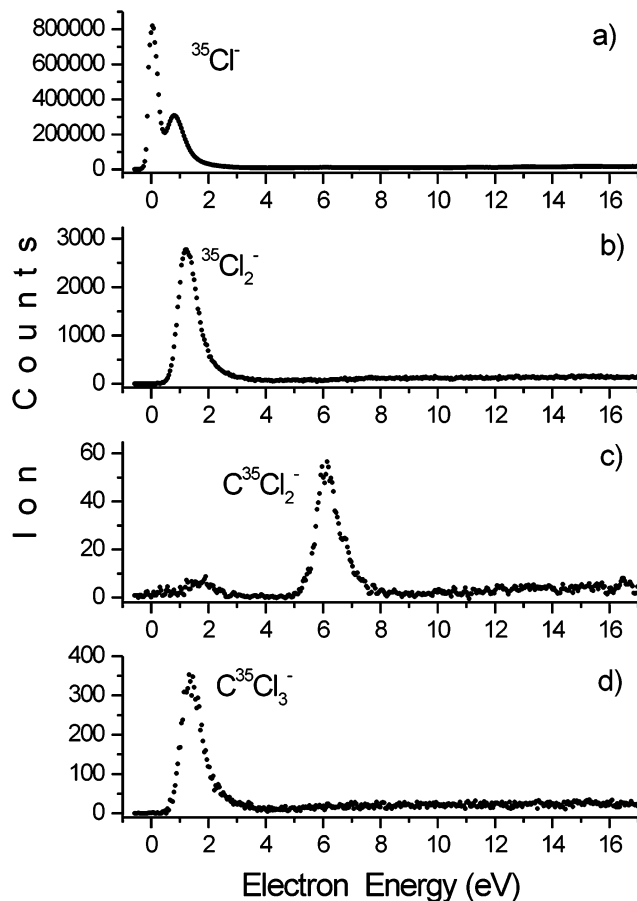


Figure 5. Effective negative ion yield curves from  $\text{CCl}_4$  obtained at the energy resolution (fwhm) 330 meV.

is a good example of why electron attachment spectra of chloromethanes should be interpreted with caution.

**Nitrobenzene.** The REC mass spectrum of nitrobenzene (Figure 8) produced by the TEM/TOF mass spectrometer contains most of the negative ions generated by resonant electron attachment to nitrobenzene reported previously.<sup>16,17,35–37</sup> Christoprou et al. were the first to publish a REC spectrum of the nitrobenzene molecule.<sup>18</sup> Those investigators observed nondissociative electron attachment to  $\text{C}_6\text{H}_5\text{NO}_2$  to form long-lived molecular anions  $\text{C}_6\text{H}_5\text{NO}_2^{\cdot-}$  ( $m/z$  123) and dissociative electron attachment to produce intense  $\text{NO}_2^-$  ( $m/z$  46) fragment ions. Prior to the current study, the most complete REC mass spectra of  $\text{C}_6\text{H}_5\text{NO}_2$  had been reported by Jäger and Henglein<sup>35</sup> and by Laramée et al.<sup>16</sup> If the negative ions with  $m/z$  104, 105, and 106 assigned by Jäger and Henglein (Figure 5 in ref 35) are respectively reassigned to  $m/z$  105, 106, and 107 (Figure 8) and the resonant curves (Figure 5<sup>35</sup>) are shifted to lower energies by  $\sim 0.15$  eV, the positions for the negative ions produced from  $\text{C}_6\text{H}_5\text{NO}_2$  in the present work (Figure 8) correspond quite well with those reported previously.<sup>35</sup>

The adjustment in the mass assignment of the three peaks observed by Jäger and Henglein<sup>35</sup> is reasonable because their

