

Lecture-6

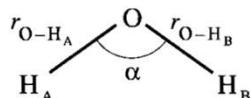
CSO202: Atoms, Photons & Molecules

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28–10. The Potential-Energy Surface for the Reaction $F(g) + D_2(g) \Rightarrow DF(g) + D(g)$ Can Be Calculated Using Quantum Mechanics

In Chapter 9, we learned that the potential energy of a diatomic molecule depends on only the distance between the two bonded atoms. Thus, the potential-energy surface for a diatomic molecule such as $D_2(g)$ or $DF(g)$ can be plotted in two dimensions by plotting the potential energy as a function of the bond length. The word “surface” is a misnomer in this case. A diatomic molecule has only one geometric parameter, the bond length. Using the term “potential-energy curve” when the potential energy depends on a single parameter and the word “surface” when the potential energy depends on more than one geometric parameter is more appropriate. Figure 28.15 shows the potential-energy curve for $D_2(g)$.

The potential energy of a polyatomic molecule depends on more than one variable because there is more than one bond length that can be varied. We will also need to specify the bond angle(s). For example, consider a water molecule. The geometry of a water molecule is completely specified by three geometric parameters, r_{O-H_A} , r_{O-H_B} , and the angle α between the two O–H bonds.



The potential energy of a water molecule is a function of these three parameters, or $V = V(r_{O-H_A}, r_{O-H_B}, \alpha)$. A plot of the complete potential-energy surface of a water molecule therefore requires four axes, one axis for the value of the potential energy and one axis for each of the three geometric parameters. The potential-energy surface is four-dimensional. Because we are limited to three dimensions for plotting functions, we cannot draw the entire potential-energy surface of a water molecule in a single plot.

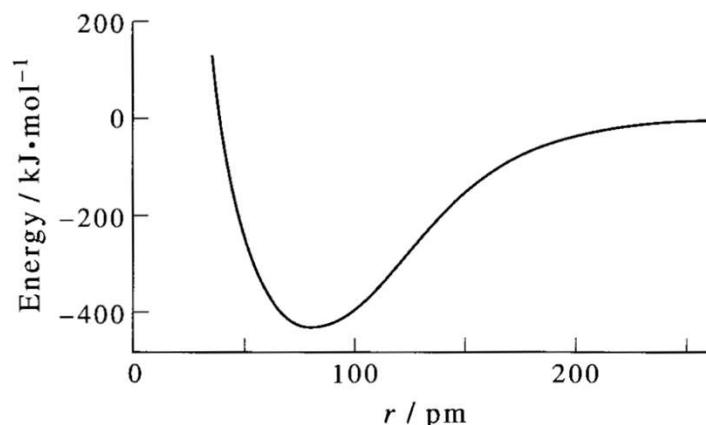
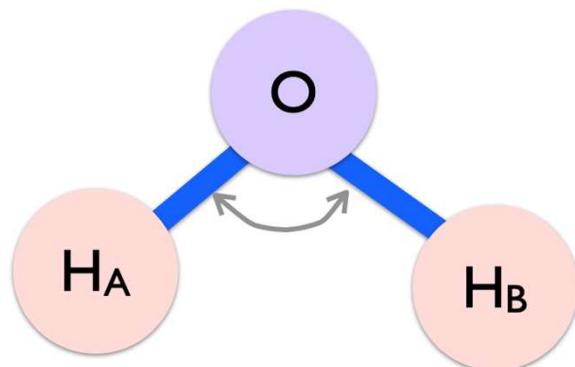


FIGURE 28.15

The potential-energy curve of $D_2(g)$. The zero of energy is defined to be that of the two separated atoms. The minimum of the potential-energy curve corresponds to the equilibrium bond length of the $D_2(g)$ molecule.

We can, however, draw parts of the potential-energy surface. We can fix one of the geometric parameters, for example, the angle α , and then draw a three-dimensional plot of $V(r_{O-H_A}, r_{O-H_B}, \alpha = \text{constant})$. Such a plot is a cross-sectional cut of the full potential-energy surface. A cross-sectional plot teaches us how the potential energy of the molecule changes when we vary some of the geometric variables while holding others constant. For example, a three-dimensional plot of $V(r_{O-H_A}, r_{O-H_B}, \alpha = \text{constant})$ as a function of r_{O-H_A} and r_{O-H_B} tells us how the potential energy of a water molecule changes when the bond lengths r_{O-H_A} and r_{O-H_B} are varied at a constant bond angle of α . If we made a series of cross-sectional plots for different values of α , we could see how the potential energy depends upon the bond angle.

- Now let us think of constructing a potential energy surface for a water molecule: again, since the internuclear distances are only important, we can easily see that we need three distances to plot the potential energy surface. $r(OH_A)$, $r(OH_B)$, $r(H_AH_B)$ in three axes and U along the fourth axis. Such a 4-D plot is difficult to make and visualize. In such case, we can fix one of the three coordinates, and see how the potential change with respect to the other two, and then repeat it for other values of the fixed coordinate.



Note: instead of $r(H_AH_B)$ we can also use the bond angle H_AOH_B

- $r(OH_A), r(OH_B), r(H_AH_B), U$

OR

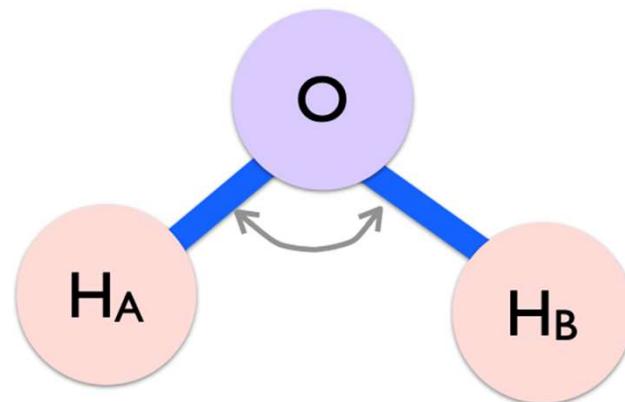
$$r(OH_A), r(OH_B), \theta(H_AOH_B), U$$

$\Rightarrow 4D$

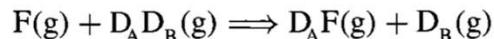
- Dimensional reduction

$r(OH_A), \theta(H_A-O-H_B), U$ for some
given value of $r(OH_B)$

$\Rightarrow 3D$



We encounter a similar limitation in viewing the potential-energy surfaces for simple chemical reactions as we did for a water molecule. Let us return to a discussion of the chemical reaction



where the subscripts A and B are used so that we can differentiate between the two deuterium atoms. When the reactants are at infinite separation, there are no attractive or repulsive forces between the fluorine atom and the $D_2(g)$ molecule, so the potential-energy surface for the reaction is the same as that for an isolated $D_2(g)$ molecule. Likewise, when the products are at infinite separation, the potential-energy surface for the reaction is the same as that for the isolated $DF(g)$ molecule. As the reaction occurs, however, r_{DF} , the distance between the fluorine atom and D_A , decreases and r_{D_2} , the distance between D_A and D_B , increases, and the potential energy depends on both distances. The potential energy also depends on the angle at which the fluorine atom approaches the $D_2(g)$ molecule. We define the collision angle β between the fluorine atom and $D_2(g)$ molecule to be that between the lines that lie along the $F-D_A$ and D_A-D_B bonds. In Figure 28.16, we show three different ways the fluorine atom can approach the $D_2(g)$ molecule: linear ($\beta = 180^\circ$), bent ($\beta = 135^\circ$), and perpendicular ($\beta = 90^\circ$).

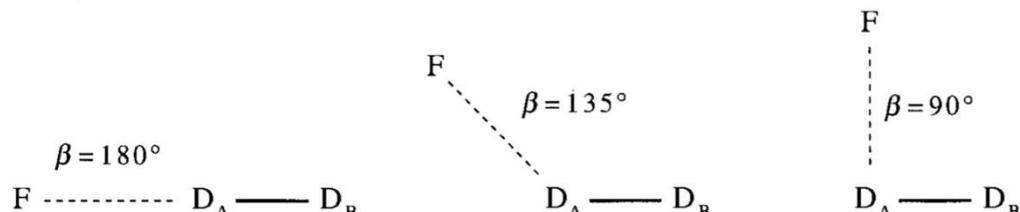
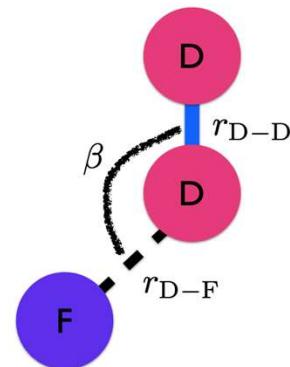


FIGURE 28.16

Three different collision angles, β , for the reactants $F(g) + D_2(g)$.

Because the potential-energy surface for this reaction depends on two distances (r_{DF} and r_{D_2}) and one collision angle (β), a four-dimensional coordinate system is needed to plot the complete surface. To view the potential-energy surface, we have to fix the value of one of the geometric parameters and then plot the dependence of the potential energy on the two remaining variables. We could make a series of such plots for different values of the fixed variable to see how the potential surface depends on all three geometric parameters.

PES for D_2+F reaction



- At least 4D PES
- PES for various values of β

The potential-energy surface for a chemical reaction can be calculated using the electronic structure techniques for polyatomic molecules. By performing such a calculation for a number of different nuclear configurations, we can obtain the potential energy as a function of the nuclear coordinates.

- Since dynamics is influenced by the underlying potential: Like in the case of a harmonic oscillator or any other moving object, we may worry about the underlying potential energy felt by the nuclei when they are moving during the process of a reaction.

For example, in case of harmonic oscillator, we could get a better physical understanding of the reaction on looking at the potential energy as a function of nuclear coordinates

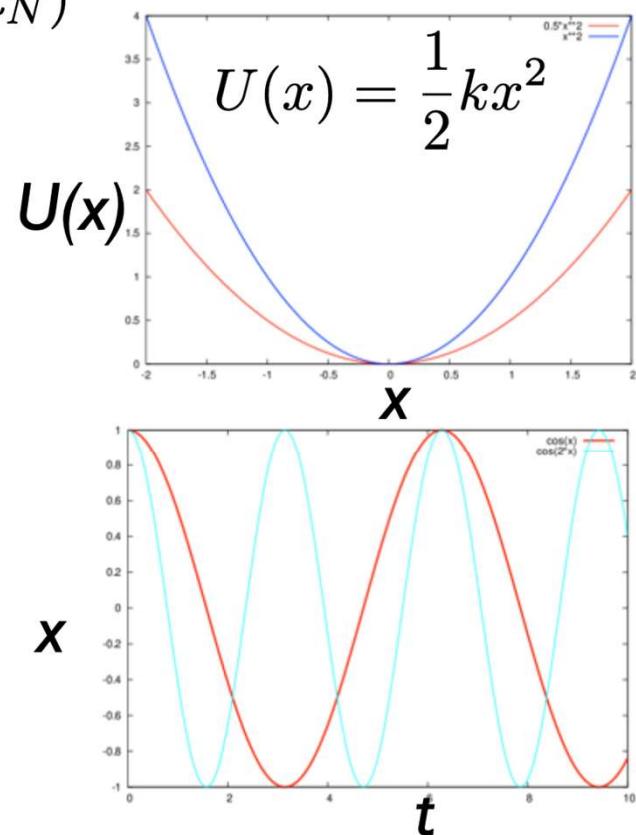
But how do we obtain this potential?

- Classical Motion:

$$E = K(\mathbf{P}_1, \mathbf{P}_2, \dots, \mathbf{P}_N) + U(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$$

$$= \sum_{I=1}^N \frac{\mathbf{P}_I^2}{2M_I} + U(\mathbf{R}_1, \dots, \mathbf{R}_N)$$

- Consider the example of a 1D harmonic oscillator: the way a harmonic oscillator is oscillating depends on the underlying potential energy surface; for e.g. as the curvature (i.e. parameter k) of the potential increases frequency of oscillation increases



- Let us look at the full quantum mechanical description of a molecular system

$$E = \langle \Psi | \hat{H} | \Psi \rangle \equiv \int d\tau \Psi^*(\tau) \hat{H} \Psi(\tau)$$

total energy ↓ total wavefunction

Hamiltonian: nuclear K.E. + electronic K.E. + electron-nucleus Coulombic interaction + electron-electron Coulombic interaction + nucleus-nucleus Coulombic interaction

Electronic motions are much faster than the nuclear motion. This is because electrons are three orders of magnitude lighter than nucleus. Thus for a nucleus, details of the electronic motion are irrelevant. Nuclei only feel the electrostatic interactions of the entire electronic cloud not of individual electrons.

Electronic distribution will adjust instantaneously with small changes in the nuclear motion.

This timescale (also called **adiabatic difference**) in the motion of nuclei and electrons allows us to solve for the electronic part of the Schrodinger equation separately, for (a given) stationary nuclear configuration



flies over elephant's head: elephant is not worried about the details of the flies flying over its head; but it certainly feels them as a whole (as a cloud)! As elephant moves, flies adjust to its movement very fast (as electron does it with nucleus)

**This is called the
Born-Oppenheimer
Approximation**

Born–Oppenheimer approximation

$$\Psi_{\text{total}} = \Psi_{\text{electronic}} \times \Psi_{\text{nuclear}}$$

- Computation of the energy and wave function of a molecule
- Born–Oppenheimer approximation allows the wave function of a molecule to be broken into its electronic and nuclear motions
- $\Psi_{\text{total}} = \text{product function}$

Schrödinger equation

Describes how the quantum state of a physical system changes in time

$$H \psi = E \psi$$

For a general quantum system

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H} \Psi(\mathbf{r}, t)$$

i **imaginary unit**

$\Psi(\mathbf{r}, t)$ **wave function**

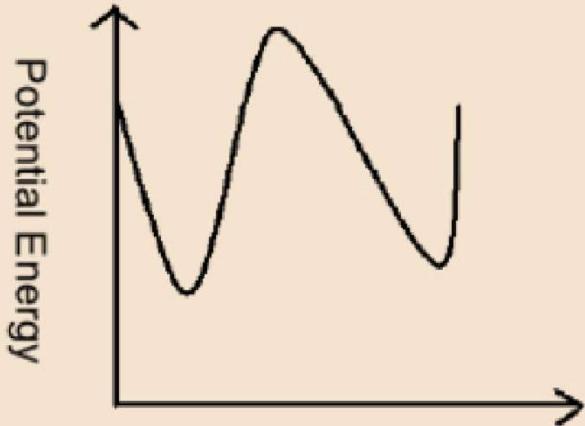
\hbar **Planck constant**

\hat{H} **Hamiltonian operator**

It's the Right time to define the Potential Energy Surface. . .

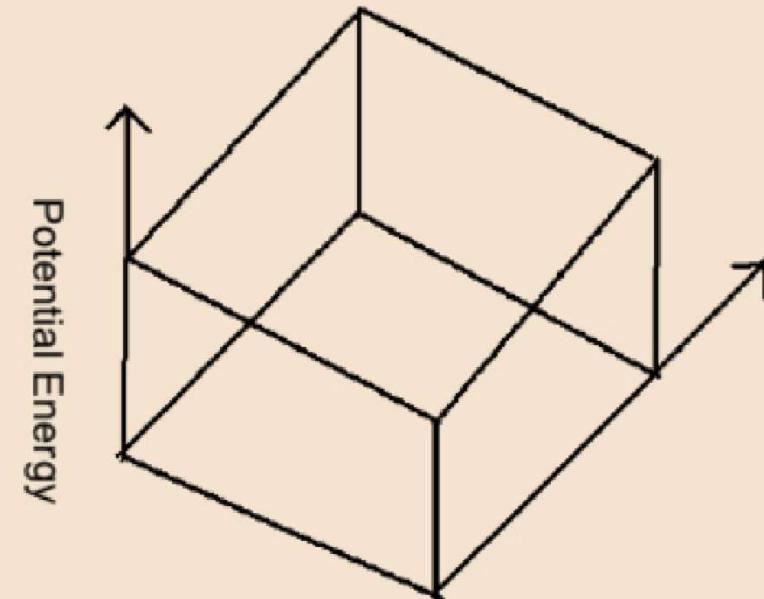
A geometric hyper surface on which the potential energy of a set of reactants is plotted as a function of the coordinates representing the molecular geometries of the system

A PES displays the energy of a molecule as a function of its geometry



Geometric Coordinate
e.g. bond length

1-D



Geometric Coordinates
e.g. bond length, bond angle

3-D

Using BO approximation (*details are not required for the purpose of the course*), one can identify that the **electronic energy** of the system (which also includes the nuclear-nuclear interaction) is identical to the potential energy felt by the nucleus for its motion (in the absence of any external fields)

$$\begin{aligned}\text{potential energy for nuclear motion} &= U(\mathbf{R}_1, \dots, \mathbf{R}_N) \\ &= E_{\text{ele}}(\mathbf{R}_1, \dots, \mathbf{R}_N)\end{aligned}$$

Electronic Hamiltonian: ~~nuclear K.E.~~ + electronic K.E. + electron-nucleus Coulombic interaction + electron-electron Coulombic interaction + nucleus-nucleus Coulombic interaction

$$\equiv \left\langle \psi_{\text{ele}} \left| \hat{H}_{\text{ele}} \right| \psi_{\text{ele}} \right\rangle$$

potential energy can thus be obtained by
solving the integral

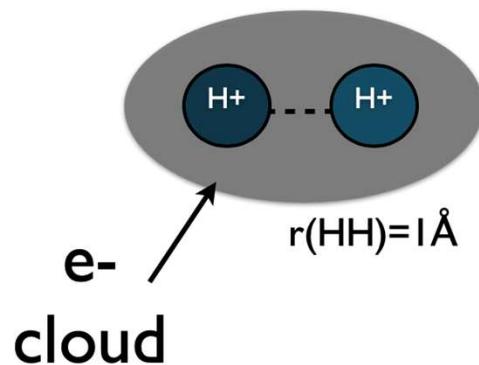
$$U(\mathbf{R}_1, \dots, \mathbf{R}_N) = \left\langle \psi_{\text{ele}} \left| \hat{H}_{\text{ele}} \right| \psi_{\text{ele}} \right\rangle$$

This integral has to be solved for a given set of nuclear positions.

Various techniques are available to solve such an integral (approximations are required here too!): some of the most popular methods include Hartree-Fock theory and Density Functional theory

Example of H_2^+

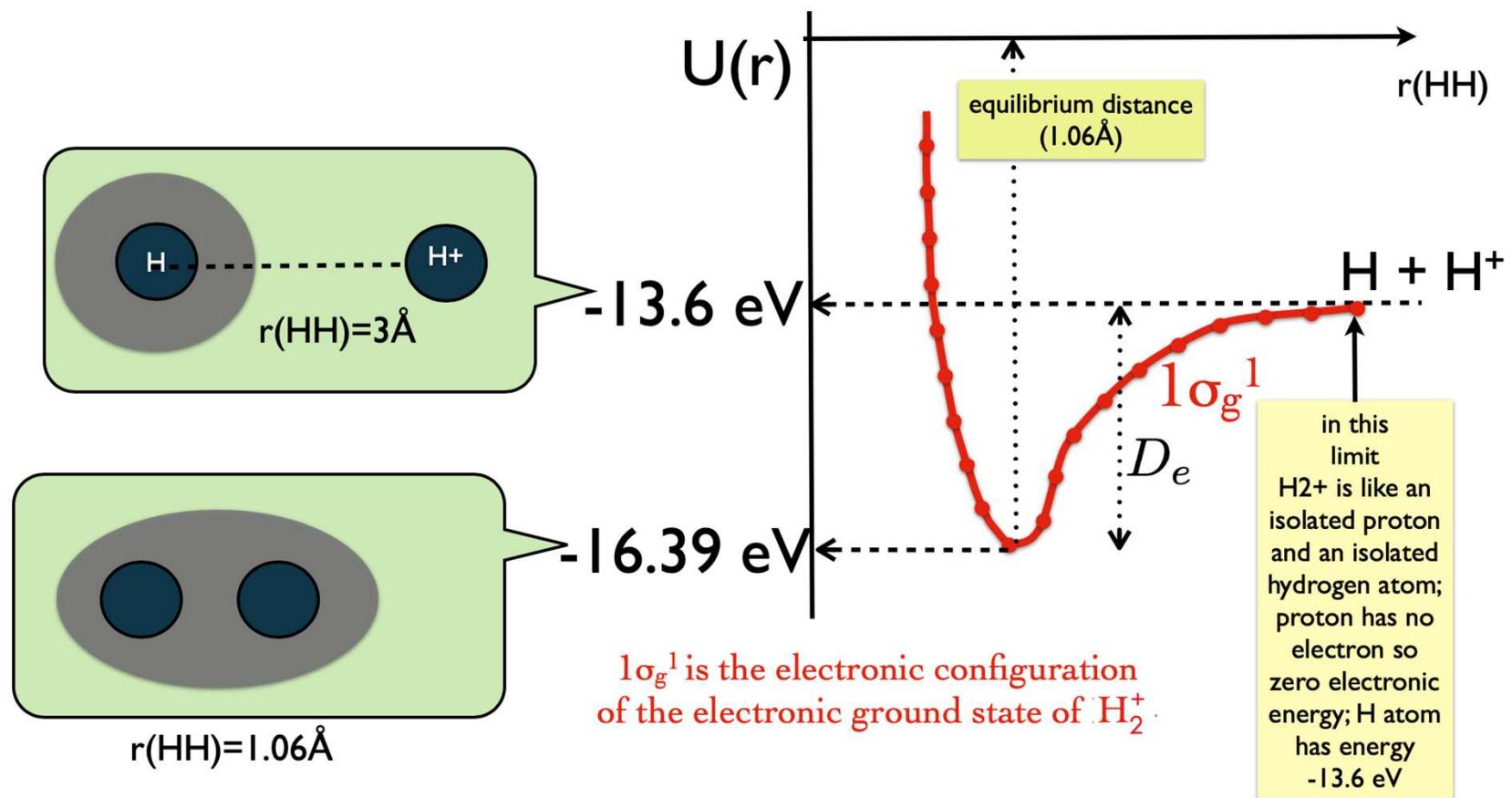
- Let us take a simple case H_2^+ (1 e- & 2 nuclei)

