INTERNATIONAL ATOMIC ENERGY AGENCY
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COLLEGE ON ATOMIC AND MOLECULAR PHYSICS: PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

(30 January - 24 February 1989)

REACTION DYNAMICS WITH LASERS

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References

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Reaction Dynamics with Lasers

I. Goals: Want to learn how chemical reactions occur.

A. What's known

1. Reactions occur!
2. Widely different rates, not predictable from ΔG
3. Studies in solution & gas phase show rate depends upon

Complex — need to simplify:
- a) Molecular Structure
- b) Solvent
- c) Concentration
- d) Temperature

→ B. Details (gas phase for simplicity)
— Thermal Energy —

1. Kinetic Theory - collision rate = $Z_{12} = n_1 n_2 \sigma_{12} \bar{v}$
   - n_1 = #/cc of species 1
   - n_2 = " " " 2
   - σ_{12} = effective cross sectional area ($\pi (r_1+r_2)^2$)
   - $\bar{v}$ = Average relative speed.

2. Reaction rate $\neq Z_{12}$

   In some cases $A + BC \rightarrow AB + C$

   $R = k[A][BC]$ $[A]$ = conc of A

   and $R \propto Z_{12}$

   Examples:
   $H + Br_2 \rightarrow HBr + Br$
   $K + HCl \rightarrow KCl + H$
   (atoms, radicals)

   These are "elementary" reactions - presumed to occur when A collides with BC

MORE COMPLEX REACTIONS

$R = k f([A],[B],[C])$

∴ REACTION NOT ELEMENTARY

EXAMPLE: $H_2 + Br_2 \rightarrow 2HBr$ (DOES NOT OCCUR ON A H_2, Br_2 COLLISION)

KNOW TO PROCEED THROUGH A SEQUENCE OF ELEMENTARY STEPS:

THIS SEQUENCE IS CALLED THE "MECHANISM"

$$\begin{cases} Br_2 + M \rightleftharpoons Br + Br + M \\ Br + H_2 \rightarrow HBr + H \\ H + Br_2 \rightarrow HBr + Br \\ H + HBr \rightarrow H_2 + Br \end{cases}$$

C. ELEMENTARY REACTIONS

KINETIC THY: $Z_{12} = n_1 n_2 \sigma \bar{v}$

RXN RATE $R = k n_1 n_2$

EXPT'L RATE

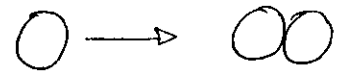
ONLY RARELY IS $k = \sigma \bar{v}$ (FROM HARD SPHERES)

ALMOST ALWAYS $k(T) \propto \exp(-E_A/RT)$

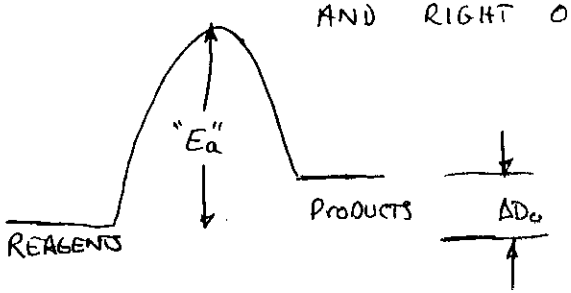
USUALLY $k(T) \equiv Z_{12} \rho \exp(-E_A/RT)$

↑ "STERIC" FACTOR

D INTERPRETATION



REACTION IF COLLISION WITH RIGHT ENERGY AND RIGHT ORIENTATION

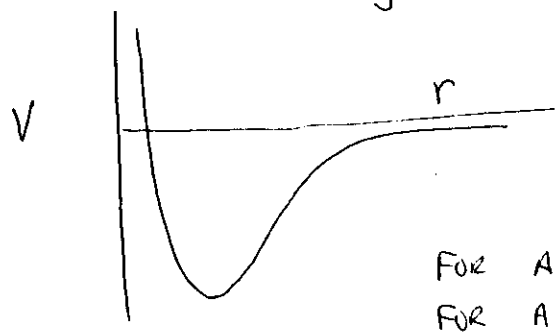


E PROBLEMS

E_A DIFFICULT TO PREDICT

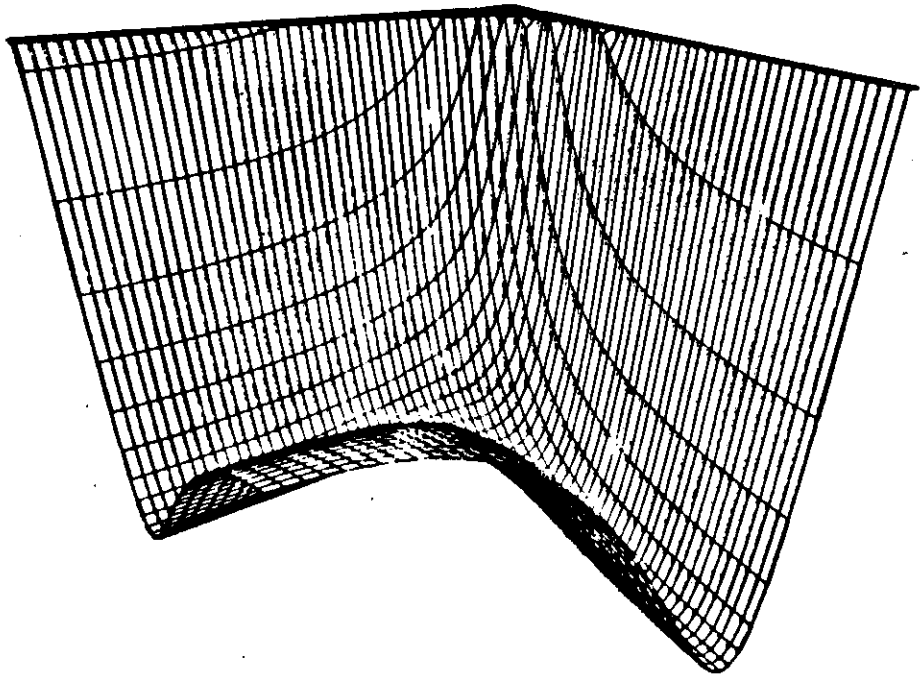
ρ IMPOSSIBLE TO PREDICT

F TURN TO THEORY ?



FOR A DIATOMIC, $V = V(r)$

FOR A TRIATOMIC, $V = V(r_1, r_2, r_3)$



II Molecular Beams – Single Collision Chemistry

Mol Beam – "Array of Molecules (atoms) moving collision free within the geometrical confines of a beam"

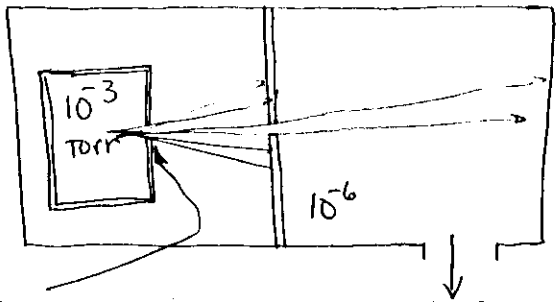
Good News:
- No wall effects
- No solvent effects
- No mitigating collisions to thermalize
- → can observe newly-born product molecule!

Ultimate Control (usually not all at the same time):
- Speed (velocity)
- Rot'l State
- Vib. State
- Orientation
- Electronic State, etc

Bad News – low signal

III Experimental Details

A. Beam Formation – Effusion



$\lambda >> D$

Molecules suffer no collisions

∴ Beam characteristic of gas at temp T

(K.E. $\sim \frac{3}{2} kT$)

~1911 Dunoyer – Molecules move in straight lines

~1920 Stern-Gerlach – Angular momentum quantized

~1947 Esterman, Simpson, Stern – Velocity Distribution

What's needed?

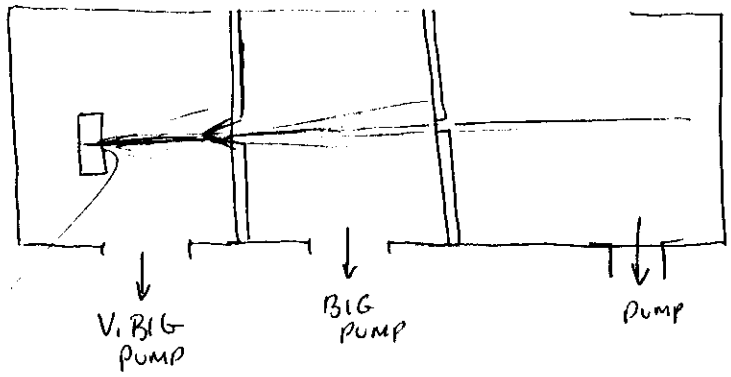
10^{-3} Torr

Beams of H, H_2, $\cdots N_2$, $N \cdots C$,

CH_3I, $CH_3^{\bullet}$, $NaCl$

And so on.

B. Beam Formation – Supersonic Beams.



$\lambda << D$

$P > 100$ Torr

hydrodynamic flow

Adiabatic expansion – gas cools

$\perp$ motion, internal motion $\Longrightarrow$ mass flow

Temperatures

Translation: motion $\perp$ to beam (few K)

Rotation: greatly cooled (few K)

Vibration: less cooled (~100K)

Hydrodynamic Flow – many collisions

All move at same speed

Seed Beam: small amt of Xe in He

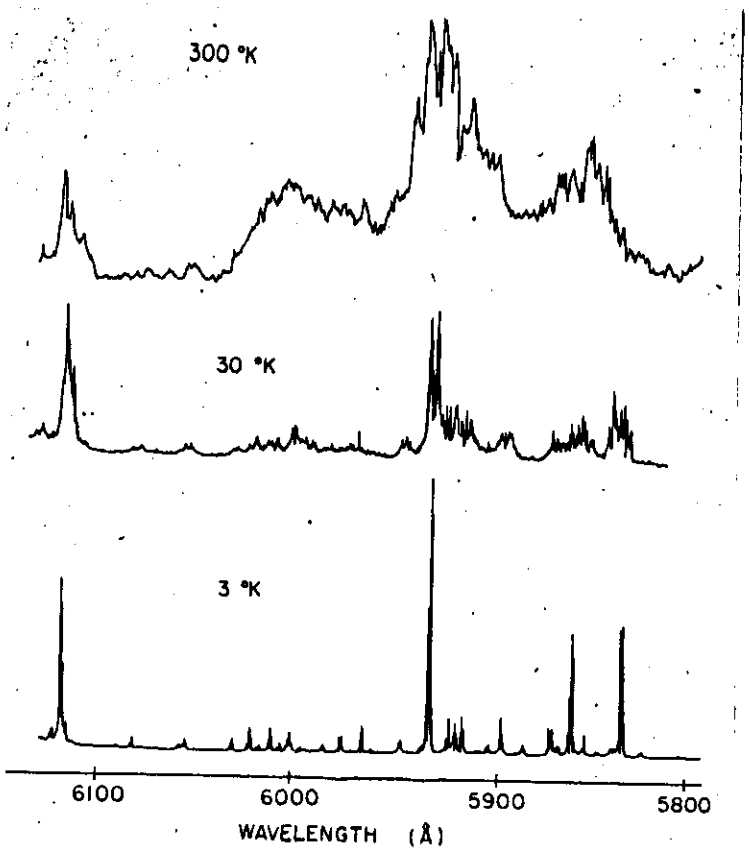
$V_{Xe} \simeq V_{He}$

But $E_{Xe} = \frac{M_{Xe}}{M_{He}} E_{He} \sim 30\, E_{He}$

Pulsed Beams

Suitable for pulsed lasers $\rightarrow$ cold!

