This chapter contains five experiments that use lasers to study the electronic structure of molecules. Experiments 5-1 through 5-4 involve the study of laser-induced fluorescence from chlorophyll solutions that can be prepared easily as described in experiment 5-1. Experiment 5-5 describes the use of a laser pendulum apparatus to study the magnetic properties of various inorganic compounds and provides insight into the electronic structure of these compounds. The phenomena studied in these experiments are best understood in terms of quantum mechanics. For this reason, this introduction describes simply and concisely some of the key results of quantum mechanics as they pertain to molecules.

Although performing the experiments in no way requires an understanding of quantum mechanics, the concepts presented here are helpful for gaining insight into the physical processes underlying the experiments. In particular, the information in “Molecular Electronic Structure” provides a theoretical basis for the phenomena studied in experiments 5-1 through 5-4. This introduction concludes with a brief discussion of how lasers work, particularly the He–Ne laser, which is used for most of the experiments in this book.

A NEW UNDERSTANDING OF LIGHT AND MATTER

The twentieth century has witnessed a revolution in the scientific understanding of light and matter and how they interact. This scientific revolution led to the discovery of the photon and to the development of the atomic model. Just as important, the laws of physics established before the twentieth century were shown to be unable to account for the existence of an atom or a photon of light.

1. We thank Professor Allan L. Smith, Department of Chemistry, Drexel University, Philadelphia, PA, for suggesting to us that He–Ne excitation of chlorophyll solutions might make a good system for studying laser-induced fluorescence.
New concepts were needed to explain physical interactions on the scale of atoms and molecules. This new science became known as quantum mechanics, and it still provides the foundation of our current understanding of atoms and molecules.

Before this century, one key assumption made by physicists was that matter and energy were clearly distinct entities. Matter consisted of particles, and radiant energy existed in the form of waves. In the early twentieth century, a series of experiments led scientists to doubt the long-accepted strict distinction between matter and energy. These experiments indicated that light could exhibit particelike properties and matter could exhibit wavelike properties.

The most sophisticated treatment of the nature of light before the twentieth century was provided by James Clerk Maxwell in the 1870s. Maxwell's equations for electromagnetic radiation state that all forms of radiation including visible light move through space as oscillating electric and magnetic fields, and that these fields arise from acceleration or deceleration of charges. Further, all electromagnetic radiation travels through a vacuum at the same speed, namely \( 3.0 \times 10^8 \text{ m/s} \) (customarily represented by the letter \( c \)), and the product of wavelength \( \lambda \) (m) and frequency \( \nu \left( \text{s}^{-1} = \text{Hz} \right) \) gives the speed of light, that is,

\[
c = \lambda \nu
\]  

(5-1)

Thus, the Maxwell equations treat light as a form of energy that travels through space as electromagnetic waves.

The first experiment to cast doubt on this model of light was Max Planck’s 1900 study of blackbody radiation, the radiant energy emitted from a solid when it is heated. Planck found that he could accurately model his data only if he assumed that the radiation was emitted in whole-number multiples of certain well-defined amounts of energy. To explain this mathematical result physically, Planck created a model in which electromagnetic radiation could be absorbed or emitted only in discrete quantities, the smallest of which was named a quantum. From his data, Planck found that the energy of a quantum \( \Delta E \) (in J) is directly proportional to the frequency \( \nu \) of the radiation, which he expressed mathematically as

\[
\Delta E = h \nu
\]  

(5-2)

The proportionality constant \( h \), now known as Planck's constant, was found experimentally to have a value of \( 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \).

Albert Einstein’s later studies of the photoelectric effect helped confirm Planck’s finding that light carried discrete quantities of energy. In fact, Einstein’s experiments indicated that light consisted of a stream of particles, which Einstein named photons. This view of light was somewhat unnerving at the time because light clearly did have wavelike properties, such as diffraction effects (see Chapter 3).

At the same time that the understanding of light was changing radically, equally important changes were being made in the understanding of the structure of matter. A series of experiments by Rutherford and others demonstrated that
matter was composed of atoms, which consisted of an extremely small, massive nucleus composed of protons and neutrons and surrounded by electrons. The distribution of the electrons around the nucleus was not well understood for several years, however.

Neils Bohr presented the first successful model of the electronic structure of atoms by proposing that electrons in hydrogen atoms travel around the nucleus in circular orbits, much like the moon orbits around the Earth. Additionally, Bohr assumed that these circular orbits could have only certain radii, implying that the hydrogen atom could exist only in certain energy states (often referred to as quantized energy states). Bohr’s model was a major breakthrough because it accurately predicted the electronic structure of hydrogen. Bohr could not extend his model to atoms other than hydrogen, however, and many experiments demonstrated that Bohr’s planetary model of electronic motion is incorrect.

A final important discovery of the early twentieth century was that electrons have a property known as spin, which gives rise to a small magnetic moment, and that electrons may have either of exactly two types of spin, which are called spin up and spin down. For more on electron spin, please see experiment 5-5.

AN INTRODUCTION TO THE THEORY OF QUANTUM MECHANICS

In the 1920s, Erwin Schrödinger (1887–1961) and several other scientists developed abstract mathematical theories that have become the foundation of modern quantum mechanics. Unlike Bohr’s theory, which could accurately model only the hydrogen atom, Schrödinger’s equation appears to model accurately the electronic structure of all atoms and molecules. The key result of quantum mechanics for chemistry is that the internal energy of atoms and molecules is quantized. Similar to Bohr’s model of the hydrogen atom, quantum mechanics predicts that the electrons in all atoms and molecules can exist only in certain well-defined energy states. An atom or molecule can undergo transitions between quantized energy states by the absorption or emission of one photon of light with an energy equal to the difference in energy between the two quantized energy levels. The experimental study of the absorption and emission of radiation by atoms and molecules is known as spectroscopy.

Unlike the Bohr model for the hydrogen atom, quantum mechanics does not predict circular orbits for electrons. In fact, quantum mechanics does not predict any regular patterns of motion (trajectories) for electrons; instead, it predicts only the probabilities of finding electrons in a certain location in space at a certain time. Abandoned was the idea of a classical trajectory (or orbit) in which the position and momentum (mass times velocity) of the electron is known at each instant. Instead, a fuzzy probabilistic picture for the electron emerged in which orbits were replaced by orbitals, a probability density of where the electron would be found if its position were measured.
Quantum mechanics can be employed to determine the quantized electronic energy levels of any atom or molecule if the potential energy of the system is known. The orbitals and energy levels of multielectron atoms are well discussed in general chemistry textbooks and will not be discussed here. Instead, we turn to the electronic structure of molecules, which provides a theoretical basis for experiments 5-1 through 5-4.

MOLECULAR ELECTRONIC STRUCTURE

Molecules can store internal energy in several different forms, all of which are quantized. The three most important forms of energy in molecules are electronic energy, vibrational energy, and rotational energy (Figure 5-1). Electronic energy includes the attraction of each electron to each nucleus and the electron-electron repulsions. Electronic energy levels for molecules generally are separated by energies that correspond to visible or ultraviolet light. Vibrational energy arises from the interactions between the nuclei. The bonds in molecules are not rigid but rather behave like springs that vibrate with a frequency proportional to the energy in the bond. Vibrational energy is also quantized, and transi-

![Electromagnetic spectrum showing location of typical electronic, vibrational, and rotational energy levels.](image)

FIGURE 5-1. Electromagnetic spectrum showing location of typical electronic, vibrational, and rotational energy levels.

