Lecture #1 of 12

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

Welcome to CHEM 267!

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This course was *brand new* at UC Irvine last time I taught it two years ago… by Zoom! Thus, the slides contained in this slide deck have been fine-tuned once, but will still evolve as the course progresses, and so, while I cannot tell you how many slides there will be in this slide deck (probably 300 – 400), what I can tell you is that… **it is going to be awesome!**

Hey Look! Slides numbers.

Helpful Pre-(non-)requisite Topics

Chemistry
- Thermodynamics
- Quantum Mechanics
- Kinetics
- Statistical Mechanics
- Electrochemistry

Physics
- General Physics
- Electricity & Magnetism
- Condensed Matter (Solid-State) Physics

Chemical Engineering
- Transport Phenomena

Materials Science and Engineering
- Theory of Diffusion
- Materials Physics

Our Calendar: **(UPDATED)** 3

Lecture Sections (7+1/10) *(Tuesdays @ 9:30-10:50am)*	**Lecture Sections (5+1/10)** *(Thursdays @ 9:30-10:50am)*	**Discussion Sections (8+1/10)** *(Fridays @ 11-11:50am)*
April 4	April 6	April 7
~~April 11~~	~~April 13~~	~~April 14~~
April 18	April 20	April 21
April 25	April 27	April 28
May 2	~~May 4~~	May 5 *(remote, or guest)*
May 9	~~May 11~~	May 12
May 16	~~May 18~~	May 19 *(remote, or guest)*
~~May 23~~	May 25	May 26
May 30	June 1	June 2
June 6 *(remote; presentations)*	June 8 *(remote; presentations)*	June 9 *(remote; presentations)*

Final Examination Period (0/1)
~~Thursday, June 15 @ 8-10am~~

… equals ~8 weeks worth of classes… out of 10

Our Syllabus: Chem 267: Photochemistry (http://www.chem.uci.edu/~ardo/photochem.html) 4

Department of Chemistry, UC Irvine, Spring 2023 *Version Date: 2023.04.03*

Instructor Professor Shane Ardo (ardo@uci.edu)
Office Hours: Mon. @ 8 – 9 am *(all remote via Zoom, through and including M5/8)*

Meeting Times
Lecture: T/Th @ 9:30 – 10:50 am in SSTR 101 *(no class on T4/11, Th4/13, Th5/4, Th5/11, Th5/18, T5/23; Zoom link should be used when feeling ill; video-recorded lectures available)*
Discussion: Fri. @ 11 – 11:50 am in HICF 100N *(remote on F5/5, F5/19 via Zoom; no class on F4/14)*
(Presentations: Last *three* meeting periods *(remote on T6/6, Th6/8, F6/9 via Zoom))*

Course Objectives
- To understand and explain the theory behind fundamental photophysical and photochemical processes
- To be able to design, perform, troubleshoot, and analyze photochemical experiments and data
- To quantitatively and qualitatively assess problems, and empirical data from the peer-reviewed literature
- To summarize and explain seminal and recent photochemical peer-reviewed literature and processes

Required Resources
Chemistry and Light by Paul Suppan (https://books.rsc.org/books/monograph/1222/Chemistry-and-Light/)
ISBN: 978-0-85186-814-1; *plus supporting information from other textbooks*
Peer-Reviewed Journal Articles and Additional Problems (http://www.chem.uci.edu/~ardo/photochem.html)

Grading *(10% of lowest score will be dropped, leaving 90% for course grade determination)*
30% *Synchronous Participation*: journal article reading and critical assessments
20% *Asynchronous Exam A* (*24 hours*; available Wed. 5/10 @ noon *through* Thurs. 5/18 @ noon)
30% *Asynchronous Exam B* (*24 hours*; available Sat. 6/10 @ noon *through* Sun. 6/18 @ noon)
20% *Synchronous e-Presentation* (~15 min per student; occurs during the last week of classes (Tues. 6/6, Thurs. 6/8, *and* Fri. 6/9))

Discussion Sessions provide opportunities to discuss important works in photochemistry… 5

