Raman Spectroelectrochemistry

Purpose of This Note

This application note discusses Raman spectroscopy and its combination with electrochemical techniques.

The theory of Raman spectroscopy and the effect of light on matter are explained. Further, the general setup for Raman spectroscopy is shown including its extension to spectroelectrochemical measurements. Gamry's measurement software and data evaluation are explained based on spectroelectrochemical experiments.

Introduction

Raman spectroscopy is a widely used spectroscopic method. Highly specific spectra of materials can be obtained which can be compared and identified by using spectral databases. Similar to IR-spectroscopy, fundamental vibrations of molecules are examined which is important for a complete understanding of chemical reactions.

However, in contrast to IR-spectroscopy, no absorption effects are observed but scattering of light. As water is a strong absorber, Raman spectroscopy is the method of choice for studying aqueous solutions compared to IR-spectroscopy. This makes it suitable for biological and medical research, e.g. analysis of the impact of drugs on biological cells.

Raman spectra can be acquired very fast. Hence it is used for a large variety of in-situ analyses. Further, it is in general a non-destructive technique depending on the intensity of the laser and duration of an experiment.

The experimental setup is simple as no sample preparation is necessary. Solid or liquid samples can be used as they are received. Experiments can be performed either inside or outside of a measurement cell through glass or plastic.

Raman Spectroscopy

Theory

When light is focused on matter, both interact in different ways with each other. Light can be absorbed, scattered, transmitted, or reflected amongst other effects which would go beyond the scope of this discussion.

In 1828, the Indian physicist Sir C. V. Raman performed a series of measurements where he focused sunlight on a liquid probe (see Figure 1).

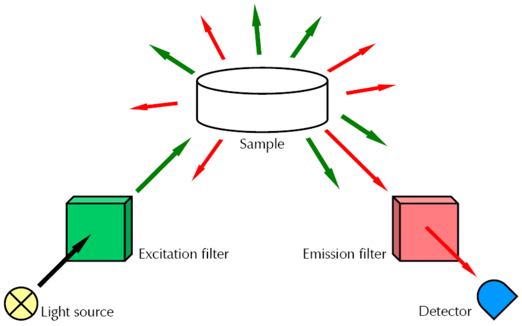


Figure 1 – Simplified setup of a Raman experiment.

He used a monochromatic filter (excitation filter) which let only light with a specific wavelength reach the probe. The measured scattered light showed a broader spectrum with additional wavelengths. A second filter (emission filter) behind the probe allowed blocking the incident wavelength. The observed residual scattered light could now be clearly distinguished from the incident light.

Light scattering

The observations which Sir Raman made can be explained by the fact that photons which are not absorbed by the probe will be scattered.

In UV-Vis absorption spectroscopy, electrons in the ground state are excited to a so-called excited electronic state. For this, the photon energy (depending on the wavelength) has to match the difference in the energy states. As a result, those absorbed wavelengths cannot be found in the transmitting light.

For more information on absorption spectroscopy, see Gamry's application notes at **www.gamry.com**:

Part 1: Basics, Setup, and Gamry's Equipment

Part 2: Experiments, Procedures, and Data Evaluation

When light is scattered, electrons are also excited from their ground state. However, the photon energy is does not have to be resonant. Molecules can be excited to a virtual energy state, see Figure 2.

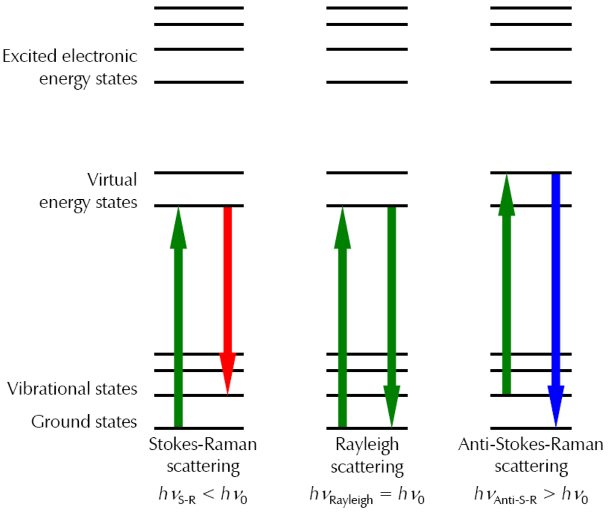


Figure 2 – Jablonski diagram showing transition of energy for Rayleigh and Raman scattering.

Scattered light itself can be distinguished between elastic and inelastic scattering. The major part scatters elastic which means that the energy (i.e. wavelength) of the incident light is equal to the emitted light. This phenomenon is referred to as Rayleigh scattering.

Only a minor part scatters inelastically where a small fraction of energy is transferred between molecule and photon. It causes changes in the polarization of the molecule which are induced by molecular vibrations. Hence energy and wavelength of incident and scattered light are not equal anymore. This effect was observed by Sir Raman in his experiments which were described in the previous section. As a result, this kind of spectroscopy is called Raman spectroscopy.

Inelastic scattering can be further distinguished between two different forms, depending on the energy state of the molecule (see Figure 2).

