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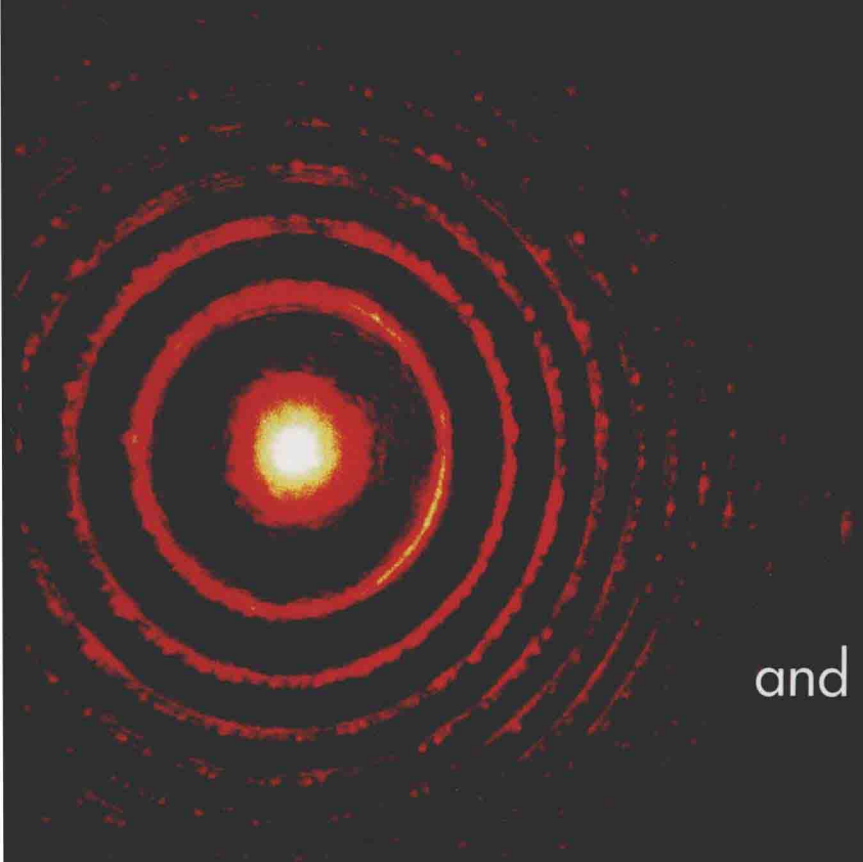
Laser Experiments

for Chemistry and Physics



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and Michael A. Duncan

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LASER EXPERIMENTS FOR CHEMISTRY AND PHYSICS

Preface

Like most scientists, the authors of this textbook have been greatly influenced by their academic backgrounds and mentors. Duncan and Compton were both undergraduate students in small liberal arts colleges (Furman University and Berea College, respectively) in which student research was a vital part of their educational experience. Performing undergraduate research was of equal importance to course work. Both authors began their research careers at the time of the development of the laser and were witness to many incredible advances in the development and applications of this new technology.

In graduate school, Compton was particularly influenced by the first year experimental research course required of every incoming graduate student (theory or experiment) in the Department of Physics at the University of Florida. In addition to experiments, Professor Alex Green included glass blowing and machine shop fundamentals in this course. Although it is not a required course, a similar experience is offered to the physics and chemistry graduate students at the University of Tennessee (UT) by Compton. Some of these experiments are included in this book. In a few instances, the laboratory experiments resulted in an area of research. For example, in the undergraduate laboratories students were required to record and analyze a Raman spectrum of CCl_4 at room temperature. Due to the thermal rovibrational population, the Stokes lines are very broad at room temperature. To resolve the isotope lines of CCl_4, one of the students in the advanced physics laboratory (Darrin Ellis) recorded a Raman spectrum of CCl_4 *submerged* under liquid nitrogen in a Styrofoam cup. Due to rovibrational cooling, the spectrum of CCl_4 under liquid nitrogen shows fully resolved isotopic contributions due to the ^{35}Cl and ^{37}Cl isotopes (see Chapter 18, Figure 18.3). A number of papers have appeared illustrating the advantages and utility of Raman Under Nitrogen (RUN). As a graduate student in 1962 working under G. S. Hurst at the Oak Ridge National Laboratory, Compton was privileged to purchase and use one of the first commercial (Bendix Corporation) time-of-flight mass spectrometers (TOF-MS). His thesis employed electron impact ionization, but after the development of the pulsed laser Compton integrated many home-built TOF-MS instruments into laser ionization experiments at ORNL and UT. In 1979, colleagues J. A. D. Stockdale and Compton formed a scientific instruments company in Oak Ridge known as Comstock, which manufactured and sold TOFs as well as electrostatic energy analyzers (ESAs). Many of these instruments have been used by researchers around the world to record multiphoton ionization mass and photoelectron spectra. This company has employed a number scientists, engineers, and machinists, which has enriched their lives as well as science in general.