… of course, there are way too many to cover, but I decided on the following as the tentative list:

(1) **F4/7**: "Generalised Förster cycle. Thermodynamic and extrathermodynamic relationships between proton transfer, electron transfer and electronic excitation", ZR Grabowski & W Rubaszewska, *J. Chem. Soc., Faraday Trans. 1*, **1977**, *73*, 11, DOI: 10.1039/F19777300011

(2) **F4/21**: "Understanding Multi-Ion Transport Mechanisms in Bipolar Membranes", JC Bui, I Digdaya, C Xiang, AT Bell & AZ Weber, *ACS Appl. Mater. Interfaces*, **2020**, *12*, 52509, DOI: 10.1021/acsami.0c12686

(3) **F4/28**: "The Application of the Marcus Relation to Reactions in Solution", WJ Albery, *Ann. Rev. Phys. Chem.*, **1980**, *31*, 227, DOI: 10.1146/annurev.pc.31.100180.001303

(4) **F5/5**: "Free Energy and Temperature Dependence of Electron Transfer at the Metal-Electrolyte Interface", CED Chidsey, *Science*, **1991**, *251*, 919, DOI: 10.1126/science.251.4996.919

(5) **F5/12**: "Nuclear, electronic, and frequency factors in electron transfer reactions", N Sutin, *Acc. Chem. Res.*, **1982**, *15*, 275, DOI: 10.1021/ar00081a002

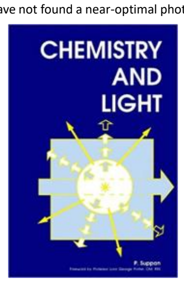
(6) **F5/19**: "Direct observation of triplet energy transfer from semiconductor nanocrystals", C Mongin, S Garakyaraghi, N Razgoniaeva, M Zamkov, FN Castellano, *Science*, **2016**, *351*, 369, DOI: 10.1126/science.aad6378

(7) **F5/26**: "Kinetics of Fluorescence Quenching by Electron and H-Atom Transfer", D Rehm & A Weller, *Isr. J. Chem.*, **1970**, *8*, 259, DOI: 10.1002/ijch.197000029

(8) **F6/2**: "Solar Fuels", JR Bolton, *Science*, **1978**, *202*, 705, DOI: 10.1126/science.202.4369.705

Our Textbook: 6

I have not found a near-optimal photochemistry textbook, and so for this year, we will use an online one



Other useful textbook resources:

- "Principles of Molecular Photochemistry", 1st edition, **2008**, ISBN: 978-1891389573, by NJ Turro, V Ramamurthy, JC Scaiano
- "Principles of Fluorescence Spectroscopy", 3rd edition, **2006**, ISBN: 978-0387312781, by JR Lakowicz
- "Solar Cell Device Physics", 2nd edition, **2010**, ISBN: 978-0123747747, by S Fonash
- "Physics of Solar Cells: From Basic Principles to Advanced Concepts", 3rd edition, **2016**, ISBN: 978-3527413126, by P Würfel & U Würfel

https://books.rsc.org/books/monograph/1222/Chemistry-and-Light

Our Syllabus (continued): 7

Topics Covered *(tentative)*

- **W1-2** **Review+** (Förster cube, Square schemes, Schrödinger equation, Internal energy, Free energy, Chemical potential, Equilibrium, Solid-state physics, Continuity of mass, Mass action, Microscopic reversibility, Activation energy, Rate-determining step, Mass transfer / Transport, Steady state)
- **W3-4** **Thermal Reactions** (Eyring–Polanyi–Evans equation, Marcus–Hush theory, Transition-state character, Reorganization energy, Linear free energy relationships, Huang–Rhys factor, Tunneling, Superexchange, Outer/inner sphere, Robin–Day classification, Self-exchange reactions, Marcus cross relations, Butler–Volmer equation, Fermi's golden rule, Marcus–Gerischer theory)
- **W5-6** **Photophysics** (Blackbody radiation, Photon properties, Conservation laws, Einstein coefficients, Jablonski diagram, Nuclear terms, Spin multiplicity, Internal conversion, Intersystem crossing, Thexi state, Kasha–Vavilov rule, Stokes shift, Franck–Condon principle, Transition dipole moment operator, Beer–Lambert law, Luminescence processes, Selection rules, Spin–orbit coupling, Heavy atom effect, E–k diagrams, Jortner energy gap law, Conical intersections, Energy transfer processes, Exciplex/Excimer, Photoluminescence spectroscopy, Inner filter effects, Emission quantum yield)
- **W7-8** **Photochemistry** (Excited-state electron/proton transfer, Förster cycle, Stern–Volmer static and dynamic quenching, Rehm–Weller equation, Diffusion-limited processes, Length/Time scales, Electromagnetic spectrum, Pump–probe transient spectroscopies, Statistical mechanics distributions, Detailed balance analysis, Photoelectrochemistry, Load line analysis)

