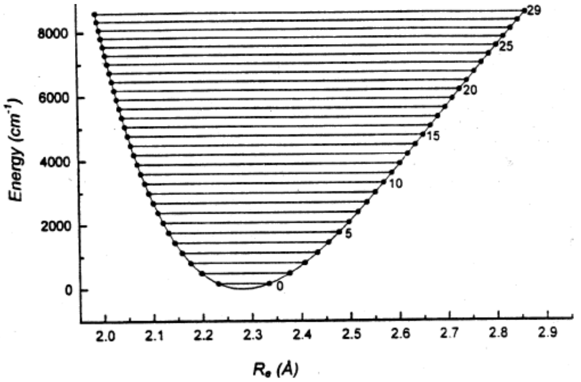
Problem Set 15
On Molecular Spectroscopy

1. The potential energy curve shown below for the ground state of the Br_2 molecule shows the vibrational levels that have been observed experimentally by laser-induced fluorescence by using continuous wave excitation in the spectral region 16,800-18,000 cm^{-1}.

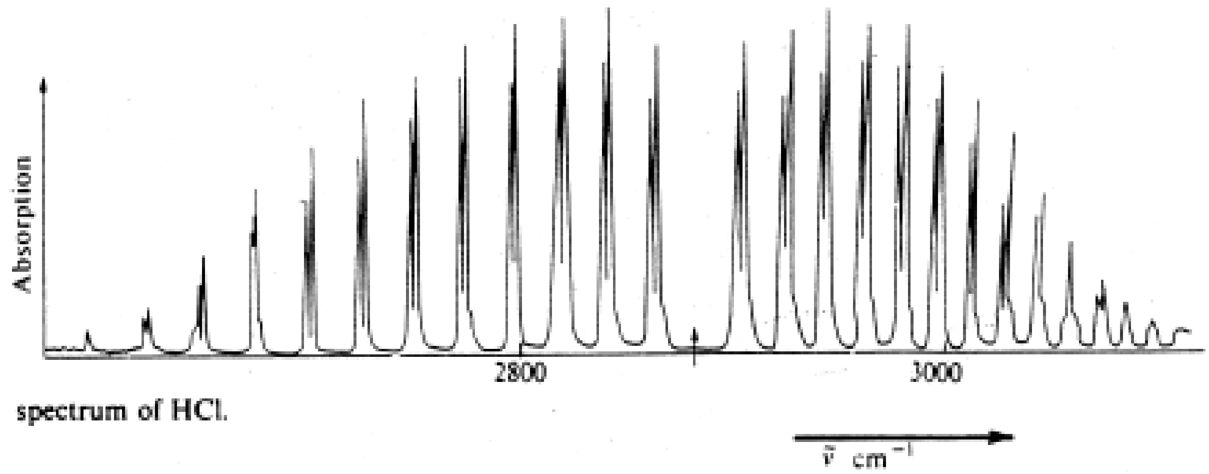


The spectra measured by Focsa, Li and Bernath, and reported in the Journal of Molecular Spectroscopy 200, 104 (2000), originate from vibrational states v' = 10-22 in the electronic excited state and involve the v" = 2-29 levels of the electronic ground state. The determined electronic ground state spectroscopic constants are shown below for the first few of the 29:

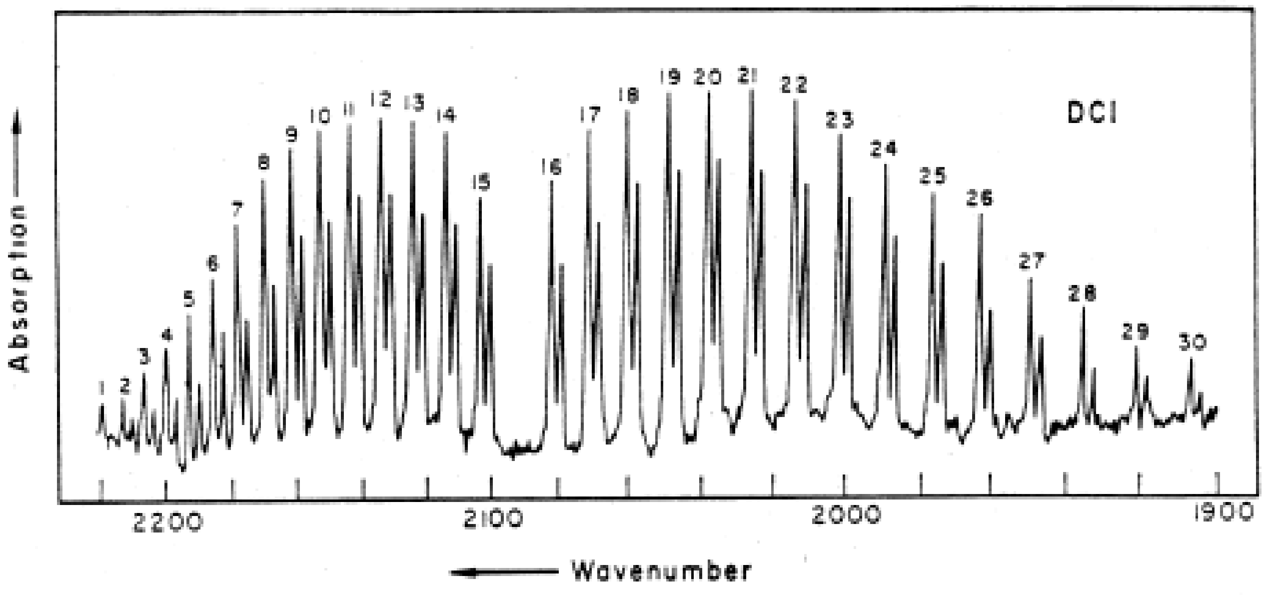
v = v"	G_v [cm^{-1} measured from $U(R_e)$]	B_v cm^{-1}
0	162.3803	0.08194837
1	485.5306	0.08162622
2	806.5050	0.08130243
3	1125.2909	0.08097696
4	1441.8750	0.08064974
5	1756.2437	0.08032069
6	2068.3828	0.07998974
7	2378.2777	0.07965681
8	2685.9132	0.07932182

From the energy expression for vibrational and rotational states in the ground electronic state of a diatomic molecule such as Br_2, determine which molecular information about the ground electronic state can be obtained from these numbers, and go ahead and try to extract them, using only these few measured quantities in the table above.

2. HCl and DCl spectra are compared below.
There are distinct differences. Enumerate the differences between the HCl and DCl spectra and explain what they are due to. In each case, assign the pairs of peaks that appear close together. What is the frequency spacing between the members of a pair due to? Calculate the frequencies of the pairs of peaks with the IUPAC number 15 and 16, given that $^{1}H^{35}Cl$ has $\nu_e = 2989.74\ cm^{-1}$ $x_e\nu_e = 52.05\ cm^{-1}$ $B_e = 10.594\ cm^{-1}$.

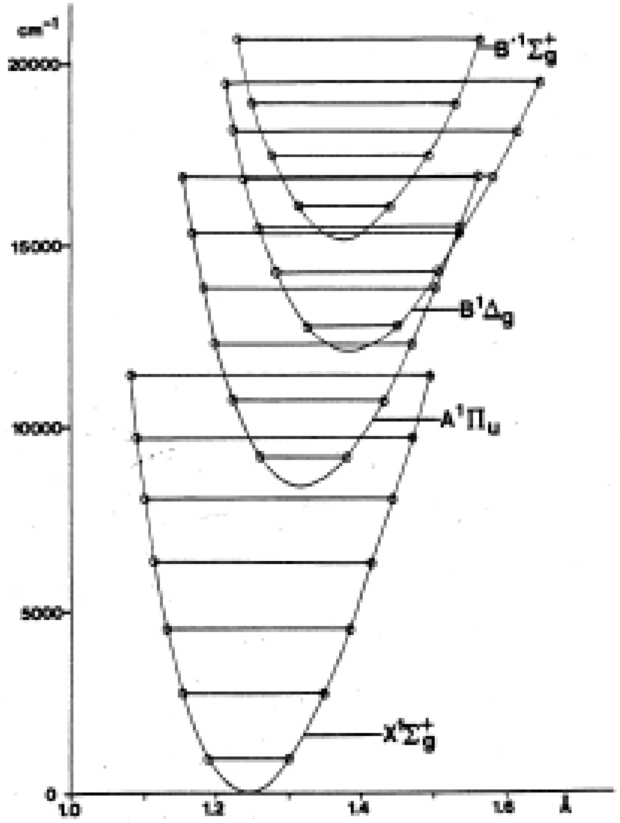


spectrum of HCl.



The deuterium chloride fundamental rotation-vibration band at 2224–1905 cm^{-1}.
The numbers on the lines refer to the IUPAC standard lines.

