K is observed in both cases. The electron impact dissociation process however exhibits a threshold energy of $\sim 50$ eV. Further studies of the wavelength dependence of these interesting photodissociation and photodesorption processes are underway.21

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Effect of molecular orientation on electron transfer

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The effect of molecular orientation on chemical reactivity has been studied in crossed beams for several systems. For $K^+$ (oriented) CF$_3$I, the KI is forward scattered for attack at the "tails" (CF$_3$) end and backward scattered for attack at the "heads" (I) end. These experimental results are nicely accounted for by the "harpoon mechanism": electron transfer from an electropositive atom to an electron accepting molecule; break-up of the negative molecular ion in the field of the incoming positive ion; and completion of reaction via the Coulomb attraction of the resulting ions. Because the decomposition of the negative ion occurs within one vibrational period, the $I^-$ ion is ejected in the instantaneous direction of the CF$_3$I axis, giving backward scattering for heads approach, forward scattering for tails approach, and also nicely accounting for the scattering from the sideways approach.

Extension of the same argument to $K^+$ (oriented) CF$_3$Br is not in complete accord with experiment, suggesting that the electron jump might be affected by the molecular orientation. Since the dominant forces after the jump are Coulombic, chemical specificity would seem indeed to be reflected in the initial transfer. To investigate this effect directly, we have studied collisions of fast K atoms with oriented CF$_3$I and CH$_3$I molecules over the CM energy range $\approx 5-25$ eV. These reactions are known to produce $K^+$ and $I^-$; we report here that for both molecules the probability of forming $K^+$ is greater for attack at the I end.

Beams of fast K atoms are generated by charge exchange of $K^+$, and after residual $K^+$ ions are swept out of the beam, the fast K atoms intersect a supersonic beam of RI molecules (R = CF$_3$, CH$_3$) which have been state selected in an inhomogeneous six-pole electric field and oriented in a uniform field. Positive ions formed in the collision are detected by one of two channeltrons (C$_{180}$ or C$_{50}$) arranged

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schematically as shown in Fig. 1. The "uniform" field is generated by two plates parallel to the RI beam with holes to pass the K atom beam, and to allow access to the channeltron cones. This arrangement was necessary both to orient the molecules and to collect the $K^+$ ions. The active channeltron cone was biased at $-1200 \text{ V}$ while its uniform plate was held at $-50 \text{ V}$. The opposing plate and cone were held at $+50 \text{ V}$, and both channeltron anodes were held at $+800 \text{ V}$.

The six-pole electric field transmits RI molecules with negative values of $(\cos \theta)$, where $\theta$ is the average classical angle between the dipole moment and the electric field. Although individual rotational states have been resolved for other molecules in a similar apparatus, our emphasis was to observe reactive scattering which, for intensity considerations required the use of neat beams resulting in a distribution of orientations. The distribution [Refs. 1(a) and 8] is broad and is calculated to have the most probable $(\cos \theta) \approx -0.15$ but in the uniform field the negative ends of all these molecules point towards the negative field plate. The orientation may be reversed by reversing the polarity of the uniform field. In the following, $0^\circ$ refers to the field configuration with the positive field plate nearest the K oven (ions counted by $C_0$), and $180^\circ$ refers to the negative field plate nearest the K oven (ions counted by $C_{180}$). For CH$_3$I the I end is negative and points towards the incoming K atoms in the $180^\circ$ configuration.

The raw signals, $S_0$ and $S_{180}$, are the six-pole (HV) focusing field (off) differences in counts, i.e., $[S_0(5 \text{ kV}) - S_0(0 \text{ kV})]$, typically a few cps. These signals are different and suggest that the threshold for electron transfer is lower at the I end (by $\approx 0.5 \text{ eV}$ for CF$_3$I), although signal limitations prevent extrapolation to threshold. Comparison between $S_0$ and $S_{180}$ is complicated by different channeltron and ion collection efficiencies. To decouple these from orientation effects, the relative detection efficiency, $F(\varepsilon) = (S_{180}/S_0)_{0 \text{ kV}}$, is measured (for each energy) using the small flux of randomly oriented molecules obtained when no voltage is applied to the six-pole field (0 kV). $F(\varepsilon)$ is roughly independent of the molecule (RI and SF$_6$) used, but because of nonreproducible contact potentials on the field electrodes and multipliers, its measurement was interspersed with measurement of $S$. The relative signal due to the oriented molecules, $S'$, is the HV on-HV off signal difference corrected for the multiplier efficiencies: $S_{180}' = S_{180} - S_0' = F \cdot S_0$.

