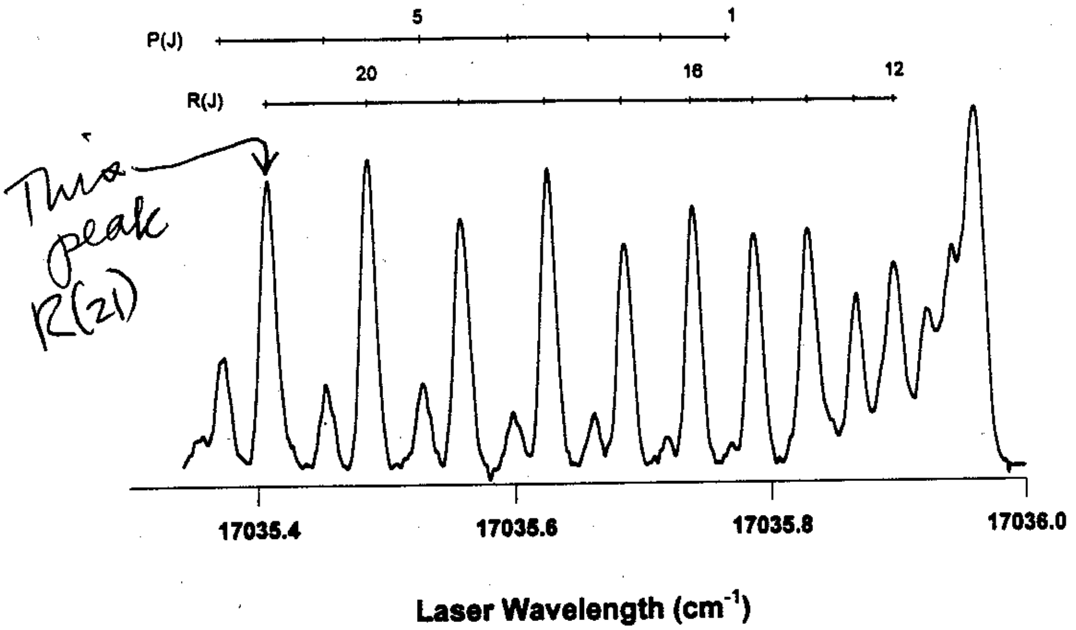
Chemistry 543

Spring 1999 Final Exam
May 6, 1999 10:00 AM -1:00 PM

1. The laser excitation spectrum near the head of the (v′ = 0,v″ = 4) band of the $X\,^1\Sigma_g^+ \rightarrow A\,(0_u^+)$ system of the Bi_2 molecule is shown below. [*J. Mol. Spectrosc.* 194, 1-7 (*1999*)].



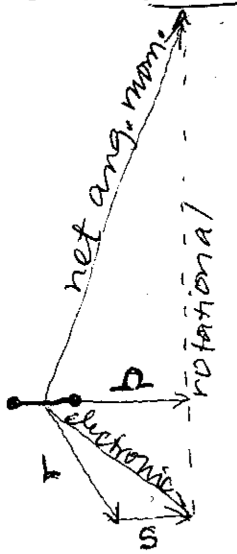
This peak R(21)

FIG. 2. Laser excitation spectrum near the head of the (v′ = 0, v″ = 4) band. Rotational levels are assigned to the *P* and *R* branch.

The bismuth dimer is the heaviest stable diatom. The Franck-Condon factors for the v″ = 2-5 and v′ = 0-4 have been reported in this paper. Answer the following questions:

Assign <u>all</u> the quantum numbers of the upper state and the lower state for the transition corresponding to the first tall peak on the left side of the spectrum.

UPPER STATE	LOWER STATE
$J' = 22$	$J'' = 21$
$v' = 0$	$v'' = 4$
$\Lambda = 0$	Λ = not a good quantum number
$S = 0$	$S =$ " "
	$\Omega = 0$ component of net ang. mom.



Write down an equation that would be used in the analysis of the peak frequencies in order to obtain the spectroscopic constants. You may use a running number m = (J+1) for one branch and -J for the other branch.

Frequency $= E'-E'' = T_e + [\nu_e'(v'+½) - \nu_e x_e'(v'+½)^2+\ldots] - [\nu_e''(v''+½) - \nu_e x_e''(v''+½)^2+\ldots]$
$+ B_v'J'(J'+1) - B_v''J''(J''+1) + \ldots = \nu_0 + B_v'J'(J'+1) - B_v''J''(J''+1) + \ldots$

For the R branch, $J' = J''+1$: Frequency $= \nu^R = \nu_0 + B_v'(J''+1)(J''+2) - B_v''J''(J''+1) + \ldots$

If as suggested, we let $m = J''+1$, then

$$\nu^R = \nu_0 + B_v'\,m(m+1) - B_v''(m-1)\,m + \ldots = \nu_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2 + \ldots$$

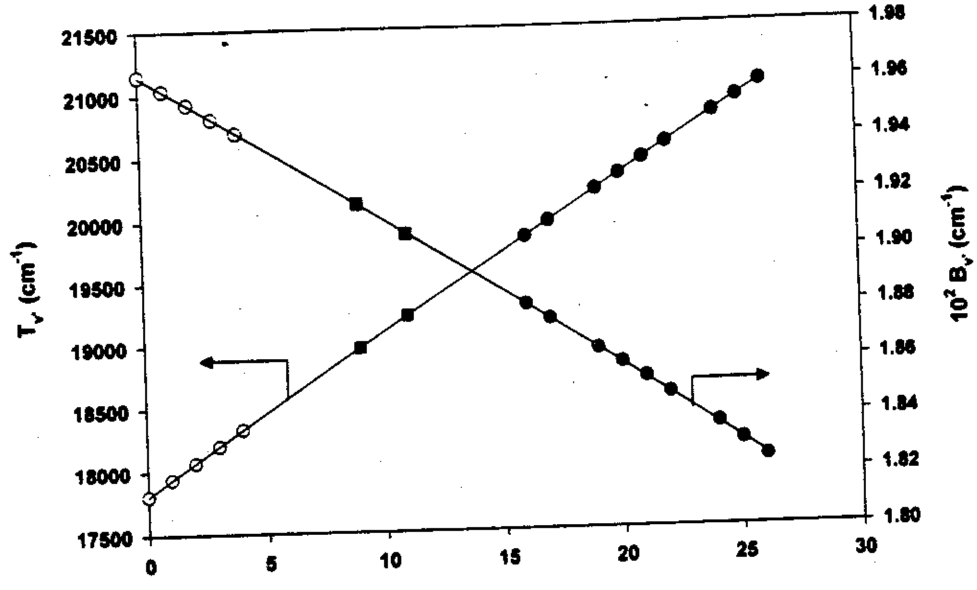
For the P branch, $J' = J''-1$: Frequency $= \nu^P = \nu_0 + B_v'(J''-1)J'' - B_v''J''(J''+1) + \ldots$

As suggested, we let $m = -J''$, then

$$\nu^P = \nu_0 + B_v'(-m-1)(-m) - B_v''(-m)(-m-2) + \ldots = \nu_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2 + \ldots$$

Answer: $\nu = \nu_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2 + \ldots$

The vibrational and the rotational term values for the upper electronic state are plotted below, using data from the present paper and previous work.



***Write down an equation that describes the vibrational term values in terms of the quantum number* v'.**

Answer: $T_v' = T_e + [\nu_e'(v'+½) - \nu_e x_e'(v'+½)^2+\ldots]$

Write down an equation that describes the rotational term values in terms of the vibrational quantum number v′.

Answer: $B_v' = B_e' - \alpha_e'\,(v'+½) + \gamma_e'\,(v'+½)^2+..$

What spectroscopic constants can be obtained from the plot above? (First <u>derive</u> the equation for the plot, then define what intercept =, slope =).

From the equation for energy given on the last page of the exam we find the equations describing the plots shown.

One equation is: $T_v' = T_e + [\nu_e'\,(v'+½) - \nu_e x_e'(v'+½)^2+...]$

From the plot we see that $\nu_e x_e'$ is negligibly small, since we find <u>a straight line</u>.

Therefore, $T_e + [\nu_e'\,(½) - \nu_e x_e'(½)^2+...] = 17\,806.8\ \text{cm}^{-1}$ (intercept) and slope = $\nu_e' = 132.38\ \text{cm}^{-1}$.

which leads to $T_e = U(R_e)' - U(R_e)'' \approx 17\,806.8 - (½)132.38 = 17\,740.6\ \text{cm}^{-1}$

The other equation is: $B_v' = B_e' - \alpha_e'\,(v'+½) + \gamma_e'\,(v'+½)^2+..$

From the plot we see that γ_e' is negligibly small, since we find <u>a straight line</u>. Thus, we can get $\alpha_e' = -\,4.991\times10^{-5}\ \text{cm}^{-1}$ (slope) and from intercept = $B_e' - ½\alpha_e'$, we get $B_e' = 0.019666\ \text{cm}^{-1}$.

The intensity observed in emission is related to the Franck Condon factors. As quoted from this 1999 paper,

$$I_{v,w} = \left(\frac{64\pi^4}{3}\right) c\,\nu_{vw} q_{vw} |R_e|^2 \left(\frac{S_J}{2J+1}\right) D(\nu_{vw})\, N_v \qquad [2]$$

v = vibrational level of emitting state, $A(0_u^+)$

w = vibrational level of ground state, $X^1\Sigma_g^+$

$I_{v,w}$ = observed LIF intensity for $v \rightarrow w$ emission band

$q_{v,w}$ = $|\langle v|w\rangle|^2$ = Franck–Condon factor for $v \rightarrow w$ emission band

ν_{vw} = frequency for $v \rightarrow w$ emission band

$|R_e|^2$ = electronic transition dipole moment

S_J = rotational linestrength

$D(\nu_{vw})$ = system spectral response (detectivity) as a function of emission frequency

N_v = concentration of emitting state, v

There is an error in this formula. What is it?

