① $$\frac{E}{hc} = U_\alpha(R_e) + Y_{00} + \nu_e\left(v+\tfrac{1}{2}\right) - \nu_e x_e\left(v+\tfrac{1}{2}\right)^2$$
$$+ B_e J(J+1) - \alpha_e\left(v+\tfrac{1}{2}\right)J(J+1)$$
neglecting $[J(J+1)]^2$ term

with all the spectroscopic constants (energies) given in cm^{-1}, including $U_\alpha(R_e)$

The G_v values given are in cm^{-1} measured from $U(R_e)$, that is,

$$162.3803\ cm^{-1} = Y_{00} + \nu_e\left(0+\tfrac{1}{2}\right) - \nu_e x_e\left(0+\tfrac{1}{2}\right)^2$$
$$485.5306\ cm^{-1} = Y_{00} + \nu_e\left(1+\tfrac{1}{2}\right) - \nu_e x_e\left(1+\tfrac{1}{2}\right)^2$$
$$806.5050\ cm^{-1} = Y_{00} + \nu_e\left(2+\tfrac{1}{2}\right) - \nu_e x_e\left(2+\tfrac{1}{2}\right)^2$$

If we pretend for the moment that G_v values are measured from $U(R_e) + Y_{00}$, then a plot of

$$y = \nu_e + (-\nu_e x_e)\, x$$

where $y = \dfrac{G_v}{v+\frac{1}{2}}$ and $x = v + \frac{1}{2}$

will provide a straight line with intercept ν_e and slope $-\nu_e x_e$

The $B_v = B_e - \alpha_e(v+\frac{1}{2})$ values in the table can be analyzed as follows by a fit to a straight line:

$y = B_e - \alpha_e x$ where $y = B_v$ $x = v+\frac{1}{2}$

intercept is B_e, slope is $-\alpha_e$

```
Br2  linear fit to Y = ve + (-vexe)X where Y = Gv/(v+0.5) X = v+.5
 9 points
 X0 = 0.0D0
  X      Y
 0.5 324.7606
 1.5 323.6870
 2.5 322.6020
 3.5 321.5117
 4.5 320.4167
 5.5 319.3170
 6.5 318.2127
 7.5 317.1037
 8.5 315.9898

 Fit to a polynomial of degree  1
 A( 0)=    .3253356E+03   cm-1   νe
 A( 1)=  -.1096773E+01   cm-1   – νexe

 POLYNOMIAL CURVE FIT OF DEGREE 1

         XACTUAL         YACTUAL          YCALC           DIFF           % DIFF

     .5000000E+00    .3247606E+03    .3247872E+03   -.2662667E-01   -.8198188E-02
     .1500000E+01    .3236870E+03    .3236905E+03   -.3453333E-02   -.1066863E-02
     .2500000E+01    .3226020E+03    .3225937E+03    .8320000E-02    .2579096E-02
     .3500000E+01    .3215117E+03    .3214969E+03    .1479333E-01    .4601392E-02
     .4500000E+01    .3204167E+03    .3204001E+03    .1656667E-01    .5170618E-02
     .5500000E+01    .3193170E+03    .3193034E+03    .1364000E-01    .4271800E-02
     .6500000E+01    .3182127E+03    .3182066E+03    .6113333E-02    .1921184E-02
     .7500000E+01    .3171037E+03    .3171098E+03   -.6113333E-02   -.1927828E-02
     .8500000E+01    .3159898E+03    .3160130E+03   -.2324000E-01   -.7354127E-02

 UNBIASED STD ERROR OF ESTIMATE FOR Y= 0.172557E-01 cm-1

 STDEV IN THE SLOPE =  0.22277E-02 cm-1
```

```
Br2  linear fit to Y = Be -ae X   where Y = Bv,  X = v+.5
 9 points
 X0 = 0.0D0
  X      Y
 0.5 0.8194837E-01
 1.5 0.8162622E-01
 2.5 0.8130243E-01
 3.5 0.8097696E-01
 4.5 0.8064974E-01
 5.5 0.8032069E-01
 6.5 0.7998974E-01
 7.5 0.7965681E-01
 8.5 0.7932182E-01
 Fit to a polynomial of degree  1
 A( 0)=   .8212085E-01 cm-1        Be
 A( 1)=  -.3282680E-03 cm-1      - αe

 POLYNOMIAL CURVE FIT OF DEGREE 1

          XACTUAL         YACTUAL          YCALC            DIFF           % DIFF

      .5000000E+00    .8194837E-01    .8195671E-01   -.8344222E-05   -.1018126E-01
      .1500000E+01    .8162622E-01    .8162845E-01   -.2226222E-05   -.2727263E-02
      .2500000E+01    .8130243E-01    .8130018E-01    .2251778E-05    .2769708E-02
      .3500000E+01    .8097696E-01    .8097191E-01    .5049778E-05    .6236456E-02
      .4500000E+01    .8064974E-01    .8064364E-01    .6097778E-05    .7561387E-02
      .5500000E+01    .8032069E-01    .8031537E-01    .5315778E-05    .6618630E-02
      .6500000E+01    .7998974E-01    .7998711E-01    .2633778E-05    .3292753E-02
      .7500000E+01    .7965681E-01    .7965884E-01   -.2028222E-05   -.2546136E-02
      .8500000E+01    .7932182E-01    .7933057E-01   -.8750222E-05   -.1103008E-01

 UNBIASED STD ERROR OF ESTIMATE FOR Y= 0.607348E-05 cm-1

 STDEV IN THE SLOPE =  0.784083E-06 cm-1
```

