

Lecture-4

CSO202: Atoms, Photons & Molecules

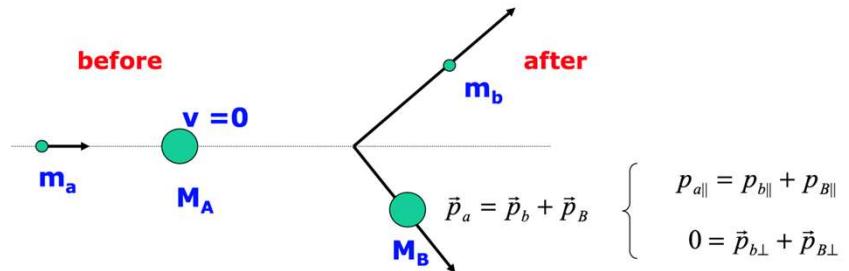
Debabrata Goswami

Molecular Beam: Reactions through Collision

Chemical Reactions Collision kinematics

Conservation laws of:

- Scalars: energy, number of particles, electrical charge,...
- Vectors: momentum, angular momentum,...



Q value:

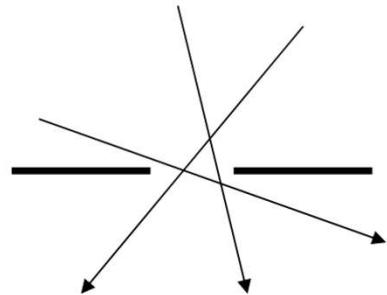
Difference of total kinetic energy before and after collision

$$Q = (E_B + E_b) - E_a$$

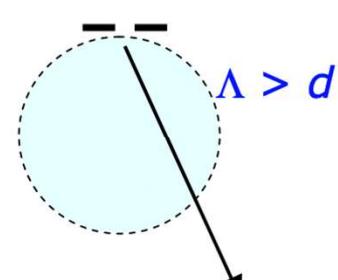
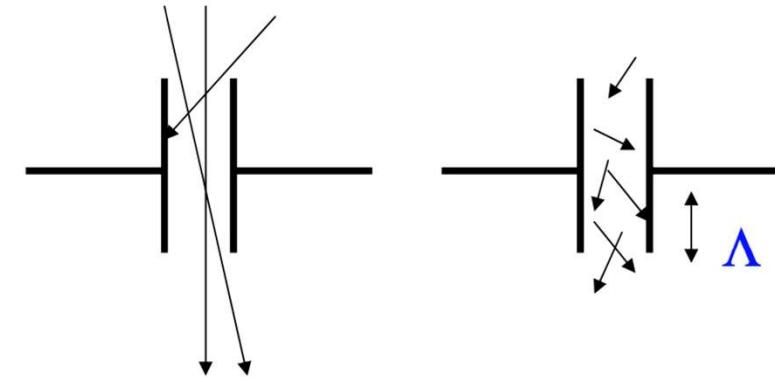
endotherm: $Q < 0$
exotherm : $Q > 0$

Emission characteristics

Aperture (diameter d)

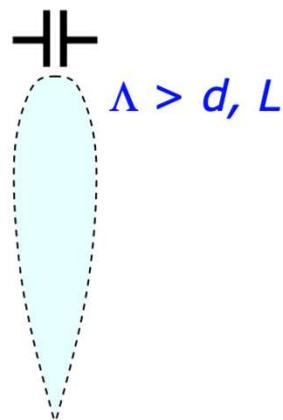


Nozzle (diameter d , length L)

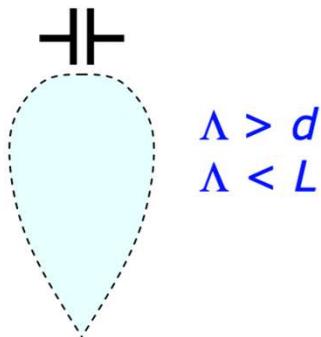


$$I(\vartheta) = \cos\vartheta$$

low density



$$\Lambda > d, L$$



high density

Effusive atomic and molecular beams

Effusive flow: low density

⇒ collisions between the particles can be neglected

$$\Lambda_{\text{Quelle}} \gg d$$

Λ: mean free path length
d: diameter of the source aperture

The collision rate **R** depends on the particle velocity **v**, target density **n** and collision cross section **σ**

$$R = v_{\text{rel}} \sigma n$$

$$\begin{aligned} \Lambda &= v/R \\ &= \frac{v}{v_{\text{rel}} \sigma n} \\ &= \frac{1}{\sqrt{2} \sigma n} \end{aligned}$$

Example:
at **T = 800 K and P = 1 mbar**

$$\rightarrow \Lambda = 8 \text{ mm}$$

The cross section **σ** is of the order of one atomic unit:

$$\begin{aligned} \sigma &\approx \pi a_0^2 \\ &= 10^{-16} \text{ cm}^2 \end{aligned}$$

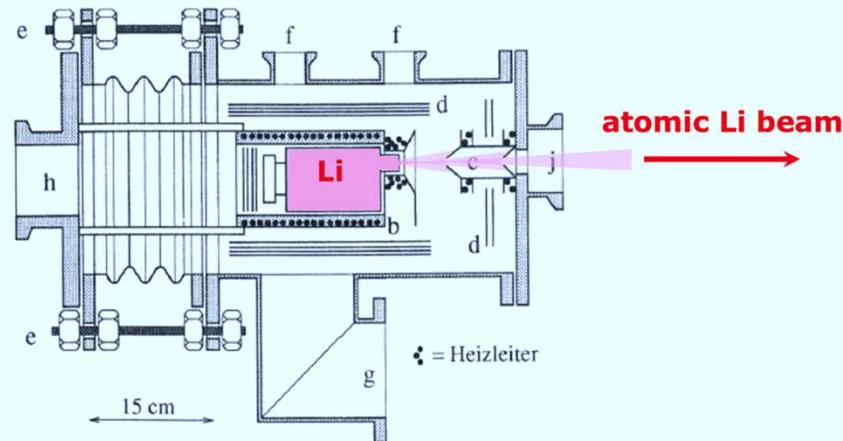
Most probable velocity in a Maxwell-Boltzmann distribution v_w

Mean velocity in the gas reservoir

$$v_w = \sqrt{2kT/m}$$

$$\bar{v} = (2/\sqrt{\pi}) v_w \approx 1.13 v_w$$

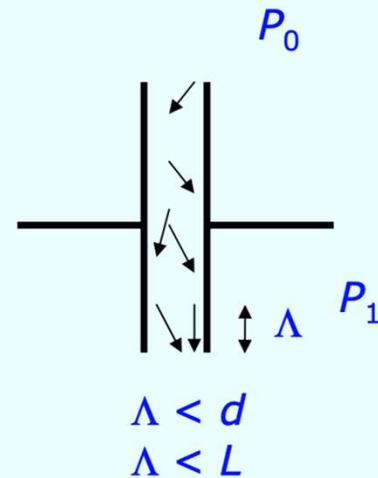
Lithium atomic (effusive) beam source with oven



- a) Li oven with heated nozzle
- b) Heating wires
- c) Skimmer
- d) Heat shielding

Supersonic gas jets

- very low divergence
- high density
- well defined velocity (cold beam: a few K)
- rather complex apparatus (vacuum system)

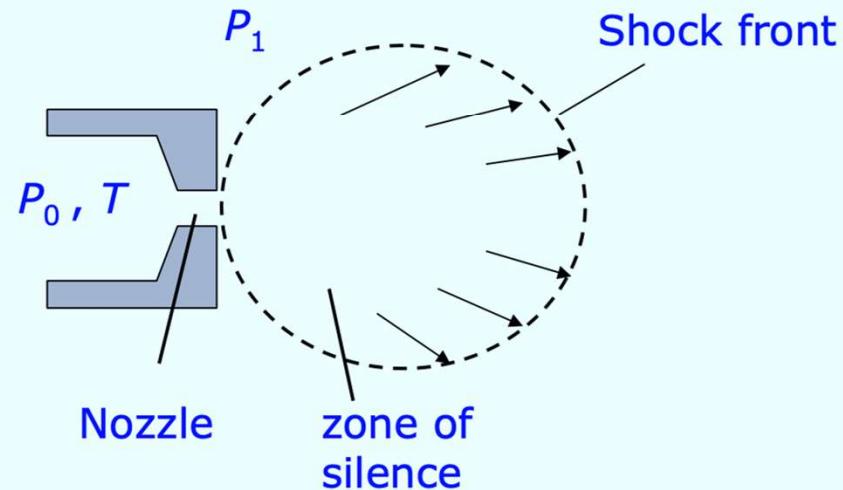


Gas expands from high pressure (P_0 1-100 bar) through a small nozzle into high vacuum (P_1)

$$\Lambda < d$$
$$\Lambda < L$$

What happens ?

- acceleration to supersonic speed
- formation of a shock front
(finite pressure P_1 in the chamber)
- internal energy (temperature) is transformed into kinetic energy



Supersonic gas jets

During the adiabatic expansion of the gas from initial pressure P_0 to P through the nozzle a part of the disordered thermal motion of the particles (given by P_0 , T_0) is transformed into directed translational energy.

