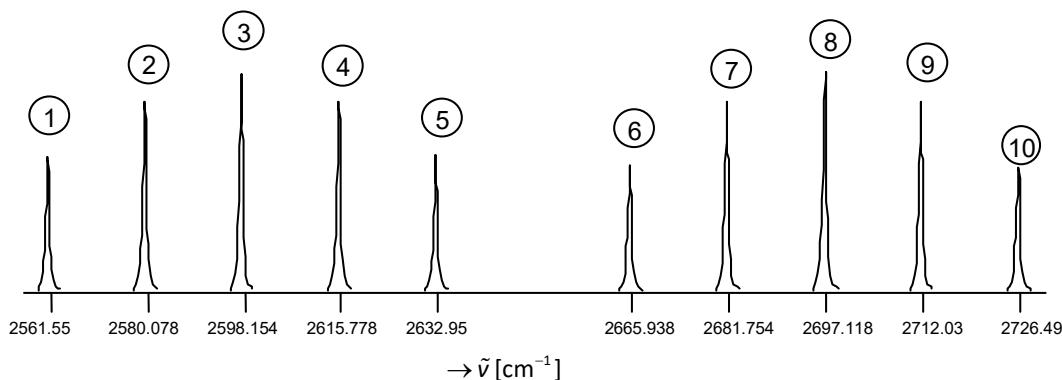


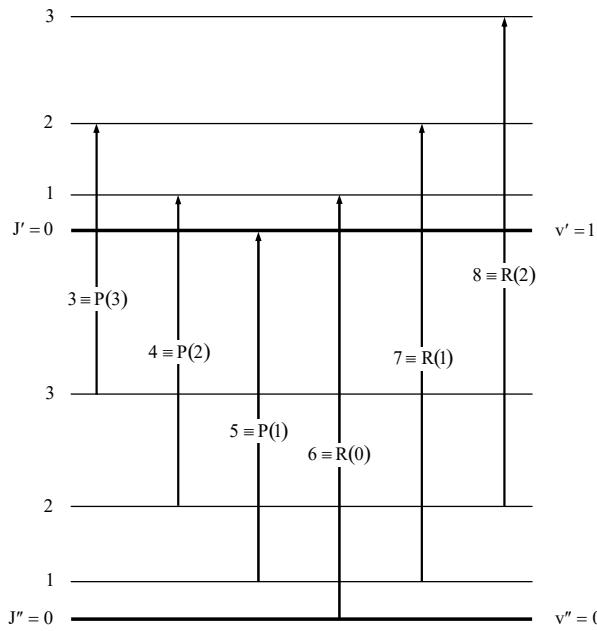
Spectroscopy

Corrections Chapter 4B

1. Shown below is an approximate infrared absorption spectrum of the diatomic molecule HBr.



- a. Draw an energy level diagram for HBr which includes the first 2 vibrational levels and the first 4 rotational levels of each vibrational level. Label the energy levels by all the appropriate quantum numbers.
- b. Indicate on your figure which levels are involved in the transitions labeled 3-8 in the HBr spectrum. Do this by drawing arrows between the pairs of levels involved and label each arrow by the number corresponding to the spectrum of HBr given above. Label each transition in your figure by the proper spectroscopic notation.
- c. From the information contained in the spectrum above, estimate a value for $\tilde{\nu}_0$, B_0 , B_1 , B_e , α and r_e . You can assume that the centrifugal distortion is small enough to neglect.



- By the method of differences by combination we can obtain B_0 and B_1 .

$$\Delta_2 F'' = R(J-1) - P(J+1) = 4B_{v'} \left(J + \frac{1}{2} \right)$$

$$\Delta_2 F' = R(J) - P(J) = 4B_{v'} \left(J + \frac{1}{2} \right)$$

We then calculate the values of $\Delta_2 F''$ and $\Delta_2 F'$ in terms of $\left(J + \frac{1}{2} \right)$ and, by linear regression on these results, we obtain :

$$\Delta_2 F'' = 33.440 \left(J + \frac{1}{2} \right) + 2.8 \cdot 10^{-14} \left[\text{cm}^{-1} \right] \Rightarrow B_0 = \frac{33.440}{4} = 8.360 \text{ cm}^{-1}$$

$$\Delta_2 F' = 32.536 \left(J + \frac{1}{2} \right) + 0.000 \left[\text{cm}^{-1} \right] \Rightarrow B_1 = \frac{32.536}{4} = 8.134 \text{ cm}^{-1}$$

We then find $\nu_0 = R(0) - 2B_1 = P(1) + 2B_0 = 2649.67 \text{ cm}^{-1}$

- By definition, $B_v = B_e - \alpha \left(v + \frac{1}{2} \right)$.

The values of $B_0 = B_e - \frac{1}{2}\alpha$ and $B_1 = B_e - \frac{3}{2}\alpha$ therefore allow us to calculate B_e and α :

$$B_e = \frac{3}{2}B_0 - \frac{1}{2}B_1 = 8.473 \text{ cm}^{-1}$$

$$\alpha = B_0 - B_1 = 0.226 \text{ cm}^{-1}$$

Finally, since

$$B_e \left[\text{cm}^{-1} \right] = \frac{h}{8\pi^2 c \mu r_e^2},$$

we can determine

$$r_e = \sqrt{\frac{h}{8\pi^2 c \mu B_e}}.$$

Suppose we have

$$^1H^79Br \Rightarrow \mu = \frac{1.008 \cdot 78.918}{(1.008 + 78.918)} = 0.995 \text{ umu}$$

We obtain (watch out for units!): $r_e = 1.414 \text{ \AA}$

3. The dissociation energy of an anharmonic oscillator can be estimated from the following expression:

$$D_e \approx \frac{\omega_e^2}{4\omega_e x_e}$$

a. Derive the expression above.

b. From the following separations of vibrational levels in CO, obtain values for ω_e , $\omega_e x_e$, and D_e .

Transition	band origin (cm ⁻¹)
$v=1 \leftarrow 0$	2138
$v=2 \leftarrow 1$	2115
$v=3 \leftarrow 2$	2091
$v=4 \leftarrow 3$	2063
$v=5 \leftarrow 4$	2038
$v=6 \leftarrow 5$	2011

As we saw in the course, the band origin for a vibrational transition $v+1 \leftarrow v$ is given by:

$$\begin{aligned} \nu_0 &= F(v+1) - F(v) = \omega_e \left(v + \frac{3}{2} \right) - \omega_e x_e \left(v + \frac{3}{2} \right)^2 - \omega_e \left(v + \frac{1}{2} \right) + \omega_e x_e \left(v + \frac{1}{2} \right)^2 \\ &= \omega_e - 2\omega_e x_e (v+1) \end{aligned}$$

So, a linear regression of these transition energies as a function of $(v+1)$ will give us a slope of $-2\omega_e x_e$ and an ordinate at the origin of ω_e .

We obtain: $\nu_0 = 2165 - 25.5(v+1) \text{ [cm}^{-1}\text{]} \Rightarrow \begin{cases} \omega_e = 2165 \text{ cm}^{-1} \\ \omega_e x_e = \frac{25.5}{2} = 12.8 \text{ cm}^{-1} \end{cases}$

We can then estimate the CO dissociation energy by the following expression :

$$D_e \approx \frac{\omega_e^2}{4\omega_e x_e} = 91800 \text{ cm}^{-1} \equiv 1098 \text{ kJ mol}^{-1} \quad (1 \text{ cm}^{-1} \equiv 11.96 \text{ J mol}^{-1})$$