As derived in class, the Einstein transition probability of spontaneous emission from state v to lower state w is $A_{vw} = (64\pi^4/3h)\nu_{vw}^3 |R_{vw}|^2$, thus the intensity of a spectral line in emission is $I_{vw} = N_v hc\nu_{vw} A_{vw}$ = energy emitted per second.

Therefore the error in the formula is that it should have ν_{vw}^4 not ν_{vw} (This error becomes rectified in Eq. [3] from the paper.) . See page 127 of Herzberg Vol. 1 which has

$I^{vw}_{\text{emission}} = (64\pi^4/3)c\nu_{vw}^4 N_v(\Sigma_{i,k}|R_{viwk}|^2) \cdot \exp[-B_v'J'(J'+1)hc/kT]/Q_{rot}$

where Q_{rot} in the high temperature limit is $\sigma\, kT/hcB_v'$ where σ is the symmetry number, that is 2 in the case of a homonuclear diatomic.

Give the formula for the rotational line strength S_J.

$I^{vw}_{\text{emission}} = (64\pi^4/3)c\nu_{vw}^4 N_v(\Sigma_{i,k}|R_{viwk}|^2) \cdot \exp[-B_v'J'(J'+1)hc/kT]/Q_{rot}$

The population of the rotational state J′ is $N_J' = (N_v/Q_{rot})(2J'+1)\exp[-B_vJ'(J'+1)hc/kT]$ where N_v' is the number of emitting molecules.

$(\Sigma_{i,k}|R_{viwk}|^2)$ gives . $|R_{elec}|^2 \bullet |\langle v|w\rangle|^2 \bullet |\langle J'|\sin\theta\cos\phi\text{, or }\cos\theta\text{, or }\sin\theta\sin\phi|J''\rangle|^2$.

By integrating over the rotor part, one obtains for $\Delta J = +1$, a factor J+1 and for $\Delta J = -1$, a factor J and zero for . $\Delta J = 0$. Thus, the **rotational line strength,** $S_J = \langle J'|\sin\theta\cos\phi\text{, or }\cos\theta\text{, or }\sin\theta\sin\phi|J''\rangle|^2 = J'+1$ or J' which together give $2J'+1$.

Give the formula for the concentration of emitting state, N_v.

N_v = number of molecules in the emissive state v, depends on the quantum yield for excitation, laser fluence, volume of excitation in the sample, etc.

Suppose you were asked to obtain $q_{v,w}$ ***from first principles, how would you do it?***

$q_{vw} = \langle v | w \rangle = \int\psi_v(v')\psi_w(v'')d\tau$. **To obtain q_{vw} from first principles**, we need to do the following:

1. Solve the Schrödinger equation for the electronic motion for several fixed values of nuclear positions. The lowest eigenvalues at these values of R, taken together provide the potential energy surface $U_w''(R)$ for the ground electronic state *X*. The set of next lowest eigenvalues together provide the PES $U_v'(R)$for the first excited electronic state *A*. The eigenfunctions are the electronic eigenfunctions $\Psi''_{elec,w}$ and $\Psi'_{elec,v}$ respectively, which vary with internuclear separation.
2. Solve numerically the one dimensional Schrödinger equation for the vibrational motion for the ground electronic state
$\{-(\hbar^2/2\mu)d^2/dx^2 + U_w''(x)\}\ \psi_w(v'') = E_w(v'')\psi_w(v'')$
and for the excited electronic state
$\{-(\hbar^2/2\mu)d^2/dx^2 + U_v'(x)\}\ \psi_v(v') = E_v(v')\psi_v(v')$
The eigenfunctions are the anharmonic vibrational wavefunctions.
3. Calculate the overlap integrals $\int\psi_v(v')\psi_w(v'')dx$. to get the Franck-Condon factors.

Show how $|R_e|^2$ ***is obtained theoretically.***

To obtain $|R_e|^2$ theoretically, we calculate $|\int\Psi''_{elec,w}\ \mu_{elec}\ \Psi'_{elec,v}\ d\tau\ |^2$ where $\mu_{elec} = \sum_i e\ z_i$ is summed over all the electronic z coordinates, and integration is over all electron coordinates and where the electronic wavefunctions $\Psi''_{elec,w}$ and $\Psi'_{elec,v}$ are functions of internuclear separation. Thus, the purely electronic transition moment depends on the centroids of the v′v″ transitions.

The paper states that Ehret and Gerber have measured $|R_e|^2 = (1.4\pm0.4\ \text{Debye})^2$, independent of internuclear separation. ***How could such a measurement be made?***

To obtain $|R_e|^2$ experimentally, we could measure <u>spontaneous lifetimes</u> of the upper state dropping to the ground state or we could measure <u>absolute intensities</u> (quite difficult). Lifetimes of rovibrational states excited by a pulsed laser (in this case, an argon ion laser will do) can be measured by observing the exponential decay of the fluorescence using a delayed coincidence method. The lifetimes in the limit of no collisions are related to the same molecular factors as are the intensities:
$(\text{lifetime of } v'J' \text{ state})^{-1} = (64\pi^4/3h)\ \sum_{v''J''}\ [S_{J'J''}/(2J+1)]q_{v'v''}\bullet\nu(v'J',v''J'')^3\ |R_e|^2$
All factors are calculable from the spectroscopic constants of the upper and lower states, including the Franck-Condon factors $q_{v'v''}$. The surprising result in this case was that $|R_e|^2 = (1.4\pm0.4\ \text{Debye})^2$, did not change with v′.

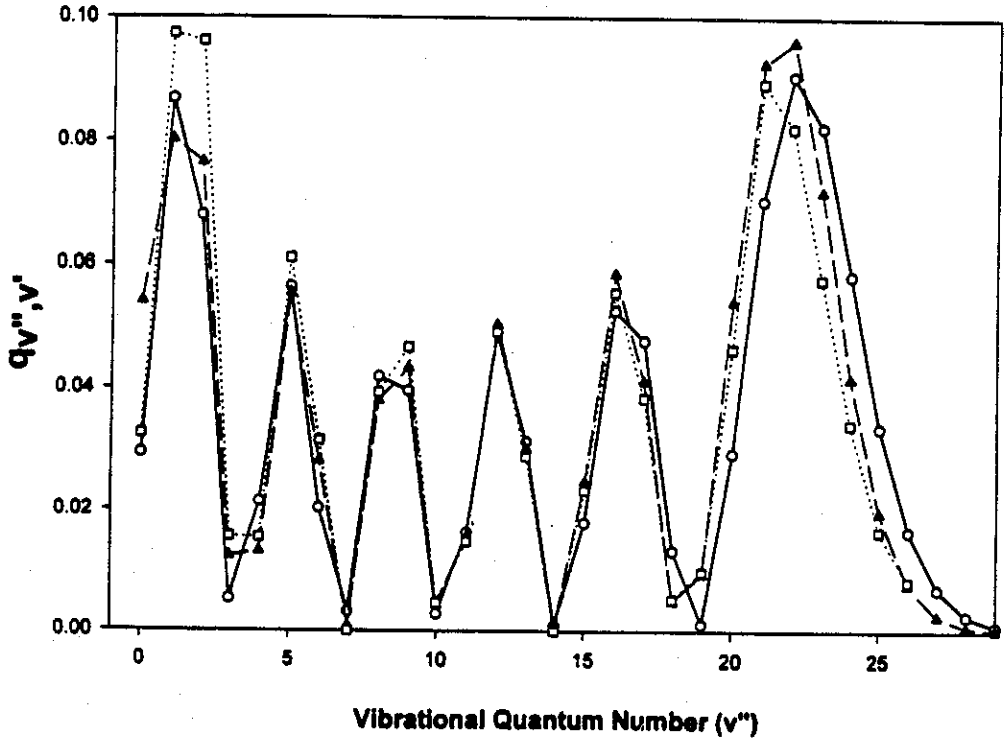
To obtain the experimental Franck Condon factors, the usual calibration procedures and forced normalization are carried out:

$$\frac{q_{vw'}}{q_{vw}} = \left(\frac{\nu_{vw'}}{\nu_{vw}}\right)^4 \left(\frac{D(\nu_{vw'})}{D(\nu_{vw})}\right)\left(\frac{I_{vw'}}{I_{vw}}\right). \qquad [3]$$

The normalization

$$\sum_{w'} q_{vw'} = 1 \qquad [4]$$

These *experimental* values are shown as (···□···) in the figure below. The Franck Condon factors were also *computed from the potential energy surfaces* using the spectroscopic constants for the upper A state and the lower X state; from the spectroscopic constants reported in this 1999 paper are shown as (– –▲– –) and from slightly different set of reported spectroscopic constants are shown as (—O—).



Explain how potential energy surfaces may be computed from spectroscopic constants.