Require less pumping



FLUORESCENCE EXCITATION SPECTRUM OF NO_2

TOP : GAS PHASE

MIDDLE : Supersonic Beam of Pure NO_2

BOTTOM : Supersonic Beam of 5% NO_2 in Ar

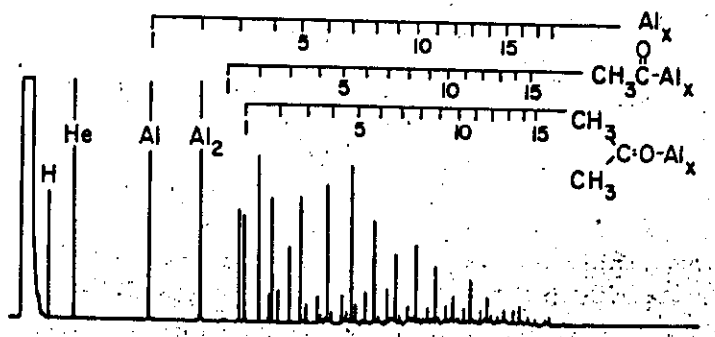


FIG. 1. Time-of-flight mass spectrum of a supersonic aluminum cluster beam produced by laser vaporization of an aluminum plug inside a pulsed supersonic nozzle. The vaporization laser beam was the second harmonic from a Nd–YAG laser (80 mJ/pulse focused to a 1 mm diam. spot on the aluminum plug). The pulsed supersonic nozzle was operated at 10 pulses per sec with a 28.5 atm backing pressure of helium. Cluster species formed in the pulsed expansion were probed 1.2 m downstream by direct photoionization using a 10 mJ cm^{-2} excimer laser beam at 1570 Å. Acetone impurity

ALKALI METAL EXPERIMENTS

- General Aspects.

For VERY RAPID Chemical Reaction, $\sigma \lesssim 20\text{-}30\ \text{Å}^2$ HARD Sphere

$\sigma \sim \pi r^2$

PRODUCT Flux for Crossed Beams $\sim 10^7\ s^{-1}$ at detector !

$S/yr \sim \pi \times 10^7 \rightarrow 10^{14}\ yr \rightarrow 10^{-9}$ Moles

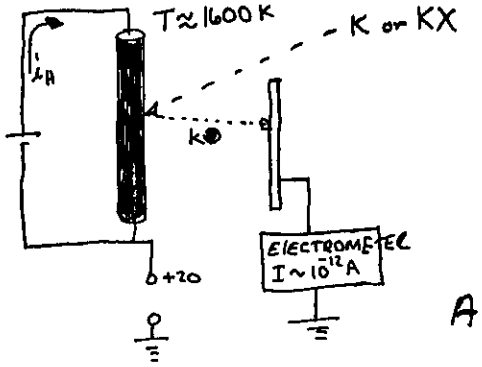
REQUIREMENTS

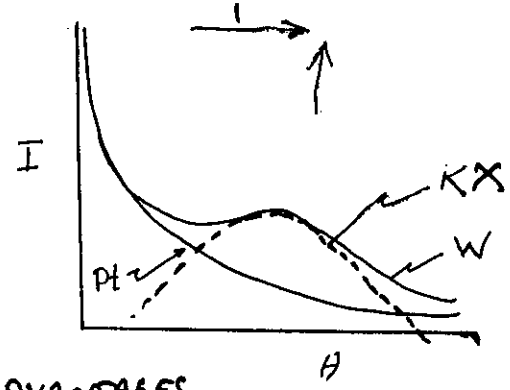
1) Reaction cross section large ATOMS O, H, ... K
2) Reagents easily generated
3) Reagents NEED TO BE DISTINGUISHED from PRODUCTS

Differential Surface Ionization (TAYLOR & DATZ)

W : IONIZES K AND KX

Pt(92%) - W(8%) IONIZES MAINLY K





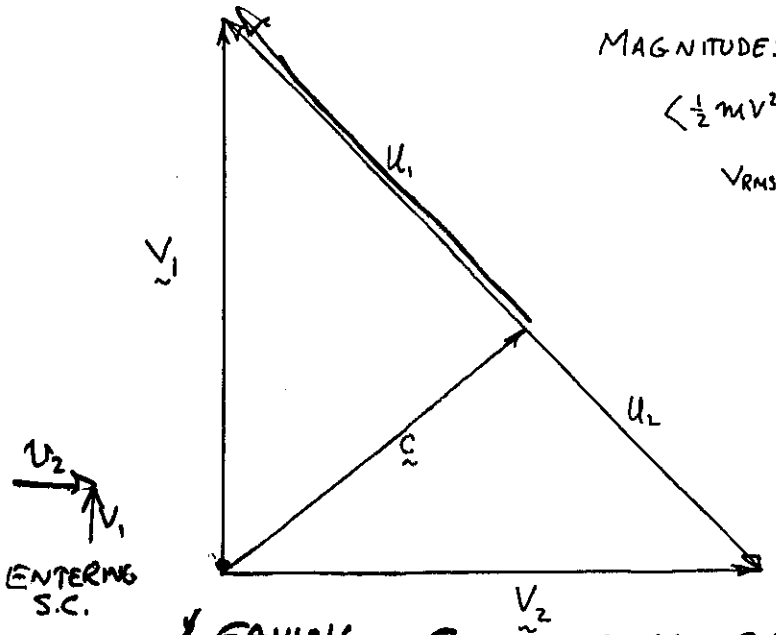
ADVANTAGES
VERY SIMPLE
VERY SENSITIVE

DISADVANTAGE
INDIRECT

III NEWTON DIAGRAMS

A. CONSERVATION of MOMENTUM

$$m_1 \underset{\sim}{V_1} + m_2 \underset{\sim}{V_2} = \text{CONST} \equiv M \underset{\sim}{C}$$



MAGNITUDES

$\langle \frac{1}{2} m V^2 \rangle = \frac{3}{2} kT$

$V_{RMS} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$

$= \left[\frac{3 \cdot 8.31 \times 10^7 \cdot 700}{39}\right]$

$= 6.7 \times 10^4$ cm/s K @ 700°K

$= 3.5 \times 10^4$ HBr @ 400 K

$$\underset{\sim}{V_r} \equiv \underset{\sim}{V_1} - \underset{\sim}{V_2} = \underset{\sim}{U_1} - \underset{\sim}{U_2}$$

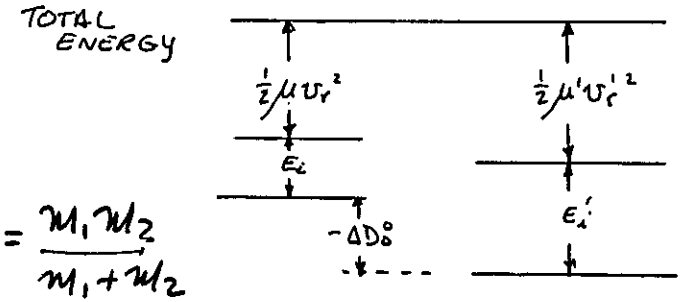
$$\underset{\sim}{U_1} + \underset{\sim}{C} = \underset{\sim}{V_1}$$

VELOCITY IN CM SYSTEM — VELOCITY OF CM SYSTEM — VELOCITY IN LAB SYSTEM

$$E = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 = \frac{M C^2}{2} + \frac{1}{2} \mu v_r^2$$

relative K.E.

B. Conservation of Energy



$\mu = \frac{m_1 m_2}{m_1 + m_2}$

REAGENTS $\mu = \frac{m_K \cdot m_{HBr}}{120} = 26.3$

PRODUCTS $\mu' = \frac{m_H m_{KBr}}{120} \sim 1.2$

$\frac{1}{2}\mu v_r^2 + \epsilon_i - \Delta D_0^\circ = \frac{1}{2}\mu' v_r'^2 + \epsilon_i'$ $\quad \Delta D_0^\circ < 0$ if exc

$\frac{1}{2}\mu' (v_r')^2 = \underbrace{\frac{1}{2}\mu v_r^2 + \epsilon_i}_{\epsilon_{IN}} - \Delta D_0^\circ - \epsilon_i'$

FOR HBr + K $\quad \Delta D_0^\circ = -0.15$ eV $\quad (1\text{eV} = 1.59\times10^{-12}$ erg

$T = \frac{1}{2}\mu v_r^2 = 8.30\times10^{-15} M v^2$ ergs

$V = 1.10\cdot10^7 \sqrt{\frac{E(\text{ergs})}{M(\text{AMU})}}$

(UNITS: M = AMU, V = km/s, E = ergs)

T = .05 eV (THERMAL)

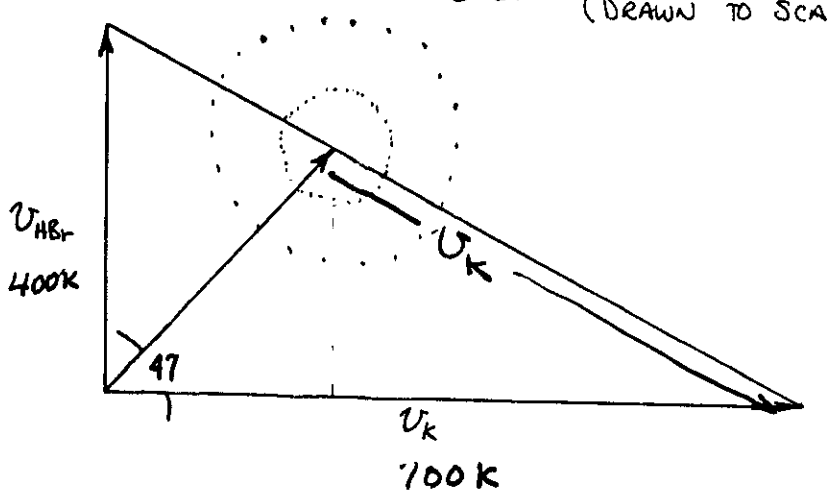
$E' = E_{ROT} = \underset{\text{(mole)}}{RT} = \underset{\text{(molecule)}}{kT} = 1.37\times10^{-16}\cdot 400 = .035$ eV

$\frac{1}{2}\mu' (V_r')^2_{MAX} = .085 + .15 = 0.23$ eV

$(V_r')_{MAX} = 1.10\times10^7 \sqrt{\frac{.23\cdot1.59\times10^{-12}}{1(2)}} = 6.65$ km/s ~4

K + HBr

DBr (DRAWN TO SCALE)



$C_K = C_K = \frac{m_K v_K}{M} = \frac{39\cdot6.7\times10^4}{120} = 2.18\times10^4$

$\underset{\sim}{C}\cdot\underset{\sim}{C} = \frac{m_K^2 v_K^2 + m_{HBr}^2 V_{HBr}^2}{M^2}$

$|C| = 3.21\times10^4 \approx 0.3$ km/s $\quad | \; u_{KBr} =$

$v_r \sim 1$ km/sec

$v_f = 6.65\times10^5$ cm/sec. -4×10^5

AFTER Collision

$m_3 u_3 + m_4 u_4 = 0$ $\quad u_3 + u_4 \equiv v_f$ $\Big\} \; u_4 = \frac{m_3 v_f}{M}$