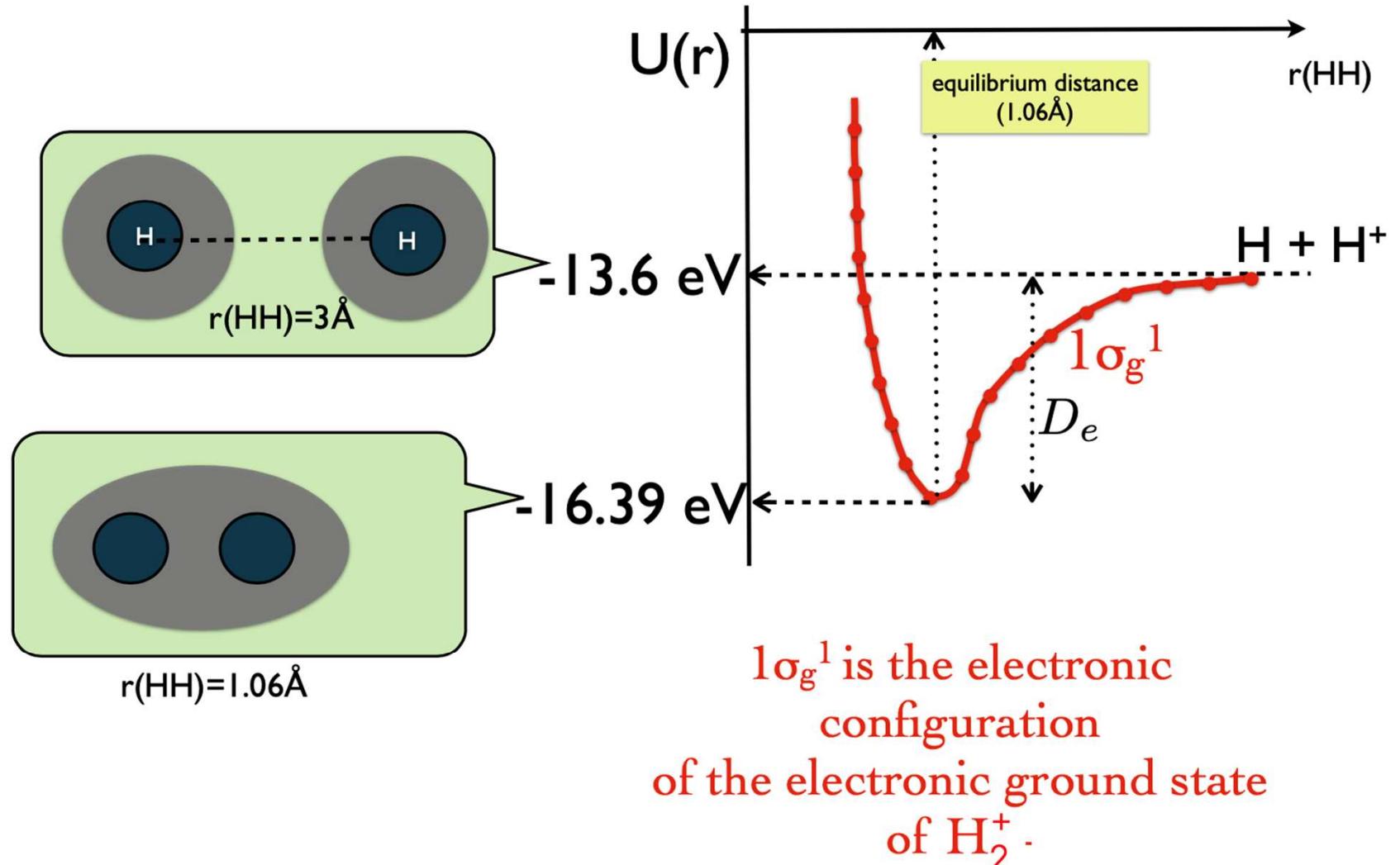


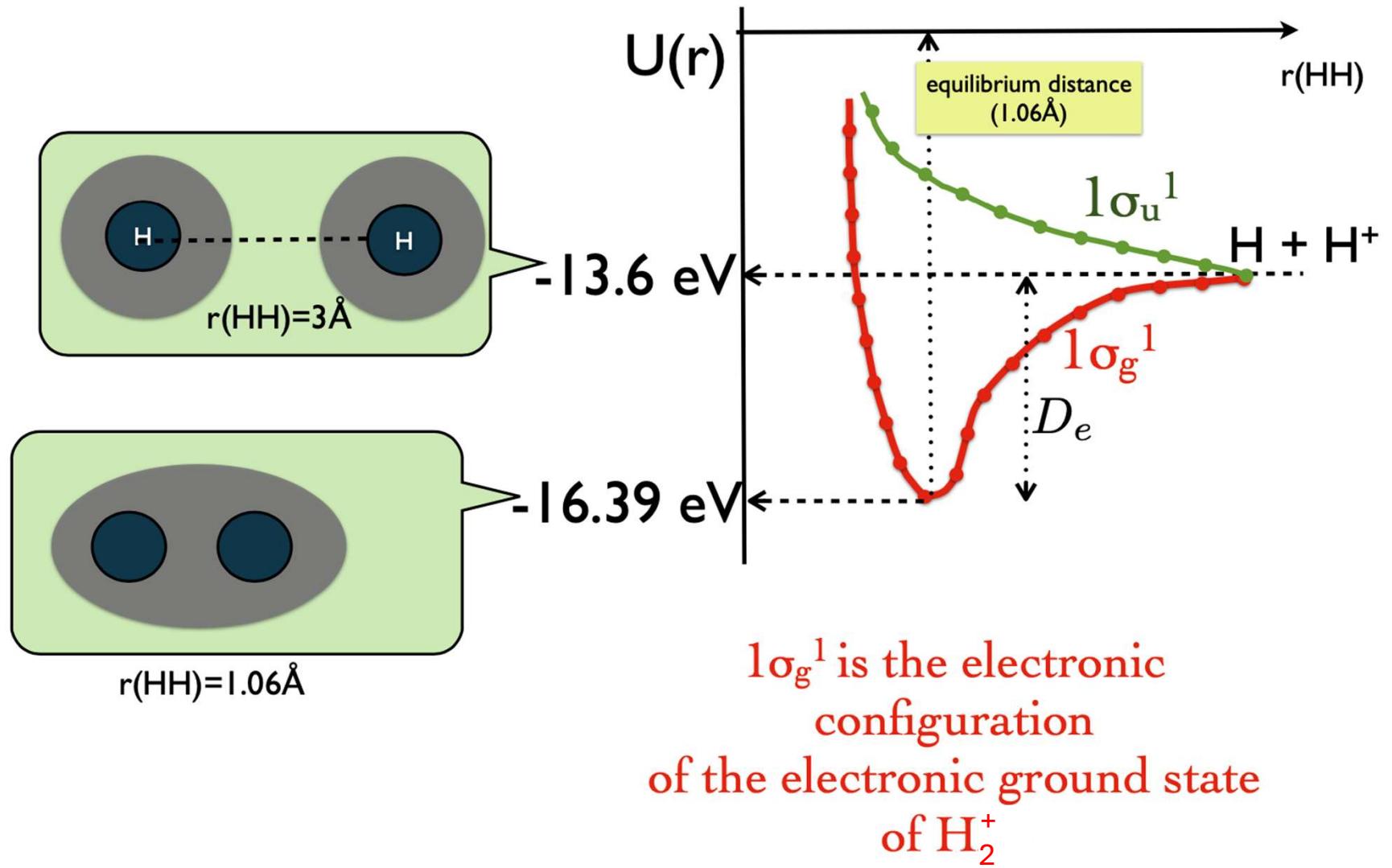
For a given distance, we can solve the electronic Schrödinger equation and obtain the electronic energy. As explained before, this will be equal to the potential felt by the nuclear motion

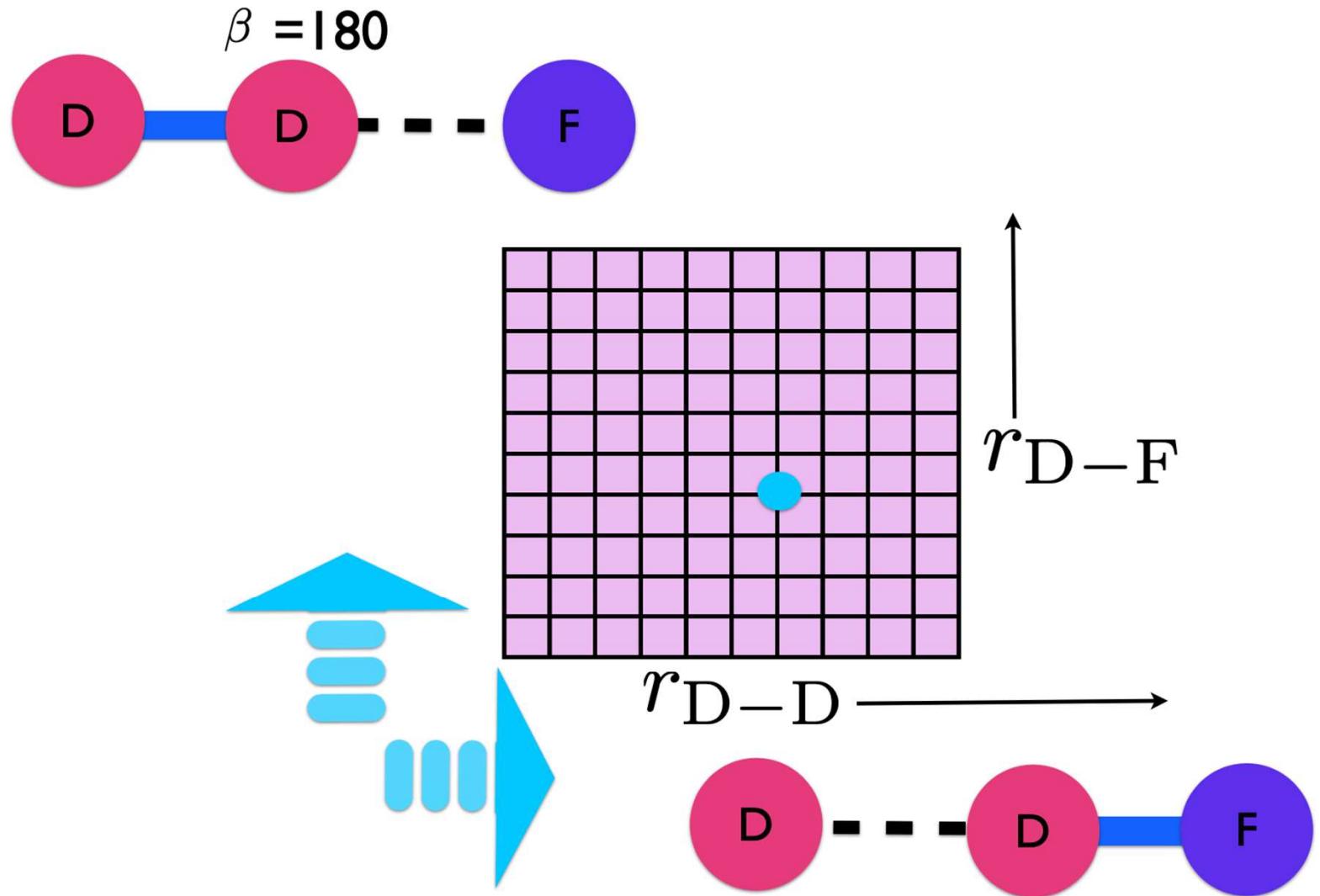
This energy depends only on the internuclear distance, and not on the actual position vector of the nucleus. This is because, the nuclear coordinates dependent terms in the electronic Hamiltonian have only coulombic interactions (between nucleus-electrons & nucleus-nucleus)

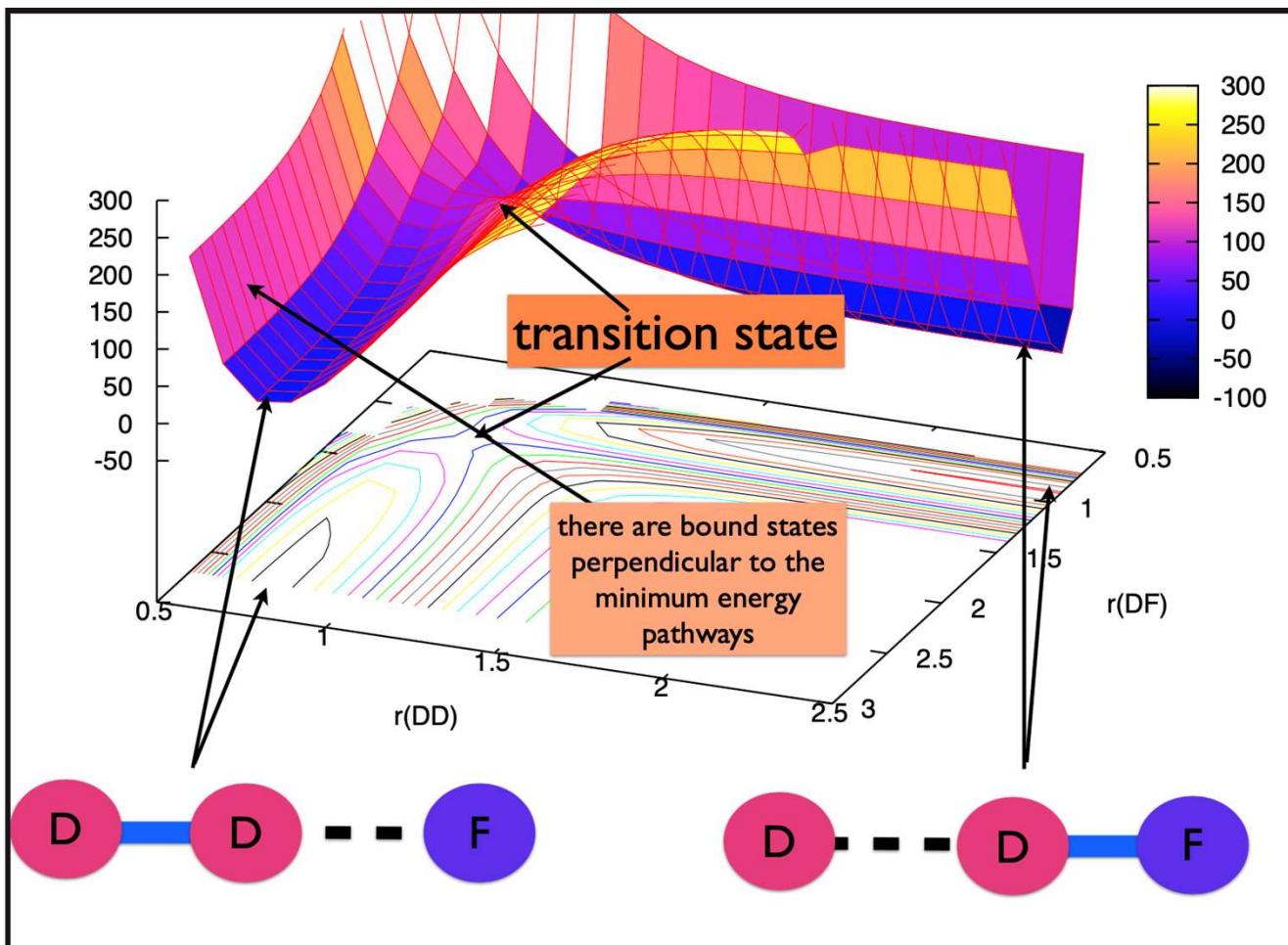
If we repeat this exercise and obtain potential energy for various distances of nucleus, we will get a potential energy surface/curve (like in the case of the harmonic oscillator)