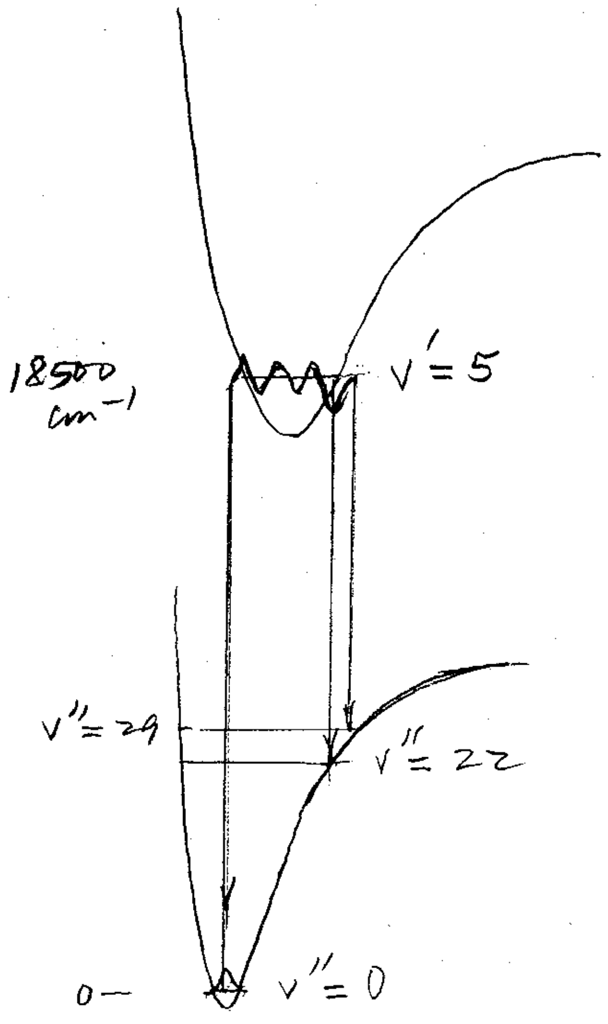
To calculate the potential energy surfaces from spectroscopic constants we need to be able to express the function $U_\alpha(R)$ in terms of B_e, ν_e , $\nu_e x_e$, α_e, etc. The first step is to find R_e from the atomic masses and B_e using the formula $B_e = \hbar^2/2\mu R_e^2$. There are several possibilities:
(1) A gross approximation is to use a Morse function $U = D_e\{1-\exp(-ax)\}^2$. The dissociation energy D_e can be obtained from a Birge-Sponer plot, and since $[d^2U_{Morse}/dx^2]_{equil} = 2a^2D_e$, the Morse parameter a can be obtained from $\nu_e = (1/2\pi)\{[d^2U/dx^2]_{equil} /\mu\}^{½}$.
(2) Klein and Rydberg have given a method for constructing the potential curve point for point from the observed vibrational and rotational levels without assuming an analytical expression for the potential function. This is the RKR method (Rydberg-Klein-Rees).
(3) Another method is to use the functional form used by Dunham, which is an expansion of U in powers of $(R-R_e)/R_e$:
(4) Another method is to use a sum of Morse potentials with fitted parameters. The last 3 methods are commonly used in the literature.

Explain how Franck Condon factors may be computed from potential energy surfaces.

Once the potential energy surfaces are known, solve numerically the one dimensional Schrödinger equation for the vibrational motion for the ground electronic state, using the PES $U_w''(x)$ as the potential energy part of the Hamiltonian.
$\{-(\hbar^2/2\mu)d^2/dx^2 + U_w''(x)\}\ \psi_w(v'') = E_w(v'')\psi_w(v'')$
and do the same for the excited electronic state
$\{-(\hbar^2/2\mu)d^2/dx^2 + U_v'(x)\}\ \psi_v(v') = E_v(v')\psi_v(v')$
The eigenfunctions of these Schrödinger equations are the anharmonic vibrational wavefunctions.
Calculate the overlap integrals $\int\psi_v(v')\psi_w(v'')dx$. to get the Franck-Condon factor for each $(v'\rightarrow v'')$ transition.

For which vibrational quantum number v′ in the upper state are the Franck Condon factors that are plotted in the above figure? Explain the variation of $q_{v''v'}$ versus v″ in the figure by using schematic drawings of the two surfaces and the transitions corresponding to the plotted FC factors.

From the Franck-Condon factors we see 5 nodes, which indicates that the upper state is v ′= 5. Here the Franck Condon factors for the v″ = 0 to 29 trace out the shape of the upper anharmonic $|\psi_v(v')|^2$., made possible by the peak of the lower vibrational wavefunctions at v″=0 occurring at a value of R coinciding with the inner maximum of the upper anharmonic function located close to the compressed oscillator classical turning point. On the other hand, the maxima at the extreme expanded oscillator configuration of the vibrational functions of the next vibrational levels v″= 1 through 29 are coinciding with various portions of the v ′= 5.wavefunction, leading to the pattern shown in page 5 of the exam. Schematically, the transitions are shown below:



2. The visible transitions of the AuCl molecule were observed at high resolution for the first time [*J. Mol. Spectrosc.* 194, 124-7 (*1999*)]. The excited AuCl molecules were produced in a microwave discharge and the spectrum was recorded with a Fourier Transform emission spectrometer. A portion of the $B(\Omega=0^+) \rightarrow X\ ^1\Sigma^+$ spectrum is shown in the figure below.

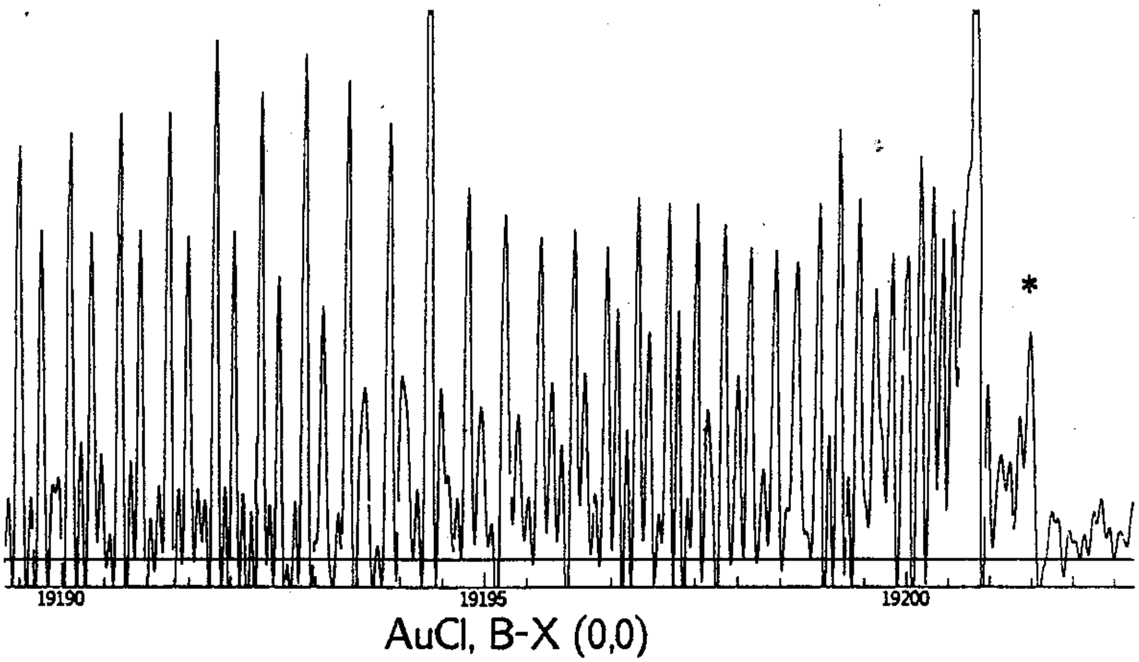


FIG. 1. A portion of the $B\ \Omega=0^+ - X\ ^2\Sigma^+$ spectrum of Au^{35}Cl. The Au^{37}Cl bandhead is marked with an asterisk.

Explain the intensity patterns of the peaks observed.

Since this is a heteronuclear diatomic molecule, there can be no nuclear spin statistics that could lead to alternation of intensities. Therefore the intensity pattern can only be due to two sets of isotopes or else to two completely different bands which just happen to overlap. The hint is in the figure caption. **The molecule containing the more abundant ^{35}Cl isotope shows consistently higher peaks than the ^{37}Cl isotopomer.** The corresponding peaks are offset due to the vibrational frequencies being different for the two isotopomers, since $\nu_e = (1/2\pi)\{[d^2U/dx^2]_{equil}/\mu\}^{½}$. The Au^{35}Cl isotopomer will have a higher observed frequency, $\nu = (T_e''-T_e'') + [G_v' - G_v''] + (F_J'-F_J'')$, since the first term is independent of mass and $[G_v' - G_v'']$ is larger by a factor, $[\mu_{37}/\mu_{35}]^{½}$, which is larger than 1. In addition, there is an effect on the rotational spacing, which is larger for the Au^{35}Cl, for both upper and lower state.
$\mu_{35} = 196.967(35)/(196.967+35) = 29.7$ amu

The spectroscopic constants for the $X\,^1\Sigma^+$ state and the $B(\Omega=0^+)$ state are shown in the table below, all values are in cm^{-1}.