Energy conservation gives for the enthalpy H (total energy):

$$H = E_{\text{therm}} + PV = 3/2 kT + kT = 5/2 kT$$

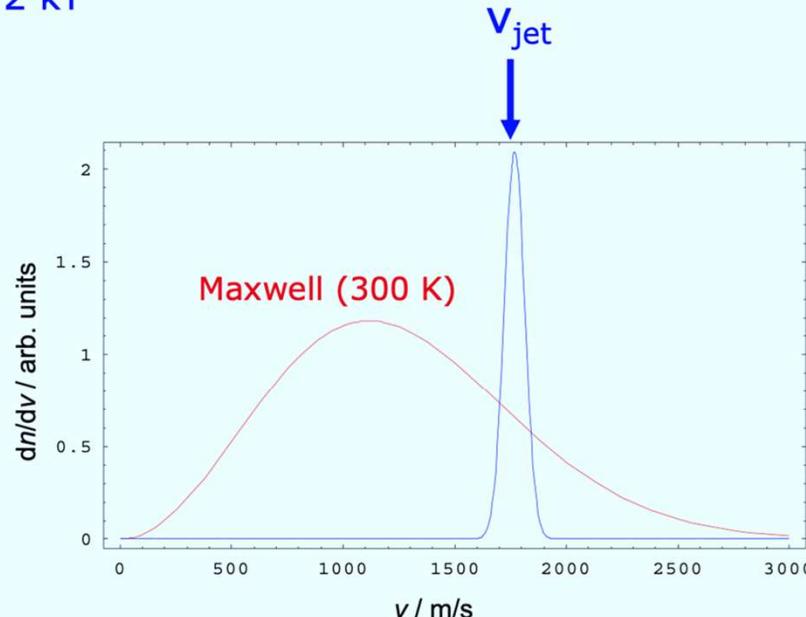
after expansion:

$$E_{\text{kin}} = 5/2 kT$$

$$v_{\text{jet}} = (5kT/M)^{1/2}$$

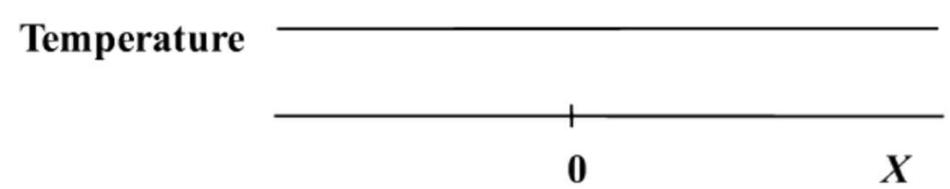
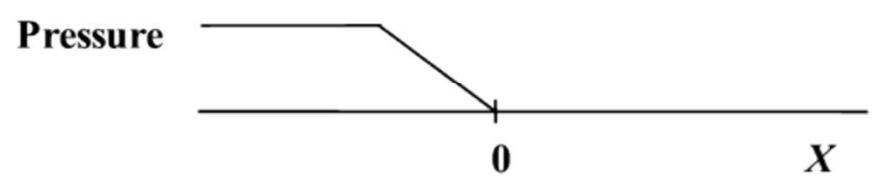
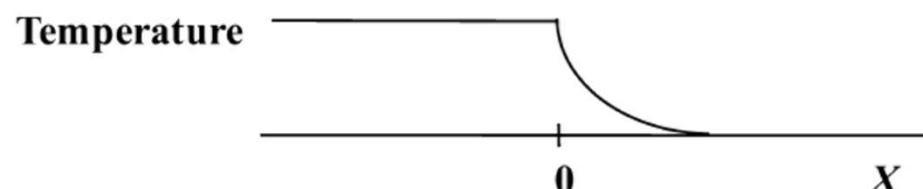
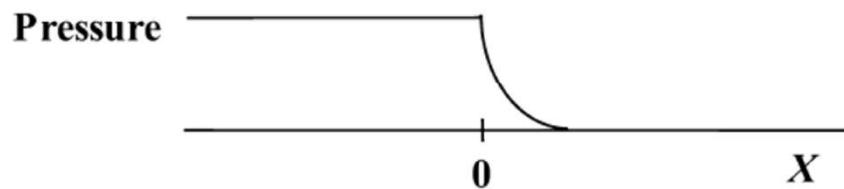
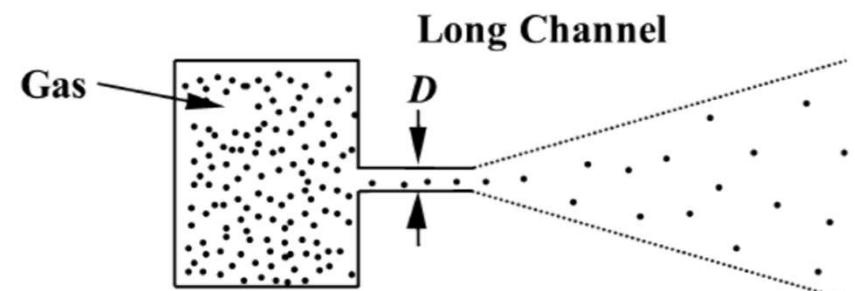
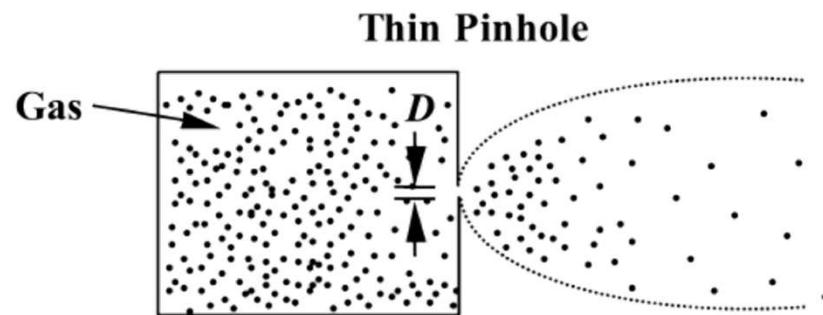
→ Temperature decreases
(adiabatic expansion)

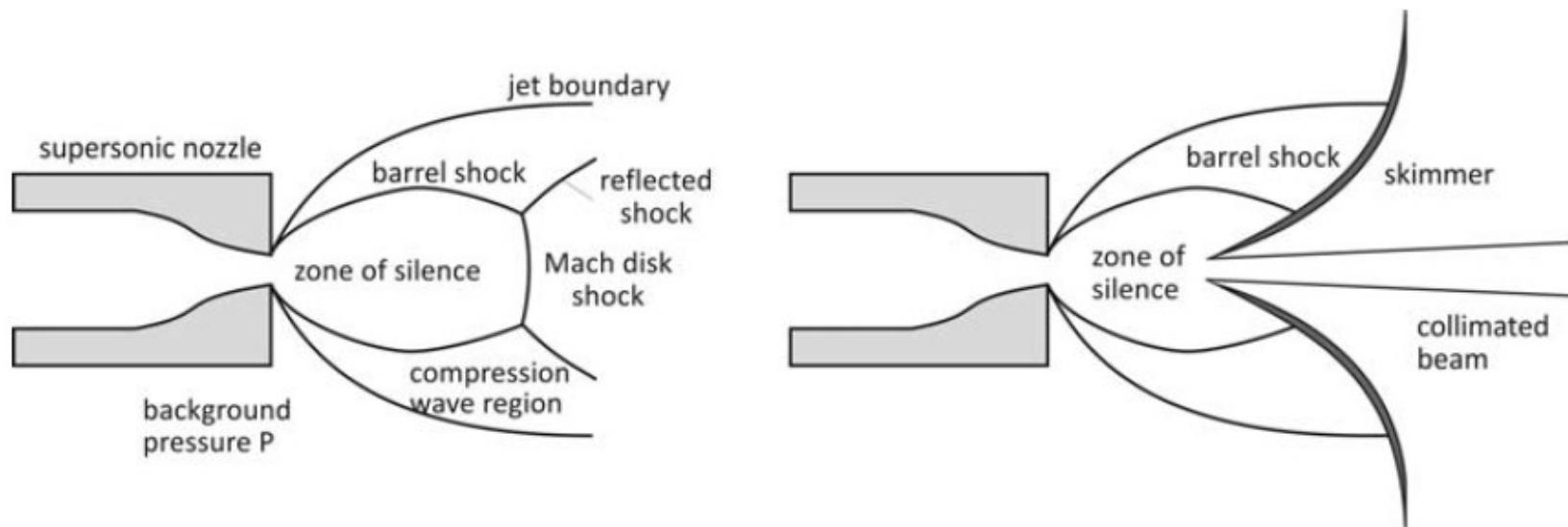
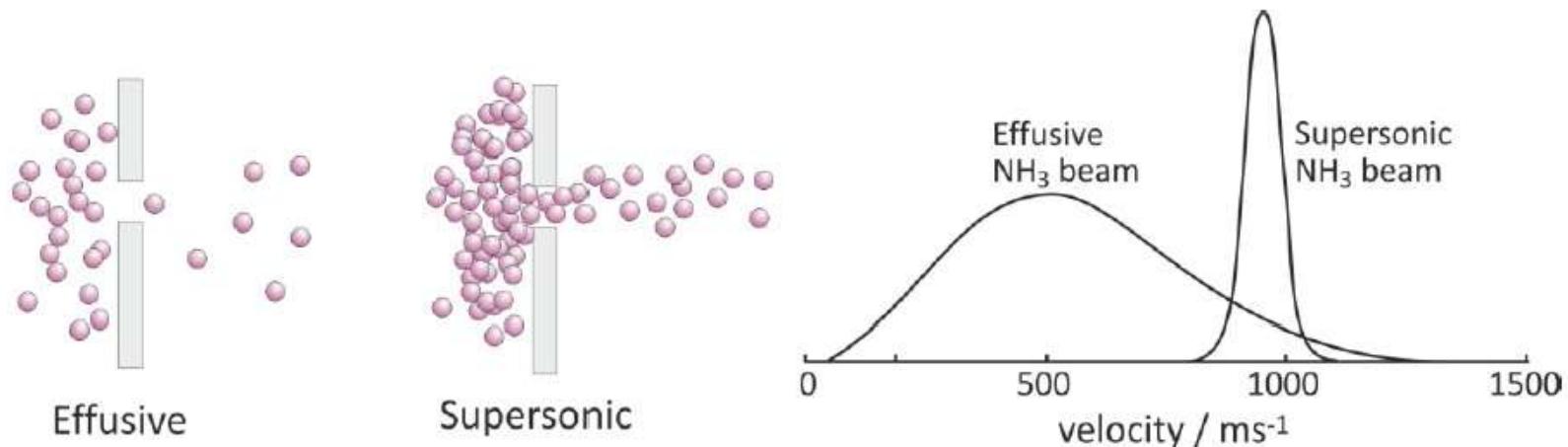
→ Kinetic energy (directed)
increases



$$E_{\text{kin}} \approx 70 \text{ meV} \text{ for expansion at } T = 300 \text{ K}$$
$$v_{\text{jet}} \approx 1700 \text{ m/s for Helium}$$

