

Week 6

Enhancing Collision Theory

6.1 Threshold Energy and Line-Of-Centers Model

5/2: • Picking up from the previous lecture...

– It follows by plugging in the energy substitutions from last time that

$$u_r f(u_r) du_r = \left(\frac{2}{k_B T}\right)^{3/2} \left(\frac{1}{\mu\pi}\right)^{1/2} E_r e^{-E_r/k_B T} dE_r$$

– Thus,

$$\begin{aligned} k &= \int_0^\infty du_r f(u_r) k(u_r) \\ &= \left(\frac{2}{k_B T}\right)^{3/2} \left(\frac{1}{\mu\pi}\right)^{1/2} \int_0^\infty dE_r E_r e^{-E_r/k_B T} \sigma_r(E_r) \end{aligned}$$

– Now assume that only those collisions for which the relative kinetic energy exceeds a threshold energy E_0 result in a collision. Thus, define

$$\sigma_r(E_r) = \begin{cases} 0 & E_r < E_0 \\ \pi d_{AB}^2 & E_r \geq E_0 \end{cases}$$

– Consequently,

$$\begin{aligned} k &= \left(\frac{2}{k_B T}\right)^{3/2} \left(\frac{1}{\mu\pi}\right)^{1/2} \int_{E_0}^\infty dE_r E_r e^{-E_r/k_B T} \pi d_{AB}^2 \\ &= \left(\frac{8k_B T}{\mu\pi}\right)^{1/2} \pi d_{AB}^2 e^{-E_0/k_B T} \left(1 + \frac{E_0}{k_B T}\right) \\ &= \langle u_r \rangle \sigma_{AB} e^{-E_0/k_B T} \left(1 + \frac{E_0}{k_B T}\right) \end{aligned}$$

– We can use

$$E_a = k_B T^2 \frac{d \ln k}{dT}$$

to relate the above to the activation energy.

- Another simplification we've made is that the reaction cross section is not constant, but actually depends on relative speed.

- Accounting for the collision geometry between the two hard spheres gives rise to the **line-of-centers model**.
- Line-of-centers model:** A model for $\sigma_r(E_r)$ in which the cross section depends on the component of the relative kinetic energy that lies along the line that joins the centers of the colliding molecules.

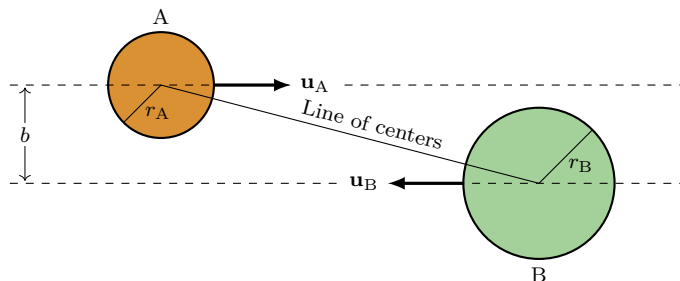


Figure 6.1: Line-of-centers model.

- If we denote the relative kinetic energy along the line of centers by E_{loc} , then we are assuming that a reaction occurs when $E_{loc} > E_0$.
- The main thrust of this model is that we are redefining E_r instead of $\sigma_r(E_r)$ overall.
- The line-of-centers model asserts that two molecules will collide only if the **impact parameter** is less than the sum of the radii of the colliding molecules.
 - In particular, we (re)define

$$\sigma_r(E_r) = \begin{cases} 0 & E_r < E_0 \\ \pi d_{AB}^2 \left(1 - \frac{E_0}{E_r}\right) & E_r \geq E_0 \end{cases}$$

- It follows from math similar to the above that

$$\begin{aligned} k &= \left(\frac{2}{k_B T}\right)^{3/2} \left(\frac{1}{\mu \pi}\right)^{1/2} \int_0^\infty dE_r E_r e^{-E_r/k_B T} \sigma_r(E_r) \\ &= \left(\frac{8k_B T}{\mu \pi}\right)^{1/2} \pi d_{AB}^2 e^{-E_0/k_B T} \\ &= \langle u_r \rangle \sigma_{AB} e^{-E_0/k_B T} \end{aligned}$$