Now to get the molecular constants from the obtained spectroscopic constants: (see last pages for eqns. (1)-(3))

(1) $$\underset{\text{cm}^{-1}}{B_e} = \frac{h}{8\pi^2 c}\,\frac{1}{\mu R_e^2} = 16.846\,\text{amu}\,\text{Å}^2\,\text{cm}^{-1} \cdot \frac{1}{\mu R_e^2}$$

(2) $$\underset{\text{cm}^{-1}\,\text{Å}^{-2}}{U''(R_e)} \equiv \left[\frac{\partial^2 U(R)}{\partial (R-R_e)^2}\right]_{R=R_e} = \frac{4\pi^2 \mu c^2 \nu_e^2}{hc} = 0.029681\,\text{amu}^{-1}\,\text{cm}\,\text{Å}^{-2} \cdot \underset{\text{amu}\ \text{cm}^{-1}}{\mu \nu_e^2}$$

(3) $$\underset{\text{cm}^{-1}\,\text{Å}^{-3}}{U'''(R_e)} \equiv \left[\frac{\partial^3 U(R)}{\partial (R-R_e)^3}\right]_{R=R_e} = \underset{\text{dimensionless}}{\left[-\frac{\alpha_e \nu_e}{2B_e^2} - 3\right]} \cdot \underset{\text{dimensionless}}{\left[\frac{\nu_e}{2B_e}\right]} \cdot \frac{\overset{\text{cm}^{-1}}{\nu_e}}{\underset{\text{Å}^3}{R_e^3}}$$

$$\frac{1}{\mu} = \frac{1}{78.9183} + \frac{1}{78.9183}$$ since ^{79}Br has mass of 78.9183 amu

$$\therefore \mu = \tfrac{1}{2}(78.9183) = 39.4591 \text{ amu}$$

From (1) and $B_e = 0.08212085\,\text{cm}^{-1}$ we get

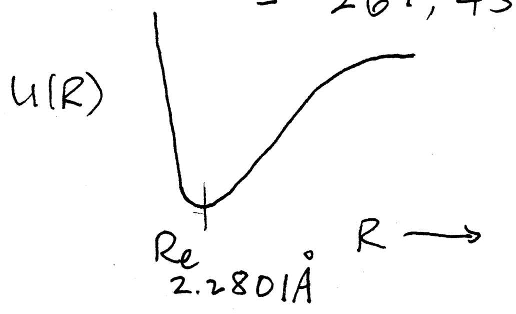
$$R_e = \sqrt{\frac{16.846}{39.4591 \times 0.08212085}} = 2.2801\,\text{Å} \pm 0.0001\,\text{Å}$$

From (2) and $\nu_e = 325.3356\,\text{cm}^{-1}$ we get

$$\underset{\text{cm}^{-1}\,\text{Å}^{-2}}{U''(R_e)} = 0.029681 \times 39.4591 \times (325.3356)^2 = 123{,}962.1 \pm 13.2\ \text{cm}^{-1}\,\text{Å}^{-2}$$

From (3) and $B_e = 0.08212085\,\text{cm}^{-1}$, $\alpha_e = 0.328768 \times 10^{-3}\,\text{cm}^{-1}$, $\nu_e = 325.3356\,\text{cm}^{-1}$ we get

$$U'''(R_e) = \left[\frac{0.3283 \times 10^{-3} \times 325.3356}{2(0.08212085)^2} - 3\right]\left[\frac{325.3356}{2(0.08212085)}\right]\frac{325.3356}{(2.28007)^3}$$
$$= 267{,}430\ \text{cm}^{-1}\,\text{Å}^{-3}$$



$U(R_e)$ = not obtained from data

$U''(R_e) = 123{,}962.1 \pm 13.2\ \text{cm}^{-1}\,\text{Å}^{-2}$

$U'''(R_e) = 267{,}430.\ \text{cm}^{-1}\,\text{Å}^{-3}$

② Pairs of peaks close together are due to
$H^{35}Cl$ (higher intensity) and $H^{37}Cl$ (lower intensity)
$D^{35}Cl$ (") and $D^{37}Cl$ (")
the intensities of the members of the close pair are proportional to the natural abundance of ^{35}Cl and ^{37}Cl, respectively, 75.53% and 24.47%. They are displaced from each other because of two factors. The more important one is that the band centers (marked with an arrow in the HCl spectrum) are different:

band center: $$\Delta E = (1+\tfrac{1}{2})\nu_e - x_e\nu_e(1+\tfrac{1}{2})^2 - \left[(0+\tfrac{1}{2})\nu_e - \nu_e x_e(0+\tfrac{1}{2})^2\right]$$
$$= \nu_e - 2\nu_e x_e$$

because ν_e and $\nu_e x_e$ are mass-dependent. The second factor is that B_e and α_e are mass-dependent also, so that not only are the band centers displaced for one μ compared to another but the spacings between rotational transitions are also different.

