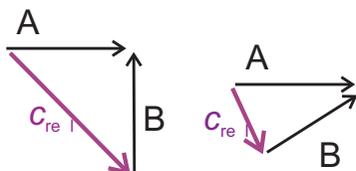# 4. Controlling reagents and characterizing products

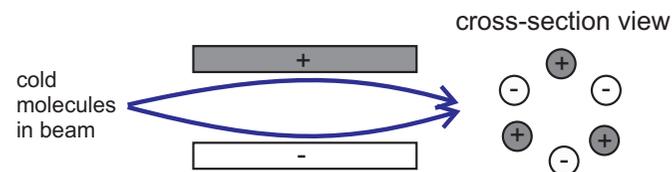## Reagent state selection in molecular beams

Selection of velocity in a molecular beam.

Achieved through the use of choppers, control of source pressure, and seeding (see above).

Relative velocity (collision energy) can also be tuned by varying the molecular beam intersection angle

Selection of internal states using inhomogeneous electric fields.

Molecule must have a dipole moment.

Focusing depends on velocity, and on $\mu \cdot \mathbf{E}$, the component of the dipole along the field (see below).

Selection of internal states using laser excitation.

Difficult to achieve high enough number densities of excited species for crossed molecular beam reactive scattering experiments.

Control of reagent orientation

Some molecules can also be **oriented** in molecular beams using a **weak static electric field**.

Molecule must have a dipole moment. Orientation relies on 1st order Stark effect. Need to select the rotational state first (see above).

The average angle between the field and the dipole is given by

$$\langle \hat{\mu} \cdot \hat{\mathbf{E}} \rangle = \langle \cos \theta \rangle = \frac{KM}{J(J+1)} \ .$$

Best heads-tails selectivity is achieved for states with $J \sim K \sim M$. Works for symmetric top molecules such as CH_3I, and some open-shell diatomic molecules such as OH.

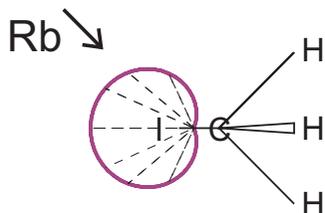Example of apparatus used to study collisions of Rg with oriented OH
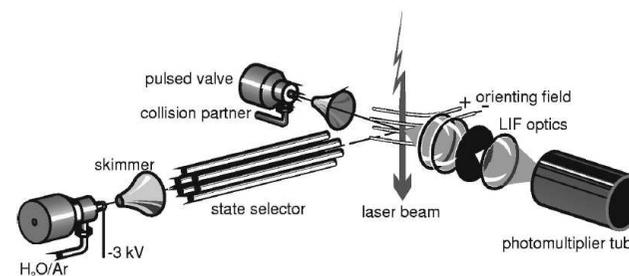
[J.J. ter Meulen and coworkers, *J. Chem. Phys.* **115**, 1843, (2001)]

Stereochemistry

Direct determination of the steric factor p.

$$Rb \ + \ CH_3I \ \longrightarrow \ RbI \ + \ CH_3$$

Look for RbI in the backward scattered direction - only see signal when I end of CH_3I is pointing towards the Rb beam.

Barrier height depends on **angle of attack, γ**.

See angle dependent line-of-centres model (Levine and Bernstein).

Not all reactions display strong steric effects, e.g., reactions which proceed on PESs without barriers tend not to.

Product state distributions

Would like to measure the **populations** in different rovibrational states of the products.

Provides information on **state-resolved cross-sections**

$$P(v', j') = \frac{\sigma_{v',j'}}{\sigma}$$

provided total cross-section σ is known.

If the velocities are not selected, but are just thermalized, then the populations provide information on the state-resolved rate constants.

The populations provide more information about the PES (see next lecture).

How do we measure?

Molecular beams provide collision free environment, i.e. no scrambling of internal states by energy transfer.

But internal state populations hard to measure in crossed beams.

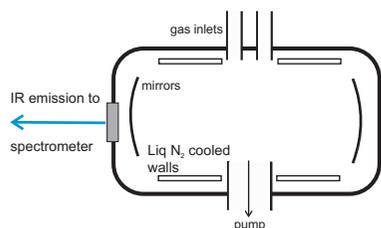Need to use other methods.

IR Chemiluminescence

Example

$$H + Cl_2 \longrightarrow HCl(v', j') + Cl$$

H atoms generated in a discharge. HCl formed rovibrationally excited - emits IR light.

Arrested relaxation experiment: 'Low' pressure (10^{-2} Pa) ensures mean free path is $\simeq$ vessel size. HCl* hits walls, sticks, and is deactivated before secondary collision.