- Impact parameter:** The perpendicular distance between the two dashed lines in Figure 6.1. Denoted by b .
- The cross section exhibits a threshold energy.
 - The dependence of the reaction cross section on the relative kinetic energy of the collision is consistent with the line-of-centers model.
- Relating E_0 to the Arrhenius equation parameters.
 - For the activation energy E_a , we have

$$\begin{aligned} E_a &= k_B T^2 \frac{d \ln k}{dT} \\ &= k_B T^2 \frac{d}{dT} \left\{ \ln \left[\left(\frac{8k_B T}{\pi \mu}\right)^{1/2} \pi d_{AB}^2 \right] - \frac{E_0}{k_B T} \right\} \end{aligned}$$

$$\begin{aligned}
 &= k_B T^2 \frac{d}{dT} \left\{ \ln T^{1/2} - \frac{E_0}{k_B T} + \text{terms not involving } T \right\} \\
 &= E_0 + \frac{1}{2} k_B T
 \end{aligned}$$

■ Tian wants us to memorize the last line above.

– Considering the line-of-centers collision model and the Arrhenius equation yields

$$A = \langle u_r \rangle \sigma_{AB} e^{1/2}$$

- Tian goes through a practice problem.

6.2 Isotropy, Internal Energy, and Center of Mass Assumptions

- 5/4: • Doing away with the assumption that the spheres are isotropic.

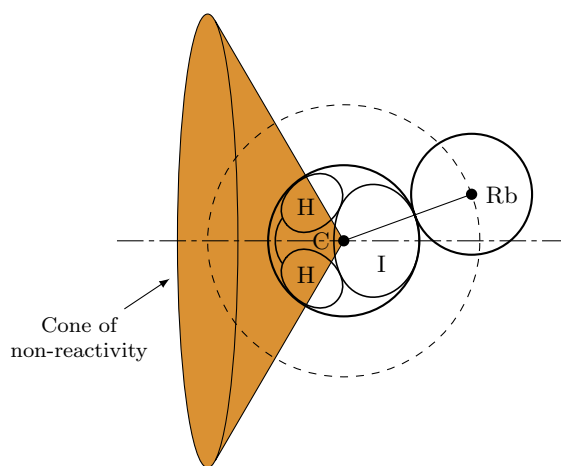
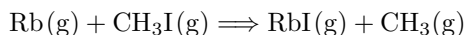


Figure 6.2: Molecules are not isotropic.

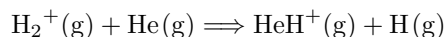
– Consider the reaction



- The rubidium atom must collide with the iodomethane in the vicinity of the iodine atom for a reaction to occur.
- Indeed, many molecules have a **cone of non-reactivity**.

- Additionally, the internal energy of the reactants can affect the cross section of a reaction.

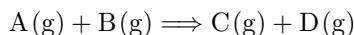
– Consider the reaction



- As the reactant molecule H_2^+ passes through different vibrational states, its reaction cross section changes.
- We only need to understand that other types of energy can have an effect qualitatively; we do not need to work with the shape of the curves quantitatively.

- A reactive collision can be described in a center-of-mass coordinate system.

– Consider the collision and subsequent scattering process for the bimolecular reaction



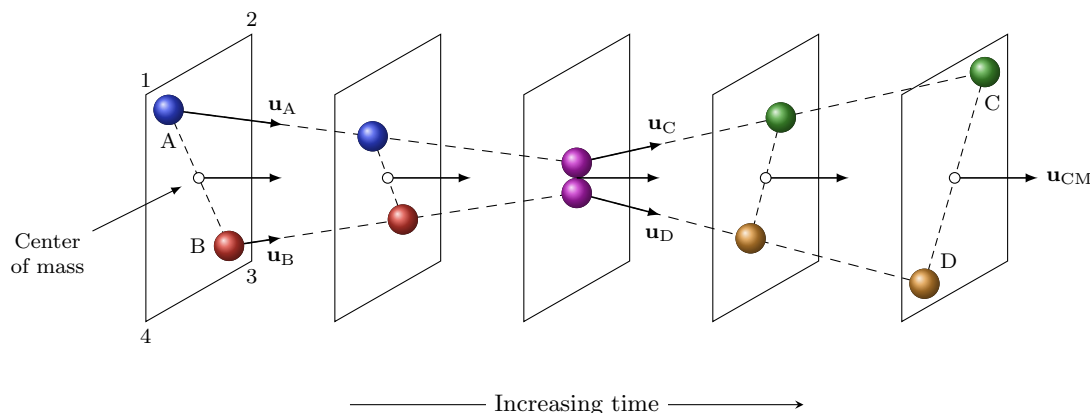


Figure 6.3: Center-of-mass coordinate system.