As an undergraduate at Furman, Duncan learned to solder from Professor Lon Knight and together they built a vacuum system for matrix isolation experiments and EPR studies of unusual radicals. At Rice University in the group of Richard Smalley, he was given the task of designing and building their first time-of-flight mass spectrometer. With virtually no electronics background, Duncan was guided by the electronics shop to the classic paper by Wiley and McLaren (*Rev. Sci. Instrum.* **26**, 1150 (1955)). After many design pitfalls and burned-out circuits, he eventually made a working instrument and incorporated it into their supersonic molecular beam machine. Other experiments and a misaligned Nd:YAG laser led inadvertently to the discovery of the laser vaporization method used to produce gas-phase clusters of metal atoms and other refractory elements. It was this laser vaporization method and the same mass spectrometer that were later employed by Jim Heath and Sean O'Brien in the Smalley group to discover C_{60}. At Georgia, Duncan has continued to design and implement new versions of time-of-flight mass spectrometers into his research, and has also developed new experiments for the undergraduate labs using these instruments, many of which are included in this book.

The authors have employed many kinds of modern lasers and laser techniques in their research and teaching laboratories. Compton was one of the first to study and employ nonlinear optical processes in atomic and molecular research and some of this early work is found in the chapters describing multiphoton ionization, stimulated electronic Raman scattering (SERS), and third harmonic generation (THG). Duncan has employed photoionization, laser desorption analysis of materials, and mass-selected ion photodissociation measurements throughout his research. Both authors have developed advanced physical chemistry laboratories at their respective universities and are deeply indebted to the numerous students who have passed through these laboratories, many of whom are now directing their own physical chemistry or physics laboratories at other universities.

This book is designed to introduce researchers to the breadth of available experiments in chemical physics that can be integrated into physics and chemistry laboratories. The authors have tried to include chapters that are fundamental to lasers and spectroscopy and provide theoretical background to the experiments described. For example, the chapters on properties of light, diffraction, etc., and rovibrational spectroscopy should be read before considering the experiments describing IR and Raman spectroscopy, optical activity, and other laser-based experiments. We hope that the enjoyment of laser experiments and their role in advancing chemistry and physics can be appreciated by a new generation of scientists through the experiments presented here.

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Michael A. Duncan, Athens, GA

Acknowledgments

The authors are grateful to the many graduate and undergraduate students who have worked in their labs over the years and have contributed to the experiments described here. Special recognition is due to the many Teaching Assistants who implemented these experiments in the undergraduate and graduate laboratories at the University of Tennessee and the University of Georgia. MAD would like to thank Professors Lionnel Carreira and Allen King, who shared ideas and provided feedback for lab experiments early in his career at Georgia. RNC is indebted to Professor Charles Feigerle for collaborations on the study of MPI of molecular iodine, to Dr. Donald Armstrong, Dr. Stewart Hager, and Dr. Jeffery Steill (Sandia Laboratory) for assisting with recording the numerous FTIR spectra, and to Dr. James Parks for sharing an experiment from the advanced physics laboratories at UT. Special thanks are also due to former masters degree student Darren Ellis for performing the first RUN spectrum in our laboratories at UT.

