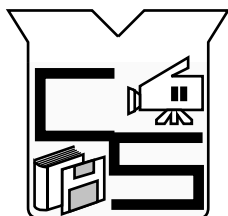
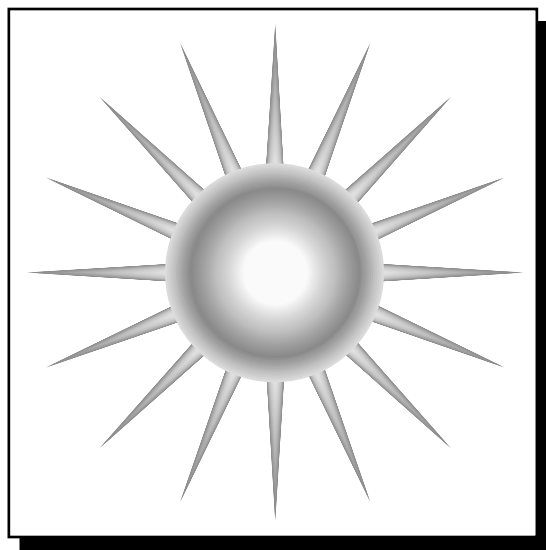


A SourceBook Module

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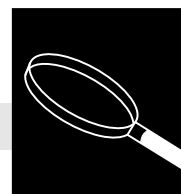


ChemSource

*Instructional Resources for Preservice and
Inservice Chemistry Teachers*

PHOTOCHEMISTRY

Topic Overview



CONTENT IN A NUTSHELL

This module emphasizes the importance of photochemical reactions and related background material necessary to understand their importance and nature. The concepts of color based on the absorption or emission of photons of specific wavelengths, of light initiating chemical reactions (sometimes unique ones) or electron flow in solid state devices, of chemical reactions producing light, of fluorescence and phosphorescence, and of quantum yields are all part of the module. Practical aspects of photochemistry include lasers, solid state solar energy devices, fluorescent lights, fabric whiteners, and new dental polymers, to name just a few. Photosynthesis is one of the most desirable photochemical reactions; ozone depletion and smog are among the least desirable. The photochemistry associated with these processes is included in this module.

PLACE IN THE CURRICULUM

This is an optional module for late in the school year, possibly after material supported by the *Reaction Rates* module is covered, although parts of the module could be used earlier as desired.

CENTRAL CONCEPTS

1. Color depends upon the selective absorption of photons (light quanta) of different wavelengths by chromophores, *i.e.*, chemical groups that absorb light. Emission of photons at specific wavelengths can also produce color. Visible light consists of photons with wavelengths between about 400-700 nm (or wavenumbers between 25,000-14,000 cm^{-1}); similar electromagnetic radiation occurs at both higher energies (<400 nm: ultraviolet, X-rays, and gamma-rays) and lower energies (>700 nm: infrared, microwave, and radiowaves).
2. Light can initiate chemical reactions by providing excited state molecules (or ions) that have sufficient energy to overcome the activation energy of the analogous thermal reactions (*e.g.*, the violent reaction that produces HCl from H_2 and Cl_2 in the presence of light). (See *Laboratory Activity 1* and *Demonstration 3*.)
3. Light activation can alter the pathways of chemical reactions, *i.e.*, provide alternate pathways to thermal reactions, different products by irradiation at different wavelengths, and the energy necessary for carrying endothermic reactions to completion.
4. Light can be used to facilitate electron flow (photoelectric effect; solar cells, see *Demonstration 4*.)
5. Light energy and the reactions activated by it can be both helpful and harmful. The protective ozone layer has been (and still is) produced photochemically from oxygen, but the layer can be destroyed by reactions of ozone with the products of chlorofluorocarbon photochemical reactions. Some polymers are synthesized through photoinitiation, while some are destroyed by photodegradation. Smog is also produced by photochemical reactions. On the other hand, the oxygen we breathe is produced by photosynthesis in plants; in fact, our entire food chain is dependent on photosynthesis (see *Biogeochemical Cycles* module).

6. Phosphorescence is effectively the emission of light (from a material exposed to radiation) that persists as an afterglow after removal of the radiation; fluorescence involves almost instantaneous (*ca.* 10^{-8} s) emission after the absorption of radiation.
7. Photoactivation in a solid crystalline material (such as AgBr) can be amplified by a factor of 10^9 - 10^{10} through energy transfer and is the basis of photography (see *Laboratory Activity 1*).
8. Photochemistry in the retina of the eye allows the transfer of visual images to the brain.
9. Quantum yield is a measure of photochemical reaction efficiency. A quantum yield of one means one chemical event per each photon absorbed. For chain reactions, a quantum yield greater than one is possible. Because of back reactions, fluorescence, and radiationless decay, a quantum yield much less than one is most common.
10. Lasers depend on photoactivation.
11. Some chemical reactions can produce light. This phenomenon is called chemiluminescence (see *Demonstration 1*).
12. The energy change (ΔE) associated with light absorption or emission is related to the frequency of the light absorbed or emitted (ν) by Planck's constant (h), *i.e.*, $\Delta E = h\nu$.

See *Reaction Rates* module.

RELATED CONCEPTS

1. The ability to read carefully and follow instructions precisely.
2. The dexterity to handle potentially hazardous solutions.
3. The only mathematical skills required for this module are arithmetic skills necessary for formulas, equations, and units.
4. Some of the concepts in this module are more easily understood if students (and teacher) have some background in energy level diagrams and/or in physics.

RELATED SKILLS

After completing their study of photochemistry, students should be able to:

1. define photochemistry.
2. identify the major regions of the electromagnetic spectrum.
3. describe the basic principles of the photographic process—light activation, development, fixation.
4. explain the reason why photographic developer leaves some silver halide unchanged.
5. give examples of photochemical processes at work in everyday life.
6. describe the basis of chemiluminescent light sticks.
7. distinguish between fluorescence and phosphorescence.

PERFORMANCE OBJECTIVES

Concept/Skills Development

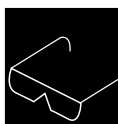


LABORATORY ACTIVITY: STUDENT VERSION

Activity 1: The Chemistry of Photography—A Survey

Introduction

Photography is based upon the fact that light can activate certain materials, in this case silver halides, to make them more sensitive to chemical reactions.



Purpose

To investigate the effect of light on silver salts; to investigate the effect of a developer on irradiated *vs.* nonirradiated silver salts; and to investigate the effect of sodium thiosulfate fixer on silver salts.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Be careful not to spill any of the silver nitrate solution on yourself, your clothes, your books, or the laboratory bench tops. Exposure to light will darken the silver material, and dark stains will form.
3. Any chemical spills should be cleaned up immediately.
4. Accidental spills on your body or clothes should be washed with large amounts of water and the incident reported to your teacher.
5. Dispose of the chemicals as directed by your teacher.

Procedure

Part I. The Effect of Light on Silver Salts

1. Number four strips filter paper from 1 to 4 with a pencil. Place 20 mL 0.1 M silver nitrate in a 250-mL beaker. Saturate each piece of filter paper with the silver nitrate solution, remove it with forceps, and place it on a piece of paper towelling. Cover the filter paper strips with another paper towel while obtaining the sodium halide solutions.
2. Place 10 mL each 0.1 M sodium chloride, 0.1 M sodium bromide, and 0.1 M sodium iodide in three separate 250-mL beakers. Quickly dip one of the pieces of silver nitrate saturated filter paper in the first beaker and remove it. Repeat with fresh strips of AgNO_3 paper for each of the other two beakers. Place all four pieces (including the piece dipped in silver nitrate only) on paper towelling. Record the appearance of each piece of filter paper. Place an opaque nonmetallic object, such as a button, on each piece of filter paper and place them in the direct rays of the sun or other bright, intense light source. Observe the appearance of the paper after 20 min. Your teacher may indicate a different time period based on the light source available to you. Save the sodium halide solutions for Parts II and III.

Part II. The Development Process

3. In a darkroom, prepare two strips of filter paper as in Steps 1 and 2 using the solution that gave you the best results in Part I. Label the strips II and III. *You do not want to expose them to general light prior to irradiation as the development process markedly increases the reactivity of light-sensitized silver halide paper.*

4. Place an opaque object in the center of each, and turn on the bright room lights for 1 min. Turn off the lights. Again, your teacher may modify this time period based on the light level in your room.
5. In the darkened room, immerse the filter papers in a 250-mL beaker containing 150 mL sulfite/glycine developing solution for 10 min. Record the changes in the papers over the 10-min period. [If working in groups, one person can do Step 7 during this time.]
6. Remove the papers from the developer solution, and place the paper labeled II on paper towelling on the table to compare with III after it has been fixed.

Part III. The Fixing Process

7. Properly dispose of the sodium halide solutions remaining in the other beakers. Wash the beakers, then thoroughly rinse them with distilled water. Place 100 mL sodium thiosulfate fixing solution in one of these 250-mL beakers. Add some (50-100 mL) distilled water to the other two beakers.
8. Rinse the paper strip labeled III in one of the beakers of distilled water. Then place the strip labeled III in the 250-mL beaker containing the fixer solution for 5 min.
9. Rinse strip in the other beaker of distilled water and place it on paper toweling.
10. Turn on the room lights and record the changes in II and III.
11. Thoroughly wash your hands before leaving the laboratory.

Data Analysis

1. What is the difference between the area covered by the opaque object and the rest of the filter paper in *Part I*?
2. What color is each of the exposed areas in *Part I*?
3. How does the silver nitrate saturated paper respond to light?
4. What sodium halide salt did you choose for *Parts II* and *III*? Why?
5. How are the papers from *Part II* and *Part III* similar to those from *Part I*? How are they different?
6. What does the final “room light” step do to the papers labeled II and III?

Implications and Applications

1. What caused the darkening of the filter papers?
2. What color is associated with each halide once it has been exposed to the light?
3. How different was the response of the silver nitrate saturated paper? Why did we observe this one?
4. What did the developer do to the silver compounds?
5. What is the main difference between the papers that were developed in *Parts II* and *III* and those that were not developed in *Part I*?
6. What does the final step of *Part II* (turning on the lights) tell you about the process? Must we complete another step to make the image permanent?
7. What causes the difference in the response of the fixed paper *vs.* the nonfixed paper to room light?
8. **Final Challenge.** What chemical reaction takes place with the silver halide in the development process?



LABORATORY
ACTIVITY:
TEACHER
NOTES

Activity 1: The Chemistry of Photography—A Survey

Major Chemical Concept

The major chemical concept being explored here is the response of silver halides to light and the subsequent chemical reduction in the photographic process.

Level

General high school chemistry.

Expected Student Background

The major prerequisite for the laboratory is the ability to read, follow instructions, make observations, and safely handle hazardous materials. Related concepts necessary for understanding this exercise include: atomic structure, ions, formula writing, equations, and an understanding of oxidation and reduction. Students should understand what the general term “halide” means.

Time

The time needed to complete the laboratory is dependent upon the intensity of light used and whether you wait until all steps are completed in one part before going on to the next. A real timesaver is to have student groups do the various parts and share the results. A darkroom is not absolutely necessary. You can manage by just darkening the classroom and using a bright desk lamp. *Part I* takes about 40 min. *Part II* takes about 20 min, and *Part III* requires about 30 min.

Safety

Read the *Safety Considerations* in the *Student Version*. When using silver nitrate be careful not to spill any on yourself as dark stains will form in time due to the exposure of the silver material to light. You should then wash your hands with a small amount of sodium thiosulfate solution followed by plenty of soap and water.

