High performance Raman spectroscopy with simple optical components

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Several simple experimental setups for the observation of Raman scattering in liquids and gases are described. Typically these setups do not involve more than a small (portable) CCD-based spectrometer (without scanning), two lenses, and a portable laser. A few extensions include an inexpensive beam-splitter and a color filter. We avoid the use of notch filters in all of the setups. These systems represent some of the simplest but state-of-the-art Raman spectrometers for teaching/demonstration purposes and produce high quality data in a variety of situations; some of them traditionally considered challenging (for example, the simultaneous detection of Stokes/anti-Stokes spectra or Raman scattering from gases). We show examples of data obtained with these setups and highlight their value for understanding Raman spectroscopy. We also provide an intuitive and nonmathematical introduction to Raman spectroscopy to motivate the experimental findings.

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I. INTRODUCTION

The Raman effect was discovered in 1928 by Raman[1] and is now a major research tool with applications in physics, chemistry, biology, and engineering.[2] In a nutshell, the Raman effect involves shining light of a given energy and observing what comes out of a sample at energies that are different from the incoming one. In this transfer of energy between the light and the sample, there is precious information about the internal excitations of the sample. Although it is possible to produce inelastic scattering with various types of internal excitations, we shall concentrate on inelastic light scattering produced by vibrations in molecules.

We can explain the Raman effect using simple mechanical analogies,[3] which should not be taken literally because they contain a number of intrinsic limitations.[4] Consider a photon, which is represented by a bouncy object in Fig. 1. This object has a certain energy, represented by its potential energy. A molecule is represented by a "block" with which the object collides. Several situations are possible. The object can bounce elastically from the block (molecule), thus finishing with the same (potential) energy that it had initially. This process corresponds to elastic scattering, which for photons is called Rayleigh scattering. In this case the direction of a photon can be changed in the scattering process but not its energy. Rayleigh scattering is schematically represented in Fig. 1(a).

Next consider the possibility of an internal degree of freedom in the molecule. This possibility is schematically represented in Fig. 1(b) by a platform attached to a spring. A photon can now "bounce" back and finish with a smaller energy than its initial one. This is done by leaving part of its energy in the vibration of the platform, as it is represented in Fig. 1(b) (by a change in the final height of the bouncing object while the platform is left oscillating). This process is the mechanical analog for a Stokes Raman process. It is also possible that the vibration was already present in the molecule before the scattering takes place. This possibility is depicted in Fig. 1(c). The activation of the vibration can be done, for example, by the effect of temperature. Hence, in this case, the photon can extract energy from the molecule and finish with a higher energy than the original one. This case corresponds to anti-Stokes Raman scattering.

In reality, the photon is usually provided by a laser, which has a well defined frequency. The change in frequency of the scattered photon provides information about the energy of the excitation that was left behind in (for Stokes) or taken from (for anti-Stokes) the molecule. The difference in energy between the scattered and incident photons is called the Raman shift. By convention, Raman shifts are positive (negative) for photons with less (more) energy than the laser and are given for historical reasons in "wavenumbers," which is one of the very many units of energy used in optical spectroscopy.

A typical Raman spectrum consists of satellite peaks around the laser frequency. Typical vibrations in molecules have energies that are only a fraction ($\sim 1/10$) of the energy of the laser. A representation of a simple Raman spectrum for only one vibration is shown in Fig. 2. Anti-Stokes scattering depends on the vibration being excited beforehand and hence is temperature dependent. If we were able to lower the temperature to $T=0$ K, anti-Stokes scattering would disappear. For $T>0$ K it is present and depends on the ratio of the energy of the vibration ($\hbar\omega_v$) to k_BT through the Boltzmann factor, i.e., $\exp(-\hbar\omega_v/k_BT)$. Usually, anti-Stokes peaks for a given vibration will be smaller than their Stokes counterparts, which is the reason for the lower intensity of the anti-Stokes peak in Fig. 2. Stokes scattering does not depend on temperature,[5] and thus the ratio of the anti-Stokes to Stokes intensity of a single vibration can be used as an estimate of the actual temperature of the molecule.[4]

Furthermore, the Stokes and anti-Stokes signals "follow" the laser in the sense that if we change it to a different one, the Stokes and anti-Stokes peaks will be at the same Raman shifts. This is because the difference between the incident and scattered photons depends only on the energy of the vibration $\hbar\omega_v$. The intensity of the peaks and the underlying background (two important issues for resonance Raman spectroscopy) do depend though on the laser. Note that the incoming photon does not need to be absorbed by the molecule to produce a Raman scattered photon. The Raman effect occurs even if the laser is at a frequency where the molecule is transparent in the conventional sense of absorp-

