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Orientation effects in cross-beam ionization reactions between potassium and symmetric-top molecules

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Rice University, 1993
RICE UNIVERSITY

ORIENTATION EFFECTS IN CROSS BEAM IONIZATION REACTIONS
BETWEEN POTASSIUM AND SYMMETRIC-TOP MOLECULES

By

GUOQIANG XING

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE

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April, 1993
Abstract

Orientation Effects in Cross Beam Ionization Reactions
Between Potassium and Symmetric-Top Molecules

By

Guoqiang Xing

Symmetric-top molecules (CF$_3$Br, CF$_3$Cl, CF$_3$H and CH$_3$Br) in a seeded supersonic nozzle beam are orientation selected by a hexapole electric field, and collide at a right angle with fast (3-40 eV) potassium atoms. The ionization reactions at two different molecular orientations are studied:

\[
\begin{align*}
K + CX_3 - Y & \rightarrow K^+ + CX_3 + Y^- \\
K + Y - CX_3 & \rightarrow K^+ + CX_3 + Y^-
\end{align*}
\]

(Tails Orientation)
(Heads Orientation)

We observed that collision ionization reactions are influenced greatly by molecular orientations. For CF$_3$Br, CH$_3$Br and CF$_3$Cl, the reactivities are greater with the heads orientation than that with the tails orientation, but for CF$_3$H, the H end is unreactive. The steric effects are more pronounced at the low energy end near the thresholds, and almost disappear at energies above 20 eV. Most importantly, we also found that the energy thresholds of these reactions are different for heads and tails orientations, indicating that the electron affinity of a molecule should be considered as an anisotropic parameter.

Some features of the experimental results are explained by the Harpoon Electron Transfer model. Further theoretical and experimental studies are required for the fully understanding of the reaction dynamics.
Acknowledgements

I would like to express my heartfelt appreciation to Professor Philip R. Brooks for his invaluable advice and guidance during the last three and a half years. At times when the equipment resisted to cooperate, it is Dr. Brooks' encouragement and patience that kept my spirit high and the research going.

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I am very grateful to my thesis committee members, Drs. John S. Hutchinson and Randall G. Hulet, for their guidance and assistance.

I am deeply indebted to my parents and family members in China. They made sacrifices and were always supportive throughout my education. Specially I want to thank my wife, Xiaolu, who is my constant source of love and support.
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1 Introduction

1.1 Overview

Chemical reaction is a process of the breaking of old chemical bonds and the forming of new ones. The properties of the reagents, such as translational energies, electronic, vibrational and rotational states, molecular orientations and so on, will affect the rate of the reaction. The goal of chemical dynamics studies is to understand microscopically the factors that govern the basic phenomena in elementary molecular reactions so that the outcomes of the chemical processes can be predicted and controlled.

Reagent orientation effects are understood by chemists' intuition. For a bimolecular reaction,

\begin{equation}
A + BC \rightarrow AB + C
\end{equation}

kinetic theory shows that, in the hard sphere approximation, the reaction rate $R$ is proportional to the product of the number densities of the reagents (BER 82).

\begin{equation}
R = k(T) n_A n_B C
\end{equation}

where the rate constant $k(T)$ is determined by

\begin{equation}
k(T) = \rho u \sigma_0 \exp(-E_a / k_B T)
\end{equation}
and $u$ is the average relative speed of the reagents, $\sigma_0$ is the collision cross section determined by the sizes of the molecule and the atom, $E_a$ is the activation energy of the reaction, $k_B$ is the Boltzmann constant, and $T$ is temperature. The so-called steric factor $\rho$ is introduced to account for the discrepancy between theoretical prediction and experimental result. It is thought that only suitable orientation geometries of the reagents can lead to reaction, and $\rho$ is the fraction of collisions with the "correct" orientation. For some simple reactions such as $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$, the steric factor $\rho$ is between 0.1 and 1, and this geometrical interpretation seems reasonable. But for some other reactions such as $\text{Br} + \text{CHCl}_3 \rightarrow \text{CCl}_3 + \text{HBr}$, the fit of experimental results requires that $\rho \ll 1$, implying that the hard sphere collision theory is inadequate to describe such reactions. Nevertheless the molecular orientation requirements this model introduces are well accepted in later theoretical development (SMI 80, BUN 66).

Potential energy surfaces were first used to describe the bimolecular exchange reaction $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ (EYR 31). The $\text{H}_3$ potential energy surface has a barrier, so energy is required to cross from the reagent region to the product region. The height of the barrier was found to vary with the reagent approach geometry; the minimum barrier occurs when the three H atoms are aligned along a straight line (collinear). This early study suggests that the macroscopic reaction rates and orientation effects can be related to the dynamics of individual reactive encounters. The activated complex theory (GLA 41) was developed in the 30's to overcome the limitations of the hard sphere collision theory. The reaction rates are governed by the potential energy surfaces at the transition state. The steric factor is not explicitly included in the expressions of reaction rate, but the orientation dependence is still present in the forms such as the entropy of activation (HAM 78, LAI 65, WES 72).
In most reactions all reagent orientations are present. Direct measurements of the steric effects require that the orientation of the reactants be preselected. Due to the rotational motion, it is difficult to orient molecules merely by applying a strong electric field (the brute force). The field strength required ($\mu E \sim kT$) would far exceed the laboratory limit ($10^7$ volt/cm at room temperature). Only at extreme conditions (e.g., rotationally cold molecules in a supersonic expansion nozzle beam) can the brute-force orientation be achieved (LOE 90, FRI 91, and LOE 92). On the other hand, inhomogeneous magnetic or electric field and polarized laser excitation techniques can be used to preselect orientation and other quantum states of the reagents (BEN 64, TOE 65, TSO 77, BRO 66, KRA 65, STO 72, AND 80, VAN 80, MOE 75, ZAR 82).

1.2 Previous Studies of Orientation Effects

Development in molecular beam and laser technologies (for reviews, see STO 82a, LEO 84) in the last 30 years makes it possible for direct experimental studies of various steric effects in chemical reactions. Kramer and Bernstein first demonstrated that polar symmetric-top molecules such as CH$_3$I can be focussed by a hexapole electric field (KRA 65). There are numerous direct experimental evidence of molecular orientations achieved by the hexapole field (see, e.g., BRO 69, GAN 87a, GAN 87b).

a) Reactions at Thermal Energies

Brooks and Jones applied the technique of hexapole focussing to study the crossed beam reactions between CH$_3$I molecules and potassium atoms (BRO 66).
(1.4) \[ K + CH_3I \text{ (oriented)} \rightarrow KI + CH_3 \]

The molecules in the beam were oriented so that the incoming K atoms could approach either the I ends (heads) or the CH$_3$ ends (tails) of the molecules. It is found that there is a significant difference in reactivity for impact of K atoms at different ends of the molecules. The iodine end is more reactive than the methyl end.

Different symmetric-top molecules such as methyl iodide (CH$_3$I), tert-butyl iodide (t-BuI), chloroform (CHCl$_3$) and trifluoromethyl iodide (CF$_3$I) were used for further study of the steric hindrance (MAR 73, BRO 73, MAR 75, BRO 79). The angular distributions of the reaction products (KI or KCl) were measured. The absence of symmetric angular distribution of the products with respect to the center of mass (CM) for all reactions shows that there is no long-lived intermediate complex.

For CH$_3$I and t-BuI (MAR 73, MAR 75), the angular distributions are similar: single peaks are found at laboratory angles of about 90° and 100° (with respect to the direction of the incoming K beam), respectively, which correspond to rebound scattering in the CM system. These results are in agreement with experimental results using un-oriented CH$_3$I molecules (HER 61). Even though the reaction products (KI) have the same angular distribution for the head and tail orientations, the iodine ends show larger reactivities for both molecules, with \( \sigma_\theta/\sigma_\gamma = 0.42 \) for t-BuI and 0.5 for CH$_3$I, where \( \sigma_\theta \) and \( \sigma_\gamma \) are the cross sections at unfavored (tails) and favored (heads) orientations, respectively. Using a hard sphere model, the larger orientation effects of t-BuI can be ascribed to the larger hindering radius of the t-Butyl (2.76Å compared to 2.54Å for methyl) and to higher degree of orientation (t-BuI is a more oblate top).
For CHCl₃ (MAR 73), intensities of backscattered KCl were found to be the same for both orientations even though the molecule is very oblate and can be better orientated (See Section 2.3). The absence of orientation effects in reactivity is apparently due to two factors: 1) there are three reaction sites (chlorine atoms) on the molecule as compared to only one (the unique halogen) on molecules such as CH₃I, and 2) the small hydrogen atom is apparently insufficient to shield the chlorine atoms.

For CF₃I (MAR 73, BRO 73), the reactivities are about the same at either end of the molecule, but the head and tail orientations result in backward and forward scattered KI, respectively. An electron transfer model (MAG 40, HER 66) (or the Harpoon Model) was introduced to explain the orientation dependence of forward and backward scattering. According to this model, an electron is transferred from the approaching K atom to the molecule at a large internuclear distance $R_C$ ($\sim 5 - 10\text{Å}$, determined by the ionization potential and vertical electron affinity of the molecule, $R_C = e^2/(IP - EA)$). The molecular ion then dissociates rapidly (much faster than the molecular rotation), ejecting I⁻ along the molecular axis, and K⁺ is dragged by the much heavier I⁻ due to the Coulomb force to form KI. So in the heads orientation, KI is scattered backward with respect to the incoming K, and in the tails orientation KI is scattered forward. The roughly equal head and tail reactivities could be a consequence of the electron jump probability being independent of the molecular orientation.

To test the Harpoon Model, reactions between potassium and CF₃I oriented sideways (molecular axis perpendicular to the relative velocity) were studied (BRO 79). The KI detector was placed in the direction parallel to the orienting field. Molecules can be oriented sideways with respect to the incoming K atom with either the I end or the CF₃ end facing the detector. The reactivities in both orientations are the same, but according to the electron transfer model,
the products (KI) will fly either *towards* or *away* from the detector, resulting in different signal levels. The experimental results confirmed this prediction.

If the totally different features observed for CH₃I and CF₃I are mainly due to the difference of electron affinities of the molecules (0.2eV for CH₃I and 1.57eV for CF₃I), it is of interest to study molecules which have electron affinities between that of CH₃I and CF₃I. For this reason, the reaction of K atoms with oriented CF₃Br (*EA = 0.91eV*) was investigated (CAR 86). The head orientation is more reactive than the tail orientation (CH₃I-like), and the head and tail orientation have peaks at different scattering angles (CF₃I-like) which indicate, respectively, backward and forward scattering of KBr. The harpoon mechanism seems to be a useful way to explain some of the reactions described above, but it must be understood that it is also a gross oversimplification of the complicated reaction process.

There is a series of experimental studies of the reaction (BEU 66, BEU 68, BEU 69, PAR 81, PAR 82, CHA 82):

(1.5) \[ \text{Rb} + \text{CH}_3\text{I} \rightarrow \text{RbI} + \text{CH}_3 \]

It is found that RbI is mostly backscattered in the CM system. At near-forward scattering angles in the CM (related to collisions with large impact parameters), the reactivity is almost independent on orientation. But at the backscattering angles, reactivity is asymmetric with respect to molecular orientation, and the head orientation contributes more to RbI intensity than the tail orientation. Detailed analysis suggests that there is a cone of nonreaction (half angle of 53° between Rb beam direction and the molecular axis) when Rb approaches CH₃I in the tail orientation. Stotle *et al.* analyzed the experimental results (STO 82b) by expanding the reaction intensity in a Legendre polynomial series. The steric
factor $f$ at a backscattering angle is determined to be about 0.38. ($f = 1$ if the reactivity is independent on orientation, and $f = 0$ if reaction occurs only when the molecules are perfectly oriented in the direction of the incoming Rb and with the I end facing Rb.) More theoretical analyses were carried out later (LEV 84, ENG 84, BER 85, CHO 85), some of the models assumed a linear dependence of the reaction activation energy on orientation and gave reasonable fit to experimental results.

Kuwata and co-workers (OHO 87) studied the reaction:

\[(1.6) \quad \text{CF}_3\text{H} \text{ (oriented)} + \text{Ar}^* \rightarrow \text{CF}_3^* + \text{Ar} + \text{H.}\]

The symmetric-top molecules are focussed by a hexapole field and the metastable Ar($^3\text{P}_{2,0}$) is produced by electron impact. Emission from CF$_3^*$ was found to be more intense when Ar* impinges on the F end, and the steric effect increases with increasing hexapole voltage.

The reaction between O$_3$ and oriented NO was also studied (VAN 80).

\[(1.7) \quad \text{NO} + \text{O}_3 \rightarrow \text{NO}_2^* + \text{O}_2 \rightarrow \text{NO}_2 + h\nu + \text{O}_2\]

It was found that when the ozone attacks the N end of the molecule (head), the chemiluminescent reaction cross section $\sigma_{h\nu}(\text{head})$ is bigger than that when O$_3$ attacks the O end (tail): $\sigma_{h\nu}(\text{head})/\sigma_{h\nu}(\text{tail}) = 1.66$.

Using laser excitation techniques, molecular alignment can be achieved. Note that molecular alignment and orientation are different, as illustrated in Figure 1.1. Using a space-fixed axis (usually the direction of the relative velocity of the colliding partners) as a reference, molecular alignment refers to the molecular axis being parallel or perpendicular to this reference direction, while molecular orientation refers to the relative position of one particular end of the
molecule with respect to the other end along the reference direction. The relative difference of total collision cross sections between perpendicular and parallel alignment are mostly small \( ((\sigma_\perp - \sigma_\parallel)/(\sigma_\perp + \sigma_\parallel) \sim 10^{-3}, \) see, e.g., STO 72 and STO 73).

Figure 1.1 Demonstration of the difference between molecular orientation and alignment. The polarity of the molecular axis is irrelevant for alignment, so molecules could have perfect alignment but no orientation at all.

b) Reactions at Higher Energies

The reactions mentioned above involving symmetric-tops and alkali atoms have been studied at thermal energies. Even though the harpoon model can explain the backward and forward scattering at different molecular orientations, it is unknown which end of the molecule preferentially receives the harpoon electron. For CF\( _3 \)Br, the lower KBr intensity at tails orientation could be due to a smaller electron jump probability (entrance channel effect) or to the fact that the CF\( _3 \) is between K\(^+ \) and Br\(^- \) and prevents the formation of KBr (exit channel effects). To probe the electron transfer process directly, Harland, Brooks, et al. studied crossed beam reactions between fast potassium atoms (\( \geq 3\text{eV} \)) and various oriented symmetric-tops (HAR 89, HAR 90, HAR 91 and BRO
At sufficiently high energies, the K$^+$ and halogen ions can escape the Coulomb attraction and ionization reactions occur:

\[ K + CX_3Y \rightarrow K^+ + CX_3 + Y^- \]  

By collecting K$^+$, the ionization reactivity was measured as a function of K beam energy and molecular orientation. Ionization is more likely for impact on the "heads" end, and the effect of orientation is greatest at low reaction energies. Extrapolation of the reactivity to low energies suggests that there might be a difference in energy thresholds between the head and the tail orientations. These preliminary experimental results could be explained solely by the exit channel effects. The harpoon electron is first transferred to the molecule (and may or may not depend on orientation). Then the intermediate molecular ion promptly and explosively decomposes, ejecting the halogen ion along the original molecular axis. In the tail orientation, the halogen ion travels in the same direction as the K$^+$, and the relative velocity between K$^+$ and Y$^-$ is smaller, leading to bigger neutralization probability and smaller K$^+$ signal, compared to that in the head orientation.

1.3 Motivation of This Work

Even though the simple harpoon model can be used to explain some of the experimental features, a few questions remain unanswered: a) Does the molecular orientation affect the electron transfer (entrance channel effects)? b) How does the reactivity depend on reaction energy? c) Most interestingly, are the energy thresholds indeed different between different molecular
orientations? d) Between different symmetric-top molecules, what are the
deciding factors for different reaction cross sections?

In answering these questions, it seems imperative to determine
accurately the energy distribution in the fast potassium beam. A broad energy
distribution would convolute any energy dependence of the orientation effect.
The nominal K beam energy has to be known precisely, too, in order to
determine the energy thresholds for certain reactions.

The lack of thorough theoretical and experimental studies on steric
effects in chemical reactions makes their full understanding difficult. In
answering some of the existing questions, each new finding always seems to
add new pieces to the puzzle. It is appropriate to conclude this chapter with a
comment (BER 87) made by three of the well-known giants (R. B. Bernstein, D.
R. Herschbach, and R. D. Levine) in the field of chemical dynamics:

Chemistry is like an impressionistic painting. If we view it from too close,
all we see is puzzling detail in myriad dabs of paint. If we look from too far, all
we see is a shimmering blur. ... At the right distance, wondrous and lovely things
appear. We can strive to make that happen as we abstract from a host of
experiments and calculations some basic facts and insights about dynamical
stereochemistry.
2 Experimental

The cross beam ionization reactions between symmetric-top molecules and the potassium atoms ($E > 3$eV) are studied in this experimental work. The molecular beam is produced by nozzle supersonic expansion, and molecular orientations are achieved by the electric hexapole and uniform orienting fields. The fast neutral K beam is generated in a resonant charge exchange source. In this chapter, a brief description of the experimental apparatus and characterizations of both the molecular and the alkali beams are provided.

2.1 The Experimental Apparatus

The overall experimental setup is shown in Figure 2.1. The vacuum system consists of several differentially pumped chambers. The pumping system is described in Table 2.1.

It is critical to have precise and reproducible alignment of the molecular beam and the hexapole axis. This is achieved by the optical bench mounting system, described in detail in H. Carman Jr's thesis (CAR 86a). An identical bench is mounted on a table outside the vacuum so that precise alignment can be done conveniently.
Figure 2.1 Diagram of the experimental setup. (Top view, vacuum pumps are not shown.)

Table 2.1 The Differential Pumping System

<table>
<thead>
<tr>
<th>Chamber</th>
<th>Diffusion Pump</th>
<th>Backing Pump</th>
<th>No. of LN2 Traps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle</td>
<td>Varian HS-10</td>
<td>Leybold D60A</td>
<td>One</td>
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<tr>
<td></td>
<td>4000 l/s</td>
<td>36.7 cfm</td>
<td></td>
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<td>CVC PMCS-6B</td>
<td>Leybold D30A</td>
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<td>1400 l/s</td>
<td>25.8 cfm</td>
<td></td>
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<tr>
<td>Hexapole Field</td>
<td>Two CVC PMC-6B</td>
<td>Varian SD-300*</td>
<td>One</td>
</tr>
<tr>
<td></td>
<td>2x1400 l/s (Baffled)</td>
<td>11 cfm</td>
<td></td>
</tr>
<tr>
<td>Scattering</td>
<td>Varian VHS-6</td>
<td>Varian SD-300*</td>
<td>One</td>
</tr>
<tr>
<td></td>
<td>2400 l/s (Baffled)</td>
<td>11 cfm</td>
<td></td>
</tr>
<tr>
<td>Potassium Beam</td>
<td>NRC SHS-2</td>
<td>Varian SD-300*</td>
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<tr>
<td></td>
<td>175 l/s</td>
<td>11 cfm</td>
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<td>K Beam Detection</td>
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<td>None</td>
<td>One</td>
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<td>Mass Spec.</td>
<td>Varian Ion Pump</td>
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<td></td>
<td>P/N 912-7006, 110 l/s</td>
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</tr>
</tbody>
</table>

* Shared by four diffusion pumps in these three chambers.

** High vacuum is first achieved by opening the gate valve to the scattering chamber.
a) The Nozzle Chamber

The nozzle chamber contains the nozzle source and the skimmer. The gas nozzle has an orifice of 200 \( \mu \text{m} \) diameter and can be heated by Ta coils. The skimmer, which is the first collimator of the beam, is an electroformed nickel cone with a 0.49 mm diameter orifice. The skimmer is glued onto a stainless steel plate which is mounted on the optical bench and sealed to the wall of the chamber by a flexible metal bellows. The nozzle assembly, also mounted on the bench, can be translated on the bench shaft via a linear motion feedthrough to adjust the nozzle to skimmer distance for optimum beam condition.

b) The Buffer Chamber

The buffer chamber consists of a beam chopper and a collimating aperture. The chopper wheel is a double blade aluminum disk with a duty cycle of 50\%. The chopper wheel is driven by a 60 Hz hysteresis synchronous motor to give a 120 Hz beam modulation. The chopper assembly is supported on an aluminum frame by six springs to damp the vibration.

A photo transistor is used to monitor the beam on/off status. The chopper disk runs between the light emitting diode (LED) and the base of the transistor, and the photo transistor circuit gives a 120 Hz square wave (high = beam off, low = beam on) as the beam modulation signal.

Between the chopper wheel and the hexapole field entrance, an adjustable iris diaphragm is mounted as the second beam collimator (the entrance aperture). While a small orifice dictates small beam intensity, a very large orifice will increase the gas load into the hexapole field region, causing beam scattering and reducing transmitted beam intensity. The orifice of the collimator is set at 5 mm diameter to achieve good signal to noise ratio while maintaining beam intensity.
c) **The Hexapole Field Chamber**

The hexapole field consists of three identical 18" long sections mounted in series. Each section has six electrodes made of 1/4" diameter fine polished stainless steel rods mounted on two Plexiglass insulators. At the end of the hexapole field, another beam collimator (the exit aperture) with an aperture of 0.35" is installed.

