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Raman Spectroscopy Under Liquid Nitrogen (RUN)

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Contents

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Robert N. Compton received degrees in physics from Berea College (BA), the University of Florida (MS), and the University of Tennessee (PhD). He was a Senior Corporate Fellow at the Oak Ridge National Laboratory from 1965 to 1995 and was a Professor of Physics and Zeigler Professor of Chemistry at the University of Tennessee until retirement in 2015. He was a Visiting Professor at the University of Aarhus, the University of Paris, and the FOM Institute in Amsterdam. In 2001, he was an Erskine Fellow at the University of Christchurch, New Zealand. As an Erskine Fellow, he also presented eight 2-h lectures on the Manhattan Project to the city of Christchurch. He is a Fellow of the APS, AAAS, and OSA. Compton received the Beams Award from the American Physical Society and the Meggers Award from the Optical Society of America. His research interests include negative ions, laser spectroscopy, and molecular chirality. He has published one other book with MA Duncan, "Laser Experiments in Chemistry and Physics" (Oxford).

Nathan I. Hammer received an Honors B.S. degree in Chemistry from the University of Tennessee in 1998 and a PhD in Physical Chemistry and Chemical Physics at the University of Tennessee in 2003. His doctoral research focused on resonant electron transfer processes, creation and manipulation of very weakly bound (0.5–50 meV) negative ions, and interaction of light with chiral systems. He was a postdoctoral researcher from 2003 to 2005 at Yale University, where he studied the spectroscopy of fundamental aqueous systems. This work resulted in 15 publications, 3 of which were in *Science* magazine, and was listed among *Science's* Top 10 Breakthroughs of 2004. Dr. Hammer then served as an Intelligence Community Postdoctoral Fellow in the Department of Chemistry at the University of Massachusetts, Amherst (2005–2007). At UMass, Dr. Hammer studied a number of fundamental nanoscale systems using single-molecule spectroscopic techniques with publications in journals including *Science* and the *Journal of the American Chemical Society*. Important accomplishments include describing blinking suppression in quantum dot nanostructures, probing the chiroptical response of single molecules, and unraveling the origins of spectroscopic defects in organic light-emitting diode (OLED) devices.

Dr. Hammer joined the University of Mississippi Department of Chemistry and Biochemistry in 2007. He received a Faculty Early Career Development (CAREER) Award from the National Science Foundation (NSF) in 2010 to spectroscopically track the evolution of noncovalent interactions from the single-molecule level to the condensed phases. As part of this grant, he developed the department's award-winning summer research program for undergraduates. Professor Hammer was named the Margaret McLean Coulter Professor of Chemistry and Biochemistry in 2020. He received the College of Liberal Arts Award for Research, Scholarship, and Creative Achievement for Senior Faculty in 2018 and the Faculty Achievement Award in 2021.

Ethan C. Lambert Ethan Lambert was born in Corinth, Mississippi, and graduated from Kossuth High School in May 2019. He enrolled at the University of Mississippi in Fall of 2019 and is currently pursuing a B.S. degree in Chemistry. He enjoys studying physical and chemical processes at the fundamental level and began research under Dr. Nathan Hammer at the beginning of his sophomore year. Ethan has used Raman spectroscopy and quantum computational chemistry to study several chemical systems, including charge transfer events, vibrational structure and symmetry, and enhancing Raman spectral signal. Ethan's current projects focus on the study of inter- and intramolecular photoinduced charge transfer events in artificial photosynthetic systems via ultrafast transient absorption spectroscopy and anisotropy. Ethan is set to graduate with an Honors B.S. in Chemistry in May 2023.

J. Stewart Hager received his PhD from the University of Tennessee in Molecular Physics. He studied high-resolution infrared spectroscopy, molecular vibrational-rotational theory, and atmospheric remote sensing. He worked with Dr. Compton as a research associate, where he helped develop the RUN technique. He served as a Senior Research Associate at Atmospheric and Environmental Research (AER) in Lexington, MA, from 2005 to 2008, where he was a team member of NASA's Active Sensing of CO_2 Emissions over Nights, Days, and Season (ASCENDS) satellite. He determined sensitivities of DIAL measurements for CO_2 due to atmospheric conditions for ASCENDS. He started the company Hager Environmental and Atmospheric Technologies, where he developed a vehicle exhaust remote sensing device called Emissions Detection and Reporting (EDAR). EDAR has been deployed in many countries, including Great Britain, Belgium, Germany, France, and Italy, and has received over 40 patents worldwide.