	$X\,^1\Sigma^+$	$B(\Omega=0^+)$
T_0	0.0	19199.2549(14)
T_1	380.7018(16)	19512.8711(15)
B_0	0.1171165(64)	0.1089616(64)
B_1	0.1165734(66)	0.1082568(64)
D_0	$0.4419(75)\times10^{-7}$	$0.5424(73)\times10^{-7}$
D_1	$0.4430(77)\times10^{-7}$	$0.5542(74)\times10^{-7}$

From an earlier observation of the 43 vibrational bands of this electronic transition, the value of $\omega_e x_e$ for $X\,^1\Sigma^+$ and $B(\Omega=0^+)$ states are known to be respectively, 1.30 cm^{-1} and 1.45 cm^{-1}.[Ferguson, Phys. Rev. 31, 969-72 (***1928***)] ***Calculate*** ω_e ***and*** r_e ***for the ground state.*** (For comparison, relativistic density functional calculations by O. D. Häberlen and N. Rösch, *Chem. Phys. Lett.* 199, 491-6 (***1992***) give values that are 99.66% and 99.18% of the values reported in the 1999 paper.)

$$T_0 = T_e + [0+\tfrac{1}{2}]\nu_e - x_e\nu_e\,[0+\tfrac{1}{2}]^2 + \ldots$$

$$T_1 = T_e + [1+\tfrac{1}{2}]\nu_e - x_e\nu_e\,[1+\tfrac{1}{2}]^2 + \ldots$$

$$T_1 - T_0 = \nu_e - 2x_e\nu_e = 380.7018\ \mathrm{cm}^{-1} - 0.0 = \nu_e - 2(1.30\ \mathrm{cm}^{-1})$$

$$\boldsymbol{\nu_e = 383.30\ \mathrm{cm}^{-1}}$$

$$B_0 = B_e - \alpha_e[0+\tfrac{1}{2}] = 0.1171165\ \mathrm{cm}^{-1}$$

$$B_1 = B_e - \alpha_e[1+\tfrac{1}{2}] = 0.1165734\ \mathrm{cm}^{-1}$$

$$B_1 - B_0 = 5.431\times10^{-4}\ \mathrm{cm}^{-1} = -\alpha_e, \qquad B_e - \tfrac{1}{2}(5.431\times10^{-4}) = 0.1171165$$

$$B_e = 0.11739\ \mathrm{cm}^{-1}, \qquad \boldsymbol{R_e = \hbar\,\{2\mu B_e\}^{-1/2} = 2.199\ \text{Å}}$$

Calculate T_e ***for the*** $B(\Omega=0^+)$ ***state.***

$T_0 = T_e + [0+½.]\nu_e - x_e\nu_e\,[0+½.]^2 + \ldots = 19199.2549$
$T_1 = T_e + [1+½.]\nu_e - x_e\nu_e\,[1+½.]^2 + \ldots = 19512.8711$
$T_1 - T_0 = \nu_e +- 2x_e\nu_e = 313.617\ \mathrm{cm}^{-1} = \nu_e +- 2(1.45\ \mathrm{cm}^{-1})$
$\nu_e = 316.517\ \mathrm{cm}^{-1}$
$T_e + [0+½.]316.517 - 1.45\,[0+½.]^2 + \ldots = 19199.2549$
$T_e = 19\,041.358\ \mathrm{cm}^{-1}$ above the v=0 level of the ground state.

3. The emission spectra of the AsI molecule radical were measured in the near-infrared spectral region with a Fourier transform spectrometer [*J. Mol. Spectrosc.* 194, 250-255 (***1999***)]. The most prominent features in the spectrum are the six band sequences in the range 800-900 nm of the transition $b^1\Sigma^+$ ($b0^+$) → $X^3\Sigma^-$ (X_10^+), shown in the figures below:

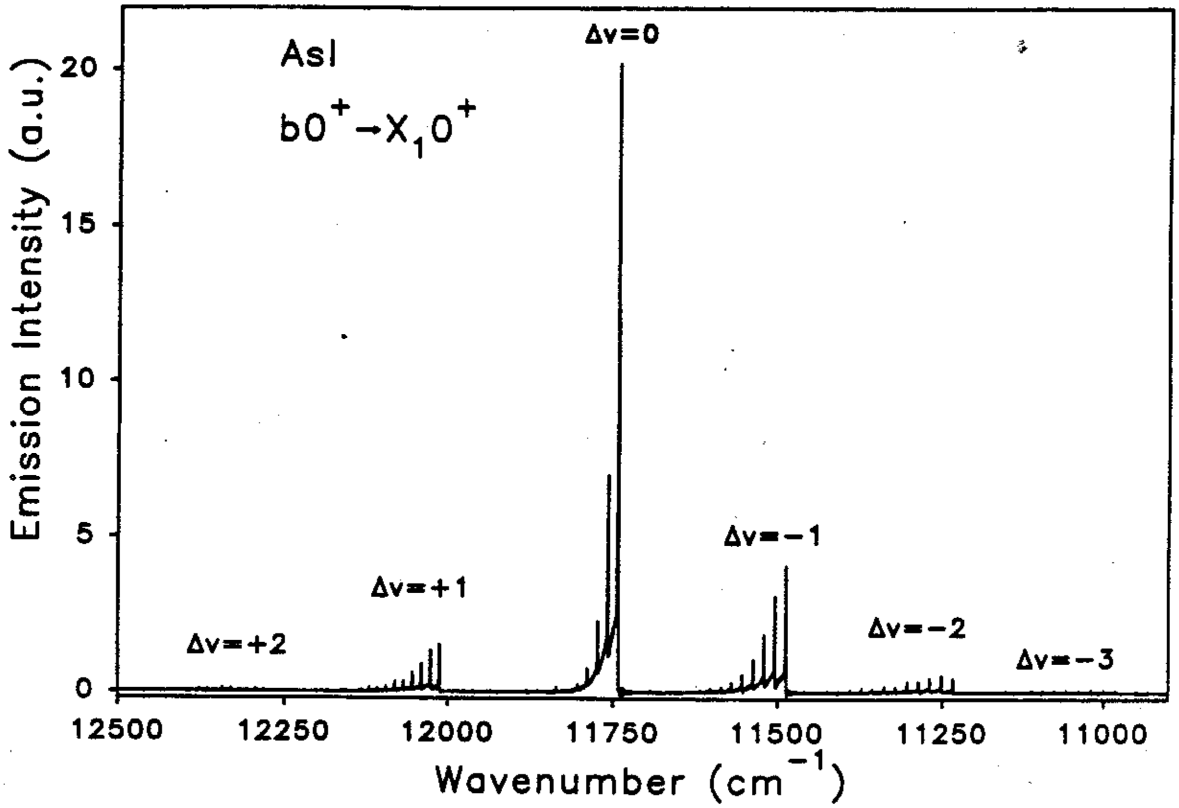
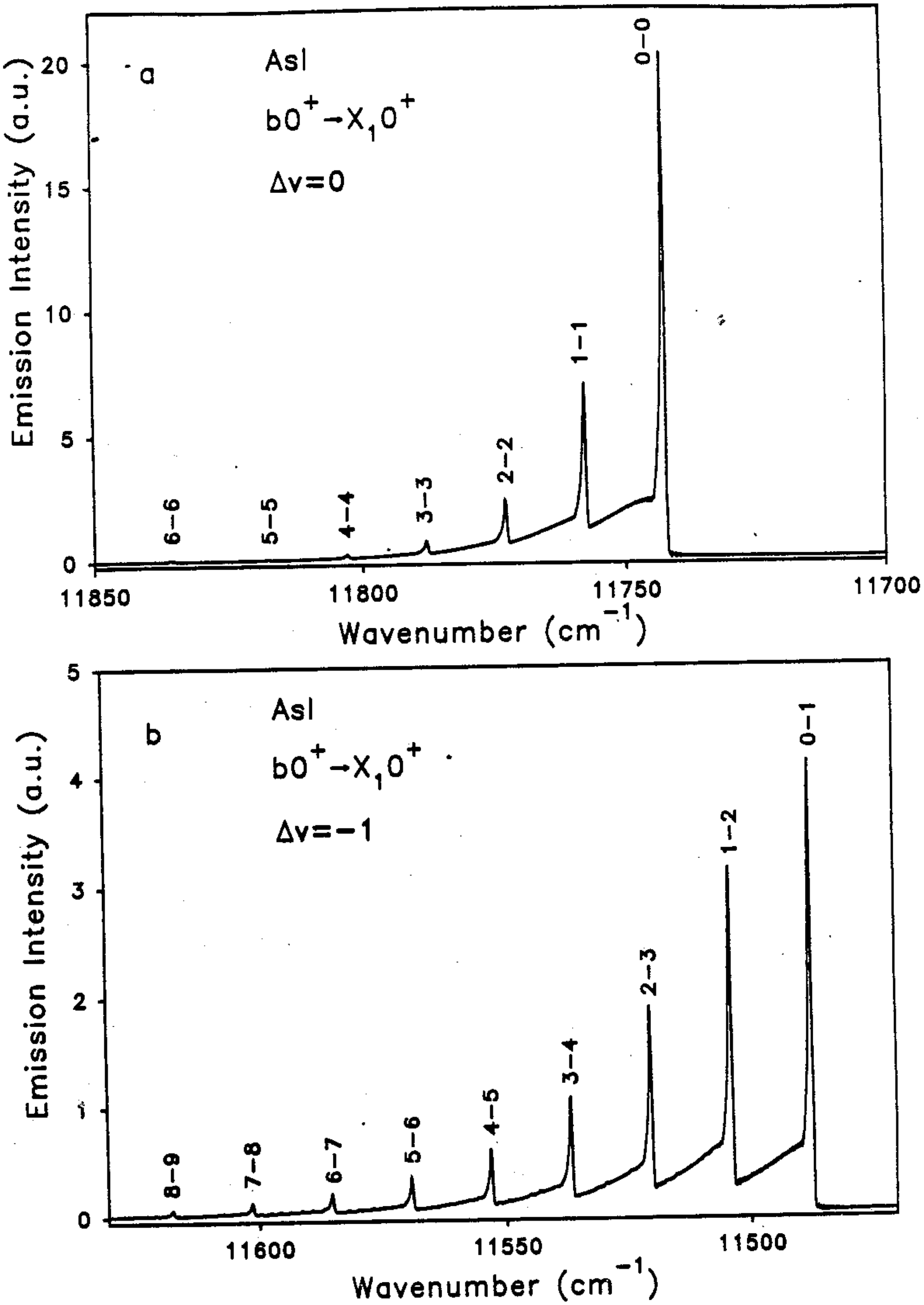


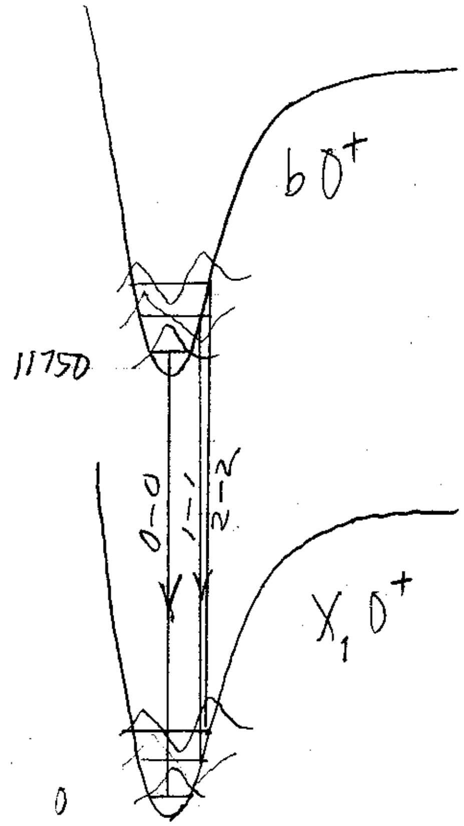
FIG. 1. Survey spectrum of the $b0^+ \rightarrow X_10^+$ transition of AsI at a spectral resolution of 0.5 cm^{-1}.