… now let's briefly peruse our course websites: https://www.chem.uci.edu/~ardo/photochem.html

Course Policies

Late assignments and make-up exams are not accepted, although *I will regrade exams upon specific request*.
Add/Drop Info (use WebReg): https://www.reg.uci.edu/calendars/quarterly/2022-2023/quarterly22-23.html
UCI Chemistry Enrollment-Related Questions: https://www.chem.uci.edu/studentaffairs/, or chemistry@uci.edu
UCI Laptop Requirements for Students: https://www.oit.uci.edu/undergrads/laptop-requirements-students/
UCI Policy on Academic Integrity and Honesty: https://aisc.uci.edu/policies/academic-integrity/
UCI School of Physical Sciences COVID-19 Student Resources: https://uci.edu/coronavirus/students/

UCI CHEM267 – Photochemistry, Spring 2023 8

Introduction and Review of Physical Chemistry

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

Review of Physical Chemistry

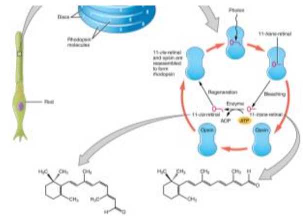
(UPDATED) 9

- **Photochemical applications**
- **Förster cube, Square schemes**
- Thermodynamics *versus* Kinetics
- Schrödinger equation, Internal energy
- Free energy, (Electro)Chemical potential, Equilibrium
- Solid-state physics terminology
- Continuity of mass
- Mass action, Microscopic reversibility
- Activation energy, Rate-determining step
- Mass transfer, Transport, Steady state

Q: What constitutes a photochemical process? 10

A: When non-thermal-equilibrium radiation interacts with matter (photophysics) to break bonds, make bonds, or perform electron transfer

Example: vision

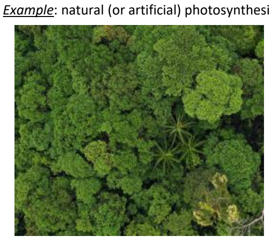


https://en.wikipedia.org/wiki/Visual_phototransduction#/media/File:1415_Retinal_Isomers.jpg

Q: What constitutes a photochemical process? 11

A: When non-thermal-equilibrium radiation interacts with matter (photophysics) to break bonds, make bonds, or perform electron transfer

Example: natural (or artificial) photosynthesis

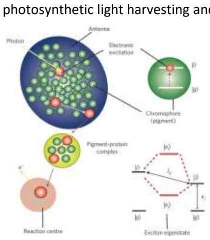


https://imgs.mongabay.com/wp-content/uploads/sites/20/2020/04/10171310/amazon_201634.jpg

Q: What constitutes a photochemical process? 12

A: When non-thermal-equilibrium radiation interacts with matter (photophysics) to break bonds, make bonds, or perform electron transfer

Example: photosynthetic light harvesting and reacting

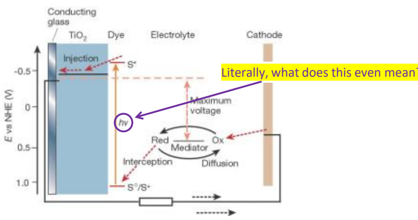


https://qph.fs.quoracdn.net/main-qimg-99e540c2a149edae724c2a02641aa62c.webp

Q: What constitutes a photochemical process? **(UPDATED)** 13

A: When non-thermal-equilibrium radiation interacts with matter (photophysics) to break bonds, make bonds, or perform electron transfer

