Since its discovery in 1928\cite{1}, Raman spectroscopy has been rapidly adopted as an analytical technique in both academia and industry. Raman arises as incident photons are scattered inelastically from an interaction with a sample (Figure 1). This change in energy is recorded as a shift in wavelength from the incident photons. Approximately one photon in a million undergo this process, requiring careful experimental setup to avoid having the signal lost in the abundant Rayleigh scattered light. As a nondestructive technique that complements IR techniques and uses much of the same hardware that was developed for the more established IR spectroscopy, Raman was quickly adopted and the field grew rapidly as early adopters could concentrate on Raman methods without needing to develop new instrumentation.

Figure 1. Raman process Jablonski diagram. Stokes shifts correspond to Raman signals.

In 1974, Fleishmann first reported enhancement effects on pyridine absorbed on a roughened silver electrode\cite{2} (Figure 2). It was quickly realized that the increase in signal was too great to be attributed to an increase in surface area, and therefore concentration of the analyte, and that other processes were at work\cite{3}. As more analytes were analyzed on these roughened silver surfaces the enhancement proved to be a universal effect, greatly increasing the observed signal. Enhancement of $10^6$ is easily achieved, with some procedures experiencing enhancement of $10^{11}$; enough for single molecule detection at zeptomolar concentrations\cite{4}. 

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**Development of Substrates for Surface Enhanced Raman Spectroscopy (SERS)**

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A vigorous attempt has been made to understand the underlying factors that lead to the enhancement of Raman signal, and to create new surfaces that would allow SERS to be better utilized in mainstream applications. The enhancement of analytical signal is now thought to arise from two effects: electronic and chemical enhancement. Electronic enhancement comprises the bulk of the signal amplification due to localized surface plasmons that are excited by the incident light. These plasmons create strong electromagnetic fields at the substrate surface which results in, on average, a $10^4$ enhancement in Raman scattering\cite{5}. Chemical enhancement contributes less to the overall signal, about 10-100x, and occurs when the analyte is chemisorbed to the metal. When this happens mixing of the frontier orbitals of the analyte and metal can occur, creating intermediate states that reduce the energy required to promote an electron into the LUMO. Chemical enhancement can also be due to charge transfer from the sample to the metal or vice versa, where electrons are transferred between the two, creating a two step excitation process\cite{3} (Figure 3).

![Figure 3. Charge transfer process](image)

An important goal in SERS research is to create reproducible surfaces that maximize the contributions of both electronic and chemical enhancements. Toward this end, many have looked toward the usage of nanoparticles to increase the localized surface plasmons in a highly reproducible way\cite{6}. The application of nanoparticles introduced the effects of so called “hot
spots” where the enhancement could be as high as $10^{14}$ by the constructive interference of nearby plasmons in narrow gaps between particles. The characterization and control of these gap distances are proving to be extremely important in SERS\cite{7}.

Figure 4. Effect of gap distances on Raman signal

While it is difficult to study the chemical enhancement effects since it occurs along with the much more intense electronic enhancement, it is possible to isolate one from another to better study the processes involved. By using graphene, the electronic effects are removed due to the lack of any curvature and so that only chemical effects remain. While developing this technique it was found that an enhancement of 2-16x could be observed while also avoiding many of the problems inherent in metal surfaces, including oxidation, poor biological compatibility, and poor surface control\cite{8}.

Many applications have taken advantage of Raman’s nondestructive nature, from archaeological examinations to quality assurance in the pharmaceutical industry. The identification of painted forgeries has been greatly enhanced through the use of Raman, which can be used to identify pigments and dyes in a questionable work. Many famous forgeries have been brought to light when a detected pigment was found that would not have been available at the supposed time of production, for example, in the Vinland Map\cite{9}. In quality control, the pharmaceutical industry has taken advantage of Raman’s speed and ability to sample through plastic packaging to greatly increase sampling of medicinal tablets over traditional wet chemistry and HPLC techniques. A high resolution Raman spectra can be obtained in a quarter of a second, and directly on the production line, so overall sample sizes are greatly increased leading to larger confidence intervals, reducing uncertainty, and saving money\cite{10}.
References