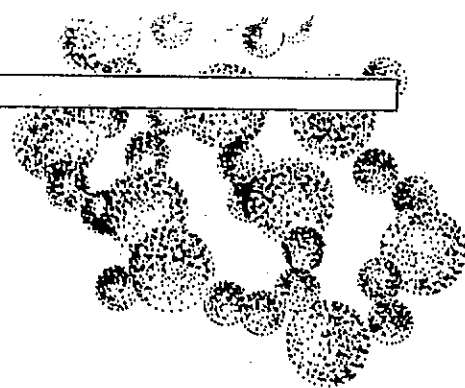


# MOLECULAR SPECTROSCOPY WORKBENCH

Henry Buijs

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## Fourier Transform Raman Spectroscopy — An Overview

In last month's column, I outlined the intended directions for the Workbench and indicated that there will be at least two articles dealing with new developments in Raman spectroscopy during the next few issues. This month's column features the first of these with a brief review of the current state of the art in Fourier transform Raman (FT-Raman) spectrometry. This article covers the main features of the technique and discusses the salient points that have led to the development of the first commercial instrument for FT-Raman.

This month's column has been written by Henry Buijs, president of Bomem, Inc., 625 Marais, Vanier, Quebec, G1M 2Y2, Canada. Buijs received his PhD in molecular physics in 1969 from the University of British Columbia. Buijs was one of the founders of Bomem in 1974, and he has been involved in various aspects of Fourier transform spectroscopy since 1962. Buijs is a member of the Chemical Institute of Canada and the Canadian Association of Physicists.

John P. Coates  
Column Editor

Raman spectra, like infrared spectra, arise from transitions associated with molecular vibrations. The spectral information acquired is governed by a different set of selection rules, and although it is not the same, the Raman spectrum is complementary to the infrared spectrum. Unlike infrared spectroscopy, however, in which absorption bands result from a net change in the dipole moment during a molecular vibration, Raman bands are the result of a change in molecular or bond polarizability. For simple molecules, selection rules define infrared activity in terms of asymmetrical modes of vibration, while Raman activity is defined in terms of symmetrical modes.

For example, in simple diatomic molecules such as hydrogen, nitrogen, and oxygen in

which the structure naturally leads to a single symmetrical mode of vibration, only Raman activity is observed. Under the right conditions of measurement, these molecules provide Raman spectra with well-defined vibrational-rotational fine structure, but do not yield infrared spectra. Water, which has a strong permanent dipole moment, exhibits an excessively strong infrared spectrum, and until recently, this characteristic has limited the use of water as a medium for analytical infrared measurements. Very short path lengths are required to provide adequate spectral windows for the study of materials in aqueous solution; this constrains the detection limits for the dissolved species. Conversely, the Raman spectrum of water is very weak, causing it to yield minimal spectral interference in the measurement of aqueous solutions. The strong absorptions of water vapor can also present a problem in the routine acquisition of FT-IR spectra unless adequate precautions are taken, such as using a dry gas purge or operating under vacuum conditions. At first glance, one might suspect that the Raman activity of oxygen and nitrogen molecules could also present a problem. This is not the case, however, because of the inherent weakness of the Raman effect in gases.

For real-world analytical situations, the simple rules based on molecular symmetry do not necessarily apply. Complex molecules have very few truly symmetrical vibrations that are purely Raman active and infrared inactive. The Raman and infrared spectra of large molecules often have the same or similar bands but with very different intensity ratios. If a molecule has a center of symmetry, then the rule — known as mutual exclusion — states that Raman active modes of vibration are infrared inactive and infrared active modes are Raman inactive. Complex molecules seldom have a center of symmetry, but typically, strong Raman bands from symmetrical vibrations are weak in the infrared spectrum. Compounds that include highly polarizable bonds, such as  $C\equiv C$ ,  $C-S$ , and  $S-S$ , also give rise to strong Raman and weak in-

frared bands. This complementary aspect of Raman and infrared spectrometry provides an excellent tool for chemical analysis and structural determinations.