3. The C_2 molecule is found in comets, interstellar clouds, the sun, and in stellar atmospheres. In the laboratory, C_2 is abundant in flames, explosions, and electrical discharges of carbon-containing molecules.
The lowest lying energies that are the eigenvalues of the electronic motion are shown to the right for the C_2 diatomic molecule.
Figure out the most intense transitions (from the ground state) in the UV-Visible absorption spectrum.
Draw a diagram of the absorption spectrum that would be observed, label the transitions in the spectrum, and explain how you arrived at the relative intensities.



potential curves of the low-lying singlet states of C_2.

4. To investigate the lateral diffusion of pyrene in a medium (such as in an organic solvent, or in phospholipid vesicles) at mole ratios of 1 pyrene to 1000 solvent molecules, we need <u>a measure of the frequency of encounters between pyrene molecules</u>.
Given the information shown in the figure, devise a spectroscopic measurement(s) that will provide us with a number that is related to the underlined quantity. An excimer is a complex formed between an electronically excited pyrene and another pyrene molecule in the ground state.

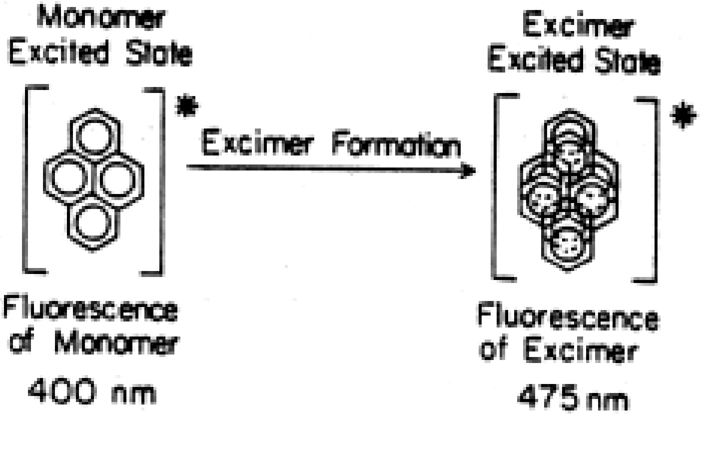


FIGURE 26. Excimer formation by pyrene. (From Soutar, A. K., Pownall, H. J., Hu, A. S., and Smith, L. C., *Biochemistry*, 13, 2828, 1974.

5. The observed and calculated intensities of the fluorescence spectrum of Xe_2 from an excited state [which dissociates into Xe($^1S_0$) + Xe(7s)] to a greound state [dissociating into ground state Xe atoms] are shown below: What conclusions can we draw from the given spectrum?

