Chemistry 543

Second Exam

April 20, 1999

1. Very little is known about the covalent states of the alkali halides. Recently [J. Mol. Spectrosc. 163, 238 (1994)] a bound state of KI was found which has an internuclear distance of 3.7356 Å and a dissociation energy of 893.1 cm^{-1}. It was given the label "C" in analogy with a similar state discovered earlier for NaI molecule. The new excited state was observed by fluorescence excitation, that is, the fluorescence is observed after excitation (from the ground electronic state X) to a particular v' of the C state. Of course, one has to be able to assign the observed bands to the correct vibrational quantum numbers in order to characterize the PES of the excited state. The progression observed in fluorescence and its simulation are shown in the Fig. below. *Interpret the fluorescence spectrum, that is, draw a labeled schematic diagram of the PE surfaces and the transitions observed here. Note the intensity pattern.*

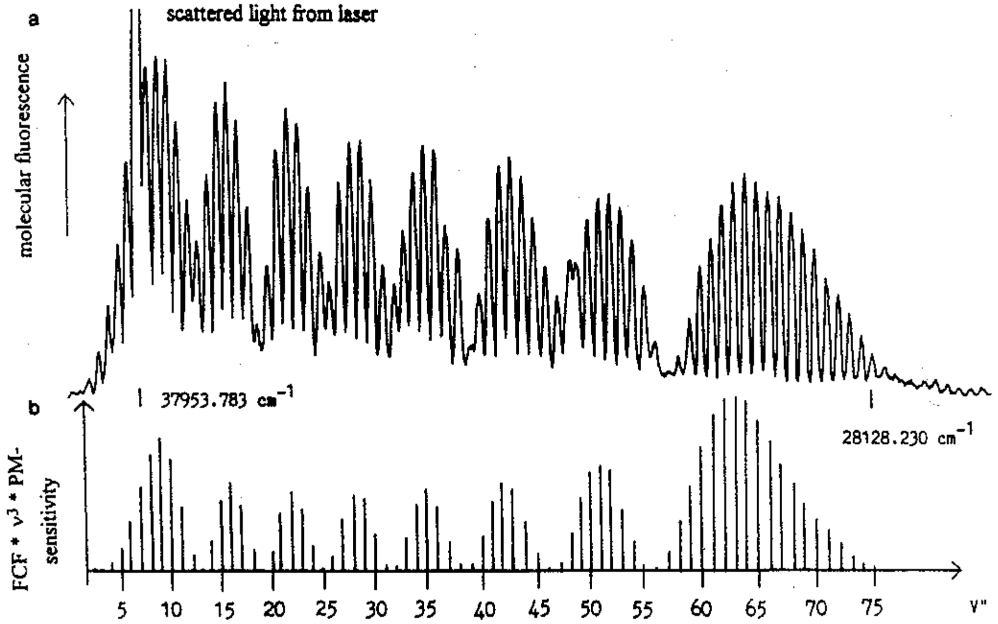
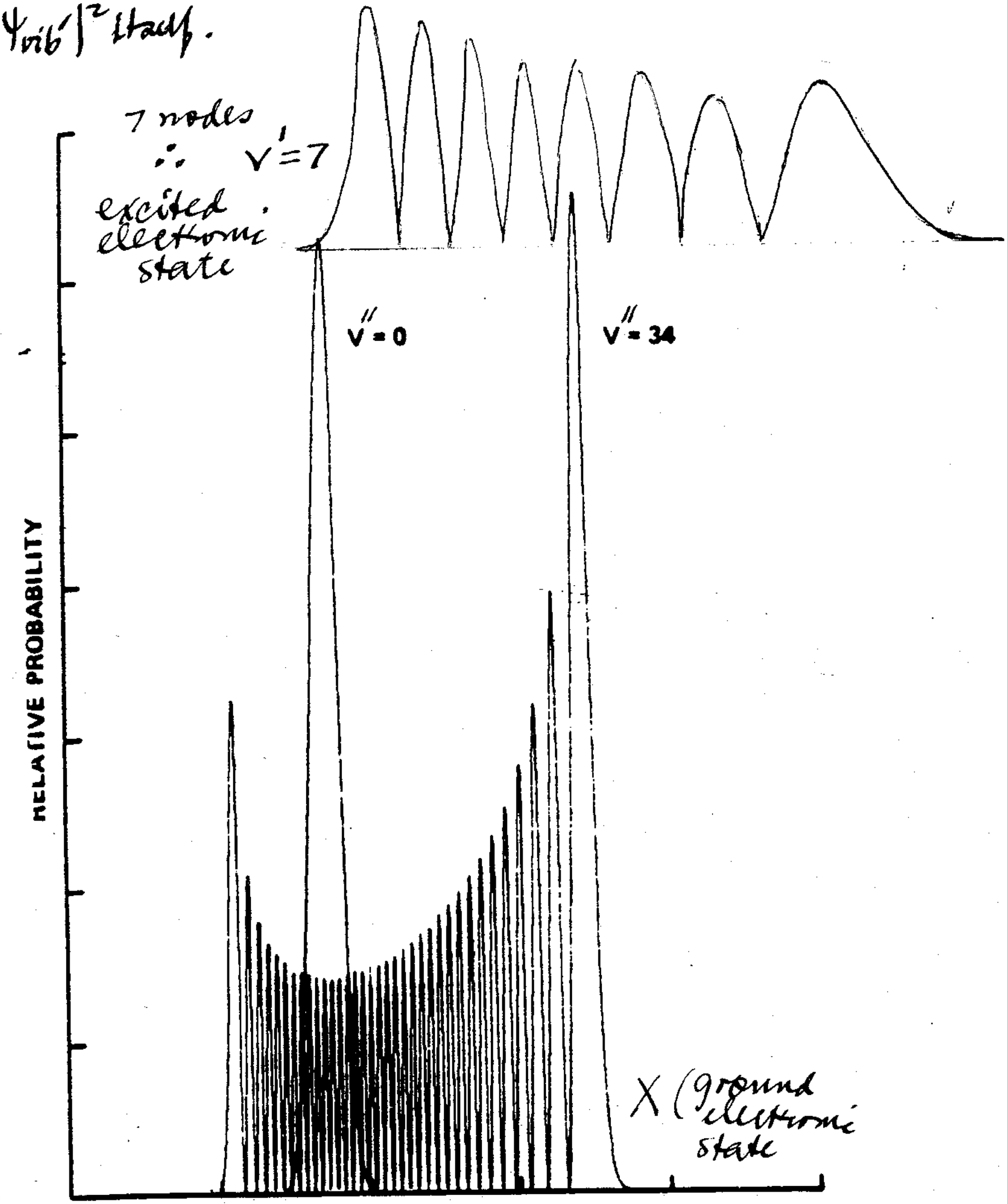


FIG. 2. Fluorescence progression (a) of KI on $C(v' = 7)-X(v'' = 7)P(72) = 37\,953.783$ cm^{-1} and its simulation in (b).