Emission spectrum (intensities versus λ) gives information about populations in v', j' states.
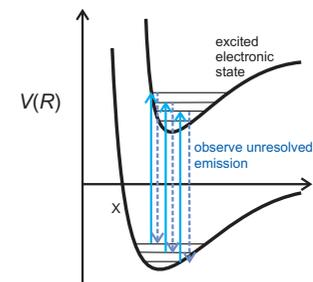
Limitations

- Need strong IR emitter (e.g., HF, HCl).
- No information of ground state.

Strengths

- Relatively universal.
- IR emission now detected by time-resolved FT-IR techniques (much more sensitive).

Laser induced fluorescence (LIF)

Excite different quantum states to an upper electronic state by varying λ_{abs}. Observe fluorescence.

The LIF spectrum is like an absorption spectrum, but with higher sensitivity. (In absorption one measures change in signal, unlike LIF.)

Note: laser based absorption methods are now being developed which have sensitivities approaching those of LIF.

Example (see more on this reaction later)

$$Ba + HI \longrightarrow BaI(v') + H$$
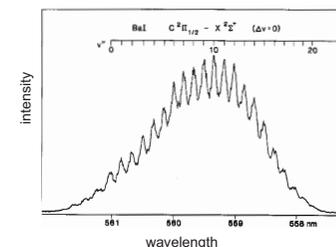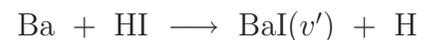
R.N. Zare and coworkers, *J. Chem. Phys.* **85** 856 (1986)

Ba and HI were generated in a molecular beam. LIF can (just) have sensitivity to detect nascent products.

Note that the upper electronic state must fluoresce.

Many excited electronic states predissociate rapidly on the timescale of emission. The quantum yield of fluorescence will then be too low for emission to be observed.

Ionization methods

Resonantly Enhanced Multi-Photon Ionization **(REMPI)**

Excite to electronic state 2 (often in two photon process), which can pre-dissociate.

$$AB^{+} + e \quad \text{ionization limit}$$

AB* — predissociation

AB ground state

X
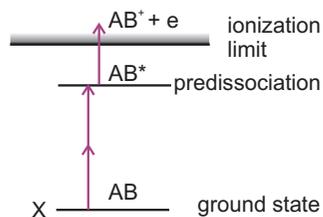
Use intense laser pulse $(\text{photons m}^{-2}\,\text{s}^{-1})$ to absorb a third photon to form ions before dissociation can occur.

Ions easily detected - highly sensitive technique.

Suitable for atoms (H, Cl, O), diatomics (HCl and O_2) and polyatomics (CH_3).

***Quantum state populations*** measured from transition intensities (like LIF).

Velocities measured by observing Doppler broadening of spectral lines (like LIF), or by time-of-flight techniques.

Note that the light mass of electrons ensures that the ionization step doesn't change the velocity of AB significantly.

Other methods

Rydberg tagging

Variant of REMPI in which the species of interest is excited to a very high-lying Rydberg state.

$$AB^{+} + e \quad \text{ionization limit}$$

AB** Rydberg state

2 — AB* predissociation

1 — AB ground state
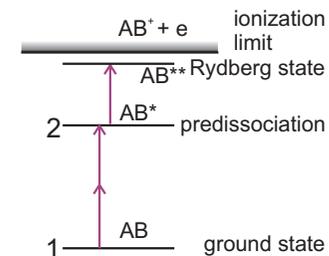
State lies sufficiently close to ionization limit to allow ionization by small electric fields.

High velocity resolution — unlike REMPI, no Coulomb repulsion between excited neutrals created within the laser focus (see H + HD example in lecture 3).
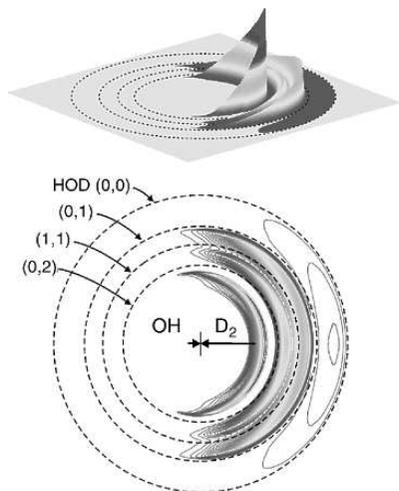
Ion Imaging

See Photochemistry lectures.

Provides a direct picture of the velocity distribution of $AB(v', j')$.

CCD camera

imaging detector

flight tube

PROBE LASER

ion optics
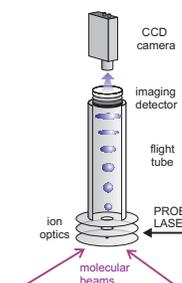
molecular beams

Example: Ne + CO inelastic scattering in Lecture 2

E.g., Selective disposal of energy into vibration

$$\mathbf{OH + D_2 \longrightarrow HOD(\nu_{bend}, \nu_{OD}) + D}$$

D atoms detected by Rydberg tagging in a molecular beam experiment — high velocity resolution.