Mass- dependence of spectroscopic constants:

Since $\nu_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ and $\frac{1}{\mu} = \frac{1}{m_H} + \frac{1}{m_{Cl}}$ for HCl

$\frac{1}{\mu} = \frac{1}{m_D} + \frac{1}{m_{Cl}}$ for DCl

$$\nu_e({}^1H^{37}Cl) = \frac{\nu_e({}^1H^{35}Cl)\cdot\left(\frac{35}{36}\right)^{1/2}}{\left(\frac{37}{38}\right)^{1/2}}$$

$\frac{1}{\mu} = \frac{1}{1} + \frac{1}{35}$ or $\mu = \frac{35}{36}$ for ${}^1H^{35}Cl$

$\mu = \frac{37}{38}$ for ${}^1H^{37}Cl$

$\mu = \frac{70}{37}$ for $D^{35}Cl$

$\mu = \frac{74}{39}$ for $D^{37}Cl$

$$= .9992\,\nu_e({}^1H^{35}Cl)$$

$$\nu_e(D^{35}Cl) = \frac{\nu_e({}^1H^{35}Cl)\cdot\left(\frac{35}{36}\right)^{1/2}}{\left(\frac{70}{37}\right)^{1/2}}$$

$$= 0.7168\,\nu_e({}^1H^{35}Cl)$$

$$\nu_e(D^{37}Cl) = \frac{\nu_e({}^1H^{35}Cl)\cdot\left(\frac{35}{36}\right)^{1/2}}{\left(\frac{74}{39}\right)^{1/2}}$$

$$= 0.7158\,\nu_e({}^1H^{35}Cl)$$

Looking at the given formula for $\nu_e x_e$ we see that $\nu_e x_e \propto \frac{1}{\mu}$. Thus

$$\nu_e x_e({}^1H^{37}Cl) = \frac{\nu_e x_e({}^1H^{35}Cl)\cdot\left(\frac{35}{36}\right)}{\left(\frac{37}{38}\right)} = 0.9985\,\nu_e x_e({}^1H^{35}Cl)$$

$$\nu_e x_e(D^{35}Cl) = \frac{\nu_e x_e({}^1H^{35}Cl)\cdot\left(\frac{35}{36}\right)}{\left(\frac{70}{37}\right)} = 0.51389\,\nu_e x_e({}^1H^{35}Cl)$$

$$\nu_e x_e(D^{37}Cl) = \frac{\nu_e x_e({}^1H^{35}Cl)\cdot\left(\frac{35}{36}\right)}{\left(\frac{74}{39}\right)} = 0.5124\,\nu_e x_e({}^1H^{35}Cl)$$

and $B_e \propto \frac{1}{\mu}$ also so the same factors hold for B_e

$$B_e({}^1H^{37}Cl) = 0.9985\,B_e({}^1H^{35}Cl)$$

$$B_e(D^{35}Cl) = 0.51389\,B_e({}^1H^{35}Cl)$$

$\alpha_e \propto \mu^{-3/2}$ from the given formula

$$\alpha_e(D^{35}Cl) = (0.51389)^{3/2}\alpha_e({}^1H^{35}Cl) = .3684\,\alpha_e({}^1H^{35}Cl)$$

R(0) means $J_{\text{lower}} = 0 \longrightarrow J_{\text{upper}} = 1$ → or $J'' = 0 \rightarrow J' = 1$

P(1) means $J_{\text{lower}} = 1 \longrightarrow J_{\text{upper}} = 0$

{double prime stands for lower
prime stands for upper

that is, the number given is the J value for the lower vibrational level, and $J_{\text{upper}} = J_{\text{lower}} - 1$ for P branch, $J_{\text{upper}} = J_{\text{lower}} + 1$ for R branch

Using the given formula:

$$E_{\text{upper}} = U(R_e) + h\nu_e(1+\tfrac{1}{2}) + [hB_e - h\alpha_e(1+\tfrac{1}{2})]J'(J'+1) + hY_{00} - h\nu_e x_e(1+\tfrac{1}{2})^2 - h\bar{D}_e[J'(J'+1)]^2$$

$$E_{\text{lower}} = U(R_e) + h\nu_e(0+\tfrac{1}{2}) + [hB_e - h\alpha_e(0+\tfrac{1}{2})]J''(J''+1) + hY_{00} - h\nu_e x_e(0+\tfrac{1}{2})^2 - h\bar{D}_e[J''(J''+1)]^2.$$

P Branch: $J' = J'' - 1$

$$h\nu_{\text{observed}} = (h\nu_e - 2h\nu_e x_e) - h[B_e - \alpha_e]2J'' - h\alpha_e(J'')^2 + 4h\bar{D}_e(J'')^3$$

$$J'' = 1, 2, 3, \ldots$$

R Branch: $J' = J'' + 1$

$$h\nu_{\text{observed}} = (h\nu_e - 2h\nu_e x_e) + h[B_e - \alpha_e]2(J''+1) - h\alpha_e(J''+1)^2 - 4\bar{D}_e(J''+1)^3$$

$$J'' = 0, 1, 2, 3, \ldots$$

Neglecting α_e and $\bar{D}_e$, spacing would be equal between P lines and R lines. $\alpha_e > \bar{D}_e$ (see given formulas and remember that $B_e/\nu_e \sim 10/3000$ for example.) Including the effect of α_e, the quadratic dependence on J'' gives an <u>increase</u> in the spacing between P branch lines as J'' increases since the term in J'' and in $(J'')^2$ are the <u>same</u> sign. On the other hand they are <u>opposite</u> in sign in the R branch so there will be a <u>decrease</u> in the spacing between R branch lines as J'' increases.

