Effect of Molecular Orientation on Indirect Ionization by Electron Impact of CH_3Cl in the $|111\rangle$ Eigenstate

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A neutral beam of oriented CH_3Cl molecules in the $|111\rangle$ rotational eigenstate is crossed with a 700-eV beam of electrons inside a uniform electrostatic field of about 20 V/cm. Ions formed directly upon impact are collected by the uniform field electrodes, but some CH_3Cl^+ ions are observed in a mass spectrometer with its ionizer turned off. These "indirect" CH_3Cl^+ ions are forward scattered, undeflected by the uniform field, and must therefore be neutral during the flight out of the uniform field. This strongly suggests that the precursor of these ions is a highly excited long-lived molecule, CH_3Cl^{**}. The "indirect" CH_3Cl^+ ion signal is greater when the electron attacks at the Cl end of the molecule.

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Considerable attention has been directed recently to studies of steric effects on reaction dynamics [1,2]. In photoionization, Kaesdorf, Schonhense, and Heinzmann have observed the stereoanisotropic ejection of photoelectrons from oriented CH_3I molecules [3]. In collisional ionization of fast K atoms with oriented CH_3I and CF_3I molecules, the formation of K^+ ions was enhanced when the K atom attacked at the I end [4]. A question arising from these studies is whether or not the electron attack leading to the reaction is dependent on the orientation of the target molecule.

Although elastic scattering of fast electrons with oriented CH_3I has been reported [5], no studies have been reported on reactive processes of electrons with oriented molecules. The basic difficulties with experiments involving charged particles are the unavoidable electrostatic interferences from the orienting field. The primary electron beam can be disturbed by the orienting field and any product ions are easily collected by the field [6]. For this latter reason, it is difficult to investigate steric effects of the direct process of ionization, but it might be possible to investigate indirect processes of ionization, in which excited neutral species are expected to be produced in the collision. This study aims at experimental clarification of steric effects on such indirect processes of ionization using oriented molecules.

Figure 1 illustrates the experimental apparatus employed in this study of the impact of electrons with oriented CH_3Cl molecules. The formation of the oriented molecules is described in detail elsewhere [7]. Briefly, a 3-ms pulsed beam of 1% CH_3Cl seeded with helium emerges from a supersonic pulse valve (*A*) at 850 Torr. The $|111\rangle$ eigenstate of the CH_3Cl molecule was selected and focused by a 2-m electrostatic hexapole field (*C*) with rod voltage $V_0=5$ kV. Here $|111\rangle$ is a set of symmetric top quantum numbers J, K, and M [8]. The 50-cm guiding field (*D*) provides an adiabatic transition from the hexapole field to the orienting field (*E*). The molecules are finally oriented in this orienting field, with electrons impacting on either the Cl end or the CH_3 end of the molecule. Random orientation of the molecules is achieved by reducing the field strength in the guiding field. The electron beam (*e* beam), with a nominal energy of 700 eV, a 40-mm-diam beam width, and total current of ca. 50 μA, was monitored 30 cm downstream on a phosphorescent screen (*F*).

The beam intensity of the primary CH_3Cl beam was measured with the mass spectrometer (*G*) tuned to the CH_3Cl^+ peak. The result is shown as the shaded area in Fig. 2, where the resolved peak in the focusing curve is due to the $|111\rangle$ state of CH_3Cl [7]. In these measurements, the molecules were ionized by electron bombardment in the mass spectrometer ionizer. The *e* beam was not running under these conditions.

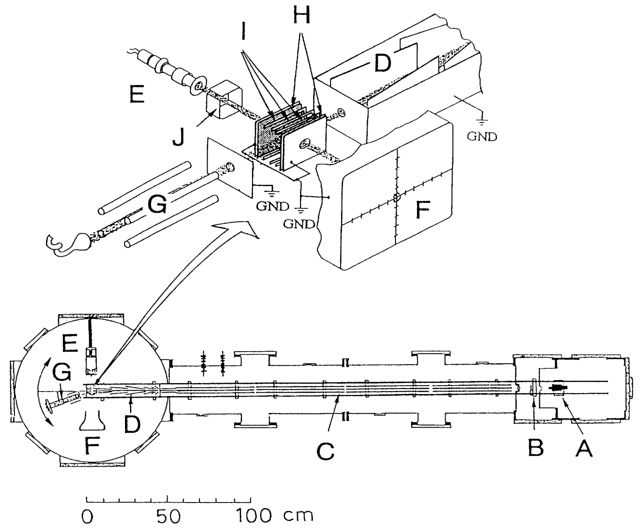

FIG. 1. Schematic view of the apparatus for electron impact with the oriented molecule. *A*, pulsed valve for CH_3Cl; *B*, beam stop; *C*, electrostatic hexapole field; *D*, guiding field; *E*, electron gun; *F*, phosphorescent screen; *G*, quadrupole mass spectrometer; *H*, orienting field; *I*, field uniformers; *J*, electron beam deflectors.