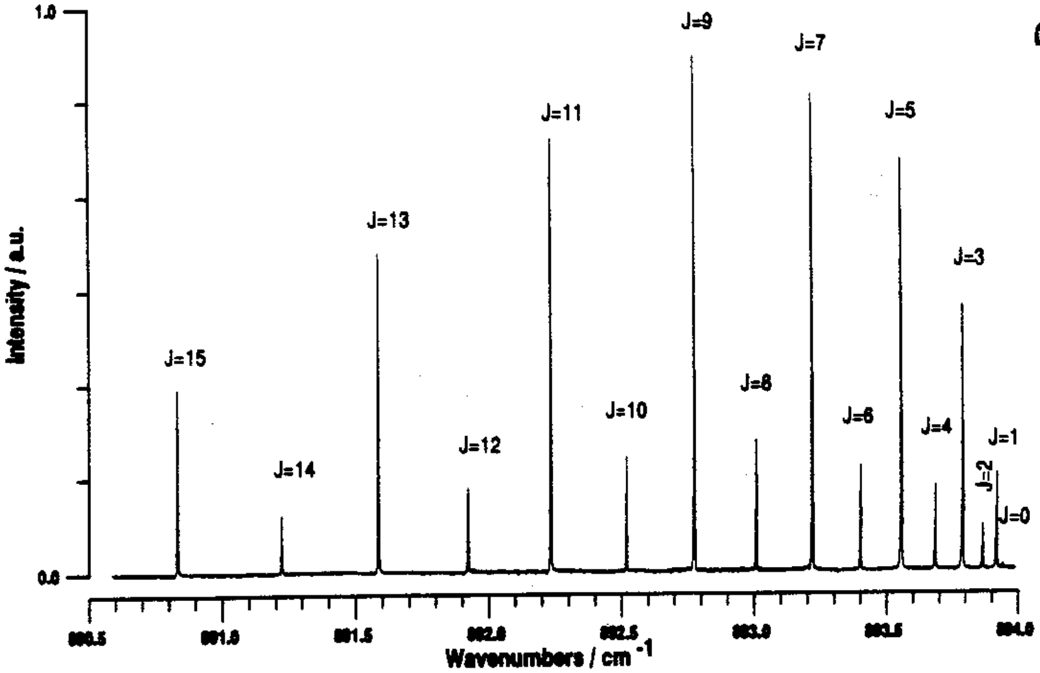
Intensity of a vibrational band in an electronic transition such as this one depends on the square of

$$\left\langle \psi''_{elec}\left(X, \text{elec. ground state}\right) \middle| e\underbrace{\sum_i z_i}_{\text{(along internuclear axis)}} \middle| \psi'_{elec}\left(\text{excited elec. state}\right)\right\rangle \cdot \int_{-\infty}^{+\infty} \psi^*_{vib'}(x)\,\psi_{vib''}(x)\,dx$$

Transitions from the excited electronic state "C" down to the ground electronic state X are <u>vertical</u> (no change in nuclear positions during electronic transition). Since the intensity depends on the overlap between the upper and lower vibrational states, and since $|\psi_{vib}|$ has maximum values at outer turning point, the overlap between the outermost part of ψ_{vib}'' "picks out" the value of ψ_{vib}' of the upper electronic state, in this example beautifully mapping out $|\psi_{vib}'|^2$ itself.



2. The high resolution stimulated Raman spectrum of F_2 molecule [J. Mol. Spectrosc. 168, 343 (1994)] is shown below. Only the region in the vicinity of the origin of the Q branch is shown here. *What equation should the frequencies be fitted to and what spectroscopic parameters can thereby be obtained?* [Hint: One answer is -0.01293658 cm^{-1}, another is 893.94 cm^{-1}.] *Explain the intensities here.*



two nuclei
ortho spin states
$\alpha\alpha$
$\beta\beta$
$\frac{\alpha\beta+\beta\alpha}{\sqrt{2}}$

para spin state
$\frac{\alpha\beta-\beta\alpha}{\sqrt{2}}$

FIG. 2. Stimulated Raman spectrum of fluorine at room temperature in the region of the origin of the Q branch of the $v = 1 \leftarrow v = 0$ band.

Since it is the $v=1 \leftarrow v=0$ fundamental band, then should fit the observed frequencies to:

$$\nu = \nu_0 + (B_1 - B_0) J(J+1) - (D_1 - D_0)[J(J+1)]^2$$

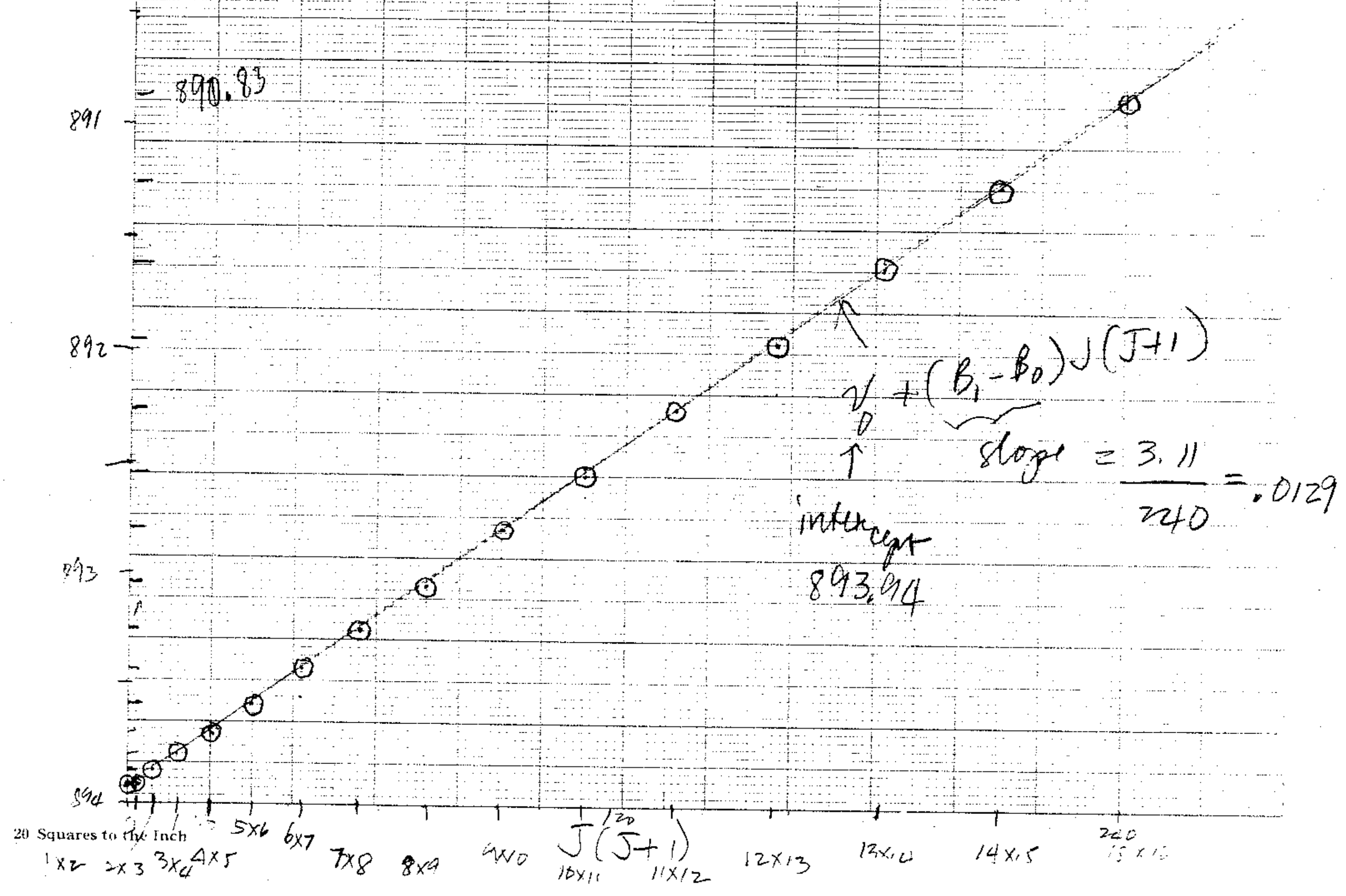
where, by subtraction using formula given on last page,

$$\nu_0 = \nu_e - 2\nu_e x_e \qquad B_1 = B_e - \tfrac{3}{2}\alpha_e \qquad B_0 = B_e - \tfrac{1}{2}\alpha_e$$

(similar definitions for D_1 and D_0 in terms of centrifugal stretching constants, but $(D_1 - D_0)$ can probably be neglected since D_e itself is very small). From such a fit of ν vs. $J(J+1)$, intercept $= \nu_0$, slope near intercept is $B_1 - B_0 = -\alpha_e$. Results are $\nu_0 = 893.94$ cm^{-1} $\alpha_e = 0.01293658$ cm^{-1}. Intensities for J odd are about 3:1 ratio to J even. ^{19}F has spin $\frac{1}{2}$ (Fermion). Total wavefunction has to be antisymmetric wrt interchange of the two F nuclei. The ground state of F_2 (a stable molecule) is $^1\Sigma_g^+$, which is symmetric (g).(+)

$$P_{AB}\Psi_{tot} = -\Psi_{tot} = (+)\psi_{elec,\,^1\Sigma_g^+} \cdot (-1)^J \psi_{rot}^J \cdot (\pm)\psi_{nuclear\ spin}$$

even goes with para while odd J with ortho


890.83
891
892
893
894
20 Squares to the Inch
1x2
2x3
3x4
4x5
5x6
6x7
7x8
8x9
9x10
10x11
11x12
12x13
13x14
14x15
15x16
120
240
J(J+1)
$\nu_0 + \underbrace{(B_1 - B_0)}_{\text{slope}} J(J+1)$
intercept
893.94
slope = $\frac{3.11}{240}$ = .0129

3. The laser spectroscopy of YF molecule characterized several singlet and triplet states. [J. Mol. Spectrosc. 169, 253 (1995)] A typical laser excitation spectrum is shown below. The band origin for the v' = 0, v" = 0 is 17517.27 cm^{-1}. *Draw an energy level diagram showing these 8 transitions P(2), ..., R(6); label every energy state with the complete set of quantum numbers.*

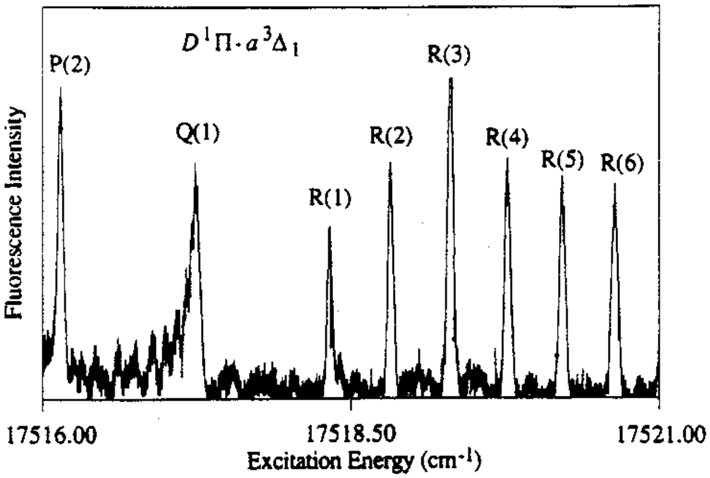
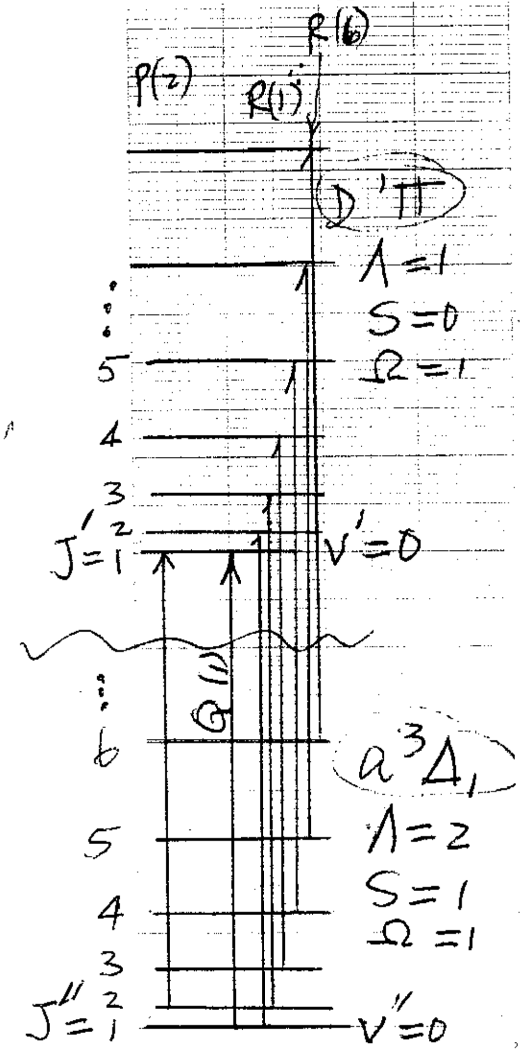


FIG. 1. Typical laser excitation spectrum for YF.