The IUPAC peaks numbered 15 and 16 are R(0) and P(1) respectively.

Using the given ν_e $\nu_e x_e$ B_e and $\alpha_e = 0.079\ \text{cm}^{-1}$ for $^1H^{35}Cl$, we find

R(0) $\nu = \nu_e - 2\nu_e x_e + 2B_e - 3\alpha_e$

for $^1H^{35}Cl$ $= 2989.74 - 2(52.05) + 2(10.594) - 3(0.079)$

$= 2906.591\ \text{cm}^{-1}$

P(1) $\nu = \nu_e - 2\nu_e x_e - 2B_e + \alpha_e$

$= 2989.74 - 2(52.05) - 2(10.594) + 0.079$

for $^1H^{35}Cl$ $= 2864.531\ \text{cm}^{-1}$

The pairs of peaks close together:

By using the formulas developed in the previous page, we find

$\nu_e(^1H^{37}Cl) = 0.9992\ \nu_e(^1H^{35}Cl) = 2987.348$

$\nu_e x_e(^1H^{37}Cl) = 0.9985\ \nu_e x_e(^1H^{35}Cl) = 51.972$

$B_e(^1H^{37}Cl) = 0.9985\ B_e(^1H^{35}Cl) = 10.578$

$\alpha_e(^1H^{37}Cl) = (0.9985)^{3/2}\alpha_e(^1H^{35}Cl) = 0.079$

R(0) for $^1H^{37}Cl$ $= 2904.323\ \text{cm}^{-1}$

P(1) for $^1H^{37}Cl$ $= 2862.327\ \text{cm}^{-1}$

R(0) for $^1H^{37}Cl$ and $^1H^{35}Cl$ differ by $2.268\ \text{cm}^{-1}$, P(1) differ by $2.204\ \text{cm}^{-1}$ nearly all of which is accounted for by the $2.236\ \text{cm}^{-1}$ difference in their band centers.

For D^{35}Cl the IUPAC peaks numbered 15 and 16 are:

$\nu_e(D^{35}Cl) = 0.7168\ \nu_e(^1H^{35}Cl) = 2143.046\ cm^{-1}$

$\nu_e x_e(D^{35}Cl) = 0.51389\ \nu_e x_e(^1H^{35}Cl) = 26.75\ cm^{-1}$

$B_e(D^{35}Cl) = 0.51389\ B_e(^1H^{35}Cl) = 5.44\ cm^{-1}$

$\alpha_e(D^{35}Cl) = (0.51389)^{3/2}\ \alpha_e(^1H^{35}Cl) = 0.029\ cm^{-1}$

R(0) for D^{35}Cl $\nu = 2143.046 - 2(26.75) + 2(5.44) - 3(.029)$

$= 2100.339\ cm^{-1}$

P(1) for D^{35}Cl $\nu = 2143.046 - 2(26.75) - 2(5.44) + 0.029$

$= 2078.695\ cm^{-1}$

③

Electronic selection rule:

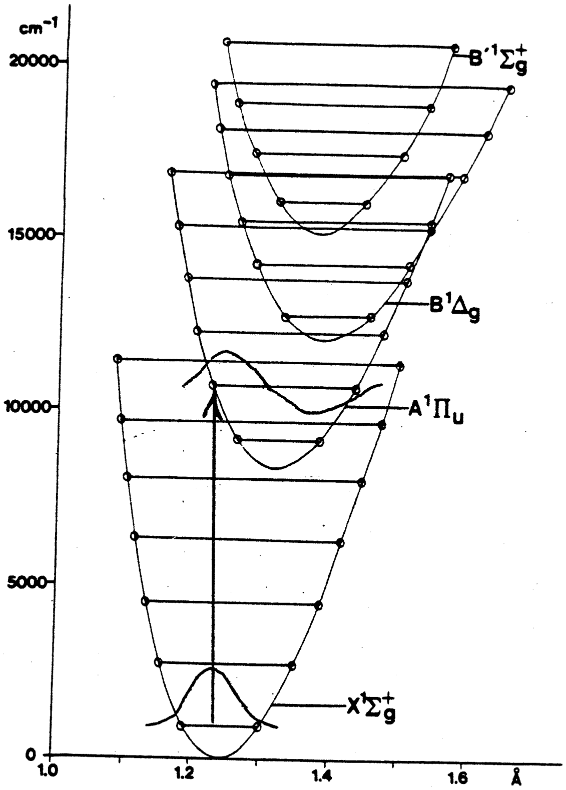
$$\int \psi^*_{\substack{\text{ground}\\ \text{electronic}}} \begin{matrix}\mu_x\\ \text{or}\\ \mu_y\\ \text{or}\\ \mu_z\end{matrix} \psi_{\substack{\text{excited}\\ \text{electronic}}}\, d\tau_e \neq 0$$