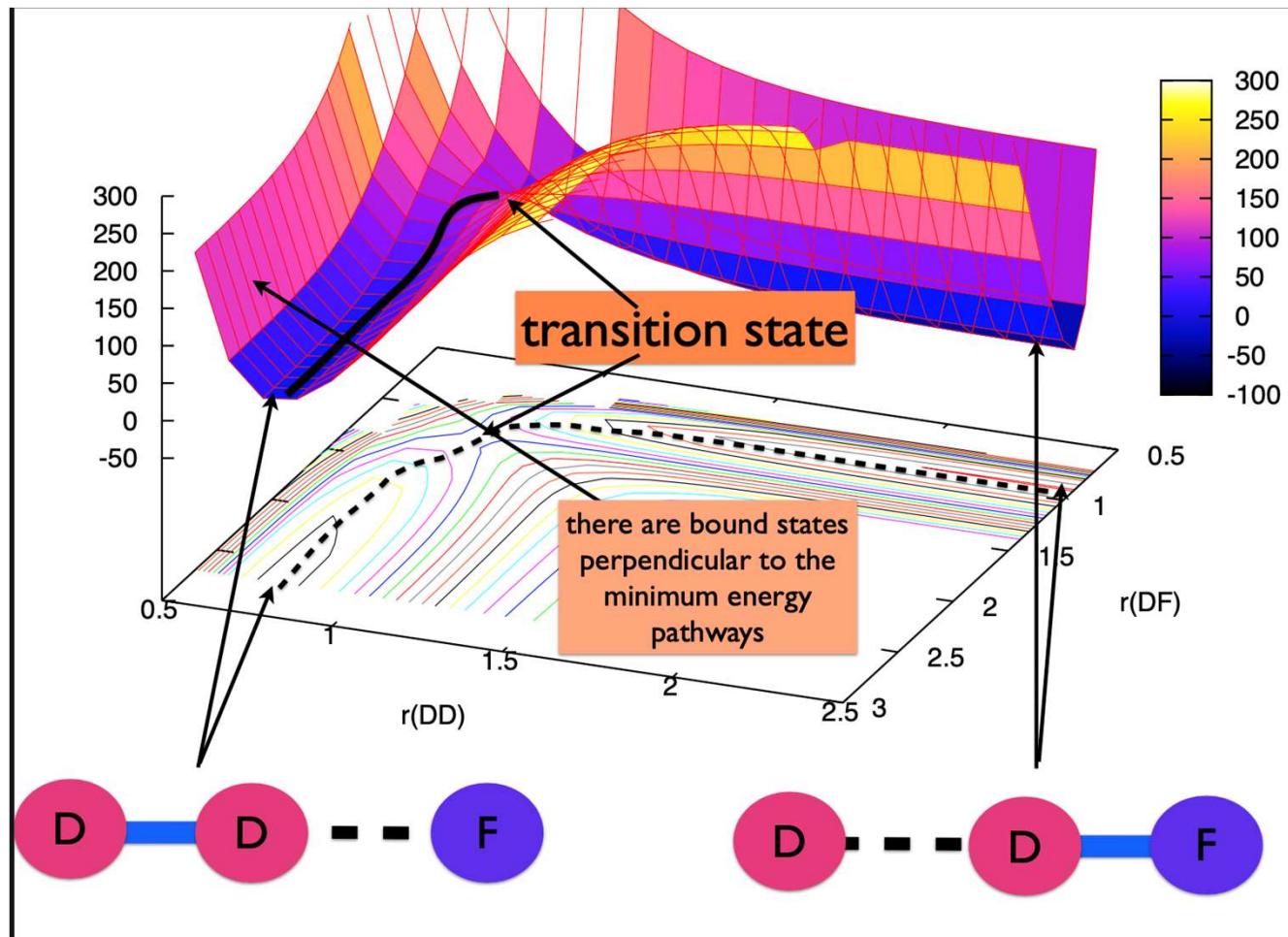


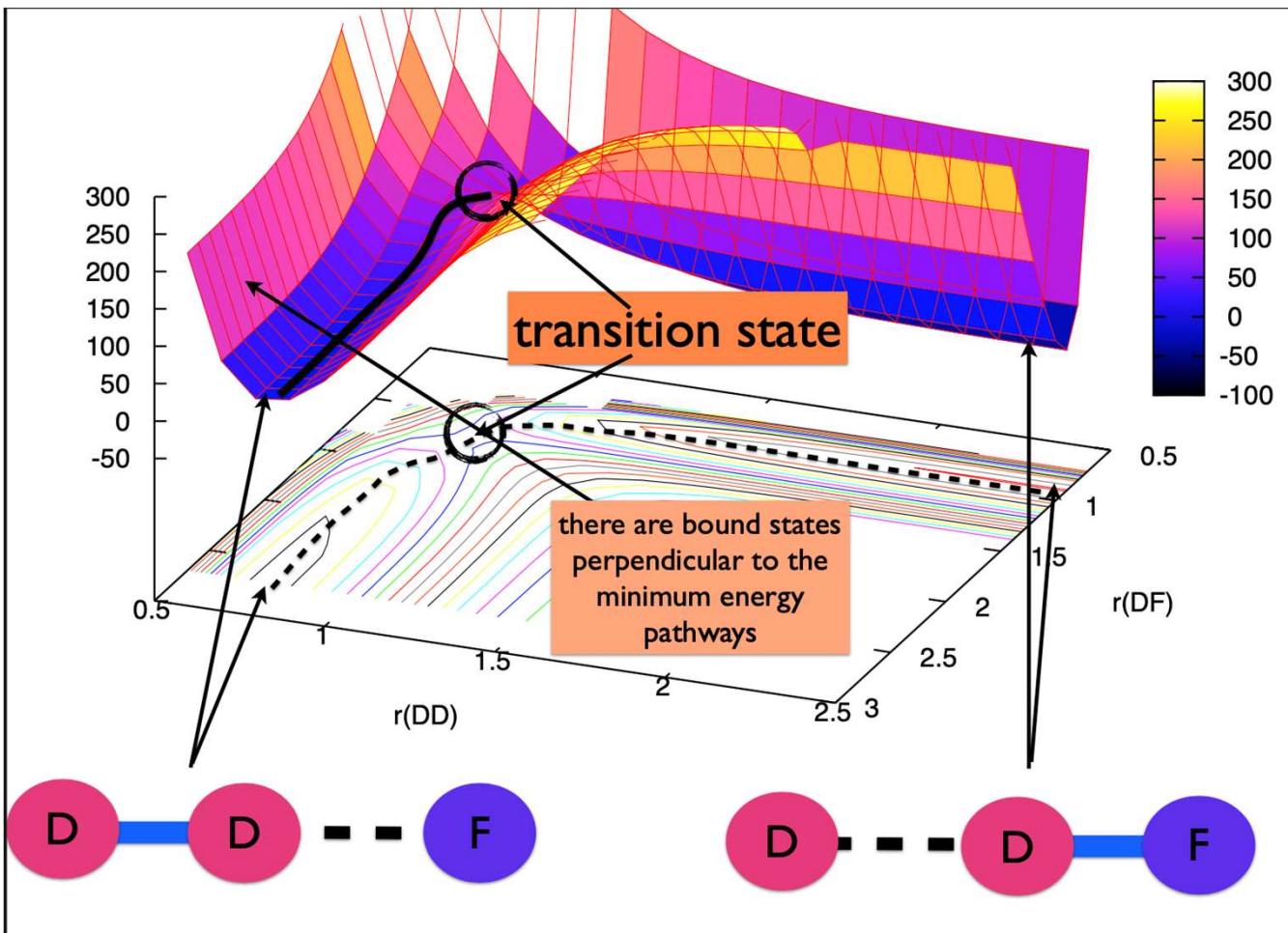


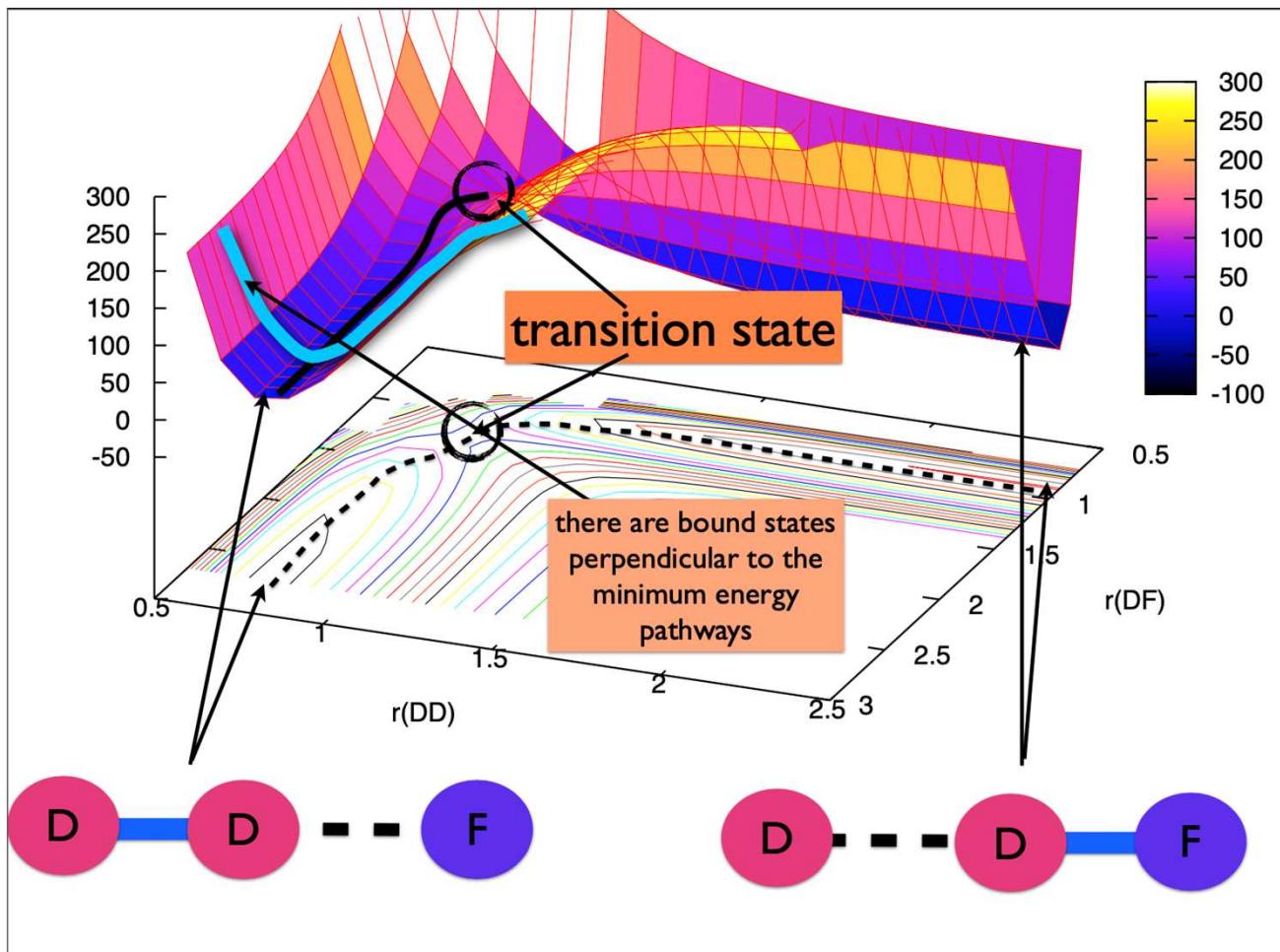


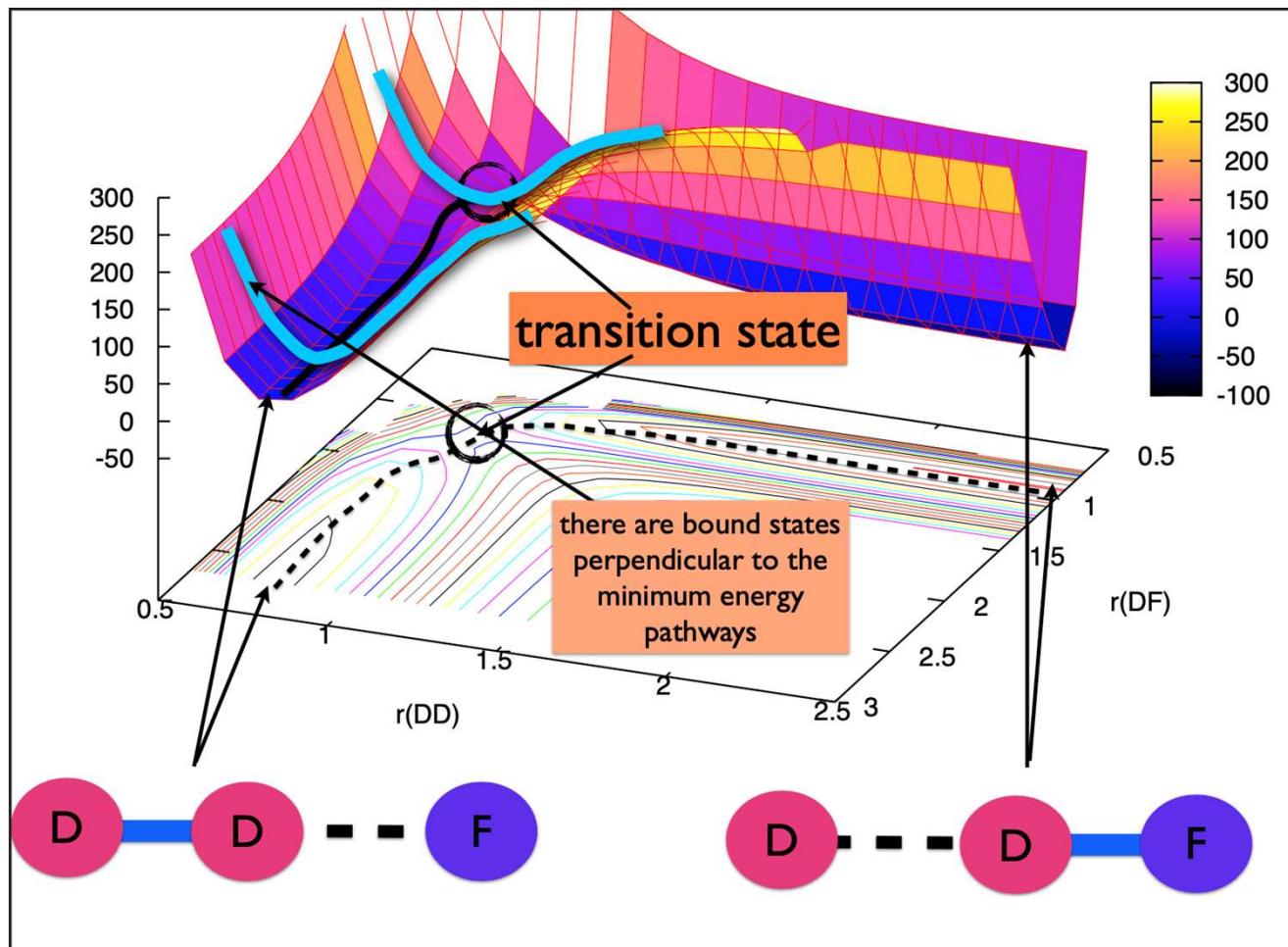












Contour Diagram of PES

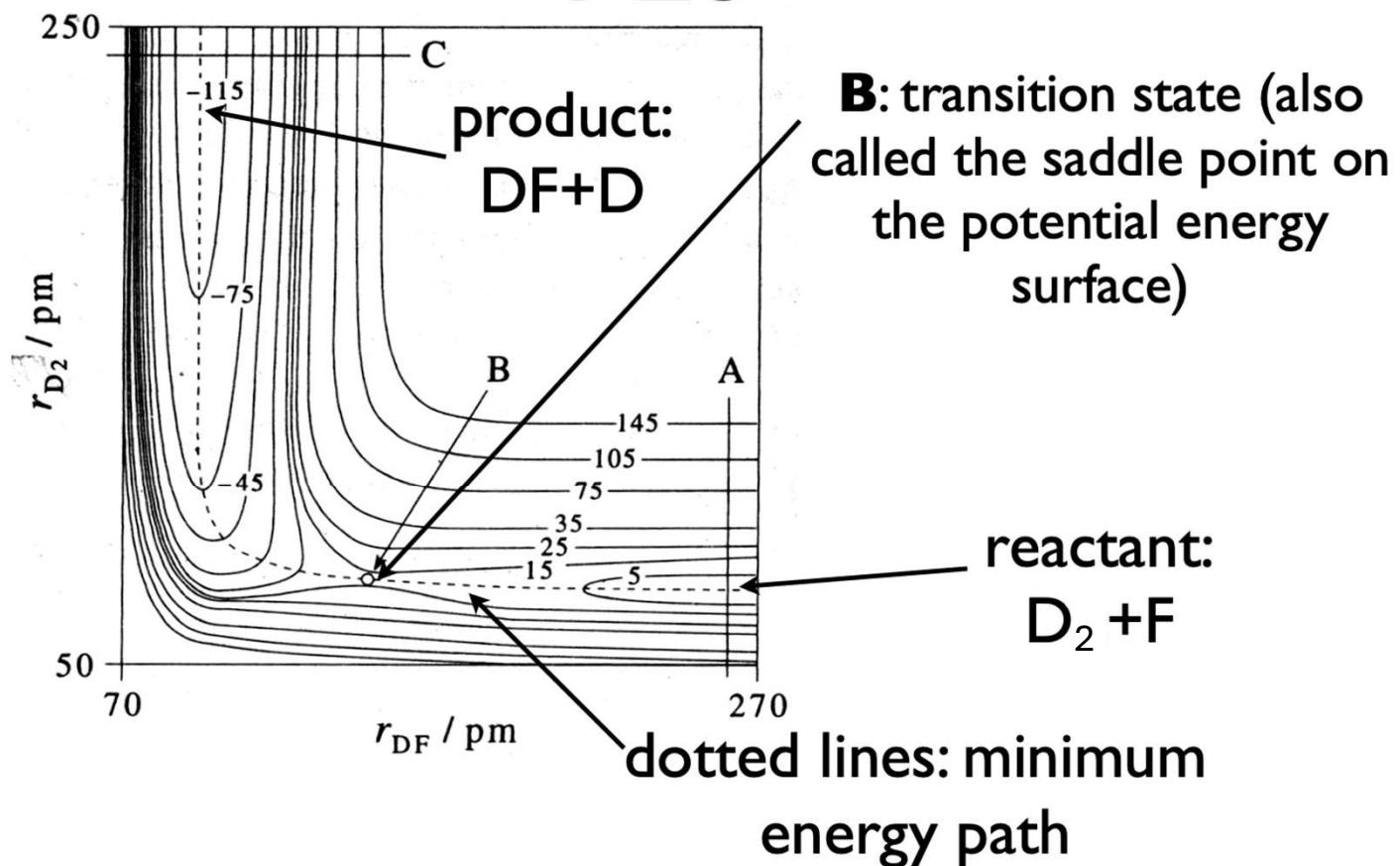
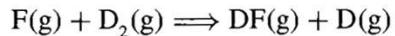


Figure 28.17

presents a contour diagram of the calculated potential-energy surface for the reaction



where the collision angle β is set to 180° , the experimental value determined from the crossed-molecular beam data (see Section 28–8). Such a geometry is said to be collinear. Each line in the contour map corresponds to a constant value of the energy. The zero of energy has been arbitrarily assigned to the reactants at infinite separation.

At $r_{DF} = A$ in Figure 28.17, the reactants are at a large separation, and the potential-energy surface is identical to the potential-energy curve for an isolated $D_2(g)$ molecule and $F(g)$ atom. In other words, if we plotted the cross-sectional plot of this surface $V(r_{D_2}, r_{DF}, \beta = 180^\circ)$ as a function of r_{D_2} , we would obtain Figure 28.15. Likewise, at $r_{D_2} = C$ in Figure 28.17, the products are at a large separation and a cross-sectional plot of $V(r_{D_2}, r_{DF}, \beta = 180^\circ)$ as a function of r_{DF} is identical to the potential-energy curve for an isolated $DF(g)$ molecule.

Let's now follow the minimum energy path from the reactants to the products, given by the dashed line in Figure 28.17. We see that as the reactants approach one another, the distance r_{D_2} remains fairly constant, the distance r_{DF} decreases, and the potential energy increases, reaching a maximum at point B. After passing through point B, the products have been formed, the distance r_{DF} decreases slightly and then remains constant, the distance r_{D_2} increases, and the potential energy decreases. The calculated potential-energy surface has an energy barrier between the reactants and products. The minimum height of this energy barrier (about $7 \text{ kJ}\cdot\text{mol}^{-1}$) occurs at point B, which is called the *transition state*. The transition state separates the reactants from the products. It sits at a unique point on the potential-energy surface. If we follow the minimum energy path from the transition state to either the separated reactants or the separated products, the energy decreases. If we move away from the transition state in the direction perpendicular to this minimum energy path, the energy increases. Thus, in one direction, the transition state is an energy maximum; in the perpendicular direction, the transition state is an energy minimum. Such points are called *saddle points* because the surface in the vicinity of the point has the shape of a saddle. The transition state for a chemical reaction usually sits at a saddle point on the potential-energy surface.

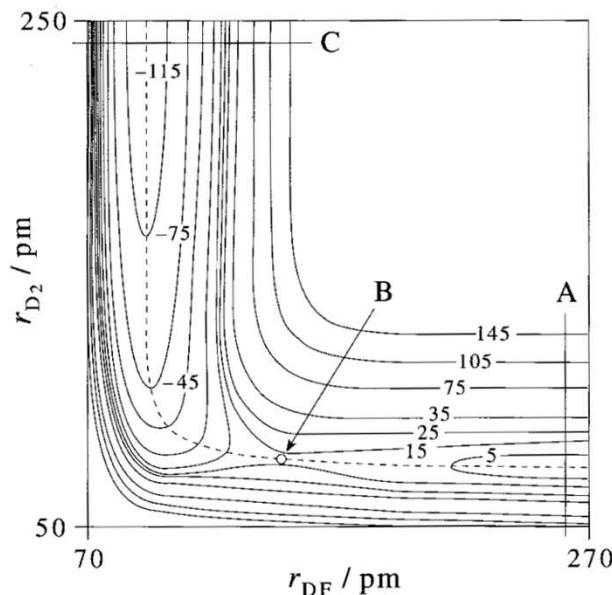


FIGURE 28.17

An energy contour map for the reaction $F(g) + D_2(g) \rightarrow DF(g) + D(g)$ at a collision geometry of $\beta = 180^\circ$, using the Born-Oppenheimer approximation to calculate the potential-energy surface. The numbers for the energy contours are in units of $\text{kJ}\cdot\text{mol}^{-1}$. The zero of energy is defined as the infinitely separated reactants. Point B is the location of the transition state of the reaction. The cross-sectional cuts through this surface indicated by the lines at A and C correspond to potential-energy curves for the isolated $D_2(g)$ and $DF(g)$ molecules, respectively. The dashed line is the minimum energy pathway for the reaction.

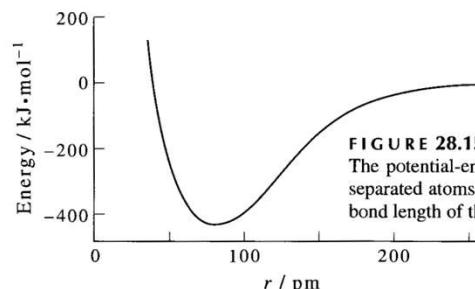


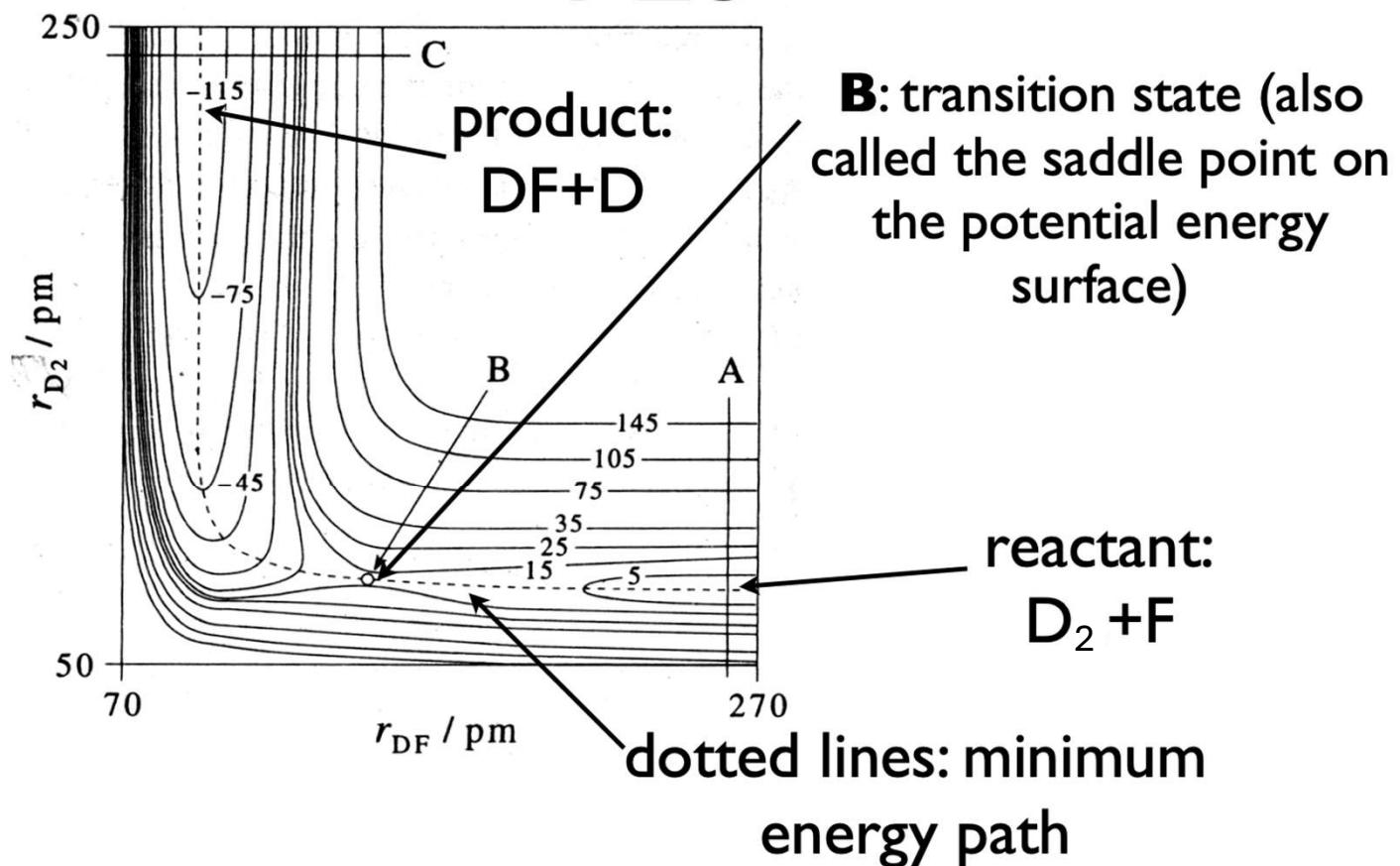
FIGURE 28.15

The potential-energy curve of $D_2(g)$. The zero of energy is defined to be that of the two separated atoms. The minimum of the potential-energy curve corresponds to the equilibrium bond length of the $D_2(g)$ molecule.

Mysteries of Lee's Experiments which we would like to solve:

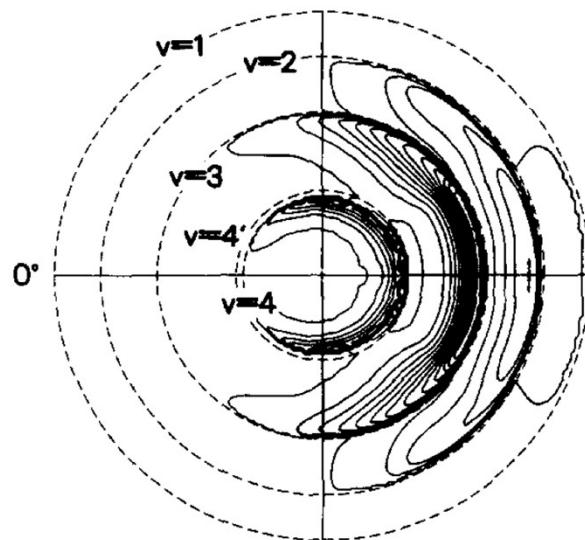
1. Why is the $D_2 + F$ reaction rebound?
2. Why is there a forward flux seen when the collision energy is increased? Why is this forward flux only observed for $v=4$?
3. Why is the population of the DF products higher for $v=3$ (and $v=4$ for some collisional energy)?

Contour Diagram of PES

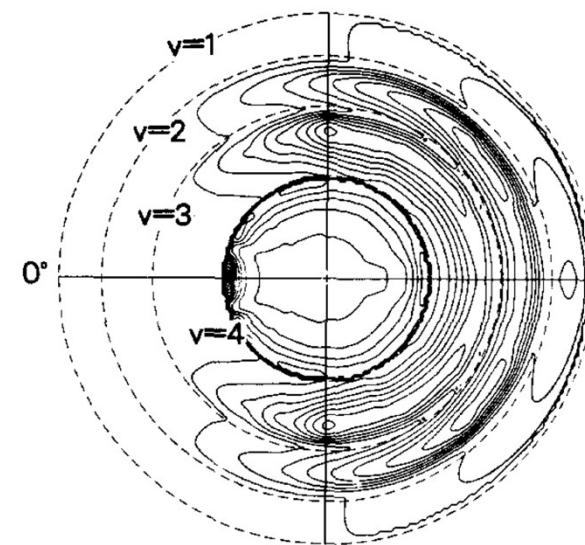


Newton diagram!

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

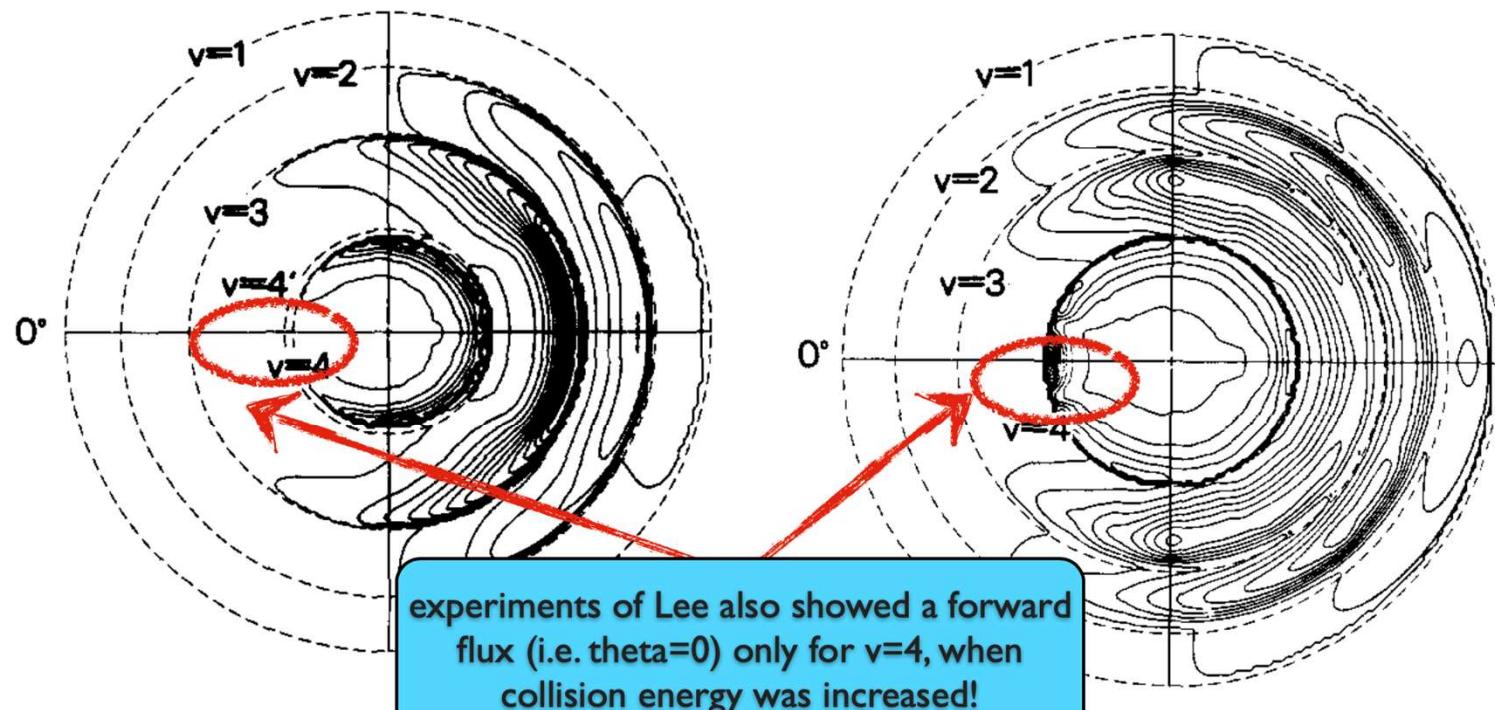


$\text{F}+\text{D}_2 \rightarrow \text{DF}+\text{D}$, 3.32 kcal/mole



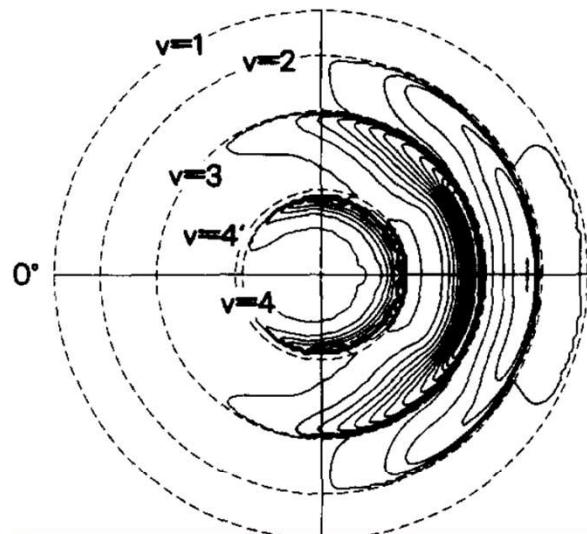
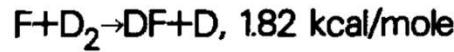
How do we understand these differences?

Rebound Reaction vs. Forward flux



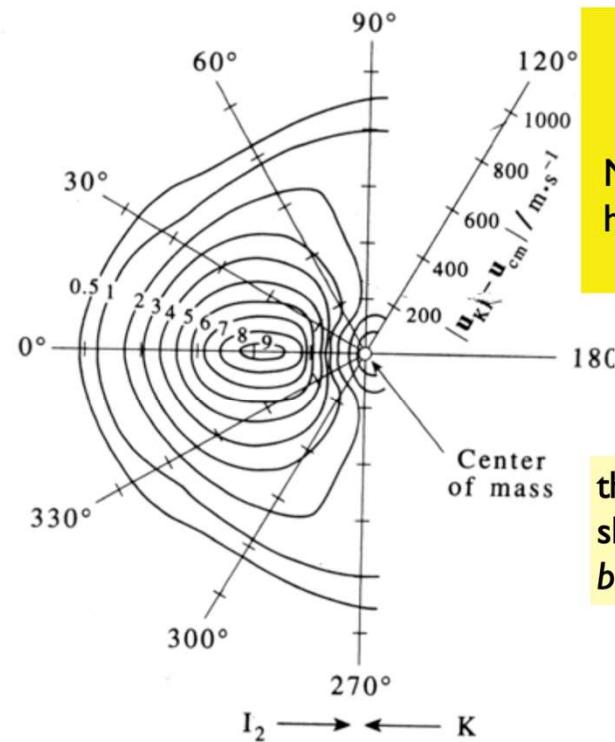
why such forward flux/scattering?