Materials (For 24 students working in pairs)

Nonconsumables

- 48 Beakers, 250-mL
- 12 Graduated cylinders, 10-mL
- 12 Forceps
- Strong light source
- Solid, nonmetallic, opaque objects that will cast definite shadows

Consumables

- 0.10 M Silver nitrate, AgNO_3 , 250 mL (4.2 g AgNO_3 per 250 mL solution)
- 0.10 M Sodium chloride, NaCl , 150 mL (0.9 g NaCl per 150 mL solution)
- 0.10 M Sodium bromide, NaBr , 150 mL (1.5 g NaBr per 150 mL solution)
- 0.10 M Sodium iodide, NaI , 150 mL (2.3 g NaI per 150 mL solution)
- 12 M Hydrochloric acid, HCl , 200 mL
- 144 Strips of filter paper (*ca.* 2 x 10 cm or cut 11 cm circles into 3 or 4 pieces)
- Paper toweling
- Developer solution, 400 mL (prepared by mixing 12 g glycine, 60 g sodium sulfite [Na_2SO_3], 60 g sodium carbonate [Na_2CO_3], and sufficient distilled water to make 400 mL of solution. You can use a commercial developer if you wish.)
- Fixer solution, 400 mL (prepared by mixing 100 g sodium thiosulfate pentahydrate [$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$], 10 g sodium metabisulfite [$\text{Na}_2\text{S}_2\text{O}_5$], and sufficient distilled water to make 400 mL solution. Use a commercial fixer if you wish.)

Advance Preparation

The most important thing you must attend to is to do the laboratory yourself with the materials you intend to use. If you find yourself without a strong light source and a total lack of sunlight, you can use an overhead projector light. You may need to use longer time periods if your light source is not very strong. Just be sure to place the opaque object on the glass top and the filter paper on top of the opaque object; the idea is to cast a shadow on the filter paper. If the experiment extends over 3 or 4 days, fresh solutions should be prepared.

Pre-Laboratory Discussion

1. Your first task is to be sure students understand the safety instructions.
2. It is important that you demonstrate the proper placement of the opaque object between the paper and the light source.
3. It is not necessary to soak the paper too long in any one solution. Indeed you should not leave it in the halide salts for more than 30s.

Teacher-Student Interaction

At the beginning of the laboratory you should monitor the use of forceps to handle the filter paper.

Anticipated Student Results

See answers to *Data Analysis* and *Implications and Applications*.

Data Analysis

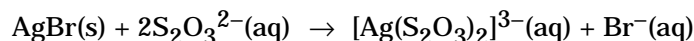
1. In Step 2 of *Part I*, the wet strips of filter paper will discolor in the light. The area covered by the opaque object will not.
2. The color of the filter paper will depend on the solution it was dipped in. The NaCl-dipped paper will become dark purple, the NaBr-dipped one will become a lighter purple, and the NaI-dipped one will become a brownish yellow.
3. Silver nitrate will turn a blush-peach color.
4. The students should choose NaCl for *Parts II* and *III* as it should provide a better contrast in *Part I*.
5. In procedure Step 5 of *Part II*, the wet strips of filter paper will show discoloration in areas where the light struck the paper and not in the area covered by the opaque object, just as in *Part I*. The use of a developer in *Parts II* and *III* makes the discoloration occur much faster. The papers become black instead of the color observed in *Part I*.
6. When the room lights are turned on in Step 10, the spots on Paper II that is light in color darkens slowly; however, the spot on Paper III does not change.

Answers to Implications and Applications

1. The substances on the filter paper were darkened by the action of light on the light-sensitive silver compounds.
2. The colors of the areas exposed to light are: silver chloride = purple, silver bromide = lighter purple-brown, silver iodide = brownish yellow.

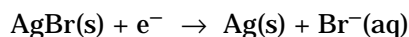


- The silver nitrate-saturated paper took a long time to discolor in the light and turned blush peach. Silver nitrate was used to show that the silver halides darkened and reacted faster.
- The developer caused the reduction of the silver halide to elemental silver. Finely divided silver is black, which is the observed color.
- The main difference between the papers from *Part I* and the other two parts is the degree of darkening and the fact that the latter two are so much blacker because the developer reduced the silver halide to elemental silver.
- The final step (turning on the lights) caused the spot to discolor because the light exposed it while some silver halide was still on the paper. This tells us that a step to make the image permanent (or fixed) is required. The step is called "fixing."
- The fixed paper did not lose the white spot while the nonfixed one did. This is because the fixing process removes the nondeveloped (nonlight-activated) silver halide from the paper so it cannot react and darken.



The sodium metabisulfite in the fixer solution acts as a stabilizer against oxidation and bacterial growth.

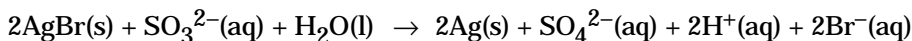
- The developer provides electrons to reduce the silver bromide:



If you used the sulfite/glycine developer, the sulfite is oxidized to sulfate:

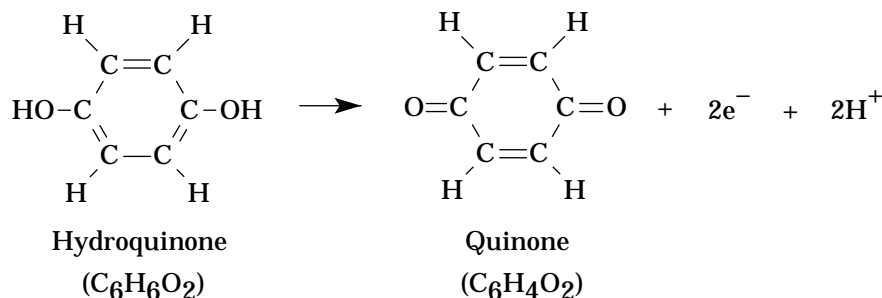


The net ionic equation for the total reaction is:

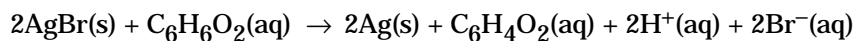


(The glycine complexes the silver of the silver halide making it more soluble and thus more easily reduced, and the carbonate neutralizes the protons formed in the sulfite oxidation.)

When the hydroquinone commercial developer reduces the silver bromide, the hydroquinone is oxidized to quinone, which can be represented as:



Overall:



Commercial developers contain other ingredients such as bases to neutralize the protons released in the above reaction.

Possible Extensions

Extensions are limited only by time. It is possible to relate exposure times to image intensity; temperature to development times and contrast; developer concentration to development times and contrast and more. Students can also investigate the different types of black and white film available commercially.

Assessing Laboratory Learning

Laboratory Practical. Have students expose film, process it, and make prints.

Written examination:

1. Why does the area where the opaque object was placed become dark when the object is removed from the paper that has not been fixed? Why does it stay white on the fixed paper? *[In the first case, when you remove the object the light shines on the silver halide that was previously under the object. Having been exposed to the light, the silver halide will be developed. The fixing process removes the silver halide from the paper, so in the second case, the silver halide was no longer there to react with the light; therefore, the paper stays white when exposed to light.]*
2. Write equations to represent the reactions of the developer with the silver halides. *[See the answer to Question 8 of Implications and Applications above.]*

CAUTION: Use appropriate safety guidelines in performing demonstrations.

Demonstration 1: Chemiluminescence

Purpose

Lightsticks can be used to demonstrate chemiluminescence as well as the temperature dependence of the chemical reaction causing chemiluminescence.

Materials

- 3 Cyalume lightsticks (available through Flinn Scientific, Aldrich Chemical, Edmund Scientific, Markson Science, safety equipment suppliers, some hardware stores, some auto supply houses, *etc.*)
- 2 Beakers, 500-mL
- Ice, 500 mL
- Hot water, 400 mL

Safety

The manufacturer claims that lightstick components are nontoxic either *via* contact with skin or ingestion. In the event that the plastic case should rupture, it is advisable to thoroughly wash solutions from skin or clothing with water.

Procedure

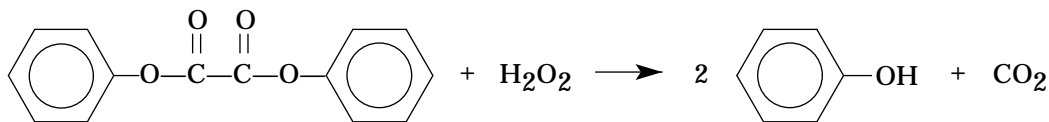
1. Activate the chemiluminescence following the instructions on the package. Typically this requires bending the plastic tube slightly in order to break the thin-walled vial inside and then shaking the tube to ensure good mixing.
2. To demonstrate the temperature effect on the chemiluminescence reaction rate, light sticks may be heated or cooled prior to activation. Immerse one of the light sticks in an ice bath for a few minutes. Place another one into a hot water bath for a few minutes. (Because of the thick plastic lightstick container, transfer of heat is slow.) Remove the lightsticks from the baths, activate by breaking the seals, and compare the light intensities with the intensity of a third lightstick kept at room temperature. Alternatively, the lightsticks may be heated or cooled prior to luminescence demonstration.

DEMONSTRATIONS

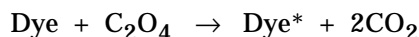


Remarks

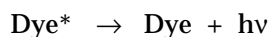
The chemiluminescence in the lightsticks is based on energy transfer between an intermediate formed in the reaction of phenyl oxalate ester with hydrogen peroxide (which is in the glass vial):



and an anthracene fluorescent dye molecule. The reaction intermediate is thought to be C_2O_4 , an unstable molecule, which reacts with the dye molecule as follows:



where Dye^* represents the activated dye molecule prior to emission, which can be written as:



where $h\nu$ represents the emitted photon of light of frequency ν . Further details of this reaction can be found in the “Cool-Light’ Chemiluminescence” article on which this demonstration is based (Shakhashiri *et al.*, 1981).

Flinn Scientific also sells a light stick kit that can be used as a chemiluminescence demonstration. “Chalk that Glows in the Dark” and “Chemiluminescent Glowing School Colors” demonstrations have also been published. Both involve suspected carcinogens and are not recommended for beginning high school teachers. However, light sticks are now available in several colors and intensities and may be substituted for the raw chemical demonstration of school colors. Still other demonstrations of chemiluminescence have been published in scientific journals and demonstration books, but almost all of them require chemicals that are either not readily available or are undesirable in the high school classroom.

An exception to this chemical quandary is the chemiluminescence quenching of quinine activity recently published by Sacksteder *et al.* (1990, December). Photophysics in a disco. *Journal of Chemical Education*, 67(12), 1065-1067. A demonstration version follows as *Demonstration 2*.

Demonstration 2: Quenching of Quinine Luminescence

Purpose

The quinine in tonic water is a fluorescent molecule that emits a blue glow when irradiated with a near-ultraviolet (long wavelength black light) source. The addition of salt quenches the fluorescence and acids such as lemon juice affect the fluorescence differently at different concentrations.

Materials

- Ultraviolet light source
- 2 Erlenmeyer flasks, 500-mL
- Volumetric flask, 50-mL
- Graduated cylinder, 100-mL
- 12 Large test-tubes
- Tonic water, 1 small bottle is sufficient
- Sodium chloride, 1 g
- Water, distilled (or tap water, if the dissolved salt level is low)

Safety

Do not stare at the black-light source. It may be injurious to your eyes.

Procedure

1. Make a "standard quinine solution" by diluting the tonic water by a factor of 10; *e.g.*, take 40 mL tonic water and dilute to 400 mL with distilled water in an Erlenmeyer flask.
2. Make a "salted quinine solution" by placing half of the standard quinine solution in a second Erlenmeyer flask containing 1 g of sodium chloride. The solution is swirled to dissolve the NaCl. (*NOTE: This procedure allows mixed solutions in Step 4 to contain the same quinine concentration.*)
3. Make a series of further dilutions of the standard quinine solution with water in large test-tubes: 12.5% (1 vol. standard : 8 vol. total solution), 25% (1 : 4), 33% (1 : 3), 50% (1 : 2), 75% (3 : 4), plus a test-tube with the full strength standard and one with just water, see following table. (These solutions can be prepared ahead of time or else the test-tubes can be marked with appropriate volume markings so that rapid dilutions are possible.) Place the quinine solution in a test-tube rack in order of ascending or descending concentration.

