http://www.simplonpc.co.uk/PO_Liners3.html

Figure 1. An antique postcard of the S.S. Narkunda sailing the deep blue sea.

The color of the sea from the author's cruise ship—the M.V. Sea Lion in the Sea of Cortez, off Baja California (with apologies to the Mediterranean).

Maryann Fitzmaurice

The Color of the Sea

Maryann Fitzmaurice

The sea, the sky and other features of the natural world have provided inspiration for many of the great scientific discoveries of humankind. The world of optics is no exception. In 1921, C.V. Raman took an oceanic voyage that led him to study the scattering of light and ultimately discover the vibrational effect that would come to bear his name.

Recently I took a vacation on a cruise ship in the Sea of Cortez off Baja California. Looking out at the fabulous blue color of the sea, I was put in mind of Chandrasekhara Venkata (C.V.) Raman, a boy genius and Palit Chair of Physics at Calcutta University by the age of 29. Raman made his first trip abroad by ship to attend the Congress of the Universities of the British Empire in London in 1921. That trip was to be of singular importance in Raman's life and the field of optics.

Prior to this journey, Raman had spent much of his time studying vibrational and acoustical effects of various kinds. During his stay in London, he visited St. Paul's Cathedral. He was fascinated by the "whispering gallery:" an acoustic phenomenon that allowed a whisper uttered on one side of the circular gallery at the base of St. Paul's great dome to be heard on the opposite side, some 43 m away. Before he left London, Raman had published one of his many letters to *Nature*[1] explaining the phenomenon and refuting an earlier theory put forward by Lord Rayleigh, 1904 Nobel laureate in physics. This simple tourist encounter is at least partly responsible for the whispering gallery mode lasers in use today ... but I digress.

Raman traveled to and from England by sea. It is said that he sat for hours on the upper deck of the ocean liner staring at the deep blue color of the Mediterranean. During the voyage, Raman conducted experiments peering into the depths of the water using the Nicol (calcium calcite polarization) prism he always carried. He sent a second letter to *Nature*, titled, "The Colour of the Sea,"[2] before even setting foot on dry land, from the S.S. Narkunda (Fig. 1) in Bombay Harbour on September 26, 1921.

Rayleigh had proposed that the ocean's blue color resulted from reflected sky light and absorption by matter suspended in the water.[3] Raman's experiments clearly showed that the blue color was independent of reflection and absorption and due instead to molecular diffraction—most likely from water molecules themselves. These simple experiments led Raman to pursue more detailed studies of light scattering once back home in Calcutta.

In 1923, Compton proved the concept put forward by Planck and Einstein that radiation is not only wave-like, but also particle-like, in nature. When a beam of radiation traverses an atom, most of the radiation is elastically scattered and therefore of unchanged wavelength. Using a graphite target, Compton showed

OSA Photo Archive

C.V. Raman was awarded the Nobel Prize in physics in 1930 for his research on light scattering and molecular vibrations.

that a small fraction of the radiation emerged in directions other than that of the incident beam due to inelastic scattering of the X-rays by electrons.[4] Inspired by Compton's discovery, Smekal predicted that photons should likewise be scattered inelastically by vibrational transitions within molecules.[5]

Raman and his colleagues at the University of Calcutta and the Indian Association for the Cultivation of Science set out to prove Smekal right. We now know that one of the characteristics of inelastic scattering is that its intensity scales to the fourth power of the energy. This meant that the inelastic scattering effect that Raman sought using visible light (about 500 nm) was at least 10 orders of magnitude weaker than that observed by Compton using X-rays (0.7 nm).

Raman observed this weak effect by using the most intense light source available at the time: the sun. In his initial experiments, he used a 7-in. reflecting telescope in combination with a short focal length eyepiece to focus sunlight onto a purified liquid or its dust-free vapor. He then used complementary yellow-green and blue-violet filters to observe the incident and scattered beams. Using this simple experimental apparatus, Raman discovered that a small amount of the incident light had been inelastically scattered by the molecules in the liquid and shifted in energy into another part of the spectrum. He later observed this shift in wavelength as additional bands on a spectrograph.