IG. 2. Spectra of the $\Delta v = 0$ and $\Delta v = -1$ sequences of the $b0^+ \rightarrow X_1 0^+$ system of AsI with assignments of the *P*-branch maxim :m^{-1}.

Draw a schematic of the potential surfaces and draw the transitions in Fig. 2a in the diagram. Be sure your drawing is consistent with everything in the figures on the previous page (intensity patterns, frequency differences, narrow P branches with sharp heads and broad R brances).

The important clues are the following:
1. This is emission: ($b0^+$) →(X_10^+). That six long sequences of bands are observed shows a rather hot vibrational population in the excited $b0^+$ state of AsI molecule.
2. The peak 0→0 has the greatest area under the peak (greatest intensity) followed by v′→v″ = 0→1, 1→2, 2→3, 2→2, ... in that order. This relative intensity pattern is typical for a transition between states with very similar potential curves and nearly equal equilibrium internuclear distances.
3. Sharp band heads are <u>in the P branch</u> in all bands, which means that $B_v' > B_v''$ uniformly, therefore $R_e'(b0^+) < R_e''(X_10^+)$ although, as mentioned above these distances are not hugely different from each other.
4. Narrow P branches and broad R branches mean that α_e is significant, a large value of α_e makes the spacing closer together in the P and farther apart in the R branch than for a rigid rotor.



The identification of the transitions and the assignment of the bands observed in this paper is unambiguous. Therefore the spectroscopic constants derived represent a first complete and reliable set of molecular constants for the low-lying states of AsI. ***From the spectra shown in the figures, which spectroscopic constants for which states would have been obtained and reported by the authors?***

The spectroscopic constants that would have been obtained are:
for the ground $X_1 0^+$ state ν_e, $x_e\nu_e$, $y_e\nu_e$

For the excited $b0^+$ state T_e, ν_e, $x_e\nu_e$, $y_e\nu_e$

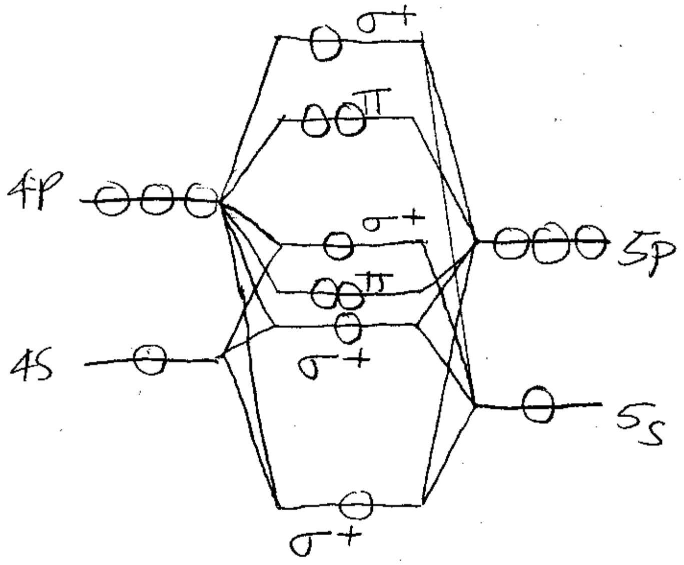
Identify the atomic states that are the dissociation limits of AsI molecule radical.

Ground electronic configuration of As atom is $[Ar]3d^{10}4s^24p^3$: This is the same valence configuration as N atom (see Problem 5) and this leads to states $^4S_{3/2}$, $^2D_{5/2,\,3/2}$ and $^2P_{3/2,\,1/2}$ Hund's rules dictate that the ground term is $^4S_{3/2}$.
Ground electronic configuration of I atom is $[Kr]4d^{10}5s^25p^5$: This is the same as one hole in the p shell which has the term symbol $^2P_{3/2,\,1/2}$:, of which the slightly lower energy is $^2P_{3/2}$, since the p shell is more than half-filled. Thus, the atomic states to which the ground state AsI molecule dissociates into are $^4S_{3/2}$ and $^2P_{3/2}$.

Draw a schematic molecular orbital diagram for this molecule, identifying the As and I orbitals involved in the bonding.

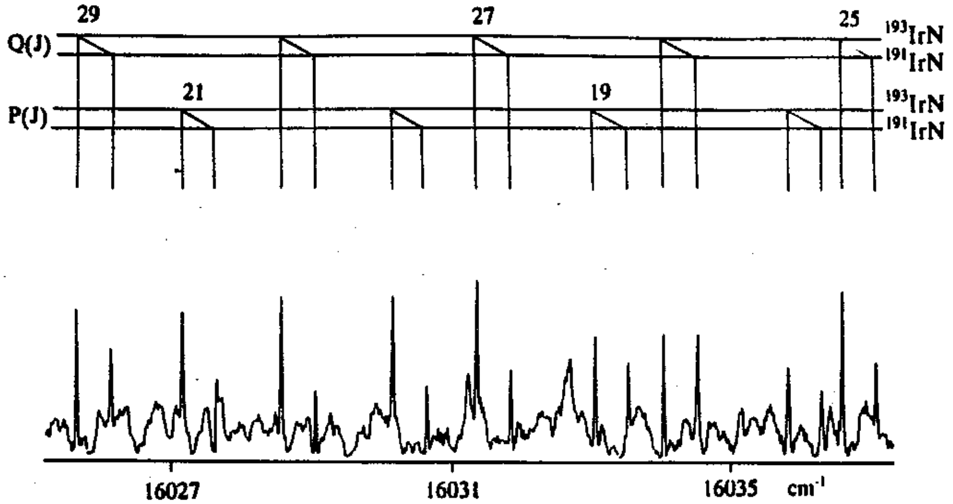
As mentioned in previous page,
As atom has electronic configuration $[Ar]3d^{10}4s^{2}4p^{3}$.
I atom has electronic configuration $[Kr]4d^{10}5s^{2}5p^{5}$.
The valence orbitals have the most compatible energies, so 4p and 5p form a bond which could have some s character (i.e., some characteristics of an sp hybrid for each atom). So the lowest bonding molecular orbital would have a mixture of $4s_{As}$, $4p_{z,As}$ and $5s_{I}$, $5p_{z,I}$, for example. The molecular orbital diagram would be as follows

As atomic orbitals AsI molecular orbitals I atomic orbitals



$C_{\infty v}$
orbitals belong to $\Sigma^+, \Sigma^-, \Pi, \Delta, \ldots$

4. Transition metal atoms have relatively high abundances in many stars and several transition metal hydrides and oxides have been detected. There is a strong possibility that metal nitrides can also be found, but without precise spectroscopic data, a meaningful search for these in the complex stellar spectra can not be made. The high resolution emission spectrum of IrN has been recently investigated in the 10,000-20,000 cm^{-1} region [*J. Mol. Spectrosc.* 193, 363-375 (***1999***)]. In spite of overlapping with strong N_2 bands present in the same region, the IrN rotational lines were easily distinguished because of their narrow linewidths and the relatively small separation between consecutive rotational lines in a branch. see for example the expanded portion of the 1- 0 band of the $A\,^1\Pi \rightarrow X\,^1\Sigma^+$ system of IrN.



An expanded portion of the 1–0 band of the $A\,^1\Pi$–$X\,^1\Sigma^+$ system of IrN with the lines of the ^{191}IrN and ^{193}IrN isotopomers marked.

Why is there a Q branch?

Because the upper electronic state has electronic angular momentum, which couples with the rotational angular momentum and makes the $\Delta J = 0$ transitions possible.

Why the Q branch overlapping the regions of the P branch? Which has the larger rotational constant, the $A\,^1\Pi$ or the $X\,^1\Sigma^+$ state? Explain.

The frequencies of the Q branch lines are given by

$\nu^Q(J'') = \nu_0 + (B_v' - B_v'')J''(J''+1)$

The Q branch overlaps the regions of the P branch, i. e., the Q branch is shaded towards the longer wavelengths, because of the less usual situation that $(B_v' - B_v'') < 0$. That is, the ground state $X^1\Sigma^+$ has a larger rotational constant.

> The molecular constants were determined by fitting the observed line positions with the customary energy level expressions for $^1\Sigma^+$ and $^1\Pi$ states. ***<u>Derive</u> these expressions for*** $F_v(J)$ ***in the*** $^1\Sigma^+$ ***case and add the required term for the*** $^1\Pi$ ***case.***

Starting from the given formula on the last page of the exam, the rotational term values are given by

$F_v(J'') = T_v + B_vJ''(J''+1) - D_v[J''(J''+1)]^2 + \ldots$ for the ground ($^1\Sigma^+$) case

$F_v(J') = T_v + B_vJ'(J'+1) - D_v[J'(J'+1)]^2 + \ldots \pm\{q\,J'(J'+1)\}$ for the $^1\Pi$ case

where the additional term reflects the electronic orbital angular momentum, q is a small number.

