Gross selection rules

1. Construct a table for the following molecules: O₂, HCl, CH₄, CO₂, N₃⁻, CH₂Cl₂, C₂H₆, H₂O, SF₆. Indicate for each of them whether you would expect to see (a) a pure rotational microwave spectrum; (b) a pure rotational Raman spectrum; (c) a vibrational (infrared) spectrum. (Hint for N₃⁻: consider with which molecule it is isoelectronic).

Rotational Microwave Spectroscopy

2. A sample of ¹²C¹⁶O was placed in a spectrometer that can cover only the wavenumber range 15—40 cm⁻¹. The spectrum obtained is shown below (from Spectra of Atoms and Molecules, P.F. Bernath, OUP, Oxford, 2005):

   ![Rotational Microwave Spectrum](image)

   a) Assign these transitions, and then
   b) determine the average separation of rotational transitions and from this calculate the CO bond length, neglecting centrifugal distortion.
   c) Finally, estimate the temperature of the gas if the fifth and seventh lines (as shown above) have the same intensity.
Rotational Raman Spectroscopy

3. An argon ion laser operating at a wavelength of 476.500 nm has been used to record the rotational Raman spectrum of H$_2$. If the rotational constant $B$ of H$_2$ is 60.80 cm$^{-1}$, at what wavelengths would you expect the first and second Stokes lines to occur?

4. The rotational Raman spectrum of a gas-phase sample of CO$_2$ is shown below (taken from http://www.ae.utexas.edu/~varghesep/PLVresearch.html):

Determine the average separation of rotational transitions and from this calculate the C-O bond length in CO$_2$, neglecting centrifugal distortion.

Useful constants: $N_A = 6.022 \times 10^{23}$ mol$^{-1}$; $k = 1.381 \times 10^{-23}$ J K$^{-1}$; $h = 6.626 \times 10^{-34}$ J s; $c = 2.998 \times 10^8$ m s$^{-1}$
1 a.m.u. $\equiv 1.66054 \times 10^{-27}$ kg; $^{12}\text{C} m = 12.000$ a.m.u., $^{16}\text{O} m = 15.995$ a.m.u.