$\boxed{u_{KBr} = \frac{1.2}{120}\cdot v_f}$

PARTITIONING of MOMENTA:

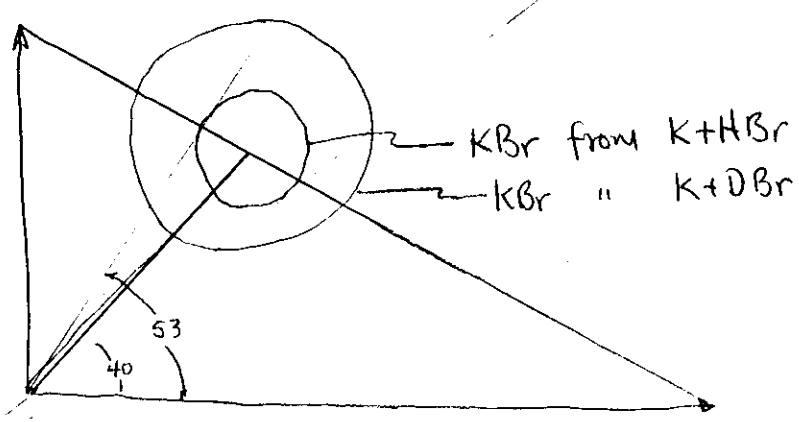
$$m_3 u_3 + m_4 u_4 = 0$$

$$u_3 - u_4 = V_f$$

$$\text{So } u_3 = \frac{m_4 v_f}{M} \Longrightarrow \frac{1 \cdot V_f}{120} \quad \text{for KBr!}$$

$$\text{So } (u_{KBr})_{MAX} = \frac{6.65 \text{ km/sec}}{120} = 5.5 \times 10^{-2} \text{ km/sec}$$

$$= 5.5 \times 10^{3} \text{ cm/sec.}$$



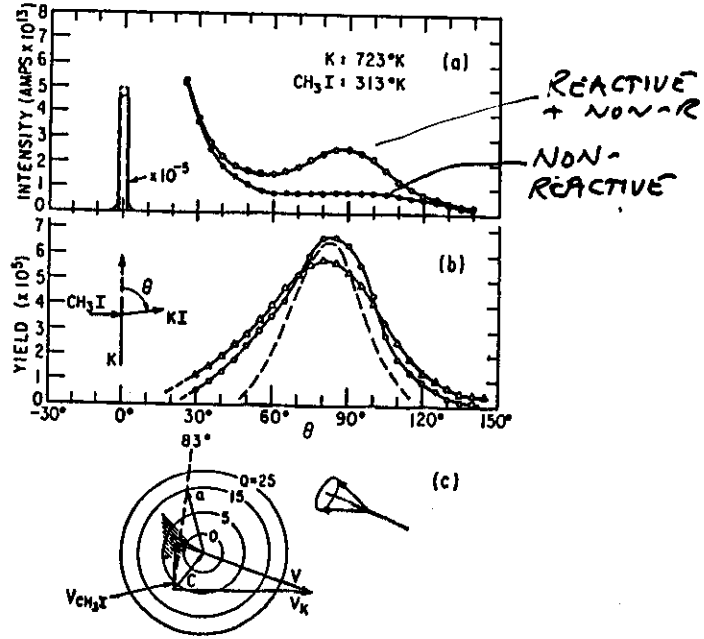


FIG. 1. Typical data and analysis: (a) Parent K beam 0.7° wide attenuated 7% by perpendicularly crossed CH_3I beam. Readings on Pt detector (solid circles) normalized to W (open circles) at parent beam peak. (b) KI distributions; circles derived from (a), triangles from a replicate experiment (four months later) using a parent K beam 2° wide and 40% attenuated. Area under curves gives collision yield. (c) Vector diagram showing most probable velocities of reactants and center of mass vector c; 50% of the KI recoil vectors appear within doubly shaded region, 90% within singly shaded region.

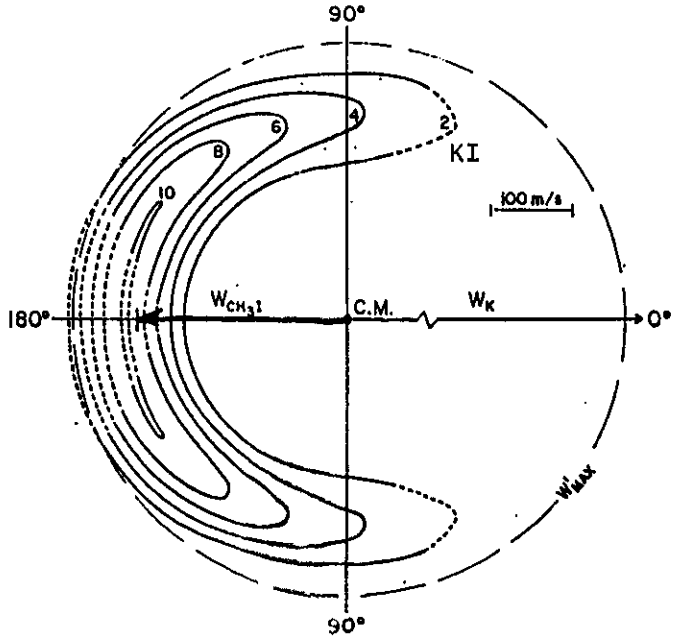
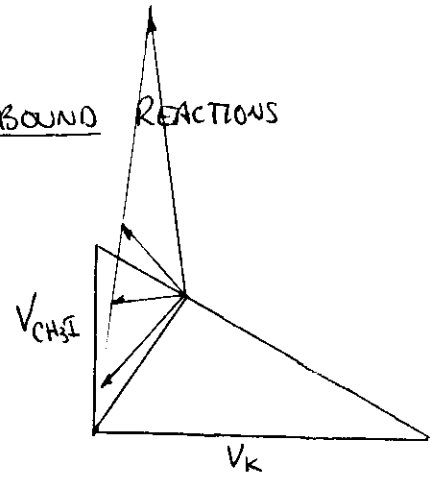
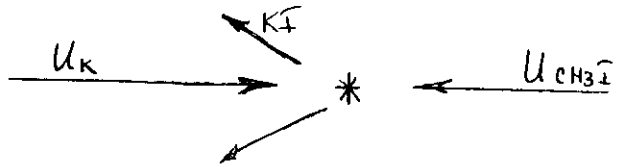


FIG. 1.—KI polar (c.m.) contour map, i.e., detailed differential cross section for the $K+CH_3I$ reaction at $\bar{E}_T = 0.12$ eV; for details, see ref. (3). Dashed contours less reliable. Outer dashed circle denotes nominal maximum KI recoil velocity (from energy conservation).

REBOUND REACTIONS

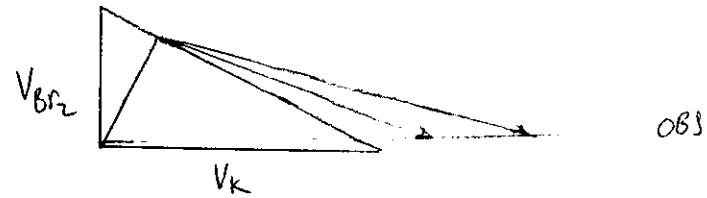


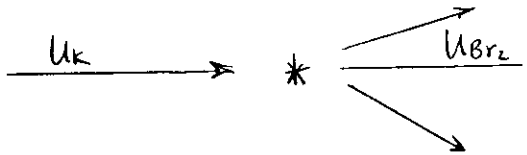


CM VIEW

KI SCATTERED BACKWARDS - NOT ISOTROPIC

STRIPPING REACTIONS





KBr FORWARD

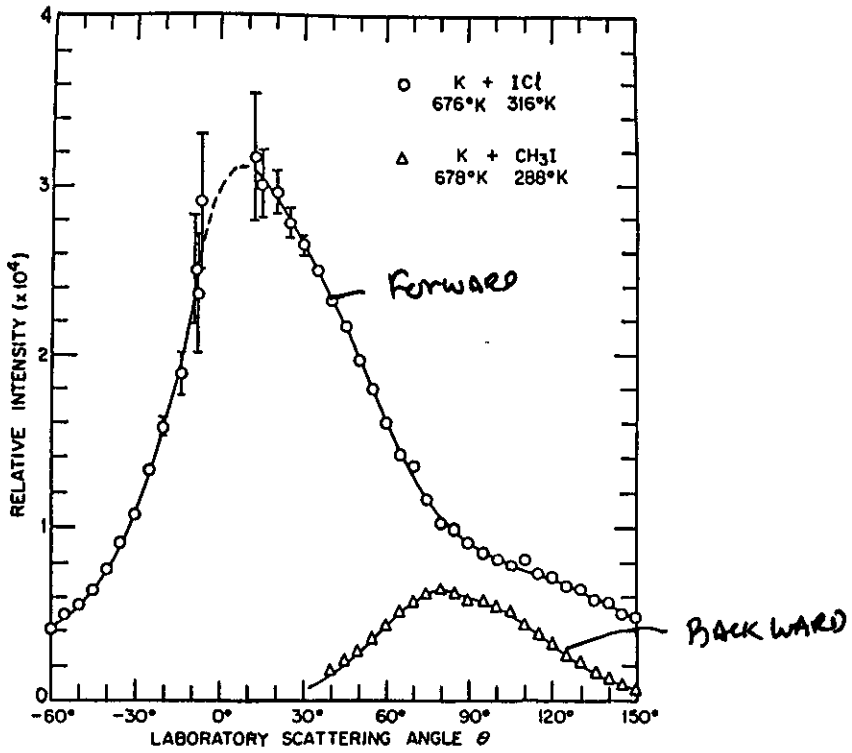


Fig. 6. Comparison of laboratory angular distributions of alkali halide product from the K + ICl and K + CH_3I reactions. The kinematic diagram applies to the K + ICl system; solid circles indicate the recoil energy E' when KI is the product, dashed circles when KCl is the product.