Raman spectra are acquired by a very different method than IR spectra. Molecules are irradiated with a monochromatic source, and the Raman spectrum is measured as radiation scattered by the sample. Raman transitions are caused by inelastic scattering and are observed as spectral lines (Stokes lines) that are shifted from the main excitation line (Rayleigh line). With the exception of signals measured by resonance enhanced and stimulated Raman techniques, the scattering intensity varies linearly with the intensity of the excitation source, and the intensity is inversely proportional to the fourth power of the wavelength of this source.

### THE FLUORESCENCE PROBLEM

The occurrence of fluorescence in many samples has prevented Raman spectroscopy from taking its rightful place in the analyst's toolbox of spectroscopic techniques. Fluorescence is observed as a broad, featureless emission that usually occurs in the visible region and is often superimposed over the entire Raman spectrum of the sample. It is most often experienced with molecules that have an uncomplicated electronic band structure and that absorb near the Raman excitation wavelength. Currently, the mechanism of fluorescence is not completely understood; however, it has been known for many years that fluorescence emission decreases rapidly as the excitation wavelength increases. This decrease is believed to be because of the increase in separation of the exciting wavelength from the wavelengths associated with the electronic transitions of the molecule. It has also been suggested that near-infrared irradiation will not induce fluorescence because the excitation wavelength is now proximi-

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mal to rotation vibration overtone bands. Electronic transitions, which would be necessary to produce fluorescence, are unlikely to occur in this region because that would imply transitions from the ground state, and these are very uncommon.

On many occasions, the sample itself may not be fluorescent but impurities may render it impractical for Raman measurements. Samples containing even traces of fluorescent material will exhibit a fluorescence spectrum so intense that the Raman spectrum is completely obscured. According to estimates, more than half of the samples that might be analyzed using Raman spectroscopy have too much fluorescence for successful analysis by conventional Raman techniques.

## CONVENTIONAL INSTRUMENTATION

Early Raman spectroscopy experiments were performed using an intense ultraviolet source in which the green line of a mercury lamp was selected for sample illumination and a spectrograph was used for photographic recording of the spectrum. In later experiments, filters and monochromators replaced the photographic recording. The introduction of relatively low-cost cw gas lasers provided the single most important advancement in modern Raman spectroscopy. The ability to obtain more efficient sample illumination from a focused laser led to improvements in the efficiency of the collection optics for the scattered radiation, in addition to allowing for more elaborate monochromator and detector systems for better stray light rejection and improved low-level light performance, especially at longer wavelengths. More recently, very efficient collection of Raman spectra has become possible by using image-intensified photodiode array detectors with the equivalent of up to 1000 parallel photomultipliers.

The magnitude of the detector problem is illustrated by the fact that the Raman scattered intensity is very small compared with the laser excitation intensity. Normally, Raman intensity can be as little as  $10^{-14}$  mW per spectral element. Typical laser power, however, is more than 100 mW. In the visible wavelength region, this property corresponds to a small number of photons/s being generated, and therefore detection by photon-counting devices is common in Raman experiments.

## FT-RAMAN SPECTROSCOPY

Historically, the high detection efficiency of photomultipliers and photon counting has meant that implementation of Fourier transform spectroscopy for the purpose of improving photon collection efficiency would be unnecessary. Furthermore, Raman spectra are generally dominated by the high-intensity Rayleigh line occurring at the laser wavelength. In the process of Fourier transformation, noise associated with Rayleigh scattering is distributed over the entire spectrum, seriously degrading the resultant spectrum.

The very large difference in intensities between the Rayleigh line and the Raman signal also produces a dynamic range problem in the detector system.

It is therefore necessary to remove the Rayleigh scattering by means of an efficient laser line rejection filter before useful FT-Raman spectra can be obtained. Such filters have recently become available (1).

