Electron-Impact Ionization of SiCl₃ Using An Improved Crossed Fast-Neutral-Beam – Electron-Beam Apparatus

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Abstract. The fast-neutral-beam technique is a versatile approach to the determination of absolute cross sections for electron-impact ionization of atoms, stable molecules as well as free radicals and metastable species. A fast neutral beam of the species under study is prepared by charge-transfer neutralization of a mass-selected ion beam and the species are subsequently ionized by an electron beam. Mass- and energy-dispersive selection separates singly from multiply charged ions and parent from fragment ions and allows the determination of partial ionization cross sections. Here we describe some major improvements that were made recently to the fast-beam apparatus that has been used extensively for ionization cross section measurements for the past 15 years in our group. Experiments using well-established ionization cross sections in conjunction with extensive ion trajectory simulations were carried out to test the satisfactory performance of the modified fast-neutral-beam apparatus. We also report absolute partial cross sections for the formation of various singly charged positive ions produced by electron impact on SiCl₃ for impact energies from threshold to 200 eV in the modified fast-beam apparatus.

1. Introduction

There is considerable interest in electron-driven collisional interactions, such as electron-impact ionization and dissociative ionization of a molecule, from both a basic science viewpoint and from the viewpoint of data needs for applications. From a theoretical point of view [1], the calculation of electron-impact cross sections for molecular ionization are beyond the capabilities of rigorous quantum mechanical calculations because of the complexity of many molecular targets and the variety of processes contributing to the ionization process. As a consequence, semi-rigorous methods are commonly used [2]. Although experimental ionization study have been carried out since the early part of the 20th century, there are still many atoms, molecules, and free radicals for which no ionization cross section data are available. The reliable determination of partial ionization cross sections are particularly challenging. Mass- and energy-dispersive elements have to be employed to separate singly from multiply charged ions and parent ions from fragment ions. Complete extraction of the product ions from the interaction region of target and electron beams (ion source), transport of the product ions through the mass- and/or energy-dispersive elements (particularly of fragment ions produced with excess kinetic energy) and their detection with 100% efficiency pose serious challenges to the experimentalist.
Märk and co-workers [3] were the first to investigate systematically the ion extraction from the ion source and ion transport through a mass spectrometer from ion source to ion detector and identified discrimination effects as the most serious problem rendering accurate absolute partial ionization cross section measurements a challenging experimental task, particularly in the case of dissociative ionization processes. Detailed investigations of the ion extraction efficiency as a function of excess kinetic energy and of the ion transport efficiency from the ion source to the detector in conjunction with ion trajectory simulations are essential in characterizing and quantifying the ability of a particular apparatus to determine reliable absolute partial ionization cross sections.

Conventional electron-impact ionization apparatus use effusive gas jets or heated ovens to produce the target beams for ionization studies. These approaches limit the list of targets to stable atoms and molecules. On the other hand, the fast-neutral-beam method, which was introduced by Cook and Peterson [4], has been shown to be a reliable experimental method for the determination of electron-impact ionization cross sections of free radicals and other short-lived and/or unstable species. Freund and co-workers [5] first described a fast-neutral-beam apparatus used extensively in absolute ionization cross section measurements for many atoms as well as for some molecules and free radicals. This apparatus, in a slightly modified version, was subsequently used in our group in a series of absolute ionization cross section measurements for many molecules and free radicals (see e.g., [6] and references therein to earlier work). Recent technological advances have made it possible to improve the performance of this apparatus significantly (i) by employing position-sensitive ion detection, which allows the determination of the product ion distribution on the face of the detector and (ii) by increasing the electron current density by more than a factor of 10 using a new dispenser-type electron emitter. The impact of these improvements and the expanded capabilities of the modified fast-beam apparatus are described in this paper along with the results of a detailed study of the electron-impact ionization of the SiCl₃ free radical.