Obtain HOD product vibrational populations
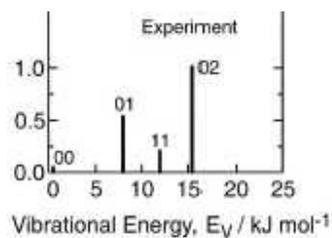
Note population inversion in OD stretch. (cf., F + H$_2$)

Observe no vibrational excitation of OH stretch.

Crim and Smith, *Phys. Chem. Chem. Phys.*, **4**, 3543, (2002).

Pump and probe methods

Alternative/complementary to crossed molecular beam method.

Particularly useful for determining nascent rovibrational quantum state populations.

$$\mathbf{Pump} \quad O_3 + h\nu \longrightarrow O(^1D) + O_2$$

$$\mathbf{Probe} \quad O(^1D) + CH_4 \longrightarrow OH(v', j') + CH_3$$

$OH(v', j')$ probed using LIF.

Use pulsed lasers (10^{-8} s) for both pump and probe steps.

Use low pressures and short pump-probe time-delay to avoid collisional energy transfer in OH.

Find significant population in all energetically accessible rovibrational states.

Example of an ***insertion reaction***. Forms highly rovibrationally excited $CH_3OH^\star$ which lives for a short time ($\leq$ a few picoseconds). See next Lecture.
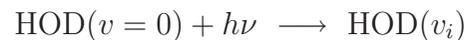
Laser excitation of reagents

Return to preparation of reagents for a moment.

Molecular beams are good for cooling molecules. In some cases rotational states can also be selected.

However, selection of vibrational levels is difficult.
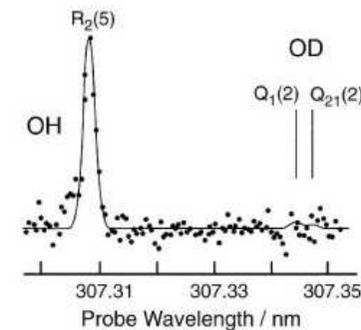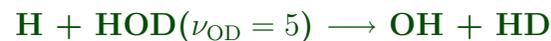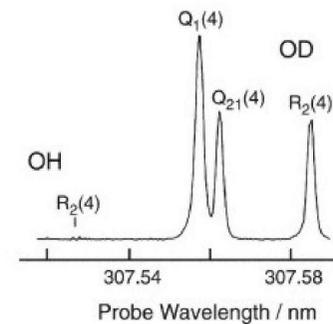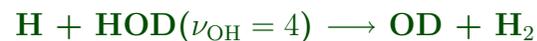
Can use **laser pump and probe** method.

Example

$$\mathrm{HOD}(v = 0) + h\nu \longrightarrow \mathrm{HOD}(v_i)$$

$$\mathrm{H} + \mathrm{HOD}(v_i) \longrightarrow \mathrm{OD/OH}(v', j') + \mathrm{H}_2/\mathrm{HD}$$

H atoms generated in a flow-system using a microwave discharge.

OH/OD probed by laser induced fluorescence.

E.g., Mode selective enhancement of reactivity

$$\mathbf{H + HOD(\nu_{OH} = 4) \longrightarrow OD + H_2}$$

$$\mathbf{H + HOD(\nu_{OD} = 5) \longrightarrow OH + HD}$$

Selectively break the vibrationally excited bond.

What about the effect of bending modes?

Is mode selectivity the exception or the rule (see IVR later)?
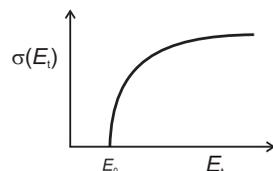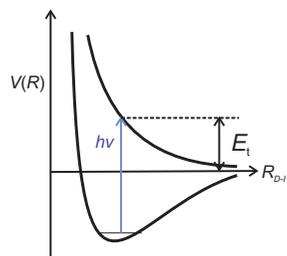
22

5. Models of reactive scattering

## Effect of Translational energy

Reactions with a barrier

DI $+ h\nu \longrightarrow$ D $+$ I

KE goes into light D atom (conservation of energy and momentum).

Vary KE of D by changing ν.

D $+$ C$_6$H$_{12}$ $\longrightarrow$ HD $+$ C$_6$H$_{11}$

Shape is dictated by energy and angular momentum conservation, $|\mathbf{L}| = \mu c_{\mathrm{rel}} b$.

