

Resonance-Raman spectroscopy— "Good vibrations" from colored compounds

In recent years, many scientific advances have enabled researchers to unravel some of the biochemical mysteries in living systems. An entirely new field of molecular structure analysis called resonance-Raman spectroscopy, recently developed at the National Research Council of Canada's Division of Chemistry, may provide other tools to probe further.

For his work in laser Raman spectroscopy and high resolution nuclear magnetic resonance, Dr. Harold J. Bernstein of the Spectroscopy Section was named the 1974 recipient of the Chemical Institute of Canada Medal. This award is presented annually as a mark of distinction to a scientist who has made an outstanding contribution to chemistry or chemical engineering in Canada.

Dr. Bernstein describes his new technique as an important bridge between atomic and electronic spectroscopy and a significant elaboration of conventional Raman spectroscopy.

The technique of conventional Raman spectroscopy as a means of studying energy states in molecules was first advanced by Sir Chandrasekhara V. Raman in 1928.

At normal temperatures, molecules are most often found in their lowest or ground state with a certain level of energy. Above this state are numerous levels of higher energy into which the molecule may be excited.

The most widely separated of these are called the molecule's electronic states, requiring large amounts of energy in the form of visible and ultraviolet radiation before a jump or transition from the ground state can occur. Still finer levels reside within each of these states. Of these, vibrational levels (which reflect, for example, the stretching or bending energy of molecular bonds) are more widely separated than rotational levels. The position of each level is designated by an integral quantum number which determines the laws molecules must obey in changing between any two energy levels.

To undergo transitions, molecules must absorb or emit only certain fixed amounts of energy, called quanta, corresponding exactly to the energy difference between particular levels. Therefore, successively larger amounts of energy are required for transitions between rotational, vibrational and electronic levels.

Spectra arising from transitions between electronic states show a characteristic principal absorption band for every compound studied.

In a simplified analogy, a molecule's electronic states may be compared to a series of high-rise buildings positioned at different elevations on the side of a hill. In a transition between any two, a person requires some source of energy, such as a train, to ascend the slope.

Several numbered floors within each building correspond to the vibrational levels designated by quantum numbers. Here the distances between levels are smaller and an elevator can provide the energy for transitions between floors. As with molecular transitions, only certain level changes are allowed. In other words, the elevator cannot leave its passengers in-between floors.

In practice, the stepping-up or stepping-down between vibrational energy levels resulting from a molecule's gaining or emitting energy is the basis of Raman spectroscopy.

In the conventional Raman experiment, a colorless substance is irradiated with monochromatic light (such as a laser beam) and the spectrum is observed at right angles to the incident beam. The frequency of the exciting beam is far removed from the principal absorption band of the substance

under study. A laser is used because it provides a uniform intensity of light along the entire length of its beam and is not restricted by the geometrical requirements of other light sources such as mercury arcs.

After contacting the sample, one part of this radiation emerges unchanged in frequency (ν_0) from the incident laser light and is observed as a Rayleigh line. However, another part is scattered by the material at different frequencies.

Stokes Raman lines are observed at slightly lower frequencies than ν_0 and result when a molecule in its ground state scatters the light with a loss of energy from the incident beam. This loss is equivalent in size to a characteristic frequency of the atomic vibrations within the molecule under study.

Conversely, anti-Stokes lines occur at frequencies higher than ν_0 and arise when a molecule initially in a higher energy level (than the ground state) scatters the incident light. Since there are fewer molecules in this higher energy level, these anti-Stokes emissions are less probable, hence, show up with lower intensity.

Used in conjunction with infrared spectral data, Raman measurements yield valuable information concerning the vibrational behavior of simple molecules as well as specific chemical bonds within more complex species. Furthermore, a study of the polarization (the planarity and orientation of its various components) of scattered light is of value in determining the symmetry of various vibrations.

On the other hand, Dr. Bernstein's resonance-Raman technique makes even more information available.

"When we first published our results in 1970," he recalls, "I received a direct call from someone who wanted to build an apparatus to try the technique. It was then picked up almost immediately and the field began to blossom into something

Dr. Harold Bernstein, Head of the Spectroscopy Section of NRC's Division of Chemistry, examines a colored liquid contained in the resonance-Raman sample cell. His resonance-Raman technique now enables scientists to obtain vibrational Raman spectra from small quantities of colored compounds.

Le Dr Harold Bernstein, Chef de la section de spectroscopie de la Division de chimie du CNRC, examine un liquide coloré contenu dans le porte-échantillon utilisé en spectroscopie Raman à résonance. Sa technique permet d'obtenir des spectres Raman vibrationnels à l'aide de petites quantités de composés colorés.