2. These types of energy are all interlinked because they all depend on the positions of the electrons and nuclei. An excellent approximation (called the Born-Oppenheimer approximation) is to treat each energy form separately and to solve for the quantized energy levels corresponding to each type of motion.
tions between vibrational energy levels are usually observed in the infrared region of the electromagnetic spectrum, which is lower in energy than the visible and ultraviolet regions. Rotational energy arises from the rotation of the molecule about its center of mass. The energy-level spacings of the quantized rotational levels are equivalent to the energies of microwave radiation, even lower in energy than infrared radiation. A typical energy-level diagram for a diatomic molecule is shown in Figure 5-2. Note that each electronic state is subdivided into vibrational energy levels, which in turn are subdivided into even smaller rotational energy levels.

Molecules may have either an odd or even number of electrons. Molecules that have an odd number of electrons are referred to as radicals and tend to be chemically unstable, that is, highly reactive. Most chemically stable molecules have an even number of electrons. In these molecules, electrons are almost always paired, such that for every electron with spin up, there is one electron with spin down. Such molecules are said to be in a singlet state. Molecules may also

3. Diatomic molecules are simple cases because they require only one quantum number each to describe their vibrational and rotational states. Larger molecules require more quantum numbers to describe their vibrational and rotational states, and the energy-level diagrams are correspondingly more complex.
occupy triplet states, in which there are two more electrons with one type of spin than there are with the other type (Figure 5-3). In all cases, the Pauli exclusion principle limits the number of electrons that may occupy any electronic energy level. Many electronic energy levels can hold only two electrons—one with spin up and one with spin down. Other electronic states, known as doubly degenerate states, can hold four electrons, two with spin up and two with spin down. Molecules that possess high symmetry can have even higher degeneracies, such as triply degenerate levels that hold six electrons, and so forth.

Electrons often occupy the lowest available electronic energy levels, and when they do, the molecule is said to be in the ground electronic state. A molecule in the ground electronic state may or may not be in the ground vibrational and rotational states (in Figure 5-2, $v$ could be greater than 0). At thermal equilibrium, the probability of finding a molecule in a particular vibrational and rotational state depends on the temperature. At higher temperatures, a molecule is more likely to occupy higher energy levels.

Because many different energy-level transitions are possible for molecules, the spectroscopy of molecules is a rich topic. Molecules can change rotational states while they remain in the same electronic and vibrational states, change both vibrational and rotational states, or change all three states. Correspondingly, absorption and emission from molecules occur in many regions of the electromagnetic spectrum. Several experiments in this chapter focus on the phenomenon of fluorescence, in which an electron changes from a higher electronic state to a lower one without changing its spin. In general, the rotational and vibrational states also change during such a transition, and the light emitted during fluorescence normally spans a broad range of frequencies.

Typically, for fluorescence to be visible, at least one electron in a molecule must be excited into a higher electronic state, from which it decays to the lower state after some period of time, during which a photon is emitted. A fluorescence experiment in the liquid or solid state can often be thought of as a four-step process, as depicted in Figure 5-4. In this example, the molecule begins in the
ground electronic state. Step 1 corresponds to the absorption of a photon of light, during which one electron enters a higher electronic energy level, and the rotational and vibrational states of the molecule may change as well. In step 2, the molecule remains in the excited electronic state but decays from a higher rotational and vibrational state to a lower one through a nonradiative process. In this step, the molecule does not emit a photon of light but instead transfers energy to surrounding molecules in the form of heat. Step 3 is fluorescence, during which the molecule may or may not return to the original rotational and vibrational state of the molecule. A final step may also occur in which the molecule in the ground electronic state decays from higher rotational, vibrational, or both states to lower ones by a nonradiative process. This diagram shows that the energy changes during absorption and fluorescence are not necessarily equal and that the frequency of the photon emitted during fluorescence is often less than the frequency of the photon absorbed, that is, fluorescence is typically “red shifted” from absorption. Experiment 5-3 provides an example of how to take advantage of this property of fluorescence.

Fluorescence is only one of several processes an excited-state molecule can undergo. Figure 5-5 shows that transitions between singlet and triplet states are also possible. A molecule in an excited singlet state may move to a triplet state by a process known as intersystem crossing, in which the spin of one of the electrons flips. In addition, an excited triplet state may decay to a lower energy singlet state (often the ground state) by emitting a photon. This phenomenon is known as phosphorescence, and it is responsible for the light emitted from many glow-in-the-dark substances. Molecules in singlet and triplet states also may return to the ground state by nonradiative decay (please see experiments 5-2 and 5-3 for more discussion of this type of nonradiative process).

4. Quantum mechanical calculations demonstrate that the lowest-lying triplet excited state is usually lower in energy than the corresponding lowest-lying excited singlet state, as depicted in Figure 5-5.
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4. Quantum mechanical calculations demonstrate that the lowest-lying triplet excited state is usually lower in energy than the corresponding lowest-lying excited singlet state, as depicted in Figure 5-5.
PRINCIPLES OF LASER OPERATION

The word LASER is an acronym for the rather forbidding phrase Light Amplification by Stimulated Emission of Radiation. The output of a laser is a beam of light that is bright, single in color, directional, and in phase. The terms intense, monochromatic, collimated, and coherent are synonymous. From its origins in the late 1950s, the laser has evolved rapidly into a great diversity of available types so that the output of current lasers spans the electromagnetic spectrum from the microwave (maser) to the X-ray.

According to quantum mechanics, atoms and molecules can exist in only discrete, quantized energy levels. Consequently, these building blocks of matter can change their energy levels by absorbing or emitting radiation that has fixed amounts of energy; that is, the radiative transitions in atoms and molecules occur...
at distinct, sharp frequencies or wavelengths and give rise to line spectra. The laser is a "quantum device" in that its characteristic monochromatic light originates from photons of a single frequency emitted as a result of some radiative transition between energy levels of the device. In fact, most lasers operate between several quantum states to produce a range of different laser frequencies that cover different regions of the electromagnetic spectrum. By proper choice of the optical elements that are an integral part of the laser device, typically one frequency can be made to dominate the others. Stated differently, the laser can be tuned and controlled to produce a beam of monochromatic light that has an extremely narrow frequency width. Sometimes, this width may approach a few hertz (Hz), far less than the frequencies of $10^{15}$ Hz that characterize light in the visible portion of the electromagnetic spectrum. For example, the helium–neon laser, a gas-filled device that produces a red beam of light when an electrical discharge excites the electrons of the helium and neon atoms inside the laser to higher energy levels, produces light at 632.8 nm in wavelength ($4.474 \times 10^{14}$ Hz in frequency). With the proper choice of optical elements, a helium–neon laser can produce green light at 543.5 nm or several frequencies of infrared light that cannot be sensed by the eye.

How, then, does the laser differ from an atomic lamp or gas discharge tube that also produces light? Many people are familiar with yellow sodium streetlights or mercury-vapor-filled fluorescent lights. In these discharge devices, light is initially produced through spontaneous emission, in which excited species make a radiative transition from higher to lower quantized energy levels on their own. The excitation process is depicted in "before" and "after" diagrams in Figure 5-6. The number 2 denotes the higher level and 1 the lower level; level 0 represents the ground state occupied almost exclusively under normal (thermal)

![Diagram](image)

**FIGURE 5-6.** The two steps "before" and "after" of the excitation of a three-level system by electron impact from the lowest level 0 to the highest level 2. The closed circles symbolize the number of atoms or molecules that occupy a quantum level.
conditions. Figure 5-7 depicts the “before” and “after” stages of spontaneous emission. The photons produced in the $2 \rightarrow 1$ transition occur spontaneously and have a frequency $\nu_{21} = (E_2 - E_1)/h$, where $h$ is Planck’s constant (see equation 5-2).

