Forensic Analysis by Raman Spectroscopy: An Emerging Technology

E. Bartick

Counterterrorism and Forensic Science Research Unit
FBI Academy, Quantico, VA, U.S.A.

Summary

This paper provides an introduction to Raman spectroscopy and shows how it has and will play a role in the analysis of forensic evidence. Raman theory, technological developments, and applications to forensic analysis are explained. The strengths and limitations of Raman are compared with infrared (IR) spectroscopy.

Introduction

Raman spectroscopy was developed by C. V. Raman (Figure 1) in 1928, but until recently has been plagued by weak Raman scattering responses compared to strong, interfering, Rayleigh scattering, plus fluorescence interferences. Developments over the past 15 years have permitted Raman spectroscopy to become more useful and easier to use. With these developments, forensic analysis by Raman spectroscopy has been an emerging technology.

Theory: Like IR, Raman is a vibrational spectroscopic method and provides complimentary information. With IR spectroscopy, incident light is absorbed as a result of the increased vibration of
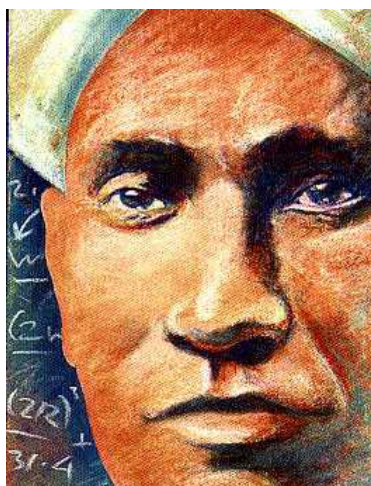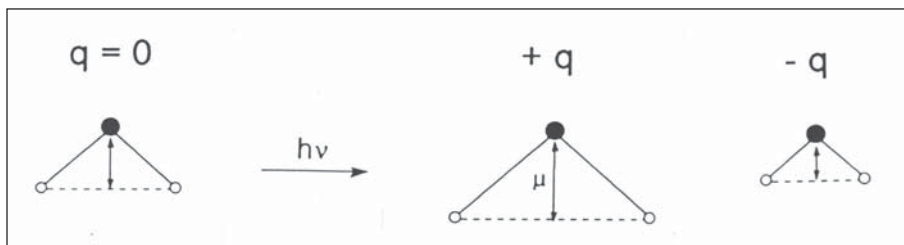

Figure 1. C.V. Raman

Figure 2. The change in dipole moment (q) is illustrated in the symmetric stretch induced by IR radiation.

the molecular dipole moments as illustrated in Figure 2. Raman shift peaks are based on a change in electron polarization (Figure 3) produced by the incident excitation light. The intensity measurement of the scattered photons produce spectra that can be compared to IR spectra in cm^{-1} (wavenumbers). Strong polar bands, like carbonyls, observed in the IR are considerably weaker in the Raman. Skeletal bonds, such as unsaturated hydrocarbons, show stronger Raman peaks than IR. Thus, the chemical structure information provided is often complimentary between the analytical methods.
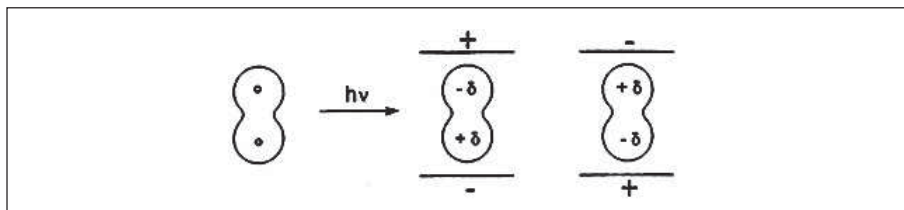

Figure 3. Polarization (d) of a diatomic molecule induced by incident light[1].

The strong, elastic, Rayleigh scattering, shown in Figure 4, is the same frequency as the incident beam (n_0). The Raman scattering is very weak (on the order of 10^{-5} compared to the intensity of the incident beam). Raman scattering has frequencies $n_0 \pm n_m$, where n_m is the vibrational frequency of a molecule. The $n_0 - n_m$ and the $n_0 + n_m$ lines are called the Stokes and anti-Stokes peaks, respectively. Therefore, in Raman spectroscopy we measure the vibrational (n_m) frequency as a shift from the incident beam frequency (n_0). Since there is no interest in the Rayleigh scattering and it overshadows the Raman peaks, it is removed. The removal of the Rayleigh scattering has historically required expensive double and even triple monochrometers. Today, these interfering peaks are conveniently removed with holographic filters.