From the figure given

R(1) is at 17,518.3 cm^{-1}
Q(1) 17,517.3
P(2) 17,516.1

J' starts at 1 because $^1\Pi$ has
$\Lambda=1$ $S=0$ $\Omega=1$ ← electronic angular momentum adds to rotational 0, 1, 2, 3, ...
to give
$J' = 1, 2, 3, 4, \ldots$

$^3\Delta_1$ has $\Lambda=2$ $S=1$ $\Omega=1$ ← electronic angular momentum adds to rotational 0, 1, 2, 3 ...
to give
$J'' = 1, 2, 3, 4, \ldots$

Therefore first Q line is for $\left.\begin{matrix} J''=1 \\ a^3\Delta_1 \\ v''=0 \end{matrix}\right\} \rightarrow \left\{\begin{matrix} J'=1 \\ D\,^1\Pi \\ v'=0 \end{matrix}\right.$

4. In each of the following, you are given limited information. In each case, state all the conclusions which can be made, based on the given information alone.

   a. The high resolution electronic absorption spectrum of a homonuclear diatomic molecule shows a vibrational band which looks like the IR spectrum of HBr, that is, having normal P and R branches.

   b. The IR spectrum of a diatomic molecule shows a Q branch.

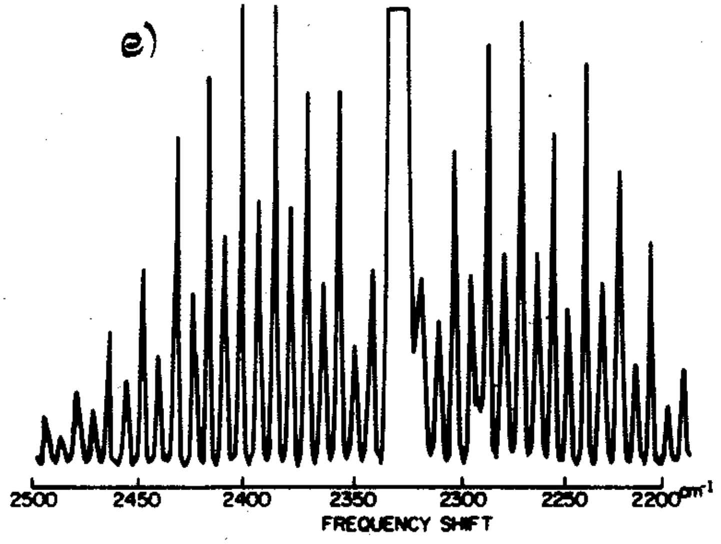
   c. The 0-0 band of the electronic spectrum of a diatomic molecule has a Q branch which tails towards the red (longer wavelength).

   d. The microwave spectrum of a molecule consists of nearly exactly equally spaced peaks 1.50 cm^{-1} apart.

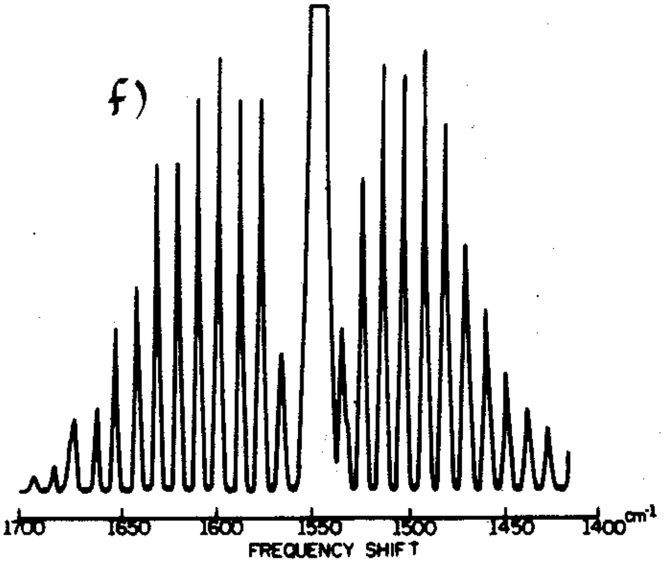
   e. The high resolution Raman spectrum of a diatomic molecule is shown below left.

   f. The high resolution Raman spectrum of a homo-nuclear diatomic molecule is shown below right.

e)



f)



④

conclusions	based on
(a) $I=0$	no alternation of intensities in homonuclear diat.
${}^1\Sigma \rightarrow {}^1\Sigma$ transition	no Q branch
$B_v' \approx B_v''$	no bandheads
(b) not ${}^1\Sigma$	Q branch
heteronuclear	IR is obs.
(c) at least one of the two electronic states involved is not ${}^1\Sigma$	Q branch
$(B_v' - B_v'') < 0$	Q on the low freq. side
$R_e' > R_e''$	
(d) molecule has permanent dipole moment	microwave obs.
$\bar{D}_e$ is very small compared to B_e	equal spacing
$B_0 = 0.75\ \text{cm}^{-1}$	spacing is $1.5\ \text{cm}^{-1}$
(e) homonuclear	alternation of intensities
$I=1$ with ratio 6:3	intensity ratio is 2:1
even J goes with orthospin states, therefore electronic ground state is $(+g)$ or $(-u)$ as in Σ_g^+ or Σ_u^-.	even J [innermost members of S and O branches are S(0) and O(2)] have higher intensity
$\nu_e - 2\nu_e x_e \approx 2335$ (center of band)	center between S(0) and O(2) is at 2335
$\bar{B} \approx 2.1\ \text{cm}^{-1}$	$12 \times 4\bar{B} = 100\ \text{cm}^{-1}$ (see figure next page)
$B_1 < B_0$ as expected	Q branch on low freq. side

(f) conclusions:

$I = 0$

$\nu_e - 2\nu_e x_e \approx 1550\ cm^{-1}$

$\bar{B} \approx 1.4\ cm^{-1}$

electronic ground state is Σ_g^- or Σ_u^+, not Σ_g^+ or Σ_u^-

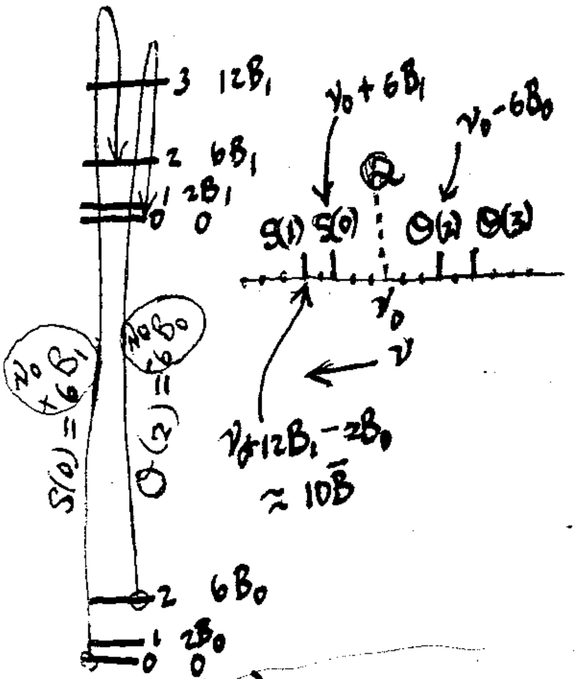
based on:

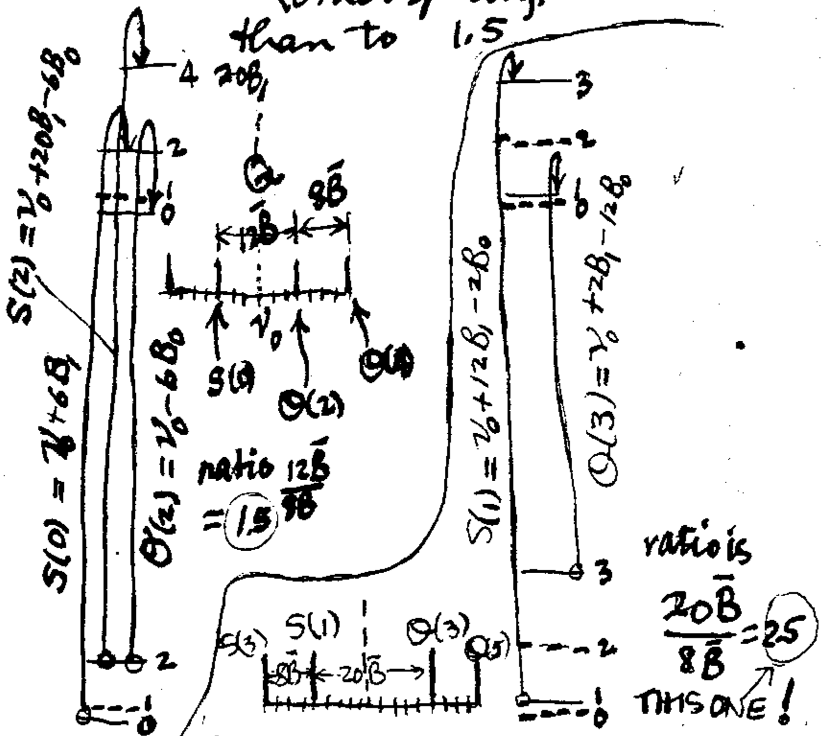
Given homonuclear but shows no alternation of intensities

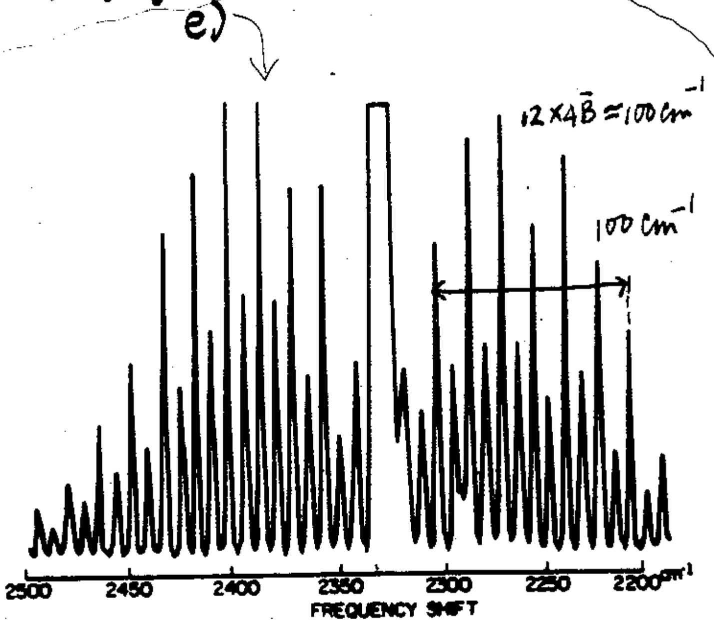
center is at $1550\ cm^{-1}$

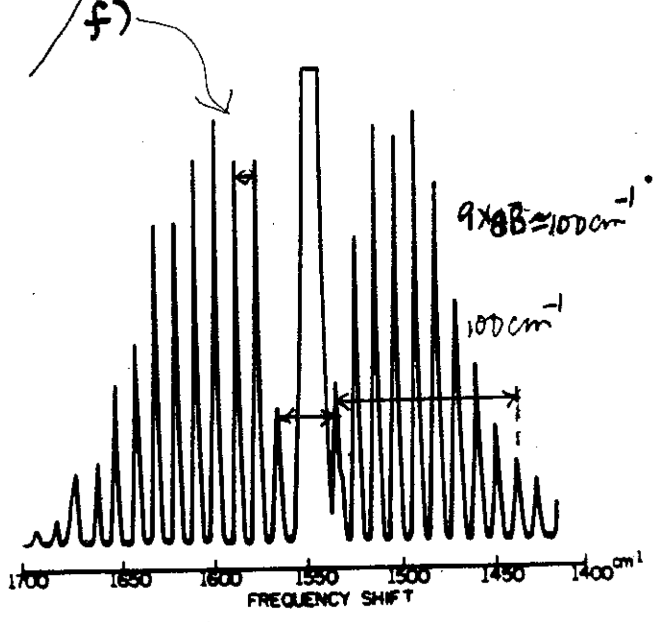
$9 \times 8\bar{B} = 100\ cm^{-1}$

ratio of $\left(\frac{\text{middle space}}{\text{other spacing}}\right)$ is closer to 2.5 than to 1.5