In a sodium street lamp, more sodium atoms are in the lower state than the upper state. Consequently, photons of yellow light that are spontaneously emitted either escape the sodium vapor in the lamp or become absorbed by some of the unexcited sodium atoms. Suppose, however, that the discharge process is able to create a population inversion, in which more atoms or molecules are in level 2 than in level 1. Then, when a photon of the resonant frequency $\nu_{21}$ passes by excited atoms or molecules in level 2, it induces them to emit radiation in an inverse process to absorption called stimulated emission (see Figure 5-8). In stimulated emission, the emitted photons have the same energy and are in phase with the stimulating photons. Consequently, a traveling wave of electromagnetic energy grows. Because of the population inversion, the system shows gain and acts to amplify the radiant energy of photons with frequency $\nu_{21}$.

A key element in laser operation is the creation of a population inversion. Such a phenomenon cannot be achieved by any amount of heating in an equilibrium manner. At equilibrium, a system at any temperature always obeys Boltzmann statistics for the population of its energy levels. Thus, the population in a level (divided by the degeneracy of that level, i.e., the number of different ways of occupying that level with the same energy) is always larger the lower the energy level is. At thermal equilibrium, no population inversions can occur. Consequently, laser action requires some nonequilibrium process, such as a flash.
of light, an electrical discharge, or a chemical reaction (explosion), for population inversion to be produced. If the population inversion is transient, the lasing duration must be finite, and the laser provides a pulsed output. If the population inversion can be maintained, the laser action can occur without time limit, and the output is a continuous wave or, as commonly abbreviated, cw.

Laser action can occur by a single pass of stimulating radiation through an active laser medium, which is characterized by having a population inversion. The result is a superradiant laser. For more efficient use of the energy stored in the active medium, however, two highly reflective mirrors are placed on opposite sides of the medium so that the stimulated radiation repeatedly bounces back and forth through the medium between the mirrors, thus increasing the effective pathlength of the active (gain) medium. The use of the optical cavity causes the laser output to have closely spaced optical modes because only an integral number of wavelengths fit inside the length of the optical cavity. For example, the spacing between modes in a helium-neon laser is typically in the megahertz range \(10^6\) Hz). These modes are so close together that they cannot be distinguished as different colors by the eye. Under special circumstances, only one mode may be selected to lase to produce a so-called single-mode laser. In the next section, we describe the helium-neon laser, a commonly used and well-known laser whose output in the red may be used to carry out most of the experiments described in this book.
THE HELIUM–NEON LASER

In 1961, Javan, Bennett, and Herriott of Bell Telephone Laboratories reported demonstrating the first continuous action laser, which was achieved by maintaining an electrical discharge in a gas mixture of helium and neon atoms (1). The lasing cavity of a typical helium–neon laser consists of a sealed tube filled with helium gas (90%) and neon gas (10%) at a total pressure of approximately 1 torr (equivalent to 1/760 of atmospheric pressure). At this low pressure, a high-voltage power supply easily maintains an electrical discharge inside the sealed cavity, thereby producing energetic electrons that travel through the gas mixture. The typical current is 10 milliamperes at 1,000 V, and the typical power is 10 W, which produces a 1-mW output beam for an overall efficiency of only 0.01% for converting electrical to coherent radiant energy.

The atomic energy levels of the rare gases are a complicated topic. The ground state of a rare gas such as helium or neon has a closed-shell configuration of electrons, 1s² for He and 1s²2s²2p⁶ for Ne, each of which gives rise to only one level, denoted 1S. Excited electron configurations of the rare gases have more than one open shell of electrons and give rise to numerous atomic energy levels. To confuse matters, the standard spectroscopic notation (2) is based more on historical than logical reasons, and the labels are best considered names for the levels that occur at certain energies.

Figure 5-9 presents the major energy levels of He and Ne that are relevant to understanding how the He–Ne laser works. The electrons in the discharge excite helium atoms from the 1s² ground-state electron configuration to the 1s²2s excited-state electron configuration, which has two long-lived (metastable) atomic energy levels, denoted 2⁴S and 2³S. The 2¹S level lies very close in energy to atomic energy levels that belong to the 1s²2s²2p⁵5s electron configuration of neon. As a consequence, the excited 2¹S helium atoms efficiently transfer by collision their energy to neon atoms to populate the upper level (denoted 3s₂) of the 632.8-nm laser transition (corresponding to 3s₂ → 2p₄). In truth, this collisional transfer process is much more efficient for exciting this level of neon than is direct electron-impact excitation of neon. Thus, the He–Ne laser works by photosensitization of Ne atoms by excited He atoms; Chapter 6 introduces a number of other examples of photosensitized energy transfer.

Because only the ground-state electron configuration 1s²2s²2p⁶ of neon is populated at room temperature, a population inversion is created between this upper level of the 1s²2s²2p⁵5s configuration of Ne and the lower-lying levels of the 1s²2s²2p³3p electron configuration of Ne. Laser action at 632.8 nm can then occur if the excited gas mixture is placed between suitable mirrors, which are commonly sealed directly to the ends of the discharge tube. As shown in Figure 5-9, 3.391-µm laser action (in the infrared) competes with the 632.8-nm laser action (in the visible) because both of these laser transitions deplete the same upper level. Increasing the intensity of the 632.8-nm laser line necessitates “spoil- ing the gain” of the 3.391-µm transition by using, for example, an infrared-absorbing mirror.
FIGURE 5-9. An energy-level diagram of helium and neon, showing the excitation mechanism and neon transitions responsible for laser action in a helium-neon laser.
The levels of the 1s²2s²2p⁵3p configuration of neon rapidly decay radiatively to levels of the 1s²2s²2p⁵3s configuration (not shown in Figure 5-9), primarily by transitions in the red portion of the spectrum. This rapid decay gives neon signs their characteristic color. This efficient emptying of the population of the lower level of the 632.8-nm laser transition is very desirable because it ensures that the population inversion between the upper and lower levels of this transition is continuously maintained as long as the electric discharge occurs in the gas mixture. Neon atoms in the long-lived levels of the 1s²2s²2p⁵3s configuration are returned to the ground-state configuration by deactivating collisions, which include collisions with the walls of the discharge tube.

The helium–neon laser transition at 632.8 nm has rather low gain, typically 2–10% per meter. Consequently, one end mirror is nearly 100% reflective, whereas the other is 99% reflective, a level that permits only 1% of the intracavity radiation to escape per round trip inside the cavity. To support laser action, the optical cavity must be carefully aligned so that the light beam inside the cavity does not escape (“walk off”) the end mirrors after repeated reflections. As a He–Ne laser is turned on, it warms up, and the dimensions of its cavity structure change over time. Typical He–Ne lasers operate in a multimode manner, and the intensity of the different modes varies as the cavity structure changes with temperature. Consequently, the He–Ne laser beam varies in intensity with time, particularly during the warm-up stage. This intensity variation can be readily detected and displayed using a power meter that records the light intensity striking its surface. Variations of several percent are typical for inexpensive, unstabilized He–Ne lasers.

A helium–neon laser can show laser action (oscillation) on more than 50 different transitions. The first He–Ne laser built by Javan, Bennett, and Herriott (1) operated at 1.1523 μm, using the 2s₂ → 2p₄ transition in the near infrared range (see Figure 5-9). Shortly thereafter, White and Rigden (3) discovered laser action in the red 632.8-nm transition; this red beam of coherent light is now familiar to us in the form of bar code readers at check-out counters and laser pointers. The He–Ne laser may also be made to operate in the green at 543.5 nm (see Figure 5-9) using the 3s₂ → 2p₁₀ transition.