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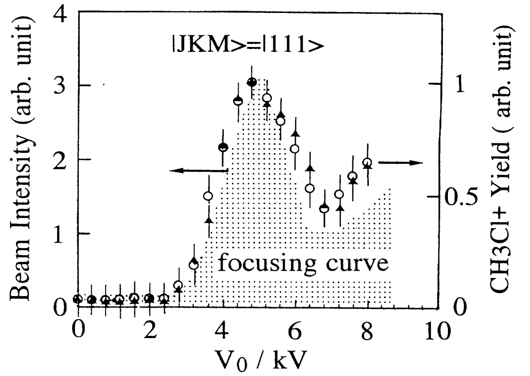

FIG. 2. Focusing curve of the primary CH_3Cl beam shown as the shaded area. The entrance slit of the mass filter was 1.4 mm. V_0 dependence of the CH_3Cl^+ yield at $\theta = 0$: The circles and triangles represent the crossed beam signals of CH_3Cl^+ for a typical two runs with the *e* beam and without mass spectrometer ionizer. The entrance slit of the mass spectrometer was 4 mm.

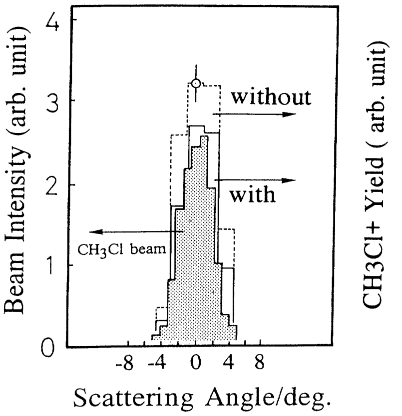

FIG. 3. Angular distributions of CH_3Cl^+ measured with and without retarding potential of the mass spectrometer to reject incoming ions. The angular distribution of the primary CH_3Cl beam is shown for comparison.

CH_3Cl^+ ions are also detected with the *e* beam on and the mass spectrometer ionizer off. Ions formed directly in the molecule-electron collision are collected on the uniform field electrodes (H), so that these "indirect" ions must arise from neutral precursors. The indirect ion signals depend linearly on the CH_3Cl beam intensity as shown by the circles (run 1) and triangles (run 2) in Fig. 2. Although the intensity of the crossed beam signals was much smaller than the original focusing curve, the normalized points of the crossed beam signals agree nicely with the focusing curve.

Figure 3 shows the angular distributions of the indirect ions. These crossed beam signals were observed by the mass spectrometer without the ionizer. A fine-mesh retarding electrode biased at +13 V to repel ions was placed at the entrance of the mass spectrometer. This retarding electrode biased was turned off and on in order to determine if the indirect ions were ions prior to entering the mass spectrometer. The angular distribution marked "with" in the figure was obtained with the retarding electrode to repel ions, and the distribution labeled "without" was obtained with the electrode grounded. The angular distribution of the primary CH_3Cl beam (obtained with the *e* beam off and the mass spectrometer ionizer on) is shown for comparison. The angular distributions of the indirect ions with and without the retarding electrode give the same pattern of forward scattering which is almost identical (after normalization) to the distribution of the primary CH_3Cl beam. It is thus concluded that the indirect ions, which are detached in the mass spectrometer as CH_3Cl^+, enter the mass spectrometer as neutral species of mass equal to that of CH_3Cl and with an angular distribution essentially the same as the primary molecular beam. These neutral species are formed in the *e*-beam–molecular-beam collision zone and must have a relatively long lifetime (≈ 60 μs) to reach the detector as neutrals. This neutral product must be excited to ionize in the mass spectrometer in the absence of the mass spectrometer ionizer. A highly excited long-lived CH_3Cl could be a precursor to the CH_3Cl^+ ion and is referred to as CH_3Cl^{**} hereafter.

The CH_3Cl beam is seeded in He, and metastable He* can be formed in the *e* beam collision, travel with the primary beam into the mass spectrometer, and then produce CH_3Cl^+ by Penning ionization. This possibility can be ruled out due to the fact that CH_3Cl^+ was observed even with pure CH_3Cl beams containing no He [9]. Secondary electrons, which are accidentally produced by the primary electron beam at electrode surfaces, might produce CH_3Cl^{**}, although it was found that indirect ions were observed only when the *e* beam and the molecular beam cross one another perfectly in the orienting field. The indirect ions are thus formed in the *e*-beam–molecular-beam collision zone.

Figure 4 shows the effect of molecular orientation on the angular distributions of indirect CH_3Cl^+. The orientation can be changed for these state-selected molecules by reversing the polarity of the uniform field: For positive polarity of the orienting field, the electron is incident on the Cl end of the molecule, and for negative polarity, the electron is incident on the CH_3 end. Each point represents the crossed beam signal count accumulated for 3600 molecular beam pulses. These distributions all show forward scattering similar to that of Fig. 3. The form of the angular distribution of the indirect ions is thus independent not only of the strength of the uniform field E but also its polarity, and again it shows that the precursors to the indirect ions must be neutral CH_3Cl^{**}.