As illustrated in Fig. 2.2, the high voltages for the hexapole field are supplied by two DC HV power modules (Spellman, Model MP15P and MP 15N) with maximum voltage outputs of ±15KV @ 0.6 mA. A digital to analog convertor (DAC) in the CAMAC crate is used to provide the inputs (0-10V) for the power supplies.

![Diagram of the computerized high voltage outputs for the hexapole field. The Op-amp 741 is used as an emitter follower to limit the current drawn from DAC.](image)

The hexapole field chamber is pumped by two CVC PMC-6B diffusion pumps with baffles cooled by liquid Freon to reduce back streaming of pump oil. Condensation of pump oil vapor on the hexapole electrodes will result in arcing under high voltages. A good vacuum in the hexapole field region is critical in reducing the background noise and increasing beam transmission. A large LN2 trap is installed to improve the pumping speed in this chamber.
d) The Scattering Chamber

The scattering chamber consists of the orienting field plates and two channeltrons used to collect the potassium ions. The molecules transmitted by the hexapole field are state-selected (see Section 2.3), and to provide a reference direction, a uniform electric field is generated by two parallel plates at the exit of the hexapole field. The distance between the two plates changes gradually to provide an adiabatic transition region from the hexapole field to the homogeneous orienting field. The plates are DC biased at opposite potentials (±50V, typically), and the direction of the field can be parallel or antiparallel to the incoming potassium beam, as shown in Fig. 2.3.

![Diagram](image)

(a) 0° Configuration  
(b) 180° Configuration

**Figure 2.3** Configurations of the homogeneous orienting fields. (a) 0° configuration, the K⁺ ions are detected by Channeltron #1; (b) 180° configuration, the ions are collected by Channeltron #2.

The K beam passes the scattering center through two openings on the orienting field plates. The diameter of the K beam is about 0.5 cm near the scattering center. Two identical channel electron multipliers (channeltron) are housed in two Plexiglass cages which are mounted on the orienting field plates.
The potassium ions produced in the collision ionization reactions are collected by one of the channeltions. The usage of a particular channeltron is determined by the direction of the field, as illustrated in Fig. 2.3. The dynode (cone) of the active channeltron is typically biased at -1400V, and the anode of the channeltron is biased at a voltage between +300 and +700V depending on the requirement on the channeltron's gain. The assembly of the uniform field plates and the channeltions is mounted on an adjustable platform and is aligned with the potassium beam.

Oil vapor contamination in the scattering chamber causes degradation of channeltron characteristics and electrostatic charge-up. (The channeltron can be reactivated by a baking-cleaning procedure developed after several tests, see Appendix.) The back-streaming of diffusion pump oil is minimized by installing the cold baffle.

e) The Potassium Beam Chamber

The potassium beam chamber contains the charge exchange oven, the ion deflection field plates and the collimating skimmer. The skimmer is surrounded with LN2 cooled copper plates to pump away the potassium vapor.

The design of the compact charge exchange oven was first made by Helbing and Rothe (HEL 68) to generate fast (> 3eV) Cs atom beams with small energy spreads. The source is easy to operate because the alkali ion production, acceleration and charge exchange with thermal alkali atoms take place in the same oven source. Alkali atoms in the vapor are first surface ionized at a hot W filament and the ions then are electrostatically accelerated within a short distance (< 1mm) to a desired energy. In a field free region, the energetic ions collide with thermal atoms, producing a beam of fast neutral alkali atoms without energy loss as a result of resonant charge exchange.
In our experiment, the oven body is made of Monel metal, and can be heated uniformly. The oven temperature is measured by an Iron/Constantan (type J) thermocouple. The cylindrical cavity in the center of the oven, serving as a potassium reservoir, is capped by a Monel flange. The oven is charged with 5 grams of potassium in a prescored glass ampule (Strem Chemicals). A tungsten filament (10 mil in diameter) is spot-welded onto two feedthroughs on the oven cap, and is DC heated to 2100°K (heating current at 5.0 A, ROS 65) to maintain a high surface ionization efficiency. A grid made of nickel mesh with 90% transparency is placed 1mm in front of the filament. The potential difference between the filament and the grid determines the energy of the final beam. The charge exchange region is about 20 mm long and the K beam exits the oven through an orifice of 1/8" diameter.

Between the oven and the skimmer, an electrostatic deflection field is applied to remove any ionic components in the beam coming out of the oven. The beam going into the scattering chamber consists of fast K atoms and the effusive thermal K atoms, but the later have no contribution to the endoergic ionization reaction because their energy is too low.

The oven is kinematically mounted on a stainless steel platform, which is extended to the scattering chamber to support the orienting field assembly. A secondary K beam skimmer mounted on this platform in the scattering chamber is found to be very effective in reducing the background noise due to scattering of the diverged potassium atoms in the beam.

f) The K Beam Detection Chamber

The K beam passes through the scattering chamber into the K beam detection chamber, which is a 6" OD and 22" long stainless steel tube pumped by a coaxial cylindrical LN2 trap.
A surface ionization detector (SID) is mounted at the end of the chamber to monitor the K beam intensity. The detector is either a 5 mil W wire or a 1/4"x1-1/2"x.005" Mo ribbon. The detector needs to be aged at elevated temperatures to maintain high ionization efficiency. The W filament detector can be aged at 2400°K for 24 hours, at 2600°K for one hour, or at 2800°K for 15 minutes. These temperatures correspond to heating currents of, respectively, 2.1A, 2.5A and 2.9A (ROS 65). Due to the current limits of the electrical feedthroughs, the Mo ribbon detector can only be aged at 15A for up to 5 minutes.

The ions coming off the surface ionization detector are collected and amplified by a Bendix magnetic electron multiplier (MEM). Figure 2.4 shows the operational principle of MEM. The electron gain of MEM is typically between $10^6$ and $10^8$ depending on the voltage applied.

Figure 2.4 Diagram of the Bendix Magnetic Electron Multiplier (MEM). The magnetic field between the Field and Dynode Strips is perpendicular to the plane of the drawing.

g) The Mass Spectrometer Chamber

The quadruple mass spectrometer is installed in the mass spectrometer...
chamber under ultra high vacuum (UHV). The chamber is linked to the main chamber by a flexible metal bellows and a high vacuum straight-through valve. The mass spectrometer is used to detect and monitor the molecular beams transmitted by the hexapole.

In Table 2.2 and Table 2.3, the dimensions along the molecular beam and potassium beam axes are summarized.

Table 2.2 Apparatus Dimensions along the Molecular Beam Axis

<table>
<thead>
<tr>
<th>Diameters of apertures and orifices</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle Orifice:</td>
<td>200 μm</td>
</tr>
<tr>
<td>Skimmer Orifice:</td>
<td>0.49 mm</td>
</tr>
<tr>
<td>Entrance Aperture:</td>
<td>5.0 mm</td>
</tr>
<tr>
<td>Hexapole Field:</td>
<td>9.47 mm</td>
</tr>
<tr>
<td>Hexapole Rod:</td>
<td>6.30 mm (1/4&quot;)</td>
</tr>
<tr>
<td>Exit Aperture</td>
<td>8.89 mm (.35&quot;)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Distances</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle to Skimmer</td>
<td>15 mm (adjustable)</td>
</tr>
<tr>
<td>Skimmer to Entrance Aperture</td>
<td>15.3 cm</td>
</tr>
<tr>
<td>Hexapole Rod (One Section)</td>
<td>45.7 cm (18.0&quot;)</td>
</tr>
<tr>
<td>Entrance Aperture to Exit Aperture</td>
<td>140.7 cm</td>
</tr>
<tr>
<td>Exit Aperture to Scattering Center</td>
<td>12.1 cm (4-3/4&quot;)</td>
</tr>
<tr>
<td>Chopper to Scattering Center</td>
<td>153.4 cm</td>
</tr>
</tbody>
</table>
Table 2.3 Apparatus Dimensions along the Potassium Beam Axis

<table>
<thead>
<tr>
<th>Diameters of apertures and orifices</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>W Filament inside the Oven</td>
<td>10 mil</td>
</tr>
<tr>
<td>K Oven Orifice</td>
<td>3.18 mm (1/8&quot;)</td>
</tr>
<tr>
<td>Primary Skimmer Orifice</td>
<td>1.27 mm (.05&quot;)</td>
</tr>
<tr>
<td>Secondary Skimmer Orifice</td>
<td>5.87 mm (.231&quot;)</td>
</tr>
<tr>
<td>Opening on Orienting Field Plates</td>
<td>15 mm</td>
</tr>
<tr>
<td>*W Surface Ionization Detector Wire</td>
<td>5 mil</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Distances</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>W Filament to Grid in the K Oven</td>
<td>1 mm</td>
</tr>
<tr>
<td>Grid to Oven Orifice</td>
<td>20 mm</td>
</tr>
<tr>
<td>Oven Orifice to Primary Skimmer</td>
<td>4.9 cm</td>
</tr>
<tr>
<td>Oven Orifice to Secondary Skimmer</td>
<td>12.2 cm</td>
</tr>
<tr>
<td>Oven Orifice to Scattering Center</td>
<td>18.4 cm (7-1/4&quot;)</td>
</tr>
<tr>
<td>Scattering Center to SID detector</td>
<td>65.3 cm</td>
</tr>
<tr>
<td>Orienting Field Plates Spacing</td>
<td>7.6 cm (3&quot;)</td>
</tr>
</tbody>
</table>

* The W wire can be replaced by a 0.005"x 1/4"x1-1/2" Mo ribbon.

2.2 The Supersonic Nozzle Beams

About half century ago, molecular beam experiments were carried out using effusive beam sources. The molecular beam is formed by effusion through a small aperture on a chamber containing a few torr of gas or vapor. The molecules inside the chamber have the Boltzmann-Maxwell velocity distribution:

\[ f(v) = \frac{4}{\sqrt{\pi}a^3}v^2\exp\left(-\frac{v^2}{a^2}\right) \]
where \( \alpha = \sqrt{\frac{2kT}{m}} \) is the most probable speed, \( m \) is the mass of the molecule and \( k \) is the Boltzmann constant. When the width of the source slit \( w \) is small compared to the mean-free path of the molecule \( \lambda \), no collision occurs as the molecules leave the source. This condition, \( w \leq \lambda \), has to be met for effusive beams. The mean-free path \( \lambda \) is determined by:

\[
(2.2) \quad \lambda = \frac{1}{\sqrt{2} n \sigma}
\]

where \( n \) and \( \sigma \) are the number density and the collision cross section of the molecules, respectively.

The rate of molecules emerging from the source is given by

\[
(2.3) \quad Q = \frac{1}{4} A n \bar{v}
\]

where \( \bar{v} = 2\alpha N \bar{v} \) is the mean velocity of the gas molecules, and \( A \) is the area of the source slit. The velocity distribution in the beam is given by

\[
(2.4) \quad f_B(v) = \frac{2}{\alpha^4} v^2 \exp(-v^2/\alpha^2)
\]

The effusive beam sources are easy to operate and their thermodynamic properties are well understood. But the beam intensity is limited by the size of the slit, and the speed distribution in the beam is very broad (Eq. (2.4)). To overcome the limitations of the effusive beams, Kantrowitz and Grey proposed in 1951 a method to generate a molecular beam with high intensity and narrowed velocity distribution — the supersonic nozzle source (KAN 51).

When a gas at a relatively high pressure (several hundred torr or more) in a chamber is expanded through a small orifice, a hydrodynamic jet is formed. During the expansion, molecules in the stream collide with each other hundreds of times before the flow is sufficiently rarefied to become collision free. Near the
collision free region a collimator (skimmer) is placed along the beam axis to sample a molecular beam. The reason for using a skimmer instead of a normal collimating slit is to reduce the collision rate between the incident molecules and the molecules reflected by the collimator. The skimmer is the first defining element of the nozzle beam and plays a role analogous to the effusive slit in an oven beam source.

The molecules in the nozzle beam are travelling with a mean velocity relative to the skimmer. The Mach number $M$, defined as the ratio between the mass flow velocity $u$ and the local speed of sound $a$, is used as an important parameter to describe the properties of the beam.

(2.5) \[ M = \frac{u}{a} \]

where $a = (\gamma k T_s / m)^{1/2}$ is the speed of sound just in front of the skimmer, $\gamma = C_p / C_v$ is the specific heat ratio, $T_s$ is the temperature in the supersonic beam and $m$ is the molecular weight.

The supersonic expansion of the molecules from the nozzle is an isentropic process. The random translational motion and internal motion (rotation, vibration) of the molecule are greatly reduced through the nozzle expansion, by being converted into mass flow velocity $u$, which is determined by conservation of energy (ABU 67):

(2.6) \[ \frac{1}{2} m u^2 = \int_{T_s}^{T_0} C_p dT \]

where $T_0$ is the temperature of the nozzle. From this equation it immediately follows that
\[ \frac{T_s}{T_0} = \frac{1}{1 + \frac{1}{2}(\gamma - 1)M^2} \]

\[ u^2 = \frac{2kT_s}{m} \frac{\gamma M^2}{2} = \frac{2kT_0}{m} \left(1 + \frac{\gamma - 1}{2}M^2\right)^{-1}\gamma M^2 \]

With a value of \( M \geq 20 \) which is obtainable, the beam temperature \( T_s \) is about 2°K for a monatomic gas \( \gamma = 5/3 \), when the nozzle is at room temperature. For polyatomic molecules \( \gamma \) is smaller and so is the cooling effect.

Fig. 2.5 shows the mass flow velocity \( u \) (in units of \( \sqrt{2kT_0/m} \)) as a function of Mach number for a monatomic gas beam. For \( M \geq 5 \), the mass flow velocity approaches the limit determined by \( (\gamma/(\gamma - 1))^{1/2} \).

![Figure 2.5 Theoretical mass flow velocity (in units of \( (2kT_0/m)^{1/2} \)) as a function of the Mach number \( M \) for a monatomic nozzle beam.](image)

The velocity distribution of the molecules emerging from the skimmer along the beam axis is assumed to be a three dimensional Maxwell-Boltzmann
distribution with the characteristic temperature $T_s$ superimposed on the stream flow velocity $u$ (AND 65):

\[ f_s(v) = N \left( \frac{v}{\alpha_s} \right)^2 \exp \left( - \frac{(v - u)^2}{\alpha_s^2} \right) \]

(2.9)

where $N$ is the normalization factor, and

\[ \alpha_s = \sqrt{\frac{2kT_s}{m}} = \sqrt{\frac{2kT_0}{m(1 + 1/2(\gamma - 1)M^2)}} \]

(2.10)

\[ \]}

Figure 2.6 Theoretical axial velocity distributions for nozzle beams of monatomic gases with different Mach numbers. The distribution for an effusive beam corresponds to $M = 0$.

Fig. 2.6 shows the axial velocity distributions for monatomic nozzle beams at different values of $M$. The velocity is in units of $(2kT_0/m)^{1/2}$, and $M = 0$ corresponds to effusive beams. This figure shows that a nozzle source beam has a much narrower velocity distribution. The percentage of the total flux that falls within 5% of the mean molecular velocity is 11%, 47% and 80% for an effusive beam ($M = 0$), nozzle beams with $M = 10$ and $M = 20$, respectively.
The nozzle beam effectively converts the random motion of the molecules into mass flow velocity. The internal motions of the molecules such as rotation and vibration are also cooled. For \( M >> 1 \) the mass flow velocity is much greater than most of the random velocities so the beam intensity through the skimmer is greatly increased and the molecules in the beam passed by the skimmer are more focussed along the beam axis. For these reasons the nozzle beam intensity is several orders of magnitude higher than the effusive beam at similar settings. The intensity ratio between nozzle and effusive beams is about \( \frac{1}{2} \gamma M^2 \) (AND 66).

Using Argon as the source gas, TOF experiments have been done previously in this lab to determine the velocity distribution in the supersonic nozzle beam. By fitting the TOF spectra, the mass flow velocity \( u \) and beam temperature \( T_s \) were determined to be 565 m/s and 1.0\(^{\circ}\)K, respectively (CAR 86a). This implies from Eq. (2.7) that the Mach number of the nozzle beam is about 30 (\( T_0 = 305^{\circ}\)K).

Details about the technical design of nozzle source and skimmer can be found in a review article by Anderson, Andres and Fenn (AND 66).

Another important application of the nozzle beam is that the nozzle gas can be a mixture — a few percent of a seed gas mixed with a carrier gas. Due to many collisions between the molecules in the space between the nozzle and the skimmer, the velocities and the temperatures of the seed and the carrier become nearly the same. In a dilute mixture the seed gas in the beam will adopt the characteristics of the carrier gas. By seeding heavy molecules in a light carrier gas, the flow velocity of the seed can be increased drastically. Using CF\(_3\)Br seeded in He as an example, the mass flow velocity of CF\(_3\)Br will be several times bigger than that in a neat CF\(_3\)Br nozzle beam, resulting in a translational energy as high as 2eV. Noble gases are usually chosen as the
carrier gas due to their chemical inactivity and large specific heat ratio \((\gamma = 5/3)\), thus the random translational and internal motion can be converted more effectively into mass flow velocity.

By seeding the beam one would expect that the beam intensity of the seed molecules will be reduced by a factor equal to the seeding ratio as compared with the pure nozzle beam. It turns out that this is not true. At the skimmer the heavier molecules have a higher Mach number so they are better focussed on the beam axis. This is the so-called 'hydrodynamic focusing' effect (AND 66). In our experiments, by using a CF\(_3\)Br(10%)/He(90%) mixture, the K\(^+\) signal (proportional to the intensity of CF\(_3\)Br) is about 1/3 to 1/2 of that of a pure CF\(_3\)Br beam with the same stagnation pressure at the nozzle.

2.3 Focusing and State Selection by Hexapole Field

Inhomogeneous magnetic and electric fields have numerous applications in atomic and molecular physics (see, e.g., RAM 56, ENG 74). In 1955, Bennewitz and co-workers suggested that electric hexapole fields can be used for focusing and state-selecting polar symmetric top molecules. This was proved later by the experiments done by Kramer and Bernstein (KRA 65) and by Brooks et. al. (BRO 66).

a) Quantum Mechanical Description of the Rotational Motion of the Symmetric-Top Molecules

The moment of inertia of any polyatomic molecule with \(n\) atoms can be described by the elliptical equation:

\[
\frac{x^2}{I_x^2} + \frac{y^2}{I_y^2} + \frac{z^2}{I_z^2} = 1
\]

(2.11)
where \( I_x, I_y \) and \( I_z \) are the moments of inertia along the directions of the principal axes, defined as:

\[
I_i = \sum_{j=1}^{n} m_i r_{ij}^2 \quad i = x, y \text{ or } z
\]

where \( r_{ij} \) is the distance from the \( j \)th atom to the \( i \) axis. The origin of the \( x\text{-}y\text{-}z \) coordinate is the center of mass of the molecule.

For a polar symmetric-top molecule, two of the principal moments of inertia are equal and the third one is along the direction of the molecular symmetry axis. The symmetry axis is labeled as the \( C \) axis, and the other two principal axes as \( A \) and \( B \) axis. For a prolate symmetric-top, \( I_A = I_B > I_C \), the top is cigar-like, such as \( \text{CH}_3\text{I}, \text{CF}_3\text{Br} \); for an oblate symmetric-top, \( I_A = I_B < I_C \) and it is pancake-like, such as \( \text{CF}_3\text{H} \) or \( \text{CCl}_3\text{H} \).

From a classical point of view, the rotational motion of the symmetric-top molecules in a weak electric field is much like that of a child's top in the gravitational field. The axis of the top precesses about its total angular momentum vector \( P \) which, in turn, precesses about the direction of the field \( Z \). The orientation angle \( \theta \), defined as the angle between the molecular axis \( z \) and space fixed axis \( Z \), will oscillate between \( \theta_{\text{min}} \) and \( \theta_{\text{max}} \), which are determined by the angles between \( P \) and \( Z \), and between \( P \) and \( z \) (CHO 86). The classical mechanics treatment gives \( 0 \leq \theta_{\text{min}} < \theta_{\text{max}} < \pi \).

Quantum mechanically, the wave function \( \Psi \) of the rotational motion of the molecule is determined by the Schrödinger equation:

\[
\hat{H}\Psi = W\Psi
\]

where \( W \) is the energy eigenvalue of the Hamiltonian \( \hat{H} \) given by
(2.14) \[ \hat{H} = \frac{P_A^2}{l_A} + \frac{P_B^2}{l_B} + \frac{P_C^2}{l_C} \]

and \( P_A, P_B \) and \( P_C \) are angular momentum operators along the three principal axes. Using \( l_A = l_B \) and \( P^2 = P_A^2 + P_B^2 + P_C^2 \), \( \hat{H} \) can be rewritten as:

(2.15) \[ \hat{H} = \frac{P^2}{l_B} + \left( \frac{1}{l_c} - \frac{1}{l_B} \right) P_C^2 \]

The wave function \( \Psi \) can be described by the three Euler angles, \( \theta, \phi \) and \( \chi \) (TOW 55). The angles \( \theta \) and \( \phi \) are the normal polar angles describing the symmetry axis of the molecule in the space fixed coordinates, and \( \chi \) is the angle of rotation around the symmetry axis fixed in the molecule. The Schrödinger equation then becomes

(2.16) \[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \Psi}{\partial \phi^2} + \left( \tan^2 \theta + \frac{C}{B} \right) \frac{\partial^2 \Psi}{\partial \chi^2} - \frac{2 \cos \theta}{\sin^2 \theta} \frac{\partial^2 \Psi}{\partial \chi \partial \phi} + \frac{W}{\hbar^2} \Psi = 0 \]

where \( B \) and \( C \) are the rotational constants defined as:

(2.17) \[ B = \frac{\hbar}{8 \pi^2 l_B}, \quad C = \frac{\hbar}{8 \pi^2 l_C} \]

and \( \hbar \) is Planck's constant.

