Surface-Aligned Ion−Molecule Reaction on the Surface of a Molecular Crystal $CD_3^+ + CD_3I \rightarrow C_2D_5^+ + DI$

Jae-Gook Lee and John T. Yates, Jr.*

Contribution from the Surface Science Center, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received August 25, 2003; E-mail: jyates@pitt.edu

Abstract: An ion−molecule reaction has been observed from a condensed molecular crystal of CD_3I using the time-of-flight electron-stimulated desorption ion angular distribution technique. The CD_3I multilayer is produced by growth on an ordered substrate. The reaction occurs between CD_3^+ ions produced by electron-stimulated desorption and neighbor CD_3I molecules in the topmost layer of the molecular crystal of CD_3I, forming product $C_2D_5^+$ ions whose desorption dynamics have been measured. The normal momentum of the product ion is close to that of the reactant ion, suggesting that the reaction is dominated by a two-body collision, i.e., the momentum of the reactant CD_3^+ ion governs the momentum of the product $C_2D_5^+$ ion. The ion−molecule reaction is of high cross section since the $C_2D_5^+$ yield is comparable to the CD_3^+ yield. It is found that the yield and directionality of the emission of the $C_2D_5^+$ product ion is governed by the molecular order that is characteristic of the molecular crystal of CD_3I. Destroying or modifying this order by using a spacer layer of H_2O diminishes the $C_2D_5^+$ product ion yield relative to the reactant CD_3^+ yield and broadens the ion emission directions.

1. Introduction

Understanding the surface properties of thin-film molecular crystals of organic molecules is an interesting new area, open for investigation by the methods of surface science. In particular, ion−molecule reactions, if they occur upon electronic excitation of a molecular crystal, could be of importance to astrophysics,[1] radiation chemistry,[2] atmospheric chemistry,[3] and plasma chemistry.[4]

A number of experiments have been performed by Madey and co-workers to understand the fundamental issue of the transmission behavior of low-energy ions through overlayers of adsorbed molecules. Studies have been made of the nature of the energy and charge-transfer process that affect the ion transport through adsorbate layers.[5−7] In a schematic illustration of the process reported in this article, shown in Figure 1, the desorbing ions, having kinetic energy <10 eV, can interact with neighbor atoms or molecules through elastic and inelastic processes. The elastic and inelastic processes that influence ion transport through molecular layers depend on the nature of the ion and its kinetic energy and on the structural and electronic

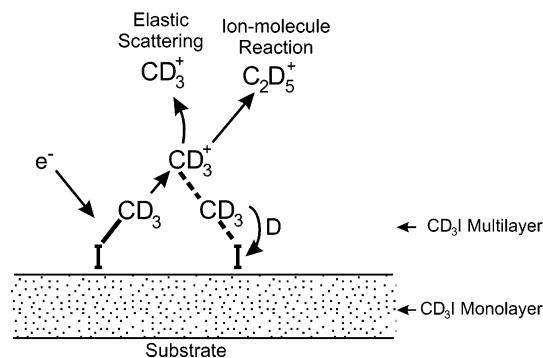Ion-Molecule Reaction at the Surface of a Molecular Crystal of CD_3I

Figure 1. Schematic of the observed ion−molecule reaction when ions desorb from a CD_3I multilayer.

properties of the collision partner. The change of total ion yield is expected to be mainly due to backscattering or large angle scattering and to charge-transfer neutralization as well as to ion−molecule reactions leading to the formation of new species.[8]

Various experimental methods have been developed to investigate specific ion−molecule reactions in the gas phase.[9] However, in a condensed layer system on a single-crystal substrate, one can expect remarkable differences between the behavior of a given molecular system in the condensed state as compared to its behavior in the gas phase.[10,11] In contrast to molecules in the gas phase, condensed molecular layers on

(1) Carson, T. R.; Roberts, M. J. *Atoms and Molecules in Astrophysics*; Academic Press: London & New York, 1972.
(2) (a) Lias, S. G.; Ausloos, P. *Ion-Molecule Reactions: Their Role in Radiation Chemistry*; Americam Chemical Society: Washington, DC, 1975. (b) Spinks, J. W. T.; Woods, R. J. *An Introduction to Radiation Chemistry*; John Wiley & Sons: New York, 1964.
(3) (a) Wayne, R. P. *Chemistry of Atmospheres*, Clarendon Press: Oxford, 1985. (b) McEwan, M. J.; Phillips, L. F. *Chemistry of the Atmosphere*; John Wiley & Sons: New York, 1975.
(4) Williams, K. L.; Martin, I. T.; Fisher, E. R. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 518.
(5) Akbulut, M.; Sack, N. J.; Madey, T. E. *Surf. Sci. Rep.* **1997**, *28*, 177.
(6) Sack, N. J.; Akbulut, M.; Madey, T. E. *Phys. Rev. Lett.* **1994**, *73*, 794.
(7) Sack, N. J.; Akbulut, M.; Madey, T. E. *Phys. Rev. B* **1994**, *51*, 4585.

(8) Azria, R.; Parenteau, L.; Sanche, L. *Chem. Phys. Lett.* **1990**, *171*, 229.
(9) *Ion-Molecule Reactions*; Flanklin, J. L., Ed.; Plenum Press: New York, 1972.

single-crystal surfaces are expected to exhibit structural properties that reflect the structure of the underlying single-crystal substrate. The alignment, orientation, and positioning of these molecules in the molecular crystal can lead to collision processes not observed in the gas phase.[10−12] This article reports the investigation of a well-known ion−molecule reaction where the process is governed by geometrical alignment of the reactant molecules. This alignment is accomplished by adsorption on a single-crystal substrate to produce a molecular crystal.

We report in this article the observation of surface-aligned ion−molecule reaction product, the $C_2D_5^+$ ion, produced by CD_3^+ ions generated by electron-stimulated desorption. The $C_2D_5^+$ ion originates from a condensed CD_3I layer adsorbed on a Cu(110) surface passivated by chemisorbed iodine atoms. The reaction between directed CD_3^+ ions and oriented overlayer CD_3I molecules produces directed $C_2D_5^+$ ion emission along the $(1\bar{1}0)$ azimuth. Only a small difference is measured in the ion emission angle and in the normal momentum of the reactant CD_3^+ and the product $C_2D_5^+$ ions. This indicates that the ion−molecule reaction dynamics are primarily governed by the initial dynamics of the reactant CD_3^+ ion as it interacts with oriented CD_3I molecules. Using an adsorbed water spacer layer on the surface, we show that the destruction of molecular alignment and orientational ordering in a subsequently formed CD_3I layer dramatically decreases the directionality and yield of $C_2D_5^+$ product ions.