Review Rebound Reactions

$K + CH_3I \rightarrow KI + CH_3$

$\sigma \sim 30\ \text{Å}^2$ (Roughly Gas-kinetic)

Conservation of Angular Momentum

$$\underset{\text{for}}{J} = \underset{\text{Orbital}}{L} + \underset{\text{Rot'l Am}}{J}$$

$\mu(V \times b)$

$b \sim 3\text{Å}$

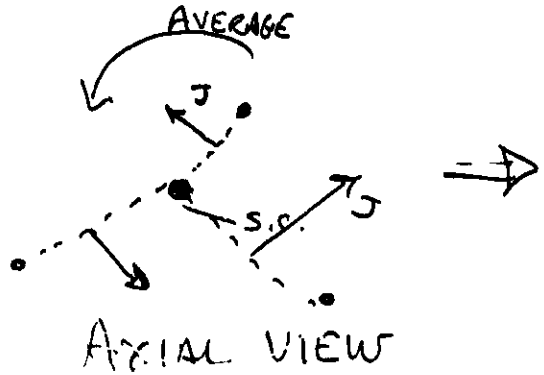
HBr $\sim 3\hbar$

$$K+HBr \quad \mu v b = \frac{40.82}{120} \times 1.67\times10^{-24} \times 5\times10^{4} \times 3\times10^{-8}$$

$$\sim 10\hbar$$

Complicated $L > J$

$L \sim J$

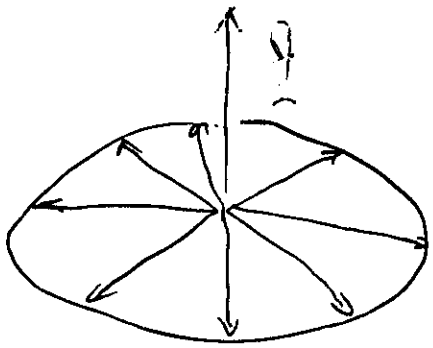


J is $\perp V_r$

"REACTIONS NOT DIRECT

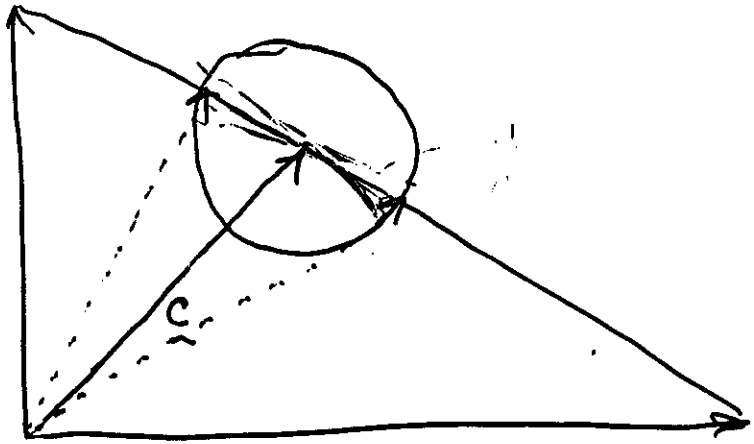
Complex ?

WATER SPRINKLER MODEL

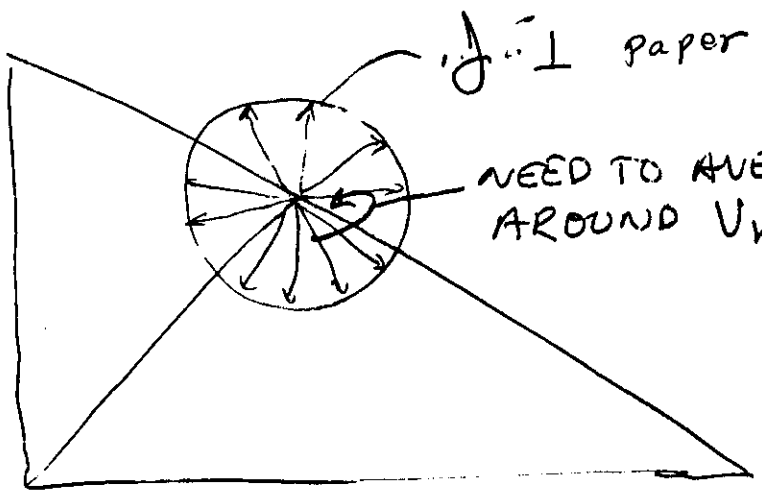


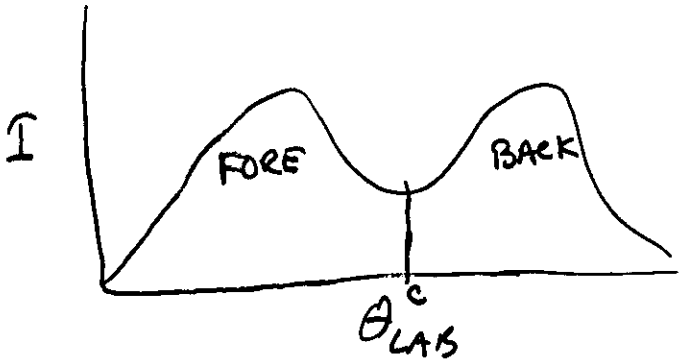
IF $\tau \gg t_{ROT}$

Might expect ISOTROPIC DIST. IN PLANE



CONCLUSION : A Long LIVED complex GIVES FORWARD-BACK SYMMETRY IN C.M. (NOT ISOTROPY)





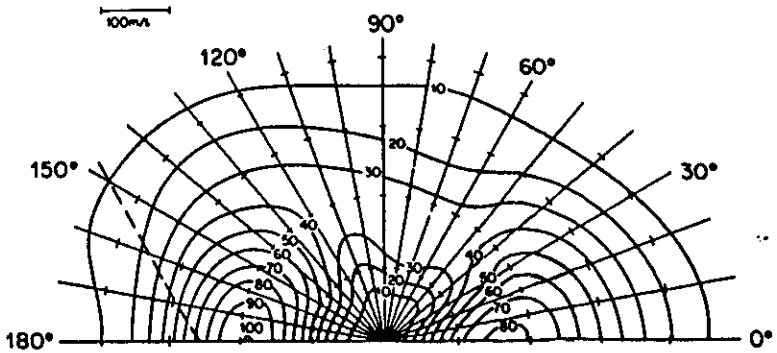


Figure 7.28. Product intensity contour diagram for CsF produced in the reaction $Cs + SF_6$ showing substantial forward–backward symmetry. (Reproduced from Riley and Herschbach 1973.)

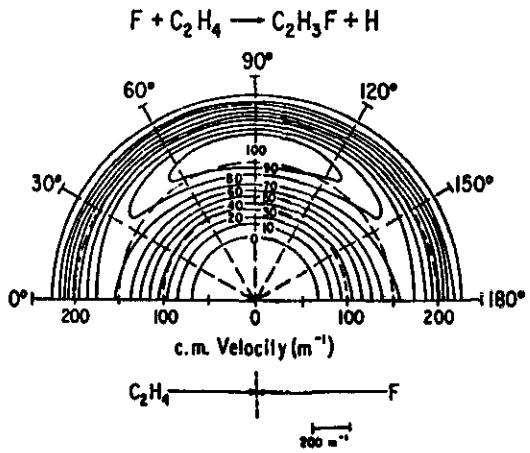


Figure 7.29. Product intensity contour diagram for C_2H_3F produced in the reaction $F + C_2H_4$. (Reproduced from Parson *et al.* 1973.)

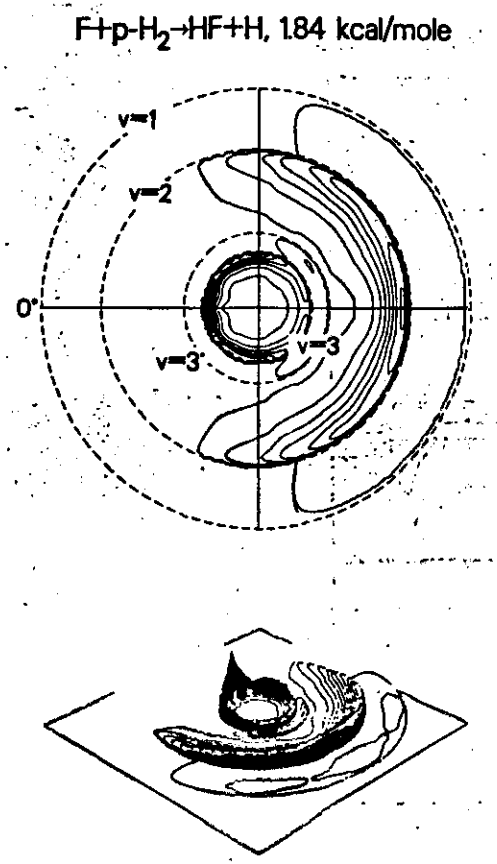
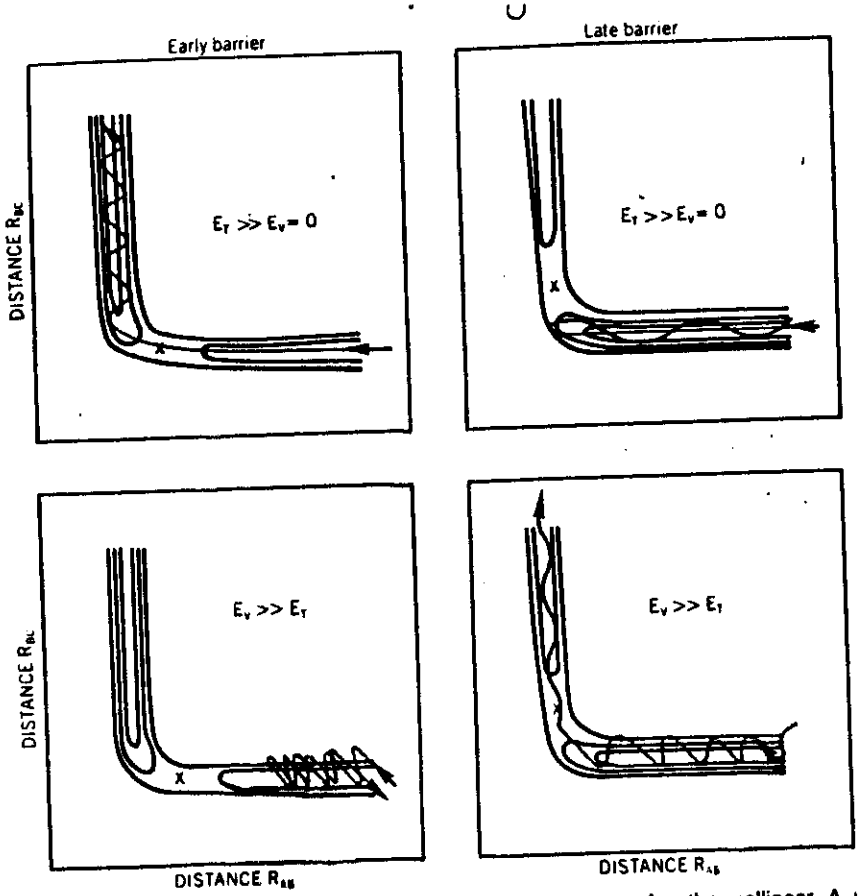


FIG. 18. Center-of-mass velocity flux contour map for F + p-H_2, 1.84 kcal/mol, with three-dimensional perspective. Lines are spaced linearly along the 3D contour according to scattering intensity.



Classical trajectories on stylized potential-energy surfaces for the collinear A + BC→AB + C reaction showing role of reagent's vibrational energy (E_V) and relative translational energy (E_T) in surmounting the activation barrier (x). In all cases the total energy exceeds the barrier height; so reaction is allowed on energetic grounds. When E_T is large (top row), reaction occurs for "early barrier" case but not for "late barrier." When E_V is large and E_T small (bottom row), reaction fails for early barrier, occurs for late barrier. Thus vibrational energy helps in surmounting a late barrier. (Adapted from J. C. Polanyi and W. H. Wong, J. Chem. Phys. 51, 1439, 1969, and reference 1.)

Figure 3

II

INTERROGATION of reagents & PRODUCTS.