The variables can be separated and \( \Psi \) can be expressed as:

(2.18) \[ \Psi(\theta, \phi, \chi) = \Theta(\theta)e^{im\phi}e^{ik\chi} \quad M, K \text{ are integers} \]

The requirement that \( \Theta(\theta) \) can be expanded in a power series of \( \cos \theta \) which must terminate at a finite order gives the rotational energy eigenvalues:

(2.19) \[ W_{JKM} = B\hbar(J + 1) + (C - B)\hbar k^2 \]

The corresponding wave function is \( \Psi_{JKM}(\theta, \phi, \chi) \) or \( |JKM> \), where the quantum
numbers \( J, K \) and \( M \) represent, respectively, the total rotational angular momentum, its projections onto the molecular axis and onto the space fixed axis (the external electric field direction, for example). Obviously \(|K| \leq J, |M| \leq J\). The mean value of \( \cos \theta \) over rotation, characteristic of the molecular orientation, is determined by these quantum numbers.

\[
(2.20) \quad <\cos \theta> = <JKM|\cos \theta|JKM> = \frac{KM}{J(J+1)}
\]

At any instant the probability of finding the molecule (whose rotational state is \(|JKM>\)) with a specific orientation with respect to the laboratory axis is given by

\[
(2.21) \quad P_{JKM}(\rho)d\rho = 4\pi^2 |\Psi_{JKM}>^* \Psi_{JKM} d\rho
\]

where \( \rho = \cos \theta \), and \( P_{JKM} \) is the distribution function of molecular orientation which is independent of \( \phi \) and \( \chi \). Using the completeness of the Legendre polynomial series, Choi and Bernstein expressed the distribution function in terms of the Legendre polynomial \( P_n(\cos \theta) \) (CHO86):

\[
(2.22) \quad P_{JKM}(\rho) = \frac{2J+1}{2} \sum_{n=0}^{2J} C_n(JKM) P_n(\rho)
\]

with \( C_n(JKM) = (-1)^{M+K} \binom{J}{K -K 0} \binom{J}{M -M 0} \) and \( \binom{J}{K 0} \) is the 3-J symbols (see, e.g., ROS 57).

As an example, using the values of \( C_n(JKM) \)'s we can express the orientation distribution functions for the \(|111>\) and \(|211>\) states:

\[
P_{111}(\rho) = \frac{1}{2} P_0(\rho) + \frac{3}{4} P_1(\rho) + \frac{1}{4} P_2(\rho)
\]

\[
P_{211}(\rho) = \frac{1}{2} P_0(\rho) + \frac{1}{4} P_1(\rho) + \frac{5}{28} P_2(\rho) + P_3(\rho) + \frac{4}{7} P_4(\rho)
\]
The Legendre polynomial has the following recurrence relations:

\[(2.23a)\quad (n + 1)P_{n+1}(x) = (2n + 1)xP_n(x) - nP_{n-1}(x)\]
\[(2.23b)\quad P_0(x) = 1, \quad P_1(x) = x\]

Figure 2.7 Orientation distribution function \(P_{JKM}(\rho)\) for \(|111\rangle\) and \(|211\rangle\) states. The average orientations of these two states are indicated by the arrows.

Fig. 2.7 shows the distribution functions \(P_{111}(\rho)\) and \(P_{211}(\rho)\). It can be seen that there are finite probabilities when \(\cos \theta\) approaches -1. This is prohibited in the classical treatment. The values of \(\langle \cos \theta \rangle\) for \(|111\rangle\) and \(|211\rangle\) states are 1/2 and 1/6, respectively. They are the direct results of Eqs. (2.20) and (2.21), which can be rewritten as:

\[(2.24)\quad \langle \rho \rangle = \int_{-1}^{1} \rho P_{JKM}(\rho) d\rho = \frac{KM}{J(J + 1)}\]
b) The Hexapole Electrostatic Field

In general the electric field potential $U$ for a $2n$-fold hyperbolic electrodes with long length can be written in cylindrical coordinates as

$$ U_n(r, \phi, z) = U_0\left(\frac{r}{r_0}\right)^n \cos n\phi $$

(2.25)

where $r_0$ is the nearest distance of the electrodes to the $z$-axis, $\pm U_0$ are the potentials of the electrodes. The potential for a hexapole field ($n = 3$) is

$$ U(r, \phi) = V_0\left(\frac{r}{r_0}\right)^3 \cos 3\phi $$

(2.26)

This ideal field distribution can be achieved by six identical electrodes biased at $+V_0$ and $-V_0$ alternatively. The cross section surface of one of the electrodes is determined by $(r/r_0)^3 \cos 3\phi = 1$. In practice, six cylindrical rods can be used, to a good approximation, to produce a hexapole field, provided that the curvature of the rods at $r_0$ is the same as that of the ideal hexapole electrode. The curvature for the $2n$-pole field at $r_0$ is $(n - 1)/r_0$. Fig. 2.8 shows the cross section of the hexapole electrodes made of six cylindrical conducting rods.

![Figure 2.8 The cross section view of a hexapole field.](image-url)
The electric field \( \mathbf{E} \) is determined by:

\[
E = -\nabla U = \frac{3V_0}{r_0^3}(e_r \cos 3\phi - e_\theta \sin 3\phi) r^2
\]

and the magnitude of the field \( E = |E| = 3V_0 r^2 / r_0^3 \) is only a function of \( r \).

A symmetric-top molecule has permanent electrical dipole moment \( \mu_0 \) along its molecular axis. Since the molecular axis precesses at very high frequencies (>10^9 Hz) around the total angular momentum \( P \), the actual force experienced by the molecule in a hexapole field will be determined by the effective dipole moment:

\[
\mu_{\text{eff}} = \mu_0 <\cos \theta>
\]

In the weak field approximation, where the electric field strength is not high enough to cause significant change in the rotational wave function \( |JKM> \), the energy change due to the field can be expressed as:

\[
W_1 = \langle JKM | \cdot \cdot \cdot | JKM \rangle = -\mu_0 E <\cos \theta> = -\mu_0 E \frac{KM}{J(J+1)}
\]

This energy shift is the so-called first order Stark Effect. In our experiments the hexapole field strength is considered within the weak field approximation limit.

The equation of motion of the molecules in the hexapole field is determined by:

\[
\frac{m \ddot{r}}{dt^2} = F = -\nabla W_1 = \mu_0 \frac{KM}{J(J+1)} \nabla E
\]

Since \( E \) is only a function of \( r \) in the cylindrical coordinates, the above equations can be simplified as:
\[(2.31a) \quad \frac{d^2 r}{dt^2} = \frac{6\mu_0 V_0}{mr_0^3} \frac{KM}{J(J+1)} r \]

\[(2.31b) \quad \frac{d\phi}{dt} = 0 \]

\[(2.31c) \quad \frac{dz}{dt} = v_{z0} \]

where \(v_{z0}\) is the initial velocity of the molecule along the \(z\)-axis.

It can be easily seen from Eq. (2.31a) that if \(KM > 0\) the molecule will exponentially diverge from the field axis and when \(KM < 0\) the radial motion of the molecules will be a harmonic oscillation with a frequency of \(\omega\) given by:

\[(2.32) \quad \omega = \sqrt{\frac{6\mu_0 V_0}{mr_0^3} |KM|}{J(J+1)} \]

It is by this harmonic motion that the symmetric-top molecules can be focussed in the field. The hexapole field only focuses those molecules in quantum states such that \(KM < 0\). Thus the molecules transmitted by the hexapole field are state-selected.

c) The Hexapole Field Transmission Function

The hexapole field transmission function can be calculated for a given field geometry. Fig. 2.9 shows the definitions of several important dimensions of the hexapole field.

The orifice of the skimmer is very small compared to the entrance and exit apertures, with radii \(r_1\) and \(r_2\), respectively, and it can be considered a point source. It takes several milliseconds for a symmetric-top molecule to traverse the length of the hexapole field, during which millions of cycles of rotations take place. It is thus a very good approximation that the value of \(<\cos \theta>\) can be used to determine the force acted on the molecule for the whole duration of
interaction, even though at any instant the value of $\cos \theta$ can range between -1 and +1.

Figure 2.9 Diagram illustrating the hexapole field dimensions used to calculate the transmission function (not properly scaled).

Assume that a molecule in state $|JKM\rangle$ ($KM < 0$) with velocity $v$ emerges from the skimmer at an angle $\alpha$ ($\alpha << 1$) with respect to the axis; at $t = 0$ it enters the hexapole field with radius $r_0$ and length $L_2$. The molecule will travel along the z-axis direction at a constant velocity $v_z = v \cos \alpha = v$, and given the initial conditions, the radial motion of the molecule can be described as:

$$r(t) = \alpha L_1 \cos \omega t + \frac{\alpha v}{\omega} \sin \omega t$$

The molecule will be transmitted by the hexapole only if its maximum radial displacement from the z-axis is smaller than the radius of the lens and smaller than the exit aperture at the end of the field. Assume that the angular distribution of beam intensity is uniform near the beam axis, and there is no beam stop at the entrance aperture. The fraction of molecules being transmitted by the hexapole field is

$$A(V_0, v, \rho) = \frac{\alpha_0^2}{\alpha_{\text{max}}^2}$$
where \( \rho = \frac{KM}{J(J+1)} \), \( \alpha_{\text{max}} = \tan^{-1}(r_1/L_1) = r_1/L_1 \) and \( \alpha_0 = \min(\alpha_1, \alpha_2) \) with

\[
\alpha_1^2 = \frac{\omega^2 r_0^2}{\nu^2(1 + \beta_1^2)}; \quad \alpha_2^2 = \frac{\omega^2 r_0^2}{\nu^2(\sin \beta_2 + \beta_1 \cos \beta_2)^2}
\]

and \( \beta_1 = \omega L_1/\nu, \beta_2 = \omega L_2/\nu \).

For a given field geometry and a molecule, the transmission function \( A \) depends on the hexapole voltage \( V_0 \), the speed \( \nu \) and the rotational state of the molecule.

To block the direct beam from reaching the scattering center, a beam stop can be placed near the entrance aperture of the hexapole lens. The diameter of the beam stop should be large enough so that the shadow it casts is bigger than the exit aperture. With such a beam stop, no molecules can be transmitted without deflection by the field.

The transmission function for a specific quantum state \( |JKM\rangle \) is given by:

\[
F_{JKM}(V_0) = \int_0^\infty A(V_0, \nu, \rho)f_s(\nu)d\nu
\]

where \( f_s(\nu) \) is the speed distribution function of the supersonic nozzle beam given by Eq. (2.9).

It follows that the total transmission function \( T(V_0) \) is:

\[
T(V_0) = \sum_{J,K,M} F_{JKM}(V_0)f_{JKM}
\]

and

\[
f_{JKM} = \frac{S(I, K)e^{-W_{\text{rot}}/kT_{\text{rot}}}}{\sum_{J=0}^{\infty} \sum_{K=-J}^{J} S(I, K)(2J + 1)e^{-W_{\text{rot}}/kT_{\text{rot}}}}
\]
where $t_{JKM}$ is the probability of the molecule being in the $|JKM\rangle$ state which is assumed to be a weighted Boltzmann distribution, $W_{JKM}$ is the rotational energy given by Eq. (2.19), $T_{rot}$ is the rotational temperature of the nozzle beam (comparable to $T_S$ in Eq. (2.7)) and $S(I,K)$ is the statistical weighting factor due to nuclear spin $I$ (TOW 55).

\begin{align}
(2.38a) \quad S(I,K) &= 4I^2 + 4I + 3 \quad \text{for } K \text{ a multiple of } 3 \\
(2.38b) \quad S(I,K) &= 4I^2 + 4I \quad \text{for } K \text{ not a multiple of } 3
\end{align}

Figure 2.10 Hexapole transmission function measured as K$^+$ count-rate in the cross-beam experiments. The solid lines are the fit from the calculated transmission functions. Left panel: CF$_3$Br, K beam energy $E_K$ is fixed at 8eV; Right panel: CH$_3$Br, $E_K = 13$eV. The finite signal levels at 0kV are due to the direct beam.

The production rate of K$^+$ in the ionization reactions between symmetric-tops and fast potassium atoms is proportional to the beam intensity transmitted by the hexapole field, and thus can be used to measure the hexapole
transmission function $T(V_0)$. Experimental results are plotted in Fig. 2.10 for CF$_3$Br and CH$_3$Br.

In the oriented molecular beam experiments, since the reaction time is much shorter than the rotational period, it is important to know the orientation distribution function of the transmitted beam, $P(\rho, V_0)$, which is given by:

\begin{equation}
P(\rho, V_0) = \sum_{J=0}^{\infty} \sum_{K=-J}^{J} \sum_{M=-1}^{J} P_{JKM}(\rho)f_{JKM}F_{JKM}(V_0)
\end{equation}

where $P_{JKM}$ is given in Eqs. (2.21) and (2.22). Utilizing Eqs. (2.24), (2.36) and (2.39) we can calculate the average molecular orientation in the transmitted beam:

\begin{equation}
\langle \rho \rangle = \frac{1}{T(V_0)} \sum_{J,K,M} \frac{K}{J(J+1)} f_{JKM}F_{JKM}(V_0)
\end{equation}

Using the actual dimensions of the field, computer programs were developed to simulate the hexapole transmission function and the orientation distribution function for different kinds of molecules. Fig. 2.11 illustrates the calculated molecular orientation function $P(\rho, V_0)$ for CF$_3$Cl at a hexapole voltage of 6KV. The average orientation of the transmitted beam, $\langle \rho \rangle$, defined in Eq. (2.40), is 0.44. No beam stop is used in our experiments and the entrance and exit apertures are set at relatively large values as listed in Table 2.2. With such beam geometries, $\langle \rho \rangle$ is not very sensitive to the hexapole field strength nor to the translational and vibrational temperatures of the beam. The intensity of the beam increases with increasing hexapole voltage, however.

Table 2.4 shows the calculated average orientations for different symmetric-top molecules at several hexapole voltages. A characteristic temperature of 10°K is used in these calculations. With very small apertures $\langle \rho \rangle$
2mm in diameter) and a beam stop, calculation predicts that the average orientation is strongly dependent on focusing voltages.

![Graph showing orientation distribution function](image)

**Figure 2.11** Calculated quantal orientation distribution function of the CF$_3$Cl beam transmitted by the hexapole field. It is normalized at $\rho = 1$, and it represents the relative probability of finding the molecular axis at a certain orientation.

**Table 2.4** Calculated Average Orientations of Different Molecular Beams Transmitted by the Hexapole Field

<table>
<thead>
<tr>
<th>Hexapole Voltage</th>
<th>CF$_3$I</th>
<th>CF$_3$Br</th>
<th>CF$_3$Cl</th>
<th>CF$_3$H</th>
<th>CH$_3$I</th>
<th>CH$_3$Br</th>
<th>CH$_3$Cl</th>
<th>CH$_3$F</th>
<th>CHCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2kV</td>
<td>0.33</td>
<td>0.34</td>
<td>0.37</td>
<td>0.53</td>
<td>0.29</td>
<td>0.33</td>
<td>0.36</td>
<td>0.40</td>
<td>0.52</td>
</tr>
<tr>
<td>4kV</td>
<td>0.39</td>
<td>0.40</td>
<td>0.42</td>
<td>0.48</td>
<td>0.31</td>
<td>0.32</td>
<td>0.33</td>
<td>0.35</td>
<td>0.48</td>
</tr>
<tr>
<td>6kV</td>
<td>0.39</td>
<td>0.42</td>
<td>0.45</td>
<td>0.46</td>
<td>0.29</td>
<td>0.28</td>
<td>0.30</td>
<td>0.36</td>
<td>0.46</td>
</tr>
<tr>
<td>8kV</td>
<td>0.38</td>
<td>0.41</td>
<td>0.45</td>
<td>0.48</td>
<td>0.26</td>
<td>0.28</td>
<td>0.31</td>
<td>0.37</td>
<td>0.48</td>
</tr>
<tr>
<td>10kV</td>
<td>0.36</td>
<td>0.40</td>
<td>0.44</td>
<td>0.48</td>
<td>0.26</td>
<td>0.29</td>
<td>0.31</td>
<td>0.36</td>
<td>0.47</td>
</tr>
</tbody>
</table>
2.4 The Fast Neutral Potassium Beam

As mentioned in Section 2.1, the fast potassium atomic beam \((E > 3\text{eV})\) is produced by a resonant charge exchange source. The structure of the oven source is shown in Fig. 2.12.

![Diagram of a charge exchange oven and a skimmer](image)

Figure 2.12 Diagrams of the potassium charge exchange source, (a), and the biasing potentials for the Tungsten filament \(W\), (b).

Inside the oven, the equilibrium potassium vapor pressure at temperatures above its melting point is given by the following formula (BOR 87):

\[
\log_{10} P(\text{kPa}) = 10.146317 - 4778.5/T - 1.1032\log T - 0.4093\times10^{-3}T
+0.29444\times10^{-6}T^2 - 0.0621\times10^{-9}T^3
\quad (373^\circ K < T < 2200^\circ K)
\]

<table>
<thead>
<tr>
<th>Temperature (^\circ\text{C})</th>
<th>95</th>
<th>100</th>
<th>105</th>
<th>110</th>
<th>115</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC Voltage (mV)</td>
<td>3.7</td>
<td>4.0</td>
<td>4.2</td>
<td>4.5</td>
<td>4.8</td>
<td>5.0</td>
</tr>
<tr>
<td>Vapor Pressure ((10^{-5}\text{torr}))</td>
<td>1.23</td>
<td>1.81</td>
<td>2.63</td>
<td>3.78</td>
<td>5.39</td>
<td>7.60</td>
</tr>
</tbody>
</table>

Table 2.5 Potassium Vapor Pressure at Several Oven Temperatures

The K vapor pressures at several oven temperatures in the operating region are listed in Table 2.5. The thermocouple voltages are referenced at the
room temperature of 24°C for type J thermocouple.

The 10 mil W filament inside the oven is DC heated at a current of 5.0A \( (V_f = 6.2\text{V}) \), and some of the potassium atoms in the vapor will be surface ionized upon striking the filament. Surface ionization can be described by the Saha-Langmuir equation (LAN 25, SAH 23, LAN 32a):

\[
\frac{n^+}{n^0} = \frac{1 - r^+}{1 - r^0} \frac{w^+}{w^0} e^{-\frac{\phi - I}{kT}}
\]

where \( n^+ (n^0) \), \( r^+ (r^0) \) and \( w^+ (w^0) \) are the number of ions (neutrals) evaporating from a surface at equilibrium, the reflection coefficients for ions (neutrals) and statistical weights for ions (neutrals), respectively. \( I \) is the ionization potential of the atoms, \( \phi \) is the work function of the surface, and \( T \) is the temperature of the surface. In molecular beam experiments where surface ionization detectors are used, the following simplified form is applied (RAM 56):

\[
\frac{n^+}{n^0} = e^{-\frac{\phi - I}{kT}}
\]

The work function of tungsten is 4.55 eV and the ionization potential for potassium is 4.34 eV, and the ionization efficiency is close to unity at thermal energies. (Molybdenum has a work function of 4.6 eV, so it can also be used as surface ionization detector for potassium.)

A positive voltage \( V_0 \) is applied to the negative post of the power supply used to heat the filament, as shown in Fig. 2.12b. The ions emerging from the surface of the filament will be accelerated to the grid which is at ground potential. The kinetic energy of the ions upon reaching the grid is determined, theoretically, by the potential difference between the center of the filament and the grid:
\[ V_{\text{diff}} = V_0 + \frac{1}{2} V_f = V_0 + 3 \text{ (volt)} \]

But due to the contact potentials of the W filament and the potassium coated surfaces of the grid and the oven walls, the actual kinetic energy of the K⁺ at the grid is about 3eV lower than \( V_{\text{diff}} \). So \( V_0 \) is an accurate measure of the K beam energy. Both the TOF experiments and the energy threshold determined by the reaction \( K + SF_6 \rightarrow K^+ + SF_6^- \) show that \( V_0 \) can be approximated as the beam energy to within 2%. 

Some of the potassium ions passed by the grid will undergo charge exchange collisions with neutral thermal potassium atoms and a beam of neutral fast K atoms is formed. The energy loss due to charge exchange is negligibly small. The distance between the filament and the grid is 1 mm, kept small to reduce the space charge spreading. The length of the charge exchange region is about 20 mm, and this is a compromise between the desire to have it much longer than the acceleration region (otherwise an appreciable fraction of ions will charge exchange before they reach the full potential) and to have it as short as possible to minimize the space charge spreading.

