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.*

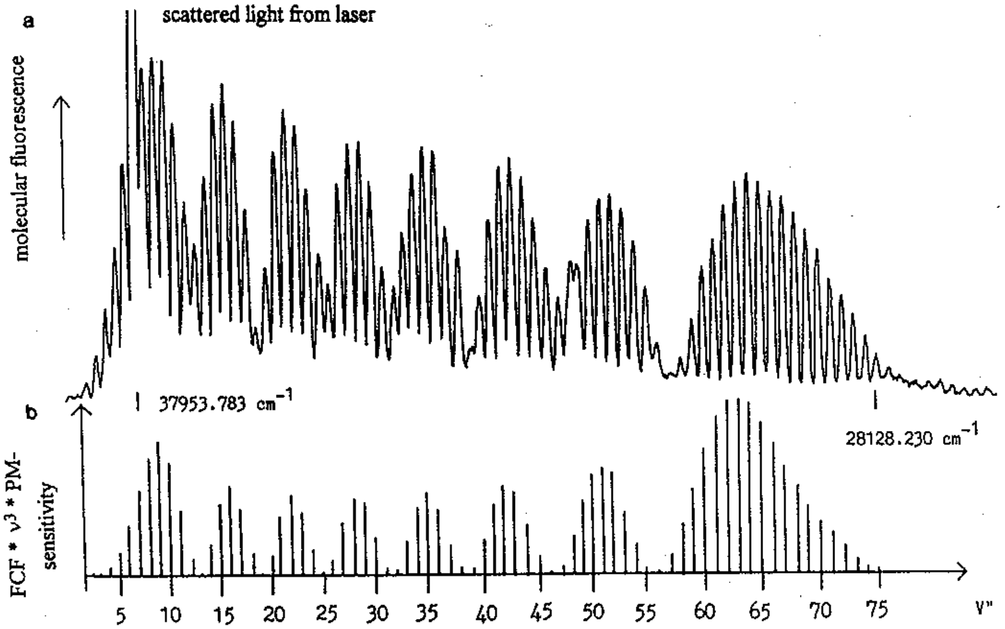


FIG. 2. Fluorescence progression (a) of KI on $C(v' = 7)-X(v'' = 7)P(72) = 37\,953.783$ cm^{-1} and its simulation in (b).

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.*

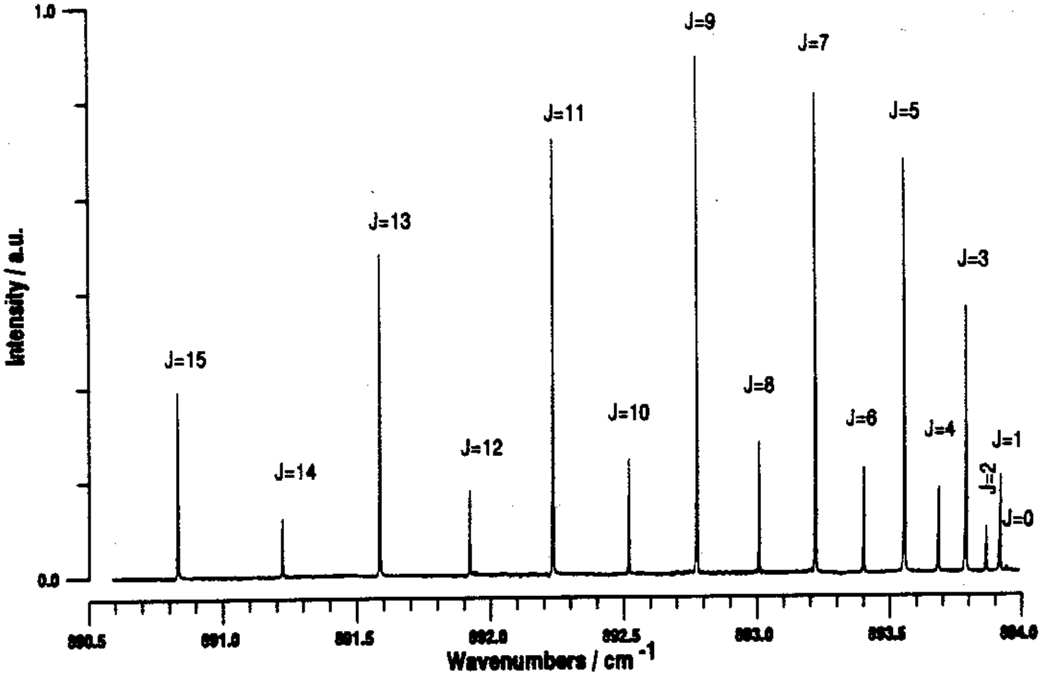


FIG. 2. Stimulated Raman spectrum of fluorine at room temperature in the region of the origin of the Q branch of the $v = 1 \leftarrow v = 0$ band.