Rebound & Stripping Mechanisms



This is an example of **rebound reactions**:
Newton's diagram has theta=180 highly populated

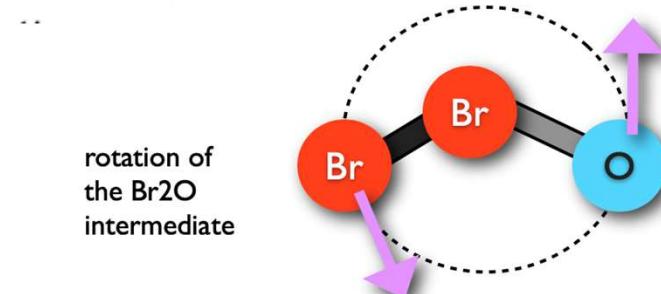
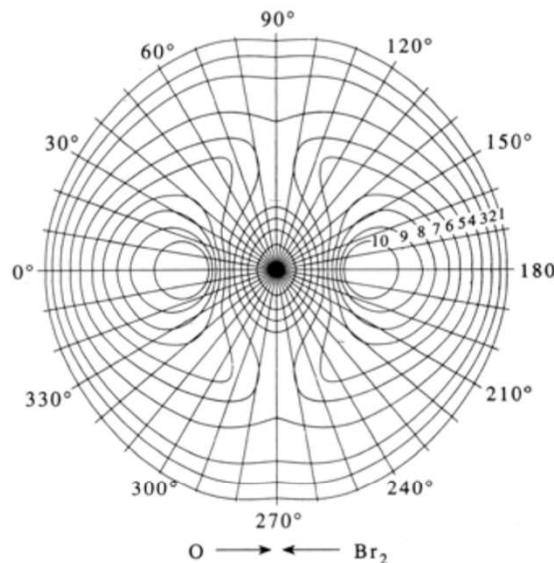
this reaction should have small b



This is an eg. of
stripping reaction.
Newton's diagram
has theta=0 highly
populated

this reaction
should have high
 b

Long-Lived Complex Mechanism

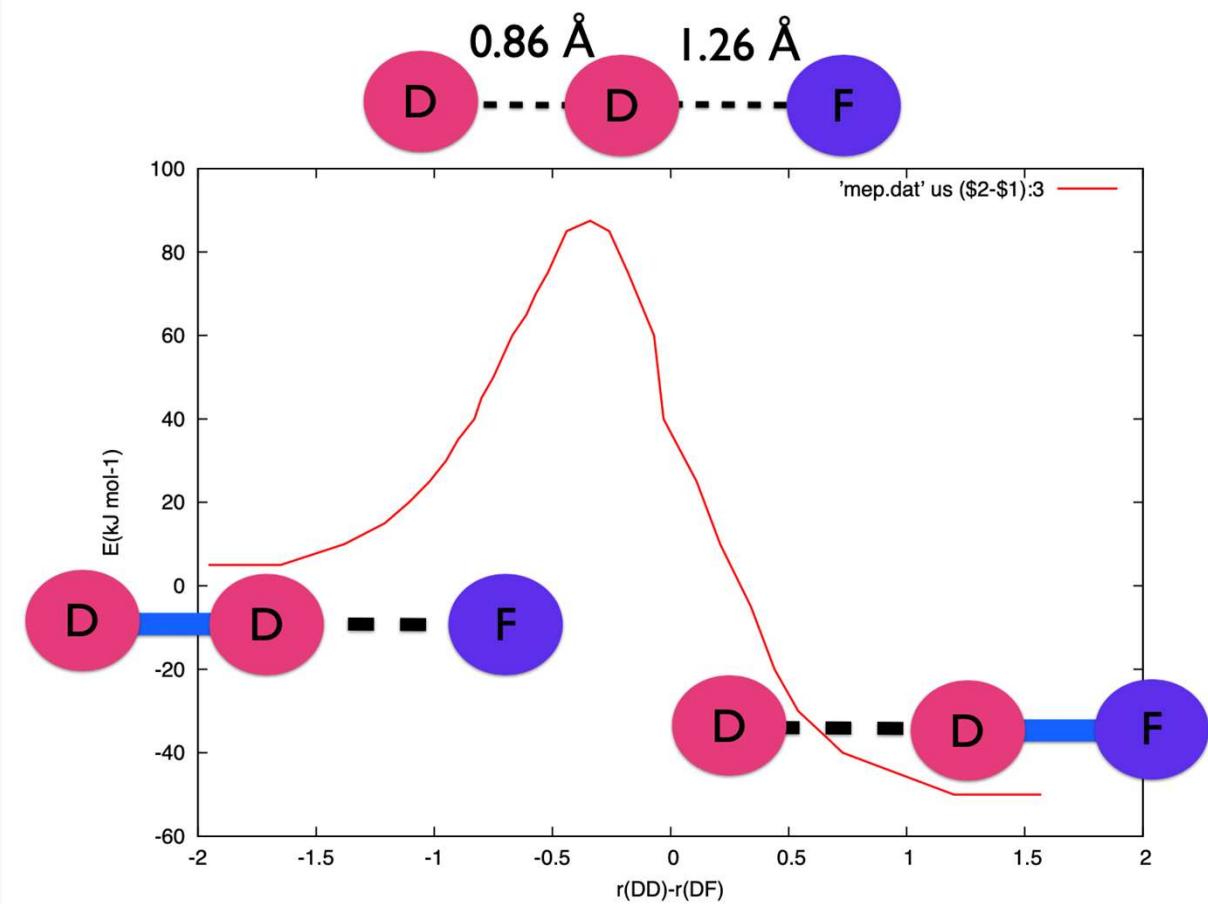


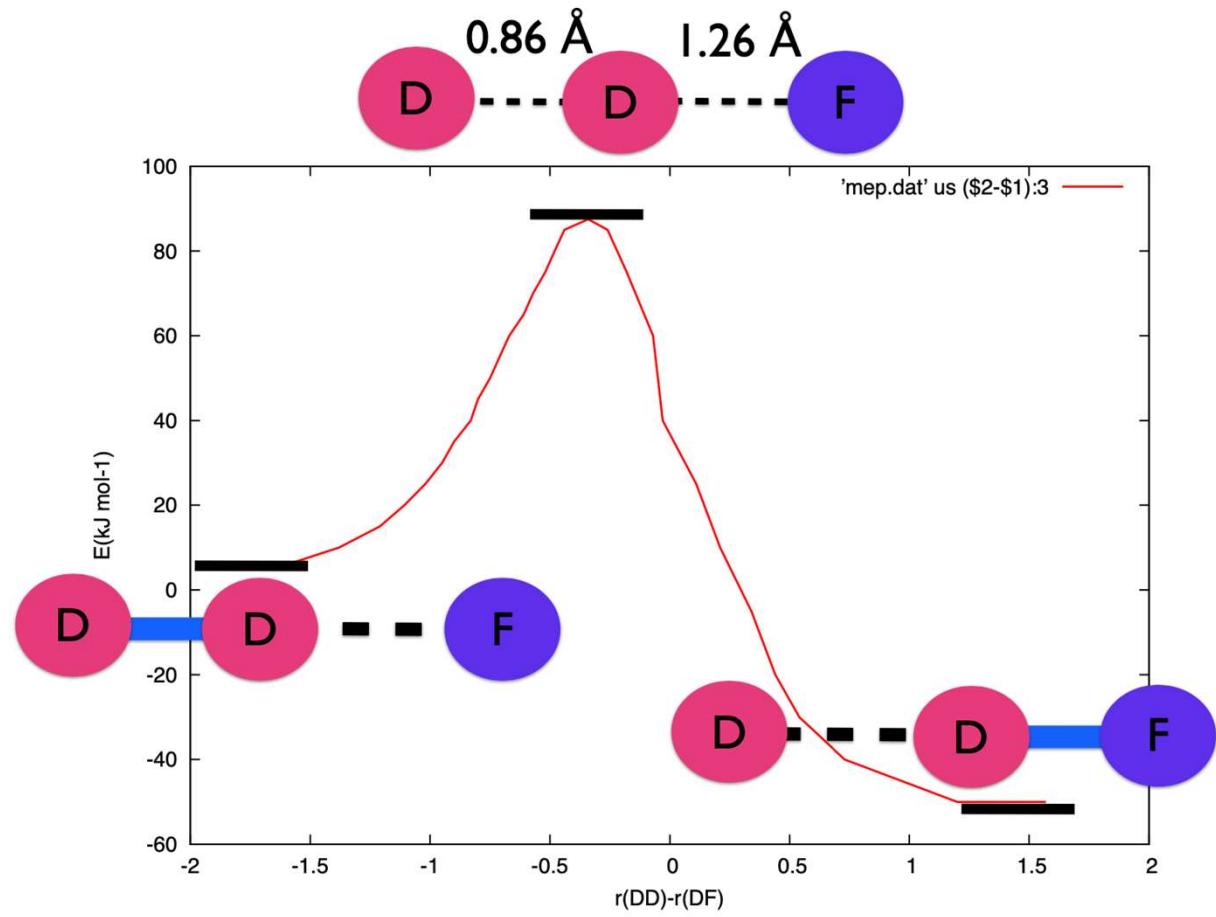
This is an example of **long-lived complex reactions:**

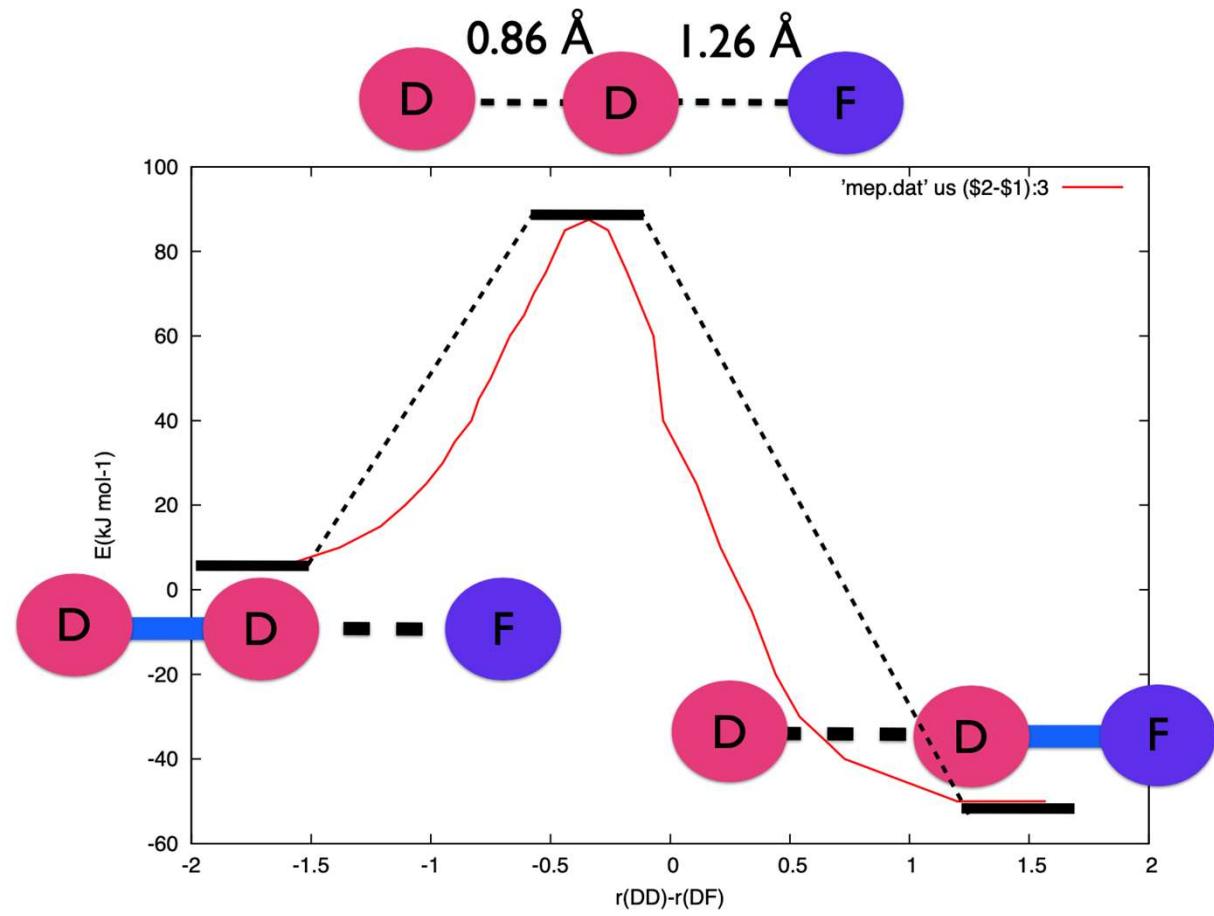
Newton's diagram is largely symmetric in both hemispheres (i.e. 0 and 180)

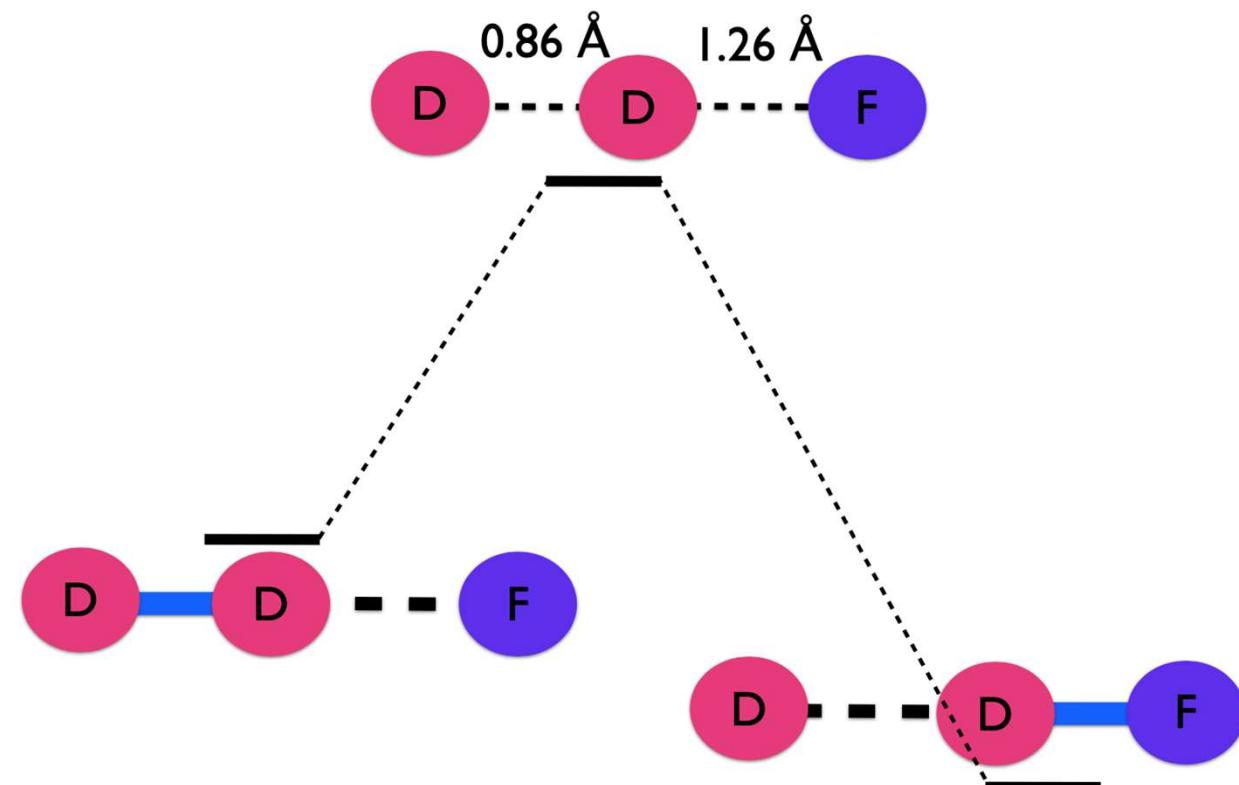
How?

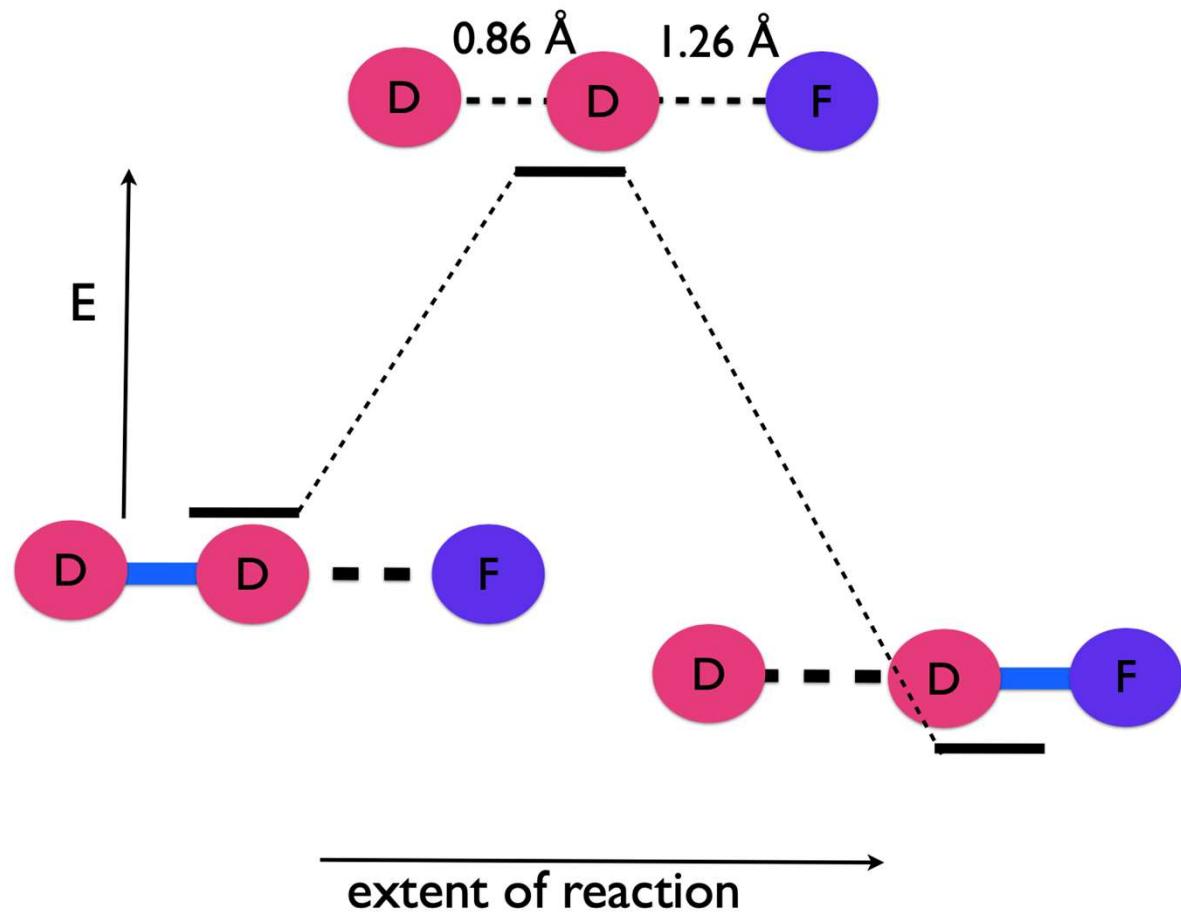
- an intermediate is formed whose life time is longer than the rotation of the intermediate
- Intermediate rotates many times before the formation of OBr (thus distribution is independent of their initial collision geometry)