The intensity of the fast potassium beam depends on the ion current emitted from the hot W filament and the resonant charge exchange cross section. In the space charge limit, the ion current is proportional to \( V^{3/2}/d^2 \), where \( V \) and \( d \) are the potential difference and distance between the filament and the grid, respectively (LAN 13, ATE 75). The charge exchange cross section increases slightly with increased energy (1eV < \( E < 50\)eV) (see, e.g., KUS 59, MAR 62). Even though the detection efficiency of the hot W SID is unity for thermal potassium (SCH 63), the surface ionization detection was experimentally shown to be energy dependent at energies above 3eV (see, e.g. STE 61, HOL 66 and POL 69).
In the present experiments, the K beam intensity is measured as the MEM output. The 5 mil tungsten SID is heated at a current of \( \sim 0.65A \), and its temperature is kept below that required to detect thermal atoms. In this mode of operation, only suprathermal atoms are detected. Figure 2.13 shows the MEM output as a function of beam energy. We found that both the detection efficiency and its energy dependence are strongly affected by the surface condition of the SID. The SID filaments with slightly different histories give different results. In the space-charge limit, the energy dependence of beam intensity is expected to obey the 3/2 power law, as experimentally observed by Aten et al. (ATE 75).

![Graph](image)

**Figure 2.13** K Beam intensity, measured as the MEM output, as a function of beam energy. The solid line is a linear fit (log-log).

Higher beam intensities can be obtained by increasing the potassium vapor pressure, but the energy distribution loses its sharpness, and a significant tail in the lower energy end develops, as observed in the TOF spectra described in the next section.
2.5 Measurement of K Beam Energy Distribution

Determination of the energy distribution of the fast potassium beam and accurate calibration of the beam energy are critical to a better interpretation of the results of crossed beam experiments, because the energy thresholds of the reactions are measured by the kinetic energy of the potassium atoms. The setup for K beam TOF experiments is shown in Figs. 2.14 and 2.15.

![Diagram of K beam experimental setup](image)

**Figure 2.14** Schematics of the K beam TOF experimental setup. SID: Surface Ionization Detector; MEM: Bendix Magnetic Electron Multiplier.

A beam chopper (an aluminum disk 4" in diameter and 1/32" thick) is placed between the scattering center and the K beam detector (SID), and is driven by an AC hysteresis synchronous motor with maximum frequency of 400Hz (TRW Globe Motors, B-2702 type). A signal generator and power amplifier provide the AC power to the motor at a frequency that can be varied continuously. The beam passing slit is 0.035" wide and 0.275" long, with its center located 1.338" from the center of the wheel. A collimator slit with the same width is placed 1-1/2" in front of the chopper to limit the beam spread. The same phototransistor as that installed in the nozzle beam is used to monitor the opening of the gate.
Ideally the chopper will provide a triangular gate with its duration inversely proportional to the chopper frequency (at 400 Hz, the FWHM is 10.4 μs), but due to the finite length of the slit and edge effects, the actual form of the gate function is slightly different and is experimentally determined.

The length of the flight path $L$ is 53.3 cm, and for a potassium atom at energy $E$, the flight time $t_f$ from the chopper wheel to the detector is given by:

$$t_f = L\sqrt{\frac{m}{2E}} = \frac{240.9(\mu s)}{\sqrt{E(\text{eV})}}$$

The pulsed K beam is detected by the SID, and the K$^+$ is then amplified by a Bendix MEM to give a sharp (several ns) electron pulse. The electron pulse
is amplified by a fast preamp and an amplifiers (Ortec 9301 and 9302), and then it is converted into a square waveform (1.0 μs wide, 2 volts high) by a pulse generator (Hewlett Packard, 8013B). A waveform digitizer (Lecroy 2256A, 1024 channels, sampling period variable from 50 ns to 5 μs) is used to record these pulses according to their delays relative to the triggering pulse.

The triggering pulse is generated from the phototransistor that monitors the gate opening, and is delayed by the Gate and Delay Generator (Ortec 416, not shown in Fig. 2.15) and the Digital Delay Generator (Berkeley Nucleonics Corp. 7020) The reason for delaying the triggering pulse is to shift the spectrum of the waveform digitizer so that only the time region of interest is recorded. In our experiments the sampling period for the waveform digitizer is set at 0.2 μs and the maximum time interval the digitizer can record is 1024x0.2 μs = 200μs. The waveform digitizer can average over up to 3x10^4 chopper cycles to produce a TOF spectrum.

Due to the limited space inside the scattering chamber, the phototransistor is not diametrically opposed to the beam opening. The offset angle ϕ0 will introduce a delay tϕ that depends on the motor frequency f:

\[
\text{(2.44)} \quad t_ϕ = \frac{ϕ_0}{2πf} \quad \text{(when motor runs clockwise)}
\]

In order to measure the delay caused by this misalignment and to determine the actual shape of the gate function, we replaced the SID with a photomultiplier tube and record the light intensity emitted from the W filament in the K oven. Since the time for light to traverse the TOF region is negligible, the delay tϕ can be determined directly as a function of chopper frequency. The motor frequency is determined by a scaler that counts the output pulses of the photo-sensor as shown in Fig 2.15. The waveform of the PMT output represents
the shape of the gate function, because the response time of PMT is in the sub-
microseconds range.

In Fig. 2.16a the slope of the linear fit is 0.07474, and from Eq. (2.44) it is
determined that $\phi_0 = 26.9^\circ$. In Fig. 2.16b the best fit of the gate function yields
the following equation:

\begin{equation}
G(t) = 1 - 1.278 \times 10^{-2} t^2 + 5.928 \times 10^{-5} t^4 - 9.848 \times 10^{-8} t^6 \quad |t| \leq 15\mu s.
\end{equation}

![Graphs](image)

**Figure 2.16** (a) Measured time of delay due to the phase shift. Solid line is a least square linear
fit; (b) Gate Function as determined by the output of the PMT, dashed curve is a smooth
polynomial fit.

Since the gate opening time is $\sim 10\%$ of the flight time ($\sim 50\mu s$), the actual
TOF spectra are convolutions of the gate function $G(t)$ and the speed distribution
function $f(v)$ (ALC 69). At time $\lambda$, molecules in the speed range from $v$ to $v + dv$
are admitted at the rate:
\[ (2.46) \quad N_{t}(\lambda, \nu)d\nu = n\nu f(\nu) g(\lambda)d\nu \]

A molecule admitted at time \( \lambda \) with speed \( \nu \) will arrive at the detector plane at time \( t (t \geq \lambda) \),

\[ (2.47) \quad \nu(\lambda, t) = \frac{L}{t - \lambda} \]

So \( N_{t}(\lambda, t) \) is the instantaneous rate at which molecules admitted by the chopper in the time interval \( \lambda \) to \( \lambda + d\lambda \) cross the detection plane at time \( t \). The speed range \( d\nu \) appearing in Eq. (2.46) is related to \( d\lambda \) by:

\[ (2.48) \quad d\nu = \left( \frac{d\nu}{d\lambda} \right) d\lambda = \frac{L}{(t - \lambda)^2} d\lambda \]

Integrating Eq. (2.46) we will get:

\[ (2.49) \quad N_{t}(t) = \int_{0}^{t} n\nu f(\nu) g(\lambda) \frac{L}{(t - \lambda)^2} d\lambda = \int_{0}^{t} n \frac{L^2}{(t - \lambda)^3} f\left( \frac{L}{t - \lambda} \right) g(\lambda) d\lambda \]

where \( N_{t}(t) \) is the number of molecules arriving at the detector plane at time \( t \). Suppose the detector and its electronics have a characteristic dynamic function:

\[ (2.50) \quad g_{d}(t) = e^{-\nu\tau} \]

then the actual measured signal is

\[ (2.51) \quad k(t) = \int_{0}^{t} g_{d}(\lambda) N_{t}(t - \lambda) d\lambda \]

To determine the energy distribution, we measured the TOF spectra and compared the overall shape of the peak with that generated by a known energy
spread. In general the peak position and broadness depend on the nominal energy, the energy spread and the time constant of the dynamic function. We assumed that the energy distribution function has the form:

\[(2.52) \quad f_E(E) = \exp\left(\frac{E - E_0}{-\Gamma \Delta E}\right) \quad \frac{E_0}{2} \leq E \leq E_0 + \Delta E\]

and it is related to the velocity distribution function by:

\[(2.53) \quad f(v) = f_E\left(\frac{1}{2}mv^2\right) \frac{dE}{dv} = mvf_E\left(\frac{1}{2}mv^2\right)\]

Figs. 2.17a and 2.17b show the TOF spectra of the K beam at nominal energies approximately 20eV and 10eV, respectively. The fitting curves are generated by computer programs using Eqs. (2.49), (2.52) and (2.53). The best fits yield \(\Delta E\) values of 0.8eV at 20eV and 0.4eV at 10eV. Since the detector dynamic function is neglected, the fitting curve gives the upper limit of the actual energy spread \(\Delta E\). From these fittings the energy spread in the beam is determined as: \(\Delta E/E_0 \leq 4\%\).

It is found that ions formed at the SID have residence times that are as large as 5\(\mu\)s, and are very sensitive to the surface condition of the detector. By biasing the detector at +150V and placing an ion repeller around the detector (also at +150V), the residence time is reduced to within 1\(\mu\)s.

To determine accurately the nominal beam energy, the residence time of the ions on the SID has to be taken into account. We used a very short flight path \((L' = 10.05 \text{ cm})\) to record another set of TOF spectra. The difference of the peak positions between the long and short flight paths is used to determine the nominal energy of the K beam:

\[(2.54) \quad E_0 = \frac{1}{2} m(t_0 - t_0')^2\]
Figure 2.17 K beam TOF spectra at nominal energies of (a): 20eV, and (b): 10eV. Solid curves are generated by using the assumed energy distribution function in Eq. (2.52) with $\Delta E = 0.8eV$ and 0.4eV, respectively.
The measured TOF peak positions ($t_0$ and $t_0'$) and their standard deviations ($\Delta t_0$) of four independent measurements are shown in Table 2.6, where $V_0$ is the biasing voltage (see Section 2.4).

**Table 2.6** The Peak Positions of TOF Spectra at Different Biasing Voltages

<table>
<thead>
<tr>
<th>$V_0$(Volt)</th>
<th>$t_0$(µs)</th>
<th>$t_0'$(µs)</th>
<th>$E_0$(eV)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>79.69 ±0.23</td>
<td>17.93</td>
<td>10.0</td>
</tr>
<tr>
<td>13.0</td>
<td>69.48 ± 0.20</td>
<td>16.16</td>
<td>13.42</td>
</tr>
<tr>
<td>14.0</td>
<td>66.62 ± 0.21</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>15.0</td>
<td>64.16 ± 0.18</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>16.0</td>
<td>62.11 ± 0.29</td>
<td>13.45 ± 0.24</td>
<td>16.12</td>
</tr>
<tr>
<td>18.0</td>
<td>58.44 ± 0.14</td>
<td>12.66 ± 0.65</td>
<td>18.21</td>
</tr>
<tr>
<td>20.0</td>
<td>55.37 ± 0.38</td>
<td>11.65 ± 0.30</td>
<td>19.97</td>
</tr>
<tr>
<td>22.0</td>
<td>52.89 ± 0.49</td>
<td>10.89 ± 0.37</td>
<td>20.63</td>
</tr>
<tr>
<td>24.0</td>
<td>50.57 ± 0.45</td>
<td>10.79 ± 0.60</td>
<td>24.12</td>
</tr>
<tr>
<td>26.0</td>
<td>48.66 ± 0.51</td>
<td>10.20 ± 0.64</td>
<td>25.80</td>
</tr>
<tr>
<td>28.0</td>
<td>46.75 ± 0.40</td>
<td>9.76 ± 0.38</td>
<td>27.89</td>
</tr>
<tr>
<td>30.0</td>
<td>45.12 ± 0.32</td>
<td>9.64 ± 0.22</td>
<td>30.32</td>
</tr>
<tr>
<td>32.0</td>
<td>43.74 ± 0.37</td>
<td>9.52 ± 0.23</td>
<td>32.59</td>
</tr>
<tr>
<td>34.0</td>
<td>42.45 ± 0.39</td>
<td>9.23 ± 0.12</td>
<td>34.58</td>
</tr>
<tr>
<td>36.0</td>
<td>41.22 ± 0.34</td>
<td>8.78 ± 0.15</td>
<td>36.27</td>
</tr>
</tbody>
</table>

* Calculated from Eq. (2.54).

Fig. 2.18 is a plot of the K beam nominal energy, calculated from the data in Table 2.6, versus the W filament biasing voltage. The actual energy of the K beam is very close (within 0.2eV) to the voltage $V_0$ applied to the W filament in the charge exchange source. The uncertainties of the nominal energy measurements are shown as error bars in the figure, and are about 2% ($\pm 0.4eV$ at 20eV), which is reasonable considering the uncertainties introduced in the
measurements for the flight path (~1%) and peak position of TOF spectra (0.3μs).

![Graph](image)

**Figure 2.18** Nominal K beam energy determined by the TOF experiments. The solid line shows the linear relationship between K beam energy and the bias voltage.

It is found that the best operating temperature of the charge exchange oven is between 95 - 105°C (corresponding to TC voltages of 3.7 - 4.2 mV). At lower and higher temperatures, the TOF spectra will lose their sharpness. As the oven temperatures exceed 120°C, a significant tail at the lower energy end develops, apparently due to the fact that an appreciable fraction of potassium ions coming off the W filament undergoes charge exchange before reaching the full potential.

We did not detect any potassium dimers in the TOF spectra within the detection limit of the measurement.
2.6 Data Acquisition and Analyses

The K+ ions generated from the reaction $K + CX_3Y \rightarrow K^+ + CX_3 + Y^-$ are collected by one of the channeltrons determined by the polarity of the orienting field, as illustrated in Fig. 2.3. The channeltrons are used in the pulse counting mode. To separate the cross beam signal from the background noise, the gas beam is modulated at 120Hz, and differential counting is achieved by using a gated Quad-Scaler (Joerger, Model SI), as shown in Fig. 2.19.

![Diagram of the cross-beam signal collection system. The beam modulation, scaler inhibition and the cross-beam signals (superposed on the background noise) are shown.]

The gas beam arrives at the scattering center with a delay with respect to the opening of the beam chopper, and the delay is determined by the mass flow velocity of the beam. Due to the velocity distribution in the gas beam, the cross beam signal is slightly broadened. An inhibition signal is generated from the beam modulation signal with a duty cycle of ~60% and a delay to accommodate the cross beam signal, as shown in Fig. 2.19.
The quad-scaler has four Signal Input channels (Channel 0 to 3) and four Inhibit Input channels (0 to 3). The pulses at each signal input channel is counted only when the voltage level is high at the corresponding inhibition channel. A real clock (218Hz) provides the inputs for Channel 0 and 1, serving as the time scales. The K+ signal from the channeltron is connected to Channel 2 and 3. The inhibition signal is applied only to Inhibition Channel 1 and 3.

We let \( C_i \) \((i = 0, 1, 2 \text{ or } 3)\) denote the count-rate at Channel \( i \), and in the background inhibit mode, as shown in Fig. 2.19, the cross-beam signal can be determined as:

\[
S = C_2 \cdot \frac{C_2 - C_3}{C_0 - C_1} C_0
\]  

The duty cycle \( \eta \) for Channel 1 and 3 \((\eta = T_C / T_0 = C_1 / C_0)\), determined by the inhibition signal, is adjusted to yield maximum signal. The delays for different gas beams are listed in Table 2.7.

**Table 2.7** Experimentally Determined Delay Settings for Different Nozzle Molecular Beams

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Molecular Weight (amu)</th>
<th>Delay (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃F</td>
<td>34</td>
<td>1.8</td>
</tr>
<tr>
<td>CHF₃</td>
<td>70</td>
<td>3.0</td>
</tr>
<tr>
<td>CH₃Br</td>
<td>95</td>
<td>2.6</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>119</td>
<td>3.0</td>
</tr>
<tr>
<td>SF₆</td>
<td>146</td>
<td>3.4</td>
</tr>
<tr>
<td>CF₃Br</td>
<td>149</td>
<td>3.2</td>
</tr>
<tr>
<td>CF₃I</td>
<td>196</td>
<td>4.0</td>
</tr>
<tr>
<td>CHF₃/He(1:9)</td>
<td>7.4*</td>
<td>1.0</td>
</tr>
<tr>
<td>CF₃Br/He(1:9)</td>
<td>15.3*</td>
<td>1.2</td>
</tr>
</tbody>
</table>

* Average molecular weight.
To a good approximation, the delay is inversely proportional to the square root of the molecular weight, suggesting that the translational energies due to the mass flow are about the same for different molecules.

The dark counts of the channeltrons are typically below 0.2 cps, and are not affected by the molecular beam or the hexapole field. The only source of noise are ions resulting from ionization of the fast potassium beam with background gases.

As tabulated below, we use $C_{nlk}$ to denote the signal rate determined from Eq. (2.55), where the subscript $n$ specifies the orienting field direction, and $l$ and $k$ represent, respectively, the on/off statuses of the molecular beam and the hexapole field. The potassium beam is on at all times. Channeltron #1 and #2 are used in the $0^\circ$ and $180^\circ$ orienting field configurations, respectively. $C_{100}$ and $C_{200}$ fluctuate statistically around zero due to background scattering of the K beam. In the experiments the two-beam signal is much stronger than the background, and $C_{100}$ and $C_{200}$ are ignored. Only $C_{110}$, $C_{111}$, $C_{210}$ and $C_{211}$ are measured. $C_{110}$ and $C_{210}$ are the signals due to collisions between potassium atoms and the molecules in the unfocussed direct beam. It can be seen, by definition, that $(C_{111} - C_{110})$ and $(C_{211} - C_{210})$ are the signals solely from the scattering between potassium atoms and oriented molecules.

<table>
<thead>
<tr>
<th>Type of Signal</th>
<th>Orienting Field Direction</th>
<th>Gas Beam</th>
<th>Hexapole Field</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{100}$</td>
<td>$0^\circ$</td>
<td>off</td>
<td>off</td>
</tr>
<tr>
<td>$C_{110}$</td>
<td>$0^\circ$</td>
<td>on</td>
<td>off</td>
</tr>
<tr>
<td>$C_{111}$</td>
<td>$0^\circ$</td>
<td>on</td>
<td>on</td>
</tr>
<tr>
<td>$C_{200}$</td>
<td>$180^\circ$</td>
<td>off</td>
<td>off</td>
</tr>
<tr>
<td>$C_{210}$</td>
<td>$180^\circ$</td>
<td>on</td>
<td>off</td>
</tr>
<tr>
<td>$C_{211}$</td>
<td>$180^\circ$</td>
<td>on</td>
<td>on</td>
</tr>
</tbody>
</table>
We define:

\[(2.56a) \quad S_0 = C_{111} - C_{110}\]
\[(2.56b) \quad S_{180} = C_{211} - C_{210}.\]

where \(S_0\) and \(S_{180}\) are proportional to the reaction rates at 0° and 180° field configurations, respectively. Because \(S_0\) and \(S_{180}\) are measured with different channeltrons at different field configurations, the K⁺ collection efficiencies and amplifications of the two channeltrons are different. Signals from un-oriented molecules can be used to determine the relative collection efficiency \(f(E)\) defined as:

\[(2.57) \quad f(E) = \frac{C_{210} - C_{200}}{C_{110} - C_{100}} = \frac{C_{210}}{C_{110}}\]

where \(E\) is the K beam energy. The biasing voltages on the channeltrons are adjusted so that \(f(E)\) is around unity (0.8 ≤ \(f(E)\) ≤ 1.5). The corrected signals are given by:

\[(2.58a) \quad S'_0 = fS_0\]
\[(2.58b) \quad S'_{180} = S_{180}\]

Orientation effects can be obtained by comparing the corrected signals, and the relative cross sections at different molecular orientations can be obtained as:

\[(2.59) \quad \sigma_0(E) = \frac{S'_0}{I_{k}(E)}; \quad \sigma_{180}(E) = \frac{S'_{180}}{I_{k}(E)}\]

where \(I_{k}(E)\) is the K beam intensity.

Because the K beam intensity varies greatly over the energy range (3 - 30eV), and its accurate measurement can not be done conveniently, we introduce the steric factor \(G(E)\) as a measure of the relative orientation effects:
(2.60) \[ G(E) = \frac{S_{180} - S_0}{S_{180} + S_0}, \quad |G| \leq 1 \]

If the reaction is not orientation dependent, the steric factor \( G \) will be zero, and in the extreme case where one orientation is totally nonreactive, \( |G| = 1 \).

The K beam energy and the hexapole field strength can be swept automatically by the PDP-11 computer. It is critical that both the potassium and molecular beam intensities are stable during different sweeps. The potassium oven is usually heated overnight at a constant heating power and the oven temperature is monitored closely during measurement. The stability of the nozzle beam intensity is maintained by an automatic pressure controller that controls the nozzle gas stagnation pressure. Sufficient pumping speed at the nozzle chamber is essential for a stable nozzle beam.
3 Theoretical Aspects of Ionization Reactions

To study the collisional ionization reactions involving oriented colliding partners, it is of interest to summarize theories already established related to ionization reactions. There are a few theoretical review articles on the ion-pair formations in ionization reactions (see, e.g., KLE 82, LAC 80, LOS 79).