Just above E_0 have enough energy to surmount barrier on PES, but need surmount **centrifugal barrier**. Only reactions at low b possible.
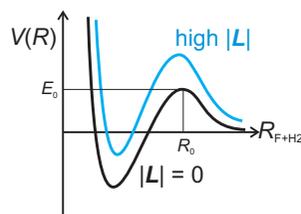
Consider an atom-atom collision (e.g., hard spheres).

Factor the translation energy (which is the total energy when the atoms are far apart) into radial and centrifugal components.
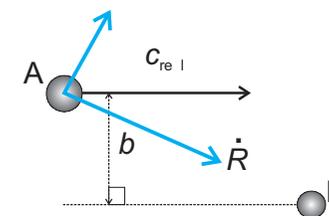
$$E_{\mathrm{t}} = \frac{1}{2}\mu\dot{R}^2 + E_{\mathrm{cent}} + V(R),$$

where (see Lecture 3)

$$E_{\mathrm{cent}} = \frac{L^2}{2I} = E_{\mathrm{t}}\frac{b^2}{R^2}.$$

Reaction can occur if the radial kinetic energy at the barrier is greater than zero, $\frac{1}{2}\mu\dot{R}^2 > 0$, i.e.

$$E_{\mathrm{t}} - E_{\mathrm{t}}\frac{b^2}{R_0^2} - V(R_0) > 0,$$

or

$$b_{\max}^2 = R_0^2\left(1 - \frac{E_0}{E_{\mathrm{t}}}\right).$$

Assuming $P(b) = 1$ for $0 \le b \le b_{\max}$, the cross-section can then be written

$$\sigma = \pi b_{\max}^2 = \pi R_0^2\left(1 - \frac{E_0}{E_{\mathrm{t}}}\right).$$

This is the **line-of-centres model** for the cross-section.

Reactions without a barrier

Already seen the $O(^1D) + CH_4$ insertion reaction. Ion-molecule reactions also often don't have barriers.

Treat the reactants as structureless atoms once more.

The long range potential for an ion - induced dipole interaction can be approximated

$$V(R) = -\frac{C_4}{R^4},$$

where C_4 is a constant.

Although there is no potential energy barrier, there is still a centrifugal barrier to surmount,

$$V_{\text{eff}} = E_t\frac{b^2}{R^2} - \frac{C_4}{R^4}.$$

By setting $dV_{\text{eff}}/dR = 0$, the location of the centrifugal barrier is at

$$R_0 = \left(\frac{2C_4}{E_t b^2}\right)^{1/2}.$$

Following the same recipe as above, at the centrifugal barrier we require $1/2\mu\dot{R}^2 > 0$ for reaction to occur. Obtain an expression for b^2_{max}, from which the cross-section can be obtained.

$$\boxed{\sigma = \pi b^2_{\text{max}} = \pi \left(\frac{4C_4}{E_t}\right)^{1/2}.}$$
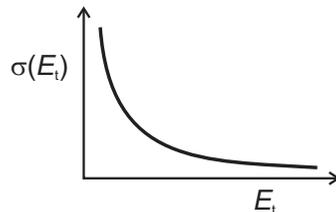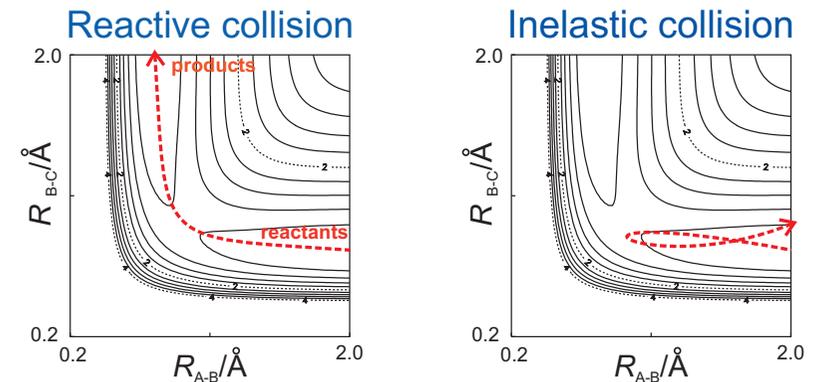

Known as Langevin model.

Potential energy surfaces (PESs)

To proceed further need to consider PES.

Just consider collinear collisions for now (no rotation) - see later.

$$H_A + H_B - H_C \longrightarrow H_A - H_B + H_C$$

Solve the classical laws of motion for a set of initial conditions - leads to a **classical trajectory** of the particles.

The two trajectories represent examples of a *reactive* collision and an *inelastic* (energy transfer) collision.
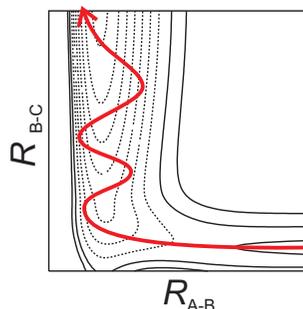
Analogy of ball rolling over a 3-D model of the PES.

