All equation, table, and figure numbers refer to the book 'Fundamentals of Molecular Spectroscopy' by Philip R. Bunker and Per Jensen.

1.1 What is the wavenumber, frequency and energy per photon of (a) visible radiation having a wavelength of 500 nm, (b) infrared radiation having a wavelength of 5 μm, and (c) microwave radiation having a wavelength of 5 cm? Quote the frequency in appropriate units such as THz or GHz, and the wavenumber in cm^{-1}.

1.2 The successive rotational energy levels of the $^{12}C^{16}O$ molecule depicted in figure 1.5 are labeled $J = 0, 1, 2, \ldots$, and to three significant figures their energy divided by hc is $E_i = 1.92J(J+1)$ cm^{-1}; the degeneracy of each level is $g_i = (2J+1)$. Calculate the numerator in the Maxwell-Boltzmann distribution function equation (1.5) for a range of values of J for temperatures T of 10, 300 and 1000 K to confirm the J-value at which the population is a maximum according to figure 1.7; in the appropriate units $k \approx 0.695$ $\text{cm}^{-1}\text{K}^{-1}$. By setting equal to zero the differential of the numerator with respect to J, determine an expression as a function of T for the value of J at which the population is a maximum. Check that this leads to the correct result for $T = 10$, 300 and 1000 K (J has to be an integer).

1.3 Translational motion of molecules gives rise to Doppler broadening of spectral lines. A Doppler-broadened line with central frequency ν_0 has a full width at half height FWHH (the frequency width of the line at half the maximum intensity) of

$$\begin{aligned} \text{FWHH} &= \frac{2\nu_0}{c}\left(\frac{2kT}{M}\ln 2\right)^{1/2} \\ &\approx 7.15\times 10^{-7}\left(\frac{T}{M/\mathrm{u}}\right)^{1/2}\nu_0, \end{aligned} \tag{1}$$

where k is Boltzmann's constant, T is the absolute temperature, M is the mass of the molecule in question, and u is the unified atomic mass unit.[1] Calculate such FWHH Doppler widths of infrared absorption lines of the H_3^+ molecule ($M/\mathrm{u} \approx 3$) and CH_4 molecule ($M/\mathrm{u} \approx 16$) at around 3000 cm^{-1} at 1000 K and at 10 K. What would the Doppler widths be for lines of these molecules at these temperatures at wavelengths around 1 cm (in the microwave region) or 100 nm (in the ultraviolet region)? The appropriate units for linewidth are cm^{-1} in the infrared and ultraviolet, and kHz in the microwave.

1.4 We describe the rotation of the molecule $^{79}\mathrm{Br}^{19}\mathrm{F}$ under the assumption that the molecule is rigid. The allowed energies of the corresponding rigid rotor are

$$E_J = h\, c\, B\, J(J+1); \quad J = 0, 1, 2, 3, \ldots,$$

with the rotational constant

$$B = \frac{h}{8\pi^2 c \mu r_e^2}\,.$$

The quantity μ is the reduced mass of the molecule and r_e is the constant internuclear distance.

Irradiation with light in the microwave region induces absorption transitions. An allowed transition from the state with the energy E_J ends in the state with the energy E_{J+1}. A progression of transitions are observed. The wavenumber interval between two neighbouring lines is independent of J. This interval is measured to have the value 0.71433 cm^{-1}. Calculate B, the moment of inertia

$$I = \mu r_e^2$$

and r_e. Calculate the wavenumber of the transition $J = 9 \rightarrow J = 10$.

[1] 1 u = $1.660\,538\,86\times 10^{-27}$ kg; also called the dalton or the atomic mass constant.