We would also like to acknowledge the special help in preparing this manuscript from Mr. Jonathan Maner (proofreading), Ms. Alex Orlowsky (figure preparation), Mr. Joshua Marks (photography), Mr. Timothy Ward and Mr. David McDonald (computational work), and Mr. Ivan Geigerman (figure preparation). We are also grateful to Drs. Sharani Roy and Jay Agarwal for a critical assessment of Chapter 15 on quantum chemistry calculations. Dr. Paul Siders is gratefully acknowledged for contributions to Chapter 22 on Fermi resonances.

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Part I

Introduction to Light, Lasers, and Optics

Elementary Properties of Light

1

Introduction

The experiments described in this book involve the use of laser light in a wide range of applications. The present chapter is an elementary introduction to the properties of light that will serve to make these experiments more understandable. This chapter, along with Chapter 2, is certainly not intended to replace a rigorous course in physical or geometrical optics; rather it is a summary of some of the important concepts and formulae in optics applied to the use of lasers in chemical physics research.

All electromagnetic (E&M) waves propagate with the same velocity in free space (which is defined as c) and differ only in frequency, ν, and wavelength, λ, through the relationship $c = \lambda\nu$. There is one report of E&M waves having a wavelength of 1.9×10^7 miles.[1] At the other extreme, the Compton Gamma Ray Observatory (GRO), a NASA satellite, has been used to detect gamma rays with wavelengths as small as 40 femtometers (40×10^{-15} meters), approximately the size of a proton.

The description of electromagnetic radiation is carried out using a classical/quantum mechanical wave/particle treatment. Certain phenomena are best described using waves and others can only be explained by treating light as particles called photons. All light phenomena can be explained by treating light as photons; however, in most cases the wave picture is easier to employ. The energy of a photon is Planck's constant h times the frequency, ν ($E = h\nu$). Photons have momentum ($p = h/\lambda$) but no mass. In 1890 Heinrich Hertz first produced radiowaves ("Maxwellian waves") in the laboratory and it was many more years before Marconi put them to good use in communications. We now know that any material object (gas, liquid, or solid) having a temperature above absolute zero (0 K) will emit photons. For so-called "black-body" radiators the temperature is related to the photon energy $h\nu$ and emitted light intensity $I(\nu,T)$ by the Planck Black-body radiation formula:

$$I(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{\left(e^{\frac{h\nu}{kT}} - 1\right)} \tag{1.1}$$

The Planck radiation law represents the power per unit area per unit solid angle per unit frequency emitted from a black body in thermal equilibrium.

Laser Experiments for Chemistry and Physics. First Edition. Robert N. Compton and Michael A. Duncan.

This function has a maximum (i.e., setting the derivative $dI(\nu,T)/d\nu = 0$ and solving for ν_{max} from equation (1.1)) corresponding to $h\nu_{max} = 2.82\ kT$. Alternately one can write this in the form of the Wien's Displacement Law as $\lambda_{max}T = 2.8977685(51)\times10^{-3}\ m\cdot K$.

The Planck radiation law is known to accurately describe the emission from stars, the heater eye on an electric stove, and even the cosmic background radiation left over from the Big Bang creation of the universe. The Cosmic Microwave Background (CMB) consists of photons left over from the Big Bang, which through multiple collisions have established a thermal "cosmic black-body" equilibrium. In Figure 1.1 the microwave cosmic background radiation data is fitted to a Planck radiation law prediction (equation 1.1) giving a temperature of 2.725 K. The data were recorded using the Far-Infrared Absolute Spectrophotometer (FIRAS) onboard NASA's Cosmic Background Explorer (COBE) satellite. [2] It is remarkable that the experimental data points lie within the line (theory) in Figure 1.1.

The black-body temperature for the data in Figure 1.1 was determined from a fit to equation (1.1), but this can also be estimated using Wien's displacement law $h\nu_{max} = 2.82\ kT$ or alternately $\nu_{max} = 58.79\ (GHz/K)T$. Using $T = 2.725$ K gives $\nu_{max} = 160.2$ GHz.

It is impossible to make a representation of the full wavelength range of E&M waves. There are regions of the spectrum yet to be explored at both the long and short wavelength regions. Figure 1.2 is an attempt to show on one scale the range of the spectrum that science has presently explored.