I. How is energy consumed?

$$k = A \exp(-E_A/RT)$$

↑ IN THERMAL EQUILIBRIUM

All Degrees of freedom Are Distributed According to Boltzmann

NEED TO DECOUPLE from EQUILIBRIUM.
CAN DO IN Beam

Simplest EXPT: Heat reagents IN BEAMS AT DIFFERT (Loesch)

EARLY EXPTS: Accelerate I_2 IN seeded beam

$$H_2 + I_2 (\text{FAST}) \longrightarrow \text{N.R.}$$

↑ SPEEDS ABOVE E_A

A. How Does VIBRATION EFFECT reactivity

EXPERIMENTAL SETUP

Odiorne
Pruett
Grabiner
Geis
Dispert

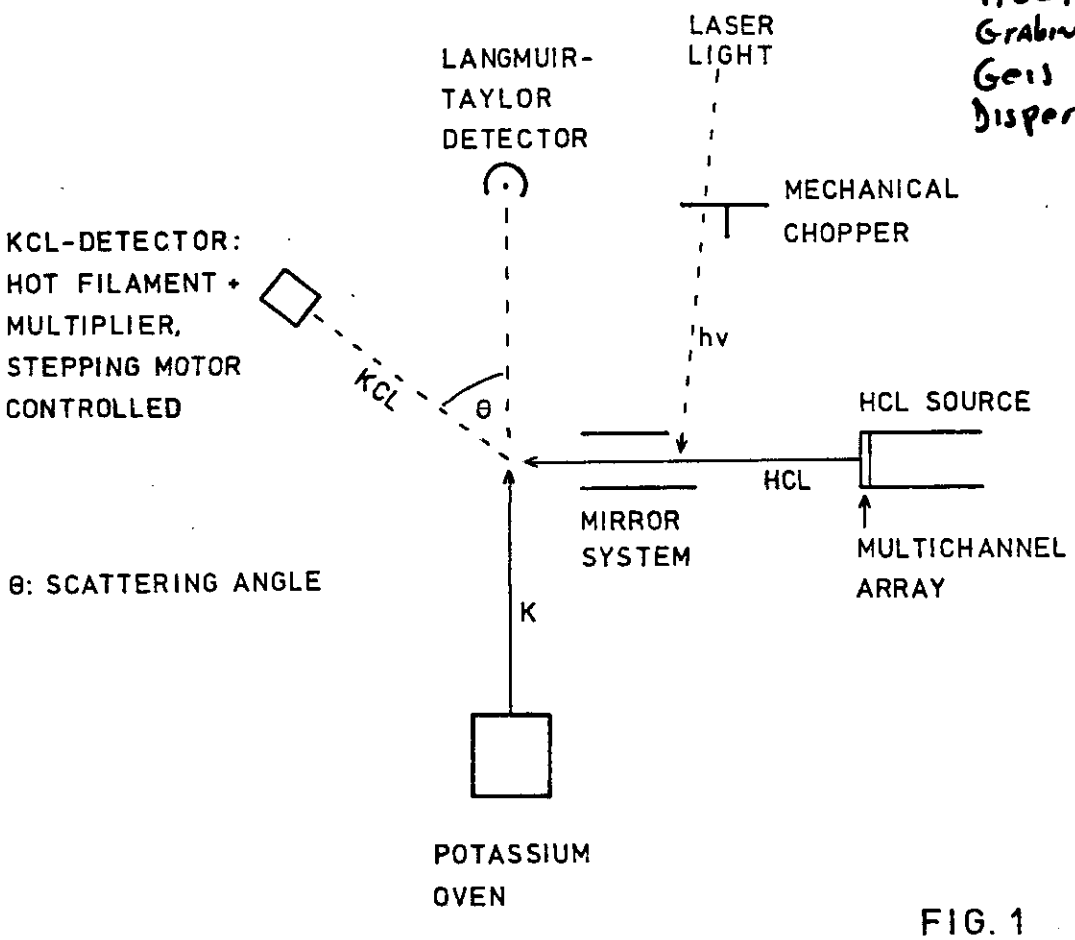
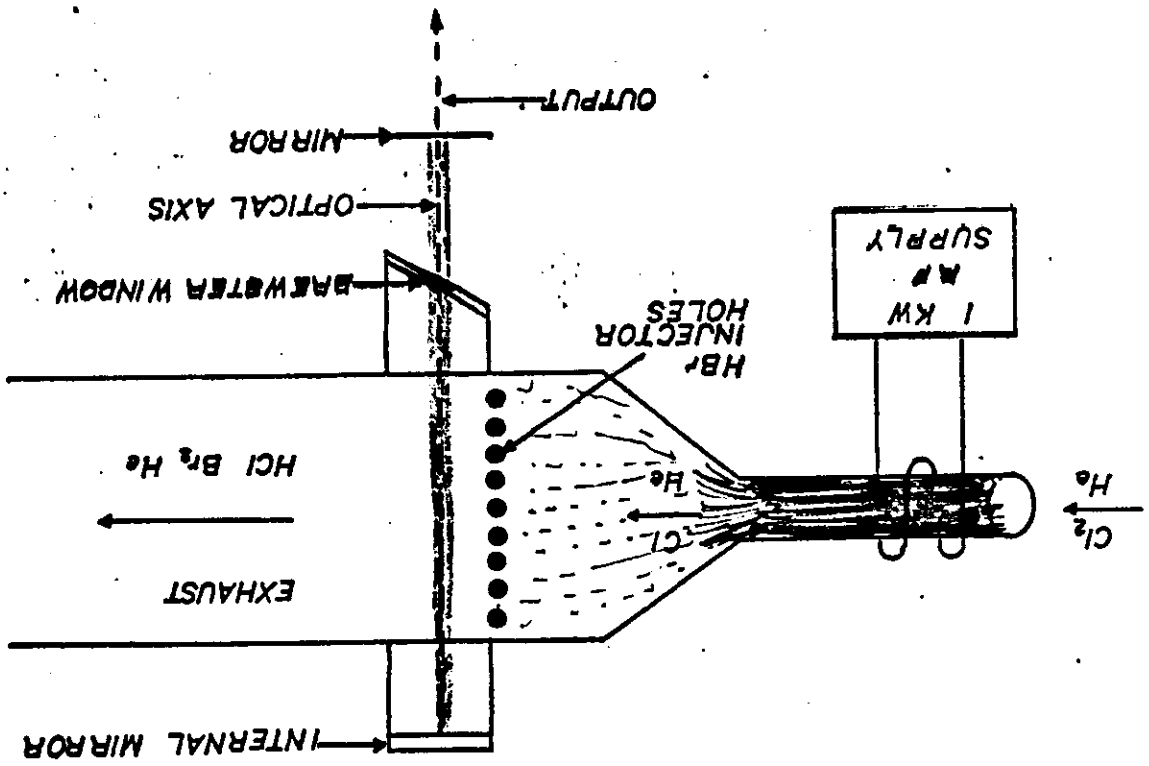