2. Experimental Section

The experiments were performed in an ultrahigh vacuum chamber with a base pressure below 1×10^{-10} Torr. The Cu single crystal, a cylindrical disk 3-mm thick, with a diameter of 10 mm, was oriented to within ±0.22° of the (110) plane. The Cu(110) crystal could be cooled to 80 K by liquid nitrogen and heated to 900 K by resistive heating. The Cu(110) crystal was cleaned by cycles of argon-ion bombardment followed by annealing to 800 K. No impurities were detected at the level of sensitivity of Auger electron spectroscopy.

The Cu(110) crystal was exposed to CD_3I (99.5%, Aldrich) for temperature-programmed desorption (TPD) and for time-of-flight electron-stimulated desorption ion angular distribution (TOF-ESDIAD) measurements at 80 K. Exposure was accomplished using a calibrated microcapillary array beam doser, which produced uniform layers while maintaining low background pressure during adsorption.[13] The typical molecular flux used was in the range of 9.0×10^{11} to 1.0×10^{13} molecules/cm²·s.

For TOF-ESDIAD measurement, the electron pulses (50-ns width, in an ~0.5-mm diameter beam) at 50 kHz containing 10^4 to 10^5 electrons with energy $E_e = 180$ eV were used to produce ionic species. An accelerating voltage of +30 V was applied to the Cu crystal in ESDIAD studies to compress the positive ion ESDIAD patterns. Damage to the adsorbed layer was minimized by using a total effective bombardment time of only about 3 s in which the total fluence of electrons was only ~4×10^{12} electrons/cm². The TOF-ESDIAD data were recorded in x, y, and t, where (x, y) are coordinates on a position-sensitive detector placed behind an array of hemispherical and planar grids and t is the time-of-flight of the desorbing particles from the crystal

to the detector.[14] The TOF-ESDIAD apparatus, described previously,[14−16] allows for the separation of multiple ion patterns corresponding to different time-of-flight windows. It is therefore possible to measure separately the ESDIAD patterns of desorbing species having different masses,[14−18] such as D^+, CD_3^+, and $C_2D_5^+$.

The ESDIAD apparatus was also used as a low-energy electron diffraction (LEED) apparatus by changing the grid polarity. This allows us to determine the azimuthal orientation of the Cu(110) crystal in laboratory coordinates and to perform digital LEED measurements for observing the ordered structure of the adsorbate overlayer.

TPD measurements were carried out using a UTI 100C quadrupole mass spectrometer with digital data acquisition during the electronically controlled temperature scan at $dT/dt = 2$ K/s, and mass multiplexing was used to monitor the desorbed products.

3. Results

3.1. Decomposition of CD_3I on the Clean Cu(110) Surface: TPD and LEED. From the results of the TPD study, most of the CD_3I molecules adsorbed on the clean Cu(110) surface dissociate to produce a surface methyl group and an iodine atom below ~140 K. The surface methyl group decomposes and reacts to yield methane, ethene, and ethane at higher temperature (~400−470 K). The adsorbed atomic iodine remains on the surface up to ~800 K.

To investigate the effect of chemisorbed iodine on the iodomethane decomposition, repeated doses of CD_3I molecules (2.3×10^{14} molecules/cm²) were employed without cleaning the surface after each TPD measurement. Following repeated exposure and heating to 773 K, the intensity of the CD_3I molecular desorption peak at 146 K increases, and the peak maximum slightly shifts to lower temperature (139 K), as shown in Figure 2a. Also, as the coverage of adsorbed iodine increases, an additional CD_3I desorption feature appears with a maximum at ~132 K. Finally, the desorption spectral family of CD_3I formed by increasing CD_3I exposure becomes unchanged for successive adsorption of CD_3I (after three cycles of exposing and heating). By comparison of the TPD peak areas, about 95% of adsorbed CD_3I molecules on the clean surface decompose at the exposure of 2.3×10^{14} molecule/cm². As shown in Figure 2b, the desorption yield of methane abruptly decreases in the opposite manner to the yield of CD_3I during the repeated exposure to CD_3I and annealing, and finally the methane desorption peak completely disappears after the fifth cycle. This result indicates that surface iodine atoms released by the thermal decomposition of CD_3I suppress further iodomethane thermal decomposition on the copper surface and that the surface becomes inert for the iodomethane decomposition. We designate this passivated fully iodine-covered Cu(110) surface as Cu(110)−I. It forms a template for the adsorption of multilayer CD_3I that exhibits an ion−molecule process following CD_3^+ formation by electron-stimulated desorption.

The chemisorbed iodine atom shows a c(2 × 2) long-range ordered structure, by LEED, as shown in Figure 3. This observation is consistent with that of another study.[19] The c(2 × 2) structure does not change by additional adsorption of CD_3I and by thermal treatment up to 800 K. For convenience, in our

(10) Polanyi, J. C.; Zeiri, Y. In *Laser Spectroscopy and Photochemistry on Metal Surfaces*; Dai, H.-L., Ho, W., Eds.; Advanced Series in Physical Chemistry; World Scientific: Singapore, 1995; Vol. 5, Part II.

(11) Polanyi, J. C.; Rieley, H. In *Dynamics of Gas-Surface Interactions*; Rettner, C. T., Ashfold, M. N. R., Eds.; Advances in Gas-Phase Photochemistry and Kinetics; Royal Society of Chemistry: Cambridge, 1991.

(12) Tripa, C. E.; Yates, J. T., Jr. *Nature* **1999**, *398*, 591.

(13) (a) Yates, J. T., Jr. *Experimental Innovations in Surface Science*; AIP Press and Springer-Verlag: New York, 1998. See also (b) Winkler, A.; Yates, J. T., Jr. *J. Vac. Sci. Technol., A* **1988**, *6*, 2929.

(14) Ahner, J.; Mocuta, D.; Yates, J. T., Jr. *J. Vac. Sci. Technol., A* **1999**, *17*, 2333.

(15) Mocuta, D.; Ahner, J.; Yates, J. T., Jr. *Surf. Sci.* **1997**, *383*, 299.

(16) Mocuta, D.; Ahner, J.; Yates, J. T., Jr. *Surf. Sci.* **1997**, *390*, 11.

(17) Ahner, J.; Mocuta, D.; Yates, J. T., Jr. *Surf. Sci.* **1997**, *390*, 126.

(18) Lee, J.-G.; Ahner, J.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 2772.