Dilution Table for 100 mL Solution

% Quinine	mL Standard quinine	mL H₂O
0	0	100
12.5	12.5	87.5
25	25	75
33	33	67
50	50	50
75	75	25
100	100	0

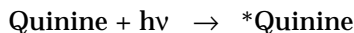
4. Make at least three sample solutions with different proportions of the standard quinine and the salted quinine solutions (*e.g.*, 9 vol. standard : 1 vol. salted, 7 : 3, and 5 : 5). Place these in a test-tube rack together with a test-tube containing the standard quinine solution and one containing the salted quinine solution.
5. In a dimly lit space (*e.g.*, in a hood or with shades drawn) irradiate the solutions, and ask students to use their eyes as fluorimeter detectors to compare the intensities of the salt-containing solutions with the dilute solutions of the standard. The intensities of the dilute solutions of the standard should be proportional to the concentrations of quinine in the solutions. Get a consensus as to the luminescence level of each of the salt-containing solutions, and come to a conclusion as to the effect of chloride ion on quinine fluorescence. [*As the chloride ion increases, the fluorescence decreases – however, it is not linear because of the nature of the mechanism. Chloride ion is said to be a quencher of quinine fluorescence.*]



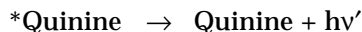
6. Add a little lemon juice to the most dilute solution of the standard (12.5%). [The intensity should increase initially, but will eventually quench the fluorescence. Adding lemon juice to the more concentrated solutions will also cause quenching. Adding of other acids will confirm that it is an acid/base effect on the quenching.]

Remarks

The fluorescence is the result of excitation of the quinine by the ultraviolet light (*i.e.*, the energy of a photon is absorbed by the quinine)

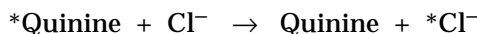


followed by emission at a lower energy.



This allows us to see the emission in the visible region of the spectrum. [Always, fluorescence occurs at lower energy than the energy of the photons that are absorbed. Most molecules lose all of the absorbed energy as heat and show no fluorescence.]

The chloride ion acts as a quencher, *i.e.*, a quinine molecule is deactivated by a collision with a chloride ion before it has a chance to deactivate by emission of radiation.



The acid-base interactions are too complicated to detail here.

In practice, the amount of chloride ion in unknown solutions can be determined by quantitatively measuring the fluorescence that is obtained with known concentrations of quinine added to the solutions. An instrument called a spectrofluorimeter is used for such measurements.

More details on this demonstration can be found in the activity by Sacksteder *et al.* (1990).

Demonstration 3: Photoreduction—The Blueprint Reaction

Purpose

To mimic the blueprint photoreaction.

Materials

0.15 M Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, 10 mL (0.19 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ per 10 mL solution)

0.10 M Iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3$, 10 mL (0.40 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ per 10 mL solution)

0.10 M Potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, 10 mL [0.33 g $\text{K}_3\text{Fe}(\text{CN})_6$ per 10 mL solution]. *NOTE: $\text{K}_3\text{Fe}(\text{CN})_6$ is commonly called potassium ferricyanide. [Potassium hexacyanoferrate(II), $\text{K}_4\text{Fe}(\text{CN})_6$, commonly called potassium ferrocyanide, gives a blue color immediately because of the mixed oxidation states and is not appropriate for this demonstration.]*

Filter paper

Strong light source

Opaque nonmetallic solid object to obstruct the photochemical reaction

Paper toweling

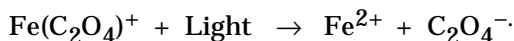
Procedure

Mix the $\text{Fe}(\text{NO}_3)_3$ solution with the $\text{H}_2\text{C}_2\text{O}_4$ solution to make a solution of iron(III) oxalate. Soak a piece of filter paper in the ferric oxalate solution, and then blot the filter paper with a paper towel. Then soak the filter paper in the $\text{K}_3\text{Fe}(\text{CN})_6$ solution. Reblot the filter paper. Place a non-metallic opaque object on the filter paper, and place it under a strong light source (or in sunlight) until a blue color is developed, which may take several minutes. Remove the filter paper from under the light source, and remove the opaque object from the paper. Rinse to remove the yellow color of the iron(III).

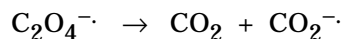
Whereas the above procedure has the advantage of doing the entire activity in front of students, an alternative procedure of allowing the paper to dry (in the dark or very dimly lit space) prior to the exposure to light is less messy but also less informative (see Summerlin & Ealy, 1985). If predried, a metal object, such as a key or a coin, can be used to make the pattern, whereas with moist paper, a redox reaction between the metal object and the iron(III) may occur.

Remarks

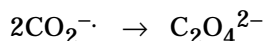
Solutions of iron(III) oxalate, $\text{Fe}_2(\text{C}_2\text{O}_4)_3$, contain several kinds of complex ions of Fe^{3+} ; for example, $[\text{Fe}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4]^+$, which can be simplified to $\text{Fe}(\text{C}_2\text{O}_4)^+$. When irradiated, this ion can transfer an electron from oxalate to iron:



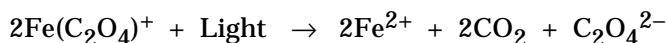
The $\text{C}_2\text{O}_4^{\cdot-}$, which is a very unstable radical anion (see *Language of Chemistry*), decomposes:



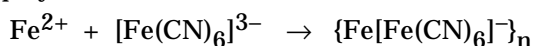
And a new $\text{CO}_2^{\cdot-}$ radical anion dimerizes to produce the oxalate anion:



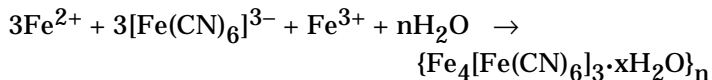
The overall reaction is:



The resulting iron(II) reacts with hexacyanoferrate(III) to produce polymeric Turnbull's blue or Prussian blue:



where the cation that balances the polyanionic charge is largely reoxidized iron(III); *i.e.*, aqueous iron(II) is readily oxidized to iron(III). Therefore, the polymer can be represented as $\{\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}\}_n$, where n is 14 to 16, and the preceding equation should probably be written as:



The polymeric structure consists of alternating Fe^{2+} and Fe^{3+} ions, each surrounded by six linear, bridging cyanide ions (*i.e.*, $\text{Fe}-\text{C}\equiv\text{N}-\text{Fe}$ bridges) in three dimensions:

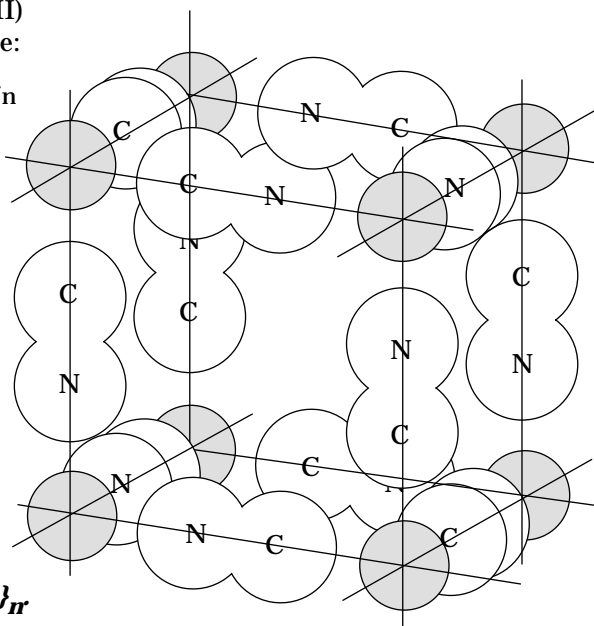


Figure 1. Polymeric structure of $\{\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}\}_n$



The blue color is due to electron delocalization in the polymer; that is, the iron(II) and iron(III) ions all try to become equivalent. (*TO THE TEACHER: Such intense broad absorption bands are called intervalence transfer bands.*) A similar blueprint demonstration, but using iron(III) ammonium citrate as the photoactive iron(III) component has been published (Summerlin & Ealy, 1989). These authors note that a black and white photonegative or an ordinary overhead transparency can also be used to make the pattern.

Other Demonstrations

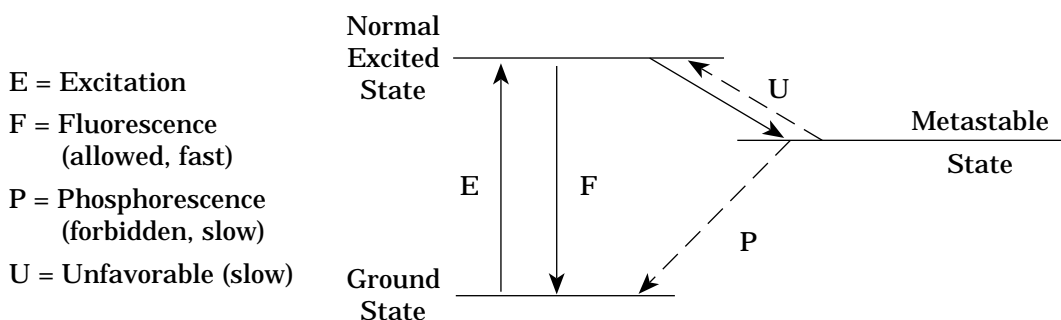
1. **Solar cells.** A titanium dioxide solar cell can be made by heating a disc of titanium metal in a flame in order to oxidize the surface to TiO_2 . Electrical leads hooked to a multimeter can be used to show that current is generated when the device is irradiated with sunlight or other bright light source. Alternatively, a standard silicon solar cell (available from Edmund Scientific) can be demonstrated in a similar manner. The current generated can be detected with a small volt/ammeter.
2. **Flashbulbs** (disposable type) can be flashed to provide an example of the generation of light by the oxidation of magnesium to magnesium oxide. *NOTE: This process is not considered chemiluminescence, but rather light generated from the heat generated in the reaction, i.e., incandescence.* (Magnesium ribbon burned in an open flame provides the same result.)
3. **Flame tests**, which are often performed in qualitative analysis or in the discussion of atomic energy levels, are appropriate for this module, too (see *Demonstration 1 in Alkali Metals* and *Activity 2 in Chemistry of Rocks, Minerals, and Gems*).
4. **Triboluminescence** demonstration has recently been suggested in *ChemMatters* (Sweeting, 1990). A Wint-O-Green Lifesaver candy disc (sugar type) is pressed between the teeth, and, in the dark, light emission can be observed. Alternatively, a pair of pliers can be used to apply the pressure (with the candy disc in a plastic bag to avoid the mess that can result if the disc shatters during the demonstration). Whereas triboluminescence produces N_2^+ , which emits primarily in the ultraviolet with only a dim blue glow in the visible, increased intensity of light is obtained by energy transfer to the methyl salicylate or oil of wintergreen, which fluoresces mainly in the blue region of the spectrum. Other types of sugar-based hard candy provide weaker visible luminescence.

GROUP AND DISCUSSION ACTIVITIES

Key Questions

1. How does light initiate chemical reactions? [*Light absorption increases the energy of the molecules, placing them in excited states, which often have enough energy to overcome the activation energy for thermal chemical reactions or to cause bond breakage.*]
2. How can light alter reaction pathways? [*Light absorption can provide enough energy to access pathways that are not attainable thermally because of other lower energy reactions, or light may provide highly reactive species such as free radicals by homolytic bond breakage. Photochemical excitation often populates other than the lowest excited states. In fact, by using different specific wavelengths, different reactive pathways can be accessed.*]

- Although ozone is decomposed photochemically it continues to exist in the atmosphere. Explain. [When ozone is decomposed photochemically by ultraviolet light: $O_3 + h\nu \rightarrow O + O_2$, the O atoms can recombine with other oxygen molecules to produce more ozone. Also, oxygen molecules can absorb ultraviolet light to produce more oxygen atoms: $O_2 + h\nu \rightarrow 2O$, which in turn can produce more ozone: $O + O_2 \rightarrow O_3$.]
- Both oxygen and ozone absorb in the ultraviolet region of the spectrum. Why do we need ozone to protect us from the sun's ultraviolet radiation, especially since there is so much more oxygen in the atmosphere than there is ozone? [Oxygen absorbs primarily in the far ultraviolet region (<200 nm) whereas ozone absorbs in the normal ultraviolet region (200–360 nm)].
- What processes in nature that are essential to us involve photochemistry? [The oxygen we breathe is produced by photosynthesis; our entire food chain depends on photosynthesis; the ozone-protecting layer about the earth depends on photochemical synthesis; photochemistry in the retina of the eye allows us to see; the warmth of the earth's surface depends on photochemical absorption of light that is then dissipated as heat; etc.]
- Has modern technology found additional uses for photochemistry? [Yes – details can be found in the Links and Connections section.]
- Why is some light emission delayed (phosphorescence)? [In addition to normal excited states that almost immediately revert back to the ground state (fluorescence), other excited states, which are metastable, also exist. If after excitation, energy transfer to such a metastable state occurs, relaxation back to the ground state is very slow. Schematically:



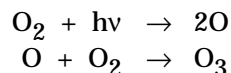
A number of other pathways also exist for the removal of the energy of excited states; therefore, most materials do not fluoresce or phosphoresce. “Allowed” and “forbidden” are quantum mechanical terms that given an indication of the probability of a reaction; a “forbidden” process is a highly improbable process.