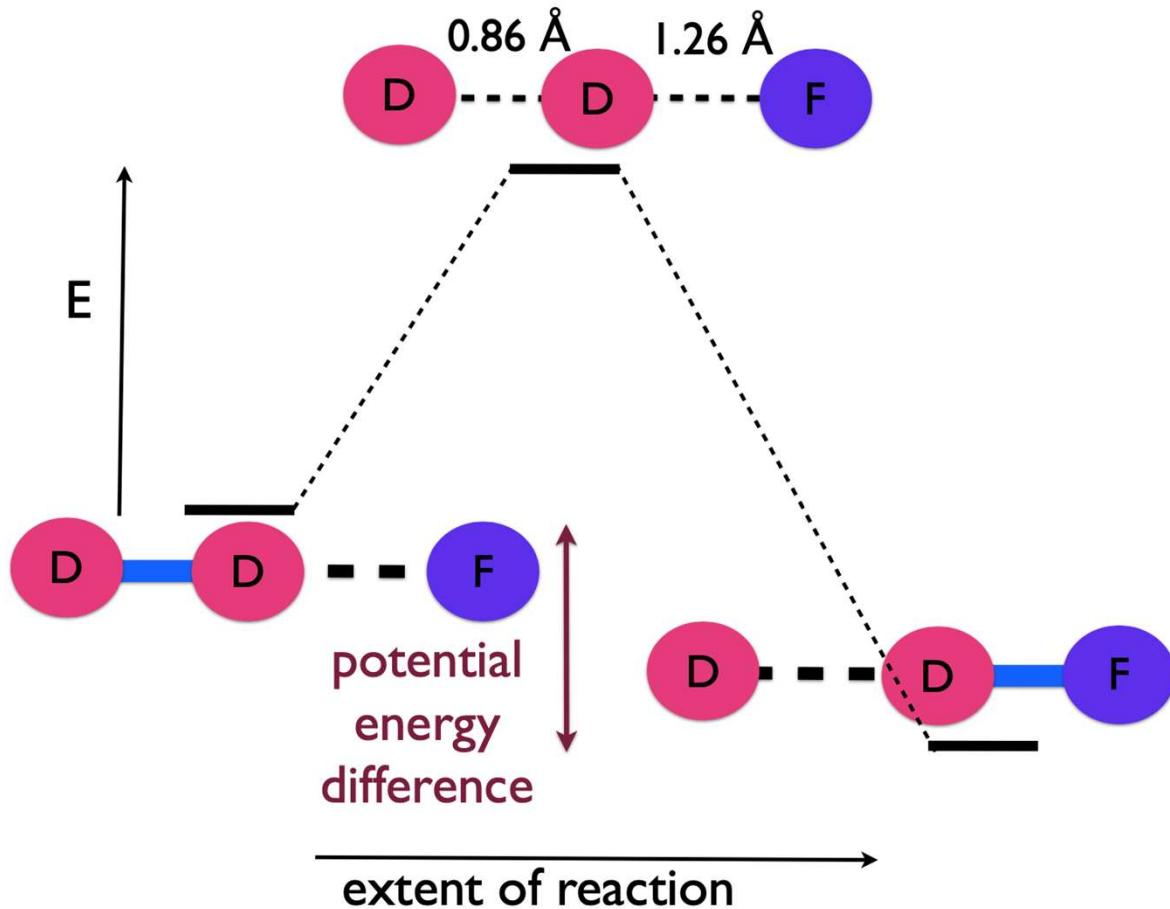


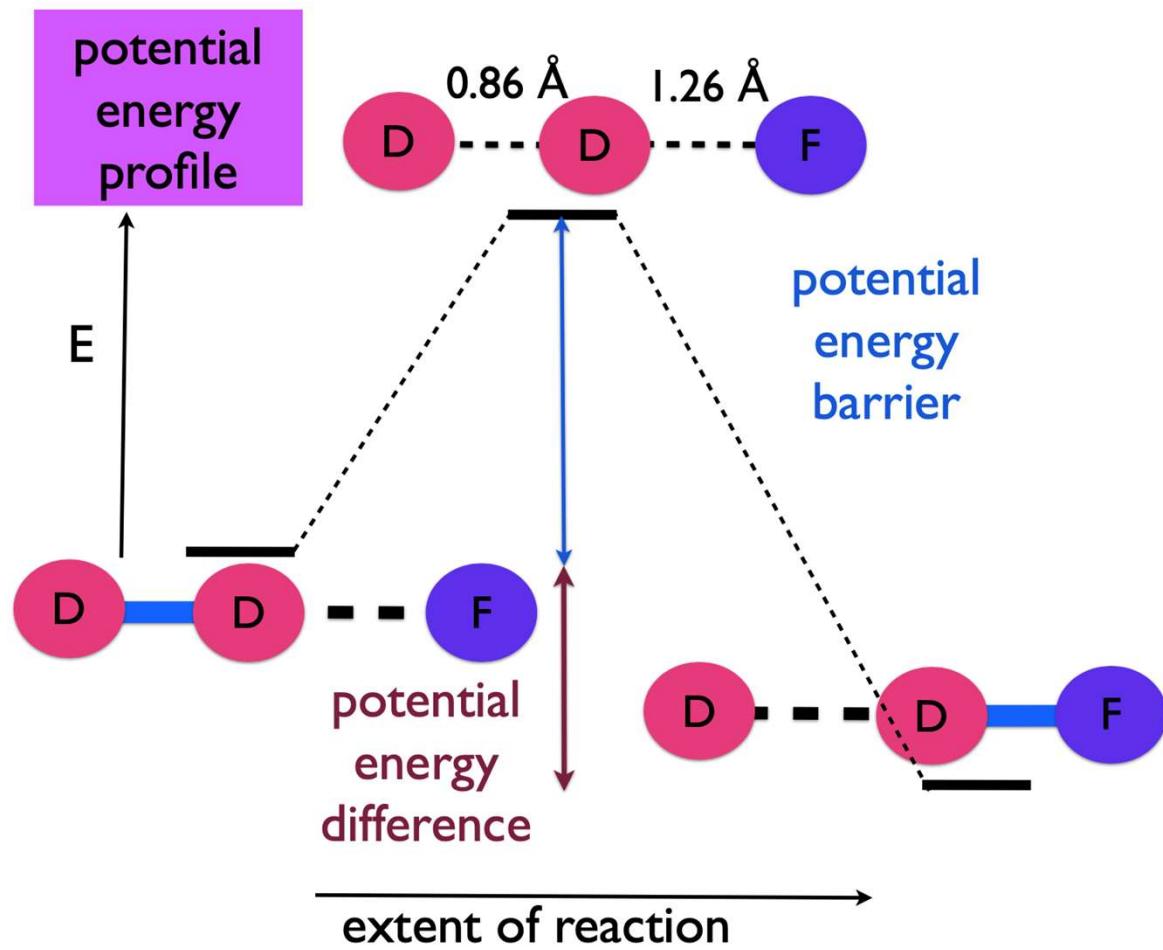


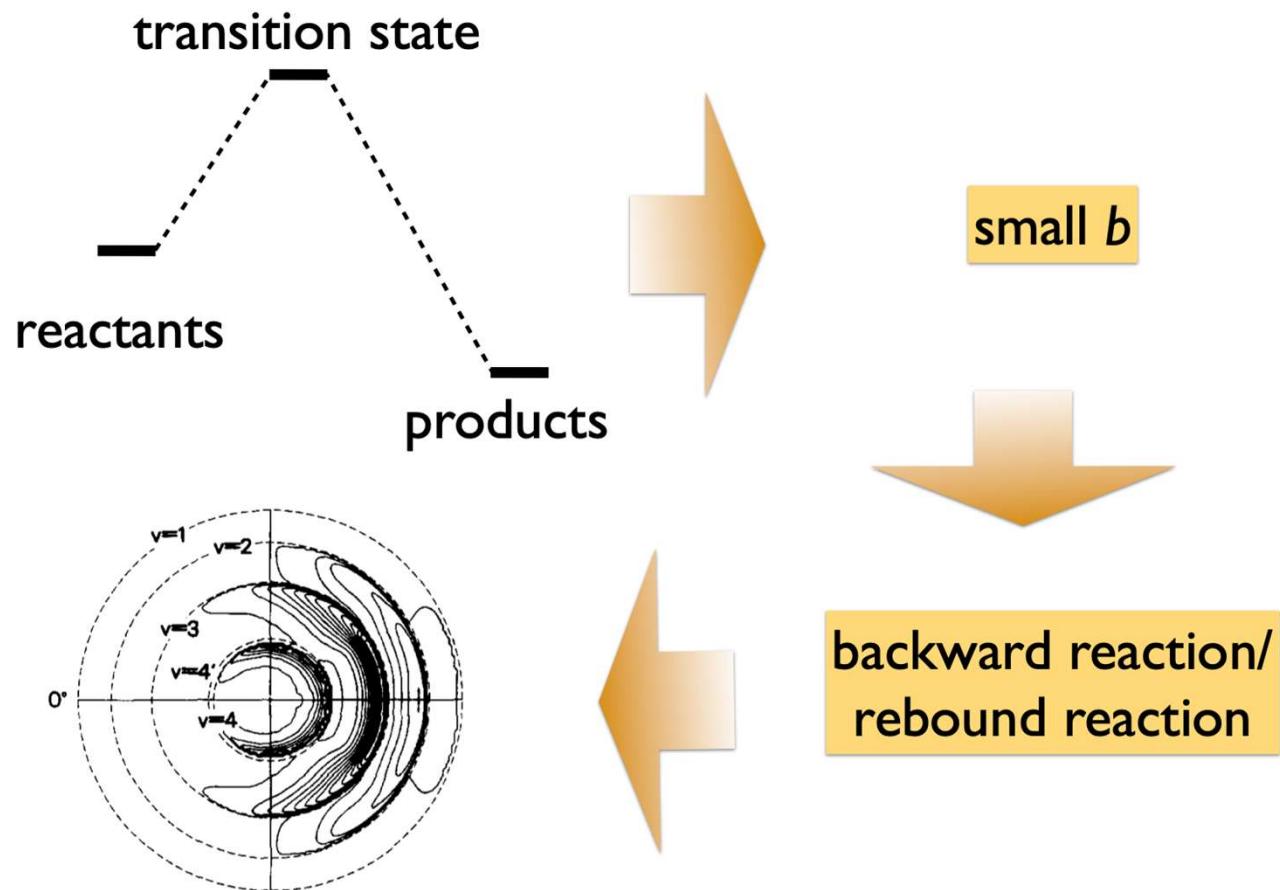


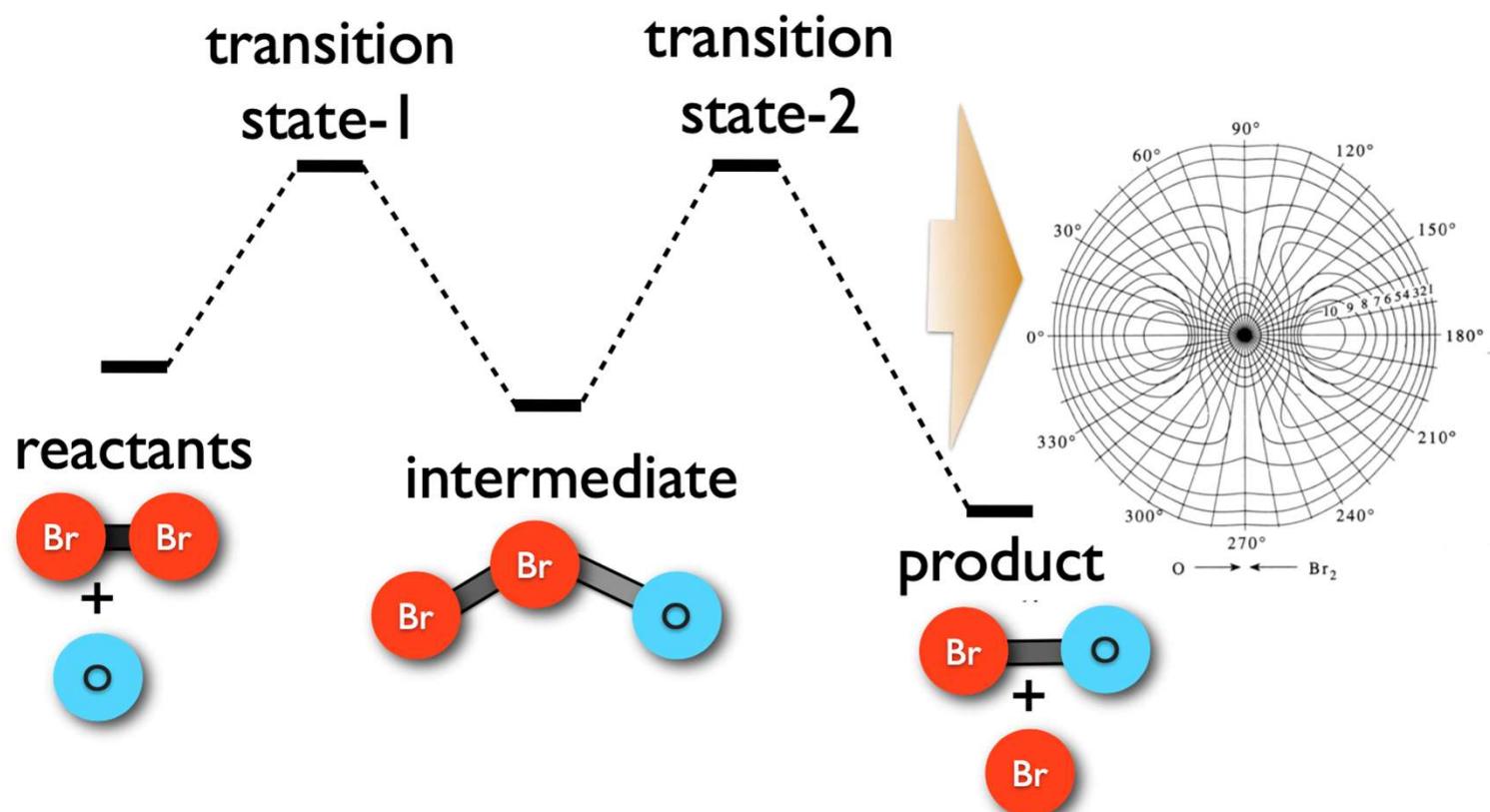








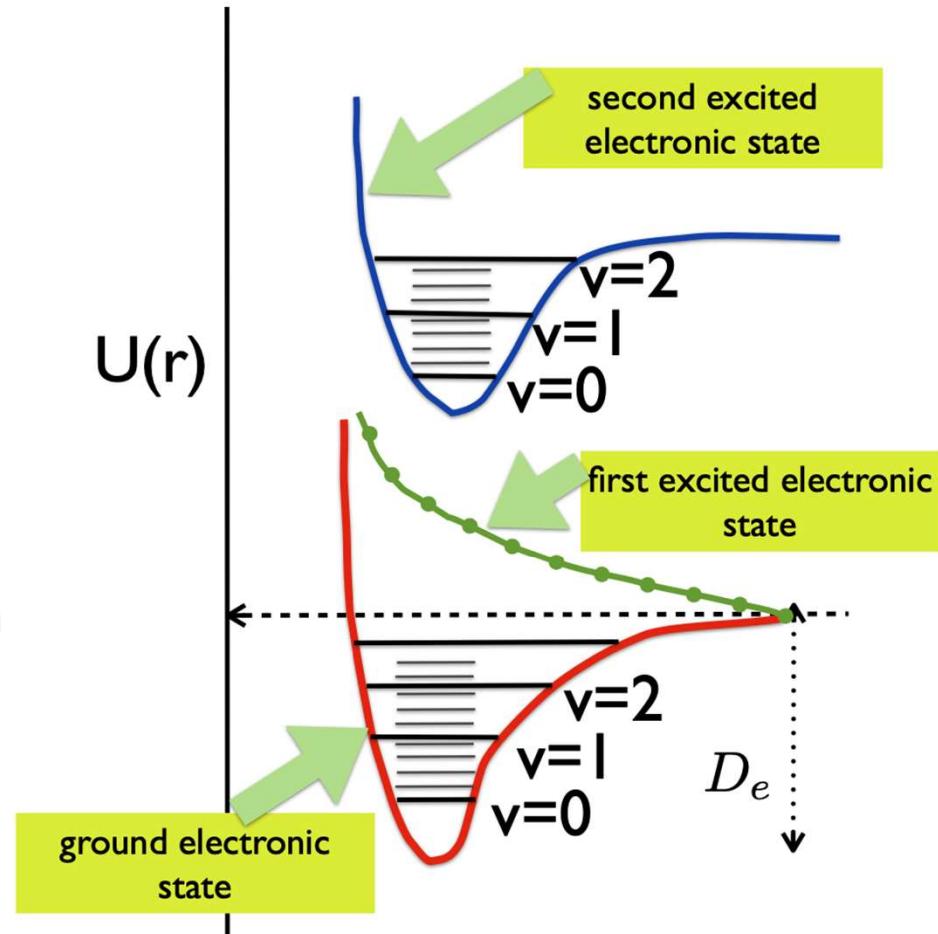




Quantum Levels

Quantum vibrational
and rotational levels

In the example (at the right side), first excited state is not a bound state (thus no vibrations, rotations possible). Molecule in the first excited state (in this example will dissociate, as that leads to lowering the potential energy)

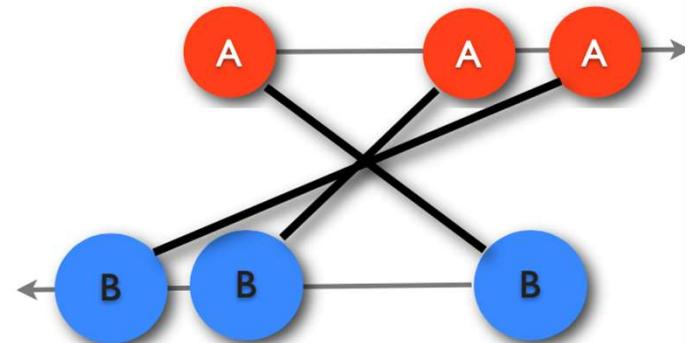


Centrifugal Barrier

For collision reactions, one important factor to account for is the orbital angular momentum. This is not the quantum mechanical orbital angular momentum, but a classical one. The orbital angular momentum that we will look in the frame work of collision reaction is the one that corresponds to line-of-centers.

From the figure on the right, it is obvious that for a head-on collision (where $b=0$), the line of centers orbital angular momentum is zero.

Thus, this angular momentum is present for all the cases where $b>0$

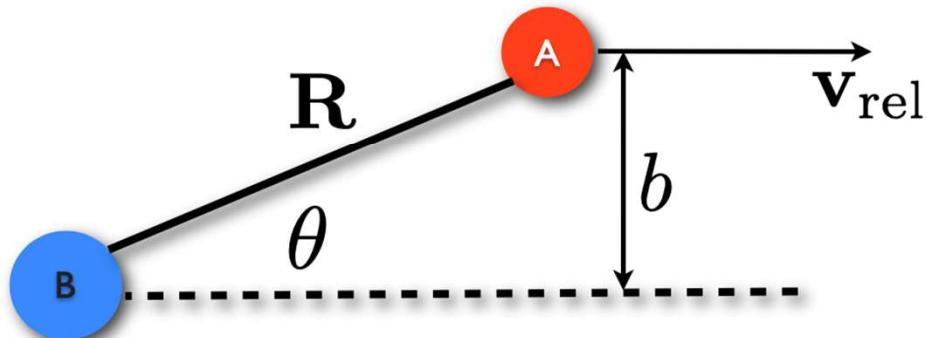


Let us now try to formulate an expression for orbital angular momentum of line-of-centers

$$\mathbf{L} = \mathbf{R} \times \mathbf{p}$$

relative linear momentum
vector separating A & B

$$|\mathbf{L}| = |\mathbf{R} \times \mathbf{p}| = |\mu \mathbf{R} \times \mathbf{v}_{\text{rel}}| = \mu v_{\text{rel}} R \sin \theta$$



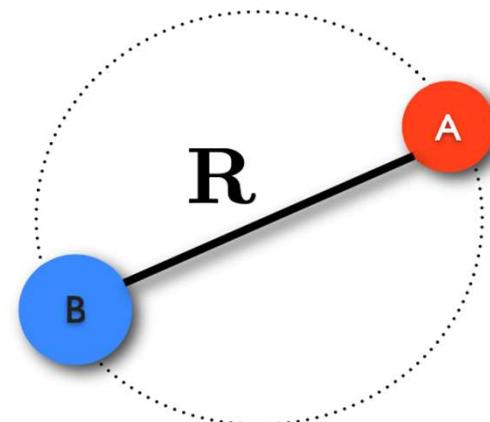
$$\Rightarrow |\mathbf{L}| = \mu v_{\text{rel}} R \sin \theta = \mu v_{\text{rel}} b$$

magnitude of orbital angular momentum depends on b , and relative velocity!

- We can neglect the contribution of quantum mechanical orbital angular momentum (usually these values are small)
- Then, total orbital angular momentum of reactants $\approx \mathbf{L}$

Then the total relative kinetic energy is given by

(remember: we don't need CM velocity as it is any way not available for reaction)



KE due to change in LOC

$$K_{\text{rel}} = \frac{1}{2}\mu\dot{R}^2 + \frac{|\mathbf{L}|^2}{2\mu R^2}$$

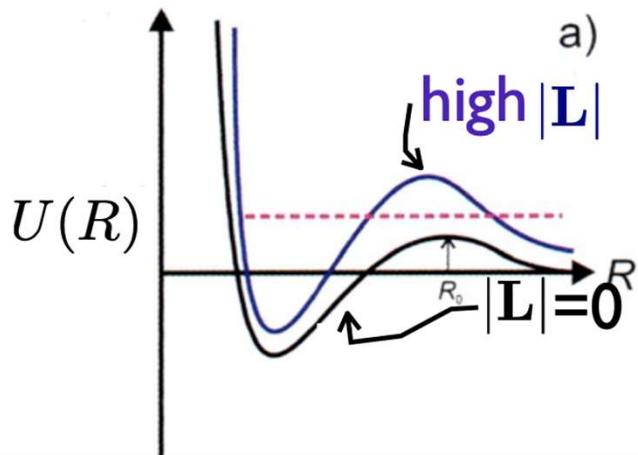
KE orbital angular momentum of LOC
This is also called centrifugal kinetic energy, K_{cent}

$$K_{\text{cent}} = \frac{|\mathbf{L}|^2}{2\mu R^2} = \frac{1}{2}\mu v_{\text{rel}}^2 \frac{b^2}{R^2} = E_c \frac{b^2}{R^2}$$

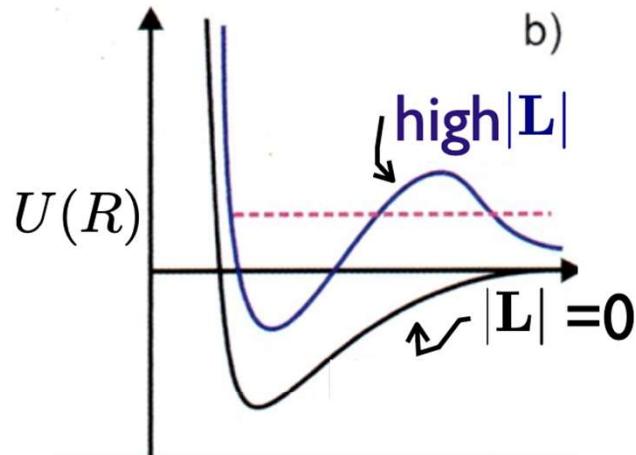
If we consider reactive collisions as elastic collisions, angular momentum is conserved during the course of collision (similar to the conservation of center of mass velocities). That is,
angular momentum of reactants=angular momentum of products.

Due to the (total) angular momentum conservation, the K_{cent} cannot be taken out from the total kinetic energy of molecule for chemical reaction (as it has to conserve!)

- In other words, K_{cent} is not available for surmounting the activation barrier. This has the effect of reducing the total energy available!
- We can think of an effective potential acting during the collision reactions: $U_{\text{eff}}(R) = U(R) + K_{\text{cent}}$



Such effect will result in increasing the effective barrier as shown above further slowing down the reaction

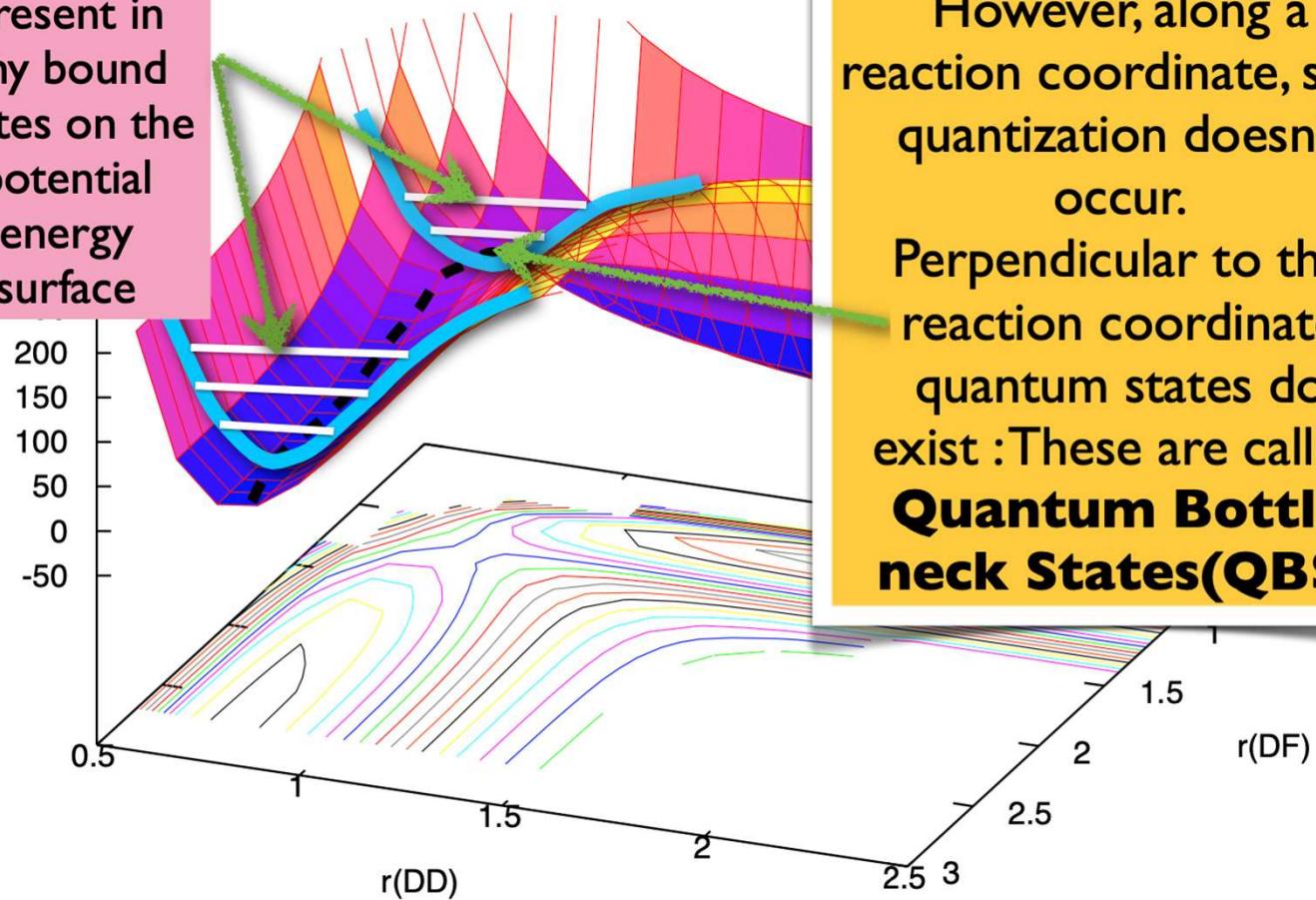


it may create barriers for cases where there is no activation barriers on the potential energy surface

Such barriers are called **centrifugal barriers**

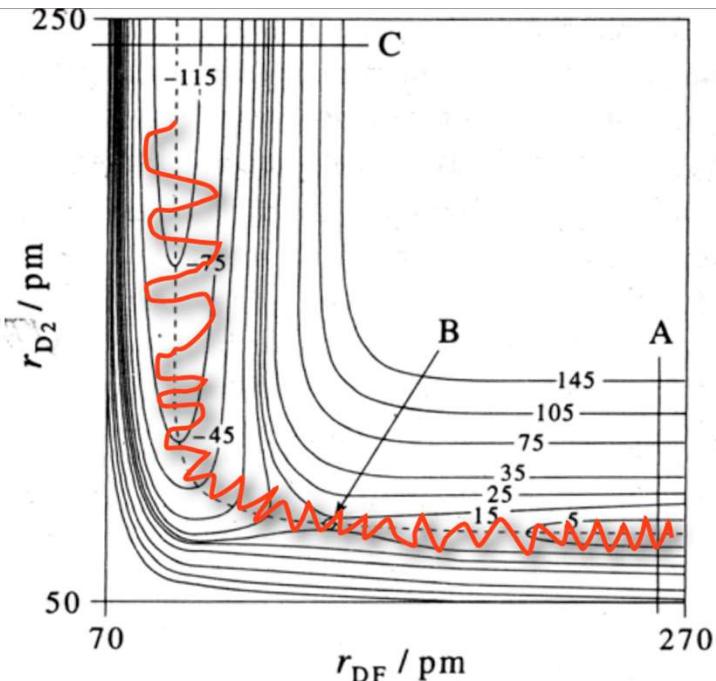
Quantum Bottleneck States

Quantized levels will be present in any bound states on the potential energy surface



However, along a reaction coordinate, such quantization doesn't occur. Perpendicular to the reaction coordinate quantum states do exist : These are called **Quantum Bottleneck States(QBS)**

See the figure at the right side. red lines are showing path taken by the reactants/products during the reaction mapped on the top of the potential energy surface. You could clearly see the vibrations perpendicular to the dotted lines (minimum energy pathway/reaction coordinate). No such vibrations are present in the direction of the dotted line)



- Energy available for the motion along the reaction coordinate (or the minimum energy pathway), doesn't (easily) flow or get distributed to the vibrational motions or rotational motions perpendicular to it. This is also true vice versa. Or in otherwords, the energy that is available for the vibrational motion perpendicular to the minimum energy pathway is not accessible for chemical reaction (remember: chemical reaction is nothing other than motion along the minimum energy pathway).