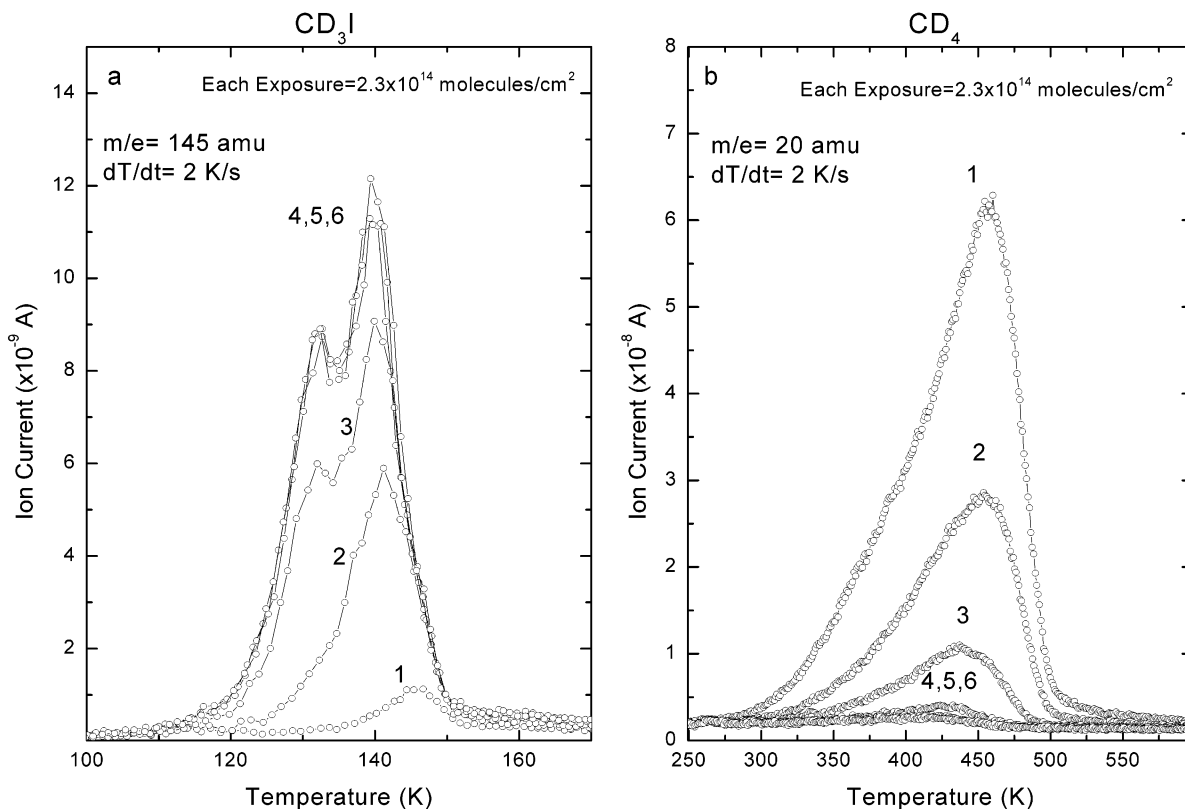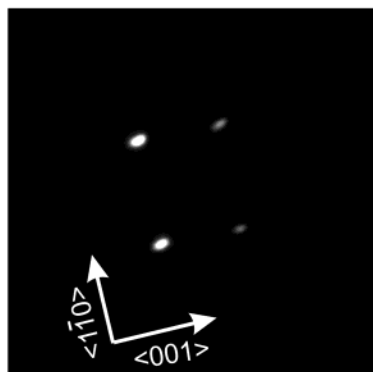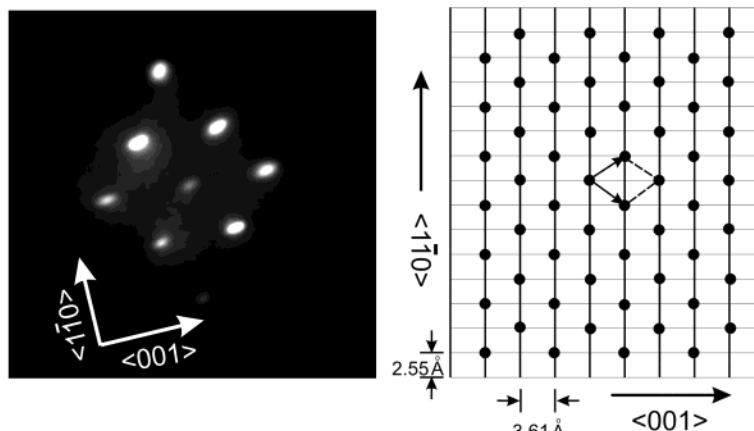(19) Johnson, C. C.; Jensen, E. T. *J. Chem. Phys.* **2000**, *112*, 5919.

TPD Spectra of CD₃I and CD₄ from CD₃I on Cu(110)

Figure 2. Thermal decomposition of CD_3I on the clean surface for 6 successive adsorption experiments.

LEED Patterns of the Clean Cu(110) and the Cu(110)-I Surface

Figure 3. Observed overlayer long-range order structure for chemisorbed iodine atom on Cu(110).

experiments to be described later, the Cu(110)−I surface was prepared by dosing ∼3 ML of CD₃I to the Cu(110) surface followed by annealing the surface to 700 K.

3.2. Adsorption of CD₃I on Cu(110)−I. On the Cu(110)−I surface, the CD₃I molecule adsorbs molecularly and desorbs at ∼140 K. The results of TPD experiments on the Cu(110)−I

surface are shown in Figure 4. At the lowest exposure (3.9×10^{13} molecules/cm²), only one desorption peak (α) is seen at 138 K. At slightly higher exposure (1.2×10^{14} molecules/cm²), the α-peak maximum slightly shifts to higher temperature and another desorption feature (β_1) appears at $T = \sim132$ K. The desorption state α saturates at an exposure of 8.1×10^{13}
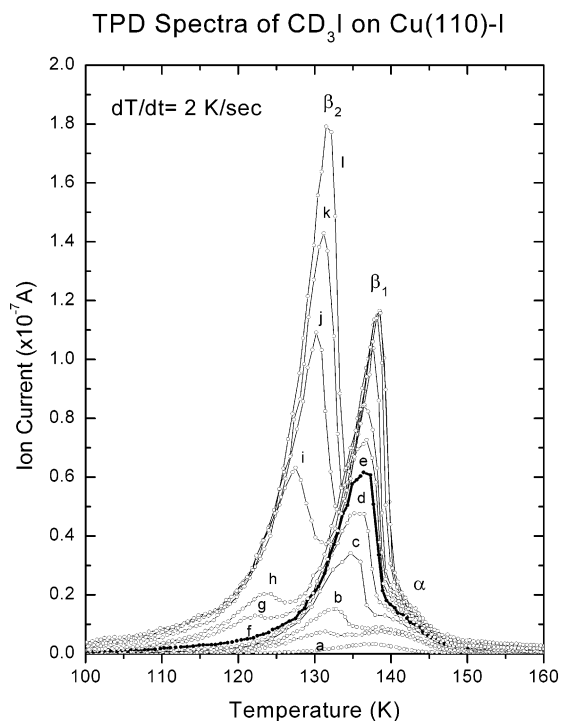
TPD Spectra of CD₃I on Cu(110)-I