Supersonic expansion reduces target temperature

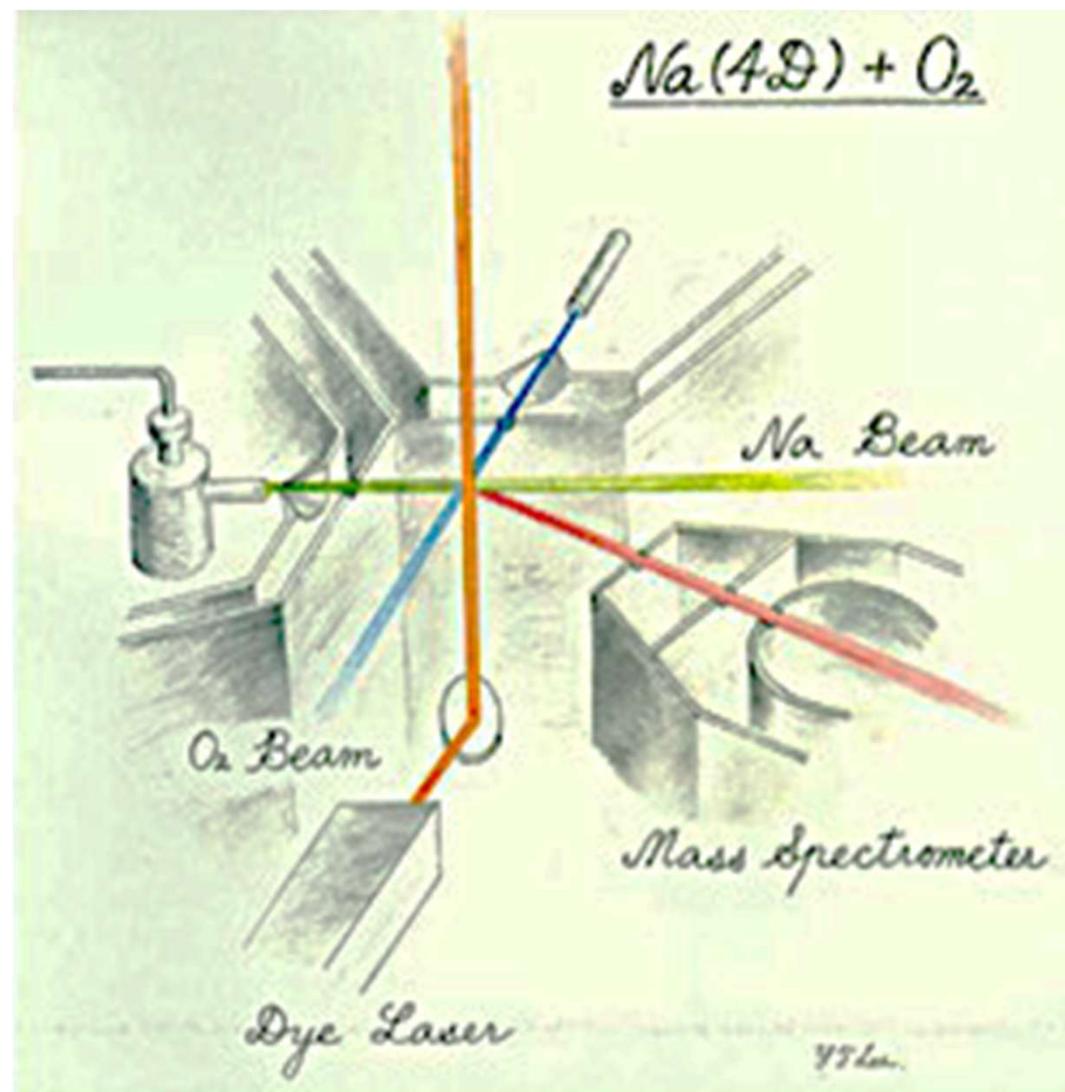
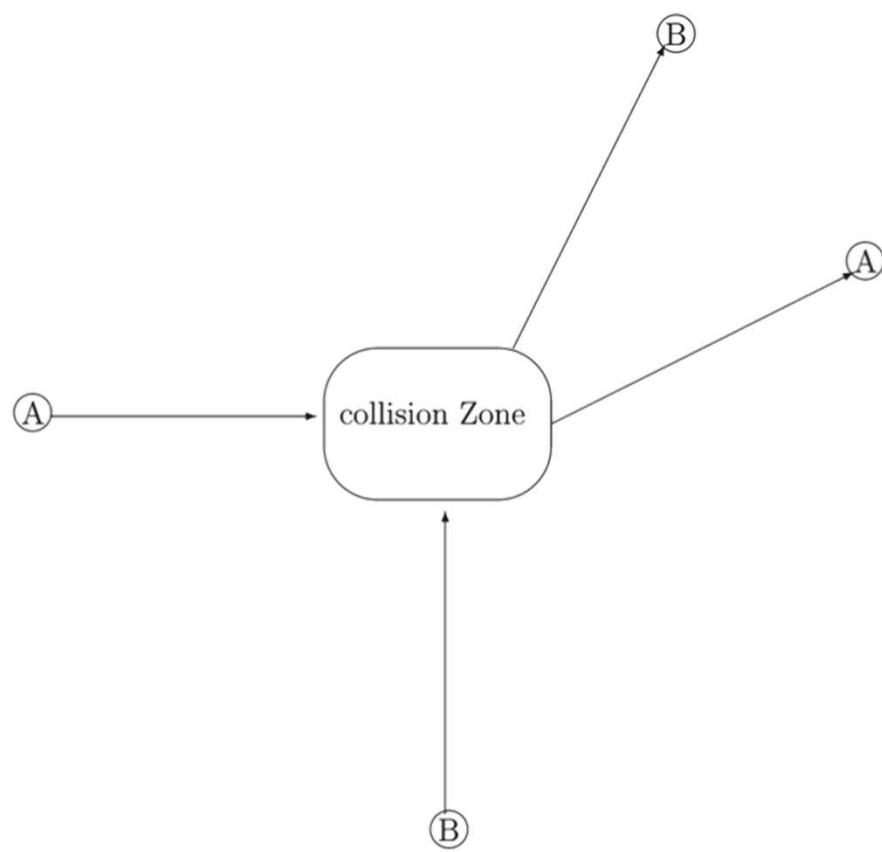