Location of the barrier

Consider an exothermic A + BC reaction.

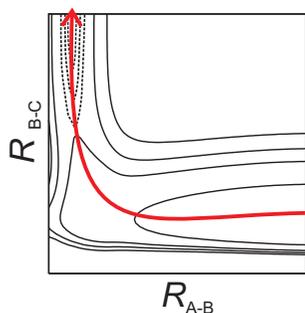### Early barrier - 'attractive release'

Barrier in entrance channel

Exothermicity released before A-B reaches equilibrium position.

Preferential release of exothermicity into product vibration (see O + CS and K + I$_2$).

Late barrier - 'repulsive' release

Barrier in exit channel

Exothermicity released as B-C extends.

Preferential release of exothermicity into product translation (see K + CH$_3$I).

Often see a mixture of the two (mixed release) types of trajectories.

## Running trajectories and microscopic reversibility

Look more carefully at trajectories.

Need to know the PES (either use a model PES, or for 'simple' reactions use fit to *ab-initio* calculated points). See Valence lectures.

Choose (randomly from a distribution) the starting positions and momenta of the atoms.

No quantization, but it is possible to predict rovibrational populations by 'binning' trajectories according to quantum mechanical momenta or energies.

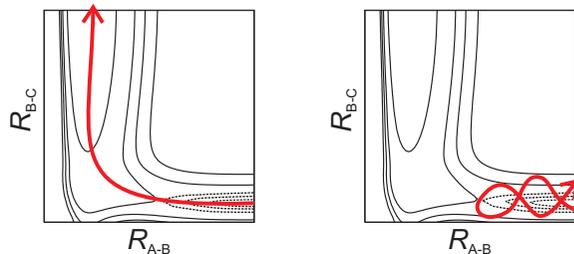Solve Newton's Laws (numerically) using $F_x = -\dfrac{\partial V}{\partial x}$.
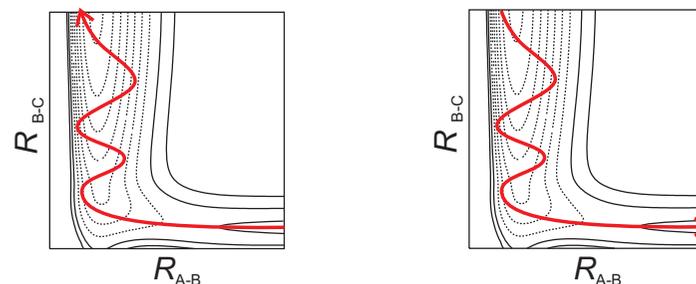
Note that trajectory is reversible (**microscopy reversibility**).

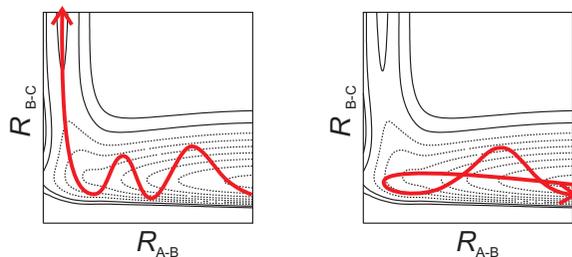## Polanyi's rules

Consider endothermic A + BC reactions

Early barrier

Kinetic energy effective in overcoming barrier (left)

Vibrational energy ineffective (right)

Late barrier

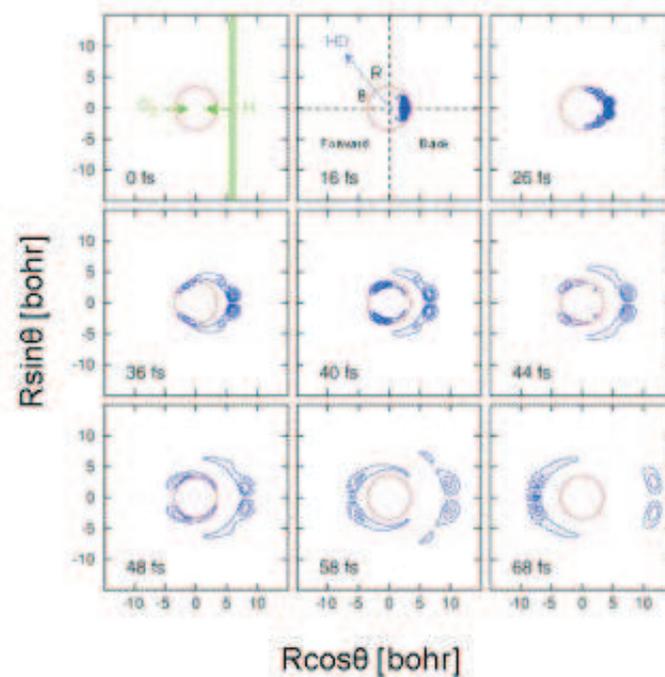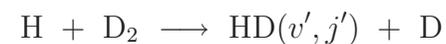Vibrational energy effective in overcoming barrier (left)

Kinetic energy ineffective (right)

K + HCl(v) and OH + H$_2$(v) provide examples of reactions with late barriers.