Modern instruments have additional advances[2]. Improved monochrometers are combined with high sensitivity Peltier cooled, charge-coupled-device
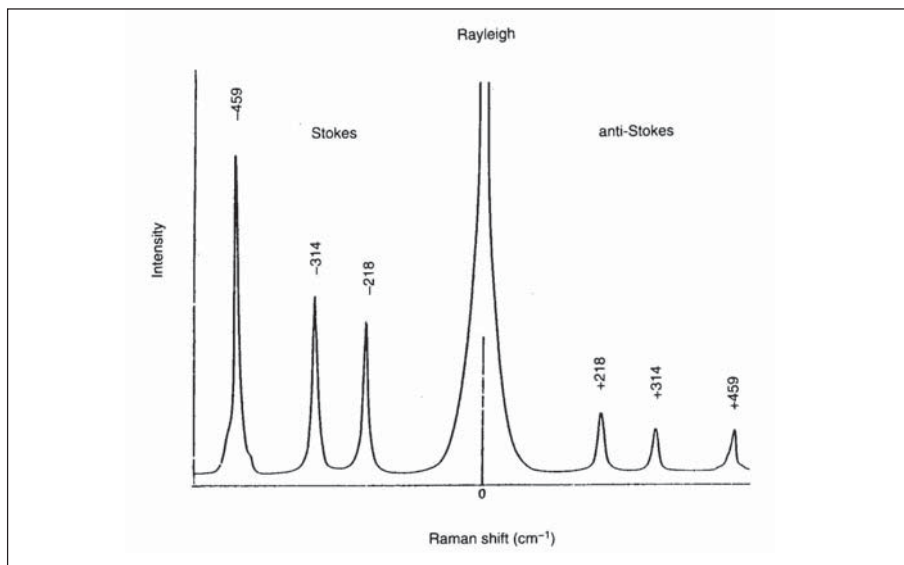
Figure 4. Raman spectrum of CCl_4 (488.0 nm excitation)[1].

(CCD) detectors. These array detectors are fast and require minimal scanning. Fluorescence effects have been reduced by several approaches. The 1064 nm near-IR (NIR) excitation laser used with Fourier transform (FT) systems causes fewer samples to fluoresce than visible wavelength lasers. However, with the lower energy, longer wavelength laser, signal averaging provided by FT systems is required to attain the desired signal-to-noise ratio of spectral results. Unfortunately, the lower scattering power of the longer wavelength excitation impedes application to microsamples that are commonly required with forensic analysis, thus limiting the use of microscopes with FT Raman. Dispersive Raman systems that use NIR lasers ranging from 780 to 840 nm have greater scattering efficiency as a result of the higher energy, shorter wavelengths. These systems have more general use compared to FT-Raman systems and have thus taken the forefront for a wide range of sample analysis. The recent technological advancements in Raman spectrometers have provided a reason for exploring this method in forensic applications.

At the *15th Meeting of the International Association of Forensic Sciences* (IAFS 1999), Raman spectroscopy was presented as an emerging technology. Papers were presented regarding Raman analysis of fibers, explosives, drugs, paints, inorganic fillers, and other materials. The technology is still emerging, and this session describes how Raman has developed since then. Instruments based on Fourier transform spectrometers and dispersive systems with and without microscope attachments have been used for

laboratory analysis. Portable instruments using fiber optic sample probes have been used at crime scenes.

Some spectroscopists have depicted Raman analysis as having advantages that make infrared analysis obsolete. These advantages include little or no sample preparation, convenient analysis of a solute in water, the capability to sample through glass, and plastic materials, and lastly the ease with which to conduct remote sampling with fiber optic probes. Since 1999, Raman methods have continued to appear, but as niche analyses and often as a compliment to infrared analysis.

During this session, papers are presented with regard to microscopical Raman analysis of fibers and noninvasive analysis of drugs, and explosives with portable instruments. Raman versus IR analysis are compared for all of these materials. Therefore, no further discussion in regard to these applications is made during this presentation.

Results

An example where Raman analysis in water was conveniently conducted was a case where several components that could be used for an explosive preparation of hexamethylenetriperoxidediamine (HMTD) were found in a suspect's possession. It was of interest to verify the presence and concentration of hydrogen peroxide in a hair colorant, WelloxideÒ. Infrared analysis by attenuated total reflectance was attempted, but only revealed a very small peak at 876 cm^{-1}, the O-O stretch of the peroxide. This small peak was almost completely masked by the water absorption band. Raman analysis showed a much stronger peak at that frequency
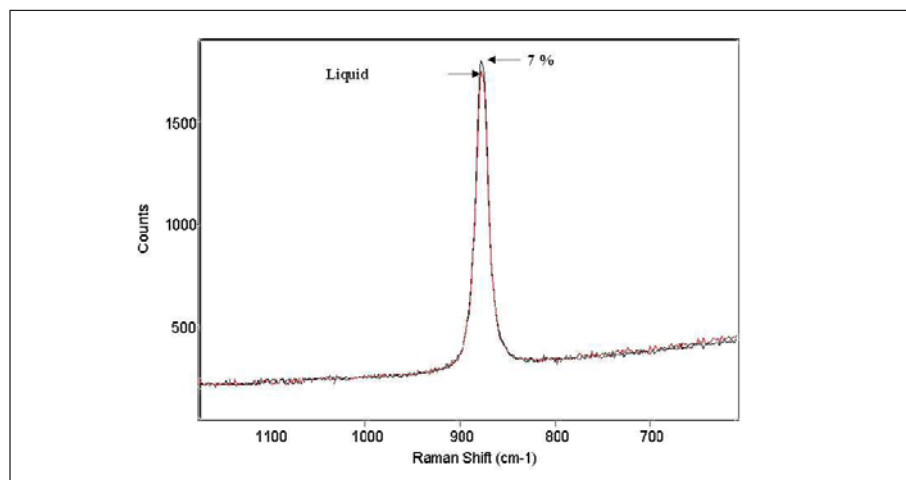
Figure 5. Suspect liquid with 7.0% w/v H_2O_2 standard in water.