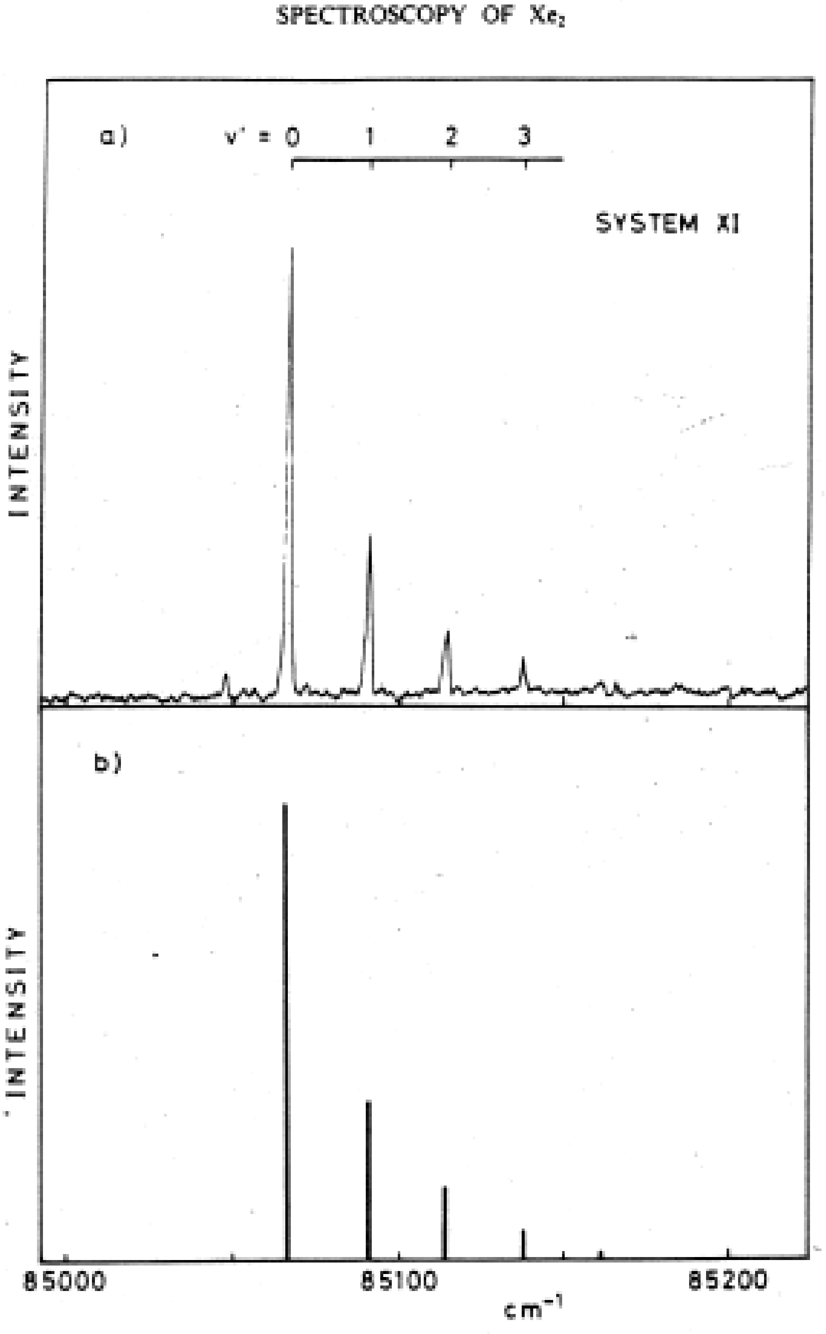


FIG. 5. (a) Fluorescence excitation specrum of the system XI. Intensity of the VUV coherent radiation is almost constant over the entire region. (b) Calculated Franck–Condon factors; $r'_e = 4.52$ Å.

6. Figure 1a shows the photoelectron spectra of H_2 and D_2 obtained by irradiation with the He I (58.4 nm) line. Figure 1b gives the potential curves of H_2 and H_2^+ ion. When an electron is removed from the neutral molecule, the nuclei find themselves suddenly in the potential field appropriate to the H_2^+ ion but still separated by the distance characteristic of the neutral H_2 molecule. The most probable change is thus a transition on the potential energy diagram from the internuclear separation of the ground state to a point on the potential energy curve of the ion vertically above this. This is the Franck-Condon principle and it determines to which vibrational level of the ion the most probable transition (strongest band) occurs. The energy corresponding to this change is called the vertical ionization potential IP_{vert}.

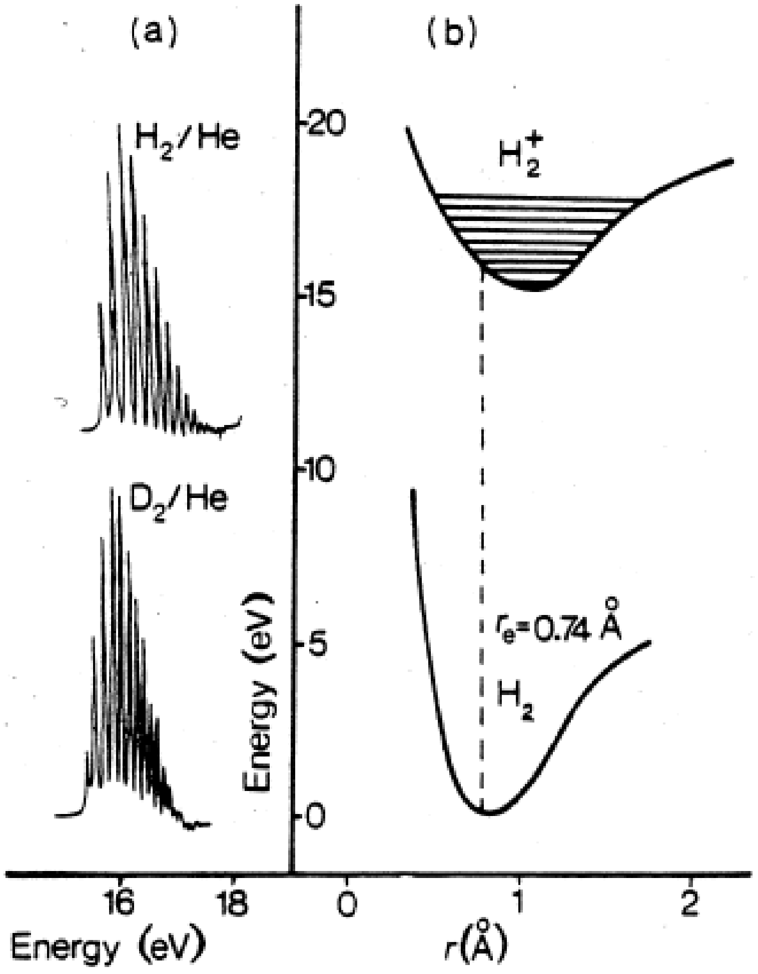


FIGURE 1. (a) Photoelectron spectra of H_2 and D_2; (b) potential energy curves showing spectra plotted along ordinate.