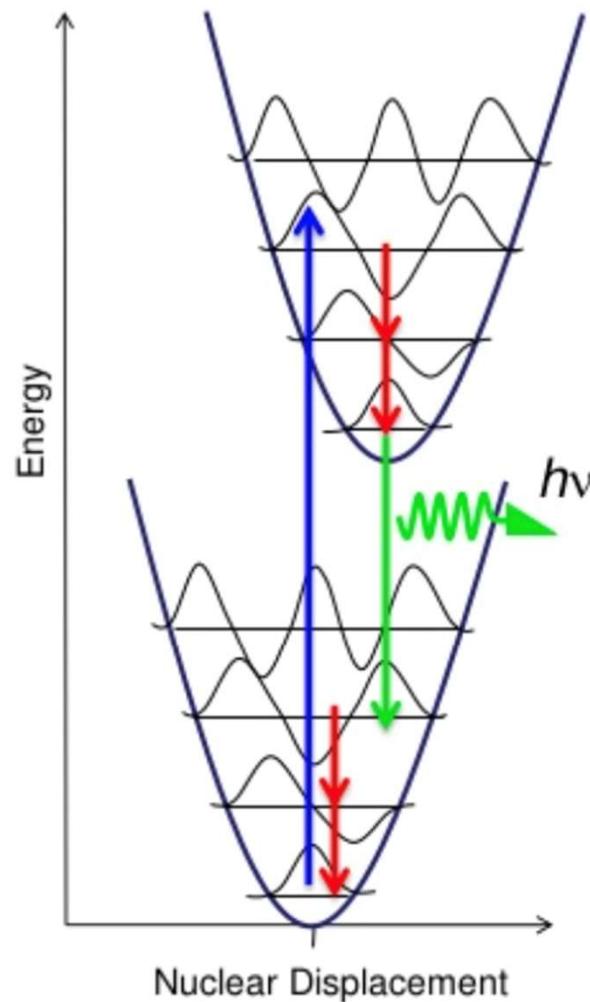
Molecular transitions

The ground state and the excited states of molecules can be represented by harmonic oscillators with quantized vibrational modes.

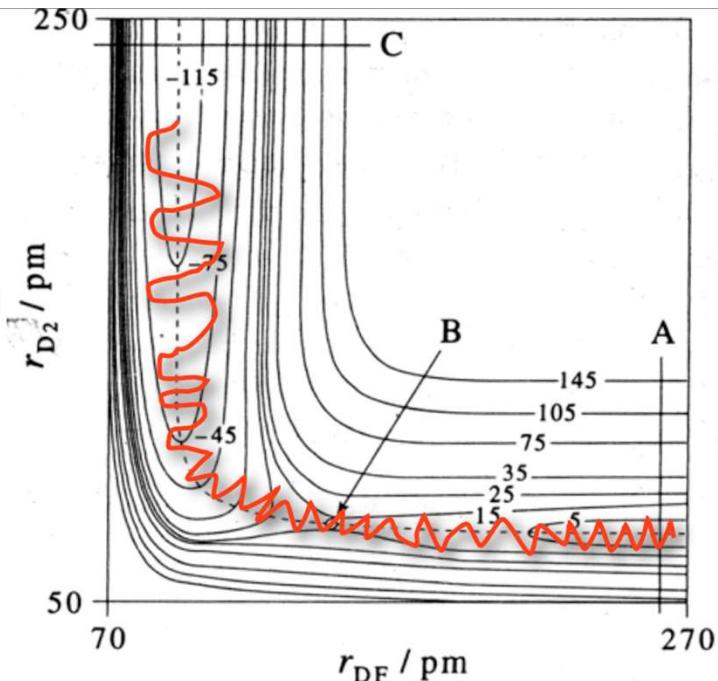
Electronic transitions are allowed between these modes.

Mass of an electron is very different from the nuclei. Thus electronic transitions occur in a stationary nuclear framework (Franck Condon Principle).

We plot electronic transitions as vertical lines, representing the same nuclear distribution in ground and excited states.

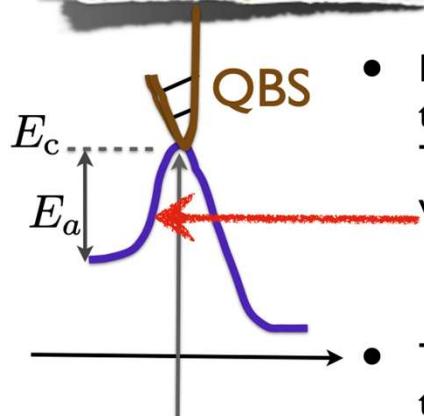


See the figure at the right side. red lines are showing path taken by the reactants/products during the reaction mapped on the top of the potential energy surface. You could clearly see the vibrations perpendicular to the dotted lines (minimum energy pathway/reaction coordinate). No such vibrations are present in the direction of the dotted line)



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Let us consider a case where there is centrifugal barrier / potential energy barrier that needs to be overcome by the reactants as shown in the figure below.



- Let us also consider a case where energy available for the reaction (E_c) is in resonance with this barrier (E_a). Then molecules will lose all its translational energy while reaching the top of the barrier.

$$E_c = E_a$$

- This results in zero velocity at the top of the transition state, resulting in slowing down the reaction for a few femtoseconds; the transition state structure will get some life time.
- This will happen only if QBS (which are perpendicular to it) do not supply energy for the translational motion along reaction coordinate. Such process can take a few tens of pico/femto seconds, giving a longer life time for the transition state structure

- This is a situation similar to the case of $\text{Br}_2 + \text{O}$ reaction, where a stable intermediate is formed, which has certain definite life time. But the transition state life time due to QBS very small.
- Similar to the case of $\text{Br}_2 + \text{O}$ formation of stable intermediates result in forward scattering! (which would otherwise only backward scatter, as expected for small b reactions)

$\text{H}_2 + \text{H}$ reaction is a good example!

Forward scattering due to slow-down of the intermediate in the $H + HD \rightarrow D + H_2$ reaction

Steven A. Harich*, Dongxu Dai*†, Chia C. Wang*‡, Xueming Yang*†§,
Sheng Der Chao||¶ & Rex T. Skodje||¶

* Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

† Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China

‡ Department of Chemistry, National Taiwan University, Taipei, Taiwan

§ Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan

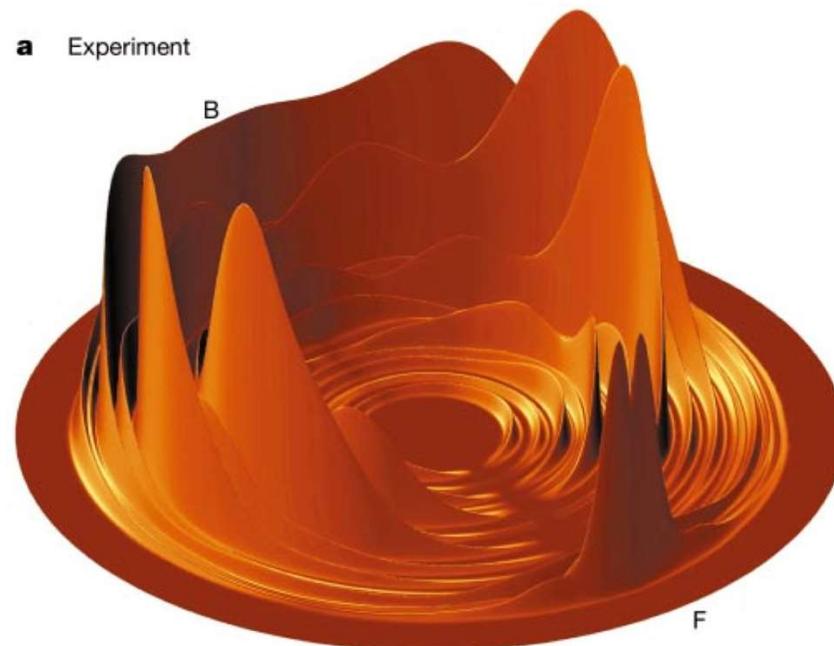
|| Institute of Molecular Science, Myodaiji, Okazaki 444-8585, Japan

¶ Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, USA

Quantum dynamical processes near the energy barrier that separates reactants from products influence the detailed mechanism by which elementary chemical reactions occur. In fact, these processes can change the product scattering behaviour from that expected from simple collision considerations, as seen in the two classical reactions $F + H_2 \rightarrow HF + H$ and $H + H_2 \rightarrow H_2 + H$ and their isotopic variants. In the case of the $F + HD$ reaction, the role of a quantized trapped Feshbach resonance state had been directly determined¹, confirming previous conclusions² that Feshbach resonances cause state-specific forward scattering of product molecules. Forward scattering has also been observed in the $H + D_2 \rightarrow HD + D$ reaction^{3,4} and attributed to a time-delayed mechanism^{3,5–7}. But despite extensive experimental^{8–12} and theoretical^{13–18} investigations, the details of the mechanism remain unclear. Here we present crossed-beam scattering experiments and quantum calculations on the $H + HD \rightarrow D + H_2$ reaction. We find that the motion of the system along the reaction coordinate slows down as it approaches the top of the reaction barrier, thereby allowing vibrations perpendicular to the reaction coordinate and forward scattering. The reaction thus proceeds, as previously suggested⁷, through a well-defined ‘quantized bottleneck state’ different from the trapped Feshbach resonance states observed before.

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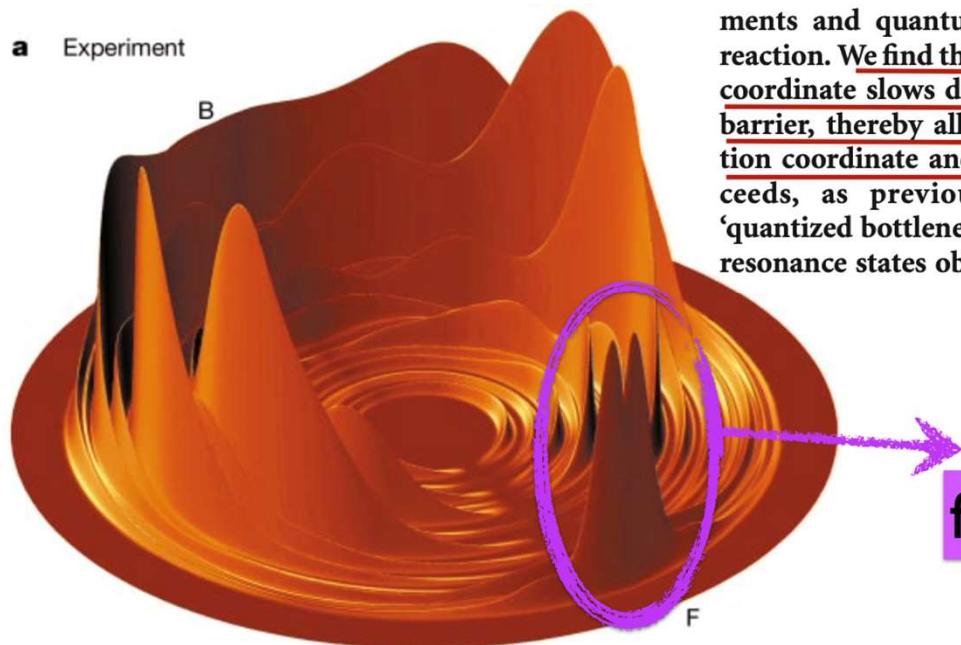
a Experiment



Forward scattering due to slow-down of the intermediate in the $\text{H} + \text{HD} \rightarrow \text{D} + \text{H}_2$ reaction

Steven A. Harich*, Dongxu Dai*†, Chia C. Wang*‡, Xueming Yang*†§,
Sheng Der Chao||¶ & Rex T. Skodje||¶

a Experiment



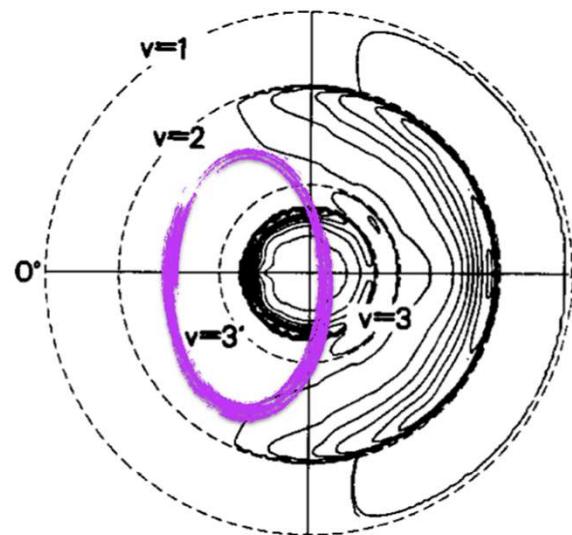
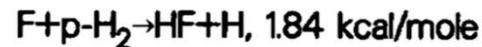
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forward scattering

Molecular beam studies of the F+H₂ reaction

D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, and Y. T. Lee

The Journal of Chemical Physics 82, 3045 (1985)



Is the forward scattering in this case due to Quantum Bottleneck States?

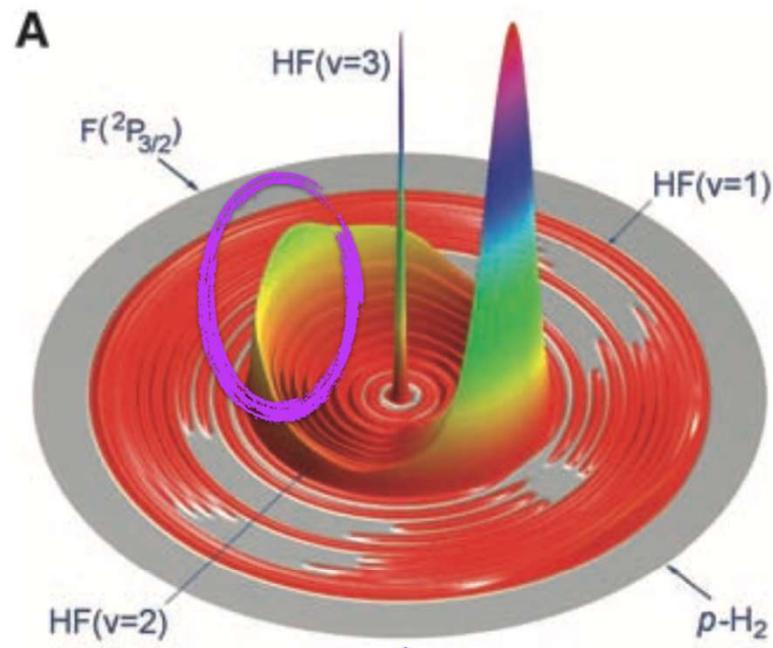
Theoretical calculations showed that it is due to quantum effects (like tunneling)

This problem was solved in 2006:

Observation of Feshbach Resonances in the $F + H_2 \rightarrow HF + H$ Reaction

Minghui Qiu,^{1,3*} Zefeng Ren,^{1*} Li Che,¹ Dongxu Dai,¹ Steve A. Harich,¹ Xiuyan Wang,¹ Xueming Yang,^{1,†} Chuanxiu Xu,⁴ Daiqian Xie,^{4,†} Magnus Gustafsson,^{5,6} Rex T. Skodje,^{5,6} Zhigang Sun,^{1,2,7} Dong H. Zhang^{1,2,7,†}

Reaction resonances, or transiently stabilized transition-state structures, have proven highly challenging to capture experimentally. Here, we used the highly sensitive H atom Rydberg tagging time-of-flight method to conduct a crossed molecular beam scattering study of the $F + H_2 \rightarrow HF + H$ reaction with full quantum-state resolution. Pronounced forward-scattered HF products in the $v' = 2$ vibrational state were clearly observed at a collision energy of 0.52 kcal/mol; this was attributed to both the ground and the first excited Feshbach resonances trapped in the peculiar $HF(v' = 3)-H'$ vibrationally adiabatic potential, with substantial enhancement by constructive interference between the two resonances.

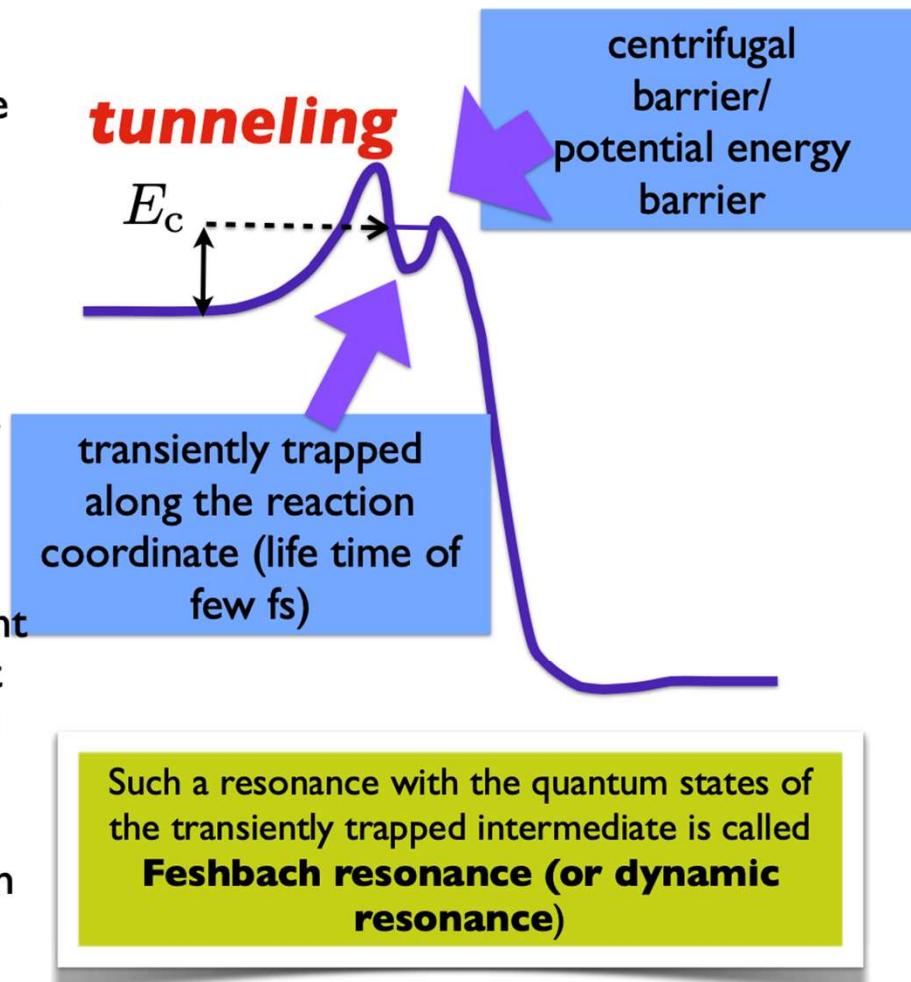


forward scattering was
seen majorly for HF($v=3$)
and also HF($v=2$)

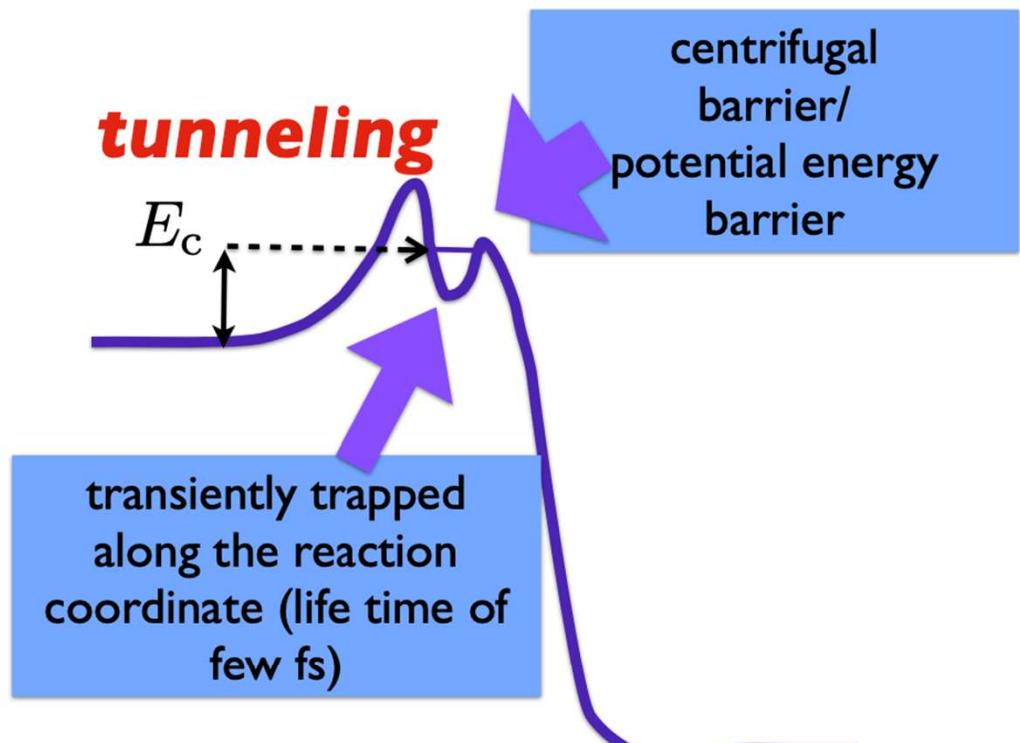
Let us consider the formation of transiently trapped structure along the reaction coordinate as shown in the figure at the right. These barriers may arise from the centrifugal & potential energy barriers

Let us also consider that there exists a vibrational/rotation state for this transient species.

When collision energy becomes resonant with the energy levels of the transient species, then the reactants can tunnel (depending on the energy level, molecules etc.; lighter molecules are easy to tunnel; tunneling usually happens close to the barrier)

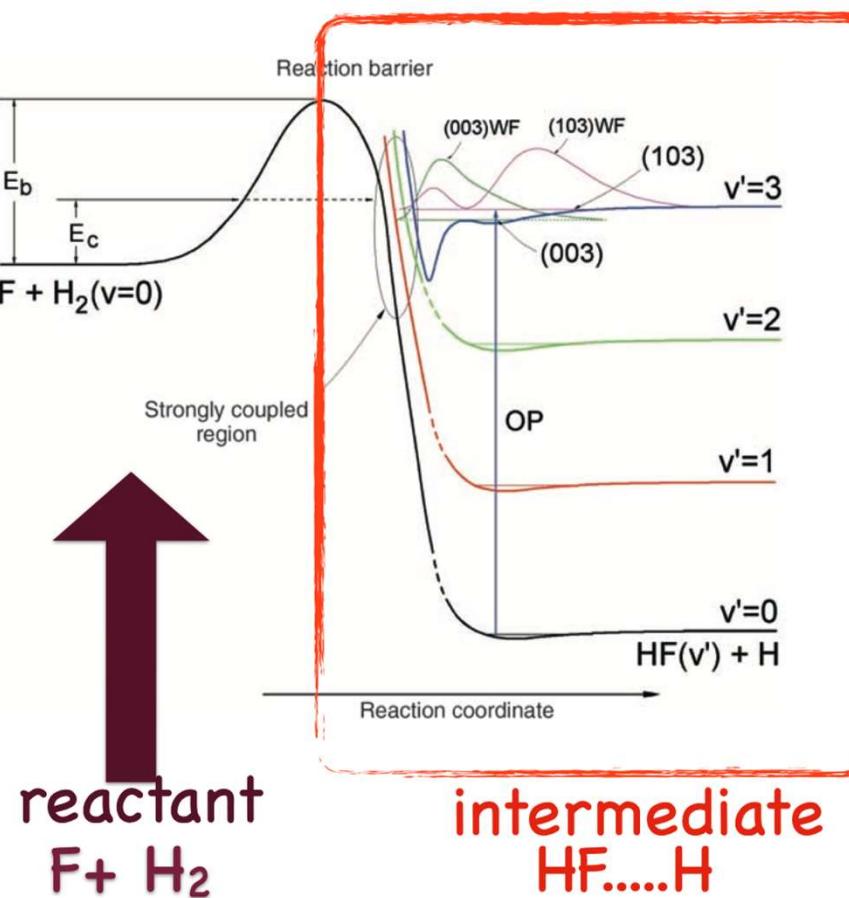


Due to tunneling, reactants form the transient intermediates even with collision energy lower than the potential energy barrier for the reaction.