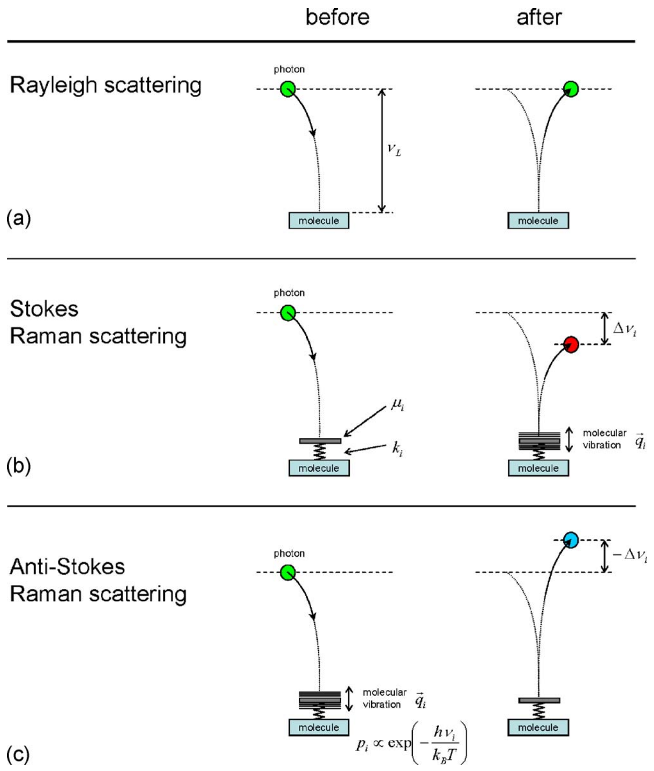

Fig. 1. (Color online) Mechanical analogs of different scattering processes. (a) Rayleigh scattering. A photon bounces from the molecule and has the same energy as the initial state, which represents elastic light scattering: Photons change directions but the energy is the same. (b) If there is a degree of freedom in the molecule (a vibration in this case), the photon can excite the vibration and finish with a lower energy than its original energy. An inelastic scattering process has occurred such that a vibration has been created in the molecule and a photon (with a lower energy) has been scattered. This process is the Stokes Raman process. (c) Alternatively, the vibration may already exist in the molecule. The photon can bounce off the molecule, taking the energy of the vibration with it and finishing at a higher energy than its original energy, corresponding to an anti-Stokes Raman process. Anti-Stokes Raman scattering depends on temperature.

tion spectroscopy. If the laser matches the energy of an electronic transition that can absorb the light, resonant Raman scattering is triggered. The intensity of Raman peaks can be boosted (up to $\sim 10^3$ in many cases) under resonance conditions. But other optical phenomena can also be triggered in resonance, such as the generation of fluorescence, which affects the observed background and can even completely swamp the Raman peaks. We shall not discuss these more complicated scenarios (from the point of view of plain Raman spectroscopy) and consider only nonresonant Raman scattering. That is, we will use a laser in the transparency region, where the phenomenon can be best understood on its own.

An elementary description of inelastic light scattering starting from the theory of optical polarizabilities has been given in Refs. 6–9. Our emphasis here is on the experimental aspects and how to observe the effect with the simplest possible setup to obtain data good enough to allow for a detailed analysis. Reference 10 reports an elementary setup for Raman spectroscopy too. However, the limitation of the elementary setup in Ref. 10 is that it does not usually allow for a quantitative analysis of the data, and stray light is a serious problem. Other elementary systems have been described[11] but use far more sophisticated setups involving fiber optics and notch filters. The system in Ref. 11 was designed to be used in combination with surface-enhanced Raman scattering (SERS).[4] The additional boost to the signal achieved by SERS sets much less stringent conditions in terms of the required optical throughput. We shall avoid any additional amplification to the signal and work with simple substances that are largely nontoxic and easily available.

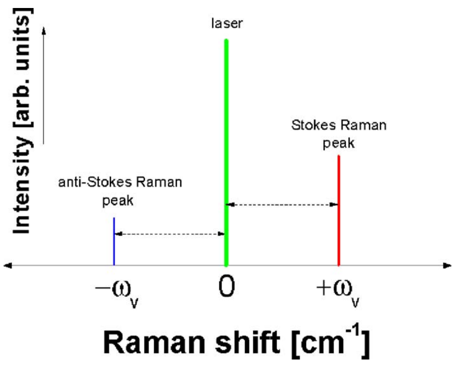

Fig. 2. (Color online) A schematic Raman spectrum for a single vibration. Stokes (anti-Stokes) peaks are redshifted (blueshifted) with respect to the laser and assigned a positive (negative) Raman shift, which are measured in wavenumbers. The laser is (by definition) at zero Raman shift. The anti-Stokes peak depends on temperature because the vibration needs to be excited before the scattering process takes place (see Fig. 1). Molecules will usually have several Raman active modes with different intensities.

