

SOLUTIONS

PROBLEM SET 12

CHM 3411, Dr. Chatfield

This turned out to be a little more complicated than I expected for an exercise, but it's not too bad.

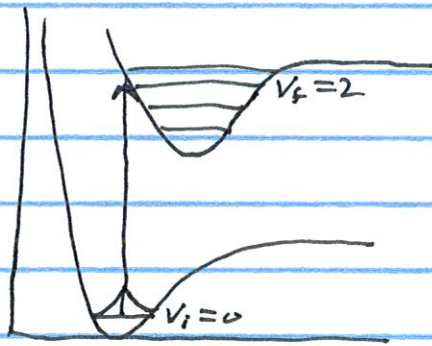
1. Franck-Condon factor = $|S(v_f, v_i)|^2$

where $S(v_f, v_i)$ is the overlap integral

$$S(v_f, v_i) = \int \psi_{v_f}^* \psi_{v_i} d\tau \quad \text{Note that } v_i \text{ is the vibr. level}$$

in the initial electronic state, and v_f is the vibr. level

in the final electronic state, e.g. for a vertical transition in absorption.



In the exercise, $\psi_{v_i} = \psi_0 = N_0 e^{-ax^2}$ and $\psi_{v_f} = N_v e^{-a(x-x_0)^2/2}$

We seek an expression (not a number!) for $|S(v_f, v_i)|^2$

$$S(v_f, v_i) = \int \psi_{v_f}^* \psi_{v_i} dx = N_0 N_v \int e^{-a(x-x_0)^2/2} \cdot e^{-ax^2} dx$$

The integrand is equal to:

$$e^{-a[\frac{3}{2}x^2 - xx_0 + \frac{1}{2}x_0^2]} = e^{-2a[3x^2 - 2xx_0 + x_0^2]}$$

It would be convenient to work this into the form: $e^{-d(x-u)^2}$ because there are formulas for evaluating the integral of that.

$$\text{Define } x_1 \text{ and } \varepsilon \text{ by } 3x^2 - 2x_0x + x_0^2 = 3(x-x_1)^2 + \varepsilon$$

$$3x^2 - 2x_0x + x_0^2 = 3x^2 - 6xx_1 + 3x_1^2 + \varepsilon$$

$$\Rightarrow x_1 = \frac{1}{3}x_0, \quad \varepsilon = \frac{2}{3}x_0^2$$

Plugging in,

$$e^{-ax^2} \cdot e^{-a(x-x_0)^2/2} = e^{-2a[3x^2 - 2x_0x + x_0^2]} = e^{-6a(x - \frac{x_0}{3})^2} \cdot e^{-\frac{4}{3}ax_0^2}$$

$$S = N_0 N_V e^{-\frac{4}{3}ax_0^2} \int_{-\infty}^{+\infty} e^{-6a(x - \frac{x_0}{3})^2} dx$$

$$\text{Define } z = x - \frac{x_0}{3} \quad dz = dx$$

$$S = N_0 N_V e^{-\frac{4}{3}ax_0^2} \int_{-\infty}^{+\infty} e^{-6az^2} dz$$

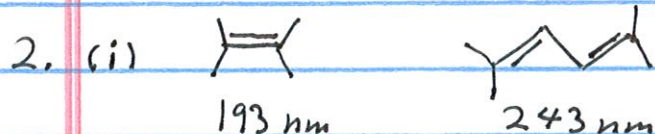
$$= 2 \int_0^{\infty} e^{-6az^2} dz = \left(\frac{\pi}{6a}\right)^{1/2}$$

$$\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a}\right)^{1/2}$$

from table

$$\Rightarrow |S(v_f, v_i)|^2 = \frac{\pi}{6a} e^{-\frac{4}{3}ax_0^2} N_0^2 N_V^2$$

Note: This is related to the fact that the product of two Gaussians is proportional to a Gaussian. Google "Gaussian Product" if you are curious.



