

Rayleigh and Raman Scattering

DAVID W. BALL

Raman spectroscopy is a widespread spectroscopic technique, yet this column hasn't covered it yet. The next few columns introduce the basics of Raman spectroscopy. This first instalment covers the fundamental physical process involved; next time, we'll look at some details of the spectroscopic technique itself.

In a column a few years back (1), we covered the three major ways that light interacts with matter: it can be transmitted, reflected, or absorbed. Here, we will modify that statement slightly.

As has been amply demonstrated, an atomic or molecular system will absorb a photon if (and only if) the energy of the photon equals the energy difference between two states of the absorbing species:

$$h\nu = E_f - E_i \quad [1]$$

where E_f is the energy of the final state, and E_i is the energy of the initial state. The absorbing species now occupies a higher-energy, or *excited*, state. The excited state will, over time, give off energy and return to a lower-energy state. The energy release may occur by emission of a photon or energy transfer to other states of the species (such as other translational, rotational, vibrational, or electronic states), and this process can occur over femtosecond to kilosecond time scales. Figure 1 is a schematic of the process.

To a tiny extent (about 1 in 10^4), a particle will absorb a nonresonant photon and simultaneously emit it. Although the incoming photon typically enters the system from a particular direction, the outgoing photon of the same energy, frequency, and wavelength can be emitted in any direction. Effectively, photons are being scattered. Although this process can be thought of as a photon bouncing off a

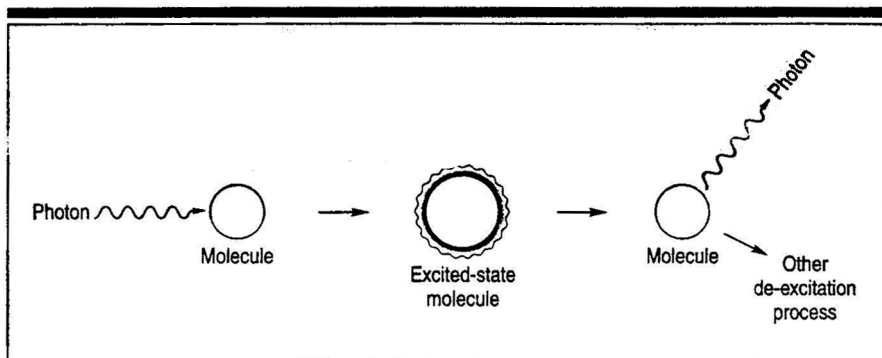


Figure 1. Schematic of a molecule absorbing a photon and then releasing energy to return to a lower-energy state.

molecule, much like pool balls rebound off each other, this is not an accurate analogy. In fact, scattering is a two-photon process, not a bouncing of a photon off a molecule. Figure 2 illustrates the process.

Scattering of this sort is called Rayleigh scattering after Lord Rayleigh, who first correctly attributed scattering to tiny particles like atoms and molecules. The ability of a molecule to induce Rayleigh scattering is related to a molecule's *polarizability*, which is the ability of a molecule's electrons to be distorted by an externally applied electric field. The amount of Rayleigh scattering at any frequency of light is proportional to the fourth power of that frequency, meaning that high-frequency light is much, much more susceptible to scattering than is lower-frequency light. This is why the sky looks blue: high-frequency blue light is scattered much more than low-frequency red light, giving the daytime sky a distinct blue color, even though the incoming sunlight spans the complete visible spectrum and more. (Reddish colors that we see toward the horizon at sunrise and sunset are caused by different optical effects, not Rayleigh scattering.)

If molecules are changing their polarizabilities (for example, the molecule may

be vibrating, and during the course of the vibration a changing polarizability may occur), another possibility exists. A photon may be absorbed and then simultaneously emitted, but in this case, the energy, frequency, and wavelength of the outgoing photon are different from those of the incoming photon. In the majority of cases, the incoming photon loses some energy, so the outgoing photon has less energy. This happens for about 1 in 10^7 photons, and this type of scattering is called Raman scattering (Figure 3).

Raman scattering was predicted by A. Smekal in 1923 and observed in 1928 by Chandrasekhara Venkata Raman, after whom the effect is named. (Raman was awarded the 1930 Nobel Physics Prize for the discovery of the Raman effect and was later knighted. Historically, Smekal's contributions appear to have been largely ignored.) Observation of the Raman effect initially was performed using mercury lamps as the source of incoming photons. With the subsequent development of lasers as very intense light sources, performing spectroscopy using the Raman effect became less laborious.

The major utility of the Raman effect is based on the fact that the amount of energy lost between the incoming and out-

going photons (ΔE_{photon}) is equal to an energy difference between two quantized energy levels of the molecules that are causing the scattering ($\Delta E_{\text{molecule}}$):

$$\Delta E_{\text{photon}} = \Delta E_{\text{molecule}} \quad [2]$$

These energy differences of the photons are independent of the initial energy, wavelength, and frequency of the incom-

ing light. Rather, the energy differences are characteristic of the molecules and thus, form the basis of Raman spectroscopy: the ability to differentiate molecules by their characteristic Raman scattering of photons.

In most cases, the net effect on two photons is that energy is lost, and the outgoing photons are shifted to lower energies. In a lesser number of instances, the

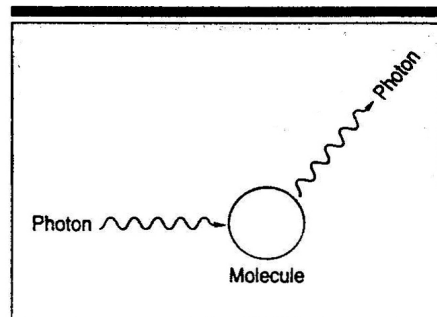


Figure 2. Schematic of Rayleigh scattering. A molecule absorbs a photon and simultaneously emits a photon of the same energy, frequency, and wavelength in any direction.

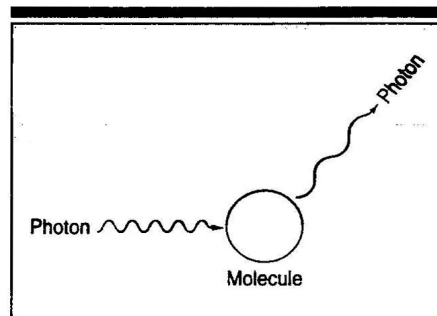


Figure 3. Schematic of Raman scattering, in which a molecule simultaneously absorbs and emits a photon. The outgoing photon has an energy that is different from that of the incoming photon. In most cases, the outgoing photon has less energy than the incoming photon.

net effect is that the outgoing photon gains energy from a molecule (which may already be in an excited state), so some photons are shifted to higher energies. But the pattern of energy shifts is the same, so a Raman spectrum ideally shows two equivalent patterns of shifts one to higher photon energies and one lower photon energies.

In our next installment, we will focus on some of the details of Raman spectroscopy itself. A goal of this column series is to show how versatile a technique it really is.

REFERENCES

- (1) D.W. Ball, *Spectroscopy* 9(6), 20–21 (1994).

David W. Ball is associate professor of chemistry at Cleveland State University (Cleveland, Ohio). He can best be contacted by e-mail at dball@popmail.csuohio.edu; he may also be reached by phone at (216) 687-2456 or by fax at (216) 687-9298. ♦