Surface Aligned Ion-Molecule Reaction: Direct Observation of Initial and Final Ion Momenta

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An ion-molecule reaction has been studied by measuring the momentum of both the reactant and the product ions. This is carried out in an ordered molecular film of CD_3I where electron stimulated desorption causes the reaction $CD_3^+ + CD_3I \rightarrow C_2D_5^+ + DI$. The close similarity of the normal momentum of CD_3^+ and $C_2D_5^+$ indicates that a sticky collision occurs in which, to within 10%, the momentum of the reactant ion is transferred to the momentum of the product ion. The measurement represents the first use of molecularly aligned species to study momentum effects in an ion-molecule reaction.

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Ion-molecule reactions are of fundamental and practical importance in many areas, such as atmospheric chemistry, astrophysics, and radiation chemistry [1]. Various experimental methods have been used to investigate specific ion-molecule reactions in the gas phase. However, in condensed layers, one can expect dynamical differences in the electronically driven dissociative behavior of molecules compared to similar processes involving gas-phase molecules [2,3]. These effects, due to molecular alignment, can lead to surface-aligned photochemistry where directed collisional effects between a photo-fragment and a neighbor molecule or a substrate atom can guide the dynamics of reaction [3,4].

It is well known that the impact of electrons on adsorbed molecules causes the desorption of ionic and neutral fragment species. This electron stimulated desorption (ESD) process induced by electronic transitions to dissociative states has been studied extensively since the 1960s [5]. For ordered overlayers on single crystal surfaces, positive and negative ionic species are often ejected in sharp beams whose direction is related closely to the chemical bond directions being ruptured by the ionization process [5]. There are a few studies of electron stimulated desorption from condensed layers [6–8] in which desorbing ions can interact and react with neighbor molecules during their escape from the surface.

In this Letter, we report the observation of a surface-aligned ion-molecule reaction product, the $C_2D_5^+$ ion. The $C_2D_5^+$ ion is produced by reaction of ESD-produced CD_3^+ ions in an ordered overlayer of CD_3I contained on a Cu(110) single crystal surface (covered with adsorbed iodine), which acts as a passive template to orient the CD_3I molecules in the multilayer. Although ion-molecule reactions on surfaces have been proposed [9–11], we believe that this is the first direct observation of such a process originating from electron stimulated desorption from surface-aligned molecules, where the momentum of ejection of the reactant ion is measured along with that of the product ion.

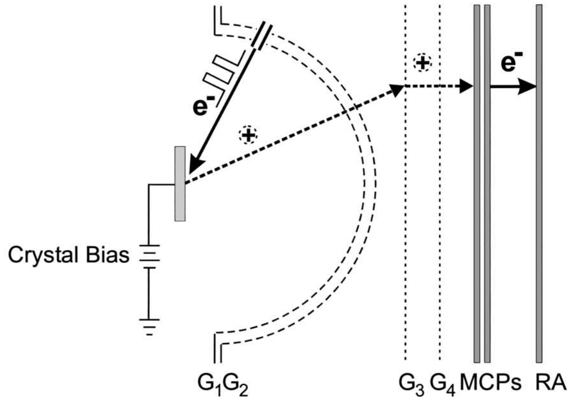
The experiments described in this paper were performed in an ultrahigh vacuum chamber with a base pressure below 1×10^{-10} mbar. The Cu single crystal, a cylindrical disk 3 mm thick, with a diameter of 10 mm, was oriented to within $\pm 0.22°$ of the $\langle 110 \rangle$ plane. The atomically clean crystal could be cooled to 80 K using liquid nitrogen, and heated to 900 K by resistive heating.

The copper crystal was exposed to CD_3I (99.5% D atom, Aldrich) at 80 K using an absolutely calibrated microcapillary array beam doser [12], which produced uniform surface layers while maintaining low background pressure during adsorption.