Despite the detection efficiency of photon-counting devices and photomultipliers, their useful wavelength ranges are limited. Fourier transform techniques, however, allow the focusing of all the collected Raman radiation onto a single detector. This multiplexing advantage — familiar to FT-IR users — reduces the requirement for very low detector noise, which in turn significantly increases the variety of detectors available. Taking advantage of some of the newer detectors, Fourier transform techniques allow Raman spectra to be collected from samples excited by lasers in the near-infrared region. The sensitivity of FT-Raman is impressive, despite both the reduction of the Raman intensity with the fourth power of wavelength and the relative noisiness of detectors in the near-infrared.

The greatest benefit of using near-infrared excitation for FT-Raman is the complete absence of fluorescence. To illustrate this point, Bruce Chase and the late Tomas Hirschfeld successfully demonstrated near-infrared FT-Raman spectra of naturally fluorescent compounds such as fluorescein, anthracene, and rhodamine (1).

The principal elements required to obtain near-infrared excited FT-Raman spectra are:

- a cw Nd<sup>3+</sup>:YAG laser operating at 1060 nm with a single-mode output power of several watts;
- a high-performance FT-IR spectrometer that operates efficiently in the near-infrared region of the spectrum from 10,000 cm<sup>-1</sup> to 6000 cm<sup>-1</sup>;
- a high-sensitivity germanium photodiode detector;
- a laser notch filter with a maximum transmittance of 0.00000001% T at the exciting laser frequency and not less than 25% transmittance at a distance of 100 cm<sup>-1</sup> from the laser exciting frequency;
- and a suitable sample cell and optics to focus the laser beam and collect Raman scattered radiation from the sample.

A commercial system based on a high-performance FT-IR spectrometer was introduced at the 1986 Pittsburgh Conference by Bomem (Vanier, Quebec, Canada). The demonstrated system, described in the May edition of the "Molecular Spectroscopy Workbook," was based on the Bomem DA3 FT-IR spectrometer with the FT-Raman components incorporated as an accessory. In this early form, the system was operated with a long wavelength visible laser — the 647-nm line of a Kr<sup>+</sup> gas laser — and featured an RG695 Schott glass filter for laser Rayleigh line rejection and an RCA silicon avalanche photodiode as the detector. The modular construction of the DA3 makes it easy to install the accessory. The sample is placed at a port in-

tended for emission studies, the line rejection filter is placed in the normal (FT-IR) sample compartment, and the detector is simply exchanged with the IR detector with the bolt-on detector modules. In later versions of the system, a Nd<sup>3+</sup>:YAG laser has replaced the Kr<sup>+</sup> gas laser. Other important instrumental considerations are the use of dynamic interferometer alignment to maintain good spectral resolution in the near-infrared region and the use of real-time numerical filtering plus Forman phase correction (using stored phase information). This last point is particularly important for the Raman measurement, because in the absence of any background fluorescence, the measured data have the same appearance as data acquired from emission studies, which suffer from the lack of a continuum background. A continuum background is necessary for the Forman phase correction method (used in many FT-IR systems), which obtains its phase information from the data. Previously, this restriction was handled by the generation of the power spectrum.

## CONCLUSION

While the FT-Raman technique can also be applied using visible laser excitation, it does not offer increased sensitivity over dispersive Raman. FT-Raman spectroscopy, however, retains a high optical throughput at high resolution, which should make it a powerful technique for gas-phase Raman spectroscopy.

Near-infrared FT-Raman spectroscopy significantly extends the applicability of Raman spectroscopy by eliminating sample fluorescence. Because fluorescence often arises from impurities in samples, this FT-Raman technique may be instrumental in making Raman spectroscopy a viable technique for industrial quality assurance applications in which sample purification is neither economical nor practical. Because FT-Raman can be implemented on FT-IR systems in a relatively simple manner, two complementary measurement techniques — IR and Raman — can be implemented on one spectrometer, making the overall system cost effective. The extensive range of FT-IR data manipulation software, which includes spectral searching and multicomponent quantitative analysis, can be conveniently applied to the Raman data without any modification and without reinventing any more wheels.

## REFERENCE

- (1) T. Hirschfeld and D.B. Chase, *Appl. Spectrosc.* 40, 133-137 (1986).

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