

## 30.8: The Velocity and Angular Distribution of the Products of a Reactive Collision

### Calculation of the speed distribution for DF molecules based upon the vibrational state of the molecule

This section describes how data from crossed molecular beam experiments allow us to describe the velocity and angular distribution of particles produced by the simple bi-molecular collision



As noted in the previous section, the internal vibrational energy of the products will affect the velocity and distribution because if DF(g) is a harmonic oscillator, then

$$E_{P(\text{trans})} + E_{P(\text{vib})} = 165 \frac{\text{kJ}}{\text{mol}}$$

and

$$E_{P(\text{vib})} = \left(v + \frac{1}{2}\right) \left(34.8 \frac{\text{kJ}}{\text{mol}}\right)$$

Thus

$$\begin{aligned} E_{P(\text{trans})} + E_{P(\text{vib})} &= \frac{1}{2} \mu_P v_{P_r}^2 + \left(v + \frac{1}{2}\right) \left(34.8 \frac{\text{kJ}}{\text{mol}}\right) \\ &= 165 \frac{\text{kJ}}{\text{mol}} \end{aligned} \quad (30.8.2)$$

The reduced mass of the products  $\mu_P$  is

$$\frac{(21.01 \text{ g/mol})(2.014 \text{ g/mol})}{21.01 \text{ g/mol} + 2.014 \text{ g/mol}} = 1.84 \text{ g/mol} = 0.00184 \text{ kg/mol}$$

so that solving for the product velocity in Equation 30.8.2 for  $v_{P_r}$  gives

$$v_{P_r} = \sqrt{\left(\frac{2}{0.00184 \text{ kg/mol}}\right) \left(1.65 \times 10^5 \frac{\text{J}}{\text{mol}} - \left(v + \frac{1}{2}\right) (3.48 \times 10^4) \frac{\text{J}}{\text{mol}}\right)}$$

It can be shown that the corresponding relative velocity of the DF molecule and the center of mass,  $|\vec{v}_{DF} - \vec{v}_{cm}|$ , is equal to  $\frac{m_D}{M} v_{P_r}$  for this reaction, with  $M = m_{D_2} + m_F$ . Table 30.8.1 shows the values of  $v_{P_r}$  and  $|\vec{v}_{DF} - \vec{v}_{cm}|$  for vibrational states  $v = 0 - 4$ .

Table 30.8.1

| Vibrational state, $v$ | relative velocity of the products, $v_{P_r}$ in m/s | $ \vec{v}_{DF} - \vec{v}_{cm} $ , in m/s |
|------------------------|---|--|
| 0                      | 12,700  | 1111                                     |
| 1                      | 11,100  | 971                                      |
| 2                      | 9270  | 811                                      |
| 3                      | 6930  | 606                                      |
| 4                      | 3200  | 280                                      |

### Analysis of Crossed Molecular Beam Data

[This link](#) takes you to the 1986 Nobel Prize acceptance lecture of Yuan Tseh Lee, in which he describes the crossed molecular beam studies that his group carried out on the reaction 30.8.1. On page 3 of the lecture, you will see a center-of-mass velocity flux contour map for the reaction. This map measures the speed distribution and the angular dispersion distribution as a result of collisions between one  $\text{D}_2$  molecule approaching from the left and one F atom approaching from the right. Moving away from the

center of the graph in any direction represents an increase in speed. The dashed line circles represent the maximum speed that a molecule in that given vibrational state can obtain. Notice that the highest vibrational state is closest to the nucleus. Thus, the map is consistent with theory, which claims that as the vibrational energy increases, the translational energy decreases.

The contour areas on the map represent a constant number of DF(g) molecules. The more closely spaced the contour lines, the greater the number of DF(g) molecules with that velocity in that vibrational state. An estimate of the population distribution is that roughly half the molecules are in the  $v = 3$  state, roughly 25% of the molecules occupy the  $v = 2$  state, and roughly 25% of the molecules occupy the  $v = 4$  state. Very few molecules occupy the  $v = 0$  or  $v = 1$  states. The fact that there are molecules with velocities between the dashed lines shows that these DF molecules are in various rotational states within each vibrational state. If  $E_{rot} = 0$  and  $J = 0$ , the molecular velocity distribution would be centered on each dashed line. But because these molecules do exist in various rotational states, their  $E_{rot}$  is greater than 0, and their translational energy is in between the energies of those molecules in rotational ground states. The distribution of vibrational states among the DF product molecules more closely resembles a normal distribution (i.e., Gaussian-like) than a Boltzmann distribution.

### ✓ Example 30.8.1

Determine the populations of the five lowest vibrational states of DF( $v$ ) relative to DF( $v = 3$ ), assuming that the distribution is in thermal equilibrium at 298 K. You can assume that the DF molecules act as harmonic oscillators with  $\tilde{\nu}_{DF} = 2907 \text{ cm}^{-1}$ .

#### Solution

If the DF(g) molecules are in thermal equilibrium, the population of vibrational states will follow a Boltzmann distribution. Therefore,

$$N(v) = e^{-\frac{(v+1/2)h\nu_{DF}}{k_B T}}$$

and

$$N(v=3) = e^{-\frac{(3+1/2)h\nu_{DF}}{k_B T}}$$

so

$$\frac{N(v)}{N(v=3)} = e^{-\frac{(v-3)h\nu_{DF}}{k_B T}}$$

| $v$ | $\frac{N(v)}{N(v=3)}$ |
|-----|-----------------------|
| 0   | $2.03 \times 10^{18}$ |
| 1   | $1.60 \times 10^{12}$ |
| 2   | $1.26 \times 10^6$    |
| 3   | 1                     |
| 4   | $7.90 \times 10^{-7}$ |

It is clear that when the molecules are at thermal equilibrium, the population of the vibrational states decreases with an increasing  $v$ , which is not the population pattern found from the experiment.

The map also shows that a majority of DF(g) molecules generally head back towards the direction from which the F atom originally approached the collision. Some even head directly back from whence they came. This type of collision is called a rebound reaction. We will see in the next section that not all reactions are rebound reactions.

A different style of contour map is shown in figure 30.8.1. In this view, the density of the dots and the intensity of their color represent the number of particles being scattered at specific angles. This map does not show the vibrational state of the DF molecules.

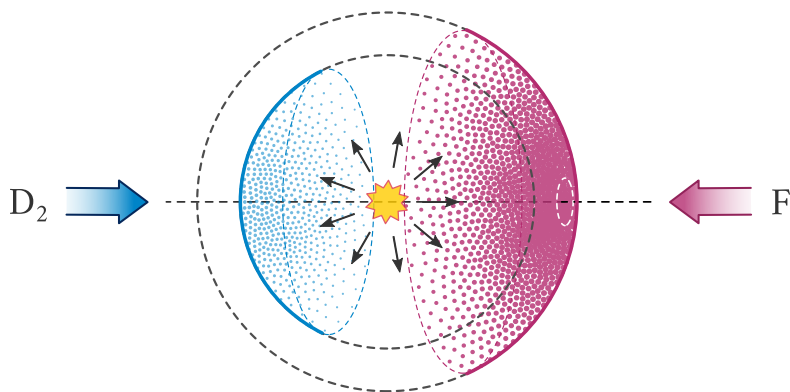


Figure 30.8.1: A center-of-mass velocity flux contour map for the reaction  $D_2 + F \longrightarrow DF + D$ . This map shows the angular dispersion distribution as a result of collisions between one  $D_2$  molecule approaching from the left and one F atom approaching from the right. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

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