5.80 Small-Molecule Spectroscopy and Dynamics
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Chemistry 5.76
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Problem Set #1

1. (a) Make the necessary conversions in order to fill in the table:

Wavelength (Å)	420			
Wavenumber (cm^{-1})		100		
Energy (J)				
Energy (kJ/mole)			490	
Frequency (Hz)				8.21×10^{13}

   (b) Name the spectral region associated with each of the last four columns of the table.

2. A 100-W tungsten filament lamp operates at 2000 K. Assuming that the filament emits like a blackbody, what is the total power emitted between 6000 Å and 6001 Å? How many photons per second are emitted in this wavelength interval?

3. (a) What is the magnitude of the electric field for the beam of a 1mW helium-neon laser with a diameter of 1 mm?
   (b) How many photons per second are emitted at 6328 Å?
   (c) If the laser linewidth is 1 kHz, what temperature would a blackbody have to be to emit the same number of photons from an equal area over the same frequency interval as the laser?

4. The lifetime of the $3^2P_{3/2} \rightarrow 3^2S_{1/2}$ transition of the Na atom at 5890 Å is measured to be 16 ns.
   (a) What are the Einstein A and B coefficients for the transition?
   (b) What is the transition dipole moment in Debye?
   (c) What is the peak absorption cross section for the transition in Å^2, assuming that the linewidth is determined by lifetime broadening?

5. (a) For Na atoms in a flame at 2000 K and 760 Torr pressure, calculate the peak absorption cross section (at line center) for the $3^2P_{3/2} - 3^2S_{1/2}$ transition at 5890 Å. Use 30 MHz/Torr as the pressure-broadening coefficient and the data in Problem 4.
   (b) If the path length in the flame is 10 cm, what concentration of Na atoms will produce an absorption (I/I_0) of $1/e$ at line center?
   (c) Is the transition primarily Doppler or pressure broadened?
   (d) Convert the peak absorption cross section in cm^2 to the peak molar absorption coefficient ϵ.

6. For Ar atoms at room temperature (20°C) and 1 Torr pressure, estimate a collision frequency for an atom from the van der Waals radius of 1.5 Å. What is the corresponding pressure-broadening coefficient in MHz/Torr?

7. Solve the following set of linear equations using matrix methods

$$\begin{aligned} 4x - 3y + z &= 11 \\ 2x + y - 4z &= -1 \\ x + 2y - 2z &= 1. \end{aligned}$$

8. (a) Find the eigenvalues and normalized eigenvectors of the matrix

$$\mathbf{A} = \begin{pmatrix} 2 & 4 - i \\ 4 + i & -14 \end{pmatrix}.$$

(b) Construct the matrix **X** that diagonalizes **A** and verify that it works.

9. Given the matrices **A** and **B** as

$$\mathbf{A} = \begin{pmatrix} -\frac{1}{3} & \sqrt{\frac{2}{3}} & \frac{\sqrt{2}}{3} \\ \sqrt{\frac{2}{3}} & 0 & \frac{1}{\sqrt{3}} \\ \frac{\sqrt{2}}{3} & \frac{1}{\sqrt{3}} & -\frac{2}{3} \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} \frac{5}{3} & \frac{1}{\sqrt{6}} & -\frac{1}{3\sqrt{2}} \\ \frac{1}{\sqrt{6}} & \frac{3}{2} & \frac{1}{2\sqrt{3}} \\ -\frac{1}{3\sqrt{2}} & \frac{1}{2\sqrt{3}} & \frac{11}{6} \end{pmatrix}.$$

Show that **A** and **B** commute. Find their eigenvalues and eigenvectors, and obtain a unitary transformation matrix **U** that diagonalizes both **A** and **B**.

10. Obtain eigenvalues and eigenvectors of the matrix

$$\mathbf{H} = \begin{pmatrix} 1 & 2\alpha & 0 \\ 2\alpha & 2 + \alpha & 3\alpha \\ 0 & 3\alpha & 3 + 2\alpha \end{pmatrix}$$

to second order in the small parameter α.

11. A particle of mass m is confined to an infinite potential box with potential

$$V(x) = \begin{cases} \infty, & x < 0, x > L, \\ k\left(1 - \frac{x}{L}\right), & 0 \leq x \leq L. \end{cases}$$

Calculate the ground and fourth excited-state energies of the particle in this box using first-order perturbation theory. Obtain the ground and fourth excited-state wavefunctions to first order, and sketch their appearance. How do they differ from the corresponding unperturbed wavefunctions?