This remarkable discovery was made on Monday, February 27, 1928, and described by K.S. Krishnan, Raman's student, in his diary:

> Went to the Association in the afternoon. Professor was there. Started studying the effect of incident light wavelength on the new scattering effect. Astonished to see that the scattered radiation has wavelength different from the incident one—wavelength higher and shorter than that of the incident radiation.[6]

Raman didn't waste any time. That Friday, March 31, 1928, he and Krishnan published another letter in *Nature*, titled, "A New Type of Secondary Radiation," which described what would later be known as the Raman effect or Raman shift.[7]

There are a number of extraordinary things about that publication: its brevity, for one—just 368 words. It was also published remarkably fast, with only five days between observation and publication—a feat that may never be repeated, even in the online era. In fact, Raman managed to get the word out even sooner: Ahead of his time, he took advantage of the 24-hour news cycle and contacted the Associated Press of India. A report of his findings was printed the next day.[8]

The amount of work that Raman and Krishnan accomplished in such a short time is amazing as well. They reported in *Nature* that: "Some 60 different common liquids have been examined in this way, and every one of them showed the effect in greater or lesser degree." Equally astonishing is the speed with which the field adopted Raman's discovery. By August of the following year, there were already 150 scientific publications related to the Raman effect.[9]

That year, 1929, Raman was nominated for the Nobel Prize in physics. But the prize went instead to Louis de Broglie for his work on the wave nature of the electron. Raman was nominated again in 1930 and, just two years after his initial experiment, he was awarded the prize at the age of 42. Although this might seem fast, it was in keeping with the wishes of Alfred Bernhard Nobel, who willed that the proceeds of his estate be "distributed in the form of prizes to those who, during the preceding year, shall have conferred the greatest benefit to mankind."[9] It was clearly Nobel's plan to reward

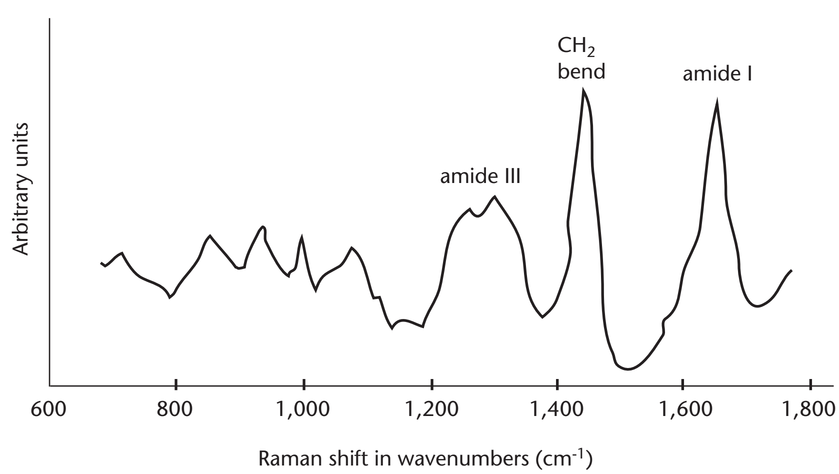

Figure 2. Raman spectrum of invasive breast cancer in human breast tissue obtained with Ti-sapphire laser excitation light at 830 nm and back-thinned, liquid nitrogen cooled CCD detector. Bands assigned to CH_2 bend, amide I and amide III molecular vibrations are shown.

recent discoveries—a concept seemingly forgotten today, when it can easily take a year or longer to publish a manuscript.