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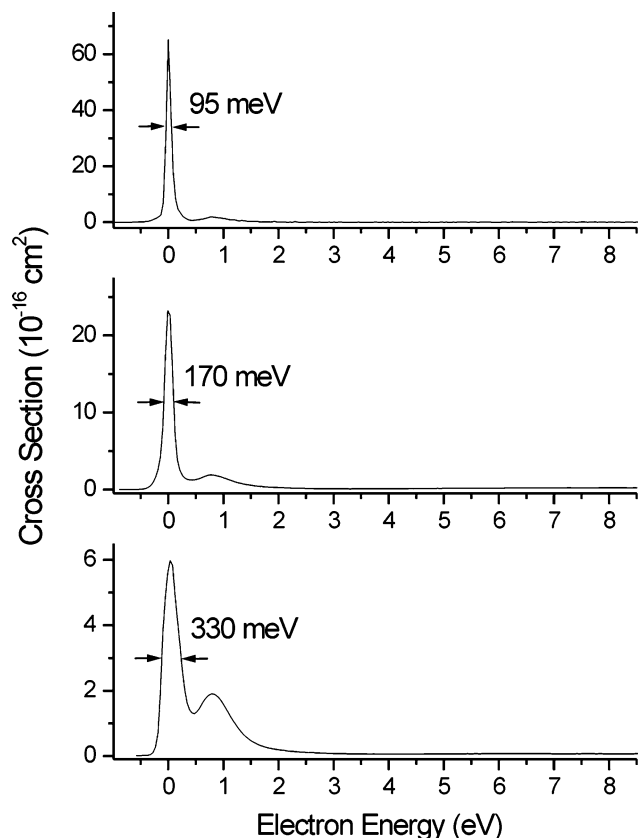


Figure 6. Cross section for the formation of  $\text{Cl}^-$  from  $\text{CCl}_4$  versus energy spread of the electron beam.

mass calibration is considerably less accurate than that obtained with the EM-TOF MS in the present study, and consequently, the mass assignments reported in this work are more likely to be correct. This action is further supported when the present data (Figure 8) are compared with that of Laramée et al.;<sup>16</sup> it is clear that the two resonances for the phenyl anion  $\text{C}_6\text{H}_5^-$  ( $m/z$  77) at 3.6 and 6.0 eV, the two intense resonances for  $\text{NO}_2^-$  at 1.2 and 3.5 eV, and the molecular ion resonance at 0.06 eV (Figure 8 in ref 16) match closely with those observed in the present work. It must be pointed out, however, that the two resonance peaks at 3.3 and 6.9 eV assigned to the molecular ion by Laramée et al.<sup>16</sup> are attributed in the present study to the  $(\text{M} - \text{H})^-$  ion  $\text{C}_6\text{H}_4\text{NO}_2^-$  at  $m/z$  122 (Figure 8h). Thus in actuality, Laramée et al.<sup>16</sup> must have recorded either the  $^{13}\text{C}^{12}\text{C}_5\text{H}_4\text{NO}_2^-$  ( $m/z$  123) or the  $m/z$  122 peak of  $\text{C}_6\text{H}_4\text{NO}_2^-$  that their TEM/quadrupole instrument could not mass-resolve from  $m/z$  123. Poor mass resolution was most likely the case. It might be further noted that the 7.7-eV resonance seen in the spectrum of pyrene shown by Laramée et al. (Figure 7 in ref 16) is for the same reason, i.e., poor mass resolution, probably also due to  $(\text{M} - \text{H})^-$  rather than the molecular anion as they assigned it.

The small adjustment in the energy scale (0.15 eV) noted above is plausible because of an ambiguity<sup>35</sup> in which the electron energy for the maximum yield of  $\text{C}_6\text{H}_5\text{NO}_2^+$  from nitrobenzene at 0 eV is shown to be at  $\sim 0.15\text{--}0.2$  eV in Figure 5.<sup>35</sup> There are two good reasons for believing that 0 eV is the correct value in their study. First, the preponderance of experimental evidence since Christopherou et al. reported the first REC spectrum of nitrobenzene indicates that the long-lived  $\text{C}_6\text{H}_5\text{NO}_2^+$  ions form from nitroben-