Figure 4. Thermal desorption spectra of CD₃I (taken at $m/e = 145$ amu) on the Cu(110)−I surface. Heating rate = 2.0 K/s. Exposures: (a) 3.9 × 10^{13} molecules/cm², (b) 1.2 × 10^{14} molecules/cm², (c) 2.0 × 10^{14} molecules/cm², (d) 3.2 × 10^{14} molecules/cm², (e) 3.9 × 10^{14} molecules/cm², (f) 4.8 × 10^{14} molecules/cm², (g) 6.0 × 10^{14} molecules/cm², (h) 6.4 × 10^{14} molecules/cm², (i) 9.3 × 10^{14} molecules/cm², (j) 1.2 × 10^{15} molecules/cm², (k) 1.4 × 10^{15} molecules/cm², and (l) 1.6 × 10^{15} molecules/cm².

molecules/cm². As the exposure of CD₃I increases, the β_1 desorption feature grows continuously even after a new desorption peak (β_2) develops at lower temperature (exposure = 4.8 × 10^{14} molecules/cm²). The saturation of the β_1 desorption state occurs at an exposure of 1.4 × 10^{15} molecules/cm². No other additional desorption features were observed at higher exposures of CD₃I.

The small desorption peak, α, may originate from random defect sites. Therefore, we assign the β_1 peak as being due to monolayer desorption and the β_2 peak as second layer or multilayer desorption. The second layer appears when the monolayer is only about 70% completed, as indicated in Figure 4 as a thicker line. This result indicates that the CD₃I adsorbed layer on the Cu(110)−I surface does not grow in a layer-by-layer growth mode, and since the adsorbate flux is almost constant across the crystal, islands of CD₃I probably form during adsorption.

The thermal desorption spectra of the CD₃I from the β_2-multilayer can be fitted to zero-order desorption kinetics, because the leading edge of the TPD spectra is invariant as a function of the initial coverage of the β_2-species. A desorption energy, 35 ± 2 kJ/mol, was obtained for the CD₃I multilayer on Cu(110)−I by leading-edge analysis.

3.3. TOF-ESDIAD Study of CD₃I on the Clean Cu(110) Surface and on the Cu(110)−I Surface. 3.3.1. Determination of Mass for Desorbing Ions.
On the clean Cu(110) surface and on the Cu(110)−I surface, only two ionic species (H⁺ and D⁺) ions were observed by TOF-ESDIAD below monolayer coverage. As the second β_2-layer begins to develop, additional desorbing particles were detected in the TOF spectrum. As
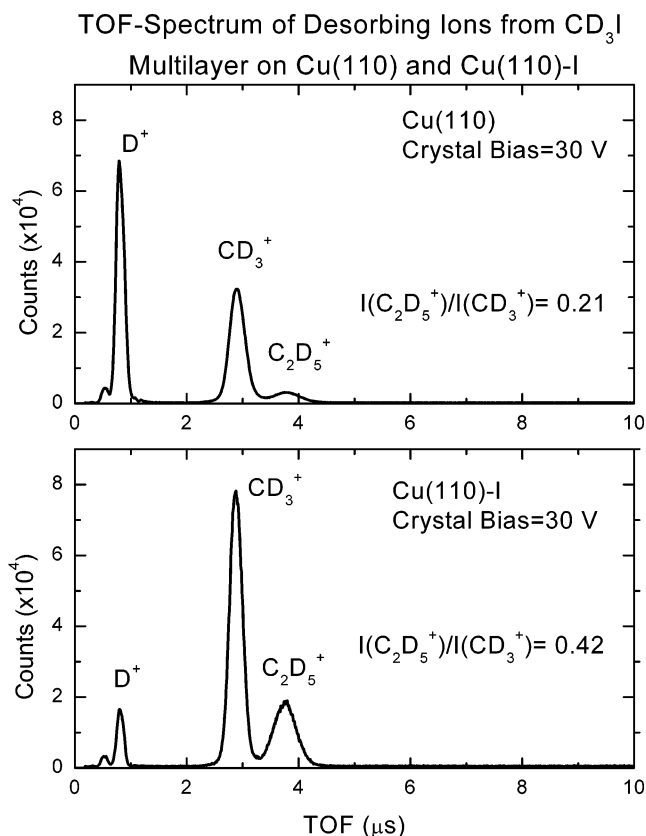
TOF-Spectrum of Desorbing Ions from CD₃I Multilayer on Cu(110) and Cu(110)-I

Figure 5. TOF spectra of desorbing ions from a CD₃I multilayer on the Cu(110) surface and on the Cu(110)−I surface.

shown in Figure 5, 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 CD₃I. The relative intensities of desorbing ions are very different on the clean surface and on the Cu(110)−I surface. The desorbing species at 0.5 and 0.8 μs were assigned as H⁺ (from a background impurity) and D⁺ ions by comparison with the time-of-flight of H⁺ and D⁺ ions from other measurements. The mass/charge ratio of the observed ions at longer flight times was determined by the dependence of flight time on the accelerating voltage. The measured ratios of mass to charge for ions at flight times of 2.7 and 3.6 μs are 18 ± 2 amu and 31 ± 4 amu, respectively. One cannot expect to produce the heaviest ion species (31 ± 4 amu) as a cracking product from electron impact ionization of CD₃I in the gas phase. Therefore, this heavy ion must originate from a chemical reaction with a neighbor molecule upon desorption from the surface. On the basis of the known gas-phase thermodynamically favorable exothermic reaction, $CH_3^+ + CH_3I \rightarrow C_2H_5^+ + HI$ ($\Delta H_r = -1.7$ eV),[2a,20] we assigned the two heavy ions as CD_3^+ (18 amu) and $C_2D_5^+$ (34 amu), respectively.