- How can chemiluminescence occur? [Although the energy released in exothermic chemical reactions is typically released as heat, if the energy released has sufficient energy for light emission in the visible region of the electromagnetic spectrum, chemiluminescence is possible.]
- Why don't all photochemical reactions have a quantum yield of unity (one)? [Whereas an excited state results each time a photon of light is absorbed, radiationless decay, fluorescence, and back reactions can all compete with the photochemical reaction and typically decrease the quantum yield below unity. On the other hand, a chain reaction can produce more than one product per photon absorbed, which can provide a quantum yield greater than unity.]

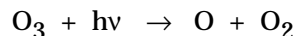


Counterintuitive Examples

1. Ozone is synthesized photochemically from oxygen in the atmosphere with ultraviolet light:



However, the ozone so produced absorbs ultraviolet radiation, which leads to the reverse of the latter reaction:



The net effect is a low steady concentration of ozone, which continually converts ultraviolet radiation to heat; this process protects us from some of the sun's ultraviolet radiation. (The absorption maximum of oxygen is about 145 nm, whereas ozone absorbs primarily between 200 and 300 nm.) (Also, see *Societal Links and Connections* below for further complications brought about by our modern life styles.)

2. A fluorescent lamp also exhibits phosphorescence. (Turn off a fluorescent lamp in the dark, and note the phosphorescent afterglow.)

TIPS FOR THE TEACHER

Language of Chemistry

absorption of electromagnetic radiation (*e.g.*, visible light) by a chemical species is associated with the molecule going to a higher energy state.

bioluminescence chemiluminescence catalyzed by enzymes, such as that observed in fireflies, glowworms, earthworms, snails, jellyfish, angler fishes, and luminescent fungi.

chemiluminescence exothermic chemical reactions that emit light rather than heat.

chromophores chemical structural parts that absorb light. For more details of the variety of ways in which color is generated (see *Appendix*).

emission of electromagnetic radiation corresponds to a chemical species in an excited electronic state going to a state of lower energy.

fluorescence and **phosphorescence** (see *Key Question 7*).

free radical uncharged atom or a molecular fragment with an unpaired electron. Many photochemical reactions produce free radicals. Radical anions (or cations) are unstable anions (or cations) with an unpaired electron analogous to neutral free radicals. $-$ and $+$ are the symbols for singly charged radical anions and cations, respectively. The dot represents the unpaired electron.

infrared spectral region on the lower energy (longer wavelength) side of the visible region of the spectrum. This region is associated with molecular vibrations and heat.

laser (Light amplification by stimulated emission of radiation) device producing sharp intense monochromatic beams of light. Atoms or molecules in excited states can be stimulated to emit radiation that is in phase with the wave that stimulated it. This emission is an amplification of the initial wave. In a large aggregation of atoms or molecules, appropriate design allows for continued amplification to produce an intense in-phase beam of monochromatic light (see *Links and Connections–Community*).

luminescence emission of light from relatively cool systems (as opposed to incandescence, which is the emission of light from systems hot enough to glow from the excitation obtained from the heat alone). Luminescent pigments exhibit colors through emission as well as absorption, whereas other pigments exhibit color solely on the basis of absorption. (The emission occurs at lower energies than the absorption.)

phosphors materials that exhibit phosphorescence or fluorescence. Originally the term applied to microcrystalline substances, but is now applied to noncrystalline materials as well.

quantum yield ratio of the number of product molecules formed to the number of photons absorbed.

triboluminescence mechanically induced emission observed when certain crystals (*e.g.*, sugar cube, hard candy or zinc sulfide) are crushed or when a ruby or sapphire crystal is cut with a diamond saw. The blue light results from the strong electric fields that result during the formation of new crystal faces. The electrons produce N_2^+ , which provides a blue luminescence. Triboluminescence also occurs when some adhesives are rapidly removed from surfaces, which also produces luminescent N_2^+ .

ultraviolet spectral region on the higher energy (shorter wavelength) side of the visible region of the spectrum. This region is associated with electron energy state changes with energy transfer to molecular vibrational modes and bond breakage.

Pattern Recognition

Relate colors with wavelengths and wavelengths with energy (see *Atomic Structure* module and Figure 2). In nanometers: 700, deep red; 650, red; 600, orange; 580, yellow; 550, green; 500, green; 450, blue; 400, violet (Nassau, 1983, p. 378).

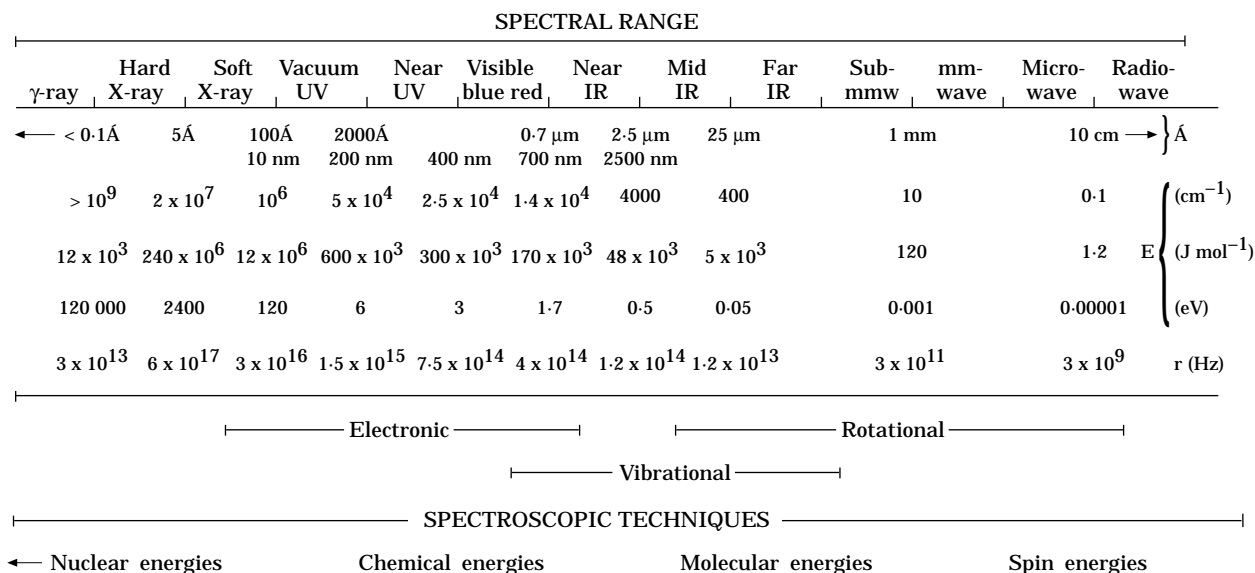


Figure 2. Electromagnetic spectrum.



Common Student Misconceptions

1. “The glow of a ‘firefly’ is from a fire.”

The glow of a ‘firefly’ is a chemiluminescent reaction.

HISTORY: ON THE HUMAN SIDE

Qualitative aspects of photochemistry were known long before the development of chemistry as a science. For example, the history of chemical luminescence goes back to 1603 when Vincenzo Cascariolo, an alchemist in Bologna, Italy, heated barite (barium sulfate) and coal together and observed that upon cooling the powder exhibited a bluish glow in the dark and that the glow could be reactivated by exposure of the powder to sunlight. He apparently had made barium sulfide, though the powder became known as *lapis solaris* (sunstone) or *phosphorus* (light bearer). Now we reserve the name phosphorus for the element, which does show phosphorescence, and call microcrystalline luminescent materials **phosphors**.

Robert Boyle, the Irish chemist better known for a gas law, is given credit for first having scientifically investigated bioluminescence in 1672, when he established that the luminescence emissions from rotting wood, rotting flesh, and fireflies require air, are cold-light systems, and can be inhibited by chemical reagents such as alcohols, ammonia, and hydrochloric acid.

Photochemistry *per se* is of more recent origin (with the possible exception of the first item in the *Humor* section). Although some alchemists compared their results in sunlight *vs.* in the dark, the fact that silver halide blackening is caused by light is thought to have been discovered in the early 1700s, and the well studied photochemical gaseous reaction between hydrogen and chlorine to produce hydrogen chloride was first noted in about 1801. However, quantitative photochemistry did not develop until after Einstein’s photoelectric effect pronouncements at the beginning of the 20th century provided a foundation on which others have developed an understanding of photochemical reactions.

The history of the photochemistry of photography is normally traced to Thomas Wedgwood, whose father started the famed line of pottery that bears their family name. In 1802, Wedgwood reported that paper or leather sensitized with silver nitrate provided temporary images when exposed to light using a primitive form of a camera, which was used for tracing images at that time. In France in 1826, Joseph Nicéphore Niépce made a “heliograph” using the change of solubility of a special asphalt when exposed to a sunlight image over several hours. He joined Louis Daguerre in a partnership in 1829, but died in 1833. In 1837, Daguerre produced his first “daguerreotype” using a silvered copper plate exposed to iodine vapor prior to its exposure to light. After the exposure to light, mercury vapors produced a silver amalgam where the silver iodide had been reduced, and sodium thiosulfate was added to remove the unexposed silver iodide, *i.e.*, to fix the image. He and Niépce’s son sold full rights for their processes to the French government in August 1839 in return for life annuities.

Meanwhile, back in England, William Fox Talbot invented a photographic process because he was unable to draw landscapes well. He was apparently unaware of the French work, or of that of Wedgwood, when in 1833-1835 he developed a light sensitive paper by soaking the paper alternately in solutions of sodium chloride and silver nitrate. He exposed the paper through a camera until the silver chloride became dark where irradiated. The unexposed portions were made less sensitive by subsequent washing with a strong sodium chloride solution. (Some of the silver chloride forms AgCl_2^- and is removed.) He later switched to sodium thiosulfate at the recommendation of Sir John Herschel, another British scientist. In January 1839, when word of the French work reached England, but several months before the details were published, Talbot rushed

publication of his “photogenic drawing” process and discussed it before the Royal Society. By 1840, Talbot had learned that much shorter exposures of light caused a latent image that could be developed into a real image, thus laying the foundation of the modern photographic process. The many more recent developments of photography which led to the field as we know it today are beyond the scope of this module.

HUMOR: ON THE FUN SIDE

1. Photochemists claim that their field is the oldest scientific field in the universe, and claim that God was the first photochemist when God said “Let there be light” and there was light. Photosynthesis was thereby initiated.
2. And did you hear about the little CHEMoron who thought that LASERS were people who sit around all day doing nothing?
3. See Sydney Harris’ new book *Einstein Simplified: Cartoons on Science* for more humor related to this module (Harris, 1989). For example: Early scientific fraud—young Thomas Edison tried to pass off a container filled with fireflies as an incandescent bulb.
4. Message on bumper stickers:
 - a. I’m in an excited state!
 - b. Be a firefly: Do chemistry by night.
5. Word Search (see *Appendix* for master copy)

~~T R I B O L U M I N E S C E N C E~~
~~C J U P P J U M M U L W Y C R O W~~
~~X E N Q H R O H P S O H P M H X A~~
~~O L E D K Q B M J K A U W Y J K V~~
~~E C N E C S E N I M U L I M E H C~~
~~R K G Q E B G D W Q G Y V L A P K~~
~~E C Q V T A E J V G J N Q E D D M~~
~~V I B U W R E S A L W R A F C J M~~
~~L K Q W A C H R O M O P H O R E S~~
~~I F Y R A N S Q I G O C H D V X C~~
~~S H F D R F T E L O I V A R T L U~~
~~P M J D O M L U G L R H Q D K E X~~
~~X D Y W I Z D E M M F K C N A L P~~

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Spectral region associated with molecular vibrations and heat.
2. Acronym for light amplification by stimulated emission of radiation.
3. Material that exhibits phosphorescence.
4. Kind of yield that measures photochemical reaction efficiency.
5. Emission of light through chemical reaction.
6. Mechanically induced emission of light.
7. Another name for “black light.”
8. Chemical groups that absorb light.
9. Halides of this metal are light sensitive.
10. $\Delta E = h\nu$ is called the Einstein-_____ relationship.