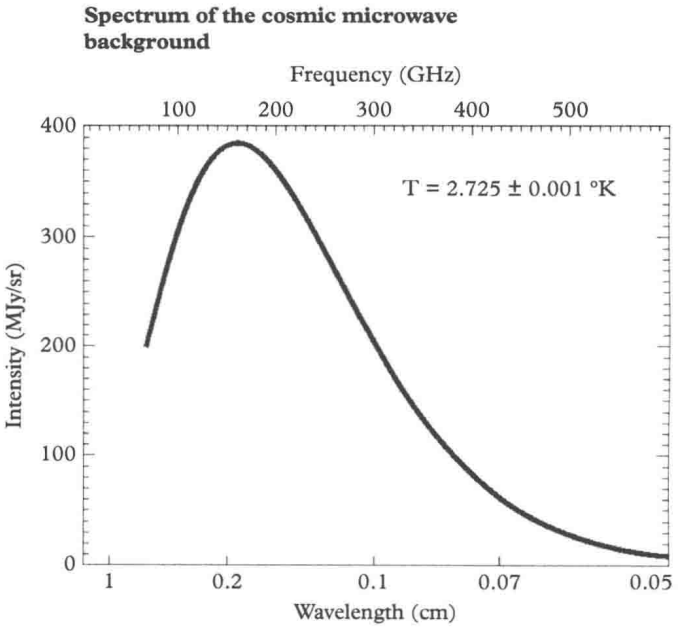

Figure 1.1 *Cosmic microwave background spectrum fit to a Planck radiation law function (equation 1). The data points are smaller than the line drawn using the Planck law. The deviations are less than 0.30% of the peak brightness, with an rms value of 0.01%. (This COBE/FIRAS image was kindly provided by COBE Science Team/NASA.)*

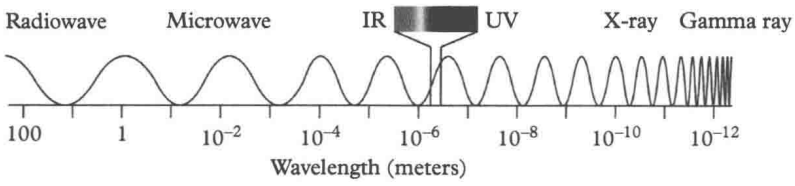

Figure 1.2 *Illustration of the known full electromagnetic spectrum of light from radiowaves to gamma rays.*

Table 1.1 *Approximate wavelength, frequency, energy, and temperature corresponding to Figure 1.2.*

E&M	Wavelength cm, except as noted	Frequency Hz	Energy eV	Energy cm^{-1}	Energy kcal/mol	Temp. K
Radiowave	> 10	$\sim 10^9$	$< 10^{-5}$	$< 0.1\ cm^{-1}$	$< 2.9 \times 10^{-4}$	< 0.03
Microwave	10 – 0.01	$\sim 10^{12}$	10^{-5} – 0.01	0.1 – 100	$3 \times 10^{-4} - 3 \times 10^{-1}$	0.03 – 30
Infrared	$0.01 - 7 \times 10^{-5}$	$\sim 10^{14}$	0.01 – 1	$10^2 - 10^4$	$3 \times 10^{-1} - 29$	30 – 4100
Visible	$7 \times 10^{-5} - 4 \times 10^{-5}$ 700 – 400 nm	$\sim 10^{15}$	~ 1 – 3	$(1.0 - 2.5) \times 10^4$	29 – 71	4100 – 7300
Ultraviolet	$4 \times 10^{-5} - 10^{-7}$ 400 – 1 nm	$\sim 10^{16}$	$\sim 3 - 10^3$	$2.5 \times 10^4 - 10^7$	$71 - 2.9 \times 10^4$	$7300 - 3 \times 10^6$
X-ray	$10^{-7} - 10^{-9}$	$\sim 10^{18}$	$10^3 - 10^5$	$10^7 - 10^9$	$10^4 - 10^6$	$3 \times 10^6 - 3 \times 10^8$
Gamma ray	$< 10^{-9}$	$> 3 \times 10^{19}$	$> 10^5$	$> 10^9$		$> 3 \times 10^8$

Maxwell was the first to show that visible light represents but a narrow component of the entire electromagnetic spectrum. From this figure we see that visible light represents only one octave out of almost 60 octaves of the known electromagnetic spectrum. This wavelength range is further described in Table 1.1 in terms of wavelength, frequency, energy, and temperature.