3.3.2. Angular Distribution of Desorbing Ions from the CD₃I Multilayer Molecular Crystal.
The angular distributions of D⁺, CD₃⁺, and C₂D₅⁺ ions from the CD₃I multilayer adsorbed on the clean Cu(110) surface are shown in Figure 6. One-beam patterns were obtained for all three species on the clean

(20) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Gas-Phase Ion and Neutral Thermochemistry*, Suppl. to *J. Phys. Chem. Ref. Data*, Vol. 17; American Chemical Society and the American Institute of Physics for the National Bureau of Standards: New York, 1988.
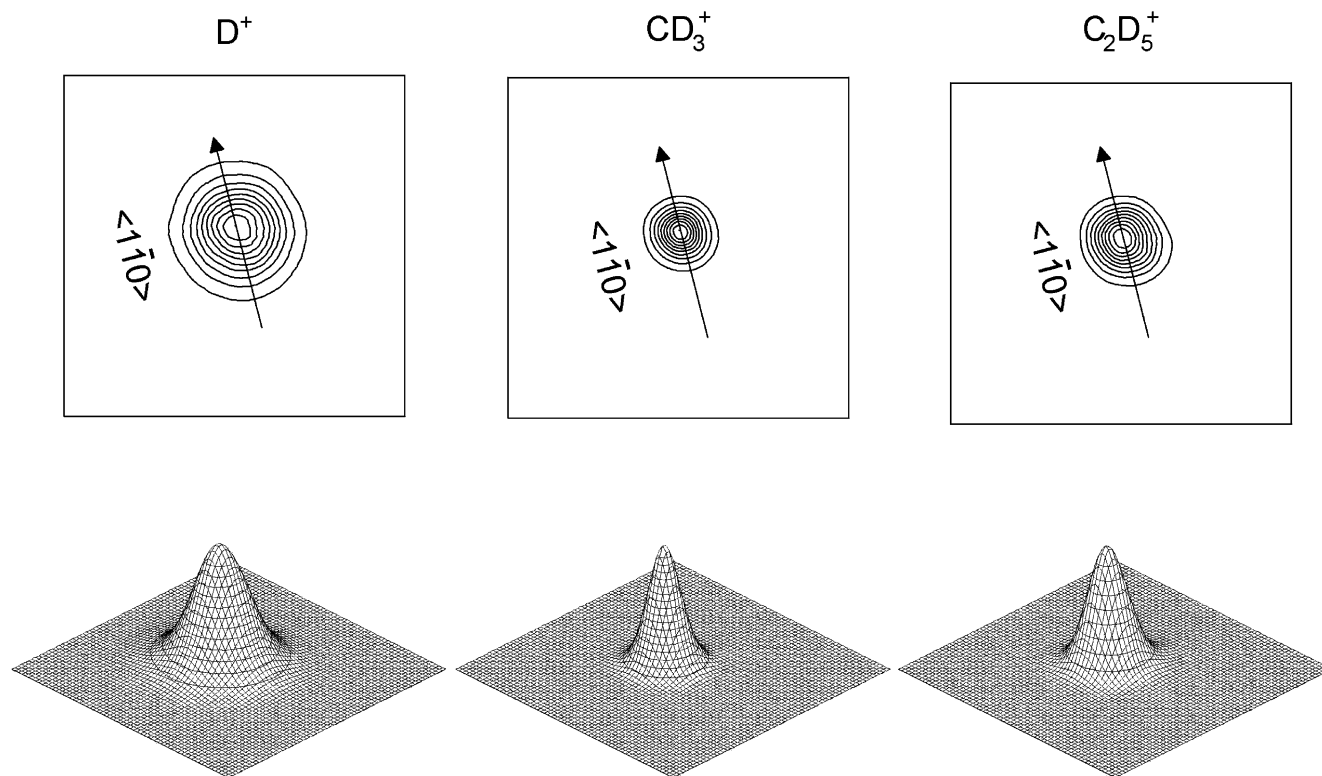
ESDIAD Patterns of Desorbing Ions from CD$_3$I on Clean Cu(110)

$$D^+ \qquad\qquad CD_3^+ \qquad\qquad C_2D_5^+$$

Figure 6. ESDIAD patterns of D$^+$, CD$_3^+$, and C$_2$D$_5^+$ ions from adsorbed CD$_3$I on the clean Cu(110). Exposure = 4.5 × 10^{15} molecules/cm^2.

Cu(110) surface. The ion yield ratio of CD$_3^+$ to C$_2$D$_5^+$ is 0.21 for all multilayer thicknesses studied.

The angular distributions of D$^+$, CD$_3^+$, and C$_2$D$_5^+$ ions from the CD$_3$I multilayer adsorbed on the Cu(110)−iodine surface are shown in Figure 7, giving a different set of patterns from those seen where CD$_3$I is adsorbed on clean Cu(110). A broad normally oriented ESDIAD pattern is seen for D$^+$ at all coverages from submonolayer to multilayer. Both the CD$_3^+$ and C$_2$D$_5^+$ ions exhibit sharp two-beam ESDIAD patterns, which are oriented parallel to the (1$\bar{1}$0) azimuth of the underlying crystal substrate. The two symmetrically oriented CD$_3^+$ emission directions are governed by the two preferred directions of the C−I bonds in the CD$_3$I multilayer molecular crystal, either from equivalent molecular orientations reversed by 180° or from two domains with reverse orientation, as has been observed in many ESDIAD studies of oriented adsorbed molecules on single-crystal surfaces.[21] Indeed, an ordered CH$_3$I multilayer on Pt(111) has been reported by Fan and Trenary.[22]

The emission angles of both CD$_3^+$ and C$_2$D$_5^+$ ions from the adsorbed CD$_3$I on Cu(110)−I with respect to the crystal normal were measured as a function of crystal bias. The ion emission angles at zero crystal bias were determined by extrapolation of the measured angle to zero crystal bias using an electrostatic model for the ESDIAD analyzer system.[23] To determine the angle between the two ion beams and the crystal normal at different crystal biases, the ESDIAD patterns were cut along the (001) azimuthal direction and fitted by two Gaussian

functions. The measured angles and initial kinetic energy at zero crystal bias were for CD$_3^+$ (13° ± 1°; 2.1 ± 0.2 eV) and for C$_2$D$_5^+$ (18° ± 1°; 1.4 ± 0.1 eV), respectively. The measured angles have been corrected for small final state effects (±1°) on the desorbing ions as well as for electrostatic effects in the ion optical system.[23−25] The normal momentum of these ions is: CD$_3^+$ (8.6 ± 0.4 (eV·amu)$^{1/2}$) and C$_2$D$_5^+$ (9.3 ± 0.3 (eV·amu)$^{1/2}$).

The coverage dependency of the ion yield for D$^+$, CD$_3^+$, and C$_2$D$_5^+$ observed from CD$_3$I on the Cu(110)−I surface from submonolayer to multilayer coverages yielding a molecular crystal is shown in Figure 8. Only D$^+$ ion desorption from the CD$_3$I submonolayer was observed. The lack of observation of heavy ions, such as CD$_3^+$ and C$_2$D$_5^+$, is attributed to an efficient neutralization process for heavy, slow-moving ions by the substrate. The D$^+$ ion emission increases until the second layer begins to form. At coverages above the monolayer, two additional ion fragments, CD$_3^+$ and C$_2$D$_5^+$, are observed with closely correlated yields. The emission of these ions from CD$_3$I is first observed at the beginning of the second (β_2) CD$_3$I layer corresponding to the TPD spectrum (e) in Figure 4, where the onset of second-layer formation is confirmed by the appearance of the β_2-desorption peak at ∼120 K in the TPD experiments and occurs when the first monolayer is 70% complete.