Answers: 1. INFRARED 2. LASER 3. PHOSPHOR 4. QUANTUM
5. CHEMILUMINESCENCE 6. TRIBOLUMINESCENCE 7. ULTRAVIOLET
8. CHROMOPHORES 9. SILVER 10. PLANCK

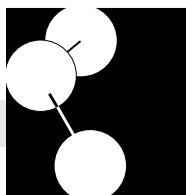
6. See cartoons at the end of module.

MEDIA

1. World of Chemistry Videocassettes. Annenberg/CPB Project, P.O. Box 1922, Santa Barbara, CA 93116-1922; (800) 532-7637; World of Chemistry Series, Atlantic Video, 150 South Gordon Street, Alexandria, VA 22304; (703) 823-2800 or QUEUE Educational Video, 338 Commerce Drive, Fairfield, CT 06430; (800) 232-2224.
 - a. "Number 17: The Precious Envelope," on the atmosphere, includes a discussion of the ozone layer. The videotape also has a short discussion of CO₂, photosynthesis and the greenhouse effect.
 - b. "Number 10: Signals from Within," focuses primarily on molecular spectroscopy. However, it has a good discussion of suntanning and sunscreens as well as the energy and types of electromagnetic radiation and the absorption of specific energies of radiation by molecules.
 - c. "Number 2: Color," emphasizes dyes and notes the use of fluorescent dyes in greenhouse windows to improve the quantity of energy absorbed by plants.
2. Videodiscs published by *JCE: Software*, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).
 - a. "Depletion of Ozone," a chapter on *The World of Chemistry: Selected Demonstrations and Animations: Disc II* (double sided, 60 min.), Special Issue 4.
 - b. "Energy States and a Sound Wave Analogy" and "Energy States and Chlorophyll," two chapters on *The World of Chemistry: Selected Demonstrations and Animations: Disc I* (double sided, 60 min.), Special Issue 3.
 - c. *Demonstrations in Organic Chemistry* (double sided, 60 min.). Special Issue 6.
3. Written materials available from ICE—Institute for Chemical Education, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, WI 53706-1396: (608) 262-3033 (voice) or (608) 262-0381 (FAX).
 - a. Topics in Chemistry: *Ozone—Chlorofluorocarbons and the Hole in the Ozone Layer*.
 - b. Topics in Chemistry: *Black and White Photography*.

INSTRUMENTATION AND EQUIPMENT

1. Light sources include the sun, sunlamp bulbs, overhead projection bulbs, ultraviolet lamps, and lasers, if available for demonstration (although not necessary).
2. Solar cell and meter to show output are available from a number of supply houses, such as Edmund Scientific.



Links/Connections

This topic is closely associated with chemical kinetics (see *Reaction Rates* module).

**WITHIN
CHEMISTRY**

Photochemistry is today quite closely allied with environmental science because of the ozone layer and smog problems, with physics (photophysics) in terms of the theoretical aspects of the subject, with medicine from the standpoint of links between skin cancer and irradiation, and with materials science in terms of the development of new lithographic procedures and new photoelectric and solar devices.

**BETWEEN
CHEMISTRY
AND OTHER
DISCIPLINES**

Personal

1. **Vision.** In the retina at the back of the eye, color is detected by three sets of cones at moderate to high light intensity. The cones have maximum sensitivity to different colors as shown in Figure 3, where "B," "G," and "R" are the blue, green, and red sensitive cones. At low light levels, light is detected by rods, which do not distinguish color, but do have much higher sensitivity as shown in Figure 3. The photochemical reaction thought to predominate at higher intensity levels is shown schematically in Figure 4, where rhodopsin is a condensation product between opsin, a large molecule of unknown structure, and 11-*cis*-retinal. Absorption of a photon into the so-called π^* level of the retinal allows rotation at the 11-position to the *trans* form shown on the right of Figure 4, providing a nerve impulse to the brain. A second photon can reverse the process, *etc.* The actual process involves at least two intermediates, and the process for dim light is even more complicated; however, the *cis-trans* conversion is involved in all cases. The cones are thought to have at least three different opsins, which provide the different energy absorption profiles necessary for color detection (see also *Organic Chemistry* and *Chemistry in Medicine* modules). Recently, workers at Brandeis University and Stanford University succeeded in isolating the pigments of human color vision by chemically synthesizing the genes for the pigments and expressing the genes in tissue culture. The opsin (protein) portion of these pigments is covalently linked to the chromophore, 11-*cis*-retinal through a lysine (an amino acid) side chain. Substitution of different amino acids at critical positions on the opsin chain can produce different absorption maxima and hence, different perceived colors. For example, substitution of an alanine for a serine at position 180 on the opsin results in a subtle but detectable difference in color vision tests. The consequences? Everyone does not see the same color! (See Borman, 1992, in *References*.)

**TO THE
CONTEMPORARY
WORLD**

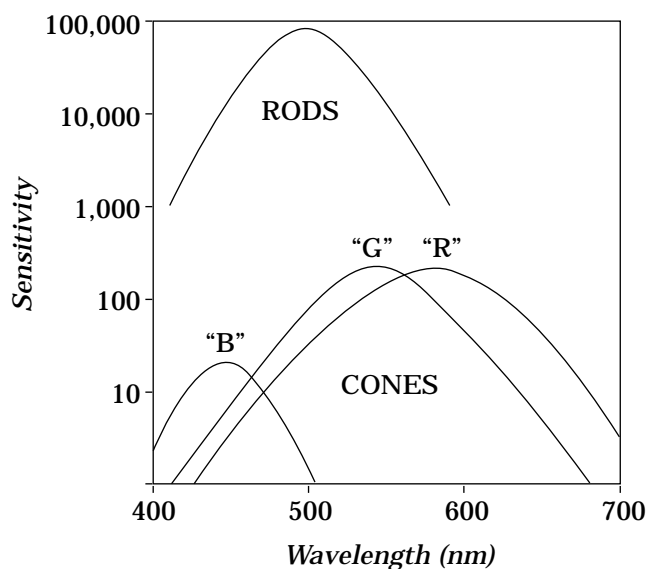


Figure 3. Sensitivity of cones and rods of the human eye.

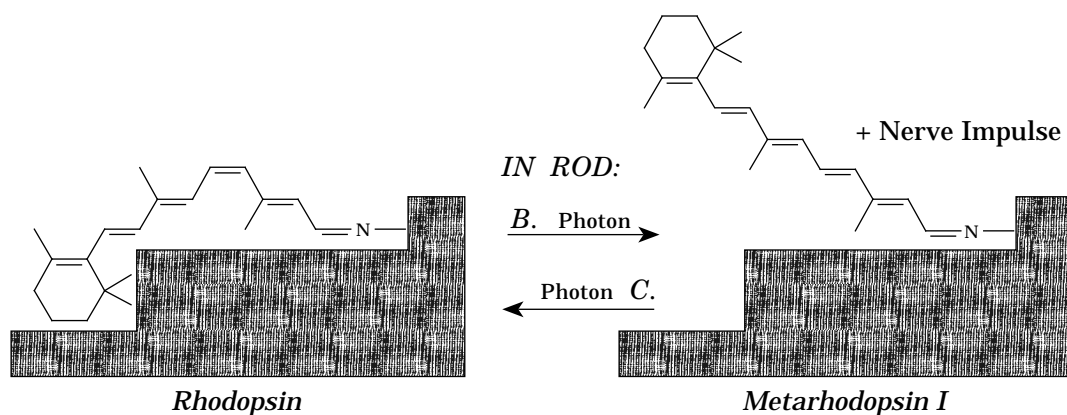
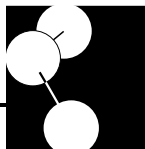


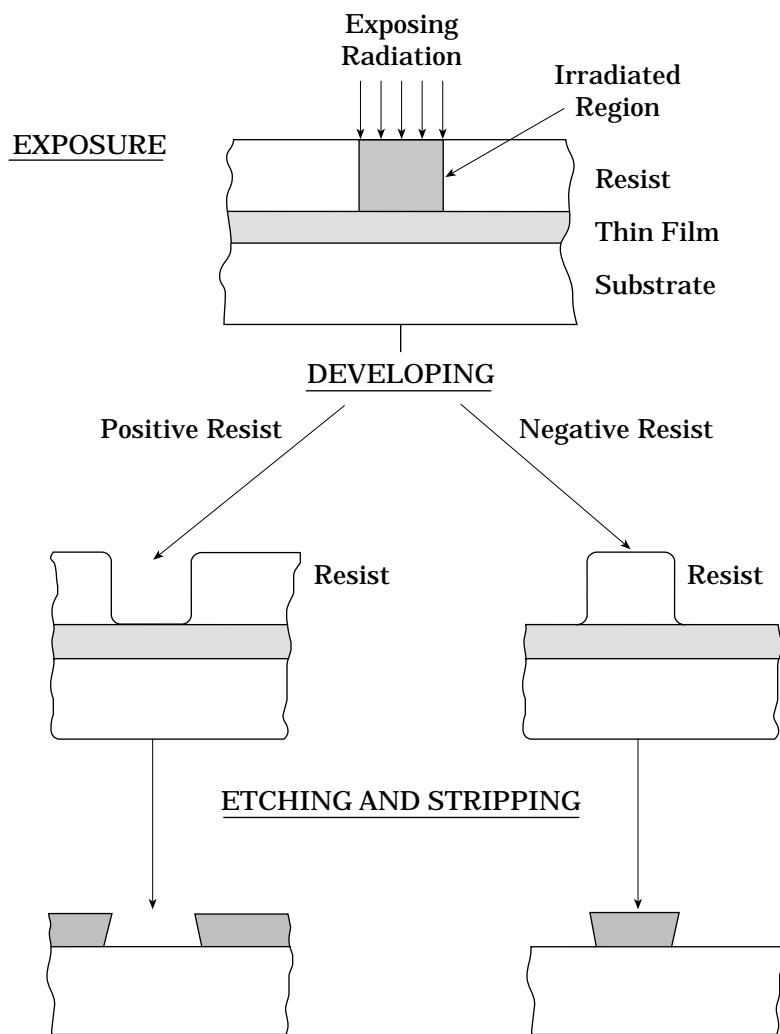
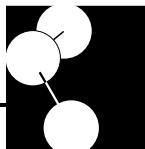
Figure 4. Light-initiated retinal chemical transformation leading to a nerve impulse.

2. **Suntanning** (and skin cancer). Exposure to the sun (or at least to ultraviolet radiation) is essential for the photochemical production of Vitamin D and for suntanning, which is based on the photochemical formation of melanin, the same pigment responsible for dark skin and black hair. However, too much ultraviolet exposure can cause skin cancer. Ultraviolet light has enough energy to modify the DNA of skin cells, which can lead to mutations, some of which are carcinogenic. *ChemCom* (Lippincott *et al.*, 1988, pp. 431–434) contains more details (see also Robbins, 1984).
3. **Photography** is probably the most common example of a photochemical process. What is not commonly understood is the chemistry of the entire process. The image is created by light exciting the electrons of silver halides. The more light a given area receives, the more electrons in that area are excited. Eventually a grain of silver bromide receives enough light to become activated and available for development. [The excited silver bromide grains can be reduced by the developer more easily than non-excited atoms.] When developed, the grains that have received enough light to be activated are reduced to black finely divided silver metal, while those areas that are not activated are not reduced. Instead, these grains of silver bromide are removed during the fixation process. In regions where only a fraction of the silver bromide grains receive enough light to be activated, gray shades develop. This light/dark contrast produces the detail in the photographic image. Because this process is based on the difference in the ability of the silver to be reduced, development times and temperatures are critical in the production of fine photographs. Excessive time spent in the developer will result in too many non-excited grains being reduced and a poor image. The second step in the process involves the fixer. The purpose of the fixer is to remove the remaining, undeveloped, silver halide compounds so the image will be “fixed” or stable (see *Laboratory Activity 1*).
4. Some **detergents** contain whiteners to make laundry appear “bright.” These compounds cause the fabric to fluoresce, that is, to emit visible radiation in response to ultraviolet radiation. The “brightener” actually emits light due to absorption of ultraviolet light from the light source. A good example of this is the “blacklight” (ultraviolet source) response of white cloth or fluorescent posters.