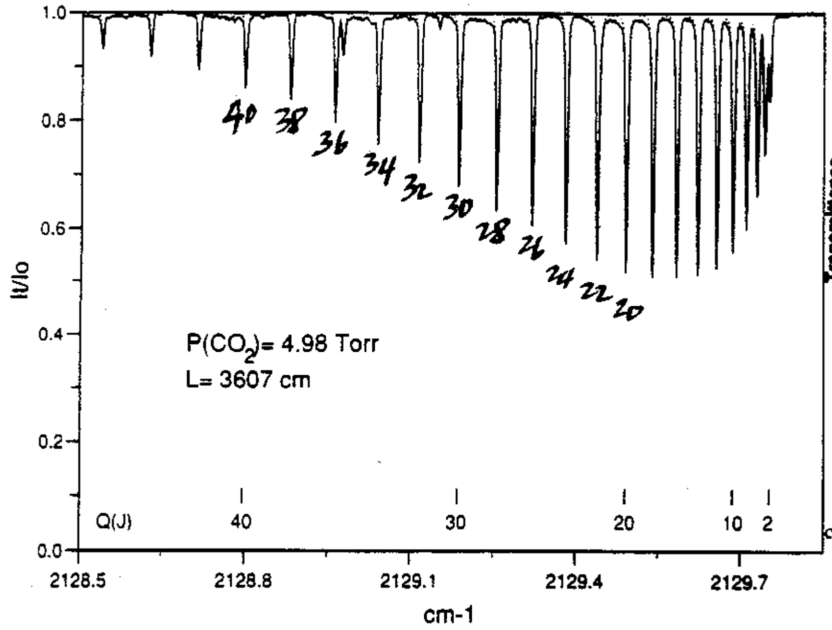








5. The $(20^00) \leftarrow 01^10$ band of CO_2 molecule has been observed [J. Mol. Spectrosc. 172, 1 (1995)] (see below). This is a combination band (the middle vibrational quantum number is of course the degenerate bend, while the first is the symmetric stretch). *What specific information can be obtained from this spectrum? Label every peak starting with the few that are assigned. Why are some peaks missing?* See also the $(40^01) \leftarrow (00^00)$ absorption spectrum [J. Mol. Spectrosc. 175, 104 (1996)] on the right for missing peaks. *Explain.*



Q-branch low pressure spectrum of the $(20^00)_I \leftarrow 01^10$ transition

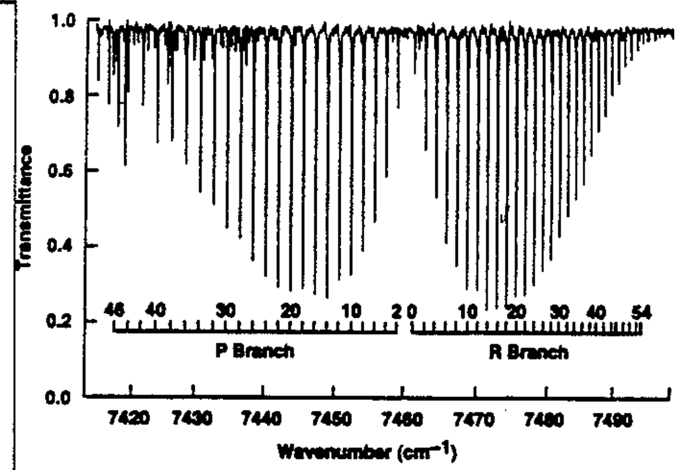


FIG. 1. Transmittance spectrum of the $(40^01)_{IV} \leftarrow (00^00)$ band at 7460 cm^{-1} obtained at Ames, using a total absorption path of 1607 m.

By subtracting 2 energy expressions we get the frequencies

$$\nu = (2\nu_e - 6\nu_e x_e)_1 - (\nu_e - 2\nu_e x_e)_2 + [-2(\alpha_e)_1 + (\alpha_e)_2]J(J+1)$$

or something very similar for polyatomic

In the plot of frequencies vs $J(J+1)$ we get $(2\nu_e - 6\nu_e x_e)_1 - (\nu_e - 2\nu_e x_e)_2$ as the intercept and $-2(\alpha_e)_1 + (\alpha_e)_2$ is the slope.

^{16}O is a BOSON $(I=0)$ which means Ψ_{tot} for CO_2 must be symmetric wrt interchange of ^{16}O nuclei

$$P_{AB}\Psi_{tot} = +\Psi_{tot} = (+)\psi_{elec}(^1\Sigma_g)\cdot(-1)^J\psi^J_{rot}(\pm)\psi_{\substack{nucl\\spin}}\cdot\psi_{vib}(\text{000 ground state is totally sym.})$$

Only even J states exist for ground vibr'l state.

even J must go with ORTHO (sym) nuclear spins

There are no PARA nuclear spin since $I=0$

6. The observation of the $A\ ^1\Sigma_u^+$ state of $^6\mathrm{Li}_2$ from v=0 to the dissociation limit was reported recently. [J. Mol. Spectrosc. 175, 340 (1996)] The PESs are shown below, illustrating the double excitation carried out. The frequencies of the band origins corresponding to transitions between v"=0 of the *X* state and v'=0 up to the dissociation limit of the *A* state are measured and tabulated. Call these frequencies $G_{v'}$ (v'=0 up to v'=dissociation limit). *Enumerate the spectroscopic quantities that can be obtained (describe how?) very accurately from these data (specify whether for the X state, the A state or other).*