The yield of CD$_3^+$ and C$_2$D$_5^+$ ions on Cu(110)−I increases sharply as the CD$_3$I exposure increases, and then the ion yield/electron becomes constant. The ion yield ratio, CD$_3^+$/C$_2$D$_5^+$ = 0.42, is constant at all exposures as the multilayer molecular

(21) Ramsier, R. D.; Yates, J. T., Jr. *Surf. Sci. Rep.* **1991**, *12*, 246.
(22) Fan, J.; Trenary, M. *Langmuir* **1994**, *10*, 3649.
(23) Gao, Q.; Cheng, C. C.; Chen, P. J.; Choyke, W. J.; Yates, J. T., Jr. *J. Chem. Phys.* **1993**, *98*, 8308.
(24) Mišcović, J.; Vukanić, J.; Madey, T. E. *Surf. Sci.* **1984**, *141*, 285.
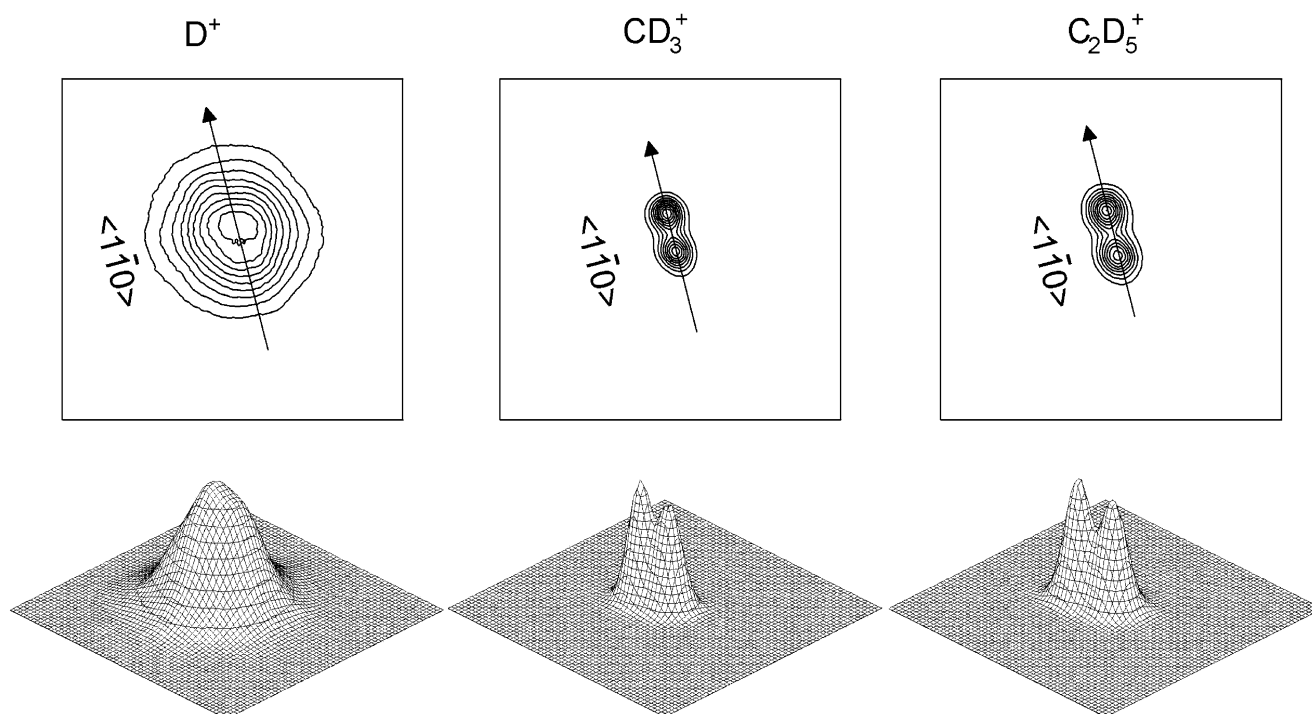(25) Mišcović, J.; Vukanić, J.; Madey, T. E. *Surf. Sci.* **1986**, *169*, 405.

ESDIAD Patterns of Desorbing Ions from CD_3I on Cu(110)-I

Figure 7. ESDIAD patterns of D^+, CD_3^+, and $C_2D_5^+$ ions from the CD_3I multilayer on the Cu(110)$-$I surface. Exposure = 4.8×10^{15} molecules/cm^2.
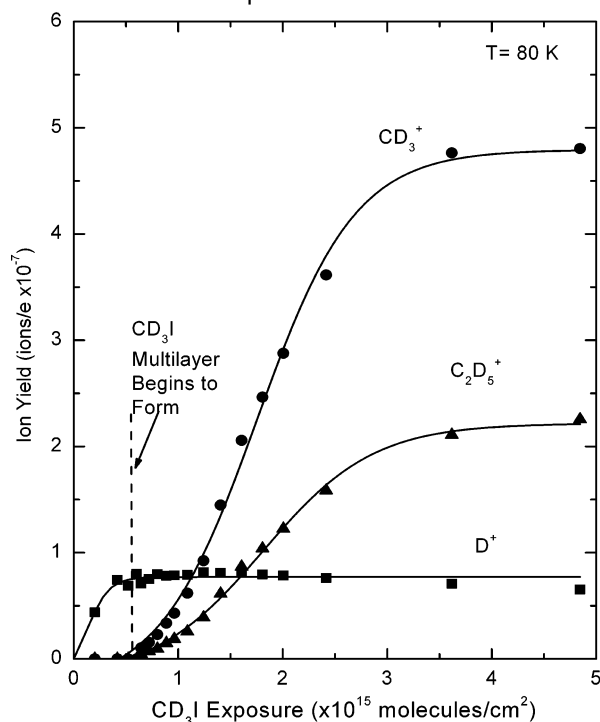

Figure 8. Ion yield from adsorbed CD_3I on Cu(110)$-$I as a function of exposure. Once a constant yield of CD_3^+ and $C_2D_5^+$ occurred, the properties of a molecular crystal of CD_3I were observed.

crystal grows in thickness, indicating that differences in ion-neutralization effects for the CD_3^+ and $C_2D_5^+$ ions as a result

of electron transfer from the metal surface are unimportant in the multilayer of CD_3I. In addition, no change of emission angle and width of the ESDIAD pattern of desorbing CD_3^+ and $C_2D_5^+$ was observed as the multilayer grows. This multilayer is therefore to be considered as an ordered molecular crystal of CD_3I, whose surface properties are invariant with thickness.