Supersonic Molecular Beam Chamber in SL-216, IIT Kanpur



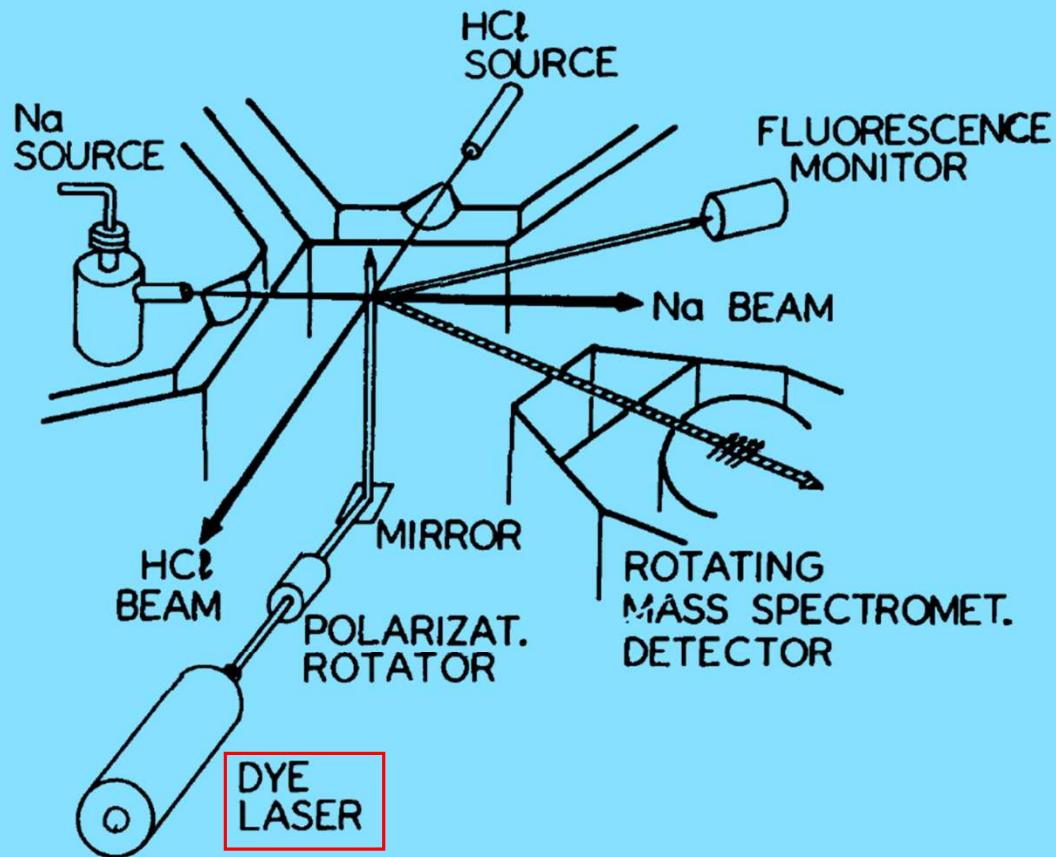
Cross Molecular Beam Experiments



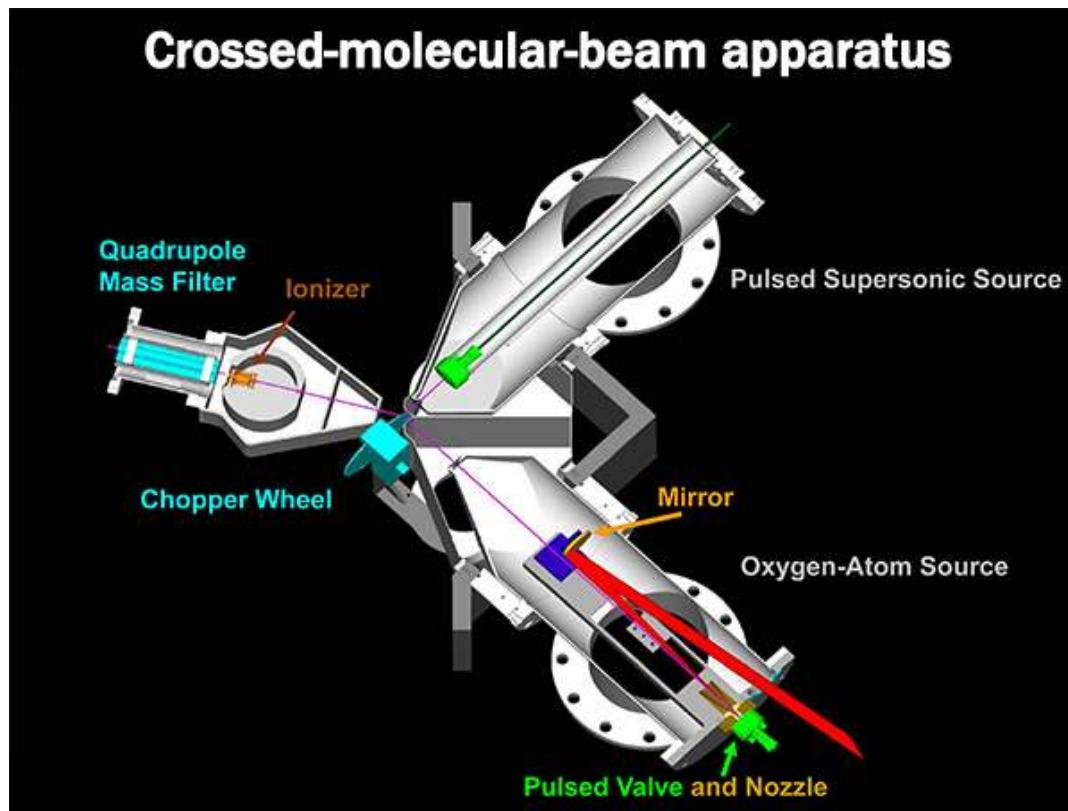
Crossed molecular beams

Y. T. Lee

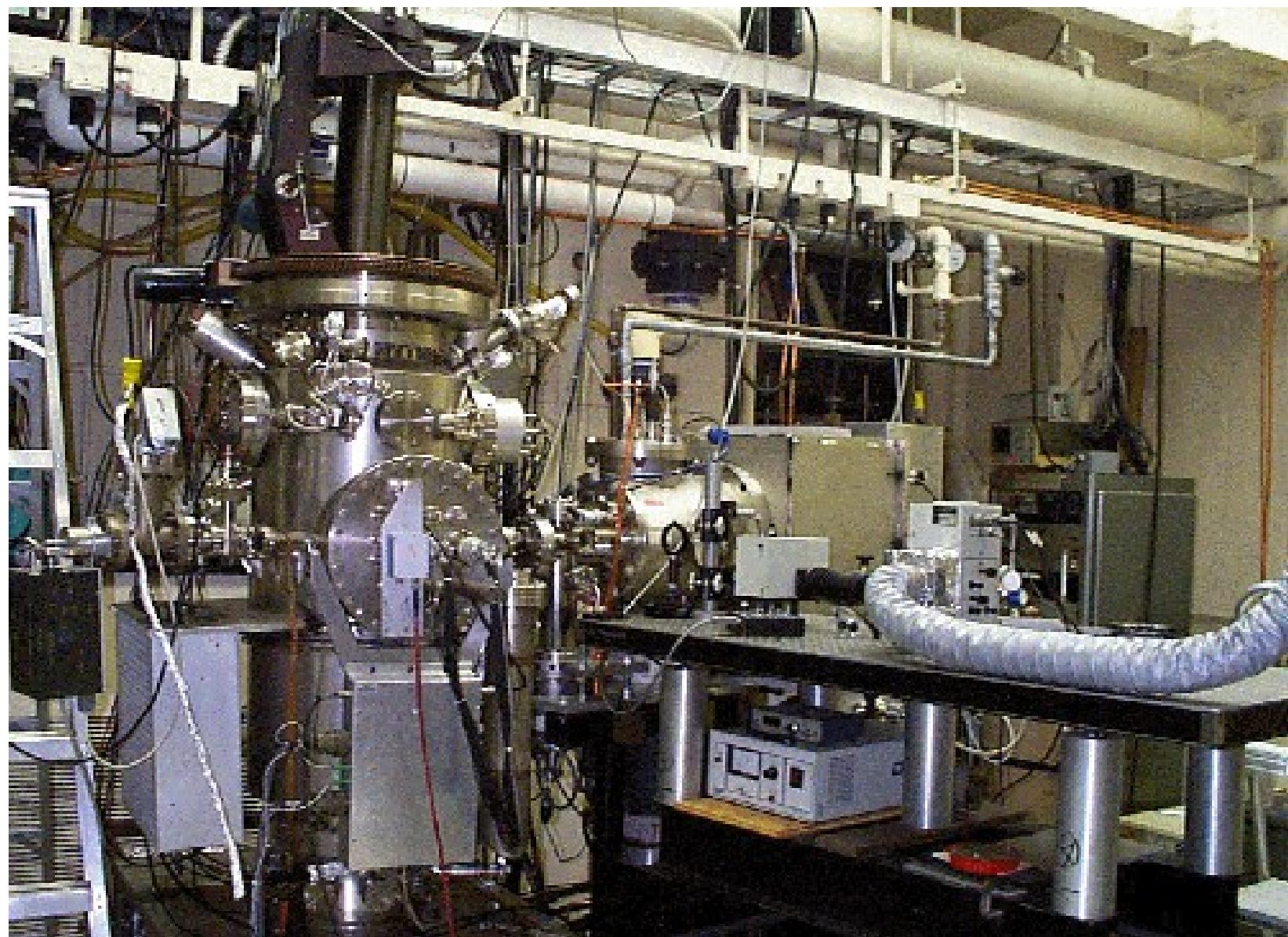
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SEPARATE HANDOUT ON LASERS



Beam generation, collision volume, detection



Consider the reaction:



This way of writing down chemical reactions, using arrows and symbols, is ‘incomplete’

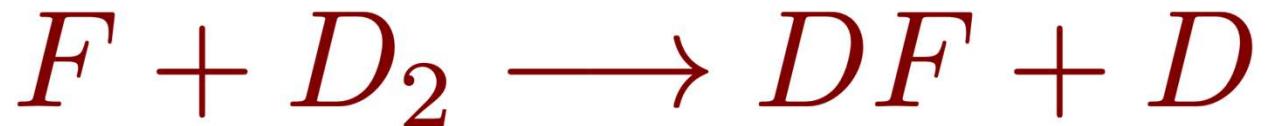
- ❖ Do rates depend on internal quantum states of the reactants?
- ❖ What are the internal quantum states of the products?
- ❖ What is the dependence of chemical reactivity on molecular orientation? Dependence on the impact of collision?
- ❖ **What is the nature of reaction intermediates and their subsequent decay dynamics in case of complex polyatomic molecular reactants?**

Molecular beam studies of the F+D₂ and F+HD reactions

D. M. Neumark,^{a)} A. M. Wodtke, G. N. Robinson, C. C. Hayden,^{b)} K. Shobatake,^{c)} R. K. Sparks,^{d)} T. P. Schafer, and Y. T. Lee

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California 94720

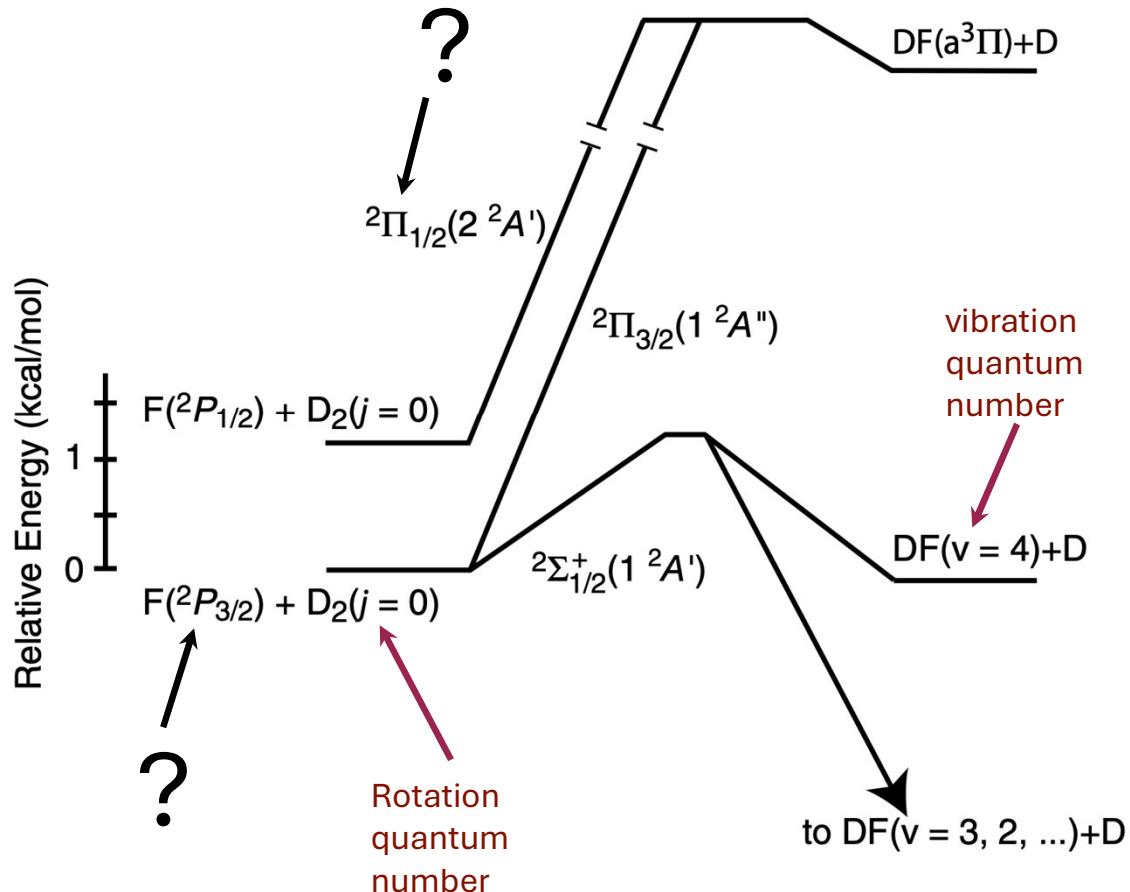
(Received 27 August 1984; accepted 13 November 1984)



Quantum state-specific study!

Does the rate depend on whether D₂ is vibrationally excited or not?

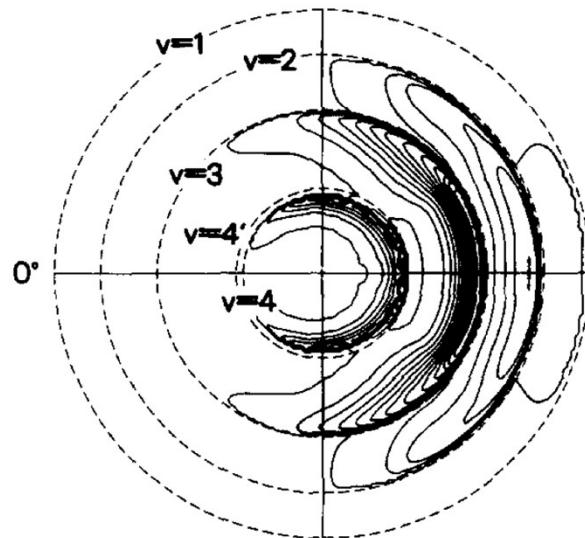
Energetics



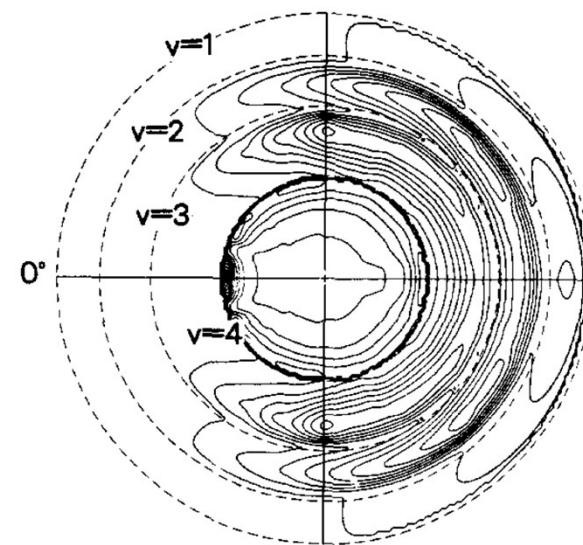
SEPERATE HANDOUT ON TERM SYMBOLS

Newton diagram!