The micro channel plate (MCP) spatial detector of the ESDIAD (electron stimulated desorption ion angular distribution) apparatus is located behind a system of spherical and planar grids as shown in Fig. 1(a), and a pulsed electron beam (180 eV, pulse width $= 50$ ns) generates desorbing positive ions from adsorbed molecules. For each ion pattern only 2×10^{12} electrons/cm^2 are employed. The positive ion ejection directions and the time-of-flight (TOF) to a resistive anode located behind the MCPs are recorded simultaneously [13]. The ion patterns shown here, composed of about 1×10^6 ions, have been compressed by means of a $+30$ V crystal bias and ion desorption angles are corrected for this effect [14]. For ion momenta studies, TOF measurements were made with a change of crystal bias from $+30$ V to $+70$ V and an extrapolation to zero bias voltage was made. The TOF-ESDIAD apparatus was also used as a low energy electron diffraction (LEED) apparatus to determine the azimuthal orientation of the Cu(110) crystal in laboratory coordinates and to perform LEED measurements for observing the ordered structure of the adsorbate overlayer.

Adsorbed CD_3I molecules on a clean Cu(110) surface thermally decompose to form an adsorbed methyl group and chemisorbed iodine near or above 150 K. The surface methyl group decomposes at a temperature of ~450 K producing methane, ethene, and ethane [15]. Adsorbed iodine remains on the copper surface up to 800 K. The initial accumulation of iodine on the Cu(110) surface by means of the decomposition of CD_3I makes the surface passivated for the decomposition of additionally adsorbed CD_3I. LEED measurements for the Cu(110)-iodine

a) TOF-ESDIAD APPARATUS



b) TOF-SPECTRUM FROM MULTILAYER CD_3I

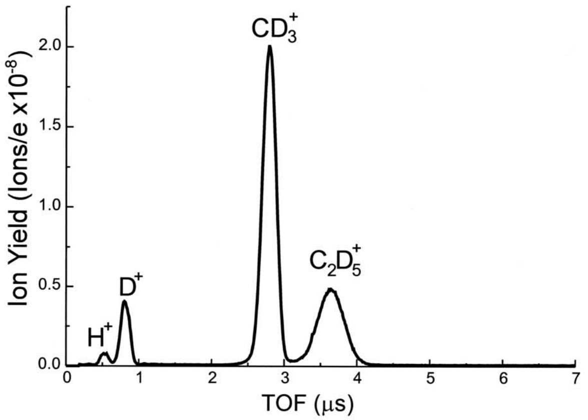


FIG. 1. (a) Schematic of the TOF-ESDIAD experimental apparatus. (b) Time-of-flight distribution for desorbing positive ions from a condensed layer of CD_3I on the Cu(110)-iodine surface.

surface indicate that the iodine overlayer exhibits a $c(2 \times 2)$ two-dimensional periodicity at full coverage of iodine. This $c(2 \times 2)$ overlayer does not change by additional exposure to CD_3I molecules followed by heating to 800 K. On the Cu(110)-I surface, CD_3I adsorbs molecularly and desorbs from the monolayer at a temperature of 140 K. The ordered iodine layer forms a template for the adsorption of an ordered multilayer of CD_3I molecules.

An example of the time-of-flight distribution from a CD_3I multilayer on the Cu(110)-iodine template is shown in Fig. 1(b). Four distinguishable ion peaks, which have peak maxima at 0.5, 0.8, 2.7, and 3.6 μs, were observed for a multilayer of CD_3I. The desorbing species at 0.5 and 0.8 μs were assigned as H^+ (from an impurity) and D^+ ions by comparison with the time-of-flight of H^+ and D^+ ions from other sources. The mass/charge ratio of the observed ions at longer flight times was measured by the dependence of flight time on the accelerating voltage, The measured ratio of mass to charge for ions at flight times of 2.7 and 3.6 μs are 18 ± 2 amu/e and 31 ± 4 amu/e, respectively. Within the error limits, we assign the ions as CD_3^+ (18 amu/e) and $C_2D_5^+$ (34 amu/e). The known gas-phase thermodynamically favorable ion-molecule reaction, $CH_3^+ + CH_3I \rightarrow C_2H_5^+ + HI$ ($\Delta H_r = -1.7$ eV) [1,16] confirms the assignment of the two heavy ions as CD_3^+ and $C_2D_5^+$, respectively.