2. Experimental Apparatus and Performance Verification

2.1 Apparatus Modifications

The fast-neutral-beam apparatus used in the present experiments (and shown in fig. 1) has been described in detail in earlier publications [5,7]. Here we only give a brief summary of two recent

Fig. 1. Schematic diagram of the modified fast-beam apparatus, which employs (i) a positive-sensitive triple-stack multi-channel plate (MCP) detector and (ii) a new dispenser-type high-current electron gun.
modifications to the apparatus and their impact on the performance of the apparatus. First, we installed a new electron gun with a dispenser-type cathode, which consists of a porous tungsten matrix of about 20% porosity as a base, interspersed uniformly with a mixture of barium and calcium aluminate as the electron emitting material. The porous metal matrix acts as a reservoir from which the emitting material can diffuse to the surface, maintain an active layer and provide a low work-function surface for the thermionic emission of electrons. The cathode is activated by indirect heating. The new emitter has the following properties:

- 1-2 A/cm² continuous emission current density
- a useful lifetime of more than 10 000 h
- no degradation of the emission current over time
- a minimal evaporation rate
- superior shock and vibration resistance
- high reliability and reproducibility of the operating characteristics

The total beam current produced by the new electron emitter is almost a factor of 10 higher than what was obtained with the previous gun with maximum beam current of well over 2 mA at energies above 50 eV (fig. 2). At beam energies of 10 eV and 4 eV, the total current is still around 20 μA and 5 μA, respectively. In addition, the size (i.e. cross section) of the electron beam produced by the new emitter in the interaction region is about 0.2 cm² compared to a beam size of 0.6 cm² produced by the old electron gun. Thus, the current density produced by the new emitter of up to 25 mA/cm² (for dc operation) exceeds that of the old gun by about a factor of 20.

![Figure 2](image.png)

Furthermore, we also replaced the channel electron multiplier (CEM), which served as ion detector with a position-sensitive, triple multichannel plate (MCP) detector in a Z-stack arrangement for maximum gain (RoentDek model DLD40 MCP detector with a delay-line anode capable of high-resolution 2D-imaging and fast timing for charged particle or photon detection at high rates with multi-hit capability). The new detector allows us to monitor the distribution of the product ions that emerge from the hemispherical analyzer on the face of ion detector. The ability to obtain the product ion distribution in addition to the total ion count is important in situations where fragment ions that are close in their mass-to-charge ratio are formed with broad excess kinetic energy distributions, which causes the individual ion distributions to overlap on the face of the detector. This was the case in our ionization studies of NO, NO₂ and N₂O, where we could not resolve the ion signals corresponding to N⁺ and O⁺ and only reported a cross section for the combined (N⁺ + O⁺) formation [5]. The experimental determination of the ion distribution on the detector face in conjunction with SIMION ion trajectory simulations allow us to deconvolute such overlapping ion distributions and obtain individual cross sections.
All other features and components of the original fast-beam apparatus and the experimental procedure to obtain absolute cross sections as described earlier [5,7] remained unchanged. In principle, the fast-beam apparatus affords the capability to measure directly all quantities that determine the absolute cross section. However, here we used the well-established Kr or Ar absolute ionization cross sections to calibrate a pyroelectric crystal. The calibrated crystal, in turn, was then used to determine the flux of the neutral target beam in absolute terms. The typical uncertainty of absolute ionization cross sections determined in the fast-beam apparatus is in the range from ±15 to ±18% [5,7].

2.2 Ion Trajectory Simulations
Extensive ion trajectory simulations using the most recent version of the SIMION charged particle simulation package [9] were carried out to help characterize and quantify the capabilities of the modified fast-beam apparatus. These simulations tracked ions formed in the interaction region of electron beam and neutral beam to the MCP detector. The electron-impact ionization in the interaction region creates product ions, which in the case of molecular targets consist of parent ions and fragment ions produced by dissociative ionization. Parent ions are formed with the same kinetic energy as the incident neutral beam and, in general, no excess kinetic energy is imparted on a parent ion in the ionization process. Fragment ions, on the other hand, are produced with a distribution of excess kinetic energies which may range from near-thermal to more than 10 eV per fragment ion. This results in fragment ions with a much wider kinetic energy spread compared to the parent ions, which, in turn, results in a much more divergent fragment ion beam. Furthermore, the two or more fragments formed in the dissociative ionization process share the initial kinetic energy, so that fragment ions travel with less than the neutral beam energy towards the detector.