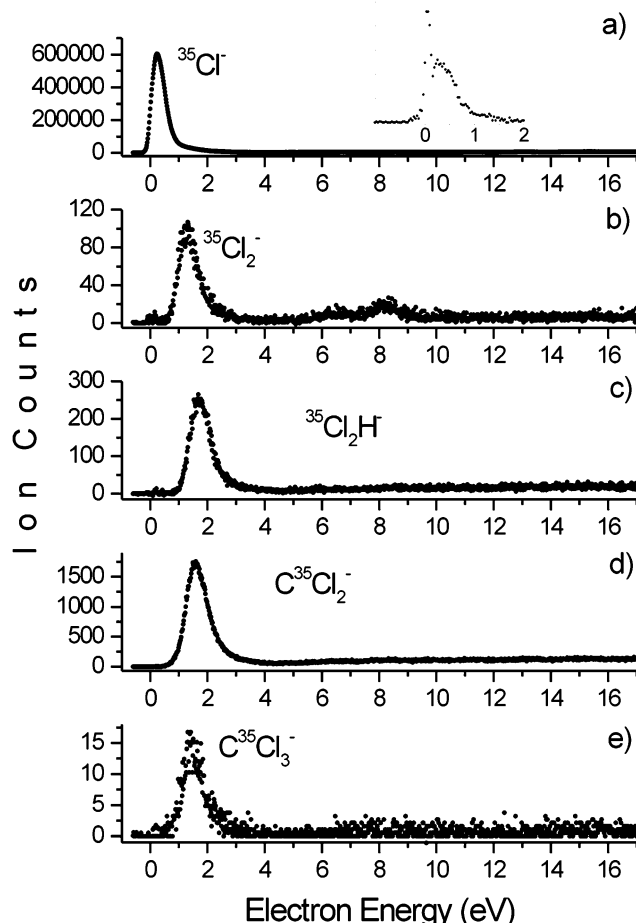


Figure 7. Effective negative ion yield curves from  $\text{CHCl}_3$  obtained at the energy resolution (fwhm) 330 meV. The  $\text{Cl}^-$  effective yield curve in the inset has been recorded at the energy resolution of 95 meV.

zene near 0 eV. Second, recent experimental evidence for the existence of a second nonzero resonant state of nitrobenzene suggests that this resonance is probably too short-lived to have been observed by Jäger and Henglein on their instrument. Specifically, the measurements by Modelli and Venuti<sup>37</sup> of both total anionic current without mass analysis and electron transmission indicate that another resonant state of  $\text{C}_6\text{H}_5\text{NO}_2^+$  is formed at  $\sim 0.4$  eV, but failure to detect this species in subsequent mass analyses led these investigators to conclude that the lifetime of the 0.4-eV resonant state is too short to be detected by mass spectrometry. Excepting the extreme intensity of the  $\text{NO}_2^-$  ions (Figure 8d) and possible contributions from impurities or background to the intensities of the ions at  $m/z$  16, 26, and 42 (Figure 8a and b), the relative cross sections found in the present study for negative ion formation agree satisfactorily with those determined previously.<sup>35</sup> Finally, the new TOF instrument's higher sensitivity has made it possible to register four additional fragment negative ion peaks in the REC mass spectrum of  $\text{C}_6\text{H}_5\text{NO}_2$  with extremely low relative intensities at  $m/z$  43, 49, 51, and 52 (Figure 8i); none of these four ions have been reported previously.<sup>16,35</sup>

## CONCLUSION

The main outcome of the present work is the design and construction of a novel mass spectrometer with a trochoidal