Raman observed the effect by eye using color filters. It is possible to observe anti-Stokes scattering in organic liquids with rudimentary optical tools (see Fig. 3). This observation is usually a much better demonstration of Raman scattering because a down-conversion in energy (Stokes scattering) can be produced by a wide variety of other processes that are not related to Raman scattering (such as a small amount of residual fluorescence, for example).

II. EXPERIMENTAL SETUPS

A modern Raman spectrometer is designed to maximize the optical throughput and to operate under vastly different scattering conditions and configurations. As mentioned, there have been a few previous pedagogical descriptions of Raman scattering as a spectroscopic tool.[6–9] Their emphasis is on the results more than the instrumentation needed to observe them, which, in most cases, involves expensive Raman systems comprising double monochromators[7] and/or holographic notch filters[8,9] and/or fiber optics.[11] We shall show hereafter how to implement a simple yet state-of-the-art system to learn basic Raman spectroscopy.

Two of the main experimental problems in obtaining Raman spectra are that the effect is weak (only a small fraction of the photons are converted into scattered ones), and Raman shifts are (typically) a small fraction of the energy of the laser ($\sim 1/10$). Accordingly, we have to observe "satellite peaks" around the laser frequency, which are several orders of magnitude weaker than the laser itself and close in energy to it. Therefore, a big part of the experimental effort to observe the Raman effect goes into removing the laser light from the detected signal. If we do not, the most likely situation is the observation of a long tail of stray light on the high and low-energy wings of the laser line, which completely swamps the Raman signals. Holographic notch filters are special "mirrors" that reflect very efficiently the laser

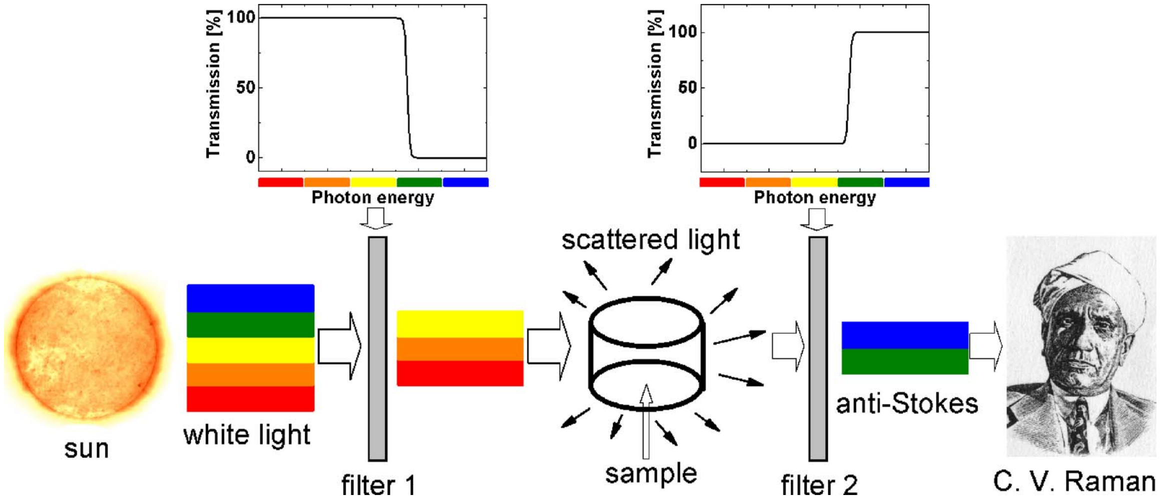

Fig. 3. (Color online) Representation of the basic experiment to observe anti-Stokes scattering. Sunlight (with components in all visible colors) is collimated and passed through a low-pass filter, that is, a filter that only allows light through up to a maximum frequency. Such a filter is represented by filter 1 (with its corresponding transmission characteristics shown at the top). This light beam is then passed through a cell with a transparent organic liquid. We can observe the scattered light with a complementary filter, that is, filter 2, which allows only light of higher frequency than the cutoff of filter 1. If we observe a glow at energies higher than the incident ones, we can conclude that it cannot be fluorescence (which is composed of smaller energies than those in the incident light) and that there must have been an inelastic "up-conversion" in energy.

while allowing all other wavelengths to go through. They are the standard choice in many modern Raman spectrometers (even simple ones) for stray light rejection.[11] Stray light can also be minimized by carefully choosing the scattering configuration. Although some of these methods will work only for certain types of samples (colorless liquids, solids, and gases), they provide the basis for a proof of principle demonstration of the effect with a minimum of complexity in the optical layout.