The coverage dependency of the ion yield for D^+, CD_3^+, and $C_2D_5^+$ observed from CD_3I on the Cu(110)-I surface from submonolayer to multilayer coverages is shown in Fig. 2. Only D^+ ion desorption from the CD_3I submonolayer was observed. The D^+ ion emission increases up to the completion of the monolayer. At coverages above one monolayer, two additional ion fragments, CD_3^+ and $C_2D_5^+$ are observed with closely correlated yields. The emission of these ions from CD_3I is first observed at the beginning of the second CD_3I layer. The onset of second-layer formation is confirmed by the appearance of a new desorption peak at 120 K in temperature programmed desorption experiments and occurs when the first monolayer is 70% complete (data not shown). The yield of CD_3^+ and $C_2D_5^+$ ions increases sharply as the CD_3I exposure increases and then the ion yield/electron becomes constant. The ion yield ratio, $CD_3^+/C_2D_5^+ = 0.42$, is constant

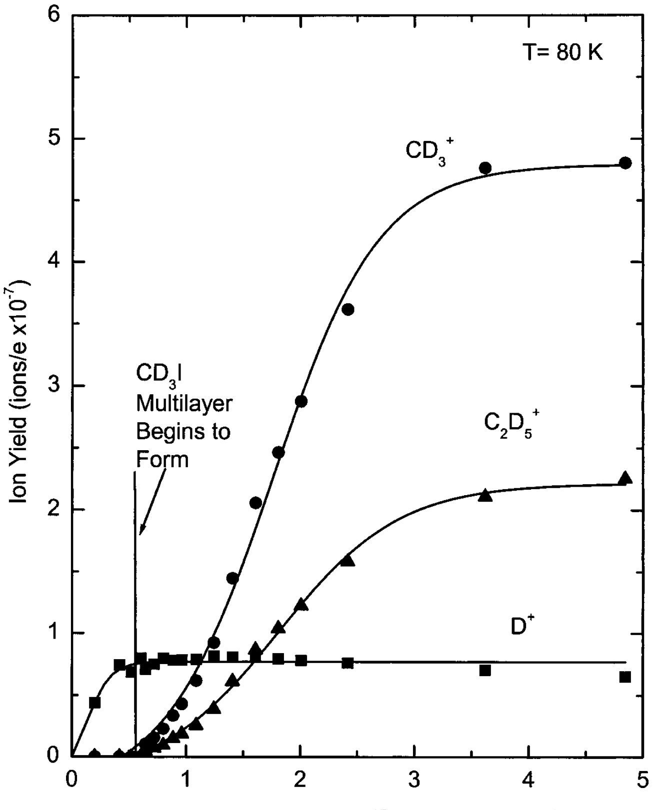


FIG. 2. Ion yield of D^+, CD_3^+, and $C_2D_5^+$ species from CD_3I on the Cu(110)-iodine surface as exposure increases.

at all exposures as the multilayer grows, indicating that differential ion-neutralization effects from electron transfer from the metal surface are unimportant in the second-layer CD_3I.

The angular distribution patterns of D^+, CD_3^+, and $C_2D_5^+$ ions from the CD_3I multilayer adsorbed on the Cu(110)-I surface are shown in Fig. 3. A broad one-beam ESDIAD pattern is seen for D^+ at all coverages from submonolayer to multilayer. Both the CD_3^+ and $C_2D_5^+$ ions exhibit sharp two-beam ESDIAD patterns which are accurately oriented parallel to the vertical plane parallel to the $\langle 1\bar{1}0\rangle$ azimuth of the underlying crystal substrate. The two symmetrically oriented CD_3^+ emission directions are closely similar to the two preferred directions of the C-I bonds in the CD_3I multilayer as has been observed in many ESDIAD studies of oriented adsorbed molecules on single crystal surfaces [5]. The measured angles from the normal and the initial kinetic energies were for CD_3^+ [13° ± 1°; 2.1 ± 0.2 eV] and for $C_2D_5^+$ [18° ± 1°; 1.4 ± 0.1 eV], respectively. The measured angles have been corrected for small final state effects on the desorbing ions as well as for electrostatic effects in the ion optical system [14,17,18]. The normal momentum of these ions is CD_3^+ $[8.6 \pm 0.4\ (\mathrm{eV} \cdot \mathrm{amu})^{1/2}]$ and $C_2D_5^+$ $[9.3 \pm 0.3(\mathrm{eV} \cdot \mathrm{amu})^{1/2}]$, indicating that to within 10% the momentum of the reactant ion is transferred to the momentum of the product ion in this reaction.