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.*

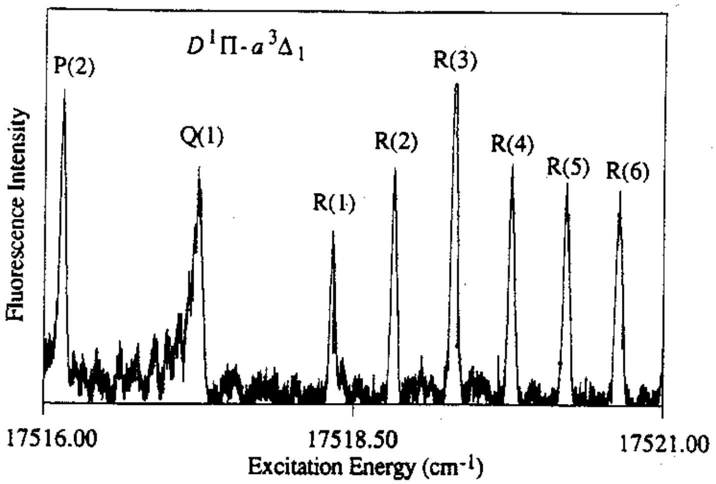
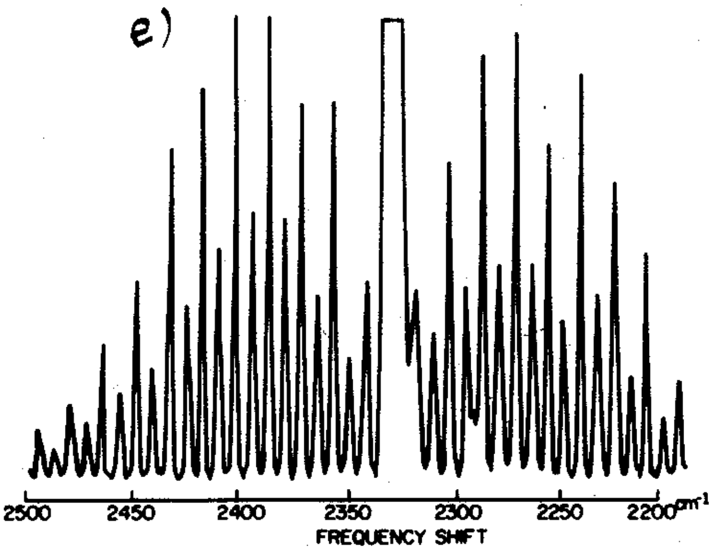
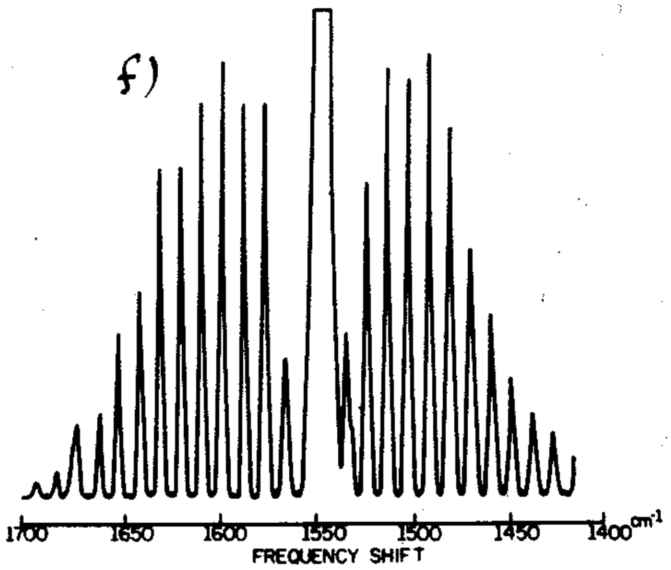


FIG. 1. Typical laser excitation spectrum for YF.