- Before the collision, A and B are traveling with velocities \mathbf{u}_A and \mathbf{u}_B , respectively.
- The collision generates molecules C and D, which then move away from each other with velocities \mathbf{u}_C and \mathbf{u}_D , respectively.
- \mathbf{R} , the location of the center of mass, is given by

$$\mathbf{R} = \frac{m_A \mathbf{r}_A + m_B \mathbf{r}_B}{M} \quad M = m_A + m_B$$

- The velocity \mathbf{u}_{cm} of the center of mass is the time derivative of the position vector. Therefore, it is given by

$$\mathbf{u}_{cm} = \frac{m_A \mathbf{u}_A + m_B \mathbf{u}_B}{M}$$

- We assume that this is an elastic collision (thus, energy is conserved).
- The total kinetic energy is given by

$$KE_{\text{react}} = \frac{1}{2} m_A u_A^2 + \frac{1}{2} m_B u_B^2$$

- Combining the fact that the relative speed of the two molecules^[1] is given by $\mathbf{u}_r = \mathbf{u}_A - \mathbf{u}_B$ with the definition of \mathbf{u}_{cm} yields

$$\mathbf{u}_A = \mathbf{u}_{cm} + \frac{m_B}{M} \mathbf{u}_r \quad \mathbf{u}_B = \mathbf{u}_{cm} - \frac{m_A}{M} \mathbf{u}_r$$

- Note that the change in plus to minus sign between the two above forms hails from our definition of relative speed as A minus B and not the other way around (as we could also very well define it). In other words, it's just a convention thing, and all that matters is that we're consistent.

- It follows that

$$\begin{aligned} KE_{\text{react}} &= \frac{m_A}{2} \left(\mathbf{u}_{cm} + \frac{m_B}{M} \mathbf{u}_r \right)^2 + \frac{m_B}{2} \left(\mathbf{u}_{cm} - \frac{m_A}{M} \mathbf{u}_r \right)^2 \\ &= \frac{1}{2} M u_{cm}^2 + \frac{1}{2} \mu u_r^2 \end{aligned}$$

- Thus, the kinetic energy is composed of two contributions: one due to the motion of the center of mass, and one due to the relative motion of the two colliding molecules.

¹In particular, the speed of molecule A relative to molecule B, as it is defined.

- We can do a similar analysis for the products to determine that

$$\text{KE}_{\text{prod}} = \frac{1}{2}Mu_{\text{cm}}^2 + \frac{1}{2}\mu'u_r'^2$$

- Note that momentum is conserved, i.e.,

$$m_A\mathbf{u}_A + m_B\mathbf{u}_B = m_C\mathbf{u}_C + m_D\mathbf{u}_D$$

- This implies that \mathbf{u}_{cm} does not change from reactants to products.
- The energy associated with the motion of the center of mass is therefore constant, and we will ignore its constant contribution to the total kinetic energy.

$$E_{\text{react,int}} + \frac{1}{2}\mu u_r^2 = E_{\text{prod,int}} + \frac{1}{2}\mu' u_r'^2$$

- $E_{\text{react,int}}$ and $E_{\text{prod,int}}$ are the total internal energies of the reactants and products, respectively.
- This internal energy takes into account all the degrees of freedom other than translation.

6.3 Experimental Techniques and the Simplest Reaction

- 5/6: • Reactive collisions can be studied using crossed molecular beam machines.

