

A water molecule can vibrate in various ways, but the easiest type of vibration to excite is the “flexing” mode in which the hydrogen atoms move toward and away each other but the HO bonds do not stretch. The oscillations of this mode are approximately harmonic, with a frequency of 4.8×10^{13} Hz. As for any quantum harmonic oscillator, the energy levels are $\frac{1}{2}hf$, $\frac{3}{2}hf$, $\frac{5}{2}hf$ and so on. There is no degeneracy to worry about (i.e. there is only one quantum state associated with each energy).

1. Calculate the probability of a water molecule being in its flexural ground state, and the probability of it being in its first excited state, assuming that it is in equilibrium with a reservoir at 300 K. Hint: You can find Z with sufficient accuracy by summing a few terms.

Solution To orient myself, I want to know if kT is small or large compared to hf .

$$hf = 32 \times 10^{-21} \text{ J}, \quad (1)$$

$$kT = 4.1 \times 10^{-21} \text{ J} \quad (2)$$

I see that hf is 7.8 times bigger than kT . Therefore, my system is rather “cold” compared to the quantum energy jump. So, I expect the probability of the first excited state to be very small, and the second excited state to be vanishingly small. Therefore, I’ll only need to compute a few terms.

$$Z = e^{-\frac{1}{2}hf/kT} + e^{-\frac{3}{2}hf/kT} + e^{-\frac{5}{2}hf/kT} + \dots \quad (3)$$

$$= e^{-\frac{1}{2}hf/kT} (1 + e^{-hf/kT} + e^{-2hf/kT} + \dots) \quad (4)$$

$$\mathcal{P}(0) = \frac{1}{1 + e^{-hf/kT} + e^{-2hf/kT} + \dots}, \quad (5)$$

$$\mathcal{P}(1) = \frac{e^{-hf/kT}}{1 + e^{-hf/kT} + e^{-2hf/kT} + \dots}. \quad (6)$$

Note, for these two probability expressions, I factored out $e^{-\frac{1}{2}hf/kT}$ from the numerator and denominator.

I could say that $\mathcal{P}(0) \approx 1$ and $\mathcal{P}(1) \approx 0$, but I’d like to estimate the finite probability that the water molecule is in the first excited state (even if the probability is very small). When I calculate with enough significant figures I find

$$\mathcal{P}(0) = 0.9996, \quad (7)$$

$$\mathcal{P}(1) = 0.0004. \quad (8)$$

2. What is the expectation value of energy, $\overline{E}_{\text{flex}}$, stored in this flexural mode when $T = 300$ K? Write your answer in terms of hf .

Solution The system spends most of the time in the ground state, so $\overline{E}_{\text{flex}} \approx \frac{1}{2}hf$. However, due to the small probability of being in the first excited state, $\overline{E}_{\text{flex}}$ is *slightly* higher than the ground state energy:

$$\overline{E}_{\text{flex}} = \frac{1}{2}hf + 0.0004hf, \quad (9)$$

3. Change the temperature so that $kT = hf$. What is the new temperature?

Solution

$$kT = 32 \times 10^{-21} \text{ J} \quad (10)$$

$$T = \frac{32 \times 10^{-21} \text{ J}}{1.38 \times 10^{-23} \text{ J/K}} \quad (11)$$

$$= 2320 \text{ K} \quad (12)$$

Water molecules start to break apart at about 3000 K (presumably, they start flexing too far). So, we can't go much higher in temperature.

4. I want to find the average energy stored in this flexural mode at this new temperature. Write down a series expression for the expected amount of energy stored in the flexural mode. Evaluate the first few terms in the series to get a number in units of hf .

Solution This time, it's a little harder to find Z . I will use a mathematical result that you might have learned from studying infinite series. (Infinite geometric series come up quite often when analyzing physical systems.)

$$Z = e^{-1/2}(e^0 + e^{-1} + e^{-2} + \dots) \quad (13)$$

$$= e^{-1/2} \frac{1}{1 - e^{-1}} \quad (14)$$

$$= e^{-1/2} \cdot 1.58 \quad (15)$$

$$\overline{E}_{\text{flex}} = E_0 \cdot \mathcal{P}(0) + E_1 \cdot \mathcal{P}(1) + E_2 \cdot \mathcal{P}(2) \dots \quad (16)$$

$$= \frac{1}{2}hf \cdot \frac{e^{-1/2}}{1.58e^{-1/2}} + \frac{3}{2}hf \cdot \frac{e^{-3/2}}{1.58e^{-1/2}} + \frac{5}{2}hf \cdot \frac{e^{-5/2}}{1.58e^{-1/2}} + \dots \quad (17)$$

$$= \frac{hf}{1.58e^{-1/2}}(0.5e^{-1/2} + 1.5e^{-3/2} + 2.5e^{-5/2} + 3.5e^{-7/2} + \dots) \quad (18)$$

$$= \frac{hf}{1.58}(0.5e^0 + 1.5e^{-1} + 2.5e^{-2} + 3.5e^{-3} + \dots) \quad (19)$$

$$= 1.1hf \quad (20)$$

$$= \frac{1}{2}hf + 0.6hf. \quad (21)$$