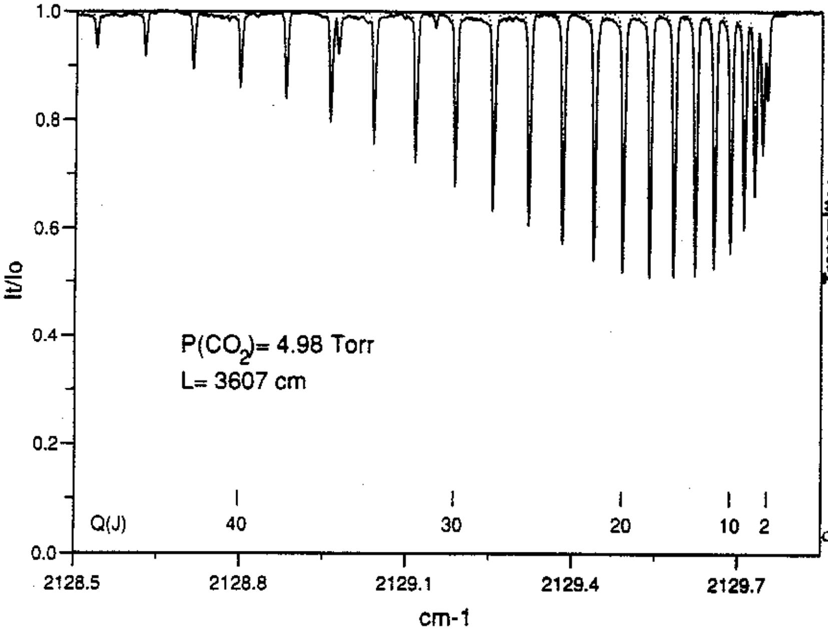
4. In each of the following, you are given limited information. In each case, state all the conclusions which can be made, based on the given information alone.

   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.





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

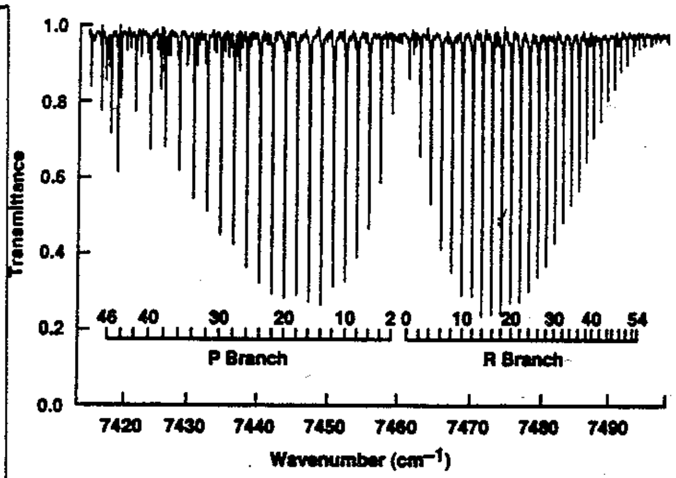


FIG. 1. Transmittance spectrum of the $(40^01)_{IV} \leftarrow (00^00)$ band at 7460 cm^{-1} obtained at Ames, using a total absorption path of 1607 m.