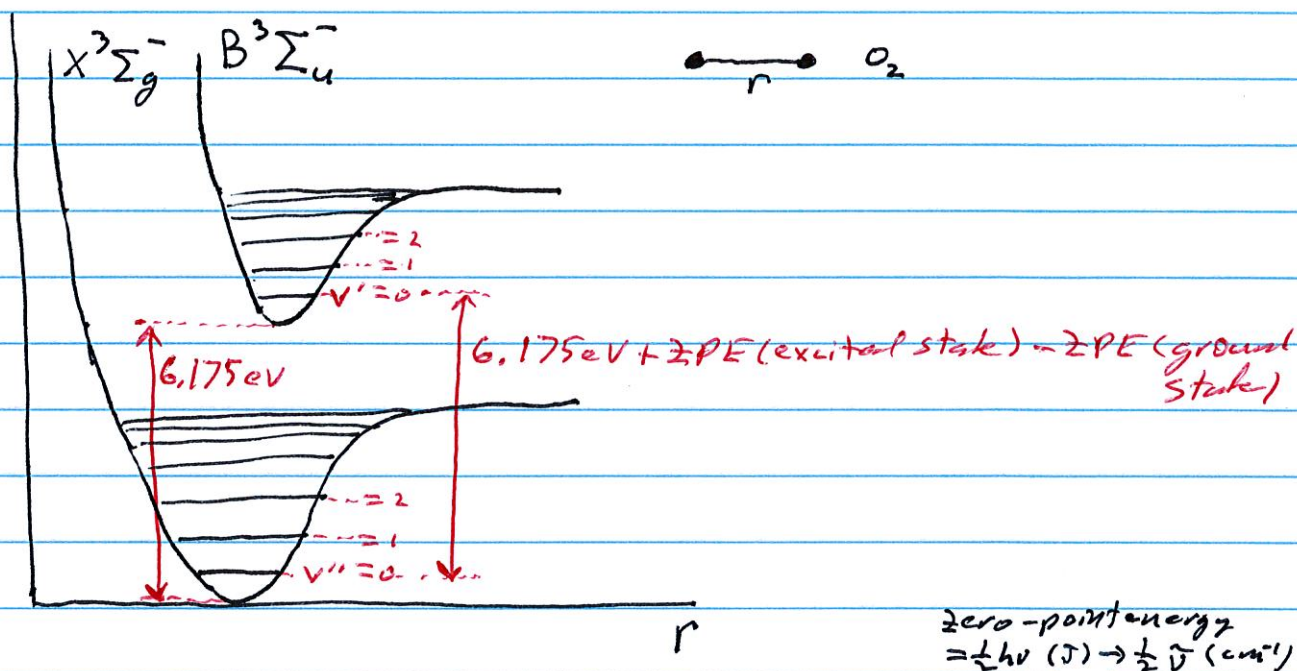
The second molecule has a longer conjugated system. This corresponds, by analogy, to a longer (albeit crooked) "box" (think of a particle-in-a-box). Therefore we anticipate a closer spacing between the HOMO and LUMO for the molecule on the right. The closer spacing corresponds to smaller ΔE , and since $\Delta E = h\nu = h \frac{c}{\lambda}$, λ will be larger.



We anticipate one $\pi^* \leftarrow \pi$ and one $\pi^* \leftarrow n$ transition. From earlier in the chapter, we know that $\pi^* \leftarrow \pi$ transitions are allowed and hence strong and occur near 180 nm, while $\pi^* \leftarrow n$ transitions are forbidden and hence weak and occur near 290 nm.

Thus the 213 nm transition is $\pi^* \leftarrow \pi$
 and ~ 320 nm is $\pi^* \leftarrow n$

3.