In our simulations, we first generate randomized values of the excess kinetic energy of a given fragment ion in a range of values for the excess energy that are known from other experiments or from literature. The energy is converted to a velocity of the fragment, whose direction is randomly selected within a 360° cone. The simulation tracks the path of each ion from the interaction through the electrostatic Einzel lens and the hemispherical analyzer taking into account the displacement of the ions due to the small transverse collimating magnetic field and the effect of the additional magnetic steering field (see fig. 1). Ions that leave the hemispherical analyzer travel an additional few centimeters before they reach the MCP detector, whose entrance has a detection area that is 46 mm in diameter and is held at a negative potential of 3 kV. The simulation ultimately determines the number of ions arriving at the detector and their position on the detector surface and calculates the transmission percentage. If an ion is lost between the interaction region and the detector, it is possible to identify the place where the ion hit a surface or was blocked.

The higher electron beam current from the new emitter and smaller interaction region result in significantly higher signal rates and a much more tightly focused product ion signature on the face of the MCP detector. This is shown in fig. 3, where we simulated the Cl− fragment ion signal from the dissociative ionization of SiCl4 (assuming an excess kinetic energy of 3 eV per Cl− fragment ion) on the face of the MCP detector for both the old and the new electron gun. In this simulation, the ratio of the signal rates was based on actual values of the beam currents obtained with respectively the old and new electron gun at an impact energy of 70 eV. The effect of the higher current of the new emitter on the signal rate is immediately obvious from the two diagrams depicted in fig. 3. We also note, that the Cl− product ion beam obtained with the new emitter is more tightly focused on the face of the MCP detector. Most importantly, the ion collection efficiency with the old emitter was already less than 100% for a 3 eV Cl− fragment ion from SiCl4 (note the ions in the left diagram that “miss” the surface area of the MCP), whereas all product ions lie well within the cross sectional area of the MCP when the new electron emitter is employed.
2.3. Test Measurements

In order to test the performance of the modified fast-beam apparatus, we carried out a series of test measurements using the rare gases (He, Ne, Ar, Kr, and Xe), for which the ionization cross sections (absolute values and cross section shapes) are well known and N\textsubscript{2}, where the significant excess kinetic energy of the N\textsuperscript{+} fragment formed in the dissociative ionization process poses a serious challenge to the capabilities of the new apparatus.

The absolute ionization cross sections of the rare gases are known with higher accuracy (±4\% for Ar, between ±5-±8\% for He, Ne, and Kr and ±12\% for Xe) than the cross section of any other atom or molecule. The partial rare gas ionization cross sections of Freund and co-workers [5] obtained with the ‘old’ fast-neutral-beam apparatus are considered among the most reliable data (see e.g. discussion in Ref. [20]). We re-measured the absolute single rare gas ionization cross sections in the new fast-neutral-beam apparatus in the following way. We determined (i) the shape of the Ar\textsuperscript{+} single ionization cross section, which has a well-established shape with a very distinct feature around 50 eV and (ii) the ratios of the cross sections for the formation of all singly charged rare gas ions at a fixed energy of 70 eV relative to the Ar ionization cross section. This was done by determining the MCP count rate that corresponds to the established absolute Ar\textsuperscript{+} cross section at 70 eV. On the basis of the rare gas ionization cross section ratios at 70 eV as obtained from Ref. [12], we then calculated the expected MCP count rates that correspond to the absolute He\textsuperscript{+}, Ne\textsuperscript{+}, Kr\textsuperscript{+}, and Xe\textsuperscript{+} cross sections at 70 eV and measured the actual count rates. The agreement between our measured and calculated count rates was excellent, all values agreeing with each other to well within the margins of error expected on the basis of the accuracy of the underlying absolute cross sections.