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).*

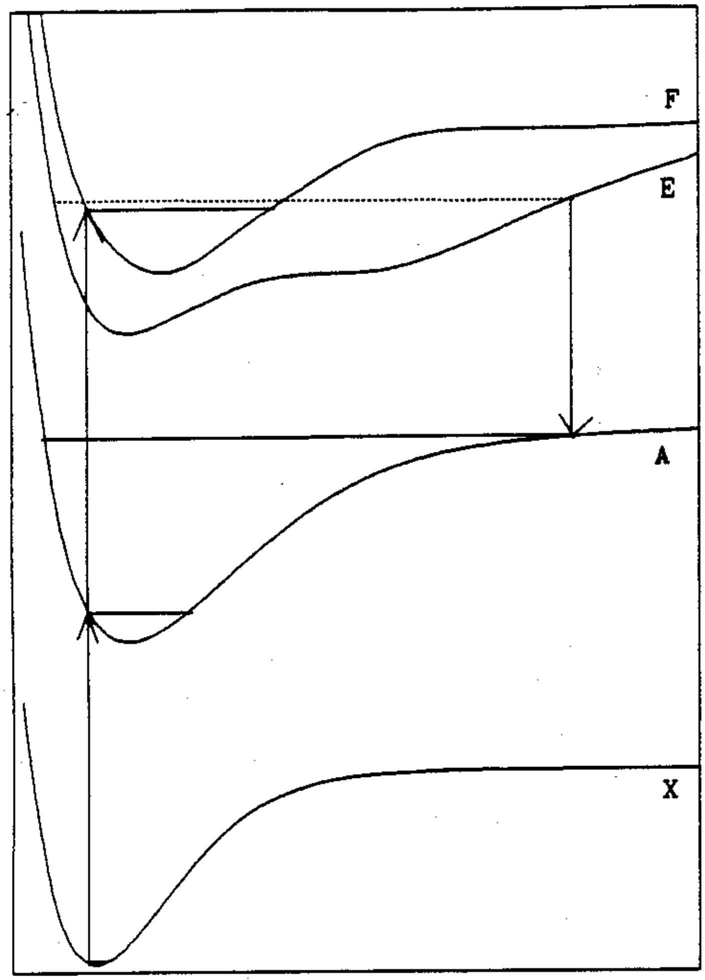


FIG. 7. Potential energy diagram showing excitation, via double resonance, from $X^1\Sigma_g^+$ through $A^1\Sigma_u^+$ (low v) to a mixed $F^1\Sigma_g^+$ and $E^1\Sigma_g^+$ level.

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 all the quantum numbers (upper and lower) of the P(5) transition in the figure. Why are the first peaks R(4), Q(4) and P(5)?*

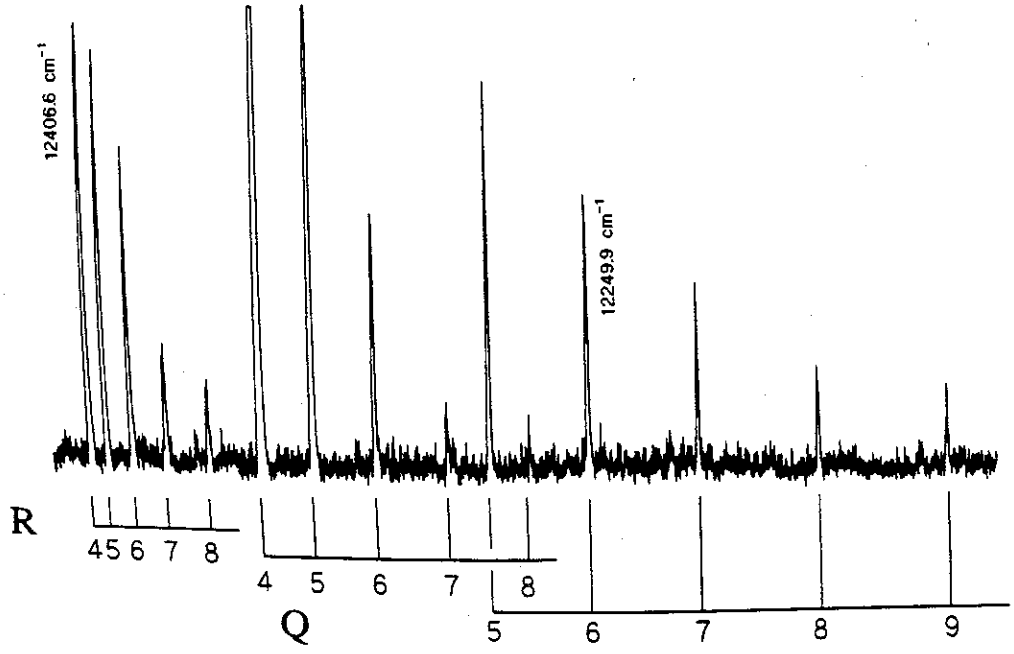


FIG. 1. Pulsed dye laser excitation spectrum of the CoH $A'^3\Phi_4$–$X^3\Phi_4$ (0, 0) band.

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?

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

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

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

$$h x_e\nu_e \equiv \tfrac{1}{4}\, B_e^2/(h\nu_e)^2 \cdot \{\, (^{10}/_3)B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2 - U^{iv}(R_e)R_e^4 \,\}$$

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

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

$$Y_{00} \equiv B_e^2/16(h\nu_e)^2 \cdot \{\, U^{iv}(R_e)R_e^4 - (^{14}/_9)B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2 \,\}$$

$$h\nu_e \equiv (h/2\pi)[\, U''(R_e)/\mu\,]^{\frac{1}{2}}$$

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