4. Discussion

4.1. Orientation of Adsorbed CD_3I on the Clean Cu(110) Surface and on the Cu(110)$-$I Surface: Growth of a Molecular Crystal of CD_3I on the Cu(110)$-$I Surface. The results of the TPD experiments indicate that the CD_3I molecule on the clean Cu(110) surface thermally decomposes upon heating to produce gaseous products, such as methane, ethene, and ethane, leaving iodine atoms on the surface. These results are consistent with those previously reported for iodomethane decomposition on the copper surface.[26,27] As a result of thermal decomposition of CD_3I, the clean copper surface is replaced by a Cu(110)$-$I surface, which exhibits a c(2 × 2) long-range overlayer structure. On this passivated Cu(110)$-$I surface, CD_3I molecularly adsorbs and desorbs at ~140 K. The desorption energy of the CD_3I multilayer on the Cu(110)$-$I surface is 35 ± 2 kJ/mol. The measured desorption energy of the multilayer is slightly smaller than the sublimation energy of solid iodomethane (40.2 ± 0.4 kJ/mol),[28,29] indicating that the multilayer

(26) Chiang, C.-M.; Wentzlaff, T. H.; Bent, B. E. *J. Phys. Chem.* **1992**, *96*, 1836.
(27) Lin, J.-L.; Bent, B. E. *J. Vac. Sci. Technol., A* **1992**, *10*, 2202.
(28) Wren, D. J.; Vikis, A. C. *J. Chem. Thermodyn.* **1982**, *14*, 435.
(29) *CRC Handbook of Thermophysical and Thermochemical Data*; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1994.
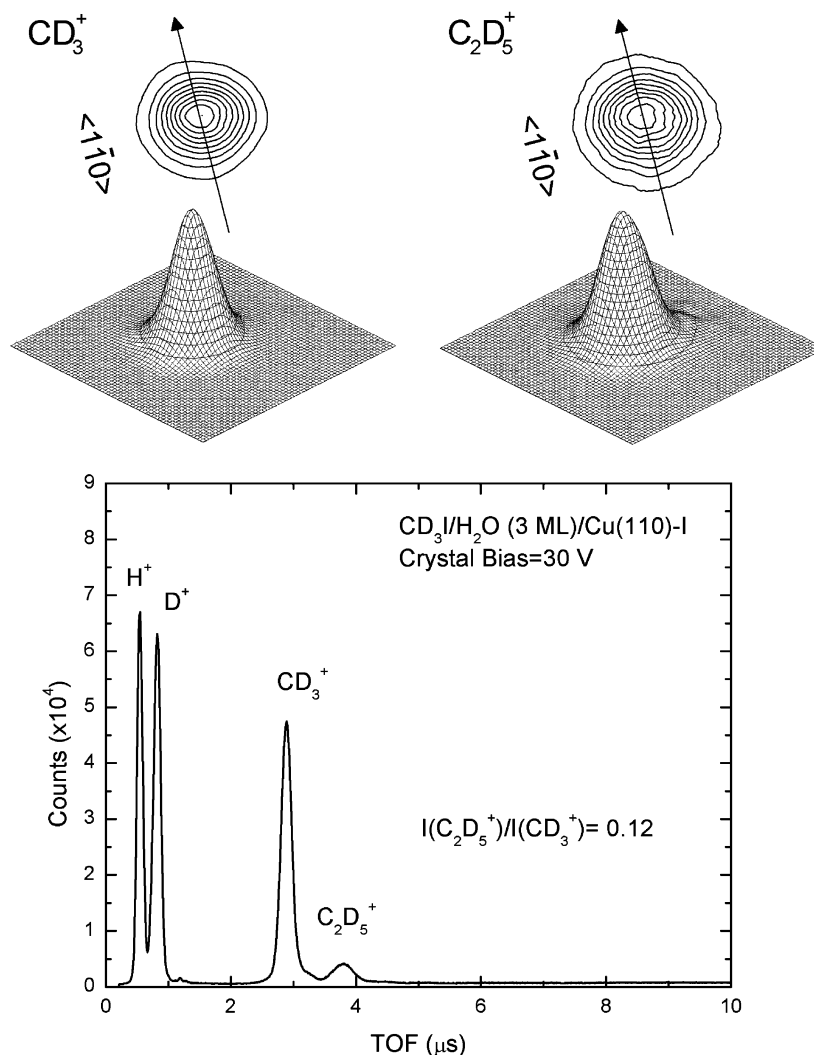
TOF-ESDIAD from Disordered CD₃I Multilayer

Figure 9. ESDIAD pattern TOF distribution of D^+, CD_3^+, and $C_2D_5^+$ ion from a disordered CD_3I multilayer. Exposure $= 4.5 \times 10^{15}$ molecules/cm^2.

structure on the Cu(110)−I surface may be different from the crystal structure of bulk CD₃I.[30]

The D⁺ ESDIAD pattern from adsorbed CD₃I in all coverage regimes on the clean Cu(110) surface and on the Cu(110)−I consists of a broad single beam centered on the crystal normal. This observation indicates that the C−D bond is randomly oriented for randomly oriented CD₃I molecules. Thus, in this framework, the summation of D⁺ beams from the randomly oriented C−D bonds averages to produce a broad normally oriented pattern. Therefore, ESDIAD cannot reliably determine the molecular orientation of adsorbed CD₃I from the D⁺ beam directions.

At coverages of above a monolayer, CD₃⁺ ion desorption also was observed on the clean Cu(110) surface as well as on the Cu(110)−I surface by TOF-ESDIAD. The emission direction of the CD₃⁺ ions is oriented parallel to the surface normal for CD₃I adsorbed on the clean surface, suggesting that the C−I bond is oriented parallel to the surface normal as seen on the Cu(111) surface.[27] However, the distribution of bond

directions is relatively broad compared to the distribution on Cu(110)−I, suggesting that some orientational disorder of adsorbed CD₃I exists when it is adsorbed on the clean Cu(110) surface. In contrast to the behavior of CD₃I on the clean Cu(110) surface, for the CD₃I on the passivated Cu(110)−I surface, the CD₃⁺ ion is emitted in two sharp beams in a plane parallel to the (1̄10) azimuth, each with a 13° tilt angle with respect to surface normal. We believe this CD₃⁺ emission pattern is characteristic of a molecular crystal of CD₃I grown on the passivated substrate.

