1 The Rigid Rotor & Microwave Spectroscopy

(a) Consider the moment of inertia for a rigid rotor composed of two masses $m_1$ and $m_2$, which lie at distances $r_1$ and $r_2$ from the center of mass, respectively:

Show that the moment of inertia $I = m_1 r_1^2 + m_2 r_2^2$ can be written equivalently as $I = \mu r^2$ where $r = r_1 + r_2$ and $\mu$ is the reduced mass.

*Hint:* Recall that by definition of the center of mass, $m_1 r_1 = m_2 r_2$.

(b) In the far infrared spectrum of H$^{79}$Br, there is a series of lines spaced by 16.72 cm$^{-1}$. Calculate the values of the moment of inertia and the internuclear separation in H$^{79}$Br.

(c) The bond length of a $^{12}$C$^{16}$O carbon monoxide molecule is 113 pm. What is the frequency of its $J = 0$ to $J = 1$ rotational transition in Hz?

2 Quantum Harmonic Oscillators & IR Spectroscopy

(a) The force constant for a $^1$H$^{19}$F molecule is 966 N/m. Calculate the frequency of light needed to excite this molecule from the ground state ($n = 0$) to the first excited state ($n = 1$) in Hertz. Calculate the zero point vibrational energy for this molecule in Joules.

(b) In the infrared spectrum of H$^{79}$Br, there is an intense line at 2559 cm$^{-1}$. Calculate the force constant of H$^{79}$Br and the period of vibration of H$^{79}$Br.
3 Ro-Vibrational Spectroscopy

(a) For a diatomic molecule with vibrational frequency $\tilde{\omega}$ (cm$^{-1}$) and rotational constant $\tilde{B}$ (cm$^{-1}$), use the rigid rotor-harmonic oscillator approximation to draw an energy-level diagram for the first four rotational levels in the $v = 0$ and $v = 1$ vibrational states. Label the quantum numbers and energy of each state. Indicate any allowed transitions between the states shown that would appear in an infrared absorption experiment. Label whether each transition falls in the $R$ or $P$ branch.

(b) Given that $B = 56000$ MHz and $\tilde{\omega} = 2143$ cm$^{-1}$ for the CO molecule, calculate the transition frequencies in wavenumbers of the first two lines of each of the $R$ and $P$ branches in the rotation-vibration spectrum of CO.

4 Bohr’s Hydrogen Atom

(a) The experimental emission lines from the hydrogen atom can be fit empirically by the Rydberg expression:

$$\tilde{\nu} = \frac{1}{\lambda} = R_H \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

which represent the transitions energies between an upper state with label $n_2$ and a lower state with label $n_1$. Experimentally Rydberg’s constant, $R_H = 109677.58$ cm$^{-1}$, is one of the most accurately known physical constants.

Bohr’s model gives the following result for the emission lines of H, in wavenumbers:

$$\tilde{\nu} = \frac{m_e e^4}{8\epsilon_0^2 c^3 h^3} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

Calculate $R_H$ using Bohr’s expression. How does this compare to the experimentally measured value? Note: It’s important to hold on to sufficient significant digits while performing this calculation!

(b) In Bohr’s model for the H atom, it is assumed that the proton is a fixed center around which the electron revolves, because the proton is much heavier than the electron. In reality, the two masses rotate around each other and we should use their reduced mass $\mu$ in place of the electron mass:

$$\mu = \frac{m_em_p}{m_e + m_p}$$

where $m_e$ is the electron mass and $m_p$ the proton mass. Recalculate the Rydberg constant using Bohr expression and the reduced mass. How well does this compare to the experimental value of $R_H$? Note: It’s important to hold on to sufficient significant digits while performing this calculation!