The observation of CD_3^+ and $C_2D_5^+$ desorbing species, both of which have their twofold symmetric angular distributions oriented in a normal plane parallel to the $\langle 1\bar{1}0\rangle$ azimuth, from the multilayer of CD_3I, leads to three important conclusions: (i) The C-I bond of the adsorbed CD_3I molecular axis is oriented in two symmetric directions parallel to the normal plane in the $\langle 1\bar{1}0\rangle$ azimuth of the underlying Cu(110) crystal at multilayer coverage indicating that the multilayer CD_3I film is epitaxially ordered; (ii) The $C_2D_5^+$ ion is observed and this ion cannot be directly produced from electron impact ionization of the CD_3I molecule; and (iii) The momentum of the $C_2D_5^+$ ion product from the ion-molecule reaction is closely similar to that of the CD_3^+ ion initially produced by ESD.

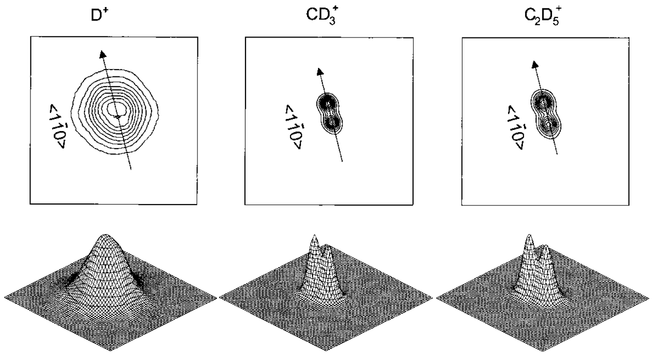


FIG. 3. ESDIAD patterns of D^+, CD_3^+, and $C_2D_5^+$ species from CD_3I on the Cu(110)-iodine surface (exposure of $CD_3I = 4.8 \times 10^{15}$ molecules/cm^2).

From the above observations we conclude that the $C_2D_5^+$ ion is produced by an ion-molecule reaction between the CD_3^+ ion and a CD_3I molecule. It is believed that ion-molecule reactions, with very few exceptions, require no activation energy, reaction taking place at rather long range (a so-called sticky collision), and that consequently the reactions are very efficient even at low temperatures [19]. The measurement of similar emission directions and normal momenta for $CD_3^+$and the $C_2D_5^+$ ions indicates that the collision between CD_3^+ and CD_3I occurs with only minor modification of the initial CD_3^+ reactant ion momentum by the ion-molecule reaction. Thus these measurements indicate that little momentum is lost to the DI species or to the condensate lattice, when the ion-molecule reaction occurs.

The observation of $C_2D_5^+$ production only when the second layer or thicker multilayer is present suggests that this process does not occur until ion-neutralization effects due to electron tunneling from the metal have been reduced by separation of the CD_3I molecules from the surface by a critical distance, allowing CD_3^+ to escape and to produce $C_2D_5^+$ which can also escape without neutralization.

An alternate postulate that a stable surface product which could yield $C_2D_5^+$ ions is produced by exposure of the CD_3I multilayer to electrons is not supported by experiments following long exposure to electrons, where the $CD_3^+/\ C_2D_5^+$ ratio was found to be invariant.