Example: dye-sensitized solar cell

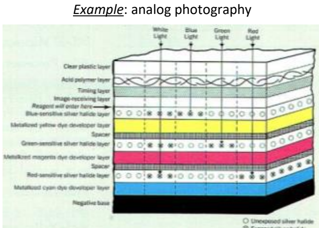


https://www.nature.com/articles/35104607

Q: What constitutes a photochemical process? 14

A: When non-thermal-equilibrium radiation interacts with matter (photophysics) to break bonds, make bonds, or perform electron transfer

Example: analog photography

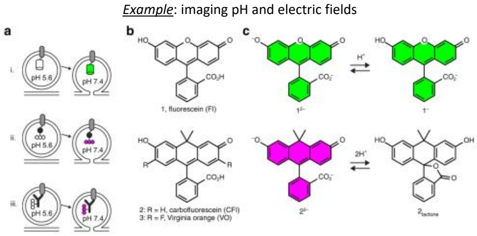


https://claresleamingblog.files.wordpress.com/2011/10/film.jpg

Q: What constitutes a photochemical process? 15

A: When non-thermal-equilibrium radiation interacts with matter (photophysics) to break bonds, make bonds, or perform electron transfer

Example: imaging pH and electric fields



https://www.nature.com/articles/s41467-017-01752-5

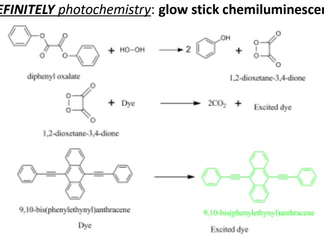
Q: What constitutes a photochemical process? 16
A: When non-thermal-equilibrium radiation interacts with matter (photophysics) to break bonds, make bonds, or perform electron transfer

__MAYBE photochemistry__: glow-in-the-dark scorpion… *__definitely photophysics__*!

https://glitchmind.com/scorpions-glow-beautifully-under-uv-light/

Q: What constitutes a photochemical process? 17
A: When non-thermal-equilibrium radiation interacts with matter (photophysics) to break bonds, make bonds, or perform electron transfer

__DEFINITELY__ *__photochemistry__*: **glow stick chemiluminescence!**



https://www.compoundchem.com/2014/10/14/glowsticks/

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so we can already conclude that photochemistry...

… is super cool *(just like electrochemistry!)*

… is quite diverse, and thus requires a wide range of chemistry, physics, and biological knowledge

… is at the heart of some very interesting, and still unexplained, scientific observations

… opens up many opportunities to innovate on new ideas and technologies

… yet is often an underexplored area of scientific endeavor

… I am not sure why this is the case

… but by being here, we are each doing something to change that!

… wow, those were some neat examples of photochemistry… **(UPDATED)** 19

… I wish I could learn more about all of them!

… Lucky you! … Lucky us!

- Synchronous e-presentation: 12 min max + 3 min for Q&A, as 6 – 8 slides *emailed to me the day before the presentation*
- One seminal and/or review publication (~70% of the time); include background and the nitty gritty of how it works; **your main goal should be to bridge information presented in the course to your topic, and to teach us something entirely new**
- One recent publication (within the last 5 years) (~30% of the time); include what the paper did, the major discovery, and a critical photochemical assessment of their data interpretation, **including at least one graph or plot of useful data**!

