Week 7

Gas-Phase Product Molecule Analysis and Intro to Lattices

7.1 Directional Scattering of the Product Molecule

- The velocity and angular distribution of the products of a reactive collision.
    - We have that

$$E'_{\text{trans}} + E'_{\text{vib}} = E_{\text{trans}} + E_{\text{vib}} - [D_e(D_2) - D_e(DF)]$$
$$= 7.62\,\text{kJ mol}^{-1} + 17.9\,\text{kJ mol}^{-1} + 140\,\text{kJ mol}^{-1}$$
$$= 166\,\text{kJ mol}^{-1}$$

    - Additionally, we know that

$$E'_{\text{trans}} + E'_{\text{vib}} = \frac{1}{2}\mu' u_r'^2 + (34.8\,\text{kJ mol}^{-1})\left(v + \frac{1}{2}\right) = 166\,\text{kJ mol}^{-1}$$

    - The relationship between the vibrational quantum number, the relative speed of the products, and the speed of DF relative to the center of mass has been tabulated.
- A contour map of the angular and speed distributions for the product molecule.
    - The contour plot.
        - The center of mass is fixed at the origin.
        - The dashed circles correspond to the maximum relative speeds a DF molecule can have for the indicated vibrational state.
        - The product molecules preferentially scatter back in the direction of the incident fluorine atom, a scattering angle of $\theta = 180°$.
        - The arrows at the bottom of the figure show the direction with which each reactant molecule approaches the other.
    - Another picture is provided, illustrating the atom-molecule reaction $F + D_2$ in which $\theta = 0°$ and $\theta = 180°$.
    - The influence of rotation.
        - Large numbers of product molecules have speeds between the dashed circles.
        - The dash circles correspond to the case where there is internal energy only in the vibrational states of the molecule, in which case the rotational energy corresponding to these circles is $E_{\text{rot}} = 0$ with $J = 0$.

■ If DF is produced in an excited rotational state, we would expect to observe a speed that has a value intermediate between two fo the dashed circles.

- Not all gas-phase chemical reactions are rebound reactions.

  – Consider the reaction
  $$K(g) + I_2(g) \longrightarrow KI(g) + I(g)$$

  ■ The product diatomic molecule in this case (KI) is preferentially scattered in the forward direction along the direction of the incident K atom.

  – Consider the reaction
  $$O(g) + Br_2(g) \Longrightarrow BrO(g) + Br(g)$$

  ■ The product molecule BrO is forward and back scattered with equal intensity.

  – Both of these observations can be read off of the contour maps of the two reactions.

7.2   Potential Energy Surfaces

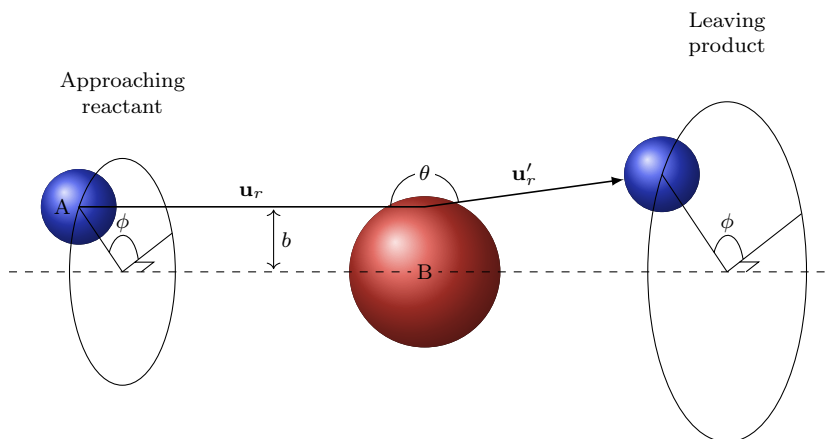5/11:   • The velocity and angular distribution of the products of a reactive collision.

Figure 7.1: Velocity and angular distributions of the products.

  – For a fixed value of the impact parameter b, the reactants and products take on all possible angles ϕ with equal probability, thereby forming a cone around the relative velocity vector $\mathbf{u}_r$.

  – The angle θ, however, depends on the dynamics of the reaction and must be determined experimentally.

- The potential energy of a polyatomic molecule depends on more than one variable.

  – D_2.

  ■ Consider the potential energy curve of D_2. 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 molecule.

  – H_2O.

  ■ The potential energy of a water molecule is a function of the three parameters r_{O-H_A}, r_{O-H_B}, and α (two bond lengths and the interbond angle). In an equation,

  $$V = V(r_{O-H_A}, r_{O-H_B}, \alpha)$$

- A plot of the complete potential energy surface of a water molecule therefore requires four axes.

• The potential energy of a chemical reaction depends on more than one variable.

F
$\beta = 180°$
F $- - - - - -$ D$_A$ —— D$_B$

F
$\beta = 180°$
D$_A$ —— D$_B$

F
$\beta = 180°$
D$_A$ —— D$_B$
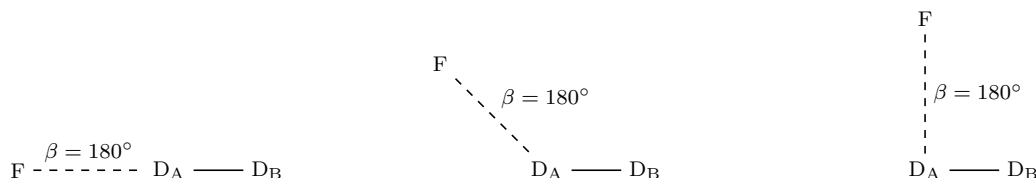
Figure 7.2: Angle of attack in F + D$_2$.

- Consider, once again, the reaction

$$F(g) + D_A D_B(g) \Longrightarrow D_A F(g) + D_B(g)$$
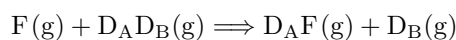
- When the reactants are at infinite separation, there are no attractive or repulsive forces between the fluorine atom and the D$_2$ molecule, so the potential energy surface for the reaction is the same as that for an isolated D$_2$ molecule.

- Likewise, when the products are at infinite separation, the potential-energy surface for the reaction is the same as the for the isolated DF molecule.

- As the reaction occurs, however, the distance between the fluroine atom and D$_A$ decreases and 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$_2$ molecule.

• As with the angular and speed distributions, we can draw an energy contour map for the reaction.

- The zero of energy is defined as the infinitely separated reactants. Point B is the location of the transition state of the reaction.

• Tian does a brief summary of Chapter 30.