The bimolecular chemical reaction process is governed by the potential energy surfaces (PES) of the reagents. Detailed knowledge of these potentials would enable us to understand features exhibited by the reaction. Since exact ab-initio calculations of PES' for molecules containing heavy atoms are not feasible so far, semi-empirical methods are usually used to construct the PES'.

3.1 Ion-Pair Formation In Atom-Atom Collisions

The simplest example is the ionization reaction between an alkali atom M (Li, Na, K, et al.) and a halogen atom X (F, Cl, Br, I). There are only two particles involved, and the reaction process can be treated in an exact way (FAI 76).

\[(3.1) \quad M + X \rightarrow M^+ + X^-\]

The total Hamiltonian $H$ can be separated approximately into two terms, in the so-called Born-Oppenheimer approximation, that represent the slow
internuclear motion $T_R$ (kinetic energy operator for the nuclei) and the fast electronic motion $H_{el}(r, R)$.

\begin{equation}
H = T_R + H_{el}
\end{equation}

The stationary wave function can be described as

\begin{equation}
\psi(r, R) = \sum_k \phi_k(r; R) \chi_k(R)
\end{equation}

where $\phi_k(r; R)$ depends parametrically on $R$, and forms a set of orthonormal electronic wave functions, and $\chi_k(R)$ is the nuclear wave function which can usually be expanded in a complete set of rovibrational wave functions. From the Schrödinger equation, $\chi_k(R)$ is determined by

\begin{equation}
(T_R + H_{kk} - E)\chi_k = \sum_{k \neq k'} (T_{kk'} + H_{kk'})\chi_k
\end{equation}

where $E$ is the total energy, and $H_{jk} = \langle \phi_j|H_{el}|\phi_k \rangle$ and $T_{jk} = \langle \phi_j|T_R|\phi_k \rangle$.

There are two basic representations used in selecting the electronic basis functions $\phi_k(r; R)$. One is the adiabatic representation which uses the eigenfunctions of $H_{el}$ as the basis functions, in this case we have

\begin{equation}
H_{kk}(R) = \langle \phi_k|H_{el}|\phi_k \rangle = E_k(R) \delta_{kk'}
\end{equation}

The $E_k(R)$ functions are the potential surfaces which govern the motion of the nuclear coordinates. The coupling between different states $k$ and $k'$ is caused by the nonadiabatic interaction $T_{kk'}$. The other representation is diabatic (or nonadiabatic) which chooses $\phi_k$'s determined at a fixed value of $R$.

\begin{equation}
\phi_k(r; R) = \phi_k(r; R_0) = \phi_k(r)
\end{equation}
The covalent wave functions of $M + X$ and the ionic wave functions of $M^+ + X^-$ are examples of the electronic basis functions in the diabatic representation. In this representation, the nonadiabatic interaction terms $T_{kk'}$ are zero and the transitions between two diabatic surfaces $H_{ij}(R)$ and $H_{kk}(R)$ are induced by the off-diagonal matrix elements $H_{jk}(R)$.

In principle the electronic and nuclear motion can be solved exactly, but since a large number of states have to be included in the calculations, few useful results can be obtained. In the classical path approximation, the nuclear motion of the colliding particles is described by some classical trajectory $R = R(t)$, and the wave function for the electronic motion $\psi(r, t)$ must satisfy the time-dependent Schrödinger equation

$$
(3.7) \quad H_{el}(r, R)\psi(r, t) = i\frac{\hbar}{2\pi} \frac{\partial}{\partial t} \psi(r, t)
$$

and it can be expanded in terms of the basis functions $\phi_k(r)$ defined in Eq. (3.6) in the diabatic representation:

$$
(3.8) \quad \psi(r, t) = \sum_k a_k(t) \phi_k(r) \exp\{-i\frac{2\pi}{\hbar} \int_0^t H_{kk}(R) dt\}
$$

Substituting Eq. (3.8) into Eq. (3.7) and using the orthonormal properties of the basis functions, the basic set of coupled equations for transition rates of the amplitudes $a_j$ can be obtained:

$$
(3.9) \quad \frac{i\hbar}{2\pi} \frac{da_j}{dt} = \sum_{k \neq j} a_k(t) H_{jk} \exp\{-i\frac{2\pi}{\hbar} \int_0^t (H_{kk} - H_{jj}) dt\}
$$

These are the so-called classical path equations (TUL 76).
Based on the classical path equations, several methods, differing in the choice of electronic coordinates and treatment of the nuclear motion, have been developed, such as the impact parameter method (KLO 84), or the surface hopping trajectory (SHT) method (TUL 71). For review of these and other methods see KLE 82.

The solution of Eq. (3.9) for an isolated, one-dimensional, two-state crossing is the Landau-Zener formula (see, e.g., LAN 32, ZEN 32, BAE 75 and JAN 76). In reaction (3.1), there are eight possible molecular states which can be formed from the two neutral particles $M(2S_{1/2})$ and $X(2P_{3/2})$: $^{1,3}\Sigma^+$ and $^{1,3}\Pi$. There is only one molecular state that can be formed by the ions $M^+(1S_0)$ and $X^+(1S_0)$: $^1\Sigma^+$, which is the ionic ground state. The potentials are one dimensional (depend only on the internuclear distance). One of the covalent states ($^1\Sigma^+$) has the same symmetry as the ionic state, and these two states will couple when the two diabatic potential surfaces intersect. At infinite internuclear distance $R$, the separation between the covalent and ionic potential curves is given by

\begin{equation}
\Delta E = IP - EA
\end{equation}

where $IP$ is the ionization potential of the alkali atom and $EA$ is the electron affinity of the halogen atom. At relatively large $R$ the van der Waals and induction forces between the particles can be neglected, so the covalent potential is zero and the ionic one is the Coulomb attraction potential: $-e^2/R$. The two curves cross at $R = R_c$ which is determined by

\begin{equation}
R_c = \frac{e^2}{\Delta E} = \frac{14.4}{\Delta E(eV)} \text{ (Å)}
\end{equation}
Figure 3.1 Illustration of the crossing of two potential curves. Dashed and solid curves are the diabatic and adiabatic potentials, respectively. Notice that the adiabatic potentials have an avoided crossing.

The Hamiltonian matrix $H$ can be expressed as the following near the curve crossing region:

$$
H = \begin{pmatrix}
H_{11} & H_{12} \\
H_{12} & H_{22}
\end{pmatrix} = \begin{pmatrix}
H_0 + \frac{1}{2} \Delta F(R - R_c) & H_{12} \\
H_{12} & H_0 - \frac{1}{2} \Delta F(R - R_c)
\end{pmatrix}
$$

where $H_{12} = H_{12}(R_c)$, $H_0 = H_{11}(R_c) = H_{22}(R_c)$, and $\Delta F = (\partial\partial R)(H_{11} - H_{22})R = R_c$. $H_{11}$ and $H_{22}$ are the diabatic covalent and ionic potentials, respectively. The adiabatic potentials can be obtained by diagonalizing the Hamiltonian matrix:

$$
V_{\pm} = \frac{1}{2} \left( H_{11} + H_{22} \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2} \right)
$$

Figure 3.1 shows the diabatic and adiabatic potential curves near the crossing region. Using Eq. (3.9) the adiabatic transition probability from the covalent to ionic state or vice versa is given by:
\[ P_a = 1 - \exp\left(-\frac{4\pi^2H_{12}^2}{\hbar |\Delta F| v \nu_{rad}}\right) \]

where \( v_{rad} = v(1 - b^2/R_c^2)^{1/2} \) is the radial velocity and \( v \) is the relative velocity of the nuclei. This is the so-called Landau-Zener (LZ) formula. (Also known as LZS formula, where \( S \) represents Stueckelberg. STU 32). The diabatic transition probability is given by: \( P_d = 1 - P_a \).

Figure 3.2 Simplified picture of the \( M + X \) scattering. Solid trajectories represent neutral systems (\( M + X \)) and dashed trajectories represent ion-pair formation. Covalent-ionic crossing occurs at distance \( R_c \) shown by the circle. The inner circle represents the repulsive core.

For an impact parameter \( b < R_c \), the crossing region will be passed twice at the same internuclear distance \( R_c \), as shown in Figure 3.2. If the first crossing is adiabatic (an electron is transferred), the collision is called ionic scattering, and if the first crossing is diabatic, it is called covalent scattering. The formation of ion-pairs requires that one crossing is diabatic and the other adiabatic. The deflection angle is larger in the ionic scattering than that in the covalent scattering, so contributions from the ionic and the covalent scattering can be separated experimentally by measuring the differential cross section (LOS 79).
Since the first and second crossings are identical, the ionic and covalent scattering have equal contributions to the ionization probability \( P_a(1 - P_a) \) and \( P_d(1 - P_d) \), respectively. So the total probability for ion-pair formation is

\[
P(b) = 2P_a(1 - P_a) = 2 \exp\left(-\frac{v_0}{\nu \sqrt{1 - b^2/R_c^2}}\right) \left(1 - \exp\left(-\frac{v_0}{\nu \sqrt{1 - b^2/R_c^2}}\right)\right)
\]

where \( v_0 = 4\pi^2 H_{12}^2/(\hbar|\Delta F|) \). The total ionization cross section can be obtained by:

\[
\sigma = \int_0^{R_c} P(b)b\,db = 4\pi R_c^2 F(v/v_0)
\]

where \( F(v/v_0) \) is a universal function that approaches zero at very low and very high velocities, and has a maximum value of 0.113 at \( v/v_0 = 2.36 \) (BAE 75).

The coupling matrix elements have been calculated for several alkali-halide systems (GRI 74, RED 74, BOT 75 and KAH 74), the results agree reasonably well with the semiempirical relation of Olson et al. (OLS 71):

\[
H_{12}^* = R_c^* \exp(-0.86 R_c^*)
\]

with \( H_{12}^* = H_{12}^*/\sqrt{IP\cdot EA} \) and \( R_c^* = (\sqrt{IP/2} + \sqrt{EA/2})R_c \). Atomic units are used in these expressions. Note that the coupling matrix element \( H_{12} \) depends exponentially on \( R_c \).

Of all the alkali-halide systems, only Na + I and Li + I have the maxima of \( F(v/v_0) \) above the energy thresholds due to the extremely large \( \Delta E \). The total ionization cross sections for these two systems have been obtained experimentally (MOU 71), and they have the same functional form as \( F(v/v_0) \). This shows that the LZ model works well for alkali-halogen atomic collisional
ionizations. Even better agreement between the LZ model and the exact calculation can be achieved if the adiabatic coupling point is used in the LZ formula instead of the diabatic cross point \((R_c)\).

### 3.2 Ion-Pair Formation in Atom-Molecule Collisions

In atom-molecule reactions such as \(M + XY \rightarrow M^+ + XY^-\), theoretical calculations are complicated by the increased total number of coordinates \((3N - 3\), with \(N\) being the total number of atoms involved in the reaction). Similar to the case of atom-atom scattering, the coupling between ionic and covalent configurations is most effective at \(R_c\) for electron transfer, where \(R_c\) is the atom-molecule distance at which the diabatic ionic and covalent potential surfaces cross. \(R_c\) is given to first order by Eq. (3.11), but \(EA\) should be the electron affinity of the molecule. Even though the transition probability can be described by a generalized LZ formula (Eq. (3.14)), molecular aspects have to be taken into account in the collision ionization process.

*Ab-initio* potential energy surfaces for the very light atom-molecule system of Li-F\(_2\) were first calculated (BAL 73). The ionic part of the surfaces can be described very well by the interaction of a Li\(^+\) ion with an F\(_2^-\) molecular ion, and by the interaction in the F\(_2^-\), which is similar to that in the free molecular ion. The calculation showed that the potential energy levels and the electron jump distances are affected by the relative orientation of the F\(_2\) molecule with respect to the Li atom, and that a larger F-F distance, achieved by vibrational excitation, leads to an enlarged electron transfer probability. For heavier molecules where *ab-initio* calculations are difficult, the features used for Li-F\(_2\) are applied to construct empirical potential surfaces. In the simplest case, diabatic potential surfaces are developed using three coordinates, \(R\), \(r\) and \(\phi\), which denote the
atom-molecule distance, the internuclear distance of the diatomic molecule and the angle between the atom and the molecular axis, respectively. The ionic potential will be an anisotropic function of $R$. The coupling matrix element between the ionic and covalent surfaces can be written as

\[(3.18) \quad H_{12} = H_{12}^0(R) \cdot f(\phi)\]

and

\[(3.19) \quad H_{12} = 1.73R_c^2 \exp(-0.875R_c^2)\]

where $H_{12}^0 = H_{12}^{0,12}\sqrt{IP \cdot EA}$ and $R_c = R_c \sqrt{2/IP}$ (HUB 76). The function $f(\phi)$ represents the angular dependence of the coupling matrix element $H_{12}$.

a) Bond Stretching in Atom-Molecule Ionization reactions

The most drastic effects on ion-pair formation in atom-molecule collisions are caused by the fact that the electron affinity of the molecules depends strongly on the bond distance, $EA = EA(r)$. The neutral molecule $XY$ and the molecular ion $XY^-$ are most likely to have different equilibrium internuclear distances, and $XY^-$ may even be dissociative. The increase of internuclear distance during the collision and its effect on the transition probability at the second crossing is referred to as "bond stretching".

As shown in Figure 3.3, the adiabatic electron affinity $EA_a$ is defined as the potential energy difference between the ground vibrational levels of $XY^-$ and $XY$. The vertical electron affinity $EA_v$ is the potential energy difference at $r(XY^-) = r(XY) = r_e$, where $r_e$ is the equilibrium internuclear distance of $XY$. Using the Br$_2$ molecule as an example (HUB 76), the equilibrium Br-Br distance is 2.28 Å, and the vertical electron affinity $EA_v = 1.47$eV, but with increasing bond distance the electron affinity first increases rapidly to a maximum of 3.8eV at $r = 3.5$ Å, and then asymptotically approach the atomic electron affinity of 3.36 eV.
Figure 3.3 Potential energy curves for $XY$ and $XY^-$. The definition of electron affinities is shown.

In atom-atom collisions, the ionic and covalent scattering have equal contributions to the total ionization cross section, but as described below, in an atom-molecule collision, the ionic scattering has a larger cross-section than the covalent scattering because of bond stretching (DEL 73, ATE 77).

The electron affinity of a molecule is usually less than that of a halogen atom, so the electron transfer will occur at a relatively smaller distance, resulting in a larger coupling matrix element $H_{12}$. From Eq. (3.14), the diabatic transition probability at the first crossing will be very small and ionic scattering is predominant. Assuming that the first crossing involves an electron transfer (ionic scattering), the internuclear distance of $XY^-$ will increase rapidly because of the repulsive potential of $XY^-$; the electron affinity will increase, and the second crossing will occur at a large atom-to-molecule distance. Consequently, the coupling matrix element $H_{12}$, which depends exponentially on $R_C$, will be much
smaller. Since the diabatic transition probability in turn is an exponential function of $H_{12}$, the increase of bond length of the molecular ion will strongly increase the diabatic transition probability at the second crossing, yielding a larger ionization cross section. For covalent scattering, on the other hand, the bond stretching only starts near the second crossing, and the ionization cross section will be small.

Due to interactions between adiabatic potential surfaces, bond stretching can occur even before the first crossing is reached (prestretching), resulting in a bigger $R_c$ and thus a larger cross section (ATE 77a, EVE 78).

Bond stretching is more important at low energy collisions when the collision time, defined as the time spent by the atom between the two crossings, is comparable to or longer than the vibrational period of the molecule. At high energies where the collision time is much shorter than the vibrational period, the molecular motion can be considered frozen during the collision, the molecular ion is formed via a Franck-Condon transition and the molecule can be treated as an atom.

b) Orientation Effects in Atom-Molecule Ionization Reaction

One of the important molecular aspects in ionization reactions is the dependence of cross section on the relative orientation of the molecules with respect to the approaching atom. As indicated in Eq. (3.18), the coupling matrix element at the crossing seam of the potential surfaces, and thus the transition probability, depends not only on the internuclear distance at the crossing but also on the orientation angle $\phi$. Theoretical calculations show that the crossing radius $R_c$ itself is a weak function of the molecular orientation (BAL 73).

The angular dependence of $H_{12}$ in Eq. (3.18), $f(\phi)$, depends on the symmetries of the intersecting surfaces (GIS 75, ZEM 75 and LAC 80), and is
assumed to be \( \cos \phi \) in the alkali-halogen case and \( \sin 2\phi \) for alkali-oxygen collision (ALE 78, GIS 75 and ZEM 75). At certain molecular orientations, \( f(\phi) = 0 \) and adiabatic transition becomes impossible \( (H_{12} = 0, P_a = 0) \). In the experimental studies of the ionization reaction \( M + Br_2 \) \((M = Cs, K \text{ and } Na) \) (BAE 73), the total cross section as a function of relative velocity has the same shape as that in the atom-atom scattering, but the position of the maximum is shifted by a factor of more than 4 toward lower reduced velocities. It was assumed that the coupling matrix element is effectively lowered by the cosine dependence on the orientation (HUB 76).

### 3.3 Alkali–Symmetric-top Ionization Reactions

Many experimental studies have been performed to investigate the collision ionization reactions between alkali atoms and symmetric-top molecules.

\[
\begin{align*}
(3.20a) \quad & M + CX_3Y \rightarrow M^+ + CX_3Y^- \\
(3.20b) \quad & M + CX_3Y \rightarrow M^+ + CX_3 + Y^-
\end{align*}
\]

Since the C-X bonding is usually stronger than the C-Y bonding, the symmetric-top can be approximated as a diatomic molecule with the \( CX_3 \) radical being treated like an atom. Ionic species other than \( CX_3Y^- \) and \( Y^- \) can also be produced as reaction products. But different reaction channels have different cross sections and energy thresholds.

a) **Predominance of the Atomic Ions as Products**

There have been numerous experimental studies of the ionization reaction between alkali atoms and un-oriented symmetric-top molecules. It is
found that reaction (3.20b) is the dominant channel. Table 3.1 summarizes some of the experimental results. It is evident that for methyl halides \((\text{CH}_3\text{X})\), no molecular ions are produced from the ionization reactions, but for trifluoromethyl halides, such as \(\text{CF}_3\text{I}\) and \(\text{CF}_3\text{Br}\), a small fraction of molecular ions can be detected.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ionic Species and Relative Intensities</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{K} + \text{CF}_3\text{I})</td>
<td>((\text{CF}_3\text{I}^+)/\text{I}^- \sim 0.05)</td>
<td>MCN 73</td>
</tr>
<tr>
<td>(\text{K} + \text{CH}_3\text{I})</td>
<td>I(^-) only, no (\text{CH}_3\text{I}^+) is found</td>
<td></td>
</tr>
<tr>
<td>(\text{Cs} + \text{CF}_3\text{X})</td>
<td>((\text{F}^-/\text{X}^-) \leq 0.05) at energies below 50eV</td>
<td>ROT 74 and</td>
</tr>
<tr>
<td>(\text{X} = \text{I}, \text{Br}, \text{Cl})</td>
<td>((\text{CF}_3\text{I}^+)/\text{I}^- \sim 0.05, (\text{CF}_3\text{Br}^+)/\text{Br}^- \sim 0.05; \text{No CF}_3\text{Cl}^+ \text{and CH}_3\text{I}^+)</td>
<td>TAN 76</td>
</tr>
<tr>
<td>(\text{M} + \text{CX}_3\text{Y})</td>
<td>((\text{CF}_3\text{I}^+)/\text{I}^- \sim 0.01, (\text{CF}_3\text{Br}^+)/\text{Br}^- \sim 0.01)</td>
<td>COM 78b</td>
</tr>
<tr>
<td>(\text{M} = \text{Cs}, \text{Na}, \text{K})</td>
<td>No (\text{CH}_3\text{Br}^+) and (\text{CH}_3\text{CN}^+)</td>
<td></td>
</tr>
<tr>
<td>(\text{K} + \text{CHCl}_3)</td>
<td>(\text{Cl}^-) is the predominant ionic species, no (\text{CHCl}_3^-) is found</td>
<td>DIS 78</td>
</tr>
<tr>
<td>(\text{e}^- + \text{CF}_3\text{I})</td>
<td>(\text{I}^- : \text{F}^-: \text{F}^+: \text{CF}_3^+ \sim 1: 0.02 : 0.0005 : 10^{-4})</td>
<td>HEN 86</td>
</tr>
</tbody>
</table>

* \(\text{CH}_3\text{CN}\) has a dipole moment of 3.92D, and theoretical calculations (CRA 67, CRA 71, GAR 70 and GAR 71) show that a molecule with \(\mu > 2.5D\) can bind an electron.

b) **Effects of Molecular Orientation**

In most experiments all molecular orientations are present and the steric effects can not be studied directly. By preselecting the orientations of the molecules, Brooks and Bernstein have studied the reactions between alkali atoms and symmetric-tops at thermal energies (cf. Chapter 1 and references therein). Strong orientation effects are shown to exist in such reactions. More recently, Harland, Brooks *et al.* (HAR 89, HAR 90, HAR 91 and BRO 92)
investigated the collision ionizations, $K + R-X \rightarrow K^+ + R + X^-$, at high energies ($>5\text{eV}$), where $R$ represents $\text{CH}_3$ or $\text{CF}_3$ radicals and $X$ is a halogen.