… this, plus discussion participation, equal 50% of your course grade, so take them seriously, but HAVE FUN!

e-Presentation… topics… include… 20

- silver-halide photography
- photolithography
- vision
- vitamin D synthesis
- ultraviolet-light-driven DNA dimerization
- natural photosynthetic ion pump
- natural photosynthetic light-harvesting complex and coherent energy transfer
- natural photosynthetic Z-scheme electron-transport chain
- nanoparticle solar fuels photocatalysis
- dye-sensitized solar cells
- excitonic solar cells with trap states
- dye lasers
- medical applications
- fluorescence microscopy pH sensing
- fluorescence microscopy electric field sensing
- long-lived phosphorescence by organic molecules
- persistent luminescence by lanthanide-doped phosphors
- chemiluminescence
- photoredox catalysis in organic synthesis
- photolabile organic radicals
- atmospheric chemistry in the ozone layer with refrigerants
- photolabile inorganic coordination compounds
- light-induced excited spin-state trapping (LIESST) spin-crossover effect
- molecular solar thermal energy storage (MOST)
- triplet-triplet annihilation upconversion
- hot/ballistic excited-state electron transfer

… **or propose your own to me**… but I really do prefer topics from this list

You will get one of your top 5 choices… more info to come later in the quarter

Course goal, i.e. the best 2-hour-long final-exam question *ever*! 21

Q: Explain processes in natural photosynthesis.

W1-2 **Review+** (Förster cube, Square schemes, Schrödinger equation, Internal energy, Free energy, Chemical potential, Equilibrium, Solid-state physics, Continuity of mass, Mass action, Microscopic reversibility, Activation energy, Rate-determining step, Mass transfer / Transport, Steady state)
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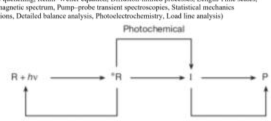
W7-8 **Photochemistry** (Excited-state electron/proton transfer, Förster cycle, Stern–Volmer static and dynamic quenching, Rehm–Weller equation, Diffusion-limited processes, Length/Time scales, Electromagnetic spectrum, Pump–probe transient spectroscopies, Statistical mechanics distributions, Detailed balance analysis, Photoelectrochemistry, Load line analysis)

From syllabus



Turro, Chapter 2, Scheme 2.1, Page 40

Course goal, i.e. the best 2-hour-long final-exam question *ever*!

22

Q: Explain processes in natural photosynthesis.

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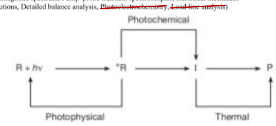
From syllabus



Turro, Chapter 2, Scheme 2.1, Page 40

<u>Course philosophy</u> (me *versus* you)

Theory/Experiments *versus* **Innovations/Processes**

I will teach the theory, history, and experimental specifics, and you will teach details of the innovations and interesting applications

Today's Critical Guiding Question

(UPDATED) 23

What are the most common particles involved in photochemical transformations, and how can we think about their thermodynamic properties and kinetic processes on an equal footing?

Förster Cube and Square Schemes

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Generalised Förster Cycle

Thermodynamic and Extrathermodynamic Relationships Between Proton Transfer, Electron Transfer and Electronic Excitation

By Zbigniew R. Grabowski* and Wiesława Rubaszewska

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland

Received 26th April, 1976

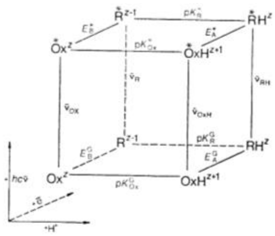
The thermodynamic quantities characterizing one electron reduction, protonation and electronic excitation, are mutually related in the ground and excited states by 6 thermodynamic (or approximate thermodynamic) cycles. The system of cycles is used to predict unknown values, and its validity may be extended to other compounds by means of extra thermodynamic (*e.g.*, Hammett-type) relations. Examples of known data concerning pK and pK^* values of protolytic equilibria for the oxidized (Ox) and reduced (R) species are evaluated, tabulated and discussed in a search for a correlation between the changes of pK on excitation (ΔpK^*) and on reduction (ΔpK_e). Both values are thermodynamically independent but a general common trend is empirically observed in several groups of systems. Some rules are derived for the excited state redox potentials and their dependence on pH, which may be useful for photochemistry.

Pre-reading assignment for first discussion session on Friday

Z. R. Grabowski & W. Rubaszewska, *J. Chem. Soc. Faraday Trans. 1*, **1977**, *73*, 11–28

Förster Cube and Square Schemes

25



Questions to ponder… NOW!

What do the thermodynamic parameters E, pK, and $\bar{\nu}$ represent?