- Fluorescent lamps** are glass tubes that are coated on the inside with one or more phosphors, *e.g.*, ZnS, and filled with a small amount of mercury vapor diluted with argon. Electricity passed through the gas excites the mercury atoms, which emit light, primarily in the ultraviolet and the blue end of the visible spectrum. The phosphors convert the radiation to lower energy radiation in the rest of the visible spectrum. With appropriate phosphor mixtures, daylight can be approximated. A particular advantage of the fluorescent lamp is its greater efficiency relative to the standard incandescent tungsten filament lamp, *i.e.*, a fluorescent lamp requires only about 30% as much electricity to produce the same amount of light. Fluorescent lighting is also cooler, as less energy is lost as heat. *CAUTION: Because of the mercury and of certain phosphors used in the lamps, proper disposal of the bulbs is important. Broken bulbs cause mercury contamination.*
- When you visit the dentist and require a filling near the front of your mouth, you may have a **polymer substance** used instead of the more common silver amalgam. The reason for this is that it is possible to color the polymer to match your teeth and thus be nondetectable. These dental polymers are hardened or “dried” by shining a strong light on them. The light provides the energy necessary to initiate the polymerization reaction.
- Light activation** is also used to produce the masks for the elaborate silkscreen designs used on T-shirts. The silkscreen process works by having ink pushed through a fabric “screen” that has been covered in areas where no dye is wanted. To achieve the elaborate designs, a film is used. A copy of the design is placed on the film, and then it is exposed to a very strong ultraviolet light for a specific, short amount of time. This process sensitizes the film in a fashion similar to the photographic process. The film is then washed with water. The film material swells and the areas where no light struck the film are washed away. The “mask” is then placed on the screen, allowed to dry, and used.
- Photoelectric effect applications.** Many materials will eject electrons when irradiated with light with appropriate energies. This phenomenon is termed the photoelectric effect or photoemission. The effective wavelengths of radiation that cause this emission of electrons vary with the materials being irradiated. It is the basis of solar cells used in some of the hand-held calculators. Silicon based cells are the most commonly used solar cells. Light energy is converted to electrical energy by the silicon cells. The energy of the photon is sufficient to move an electron into a conducting band.

Television cameras are also based on light induced electron emission at specific points on a two-dimensional solid-state photoelectric array. In color cameras, sensitivity at three different energies is required to differentiate between red, green, and blue light at each point on the array. Electronic circuitry allows for the rapid scanning of the various points of the photoelectric array.

- Photolithography applications.** The printed circuits used in calculators and personal computers take advantage of photochemical reactions during their manufacture. Typically, a semiconducting silicon wafer, which is the heart of the memory chip, has its surface oxidized to silica, SiO₂, which is an insulator. In order to conduct a current to the silicon, the silica must be



selectively etched. Typically, a photosensitive polymer (a resist) is placed on the silica surface and selectively irradiated through a mask. If a positive resist has been used, the irradiated portions of the resist are broken into short segments (undergo scission) and are more readily dissolved by a developer that removes the irradiated portions. Conversely, if a negative resist has been used, the irradiated portions of the resist become crosslinked and insoluble. Therefore, a developer removes the nonirradiated portions of the resist. After development, an etchant (*e.g.*, HF) etches the silica from the silicon surface in the regions in which the resist had been removed. Doping of the silicon or adding a metal for connections is thus made very specific. The present devices have many more steps and include multilayers, but photolithography is a central part of all such processes (see Figure 5, which details this procedure).

Figure 5. The schematic diagram showing the formation of a polymeric relief image using lithography.

Community

1. **Lasers.** Light amplification by stimulated emission of radiation devices produce sharp intense monochromatic beams of light, which are being used in a variety of devices today. Atoms or molecules in excited states can be stimulated to emit radiation that is in phase with the wave that stimulated it. This emission is an amplification of the initial wave. In a large aggregation of atoms or molecules, appropriate design allows for continued amplification to produce an intense in-phase beam of monochromatic light.

Types of lasers in use today include the now classic photochemically activated (optically pumped) solid lasers, which have been used for precise control as in laser eye surgery, extremely high temperature melting and welding, accurate alignment measurements, holography, *etc.* A figure of such a laser is shown in Figure 6 (The New Encyclopædia Britannica, 1986).

The heart of a typical laser consists of a rod of a material containing an ion that absorbs and emits photons (light quanta). Examples: the ruby laser—chromium(III) in an artificial sapphire crystal (Al_2O_3), and the neodymium laser—neodymium(III) in an artificial sapphire crystal. The rod has polished mirror-coated ends to reflect the laser light and has a small hole in one mirror

to allow light through to the Q-switch, which reflects the light back through the crystal until it is at a high level and then opens to emit the optically pumped beam. The flash lamp that pumps the laser crystal is a high intensity lamp, either wound around the crystal as shown or positioned beside the crystal and/or focused onto the crystal. The emerging beam is coherent (monochromatic in-phase) radiation. Such laser beams are used by scientists, engineers, surveyors, and others who need sharp light beams.

Semiconductor diode lasers produce a laser beam at the junction between two dissimilar (n and p) semiconductors when a large electrical current is passed through the device. Although the power is lower than the lasers noted above, the low cost of these small efficient lasers has revolutionized telephone communications (laser light transmission through glass fibers), the record industry (audio compact disc systems), publishing (laser printers), optical memory, *etc.* (see *Materials Science* module for a discussion of semiconductors). Related types of lasers include liquid lasers, tunable dye lasers, and gas lasers. Most encyclopedias provide details on these types of lasers.

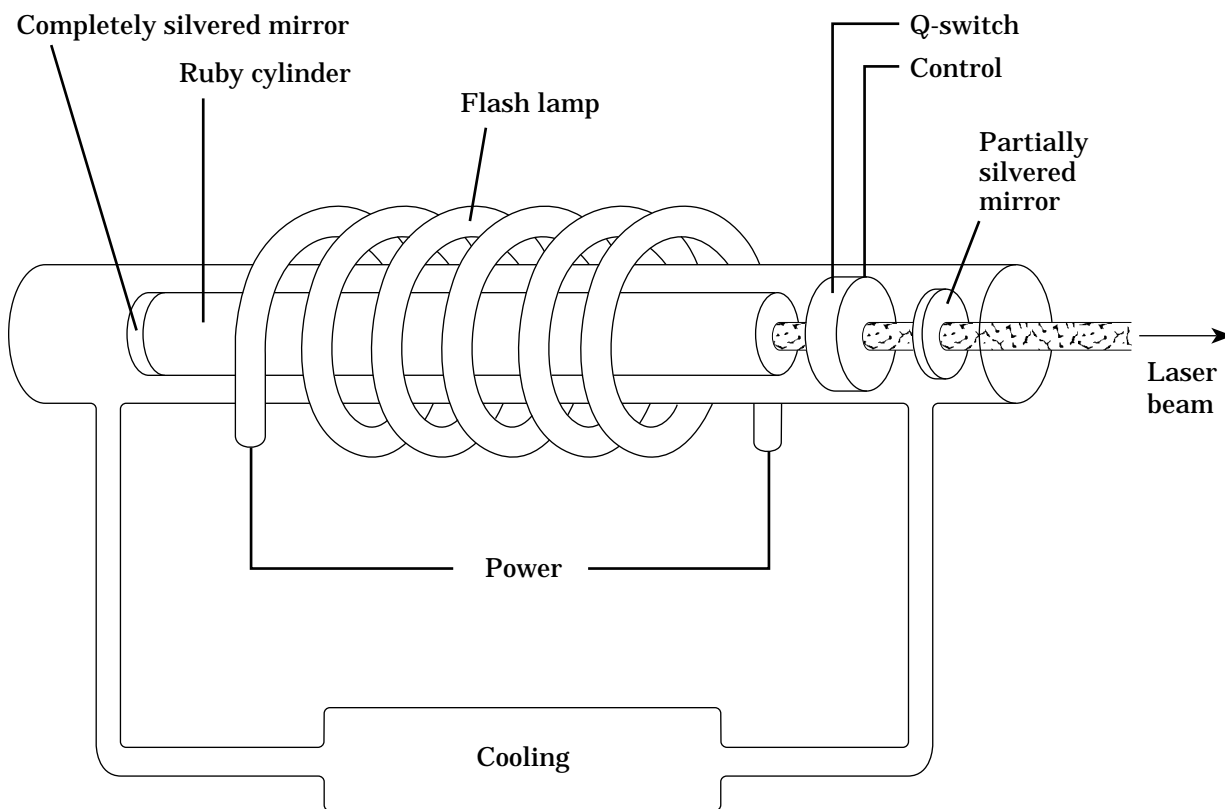
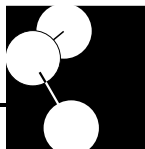


Figure 6. Q-switch, a special switching device that produces giant output pulse. In this example, a ruby laser is being used.

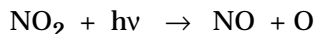
2. **Photochemical separation of isotopes** (uranium enrichment). The low temperature vibration of uranium-235 hexafluoride at 629 cm^{-1} can be selectively irradiated relative to the vibration of uranium-238 hexafluoride at 628 cm^{-1} or vice versa. Because of the narrow line widths possible with lasers, selective ionization followed by chemical reaction is possible. Details of this and related isotope separations can be found elsewhere (Coyle *et al.*, 1982; Andrews, 1986; Spindel & Ishida, 1991).



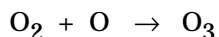
3. **Photoelectric effect applications** (see also *Personal* section). Xerography or photocopying is based on the localized charges that can be induced on a selenium drum by light absorption. An encapsulated graphite powder is selectively transferred to paper based on the charge differences.
4. **Photomultipliers** are electron emitters that have a set of secondary emitters built into the same device to provide amplification of the light signal and are used for light intensity measurements in a wide variety of applications, such as electric eyes, spectrophotometry, scintillation counters, facsimile transmission, and industrial controls.
5. **Photolithography** including photoengraving, photoetching, printed circuits, and other related procedures all depend on photochemical reactions. The blueprint process (*Demonstration 2*) is just one example. Photochemically reduced dichromate in the presence of a number of substances, such as egg albumin, forms insoluble crosslinked materials. The irradiated portion is the background part of the master copy, and the nonirradiated portion is the print area. The more soluble nonirradiated portion of the albumin coating is removed. The chromium polymer protects the irradiated portion of the plate when an etchant is then applied. The result is a bas-relief (gravure or intaglio) plate. Ink is applied over the entire plate and scraped from the nonbas-relief areas. Pressure and capillary action are then used to transfer the ink to the paper.

Societal (Science/Technology/Society; Current Events)

1. Smog. The automobile produces NO, which in turn is oxidized to NO₂ in the atmosphere, producing the brown color of smog. Sunlight photochemically dissociates NO₂ to NO and oxygen atoms:

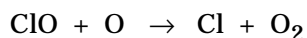
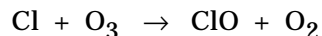
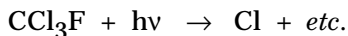


These oxygen atoms react with oxygen molecules to produce ozone:

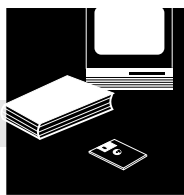


This is the photochemical component of smog.

2. Ozone. Inasmuch as ultraviolet radiation has enough energy to break chemical bonds, life on earth is blessed with an atmosphere that absorbs much of the ultraviolet radiation. Oxygen absorbs the far ultraviolet radiation, and ozone absorbs radiation in the near ultraviolet region. However, other materials in the atmosphere are causing a decrease in the stratospheric ozone layer. Free radicals from photochemical reactions of chlorofluorocarbons (Freons), nitrogen oxides, and methane in the atmosphere can react with ozone to form oxygen gas and other oxides. To illustrate:



Note that at the end of the sequence a Cl radical is still available to react with another ozone molecule. Estimates that 1000 ozone molecules are destroyed by each chlorine atom have been made by considering other species with which the chlorine atoms can react and their concentrations in the atmosphere (Coyle *et al.*, 1982; Lippincott *et al.*, 1988, pp. 370–372).