where $\mu_x = \sum_i^{\text{all electrons}} x_i e$ dipole moment operator

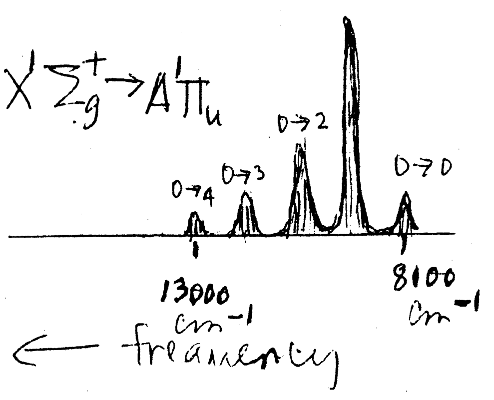
similarly for μ_y and μ_z

For a homonuclear diatomic this integral does not go to zero if the integrand does not change sign when $(x,y,z) \longrightarrow (-x,-y,-z)$ the inversion operation (a symmetry operation) is carried out. The variable x itself changes sign the ${}^1\Sigma_g^+$ wavefunction does not change sign (gerade) Therefore the electronic excited state has to be ungerade (u) so that the integrand does not change sign. Only $A\,{}^1\Pi_u$ state fits. UV-Vis spectra come from electric dipole transitions like this. The transition integral is

$$\int \psi^*_{{}^1\Sigma_g^+} \begin{matrix}\mu_x\\ \text{or}\\ \mu_y\\ \text{or}\\ \mu_z\end{matrix} \psi_{{}^1\Pi_u}\, d\tau_e \cdot \int \psi^*_{vib''} \psi_{vib'}\, d\tau_{vib} \cdot \int \text{rotational part}$$



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



The most intense are $v''=0$ to $v'=1$ and $v''=0$ to $v'=2$ because these provide the largest overlap $\int \psi_{v'}^* \psi_{v''}\, d\tau_{vib}$ in the transition moment integral

④ The 400 nm fluorescence intensity is proportional to the number of excited monomers. The 475 nm fluorescence intensity is proportional to the number of dimers (excimers). Measure these intensities simultaneously. The ratio

$$\frac{\text{Intensity}_{475\,\text{nm}}}{\text{Intensity}_{400\,\text{nm}}} = \frac{\text{dimer concentation}}{\text{monomer concentration}}$$

gives a measure of the frequency of encounters between pyrene molecules. This will be a function of pyrene concentration. In more viscous solvents one expects diffusion of pyrene to be slower so that a higher concentration of pyrene in that solvent would be required to obtain a given dimer/monomer ratio. At such concentrations as in this problem (≈ 1 pyrene : 1000 solvent), dimer formation can be assumed to be diffusion controlled.

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 ground state [dissociating into ground state Xe atoms] are shown below.