In case one, the molecule is initially in its ground state. After excitation, the molecule falls back to a vibrational energy state above the ground state. As a result, the emitted photon has less energy than before and the scattered light will shift to a higher wavelength. This effect is called Stokes-Raman-scattering.

Case two assumes that the molecule is already in a higher vibrational state. After excitation, the photon falls back to the molecule's ground state. The emitted photon has a higher energy than before. The wavelength shifts to lower values. This effect is called Anti-Stokes-Raman scattering.

Latter one is mostly weaker than Stokes-Raman scattering as most molecules are initially in their ground state. Hence Stokes-Raman scattering is mainly measured in Raman spectroscopy.

Note: Please note that inelastic scattering must not be confused with fluorescence. Raman-scattering involves excitation to a virtual energy state. In contrast, fluorescence is induced by excitation to an excited electronic state and relaxation to the ground state.
As both effects can occur simultaneously, fluorescence can disturb Raman measurements.

Measurement setup

Figure 3 shows a general setup for spectroscopic and spectroelectrochemical Raman experiments. It consists of a Raman spectrometer, measurement cell, potentiostat, and computer.

The light source of a Raman spectrometer is in general a laser with a specific wavelength. The laser's wavelength can range from the Ultraviolet to the visible and near-Infrared range depending on the application.

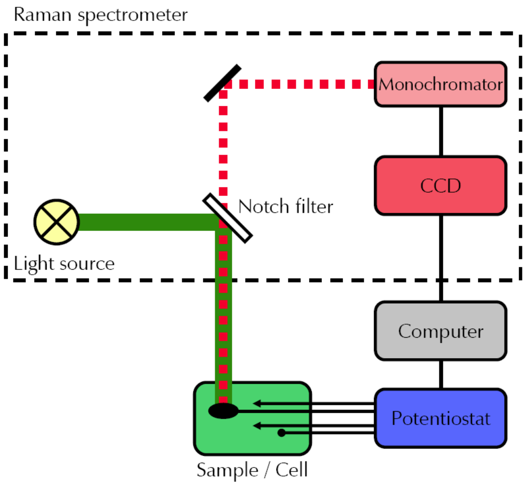


Figure 3 – Experimental setup for spectroelectrochemical Raman experiments.

The light beam is focused on a dichroic filter (Notch filter). The filter reflects the light beam to the sample in a right angle. The resulting Raman scattering is focused back to the dichroic filter. It serves as band-stop filter whereby the incident light from the light source is nearly completely attenuated. Only light with a different wavelength, i.e. Raman scattered light can pass the filter unaltered.

The measured light is redirected by mirrors to a monochromator which uses grating to diffract the beam into a narrow band of wavelengths. The photo current from each wavelength section is then measured at the detector. In general, a CCD detector (charged-coupled devices) is used which converts the measured photo current into electric current. Finally, the measured data can be saved and evaluated on a computer by using appropriate software.

For spectroelectrochemical measurements, the target sample is used as working electrode. Reference and counter electrode complete the electrochemical cell. All electrodes are connected to a potentiostat which is also connected to a computer.

Using appropriate software enables simultaneous recording of spectroscopic and electrochemical data and subsequent data evaluation.

For more information on Gamry's spectroelectrochemical equipment, please visit: **www.gamry.com/products/spectroelectrochemistry**

Raman spectrum

In Raman spectra, the intensity of measured Raman scattering is plotted versus the Raman shift. The Raman shift is defined as difference between the measured frequency of scattered light and incident light beam. Hence Raman spectra are independent of the wavelength of the light source.

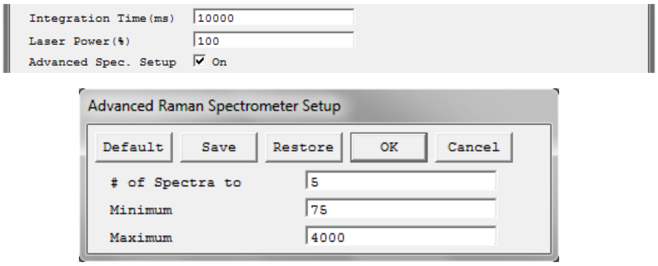
However, instead of using the wavelength, the Raman shift is given as change of the wavenumber $\bar{\nu}$ (cm^{-1}) which is inversely proportional to the wavelength.

Measurements

The following sections describe the interface of Gamry's Framework. All relevant parameters which can be set for spectroscopic Raman experiments are explained. Further, a practical example of a chronoamperometric Raman experiment is shown.

Setup parameters

The setup window for spectroelectrochemical Raman experiments in Gamry's Framework is similar to standard electrochemical setups. It contains three additional lines (see Figure 4).


Integration Time(ms) 10000
Laser Power(%) 100
Advanced Spec. Setup ☑ On

Advanced Raman Spectrometer Setup

# of Spectra to 5
Minimum 75
Maximum 4000

Figure 4 – Section of Framework's interface for spectroelectrochemical Raman experiments.

The *Integration Time* is given in milliseconds and indicates how long a single spectrum is recorded. Longer integration times increase the signal's intensity and reduce the signal-to-noise ratio. However, the electrode is also longer exposed to the laser which can alter it. Further, the detector can be saturated when using longer integration times which results in cut off signals.