Assign the H_2 bands and the D_2 bands with appropriate quantum numbers lower→upper. Why are the D_2 intensities and spacings different from H_2?

7. Explain why the emission and absorption bands of anthracene appear as mirror images. Since this molecule has a very complicated potential surface, you may use a diatomic molecule potential surface to illustrate your answer.

Polycyclic Hydrocarbons

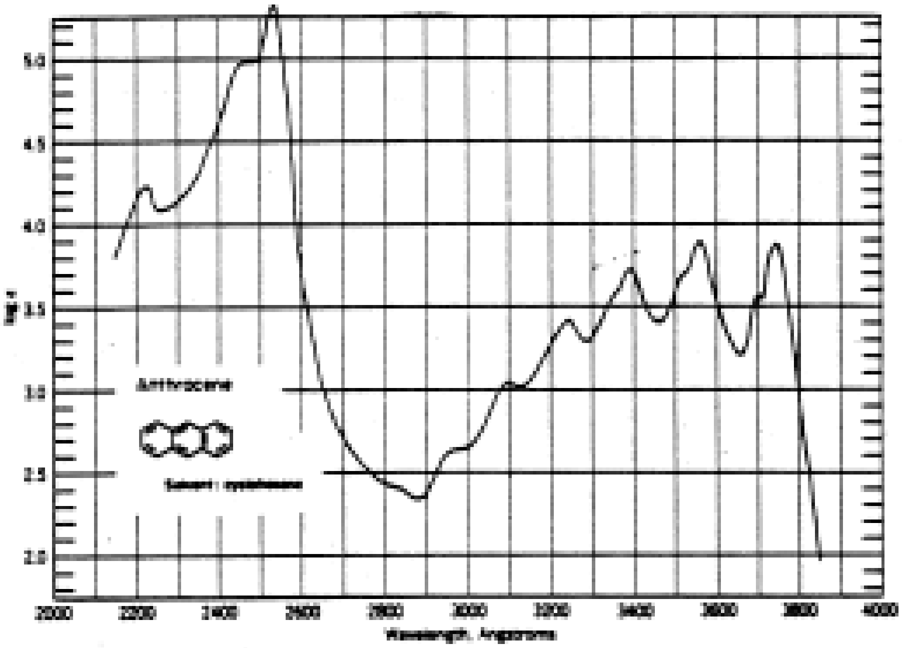
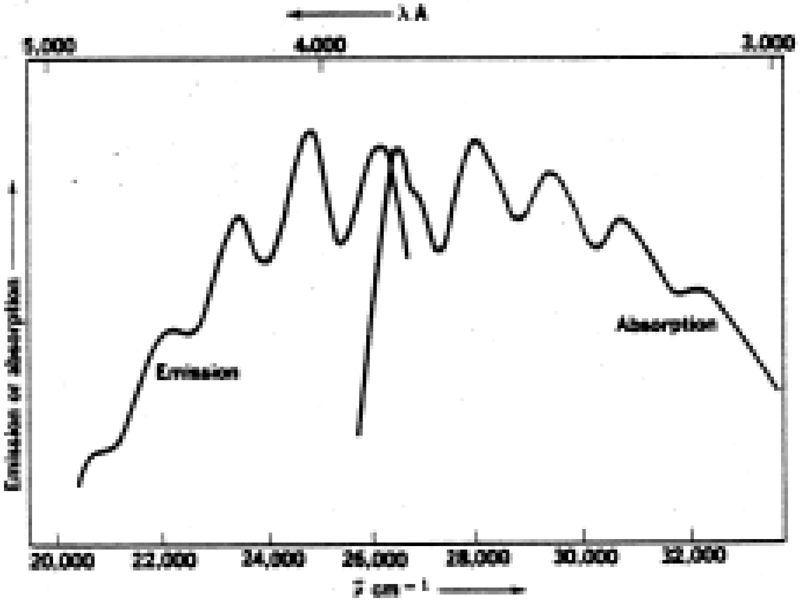
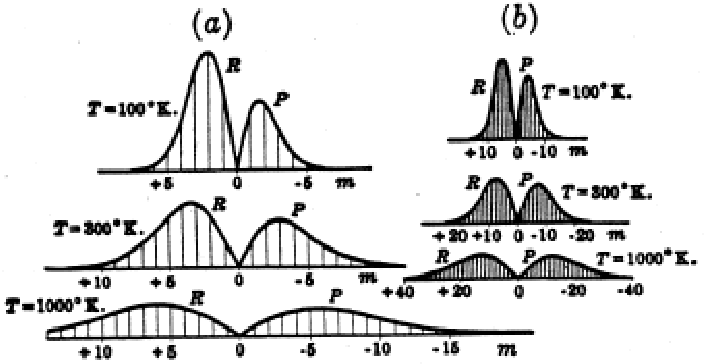