A. A simple Raman system

We used an Ocean Optics HR4000 high-resolution spectrometer with the H11 grating, 100 μm slit size, and set the wavelength range to 545–663 nm. This portable spectrometer is about the size of the palm of a hand and costs ~\$3000–\$4000. The detection range can be chosen by the user prior to delivery and needs to be selected according to the typical ranges of Stokes shifts that one desires to observe, which will vary according to the laser used. We used a 5 mW, 532 nm laser pointer, a Spectra-Physics Ar^+ laser (tuned at 514.5 nm), and 5 and 30 mW HeNe (633 nm) lasers. The smallest lasers such as the 5 mW, 532 nm make the system very portable (it can fit in a suitcase). The bigger and more powerful lasers were used for convenience and availability in our laboratory and do not impose any serious restriction on the portability and performance of the system. There are lasers that emit as much as ≈500 mW at 532 nm (green) and are portable and battery operated. The choice of laser is a matter of convenience, but any laser above ~5 mW in the green-red region is usable.

The fixed observation window chosen for our spectrometer (545–663 nm) allows different types of experiments to be done. The 532 and 514 nm green lines fall outside the range of the spectrometer, thus reducing to some degree problems with stray light. The spectrometer allows us to see the Stokes-side of the spectrum (see Fig. 2) in the ranges of ~1100–4370 cm^{-1} for 514 nm and ~450–3715 cm^{-1} for 532 nm, respectively. The latter is a very useful range to observe typical "fingerprint" Raman modes of organic molecules, which usually span the range of ~300–1700 cm^{-1}. It is also useful to observe the Raman signals of typical gases such as hydrogen (~2230 cm^{-1}) and oxygen (~1650 cm^{-1}). The choice of a 514 nm laser misses part of the fingerprint region of organic molecules but is better suited for the study of gases such as N_2 and O_2 by being in a range further away from the laser and thus minimizing stray light problems.

The 633 nm HeNe laser is in the middle of the detection range of the spectrometer and allows us to demonstrate the possibility of observing simultaneously Stokes and anti-Stokes peaks (see Fig. 2). The simultaneous observation of both types of scatterings (Stokes and anti-Stokes) is the most challenging as far as stray light is concerned, assuming that notch filters or any other sophisticated light rejection elements are not used (the laser falls in the middle of the detection range of the spectrometer).

B. 90°-scattering configuration

The simplest of our two setups is the 90°-scattering configuration. In this case, we set up the spectrometer at right angles to the laser beam as it passes through the sample. A lens is used to collect the signal from the sample, and another lens is used to focus the signal into the spectrometer (see Fig. 4). It is possible to create an image of the beam in the sample onto the entrance slit of the spectrometer by using only one lens. However, the use of two lenses gives more flexibility because the beam in between the two lenses is parallel to the optical axis, and the separation between the lenses can be varied while producing the same image on the entrance slit. This gives more flexibility to set up the optical components at the right positions and allows for the spectrometer and the lens closer to it to be optimized (with a distant light source, for example) and left untouched from then on, thus reducing the problem to the positioning of the collecting lens and the sample. The spectrometer was designed to couple to an optical fiber, but it is preferable to

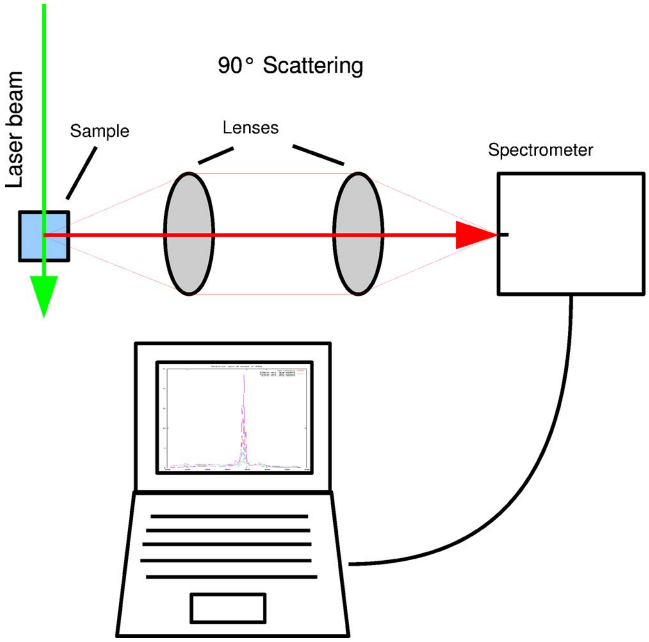

Fig. 4. (Color online) A representation of the 90°-scattering configuration. The two lenses project an image of the laser beam inside the sample onto the entrance slit of the spectrometer. A slightly improved version of the same system can accommodate a suitable color filter in between the two lenses, which can be used to further reduce any remaining laser stray light reaching the entrance slit, thus allowing only the Raman scattered light to be analyzed in the spectrometer.

obtain a signal by focusing light onto the entrance slit directly. The laser can be focused into the transparent sample by using a third lens in the laser path, but this is not usually necessary and does not provide substantial gains. The sample needs to be in a cuvette made from a nonfluorescent glass such as quartz with four transparent sides. A schematic of the layout of the system is given in Fig. 4.