As mentioned earlier, in these ionization reactions the first crossing between the ionic and covalent potential surfaces is almost totally adiabatic, so the total ionization cross section depends on the $LZ$ diabatic transition probability at the second crossing. According to Eq. (3.14), $P_d = \exp(-\kappa/k)$, where $\kappa$ is related to the coupling matrix element $H_{12}$. Earlier studies of thermal energy collision reactions suggest that the molecular ions ($RX^-$), which are the intermediate species of the reaction, dissociate explosively (within a vibrational period) after the electron jump, and $X^-$ is ejected along the molecular axis. The relative velocities between $K^+$ and $X^-$, $v$, will be different for heads and tails orientations. In the heads orientation, for example, $X^-$ is ejected in the direction opposite to that of the incoming potassium atom. The increased relative velocity between $K^+$ and $X^-$ gives a large diabatic transition probability $P_d$. The heads-to-tails ratio of the total ionization cross section can be given approximately as (Eq. (7) of HAR 91):

\begin{equation}
R = \frac{\sigma_H}{\sigma_T} = \frac{P_d(H)}{P_d(T)} = \exp(\kappa \Delta v / v^2)
\end{equation}

where $\Delta v = v_H - v_T$, $v^2 = v_H v_T$, $v_H$ and $v_T$ denote the relative velocity between $K^+$ and $X^-$ in heads and tails orientations, respectively. From experimental results, straight lines are indeed found in the plot of $\ln(R)$ versus $1/E$, where $E = 1/2\mu v^2$ is the collision energy.

In conclusion, from experimental investigations and theoretical calculations, a general understanding of the features of reaction dynamics in collision ionizations has been achieved. In a two-state approximation, electron
transfer takes place near the diabatic crossing of the intersecting potential surfaces. The generalized LZ formula, in which the coupling matrix element is orientation dependent, can be used to calculate the probability of electron transfer. Bond stretching and molecular orientation are two of the essential molecular aspects in collisional ionizations.
4 Results

In the present experiments, collisional ionization reactions between oriented symmetric-top molecules (CF$_3$Br, CF$_3$Cl, CF$_3$H and CH$_3$Br) and fast potassium atoms ($E > 3$eV) are studied:

(4.1a) $K + CX_3Y \rightarrow K^+ + CX_3Y^-$
(4.1b) $K + CX_3Y \rightarrow K^+ + CX_3 + Y^-$.

The molecules are seeded with helium at the same molecular concentration (10% of seed gas, 90% of He) in the nozzle supersonic beams. Typical experimental conditions are listed in Table 4.1.

The K$^+$ ions produced from these reactions are collected to measure the total ionization cross section. For all the molecules we studied, we found that the ionization reactivities are strongly affected by molecular orientations. The steric effects are more pronounced at the low energy end above the thresholds. Due to improved S/N, the energy thresholds of the reactions can be determined directly. Our experimental results show unambiguously that the energy thresholds are different for heads and tails orientations, and the apparent molecular electron affinity is orientation dependent in collision ionization reactions.
Table 4.1 Typical Experimental Conditions for the Study of Crossed Beam Reactions

<table>
<thead>
<tr>
<th>Vacuum Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle Chamber</td>
</tr>
<tr>
<td>Buffer Chamber</td>
</tr>
<tr>
<td>Hexapole Field Chamber</td>
</tr>
<tr>
<td>K Beam Chamber</td>
</tr>
<tr>
<td>Scattering Chamber</td>
</tr>
</tbody>
</table>

Nozzle Beam (*Seeded in He at Molecular Concentration of 10%*)

| Stagnation Pressure | 80 torr |
| Nozzle Temperature  | $\sim 270^\circ K^*$ |
| Modulation by the Chopper | 50% Duty Cycle @ 120 Hz |
| Hexapole Voltages   | $\pm 8$ kV |
| Orienting Field     | $\pm 13$ V/cm ($\pm 50$ V on the Plates) |

Fast Potassium Beam

| W Filament (10 mil) | 2100$^\circ$K (5 Amp @6VDC) |
| Oven Body Temperature | 105$^\circ$C (TC Voltage @4.2mV) |

Signal Detection

| Active Channeltron Bias | Anode: +500 V |
| Inactive Channeltron Bias | Cathode (Cone): -1300V |
| Bendix Electron Multiplier Max. Bias | Floating |
| Signal Counting Time | 30 sec/point ** |

* The nozzle is not heated, due to gas expansion and the radiation of the LN$_2$ trap, the nozzle is below room temperature.

** The counting time at lower energies is increased to improve S/N.
4.1 Relative Cross Sections of the Reactions

a) CF₃Br

Because trifluoromethyl bromide (CF₃Br) is known to have larger reaction cross sections than methyl halides such as CH₃Br, or CH₃Cl, this molecule is used first for signal optimization in the ionization reactions. Figure 4.1a shows the relative ionization reaction cross section as a function of molecular orientation and potassium beam energy. As described in Chapter 2 (Eq. (2.59)), the relative cross section is obtained by dividing the corrected K⁺ signal by the K beam intensity. Because the beam monitor was sensitive to the energy of the fast K beam, the K beam intensity is assumed to be space-charge limited as determined by Aten, et al. (ATE 75), and the intensity is thus proportional to \(E^{3/2}\), where \(E\) is the energy of the potassium beam.

The open circles and filled triangles in Fig. 4.2a represent the 0° and 180° orienting field configurations, respectively. Because the bromine end of the molecule is less electronegative than the fluorine end, the dipole moment of the molecule should point from the CF₃ radical end toward the Br end (F₃CBr⁺). This was first suggested by Brooks (BRO 69) for the analogue CF₃I molecule to explain the reaction asymmetry, and was later experimentally confirmed by Gandhi and Bernstein (GAN 88). So for CF₃Br, the 0° field configuration corresponds to the "heads" orientation with the Br end closest to the incoming K atom. Fig. 4.1a shows clearly that the Br end of the molecule is more reactive than the CF₃ end.

To better illustrate the energy dependence of the ionization cross section at the low energy end, a log-log plot is drawn from the same set of data, as shown in Fig. 4.2b. Large orientation effects are apparent at K beam energies below 5eV.
Figure 4.1 (a) Relative ionization cross section for the reaction of $K + CF_3Br$. Open circle: 0° Orientation (heads); Filled triangle: 180° Orientation (tails). (b) Same as (a), except that log-log scale is used to emphasize the lower energy region. The relative cross section is obtained by dividing the corrected $K^+$ signal by $K$ beam intensity ($\propto E^{3/2}$, where $E$ is the $K$ beam energy).
The data points shown in Figs. 4.1 are mainly from three sweeps over an energy range between 5eV and 26eV. The counting time at each point is 30 seconds, and to improve S/N, longer counting times are used at additional lower energy points. The typical statistical error for each point is smaller than the size of the symbol in the plots. But because of beam intensity drifts (~5%), the resultant cross sections shift a little between different sweeps. At each energy point, the K⁺ signals from the collisions between the fast K atoms and the molecules in the direct nozzle beam are averaged over three sweeps to determine the relative collection efficiencies of the channeltrons.

![Graph](image)

**Figure 4.2** Relative ionization cross section of the reaction K + CH₃Br. Open circles: 0° Orientation (tails); Filled triangles: 180° Orientation (heads).

b) CH₃Br

The relative ionization cross sections for the reaction between potassium and CH₃Br is shown in Figure 4.2. Due to the different electronegativities of Br, F and H, the direction of the electric dipole moment of CH₃Br is reversed
(+H₃CBr⁻) compared to that of CF₃Br. For CH₃Br, the 0° orienting field configuration is the tails orientation (CH₃ facing the incoming K). The same convention for the plot as for CF₃Br in Fig. 4.1 was used, with open circles and filled triangles representing 0° and 180° field configurations, respectively. Fig. 4.2 shows that for CH₃Br the reaction cross section is larger at the 180° orienting field configuration, so the Br end (heads) is more reactive than the CH₃ end, despite the reversal of the dipole moment with respect to CF₃Br. The reactivity differences between the two orientations are noticeably smaller, however.

Comparison of the results of CF₃Br and CH₃Br shows that for CF₃Br the 0° field configuration is more favorable for ionization, and for CH₃Br the 180° field configuration is more favorable. This obviously eliminates any thought that the asymmetry of reactivity may originate simply from the polarity change of the orienting field. In fact, due to the opposite directions of the dipole moments, the same orienting field configuration corresponds to different molecular orientations for CF₃Br and CH₃Br, with respect to the incoming potassium atom. Figs. 4.1 and 4.2 show that the Br end is more reactive for both molecules. These experimental findings, together with those for SF₆ as described in Appendix III, prove unquestionably that the different reactivities obtained at the two orienting field configurations are truly molecular effects, and orientations of the polar symmetric-top molecules are indeed achieved by the hexapole and the uniform orienting fields.

c) CF₃Cl and CF₃H

The relative cross sections for the reaction of potassium with oriented CF₃Cl and CF₃H are plotted in Figs. 4.3 and 4.4, respectively. The directions of the dipole moments of these molecules are similar to that of CF₃Br (+F₃CCl⁺,
Figure 4.3 Relative ionization cross section for the reaction K + CF$_3$Cl. Open circles: 0° orientation (heads); Filled triangles: 180° orientation (tails).

Figure 4.4 Relative ionization cross section for the reaction K + CF$_3$H. Open circles: 0° orientation (heads); Filled triangles: 180° orientation (tails).
-F_3CH^+), so the 0° orienting field configuration corresponds to heads orientation with the Cl end or the H end of the molecule facing the approaching K atom.

For CF_3Cl, the Cl end is more reactive, similar to CF_3Br; and for CF_3H, however, the F end (tails) is more reactive than the H end of the molecule. This result for CF_3H agrees with earlier experimental findings (HAR 91) and is similar to the result for the CCl_3H molecule (MAR 73). We assumed that due to the small electron affinity of hydrogen (0.8 eV) as compared to that of fluorine (3.45 eV), the F^- ions will be preferentially formed instead of the H^+ ions in the following reaction:

\[ 4.2 \quad K + CF_3H \rightarrow K^+ + CF_2H + F^- \]

d) Comparison

The ionization cross sections for all four molecules have the same energy dependence similar to a typical endoergic reaction: the reactivity rises sharply above the threshold at the low energy end and decreases monotonically at higher energies after reaching a maximum (see, e.g. MOU 74, TAN 76). The cross sections shown in Figs. 4.1 - 4.4 also indicate that the orientation effects are energy dependent. The steric effects are more pronounced at the low energy end and almost disappear at energies above 20eV. The differences in cross section among the four molecules we studied are illustrated in Fig. 4.5, and Table 4.2 summarizes the orientation averaged relative cross sections at K beam energy of 26eV. We assumed that the beam intensities are the same for different measurements. Due to the beam intensity shifts, the actual relative cross sections could differ by up to 20% from those shown in Fig.4.5 and Table 4.2. The CF_3Br molecule has the largest cross section, while CF_3H has the smallest.
<table>
<thead>
<tr>
<th>Molecule</th>
<th>CF$_3$Br</th>
<th>CF$_3$Cl</th>
<th>CF$_3$H</th>
<th>CH$_3$Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Cross Section*</td>
<td>1.00</td>
<td>0.49</td>
<td>0.32</td>
<td>0.51</td>
</tr>
</tbody>
</table>

* Relative to the orientation averaged signals of CF$_3$Br at the K beam energy of 26eV, at which the steric effects almost disappear.

![Graph](image)

**Figure 4.5** Rough comparison of the ionization cross sections among the four molecules. Solid line: 180° orienting field configuration; Dashed line: 0° orienting field configuration. Note that the abscissa is the CM energy.

### 4.2 Determining the Steric Factor $G$

As shown in Fig. 4.5, the cross sections of the ionization reactions depend strongly on the beam energy. In order to determine the relative magnitude of the orientation effects, the steric factor $G$ is calculated using the same set of data from which Figs. 4.1 - 4.4 are drawn. The steric factor $G$ is defined as:
\[ G(E) = \frac{S'_{180} - S'_{0}}{S'_{180} + S'_{0}}, \quad |G| \leq 1 \]

where \( S'_{0} \) and \( S'_{180} \) are the corrected signals with K beam energy \( E \) at the 0° and 180° orienting field configurations, respectively (see Chapter 2). Note that the absolute K beam intensity is not required to be known in order to determine the steric factor \( G \). If there is no orientation effect, \( G = 0 \), and \( |G| = 1 \) if one orientation becomes totally nonreactive. The negative (positive) values of \( G \) imply that the reactivity is smaller (greater) in the 180° field configuration.

![Graph showing steric factor G for CF₃Br and CH₃Br as a function of K beam energy.](image)

**Figure 4.6** The Steric Factor G for CF₃Br and CH₃Br as a function of K beam energy. Open Circle: CF₃Br; Solid Diamond: CH₃Br.

The energy dependence of the steric effects for CF₃Br and CH₃Br is illustrated in Fig. 4.6, and Fig. 4.7 shows the steric factors for CF₃Cl and CF₃H. For CF₃Br, CF₃Cl and CH₃Br, the steric factor \( G \) approaches ±1 at lower energies, indicating that as the collision energy is reduced, the reactivity
disappears first at the CF$_3$ or the CH$_3$ end of the molecule. This is a direct indication that the energy thresholds in the tails orientation is higher than that with the heads orientation. Considering the broad distribution of molecular orientations in the focussed beams, it is evident that the reactivity is strongly suppressed in the unfavored orientations. For CF$_3$H, the steric factor $G$ is positive, showing that the H end (heads) is unreactive. The magnitude of $G$ is smaller for CF$_3$H than the other three molecules, apparently because of the smaller steric hindrance of the hydrogen atom and the three reactive F atoms in the molecule.

![Steric Factor G vs K Beam Energy](image)

**Figure 4.7** The Steric Factor $G$ for CF$_3$Cl and CF$_3$H as a function of K beam energy. Open Circle: CF$_3$Cl; Solid Diamond: CF$_3$H.

Figs. 4.6 and 4.7 show that the steric factors of all four molecules have about the same energy dependence. The greatest orientation effects ($|G| = 1$) occur near the reaction thresholds, and the orientation effects decrease monotonically with increasing collision energies.
Figure 4.8 The measured hexapole field dependence of the steric factor $G$ for $\text{CF}_3\text{Br}$. The dashed curve is calculated from the hexapole transmission functions that take into account the unfocussable molecules ($\text{KM} > 0$).

We also changed the hexapole field strength to study the field dependence of the steric effects. The results for $\text{CF}_3\text{Br}$ is shown in Fig. 4.8. The steric factor $G$ remains the same at hexapole voltages above $\sim 5\text{KV}$. At voltages below $5\text{KV}$, however, the steric factor increases with decreasing hexapole voltage, which seems to contradict the early establishment that neither the orientation distribution nor the average orientation is sensitive to the hexapole field strength due to the large entrance and exit apertures in the focussing lens. Further analysis shows that since there is no beam stop along the hexapole axis, some molecules in the $\text{KM} > 0$ states, which are defocussed, will still enter the reaction region at lower hexapole voltages, and the apparent increase in steric effect at low hexapole voltages is merely the consequence of under-compensation of these diverging molecules with $\text{KM} > 0$. 
The intensity of the diverging molecules transmitted by the hexapole field can be calculated. To a first order approximation, we assumed that the molecules in the $KM > 0$ states have a uniform velocity equal to the mass flow velocity and have an averaged orientation $<\cos\theta> \sim 0.4$, similar to that of the $KM < 0$ molecules (see Table 2.4). With respect to the incoming $K$ atom, reversing the direction of the orienting field is equivalent to changing the rotational states of the molecules from $KM < 0$ to $KM > 0$ or vice versa. When molecules in the $KM > 0$ states are accounted for in calculating the steric factor $G$, the resultant field dependence, shown as the dashed curve in Fig. 4.8, agrees well with the experimental results.

For $\text{CH}_3\text{Br}$, the steric factor increases slightly at lower hexapole voltages, which can again be explained by the effect of the diverging molecules. Calculations indicate that due to the large molecular dipole moment (1.85D, as compared to 0.65D for $\text{CF}_3\text{Br}$), the molecules at $KM > 0$ states diverge rapidly in the hexapole field, and their intensity become negligible when the voltage on the hexapole exceeds about 1.6KV.

### 4.3 Determining the Energy Thresholds of the Reactions

From earlier studies on ten symmetric-top molecules (HAR 91), different energy thresholds were suspected in the heads and tails orientations. The fact that the steric factor $G$ approaches ±1 at low energies in the present experiments shows that the energy thresholds are indeed different for different orientations. To directly determine the energy thresholds, potassium ions from the cross beam reactions were collected for much longer times (up to 30 minutes per point) at energies near the thresholds. The energy thresholds in the
heads and tails orientations were obtained for all four molecules, as shown in Figs. 4.9 - 4.12, for CF$_3$Br, CH$_3$Br, CF$_3$Cl and CF$_3$H, respectively.

Assuming that near the threshold the reactivity increases linearly with the collision energy, linear fits of the relative cross sections at the low energy end give the energy thresholds for each orientation, as listed in Table 4.3. The K beam energy in the Lab system is converted to the CM energy by using Eq. (A2.3) in Appendix II, taking into account the translational energies of the gas molecules.

Table 4.3 Experimental Energy Thresholds for the Ionization Reactions

<table>
<thead>
<tr>
<th>Molecule (Orientation)</th>
<th>CF$_3$Br Heads</th>
<th>Tails</th>
<th>CF$_3$Cl Heads</th>
<th>Tails</th>
<th>CF$_3$H Heads</th>
<th>Tails</th>
<th>CH$_3$Br Heads</th>
<th>Tails</th>
</tr>
</thead>
<tbody>
<tr>
<td>E$_{th}$ (LAB)$^a$ (eV)</td>
<td>4.10</td>
<td>4.85</td>
<td>6.18</td>
<td>7.11</td>
<td>12.42</td>
<td>11.94</td>
<td>5.50</td>
<td>5.80</td>
</tr>
<tr>
<td>E$_{th}$ (CM)$^b$ (eV)</td>
<td>3.44</td>
<td>4.03</td>
<td>4.73</td>
<td>5.41</td>
<td>8.25</td>
<td>7.94</td>
<td>4.15</td>
<td>4.36</td>
</tr>
</tbody>
</table>

a: Uncertainties are ±0.2eV, except CF$_3$H, whose E$_{th}$(LAB) has an error of ~±0.6eV.
b: Uncertainties are ±0.2eV, except CF$_3$H, whose E$_{th}$(CM) has an error of ~±0.4eV.

For symmetric-top molecules, reactions (4.1a) and (4.1b) usually have the lowest thermodynamic energy thresholds in the CM system, which are given respectively as:

(4.3a) \[ E_{th} = IP(K) - EA_v(CX_3Y) \]
(4.3b) \[ E_{th} = IP(K) + D(CX_3-Y) - EA(Y) \]

where \( IP, EA \) and \( D \) represent the ionization potential, the electron affinity and the bond dissociation energy, respectively.
**Figure 4.9** Direct determination of the energy thresholds for the reaction $K + CF_3Br \rightarrow K^+ + CF_3Br$. Open Circles: heads orientation; Solid Triangles: tails orientation.

**Figure 4.10** Determination of the energy thresholds for the reaction $K + CH_3Br \rightarrow K^+ + CH_3 + Br$. Open circles: $0^\circ$ orientation (tails); Filled triangles: $180^\circ$ orientation (heads).
Figure 4.11 Determination of the energy thresholds for the reaction $K + CF_3Cl \rightarrow K^+ + CF_3 + Cl$. Open circles: $0^\circ$ orientation (heads); Filled triangles: $180^\circ$ orientation (tails).

Figure 4.12 Energy thresholds for the reaction $K + CF_3H \rightarrow K^+ + CF_2H + F^-$. Open circles: $0^\circ$ orientation (heads); Filled triangles: $180^\circ$ orientation (tails).
It is known (COM 78b) that for the ionization reaction between alkali atoms and CF$_3$Br molecules, both of the following reaction channels exist:

(4.4a) \[ K + CF_3Br \rightarrow K^+ + CF_3Br^- \]
(4.4b) \[ K + CF_3Br \rightarrow K^+ + CF_3 + Br^- \]

and reaction (4.4a) has a smaller cross section and a lower energy threshold than reaction (4.4b). At collision energies below the threshold of reaction (4.4b), all the potassium ions are produced through the first reaction channel. Thus we assumed that the observed energy thresholds for CF$_3$Br correspond to reaction (4.4a). Applying Eq. (4.3a), the vertical electron affinities of the CF$_3$Br molecule with heads and tails orientations are obtained from the observed energy thresholds: \( EA_V \) (heads) = 0.90 ± 0.2eV; \( EA_V \) (tails) = 0.31 ± 0.2eV. These results show that the vertical electron affinity of the molecule is orientation dependent, and should not be treated as an isotropic "thermodynamic" parameter. The tail end of the molecule may have a higher potential barrier than the head end, resulting in a greater energy threshold and a smaller vertical electron affinity.