More information on lasers may be found in references 4–9.
The levels of the $1s^22s^22p^53p$ configuration of neon rapidly decay radiatively to levels of the $1s^22s^22p^53s$ configuration (not shown in Figure 5-9), primarily by transitions in the red portion of the spectrum. This rapid decay gives neon signs their characteristic color. This efficient emptying of the population of the lower level of the 632.8-nm laser transition is very desirable because it ensures that the population inversion between the upper and lower levels of this transition is continuously maintained as long as the electric discharge occurs in the gas mixture. Neon atoms in the long-lived levels of the $1s^22s^22p^53s$ configuration are returned to the ground-state configuration by deactivating collisions, which include collisions with the walls of the discharge tube.

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A helium–neon laser can show laser action (oscillation) on more than 50 different transitions. The first He–Ne laser built by Javan, Bennett, and Herriott (1) operated at 1.1523 μm, using the $2s_2 \rightarrow 2p_4$ transition in the near infrared range (see Figure 5-9). Shortly thereafter, White and Rigden (3) discovered laser action in the red 632.8-nm transition; this red beam of coherent light is now familiar to us in the form of bar code readers at check-out counters and laser pointers. The He–Ne laser may also be made to operate in the green at 543.5 nm (see Figure 5-9) using the $3s_2 \rightarrow 2p_{10}$ transition.

More information on lasers may be found in references 4–9.
REFERENCES

EXPERIMENT 5-1

EXTRACTION OF CHLOROPHYLL FROM FRESH SPINACH

Experiments 5-2, 5-3, and 5-4 study the fluorescent properties of chlorophyll. In this experiment, chlorophylls a and b are extracted from fresh spinach and laser-induced fluorescence from these compounds is observed.

DEGREE OF DIFFICULTY
Experimental: moderate
Conceptual: easy

MATERIALS
- Erlenmeyer flasks
- beakers
- mortar and pestle
- separatory funnel, 125 mL
- round-bottom flask, 150 mL
- rotovap or steam bath
- column chromatography equipment ( buret is sufficient)
- glass wool
- 10 g of alumina powder (aluminum oxide)
- 10 g of anhydrous magnesium sulfate
- 150 mL of heptane (hexane is an acceptable substitute) (Sigma product #H9629. Approx. $18 for 1 liter)
- 5–10 fresh spinach leaves
- 10 g of sand
- He–Ne laser (or other laser with wavelength very near 633 nm)
- cut-off filter, 665 nm or 645 nm (if available) (Available from Corion Corp., 73 Jeffrey Ave., Holliston, MA 01746-2082. Listed as “Schott filter glass,” LG-650 or LG-675. Approx. $20 for a 1-in.-diameter filter)

PROCEDURE

Extraction of Chlorophyll from Spinach Leaves

1. Grind 4 or 5 large spinach leaves in a pool of heptane using a mortar and pestle. A pinch of sand may aid the process. Pour off the green organic extract, and filter it using a piece of filter paper and a funnel.

2. To remove impurities, extract the heptane solution with water in a separatory funnel. Repeat the washing procedure, and then pour the green heptane solution into an Erlenmeyer flask with 10 g of anhydrous magnesium sulfate. Let the solution sit for several minutes.
3. Pour off the heptane solution into a round-bottom flask. Concentrate the solution in
the flask by heating it in a water bath at a temperature below 50° C (by swirling or
using a rotovaporator) until approximately 1 mL of the solution remains. Reduce
the temperature to below 40° C, and allow the solution to evaporate to dryness.

4. Dissolve this residue with 2 mL of heptane and set aside.

Preparation of the Alumina Column

5. Place a small amount of glass wool at the bottom of a chromatography column, and
fill the column two-thirds full with heptane. Make a one-half-inch plug of sand
above the glass wool by slowly pouring in sand and allowing it to settle to the
bottom.

6. Slowly pour in alumina powder while tapping on the sides of the column to prevent
clumping and bubble formation. Make sure the liquid level never falls below the
column packing. Drying of the column leads to cracking, which makes the column
perform poorly. After all of the alumina has been added, open the stopcock and
allow the heptane to drain slowly to allow the column to settle. Drain the heptane
until it just covers the packing.

Purification of the Chlorophyll

7. Pipette the green extract from step 4 onto the top of the column, and drain the
column slowly until the alumina is nearly exposed. Add 5 mL of heptane to the
column, and allow it to drain as well. Add another 5 mL of heptane and a small
amount of sand to the column. Fill the column to the top with heptane. Caution:
ever let the liquid level fall below the level of the alumina.

8. Drain the solvent through the column and collect the various fractions (the colored
bands that pass through the column) in separate flasks. You may wish to weigh
several of the flasks in advance to ease preparation of the chlorophyll solutions in
step 9. The yellow–green carotenes come off first followed by the two chlorophylls,
a and b (green). Experiments 5-2 through 5-4 use the chlorophyll fractions. Conse-
quently, do not contaminate any of the green fractions with the yellow carotenes.
Distinguishing between chlorophyll a and b is not necessary.

9. Evaporate the chlorophyll fractions to a green residue without heating them above
45° C. Determine the mass of each residue. Use these residues immediately to pre-
pare stock solutions of chlorophyll (MW ≈ 900) in heptane. The choice of concen-
tration of these solutions is up to the experimenter; we prepared stock solutions of
concentration 1.30 × 10⁻³ M. These solutions should be capped and refrigerated
until needed.

10. Irradiate the chlorophyll solutions of varying concentrations with a red laser, and
observe the fluorescence at 90° to the incident laser beam. Confirm that the light
arises from fluorescence and not scattering (i.e., that it has a longer wavelength than
the incident light) by viewing the cuvette through a 665- or 645-nm cut-off filter.
HAZARDS AND PRECAUTIONS

Heptane is flammable and will irritate the skin upon exposure. Exercise caution when heating heptane solutions; use a boiling stone and a sand bath. Never use flames! Wear gloves when handling these substances, and avoid breathing their vapors. The remaining substances are believed to be of low toxicity and present no hazards known at this time. Wear eye protection at all times.

DISPOSAL

All solids can be disposed of as trash. Any heptane solutions should be disposed of as organic waste.

DISCUSSION

The column chromatography system described in the procedure is conceptually identical to the column prepared in experiment 4-1. The laser-based detection system is unnecessary in this experiment because the desired compounds are colored. Please refer to the discussion section of experiment 4-1 for background information on chromatography.

Figure 5-1-1 shows the structures of chlorophylls a and b. These molecules are examples of coordination compounds, which have in common a metal ion coordinated to an organic compound. Coordination compounds include such diverse compounds as hemoglobin and vitamin B₁₂ and are essential in many biological processes, such as the transport of oxygen, electron transfer, and catalysis.

Chlorophyll is the component in photosynthesis that traps solar energy so that it can be used to drive the production of carbohydrates from carbon dioxide and water. Chlorophyll a and b absorb strongly in the red region of the spectrum and have peak

![Molecular structure of chlorophyll](image-url)

FIGURE 5-1-1. Molecular structure of chlorophyll. When R = CH₃, the compound is chlorophyll a; when R = CHO, the compound is chlorophyll b.
absorptions near 650 nm (Figure 5-1-2). The absorption spectra for chlorophylls a and b differ somewhat, and these two types of chlorophyll complement each other in absorbing sunlight.

During photosynthesis, once a photon is absorbed by a chlorophyll molecule, the energy from that absorption is quickly transferred to the chloroplasts, where it is used to drive chemical processes. When the chlorophyll is extracted from leaves, however, the absorbed energy can no longer be trapped, and the chlorophyll reemits the energy by fluorescence. The chlorophyll solutions prepared in this experiment strongly absorb the 632.8-nm light from a He–Ne laser, and the fluorescence maximum lies at approximately 685 nm. The fluorescence can be distinguished from scattered laser light by use of a filter. Unlike many synthetic dyes, chlorophyll is nontoxic, plentiful, and cheap. For these reasons, chlorophyll is an ideal substance for studying absorption and fluorescence phenomena in the laboratory.
EXPERIMENT 5-2

FLUORESCENCE VS. CONCENTRATION

This experiment examines the intensity of fluorescent light in a series of solutions of different chlorophyll concentrations to determine the dependence of fluorescence intensity on concentration.