(Figure 5). Thus, the method showed a stronger confirmation of the peroxide. With a set of peroxide standards, the concentration was determined as 6.7% in water[3].

Researchers are beginning to demonstrate the usefulness of Raman analysis for organic and inorganic pigment identification in paint[4]. Figure 6 compares IR and Raman paint spectra of a yellow acrylic melamine enamel automotive paint. The IR spectrum in Figure 6A clearly shows the resin binder features. The N-H stretch, near 3350 cm^{-1}, the C-H stretches near 3000 cm^{-1}, the C=O stretch near1730 cm^{-1}, the C-N stretch near 1540 cm^{-1}, and the typical C-O envelope from 1300-1000 cm^{-1} are observed in the IR. Of particular interest to paint analysis are any contributions by pigments. The weak, broad band at 868 cm^{-1} appears to be contributed by chrome yellow, as shown in the 6B reference spectrum. However, because of the band's comparatively low intensity and lack of detail in the paint spectrum, it would be difficult to positively identify chrome yellow by
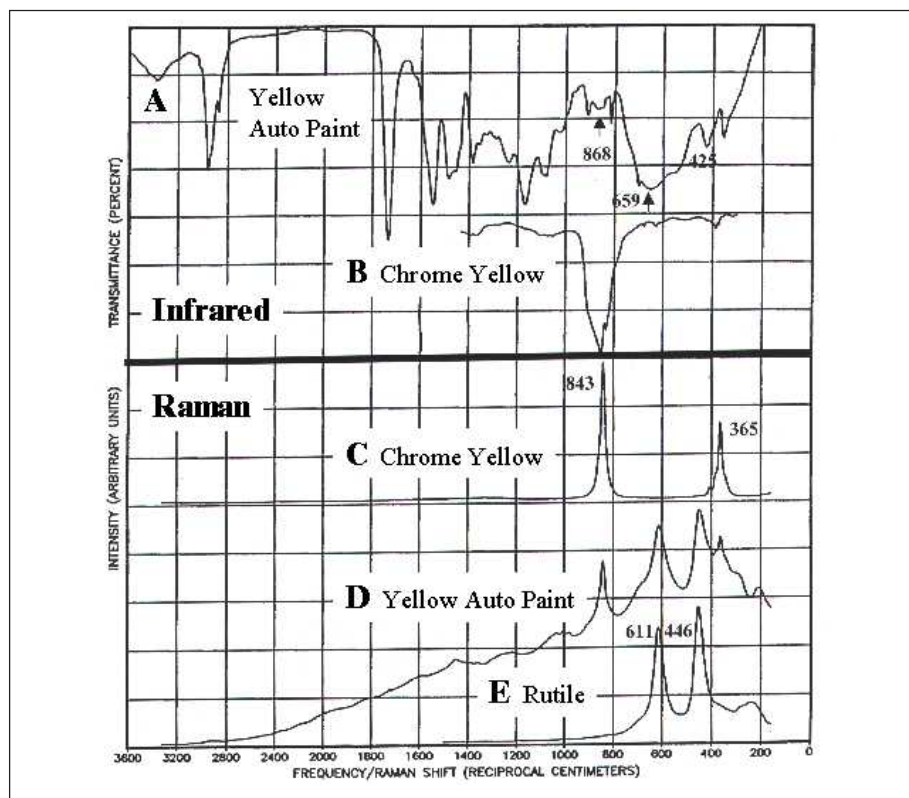

Figure 6. Yellow automotive paint spectra by Raman and IR. (Figure contributed by E. Suzuki.)

this method alone. The peaks labeled at 659 and 425 cm^{-1} are rutile, a crystal form of titanium dioxide. Figure 6D is the Raman spectrum of the yellow automobile paint. The major peaks 843 and 365 cm^{-1} match up with the Raman spectrum of chrome yellow shown in 6C. Peaks at 611 and 446 cm^{-1} are contributed by rutile, as shown in 6E. With Raman, the high scattering efficiency of some pigments, relative to those of binders, helps to easily determine the pigment components, since interfering binder peaks are not a problem.

Conclusion

Raman spectroscopy has proven itself useful in certain forensic areas. C. V. Raman would be amazed at the current capabilities. The advantages are being recognized, and Raman spectrometers are starting to find use in forensic analysis. Yet, every technology has its strengths and its limitations, and these are evident in the papers presented at this session.

References

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