Raman Spectroscopy

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Raman spectroscopy is one of the most versatile methods of molecular analysis. The Raman effect consists of the appearance of displaced lines in the spectrum of monochromatic light scattered by substances. The Raman scattered radiation is spectrally shifted by an amount which corresponds to the vibrational or rotational energy for a transition of the molecule in question. The magnitudes of these displacements provide an unambiguous identification ("fingerprint") of the measured species. The amount of light which is scattered at a given wavelength (intensity of the spectral line) is a measure of molecular concentration.

In the years immediately following its discovery in 1928, the Raman effect was very popular for the solution of molecular structure problems that could not be conveniently undertaken by the techniques which were available at that time. Specifically, during that period, the simplicity of photographic spectroscopy made Raman much more desirable than the complicated and difficult procedures of infrared methods. In the late 1940s, however, automatically recording infrared instruments became available and the interest in Raman waned. This remained the situation until the early 1970s when the advent of lasers and improved Raman instrumentation once again placed Raman spectroscopy on a par with infrared techniques.

Lasers provide many advantages over their predecessor, the mercury arc. They are high intensity, narrowbanded monochromatic sources which give "clean" well-resolved spectra with good signal to noise. They are less extended, and this greatly reduces or eliminates problems due to stray light contamination. They operate in either the cw or pulsed mode, making it possible to optimize both irradiation conditions and/or signal handling for a particular measurement scenario. Lasers, or lasers coupled to dye lasers and/or harmonic generators, provide a multiplicity of wavelengths, which often makes it possible to circumvent two of the major Raman problems, fluorescence and absorption.

Optical engineering has greatly improved the performance of Raman spectrometers. Throughput matching, better optical components, and improved coatings have reduced light losses. Upgraded optical designs have increased illumination and collection efficiency while maximizing stray light rejection. New fast scanning and multiplexing systems can reduce analysis time and/or improve signal to noise.

Computer-based systems have greatly improved data handling and processing. Point-by-point addition, subtraction, multiplication, division, and/or overlay of spectra are possible. Spectral search and correlation are easily implemented as is automatic system calibration. In addition, the computer can be used to control the spectrometer and perform "housekeeping" functions.

Raman spectroscopy in the 1980s can be used for routinely performing qualitative and quantitative measurement or can be extended to solving complex analytical problems such as determining chemical structure. Gases, vapors, aerosols, liquids (including aqueous solutions), and solids can be analyzed by this technique. Cryogenic and high temperature measurements can be made, including *in situ* identification and quantification of combustion products in flames. Modern systems can compensate for the weak Raman interactions. Present-day sensitivities are sufficient for most analytical requirements. In gases and liquid samples, specific species can be detected to the one-part-per-million range or below. Solid samples as small as a cubic micrometer in volume can be measured. Futhermore, Raman is one of the few techniques amenable to both laboratory and single-ended remote measurements. In the latter case, analyses can be made at several kilometers where a line of sight exists.

The long-term success of Raman spectroscopy depends on both scientists and engineers. There is a need to establish a line of communications between the participants. This first special issue of *Optical Engineering* devoted to Raman spectroscopy contains articles by scientists active in the field. It is intended to introduce the engineer to the Raman approach. It is anticipated that future issues will provide a medium for dialogue between the two disciplines.