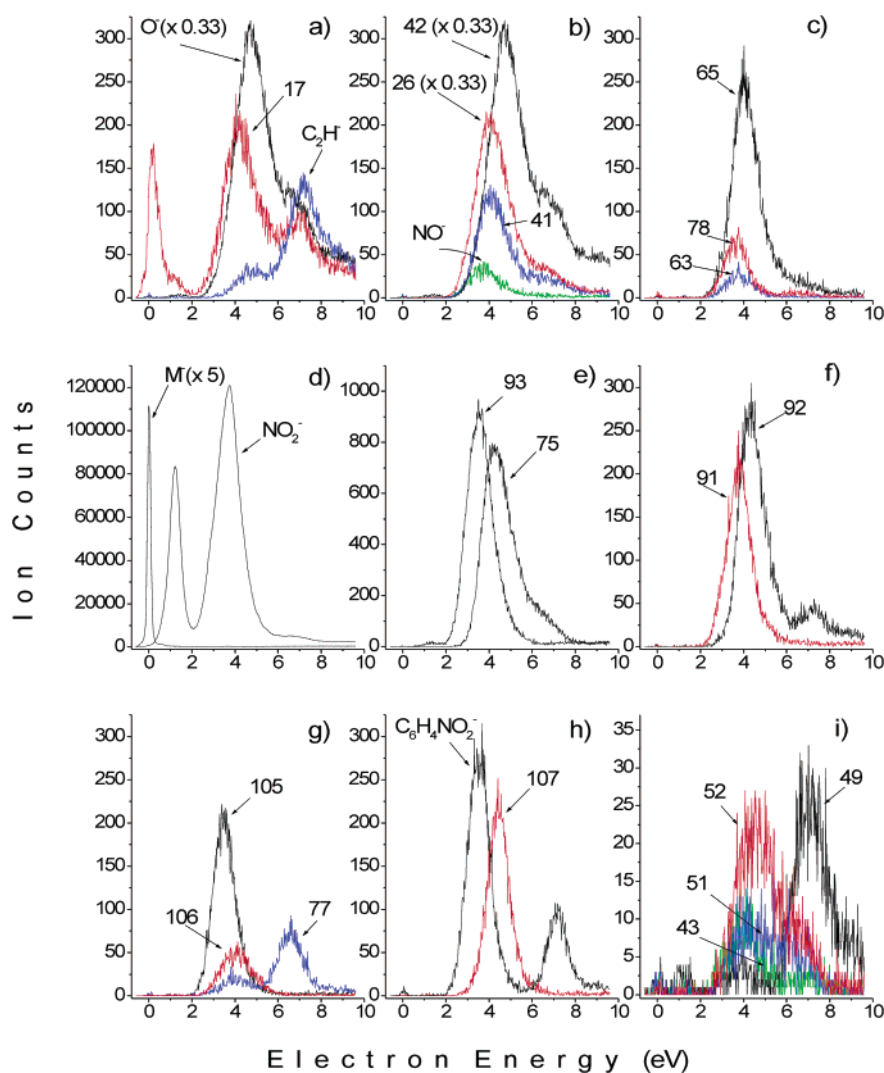
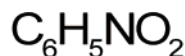


Figure 8. Effective negative ion yield curves from nitrobenzene obtained at the energy resolution (fwhm)  $\sim 180$  meV.

electron monochromator and a reflectron-TOF analyzer and the demonstration that this instrument can be used to obtain resonant electron capture mass spectra as rapidly as by any other spectroscopic method. Critical comparison between the experimental data obtained with this instrument and that found in the literature shows that rapid scanning of the ionizing electrons' energy does not influence the resolution or accuracy of the spectra obtained though sensitivity may diminish at very high electron energy scan rates.<sup>27</sup>

Although more development is required, prospects for useful application of REC TOF mass spectrometry are promising. The reflectron-TOF analyzer's sensitivity and exceptional acquisition speed suggest that interfacing with a gas chromatograph is possible. Cross sections for some negative ions of the chloromethanes were found in a very early study by Spence and Schulz to depend strongly on temperature.<sup>29</sup> The new instrument's capability for acquiring all of the negative ions produced from a compound in a matter of seconds could be exploited for conducting temperature-dependent experiments in which the effective

yield curves for all of the negative ions must be recorded under identical conditions. Accurate determination of the enthalpy of ion formation requires knowledge of the translational energy released during a dissociation event. In principle, the TOF analyzer could be used to measure excess translational energies as was first demonstrated by Illenberger.<sup>38</sup> This would require that the ion source be operated in a pulsed mode. Finally, a complete thermochemical description of the dissociative electron attachment to polyatomic molecules requires information about the vibrational excitation of the dissociation products formed. In principle, measurements of ion lifetimes give this information, at least with respect to the charged counterpart of the dissociative capture event. Studies applying Edelson's method<sup>39</sup> for determining the lifetimes of negative ions should be possible with the new TEM/TOF mass spectrometer.

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