Quantum mechanical calculations

Possible for light systems.

Provides important information about role of zero point energy, tunnelling and other exotic QM effects.

$$\text{H} \; + \; \text{D}_2 \; \longrightarrow \; \text{HD}(v', j') \; + \; \text{D}$$

S.C. Althorpe and coworkers *Nature* **416** 67 (2002)

Importance of tunnelling in the F + H$_2$ reaction already discussed.

Role of kinematics

To preserve the model of a ball rolling a 3-D model of the PES need to take into account masses of reactants and products.

Instead of plotting the PES with 90° coordinates, the coordinates should be **skewed** at an angle β, defined for an A + BC reaction as

$$\cos^2 \beta = \frac{m_A m_C}{m_{AB} m_{BC}} \,.$$
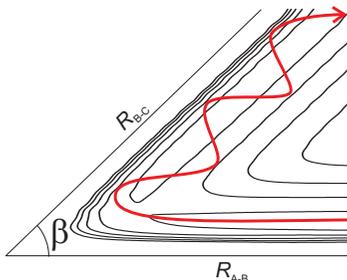
So for a reaction

$$\mathcal{L} \; + \; \mathcal{H}\mathcal{H}' \; \longrightarrow \; \mathcal{L}\mathcal{H} \; + \; \mathcal{H}' \qquad \beta \sim 90°$$

while for

$$\mathcal{H} \; + \; \mathcal{L}\mathcal{H}' \; \longrightarrow \; \mathcal{H}\mathcal{L} \; + \; \mathcal{H}' \qquad \beta \ll 90°$$

where $\mathcal{H}$ =a heavy atom, $\mathcal{L}$ =a light atom.

For example, for

$$\text{Cl} \; + \; \text{HI} \; \longrightarrow \; \text{HCl} \; + \; \text{I}$$

$\beta \; = \; 10.7°$. One finds 70% of the available energy in this reaction is channelled into vibrational excitation, in spite of the barrier being late.

Polanyi's 'rules' (and the reverse of them) only apply to reactions involving light attacking or departing atoms.

Angular momentum conservation

Again focus on A + BC reaction, and think about role of masses in context of angular momentum conservation.

Recall

$$\mathbf{J}_{\text{tot}} = \mathbf{j}_{BC} + \mathbf{L} = \mathbf{j}'_{AB} + \mathbf{L}' \,.$$

Take a reaction

$$\mathcal{H} \; + \; \mathcal{H}'\mathcal{L} \; \longrightarrow \; \mathcal{H}\mathcal{H}' \; + \; \mathcal{L} \,,$$

for which $\beta \sim 90°$, the mass combination favours $\mathbf{L} \gg \mathbf{j}_{BC}$, while for the products $\mathbf{j}'_{AB} \gg \mathbf{L}'$. Thus we can write

$$\mathbf{L} \; \longrightarrow \mathbf{j}'_{AB} \,,$$

i.e. **propensity for the reactant orbital angular momentum to be channelled into product rotational angular momentum** (see later).
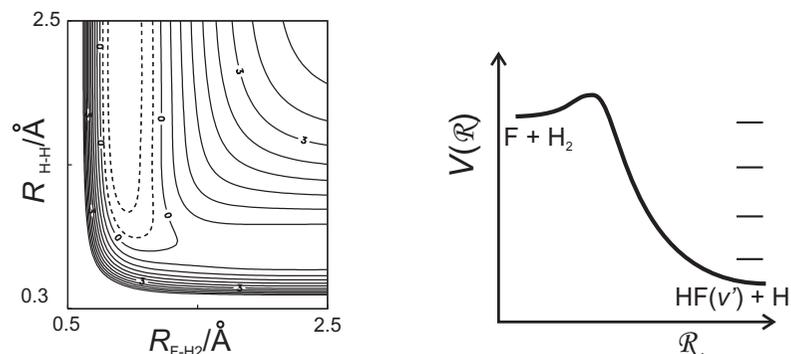
Similarly for the mass combination

$$\mathcal{H} \; + \; \mathcal{L}\mathcal{H}' \; \longrightarrow \; \mathcal{H}\mathcal{L} \; + \; \mathcal{H}' \,,$$

