Chapter 10 (cont.) 11/30/01

Just as $\Delta p \, \Delta x \geq \hbar/2$

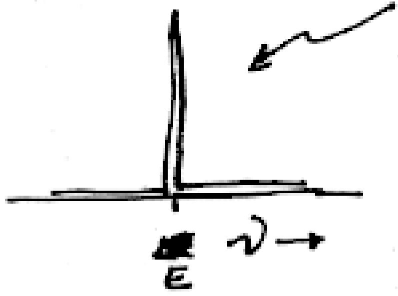
So

$$\Delta E \, \Delta t \geq \hbar/2$$

uncertainty of its energy

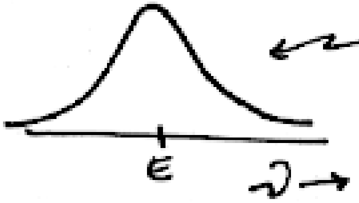
time interval of observation

thus instead of



Everything we've said predicts this

We have



We see this...

E = energy of transition

This one contributor to linewidth

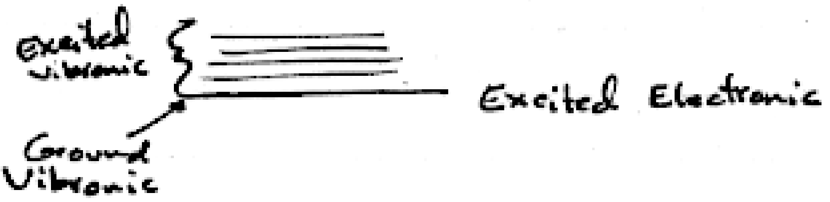
Environment can have local variations, so that each molecule has a slightly different E for the transition

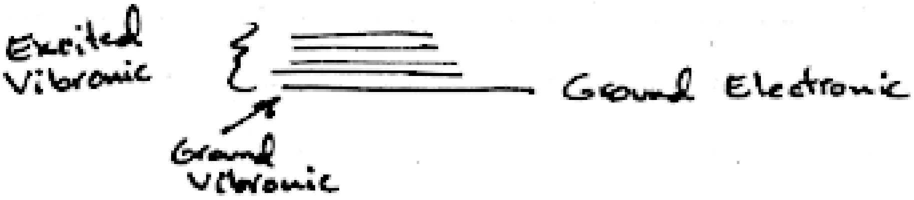
leading also to

Final linewidth can be mostly one, the other, or a mix, depending...

Finally just as their are quantized electronic states, there are also quantized vibronic states (lower E) and quantized rotational states (still lower)

Thus





Diatomic

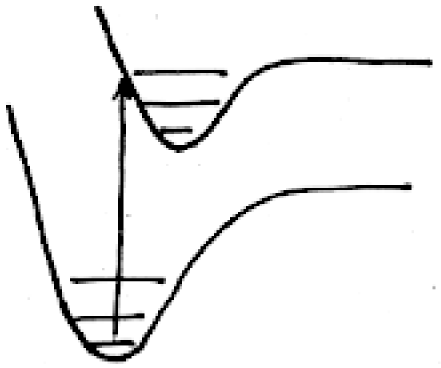
X—Y

⇐ NOT IN THE BOOK (BUT IMPORTANT!) ⇒

Finally (*really*) if excited e^- state is moving one electron from a *bonding* to an *antibonding* orbital, then we'd expect bond distance to increase.

Similarly, vibration leads to fluctuating bond lengths.

BUT e^- moves much faster than nuclei (*much* heavier)



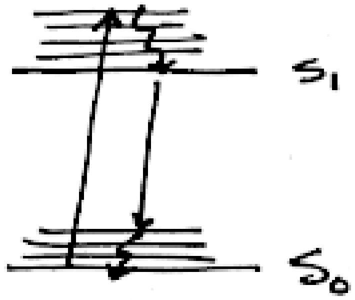
⇑

&

Born-Oppenheimer

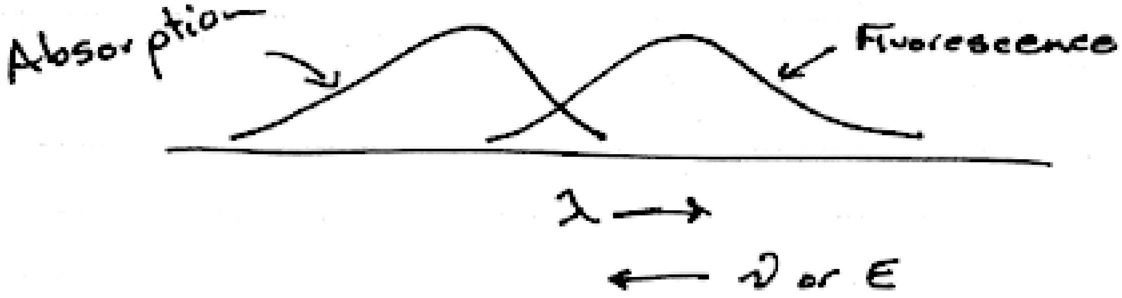
x → (internuclear distance)

Consequently, we usually have

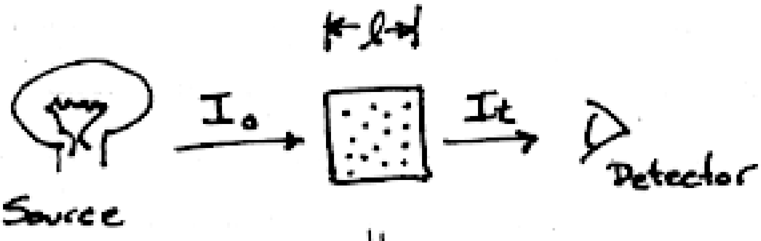


Energy of absorption is always higher than energy of flourescence

Wavelength of absorption is always lower than wavelength of fluorescence.



Beer-Lambert (p. 543)



→ Fractional decrease in intensity

$$-\frac{dI}{I} = \alpha\, c\, dx$$

proportionality

Conc of absorber

$$-\int_{I_0}^{I_t} \frac{dI}{I} = \alpha c \int_0^{\ell} dx$$

cell path length

$$\ln \frac{I_0}{I_t} = \alpha c \ell$$

changes due to ln → log change

$$I_t = I_0 e^{-\alpha c \ell}$$

OR

$$\text{ABSORBANCE} = \underbrace{A = \log \frac{I_0}{I_t} = \varepsilon c \ell}_{\text{MOST COMMON FORM}}$$

ε = "extinction coefficient"

ε has a wavelength (energy) dependence so

$$A_\lambda = \varepsilon_\lambda c \ell$$

↑ indep of c and ℓ
characteristic of the sample

Read about
isosbestic point
p. 545-547