Chapter 1
Introduction

Since the discovery of the Raman effect in 1928, Raman spectroscopy has proven to be a powerful tool for the characterization of molecular structure in the gaseous, liquid, and solid phases. Raman and IR spectroscopy provide complementary information on molecular vibrations; in cases of high symmetry however the two methods are mutually exclusive. The selection rules for the interaction of light and matter predict that asymmetric vibrations are excited in IR absorption and symmetric vibrations are active in Raman scattering. Together these spectroscopies have been essential techniques used for the structural analysis of organic and inorganic molecules since 1930s. In recent years, Raman spectroscopy has also proven to be a useful tool for the analysis of biological systems. Conformational changes of peptides and proteins in aqueous solutions, as well as nucleic acids and polynucleotides, have been studied. A general discussion of the comparisons of Raman and IR spectroscopy can be found in the books by Ingle and Crouch [1] and Nakamoto [2].

The Raman effect was discovered by its namesake, Sir Chandrasekhara Venkata Raman, in 1928 by using sunlight as the excitation source focused onto a sample. The weakly scattered light was detected with the aid of his eye through a telescope. The fact that such a feeble effect was detected is a testament to Raman's brilliance as well as to the sensitivity of the human eye. Raman received the Nobel Prize only 2 years after his discovery.

Early Raman studies concentrated on the development and use of more intense and higher resolution light sources. The earliest Raman spectra were collected using resonance lamps as well as low-pressure mercury-arc light sources. The development of the powerful Ar^+ and Kr^+ ion lasers having power outputs in the blue/green (488, 514.5, 351.1 nm) and red (most prominent lines being 521, 568, and 647 nm) regions of the electromagnetic spectrum, respectively, has afforded great improvement in Raman scattering sensitivity and resolution. These and other lasers, together with the improvements in modern dual, double-grating, spectrometers, and position

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sensitive photodetectors, have greatly expanded the application of Raman spectroscopy.

The introduction of the laser in Raman spectroscopy has allowed for the development of many new innovations in the field: resonance Raman spectroscopy, nonlinear Raman scattering, stimulated Raman scattering, coherent anti-stokes Raman spectroscopy (CARS), etc. In addition, the ability to tightly focus laser light has allowed for the development of micro-Raman spectroscopy techniques. The Raman microprobe couples a Raman spectrometer with an optical microscope in order to study surface layers such as polymers, thin films, nanostructured materials, and biological molecules. Laser improvements however are followed by new experimental challenges. A major difficulty in the application of Raman spectroscopy is the potential for laser damage to the material under investigation. It is seldom possible to use the full laser power available in a Raman study, especially if the sample is strongly absorbing at the frequency of the laser line. Sample heating effects such as sublimation, evaporation, and oxidation are serious limitations to Raman spectroscopy in all phases.

To combat the negative effects of employing high laser power, several methods have been developed. For liquids, a rotating cell is often used to avoid over-heating of the sample, but this is not practical for inhomogeneous solid-state samples. Raman spectroscopy of cooled samples under vacuum is presently a very common method requiring low-temperature cells and vacuum pumping. Oxidation effects are sometimes reduced by blowing dry nitrogen or argon gas over the irradiated sample or maintaining the sample at low temperature under a vacuum. Co-deposition of the molecules under investigation with a cold host bath (e.g., Argon) is often used as well [3]. Surface-enhanced Raman spectroscopy (SERS) offers a substantial solution for eliminating laser-induced harm to the sample. SERS is a relatively recent technique that can result in an enhancement of roughly 10^4–10^6 in Raman signal intensity for some molecules [4]. The theoretical limits for nonresonance-enhanced SERS is approximately 10^{11} while resonance enhancement (SERRS) can increase this limit to as high as 10^{14}. Thus, lower laser power can be employed in order to yield the same signal intensities thereby reducing the damaging effects of the laser. Similarly, lower limits of detection sensitivity are possible with these techniques. This method requires the application of a small layer of the molecules of interest on a roughened metal surface. Although many experimental studies have been devoted to understanding the SERS process and some theoretical explanations have been put forward, it is fair to say that SERS is not completely understood and the interactions with the metal surface are known to shift vibrational energies, sometimes significantly [5]. The application and development of SERS, while limited, represents a major advance in the field.

These methods, while effective, are complex in nature and often costly. In this book, we describe a simple method of performing Raman spectroscopy of samples submerged *under* liquid nitrogen (−195.79 °C: 77 K; −320 °F) which reduces or eliminates some of the problems described above. Cooling the sample to liquid nitrogen temperature exhibits great improvements in sensitivity and spectral resolution over room temperature Raman spectroscopy. It also allows the selection of the