The ground state $X\,^1\Sigma^+$ of IrN arises from the electron configuration $(1\sigma)^2\,(2\sigma)^2\,(1\pi)^4\,(3\sigma)^2\,(1\delta)^4$, whereas the $A\,^1\Pi$ state arises from the configuration $(1\sigma)^2\,(2\sigma)^2\,(1\pi)^4\,(3\sigma)^2\,(1\delta)^3\,(2\pi)^1$, where only the atomic valence shells have been included. ***Identify which of these molecular orbitals are the bonding, nonbonding, and antibonding ones.***

Here 3σ and 1δ are mainly the bonding and nonbonding orbitals, respectively, and 2π is an antibonding orbital.

5. Ab initio configuration interaction calculations have resulted in the theoretically calculated potential energy curves of CuN [*J. Mol. Spectrosc.* 194, 8-16 (*1999*)] shown below.

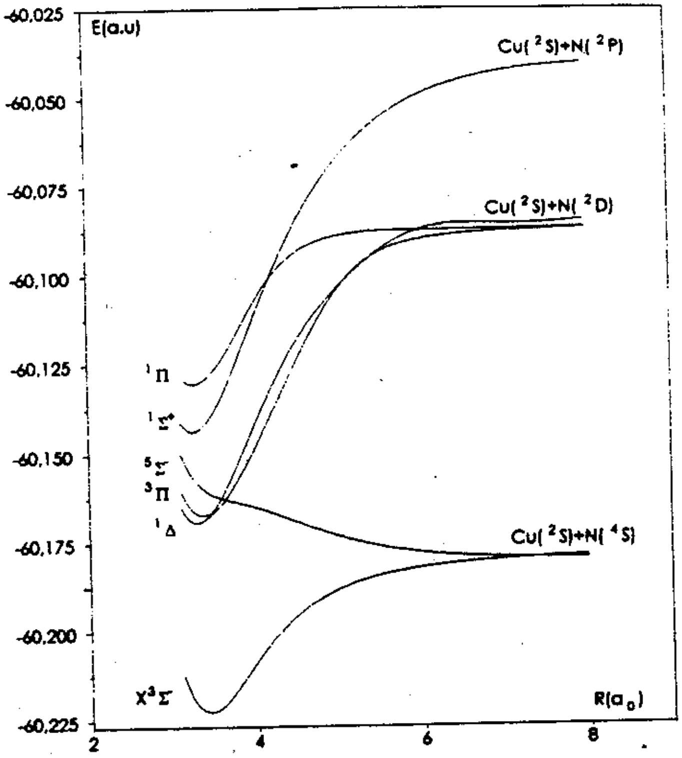


FIG. 2. CIPSI potential energy curves for the ground and excited states of CuN.

Starting from the electronic configurations of the atoms, derive the atomic states of Cu and N to which the CuN molecules dissociate.

Electronic configuration of Cu $(\underbrace{1s^2 \ldots 3d^{10}}_{\text{closed shells}} 4s^1)$ $\left.\begin{matrix} l=0 \\ s=\frac{1}{2} \end{matrix}\right\}$ ^2S

Electronic configuration of N $(\underbrace{1s^2 2s^2}_{\text{closed shells}} 2p^3)$ 3 equivalent electrons in p orbital:

m = 1			↑	↓	↑↓	↑↓	↑↓	↑↓	↑	↓			↓	↑	↓	↑	↓	↑	↑	↓
m = 0	↑	↓			↑	↓			↑↓	↑↓	↑↓	↑↓	↑	↓	↓	↑	↑	↓	↑	↓
m = −1	↑↓	↑↓	↑↓	↑↓			↑	↓			↑	↓	↑	↓	↑	↓	↓	↑	↑	↓
M_L	−2	−2	−1	−1	2	2	1	1	1	1	−1	−1	0	0	0	0	0	0	0	0
M_S	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	+½	−½	−½	+½	−½	+½	+3/2	−3/2
L=2, S=½	x	x	x	x	x	x	x	x					x	x						
L=1, S=½									x	x	x	x			x	x				
L=0, S=3/2																	x	x	x	x

$L=2, S=\frac{1}{2}: J=\frac{5}{2}, \frac{3}{2}$ $^2D_{5/2, 3/2}$ (6+4 microstate)

$L=1, S=\frac{1}{2}: J=\frac{3}{2}, \frac{1}{2}$ $^2P_{3/2, \frac{1}{2}}$ (4+2 microstate)

$L=0, S=\frac{3}{2}: J=\frac{3}{2}$ $^4S_{3/2}$ (4 microstates)

} 20 microstate

Starting from the atomic states of the separated atoms, <u>derive</u> the molecular states of the CuN molecule that can result from these combinations.

separated atoms								molecular
Cu	N	S_1	S_2	S	M_{L_1}	M_{L_2}	Λ	Term Symbol
^2S	^4S	$\frac{1}{2}$	$\frac{3}{2}$	2, 1	0	0	0	$^5\Sigma$ $^3\Sigma$
^2S	^2D	$\frac{1}{2}$	$\frac{1}{2}$	1, 0	0	± 2	2	$^3\Delta$ $^1\Delta$
					0	± 1	1	$^3\Pi$ $^1\Pi$
					0	0	0	$^3\Sigma$ $^1\Sigma$
^2S	^2P	$\frac{1}{2}$	$\frac{1}{2}$	1, 0	0	± 1	1	$^3\Pi$ $^1\Pi$
					0	0	0	$^3\Sigma$ $^1\Sigma$

Figure shows

$^2S + {}^4S \longrightarrow {}^5\Sigma^- \quad {}^3\Sigma^-$

$^2S + {}^2D \longrightarrow {}^3\Pi \quad {}^1\Delta \quad {}^1\Pi$

(not shown are $^3\Delta$, $^3\Sigma$, $^1\Sigma$)

$^2S + {}^2P \longrightarrow {}^1\Sigma^+$

(not shown are $^3\Pi$, $^1\Pi$, $^3\Sigma$)

Starting from the ground molecular electronic configuration, $(1\sigma)^2\,(2\sigma)^2\,(1\pi)^4\,(1\delta)^4\,(2\pi)^2\,(3\sigma)^1\,(4\sigma)^1$, where only the atomic valence shells have been included, that is, N: $(1s)^2$ and Cu: $(1s)^2\,(2p)^6\,(3s)^2\,(3p)^6$ are not included, ***<u>derive</u> the molecular electronic states that can result.***

Outside the closed shells there are only $\pi^2\,\sigma\,\sigma$

Do them separately

π^2

$\lambda=1$	↑↓		↑	↓	↑	↓
$\lambda=-1$		↑↓	↑	↓	↓	↑
Λ	2	-2	0	0	0	0
M_S	0	0	1	-1	0	0
$^1\Delta$	x	x				
$^3\Sigma$			x	x	x	
$^1\Sigma$						x

$\sigma\sigma$

$\lambda=0$	↑	↑	↓	↓
$\lambda=0$	↓	↑	↓	↑
Λ	0	0	0	0
M_S	0	1	-1	0
$^3\Sigma$	x	x	x	
$^1\Sigma$				x

Combine them to get

π^2 $\sigma\sigma$ overall

$^1\Delta + {}^3\Sigma \rightarrow {}^3\Delta \left\{ \begin{array}{l} \Lambda=2 \\ S=1 \end{array} \right.$

$^1\Delta + {}^1\Sigma \rightarrow {}^1\Delta \left\{ \begin{array}{l} \Lambda=2 \\ S=0 \end{array} \right.$

$^3\Sigma + {}^3\Sigma \rightarrow \begin{array}{l} ^5\Sigma \\ ^3\Sigma \\ ^1\Sigma \end{array} \left. \right\} \begin{array}{l} \Lambda=0 \\ S=2,1,0 \end{array}$

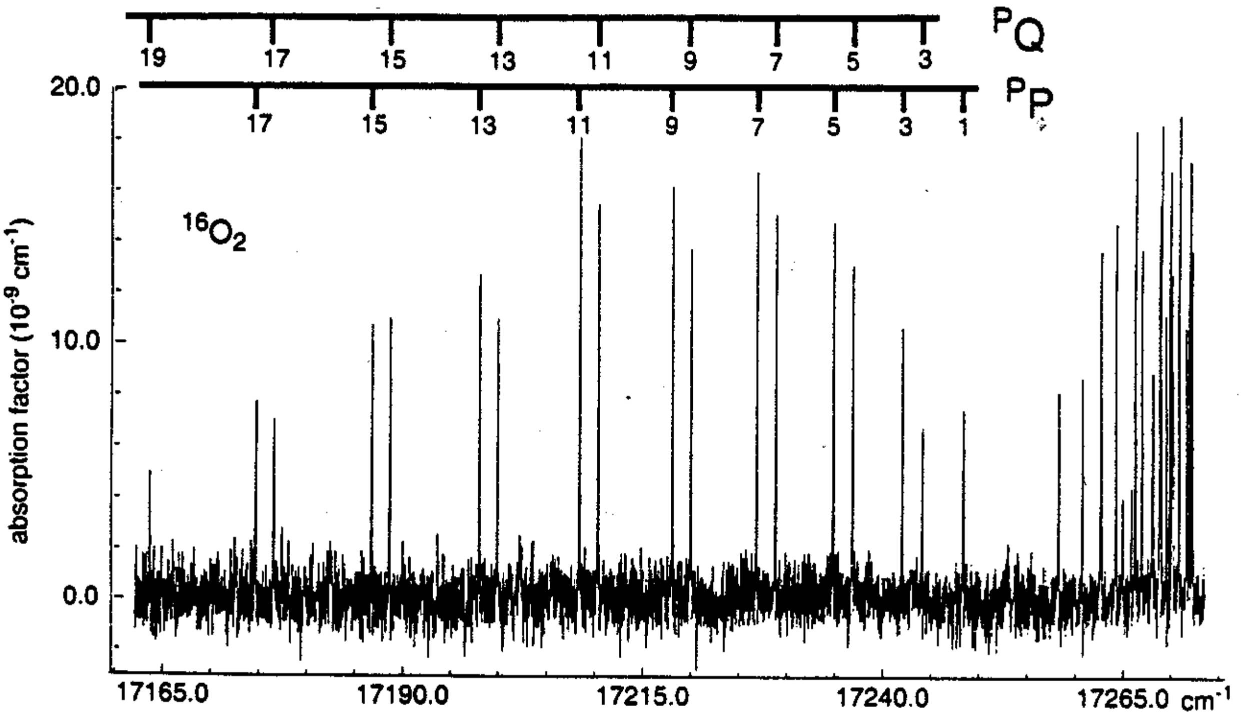
$^3\Sigma + {}^1\Sigma \rightarrow \begin{array}{l} ^3\Sigma \\ ^1\Sigma \end{array} \left. \right\} \begin{array}{l} \Lambda=0 \\ S=1 \end{array}$