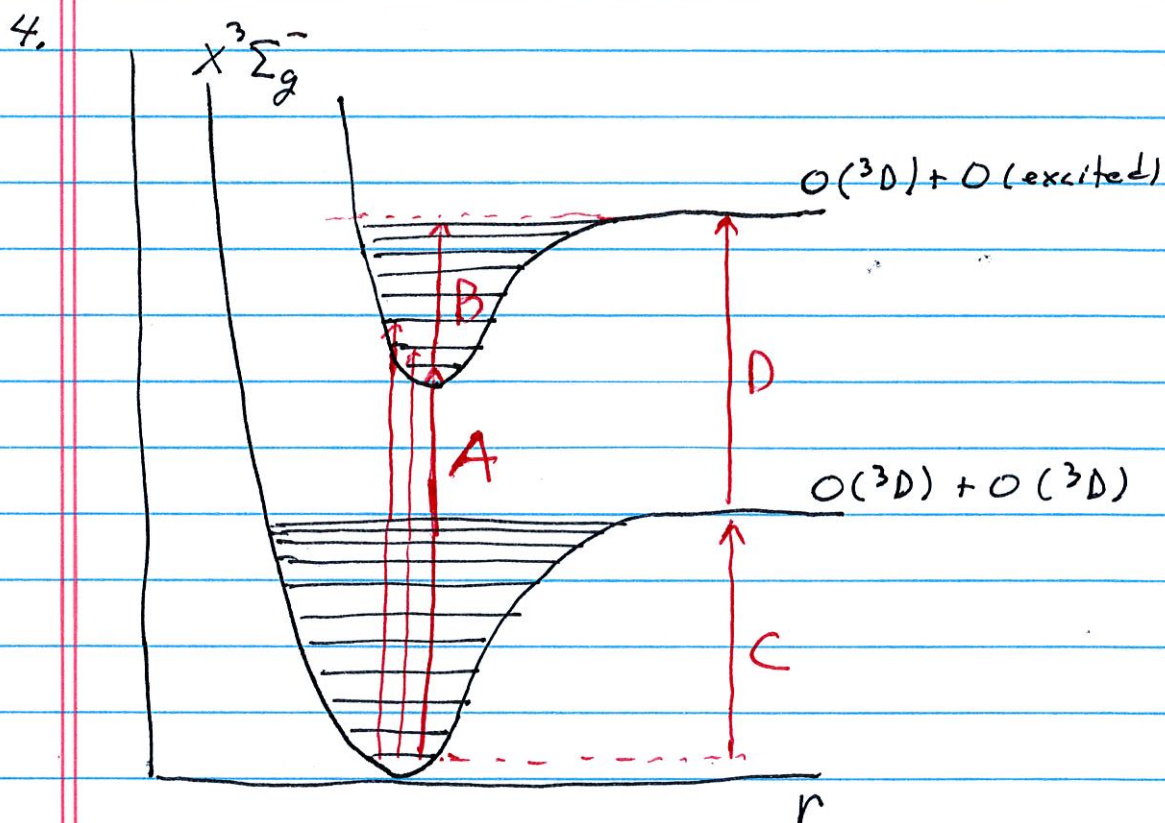
In electronic ground state, $\tilde{\nu}'' = 1580 \text{ cm}^{-1} \Rightarrow \text{ZPE} = 790 \text{ cm}^{-1}$
 excited .. , $\tilde{\nu}' = 700 \text{ ..} \Rightarrow \text{ZPE} = 350 \text{ ..}$

Lowest-energy transition is labeled (0,0), which stands for $v'=0 \leftarrow v''=0$. The frequency of this transition is:

$$\tilde{\nu}_{00} = 6.175 \text{ eV} + 350 \text{ cm}^{-1} - 790 \text{ cm}^{-1}$$

Convert units: $1 \text{ eV} = 80657.73 \text{ cm}^{-1}$

$$\tilde{\nu}_{00} = 49,366 \text{ cm}^{-1}$$



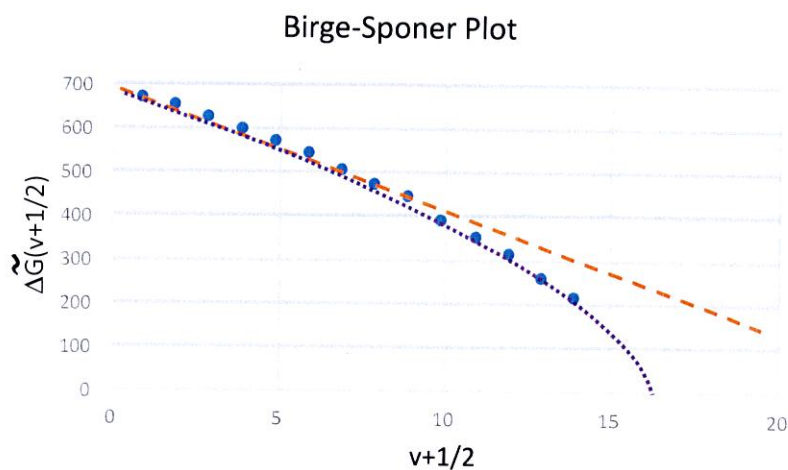
$A =$ First Schumann-Runge line $= 50,062.6 \text{ cm}^{-1}$
 $B = \tilde{D}_0$ for upper state (from Birge-Sponer plot)
 $D =$ energy of excited O atom formed by upper state dissociation $= 190 \text{ kJ/mol}$
 $C = \tilde{D}_0$ for ground (lower) state

$$C = A + B - D \text{ (will need to convert units)}$$

For the Birge-Sponer plot, note that the difference between consecutive Schumann-Runge lines is equivalent to a $v \rightarrow v+1$ excitation in the upper state. Therefore we plot the difference between S-R frequencies vs $v + \frac{1}{2}$. This gives

us a $\Delta \tilde{G}_{v+\frac{1}{2}}$ vs $v+\frac{1}{2}$ plot for the upper states.