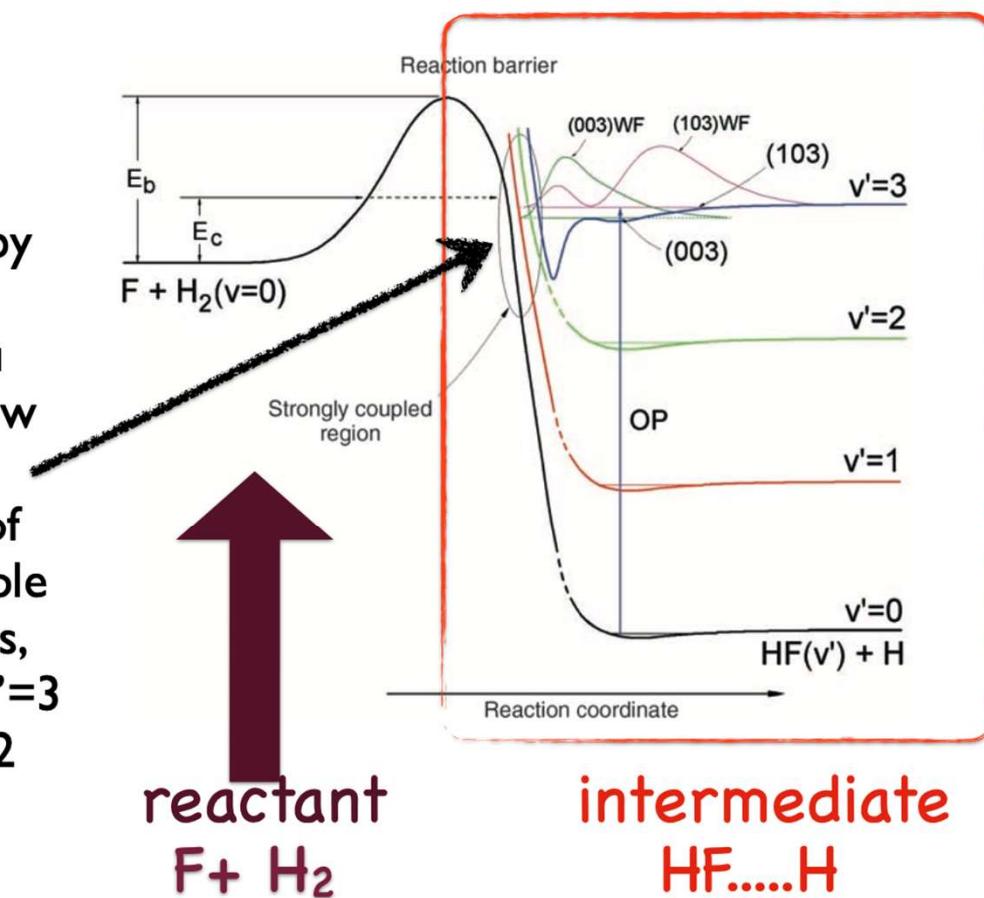
In the case of F+H₂ reaction, it was identified that a weakly bound (HF...H) complex form during the reaction, and has a definite life time

This complex has similar behavior of HF, but coordinated weakly to the H atom that will be cleaved from the H₂



relative energy of $\text{F} + \text{H}_2$ reactants are in resonant with $v'=3$ energy levels of $\text{HF}\dots\text{H}$ complex, former will tunnel to form $\text{HF}\dots\text{H}$ with $v'=3$).

It has also found by theoretical calculations (you don't need to know how), potential energy surfaces of $v'=2$ and $v'=3$ couple each other. By this, some $\text{HF}\dots\text{H}$ with $v'=3$ can "leak" to $v'=2$ state



Because of this, HF...H intermediates are formed with $v'=3$ and $v'=2$ (with varying amount depending on the coupling of potential energy surface). [Details on this is beyond the purpose of this course]

Due to the stability of the HF...H intermediate (as also indicated by the shallow potential energy wells for each of the vibrational states in the figure before), we can expect that the HF...H molecules with $v'=3$ and $v'=2$ could result in backward and forward scattering

This is exactly what is seen in experiments (see 5 slides before)

Note: HF...H in a v' vibrational state will always decay to HF molecule with v' state.

This is because, within the molecular beam setup, HF molecules formed are not undergoing collisions till they reach the detector.

Due to lack of collisions with in the HF molecules, they retain their vibrational levels; thus $v=2$ & $v=3$ are highly populated.

This is the reason for a non-Boltzmann distribution

PERSPECTIVE

Quantum Dynamics of Chemical Reactions

David C. Clary

Substantial recent progress has been made in developing theory to account for quantum effects on chemical reactions.

Theoretical and computational methods are widely used to study chemical reactions in the gas phase (1, 2). Current methods enable useful and reliable calculations on the rates of chemical reactions and are also used to predict more detailed aspects of the dynamics and mechanisms of reactions that can be observed with methods such as laser spectroscopy and molecular beams (3).

The ease with which any such calculations can be performed depends on the topology of the potential energy surface (i.e., the energy of the electrons in a system of atoms that varies as the positions of the atoms are changed). If there is no energy barrier to reaction, very simple theories are often easily applied, and quantum dynamical effects can be minimal (4, 5). Also, the method of classical molecular dynamics is widely applicable when quantum tunneling and vibrational zero point energy effects are not important (6).

The most challenging reactions are those for which there is an energy barrier to the reaction and in which hydrogen or deuterium atoms are explicitly involved in bond breaking and bond formation. For these reactions, quantum tunneling through the energy barrier can be a major effect, and quantum dynamics methods need to be used.

The starting point for quantum dynamics calculations is the Schrödinger equation, which

needs to be solved for the electrons and nuclei taking part in the chemical reaction. Because the equation cannot be solved analytically, theories

are required that allow for an efficient numerical solution. The Born-Oppenheimer approximation usually applies, allowing the electronic and nuclear motion to be treated in separate calculations. A potential energy surface is first computed through solving the Schrödinger equation for the electrons, with the atoms held in fixed positions. It is expensive computationally to calculate the electronic energies for molecular geometries that involve bonds being broken and formed in chemical reactions, and only the most sophisticated ab initio electronic structure methods yield reliable reaction barriers (7, 8).

Even if the required electronic structure calculations can be carried out accurately, it is not a trivial task to fit the electronic energies to

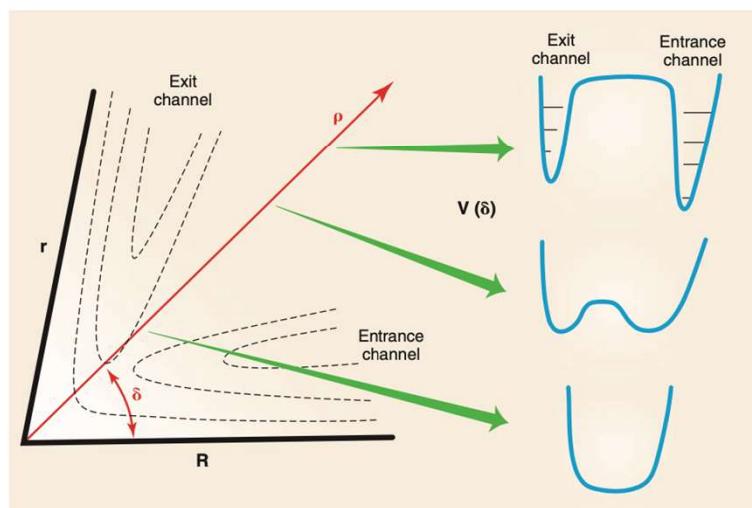


Fig. 1. Schematic diagram of a potential energy surface for a colinear atom + diatom reaction, with bonds being broken (r) and formed (R). A transformation is made of (R, r) to the polar (hyperspherical) coordinates (ρ, δ) . The potentials $V(\delta)$ in the angular variable δ for three different values of ρ are also shown. The quantum wave function is integrated along the hyperradius ρ and, for fixed values of ρ , vibrational energy levels are obtained for each value of $V(\delta)$. When ρ is large, these levels correspond to the vibrational states of reactants or products.

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Conclusion

The ideal theory for treating bimolecular reactions involves accurate quantum dynamics using accurate potential energy surfaces. As has been described here, calculations with this approach can be done on reactions involving up to four atoms but more approximate methods are normally needed for more complicated reactive systems. These definitive calculations are providing insight into the detailed mechanisms of chemical reactions.

As methods are developed and computers get more efficient it is inevitable that the range of the rigorous quantum theory will improve. A key aspect will be the interface with the most accurate electronic structure methods to produce

truly direct quantum dynamics methods that can be applied to more complicated reactions for which analytical potential energy surfaces are not available. Another area where there is a need for intensive research is in the rigorous treatment of transitions between electronic states in chemical reactions. Even for simple benchmark reactions such as $F + H_2$ this treatment is needed to explain some experimental results. There is no doubt that the theoretical study of reaction dynamics will be a very active research area for many years to come.

ACKNOWLEDGMENTS. This work was supported by the Engineering and Physical Sciences Research Council and Office of Naval Research Grant N00014-05-1-0460.

David Clary (2008)

Molecular Beam Studies of Elementary Chemical Processes

YUAN TSEH LEE

Conclusion

The experimental investigation of elementary chemical reactions is presently in a very exciting period. The advance in modern microscopic experimental methods, especially crossed molecular beams and laser technology, has made it possible to explore the dynamics and mechanisms of important elementary chemical reactions in great detail. Through the continued accumulation of detailed and reliable knowledge about elementary reactions, we will be in a better position to understand, predict, and control many time-dependent macroscopic chemical processes that are important in nature or to human society.

In addition, because of recent improvements in the accuracy of theoretical predictions based on large-scale ab initio quantum mechanical calculations, meaningful comparisons between theoretical and experimental findings have become possible. In the remaining years of the 20th century, there is no doubt that the experimental investigation of the dynamics and mechanisms of elementary chemical reactions will play a very important role in bridging the gap between the basic laws of mechanics and the real world of chemistry.

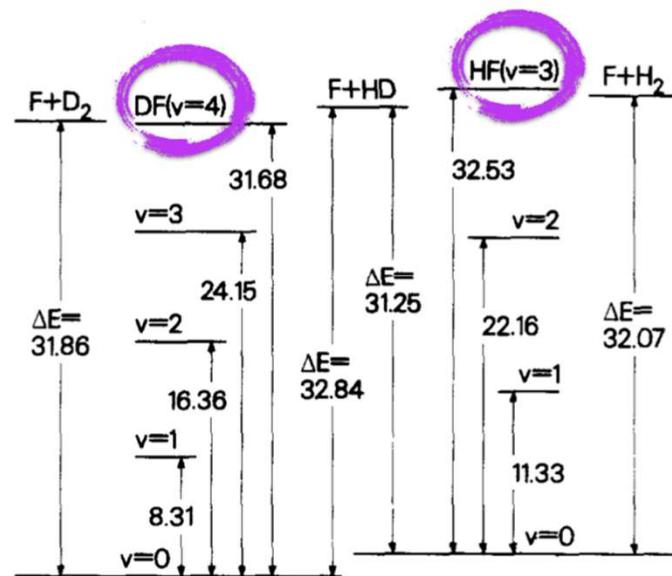
Similar observations were also made for D₂+F and DH+F reactions.

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

D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, K. Shobatake, R. K. Sparks, T. P. Schafer, and Y. T. Lee

Citation: *The Journal of Chemical Physics* **82**, 3067 (1985); doi: 10.1063/1.448255

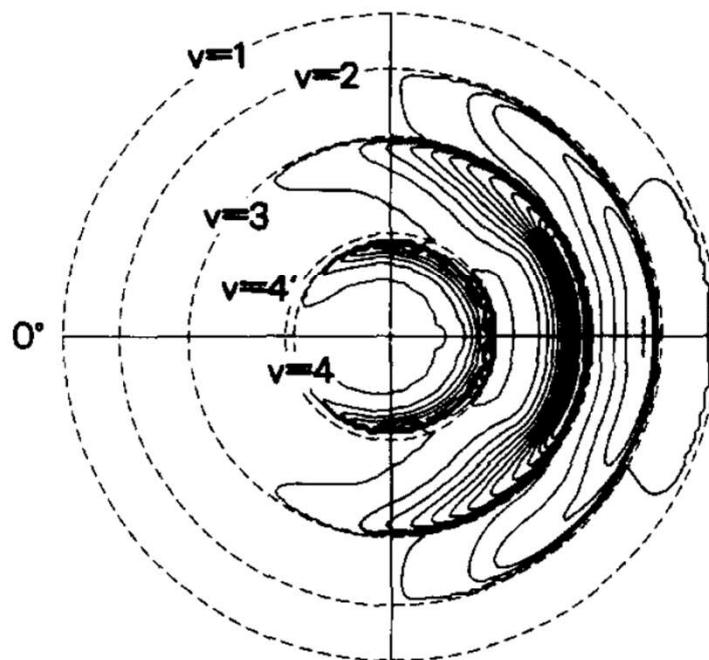
- Note: as you notice from the right hand side figure on the energy levels of DF and HF, the levels $v < 3$ are only accessible for low energy collisions, while for HF $v < 3$ are only accessible. This is due to the difference in mass of D and H.
- Thus, if D₂+F also shows Feshbach resonance, then we can expect similar forward scattering for $v=4$ & $v=3$ of DF



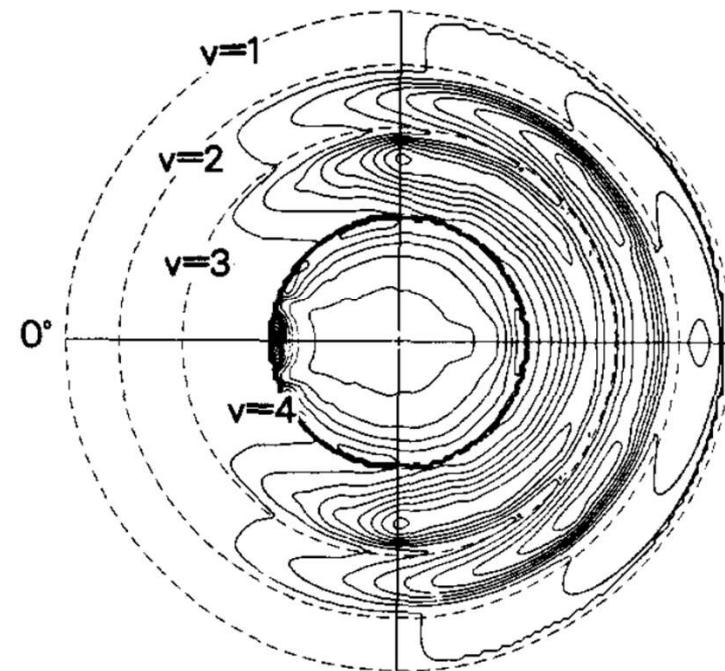
However, forward resonance is not seen for neither $v=4$ or any other $v < 4$! However, forward scattering is seen for $v=4$ when collision energy is increased to 3.32 kcal/mol (see the figures below).

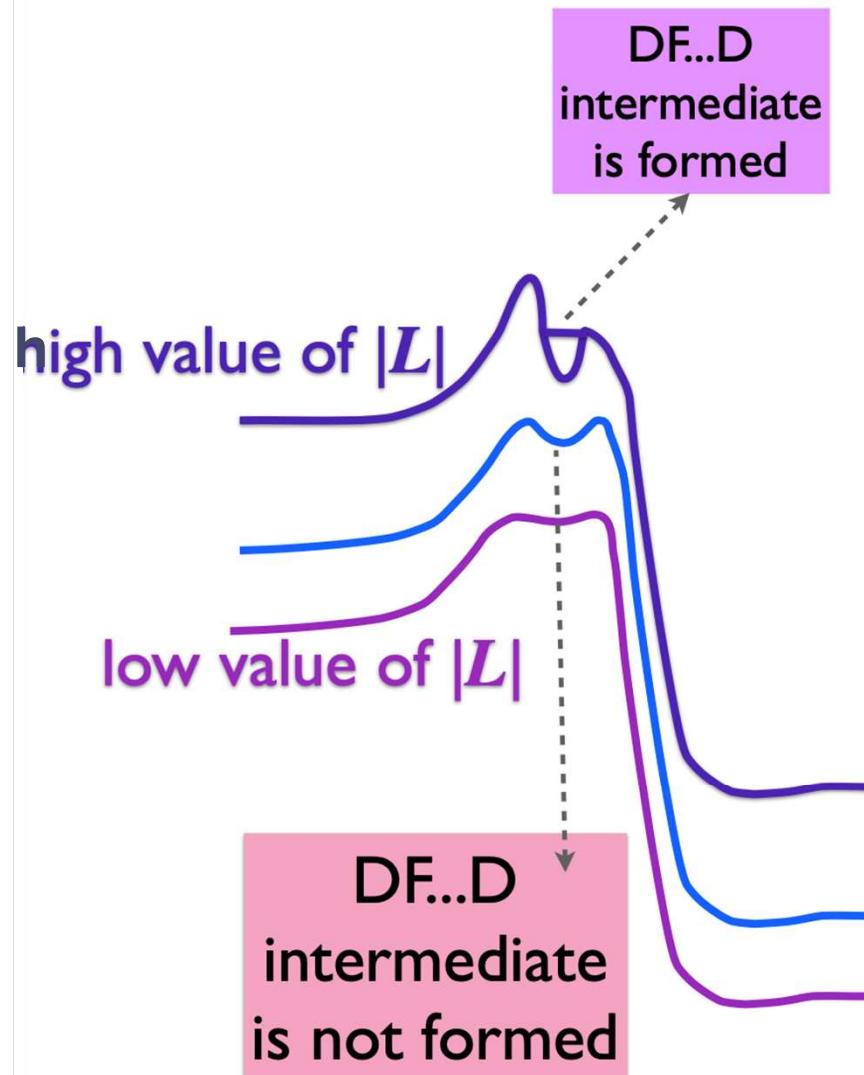
Why?

$F + D_2 \rightarrow DF + D, 1.82 \text{ kcal/mole}$

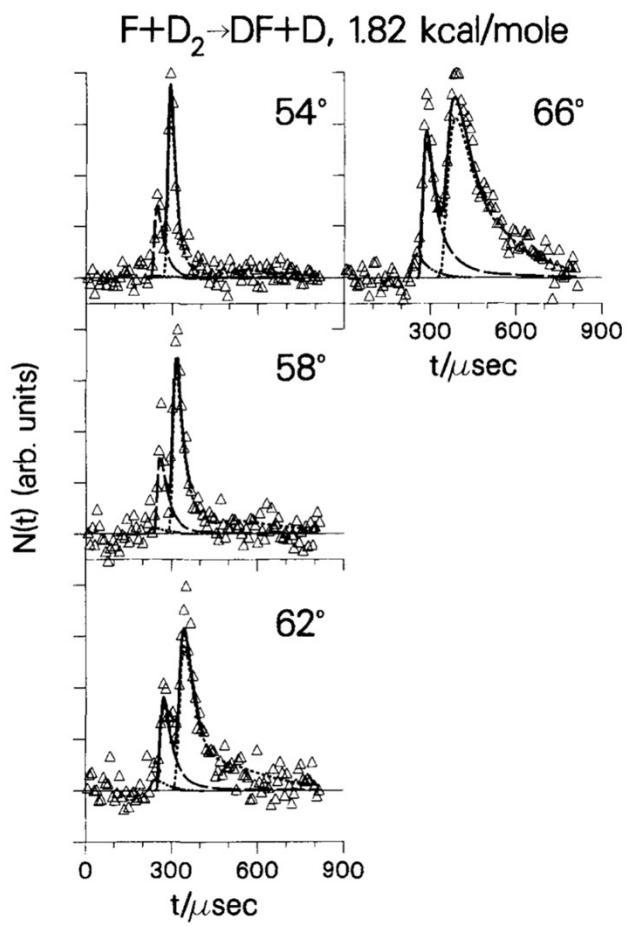
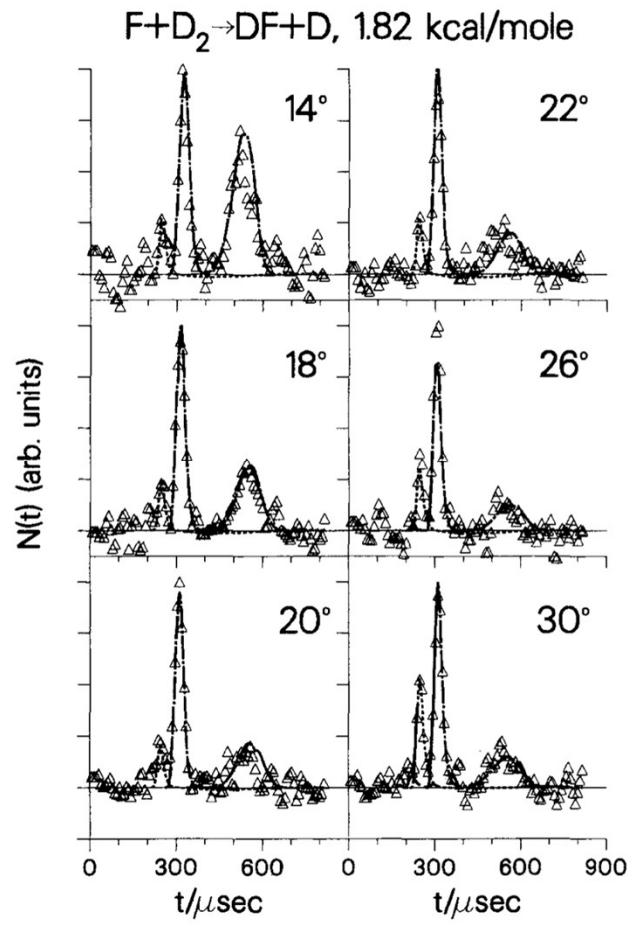


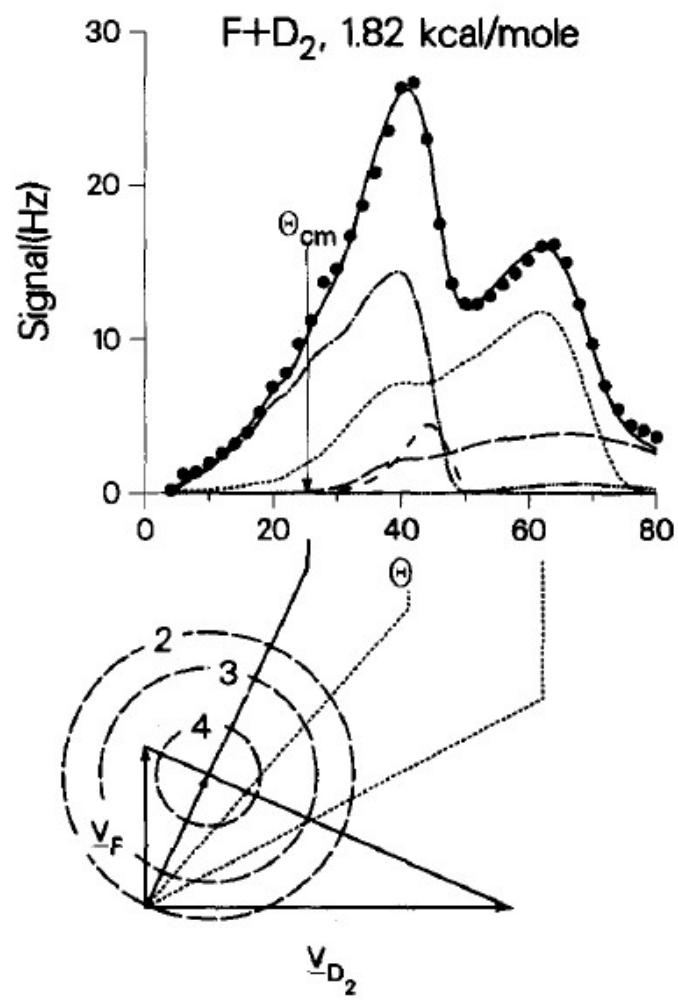
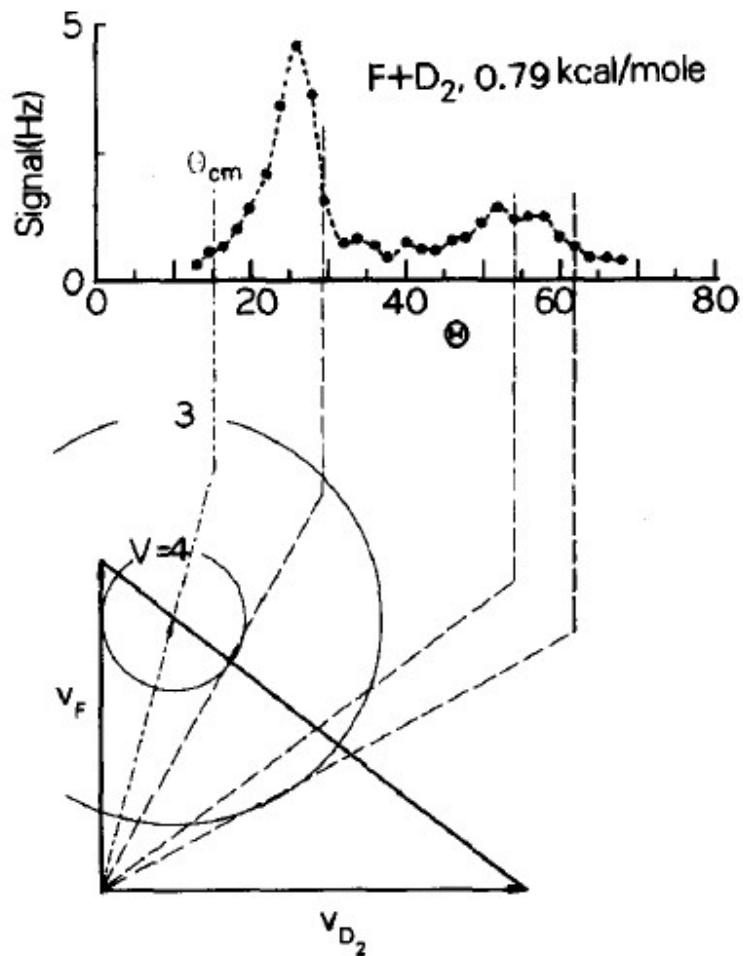
$F + D_2 \rightarrow DF + D, 3.32 \text{ kcal/mole}$