Several groups have employed mass-selective techniques to measure partial ionization cross sections for the formation of N\textsubscript{2}\textsuperscript{+} and N\textsuperscript{+} ions from N\textsubscript{2} (see e.g. Peterson [11] and Freund et al. [12]). While the N\textsubscript{2}\textsuperscript{+} parent ions are formed with thermal or near-thermal kinetic energy, the dissociative ionization leading to N\textsuperscript{+} produces fragment ions with a broad excess kinetic energy distribution [1] as evidenced by a N\textsuperscript{+} appearance energy of about 30 eV, which is significantly higher than the thermochemical minimum energy of 24.3 eV required to produce N\textsuperscript{+} from N\textsubscript{2}. We combined SIMION ion trajectory modeling for the formation of N\textsuperscript{+} ions from N\textsubscript{2} in the modified fast-beam apparatus with measurements of all partial N\textsubscript{2} ionization cross sections. We simulated the N\textsuperscript{+}/N\textsubscript{2} ion distribution on the MCP detector with the excess kinetic energy as a free parameter and compared the simulated distribution with measured distributions. A comparison between the measured and simulated ion distributions on the face of the MCP detector reveals (at least qualitative) information about the actual excess kinetic energy distribution and provides a measure of the ion collection efficiency under various operating conditions. Up to an excess kinetic energy of 4.65 eV per N\textsuperscript{+} ion, we could
demonstrate a 100% N⁺ ion collection efficiency. Subsequently, we carried out absolute ionization cross section measurements of N₂ in the modified fast-beam apparatus measuring the N₂⁺ and (N⁺ + N₂++) partial cross sections as well as the respective appearance energies. The results agreed with the accepted cross section values to better than ±5% and to better than ±0.5 eV for the appearance energies.

3. Results and Discussions
We now present the results of the absolute partial ionization cross section measurements for the SiCl₃ free radical from threshold to 200 eV using the modified fast-beam apparatus. Figure 4 shows the measured partial cross sections for the formation of the SiCl₃⁺ parent ion and all singly charged fragment ions SiCl₂⁺, SiCl⁺, Si⁺, and Cl⁺. These partial ionization cross sections along with the total single SiCl₃ ionization cross section are also summarized in Table 1 in the Appendix. Cross sections for the formation of doubly charged ions are not reported here. Similar to what was found in the case of SiCl₄ [6], the maximum values of the cross sections for the formation of doubly charged ions from SiCl₃ are less than 0.1 x 10⁻²⁰ m².

![Fig. 4. Absolute partial cross sections for the formation of the singly charged ions SiCl₃⁺ (diamonds), SiCl₂⁺ (circles), SiCl⁺ (squares), Cl⁺ (inverted triangles) and Si⁺ (triangles) as a function of electron energy from threshold to 200 eV. The absolute cross sections have margins of uncertainty of ±15% (see text), which are not shown.](image)

