Exercise 09

Name:	Matriculation number:
Name:	Matriculation number:

Results:

9.1	of 10 P
9.2	of 10 P
9.3	of 10 P
total	of 30 P

General instructions

- Submit your solution to Luca Donati (R. 35.17) before **Thursday 30. June at 8.15 am**.
- Fill out this cover sheet and submit it along with your solution.
- Show how you arrived at your answer.

9.1 Relative populations of the rotational energy levels (10 P)

The relative populations of the rotational energy levels of unsymmetric diatomic moleule are given as

$$p_J = \frac{N_J}{N} \quad \sim \quad (2J+1)\exp\left[-J(J+1)\frac{\Theta_{\text{rot}}}{T}\right] . \tag{1}$$

(a) Show that the level with the highest relative population is

$$J_{\text{max}} = \sqrt{\frac{T}{2\Theta_{\text{rot}}}} - \frac{1}{2}$$

(b) Plot J_{max} as a function of temperature for

- $^1H^{19}F$, $\Theta_{\text{rot}} = 60.875$ K
- $^1H^{35}Cl$, $\Theta_{\text{rot}} = 15.021$ K
- $^1H^{81}Br$, $\Theta_{\text{rot}} = 12.012$ K
- $^1H^{127}J$, $\Theta_{\text{rot}} = 9.246$ K

9.2 Rotational-vibrational spectrum of CO (10 P)

In this exercise, you will calculate the rotational vibrational spectrum of $^{12}C^{16}O$ for the vibrational transition $\nu = 0 \rightarrow \nu' = 1$. The characteristic temperatures for vibration and rotation are

$$\begin{aligned} \Theta_{\text{vib}} &= 3112 \text{ K} \\ \Theta_{\text{rot}} &= 2.766 \text{ K} \end{aligned} \tag{2}$$

(a) Calculate the frequency of the fundamental vibrational transition $(\nu = 0, J = 0) \rightarrow (\nu' = 1, J' = 0)$. Is this transition observed in the spectrum? Why?

(b) Calculate and plot the relative populations of the rotational states in the vibrational ground state.

(c) Calculate the frequencies in the R-Branch.

(d) Calculate the frequencies in the P-Branch .

(e) Sketch the spectum.

9.3 Ortho- and para-hydrogen (10 P)

Molecular hydrogen (H_2) occurs in two isomeric forms, one with its two proton spins aligned parallel (orthohydrogen), the other with its two proton spins aligned antiparallel (parahydrogen). Parahydrogen is in a lower energy state than is orthohydrogen. At room temperature and thermal equilibrium, thermal excitation causes hydrogen to consist of approximately 75% orthohydrogen and 25% parahydrogen. The rotational energies are given by

$$E_J = \frac{J(J+1)\hbar^2}{2I}$$

with $2J+1$ fold degeneracies.

(a) Determine the rotational partition functions z_p and z_o respectively for the para- and orthohydrogen.

(b) Determine the rotational partition function for an equilibrium mixture. (Hint: be careful to the degeneracies)

(c) How can be approximated for high temperature?

(d) Determine and plot the heat capacity.

(e) Determine and plot in a mixture of gas at equilibrium, the ratio of ortho- to para-hydrogen.