$^1\Sigma + {}^1\Sigma \rightarrow {}^1\Sigma \left\{ \begin{array}{l} \Lambda=0 \\ S=0 \end{array} \right.$

$\Uparrow$

the molecular electronic states

6. The $b\,^1\Sigma_g^+ \rightarrow X\,^3\Sigma_g^-$ red atmospheric system of the O_2 molecule is, despite its small oscillator strength, of importance for light scattering and extinction studies of the Earth's atmosphere. For this reason this band system has been the subject of many studies, the latest of which was the high resolution study of reported in [*J. Mol. Spectrosc.* 193, 442-445 (***1999***)] . The (3,0) bands of this system for the $^{16}O_2$ and the $^{18}O_2$ molecules are shown below.



The molecular constants of the $X\,^3\Sigma_g^-$ v = 0 ground state are very accurately known from previous work, these can be kept constant in the analysis to find the molecular constants for the $b\,^1\Sigma_g^+$ state. ***Why is the oscillator strength so small for this band system?***

Because it is a triply forbidden transition

$\Delta S = 0$
$g \leftrightarrow u$
$\Sigma^+ \leftrightarrow \Sigma^+$
$\Sigma^- \leftrightarrow \Sigma^-$

selection rules for electric dipole transitions

Explain the meaning of the labels ^{P}P and ^{P}Q in the P branches of $^{16}O_2$ and ^{R}R and ^{R}Q in the R branches of $^{16}O_2$ spectra shown.

The lower electronic state is $^3\Sigma_g^-$ has only N''= odd rotational levels since ^{16}O nucleus is a boson, with nuclear spin = 0. The total wavefunction has to be symmetric (does not change sign) with respect to interchange of any two bosons.
$P_{AB}\,\Psi_{elec}(^3\Sigma_g^-)\bullet\Psi_{vibr}(R-R_e)\bullet\Psi_{rot\ N''M''}(\theta,\phi)\bullet\Psi_{elec\ spin}\bullet\Psi_{nuclear\ spin}(A,B)$
that is, $(g)(-)$ $\bullet(+)$ $\bullet(-1)^{N''}$ $\bullet(+)$ $\bullet$(ortho only) must be +
which can only be true if N''= odd.
The upper electronic state is $^1\Sigma_g^+$ has only N'= even rotational levels
since $(g)(+)$ $\bullet(+)$ $\bullet(-1)^{N'}$ $\bullet(+)$ $\bullet$(ortho only) must be +
which can only be true if N'= even. Since there is only rotational angular momentum in this upper state, $J' = N'$.
The only combinations that are observable in this case,
since N''= odd only, and $J''= N''+1$, N'', or $N''-1$ and N'= even only, $J''= N'$
are the following:

notation	superscript means	P, Q, or R means
^{P}P	$N' = N'' -1$	$J' = J'' -1$
^{P}Q	$N' = N'' -1$	$J' = J''$
^{R}Q	$N' = N'' +1$	$J' = J''$
^{R}R	$N' = N'' +1$	$J' = J'' +1$

Provide the quantum numbers of the upper and lower state of the first marked line (19) on the left side of the top spectrum

The notation for this line $^{P}Q(19)$: Since only odd N'' exist for the lower state this number (19) must correspond to N''.

UPPER STATE	LOWER STATE	
$N' = 18$	$N'' = 19$	superscript P
$J' = 18$	$J'' = 18$	Q branch
$\Lambda' = 0$	$\Lambda'' = 0$	Σ
$S' = 0$	$S'' = 1$	$^1\Sigma$ and $^3\Sigma$
$v' = 3$	$v'' = 0$	given it is a (3,0) band

7. The cyanogen (NCCN) molecule is an important constituent of flames. For this reason this molecule has been the subject of many studies, the latest of which was the high resolution infrared spectra of various isotopomers of cyanogen reported in [*J. Mol. Spectrosc.* 193, 183-194 (*1999*)] . The table summarizing the nuclear spin statistical weights in this paper is reproduced below. Parity *e* is (+) and *f* is (–)

TABLE 1
Relative Nuclear Spin Statistical Weights for Cyanogen[a]

State	Parity	*J*	$^{12}C_2{}^{14}N_2$	$^{12}C_2{}^{15}N_2$	$^{13}C_2{}^{15}N_2$	$^{13}C_2{}^{14}N_2$
g	*e*	Even	2	1	5	5
		Odd	1	3	3	7
	f	Even	1	3	3	7
		Odd	2	1	5	5
u	*e*	Even	1	3	3	7
		Odd	2	1	5	5
	f	Even	2	1	5	5
		Odd	1	3	3	7

[a] For the non-centrosymmetric isotopomers there is no *g-u* distinction and all rovibrational levels have the same nuclear spin statistical weight.

Derive the entries for the $^{13}C_2{}^{15}N_2$ isotopomer in this table, defining all the symmetry terms used.

^{13}C has spin 1/2, ^{15}N has spin 1/2. Both are fermions. The total wavefunction has to be antisymmetric (must change sign) with respect to interchange of any two fermions, therefore the total wavefunction has to be symmetric (must not change sign) with respect to two such interchanges.

$$P_{AB}\,P_{RS}\,\Psi_{elec}({}^1\Sigma_g{}^{+})\bullet\Psi_{vibr}(_{\text{gor u}}{}^{\text{parity e(+) or f(-)}})\bullet\Psi_{rot\,N''M''}\,(\theta,\,\phi)\bullet\Psi_{elec\,spin}\bullet\Psi_{13C}(A,B)\bullet\Psi_{15N}(R,\,S)$$

that is, $(g)(+)\bullet(g)(e)\quad\bullet(-1)^{J''}\quad\bullet(+)\quad\bullet(\text{ortho or para})\bullet(\text{ortho or para}) = +$

For spin 1/2 the nuclear spin states are *para*: $\{\alpha(A)\beta(B)-\beta(A)\alpha(B)\}/\sqrt{2}$

ortho:
$\alpha(A)\,\alpha(B)$
$\beta(A)\,\beta(B)$
$\{\alpha(A)\beta(B)+\beta(A)\alpha(B)\}/\sqrt{2}$

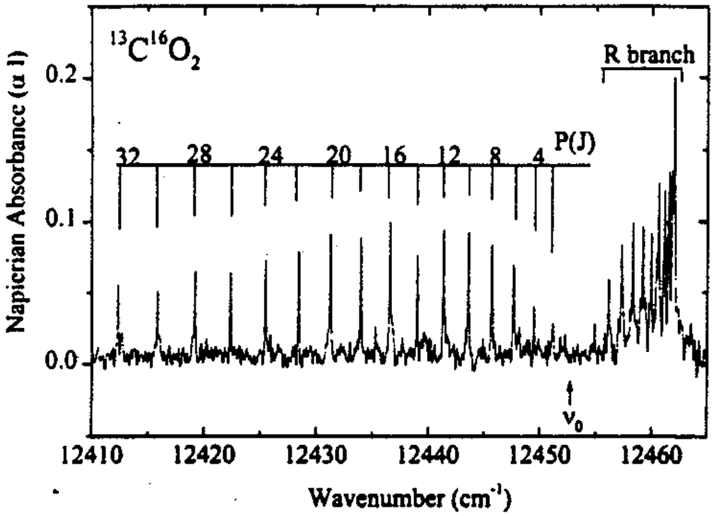
with statistical weights of 1 and 3

First table entry:
(g)(+) •(g)(+) •$(-1)^{even}$•{(*para*)(*para*) or (*ortho*)(*ortho*)} in order to get + sign .
The statistical weight is {(1)(1) + (3)(3)} = 10
The next table entry:
(g)(+) •(g)(+) •$(-1)^{odd}$•{(*para*)(*ortho*) or (*ortho*)(*para*)} in order to get + sign .
The statistical weight is {(1)(3) + (3)(1)} = 6
The next table entry:
(g)(+) •(g)(-) •$(-1)^{even}$•{(*para*)(*ortho*) or (*ortho*)(*para*)} in order to get + sign .
The statistical weight is {(1)(3) + (3)(1)} = 6
And so on. The statistical weight of 10 goes with the positive result for the factors (g)(+) •(g or u)(+ or -) •$(-1)^{\text{even or odd}}$ and the statistical weight of 6 goes with the negative result for these factors. Therefore, the statistical weights should be 10,6,6,10,6,10,10,6 respectively from top to bottom for the column $^{13}C_2{}^{15}N_2$.
The table shows statistical weights of the same ratio: 5,3,3,5,3,5,5,3.

Given that the equilibrium bond length of the N-C bond is 1.157Å ***and that for the C-C bond is*** 1.380Å ***, calculate the moments of inertia of the various isotopomers given in the table.***

$^{14}N—^{12}C—^{12}C—^{14}N$
1.157 1.380 1.157 Å center of mass is at the midpoint of the C-C bond.
$I = \sum_i m_i r_i^2 = 2\{14(1.157+0.690)^2 + 12(0.690)^2\}$
To get the others, just use different masses for C and N isotopes. Center of mass has to be shifted when the isotopomer does not have a center of symmetry.