SPECTROSCOPY OF Xe_2

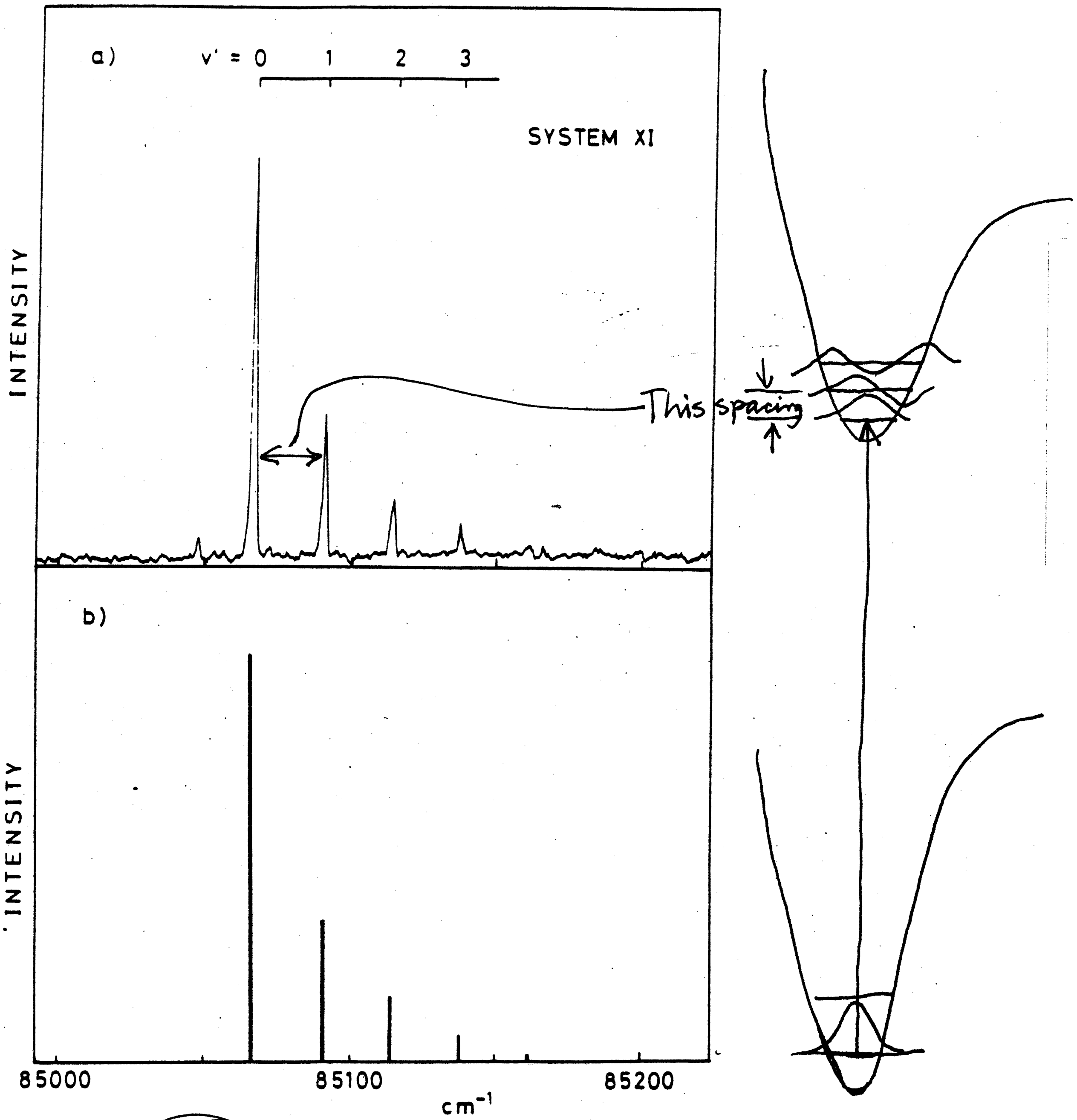


FIG. 5. (a) Fluorescence excitation specrum of the system XI. Intensity of the VUV coherent radiation is almost constant over the entire region. (b) Calculated Franck–Condon factors; $r'_e = 4.52$ Å.

Excite from $v''=0$ and watch fluorescence from excited states that have been reached.

The excited and ground states have nearly the same R_e, $v'=0$ and $v''=0$ are vertically superposable

⑤ What conclusions can we draw from the given spectrum? (answer is on previous page).

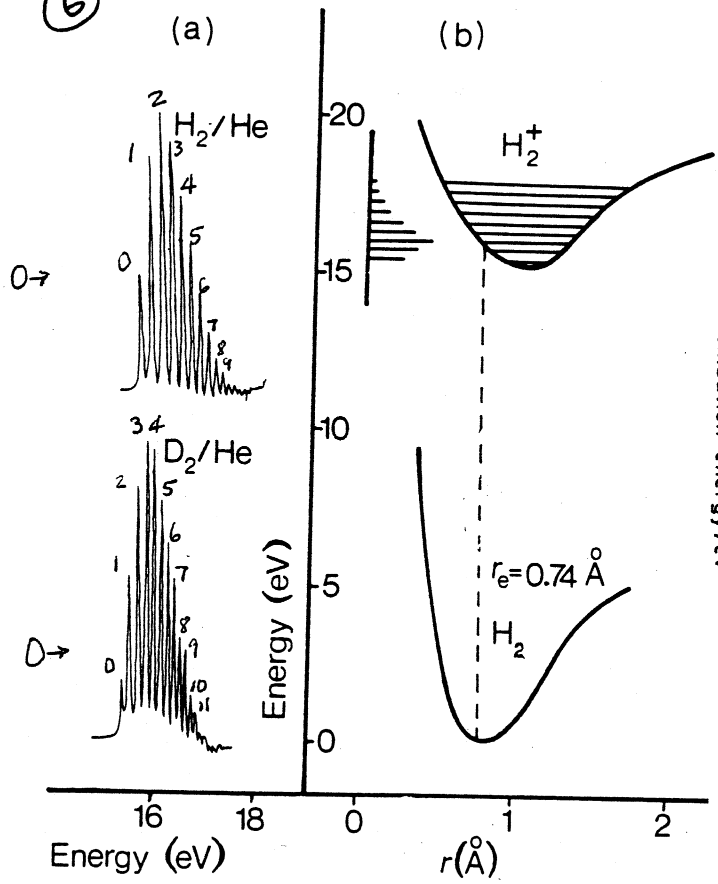
ASIDE: Note that the entire spectrum is only about 100 cm^{-1} from $v'=0$ to $v'=4$, that is, of the same order of energy spacings as rotational levels of H_2. This diatomic molecule has a very small force constant, a very weak bond in Xe_2 diatomic molecule (a so-called van der Waals dimer).

To explain the spectrum we need maximum overlap between $v'=0$ and $v''=0$ wavefunctions and decreasing overlap between $v'=1$ and $v''=0$ and also between higher v' and $v''=0$.

Intensities are proportional to squares of:

$$\int \underset{\text{upper electronic}}{\psi^*_{upper}} \, \mu \, \underset{\text{lower ground electronic state}}{\psi} \, d\tau_e \cdot \int \underset{\text{in upper electronic}}{\psi^*_{v'}} \, \underset{\text{in ground electronic state}}{\psi_{v''=0}} \, d\tau_{vib}$$