DEGREE OF DIFFICULTY

Experimental: moderate
Conceptual: moderate

MATERIALS

- He–Ne laser (or other laser with wavelength very near 633 nm)
- cuvette and holder
- light-detection system
- test tubes, graduated cylinders, or volumetric flasks
- Schott cut-off filters, RG665 or RG645 (Available from Corion Corp., 73 Jeffrey Ave., Holliston, MA 01746-2082. Listed as “Schott filter glass,” LG-650 or LG-675. Approx. $20 for a 1-in.-diameter filter)
- 0.45-μm filter (if available)
- chlorophyll solution (from experiment 5-1)
- heptane (Sigma product #H9629. Approx. $18 for 1 liter)
- beam splitter (if available)

PROCEDURE

1. Assemble the apparatus as described in step 1 of experiment 5-3 and depicted in Figure 5-3-1.

2. Prepare six to eight dilutions of chlorophyll (MW ≈ 900) from the stock solution (prepared in experiment 5-1) and heptane. Recommended concentrations are from 1.3 × 10^{-3} M to 4.0 × 10^{-3} M. Prepare at least 3 mL of each chlorophyll solution. Filter the solutions with a 0.45-μm filter, if available.

3. Fill the cuvette with the most dilute sample and irradiate it with red laser light. Record the fluorescence intensity.

4. Repeat this procedure using the other dilutions. When changing solutions, empty the cuvette, and rinse it with a small amount of the new solution from a clean pipette before filling the cuvette with the new solution. Be sure not to move the sample holder when changing solutions.

5. Prepare a plot of fluorescence intensity vs. concentration of chlorophyll.
HAZARDS AND PRECAUTIONS

Heptane is flammable and will irritate the skin upon exposure. Keep all of the organic solutions away from open flames, wear gloves when handling them, and avoid breathing their vapors. The other substances are believed to be of low toxicity and present no hazards known at this time. Wear eye protection at all times.

DISPOSAL

The chlorophyll solutions should be disposed of as organic waste.

DISCUSSION

Figure 5-2-1 is a plot of fluorescence intensity as a function of chlorophyll concentration. At low concentration, the intensity rises rapidly and nearly linearly with concentration, whereas at higher concentration, the intensity approaches a constant value.
HAZARDS AND PRECAUTIONS

Heptane is flammable and will irritate the skin upon exposure. Keep all of the organic solutions away from open flames, wear gloves when handling them, and avoid breathing their vapors. The other substances are believed to be of low toxicity and present no hazards known at this time. Wear eye protection at all times.

DISPOSAL

The chlorophyll solutions should be disposed of as organic waste.

DISCUSSION

Figure 5-2-1 is a plot of fluorescence intensity as a function of chlorophyll concentration. At low concentration, the intensity rises rapidly and nearly linearly with concentration, whereas at higher concentration, the intensity approaches a constant value.

![Fluorescence vs Concentration Graph]

**FIGURE 5-2-1.** Concentration dependence of chlorophyll fluorescence.
The qualitative form of the concentration dependence of fluorescence for chlorophyll is observed for many different molecules. In fact, the relationship between fluorescence intensity and concentration can be modeled for many systems according to a fairly simple equation:

\[ F = \Phi I_o (1 - e^{-\epsilon bc}) \]  

(5-2-1)

where \( F \) is the intensity of fluorescence, \( I_o \) is the intensity of incident light, \( \epsilon \) is the molar absorptivity (a constant for any particular compound at a particular wavelength), \( b \) is the pathlength of the cell, and \( c \) is the molar concentration. The (dimensionless) constant \( \Phi \) is the quantum efficiency and has been defined as the number of quanta of radiation fluoresced by a sample divided by the number of quanta absorbed. Thus, the quantum efficiency represents the fraction of molecules that fluoresce from the excited state as opposed to decay by nonradiative processes. This formula accurately predicts that the fluorescence intensity will approach a maximum value \( \Phi I_o \) as \( c \) becomes large.

Formula 5-2-1 also predicts the linear relationship between fluorescence and concentration at low concentration, since it can be shown (using a Taylor series expansion) that

\[ e^x \approx 1 + x \]  

(5-2-2)

for small \( x \) (in this case, low concentration). Using this expansion in equation 5-3-1, we find

\[ F = \Phi I_o \epsilon bc \]  

(5-2-3)

The interested student may wish to use these relationships to model the chlorophyll fluorescence.
FLUORESCENCE QUENCHING

This experiment examines the phenomenon of quenching, which occurs when a substance in solution (the "quencher") interacts with excited-state molecules to decrease the intensity of fluorescent light.

DEGREE OF DIFFICULTY

Experimental: moderate
Conceptual: moderate

MATERIALS

- He–Ne laser (or other laser with wavelength very near 633 nm)
- cuvette and holder
- light-detection system
- test tubes, graduated cylinders, pipettes
- cut-off filter, 665 nm or 645 nm (Available from Corion Corp., 73 Jeffrey Ave., Holliston, MA 01746-2082. Listed as "Schott filter glass," LG-650 or LG-675. Approx. $20 for a 1-in.-diameter filter)
- 0.45-μm filter (if available)
- stock chlorophyll solution (from experiment 5-1)
- heptane
- beam splitter (if available)
- 1 g of sodium iodide (NaI)
- 1 g of p-benzoquinone (Sigma product #B1266. Approx. $20 for 25 g)
- 50 mL of acetone (optional)
- 50 mL of propylene glycol (or other high-viscosity solvent) (optional)

PROCEDURE

1. Assemble the apparatus as shown in Figure 5-3-1. Optimally, a cuvette holder such

![Diagram of experimental setup](image)

FIGURE 5-3-1. Schematic diagram of experimental setup for detecting fluorescence from chlorophyll solutions.
as the one in Figure 1-3 can be modified to hold the cut-off filter next to the 90° face of the cuvette. Position the photodiode (or other light-measuring device) as close to the cuvette as possible, and make certain that the laser beam passes adjacent to the photodiode. Use the beam splitter to monitor the laser output power, and take measurements only when the power is at some fixed value.

2. Prepare “spiked” solutions of heptane by adding small amounts of NaI or p-benzoquinone. Useful concentrations for these two quenchers are up to 0.5 M for NaI and up to 0.15 M for p-benzoquinone.

3. Evaporate several 2-mL samples of the stock solutions of chlorophyll in heptane (from experiment 5-1) to a green residue without heating beyond 45° C. Dissolve the residues in 2.0 mL of the various spiked solutions. Prepare at least one solution without any quencher as a control. Filter the solutions with a 0.45-μm filter, if available.

4. Measure the fluorescent light intensity for the spiked chlorophyll solutions and the control.

5. (Optional) Repeat the experiment with either acetone or propylene glycol as the solvent to measure the effects of viscosity on quenching.

6. Prepare plots of fluorescence intensity vs. concentration for each quencher and solvent used.

HAZARDS AND PRECAUTIONS

Heptane is flammable and irritates the skin upon exposure. Exercise caution when heating heptane solutions; use a boiling stone and a sand bath. Never use flames! Keep all of the organic solutions away from open flames, and avoid skin contact and breathing their vapors. p-Benzoquinone is a skin and eye irritant and a suspected carcinogen. Wear eye protection at all times.

DISPOSAL

The chlorophyll solutions should be disposed of as organic waste.