In collision ionizations where all molecular orientations are present, the resultant energy threshold (and thus the electron affinity) is determined from only those collisions where the molecules have the favorable orientations. Taking this into consideration, the vertical electron affinity of CF$_3$Br (heads) determined from our experiment is in good agreement with previous results of \( EA_V = 0.91 \pm 0.2 \) eV (COM 78b) from the reaction of Na + CF$_3$Br.

The direct determination of the energy threshold for reaction (4.4b) for CF$_3$Br is complicated by the competition between the two reaction channels. Deconvolution of the total cross section requires knowledge of the energy dependence of the cross sections for both channels. In a similar experiment
using un-oriented CF$_3$Br molecules (COM 78b), the onset of the Br$^-$ ions is 0.54 eV higher than that of CF$_3$Br$^-$.

In previous experiments (see, e.g., MCN 73, COM 78b, and TAN 76), the CH$_3$Br$^-$ and CF$_3$Cl$^-$ molecular ions were not detected at all in collision ionization reactions, even though in the same experiment the CF$_3$I$^-$ and CF$_3$Br$^-$ ions in appreciable amount could be detected. Thus we assumed that for CH$_3$Br and CF$_3$Cl the potassium ions are produced from only one reaction channel:

$$(4.5) \quad K + \text{CH}_3\text{Br} \rightarrow K^+ + \text{CH}_3 + \text{Br}^-$$

$$(4.6) \quad K + \text{CF}_3\text{Cl} \rightarrow K^+ + \text{CF}_3 + \text{Cl}^-.$$  

For CF$_3$H, the dissociation energy of the C-F bond is quite large (~5.4eV), and the reduced mass of the K-CF$_3$H system is smaller than those involving other heavier symmetric-tops, so the energy conversion ratio from the LAB system to the CM system is also smaller (see Eq. (A2.3) in Appendix II). As a result, the K beam energy thresholds for the reaction exceed 10eV. At such high energies, the background noise due to the scattered potassium beam is very high. Because of the limited S/N, only the upper limits of energy thresholds for reaction (4.2) are estimated, as shown in Fig. 4.12.

In Table 4.4, the molecular constants and the expected energy thresholds are listed. For CF$_3$Cl, CF$_3$H and CH$_3$Br, the asymptotic energy thresholds of the ionization reactions are given by Eq. (4.3b), and the experimentally determined energy thresholds for both orientations are higher than the asymptotic values. As will be discussed in the next chapter, the electron transfer occurs at potential energies above the dissociation limit of the molecular ion, and higher energy thresholds than those given by Eq. (4.3b) are expected due to the partitioning of the dissociation energies.
Table 4.4 Summary of Molecular Constants and Energy Thresholds

<table>
<thead>
<tr>
<th>Molecule</th>
<th>CF$_3$Br</th>
<th>CF$_3$Cl</th>
<th>CF$_3$H</th>
<th>CH$_3$Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Mass (amu)</td>
<td>149.0</td>
<td>104.4</td>
<td>70.0</td>
<td>95.0</td>
</tr>
<tr>
<td>Dipole Moment (Debye$^0$)</td>
<td>0.65$^a$</td>
<td>0.50$^a$</td>
<td>1.65$^a$</td>
<td>1.81$^a$</td>
</tr>
<tr>
<td>C-Y Bond Energy D (eV)</td>
<td>2.86$^c$</td>
<td>3.40$^c$</td>
<td>5.38$^d$</td>
<td>2.90$^c$</td>
</tr>
<tr>
<td>$\gamma = E(CM)/E(LAB)$</td>
<td>0.792$^g$</td>
<td>0.728$^g$</td>
<td>0.642$^g$</td>
<td>0.709$^g$</td>
</tr>
<tr>
<td>Molecular EA (eV)</td>
<td>0.91$^f$</td>
<td>—</td>
<td>—</td>
<td>-0.469$^g$</td>
</tr>
</tbody>
</table>

For Reaction K + CX$_3$Y → K$^+ + CX_3 + Y^-$:

<table>
<thead>
<tr>
<th>Thermodynamic Energy Threshold (eV)</th>
<th>3.84$^h$</th>
<th>4.13$^h$</th>
<th>6.27$^h$</th>
<th>3.88$^h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ih}(CM)$ (eV) (heads)</td>
<td>—</td>
<td>4.73$^i$</td>
<td>$\leq 8.25$</td>
<td>4.15$^i$</td>
</tr>
<tr>
<td>(Observed) (tails)</td>
<td>—</td>
<td>5.41$^i$</td>
<td>$\leq 7.94$</td>
<td>4.36$^i$</td>
</tr>
</tbody>
</table>

For Reaction K + CX$_3$Y → K$^+ + CX_3Y^-$:

| $E_{ih}(CM)$ (eV) (heads)         | 3.44$^j$ | —        | —        | —        |
| (Observed) (tails)                | 4.03$^j$ | —        | —        | —        |
| Mol. EA (eV) (heads)              | 0.90$^j$ | —        | —        | —        |
| (Observed) (tails)                | 0.31$^j$ | —        | —        | —        |

---

**Notes:**

- b: 1 Debye = 10$^{-18}$ cgs unit = 3.33564x10$^{-30}$ Coulomb-meter.
- c: LIA 78, and PAU 60.
- d: The bond energy CHF$_2$-F is determined from values of the heat of formation:
  \[ D(CHF$_2$-F) = \Delta H^f(CHF$_2$) + \Delta H^f(F) - \Delta H^f(CHF$_3$) \]
  with \[ \Delta H^f(CHF$_2$) = -2.56eV; \Delta H^f(F) = 0.82eV; \Delta H^f(CHF$_3$) = -7.12eV, \]
  all values are at 298°K and are from ref. a.
- e: $\gamma = M/(M_K + M)$, see Eq. (A2.3) in Appendix II.
- f: COM 78b.
- g: MOU 74;
- h: Calculated from Eq. (4.3b), with IP = 4.34 eV for K, EA = 3.45, 3.61 and 3.36 eV for F, Cl and Br, respectively.
- i: See Table 4.3.
- j: Calculated from Eq. (4.3a).
4.4 Summary

In conclusion, large orientation effects are observed in the cross beam ionization reactions between potassium atoms and symmetric-top molecules. For CF$_3$Br, CF$_3$Cl and CH$_3$Br, the heads orientation with the Br or Cl end of the molecule facing the approaching K atom is favored for ionization. For CF$_3$H, the F end is more reactive. The orientation effects are more pronounced at the lower energy end. At energies above 20eV, the orientation asymmetry in reactivity almost disappears. Among the four molecules, the CF$_3$Br molecule has the largest cross section while the CF$_3$H molecule has the smallest cross section. Most importantly, our experimental results show unambiguously that the reaction thresholds are orientation dependent.
5 Discussion and Conclusions

The experimental results presented in Chapter 4 show that molecular orientation plays an important role in the collision ionization reactions, \( K + CX_3Y \rightarrow K^+ + CX_3Y^- \rightarrow K^+ + CX_3 + Y^- \). We believe that the reaction process starts with an electron transfer as the potassium atom approaches the molecule, followed by the rapid dissociation of the intermediate molecular ion. The ionic species are produced only if the kinetic energy of the relative motion is great enough to overcome the Coulomb attraction.

5.1 General Description of the Ionization Reaction Process

As mentioned in Chapter 3, the collision ionization process involves two crossings of the ionic and covalent potential surfaces. Figure 5.1 is a simplified diagram of a collision trajectory of K atom leading to ionization. The first crossing occurs at an atom-molecule distance of \( R_{ct1} \) determined as:

\[
R_{ct1} = \frac{14.4}{IP - EA_v} \text{Å}
\]

where \( IP \) is the ionization potential of the potassium atom and \( EA_v \) is the vertical electron affinity of the \( CX_3Y \) molecule. The electron affinity of the molecule is less than that of the halogen atoms, and \( R_{ct1} \) is small (≤ 4Å). According to the generalized Landau-Zener formula (see Eqs. (3.14), (3.18) and (3.19)), the
diabatic transition probability is exponentially dependent on the coupling matrix element $H_{12}$, which in turn depends exponentially on $R_c$. Calculations, detailed in Appendix IV, suggest that the first crossing is almost totally adiabatic ($P_d \sim 1$), so $K^+$ and $CX_3Y^-$ should be formed after the first crossing.

Figure 5.1 A simplified view of a collision trajectory of the K atom leading to ionization. The dashed line represents the path of $K^+$. The potential surface crossings occur at $R_{c1}$ and $R_{c2}$ as the potassium atom approaches and departs the molecule, respectively. Note that the internuclear distances of $R_{c1}$ and $R_{c2}$ may refer to different coordinates.

The molecular anion is expected to undergo rapid dissociation, ejecting the halogen ion $Y^-$ along the original molecular axis. If the dissociation is completed before the second crossing is reached, only the atomic ions are involved in the second crossing and the internuclear distance $R_{c2}$ can be determined as

$$R_{c2} = \frac{14.4}{IP - EA} \text{ (Å)}$$

where $EA$ is the electron affinity of the halogen $Y$, and is larger than the vertical electron affinity of the molecule. So $R_{c2} > R_{c1}$, and the calculation in Appendix IV shows that the second crossing is diabatic ($P_d \sim 1$) and the electron will stay on the halogen atom. Even if the molecular anion is still in the process of dissociation at the second crossing, the electron affinity of the molecular
complex will still be greater than the free molecule due to bond stretching, and the diabatic transition probability will be enhanced.

The orientation dependence of the coupling matrix element, and the short-range forces between the potassium atom and the molecule have been ignored in estimating the LZ transition probabilities. At collision energies near the thresholds, molecular orientation becomes the dominant effect, as we experimentally observed.

5.2 Acceptance Site of the Harpoon Electron

A polar symmetric-top molecule possesses a permanent electric dipole moment. From an electrostatic point of view, an electron will be attracted by the positive end of the molecule. The experimental results for K + CH$_3$Br and K + CF$_3$H show that the negative ends (Br and F) of the molecules are more reactive (see Figs. (4.2) and (4.4)). It seems that the harpoon electron does not just simply jump to the positive end of the molecule.

It is helpful to know the location of the unpaired electron in the molecular anion. Because the molecular ions are generally unstable in the gas phase, the electron spin density distribution of the CF$_3$X$^-$ ions ($X = $ I, Br and Cl), produced by $\gamma$ irradiation at 77° K of solid solutions containing up to 5% of the CF$_3$X parent compounds in various solvents, was studied by using ESR spectroscopy (HAS 77). It was revealed that the unpaired electron resides in an $a_1(\sigma^*)$ antibonding orbital which is composed largely of the $p$ orbitals from carbon and the unique halogen ($X$) that lies along the $C_3v$ symmetry axis of the molecular ion. Furthermore the spin density in the $p_\sigma$ orbital of $X$ in CF$_3$-X$^-$ is found to be four times larger than the corresponding spin density associated with the same halogen in CH$_3$-X$^-$ (SPR 71, MIS 73 and FUJ 74), so the CF$_3$-X$^-$ species are
probably more stable than CH$_3$X$^-$. The absence of CH$_3$X$^-$ ions as products in collision ionization reactions (see Table 3.1) supports this finding. Furthermore, the photoelectron spectra (TUR 70 and BAK 72) and collision energy loss profiles (CAS 79) also show that the lowest unoccupied orbital of the CH$_3$I molecule is the $\sigma^*$ orbital between C and I, and this orbital lies about 4.5 eV above the highest occupied orbital ($n$(I), cf. Fig. 3 of CAS 79).

It can be rationalized that the Harpoon electron will jump preferentially to the lowest unoccupied orbitals in a molecule, and since the molecule CX$_3$Y is anisotropic, the electron jump is probably orientation dependent.

5.3 Orientation Effects In the Exit Channel

As mentioned in Chapter 3, the steric effects observed in the collision ionization reactions can be explained by the relative motions of the ions in the exit channel (HAR 91). Figure 5.2 illustrates the relative velocities of between potassium and halogen ions in the heads and tails orientations.

![Diagram](a) Heads Orientation (b) Tails Orientation

Figure 5.2 An illustration of the relative velocities between K$^+$ and Y$^-$ in the heads and tails orientations. For K atom incident on the head end of the molecule CX$_3$Y (heads orientation), the relative velocity will be greater, reducing the chances of the electron returning to the K$^+$. 
The halogen ion is ejected from the intermediate molecule along its original axis, so in the heads orientation it travels in the direction opposite to the incoming potassium ion, yielding a large relative velocity. On the other hand, the halogen and potassium ions travel in the same direction in the tails orientation, and the relative velocity is reduced. Because the LZ diabatic transition probability at the second crossing depends exponentially on the inverse of the relative velocity, the heads orientation will have a larger cross section for forming ions than the tails orientation. Harland et al. (HAR 91) established that (see Eq. (3.21)) the heads-to-tails ratio $R$ of the cross sections depends exponentially on the inverse of the collision energy ($\log R \propto 1/E$).

As shown in Fig. 5.3, the linear dependence between $\ln(R)$ and $1/E$ indeed exists for $\text{CH}_3\text{Br}$, $\text{CF}_3\text{Cl}$ and $\text{CF}_3\text{H}$ at energies a few eV's above the energy thresholds.

But for $\text{CF}_3\text{Br}$ only, a much better linear relationship can be found between $\ln R$ and $1/(E - E_0)$, where $E_0$ is roughly the energy threshold for the heads orientation. This different behavior between $\text{CF}_3\text{Br}$ and other molecules probably arises because of the following: among the four molecules, $\text{CF}_3\text{Br}$ has the largest electron affinity and thus the smallest energy threshold. The first crossing of the ionic and covalent potential surfaces will therefore occur at the largest internuclear distance (Eq. (5.1)). $\text{CF}_3\text{Br}$ also has the largest molecular mass and the smallest relative velocity, so the time between the two crossings will be the longest for $\text{CF}_3\text{Br}$. Before the second crossing is reached, a significant amount of translational energy may already be consumed in overcoming the Coulomb attraction, so the relative velocity between the ionic species at the second crossing could be much smaller than the initial relative velocity.
Figure 5.3  Plots of \( \ln(R) \) vs. \( 1/E \) for CH\(_3\)Br, CF\(_3\)Cl, CF\(_3\)H and CF\(_3\)Br. \( R \) is the cross section ratio between the heads and tails orientations, \( R = \sigma_H/\sigma_L \). The arrows indicate the locations of the energy thresholds. For CF\(_3\)Br, the abscissa is \( 1/(E - E_{th}) \) and \( E_{th} = 4.1 \text{eV} \).

As the energy nears the thresholds, \( \ln R \) no longer linearly depends on \( 1/(E - E_{th}) \) or \( 1/E \) for all four molecules, as shown in Fig. 5.3. This suggests that...
at energies near the threshold, the difference in energy threshold between the heads and tails orientations becomes more important and the approximation used to derive Eq. (3.21), namely \( \Delta \nu = \nu_H - \nu_T, \nu^2 = \nu_H \nu_T \), will not be valid. So our experimental results suggest that the application of Eq. (3.21) should be restricted to energies a few eV's above the thresholds.

5.4 Study of the Potential Energy Surfaces of the Molecules

As shown in Fig. 4.5, the ionization cross section \( \sigma \) and its energy dependence vary between different symmetric-top molecules, especially at energies near the thresholds. Since both the electron transfer and the subsequent dissociation of the molecular anion are affected by the potential energy surfaces of the free and electron-attached molecule, a general knowledge of these potentials will be very helpful in understanding the energy and orientation dependence of the reaction cross section near the thresholds.

In the thermal energy reactions between alkali atoms and methyl halide molecules, \( M + CH_3X \rightarrow MX + CH_3 \), translational energy thresholds still exist even though the reactions are exoergic (see, e.g. BER 73, PAN 78, and WU 78). Using one-dimensional diabatic potentials for \( CH_3X \) and \( CH_3X^- \), which depend only on the C-X bond distance, Wu found that the experimentally observed energy barrier (or the activation energy) for electron transfer can be approximated as the energy difference between the zero point energy of the molecule and the crossing point energy of the two diabatic potential curves (WU 79).

The potential energy curves for the molecules we studied can be constructed by using a diatomic approximation. The CX\(_3\) radical is treated as a
single atom, and the molecule CX₃Y can be treated as a diatomic molecule. The Morse potential for a diatomic molecule AB is used in the expanded form:

\[ U(AB) = -2D₀ \exp(-β(r - r₀)) + D₀ \exp(-2β(r - r₀)) \]  

(5.3)

in our case \( D₀ \) is the bond dissociation energy of CX₃-Y, \( r₀ \) is the equilibrium C-Y distance, \( β = ν₀(2π²μ/ID₀)^{1/2} \) with \( ν₀ \) being the fundamental vibration frequency characteristic of the C-Y stretching mode, and \( μ \) the reduced mass. The zero potential energy is referenced at infinite separation. The first term in the equation represents the attraction force, while the second term denotes the repulsion of the nuclei.

By studying the dissociative thermal electron attachment for a collection of methyl halide molecules, Wentworth et al. developed a simple potential function for the molecular ion AB⁺ (WEN 69):

\[ U(AB⁺) = -2kD₀ \exp(-β(r - r₀)) + D₀ \exp(-2β(r - r₀)) - EA \]  

(5.4)

where \( EA \) is the electron affinity of atom Y and \( k \) is an empirical constant depending on the molecular properties:

\[ k = \frac{1}{2} \cdot \frac{E₀ + EA \sqrt{1 - (EA - E₀)/(D₀ + 1/2ν₀)}}{2(EA - E₀)} \]

(5.5)

with \( E₀ \) being a constant of 0.662 eV.

The parameters used to construct the energy curves are summarized in Table 5.1, and the potential curves are plotted in Fig. 5.4. Table 5.1 also includes the values of \( ΔE \), defined as the difference between the potential energy at the curve crossing point and the minimum potential of the neutral molecule at equilibrium distance, as illustrated specially in the plot of the potential curves of CF₃Br.
Figure 5.4 Potential energy curves for CF$_3$Br, CH$_3$Br, CF$_3$Cl and CF$_3$H. For all four molecules, the energy barrier $\Delta E$ can be observed from these figures. The values of $\Delta E$ are listed in Table 5.1.
Table 5.1 Parameters Used to Construct the Potential Curves of the Molecules.

<table>
<thead>
<tr>
<th>CX3Y</th>
<th>$\tilde{v}_{0,CX3-Y}$ (cm$^{-1}$)</th>
<th>$r_0$ (Å)</th>
<th>$D_0$ (eV)</th>
<th>$1/\beta$ (Å)</th>
<th>$EA$ (eV)</th>
<th>$\Delta E$ (eV)</th>
<th>$k$</th>
<th>$\sigma$ (rel.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$Br</td>
<td>350$^a$</td>
<td>1.908$^a$</td>
<td>2.86$^c$</td>
<td>0.585</td>
<td>3.363$^f$</td>
<td>0.221</td>
<td>0.17</td>
<td>1.00$^g$</td>
</tr>
<tr>
<td>CF$_3$Cl</td>
<td>470$^a$</td>
<td>1.751$^a$</td>
<td>3.40$^c$</td>
<td>0.600</td>
<td>3.613$^f$</td>
<td>0.159</td>
<td>0.46</td>
<td>0.49$^g$</td>
</tr>
<tr>
<td>CH$_3$Br</td>
<td>611$^b$</td>
<td>1.939$^b$</td>
<td>2.95$^a$</td>
<td>0.584</td>
<td>3.363$^f$</td>
<td>0.185</td>
<td>0.28</td>
<td>0.51$^g$</td>
</tr>
<tr>
<td>CF$_2$H-F</td>
<td>1152$^a$</td>
<td>1.332$^a$</td>
<td>5.38$^d$</td>
<td>0.392</td>
<td>3.448$^f$</td>
<td>-0.0515</td>
<td>2.60</td>
<td>0.32$^g$</td>
</tr>
</tbody>
</table>

a: SVE 74; b: HER 66a; c: LIA 78, and PAU 60; d: see note d of Table 4.4; e: WEN 69; f: BER 63; g: See Table 4.2.

Even though the potentials are diatomic approximations involving empirical constants, the energy barrier $\Delta E$ shows a clear trend among the molecules studied: CF$_3$Br < CH$_3$Br < CF$_3$Cl < CF$_3$H. The relative ionization cross sections obtained from our experiments, as listed in Table 5.1, have the reverse order: CF$_3$Br > CH$_3$Br > CF$_3$Cl > CF$_3$H. Since the potential of CX$_3$Y$^-$ is highly repulsive near the crossing region, even a small increase in bond length will cause a large change of vertical electron affinity. For CF$_3$Cl and CF$_3$H, the vibrational barrier is so large that a negative electron affinity is expected, and the electron transfer will occur at smaller atom-molecule distances, leading to smaller ionization cross section.

By studying the collision ionization reactions between alkali atoms and various molecules, the molecules can be categorized into two classes (KLE 82), mainly due to the difference in the potential energy surfaces. Figure 5.5 shows the potential curve crossings for two different types of diatomic molecules. In Fig. 5.5a, there is no potential barrier on the lower adiabatic potential surface, as is the case for molecules like H$_2$, N$_2$, NO and SF$_6$. On the other hand, if the equilibrium internuclear distance of XY$^-$ is significantly larger than that of XY,
and the coupling matrix element is sufficiently small, the lower adiabatic potential curve can have a vibration barrier, as shown in Fig. 5.5b. Methyl halide molecules and the halogen molecules are believed to have such barriers.

