The Raman Effect: A Large-Scale Lecture Demonstration

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Abstract: This article describes a lecture demonstration of the Raman effect. It presents a method for using a simple arrangement of optical components to project Raman lines from liquid samples. The Raman lines are visible as different colors of light projected on a screen several meters away. The demonstration is appropriate for physical, analytical or instrumental analysis courses.

Introduction

Raman spectroscopy has long been thought to be an extremely difficult experiment to demonstrate, to perform, to explain, and to understand. This difficulty is part of the reason for the dearth of papers in the chemical education literature on this subject [1]. Some of the papers discuss a dry-lab application of Raman spectroscopy because of a general lack of Raman spectrometers at most undergraduate institutions. Within the last three decades, Raman spectroscopy has been utilized far more frequently because of its wide range of applications (especially to aqueous solutions), its complementary nature to infrared spectroscopy, and its simplification due to technological advances such as the development of lasers, notch filters, and array detectors. Raman spectroscopy has also become one of the fundamental techniques in the study of surfaces and colloids.

This article describes a lecture demonstration of the Raman effect for use in analytical or physical chemistry classes. The demonstration provides physical chemistry instructors a method for showing the effects of Raman scattering in the classroom with ease, and without the need for expensive spectrometers and electronics. Originally, this demonstration was developed as part of a digital video disk (DVD) project funded by the National Science Foundation. In that project, titled “Physical Chemistry in Practice,” current applications of techniques and phenomena taught in the physical chemistry classroom are brought to life for students through video animations and computer analysis of authentic data. The DVD modules showcase scientists and their research, and link their research with the theory that students are exposed to in the classroom. Computer applications included with the DVD allow students to solve physical chemistry problems related to the experiments discussed in the video segments, and to analyze authentic data from those experiments. The Raman demonstration described here is used on the DVD as an introduction to a module on surface-enhanced Raman spectroscopy (SERS). That module discusses the use of this technique to detect very low concentrations of excitatory amino acids in rat brains after a head injury [2–5]. As part of the module, students are introduced to the basics of Raman spectroscopy using this lecture demonstration, then to the fundamentals of SERS, and finally, introduced to the amino-acid-detection research.

Theory

The interaction of light with molecules can occur through a variety of mechanisms including absorption, emission (both spontaneous and stimulated), and the two-photon Raman process. The Raman process involves a net transition between two rotational or vibrational energy levels of a molecule, just as absorption and emission spectra do. Absorption and emission spectroscopies directly probe the difference in energy between two energy levels using a single photon. The energy of that photon is the energy difference for the transition between levels (Figure 1). The energy difference between the two *real* states is observed because the electric dipole of the photon interacts with the electron distribution within the molecule.

In the Raman process, the molecule interacts with the photon in an inelastic scattering event. During the scattering event, the molecule takes the energy of the incoming photon, and can add or subtract from the photon energy by one of the energy-level differences within the molecule. The energy of the incoming photon is not required to be in resonance with a real energy-level difference in the molecule because the incident photon will not be absorbed and reemitted, but simply scattered. The scattering occurs from a “virtual state” and the scattered photon will be the transition from this off-resonance virtual state to a real state. This scattering process yields a resulting photon whose energy may differ from that of the initial photon by the energy differences within the molecule (Figure 2).

In the Raman process, an electric dipole is induced in the molecule as a function of the incident electric field, $\boldsymbol{E}_\mathrm{i}$. In conventional Raman spectroscopy, that induced dipole is a linear function of this electric field and the molecular polarizability, α, as follows: $\mu = \alpha \boldsymbol{E}_\mathrm{i}$ [6–8]. However, when a pulsed laser is used, and focused as tightly as it is in the apparatus described below, the field strengths are extremely large, and can be as much as 5 orders of magnitude larger than in a continuously operated (nonpulsed) laser. As a result, the

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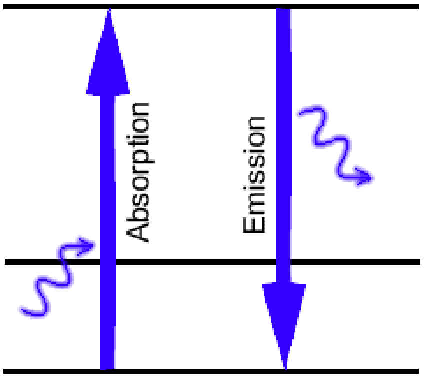

Figure 1. Schematic showing a conventional absorption spectroscopy process. The incident radiation which is absorbed causes a transition between two real states, requiring radiation to be at the exact energy of the difference between the initial and final states. A spontaneously emitted photon will have an energy equal to the difference between two real states.