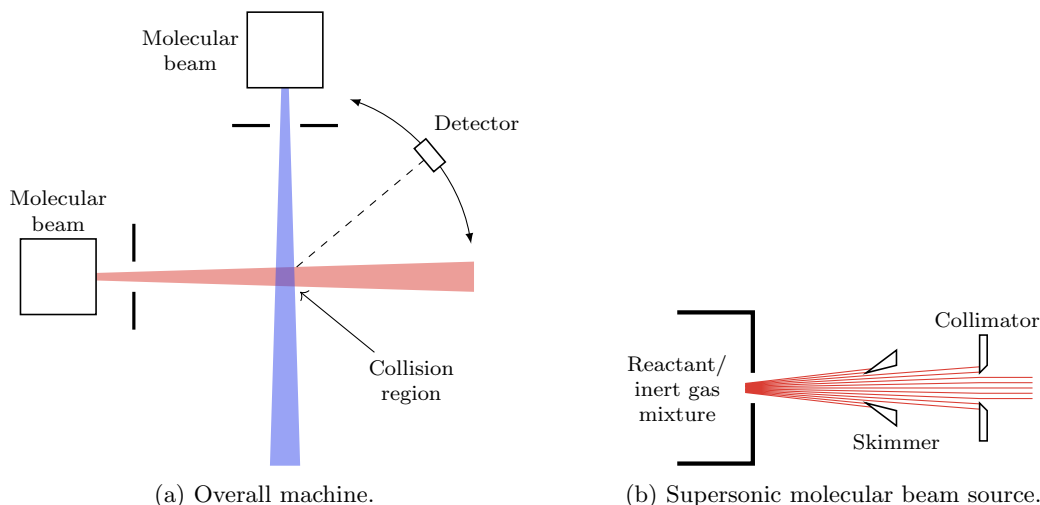
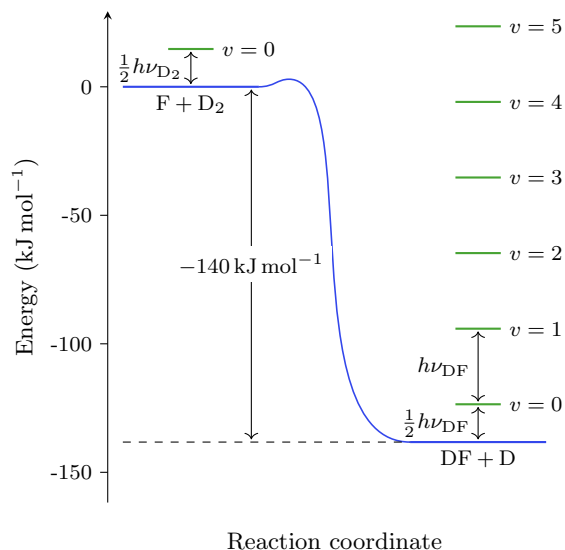
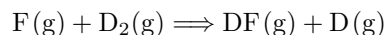


Figure 6.4: Crossed molecular beam machines.

- Figure 6.4a depicts the overall setup in a crossed molecular beam machine. Each reactant is introduced into the vacuum chamber by a molecular beam source. The two molecular beams collide at the collision region.
- Figure 6.4b depicts a supersonic molecular beam source. The reactant is expanded along with an inert gas through a small orifice into the vacuum chamber. A skimmer is used so that a collimated beam of molecules is directed toward the collision region.
- The product molecules are detected using a mass spectrometer.
- A supersonic molecular beam has several important advantages that make it ideal for crossed-beam studies.
 - The supersonic expansion generates a collection of molecules with a high translational energy but a very small spread in molecular speeds.

- In addition, molecules can be prepared with low rotational and vibrational energies.
- If we measure the number of molecules of a particular reaction product that arrive at the detector as a function of time after the collision, we can resolve the velocity distribution of the product molecules.
- If we measure the total number of product molecules as a function of scattering angle, we can determine the angular distribution of the product molecules.

- The reaction

Figure 6.5: Energy diagram for $\text{F} + \text{D}_2$.

- Figure 6.5 depicts the energy of the lowest vibrational state of D_2 and the energies of the first six vibrational states of DF .
 - In drawing these energy states, we have tacitly assumed that the vibrational motion of both D_2 and DF is harmonic.
- The difference between the ground electronic state energies of D_2 and DF is

$$D_e(\text{D}_2) - D_e(\text{DF}) = -140 \text{ kJ mol}^{-1}$$

- The reaction has an activation energy barrier of about 7 kJ mol^{-1} .
- Moreover, we have that

$$E_{\text{tot}} = E_{\text{trans}} + E_{\text{int}} = E'_{\text{trans}} + E'_{\text{int}}$$

where E_{int} is the internal energy of the reactants, E_{trans} is the relative translational energy of the reactants, E'_{int} is the internal energy of the products, and E'_{trans} is the relative translational energy of the products.

- Additionally, note that

$$E_{\text{int}} = E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} \qquad E'_{\text{int}} = E'_{\text{rot}} + E'_{\text{vib}} + E'_{\text{elec}}$$

i.e., that $E_{\text{int}}, E'_{\text{int}}$ are the sum of the rotational, vibrational, and electronic energies of the reactants and products, respectively.

