Effect of molecular orientation on electron impact ionization and fragmentation

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Relative ionization cross sections have been determined for the production of the molecular ion CH_3Cl^+ and the fragmentation product CH_3^+ from the 200 eV electron impact ionization of spatially oriented CH_3Cl molecules in a cross beam experiment. The ionization cross section for CH_3Cl^+ formation is higher at the positive end, or CH_3 end, of the molecule while the cross section for formation of the CH_3^+ fragmentation product is independent of spatial orientation, within experimental uncertainty. © *1994 American Institute of Physics.*

The effect of molecular orientation on chemical reactivity,[1] chemiluminescence,[2] photoionization,[3] Rydberg molecule formation[4] and, more recently, electron scattering[5] have been studied. The orientation asymmetry in most systems investigated has been significant, despite the use of oriented beams characterized by a distribution of spatial orientation.[1] In this communication we report preliminary results of an investigation into the effect of molecular orientation on electron impact ionization and fragmentation with results for the prolate symmetric top molecule CH_3Cl. We can report a significant asymmetry in the total ionization cross section for CH_3Cl. Using a mass insensitive detector the cross section for ionization at the CH_3 end of the molecule is 2.3 times higher than for ionization at the Cl end. This is close to the ratio of 2.6 found for the formation of the molecular ion, CH_3Cl^+ using a mass filter detector. A ratio close to 1.0 is measured for the CH_3^+ fragment, i.e., the cross-section for the formation of the CH_3^+ fragmentation product is independent of electron–molecule orientation along the molecular axis, within experimental uncertainty.

Electron impact ionization was first used in mass spectrometry by Dempster[6] in 1918 in an attempt to generate reproducible mass spectra for use in analytical chemistry, an application of mass spectrometry suggested by J. J. Thomson[7] in 1913. Despite 80 years of experience in electron impact ionization, absolute ionization cross sections cannot be routinely measured, fragmentation patterns are not always predictable using chemical intuition, and theoretical models of electron impact ionization fail to deliver either acceptable cross sections or fragmentation patterns (mass spectra). The study of electron impact ionization of spatially oriented molecules has been initiated in order to gain a deeper insight into the electron impact ionization process and to provide data to test theoretical models.

Experiments are carried out using crossed beams of spatially oriented CH_3Cl and near-monochromatic electrons, see Fig. 1. The molecular beam is produced by the expansion of CH_3Cl at 288 K from a stagnation pressure of 1200 Torr through a 70 μm nozzle in a pulsed General Valve Series 9 electromagnetic valve with an open time of 1.2 ms at a 10 Hz repetition rate. The supersonic beam enters a buffer chamber through a 1.0 mm entrance skimmer and exits through a 3.6 mm skimmer that serves as the entrance orifice to a 0.833 m long hexapole filter with an inscribed radius of 5.5 mm (a

second hexapole with an inscribed radius of 7.5 mm was used in some experiments). The inhomogeneous hexapole electric field (typically 10^6 V m^{-1}) transmits a focused beam of upper Stark-state selected CH_3Cl molecules through a 8.0 mm diameter exit aperture into a weak homogeneous orienting electric field (2000 V m^{-1}) maintained between parallel field plates 200 mm long and 10 mm apart. The molecular beam is detected on axis by a Vacuum Generators SXP300 quadrupole mass filter which is also used as a mass sensitive ion detector after replacement of the ion source and lens with an Einzel lens assembly. An Amptektron Model 501-L low energy ion detector, which can be rotated about the electron beam–molecular beam intersection, is used for measuring beam profiles, alignment of the electron beam with respect to the molecular beam and as a mass insensitive detector for low energy ion counting. Deconvolution of the CH_3Cl arrival time distribution gave a mean flow velocity of 543 m s^{-1} and a translational temperature of 29 K.[8] The on-axis quadrupole produced a mass spectrum dominated by the molecular ion, CH_3Cl^+ (100), with CH_3^+(30) as the only other significant ion signal.

The electron beam is generated by an electron gun housed in a stainless steel chamber protruding into the scattering chamber. The gun has been designed to deliver pencil beams of 2–3 mm diameter over the energy range 20–300
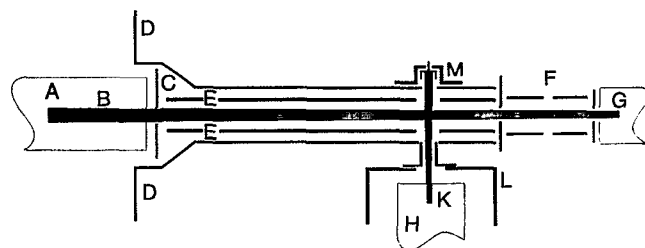
FIG. 1. Diagram of the beam crossing region: A—hexapole; B—molecular beam; C—hexapole exit aperture; D—shielding plates; E—homogeneous field plates; F—ion guiding lens; G—quadrupole mass filter; H—electron gun; K—electron beam; L—shielded electron gun chamber; M—shielded electron collector. Mesh shields at ground potential below the field plates and a copper shield at ground potential held at liquid nitrogen temperature above the field plates are not shown.

eV ($\lambda = 2.7$ to 0.7 Å) with an electron energy distribution of <0.2 eV FWHM. The electron beam is directed through a cylindrical snout which penetrates from the end of the chamber to the nearside homogeneous field plate. It passes through 10.0 mm diam apertures in the field plates and enters a shielded Faraday cup coated with colloidal graphite (aquadag). The snout, homogeneous, field plates, top and bottom shielding plates and shielding grids are all coated with colloidal graphite. In these experiments the electron beam was operated in continuous mode with a beam current of <300 nA at 200 eV (0.87 Å) to minimize space charge effects. The field plates were energized at ± 20 V/gnd, and gnd/± 20 V combinations for field reversal and hence orientation reversal.