In terms of their absolute magnitude, the partial ionization cross sections can be grouped into three categories: (1) the SiCl⁺ and Cl⁺ cross sections, which have the largest maximum cross section values (above 3.5 x 10⁻²⁰ m²), (2) the SiCl₂⁺ and SiCl₃⁺ cross sections whose maximum values are slightly above 2 x 10⁻²⁰ m², and (3) the Si⁺ cross section with a maximum value of about 1.51 x 10⁻²⁰ m². The parent SiCl₃⁺ cross section curve has a threshold of about 12.3 eV and rises to its maximum of 2.14 x 10⁻²⁰ m² at an energy of slightly less than 50 eV. The curve then exhibits a slight decline followed by a second maximum of similar magnitude at about 80 eV and subsequently gradually declines to about 1.6 x 10⁻²⁰ m² at 200 eV. The SiCl₂⁺ cross section has a threshold of about 13 eV and rises in a fashion similar to SiCl₃⁺ cross section, but exhibits only one maximum of 2.4 x 10⁻²⁰ m² at about 70 eV. The SiCl⁺ cross section rises from a threshold of about 14.8 eV to a narrow maximum of 3.7 x 10⁻²⁰ m² at about 55 eV and declines to a value of slightly less than 2.6 x 10⁻²⁰ m² at 200 eV. The Cl⁺ and Si⁺ cross sections have both threshold of slightly less than 20 eV. The Cl⁺ cross section has a fairly sharp maximum of 3.6 x 10⁻²⁰ m² at 70 eV. By contrast, the Si⁺ cross section has a broad maximum of 1.5 x 10⁻²⁰ m² around 80 eV and a much more gradual decline towards higher impact energies. The shape of the SiCl₄⁺ cross section with a double-maximum structure is similar to what was observed earlier for selected partial SiCl₄ cross sections [6] as well as for some partial cross sections of other Cl-containing...
molecules, such as TiCl$_4$ [13], and Cl$_2$ [14]. The low-energy maximum may be indicative of the presence of indirect ionization channels such as autoionization.

Figure 5 shows the experimentally determined total single SiCl$_3$ ionization cross section curve (i.e. the sum of all the partial cross sections for the formation of singly charged ions) in comparison with the calculated total single SiCl$_3$ cross section using the DM formalism. As can be seen, the agreement between measured and calculated total single ionization cross sections is very good in terms of the cross section shape, but less satisfactory in terms of the absolute cross section magnitude. The calculated cross section exceeds the measured cross section at all impact energies above about 30 eV. The discrepancy is largest, about 20% in the region of the cross section maximum. Note that the overall uncertainty in the experimentally determined cross section is about ±17% at 70 eV and is given by the sum of the uncertainties in the relative partial cross sections (added in quadrature) and the uncertainty in the absolute cross section calibration. The level of agreement between calculated and experimentally determined SiCl$_3$ cross section is similar to what was found for other polyatomic molecules (see e.g., Deutsch et al. [2]). We note, however, that by contrast the agreement between calculated and experimentally determined (maximum) cross section for SiCl$_4$ [6] and for SiCl$_2$ and SiCl [15] was better than 5%.

4. Conclusions
Two recent improvements to the fast-beam apparatus that has been used extensively for ionization cross section measurements for the past 15 years in our group have been described, a new high-current electron emitter and a position-sensitive MCP detector. Experiments using well-established ionization cross sections in conjunction with extensive ion trajectory simulations were carried out to test the satisfactory performance of the modified fast-neutral-beam apparatus. We report measured absolute partial cross sections for the formation of all singly charged ions following electron impact on SiCl$_3$ from threshold to 200 eV using the modified apparatus. The maximum cross section values range from 1.5 – 4 x 10$^{-20}$ m$^2$. Several partial cross section curves show a prominent structure around 30 eV, which may be indicative of the presence of indirect ionization channels such as autoionization. A comparison between the experimentally determined total single SiCl$_3$ cross section and a calculated cross section using the DM formalism shows that the calculated cross section lies systematically above the experimental data. The discrepancy of 20% is similar to what was found previously for other polyatomic molecules, but is larger than the excellent agreement that was found for SiCl$_4$, SiCl$_2$, and SiCl.
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Table 1. Absolute partial and total single electron impact ionization cross sections for SiCl$_3$ as a function of electron energy from threshold to 200 eV.