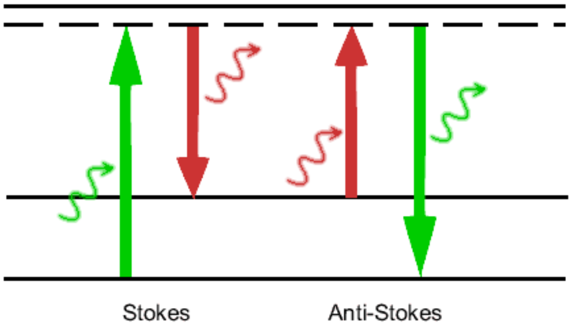

Figure 2. Schematic showing the Raman process into a "virtual state." The emitted photon differs in energy from the incident photon by an energy corresponding to the difference in energy between the final state and the initial state of the molecule. The Stokes photons have a lower energy than the incident photon, by a value equal to the energy difference between states in the molecule. The anti-Stokes photons have a higher energy than the incident photons, also corresponding to the differences in energy in the molecule. The anti-Stokes emission usually has a lower intensity because the scattering process must initiate in a higher energy state, which has a lower Boltzmann population.

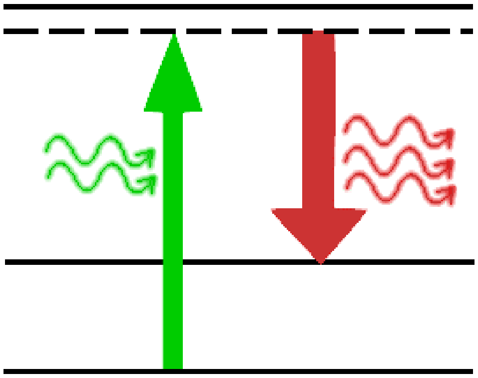

Figure 3. A schematic showing the amplification effect that can occur when the population inversion is very large due to a very large incident radiation field. The emission becomes a stimulated emission.

induced dipole is no longer a linear function of the incident electric field, but has higher order contributions as well. This nonlinear effect can result in a *stimulated* coherent output photon at a frequency corresponding to the difference between the incident photon and the molecular energy differences. Because it is a stimulated process, there is an amplification effect (Figure 3) and the process is sometimes referred to as a "Raman laser." However, for the purpose of providing a visual presentation of the Raman effect, the subtleties between the stimulated and spontaneous processes will not hinder the use of this demonstration in the classroom.

Description

Raman spectroscopy provides the opportunity to examine processes that cannot be examined in one-photon spectroscopies because of the different selection rules. Unfortunately, the myths of expense, difficulty, and inapplicability surrounding Raman spectroscopy have made incorporation of Raman spectroscopy into the curriculum a rare event. In the demonstration described here, the Raman spectrum of a number of pure liquids is used to visually display the Raman effect using stimulated Raman photons. In general, Raman spectra are not seen with the naked eye because they are difficult to observe. The process requires a very intense incoming light source and an extremely light-tight system. Even a small amount of stray light in the spectrometer can mask the scattered Raman photons, which may be thousands to millions of times less intense than the incoming light source.

The development of monochromatic high-intensity laser beams now makes Raman spectroscopy more viable within the laboratory. The technological advances are important because the intensity of the scattered Raman signal is proportional to the number of watts per cm^2 of the incoming photon source and the density of the scatterer. Specifically, the scattered intensity is equal to $I_o(8\pi^4 N\alpha^2)/(\lambda^4 R^2)$, where I_o is the incident intensity, N is the density of the scatterer, α is the polarizability, λ is the incident wavelength, and R is the distance to the detector. The R^2 term is simply an issue of detected intensity, rather than emitted intensity, and has the typical inverse square relation for any light source. The inverse λ^4 relation would seem to suggest that the signal intensity could simply be increased by using a shorter wavelength incident source. However, as the incident wavelength decreases, fluorescence from the sample becomes likely. If fluorescence is induced in the sample, this process will obscure the Raman scattered photons. In fact, this is another reason why it is optimal to select a wavelength that is *off*-resonance, so that absorption and subsequent fluorescence are minimized.