DISCUSSION

In addition to fluorescence, several processes can return an excited-state molecule to the ground state without emitting light; these processes are known as nonradiative processes. In a typical nonradiative process, the energy of the excited electronic state of a molecule is either transferred to other molecules or redistributed inside the molecule. The mechanisms of these processes are often complex and not well understood. Nonradiative processes compete with fluorescence in the sense that for any given sample of molecules in an excited electronic state, a certain fraction will fluoresce and the rest will return to the ground state through nonradiative processes. The ratio of these two processes is different for every molecule and may be expressed in terms of the fluorescence quantum yield (Φ), which is defined as the number of photons of light fluoresced by a
sample divided by the number of photons absorbed. Values of \( \Phi \) range from nearly 1 for some laser dyes to nearly 0 for molecules that hardly fluoresce.

The quantum yield for a particular molecule depends on the environment of the molecule, that is, the solvent, temperature, pH, and other factors that affect interaction between the excited-state molecule and its surroundings. This experiment examines the effects of two different quenchers that promote nonradiative processes in the chlorophyll solutions. For sodium iodide, the iodide ions in solution interact with the excited-state chlorophyll molecules to promote conversion of the singlet state to a triplet state, which then decays to the ground state by other nonradiative processes.\(^1\) Figure 5-3-2 presents a plot of the extent of fluorescence quenching against concentration of iodide ion.

\[
\begin{align*}
\text{Fluorescence intensity (arbitrary units)} & \\
2.81 \times 10^{-4} \text{ M chlorophyll} & \\
1.85 \times 10^{-4} \text{ M chlorophyll} & \\
\end{align*}
\]

**Figure 5-3-2.** Quenching of chlorophyll fluorescence by sodium iodide.

---

1. The mechanism for this interaction is that the iodide ion is paramagnetic and has a permanent magnetic dipole moment, which allows it to interact with the electrons in the chlorophyll molecule so as to change the spins of the outermost electrons from spin antiparallel (singlet state) to spin parallel (triplet state). More information on electron spin and magnetic moments is presented in experiment 5-5.
Fluorescence also depends to some extent on the viscosity of the medium. As can be seen in Figure 5-3-3, fluorescence quenching caused by α-benzoquinone is greater in the low-viscosity acetone solution than in the higher viscosity propylene glycol solution. In the high-viscosity solution, the chlorophyll and quenching molecules move more slowly, and the probability is lower that an excited-state chlorophyll molecule will come in close contact with a quencher molecule before it fluoresces. Thus, quenching is a less-efficient process in viscous media.

Quenching plays a very important role in photosynthesis. For photosynthesis to be efficient, the potential energy gained by the absorption of photons must be prevented from being reradiated as fluorescence. Quenching occurs during photosynthesis when the chlorophyll comes in contact with a chloroplast, and the energy of the excited state leads to charge separation, which is then used to drive chemical reactions.
The dependence of fluorescence depolarization on temperature is investigated, providing insight into the dynamics of chlorophyll molecules in solution.

**DEGREE OF DIFFICULTY**

Experimental: moderate  
Conceptual: moderate

**MATERIALS**

- He–Ne laser (or other laser with wavelength very near 633 nm)  
- light-detection system  
- cuvette holder  
- beam splitter (if available)  
- water bath and ice bath  
- thermometer  
- 2 polarizers  
- hot plate  
- chlorophyll solution (from experiment 5-1)

**PROCEDURE**

1. Set up the apparatus as shown in Figure 5-4-1. Although not required, continual monitoring of the temperature of the chlorophyll solutions while taking light intensity measurements is particularly convenient. Place one polarizer in the path of the incident laser light and the other parallel to the first in front of the photodiode at 90° to the incident beam. Using a cuvette holder such as the one in Figure 1-3, which is

![Diagram of experimental setup](image)

**FIGURE 5-4-1.** Schematic diagram of experimental setup for detecting depolarization of fluorescence from chlorophyll solutions.
modified to hold the polarizer next to the 90° window of the cuvette, may be helpful. Use the beam splitter to monitor the power output of the laser, and take data only when the power is at some fixed value.

2. Prepare a solution of chlorophyll that gives strong fluorescence upon irradiation by a red laser (see Figure 5-3-1). Measure the light intensity at 90° to the incident beam as a function of the temperature of the chlorophyll solution over a temperature range of 0° to 45° C. One easy way to make these measurements is to heat the solution to 45° C and then measure the fluorescent light intensity as the temperature drops. An ice bath can be used to bring the solution to 0° C. Realize, however, that during the cooling process, the solution is not at thermal equilibrium, and the temperature is not uniform throughout the sample. Use the light meter to monitor the laser output and ensure that all readings are made at the same output.

3. Plot the light intensity at 90° vs. temperature.

HAZARDS AND PRECAUTIONS

Heptane is flammable and irritates the skin upon exposure. Keep all of the organic solutions away from open flames, and avoid skin contact and breathing their vapors. Keep all flammable material away from open flames. Wear eye protection at all times.

DISPOSAL

The chlorophyll solutions should be disposed of as organic waste.

DISCUSSION

In this experiment, ground-state chlorophyll molecules are excited to a higher energy, singlet electronic state by absorption of the light radiation from the laser. This electronic transition occurs by an interaction between the electromagnetic field of the light and the electrons in the molecule. The oscillating electric field of the light causes the electrons in the molecule to oscillate at the same frequency. The additional energy gained by this interaction allows the molecule to enter an excited state, if the energy of the photon matches the difference in energy between the two quantum mechanical levels according to the fundamental relation $\Delta E = h \nu$.

Because the absorption of light results from an interaction with the electric field of the incident light, the molecule, not surprisingly, retains a memory of the polarization of the incident light. The electrons in the molecule not only vibrate with the same frequency as the incident light, they also vibrate with the same polarization (i.e., they vibrate in the same direction as the electric field of the light). When the excited-state molecule fluoresces, the electric field of the emitted light is oriented in the same direction that the electrons were oscillating in the molecule. If the molecule did not rotate between the time it absorbs and the time it emits a photon, then the electric field of the incident light and the fluorescent light would be oriented in the same direction. In other words, the polarizations of the incident and fluorescent light would be the same.

Of course, excited molecules in solution do not remain stationary but rotate chaotically because of interactions (collisions) with the solvent molecules. Molecules remain
in the excited state for a small but finite amount of time, and in general, we cannot assume the molecules do not rotate during this time. In this experiment, linearly polarized light irradiates a sample of chlorophyll molecules. If the lifetime of the excited state is long compared with the rotation speeds of the molecules in solution, the fluorescent light will be almost completely depolarized, that is, it will retain almost no memory of the polarization of the incident light. The fluorescent light can be expected to remain highly polarized only if the lifetime of the excited state is shorter than the time required for chlorophyll molecules to rotate significantly in solution or if it were possible to observe the fluorescence emitted just after excitation. Chlorophyll is a large, bulky molecule and thus tends to rotate slowly in solution. Accordingly, the extent of fluorescent depolarization for chlorophyll is relatively low at room temperature. Increasing the temperature increases the energy of the solvent molecules as well as the chlorophyll molecules, and on average the excited chlorophyll molecules rotate faster in solution, increasing the extent of depolarization.

In this experiment, the extent of fluorescent depolarization is measured indirectly by positioning the second polarizer to transmit light preferentially with the same polarization as the incident light. As the extent of depolarization increases, the intensity of light at the detector decreases. Little interference in these measurements would be expected from scattered laser light. As explained in the introduction to Chapter 2, almost all light scattered at right angles to the laser beam should have the same polarization as the incident light and be transmitted through the polarizer. Depolarization of scattered light is normally caused by multiple scattering and molecular anisotropy, and these factors do not depend on temperature.

