Week 7

Gas-Phase Product Molecule Analysis and Intro to Lattices

7.1 Directional Scattering of the Product Molecule

5/9:

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

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

  - 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 $\text{F} + \text{D}_2$ 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
    $$\mathrm{K(g) + I_2(g) \longrightarrow KI(g) + I(g)}$$
    - 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
    $$\mathrm{O(g) + Br_2(g) \Longrightarrow BrO(g) + Br(g)}$$
    - 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.