The apparatus used to generate a stimulated Raman photon is shown schematically in Figure 4. All the optics can be purchased from Edmund Scientific for under $200. The laser was purchased from Continuum Laser for about $10,000, but equivalent models may be available from this or other vendors at a lower price. For this demonstration, the 532-nm (green) pulsed output of a frequency-doubled Nd:YAG laser is used as the incoming photon. Our laser generates 10–15-mJ, 6-ns pulses of green light at a 20-Hz repetition rate. The laser output is directed along a beam path defined by a pair of irises for collimation. Also in the beam path are a pair of convex

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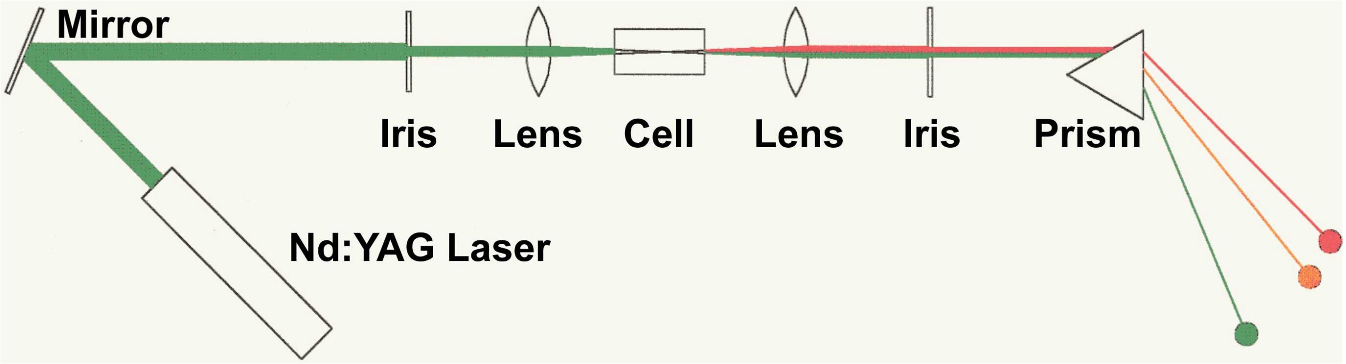

Figure 4. A schematic of the apparatus used in this demonstration. The 532-nm Nd:YAG laser output is directed through an iris and collimating lens, and into the sample. The majority of the incident radiation, as well as the Raman scattered photons at different wavelengths, exit the sample and pass through a second lens and iris, and are then dispersed through the prism onto a screen. On the screen they are seen as separate dots of different colors.

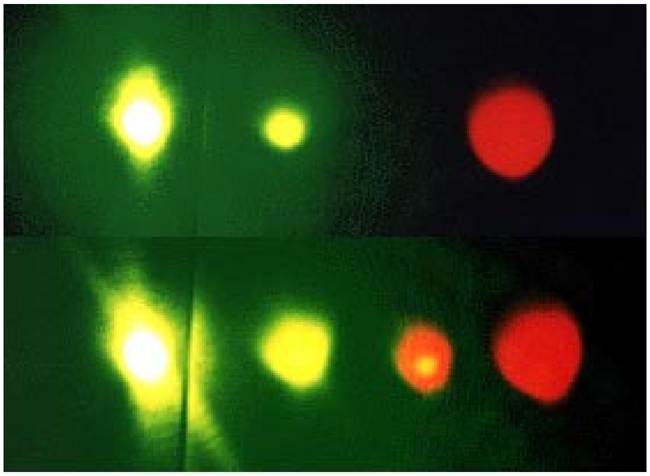

Figure 5. A composite photo showing the different wavelengths and physical positions for the Stokes photons from toluene (top) and benzene (bottom). The conditions were identical for both spectra. The spot on the far left in each spectrum arises from the nonscattered, or Rayleigh, photons. The positions on the screen are different for the different colors due to separation by the prism used in the apparatus. However, the positions for the spots from toluene and benzene are almost identical, while the differences between the spectra of these two molecules is seen primarily as a difference in spot intensity.