The collecting optics requires some attention because it has a direct effect on the efficiency of system. The spectrometer has a numerical aperture of 0.125 $(f/4)$,[12] which places a limit above which increases in the numerical aperture of the collection optics are not realized in the signal. Ideally, the collection optics will have a numerical aperture[12] matched to the spectrometer, but small differences in either direction do not significantly affect the performance and can be compensated in many cases by changes in the integration time needed to obtain the signal. Other important considerations in selecting appropriate lenses are practical ones such as using lenses with short focal lengths to keep the size of the system to a minimum. We obtained very good results with two achromatic 25 mm diameter lenses with focal lengths of 50 mm for both the collecting and focusing lenses, but we also found satisfactory results using two ×10 microscope objectives (NA=0.1) back-to-back and mounted on a common frame.

It is necessary to be able to finely adjust the position of the lenses and the spectrometer with respect to the laser beam. Having the two lenses connected together will aid in this adjustment. The distance between the spectrometer and focusing lens should be adjustable to ensure optimal coupling. It is also convenient to direct the laser onto the sample via at least one external mirror to allow the position of the beam to be more easily moved without physically moving the laser. There are some easy ways of ensuring optimal alignment, such as the use of a highly fluorescent substance in the cuvette (for example, Rhodamine 6G with a green laser or Nile Blue with a red laser) to provide instant feedback on the changes being made to the system. It is also possible to use the Raman signal of some transparent liquids such as ethanol to optimize the system, although the feedback in this case will be slower due to the longer integration times required in the acquisition (∼10 s). Once the position of the lenses is optimized and the throughput checked (with a fluorescent probe, for example), the system can be used to obtain Raman spectra of transparent liquids in this configuration. Examples of spectra generated in a 90° configuration with different lasers are given in Figs. 6, 7 and 11 and are discussed in Sec. III.

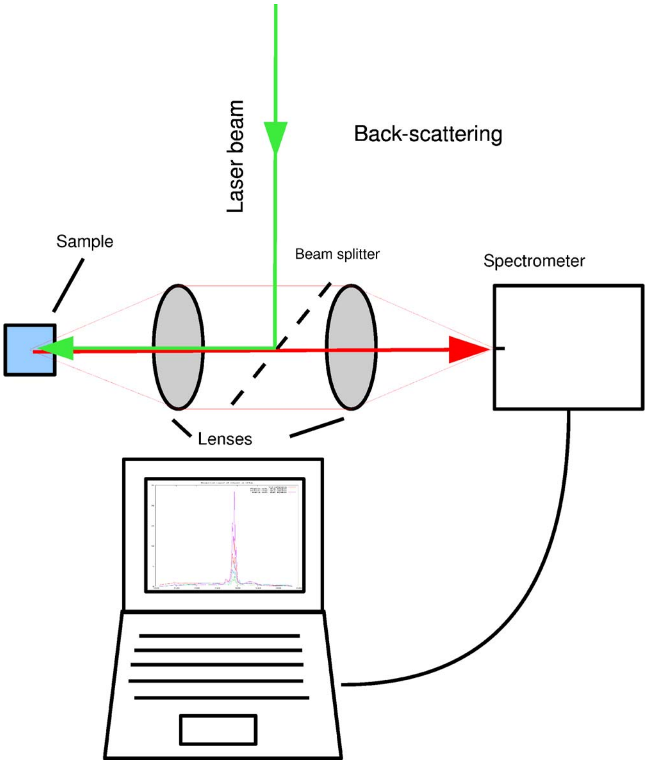

Fig. 5. (Color online) A representation of the back-scattering configuration. An optional color filter may be inserted between the beam-splitter and the lens on the right. This configuration has the advantage of being self-focusing because the same lens that delivers the laser on the left is the one that collects the image to be projected onto the entrance slit of the spectrometer. This situation comes at the price of using a beam-splitter (with the subsequent loss in intensity on both reflection and transmission). Back-scattering is the best choice in many situations where the 90°-scattering configuration (see Fig. 4) is not feasible (due to the sample's characteristics) and produces too much stray light.