for which $\beta \ll 90°$, angular momentum conservation often reduces to

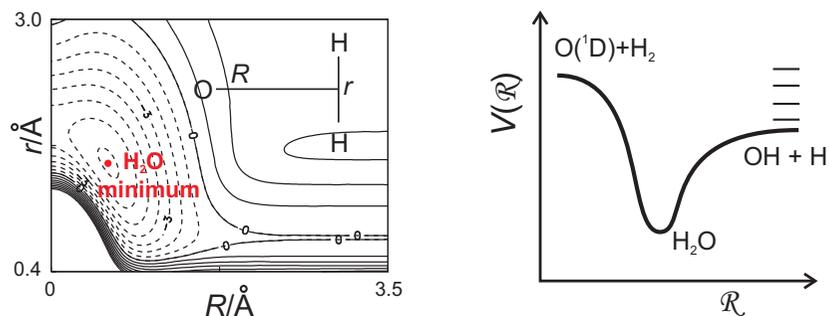$$\mathbf{L} \; \longrightarrow \mathbf{L}' \,,$$

i.e. **propensity for conservation of orbital angular momentum**.

Direct versus indirect reactions

So far considered only trajectories for **direct** processes.

What about trajectories on a PES with deep well. Formation of an intermediate **complex**.

Trajectories can get trapped in the well. If trapped for a long time relative to rotational period ($\sim 10\,\text{ps}$) recall you get a forward backward symmetric DCS.

Statistical products state distributions

If complex survives for many **vibrational periods** ($\sim 100\,\text{fs}$) the vibrational energy can become completely randomized.
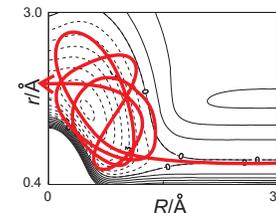
Process is known as **intramolecular vibrational redistribution, (IVR)**.

Under these conditions the product quantum states may also be randomly or **statistically** populated (i.e. every 'state' has an equal probability of being populated).

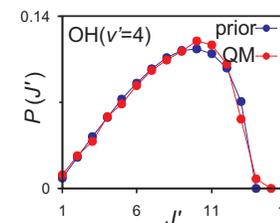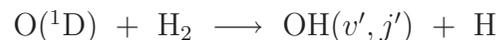Calculate most easily using **prior distribution**. Ignore angular momentum conservation.

Probability of finding J' is $(2J'+1)$

Probability of finding translational energy, E_t' is $\propto E_t^{1/2}$

Therefore

$$P(v', J') = (2J'+1)\left[E_{\text{avl}} - E_v' - E_r'\right]^{1/2},$$

where E_{avl} is the total energy available to the products.

$$O(^1D) \ + \ H_2 \ \longrightarrow \ OH(v', j') \ + \ H$$

6. Probing transition states

Measurement of the opacity function

Look at angular momentum constraints once more.

$$\text{Ba} + \text{HI} \longrightarrow \text{BaI} + \text{H}$$

Example of reaction with light departing atom for which $\mathbf{L} \rightarrow \mathbf{j}'$.
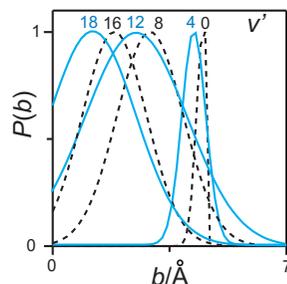
Measure distribution of product J', $P(J')$ (using LIF) at a well defined c_{rel} (in a molecular beam)

$$P(J') \equiv P(L)$$

But

$$|\mathbf{L}| = \mu c_{\text{rel}} b = \hbar \sqrt{L(L+1)} \simeq \hbar(L+1/2)$$
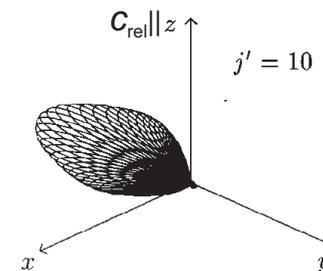
So $P(L)$ transforms directly into $P(b)$

Low impact parameter collisions lead to generation of the highest BaI vibrational excitation.
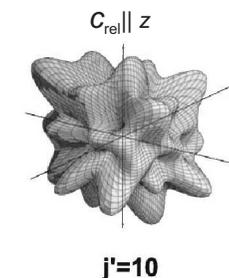
Angular momentum alignment

Another manifestation of angular momentum conservation. Again focus on A + BC reactions.

Angular momentum is a vector. What direction does $\mathbf{j}'$ point after reaction?

$$\text{H} + \text{D}_2 \longrightarrow \text{HD}(\mathbf{j}') + \text{D}$$

The zx-plane (the 'scattering' plane) contains both c_{rel} and c'_{rel}. Data imply the ***direct reaction is highly coplanar***.

