Exercise 1: Rotational Spectra

Sample Solution

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1. Calculate the absorption cross sections in the microwave spectral range for the following molecules (Figure 2):

- HCl, ClO, CO, N_2O, O_3

Questions and answers:

- Estimate the rotational constant B for HCl and for CO.
  - $B_{\text{HCl}} \approx 300\,\text{GHz}$
  - $B_{\text{CO}} \approx 60\,\text{GHz}$
- Why is B larger for HCl than for CO?
  - The reduced mass μ is larger for CO. This is caused by a larger molecule in general and a smaller mass difference of the atoms inside the molecule (see Figure 1).
- Do you have any idea why N_2O behaves like a diatomic molecule — and O_3 not?
  - The angles between the atoms inside the molecule differ. N_2O has flat angles and therefore momentums of inertia like a linear molecule ($I_A = 0, I_B = I_C$). O_3 has a more complex structure with differing momentums of inertia ($I_A \neq I_B \neq I_C$).
- Calculate the reduced mass of the different molecules from the masses of the individual atoms. For the diatomic molecules this is trivial. For N_2O, I think the appropriate mass can be found by careful thinking. You can ignore O_3.
  - The reduced mass μ for a diatomic molecule is given by $\mu = \frac{m_1 m_2}{m_1+m_2}$. The atomic masses of the relevant atoms are H $(1\,u)$, Cl $(35\,u)$, C $(12\,u)$, O $(16\,u)$ and N $(14\,u)$. For the regarded molecules the reduced masses are:

$$\mu(\text{HCl}) = 0.972\,u$$
$$\mu(\text{ClO}) = 10.98\,u$$
$$\mu(\text{CO}) = 6.857\,u$$
$$\mu(\text{N}_2\text{O}) \approx 7.5\,u$$

- Calculate the bond length of the various molecules (except O_3) from the reduced mass and the rotational constant. Verify your result with Google. Again N_2O needs some extra thinking.
  - For each molecule, the rotational constant B can be found using Figure 2. The rotational constant (for frequencies) is defined as

$$B = \frac{h}{8\pi^2 I} \quad with \quad I = \mu r_0^2$$

    The equations can be combined and solved for r_0 which is the bond length of the regarded molecule.

$$r_0(\text{HCl}) = 132\,pm$$
$$r_0(\text{ClO}) = 158\,pm$$
$$r_0(\text{CO}) = 111\,pm$$
$$r_0(\text{N}_2\text{O}) \approx 233\,pm$$

- Play with different temperatures. How does the rotational spectrum change? Can you explain the changes?
  - Different temperatures lead to different distributions of energy states. With higher temperatures the amount of molecules in high energy states increases and absorption lines at higher frequencies get stronger. When observing very cold temperatures all molecules are in the lowest energy state ($i = 0$) and only one absorption line at the lowest frequency is left.

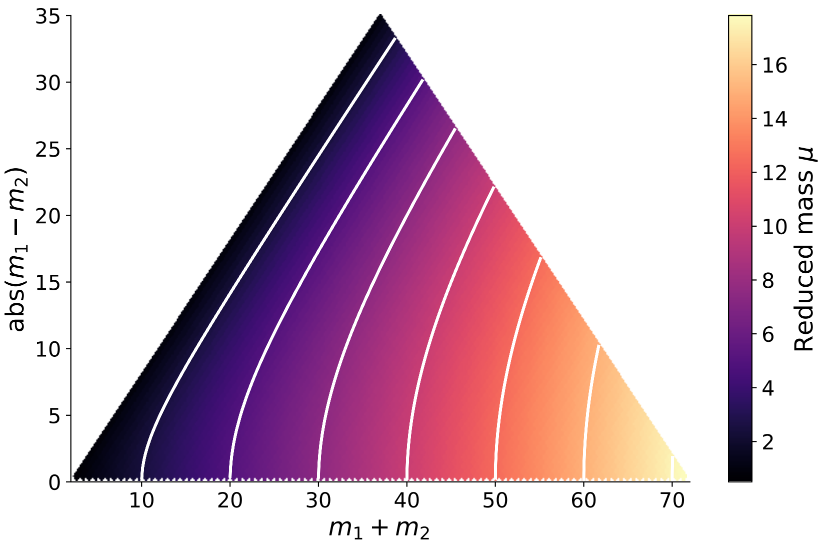

Figure 1: Reduced mass μ as a function of total mass and mass difference.

