

# CSO202—Atoms, Molecules & Photons

## Quiz – 1 (MM: 15)

(Aug. 30 2024, 9:00 AM – 9:30 AM, L2 & L4)

1. In the hard sphere reactive collision model, the collision cross section ( $\sigma$ ) and the radii of the colliding atoms or molecules ( $r_1$  and  $r_2$ ) are important in deciding the nature of the reaction. For the reaction to be of the rebound type, what would be the required relationship between  $\sigma$ ,  $r_1$ , and  $r_2$ ?

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**Ans.** For the reaction to be of the rebound type:  $\sqrt{\frac{\sigma}{\pi}} < (r_1 + r_2)$ , for all  $r_1$  and  $r_2$ .

2. The concentric circles in the Newton Diagram correspond to the maximum expected speeds for the product molecule in the specific vibrational state (e.g.,  $v = 0, 1$ , etc.) when the rotational quantum number,  $J = 0$ . What would be the change in the radius ( $r$ ) of the product distribution for any specific concentric circle (consider the  $v = 0$  case), when the relative translational energy of the reactants is doubled?

2

**Ans.** Radius ( $r$ ) will increase by  $\sqrt{2}$

3. Consider the Reaction-1:  $O(g) + Br_2(g) \rightarrow BrO(g) + Br(g)$ , where Newton's diagram is largely symmetric in both hemispheres.

This contrasts with Reaction-2:  $K(g) + I_2(g) \rightarrow KI(g) + I(g)$ , where Newton's diagram is in the forward direction for the relative translational energy of the reactants is  $15.13 \text{ kJ.mol}^{-1}$ . Based on this, fill in the blacks in the following statements:

- a. Reaction-1 is an example of \_\_\_\_\_ (1) \_\_\_\_\_ reaction, where the reaction progresses through an intermediate that rotates many times before the product formation and thus the distribution is \_\_\_\_\_ (2) \_\_\_\_\_.

2

**Ans.** (1) long-lived complex; (2) independent of their initial collision geometry

- b. Reaction-2 is an example of \_\_\_\_\_ (1) \_\_\_\_\_ reaction where the reaction cross section is larger than the collision impact parameter and is dominated by \_\_\_\_\_ (2) \_\_\_\_\_.

2

**Ans.** (1) stripping reaction; (2) forward scattering

4. Consider an ultrafast Ti:Sapphire laser operating at 76 MHz, with a pulse width of 6 fs centered at a wavelength of 800 nm. Measuring such a short pulse is only possible if it is correlated with itself. You could treat the laser to output TEM<sub>00</sub> mode and the temporal profile to be Gaussian so that it follows the condition for transform-limit as:  $\Delta\nu \cdot \Delta t = 0.44$ .

- a. What is the spectral bandwidth  $\Delta\lambda$  (in nm) of this laser around 800 nm under the transform-limited condition?

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$$\text{We know: } \nu\lambda = c; \quad \Rightarrow \quad \nu = \frac{c}{\lambda}$$

$$\text{i. e. } \Delta\nu = -\frac{c}{\lambda^2} \Delta\lambda$$

Thus, Spectral Bandwidth Value is related to frequency width as :  $\Delta\lambda = \frac{\lambda^2}{c} \Delta\nu$

For a transform-limited Gaussian Pulse:  $\Delta\nu \cdot \Delta t = 0.44$ ;  $\Rightarrow \Delta\nu = \frac{0.44}{\Delta t}$

For a  $\Delta t = 6 \text{ fs}$  pulse centered at  $\lambda = 800 \text{ nm}$ , Spectral Bandwidth,  $\Delta\lambda = \left(\frac{\lambda^2}{c}\right) \left(\frac{0.44}{\Delta t}\right) =$

$$\frac{(8 \times 10^{-7})^2}{3 \times 10^8} \left(\frac{0.44}{6 \times 10^{-15}}\right) = 0.1956 \times 10^{-7} \text{ m} = 156.48 \text{ nm}$$

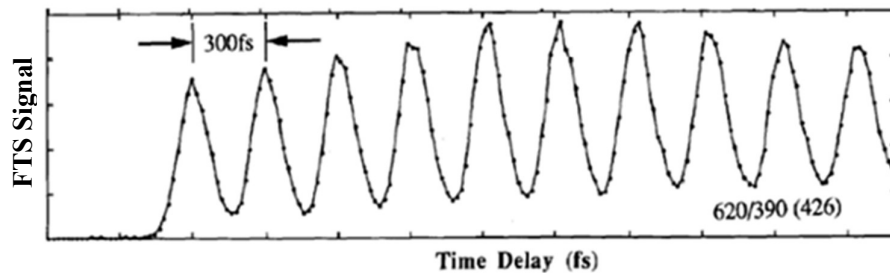
Now let us consider how the spectral bandwidth (in nm) would change if we examine the CPM laser used by Zewail, which has a center wavelength of 600 nm. So, specifically:

- b. What would the spectral bandwidth value (in nm) be if the center wavelength of the laser is 600 nm while maintaining the same pulse width of 6 fs?