- Lastly, note that $E_{\text{elec}} = -D_e(\text{D}_2)$ and $E'_{\text{elec}} = -D_e(\text{DF})$.

6.4 Chapter 30: Gas-Phase Reaction Dynamics

From McQuarrie and Simon (1997).

- 5/18:
- An underlying assumption of the step model for $\sigma_r(E_r)$.
 - All molecular collisions with relative energy E_r yield the same reaction cross section.
 - Reality: Not all molecular collisions are head-on; some are more grazing. In a head-on collision, the molecules come to a stop and, in principle, all the relative kinetic energy becomes available for reaction. In contrast, a grazing collision provides almost no energy for reaction.
 - **Line-of-centers model** (for $\sigma_r(E_r)$): A model in which the reaction cross section depends on the component of the relative kinetic energy that lies along the line that joins the centers of the colliding molecules. *Given by*

$$\sigma_r(E_r) = \begin{cases} 0 & E_r < E_0 \\ \sigma_{AB} \left(1 - \frac{E_0}{E_r}\right) & E_r \geq E_0 \end{cases}$$

- Derivation of the line-of-centers model.

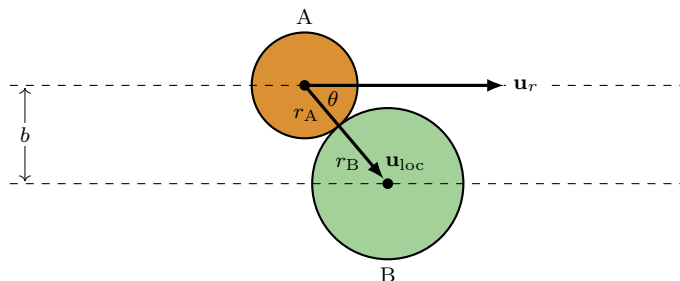


Figure 6.6: Line-of-centers model derivation.

- Qualitative observations and definitions.
 - From the reference frame of molecule B, molecule A approaches with relative speed $\mathbf{u}_r = \mathbf{u}_A - \mathbf{u}_B$ and relative kinetic energy $E_r = \mu u_r^2/2$.
 - Applying the line-of-centers coordinate system, molecule A approaches molecule B along the loc (line of centers) axis with speed \mathbf{u}_{loc} .
 - They will collide if the **impact parameter** b is less than the sum of the two radii $r_A + r_B = d_{AB}$.
 - The impact parameter determines the energy of the collision on a scale of zero to E_r . In particular, if $b = 0$, then $E_{loc} = E_r$, and if $b \geq d_{AB}$, $E_{loc} = 0$, where E_{loc} denotes the relative kinetic energy along the line of centers.
 - Naturally, a reaction will occur iff $E_{loc} \geq E_0$.
- Mathematical derivation (Fogler & Gürmen, 2008).
 - We have from basic trigonometry that

$$\cos \theta = \frac{u_{loc}}{u_r} \qquad \sin \theta = \frac{b}{d_{AB}}$$

- Thus, we know that

$$u_{loc}^2 = u_r^2 \cos^2 \theta = u_r^2 (1 - \sin^2 \theta) = u_r^2 \left[1 - \left(\frac{b}{d_{AB}} \right)^2 \right]$$

and hence

$$E_{loc} = \frac{1}{2} \mu u_{loc}^2 = \frac{1}{2} \mu u_r^2 \left[1 - \left(\frac{b}{d_{AB}} \right)^2 \right] = E_r \left[1 - \left(\frac{b}{d_{AB}} \right)^2 \right]$$

- Now recall that a chemical reaction only takes place if $E_{\text{loc}} \geq E_0$. By the above, an equivalent requirement for a chemical reaction to take place is that

$$\begin{aligned}
 E_r \left[1 - \left(\frac{b}{d_{\text{AB}}} \right)^2 \right] &\geq E_0 \\
 \left(\frac{b}{d_{\text{AB}}} \right)^2 &\leq 1 - \frac{E_0}{E_r} \\
 \left| \frac{b}{d_{\text{AB}}} \right| &\leq \sqrt{1 - \frac{E_0}{E_r}} \\
 |b| &\leq d_{\text{AB}} \sqrt{1 - \frac{E_0}{E_r}}
 \end{aligned}$$

i.e., that the impact parameter lie within some range, specifically one whose width is determined by the total energy of the reactants E_r and is at most d_{AB} (in the case of infinite reactant energy).