Figure 1 shows the ratio of corrected signals, $G = S_{180}'/S_0'$ for CH$_3$I and CF$_3$I vs CM energy (mass factor x lab energy$^{11}$). Both molecules exhibit a pronounced steric effect near threshold. For CH$_3$I, G is greater than one, showing that production of K$^+$ is most efficient when K is incident on the negative end (I) of CH$_3$I. For CF$_3$I, impact at the positive end is most effective, and this is once again the I end of the molecule.$^{12}$ No effect of focusing voltage was observed for SF$_6$, a spherical top not focused by the six-pole field, showing that the results are due to focused molecules.

The curves in Fig. 1 are calculated using a line-of-centers energy dependence of the cross section, $\sigma = \sigma_0 (1 - E_r/E)$, for each orientation. $E_r$ are the thresholds for the I or R ends and are very roughly determined by fitting the data: $E_r \approx 4.0 \text{ eV}$, and $E_r \approx 3.3 \text{ eV}$.

We conclude that the electron jump is not governed solely by the polarity of the molecule, otherwise G would show the same behavior for the two cases. In both cases the negative molecular ion fragments$^9$ and the major product is the I$^-$ ion, so the electron seems to prefer to jump to the leaving group. The electron jump and ion decomposition thus seem to be concerted processes, suggesting that K atom attack at the I end may cause a distortion of the molecule which facilitates its decomposition. The nominal threshold energy for the I end of these molecules (as fitted above) is consistent with the thermodynamic threshold for I$^-$ production ($E_r = IP + AD - EA = 4.34 + 2.0 - 3.06 = 3.3 \text{ eV}$)$^{13,14}$ This notion parallels the suggestion of Los and co-workers$^{14}$ that in collisional ionization of halogens, the halogen bonds stretch during the electron jump, increasing the effective electron affinity of the molecule.

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Picosecond multiphoton ionization of molecular clusters

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Many spectroscopic techniques have been applied to the detection and study of van der Waals (vdW) molecules and larger clusters. Of these, mass-resolved multiphoton ionization (MPI) spectroscopy has potentially the most versatility. Its advantages include high sensitivity, moderately high resolution, and species selectivity (especially important in cluster studies). Additionally, photoelectron spectroscopy following MPI can yield spectroscopic details of ionic states. Unfortunately, one disadvantage of the technique is the extensive fragmentation often accompanying ionization. Although fragmentation is also a problem with other ionization techniques (e.g., electron impact), additional dissociation pathways arise when using intense lasers. These include absorption of additional photons by the parent ion or fragment ions, or resonances with dissociative states in the neutral manifold. These dissociative pathways may preclude the use of MPI techniques in many cases.

In an effort to improve the generality of multiphoton ionization investigations of weakly bound species, we have begun a systematic investigation of picosecond MPI of van der Waals molecules and clusters. To our knowledge, no previous picosecond ionization studies of clusters have been reported. We present here preliminary results involving MPI of the cluster series \((\text{NO})_n\) \((n = 1-4)\) and \(\text{Ar}_n\text{I}_2\) \((n = 1-10)\). Previous MPI studies using nanosecond lasers have not been successful, presumably due to fast dissociation processes. The use of high peak power lasers and/or nonresonant ionization allows MPI techniques to supplement electron impact ionization in the study of cluster distributions. Additionally, dynamical and spectroscopic information may be obtained with the laser technique.

The pulsed supersonic nozzle (R. M. Jordan Co.), Wiley-McLaren-type time-of-flight (TOF) mass spectrometer, and vacuum system are similar to those described elsewhere. The laser system consists of a Nd:YAG laser (Quantel, YG571C Nano-Pico) which delivers 1.2 J in a 10 ns pulse (Q-switched) or 75 mJ in a 20 ps pulse (mode-locked) at the 1064 nm fundamental wavelength. In either operating mode, the second, third, or fourth harmonics (532, 355, or 266 nm) are available. Other wavelengths may be obtained by Raman shifting. In addition, a short-cavity dye laser (Quantel, PTL-10) provides tunable, picosecond pulses in the red (580–710 nm) which may be frequency-doubled or mixed. The laser beam is typically focused by a 50 mm lens into the expanding gas. The TOF spectrum is observed for each shot with a digitizing oscilloscope (Tektronix 11402). The signal-to-noise ratio is improved by averaging spectra from ~100 consecutive laser shots.

A number of different atomic and molecular cluster species have been studied in several wavelength regions. Figure 1 shows two representative TOF spectra, each chosen to illustrate a particular point concerning picosecond MPI. Each spectrum will be discussed in turn.

Because of the importance of NO in atmosphere chemistry, its vDW molecules have been the subject of many spectroscopic studies. In particular, the nitric oxide dimer is readily formed in supersonic nozzles, and the dimer ion is known to be stable. However, in spite of several studies of