The formation of sharp beams of CD_3^+ and $C_2D_5^+$ is dependent on the structure of the CD_3I multilayer. To illustrate this point, in Fig. 4, a spacer layer of 3 ML of H_2O was used above the Cu(110)-I template surface to support a condensed layer of CD_3I. The CD_3^+ and $C_2D_5^+$ ESDIAD patterns change significantly to broad one-beam patterns oriented normally to the surface, indicative of CD_3I structural disorder, and the ion yield ratio changes from $C_2D_5^+/\ CD_3^+ = 0.42$ to a ratio of 0.12 for the H_2O spacer layer. This indicates that the water spacer layer does not transmit information about the underlying template structure to the condensed CD_3I layer, and that CD_3I epitaxy does not occur in this case. The decrease in the relative yield of $C_2D_5^+$ to CD_3^+ for the disordered CD_3I layer indicates that the efficiency of the ion-molecule reaction is significantly favored by the ordering of molecules in the condensed films.

In summary, we have employed a passivated single crystal metal surface as a template to epitaxially grow a multilayer of CD_3I molecules. The C-I bond directions in the ordered condensed multilayer of CD_3I are tilted in a normal plane parallel to the $\langle 1\bar{1}0\rangle$ azimuth. The reaction between directed CD_3^+ ions (produced by ESD) and overlayer CD_3I molecules induces directed $C_2D_5^+$ ion

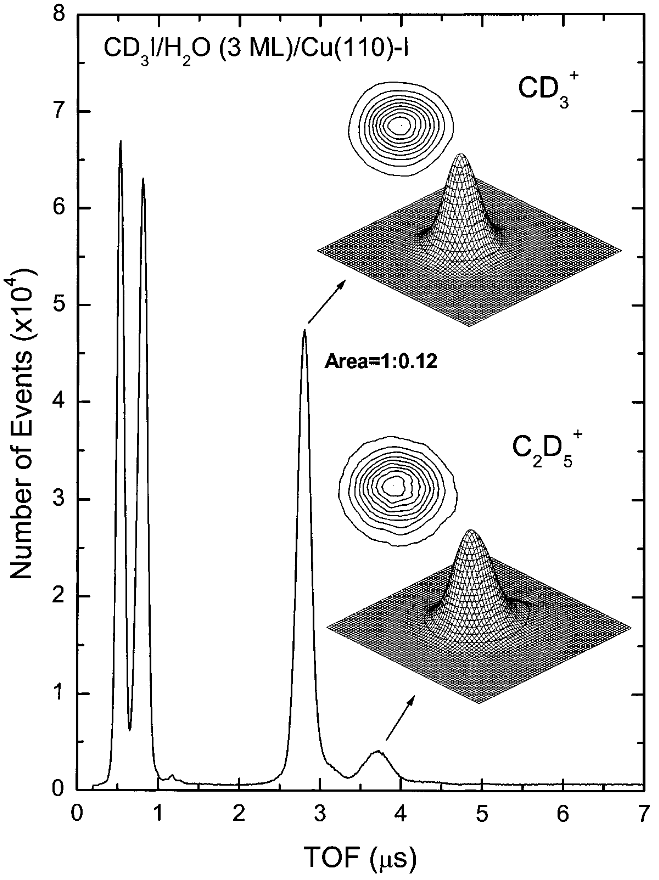


FIG. 4. TOF-ESDIAD pattern from a disordered CD_3I multilayer (3.5 ML) on top of 3 ML of H_2O on Cu(110)-iodine.

formation. Only small differences are observed in the ion emission direction and the normal momentum of the CD_3^+ and the $C_2D_5^+$ ions, indicating that the ion-molecule reaction dynamics are governed by the initial dynamics of the parent CD_3^+ ion which undergoes a high cross section or sticky collision with neighbor CD_3I molecules. This work provides the first example of the use of oriented adsorbed molecules to produce directed reactant and product ion beams in an ion-molecule reaction, and the measurement of the momentum of each. For the reaction $CD_3^+ + CD_3I$, it is found that the momentum of the CD_3^+ reactant ion is closely similar to the momentum of the product $C_2D_5^+$ ion in the ion-molecule reaction. The generality of this observation remains to be investigated in other ion-molecule reactions.

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