FIG. 11-23 The absorption and fluorescent emission spectrum of anthracene dissolved in dionane showing the occurrence of the emission band at longer wavelengths, . [From G. Kortum and B. Finckh, Z. physik Chem. B52, 263 (1942).]



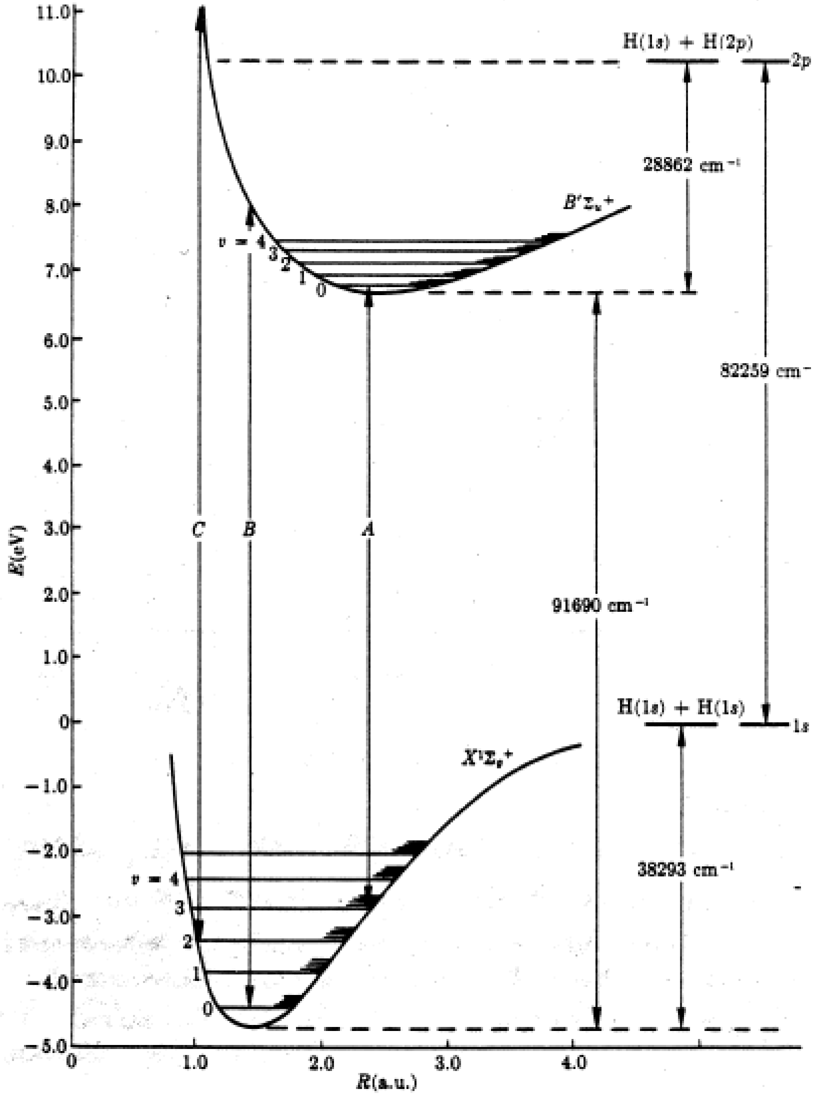
8. The HCl intensity distribution changes with temperature (see below). Explain with equations, how to calculate the relative intensities at 100 K, also at 1000 K.