C. Back-scattering configuration

The other setup we used is the back-scattering configuration, which utilizes a beam-splitter to direct the laser beam along the optical axis of the collection optics (see Fig. 5). The layout is the same as in the 90° configuration, except that the beam-splitter is inserted between the two lenses. This insertion causes the laser beam to pass through the collecting lens onto the sample. From there the system works as before (though only some of the collected light passes through the beam-splitter). This layout is slightly more complicated than the 90°-scattering but is still easy to implement. The signal provided in this configuration is typically larger than in 90°-scattering because the excitation and collection volumes in the sample are automatically aligned in this case. But the back-scattering configuration has typically more influence from stray light (which appears as a noisy background in the spectra) due to reflections of the laser on the lenses and cuvette (which enter the spectrometer and produce a dim speckle pattern on the detector). This background can be largely reduced by inserting a simple color (edge) filter between the beam-splitter and the focusing lens. The appropriate filter is chosen according to the laser line being used and greatly attenuates the laser light while allowing the Stokes side of the scattered light to go through. The presence of the filter usually results in a considerable reduction in noise and background level and only slightly reduces the intensity of the Raman peaks. Hence the use of such a filter is recommended in most situations. However, it is not possible to use a filter when attempting to see anti-Stokes Raman lines or lines very close to the laser. Examples of spectra taken in a back-scattering configuration are shown in Fig. 8–10.

III. EXAMPLES OF EXPERIMENTALLY OBTAINED RAMAN SPECTRA

The best candidates for samples to demonstrate the performance of these systems are clear liquids. There are many common substances that fit the description that are easily available, mostly nontoxic, and easy to handle. Clear solids and gases also make good samples, though signals from gases tend to be weak because of their much smaller density. Solids might have issues with reflections of the laser producing stray light, especially in back-scattering without a color filter. Different liquids may be chosen to provide a range of different Raman modes. We will discuss some simple examples of data we collected with both setups.

A. Common liquids and solid samples

When the laser is outside the range of the spectrometer, stray light issues become less of a problem. Transparent liquids, such as water, ethanol, and toluene, are good samples because they generate little stray light, are readily available, and have strong enough Raman signals to be seen with low-powered lasers in a reasonably short time (typical integration times used for the spectra were ≈60 s). Examples of Raman spectra for these liquids are shown in Figs. 6 and 7 in the 90° configuration and in Fig. 8 for back-scattering.

Figure 6(a) shows that it is possible to measure the Raman spectrum of small solid samples, in this case the tip of a diamond scribe (to cut glass). The measurement of a small diamond attached to metallic surface introduces a lot more stray light into the system due to multiple reflections in the tiny crystal and the substrate. As can be seen, the system is still able to detect the only Raman active peak of diamond (at ≈1342 cm^{-1}) above the stray light background. The small size of the sample does not allow for easy alignment, especially in 90°-scattering as shown here.

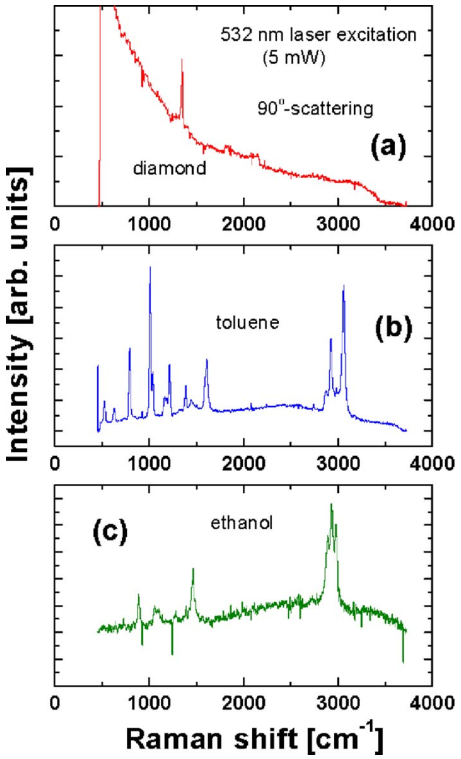

Fig. 6. Results with 90°-scattering and a 532 nm laser. No color filter was used for these samples. The samples were (a) the tip of a diamond scribe and [(b) and (c)] clear liquids. The diamond spectrum contains much stray light produced by the multiple reflections in the small diamond crystal. This light does not prevent the only Raman peak of diamond (at ≈1342 cm^{-1}) from being visible above the stray light background. (Diamond has only one Raman active mode, which is the zone-centered $k=0$ optical vibration of the crystal.)

A polymer such as Perspex can be used as an example of scattering from a solid sample. Because Perspex is transparent and can be shaped into larger geometries with clear faces, it does not scatter as much light as a tiny diamond and pro-