References

Module developed by R. D. Archer, W. G. Cumming, and A. M. Rennert, the New England team.

Andrews, D. L. (1986). *Lasers in chemistry*. Berlin: Springer-Verlag.

This book details various types of lasers and their uses in chemistry.

Ashcroft, K. (1976). *Chemistry of photography*. Ontario: Book Society of Canada.

A simply written book on photography, which can be recommended in spite of an incorrect equation for the quinone chemical development reaction.

Baumann, M. G. D., Wright, J. C., Ellis, A. B., Kuech, J., and Lisensky, G. C. (1992). Diode lasers. *Journal of Chemical Education*, 69, 89-95.

A fairly detailed discussion of diode lasers and the theory behind them. Very good for teachers who understand energy level diagrams.

Borman, S. (1992, April 6). New light shed on mechanism of human color vision. *Chemical and Engineering News*, 70, 27-29.

Article describes first isolation of pigments of human color vision and how they may help us understand color vision deficiencies.

Calvert, J. G., and Pitts, J. N., Jr. (1966). *Photochemistry*. New York, NY: Wiley.

An excellent resource in photochemistry. Too sophisticated for direct use by most high school students.

Coyle, J. D., Hill, R. R., and Roberts, D. R. (Eds.). (1982). *Light, chemical change, and life: A source book in photochemistry*. Milton Keynes, England: Open University Press.

This book is an excellent elementary text on photochemistry. It is both authoritative and readable.

Drummond, A. H., Jr. (1989, December). Automatic sunglasses. *ChemMatters*, 7, 4-6.

Photochemical reactions of photochromic glass.

Harris, S. (1989). *Einstein simplified. Cartoons on science*. New Brunswick, NJ: Rutgers University Press.

Lippincott, W. T. (Principal Investigator) and American Chemical Society Team. (1988). *ChemCom: Chemistry in the community*. Dubuque, IA: Kendall/Hunt.

This text is written with the nonscientist in mind; therefore, treatments of practical importance are easy for students to understand.

Nassau, K. (1983). *The physics and chemistry of color: The fifteen causes of color*. New York, NY: Wiley.

An excellent reference book on color, its causes and applications. Whereas much of the material is quite appropriate, the chemistry is too deep for most high school students.

The New Encyclopædia Britannica. (1986). Chicago: Encyclopedia Britannica.

"Luminescence," "Photochemical Reactions," "Photoelectric Effect," "Photoengraving," and "Photography, Technology of" articles provide much more detail on these topics than has been presented in this module.



Noyes, W. A., Jr., and Leighton, P. A. (1966). *The photochemistry of gases*. New York, NY: Dover.

A classic that was originally published by Reinhold in 1941. Much of the basic photochemistry of ordinary gases was already known at that time.

Perkins, P. (1993, September). Introduction to photochemistry. *Chem 13 News*, p. 15. "Photography." A review of the development of black and white photography. Available from Institute for Chemical Education, University of Wisconsin/Madison, Madison, WI 53706. Order No. 91-004.

Robbins, D. K. (1984, April). The sunworshippers. *ChemMatters*, 2, 4-7.

This article treats the effects of the sun's radiation on the skin and the efficacy of sun-blocking agents.

Shakhashiri, B. Z., Williams, L. G., Dirreen, G. E., and Francis, A. (1981). "Cool-light" chemiluminescence. *Journal of Chemical Education*, 58, 70-72.

Spindel, W., and Ishida, T. (1991). Isotope separation. *Journal of Chemical Education*, 68, 312-318.

This article contains an excellent section on laser isotope separation (LIS).

Summerlin, L. R., and Ealy, J. (1985). *Chemical demonstrations* (Vol. 1). Washington, DC: American Chemical Society.

See pp. 113-114 in this reference for demonstration related to this module.

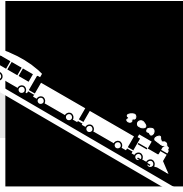
Sweeting, L. (1990, October). Light your candy. *ChemMatters*, 8, 10-12.

This article discusses the origins of triboluminescence.

Thompson, L. F., Willson, C. G., and Bowden, M. J. (1983). *Introduction to microlithography* (American Chemical Society Symposium Series No. 219). Washington, DC: American Chemical Society.

Woodin, R. L., Bomse, D. S., and Rice, G. W. (1990, December 17). Lasers in chemical processing. *Chemical and Engineering News*, 69(51), 20-31.

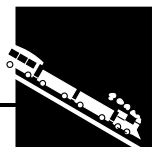
An article that shows the extreme importance of lasers in the chemical industry.



Appendix

- **Transparency Masters**
 1. Wavelengths of Commercial Lasers (Andrews, 1986, p. 164; Woodin *et al.*, 1990)
 2. Laser Wavelength Coverage
 3. Solar Spectral Radial Distribution (Coyle *et al.*, 1982, p. 10)
 4. Fifteen Causes of Color (Nassau, 1983, p. 23)
 5. Causes of Color
 6. Excitation, Fluorescence, and Phosphorescence
 7. Word Search

- **Humor**



Wavelengths of Commercial Lasers

λ/nm	Laser	λ/nm	Laser	λ/nm	Laser
157	Fluorine	441.6	Helium-cadmium	534	Manganese
173.6	Ruby x 4	454.5	Argon	539.5	Xenon
193	Argon fluoride	457.7	Krypton	543.5	Helium-neon
222	Krypton chloride	457.9	Argon	568.2	Krypton
231.4	Ruby x 3	461.9	Krypton	578.2	Copper
248	Krypton fluoride	463.4	Krypton	595.6	Xenon
266	Neodymium x 4	465.8	Argon	628	Gold
308	Xenon chloride	468.0	Krypton	632.8	Helium-neon
325	Helium-cadmium	472.7	Argon	647.1	Krypton
333.6	Argon	476.2	Krypton	657.0	Krypton
337.1	Nitrogen	476.5	Argon	676.5	Krypton
347.2	Ruby x 2	476.6	Krypton	687.1	Krypton
350.7	Krypton	482.5	Krypton	694.3	Ruby
351	Xenon fluoride	484.7	Krypton	722	Lead
351.1	Argon	488.0	Argon	752.5	Krypton
353	Xenon fluoride	495.6	Xenon	799.3	Krypton
355	Neodymium x 3	496.5	Argon	904	Gallium arsenide
356.4	Krypton	501.7	Argon	1060	Nd:glass
363.8	Argon	510.5	Copper	1064	Nd:YAG
406.7	Krypton	514.5	Argon	1092.3	Argon
413.1	Krypton	520.8	Krypton	1152.3	Helium-neon
415.4	Krypton	528.7	Argon	1315	Iodine
428	Nitrogen	530.9	Krypton	1319	Nd:YAG
437.1	Argon	532	Neodymium x 2	3391	Helium-neon
				3508	Helium-xenon

2608-3093 (21 lines)

3493-4100 (37 lines)

5090-6130 (14 lines)

Hydrogen fluoride

Deuterium fluoride

Carbon monoxide

a 9160-9840 (45 lines)

10400-11040 (58 lines)

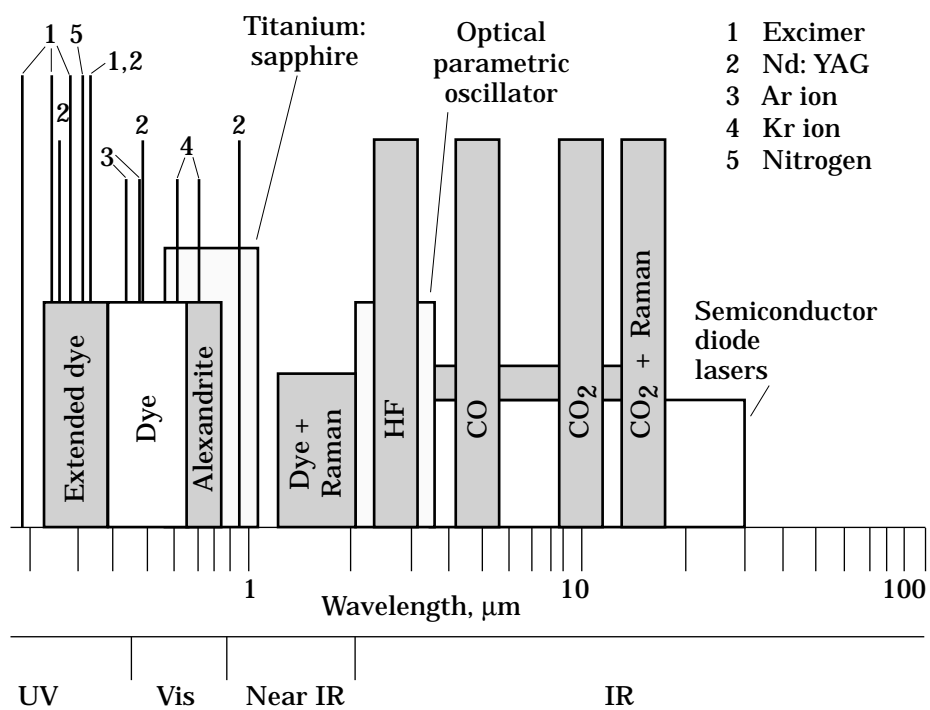
a 10070-11020 (50 lines)

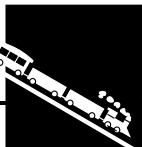
Carbon dioxide

Nitrous oxide

Carbon dioxide

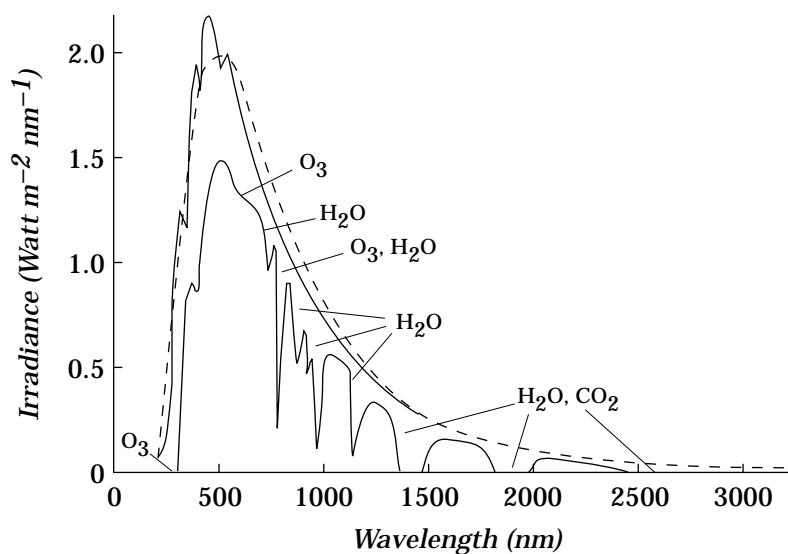
Laser Wavelength Coverage





Solar Spectral Radial Distribution

Note that the detection limits of the human eye exactly match the maximum in this curve, indicating an evolutionary link between the development of vision and the environment.



Fifteen Causes of Color

Vibrations and Simple Excitations

1. **Incandescence** Flames, lamps, carbon arc, limelight
2. **Gas Excitations** Vapor lamps, lightning, auroras, some lasers
3. **Vibrations and Rotations** Water, ice, iodine, blue gas flame

Transitions Involving Ligand Field Effects

4. **Transition Metal Compounds** Turquoise, many pigments, some fluorescence, lasers, and phosphors
5. **Transition Metal Impurities** Ruby, emerald, red iron ore, some fluorescence and lasers

Transitions between Molecular Orbitals

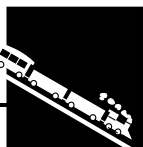
6. **Organic Compounds** Most dyes, most biological colorations, some fluorescence and lasers
7. **Charge Transfer** Blue sapphire, magnetite, lapis lazuli, many pigments

Transitions Involving Energy Bands

8. **Metals** Copper, silver, gold, iron, brass, “ruby” glass
9. **Pure Semiconductors** Silicon, galena, cinnabar, diamond
10. **Doped or Activated Semiconductors** Blue and yellow diamond, light-emitting diodes, some lasers and phosphors
11. **Color Centers** Amethyst, smoky quartz, desert “amethyst” glass, some fluorescence and lasers.

