Photochemistry

Interaction of light with matter

Study process

Use process to identify what’s happening
Processes

Grotthus-Draper

Light must be absorbed to be photochemically active

Einstein-Stark

One photon/molecule Superceded by lasers

Beer’s Law

\[ \frac{I}{I_0} = e^{-\varepsilon cl} \]
\[ \frac{I}{I_0} = e^{-\sigma pl} \]

\( \varepsilon \) molar extinct. Coeff \( M^{-1} \cdot cm^{-1} \)

\( \sigma \) absorption cross sect. \( cm^2 \)

\( \varepsilon \approx 6000 \ M^{-1} \cdot cm^{-1} \)

\( \sigma \approx 10^{-17} \ cm^2 \)
Absorption

$\Delta E = h\nu$

Selection Rules

$\Delta J = \pm 1$  \(\text{Ir, } \mu\text{wave}\)

$\Delta S = 0$  \(\text{Visible, } \text{uv}\)

Franck-Condon effect
Franck-Condon Effect

Nuclei move slowly compared to electrons
For a shu \( \Delta v = \pm 1 \), and all spacings are equal.

For the real HCl molecule, \( \Delta v = \pm 1 \) is *highly* favored.

Spacings are not equal.

- \( 2576 \text{ cm}^{-1} \)
- \( 2679 \text{ cm}^{-1} \)
- \( 2782 \text{ cm}^{-1} \)
- \( 2889 \text{ cm}^{-1} \)
Overtones are a result of $\Delta v = \pm 2, \pm 3$ etc. They are $\approx 1000 \times$ less intense.
Absorption & Emission

Absorption
\[ X + h\nu \rightarrow X^* \]
\[ R_{\text{abs}} = B_{12}\rho[X] \]

Radiation
\[ X^* \rightarrow X + h\nu \]
\[ R_{\text{spont}} = A_{21}[X^*] \]

Stimulated emission
\[ X^* + h\nu \rightarrow X + 2h\nu \]
\[ R_{\text{stim}} = B_{21}\rho[X^*] \]

Quenching
\[ X^* + Q \rightarrow X + Q' \]
\[ R_Q = k_Q[Q][X^*] \]
Types of Absorptions for diatomic molecules

bound - bound

bound - bound

bound - bound

bound - unbound

bound - unbound

predissociation
Fluorescence Quenching

\[ A + h\nu \rightarrow A^* \quad \text{R \quad Excitation} \]
\[ A^* \rightarrow A + h\nu \quad k_f \quad \text{Fluorescence} \]
\[ A^* \rightarrow \text{products} \quad k_d \quad \text{Decomposition} \]
\[ A^* + Q \rightarrow A + Q' \quad k_q \quad \text{Quenching} \]
\[ Q \rightarrow Q' \]
assume rate of excitation is constant (steady light)

\[
\frac{dA^*}{dt} = R - k_f[A^*] - k_q[A^*][Q] = 0 \quad \text{steady state}
\]

\[
[A^*] = \frac{R}{k_f + k_q[Q]}
\]

Quantum yield is \( \phi = \text{fluorescence rate/absorption} \)

\[
\phi = \frac{k_f[A^*]}{R} = \frac{k_f}{k_f + k_q[Q]}
\]
in absence of $Q$

$$I_f = I_f^0 = k_f[A^*] = \frac{k_f R}{k_f + k_q[Q]} = R$$

Compare with & without $Q$, keeping $R$ const

$$I_f = k_f[A^*] = k_f \frac{R}{k_f + k_q[Q]}$$

$$\frac{I_f}{I_f^0} = \frac{[A^*]}{[A^*]^0} = \frac{k_f}{k_f + k_q[Q]} \frac{R}{R} = \frac{k_f}{k_f + k_q[Q]}$$

Reciprocal gives

$$\frac{I_f^0}{I_f} = 1 + \frac{k_q}{k_f} [Q] = 1 + k_q [Q] \tau$$

Plotting $\frac{I_f^0}{I_f}$ vs $[Q]$ gives $k_q \tau$ as slope
Pulsed Mode

**Time dependence (after pulse)**

\[
\frac{dA^*}{dt} = -k_f[A^*] - k_d[A^*] - k_q[A^*][Q]
\]

\[
\frac{dA^*}{dt} = -k_{obs}[A^*] \quad k_{obs} = k_f + k_d + k_q[Q]
\]

\[
\frac{[A^*]}{[A^*]^0} = \exp(-k_{obs}t) = e^{-t/\tau}
\]

**plot** \(k_{obs} vs [Q]: \) slope is \(k_q\); intercept is \((k_f+k_d)\)

Stern-Volmer plot
Laser measurements

Rice expts done with laser absorption

Other kinetic methods

LIF

Multiphoton ionization

Time response

Kinds of lasers

Chemical lasers

\[ i-C_3H_7I + h\nu = I^* + \cdot C_3H_7 \]

\[ I^* \rightarrow I + h\nu \quad 1.3\mu \quad \text{Joules/\mu s} \rightarrow \text{MW} \]
excitation

fluorescence

intersystem crossing

collisional relaxation

phosphorescence

Singlet Levels

Triplet Levels
The graph shows the potential energy $V(R)$ in eV as a function of the interatomic distance $R$ in Å. The graph is divided into three regions: Ionic, Covalent, and Diabatic.

- **Ionic Phase**: This region is characterized by a sharp drop in potential energy as the distance $R$ increases. The ionic bond is represented by the separation between sodium ($\text{Na}^+$) and iodine ($I^-$).
- **Covalent Phase**: In this phase, the potential energy decreases more gradually with increasing distance $R$. The covalent bond is typically stronger than the ionic bond.
- **Diabatic Phase**: This phase shows a transition with a sudden change in potential energy, indicating a change in the electronic configuration.
$P_{LZ} = \exp\left\{ -\frac{4\pi^2 H_{ic}^2}{\hbar v_r \frac{\partial}{\partial r} (V_{cov} - V_{ion})} \right\}$
\[ \text{Potential Energy (10^3 cm}^{-1}) \]

\[ \text{Internuclear Separation (Å)} \]

\[ \text{Na}^* + \text{I} \]