Thermal Physics

Rotational motion of CO_2

Problem 1.- Sketch the heat capacity of rotational motion of the CO_2 molecule as a function of temperature.

Solution: The CO_2 molecule is linear and has a moment of inertia $I = 7.17\times10^{-46}$ kg m^2, so the value of ε_o is given by:

$$\varepsilon_o = \frac{\hbar^2}{2I} = \frac{(1.05\times10^{-34}\,\text{Js})^2}{2(7.17\times10^{-46}\,\text{kgm}^2)} = 7.68\times10^{-24}\ \text{J}$$

If we wanted to express this energy in terms of a temperature, the result would be:

$$T_o = \frac{\varepsilon_o}{k_B} = \frac{7.68\times10^{-24}\,\text{J}}{1.38\times10^{-23}\,\text{J/K}} = 0.557\ \text{K}$$

We determined an approximation for the rotational heat capacity of linear molecules at high temperature, which is equal to 1. We expect the same in CO_2 at temperatures higher than 0.557 K.

We also deduced an approximation for low temperature using only the first two energy levels of the molecule. We found the following expression:

$$C_V \approx 12\left(\frac{\varepsilon_o{}^2}{\tau^2}\right)e^{-2\varepsilon_o/\tau}$$

However, there is an important consideration in CO_2: due to Bose statistics of the oxygen atoms, **levels with j-odd are forbidden.** So the first two energy levels correspond to j=0 and j=2. This gives us the approximate partition function:

$Z = 1 + 5e^{-6\varepsilon_o/\tau}$ and $\log(Z) \approx 5e^{-6\varepsilon_o/\tau}$

So the energy will be:

$$U = \tau^2\frac{\partial \log(Z)}{\partial\tau} \approx \tau^2\frac{\partial \log(5e^{-6\varepsilon_o/\tau})}{\partial\tau} = \tau^2 5e^{-6\varepsilon_o/\tau}\left(\frac{6\varepsilon_o}{\tau^2}\right) = 30\varepsilon_o e^{-6\varepsilon_o/\tau}$$

This expression allows us to find the heat capacity:

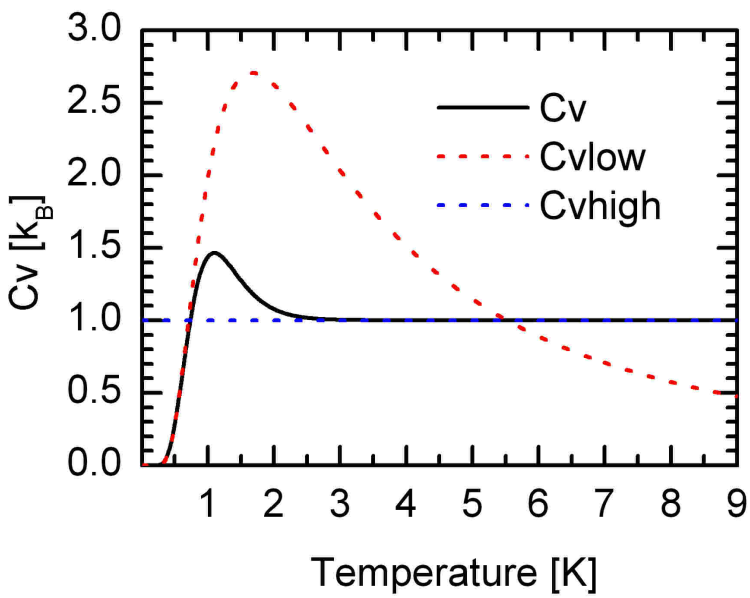
$$C_V = \frac{\partial U}{\partial\tau} \approx \frac{\partial 30\varepsilon_o e^{-6\varepsilon_o/\tau}}{\partial\tau} = 180\left(\frac{\varepsilon_o{}^2}{\tau^2}\right)e^{-6\varepsilon_o/\tau}$$

In terms of T_o, this becomes:

$$C_V = 180\left(\frac{T_o^{\,2}}{T^2}\right)e^{-6T_o/T}$$

Where T is the temperature in kelvin.

A schematic of these two approximations would be the blue and red dotted lines in the following figure. The actual heat capacity can be calculated by approximating the partition function with 30 or more elements, in which case we get the solid black line in the figure:



It is clear that for low temperature (less than 0.8K) the approximation with two elements of the partition function fits the actual C_V very well. We can say the same about the other approximation for high temperature. In normal conditions, with CO_2 at room temperature, only this high-T approximation is observed, with a rotational heat capacity of 1 (or $1k_B$ in conventional units).

Other effects contribute to give CO_2 a larger heat capacity: Linear kinetic energy will contribute 3/2, as in the case of a mono-atomic gas, and vibrational kinetic energy will add about 0.9 at room temperature.

Notice that due to the quantum nature of the rotational energy, there is a transition in the heat capacity at around 1 K. Is there any chance of observing this quantum effect? CO_2 becomes a solid at about 190K (at a pressure of 1 atm), so you would have to design a clever experiment to get gaseous CO_2 at such a low temperature.