Theory and experiments hinted on the occurrence of Feshbach resonance at collision energy 3.32 kcal/mol. This means, Feshbach resonance is occurring only for high values of collision energy. This can be ascribed to the fact that, at high values of collision energy, values of $|L|$ is such that the corresponding centrifugal barriers create transiently stabilized DF...D complex. For low values of collision energy, and thus low $|L|$, centrifugal barriers are such transient species are not formed (as indicated in the figure here)





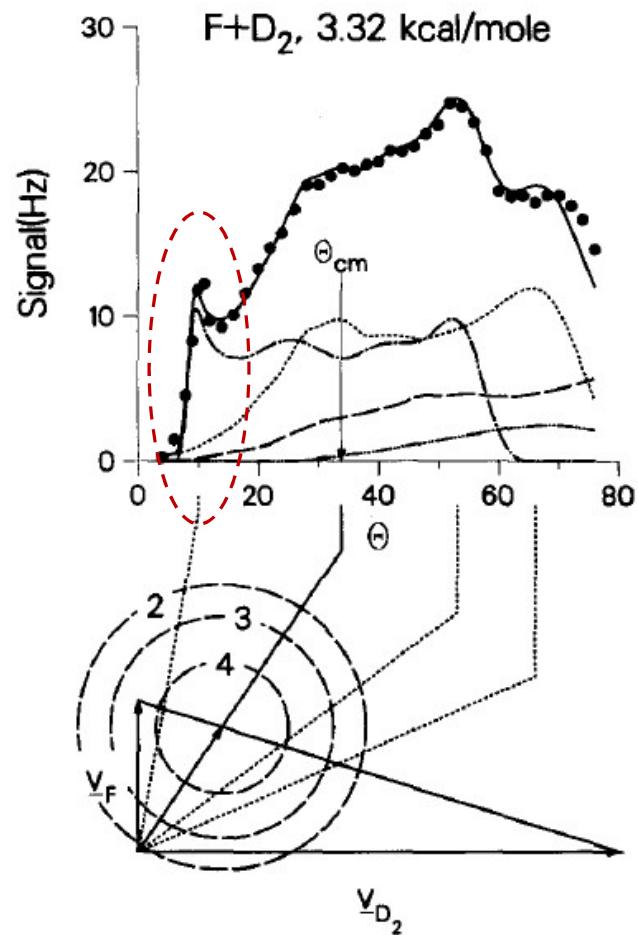
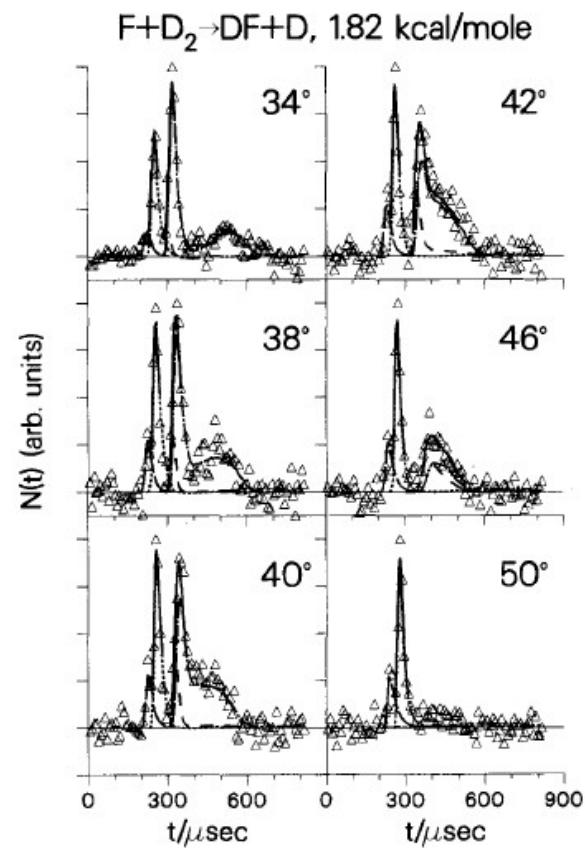
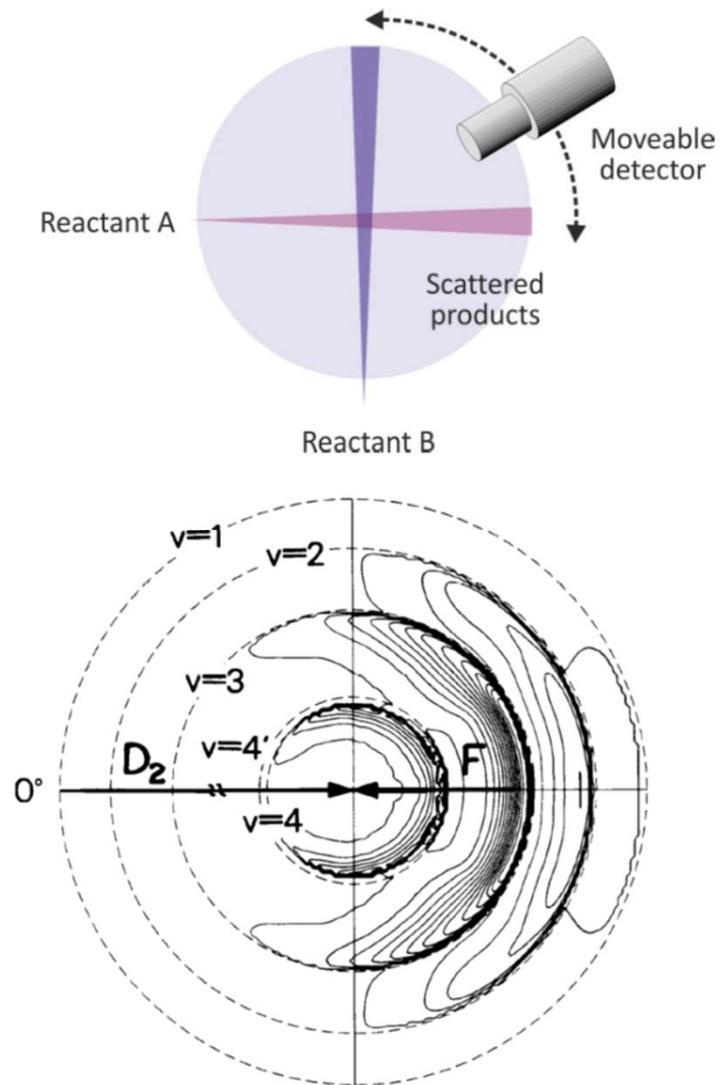
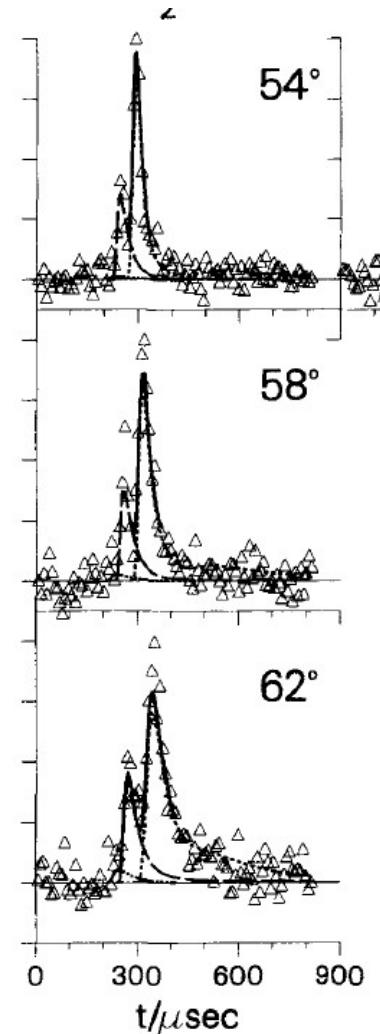
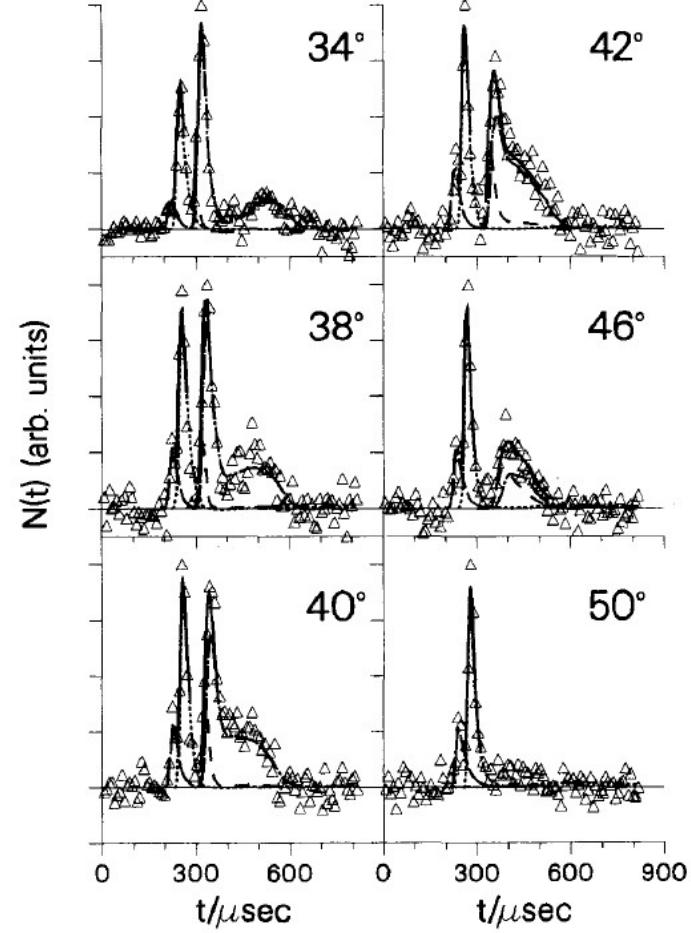
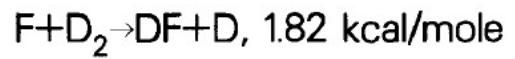
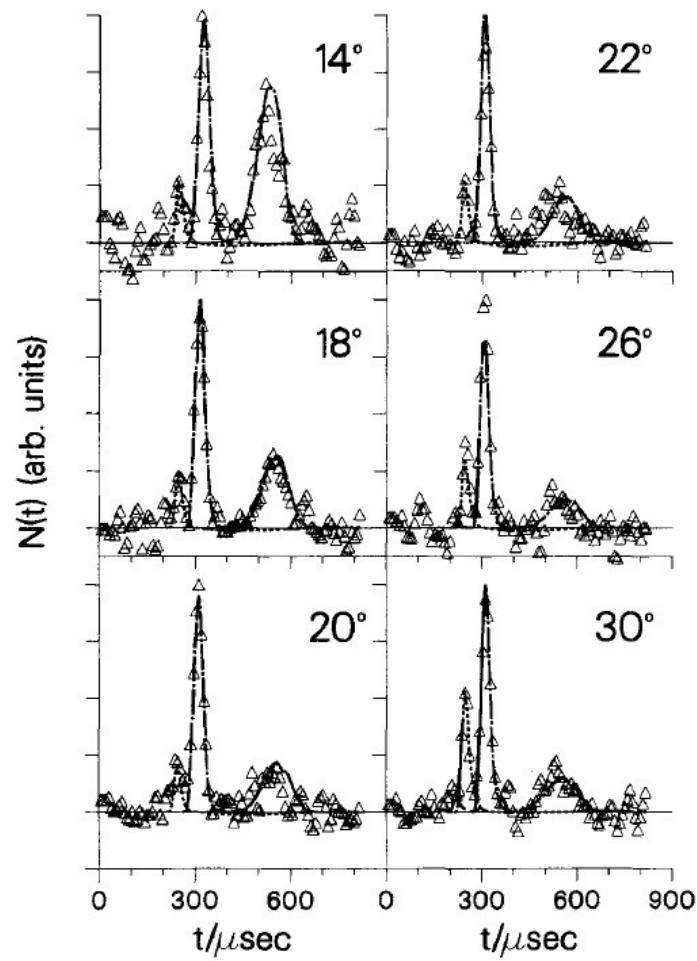
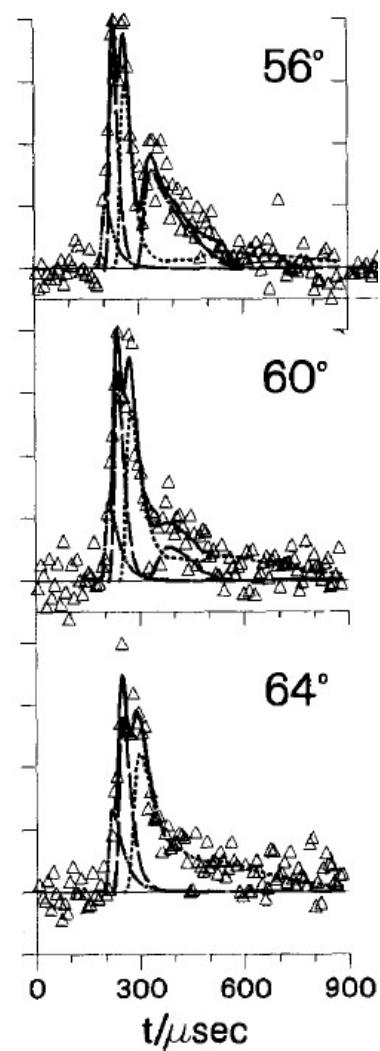
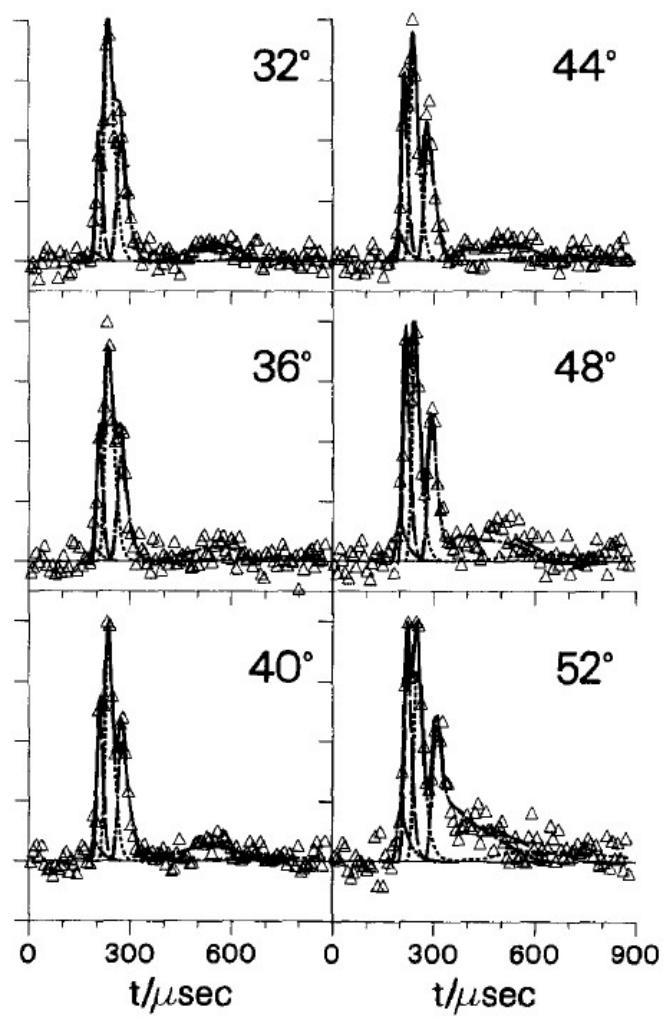
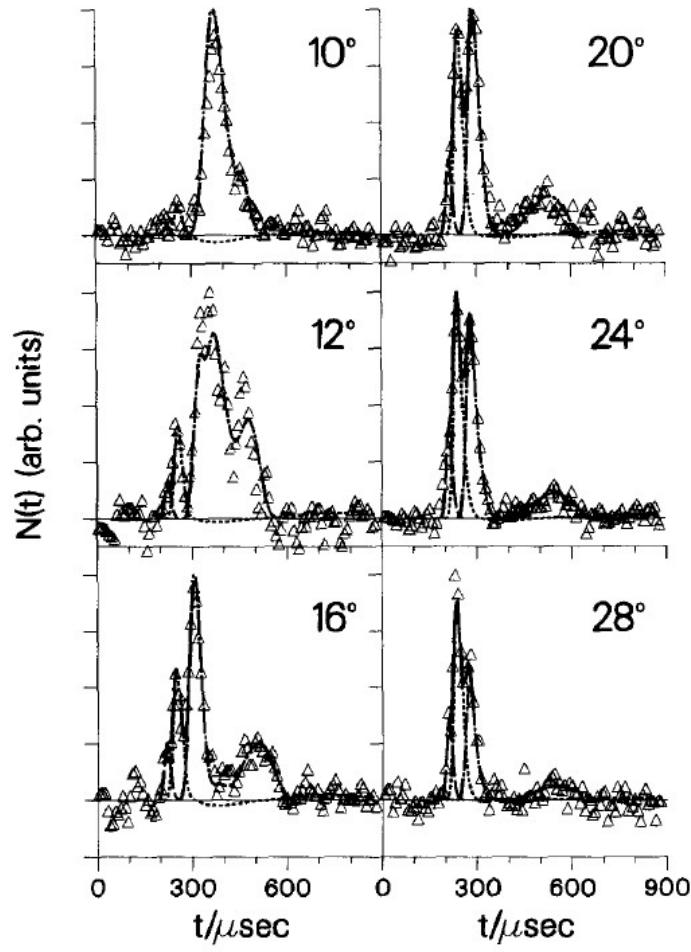
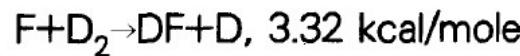


FIG. 3. LAB angular distribution for $\text{F} + \text{D}_2$, 3.32 kcal/mol, showing computer-generated fit (no $v = 4'$ state here).

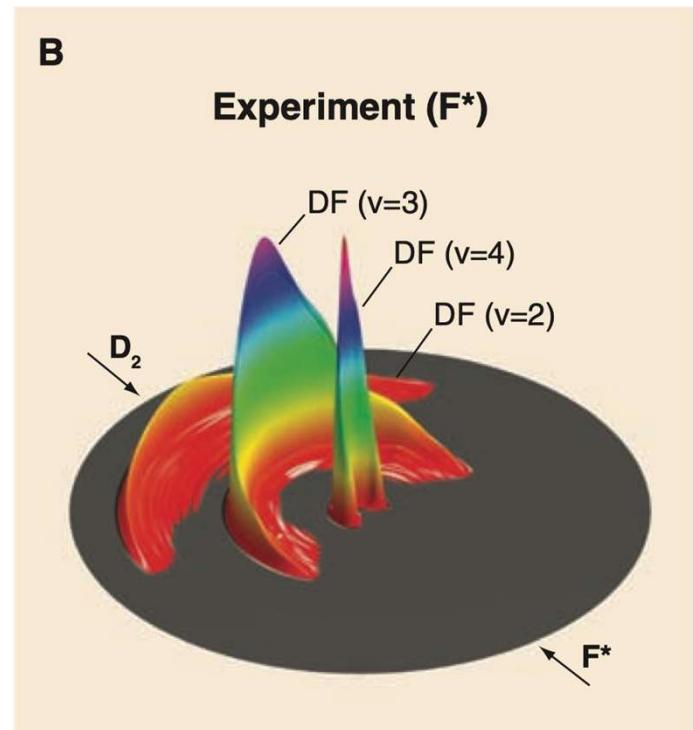
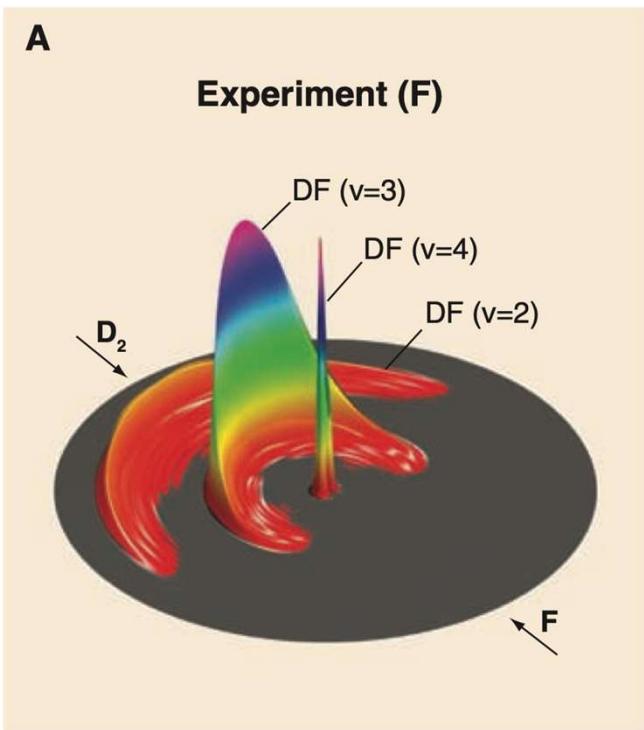


Neumark et al *J. Chem. Phys.* **1985**, *82*, 3067

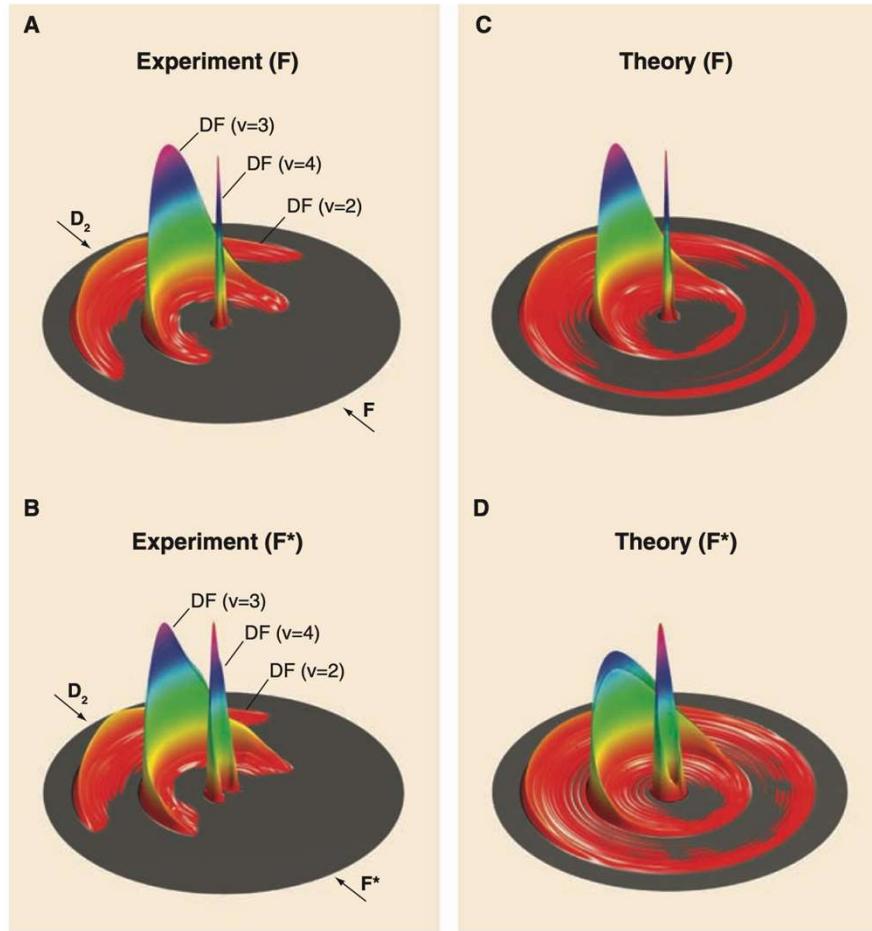




What about F^* ?



Conservation principles!



Mysteries of Lee's Experiments

1. Why is the $D_2 + F$ reaction rebound? 

2. Why is there a forward flux seen when the collision energy is increased? Why is this forward flux only observed for $v=4$? 

3. Why is the population of the DF products higher for $v=3$ (and $v=4$ for some collisional energy)? 