FIG. 1



DRIVING REACTION $Cl+HBr \xrightarrow{v=1} HCl+Br$

SCHEMATIC HYDRODYNAMIC
GAS HCl LASER

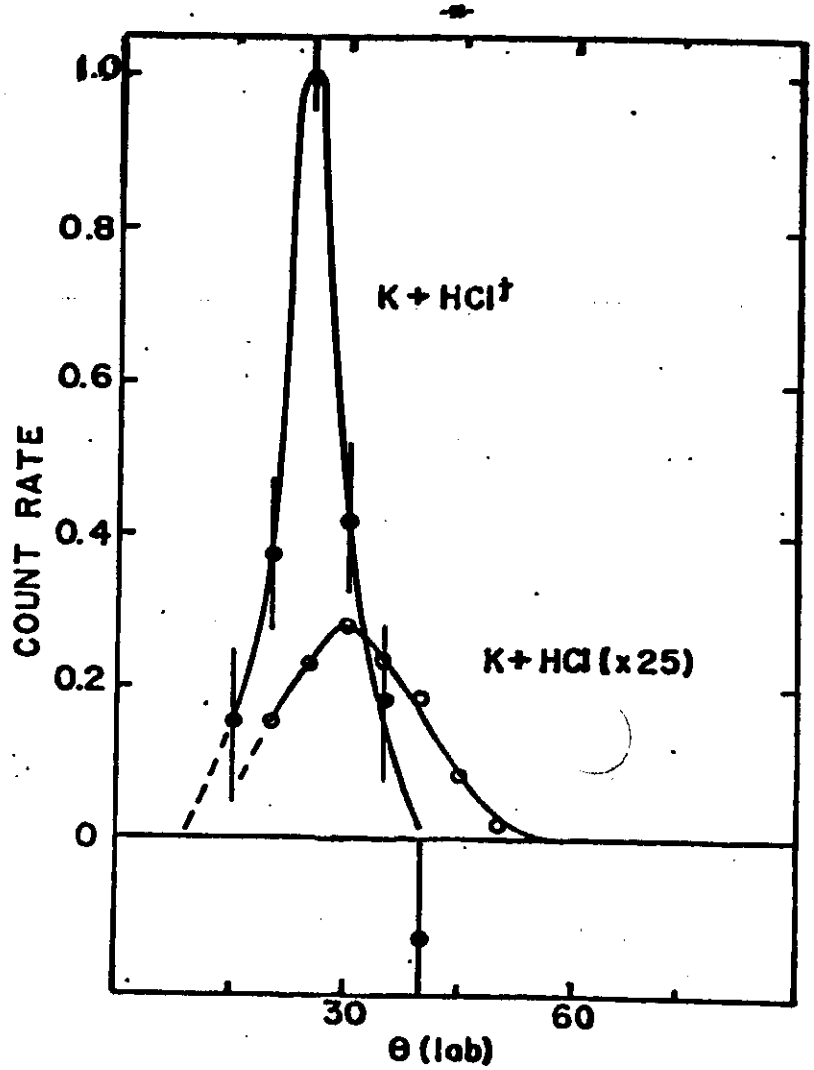
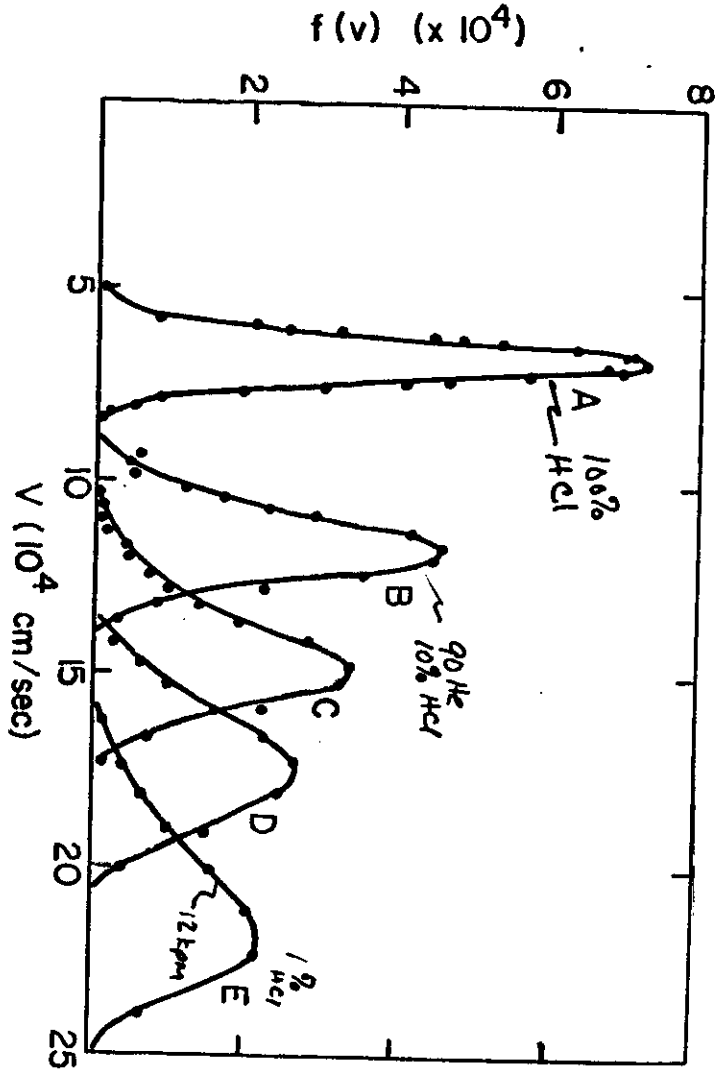
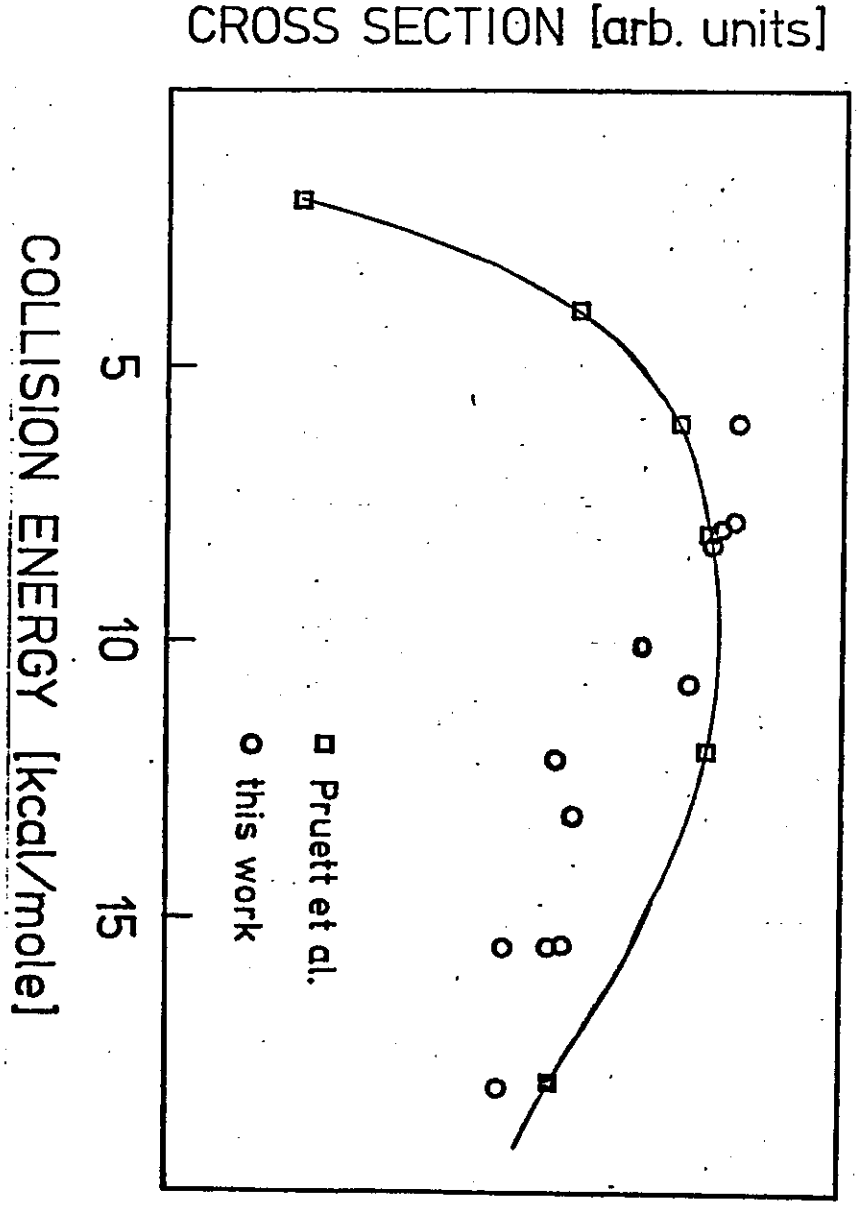
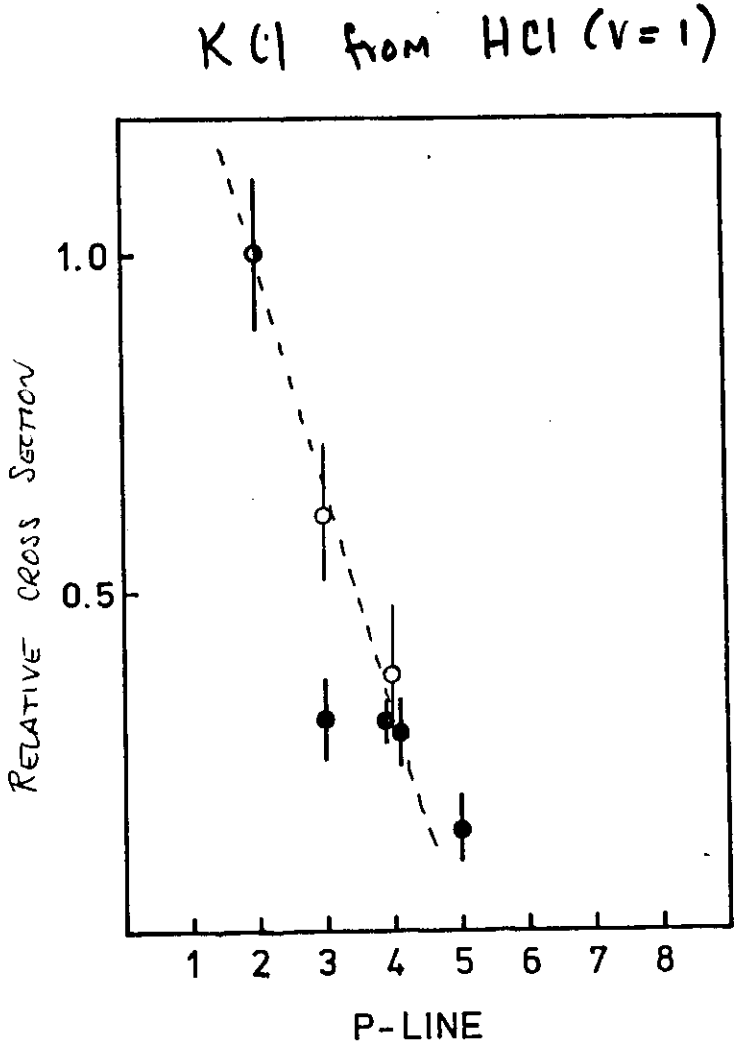


Figure 21a. Angular distribution of KCl from KI and KCl*.




CROSS SECTION [arb. units]
COLLISION ENERGY [kcal/mole]
5
10
15
□ Pruett et al.
o this work


KCl from HCl (v=1)
RELATIVE CROSS SECTION
1.0
0.5
1 2 3 4 5 6 7 8
P-LINE

Summary of Results for K+HCl

1. $\Delta D_0^\circ \sim 0$
2. $K + HCl\ (v=0) \rightarrow KCl + H \qquad \sigma \approx 0.1\ \text{Å}^2$
3. $K + HCl\ (v=1) \rightarrow KCl + H \qquad \sigma \approx 10\ \text{Å}^2$

3a) $K + HCl\ (v=0)\ (\text{FAST}) \rightarrow KCl + H \qquad \sigma \sim 1\ \text{Å}^2$

Rotational energy inhibits reaction

$\sim 2^{-1}/h$

K+HF (Loesch)