Figure 5-4-2 shows a typical plot of light intensity at 90° vs. temperature. As ex-

![Figure 5-4-2](image_url)
pected, the fluorescent light is significantly more polarized at lower temperatures than at higher temperatures. The extent of depolarization increases approximately linearly with temperature (at least over the temperature range studied), which reflects the effect of increasing temperature to increase the fraction of molecules that have rotated appreciably before emitting.
MAGNETIC SUSCEPTIBILITY MEASUREMENTS

A laser pendulum apparatus is constructed and used to measure the magnetic properties of powdered crystalline samples.

**DEGREE OF DIFFICULTY**

Experimental: difficult
Conceptual: difficult

**MATERIALS**

- laser
- computer-interfaced light-detection system
- permanent magnet¹
- 1-mL vials with plastic caps
- ring stand and clamps
- mortar and pestle
- various inorganic compounds (such as those listed in Table 5-5-1)
- thread
- epoxy

**PROCEDURE**

1. Pierce a plastic vial cap, insert one end of a 0.28-m thread into the cap, and affix the end to the cap, using epoxy. Attach a vial to the cap, and suspend the vial by the string so that it is free to swing. Align the permanent magnet (1-in. pole gap or smaller) as shown in Figure 5-5-1, and make sure that the sample sits in the upper quarter of the magnet’s gap when at rest. Align the laser and the photodiode of the light-detection system with the hanging vial. A small drop of glue may be used on the thread to make a larger light block if the thread is too narrow to be “seen” by the photodiode.

2. Prepare test samples by finely grinding crystals of the various inorganic substances listed in Table 5-5-1 with a mortar and pestle. Add approximately 0.2 g of each to the vials. Carefully clean the mortar and pestle after grinding each sample to avoid contaminating the samples. Cap the vials after adding the samples.

---

1. The magnet we used had a 1-inch pole gap and a field strength of 5 kG. Magnets with these specifications are difficult to find commercially, however. The rare earth magnets that have recently become commercially available have very high field strengths and are economical to use. Two of them could be mounted approximately 1 inch apart to generate approximately the same magnetic field.
FIGURE 5-5-1. Schematic diagram of laser pendulum apparatus for measuring magnetic susceptibilities.

3. Test the laser-detection system using one of the samples. Once the positions of the magnet, laser, and photodiode are optimized, do not move them. To avoid interfering with the other equipment, change samples by snapping off the cap and snapping on a new vial.

4. Swing the sample through small angle displacements, and record the photodiode response on the computer to determine the period of the pendulum with each compound. Keep the method of swinging and the swing arc as uniform as possible for all samples.

TABLE 5-5-1. MAGNETIC SUSCEPTIBILITY RESULTS: EXPERIMENTAL vs. LITERATURE VALUES

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_M$ Observed$^a$</th>
<th>$\mu_M$ Literature$^b$</th>
<th>$n$ Calc$^c$</th>
<th>$n$ Theory$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCl$_2$</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnCl$_2$</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuBr$_2$</td>
<td>1.81</td>
<td>1.28$^g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuSO$_4$$\cdot$5H$_2$O</td>
<td>1.88</td>
<td>1.88$^g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(NO$_3$)$_2$$\cdot$6H$_2$O</td>
<td>2.88</td>
<td>3.24$^g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrCl$_3$$\cdot$6H$_2$O</td>
<td>3.89</td>
<td>4.08$^g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoCl$_2$$\cdot$4H$_2$O</td>
<td>4.87</td>
<td>4.87$^g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(OAc)$_2$$\cdot$4H$_2$O</td>
<td>4.99</td>
<td>4.98$^g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeSO$_4$$\cdot$7H$_2$O</td>
<td>6.22</td>
<td>5.22$^g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_2$Fe(CN)$_6$$\cdot$3H$_2$O</td>
<td>0</td>
<td>0$^e$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>K$_2$Fe(CN)$_6$</td>
<td>2.69</td>
<td>2.4$^g$</td>
<td>1.87</td>
<td>1</td>
</tr>
<tr>
<td>Ni(NH$_3$)$_6$Br$_2$</td>
<td>3.20</td>
<td>3.24$^f$</td>
<td>2.35</td>
<td>2</td>
</tr>
<tr>
<td>K$_2$Cr(C$_2$O$_4$)$_3$$\cdot$3H$_2$O</td>
<td>3.80</td>
<td>3.75$^g$</td>
<td>2.92</td>
<td>3</td>
</tr>
<tr>
<td>Fe(NH$_4$)$_2$SO$_4$$\cdot$6H$_2$O</td>
<td>5.49</td>
<td>5.26$^h$</td>
<td>4.58</td>
<td>4</td>
</tr>
</tbody>
</table>

$^a$Total magnetic moment in Bohr magnetons calculated as described in discussion section.
$^b$Calculated from $\chi_M$ values with the assumption that the magnetic polarizability is negligible.
$^c$Calculated from $\mu_{M}$ (observed) with the assumption that the orbital contribution to $\mu_{M}$ is negligible.
$^d$Number of unpaired electrons according to reference 4.
$^e$According to reference 5.
$^f$According to reference 6.
$^g$According to reference 7.
$^h$According to reference 8.
HAZARDS AND PRECAUTIONS

Tin (II) chloride is corrosive and skin absorbable. Nickel (II) nitrate hexahydrate is a strong oxidizer. Most chromium salts are carcinogens. Many of the other substances are toxic or suspected carcinogens. Review the Material Safety Data Sheets for each compound used. Wear gloves when handling the compounds, and do all sample grinding in a fume hood. Wear eye protection at all times.

DISPOSAL

Chromium salts and some cyano-containing compounds require special disposal procedures. All other substances can be flushed from the glass vials with water and disposed of in an aqueous waste container. Follow established procedures for handling and disposal of aqueous wastes.

DISCUSSION

The magnetic properties of a compound provide clues to its electronic structure particularly whether or not all of its electrons are paired. A fundamental measurement of magnetic behavior is the magnetic susceptibility of a substance, which measures how much its magnetic moment changes in the presence of a magnetic field. In this experiment, the origins and implications of this effect are examined. The laser-pendulum apparatus used here replaces the more costly and complex Gouy or Faraday balances traditionally used for measurement of the effects of an applied magnetic field (1).

One important result of classical electromagnetism is that spinning and rotating charges have associated magnetic moments. Many molecules have small magnetic moments ($\mu_M$) that arise from two sources: the magnetic moments of the electrons themselves ($\mu_{\text{spin}}$) and the magnetic moment that arises from the orbital motion of the electrons around the nuclei ($\mu_{\text{orb}}$):

$$\mu_M = \mu_{\text{spin}} + \mu_{\text{orb}}$$  \hspace{1cm} (5-5-1)

The magnetic moment that arises from the orbital motion of an electron depends on the particular orbital the electron occupies and cannot be computed easily. For the substances used in this experiment, however, the orbital contribution to the magnetic moment is far smaller than the contribution of the electron spin, and as a rough approximation it may be assumed that the magnetic moment arises solely from the spins of the unpaired electrons; that is,

$$\mu_M \approx \mu_{\text{spin}}$$  \hspace{1cm} (5-5-2)

When this relationship holds true, the magnetic moment is sometimes called a spin-only magnetic moment.