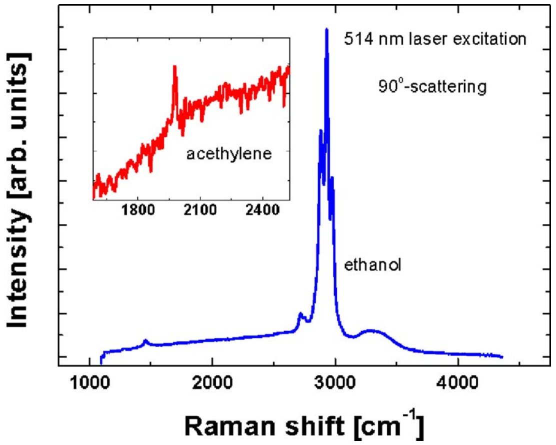

Fig. 7. Some results for 90°-scattering of a liquid and a gas (acetylene) in a cell using a different green laser than that used to generate Fig. 6. These spectra were taken without a color filter and with the Ar^{+} -laser at 514 nm. Acetylene (inset) is used in a glass ampule properly loaded and sealed beforehand. The range of Raman shifts visible to the spectrometer depends on the frequency of the incident laser, and hence some of the peaks for ethanol shown in Fig. 6 are not visible here.

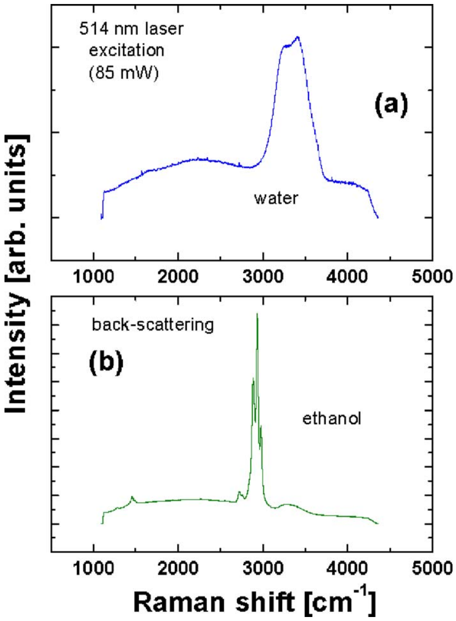

Fig. 8. Results for clear liquids using back-scattering and the 514 nm line of an Ar$^+$-laser. A color filter was in place to reduce stray light.

vides a spectrum with much less stray light. An example in the back-scattering configuration is shown in Fig. 9.

B. Gases

Another possibility, and the one that provides the weakest signals, is to use some conventional gases as samples. Not only is the cross section for abundant gases (such as nitrogen) intrinsically small, but the density is much smaller than typical values for solids or liquids too. The combination of the small intrinsic Raman signals and the much smaller density results in very weak signals, which set a stringent test for the detection capabilities of a Raman system. Gases also present several practical experimental difficulties because it is more difficult to contain gases (as samples) than liquids or solids. This problem is not insurmountable with the use of an ampule that can be sealed with the gas inside. It is preferable if the ampule (or cell) where the gas is contained has flat surfaces to avoid unnecessary problems with the focusing optics.

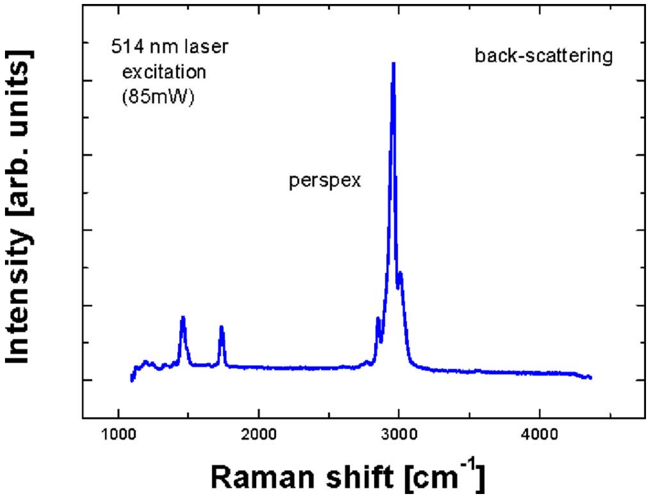

Fig. 9. Signal of Perspex in back-scattering with an Ar$^+$-ion laser excitation at 514 nm. The spectrum was taken with a color filter and is an example of Raman spectra in a solid polymer sample. The dominant peaks seen in the spectrum at $\approx 3000\ \mathrm{cm}^{-1}$ come from hydrogen stretching C–H modes in the structure of the polymer.

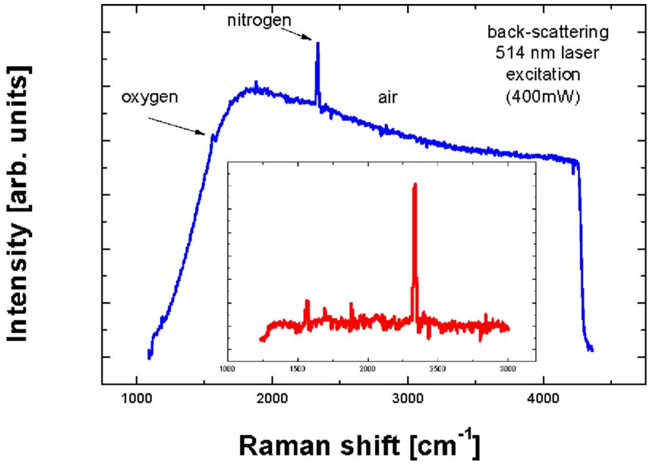

Fig. 10. Demonstration of signals from gases. Signals from both nitrogen and oxygen are visible. The inset shows the peaks with the background subtracted off (Ref. 14). This measurement used the Ar$^+$-laser at 514 nm in back-scattering with a color filter in place. Nitrogen and oxygen gases have very low signals due to their low density and small intrinsic Raman cross-sections.