Collisions involving neutral reactants are unaffected by the presence of a uniform electric field in the crossing region. This is not the case where charged particles are involved. Ions formed between the homogeneous field plates would be accelerated toward the field plate of opposite polarity and be discharged. The K^+ ion products produced in collisions between fast K atoms and oriented symmetric top molecules[1(d)] were collected using channeltrons protruding through the field plates. This approach cannot be used for electron (or ion) impact where the proximity of the channeltron cones to the beam crossing would shatter the electron (ion) beam integrity and the geometry of the beam crossing volume. In these experiments one of the homogeneous field plates is maintained at ground potential and the second is set at ± 20 V. Molecules are oriented such that the negative end of the dipole points toward the ground field plate when the configuration is gnd/+20 V and toward the energized field plate when the configuration is set to gnd/-20 V. In an experiment, the energized field plate is dropped to <0.1 V from ground (polarity preserved) in <100 ns as the leading edge of the gas pulse reaches the electron beam. Typically, the segment of oriented beam between the homogeneous field plates at the time the field is collapsed corresponds to 300 μs in flight time. Ions produced by the electron impact ionization of this 300 μs segment of spatially oriented beam are gated at a detector located 25 mm downstream on the molecular beam axis. A second gate of equal width intercepts ions produced from the electron impact ionization of a second 300 μs slice from the trailing segment of the gas pulse which did not sample the orienting field. This is repeated with the hexapole high voltage switched off and the rods set to ground potential, i.e., in the absence of the inhomogeneous field in the hexapole. This mode of operation assumes the integrity of the spatial orientation following collapse of the orienting field, at least on the μs time scale. Experiments designed to specifically explore this have not been performed, although the observation of reproducible orientation effects for symmetric top molecules and the absence of an effect for argon and the spherically symmetric molecule SF_6 under identical experimental conditions lends support to this assumption, at least qualitatively. The results for CH_3Cl are independent of the field plate polarity used, i.e., +20 V/gnd gives the same results as gnd/-20 V and gnd/+20 V gives the same result as -20 V/gnd.

The raw signals measured in the experiment are: (i) ion

TABLE I. Steric factors and steric ratios for 200 eV electron impact ionization of CH_3Cl, Ar, and SF_6 using a quadrupole mass filter detector.

System	Ion	$G = (S_- - S_+)/(S_- + S_+)$	S_+/S_-
CH_3Cl	CH_3Cl^+	-0.42 ± 0.12	2.58 ± 0.81
	CH_3^+	-0.01 ± 0.14	1.07 ± 0.36
Ar	Ar^+	~0	~1
SF_6	SF_6^+	~0	~1

counts, hexapole on, homo field on, for the +end of the molecule, $S_{h\nu,+}$; (ii) ion counts, hexapole off, homo field on, for the +end of the molecule, $S_{0,+}$; (iii) ion counts, hexapole on, homo field on, for the $-$end of the molecule, $S_{h\nu,-}$; and (iv) ion counts, hexapole off, homo field on, for the $-$end of the molecule, $S_{0,-}$.

S_+ is then defined $S_{h\nu,+} - S_{0,+}$ and S_- is given by $S_{h\nu,-} - S_{0,-}$. The ratio, $S_{0,+}/S_{0,-}$, should ideally be unity but in practice it degrades from unity with time according to the condition of the electron gun and the elements making up the beam crossing region. The steric effect is expressed either as the steric ratio, S_+/S_-, which is equivalent to the ratio of the corrected signal for ionization at the positive end of the dipole to the signal for ionization at the negative end of the dipole, or as the steric factor $G = (S_- - S_+)/(S_+ + S_-)$ where $-1 \leq G \leq 1$. Equal ionization probability at both ends of the molecule would give $G = 0$, preferential ionization at the positive end of the molecule would give a negative value for G and preference at the negative end a positive value for G.

Ions are counted over a 300 s period at a 10 Hz repetition rate with 300 μs gates. For CH_3Cl, total ion counts are around 2000 for S_+ and 600 for S_-. The ion signals with hexapole on and hexapole off, with the homogeneous field plates grounded, are typically around 1000 and 350 counts, respectively, resulting from a threefold signal enhancement for a CH_3Cl beam through the hexapole inhomogeneous field. The data for CH_3Cl shown in Table I represent the average of 35 repeated determinations involving numerous disassembly—cleaning—assembly cycles of the machine, two different hexapoles, and experiments in which the energized electrode was both positive and negative. The ion counts for the spherically symmetric species Ar and SF_6 are independent of the hexapole high voltage and the homogeneous field conditions and since S_+ and S_- are small and almost equal for Ar and SF_6 under the same conditions as the CH_3Cl experiments, the steric ratios and factors are shown in the table as ~0 and ~1, respectively.

These experiments have shown that electron impact ionization is more efficient at the positive end of the CH_3Cl molecule for molecular ion formation and independent of orientation for the fragment ion CH_3^+. Although the distribution of orientations within the molecular beam is broad, the positive end of all molecules point toward the positive field plate and the negative end toward the negative field plate. Irrespective of the polarity on the field plates, the beam includes a substantial fraction of molecules which can best be described as sideways oriented.[1] In the case of CH_3^+ formation, a G factor of close to zero may point to the domination of sideways orientation in the fragmentation channel. Mol-

ecules of the general series CH_3X and CF_3X are currently under investigation, the emergence of a coherent pattern will facilitate the construction of a theoretical model.

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