Thus, the orientation of the adsorbed CD₃I molecule on the clean Cu(110) surface appears to be different from the orientation in the multilayer on the Cu(110)−I surface. On the Cu(110)−I surface, the C−I bond tilts 13° with respect to the surface normal. We noticed that in layers of bulk CD₃I the C−I bond tilts 20° with respect to the normal of the (001) crystal plane.[30]

From the results of TPD and ESDIAD, it is concluded that the Cu(110)−I surface (c(2 × 2) overlayer structure) leads to preferential CD₃I molecule orientation with the molecular plane

(30) Kawaguchi, T.; Hijikigawa, M.; Hayafuji, Y.; Ikeda, M.; Fukushima, R.; Tomhe, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 53.

oriented parallel to the $(1\bar{1}0)$ azimuth and with an outward-directed C−I bond orientation.

4.2. Ion−Molecule Reaction. The results of TOF-ESDIAD study for adsorbed CD_3I on the clean Cu(110) surface and on the Cu(110)−I surface provide the following interesting features for the ion−molecule reaction being observed: (1) the observation of the desorbing $C_2D_5^+$ ion that cannot be directly produced from electron impact ionization of the CD_3I molecule; (2) the small normal momentum difference (within 10%) observed between the CD_3^+ ion and the $C_2D_5^+$ ions; and (3) the constant intensity of the $C_2D_5^+$ ion compared to that of CD_3^+ at larger multilayer thicknesses, indicating that the properties of a bulk molecular crystal of CD_3I are being observed for layers several monolayers thick.

4.2.1. The Observation of the Ion−Molecule Reaction from the Condensed Layer. We conclude that the $C_2D_5^+$ product ion is a direct consequence of the ion−molecule reaction between CD_3^+ and CD_3I molecules in the second layer and in the multilayer of CD_3I. This direct process is consistent with the fact that the CD_3^+ and $C_2D_5^+$ ion yields are constant over the entire range of coverage studied. In addition, as extensive electron bombardment damage is purposely carried out on the thick multilayers of CD_3I, no change in the yield of $C_2D_5^+$ and CD_3^+ is observed. Other postulates of a chemical reaction prior to electron-induced excitation or to electron-induced chemical reactions yielding species such as C_2D_5I are inconsistent with these observations.

The measurement of similar ion emission directions for CD_3^+ and $C_2D_5^+$ and similar normal momenta for both the reactant and product ions indicates that the collision between CD_3^+ and CD_3I occurs with only minor modification of the initial CD_3^+ momentum by the ion−molecule reaction. Thus, these measurements indicate that little momentum is lost to the product DI species or to the condensate lattice when the ion−molecule reaction occurs.

4.2.2. The Depth of Origin of Desorbing Ions. The shape and width of the CD_3^+ and $C_2D_5^+$ ESDIAD beams are little influenced by the coverage of the second layer, and as may be seen in Figure 8. The intensity of the ions becomes independent of the multilayer thickness after a thickness of several layers is reached. As the low-energy electron that is responsible for the ionization process can penetrate into a depth of several monolayers, these results indicate that the ion−molecule reaction observed here is occurring primarily in the topmost layer of the condensed molecular solid overlayer when its thickness reaches about 3 ML. The constancy of the ion yields as a function of CD_3I layer thickness also indicates that neutralization by the substrate is unimportant on the thicker condensed overlayers.

4.2.3. Surface-Aligned Effect and H_2O Layer Effect. The difference in relative $C_2D_5^+$ to CD_3^+ ion yield on the different surfaces (0.21 on clean Cu(110) and 0.42 on Cu(110)−I) indicates that the efficiency of the ion−molecule reaction is strongly affected by molecular orientation. To investigate how the formation of the CD_3^+ and $C_2D_5^+$ ions is dependent on the overlayer structure, we performed a layer-type experiment in which CD_3I molecules were deposited on 3 ML of H_2O condensed on the Cu(110)−I surface, as shown in Figure 9. In this experiment, we observed that both CD_3^+ and $C_2D_5^+$ ion ESDIAD patterns change to a broad one-beam pattern from the

two-beam pattern aligned parallel to the $(1\bar{1}0)$ direction and that the $C_2D_5^+/CD_3^+$ abruptly decreases from 0.42 without the water overlayer to 0.12 on the water overlayer. In addition, the half width of the ESDIAD pattern from CD_3I/H_2O is wider compared to that of the ESDIAD pattern from the CD_3I on the clean Cu-(110) surface and on the passivated Cu(110)−I substrate. This experiment indicates that the H_2O spacer layer causes CD_3I condensation to become disordered as the recognition of the underlying Cu(110)−I substrate is eliminated or modified by the H_2O spacer layer. In addition, the enhanced H^+ yield from the CD_3I/H_2O may indicate that H^+ is evolved from H_2O in the spacer layer or H_2O admixed with CD_3I. Therefore, the yield of the ion−molecule reaction is strongly influenced by the structure of the molecular solid from which it originates, and the direction of ejection of the reactant CD_3^+ ions relative to the orientation of the reactant CD_3I molecules is of importance in governing the yield of the ion−molecule reaction.

5. Summary

The following results have been obtained from the study of adsorbed CD_3I on the clean Cu(110) and on the Cu(110)−I surface.

1. An ion−molecule reaction has been observed from a condensed molecular crystal of CD_3I produced by growth on an ordered substrate. The reaction occurs between CD_3^+ ions ejected by electron-stimulated desorption and neighbor CD_3I molecules in the topmost layer of the crystalline molecular crystal of CD_3I, producing product $C_2D_5^+$ whose desorption dynamics have been measured.

2. The ion−molecule reaction occurs with little change between the normal momentum of the reacting ion and the product ion, indicating that the reaction is dominated by a two-body collision, i.e., the momentum of the reactant CD_3^+ ion governs the momentum of the product $C_2D_5^+$ ion.

3. The ion−molecule reaction is of high cross section since the $C_2D_5^+$ yield is comparable to the CD_3^+ yield.

4. It is found that the yield and directionality of the emission of the $C_2D_5^+$ product ion is enhanced by the molecular order that is characteristic of the molecular crystal of CD_3I. Destroying or modifying this order by using a spacer layer of H_2O diminishes the $C_2D_5^+$ product ion yield relative to the reactant yield and destroys the molecular order of the layer.

5. The chemistry of CD_3I thermal decomposition on Cu(110) has been studied, and it has been found that a c(2 × 2) monolayer of chemisorbed I passivates the Cu(110) surface for CD_3I thermal decomposition.

6. The growth of a molecular crystal of CD_3I on top of the iodine-passivated Cu(110) surface has been observed, and it is demonstrated that ESDIAD is an excellent tool for studies of the structural character of the outermost layers of a thick molecular crystal.

A preliminary report of this effect has been presented elsewhere.[31]

(31) Lee, J.-G.; Hong, S.-H.; Ahner, J.; Yates, J. T., Jr. *Phys. Rev. Lett.* **2002**, *89*, 253202.