Theory of Raman Spectroscopy

DAVID W. BALL

In the previous column (1) we discussed two additional phenomena arising from the interaction of light with matter. One was *Rayleigh scattering*, a two-photon process having a net effect of changing the direction of, or scattering, light, while keeping its frequency constant. Because of this, Rayleigh scattering is a form of elastic scattering. The other was *Raman scattering*, a two-photon process having net effects of scattering photons but changing their frequency. This changing in frequency — characteristic of inelastic scattering — provides a basis for a form of spectroscopy. (We did not consider some other forms of scattering, like Brillouin or Mie scattering. Perhaps we'll discuss those in a future column.)

What causes the scattering of a photon? It turns out that the key property of a molecule scattering a photon is the molecule's polarizability. The polarizability, α, represents the ability of an applied electric field, E, to induce a dipole moment, μ_{in}, in an atom or molecule:

$$\mu_{in} = \alpha E \qquad [1]$$

For example, large atoms such as xenon have a strong polarizability because their electron clouds — distant from the xenon nucleus — are relatively easy to distort with an applied electric field. Helium atoms, which are smaller and more compact, have a small polarizability. Polarizabilities for atoms are isotropic (that is, the same in all directions), whereas polarizabilities for molecules may vary with position about the molecule, depending on the molecule's symmetry. Thus, you may see polarizabilities labeled with Cartesian coordinates to indicate the particular direction to which polarizability refers.

A photon of light can act as an induced electric field (remember that the formal name for light is *electromagnetic radiation*), so equation 1 applies when light interacts with atoms and molecules. However, certain actions of a molecule occur with concurrent changes in the polarization of the molecule — motions like rotations and vibrations. That is, in some cases, the polarization of the molecule changes.

Mathematically, this is fairly straightforward to show, although I warn you, the equations can get a little long! At a molecule's equilib-

rium nuclear geometry, the polarizability is some value, α_0. At some distance, Δr, away from the molecule's equilibrium geometry, the instantaneous polarization α is given by

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial r}\right)\Delta r \qquad [2]$$

where the derivative

$$\left(\frac{\partial \alpha}{\partial r}\right)$$

represents the change in polarizability with change in position. Of course, if the molecule is vibrating or rotating in some sinusoidal fashion, Δr can be written as some sinusoidal (that is, sine- or cosine-based) function in terms of the frequency of the vibration, ν, and the time, t:

$$\Delta r = r_{max}\cos(2\pi \nu t) \qquad [3]$$

where r_{max} is the maximum vibrational amplitude. Light that has a particular frequency, ν_{in}, is inducing an electric field, E, that also has sinusoidal behavior:

$$E = E_{max}\cos(2\pi \nu_{in} t) \qquad [4]$$

Here, E_{max} is the maximum electric field frequency. Now we will bring this all together. Equations 2, 3, and 4 can be substituted for α, Δr, and E, respectively, into equation 1 to get:

$$\mu_{in} = \alpha_0 E_{max}\cos(2\pi \nu_{in} t) + E_{max} r_{max}\left(\frac{\partial \alpha}{\partial r}\right)\cos(2\pi \nu t)\cos(2\pi \nu_{in} t) \qquad [5]$$

This expression looks complicated, but you should be able to verify easily that we've simply substituted for α, Δr, and E.

Now we go back to high-school geometry (and you thought high-school geometry was useless!) to get a relationship for a product of two cosines, which is what the second term in equation 5 is.

$$\cos a \times \cos b = \tfrac{1}{2}(\cos(a + b) + \cos(a - b)) \qquad [6]$$

In comparing equations 5 and 6, we see that a is $2\pi \nu_{in} t$ and b is $2\pi \nu t$. Substituting, then, for the product of the two cosines in equa-

David W. Ball *is an associate professor of chemistry at Cleveland State University in Ohio. He can be reached by phone at (216) 687-2456 or by e-mail at d.ball@csuohio.edu.*

tion (5), we get

$$\mu_{in} = \alpha_0 E_{\max} \cos(2\pi v_{in} t) + \frac{E_{\max} r_{\max}}{2} \left(\frac{\partial \alpha}{\partial r} \right) \left(\cos(2\pi t(v_{in} + v)) + \cos(2\pi t(v_{in} - v)) \right)$$

[7]

This final expression can be used as the dipole moment operator in a transition moment integral, but we won't construct that expression. Let's just analyze the terms in equation 7 and see what they imply.

The first term contains the variable v_{in}, which is the frequency of the incoming light. This term relates to the *outgoing,* scattered photon that has the same frequency as the incoming photon. That is, this term ultimately explains Rayleigh scattering. The second term contains two cosines. One contains the variable $v_{in} + v$, which relates to an outgoing, scattered photon that increases in frequency by some amount, v, which is the frequency of the molecular motion. The last cosine term contains the variable $v_{in} - v$, which relates to a scattered photon that decreases its frequency by the same amount, v. These two terms ultimately explain Raman scattering. The two terms show that incoming photons will shift their frequencies, up *and* down, by amounts equal to certain motions of the molecules. This is the basis of Raman spectroscopy.

Equation 7 also gives a gross selection rule for what are called *Raman-active motions.* Notice the term

$$\left(\frac{\partial \alpha}{\partial r} \right)$$

in the second term that is multiplying the last two cosine terms. That derivative, remember, is the change in the polarizability with nuclear position. If that derivative equals zero, the entire second term is zero and there will be no Raman scattering. Thus, we have as a gross selection rule: A molecular motion will be Raman-active only if the motion occurs with a changing polarizability.

Unlike dipole-moment changes (which are the basis for other forms of spectroscopy, as we discussed in an earlier column), polarizability changes can be challenging to visualize, but with enough examples and practice it can be done. Some textbooks and spectroscopy references go through these steps.

Next time, we'll discuss the different ways that Raman scattering is applied as a spectroscopic method.

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REFERENCES

(1) D. Ball, *Spectroscopy* **16**(2), 28-30 (2001). ◆

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