Intensity Distribution in Rotation-ration Bands in Absorption at 100° K., 300° K., 1000° K. (*a*) For $B = 10.44$ cm^{-1} (HCl). (*b*) $B = 2$ cm^{-1}. The wave number scale of the cissae, which is not explicitly given, is the same for the diagrams. The lines are drawn with the sepa-ion that they would have if the constant B were same in the upper and lower states. m is the ning number of the lines Note that ger wave lengths are to the right in this figure.

9. Some H_2 molecule and H atom electronic states are shown below right:

We have found the expression for the energy eigenvalues for H atom in class. What does the difference 82 259 cm^{-1} correspond to? Draw the absorption and emission spectra in the ultraviolet region which can be predicted from the levels shown. Mark in your spectrum the A, B, C transitions shown in the figure at the right. What indications are there about the relative H-H bond strengths in the excited state and the ground state? Explain.



$$E = U_{\alpha}(R_e) + (v+½)\nu_e - x_e\nu_e\,(v+½)^2 + y_e\nu_e\,(v+½)^3 + B_eJ(J+1) - D_e[J(J+1)]^2 - \alpha_e(v+½)J(J+1) + Y_{00}$$

where all spectroscopic quantities are expressed in energy units (or the corresponding frequency or wavenumbers). In energy units,

$$B_e \equiv \hbar^2 / 2\mu\, R_e^2$$

$$hx_e\nu_e \equiv ¼\, B_e^2/(h\nu_e)^2 \cdot \{\, ({}^{10}/_{3})B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2 - U^{iv}(R_e)R_e^4 \,\}$$

$$D_e \equiv 4\, B_e^3/(h\nu_e)^2$$

$$\alpha_e \equiv -\, 2\, B_e^2/h\nu_e \cdot \{3 + 2\, B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2\}$$

$$Y_{00} \equiv B_e^2/16(h\nu_e)^2 \cdot \{\, U^{iv}(R_e)R_e^4 - ({}^{14}/_{9})B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2 \,\}$$

$$h\nu_e \equiv (h/2\pi)[\, U''(R_e)/\mu\,]^{½}$$

Energy Conversion Factors 300 MHz = 0.01 cm^{-1}, 208.5 cm^{-1} = 300 K

		erg	eV	cm^{-1}
1 erg	=	1	6.2415×10^{11}	5.0340×10^{15}
1 eV	=	1.6022×10^{-12}	1	8065.5
1 cm^{-1}	=	1.9865×10^{-16}	1.23985×10^{-4}	1
1 kcal/mole	=	6.9478×10^{-14}	4.3364×10^{-2}	349.75
1 hartree	=	4.3598×10^{-11}	27.212	219,474.6

		kcal/mole	hartree
1 erg	=	1.4393×10^{13}	2.2937×10^{10}
1 eV	=	23.060	3.6749×10^{-2}
1 cm^{-1}	=	2.8591×10^{-3}	4.55634×10^{-6}
1 kcal/mole	=	1	1.5936×10^{-3}
1 hartree	=	627.51	1

How to obtain molecular constants from spectroscopic constants

(1) *If B_e is given in cm^{-1} and masses in amu, how to find the R_e in Å ?*

$$E_{rot} = B_e J(J+1) \qquad \text{where } B_e = \frac{\hbar^2}{2\mu R_e^2}$$

$$hcB_e = \frac{\hbar^2}{2} \bullet \frac{1}{\mu R_e^2}$$

$$\underset{\text{cm}^{-1}}{B_e} = \frac{h}{8\pi^2 c} \bullet \underset{\text{amu Å}^2}{\frac{1}{\mu R_e^2}}$$

$$\frac{h}{8\pi^2 c} = \frac{6.62618\text{x}10^{-34}\text{ J s}}{8\pi^2 \text{ x } 3\text{ x}10^{8}\text{ ms}^{-1}} \bullet \frac{\text{m}^2\text{ kg s}^{-2}}{\text{J}} \bullet \left[\frac{10^{10}\text{ Å}}{1\text{ m}}\right]^2$$

$$\bullet \frac{6.0224\text{x}10^{23}\text{ amu}}{1\text{ g}} \bullet \frac{10^3\text{ g}}{1\text{ kg}} \bullet \frac{1\text{ m}}{10^2\text{ cm}}$$

$$\frac{h}{8\pi^2 c} = 16.846\text{ amu Å}^2\text{ cm}^{-1}$$

$$\underset{\text{cm}^{-1}}{B_e} = (16.846\text{ amu Å}^2\text{ cm}^{-1}) \bullet \underset{\text{amu Å}^2}{\frac{1}{\mu R_e^2}}$$