- It is this observation that motivates our definition of the **reaction diameter**. The physical meaning of this quantity is analogous to that of the collision diameter: Whereas the collision diameter defined a cylinder in which other molecules had to lie to *collide* with one molecule in particular (see Figure 2.1), the reaction diameter defines a cylinder (the **reaction cylinder**) in which other molecules must lie to *react* with one molecule in particular.
- One consequence of this physical interpretation is that $\sigma_r(E_r) = \pi b_{\text{crit}}^2$, i.e., that the reaction cross section is a perpendicular cross section of the reaction cylinder in much the same way that the collision cross section is a perpendicular cross section of the collision cylinder.
- Another consequence is that two molecules with impact parameter equal to b_{crit} will have *just enough* energy to react, and no more. In other words, they will possess exactly E_0 units of energy. Mathematically,

$$E_0 = E_r \left[1 - \left(\frac{b_{\text{crit}}}{d_{\text{AB}}} \right)^2 \right]$$

- Solving the above for b_{crit}^2 and substituting into the definition of $\sigma_r(E_r)$ in terms of b_{crit} yields

$$\sigma_r(E_r) = \pi d_{\text{AB}}^2 \left(1 - \frac{E_0}{E_r} \right) = \sigma_{\text{AB}} \left(1 - \frac{E_0}{E_r} \right)$$

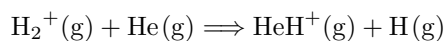
for the case where $E_r \geq E_0$, as desired. We will naturally still take $\sigma_r(E_r) = 0$ when $E_r < E_0$.

- **Impact parameter:** The perpendicular distance between the paths along which the two molecules travel. *Denoted by b .*
- **Reaction diameter:** The largest value of the impact parameter at which two molecules of combined energy E_r will still react. *Denoted by b_{crit} . Also known as **critical impact parameter**.*
- McQuarrie and Simon (1997) gives an example of a bimolecular gas phase reaction for which the relationship between the reaction cross section and the collision energy is as described by the line-of-centers model.
- Substituting the reaction cross section as defined by the line-of-centers model into the integral defining k yields

$$k = \langle u_r \rangle \sigma_{\text{AB}} e^{-E_0/k_B T}$$

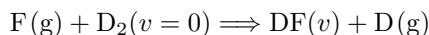
- McQuarrie and Simon (1997) relates E_0 to the Arrhenius equation parameters as in class.
- Upon reviewing experimentally determined collision cross section functions for a number of reactions, we can conclude that even the line-of-centers model is insufficient, and we need to move beyond simple hard-sphere collision theories.

- An underlying assumption of all hard-sphere models.
 - Every collision with sufficient energy is reactive, regardless of orientation.
 - Reality: A specific orientation of components is typically required for molecules that are not spherically symmetric.
- McQuarrie and Simon (1997) discusses the $\text{Rb(g)} + \text{CH}_3\text{I(g)}$ reaction from class and Figure 6.2.
- An underlying assumption of all hard-sphere models.
 - Only the translational energy of reacting molecules affects the reaction cross section.
 - Reality: The presence or lack thereof of internal energy, as well as how it's distributed between the rotational, vibrational, and electronic states, plays an integral role in determining the reaction cross section. Additionally, internal energy changes can occur during the course of a reaction.
- An analysis of the following reaction with the hydrogen molecular ion in different vibrational states.