1

$$\text{For a } \Delta t = 6 \text{ fs pulse centered at } \lambda = 800 \text{ nm, Spectral Bandwidth, } \Delta\lambda = \left(\frac{\lambda^2}{c}\right) \left(\frac{0.44}{\Delta t}\right) = \frac{(6 \times 10^{-7})^2}{3 \times 10^8} \left(\frac{0.44}{6 \times 10^{-15}}\right) = 0.088 \times 10^{-7} \text{ m} = 88 \text{ nm}$$

5. In the Femtosecond Transient Spectroscopy (FTS) of  $\text{I}_2$  photodissociation studied by Zewail's group, the observed fluorescence showed oscillations in time as follows:



2

Estimate the fundamental vibrational wavenumber (in  $\text{cm}^{-1}$ ) of  $\text{I}_2$  as per this observed oscillatory fluorescence signal.

Ans.

fundamental vibrational  
wave number  $= \bar{\nu} = 1/\lambda = \frac{\nu}{c}$   
 $= \frac{1}{\tau c}$

Given that  $\tau = 300 \text{ fs}$   
 $c = 3 \times 10^8 \text{ ms}^{-1}$

then,  $\bar{\nu} = \frac{1}{300 \times 10^{-15} \times 3 \times 10^8 \times 10^{-2}} \text{ cm}^{-1}$

$\boxed{\bar{\nu} = 111 \text{ cm}^{-1}}$

OR

$\bar{\nu} = f/c$

$\Rightarrow \bar{\nu} = \frac{10^{15}}{300 \times 3 \times 10^8} \text{ m}^{-1}$

$= \frac{10^5}{9} \text{ m}^{-1} = \frac{10^3}{9} \text{ cm}^{-1}$

$\bar{\nu} = \frac{10^3}{9} \text{ cm}^{-1} = 111.11 \text{ cm}^{-1}$

$f = \frac{1}{300 \text{ fs}} = \frac{10^{15}}{300} \text{ sec}^{-1}$   
 $c = 3 \times 10^8 \text{ m/s}$

6. PhotoActivated Localization Microscopy (PALM) allows obtaining images with a resolution beyond the diffraction limit. Developed by Eric Betzig and William E. Moerner around the year 2000, it was one of the two techniques awarded the 2014 Nobel Prize in Chemistry. The STimulated Emission Depletion (STED) microscopy developed by Stefan Hell as early as 1994, was the other technique chosen for the 2014 Chemistry Nobel Prize. Give at least one specific similarity and one specific difference between these two super-resolution techniques.

**Ans.** Any of the following bulleted point pairs can be treated as the possible solution (one from Similarly & one from Dissimilarity):

#### **SIMILARITY**

- Both the super-resolution techniques are limited by the photobleaching of the fluorophores used.
- Both use fluorescent dyes

#### **DISSIMILARITIES**

- PALM method uses mathematical models to reconstruct a sub-diffraction-resolved image from many sets of diffraction-limited images while STED achieves its super-resolution by directly modifying the point spread function (PSF) through structured illumination.
- PALM requires data processing for offline localization resulting in super-resolution while for STED no data-processing post-measurement is needed as the raw data is final
- STED microscopy is a point scanning confocal-based technique while the PALM method is a widefield technique with random laser activation of fluorophores
- STED modifies the point spread function (PSF) and enhances the achievable resolution while PALM is a widefield fluorescence microscopy imaging method in contrast to point scanning techniques, such as laser scanning confocal microscopy
- STED utilizes a deterministic functional technique that exploits the non-linear response of fluorophores while PALM is based on the principle of separation of individual emitters in time to determine their precise positions
- STED uses the selective deactivation of fluorophores while PALM exploits the stochastic blinking phenomena of fluorophores like the Green Fluorescent Proteins (GFP)
- STED minimizes the area of illumination at the focal point while for PALM, Photo-convertible fluorescent proteins are able to change their fluorescence emission spectrum from one maximum to another
- The achievable resolution in the STimulated Emission Depletion (STED) microscopy is highly dependent on the laser intensities used in this microscopy while for PALM, Photo-switchable fluorescent proteins can be switched “on and off” with the help of light pulses of two different wavelengths
- For PALM, Photo-activatable fluorescent proteins can be switched “on” from a nonfluorescent state to a fluorescent state in the blue ultraviolet spectrum while the achievable resolution in the STimulated Emission Depletion (STED) microscopy could be theoretically unlimited for a sufficiently powerful depletion laser that induces stimulated emission