The *Laser Power* is given in percent. The signal intensity increases with increasing power level. However, higher laser power can alter or destroy the sample.

If the advanced spectrometer setup is checked, an additional window appears after pressing "OK". This setup gives the user the possibility to adjust additional settings.

The first line adds an average function. When measuring, multiple Raman spectra are recorded and averaged to one spectrum. This method increases the measurement time and leads to a longer exposure time of the laser. However, signal-to-noise ratio and the resolution can be improved. In addition, cut off peaks can be avoided.

The *Minimum* and *Maximum* parameters adjust the wavenumber range (in cm^{-1}) of the Raman spectrum which is displayed during a measurement. However, the complete wavenumber range (173 cm^{-1} to 4000 cm^{-1}) is saved in the final measurement file.

Gamry's SPECTRO software package (Framework revision 6.20) includes currently two different Raman experiments:

Raman Chronoamperometry

Raman Cyclic Voltammetry

Raman Chronoamperometry

This section discusses Raman experiments with PEDOT:PSS (Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)). This conductive polymer is mostly used in LEDs as hole-injection layer.

Figure 5 shows Raman spectra at different potentials during several chronoamperometric experiments with PEDOT:PSS. The polymer was applied on a metal surface as thin film. An aqueous solution of sodium sulfate served as electrolyte. The electrolyte was nitrogen-purged before measuring. Graphite was used as counter electrode and a Ag/AgCl electrode was used as reference electrode.

The integration time was set to 20 s and five spectra where averaged, resulting in an exposure time of 100 s for each saved spectrum. The laser power was reduced to 50 %.

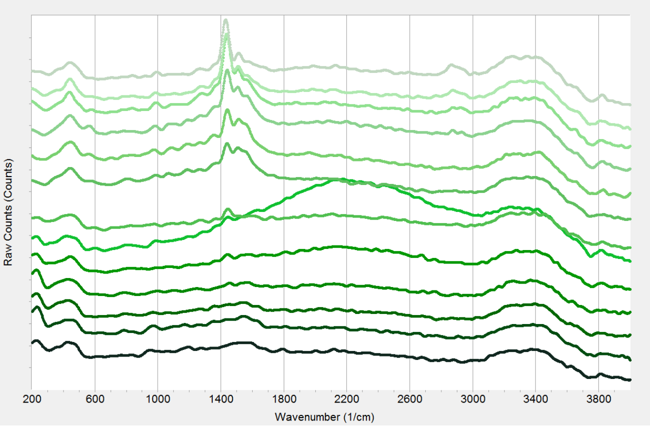


Figure 5 – Raman spectra of PEDOT:PSS at different potentials from 0.6 V to -0.6 V (bottom to top) during chronoamperometric Raman experiments.

Note: In order to illustrate changes in the Raman spectra better, absolute raw count values are ignored. All graphs are displayed one above each other.

The polymer was reduced in several steps from 0.6 V to -0.6 V (from bottom to top in 0.1 V steps). When decreasing the potential, a peak at 1447 cm^{-1} begins to appear which is getting more intense at negative potentials. In addition, the peak shifts by -17 cm^{-1} between 0 V and -0.6 V. Three weaker bands appear at about 1520 cm^{-1}, 1570 cm^{-1}, and 2870 cm^{-1}.

Literature research[1] reveals that the strong peak at 1447 cm^{-1} can be assigned to ring C-C stretching vibrations from PEDOT. The negative shift can be assigned to an increase in the conjugation length of oxidized parts to their neutral state during reduction.

Reduction of PEDOT can lead to reduced efficiency and long-term stability of LEDs. During operation of LEDs, electrons are withdrawn from PEDOT and form electron holes in the polymer layer. Vice-versa, electrons are injected into the electron-transporting layer near the cathode. Recombination between electrons and electron holes lead then to emission of radiation. However, recombination does not always occur. Electrons can migrate to the PEDOT-PSS layer and reduce PEDOT.

By combination of electrochemical techniques and Raman spectroscopy, more information can be obtained simultaneously. These can be combined to get a detailed description of reaction mechanisms.

[1] S. Sakamoto, M. Okumura, Z. Zhao, Y. Furukawa, *Raman spectral changes of PEDOT–PSS in polymer light-emitting diodes upon operation*, Chem. Phys. Lett., volume 412, issues 4–6, pages 395-398, 2005.

Conclusion

This application note describes the theory of Raman spectroscopy. The setup for Raman experiments including its extension to spectroelectrochemical measurements is described. Gamry's Raman interface and important setup parameters are discussed by means of chronoamperometric Raman experiments.

The effect of electrochemical reduction of PEDOT:PSS – a conductive polymer which is used in LEDs – is discussed. The measurements show that Raman spectroscopy in combination with electrochemical techniques is a helpful tool to investigate changes in the electronic state of molecules during electrochemical processes.

Structural information can be obtained for better understanding of different reaction mechanisms. Highly specific Raman spectra exhibit detailed information about the current system. By using spectral databases, materials can be compared and identified.

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