The magnetic moment of an electron arises from its intrinsic spin of $s = 1/2$ and, by quantum mechanics, is given to be

$$\mu_{\text{one e^-}} = \frac{2\mu_B}{\sqrt{s(s+1)}}$$  \hspace{1cm} (5-5-3)

where $\mu_B$ is a constant known as the Bohr magneton and $s = 1/2$. Electrons with opposite spins have magnetic moments oriented in opposite directions, and the magnetic
moments of any paired electrons cancel each other. Substances with unpaired electrons have permanent magnetic moments that arise from electron spins. If we define \( S \), the total spin quantum number, as the sum of all the spins in an atom or molecule, then the total magnetic moment is

\[
\mu_{\text{spin}} = 2\mu_B\sqrt{S(S+1)} \tag{5-5-4}
\]

Since the spin on the electron is 1/2, the number of unpaired electrons \( n \) is related to \( S \) by

\[
S = n/2 \tag{5-5-5}
\]

and equation 5-5-4 can be rewritten as

\[
\mu_{\text{spin}} = \mu_B\sqrt{n(n+2)} \tag{5-5-6}
\]

Thus, a measurement of the value of \( \mu_M \) can be used to deduce \( n \), the number of unpaired electrons in a molecule, provided that \( \mu_{\text{orb}} \) is negligible.

The value of the magnetic moment of a substance can be determined indirectly by observing how the substance interacts with a magnetic field. When any substance is placed in a permanent magnetic field, the field induces a magnetic moment in the object that depends largely on the magnetic moment of the substance. The strength of the induced magnetic field \( (B) \) can be related to the strength of the external magnetic field \( (H) \) according to the relationship

\[
B = H(1 + 4\pi\chi) \tag{5-5-7}
\]

where \( \chi \) is the magnetic susceptibility per unit volume, a dimensionless quantity that represents the intensity of magnetization per unit field strength. A more useful quantity than \( \chi \) for performing calculations is the molar magnetic susceptibility \( \chi_M \), which is defined as the magnetic susceptibility times the molar volume of the substance:

\[
\chi_M = \chi \left( \frac{M}{\rho} \right) \tag{5-5-8}
\]

where \( M \) is the molecular weight (g/mol) of the substance, \( \rho \) is the density (g/cm\(^3\)), and \( \chi_M \) has units of cm\(^3\)/mol.

The molar magnetic susceptibility is related to the magnetic moment of a particular substance by

\[
\chi_M = N \left( \alpha_M + \frac{\mu_M^2}{3kT} \right) \tag{5-5-9}
\]

where \( N \) is Avogadro's number, \( k \) is Boltzmann's constant, \( T \) is temperature, \( \alpha_M \) is the magnetic polarizability, and \( \mu_M \) is the magnetic moment. The magnetic polarizability is an inherent property of substances and is generally small and negative, whereas the value of the magnetic moment is large and positive. Thus, substances without a permanent magnetic moment have a value of \( \chi_M \) that is small and negative, which means that the magnetic moment induced in the substance points in a direction opposite to the external field and acts to cancel the field strength inside the object. These substances are called diamagnetic. For substances that have a permanent magnetic moment, the positive \( (\mu_M^2/3kT) \) term far outweighs the negative \( \alpha_M \) term at room temperature. These sub-
stances are called paramagnetic, and the induced magnetic field points in a direction parallel to the external field and acts to enhance the magnetic field in the substance.

For many paramagnetic substances, the \( \alpha_m \) term is so much smaller than the \( \left( \mu_m^2 / 3kT \right) \) term as to be negligible. In this case, equation 5-5-9 can be rewritten as

\[
\mu_m = \sqrt{\frac{3kT\chi_m}{N}}
\]  

(5-5-10)

By evaluating the constants explicitly, we obtain

\[
\mu_m = 2.84\sqrt{\chi_m T}
\]  

(5-5-11)

in units of Bohr magnetons. Thus, for the substances studied in this experiment, the value of \( \chi_m \) directly reflects the number of unpaired electrons (2,3).

The laser pendulum system used in this experiment allows for a remarkably simple determination of the molar magnetic susceptibility. In the absence of an external field, the period of a simple pendulum \( (\tau) \) can be approximated by

\[
\tau = 2\pi \sqrt{\frac{\ell}{g}}
\]  

(5-5-12)

where \( \ell \) is the length of the string and \( g \) the gravitational constant. When a paramagnetic sample swings back and forth in an inhomogeneous magnetic field, an additional force is developed that is proportional to \( \chi H^2 \), and this force always acts to pull the pendulum into the region of highest magnetic field strength. This extra force acts in the same direction as the gravitational force on the sample, and the pendulum behaves as if the value of \( g \) had increased to a value \( g' \). Specifically, the period of the pendulum is shortened and the new period \( \tau' \) is given by

\[
\tau' = 2\pi \sqrt{\frac{\ell}{g'}}
\]  

(5-5-13)

Solving equations 5-5-12 and 5-5-13 for \( g \) and \( g' \) gives

\[
g = \frac{4\pi^2 \ell}{\tau^2}
\]  

(5-5-14)

and

\[
g' = \frac{4\pi^2 \ell}{\tau'^2}
\]  

(5-5-15)

Subtracting these two equations yields

\[
\Delta g = g' - g = 4\pi^2 \ell \left( \frac{1}{\tau^2} - \frac{1}{\tau'^2} \right)
\]  

(5-5-16)

The value of \( \Delta g \) multiplied by the mass \( m \) of the sample is equivalent to an effective weight change of the sample

\[
\Delta W = m \Delta g
\]  

(5-5-17)

As mentioned previously, the effective weight change should be proportional to \( \chi \)

\[
\chi \propto \Delta W
\]  

(5-5-18)
implying that

\[ \chi_M \approx \Delta W \left( \frac{M}{\rho} \right) \]  

(5-5-19)

The procedure used to determine the magnetic moment of an unknown sample is to measure the period of the pendulum with and without the sample, calculate the value of \( \Delta W \), and then compare the \( \Delta W \) to a standard with a known molar magnetic susceptibility. For this experiment, a useful standard is \((\text{CoCl}_2 \cdot 6\text{H}_2\text{O})\), whose molar magnetic susceptibility \( (\chi_M)_S \) is \(9710.0 \times 10^{-6} \text{ cm}^3/\text{mol}\). Using formulas 5-5-19 and 5-5-11, the magnetic moment of an unknown sample can be related to the standard reference sample by

\[ \mu_M = 2.84 \left[ \frac{\Delta W}{\Delta W_S} \left( \frac{\rho_s}{\rho} \right) \left( \frac{M_s}{M} \right) (\chi_M)_S T \right]^{1/2} \]  

(5-5-20)

where the subscript \( S \) refers to the standard, and the magnetic polarizability of the sample is assumed to be negligible.

To summarize, the laser and computer-interfaced light-detection system can be used to make sensitive measurements of the period of the pendulum. The difference between the period of the pendulum with and without the sample is used in the calculation of an effective weight change (equations 5-5-16 and 5-5-17). This effective weight change can be compared with the weight change of a standard with a known magnetic susceptibility, and can thus be used in the calculation of the magnetic moment of the sample (equation 5-5-20). Assuming that the magnetic moment of the sample arises from electron spin alone, the effective number of unpaired electrons can be calculated according to equation 5-5-6.

Table 5-5-1 compares the experimental values of \( \mu_M \) determined for 14 compounds with their literature values. The accuracy achieved using this technique was less than that reported using the standard Gouy balance method, but with a little practice and experimental optimization, accuracies of up to 95\% can be achieved. For the final five octahedral complexes, the table also shows calculated and theoretical values for the number of unpaired electrons \( n \). The reasonably large discrepancies between the calculated and theoretical values arise partly from experimental error but also indicate that these compounds have significant orbital contributions to their magnetic moments.

REFERENCES

LASER
EXPERIMENTS FOR BEGINNERS

Richard N. ZARE • Bertrand H. SPENCER • Dwight S. SPRINGER • Matthew P. JACOBSON