

## 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  $\theta = 180^\circ$ .
- 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  $\theta = 0^\circ$  and  $\theta = 180^\circ$ .

– 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
$$\text{K(g)} + \text{I}_2\text{(g)} \longrightarrow \text{KI(g)} + \text{I(g)}$$
■ 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
$$\text{O(g)} + \text{Br}_2\text{(g)} \Longrightarrow \text{BrO(g)} + \text{Br(g)}$$
■ 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.

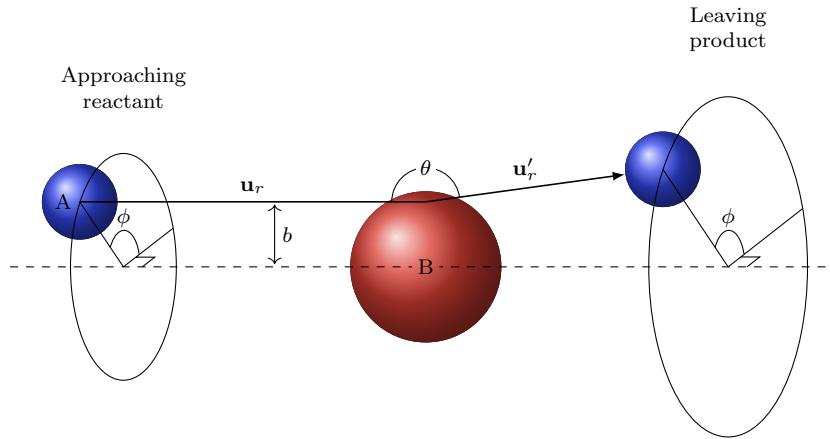
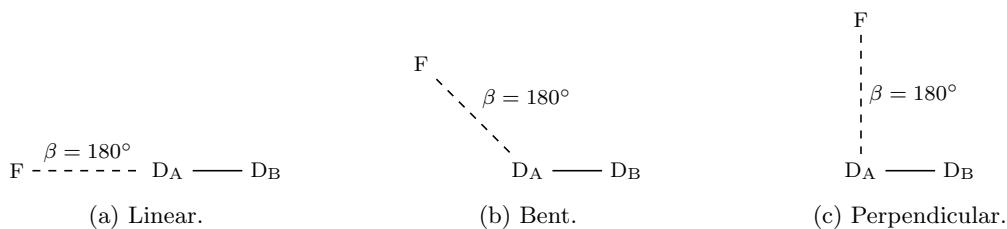


Figure 7.1: Velocity and angular distributions of the products.

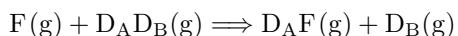
- For a fixed value of the impact parameter  $b$ , the reactants and products take on all possible angles  $\phi$  with equal probability, thereby forming a cone around the relative velocity vector  $\mathbf{u}_r$ .
- The angle  $\theta$ , however, depends on the dynamics of the reaction and must be determined experimentally.
- The potential energy of a polyatomic molecule depends on more than one variable.
  - $\text{D}_2$ .
    - Consider the potential energy curve of  $\text{D}_2$ . 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  $\text{D}_2$  molecule.
  - $\text{H}_2\text{O}$ .
    - The potential energy of a water molecule is a function of the three parameters  $r_{\text{O}-\text{H}_A}$ ,  $r_{\text{O}-\text{H}_B}$ , and  $\alpha$  (two bond lengths and the interbond angle). In an equation,

$$V = V(r_{\text{O}-\text{H}_A}, r_{\text{O}-\text{H}_B}, \alpha)$$

- 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.

Figure 7.2: Angle of attack in  $\text{F} + \text{D}_2$ .

- Consider, once again, the reaction



- When the reactants are at infinite separation, there are no attractive or repulsive forces between the fluorine atom and the  $\text{D}_2$  molecule, so the potential energy surface for the reaction is the same as that for an isolated  $\text{D}_2$  molecule.
- Likewise, when the products are at infinite separation, the potential-energy surface for the reaction is the same as that for the isolated  $\text{DF}$  molecule.
- As the reaction occurs, however, the distance between the fluoroine atom and  $\text{D}_A$  decreases and the distance between  $\text{D}_A$  and  $\text{D}_B$  increases, and the potential energy depends on both distances.
- The potential energy also depends on the angle at which the F atom approaches the  $\text{D}_2$  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.

