4.8. RAMAN SPECTROSCOPY

Raman spectroscopy is a technique for studying molecular vibrations by light scattering. Raman spectroscopy complements IR absorption spectroscopy because some vibrations, as we have seen, do not result in absorptions in the IR region. A vibration is only seen in the IR spectrum if there is a change in the dipole moment during the vibration. For a vibration to be seen in the Raman spectrum, only a change in polarizability is necessary.
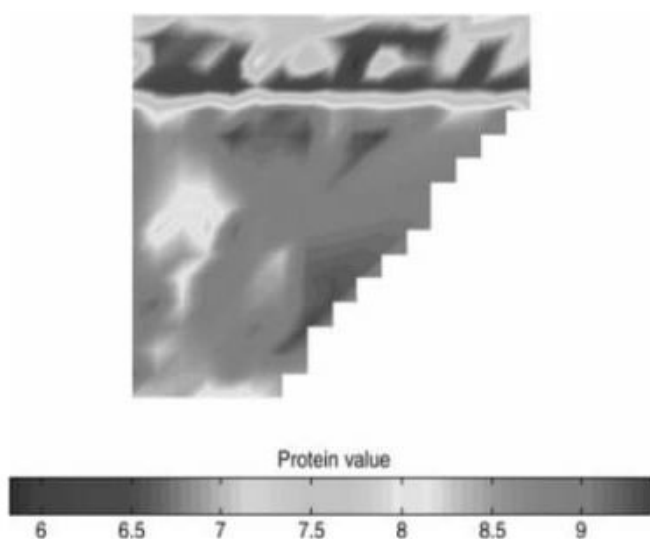

Protein value

| 6 | 6.5 | 7 | 7.5 | 8 | 8.5 | 9 |

Figure 4.59 This figure is a false-color map of the field during a corn harvest showing the differences in protein content for corn from different parts of the field. The bar under the map runs from blue on the left to red on the right. The top rectangle of the map is primarily blue (dark) and green (light), indicating 6–7% protein. The irregular spot in the middle left section is yellow (about 8% protein), while the rest of the lower portion is red and orange (8.5–9% protein). (Reprinted from von Rosenberg et al., with permission from Advanstar Communications, Inc.)
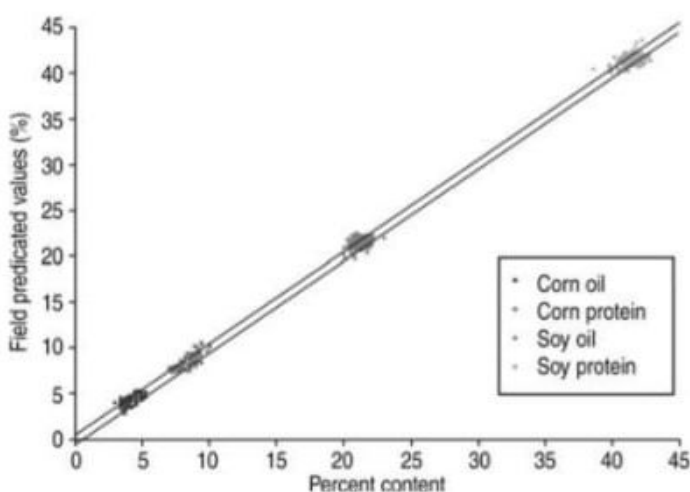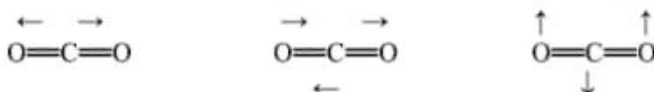
Figure 4.60 Correlation plot of the oil and protein values measured by the NIR field grain analyzer and the laboratory reference method (combustion analysis). (Reprinted from von Rosenberg et al., with permission from Advanstar Communications, Inc.)