(2) *If vibrational frequency ν_e and the U(R) potential energy function are given in cm^{-1} and masses in amu, how to find the second derivative of U(R) at the equilibrium bond length in units of cm^{-1} $Å^{-2}$?*

$$hc\nu_e = (h/2\pi)\left[U''(R_e) / \mu\right]^{1/2}$$

$$U''(R_e) = \left[\frac{\partial^2 U(R)}{\partial R^2}\right]_{R_e} = 4\pi^2\mu c^2 \nu_e^2 \qquad \text{U(R) in joule per molecule}$$

$$\underset{\text{J Å}^{-2}}{U''(R_e)} = \underset{\text{amu (cm}^{-1})^2}{4\pi^2\mu\nu_e^2} \bullet (3\text{x}10^8\text{ m s}^{-1})^2 \bullet \frac{1\text{ kg}}{6.022\text{x}10^{26}\text{ amu}} \bullet \left[\frac{1\text{ cm}}{10^8\text{ Å}}\right]^2$$

If U(R) is in cm^{-1}, then we want $U''(R_e)$ in units of cm^{-1} Å^{-2}. To get this,

$$\underset{\text{cm}^{-1}\,\text{Å}^{-2}}{U''(R_e)} = \frac{4\pi^2\mu\nu_e^2}{hc}$$

$$= \underset{\text{amu cm}^{-1}}{4\pi^2\mu\nu_e^2} \bullet (3\text{x}10^8\ \text{m s}^{-1})^2 \bullet \frac{1\ \text{kg}}{6.022\text{x}10^{26}\ \text{amu}} \bullet \left\lceil \frac{1\ \text{cm}}{10^8\ \text{Å}} \right\rfloor^2$$

$$\bullet \frac{1}{6.62618\text{x}10^{-34}\ \text{J s}\ \text{x}\ 3\text{x}10^{10}\ \text{cm s}^{-1}} \bullet \frac{1\ \text{J}}{\text{m}^2\ \text{kg s}^{-2}}$$

$$\underset{\text{cm}^{-1}\,\text{Å}^{-2}}{U''(R_e)} = (\ 0.029681\ \text{amu}^{-1}\ \text{cm Å}^{-2}\ ) \bullet \underset{\text{amu}}{\mu}\ \underset{(\text{cm}^{-1})^2}{(\nu_e)^2}$$

(3) *If the vibrational-rotational coupling constant frequency α_e is given in cm $^{-1}$ and masses in amu, how to find the third derivative of U(R) at the equilibrium bond length in units of cm $^{-1}$ Å^{-3} ?*

$$\alpha_e = -\frac{2B_e^2}{h\nu_e} \bullet \left\lceil 3 + \frac{2B_e\ U'''(R_e)\ R_e^3}{(h\nu_e)^2} \right\rfloor$$

Rearrange to find

$$\underset{\text{cm}^{-1}\,\text{Å}^{-3}}{U'''(R_e)} = \left\lceil \frac{\partial^3 U(R)}{\partial R^3} \right\rfloor_{R_e} = \underset{\text{dimensionless}}{\left\lceil -\frac{\alpha_e\,\nu_e}{2B_e^2} - 3 \right\rfloor} \bullet \underset{\text{dimensionless}}{\left\lceil \frac{\nu_e}{2B_e} \right\rfloor} \bullet \underset{\text{cm}^{-1}\,\text{Å}^{-3}}{\left\lceil \frac{\nu_e}{R_e^3} \right\rfloor}$$

Some conversion factors

$$\underset{\text{J per molecule}}{\Delta E} = h\nu = 6.62618\text{x}10^{-34}\ \text{J s} \bullet \underset{\text{s}^{-1}\text{ or Hz}}{\nu}$$

$$\underset{\text{J per molecule}}{\Delta E} = 6.62618\text{x}10^{-34}\ \text{J s} \bullet \frac{\text{s}^{-1}}{\text{Hz}} \bullet \frac{10^6\ \text{Hz}}{1\ \text{MHz}} \bullet \underset{\text{MHz}}{\nu}$$

$$\underset{\text{J per molecule}}{\Delta E} = hc(1/\lambda) = 6.62618\text{x}10^{-34}\ \text{J s} \bullet 3\text{x}10^8\ \text{m s}^{-1} \bullet \frac{10^2\ \text{cm}}{1\ \text{m}} \bullet \underset{\text{cm}^{-1}}{(1/\lambda)}$$

1 eV = 8065.46 cm^{-1} 1 eV per molecule = 96, 485 J mol^{-1}