Geometrical and Physical Optics

12. **Dispersive Refraction, Polarization, etc.** Rainbow, halos, sun dogs, green flash of sun, “fire” in gemstones
13. **Scattering** Blue sky, red sunset, blue moon, moonstone, Raman scattering, blue eyes and some other biological colors
14. **Interference** Oil slick on water, soap bubbles, coating on camera lenses, some biological colors
15. **Diffraction** Aureole, glory, diffraction gratings, opal, some biological colors, most liquid crystals



Causes of Color*

Vibrations and Simple Excitations

Incandescence

Gas Excitations

Vibrations & Rotations

Electronic Energy Levels in Ions or Molecules

Transition Metal Compounds

Transition Metal Impurities

Organic Compounds

Charge Transfer

Transitions Involving Energy Bands

Metals

Pure Semiconductors

Doped or Activated Semiconductors

Color Centers

Geometrical and Physical Optics

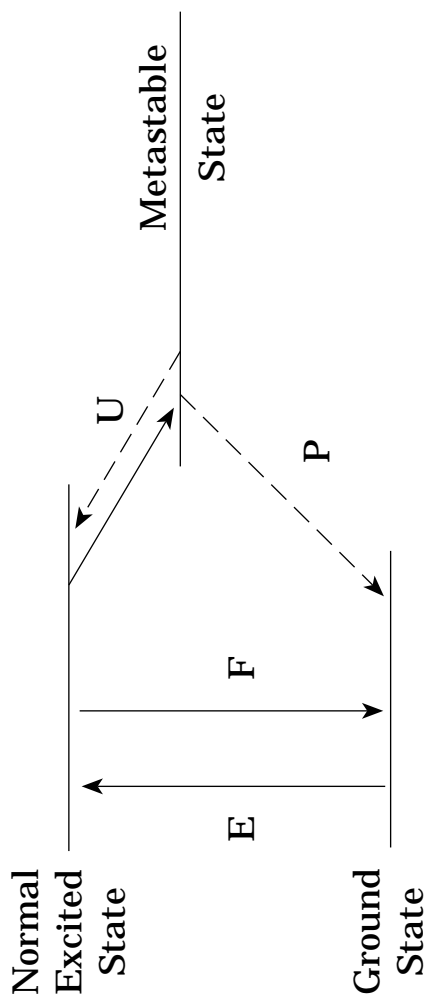
Dispersive Refractions, Polarization, *etc.*

Scattering

Interference

Diffraction

***Transparency 4 has more details.**

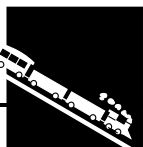
Excitation, Fluorescence, and Phosphorescence

E = Excitation

F = Fluorescence
(allowed, fast)

P = Phosphorescence
(forbidden, slow)

U = Unfavorable (slow)



Word Search

T R I B O L U M I N E S C E N C E
C J U P P J U M M U L W Y C R O W
X E N Q H R O H P S O H P M H X A
O L E D K Q B M J K A U W Y J K V
E C N E C S E N I M U L I M E H C
R K G Q E B G D W Q G Y V L A P K
E C Q V T A E J V G J N Q E D D M
V I B U W R E S A L W R A F C J M
L K Q W A C H R O M O P H O R E S
I F Y R A N S Q I G O C H D V X C
S H F D R F T E L O I V A R T L U
P N J D O M L U G L R H Q D K E X
I D Y W I Z D E M M F K C N A L P

Words about the concepts in this module can be obtained from the clues given.
Find these words in the block of letters:

1. Spectral region associated with molecular vibrations and heat.
2. Acronym for light amplification by stimulated emission of radiation.
3. Material that exhibits phosphorescence
4. Kind of yield that measures photochemical reaction efficiency.
5. Emission of light through chemical reaction.
6. Mechanically induced emission of light.
7. Another name for "black light."
8. Chemical groups that absorb light.
9. Halides of this metal are light sensitive.
10. $\Delta E = h\nu$ is called the Einstein-_____ relationship.

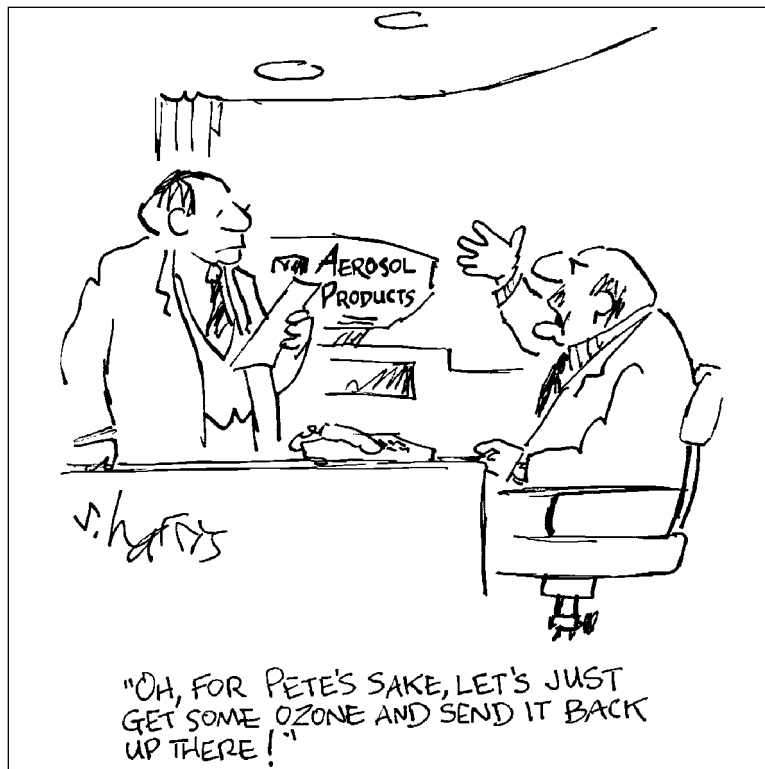
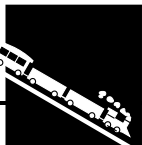
THE FAR SIDE

By GARY LARSON



The bozone layer: shielding the rest of the solar system from the Earth's harmful effects.

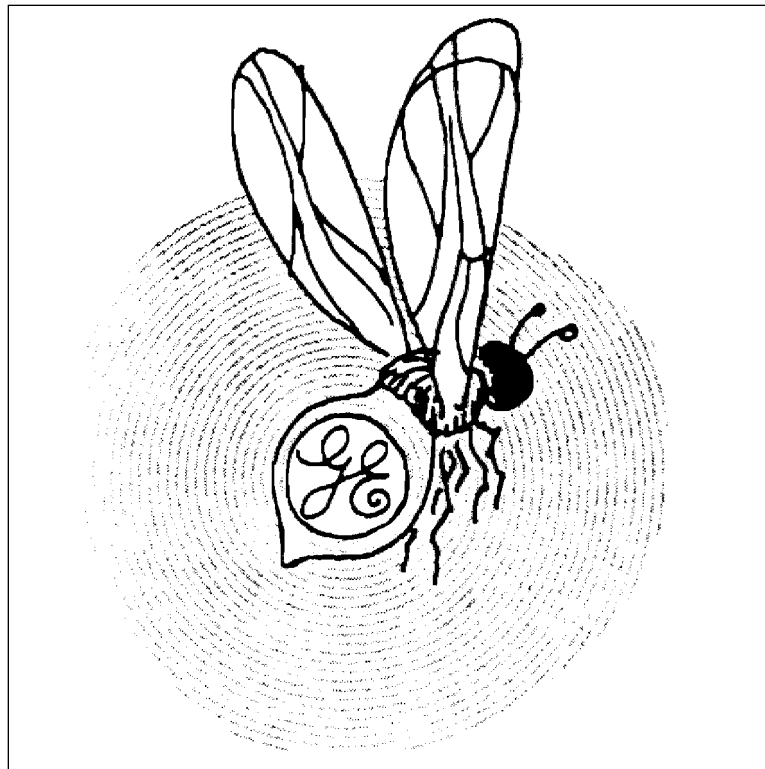
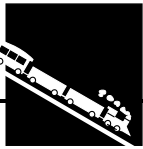
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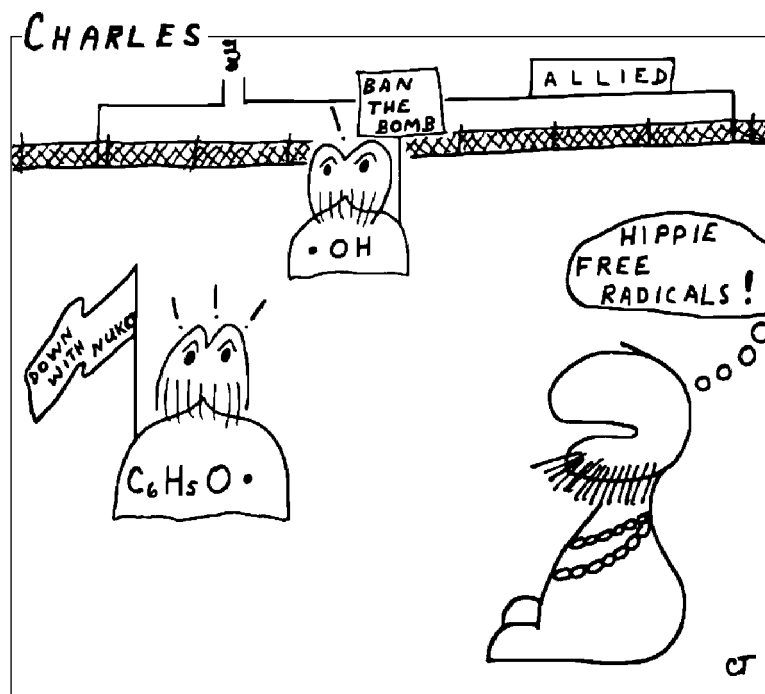
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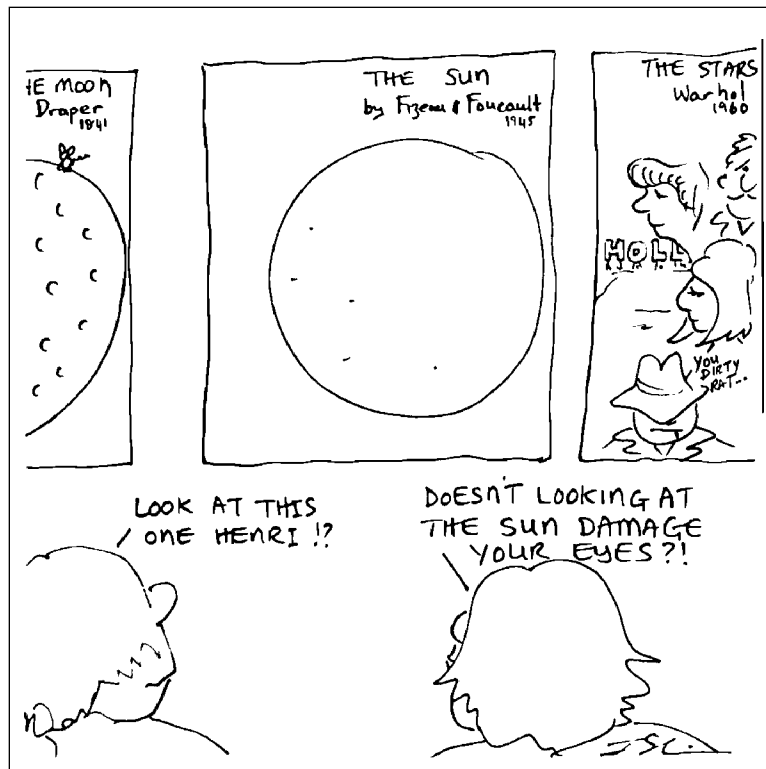
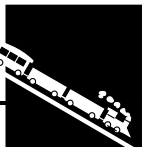
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