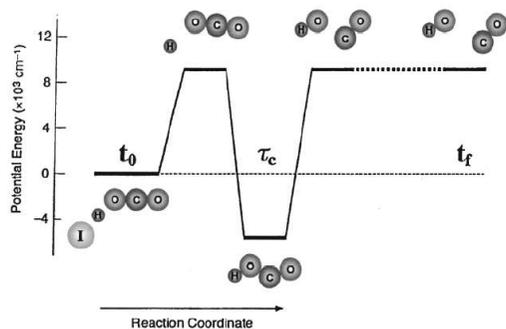$$\text{O}(^1\text{D}) + \text{HD} \longrightarrow \text{OH}(\mathbf{j}') + \text{D}$$

This ***insertion reaction behaves very differently - highly non-coplanar***.

These are calculated data, but can be measured using polarized light.

Aoiz and de Miranda and coworkers, *J. Chem. Phys.* **114**, 8329, (2001); **111**, 5368, (1999).

Half-collisions and controlling the impact parameter

Make **van der waals complex** of IH—OCO by co-expansion of HI and CO_2 in a molecular beam.

Start $H + CO_2$ reaction by laser flash photolysis of HI. Monitor OH products by LIF as a function of time.
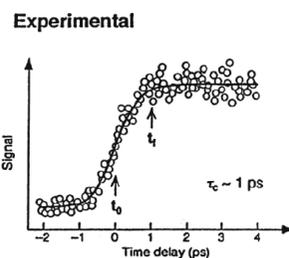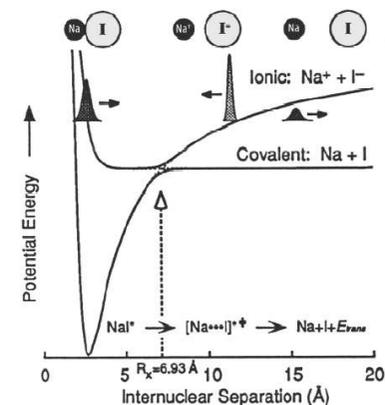

Reaction proceeds *via* HOCO complex. Survives for about 1 ps. Results can be modelled using a statistical model of reaction rates.
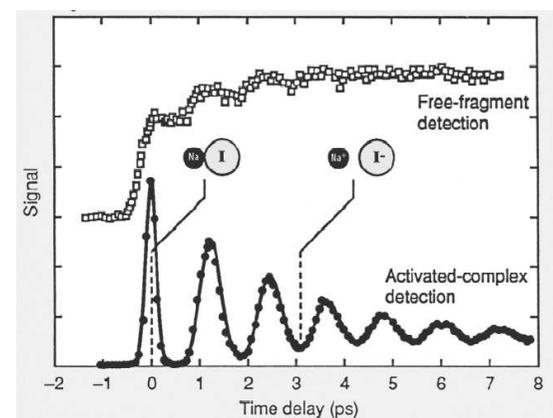
A.H. Zewail, *J. Phys. Chem. A* **104**, 5660, (2000)

Femtochemistry

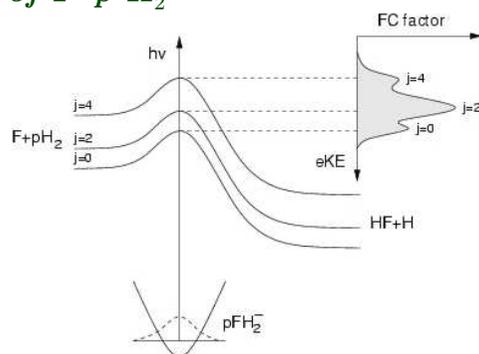Similar to a harpoon reaction, but in **half collision**.

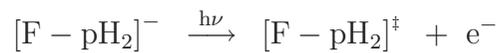Crossing between the ionic and covalent potential energy curves.

A.H. Zewail, *J. Phys. Chem. A* **104**, 5660, (2000)

Observing the Transition State Region.
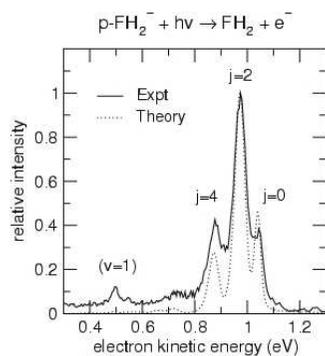
Photoelectron spectroscopy of F–p-H_2^-

Measure the kinetic energies of the ejected photoelectrons

$$[F - pH_2]^- \xrightarrow{h\nu} [F - pH_2]^{\ddagger} + e^-$$

The neutral products are produced in geometries very close to those of the transition state for the reaction $F + pH_2 \rightarrow HF + H$.

The spectrum suggests that the transition state is bent.

Manolopoulos and Neumark and coworkers, *Science*, **262**, 1852, (1993).