VIB enhancement decreases with increasing E

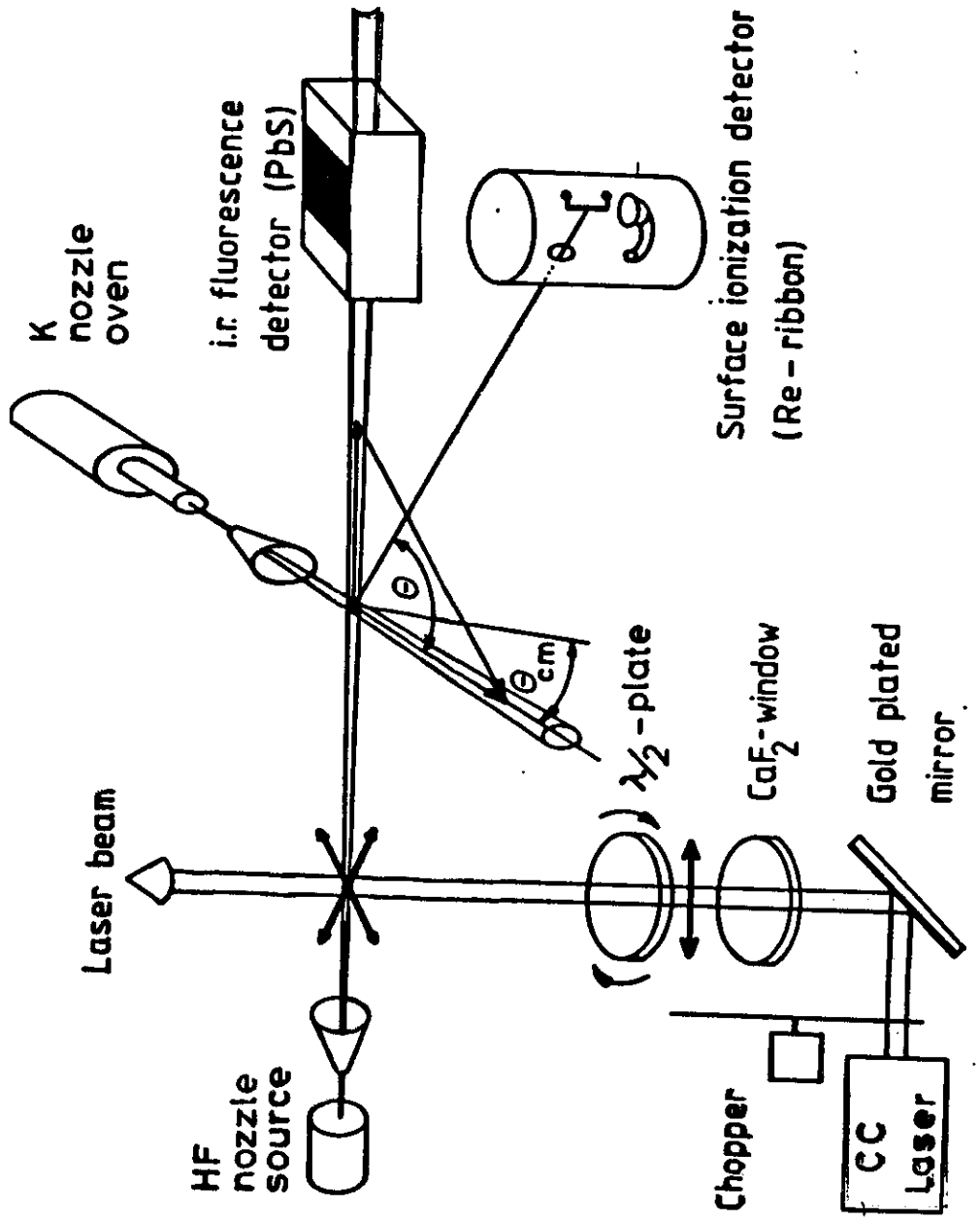
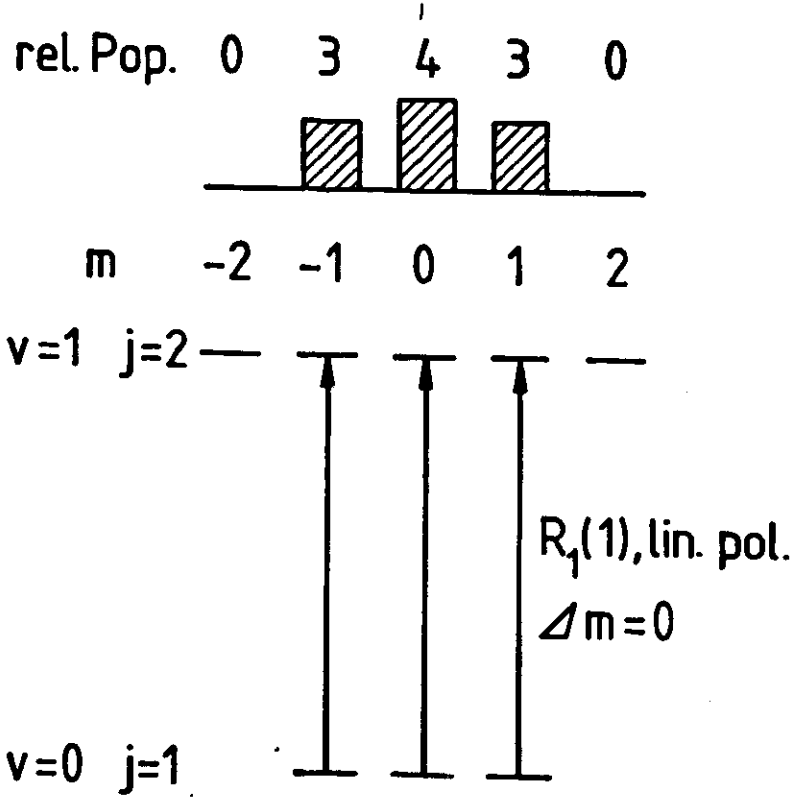
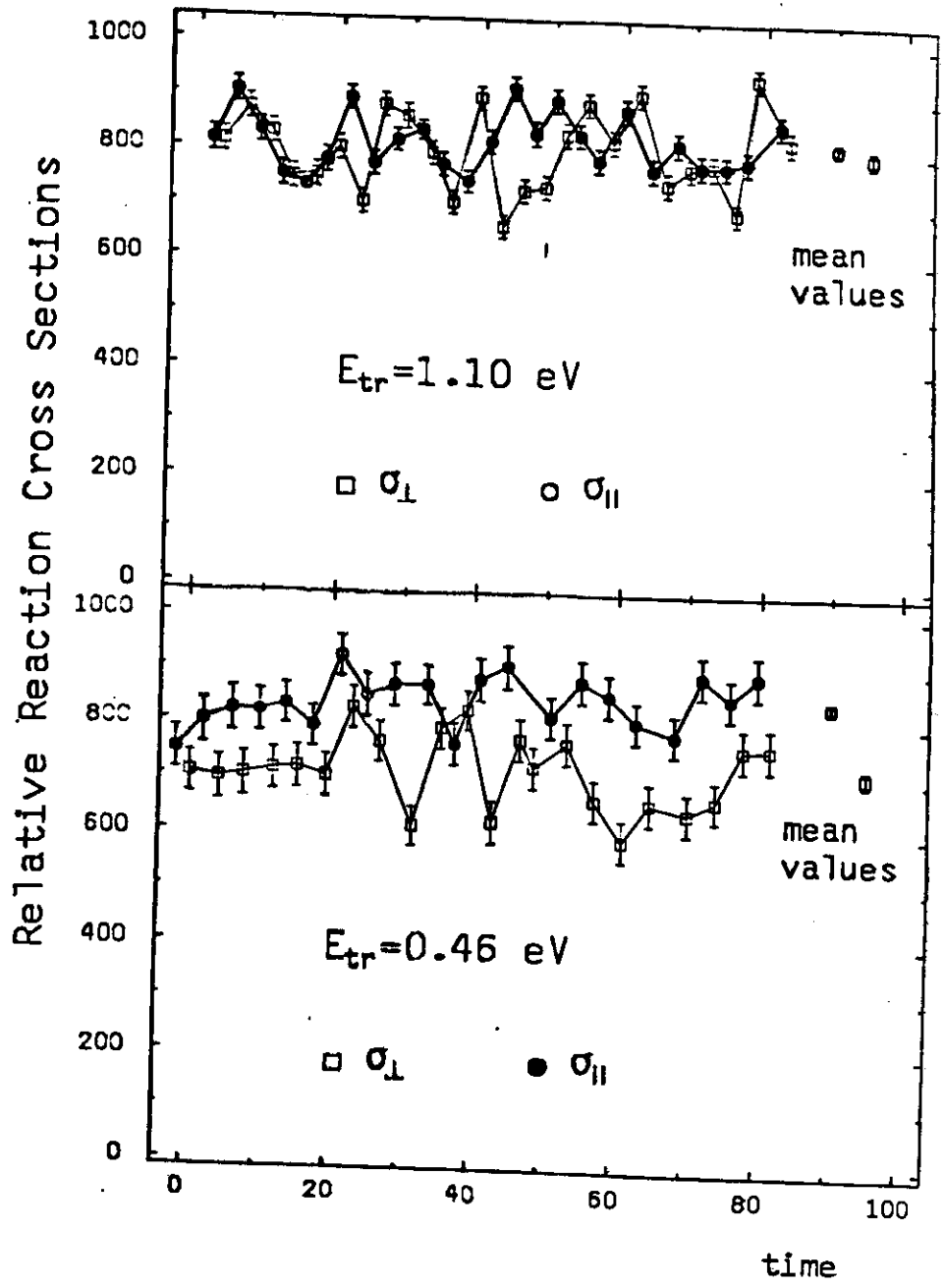
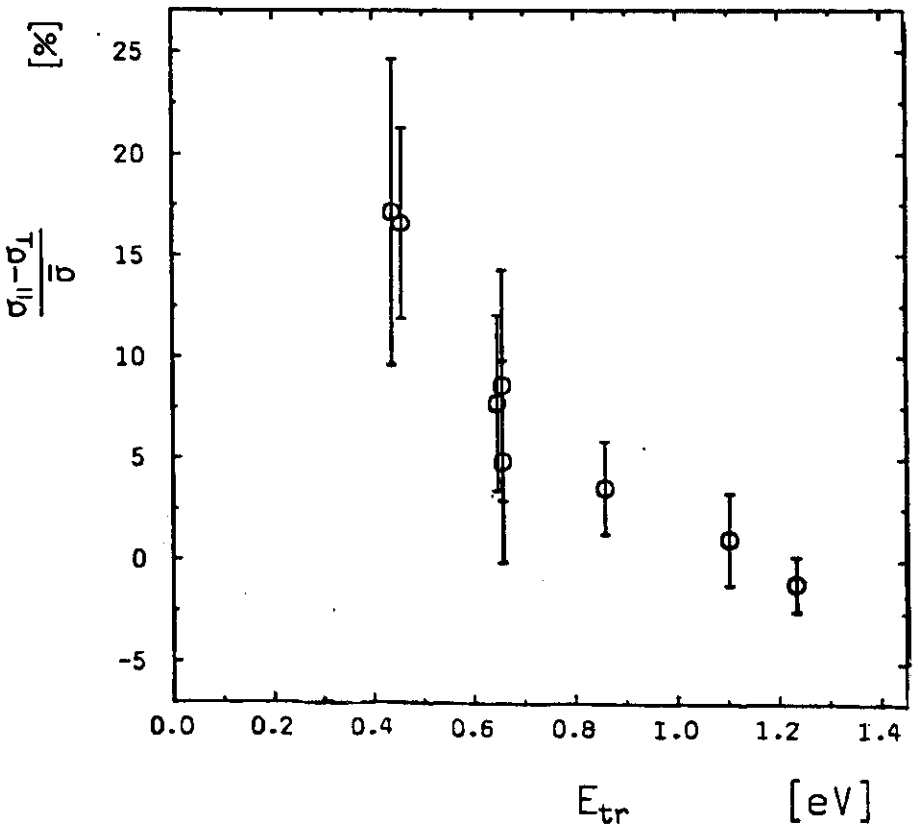


Fig. 1


rel. Pop. 0 3 4 3 0
m -2 -1 0 1 2
v=1 j=2
v=0 j=1
R1(1), lin. pol.
Δm=0


Relative Reaction Cross Sections
1000
800
600
400
200
0
mean values
Etr=1.10 eV
□ σ⊥ ○ σ∥
Etr=0.46 eV
□ σ⊥ ● σ∥
0 20 40 60 80 100
time



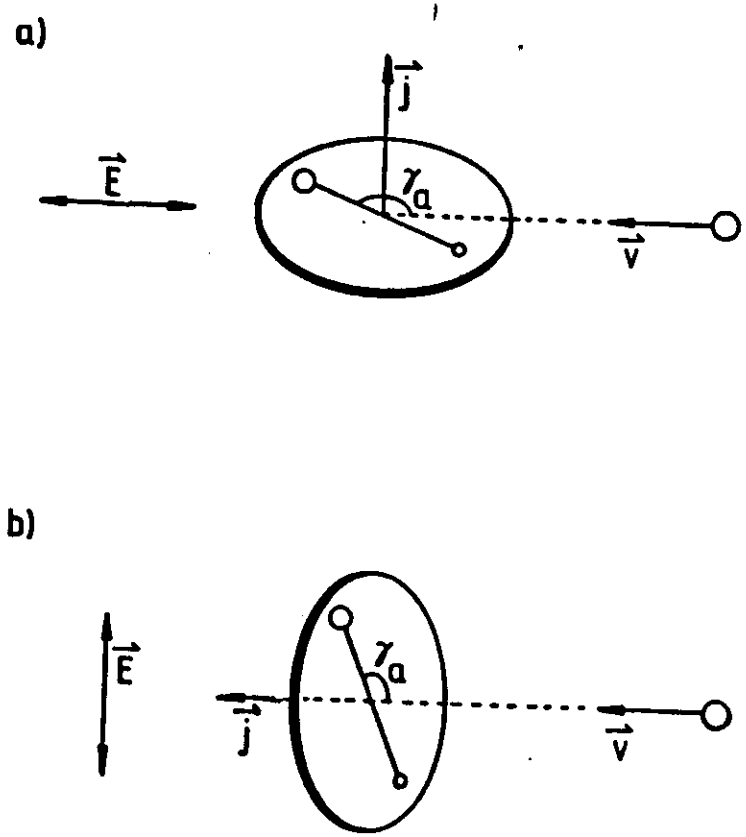


Fig. 7

II How is energy disposed?
(not much known before beam expts)

Early evidence

Angular Distribution of Products
Velocity Dist.
IR Chemiluminescence (Polanyi)
Beam Deflection

$Cs + SF_6 \rightarrow CsF + SF_5$

Deflected in Rabi-type machine
$T_{VIB} \sim$ Boltzmann
$\Rightarrow$ Long lived complex