That is, only a distortion of the electron cloud around the vibrating atoms is required. Distortion becomes easier as a bond lengthens and harder as a bond shortens, so the polarizability changes as the bound atoms vibrate. As we learned earlier in the chapter, homonuclear diatomic molecules such as Cl_2 do not absorb IR radiation, because they have no dipole moment. The Cl—Cl stretching vibration is said to be *IR-inactive*. Homonuclear diatomic

That is, only a distortion of the electron cloud around the vibrating atoms is required. Distortion becomes easier as a bond lengthens and harder as a bond shortens, so the polarizability changes as the bound atoms vibrate. As we learned earlier in the chapter, homonuclear diatomic molecules such as Cl_2 do not absorb IR radiation, because they have no dipole moment. The Cl—Cl stretching vibration is said to be *IR-inactive*. Homonuclear diatomic molecules do change polarizability when the bond stretches, so the Cl—Cl stretch is seen in Raman spectroscopy. The Cl—Cl stretching vibration is said to be *Raman-active*. Some molecular vibrations are active in IR and not in Raman, and vice versa; many modes in most molecules are active in both IR and Raman. Looking at CO_2 again, shown below, the mode on the left is the IR-inactive symmetric stretch, while the other two asymmetric vibrations are both IR-active. The symmetric stretch is Raman-active.

$$\overset{\leftarrow\quad\rightarrow}{O{=}C{=}O} \qquad \overset{\rightarrow\quad\rightarrow}{\underset{\leftarrow}{O{=}C{=}O}} \qquad \overset{\uparrow\qquad\uparrow}{\underset{\downarrow}{O{=}C{=}O}}$$

4.8.1. Principles of Raman Scattering

When radiation from a source is passed through a sample, some of the radiation is scattered by the molecules present. For simplicity, it is best to use radiation of only one frequency and the sample should not absorb that frequency. The beam of radiation is merely dispersed in space. Three types of scattering occur. They are called *Rayleigh scattering*, *Stokes scattering*, and *anti-Stokes scattering*. Most of the scattered radiation has the same frequency as the source radiation. This is Rayleigh scattering, named after Lord Rayleigh, who spent many years studying light scattering. Rayleigh scattering occurs as a result of elastic collisions between the photons and the molecules in the sample; no energy is lost on collision. However, if the scattered radiation is studied closely, it can be observed that slight interaction of the incident beam with the molecules occurs. Some of the photons are scattered with less energy after their interaction with molecules and some photons are scattered with more energy. These spectral lines are called *Raman lines*, after Sir C.V. Raman, who first observed them in 1928. Only about 1 photon in a

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million will scatter with a shift in wavelength. The Raman–Stokes lines are from those photons scattered with less energy than the incident radiation; the Raman–anti-Stokes lines are from the photons scattered with more energy. The slight shifts in energy and therefore, slight shifts in the frequencies of these scattered photons are caused by inelastic collisions with molecules. The differences in the energies of the scattered photons from the incident photons have been found to correspond to vibrational transitions. Therefore the molecules can be considered to have been excited to higher vibrational states, as in IR spectroscopy, but by a very different mechanism. Figure 4.61 shows a schematic diagram of the Rayleigh and Raman scattering processes and of the IR absorption process.