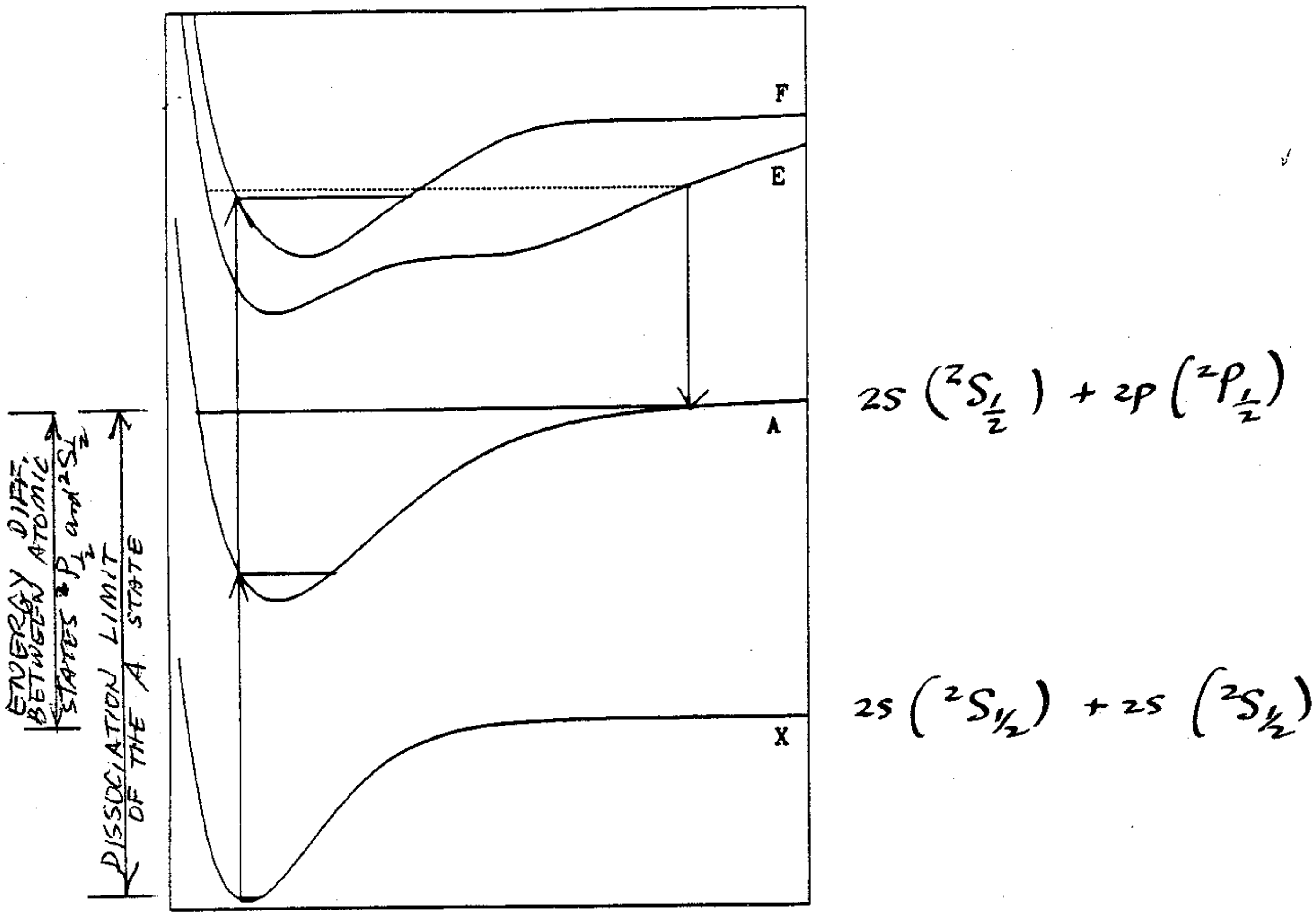


FIG. 7. Potential energy diagram showing excitation, via double resonance, from $X^1\Sigma_g^+$ through $A^1\Sigma_u^+$ (low v) to a mixed $F^1\Sigma_g^+$ and $E^1\Sigma_g^+$ level.

1. Can get D_0 dissociation energy for the ground electronic (X) state by taking the difference:

DISSOCIATION LIMIT OF STATE A

$-\ (^2P_{1/2} - {}^2S_{1/2})_{Li\ atom}$

D_0 for the X state

Problem 6 continued:

2. Take the differences of the frequencies: $[G_{(v+1)'} - G_{v'}]$ Plot these differences against v', starting from $v'=0$. The area under the curve [if a straight line the area $= \frac{1}{2}(\underset{\substack{\uparrow \\ x\text{ intercept}}}{V_{max}})(\Delta \underset{\substack{\uparrow \\ y\text{ intercept}}}{G_{max}})$] is D_0 for the A state. Or else plot the same $[G_{(v+1)'} - G_{v'}]$ values against $(v'+\frac{1}{2})$ in which case [again if straight line the area = $\frac{1}{2}$ (x intercept)(y intercept)] the area gives D_e for the A state.

3. Analysis of individual G_v - by least squares fitting to $G_{v'} = \nu_e'(v'+\frac{1}{2}) - \nu_e'x_e'(v'+\frac{1}{2})^2 + \nu_e'y_e'(v'+\frac{1}{2})^3$ will provide ν_e' $\nu_e'x_e'$, and $\nu_e y_e'$ for the A state very accurately.

7. The (0,0) band of CoH is reported in J. Mol. Spectrosc. 173, 100 (1995), shown below. The ground state has been identified as $X\,^3\Phi_4$, v=0 level. *Specify* *<u>all the quantum numbers</u>* *(upper and lower) of the P(5) transition in the figure. Why are the first peaks R(4), Q(4) and P(5)?*

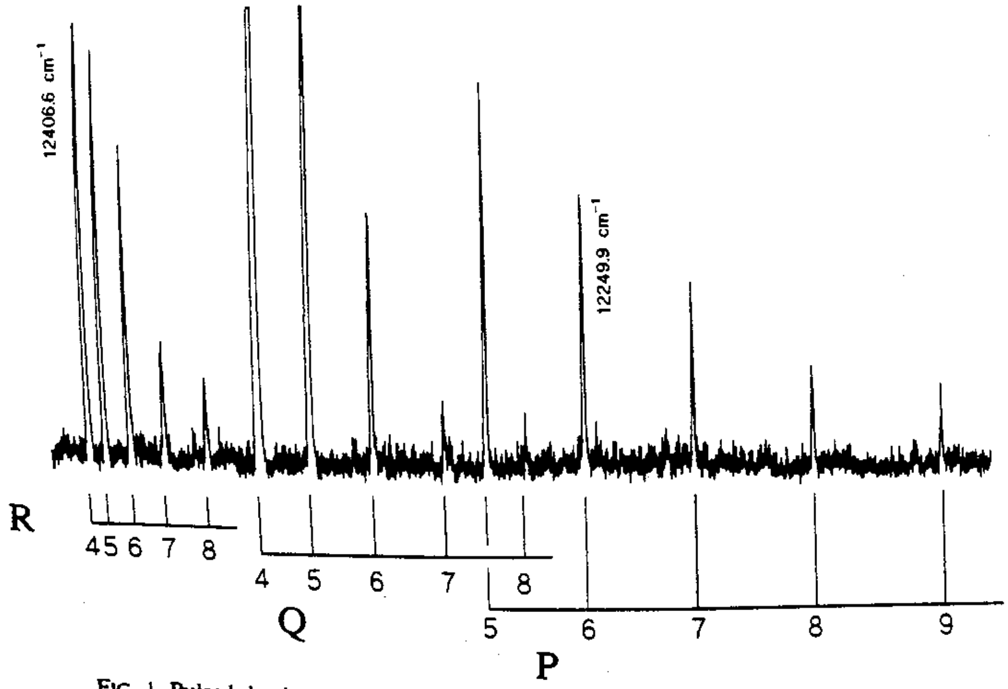
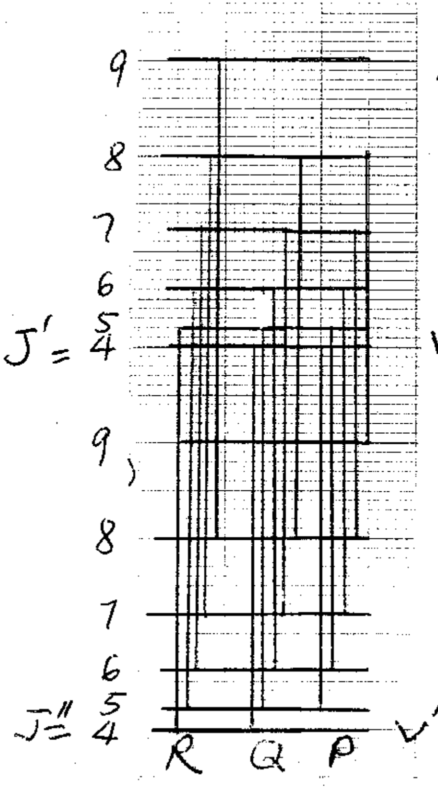


