CHEM 352: Examples for chapter 6.

1. Consider a diatomic molecule and denote the equilibrium bond lengths for the ground and excited electronic states by R_e and R_e'. Given the force constants for both states are equal, calculate the 0-0 transition Franck-Condon factor and show that this transition is most intense when $R_e = R_e'$.

Solution:

We need to calculate the overlap integral (S) between the two vibrational wavefunctions that are centered at R_e and R_e':

$$\psi_g = \left(\frac{1}{\alpha\pi^{3/2}}\right)^{1/2} \exp\left(-y^2/2\right) \text{ and } \psi_e = \left(\frac{1}{\alpha\pi^{3/2}}\right)^{1/2} \exp\left(-y'^2/2\right)$$

where $y = (R - R_e)/\alpha$, $y' = (R - R_e')/\alpha$, and $\alpha = \left(\hbar^2/(mk)\right)^{1/4}$. Then the overlap integral can be written as:

$$S = \int_{-\infty}^{\infty} \psi_g(R)\psi_e(R)dR = \frac{1}{\pi^{1/2}}\int_{-\infty}^{\infty} \exp\left(-(y^2 - y'^2)/2\right) dy$$

Substituting $\alpha z = R - \frac{1}{2}\left(R_e - R_e'\right)$ this becomes (change of variables):

$$S = \frac{1}{\pi^{1/2}} \exp\left(R_e - R_e'\right)/\left(4\alpha^2\right) \int_{-\infty}^{\infty} \exp\left(-z^2\right) dz$$

From integral table book we can find that the above integral is equal to $\sqrt{\pi}$ and hence the overalp is:

$$S = \exp\left(R_e - R_e'\right)^2/\left(4\alpha^2\right)$$

The Franck-Condon factor obtained by squaring the overlap integral:

$$S^2 = \exp\left(R_e - R_e'\right)^2/\left(2\alpha^2\right)$$

This expression reaches maximum value (one) when $R_e = R_e'$ (equal bond lengths).

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2. Consider a pulsed laser that operates at 532 nm wavelength, which has 0.10 J energy per pulse and 3.0 ns pulse length. What is the average power

and the number of photons in one pulse?

Solution:

To get the average power (P), we simply divide the pulse energy by the pulse length:

$$P = \frac{0.10 \text{ J}}{3.0 \times 10^{-9} \text{ s}} = 3.3 \times 10^{7} \text{ J/s}$$

Note that J/s = W. The energy of one $\lambda = 532$ nm photon is (E):

$$E = \frac{hc}{\lambda} = \frac{6.626076 \times 10^{-34} \text{ Js} \times 2.99792458 \times 10^{8} \text{ m/s}}{532 \times 10^{-9} \text{ m}} = 3.73392^{-19} \text{ J}$$

To get the number of photons divide the total pulse energy by the single photon energy:

$$n = \frac{0.10 \text{ J}}{3.73392^{-19} \text{ J}} = 2.7 \times 10^{17} \text{ photons}$$

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3. N_2 molecules are irradiated with 58.43 nm wavelength electromagnetic radiation and it was observed tat the photoelectrons ejected had a kinetic energy of 5.63 eV. What was the ionization energy for these electrons? How does this compare with the ionization energy of N_2 and what does it say about the orbital from which the photoelectrons came from?

Solution:

The energy of the incident photons (E) is:

$$E = \frac{hc}{\lambda} = \frac{6.626076 \times 10^{-34} \text{ Js} \times 2.99792458 \times 10^{8} \text{ m/s}}{58.43 \times 10^{-9} \text{ m}} = 4.000 \times 10^{-18} \text{J} = 21.22 \text{ eV}$$

Since we have the energy conservation condition: $h\nu = \frac{1}{2}m_e v^2 + I$ (m_e is the electron mass). Plugging in the numbers we get: 21.22 eV = 5.63 eV + I where the kinetic energy is $\frac{1}{2}m_e v^2 = 5.63$ eV. Solving for for I gives 15.59 eV. From NIST chemistry webbook (https://webbook.nist.gov/chemistry/) we can see that the experimental value for N_2 ionization energy is 15.58 eV, which is almost exactly the value observed. Therefore the photoelectrons originated from the HOMO orbital of N_2.

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4. Consider vibrationally resolved electronic spectrum of a diatomic molecule. What does the Franck-Condon principle say about the relative bond lengths between the excited and ground electronic states if there is: a) just one line, b) one line with a pattern of decaying lower intensity lines, or c) line pattern that first increases in intensity and then decays.

Solution:

a) This means that the bond lengths are equal. Only 0-0 transition observed.
b) The bond lengths are very close to each other so that the 0-0 transition dominates but the smaller lines originate from the small difference in bond lengths.
c) The difference in the bond lengths is significant, which means that the 0-0 transition has low intensity and the Franck-Condon overlaps first increase to reach a maximum and then after this it starts to decrease.
Note that some times also "hot bands" can also contribute where emission takes place from multiple vibrational states of the excited state.