The energy of the source photons is given by the familiar expression $E = h\nu$. If a photon collides with a molecule, the molecule increases in energy by the amount $h\nu$. This process is not quantized, unlike absorption of a photon. The molecule can be thought of as existing in an imaginary state, called a virtual state, with an energy between the ground state and the first excited electronic state. The energies of two of these virtual states are shown as dotted lines in Fig. 4.61. The two leftmost arrows depict increases in energy through collision for a molecule in the ground state and a molecule in the 1st excited vibrational state, respectively. The arrows are of the same length, indicating that the interacting photons have the same energy. If the molecule releases the absorbed energy, the scattered photons have the same energy as the source photons. These are the Rayleigh scattered photons, shown by the two middle arrows. The molecules have returned to the same states they started from, one to the ground vibrational state and the other to the first excited vibrational state. The arrows are the same length; therefore the scattered photons are of the same energy.
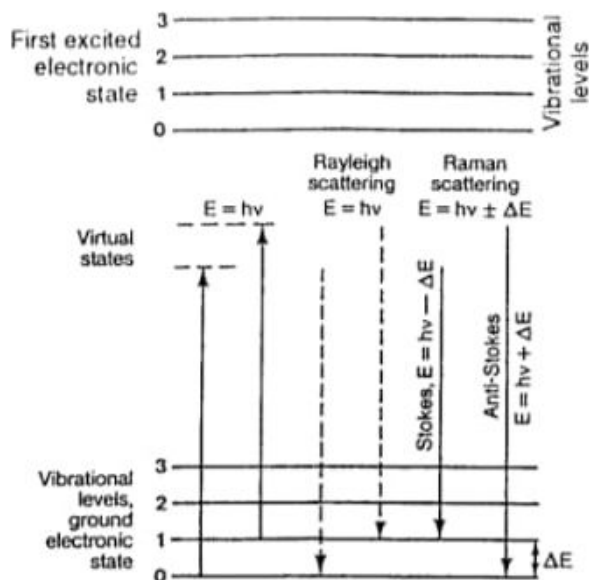
Figure 4.61 The process of Rayleigh and Raman scattering. Two virtual states are shown, one of higher energy. Rayleigh and Raman scattering are shown from each state. Normal IR absorption is shown by the small arrow on the far right marked ΔE, indicating a transition from the ground state vibrational level to the first excited vibrational level within the ground electronic state.

If the molecule begins to vibrate with more energy after interaction with the photon, that energy must come from the photon. Therefore, the scattered photon must decrease in energy by the amount equal to the vibrational energy gained by the molecule. That process is shown by the second arrow from the right. Instead of returning to the ground vibrational state, the molecule is now in the first excited vibrational state. The energy of the scattered photon is $E - \Delta E$, where ΔE is the difference in energy between the ground and first excited vibrational states. This is Raman scattering, and the lower energy scattered photon gives rise to one of the Stokes lines. Note that ΔE is equal to the frequency of an IR vibration; if this vibration were IR-active, there would be a peak in the IR spectrum at a frequency equal to ΔE. In general, the Raman–Stokes lines have energies equal to $E - \Delta E$, where ΔE represents the various possible vibrational energy changes of the molecule. This relationship can be expressed as:

$$E - \Delta E = h(v - v_1) \tag{4.13}$$

where v is the frequency of the incident photon and v_1 is the *shift* in frequency due to an energy change ΔE. Several excited vibrational levels may be reached, resulting in several lines of energy $h(v - v_1)$, $h(v - v_2)$, $h(v - v_3)$, and so on. These lines are all shifted in frequency from the Rayleigh frequency. The Stokes lines, named after Sir George Gabriel Stokes, who observed a similar phenomenon in fluorescence, are shifted to lower frequencies than the Rayleigh frequency. The Raman shifts are completely independent of the wavelength of the excitation source. Sources with UV, visible, and NIR wavelengths are used, and the same Raman spectrum is normally obtained for a given molecule. There are exceptions due to instrumental variations and also if a resonance or near-resonance condition applies at certain wavelengths (Section 4.8.4).

Less commonly, the molecule *decreases* in vibrational energy after interacting with a photon. This might occur if the molecule is in an excited vibrational state to begin with and relaxes to the ground vibrational state. In this case, the molecule has given energy to the scattered photon. The photon is shifted to a frequency higher than the incident radiation. These higher frequency lines, the Raman–anti-Stokes lines, are less important to analytical chemists than the Stokes lines because of their lower intensity. One exception to this is for samples that fluoresce strongly. Fluorescence interferes with the Stokes lines but to a much lesser extent with the anti-Stokes lines.

It is convenient to plot the Raman spectrum as intensity vs. shift in wavenumbers in cm^{-1}, because these can be related directly to IR spectra. The Raman shift in cm^{-1} is identical to the IR absorption peak in cm^{-1} for a given vibration, because both processes are exciting the same vibration. The Raman spectrum for benzene is shown in Fig. 4.62, along with the related IR transmission spectrum.