When King Gustav V of Sweden awarded Raman his Nobel Prize on December 11, 1930, Raman began his Nobel lecture on "The Molecular Scattering of Light," with an introduction he titled "The Colour of the Sea." In it, he said:

> A voyage to Europe in the summer of 1921 gave me the first opportunity of observing the wonderful blue opalescence of the Mediterranean Sea. It seemed not unlikely that the phenomenon owed its origin to the scattering of sunlight by the molecules of the water. To test this explanation, it appeared desirable to ascertain the laws governing the diffusion of light in liquids, and experiments with this object were started immediately on my return to Calcutta in September 1921. It soon became evident, however, that the subject possessed a significance extending far beyond the special purpose for which the work was undertaken, and that it offered unlimited scope for research. It seemed indeed that the study of light scattering might carry one into the deepest problems of physics and chemistry…[10]

Raman spectroscopy quickly became the technique of choice for conducting molecular vibrational studies. However, after World War II, it fell out of favor and was largely replaced by then-simpler infrared and near infrared spectroscopy techniques. Like the technique it inspired, the S.S. Narkunda fell on bad times. After being pressed into use as a troop carrier, it was sunk by the German Lufthansa in 1942.

Fortunately, recent instrumentation advances, including high intensity, tunable, titanium-sapphire lasers and back-thinned, liquid nitrogen cooled CCD detectors, have once again brought C.V. Raman and his "effect" to the scientific forefront. The Raman spectra we analyze today using this advanced instrumentation look little like the bands Raman and Krishnan first saw in their Calcutta laboratory (Fig. 2). The Raman bands in these modern spectra represent a chemical fingerprint of the molecular species examined.

Raman spectroscopy had its first biomedical impact in the fields of biochemistry and biophysics, where it was used for key chemical and structural studies of DNA, lipid membranes, hemoglobin and enzymes. However, perhaps its greatest impact will be in clinical medicine. It is now being used to probe intact living cells and tissues. In fact, Raman techniques are currently being developed for painless transcutaneous monitoring of blood glucose in diabetics,[11] identification of vulnerable atherosclerotic plaques in the coronary arteries of patients at risk for heart attacks[12] and the real time *in vivo* diagnosis of breast cancer.[13]

I will close with one final light touch. When I was introduced to Raman spectroscopy years ago, I had never heard of C.V. Raman or his effect. My only association with the name was Ramen noodles—the thin, flat noodles in those cheap, instant soups on which I, and many other impoverished students, had survived in graduate school. In an odd twist of fate, Raman spectroscopy has become a popular tool in industry; it is now used for quality control in the manufacture of starchy foods such as—you've got it—Ramen noodles!

Maryann Fitzmaurice, M.D., Ph.D. (maryann.fitzmaurice@case.edu) is assistant professor of pathology at the University Hospitals of Cleveland and Case Western Reserve University in Cleveland, Ohio.

References

1. C.V. Raman, Nature **108**, 42 (1921).
2. C.V. Raman, Nature **108**, 367 (1921).
3. J.W. Rayleigh, Phil. Mag. **4**, 107-20, 274-9 (1871).
4. A.H. Compton, Phys. Rev. **21**, 483 (1923).
5. A. Smekal, Naturwissenschaften **11**, 873 (1923).
6. V.P.N. Nampoori, *A co-traveler of light, colour and beauty: Life and work of C.V. Raman*, www.photonics.cusat.edu/Article5.html.
7. C.V. Raman and K.S. Krishnan, Nature **121**: 501-2 (1928).
8. C.V. Raman, Indian J. Phys. (March 31,1928).
9. R. Singh and F. Riess, *Sir C.V. Raman and the story of the Nobel Prize.* http://www.iisc.ernet.in/~currsci/nov10/articles33.htm.
10. C.V. Raman, *"The molecular scattering of light,"* Nobel Lecture, December 11, 1930. Nobel Lectures. Physics 1922-1941, Elsevier Publishing Company, Amsterdam, 1965. http://nobelprize.org/physics/laureates/1930/raman-lecture.pdf.
11. A.M.K. Enejder et al., Opt. Lett. **27**, 2004 (2002).
12. H.P. Buschman et al., Cardiovascular Pathology, **10**, 59-68 (2001).
13. A.S. Haka et al., Proc. of the European Conference on Biomedical Optics, in press.