- For the vibrational states $v = 0, \dots, 3$, there is a threshold energy of about 70 kJ mol^{-1} .
 - For vibrational states $v = 4, 5$, there is no threshold energy.
 - This is because these higher vibrational states can lend more than the threshold energy worth of energy to the reaction, so no supplementary translational motion is needed.
 - McQuarrie and Simon (1997) discusses the center-of-mass coordinate system.
 - The energy and momentum conservation laws allow us to define the velocity of the products.
 - They do not, however, allow us to define the angle at which the products scatter.
 - We will soon see that the scattering angles are often highly **anisotropic**.
 - **Anisotropic** (entity): An object or substance the properties of which vary by the direction in which they're measured.
 - **Crossed molecular beam method**: An experimental setup designed to cross a beam of A molecules with a beam of B molecules at a specific location inside a large vacuum chamber before detecting the product molecules with a mass spectrometer.
 - “In some crossed molecular beam machines, the detector can be rotated in the plane defined by the two molecular beams, thereby allowing the measurement of the angular distribution of the scattered products” (McQuarrie & Simon, 1997, p. 1244).
 - “A supersonic molecular beam can be generated by taking a high-pressure, dilute mixture of the reactant molecule of interest in an inert carrier gas (He and Ne are commonly used) and pulsing the mixture through a small nozzle into the vacuum chamber” (McQuarrie & Simon, 1997, p. 1244).
 - Crossed molecular beam experiments can be used to measure reaction cross sections: We alter the relative velocities (and hence collision energies) of the reactants and record the product yield.
- 5/19:
- **Potential energy diagram**: A diagram that indicates how the potential energy changes as the reaction proceeds along the reaction coordinate.
 - McQuarrie and Simon (1997) discusses the potential energy diagram for the $\text{F} + \text{D}_2$ reaction (Figure 6.5).
 - Using the conservation of energy, we can calculate that $v \leq 4$ for the product DF.
 - Additionally, we can experimentally measure the vibrational state of DF because molecules with a higher vibrational state must have more of their energy internal instead of as translational, meaning that they move slower.

- Example: Consider the reaction



where the relative translational energy of the reactants is 7.62 kJ mol^{-1} . Assume the reactants and products are in their ground electronic [$D_e(\text{D}_2) - D_e(\text{DF}) = -140 \text{ kJ mol}^{-1}$] and rotational states. Treat the vibrational motion of D_2 and DF as harmonic with $\tilde{\nu}_{\text{D}_2} = 2990 \text{ cm}^{-1}$ and $\tilde{\nu}_{\text{DF}} = 2907 \text{ cm}^{-1}$. Determine the range of possible vibrational states of the product.

- We apply conservation of energy.

$$\begin{aligned} E_{\text{reactants}} &= E_{\text{products}} \\ E_{\text{trans}} + E_{\text{vib}} + E_{\text{elec}} &= E'_{\text{trans}} + E'_{\text{vib}} + E'_{\text{elec}} \\ E_{\text{trans}} + E_{\text{vib}} - D_e(\text{D}_2) &= E'_{\text{trans}} + E'_{\text{vib}} - D_e(\text{DF}) \end{aligned}$$

- We are given in the problem statement that $E_{\text{trans}} = 7.62 \text{ kJ mol}^{-1}$, $E_{\text{vib}} = \frac{1}{2}h\nu_{\text{D}_2}$ ($v=0$ for D_2), and $D_e(\text{D}_2) - D_e(\text{DF}) = -140 \text{ kJ mol}^{-1}$. Moreover, since

$$\nu_{\text{D}_2} = \frac{c}{\lambda} = \frac{c}{1/\tilde{\nu}} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{1/2.99 \times 10^5 \text{ m}^{-1}} = 8.96 \times 10^{13} \text{ s}^{-1}$$

we have that

$$E_{\text{vib}} = \frac{1}{2}h\nu_{\text{D}_2} = \frac{1}{2} \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) (N_{\text{A}} \text{ mol}^{-1})(6.626 \times 10^{-34} \text{ J s})(8.96 \times 10^{13} \text{ s}^{-1}) = 17.9 \text{ kJ mol}^{-1}$$

- Thus, we know that

$$\begin{aligned} E'_{\text{vib}} &= E_{\text{trans}} + E_{\text{vib}} - [D_e(\text{D}_2) - D_e(\text{DF})] - E'_{\text{trans}} \\ &= 7.62 \text{ kJ mol}^{-1} + 17.9 \text{ kJ mol}^{-1} + 140 \text{ kJ mol}^{-1} - E'_{\text{trans}} \\ &= 166 \text{ kJ mol}^{-1} - E'_{\text{trans}} \end{aligned}$$

- Since $E'_{\text{trans}} \geq 0$, we must have $E'_{\text{vib}} \leq 166 \text{ kJ mol}^{-1}$. This combined with the fact that

$$E'_{\text{vib}} = \left(v + \frac{1}{2} \right) h\nu_{\text{DF}} = \left(v + \frac{1}{2} \right) (34.8 \text{ kJ mol}^{-1})$$

reveals that $v \leq 4$, where $h\nu_{\text{DF}}$ is evaluated analogously to how we computed $h\nu_{\text{D}_2}$.

- Note that this result is in agreement with Figure 6.5.