The lifetime of CH_3Cl^{**} observed here is estimated to be longer than ≈ 60 μs. Lifetimes of typical high-Rydberg molecules are known to be much shorter [10]. But recently, Tarr, Schiavone, and Freund have observed

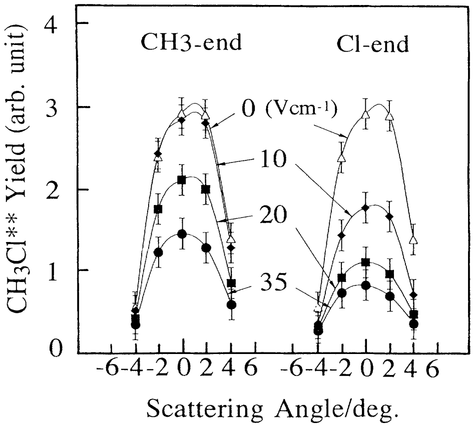

FIG. 4. Angular distributions of CH_3Cl^+ as functions of the strength of the orienting field and its polarity which determines the molecular orientation on electron impact.

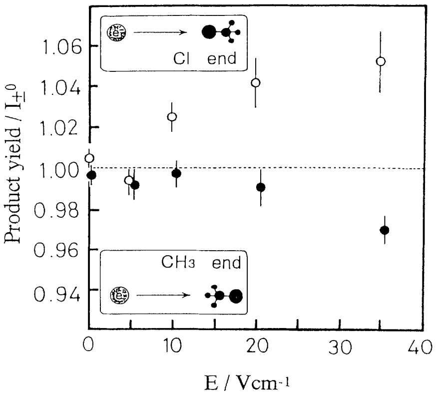

FIG. 5. E dependencies of I^0_+ for the Cl-end and I^0_- for the CH_3-end orientations.

long-lived high-Rydberg molecules in the electron impact of H_2, CO, etc., with lifetimes on the order of 100 μs [11,12]. The CH_3Cl^{**} formed in the present study could be such a long-lived high-Rydberg molecule, but further evidence is necessary to substantiate this assertion.

The main objective of the present study was the experimental elucidation of the steric effect on the formation of indirect CH_3Cl^+. As seen in Fig. 4, the yield of indirect CH_3Cl^+ decreases considerably with E. This reduction is believed to be partly a result of changes in the effective intensity of the e beam in the orienting field, although the electrodes of the field are shielded carefully to avoid such effects. It is also possible that the product CH_3Cl^{**} is ionized in the uniform field (and is swept out of the detected beam) as the electric field strength in the uniform field is raised.

In order to decouple the effect of molecular orientation from other effects, we probed the effect of the guiding field (D) on the signal. The hexapole field selects molecules in specific $|JKM\rangle$ states, and the guiding field is present to ensure that the electric field changes smoothly from the strongly inhomogeneous field of the hexapole to the uniform field of the collision region. This ensures that the state-selected molecules make an adiabatic transition into the collision region and that J, K, and M are maintained. If the guiding field is eliminated, the state-selected molecules do not make adiabatic transitions into the uniform field, and the orientation becomes scrambled. Thus by turning the guiding field off, we can destroy the orientation of the molecules without altering the beam intensity. The effect of orientation can now be obtained by normalizing the signals to the signal obtained with the guiding field off: For positive polarity of the orienting field,

$$I^0_+(E) = I_+(E,\text{on})/I_+(E,\text{off}) ; \tag{1}$$

for negative polarity of the orienting field,

$$I^0_-(E) = I_-(E,\text{on})/I_-(E,\text{off}) , \tag{2}$$

where $I_+(E,\text{on})$ represents the sum over the angular distributions in Fig. 4 for positive polarity of the uniform field with field strength E, and the guiding field on. Other terms are similarly defined. For positive polarity of the orienting field, the electrode nearest the electron gun is held negative, corresponding to the electron attack at the Cl end of the molecule (Cl-end orientation). Negative polarity corresponds to the close electrode held positive and to the electron attack at the CH_3 end of the molecule (CH_3-end orientation). The terms "on" and "off" in parentheses indicate the condition of the guiding field. The molecules are oriented with the guiding field on and randomized when the guiding field is off.

Figure 5 shows the behavior of the I^0_+ and I^0_- thus obtained. At zero orienting field, no difference was observed between I^0_+ and I^0_-, because the molecular orientation is randomized when the orienting field is zero. As E is increased, I^0_+ and I^0_- begin to show opposite behavior due to the different orientation of the molecule. The normalized yields of CH_3Cl^+ for the Cl-end orientation clearly give larger values than those for the CH_3-end orientation and explicitly show the effect of molecular orientation in the electron impact collision.

As mentioned, He metastable atoms were observed under the same crossed beam conditions, but no steric effect is observed when pure He was employed in place of the 1% CH_3Cl/He mixture of the molecular beam. For the pure He beam, both I^0_+ and I^0_- are 1, even with the orienting field on. As previously described, the indirect ions are observed in the absence of He, so both the formation and steric effect for the production of CH_3Cl^+ depend on the CH_3Cl molecule itself.

It is thus concluded that the effect of molecular orientation on indirect ionization of CH_3Cl by electron impact can be observed in the present study. Further studies for clarifying causes of this preference for ionization on impact at the Cl end of the molecule would be very important from the theoretical and experimental points of view [13,14].

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