The visible spectrum ranges in wavelength from approximately 400 to 700 nm. The sensitivity of the human eye to visible light depends upon the observer and the time of day. Figure 1.3 shows the relative sensitivity curves for the *standard observer* as defined by the International Commission on Illumination. The International Commission on Illumination, which was established in 1913 and based in Vienna, Austria, is the international authority on light, illumination, and color.

A complete description of the sensitivity of the eye can be found in the book by Williamson and Cummins.[3] As mentioned before, visible light is but a narrow and somewhat ill-defined region of the spectrum. The curves in Figure 1.3 are ill-defined in the sense that the relative sensitivity of the eye for humans can only be considered for a *standard observer*. The standard curve also varies under different light levels because of the sensitivity difference of the rods and cones covering the retina. The rod system is about 1000 times more sensitive than the

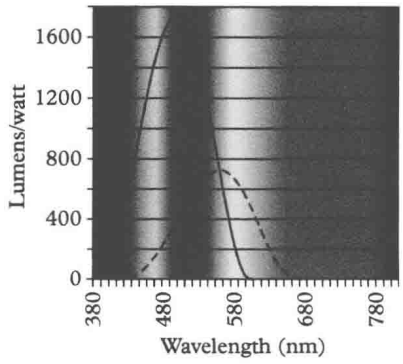

Figure 1.3 *Relative sensitivity of the human eye of a standard observer as a function of wavelength under conditions of daylight vision (photopic, dashed line) and night vision (scotopic, solid line).*

cones and as a result the relative color sensitivity differs for night vision (scotopic) and daylight vision (photopic) as shown in Figure 1.3. An interesting experiment to demonstrate the varied sensitivities of the human eye is to have a number of people with their eyes dark-adapted observe the heaters on an electric stove as the stove is turned on in the dark. Some individuals will notice that the stove begins to appear red before others. The onset of first observing red light depends on the sensitivity of each individual to long wavelength light.

Maxwell's Equations

In 1873, Maxwell considered the accumulated body of experimental observations concerning electricity and magnetism uncovered by Gauss, Faraday, Biot-Savart, Hertz, Ampere, and others and combined all of these empirical laws into one unifying theory of electricity and magnetism. Maxwell's equations can be written for a medium of dielectric constant ε and charge density ρ in which a current J flows as

$$\begin{aligned}
&\nabla \cdot \vec{D} = \rho && \text{Gauss' Law} \\
&\nabla \cdot \vec{B} = 0 && \text{Gauss' Law of Magnetism} \\
&\nabla \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} && \text{Ampere's Circuit Law} \\
&\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} && \text{Faraday's Law of Induction}
\end{aligned} \tag{1.2}$$

in the MKS (meter–kilogram–second) system of units, where $\vec{D} = \varepsilon\vec{E}$, $\vec{B} = \mu\vec{H}$, ε and μ are the electric permittivity and magnetic permeability of the medium, and ∇ is the gradient operator. It is easy to show from Maxwell's four equations above that electromagnetic waves consist of perpendicular $\vec{E}$ and $\vec{B}$ fields traveling in a direction mutually orthogonal to $\vec{B}$ and $\vec{E}$ with a velocity equal to c in a vacuum. Since $\varepsilon = \varepsilon_0$ and $\mu = \mu_0$ in a vacuum and the divergence of the electric field is zero we can write

$$\begin{aligned}
&\nabla \cdot \vec{E} = 0 \\
&\nabla \times \vec{B} = \mu_0 \varepsilon_0 \frac{\partial \vec{E}}{\partial t} \\
&\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}
\end{aligned} \tag{1.3}$$

Upon taking curl (∇_x) of $\vec{E}$ twice and collecting terms it is easy to show that

$$\nabla \times \nabla \times \vec{E} = \nabla\left(\nabla \cdot \vec{E}\right) - \nabla^2 \vec{E} \tag{1.4}$$