$\text{F}+\text{D}_2 \rightarrow \text{DF}+\text{D}$, 1.82 kcal/mole



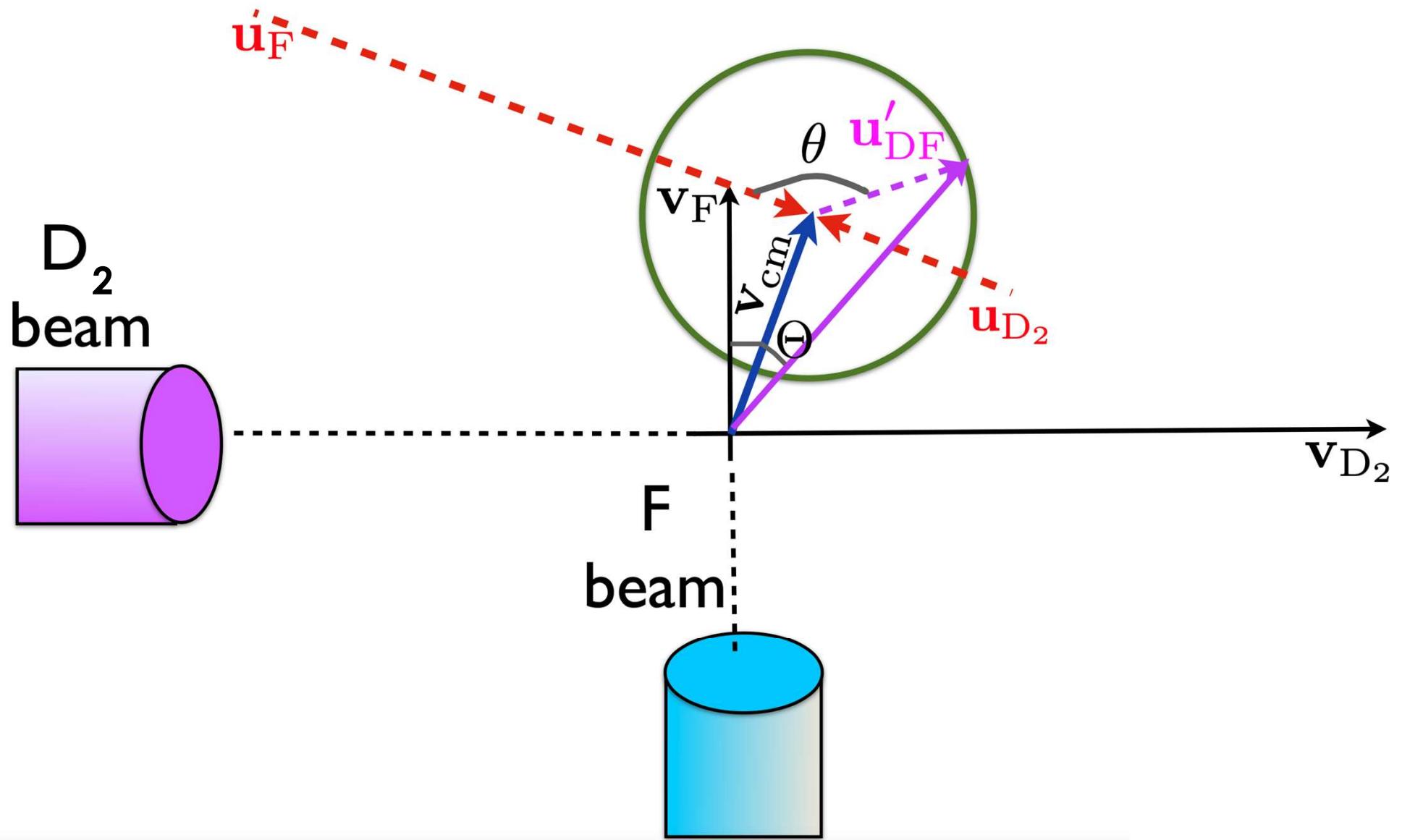
$\text{F}+\text{D}_2 \rightarrow \text{DF}+\text{D}$, 3.32 kcal/mole



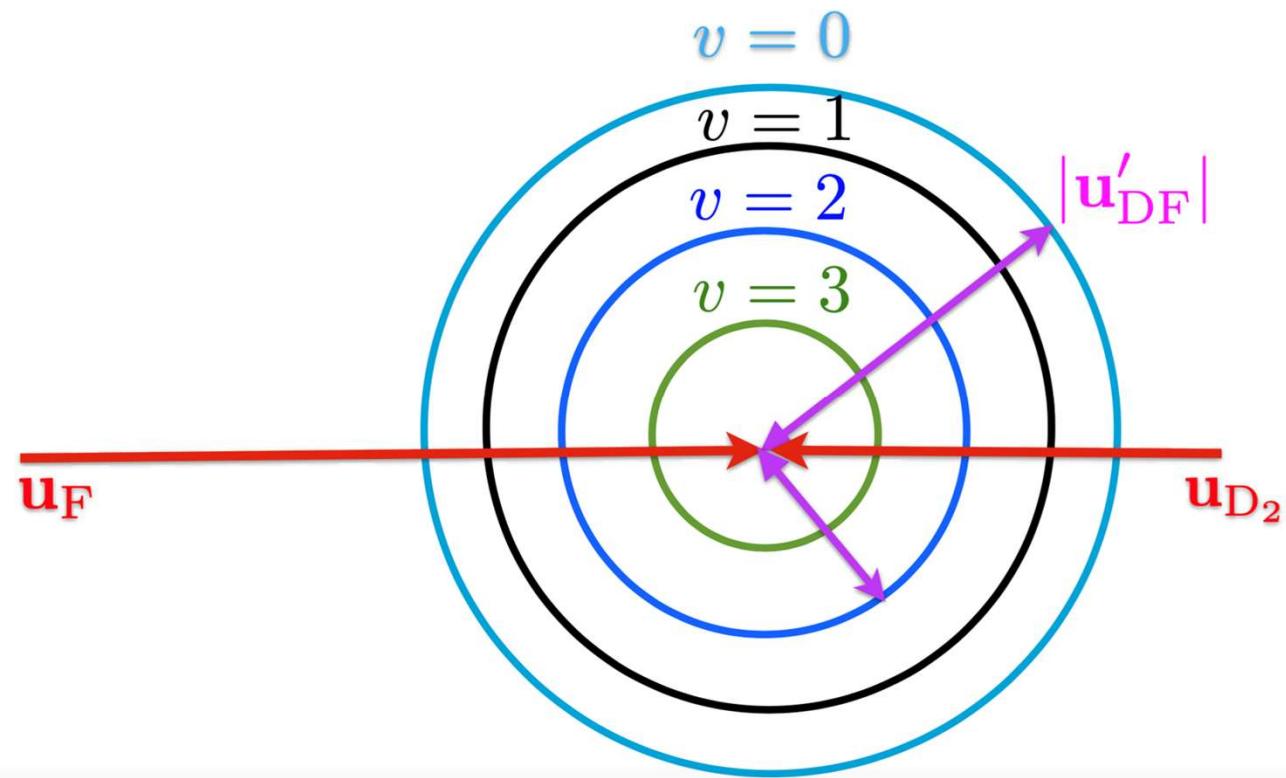
How do we understand these differences?

Questions

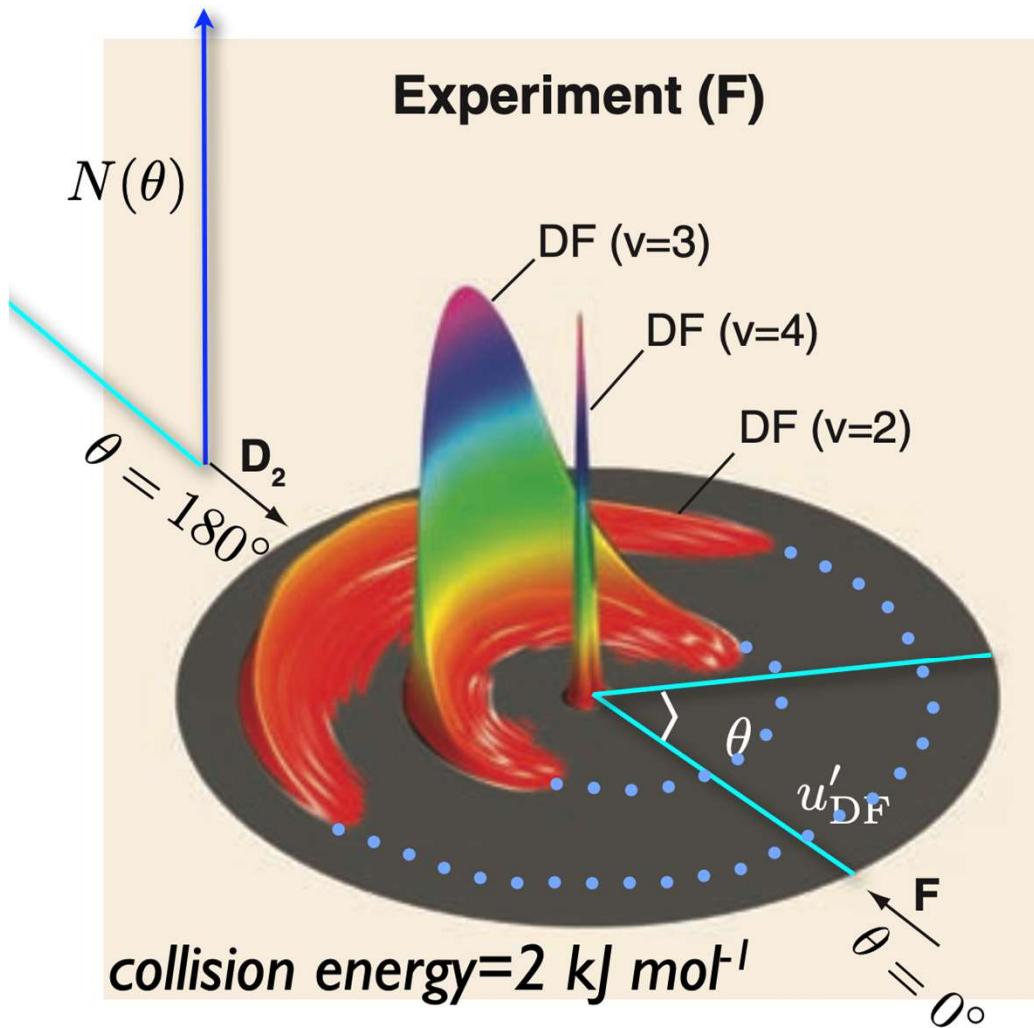
- Are quantum effects important?
- Are the DF molecules Boltzmann distributed?
- Mechanism?
- Isotopic analogs are similar?