$v+\frac{1}{2}$ wavenumber	$\tilde{G}(v+\frac{1}{2})$	$\Delta \tilde{G}(v+\frac{1}{2})$
0.5	50062.6	662.8
1.5	50725.4	643.6
2.5	51369.0	619.6
3.5	51988.6	590.4
4.5	52579.0	564.4
5.5	53143.4	536.2
6.5	53679.6	497.4
7.5	54177.0	464.8
8.5	54641.8	436.4
9.5	55078.2	381.8
10.5	55460.0	343.1
11.5	55803.1	304.2
12.5	56107.3	253.0
13.5	56360.3	210.3
14.5	56570.6	175.0
15.5		80.0
SUM		6763.0 cm^{-1} 0.8385 eV



Note that the data curve, with increasing curvature as $v+\frac{1}{2}$ increases. \tilde{D}_0 for the upper state is given by the sum (which equals the area under the curve, approximately). The last two $\Delta \tilde{G}_{v+\frac{1}{2}}$ values were estimated by reading from the purple curve drawn on the plot.

$$\Rightarrow \tilde{D}_0 (\text{upper state}) = 6763.0 \text{ cm}^{-1} = 0.8385 \text{ eV}$$

$$(1 \text{ eV} = 8065.73 \text{ cm}^{-1})$$

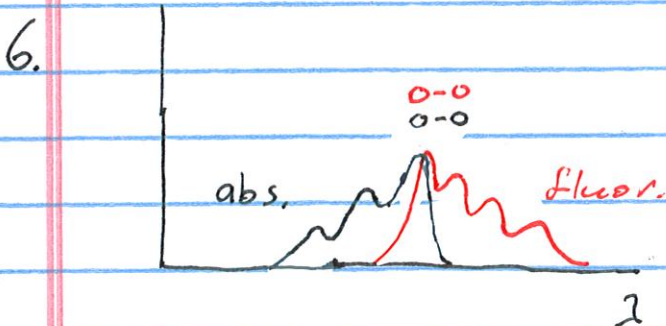
Also note that $D = 190 \text{ kJ/mol} = 15,882.7 \text{ cm}^{-1}$
($1 \text{ kJ/mol} = 83.593 \text{ cm}^{-1}$)

We can now calculate \tilde{D}_0 for the ground state:

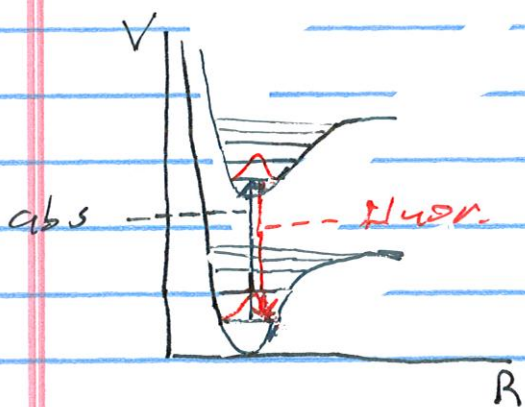
$$\begin{aligned}\tilde{D}_0(X^3\Sigma_g^-) &= A+B-D = (50,062.6 + 6763.0 - 15,882.7) \text{ cm}^{-1} \\ &= 40,942.9 \text{ cm}^{-1} \\ &= 5.076 \text{ eV}\end{aligned}$$

5. ${}^2\Pi_g \leftarrow {}^2\Pi_u$ is an allowed transition.

Therefore it is an example of fluorescence.



This is a little unusual because the peaks for the 0-0 transition are the most intense. This implies that R_e (lower state) and R'_e (upper state) are nearly the same.



- The vertical transition is to the center of the ground vibr. levels in both electronic states.
- The 0-0 absorption and fluorescence peaks are slightly offset due to solvent effects.
- The fluorescence peaks become more closely spaced as N increases. ($v=0 \rightarrow v$ transitions)
- The absorption peaks become more closely spaced as v' increases ($v' \leftarrow v=0$ transitions)

7. For laser action, a population inversion must be created in the gain medium. This requires (1) a short-lived state accessible from the ground state via a pump laser and (2) a metastable state. The metastable state must be quickly created from the short-lived excited state via radiationless decay, in which case lasing occurs between the metastable state and the ground state. This constitutes one kind of 3-level laser. A 4-level laser is even more robust.

The second requirement is that the laser radiation be partially confined to an optical cavity so that the laser frequency band is further narrowed to one of the cavity's resonant frequencies.