### 7.3 Lattice Structure

5/13:

- The unit cell is the fundamental building block of a crystal.
  - We can think of a crystal as a two- or three-dimensional lattice.
  - Either way, we can identify blocks in the lattice that form a regularly repeating structure.
- **Face-centered cubic (unit cell):** The following unit cell. *Also known as FCC, cubic close-packing. Structure*

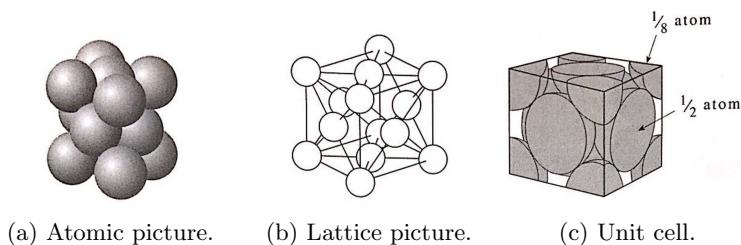


Figure 7.3: Face-centered cubic unit cell.

- Figure 7.3a shows the set of atoms that contribute to a unit cell of the crystal. The unit cell, itself, is a cube however (see Figure 7.3c).
- Figure 7.3b shows the unit cell for a three-dimensional lattice model of copper, where each point of the crystal is associated with a lattice point.
- Figure 7.3c shows the fractions of each copper atom shown in Figure 7.3a that contribute to the unit cell of the crystal.
- There are four atoms per unit cell (six half-atoms and eight eighth-atoms).
- Example: The packing of copper atoms in a copper crystal gives a face-centered cubic unit cell.

- **Body-centered cubic (unit cell):** The following unit cell. *Also known as BCC. Structure*

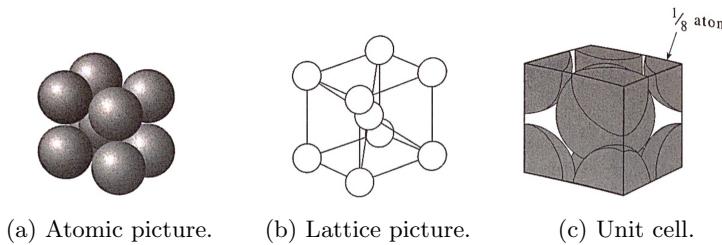


Figure 7.4: Body-centered cubic unit cell.

- There are two atoms per unit cell.
- Example: The packing of potassium atoms in a crystal.

- **Primitive cubic (unit cell):** The following unit cell. *Also known as simple cubic. Structure*

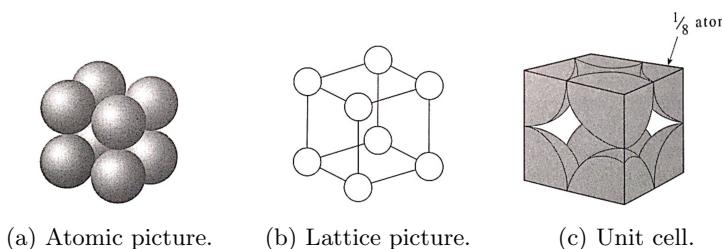


Figure 7.5: Body-centered cubic unit cell.

- There is one atom per unit cell.
- Example: The packing of polonium atoms in a crystal.

- **Unit cell:** The simplest repeating unit in the crystal. *Structure*

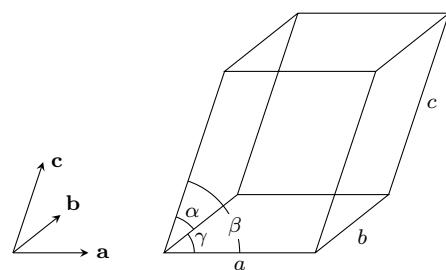


Figure 7.6: Unit cell.

- Opposite faces of a unit cell are parallel.
- The edge of the unit cell connects equivalent points.
- Unit cells all have the same general shape.
  - We take the bottom left corner of the unit cell to be the origin of the  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$  coordinate system.
  - The unit cell is defined by the distances  $a$ ,  $b$ , and  $c$  (which give its length along the  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  axes, respectively) and the angles  $\alpha$ ,  $\beta$ , and  $\gamma$  (which lie between the three pairs of axes).
  - Note that henceforth unless stated otherwise, the  $\mathbf{a}$  axis points to the right, the  $\mathbf{b}$  axis points back, and the  $\mathbf{c}$  axis points up, as in Figure 7.6.
- Tian gives examples of unit cells for crystals containing more than one atom as well as what kinds of crystals take these structures.
- **Bravais lattices:** The fourteen distinct unit cells necessary to generate all possible crystal lattices.
  - The French physicist August Bravais proved that only the Bravais lattices are needed to generate all possible structures.
- We can interpret the points in the unit cell as atoms or molecules. For example, crystalline  $C_{60}$  forms a face-centered cubic unit cell.
- **Miller indices:** The three indices that we use to specify parallel planes through a crystal lattice. *Denoted by  $h$ ,  $k$ ,  $l$ . Given by*

$$h = \frac{a}{a'} \quad k = \frac{b}{b'} \quad l = \frac{c}{c'}$$

where the plane in question intersects the  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  axes of the unit cell at points  $a'$ ,  $b'$ , and  $c'$ , respectively.