⑥



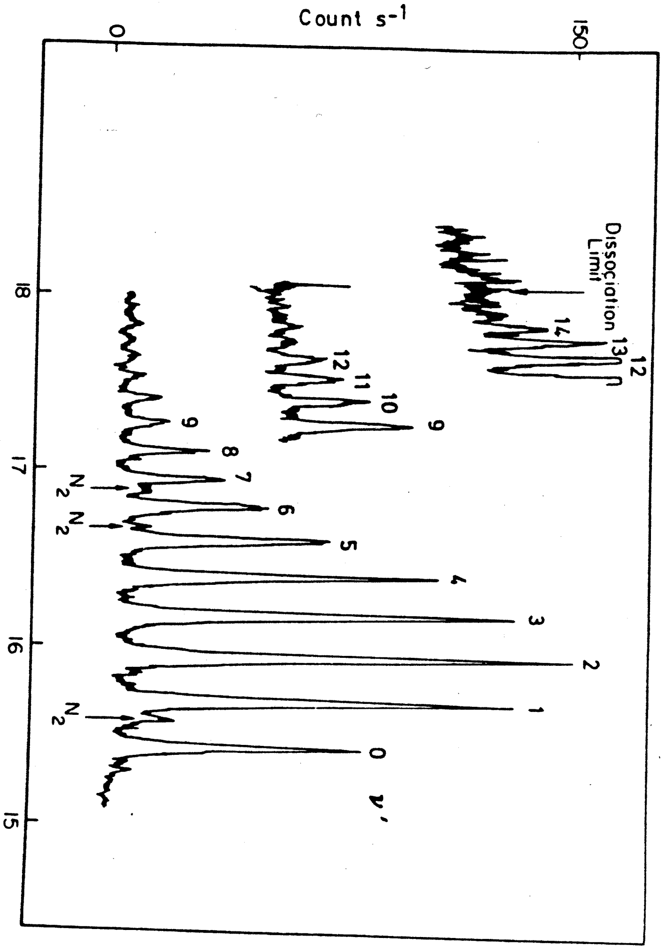


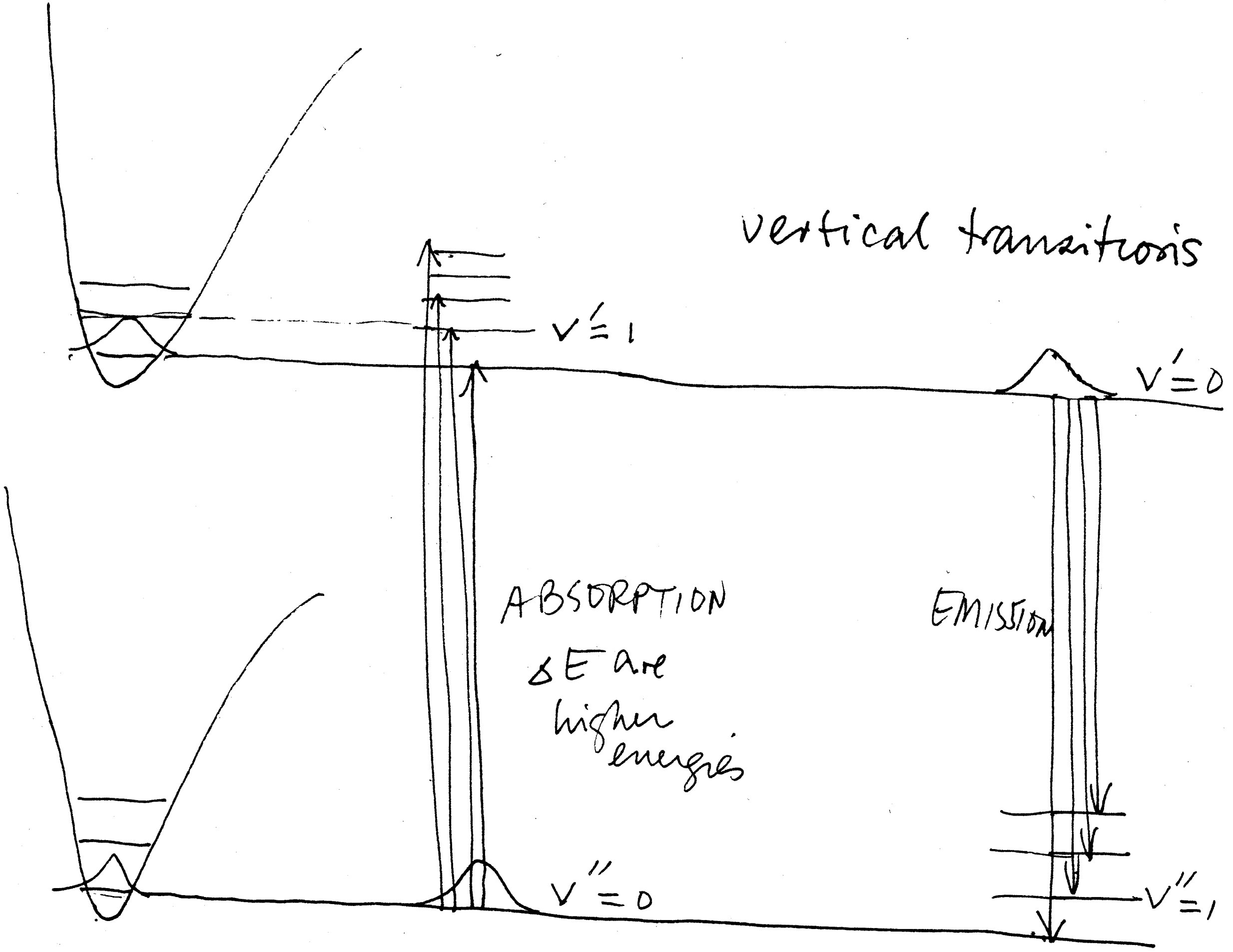
FIGURE 1. (a) Photoelectron spectra of H_2 and D_2; (b) potential energy curves showing spectra plotted along ordinate.