![Potential Energy Graphs](image)

**Figure 5.5** Potential curves for two diatomic molecules XY at the ionic-covalent crossings. Solid and dashed curves are adiabatic and diabatic potentials, respectively. (a) No vibration barrier at the lower adiabatic potential curve; (b) A vibration barrier exists at the lower adiabatic potential curve.

For the molecules with a vibrational barrier, the process of bond stretching will always be important in ionization reactions. The energy barrier is overcome by vibration excitation induced by the collision. These translation-to-vibration energy transfer processes in molecular collisions are discussed by Nikitin (NIK 74). Generally, in the energy region of our interest \((E \leq 10\text{eV})\), the short-range interaction between the atom and the molecule contributes the most to the vibrational excitation and the energy transfer is expected to be affected by the molecular orientation.
Moutinho et al. have studied the ionization reactions of potassium atoms with CH₃Br, CH₃I and Br₂ (MOU 74, MOU 79). Near the energy threshold, increasing the vibrational energy increases the ionization cross section more than does a comparable amount of translational energy. It was suggested that in the energy threshold region, bond stretching is critical and translational energy is not effectively converted into vibrational energies. However, for molecules with no vibrational barrier, the vibration can adjust adiabatically to the electron transfer, and translational energy and the energy of internal motion are equally effective in enhancing ionization cross section near the threshold (see, e.g., HUB 75, for the reaction between alkali atom and SF₆).

Using Eq. (3.13), the height of the barrier on the lower adiabatic potential surface, $E_b$, can be determined as $E_b \sim \Delta E - H_{12}$, where $H_{12}$ is the coupling matrix element between CX₃Y and CX₃Y⁺, and is likely to be orientation dependent.

Analysis of the potential curves suggests that the ionization cross section will be determined mainly by the vibrational excitation of the molecule to overcome the energy barrier in the adiabatic potential surface. For CF₃Br, the vibrational barrier is very small, $< 0.17$ eV, resulting in a large cross section. For CF₃H, the vibrational barrier exceeds an electron-volt, and only those collisions with very small impact parameters lead to excitation of sufficiently high vibration levels, resulting in a small ionization cross section. For the four molecules studied, the magnitudes of the cross sections indeed reflect the relative heights of energy barriers in the molecules. Furthermore, the vibrational barrier is likely to be orientation-dependent due to the anisotropic coupling matrix element between CX₃Y and CX₃Y⁺, leading to different electron affinities and ionization cross section at heads and tails orientations near the thresholds.
5.5 Analysis of Ionization Reaction Energy Thresholds

The energy threshold for the reaction $K + CX_3Y \rightarrow K^+ + CX_3Y^-$ is determined as

$$(4.3a) \quad E_{th} = IP - EA_v$$

where $E_{th}$ is the CM energy, $IP$ is the ionization potential of potassium atom, and $EA_v$ is the vertical electron affinity of the molecule. For CF$_3$Br, the observed energy thresholds for the ionization reactions are different for heads and tails orientations, as shown in Fig.4.9, indicating that molecular electron affinity is an anisotropic parameter. The electron affinity in the tails orientation is smaller than that in the heads orientation, suggesting the following consequences: a) according to Eq. (5.1), the covalent and ionic potential surfaces intersect at a reduced $K$–CF$_3$Br distance $R_c$ in the tails orientation and the electron transfer probability will be smaller at the first crossing, and b) the Coulomb attraction potential which $K^+$ and CF$_3$Br$^-$ have to escape is greater ($e^2/R_c$) in the tails orientation than that in the heads orientation.

The dominant reaction process, $K + CX_3Y \rightarrow K^+ + CX_3 + Y^-$, has energy thresholds given in the asymptotic limit as

$$(4.3b) \quad E_{th} = IP + D - EA$$

where $D$ is the CX$_3$-Y bond dissociation energy and $EA$ is the electron affinity of the halogen atom Y. For CF$_3$Br, the threshold for this reaction was not determined from our experimental result due to overlapping with other reaction channels. For CH$_3$Br, CF$_3$H and CF$_3$Cl, the reaction thresholds determined from the experiments, listed in Table 4.4, are larger than those given by Eq.
(4.3b). An inspection of the potential curves of the molecules, as shown in Fig. 5.4, suggests that the electron transfer occurs at a potential energy above the dissociation asymptote of the molecular ion. Figure 5.6 is a plot of the typical potential curves for $\text{CX}_3\text{Y}$ and $\text{CX}_3\text{Y}^-$. 

![Potential Energy Diagram]

**Figure 5.6** An illustration of the excessive potential energy of the molecular ion after the electron transfer. The molecular ion is formed on the repulsive wall of the potential surface above the dissociation limit.

Due to the van der Waals and inductive forces, the molecule can be excited to an energy of $\Delta E_0$ relative to the ground vibration level before the electron transfer. The excess potential energy of the molecular ion, with respect to that of $\text{CX}_3 + \text{Y}^-$ at infinite separation, can be obtained as:

$$\epsilon = \text{EA} - D - \text{EA}_v + \Delta E_0$$  

(5.6)

where $\text{EA}$ is the electron affinity of the halogen $Y$, $D$ is the $\text{CX}_3\text{-Y}$ bond dissociation energy and $\text{EA}_v$ is the vertical electron affinity of the molecule. A
certain fraction of the energy $\epsilon$ is partitioned to the CX$_3$ radical as translational and possible vibrational energies. The additional energies gained by the radical will not contribute to the relative motion of the K$^+$ and Y$^-$ ions. Therefore, the observed energy thresholds should be expected to be higher than those thermodynamic values given in Eq. (4.3b).

If we can determine the total energy of the radical CX$_3$ in the CM system, the apparent energy threshold can be obtained. But even with the radical being counted as a single particle, the dissociation process is a three-body problem, and analytical solutions of the kinematic equations cannot be obtained. In general, the partition of the dissociation energy is affected by several parameters, such as the relative strength of the repulsive force as compared with the Coulomb attraction, the life-time of the molecular ion, and the collision geometries (the impact parameter and the molecular orientation).

For CF$_3$Br, we were able to determine its vertical electron affinities from the onsets of the molecular ions in the heads and tails orientations. If for CF$_3$Cl, CF$_3$H and CH$_3$Br, the vertical electron affinity is also orientation dependent, Eq. (5.6) suggests that the apparent energy thresholds for producing atomic ions will be different for heads and tails orientations, which coincides with our experimental results (see Table 4.4).

5.6 Conclusions

From our experimental results, we can conclude the following:

a) The ionization cross sections in the collisions between potassium atoms and symmetric-tops are strongly orientation dependent, and the steric effects are more pronounced at energies near the thresholds.
b) The energy thresholds are different in the tails and heads orientations, so the vertical electron affinity of a molecule should be considered as an anisotropic parameter.

c) The harpoon electron does not simply jump to the positive end of the electric dipole of the molecule. For CF$_3$H and CH$_3$Br, the Br and F ends, which are the negative ends of the molecular dipoles, are more reactive. The harpoon electron is likely to reside in the a$_1$(σ*) antibonding orbital between the carbon and the unique halogen atom along the symmetry axis of the molecule.

d) The difference in relative ionization cross sections among the molecules can be related to the vibrational energy barriers in the molecules, and near the energy threshold bond stretching is important for vibration excitation.

e) At higher collision energies (a few eV’s above the thresholds), the steric effect can be explained mainly by the relative motions of the charged particles in the exit channel.

The present experimental studies of ionization reactions using oriented molecules provide new information for the better understanding of the steric effects in chemical reactions. The reaction dynamics in collisions involving polyatomic molecules are complicated by the internal motions of the molecules and by the presence of multiple reaction channels. In future experiments, efforts need to be made to improve the average orientation of the molecules in the supersonic nozzle beam so the tails and heads orientations will be better representations of the ideal molecular orientation geometries. If the S/N ratio can be improved even further, by coincidence counting of both positive and negative ionic products, for example, it is possible that the reactivity between alkali atoms and symmetric-top molecules in a single |JKM> state can be investigated, and the orientation-dependent reaction opacity function can be
obtained directly. The energy dependence of the ionization cross section, which carries useful information about the reaction dynamics, can be determined quantitatively if the absolute intensity of the potassium beam is calibrated accurately. More importantly, by collecting and mass-analyzing the negative ions produced in the ionization reaction, the steric effects in different reaction channels can be studied separately.
Appendix I

Procedure for Channeltron Reactivation

As mentioned in Section 2.1, the characteristics of the channel electron multipliers (channeltrons, Detector Technology, Inc., Model 206-10C) used to collect potassium ions tend to degrade, probably due to pump oil contamination. The normal resistance of the channeltron is about 200MΩ, and the electron gain is about $10^7$. After numerous tests, we found that the totally "dead" channeltrons (no output pulse at voltages up to 3kV across the dynode and anode) can be reactivated effectively by the following procedure:

1) Put the channeltron in a clean beaker and place them in an oven at room temperature. Increase the oven temperature to 350°C, and bake the channeltron in air at 350°C for about 80 minutes. Turn off the oven and let it cool down normally to room temperature.

2) Using a ventilated hood, mix solutions of 6ml 30% hydrogen peroxide, 6ml 88% formic acid (HCOOH) and 240ml of deionized water in a 250ml beaker. Heat the solution to 80°C on a hot plate.

3) Put the baker on a thermal insulator and place the channeltron in the solution for 5 minutes.
4) Place the beaker under the tap and overflow rinse with warm tap water for 5 minutes.

5) Remove the channeltron from the warm water and immediately rinse in deionized water with a polyethylene squirt bottle. Keep rinsing for at least one minute.

6) Blow the channeltron dry with oil-free dry nitrogen and bake in 80°C oven in air for 15 minutes.

Step 2) through 6) are the recommended cleaning procedures for Galileo bakeable channeltrons. We found both the high temperature baking and the subsequent cleaning are necessary for the reactivation. Some of the channeltrons are coated with lead oxides, and the following reactions are known to happen at elevated temperatures, which may alter the channeltron characteristics:

\[2\text{PbO} + \text{H}_2 \rightarrow \text{Pb}_2\text{O} + \text{H}_2\text{O} \ (235^\circ\text{C})\]
\[2\text{PbO}_2 \rightarrow 2\text{PbO} + \text{O}_2 \ (350^\circ\text{C} \text{ in air})\]

It is also possible that the oil contamination inside the channeltron is effectively removed by being baked at high temperatures. The diffusion pump oil (Convoil, CVC Products, Inc.) has a boiling point of 360°C at 1 atm.
Appendix II
LAB-to-CM Energy Conversions

The ionization reactions between the symmetric-top molecules and the fast potassium atoms occur when the two beams cross at a right angle. The collision energy in the CM system can be calculated from the translational energies of the molecules and the atoms in the LAB system.

The energy of the potassium beam $E_K$ is determined by the TOF experiments as described in Chapter 2, and the translational energy of the symmetric-top molecules, $E_{mol}$, in the seeded supersonic expansion beam is given by the energy conservation, in analogy to Eq. (2.6):

\[
E_{mol} = \frac{1}{2} \overline{m} u^2 = \int_{T_s}^{T_0} \overline{C_p} dT
\]

where $\overline{m}$ and $\overline{C_p}$ are the average molecular weight and specific heat of the gas mixture, respectively, and $u$ is the mass flow velocity of the molecules.

The collision energy in the CM system is given by:

\[
E_{CM} = \frac{1}{2} \mu v_{rel}^2 = \frac{1}{2} \frac{M_K M}{M_K + M} (v_K^2 + u^2)
\]

where $M$ is the mass of the molecule and $M_K$ is the mass of K atom.

Using $E_K = \frac{1}{2} M_K v_K^2$ and Eq. (A2.1), the CM energy is related to K beam energy as:

\[
E_{CM} = \frac{M}{M_K + M} (E_K(LAB) + E_0)
\]
where $E_0 = \frac{M_K}{M} E_{mok}$ with values of 0.24, 0.32, 0.43 and 0.35eV for CF$_3$Br, CF$_3$Cl, CF$_3$H and CH$_3$Br, respectively. The conversion ratio, $M/(M_K + M)$, is determined by the molecular mass, and among the four symmetric-top molecules we studied, CF$_3$Br has the largest molecular mass, so the conversion ratio is the highest (0.792) for CF$_3$Br. For a given potassium beam energy, the K + CF$_3$Br system has the greatest CM energy.

Eq. (A2.3) can also be used for the energy conversion in the ionization reactions between potassium atoms and the spherically symmetric-top SF$_6$ molecules in a neat nozzle expansion beam. Since the mass flow velocity of SF$_6$ is small in a neat nozzle beam, $E_0$ can be neglected, resulting in an error of only 0.03eV in $E_{CM}$. 
Appendix III
Study of the Ionization Reaction $K + SF_6$

In the cross beam experiments, because that the $K^+$ ions are collected in an orienting field and in the vicinity of the hexapole field ($10^4$ volt/cm or higher), it is necessary to establish that any orientation asymmetry of $K^+$ signals in reaction (4.1) is not caused by these fields. To investigate the possible artifacts, we studied the ionization reaction between potassium atoms and $SF_6$ molecules in a neat nozzle beam:

$$ (A3.1) \quad K + SF_6 \rightarrow K^+ + SF_6^- $$

Spherical tops like $SF_6$ have no permanent electric dipole moment, and can not be focussed by the hexapole field. Therefore neither the hexapole or the uniform field affects the $SF_6$. By varying the focussing and the orienting fields, any change in the $K^+$ signal will originate from these fields, and is regarded as an artifact. The $K^+$ signal level was found to be independent of the hexapole field. The operational voltages on the two channeltrons were chosen to give approximately equal signals. As the K beam energy is increased, the collection efficiency of Channeltron #2 is enhanced and this effect is accounted for as the relative collection efficiency (see Eq. (2.57)).

We also determined the energy threshold of reaction (A3.1) which is given in the CM system as:
where \( IP \) and \( EA \) denote the ionization potential of potassium and the electron affinity of \( \text{SF}_6 \), respectively. The electron affinity of \( \text{SF}_6 \) was measured independently by several groups (0.75 ± 0.1 eV, LEF 74; 0.46 ± 0.1 eV, COM 78; and 0.32 ± 0.15 eV, HUB 75), and the average of these results is used, \( EA_{\text{SF}_6} = 0.51 ± 0.2 \text{ eV} \). Given the value of 4.34 eV for \( IP \), we get \( E_{th}(\text{CM}) = 3.83 \text{ eV} \). The K beam energy threshold in the LAB system is obtained by using Eq. (A2.3) in Appendix II, resulting in \( E_{th}(\text{LAB}) = 4.85 \text{ eV} \).

![Graph](image)

**Figure A3.1** \( \text{SF}_6 \) reactivity as a function of K beam energy. Open Circle: 0° configuration; Filled diamond: 180° configuration. Different slopes are due to the slightly different collection efficiencies of the channeltrons. From the plot above, we get \( E_{th}(\text{LAB}) = 4.75 ± 0.2 \text{ eV} \) for both configurations.

Figure A3.1 shows the reactivity for reaction (A3.1) as measured by the K+ count-rates. For both the 0° and 180° field configurations, the same energy
threshold of $4.75 \pm 0.2$ eV is obtained, in very good agreement with the expected value of 4.85 eV.

From the experiments using SF$_6$, we have established that there is no artifact in the ion collection system, and the hexapole and orienting fields do not create any side effects. Furthermore, the close agreement of the energy thresholds obtained from the literature and our experiments shows that the energy calibration of the K beam by the TOF experiments is accurate to within about $\pm 0.2$ eV at 5 eV.
Appendix IV
Estimation of the LZ Transition Probabilities

In collision ionization reactions, the ionic and covalent potential surfaces cross twice as the colliding partners approach and depart from each other. Ions are formed if one of the transitions is adiabatic and the other is diabatic. Electron transfer occurs if the transition at the first crossing is adiabatic, and the transition probabilities can be calculated by using the generalized Landau-Zener formula. Using Eqs. (3.17) - (3.19), the coupling matrix element can be derived as:

\[(A4.1) \quad H_{12} = 55.32 \frac{\sqrt{EA}}{4.34 - EA} \exp(-\frac{13.43}{4.34 - EA}) \cdot f(\phi) \ (eV)\]

where the molecular electron affinity \( EA \) is in units of eV, \( 0 \leq |f(\phi)| \leq 1 \), and the ionization potential of 4.34 eV for K has been used. Assuming that in the crossing region the short range forces between the K atom and the molecule are still negligible, the term \( \Delta F \) in Eq. (3.14) will be \( e^2/R_c^2 = (IP - EA)/R_c \), and Eq. (3.14) becomes:

\[(A4.2) \quad P_a = 1 - \exp(-1.893 \times 10^7 \frac{EA \cdot f^2(\phi)}{\sqrt{E_K (1 - b^2/R_c^2)(4.34 - EA)^4}} \exp(-\frac{26.86}{4.34 - EA}))\]

where \( b \) is the impact parameter, and \( E_K \) is the K beam energy in the lab system. For collisions with larger impact parameters \( (b \sim R_c) \), the denominator in
the exponent will be small, leading to total adiabatic transition \((P_a \sim 1)\). The electron transfer probability \(P_a\) would be the least at \(b = 0\). We let \(f(\phi) \sim 1\) and \(b = 0\) to estimate the lower limit of \(P_a\). The values of \(P_a\) at different molecular electron affinities are generally close to 1, so the diabatic probabilities \(P_d = (1 - P_a)\) are shown in Table A4.1.

**Table A4.1** Estimated Diabatic Transition Probability at the First Crossing in the Reaction \(K + CX_2Y\) (K beam energy = 5eV)

<table>
<thead>
<tr>
<th>(EA (eV))</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>1.4</th>
<th>1.8</th>
<th>2.2</th>
<th>2.6</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_{12}/f(\phi) (eV))</td>
<td>0.23</td>
<td>0.29</td>
<td>0.38</td>
<td>0.32</td>
<td>0.30</td>
<td>0.23</td>
<td>0.15</td>
<td>0.072</td>
<td>0.023</td>
<td>0.003</td>
</tr>
<tr>
<td>(P_d = 1 - P_a^*)</td>
<td>2(-4)</td>
<td>2(-7)</td>
<td>3(-9)</td>
<td>3(-10)</td>
<td>3(-10)</td>
<td>4(-8)</td>
<td>9(-5)</td>
<td>4(-2)</td>
<td>6(-1)</td>
<td>9.8(-1)</td>
</tr>
</tbody>
</table>

* The number inside the parentheses denotes order of magnitude. e.g., 2(-4) = 2x10^{-4}.

Using un-oriented molecules, previous experiments have determined the electron affinities for several symmetric-tops: 0.91 eV for CF\(_3\)Br, 1.57eV for CF\(_3\)I (COMP 78b) and 0.26 eV for CH\(_3\)I (MOU 74). For these molecules, the diabatic transition probabilities given by the LZ formula are extremely small, so the first crossing is almost exclusively adiabatic and electron transfer occurs.

For molecules with very small or even negative electron affinities (e.g., CH\(_3\)Br has an electron affinity of -0.46 eV, MOU 74), the formula to calculate the matrix element has to be modified. A simple exponential relation between \(H_{12}\) and \(R_c\) has been suggested for O\(_2\) (Eq (6.7) in KLE 82) for which the electron affinity is near zero.

If the first crossing is mainly adiabatic, large ionization cross sections are expected. The intermediate molecular ion, formed on the repulsive wall of the potential after the electron transfer, is expected to undergo rapid dissociation within a vibrational period. If the dissociation is completed before the second
crossing point is reached, only the atomic ions (K⁺ and Y⁻) are involved at the second crossing. Since the electron affinity of a halogen atom is very large (3.45, 3.61, 3.36 and 3.06eV for F, Cl, Br and I, respectively), calculation from the LZ formula reveals that the outgoing transition between the ionic and covalent potential surfaces is nearly totally diabatic: \( P_d = 0.968 \) for \( EA = 3.0 \text{eV} \), \( P_d = 0.998 \) for \( EA = 3.2 \text{eV} \), and approaches unity at electron affinities greater than 3.3eV. A diabatic transition at the second crossing means that the electron stays on the halide and does not return to the alkali ion. If at the second crossing the dissociation is not completed, the electron affinity of the molecular complex will still be much larger than that of the free molecule due to bond stretching, and the diabatic transition probability will be enhanced.

On the other hand, if the first crossing is mostly diabatic, the bond stretching of the molecule is much less than that of the molecular ion, and the second crossing is similar to the first. In such case the total ionization cross section will be limited by the small electron jump probability.

Note that from the calculations above one should not conclude that the molecular orientation has little effect at the first crossing. First, the LZ transition probability is exponentially dependent on the coupling matrix element which in turn depends exponentially on \( R_c \). The choice of the constants in the empirical relation between \( H_{12} \) and \( R_c \) (the factors of 1.73 and 0.875 in Eq. (3.19)) has a big effect on the final transition probability. The direct application of the LZ formula tends to devaluate the actual orientation effect. Second, we have ignored the short-range forces in the above calculations. For molecules with small or negative electron affinities, \( R_c \) will be small and our approximation will likely become invalid. At energies near the threshold, the adiabatic transition probability will be smaller and the effect of molecular orientation becomes the dominant factor, as we experimentally observed.
Bibliography