- Three basic types of planes.

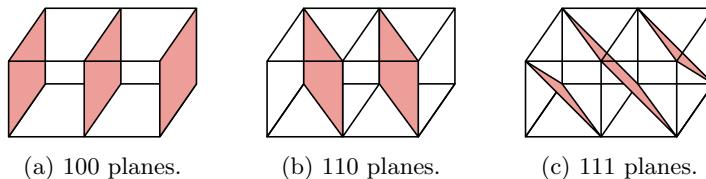


Figure 7.7: Basic lattice planes.

- Why are they called as such? Esp. where are the zeros coming from?
- Denoting more complicated types of planes.

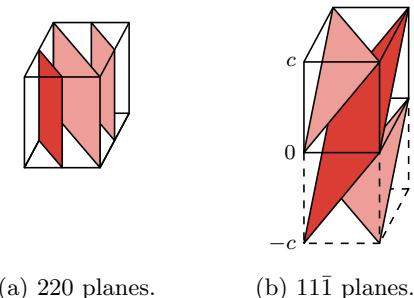


Figure 7.8: More complicated lattice planes.

- In Figure 7.8a, we denote by 220 the darkened plane and implicitly identify planes that are stacked twice as close together as in Figure 7.7b.
  - Note that  $h = a/a' = a/(a/2) = 2$  and  $k = b/b' = b/(b/2)$  is where the twos are coming from.
- In Figure 7.8b, we denote by  $11\bar{1}$  the darkened plane. The  $\bar{1}$  denotes a Miller index of *negative* one, corresponding to  $c' = -c$  (notice how the darkened plane does not intersect the **c** axis within the unit cell, but rather extends down to the axis' negative region).
- The lattice plane spacing can be determined.
  - The perpendicular distance between adjacent  $hkl$  planes for an orthorhombic unit cell.
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$
  - For a cubic unit cell,
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$
  - For a tetragonal unit cell,
$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$
  - For a hexagonal unit cell,
$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$
  - For a rhombohedral unit cell,
$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$$
  - For a monoclinic unit cell,
$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$
  - For a triclinic unit cell,
$$\frac{1}{d^2} = \frac{1}{V^2} (S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

where

$$\begin{array}{ll} S_{11} = b^2 c^2 \sin^2 \alpha & S_{12} = abc^2(\cos \alpha \cos \beta - \cos \gamma) \\ S_{22} = a^2 c^2 \sin^2 \beta & S_{23} = a^2 bc(\cos \beta \cos \gamma - \cos \alpha) \\ S_{33} = a^2 b^2 \sin^2 \gamma & S_{13} = ab^2 c(\cos \gamma \cos \alpha - \cos \beta) \end{array}$$

## 7.4 Chapter 30: Gas-Phase Reaction Dynamics

*From McQuarrie and Simon (1997).*

- 5/21:
- We will now build a molecular picture of the  $F + D_2$  chemical reaction from the crossed molecular beam data. We take  $E_{react} = 7.62 \text{ kJ mol}^{-1}$  throughout the following, as per the previous example.
  - The *angle* with which the molecules reach the detector.

- As per Figure 6.3 and the associated discussion,  $\mathbf{u}'_{DF}$  and  $\mathbf{u}'_D$  are not independent but are related by the conservation laws for mass, momentum, and energy.
- However, even though this means that DF and D could theoretically part ways in any manner consistent with these three laws, in reality, they will go their separate ways in some directions far more often than others, as dictated by the dynamics of this particular reaction.
- Let's consider these dynamics in greater detail, as facilitated by Figure 7.1.
  - In this picture, we take as our reference frame the perspective of spherically symmetric molecule B and let A approach.
  - For  $b$  fixed, the distribution in  $\phi$  will be cylindrically symmetric.
  - However, the angle  $\theta$  will vary.

5/22:

- The *speed* at which the molecules hit the detector.

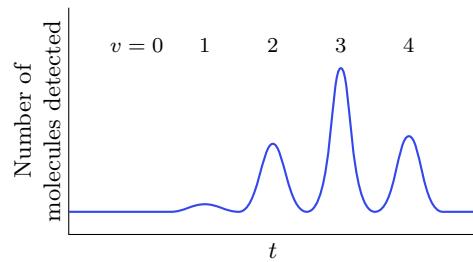


Figure 7.9: DF speed distribution.

- Additionally, as per the previous example, DF can be produced in vibrational states zero through four.
- McQuarrie and Simon (1997) does a worked example, showing quantitatively how the speed of the DF molecule depends on its vibrational state.
- Experimentally, these results show up as separate peaks, each corresponding to a vibrational energy level, in Figure 7.9, which gives the collision frequency of DF molecules with the detector over time.
  - Notice that the molecules with the least vibrational energy have the most translational energy, and hence move the fastest and appear first.