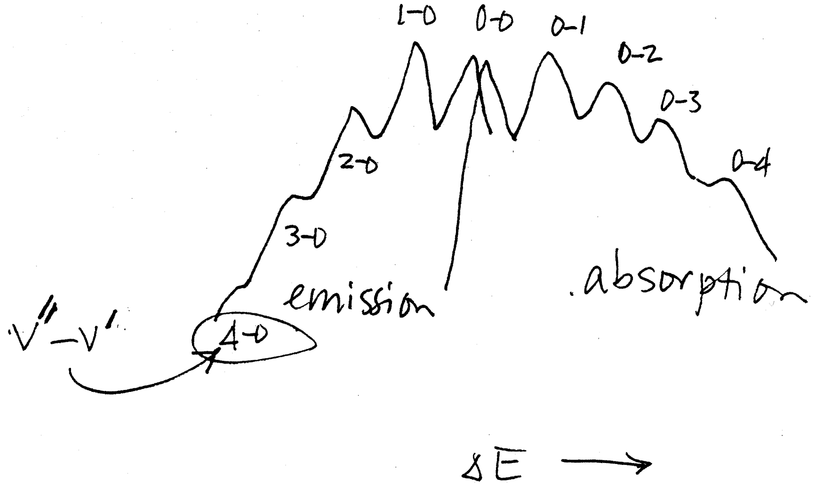
The same point on the potential energy curve of the ion corresponds to a higher vibrational quantum number for D_2^+ than for H_2^+ because the vibrational spacings depend on

$\nu_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ $\frac{1}{\mu} = \frac{1}{2} + \frac{1}{2}$ for D_2^+ → smaller ν_e, closer vibrational spacing

$\frac{1}{\mu} = \frac{1}{1} + \frac{1}{1}$ for H_2^+

⑦


vertical transitions
v'=1
v'=0
ABSORPTION
ΔE are higher energies
EMISSION
v''=0
v''=1


1-0
0-0
0-1
0-2
0-3
0-4
2-0
3-0
4-0
emission
absorption
v''-v'
ΔE →

⑧ Intensity is proportional to the number of molecules present in a particular lower energy level from which transition occurs

For the same J at two different temperatures the intensities are related as

Such as 100K and 1000K

$$\frac{I_{T_1}}{I_{T_2}} = \frac{e^{-BJ(J+1)/k_B T_1}}{e^{-BJ(J+1)/k_B T_2}}$$

At a given temperature, different J, the intensities are related as

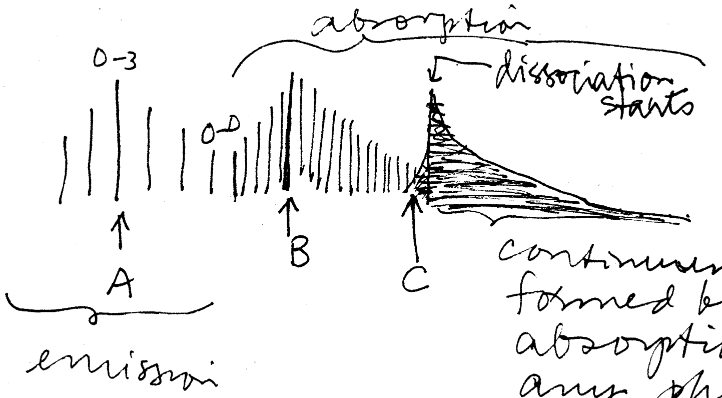
$$\frac{I_{J_1}}{I_{J_2}} = \frac{(2J_1+1)\, e^{-BJ_1(J_1+1)/k_B T}}{(2J_2+1)\, e^{-BJ_2(J_2+1)/k_B T}}$$

the $(2J+1)$ factors come from the number of states that exist $M_J = -J, -J+1, \ldots 0, \ldots +J$ with the same energy eigenvalue.

As the temperature increases, the populations of the upper J'' levels relative to the lower ones J'' increase, so more lines are observed in the P and R branches at higher temperatures. The temperature can be determined from the envelope of the P and R branches if the identity of the molecule is known, even if the rotational transitions cannot be individually measured.

⑨ (a) $$82\,259\ \text{cm}^{-1} = \underbrace{-\frac{1}{2^2}\frac{e^2}{2a_0}}_{\substack{\text{H atom}\\ n=2}} \quad - \underbrace{\frac{1}{1^2}\frac{e^2}{2a_0}}_{\substack{\text{H atom}\\ n=1}}$$

(b)



continuum formed by absorption of *any* photon energy that corresponds to dissociation of H_2 molecule into H atoms

Intensities of vibrational bands are according to
$$\int_{-\infty}^{+\infty}\psi^*_{v''}(x)\,\psi_{v'}(x)\,dx$$
for vertical transitions (no change in $x = R - R_e$) during electronic transition

(c) Relative bond strengths are indicated by the dissociation energies:

Ground electronic state $D_e = 38\,293\ \text{cm}^{-1}$

Excited electronic state $D_e = 28\,862\ \text{cm}^{-1}$

which, not surprisingly, are also associated with shorter bond length (R_e) for ground state and longer bond length for the excited state