Theoretically expected points if products are at a vibrational level v and in rotational and electronic ground state



What do we find experimentally?



We can assign the peaks to various vibrational states based on our theoretical estimates (dotted blue color) of u'_DF

Contour Diagrams:

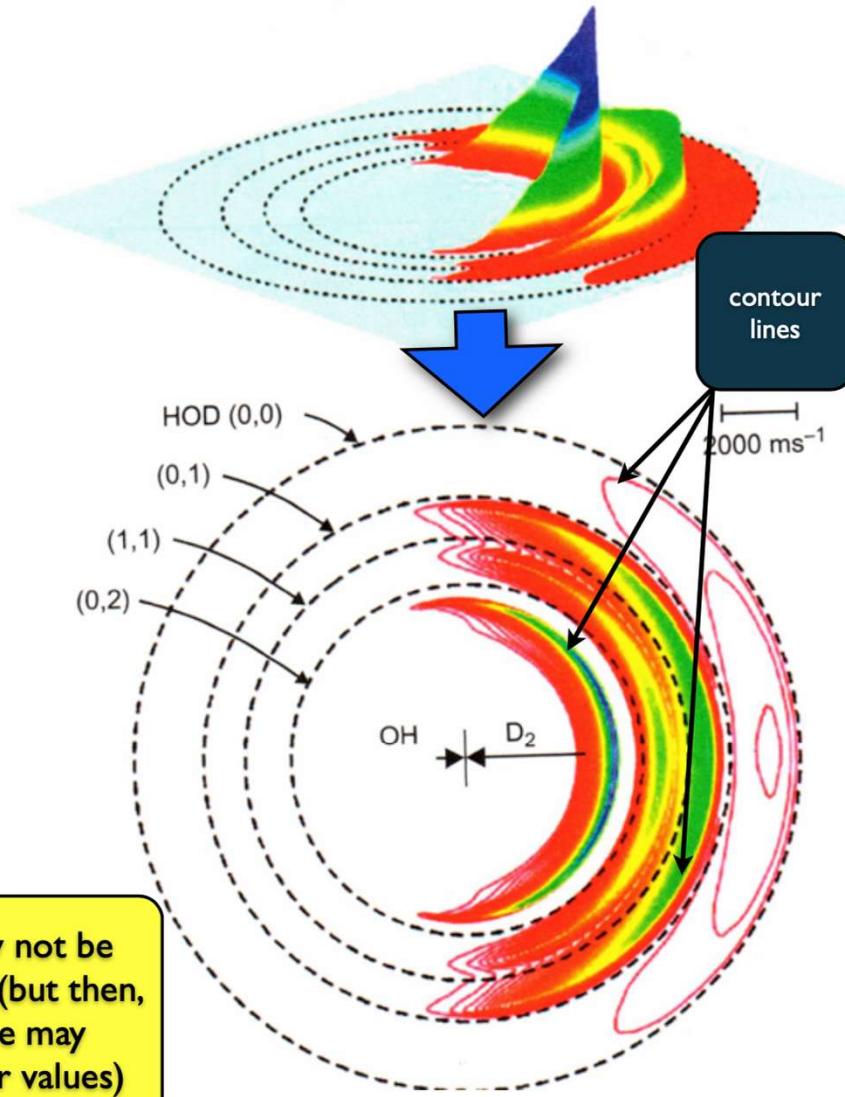
$N(\theta)$ values as contours lines:
contour diagram will help to see a 3D-graph 2D.

Here contour values are color coded (with high values of $N(\theta)$ in blue and low values of $N(\theta)$ in red).

Intermediate values are in other colors;
 $N(\theta)$ value decreases on going from
blue \rightarrow cyan \rightarrow green \rightarrow yellow \rightarrow red

steeper the curve,
closer the contour lines are.

Contour lines may not be color coded always (but then, each contour line may accompany contour values)



How is Newton's Diagram constructed?

- Center of mass velocity is conserved during the entire course of the collision reaction.
This allows us to define a coordinate system with respect to center of mass velocity.



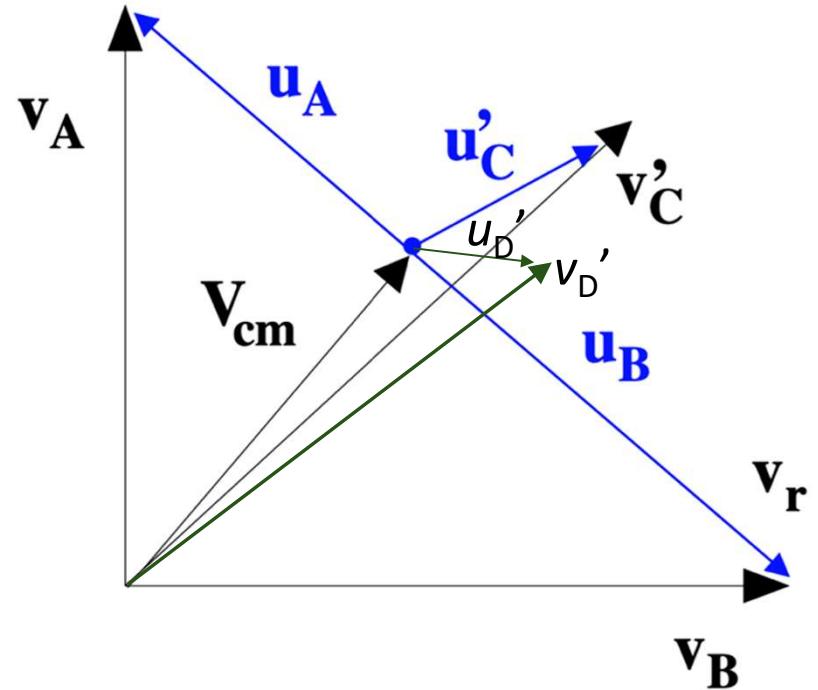
This can be represented as follows:

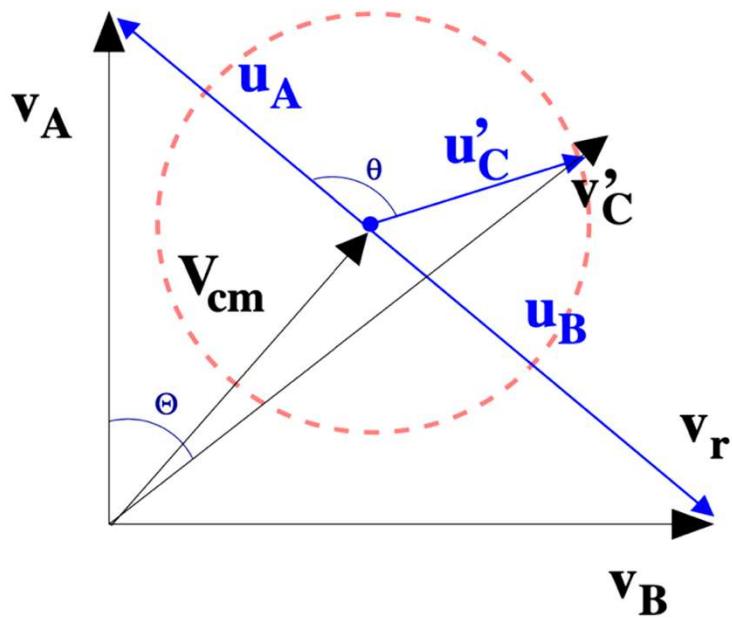
We can derive the following relations from such a diagram:

$$u'_C = \frac{m_D}{M} v'_r \quad (1)$$

$$u'_D = \frac{m_C}{M} v'_r \quad (2)$$

where $v'_r = |\mathbf{v}'_C - \mathbf{v}'_D|$





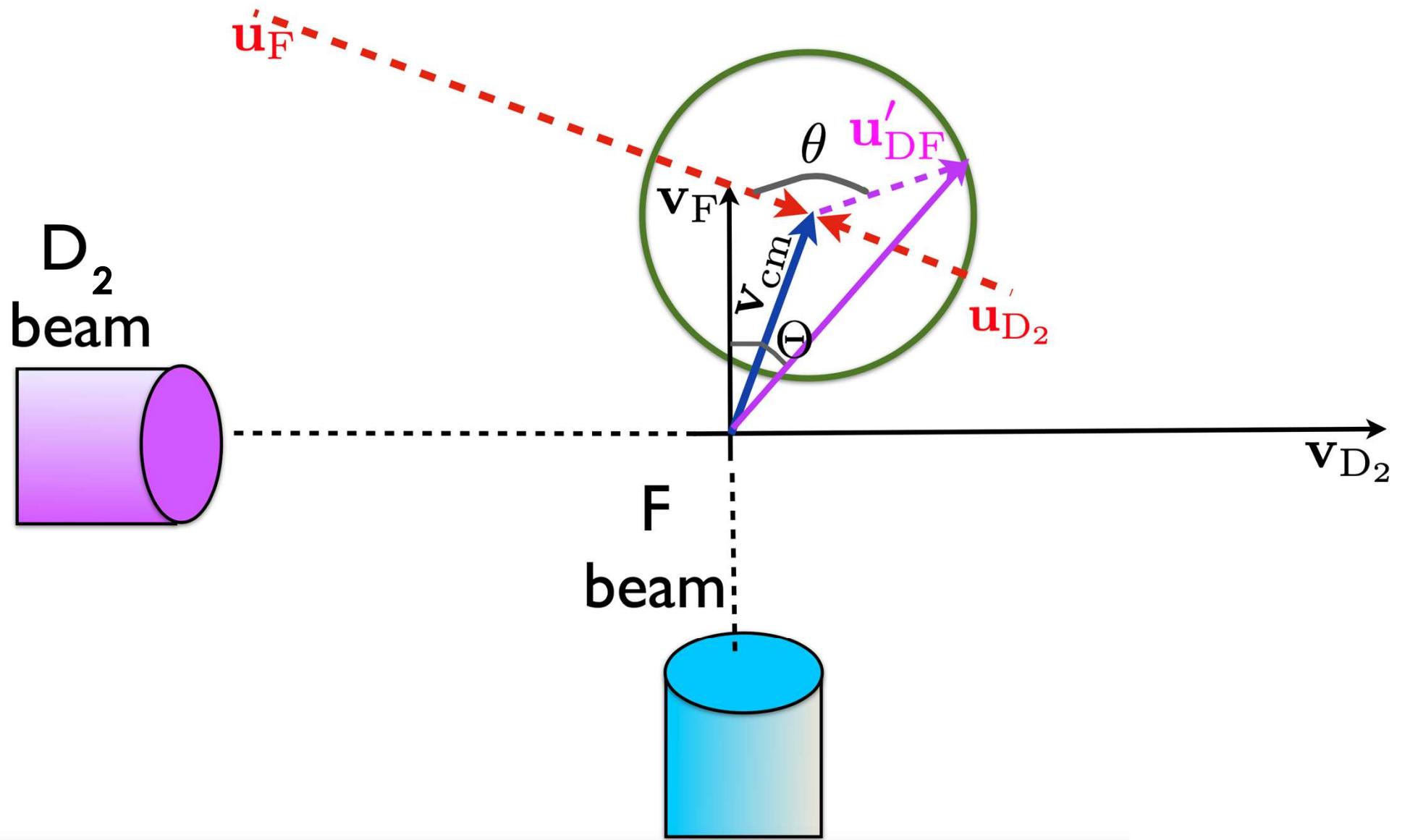
This means that the translational kinetic energy of the product is dependent not only on the translational kinetic energy of the reactant molecules, but also on the internal energies of the reactants and the products. Thus, the radius of the circle (i.e., u'_C) will depend on which vibrational, rotational and electronic state the product molecule will be.