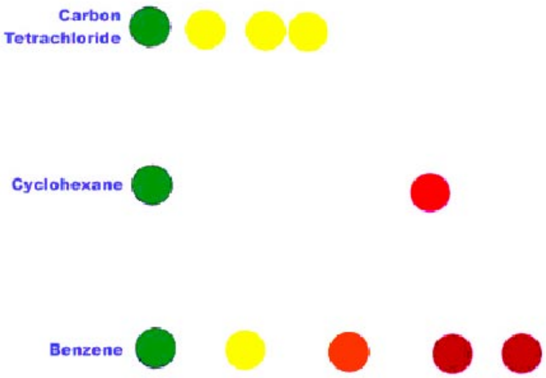

Figure 6. A diagrammatic representation of the positions and approximate colors of the Stokes photons from carbon tetrachloride, cyclohexane, and benzene. The green spots represent the nonscattered, or Rayleigh, photons and have been lined up to show the differences in physical position of the spots for each sample.

lenses of the same focal length (200 mm) spaced 2 focal lengths apart. This arrangement causes the laser light to be focused and then recollimated by the lenses, increasing the incident electric field at the focal point of the lenses, and thus increasing the Raman scattered signal. The sample is placed in a 10-cm cell located at the focal point of the two lenses so as to give the maximum signal. This cell size simplifies positioning. Raman scattering has been successfully observed from carbon tetrachloride, cyclohexane, benzene, and toluene, although only poorly from CCl_4. The samples used are pure liquids. Gases can also be used, though the Raman signal intensity is lowered by the reduced density of the scattering material.

Photons that are scattered through the stimulated Raman process are both spatially and temporally coincident with the incoming photon, with only the difference in energy to separate them. That energy difference corresponds to a different frequency and corresponding wavelength. There are also some photons that are not scattered, passing straight through the sample, and some photons that are scattered by $\Delta v = 0$ and $\Delta J = 0$, which are known as Rayleigh scattered photons. The Raman scattered photons need to be separated from the nonscattered, or Rayleigh, photons. The separation is accomplished by passing the light through an equilateral prism and projecting the photons over a 5-meter distance onto a white screen. The separation allows your eye to see the scattered photons separated from the other photons by wavelength, and by a visible physical separation on the screen. Figure 5 shows a superposition of photographs of the resulting projected photons from benzene and toluene. Figure 6 shows a diagram of the positions and approximate colors of the separated photons from carbon tetrachloride, cyclohexane, and benzene.

The green spot is the incident laser radiation, which is mostly transmitted through the sample. The other spots are the Raman scattered photons. The energy difference between the colors corresponds to the energy difference between two of the vibrational energy levels in the molecule. In addition, the pattern and intensity of the spots allow a qualitativeidentification of the molecule. Using the apparatus described here, these spots are readily observable in a classroom environment with the room lights turned off.

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Notes on Safety

The Nd:YAG laser used in this demonstration is a Class IV laser product, capable of producing severe eye damage, even from a small percentage of the beam. Extreme care must be taken to block ***all*** stray reflections off optics used in the demonstration. Fortunately, these reflections usually stay in the plane of the beam path, so that beam blocks are easily mounted at the ends of the beam path and around the prism to catch most reflections. In addition, these stray reflections can be blocked by placing smoked Plexiglas shields around the apparatus. When preparing the apparatus to demonstrate this experiment, the demonstrator should use safety goggles. Each demonstrator is responsible for ensuring that the reflections in their demonstration apparatus will not harm those in the room.

Applications

Even though this demonstration was originally designed for inclusion in the *Physical Chemistry in Practice* DVD, it has useful applications as a lecture demonstration in both physical chemistry and instrumental analysis courses. In physical chemistry, students will usually be taught the theory behind infrared spectroscopy, and the corresponding selection rules, as a probe of molecular vibrations. They may be taught the selection rules and theory for rotational and vibrational Raman spectroscopy as well. Some discussions of molecular polarizability, the induced dipole moment, and the regions of the Raman spectrum will likely be included. This instruction will typically be highly mathematical. In the laboratory, only a fraction of students in undergraduate physical chemistry courses will be able to carry out Raman experiments because the cost of the apparatus is usually prohibitive to most institutions. Even those students who do have the opportunity to carry out a Raman experiment will see little more than a black-box setup, with output in the form of a graphical waveform resulting from the signal from a photodiode, PMT, or CCD detector.

For physical chemistry students, this demonstration will serve as a bridge between the theory they learn in the course and the spectrum that results from the black-box apparatus in the laboratory. In addition, it will serve to show them a simplified version of the apparatus itself, with many of the advanced components either removed or simplified to no more than mirrors, lenses and prisms. For students in an instrumental analysis course, this "simplified apparatus" aspect of the demonstration will be most useful. In the DVD, students are shown the simple experiment as described in this demonstration. They are then immediately shown how the optical components from this are related to the components in a commercial Raman instrument. In both courses, this demonstration will help students in making the connection between the complex, abstract aspects of Raman spectroscopy, and a simple, concrete picture.

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