| Electron Energy (eV) | SiCl$_3^+$ | SiCl$_2^+$ | SiCl$^+$ | Si$^+$ | Cl$^+$ | Total (single) |
|---------------------|------------|------------|----------|--------|--------|----------------|
| 12                  | --         | --         | --       | --     | --     | --             |
| 14                  | 0.01       | 0.0001     | --       | --     | --     | 0.0101         |
| 16                  | 0.15       | 0.30       | --       | --     | --     | 0.45           |
| 18                  | 0.35       | 0.58       | 0.20     | 0.004  | --     | 1.13           |
| 20                  | 0.60       | 0.78       | 0.58     | 0.10   | 0.07   | 2.13           |
| 22                  | 0.87       | 1.01       | 0.91     | 0.17   | 0.27   | 3.22           |
| 24                  | 1.07       | 1.18       | 1.37     | 0.31   | 0.54   | 4.472          |
| 26                  | 1.24       | 1.38       | 1.70     | 0.39   | 0.82   | 5.53           |
| 28                  | 1.47       | 1.53       | 1.90     | 0.46   | 1.04   | 6.40           |
| 30                  | 1.63       | 1.65       | 2.17     | 0.58   | 1.24   | 7.27           |
| 32                  | 1.75       | 1.78       | 2.41     | 0.66   | 1.48   | 8.07           |
| 34                  | 1.86       | 1.87       | 2.73     | 0.79   | 1.62   | 8.88           |
| 36                  | 1.92       | 1.93       | 2.95     | 0.86   | 1.79   | 9.46           |
| 38                  | 2.00       | 1.99       | 3.21     | 0.98   | 2.00   | 10.17          |
| 40                  | 2.05       | 2.04       | 3.32     | 1.053  | 2.19   | 10.64          |
| 42                  | 2.07       | 2.08       | 3.431    | 1.11   | 2.34   | 11.03          |
| 44                  | 2.11       | 2.11       | 3.48     | 1.15   | 2.51   | 11.37          |
| 46                  | 2.13       | 2.16       | 3.53     | 1.20   | 2.64   | 11.65          |
| 48                  | 2.14       | 2.19       | 3.56     | 1.25   | 2.79   | 11.94          |
| 50                  | 2.13       | 2.23       | 3.64     | 1.28   | 2.90   | 12.19          |
| 52                  | 2.12       | 2.28       | 3.68     | 1.31   | 3.07   | 12.47          |
| 54                  | 2.13       | 2.30       | 3.71     | 1.35   | 3.18   | 12.68          |
| 56                  | 2.12       | 2.33       | 3.71     | 1.38   | 3.30   | 12.84          |
| 58                  | 2.12       | 2.35       | 3.70     | 1.41   | 3.38   | 12.96          |
| 60                  | 2.12       | 2.36       | 3.68     | 1.44   | 3.44   | 13.05          |
| 62                  | 2.13       | 2.37       | 3.66     | 1.46   | 3.50   | 13.13          |
| 64                  | 2.12       | 2.38       | 3.66     | 1.47   | 3.54   | 13.17          |
| 66                  | 2.12       | 2.38       | 3.63     | 1.48   | 3.58   | 13.19          |
| 68                  | 2.13       | 2.38       | 3.62     | 1.49   | 3.58   | 13.21          |
| 70                  | 2.14       | 2.39       | 3.60     | 1.50   | 3.60   | 13.22          |
| 80                  | 2.14       | 2.39       | 3.53     | 1.51   | 3.59   | 13.16          |
| 90                  | 2.11       | 2.36       | 3.46     | 1.50   | 3.53   | 12.97          |
| 100                 | 2.08       | 2.33       | 3.35     | 1.49   | 3.43   | 12.69          |
| 110                 | 2.03       | 2.28       | 3.28     | 1.47   | 3.33   | 12.40          |
| 120                 | 1.99       | 2.21       | 3.19     | 1.45   | 3.19   | 12.04          |
| 130                 | 1.95       | 2.15       | 3.11     | 1.43   | 3.07   | 11.71          |
| 140                 | 1.91       | 2.08       | 3.04     | 1.39   | 2.94   | 11.36          |
| 160                 | 1.82       | 1.95       | 2.88     | 1.33   | 2.67   | 10.65          |
| 180                 | 1.71       | 1.81       | 2.72     | 1.28   | 2.41   | 9.95           |
| 200                 | 1.61       | 1.67       | 2.56     | 1.21   | 2.14   | 9.19           |