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2. Investigate other molecules!
3. Show for a diatomic molecule that the moment of inertia is given by $I = \mu r_0^2$.

$$I = \sum_i m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2$$

The center of gravity is defined as $m_1 r_1 = m_2 r_2$. Insert this and you get

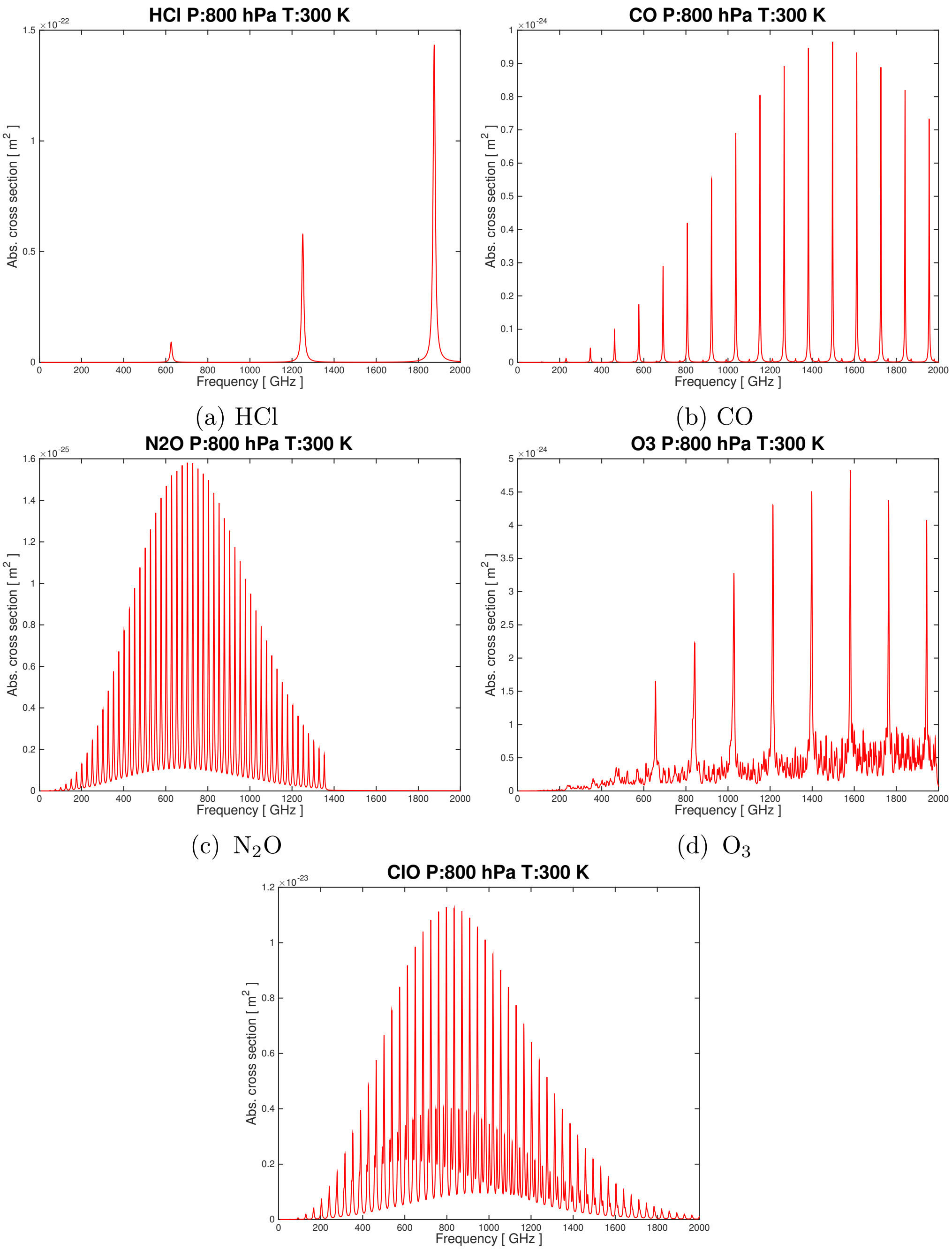
$$\begin{aligned} I &= m_2 r_2 r_1 + m_1 r_1 r_2 \\ &= r_1 r_2 (m_1 + m_2) \qquad (1) \end{aligned}$$

We can do more with the center of gravity equation:

$$\begin{aligned} m_1 r_1 = m_2 r_2 &= m_2 \overbrace{(r_0 - r_1)}^{\text{from def.}} = m_2 r_0 - m_2 r_1 \\ (m_1 + m_2) r_1 &= m_2 r_0 \\ r_1 &= \frac{m_2 r_0}{m_1 + m_2} \qquad (2) \\ r_2 &= \frac{m_1 r_0}{m_1 + m_2} \qquad (3) \end{aligned}$$

Insert (2) and (3) into (1):

$$\begin{aligned} I &= \frac{m_2 r_0 \; m_1 r_0 \; (m_1 + m_2)}{(m_1 + m_2)(m_1 + m_2)} \\ &= \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2 \qquad \square \end{aligned}$$



(a) HCl

(b) CO

(c) N_2O

(d) O_3

(e) ClO

Figure 2: Absorption cross sections of the molecules HCl, ClO, CO, N_2O and O_3.