We show an example of gas measurement for acetylene, a simple and nontoxic gas, in the 90°-scattering configuration in the inset of Fig. 7. The other simpler option is to look at gases present in air, such as nitrogen or oxygen. Both are weak Raman scatterers, but it is possible to see a signal, as shown in Fig. 10. Longer integration times are typically required for these measurements, but good quality data can be obtained with ≈ 100 mW incident power and integrations times of the order of ~ 1 min. The background in Fig. 10 is spurious and comes predominantly from stray light. Backgrounds of this sort can be removed in a subsequent postprocessing of the data, thus leaving a clean Raman spectrum that can be used to monitor nitrogen/oxygen ratios in air. Raman spectroscopy has numerous applications in remote gas sensing, and oxygen and nitrogen are among the weakest signals we can hope to detect.

C. Anti-stokes Raman scattering

As mentioned, it is possible to observe both Stokes and anti-Stokes Raman scattering at the same time in the 90° configuration using an appropriate laser and a substance with low-energy Raman modes, such as 2-bromo-2-methylpropane (2B2MP).[13] For the range of our spectrometer, a 633 nm laser works well because the laser is within the range the spectrometer can detect and has enough leeway on both sides of the laser wavelength to see low-frequency Raman modes on both Stokes and anti-Stokes sides (see Fig. 11). The use of a transparent liquid is important because it helps to minimize the (stray) laser light scattered into the system. The 90° configuration ensures that a minimum of stray light enters the system because the only laser light that might enter the spectrometer is the light scattered from the liquid itself (typically by impurities or small density fluctua-

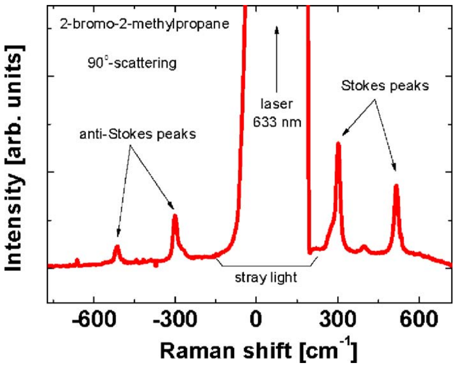

Fig. 11. Demonstration of Stokes and anti-Stokes Raman peaks in the transparent liquid 2-bromo-2-methylpropane (2B2MP). The laser used was a 633 nm HeNe laser, and the configuration was 90°-scattering without a color filter. Despite a region of (inevitable) stray light around the laser wavelength, the presence of Stokes and anti-Stokes scattering for two modes of 2B2MP is clearly seen. The central region (around 0 cm^{-1}) is the combination of stray light and Rayleigh scattering.

tions) and some of the light entering and exiting the cuvette. The region around the laser in Fig. 11 contains some unavoidable stray light, but it does not prevent the observation of two Raman modes of 2B2MP with their corresponding anti-Stokes peaks on the other side.

The ratio of the anti-Stokes (I_{aS}) to Stokes signal (I_{S}) of a Raman peak is given by $I_{\mathrm{aS}}/I_{\mathrm{S}}=\exp(-\hbar\omega_v/k_BT)$.[4,15,16] The ratios of the two peaks in Fig. 11 can be used to obtain two estimates of the temperature of the liquid. The temperature obtained from intensity ratios of the anti-Stokes to Stokes ratios of either the ≈ 300 or ~ 516 cm^{-1} modes of 2B2MP is slightly higher than room temperature (≈ 45 °C). This value is within the accuracy expected for this method (and it might also be revealing a slight laser-heating effect in the liquid). Temperature determinations with this method are inaccurate because the exponential $\exp(-\hbar\omega_v/k_BT)$ is very sensitive to small changes in T. Although this method is not the preferred way to measure the temperature of a room, the example highlights the concept of measuring temperatures with a spectroscopic tool. Raman spectroscopy is one of the preferred options for temperature estimations and chemical sensing using a remote optical system and is very important in studying chemical reactions in flames or plasmas[17] and the temperature of mechanical parts that move at high speed (such as blades in turbines),[18] where it is impossible to attach a thermometer or an electronic sensor.

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