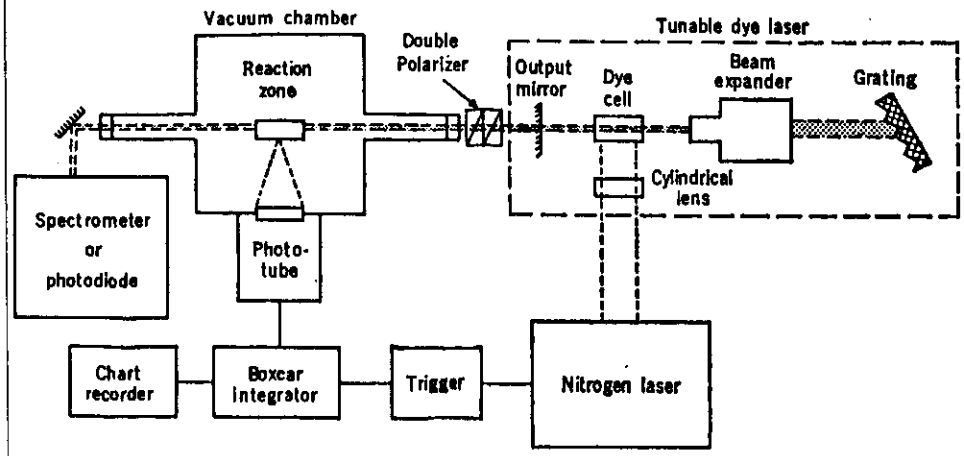


Fig. 4. Schematic of a laser-induced fluorescence apparatus. In this arrangement, the reaction zone is being directly irradiated. [Adapted from Cruse *et al.* (*36*)]

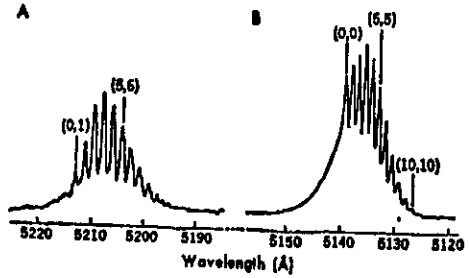
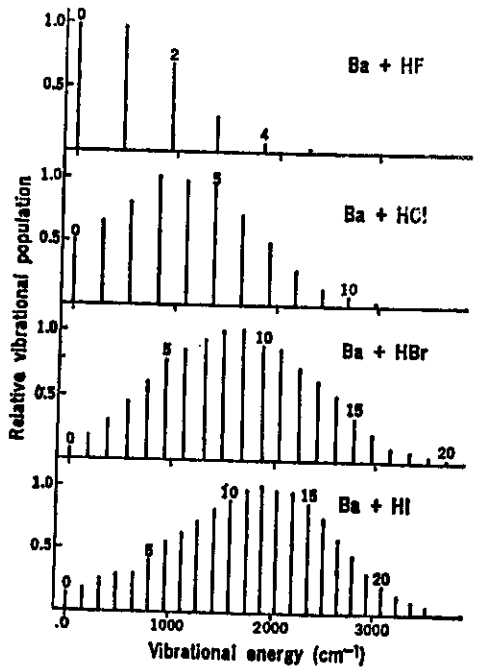


Fig. 5 (left). Excitation spectrum of BaCl for the $Ba + HCl \rightarrow BaCl + H$ reaction. The band heads of the $C\ ^2\Pi_{3/2} - X\ ^2\Sigma^+$ $\Delta v = v' - v'' = -1$ (A) and 0 (B) sequences are marked; the coordinate scale of (A) was six times more sensitive than that of (B). [Adapted from Cruse *et al.* (*36*)] Fig. 6 (right). Relative BaX vibrational populations for the reactions $Ba + HX \rightarrow BaX + H$. For each reaction, the populations have been normalized so that the population of the most probable level equals unity. [Adapted from Cruse *et al.* (*36*)]



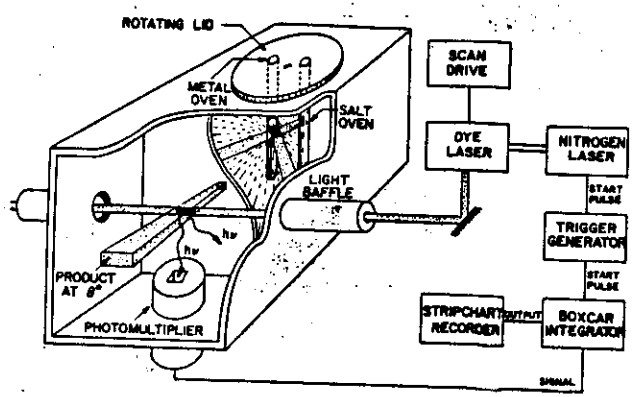


FIG. 1. Schematic representation (partial cutaway) of the experimental apparatus. The beam sources are mounted perpendicular to each other on a rotating lid (beam collimators are not shown for simplicity). Only product molecules at an angle θ from the Ba beam are allowed to enter the laser detection region. By changing the angle θ and by scanning the laser wavelength, product angular distributions of individual internal states are obtained.

Fit of Model Angular Distributions to Data

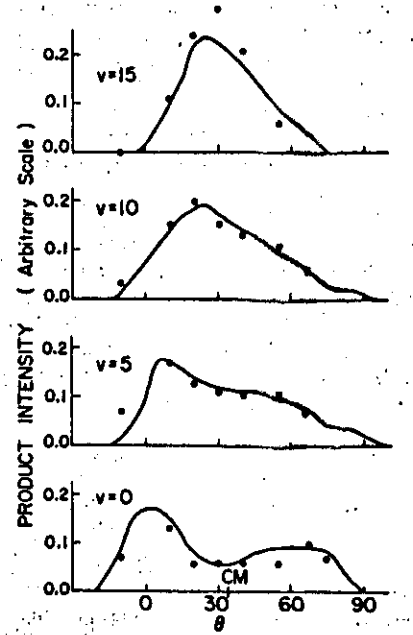
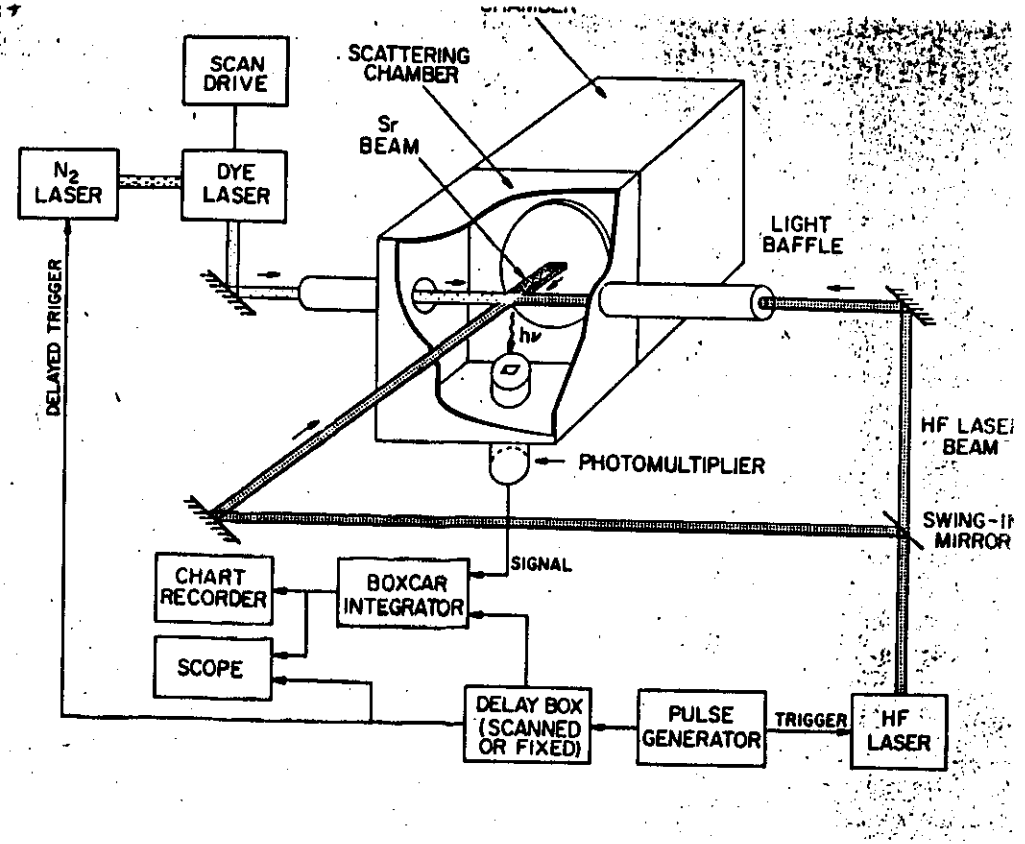


FIG. 4. The BaCl product density distribution of selected v levels as a function of the scattering angle θ. The closed circles are the experimental data and the solid curves are the best fit using the model of an exponentially decaying prolate complex ($\tau = \frac{1}{2}$ revolution).



APPARATUS of KARNY & ZARE

FOR LASER EXCITING HF AND OBSERVING SrF (or CaF) by laser-induced fluorescence from reactions

$$(Ca, Sr) + HF(DF) \longrightarrow (Ca, Sr)F + H(D)$$

ctions of Ca and Sr with HF and DF

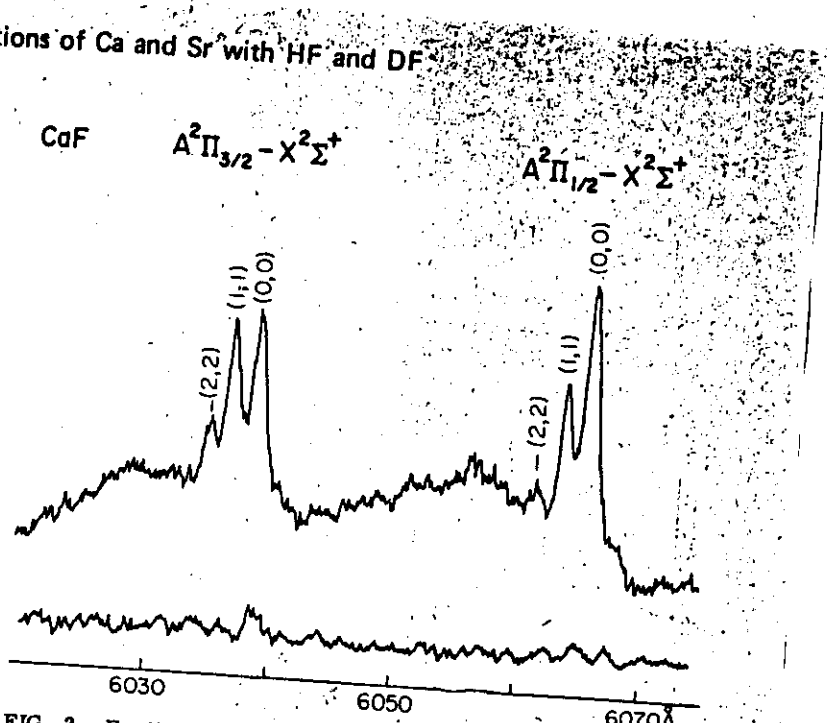


FIG. 3. Excitation spectra of the CaF products resulting from the Ca + HF ($v = 1$) reaction (top trace) and the Ca + HF ($v = 0$) reaction (bottom trace).

RETTNER & ZARE

EMISSION

$Ca(^1P_1) + HCl \rightarrow CaCl\ A^2\Pi\ \lambda = 620\ nm$

$\rightarrow CaCl\ B^2\Sigma\ \lambda = 594\ nm$