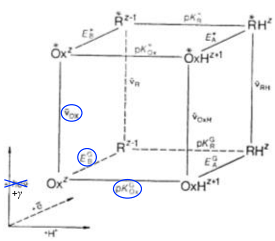
How are they related?

What is the reference state for each?

Z. R. Grabowski & W. Rubaszewska, *J. Chem. Soc. Faraday Trans. 1*, **1977**, *73*, 11–28

Förster Cube and Square Schemes

(UPDATED) 26



Questions to ponder… NOW!

What do the thermodynamic parameters E, pK, and $\bar{\nu}$ represent?

- $E = E^{o}$ (standard-state reduction potential)
- $pK = pK_a = -\log K_a$ (acid dissociation constant)
- $\bar{\nu} = \frac{1}{\lambda}$ (wavenumber)

How are they related?

- **Redox:** $E^{o} = -\Delta G^{o}/nF$
- **Acidity:** $pK_a = -\log K_a = \Delta G^{o}/(2.303RT)$ ← ln 10
- **Light:** $hc\bar{\nu} = \frac{hc}{\lambda} = h\nu = E_{photon}$

What is the reference state for each?

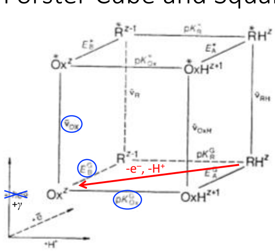
- $E^{o}(H_3O^+(aq)/H_2) = 0$; $pK_a(H_3O^+(aq)) = 0$; 0

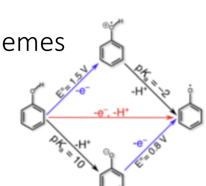
… let's backtrack a bit… before we add light…
… one must understand dark thermal processes…

E. C. Meister, M. Willeke, W. Angst, A. Togni & P. Walde, *Helv. Chim. Acta*, **2014**, *97*, 1–31
T. P. Silverstein & S. T. Heller, *J. Chem. Educ.*, **2017**, *94*, 690–695

Förster Cube and Square Schemes

27





Does this obey Hess' law?

- **Redox:** $E^{o} = -\Delta G^{o}/nF$
- **Acidity:** $pK_a = -\log K_a = \Delta G^{o}/(2.303RT)$
- **Thus,** $E^{o} = -pK_a \times (2.303RT/nF) = -59.2\text{mV} \times pK_a$

Does Bottom Route = Top Route?

- -0.0592V(10) + –0.8V = –1.5V + -0.0592V(-2)**?**
- -0.59V + -0.8V ≈ -1.5V + 0.12V… so, ~yes!

… anyway… but is the concerted path possible?

R. Tyburski, T. Liu, S. D. Glover & L. Hammarström, *J. Am. Chem. Soc.*, **2021**, *143*, 560–576

Förster Cube and Square Schemes

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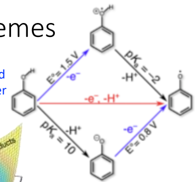

... oh, I see... by moving oppositely charged species in a concerted fashion, electrostatic (Born solvation) energy will be much smaller

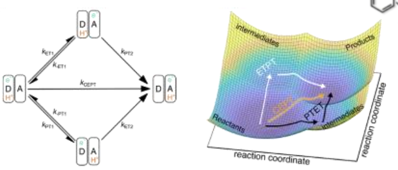

Figure 2. (Left) Square scheme that summarizes the mechanisms by which proton-coupled electron transfer can proceed. The edges of the square show the sequential mechanisms with ETPT and PTET on the top and bottom, respectively. The pathway bisecting the square is concerted, where e^- and H^+ are transferred without the formation of an intermediate species. Note that the donor and acceptor units for ET and PT can be the same or different species. (Right) Illustration of the three main mechanisms for PCET, each with a distinct transition state.

... and this can constitute a ground-state, or excited-state, free energy landscape (potential energy surface)

R. Tyburski, T. Liu, S. D. Glover & L. Hammarström, *J. Am. Chem. Soc.*, **2021**, *143*, 560–576