$$E = E_T + E_I = E'_T + E'_I$$

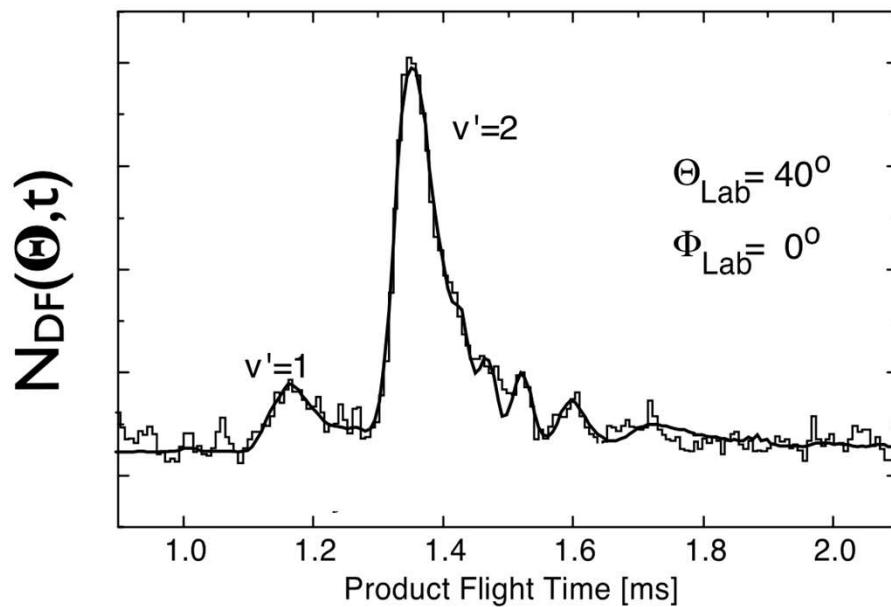
where the internal energy is given by

$$E_I = E_R + E_V + E_E \quad (\text{rotational} + \text{vibrational} + \text{electronic})$$

- We can calculate the magnitude of the vector u'_C (i.e., u'_C) knowing translational energy of the product $E_{T'}$, which in turn can be estimated using the total energy conservation ($E = E_T + E_I = E_{T'} + E'_I$)
- E is the total energy, E_I is the internal energy and E_T is the translational kinetic energy
- A superscript prime indicates product, otherwise it represents reactants
- This implies that although we cannot *predict* how the vector u'_C will be oriented though we can find that by performing an experiment, we can *predict* that this vector has the magnitude u'_C
- In the point of view of the molecular beam experiments, we can predict that the products could ideally be seen anywhere in the circle (as shown in the figure) with radius u'_C
- There are some preferred values of ϑ , and it depends on the details of the mechanism of reaction, but the circle is predictable irrespective



Detector measures the time-of-flight (TOF)
spectrum of a product species
 $N_{DF}(\Theta, t)$



$v'=1$
has high
velocity and
reaches first

$v'=2$ is
slower

from time of flight

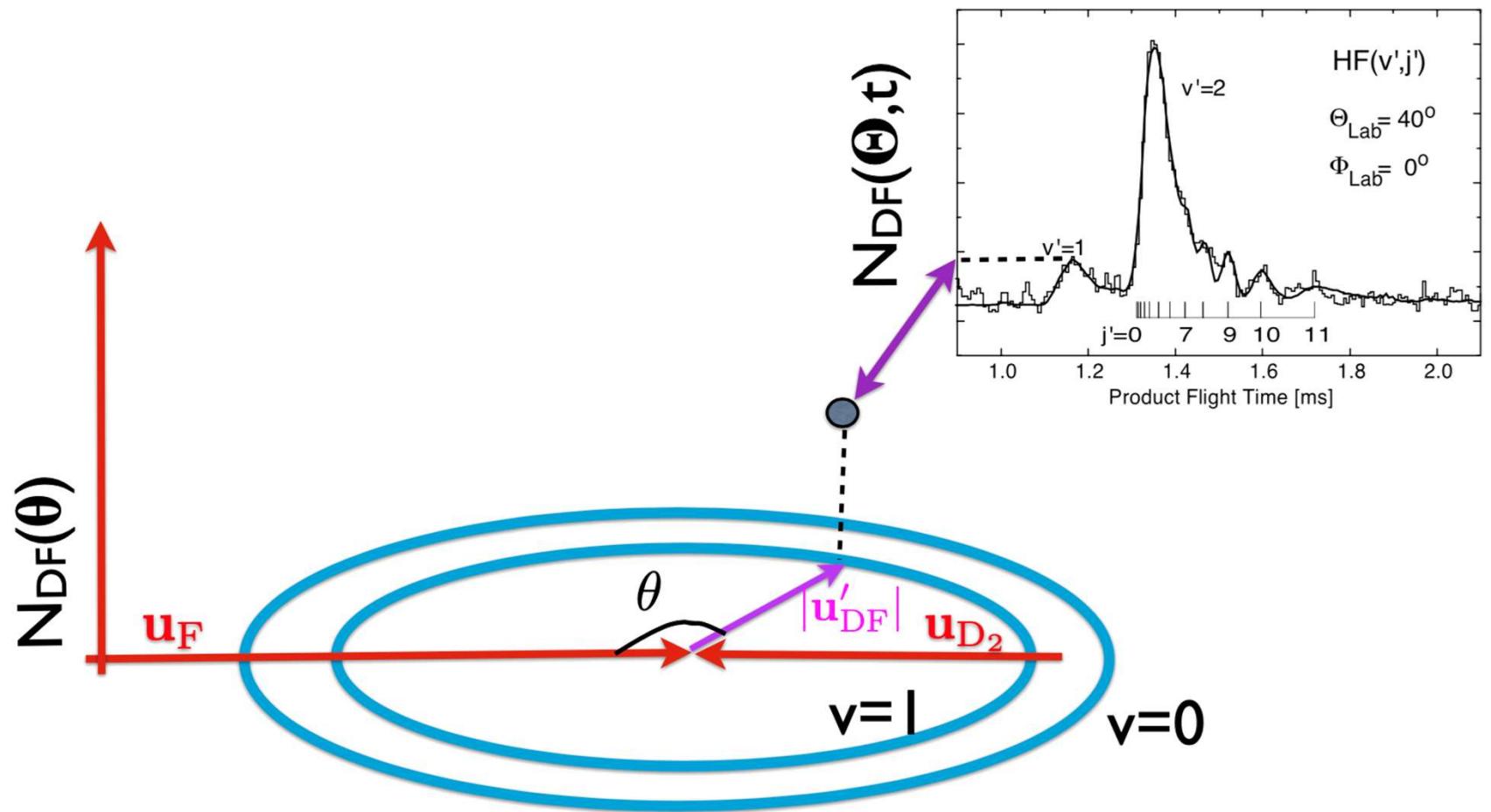


$$N_{DF}(\Theta, v) \implies N_{DF}(\theta, u)$$

(LAB frame)

(CM frame)

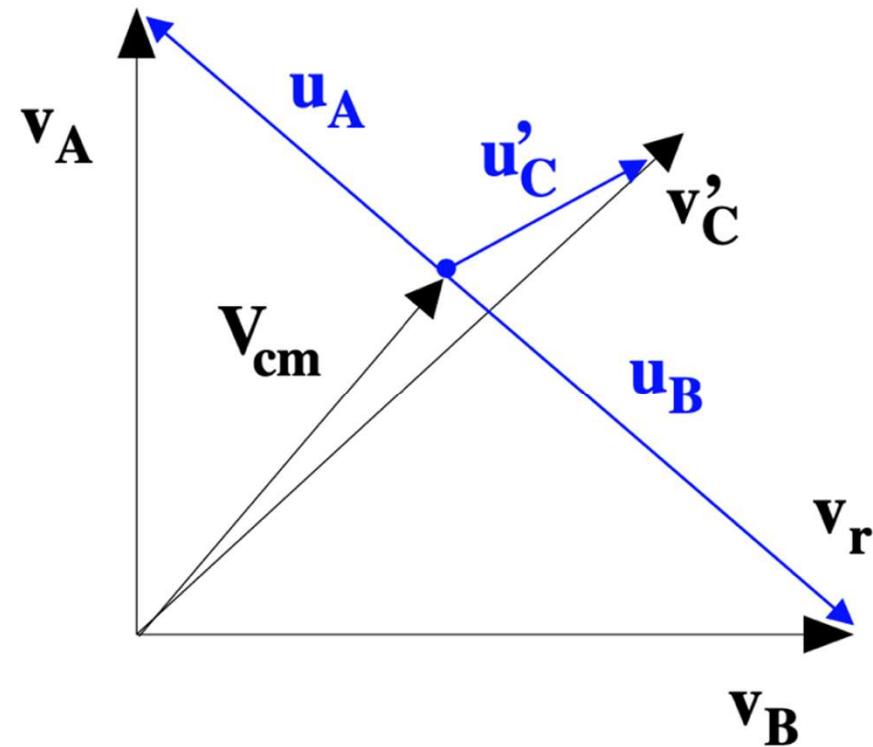
This transformation is mathematically possible
(Jacobian)



The $F + D_2$ and $F + HD$ reactions were investigated in a high resolution crossed molecular beams experiment at several collision energies. The DF product from both reactions was predominantly backward scattered although some forward scattered $DF(v = 4)$ was observed at the highest energy studied. The HF angular distributions from $F + HD$ were quite different, showing considerable forward scattered ($v = 3$) and no other identifiable structure. These results disagree with classical trajectory studies, which predict only small variations in the product angular distributions among $F + H_2$ and its isotopic variants. They agree, however, with the predicted dependence of dynamical resonance effects on isotopic substitution. The results therefore support the conclusions drawn in the previous paper regarding the role of dynamical resonances in the $F + H_2$ reaction.