FIG. 1. Pulsed dye laser excitation spectrum of the CoH $A'^3\Phi_4$–$X^3\Phi_4$ (0, 0) band.

Rotational constants
$B\,(A'\,^3\Phi_4) < B(X\,^3\Phi_4)$.
is clear from the relative frequencies of the above lines



$\Lambda = 3$
$S = 1$ $(A'\,^3\Phi_4)$
$\Omega = 4$

$v' = 0$

$$E(J) = T_v + B_v[J(J+1) - \Omega^2] - D_v[J^2(J+1)^2 - \Omega^4]$$

net electronic angular momentum of both states is 4. When rotational quantum number is added to it J starts at 4

$\Lambda = 3$
$S = 1$ $(X\,^3\Phi_4)$
$\Omega = 4$

$v'' = 0$

8. For a diatomic molecule, which of the quantities listed on the right (include all which apply) are factors in the absolute intensities of:

a. the P(J) peak in the IR spectrum

b. the fundamental band in the IR spectrum

c. the 0-1 band in the UV or visible spectrum

d. the J peak in the microwave spectrum

e. the first overtone band in the IR spectrum

f. the second overtone band in the IR spectrum

g. the J peak in the rotational Raman spectrum

h. the Q(J) peak in the Raman spectrum

$\langle \psi_{elec}(X^1\Sigma_g^+) \,|\, e\sum_i x_i \,|\, \psi_{elec}(X^1\Sigma_g^+) \rangle$

$(d\mu/dR)_e$

$(d^2\mu/dR^2)_e$

$(d^3\mu/dR^3)_e$

$U(R_e)$

$(dU(R)/dR)_e$

$(d^2U/R)/dR^2)_e$

$(d^3U(R)/dR^3)_e$

$(d^4U(R)/dR^4)_e$

α_{ave}

$(d\alpha/dR)_e$

$(d(\alpha_{||}-\alpha_{\perp})/dR)_e$

$(d^2\alpha/dR^2)_e$

$\langle v' \,|\, (R-R_e) \,|\, v'' \rangle$

$\langle v' \,|\, (R-R_e)^2 \,|\, v'' \rangle$

$\langle v' \,|\, (R-R_e)^3 \,|\, v'' \rangle$

$\langle v' \,|\, (R-R_e)^4 \,|\, v'' \rangle$

$\langle v' \,|\, (R-R_e)^5 \,|\, v'' \rangle$

$\exp(-h\nu/kT)$

$J(J+1)$

$2J+1$

$\int_{-\infty}^{+\infty} \Psi_{v'}^*(x)\, \Psi_{v''}(x)\; dx$

$\exp(-BJ(J+1)/kT)$

$\langle \Psi_{elec}(X^1\Sigma_g^+) \,|\, e\sum_i x_i \,|\, \Psi_{elec}(A) \rangle$

other?

⑧ a) P(J) in IR spectrum

$$\left(\frac{du}{dR}\right)_e \langle 0|(R-R_e)|1\rangle (2J+1)\ \exp(-BJ(J+1)/kT)$$

b) $$\left(\frac{du}{dR}\right)_e \langle 0|(R-R_e)|1\rangle \exp(-h\nu/kT)$$

c) $$\langle \Psi_{elec}(X^1\Sigma_g^+)|e\sum_i x_i|\Psi_{elec}(A)\rangle * \int_{-\infty}^{+\infty}\Psi_{v'}^*(x)\Psi_{v''}(x)\,dx$$

d) J microwave

$$(2J+1)\exp(-BJ(J+1)/kT)\langle\Psi_{elec}(X^1\Sigma_g^+)|e\sum_i x_i|\Psi_{elec}(X^1\Sigma_g^+)\rangle$$

e) first overtone

$$\left(\frac{d^2u}{dR^2}\right)_e\langle 0|(R-R_e)^2|2\rangle + \left(\frac{du}{dR}\right)_e\langle 0|(R-R_e)^4|2\rangle\left(\frac{d^3U(R)}{dR^3}\right)_e$$

f) $$\left(\frac{d^3u}{dR^3}\right)_e\langle 0|(R-R_e)^3|3\rangle + \left(\frac{du}{dR}\right)_e\langle 0|(R-R_e)^5|3\rangle\left(\frac{d^4U(R)}{dR^4}\right)_e$$
$$+\left(\frac{d^2u}{dR^2}\right)_e\langle 0|(R-R_e)^5|3\rangle\left(\frac{d^3U(R)}{dR^3}\right)_e$$

g) J peak in rotational Raman

$$\alpha_{ave}\exp[-BJ(J+1)/kT](2J+1)\ ..$$

h) Q(J) in Raman

$$\left(\frac{d\alpha}{dR}\right)_e\langle 0|(R-R_e)|1\rangle \exp(-BJ(J+1)/kT)(2J+1)*$$

$\exp(-h\nu/kT)$ for antistokes

Each of above multiplied by $\underset{\text{ortho}}{(I+1)(2I+1)}$ or $\underset{\text{para}}{I(2I+1)}$ or $(2I+1)^2$ if heteronuclear.

Then, to get intensities: square everything.