8. The $(1\ 0^0\ 5)_{\mathrm{1st\ or\ 2nd}} \rightarrow (0\ 0^0\ 0)$ band of $^{13}C^{16}O_2$ molecule has been reported in [*J. Mol. Spectrosc.* 193, 204-212 (***1999***)] . The figure below, taken from this paper shows the intracavity laser spectrum taken of 200 Torr of gas in the cell under conditions which gives an equivalent path length of 13.5 km.



The 1st or 2nd (subscript 1 or 2) notation refer to the first or second member of the Fermi dyad that result from coupling of the nearly degenerate $(1\ 0^0\ 5)$ and the $(0\ 2^0\ 5)$ vibrational states. The Fermi dyad resulting from the near degeneracy of $(1\ 0^0\ 0)$ and $(0\ 2^0\ 0)$ of $^{12}C^{16}O_2$ is the most well known case. ***Explain the notation used for the upper combination state in the figure.***

There are 3 frequencies, two of which are degenerate (the bending modes).

(10^05):	ν_1	ν_2	ν_3
	$v_1=1$	$v_{2a}=0$	$v_3=5$
		$v_{2b}=0$	

0^0 means $(v_{2a}+v_{2a}) = 0$ and $\ell = 0$.

Derive the expression for G_v in this case.

$$G_v = \nu_{1e}\,(v_1+\tfrac{1}{2}) - (x_e\nu_e)_{11}\,(v_1+\tfrac{1}{2})^2 + \ldots$$
$$+\nu_{3e}\,(v_3+\tfrac{1}{2}) - (x_e\nu_e)_{33}\,(v_3+\tfrac{1}{2})^2 + \ldots$$
$$+\nu_{2e}\,(v_{2a}+v_{2b}+1) - (x_e\nu_e)_{22}\,[(v_{2a}+\tfrac{1}{2})^2 + (v_{2b}+\tfrac{1}{2})^2 + (v_{2a}+\tfrac{1}{2})(v_{2b}+\tfrac{1}{2})] + \ldots$$

Given the experimental numerical values in cm^{-1} ***in Table 7 below*****,**

TABLE 7

Observed and Calculated Wavenumbers (in cm^{-1}) for the $(1\ 0^0\ 5)_2$–$(0\ 0^0\ 0)$ Band of $^{13}C^{16}O_2$ Centered at 12 341.058 cm^{-1}

	P(J)			R(J)		
J	Obs. (cm^{-1})	Obs.–SP ($\times 10^{-3}$cm^{-1})	Obs.–GIP ($\times 10^{-3}$cm^{-1})	Obs. (cm^{-1})	Obs.–SP ($\times 10^{-3}$cm^{-1})	Obs.–GIP ($\times 10^{-3}$cm^{-1})
4				12344.546	-0.7	-38
6				12345.762	13	-26
8	12334.056	14	26	12346.831	-9	-52
10	12331.993	-20	-62	12347.819	-3	-49
12	12329.869	-4	-49	12348.691	-3	-51
14	12327.614	-10	-58	12349.465	10	-42
16	12325.281	16	-35	12350.111	4	-50
18	12322.792	4	-59	12350.650	0.7	-56
20	12320.226	7	-49	12351.105^a	23	-35
22	12317.519	-13	-71	12351.406	0.2	-57
24				12351.634	13	-42
26	12311.823	-11	-67	12351.713	-14	-66
28				12351.713	12	-57

show how to determine G_v, B_v, D_v

$\nu^P(J'') = \nu_0 - (B_v'+B_v'')J'' + (B_v'-B_v'')J''^2$ from which we can get
$\{\nu^P(J'') - \nu_0\}/J'' = -(B_v'+B_v'') + (B_v'-B_v'')J''$
We can plot $\{\nu^P(J'') - \nu_0\}/J''$ versus J'' to get a straight line.
In the table ν_0 is given (12 341.058 cm^{-1}) and each one of the entries under the column P(J) : Obs (cm^{-1}) is a value of $\nu^P(J'')$ for the corresponding J''.
So we take (12 334.056-12 341.058)/8 cm^{-1} and $J''=8$ as one point, and so on with the other points.
From the straight line fit we get intercept = $-(B_v'+B_v'')$
and slope = $(B_v'-B_v'')$, from which we obtain both **B_v' and B_v''**.
$G_v'' = 0.0$ by definition, and
$G_v' = \nu_0$, is given, =12 341.058 cm^{-1}.
D_v' and D_v'' are very small and can be obtained by multiparameter fitting of the tabulated [J, P(J)] values, that is, $[J'', \nu^P(J'')]$, to the equation
$\nu^P(J'') = \nu_0 - (B_v'+B_v'')J'' + (B_v'-B_v'')J''^2 - (D_v'-D_v'')J''^2 + 2(D_v'+D_v'')J''^3$

9. The high resolution infrared study of the ν_{14}, ν_{17}, and ν_{18} of $^{11}B_2H_6$ and $^{10}B^{11}BH_6$ molecules has been reported in [*J. Mol. Spectrosc.* 191, 331-342 (*1998*)]. The figure below, taken from this paper shows the diborane molecule and the symmetry species of the normal modes.

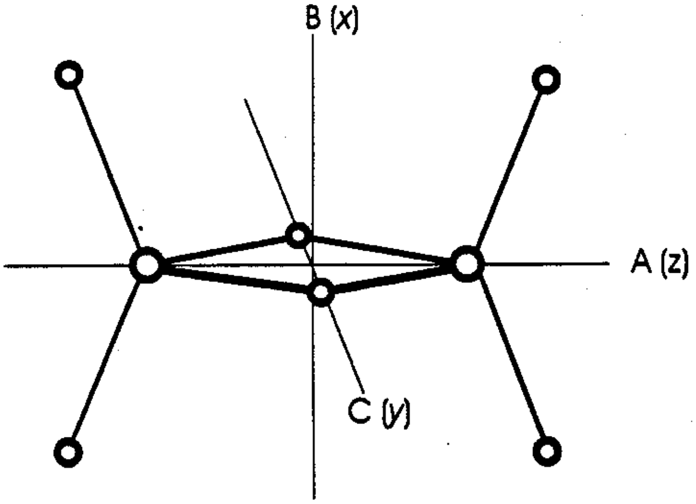


FIG. 1. Model of the diborane molecule showing the position of the atoms and the inertial axes.

TABLE 1

D_{2h} Point Group for $^{11}B_2H_6$ and $^{10}B_2H_6$

	I	C_2^z	C_2^x	C_2^y	i	σ_{xy}	σ_{yz}	σ_{xz}		
A_g	1	1	1	1	1	1	1	1		$\nu_1, \nu_2, \nu_3, \nu_4$
A_u	1	1	1	1	-1	-1	-1	-1		ν_5
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	ν_{15}
B_{1u}	1	1	-1	-1	-1	-1	1	1	T_z	$\nu_{16}, \nu_{17}, \nu_{18}$
B_{2g}	1	-1	-1	1	1	-1	-1	1	R_y	ν_{11}, ν_{12}
B_{2u}	1	-1	-1	1	-1	1	1	-1	T_y	ν_{13}, ν_{14}
B_{3g}	1	-1	1	-1	1	-1	1	-1	R_x	ν_6, ν_7
B_{3u}	1	-1	1	-1	-1	1	-1	1	T_x	ν_8, ν_9, ν_{10}

Derive these results, i.e., derive the irreducible representations of the normal vibrations of the diborane molecule.

We start with Cartesian displacement coordinates (represented by arrows) at each atom in the molecule as the basis for a reducible representation that includes all the 3N nuclear motions of the molecule (translation, rotation, vibration). We find the characters $\chi_\Gamma(R_k)$ of this reducible representation, by observing the contributions from the arrows on the atoms not shifted by the symmetry operations of the point group D_{2h}

	I	C_2^z	C_2^x	C_2^y	i	σ_{xy}	σ_{yz}	σ_{xz}
Γ_{cart}	8(3)	2(-1)	0	2(-1)	0	2(+1)	4(+1)	6(+1)

Then we find the irreducible representations that can be found in this reducible rep by means of a similarity transformation, using

$$a_i = (1/h)\sum_k \chi_i(R_k)\,\chi_\Gamma(R_k)$$

$a(A_g) = (1/8)[24-2-2+2+4+6] = 4$
$a(A_u) = (1/8)[24-2-2-2-4-6] = 1$
$a(B_{1g}) = (1/8)[24-2+2+2-4-6] = 2$
$a(B_{1u}) = (1/8)[24-2+2-2+4+6] = 4$
$a(B_{2g}) = (1/8)[24+2-2-2-4+6] = 3$
$a(B_{2u}) = (1/8)[24+2-2+2+4-6] = 3$
$a(B_{3g}) = (1/8)[24+2+2-2+4-6] = 3$
$a(B_{3u}) = (1/8)[24+2+2+2-4+6] = 4$
$\Gamma_{\text{cart}} = 4A_g + A_u + 2B_{1g} + 4B_{1u} + 3B_{2g} + 3B_{2u} + 3B_{3g} + 4B_{3u}$
From the character table we get,
$\Gamma_{\text{trans}} = B_{1u} + B_{2u} + B_{3u}$
$\Gamma_{\text{rot}} = B_{1g} + B_{2g} + B_{3g}$
by difference,
$\Gamma_{\text{vib}} = 4A_g + A_u + B_{1g} + 3B_{1u} + 2B_{2g} + 2B_{2u} + 2B_{3g} + 3B_{3u}$
are the irrreducible representations of the normal vibrations of diborane molecule.