How is Newton's Diagram constructed?

Center of mass velocity is conserved during the entire course of the collision reaction. This allows us to define a coordinate system with respect to center of mass velocity. This can be represented as follows:



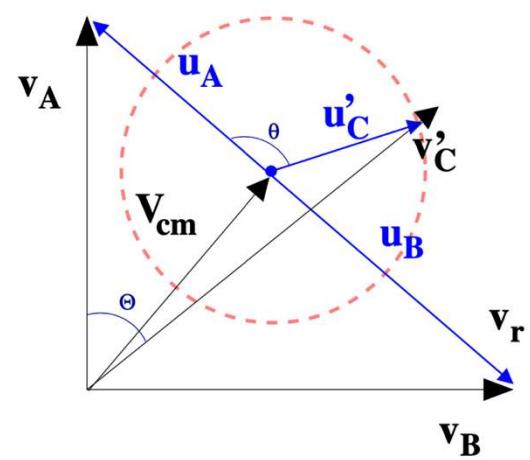
We can derive the following two relations from such a diagram:

$$u'_C = \frac{m_D}{M} v'_r \quad (1)$$

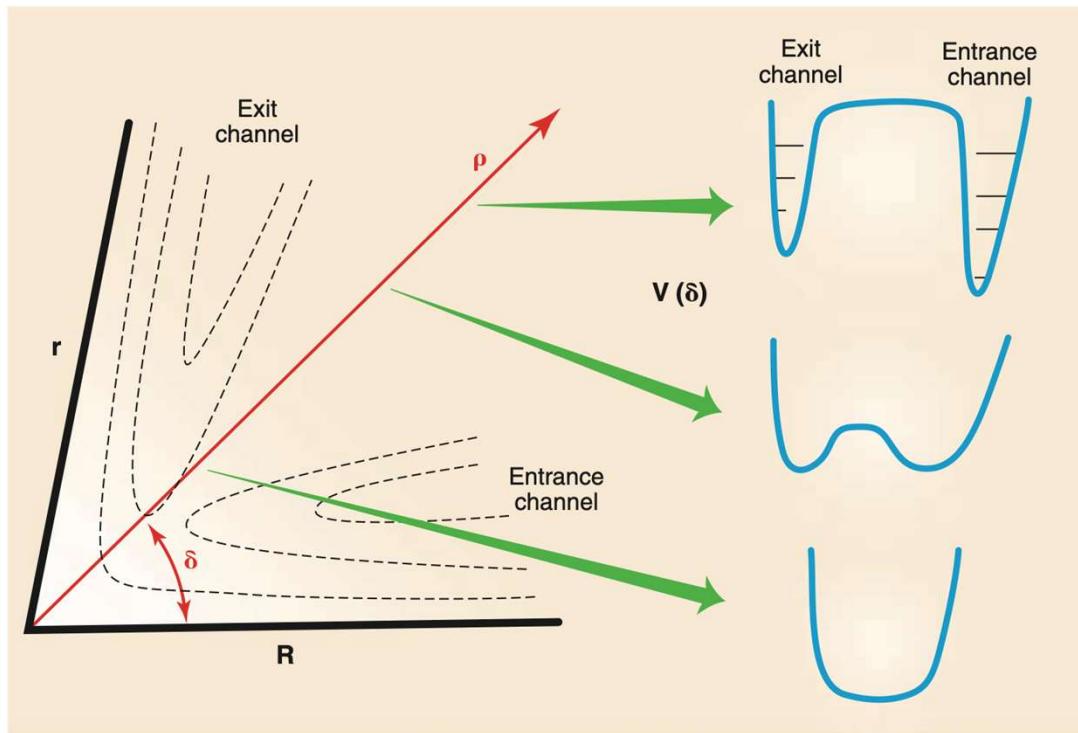
$$u'_D = \frac{m_C}{M} v'_r \quad (2)$$

$$\text{where } v'_r = |\mathbf{v}'_C - \mathbf{v}'_D| \quad (3)$$

We can calculate the magnitude of the vector $\mathbf{u}_{C'}$ (i.e. $u_{C'}$) knowing translational energy of the product $E_{T'}$, which in turn can be estimated using the total energy conservation ($E = E_T + E_I = E_{T'} + E_I$). E is the total energy, E_I is the internal energy and E_T is the translational kinetic energy. Here a superscript prime indicates that for product, otherwise for reactants. This implies that although we cannot *predict* how the vector $\mathbf{u}_{C'}$ will be oriented though we can find that by performing an experiment, we can *predict* that this vector has the magnitude $u_{C'}$: see the figure below. In the point of view of the molecular beam experiments, we can predict that the products could ideally be seen anywhere in the circle (as shown in the figure below) with radius $u_{C'}$. There are some preferred values of ϑ , and it depends on the details of the mechanism of reaction but the circle is predictable irrespective.

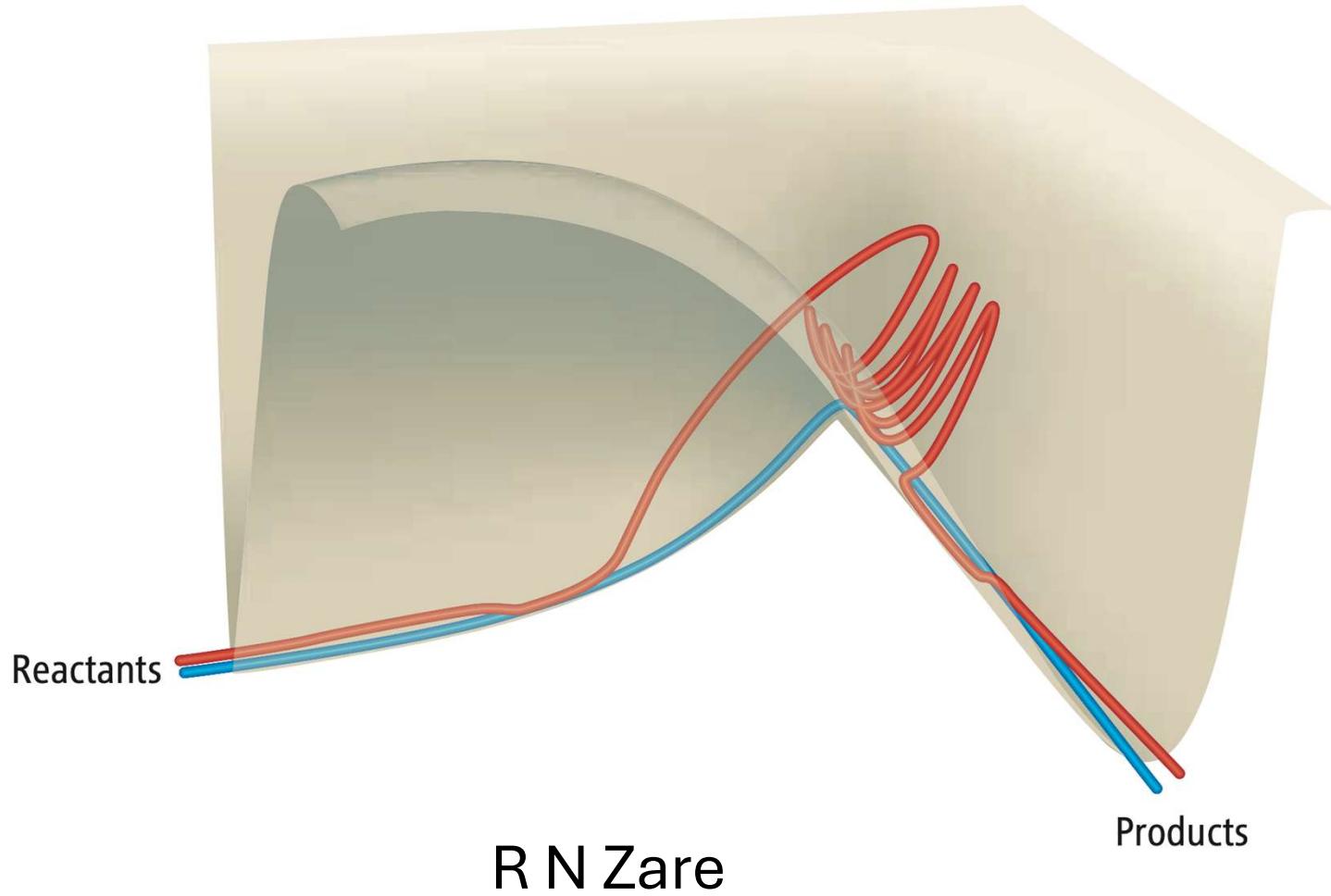


Potential energy surface



For Molecules: E(electronic) > E(vibrational) > E(rotational)

Remember: No vibrational or rotational for Atoms!



CHAPTER 28

PHYSICAL CHEMISTRY A MOLECULAR APPROACH

Donald A. McQuarrie • John D. Simon



1997 Edition

Gas-Phase Reaction Dynamics

Bimolecular gas-phase reactions are among the simplest elementary kinetic processes that occur in nature. In this chapter, we will examine some of the current models that are used to describe the molecular aspects of bimolecular gas-phase reactions. First, we will modify the collision theory presented in Chapter 25 and define the rate constant in terms of a reaction cross section. We will then examine experimentally measured reaction cross sections for several gas-phase reactions. The simplest gas-phase reaction is the hydrogen exchange reaction $H_A + H_B - H_C \Rightarrow H_A - H_B + H_C$. This reaction has been studied in great detail and the experimental data for it are often used to test theories of gas-phase chemical reactions.

In this chapter, however, we have chosen to focus our discussion on the reaction $F(g) + D_2(g) \Rightarrow DF(g) + D(g)$. From a study of this reaction, we will not only learn the same concepts that underlie the $H(g) + H_2(g)$ exchange reaction but will also learn about molecular processes that can occur in reactions in which $\Delta_r U^\circ < 0$. The reaction $F(g) + D_2(g)$ therefore serves as an excellent system for studying the molecular details of gas-phase reactions. We will examine data obtained from crossed molecular beam spectroscopy experiments and learn how such measurements reveal the chemical dynamics of reactive collisions. We will then see that contemporary quantum-mechanical calculations can provide a detailed description of the reaction path by which the $F(g) + D_2(g)$ reactants become the $DF(g) + D(g)$ products.