# CSO202A: Atoms, Molecules, & Photons

Instructors:

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| CSO202A<br>3-1-0-0<br>SO | | Atoms, Molecules, and Photons | D. Goswami (I/C)<br>P. Sen | MWTh<br>12:00-12:50<br><br>Tutorial<br>F 17:10-18:00 |

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| Release of First Course Handout | January 12, 2021 |
| Online Classes Commence | January 13, 2021 |
| Adding a Course | January 13-19, 2021 |
| Mid Sem Recess | February 28-March 4, 2021 |
| Last date for Dropping/De-registration of Regular Courses and Modular Courses (Second Half) | April 15, 2021 |
| Classes End | April 30, 2021 |
| Mid Semester Examination | February 21-27, 2021 |
| End Semester Examination | May 3-12, 2021 |

Working days for the Semester are as follows:

M: 13 (12+ 1 Sat, January 30, 2021), T: 13 (12+1 Sat, March 13, 2021), W: 13, Th: 14, F: 14

**Lecture Hours:** ~36 (UPLOADED PERIODICALLY ONLINE)

**Evaluation:**

**Assignments**: 20%
**Midsem**: 40%
**Endsem**: 40%

**Note**: Given the prevailing uncertainties, evaluation procedures might get modified as per Institute advisory from time to time.

**Reference text**: Nobelprize.org: Nobel Prizes in Chemistry 1986, 1999, 2007, 2014; *G. Scholes*: Atomic and Molecular Beam Methods: Volume 1; Oxford University Press (1988); *McQuarrie & Simon*, Physical Chemistry - a molecular approach. Our library has a few copies. Note though that this course has no official text, the instructors will provide reading material/notes from time to time and point our relevant internet resources for additional help.

**Homework**: A few homeworks, appropriately dispersed throughout the semester, will be provided. These need not be turned in! Discussion of the solutions will be done during tutorial hours.

**Assignments**: Each module will end with an assignment that needs to be submitted for evaluation.

## Objective

Convey the excitement of modern physical chemistry through presenting and analyzing some of the key experiments. What concepts are needed to understand the experiments and their impact?

1. Diversity of chemical reactions - gas phase, on surfaces, and in solutions.
2. Timescales, length scales, and energetics.

## Modules

Following modules will be covered:

- Dynamics of elementary reactions in gas phase. Focus on molecular beam experiments for which Herschbach, Lee, and Polanyi got the Nobel in 1986. Illustrate the key concepts using the the elementary atom molecule reactions. History goes back to Arrhenius, if not earlier, Hinshelwood, Semenov, Norrish, Porter, etc. Collisions, rates, and models.
- Ultrafast reactions – Femtochemistry: Zewail's (Nobel prize 1999) work on transition states – "measuring the immeasurable" (nuclear motions). Focus on bond breaking in the ICN molecule.
- Reactions on surfaces. Focus on the key insights coming from Ertl's (Nobel prize 2007) landmark experiment on the important Haber process of $NH_3$ synthesis.
- As it would have become apparent from the earlier modules, the ability to observe better and better with higher detail is also a key part of understanding chemistry. "Seeing the unseen" led to the 2014 Nobel prize in super-resolution microscopy that was awarded jointly to Eric Betzig, Stefan W. Hell and William E. Moerner "for the development of super-resolved fluorescence microscopy." We will focus on how the fundamental "diffraction-limit" barrier was circumvented to achieve the super-resolution.

## Game plan

1. Total of about 9 lectures per module (flexible).
2. First lecture is a presentation - experiment, history, importance, breakthrough,..
3. Remaining lectures building concepts required to understand outcome of the experiment.

## MODULE I - Dynamics of elementary gas phase reactions

Focussing on a few classic developments [Polanyi JCP 54, 2410 (1971); Lee JCP 82, 3067 (1985); Herschbach JCP 51, 1439 (1969)]

- Molecular beams, collision theory, crude hard sphere model - what radii to choose?
- Energetics - exothermic or endothermic? Do rates depend on internal quantum states of the reactants? Partitioning of total energy into collision and internal energies.
- *Potential energy diagram, accurate ground electronic states of some systems with many electrons, their dissociation energy, diatomic rovibrational energy levels – importance of anharmonicity and rotational-vibrational couplings. Spectroscopy (microwave, IR & photoelectron) reveals the necessary data? How accurate is theory?*
- *Potential energy surface - how is it obtained? Difficulties? Born-Oppenheimer approximation, term symbols and notation.*
- Energy and momentum conservation, relative and center of mass motion, velocity diagrams.
- On the Boltzmann distribution of internal states of a diatomic molecule.
- On the breakdown of Born-Oppenheimer (BO) principle in an elementary reaction.
- What do we learn about the mechanism? Any surprises? Is classical mechanics helpful? Quantum effects? (non BO, zero-point energies,...)

## MODULE II - Ultrafast reactions: Femtoscale & clocking the Transition states

Focusing on the classic experiments [Dantus et al. JCP 87, 2395 (1987) & Rose et al. JCP 88, 6672 (1988). First one on ICN and the second one on NaI.]

- Timescales & length scales - importance of femtosecond spectroscopy.
- Concept of transition states - figment of imagination? Convenient notion or reality?
- *Potential surfaces of diatomics - bound, repulsive etc. Crossing and violation of Born-Oppenheimer in case of NaI. Covalent versus ionic channels of dissociation. Extent of covalent/ionic mixing of a diatomic MO (Coulson level description).*
- *Structure and bonding in the linear triatomic ICN. Bond strengths - why break the I--C bond?*
- Lasers - pump and probe. Detection of the laser induced fluorescence - why and how? To pulse or not to pulse? Notion of coherence.
- Concept of wavepackets, Franck-Condon excitation - classical and quantum models for the bond breaking process. Connection to the time-domain spectroscopy and time-dependent Schroedinger equation.

## MODULE III - Reactions on surfaces

Focusing on the classic experiments of Gerhard Ertl [Nobel lecture & Angew. Chem. 29, 1219 (1990)].

- Introduction to ammonia synthesis - thermodynamics & Haber-Bosch process.
- Concept of heterogeneous catalysis - what are the elementary steps? Langmuir’s work, chemisorption and introduction to surfaces.
- *Bonding in $N_2$ and $NH_3$ - energetics of surface catalyzed reactions. How surface breaks the strong $N_2$ bond?*
- *Experimental techniques - photoelectron spectroscopy, etc.*
- Molecular level understanding of the reaction - dynamics?.

## MODULE IV – Super-resolved fluorescence microscopy

Focusing on a few classic developments [Hell Opt. lett. 19, 780 (1994); Betzig Science 313, 1642 (2006); Moerner PNAS 104, 12596 (2007)].

- Concept of ‘diffraction limit’ or the Abbe limit in optical microscopy.
- *First approach use patterned illumination to spatially modulate the fluorescence behavior of molecules within a diffraction-limited region, such that not all of them emit simultaneously, thereby achieving subdiffraction limit resolution.*
- *Second approach is of single-molecule imaging, using photoswitching or other mechanisms to stochastically activate individual molecules within the diffraction-limited region at different times.*
- *Images with subdiffraction limit resolution are then reconstructed from the measured positions of individual fluorophores*
- Understanding these concepts of Super-Resolution Fluorescence Microscopy by Single-Molecule Switching or through structured illumination and their limitations, if any.