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RAMAN SPECTROSCOPY: A MODERN TECHNIQUE FOR MATERIAL PROPERTIES IDENTIFICATION

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Abstract: *Raman Spectroscopy has become a powerful analytical and research tool with assertion in almost all natural sciences and a wide range of technical and industrial branches Due to a technical advancement and novel engineering solution this technique is one of the most essential laser spectroscopic methods. This paper introduces the basic principle and demonstrates great applicability of Raman spectroscopy. Others currently examined applications are also presented.*
Key words: *Raman spectroscopy, spectrum, shift, identification*

1. INTRODUCTION

Essential knowledge and insight into the world of atoms and molecules dimensions we have today is without question a result of laser spectroscopic research. Especially Raman spectroscopy (RS) is a powerful analytic method providing detailed and specific information on a molecular level. In regard of its versatility this method can offer information that can be below possibilities of other spectroscopic methods (Schmitt & Popp, 2007).

Raman effect was discovered almost one hundred years ago. However, renaissance of RS is coming even in the last two decades hand in hand with technical advancements as are new extremely sensitive detection devices latest developments, efficient filters and laser technology designs (Pitt et al., 2005). The fact, that RS is a very flexible method in majority of science and technical branches, has been repeatedly proven during the last few decades.

A structure and a composition of materials influence their physical utility properties and consequently characteristics of products fabricated from these materials. In many cases strict and specific conditions that must be complied are given. Critical properties on the possibility borders of examination must be attested. RS is a powerful tool for such verification within a wide range of scientific disciplines. This rapid method allows quick identification of materials, gives information on the structure, spatial arrangement of molecules and structural analyses. Analogically to the fact that every human being in the world has different – unique – fingerprints by which they can be identified, also every individual substance has its own unique Raman spectrum characteristic only for the respective substance. RS also enables observation of the structural changes dynamics, mapping, depth scanning and with Infrared spectroscopy is a complementary spectroscopic method.

Indisputable advantage of RS is that the method is non-destructive, non-contact and highly sensitive with resolution in the order of μm and is applicable to a wide range of substances (liquids, transparent solids, gases) with no need for sample preparation in most cases. It is possible to explore aqueous solutions since water does not generally interfere with Raman spectral analysis. The intensity of spectral features is directly proportional to the particular species concentration. The standard spectral range ideal for both organic and inorganic samples covers from 100 cm^{-1} to 3200 cm^{-1}.

In spite of many advantages a well known competing process can appear along with the Raman scattering: fluorescence. Raman spectra, for instance, of certain biological samples are often masked by fluorescence when visible wavelengths of laser are used. Selection of suitable laser wavelengths with a lower energy photon is mostly a feasible solution. The interfering luminescence background can be in some cases reduced by "bleaching", i.e. prolonged sample illumination with the laser beam antecedent to concrete measurement (Demuth, et al., 1995).

Currently the most commonly used Raman spectrometers are combined with microscopes. Then only a very small volume (about ones of μm in diameter) of a sample is needed for collecting Raman spectra when using Raman microscopy. This interconnection yields many benefits.

2. THEORETICAL BACKGROUND

RS is based on Raman effect, which was named in honour of one of its discoverers, the Indian scientist Sir Chandrasekhara Venkata Raman (1928). The Raman effect occurs when a monochromatic light is shone on a researched material. A major part of light beam usually from near infrared, visible or near ultraviolet range is scattered without changes in frequency, i. e. Rayleigh (elastic) scattering, a part is absorbed and a remained tiny fraction, important for origin of the spectra, is inelastically scattered. After interaction of the photon with the molecule, particularly with the electron cloud and the bonds of the molecule, the photon evokes molecule excitation from the ground state to a virtual energy state. When the molecule relaxes it emits a photon and it returns to a different vibrational or rotational state. The energetic difference, between the ground state and the final state, results in a shift in the emitted photon's wavelength.

If the molecule absorbs energy, i.e. the final state is more energetic than the initial state then the emitted photon of a higher wavelength will generates a Stokes line. If the molecule loses energy, the emitted photon of a lower wavelength will generates an anti-Stokes line. These wavelength shifts carry analytical information on the differences between the individual quantum levels and play the key role in substance identification.

Mostly only a more intensive (Stokes) part of the spectrum is measured. Both Stokes and anti-Stokes are approximately symmetrical towards the zero shift of the wavelength that corresponds with the incident laser line wavelength. Distribution of the lines in the spectrum informs about a sort of the bonds in the molecule. Every individual substance has its own unique Raman spectrum characteristic only for the respective substance.

Raman scattering is detected as intensity as a function of wavelength (measured in nm) or a Raman frequency shift (measured in cm^{-1}). Intensity of the Raman scattering depends on several factors as the excitation wavelength of the used laser, used excitation power, changes in polarizability, the amount of Raman active molecules illuminated by the laser beam and temperature. The intensity of a Raman-band is theoretically described by George Placzek (Placzek, 1934).

In spite of the fact, that the particularity of RS is remarkable, the conversion efficiency of Raman effect is rather poor, since only a scarcity (about 10^{-7}) of the initial photons are inelastically scattered. Hence the detection of very low concentrated molecules is limited.

In order to enhance sensitivity, to improve intensity, to reach better spatial resolution and other improvements number of variation of RS has been developed: Surface Enhanced RS, Resonance RS, Transmission RS, Spontaneous RS, Tip-Enhanced RS et al.

3. APPLICATIONS

Raman spectroscopy finds application in many scientific and industrial disciplines and branches such as

- Chemistry – RS provides a fingerprint for identification of a molecule, since vibrational information is specific to the chemical bonds and symmetry of molecules.
- Material sciences – RS is one of the best-known methods, is of central importance for all the specification and structural analysis of almost all kind of materials (amorphous, partially crystallic, transparent, non-transparent samples, samples with different surface textures).
- Nanotechnology – RS provides determination of nanocrystal, chirality, semidiameters in nanomaterials.
- Semiconductor industry – RS allows semiconductor impurities determination in silicone substrates and diamond-like carbon coatings (a point measurement on silicone can be obtained in less than 0.1 s), identification of defects particles on the material surfaces. Such results notably affect device yields and the economics of the process line.
- Solid state physics – materials characterization, finding the crystallographic orientation, etc.
- Criminology, security forces – identification of unknown or hazardous substances, by instance detection of explosives or drugs by airport security, etc.
- Forensic sciences – identification of trace amounts of substances in evidential materials, etc.
- Geology and mineralogy – identification of the principal mineral phases, classification of rocks, etc.
- Pharmaceutical industry – development, production and control of pharmaceuticals, etc.
- Medicine, biology – DNA analyses, prognoses and diagnoses of carcinomas, study of biological systems, etc.

Followed issues are solved at the present time using Renishaw inVia Basis Raman microscope with the 514 nm excitation Ar^+ laser at Faculty of Applied Informatics, Tomas Bata University in Zlin.

Application of Multi-Walled Carbon Nanotube (MWCNT) for the purpose of conducting layers creation is investigated. RS is very useful in the detection of carbon form in fundamental research and also in industrial usage. This technique is able to distinguish different forms of carbon (Fig.1.), because of evident Raman spectral variances, and also map them. While, for example, SEM indicates only presence of elemental carbon in the sample (Pitt et al., 2005). Different concentrations of MWCNT affect properties of electric conductivity of layers, which are used for shielding electromagnetic fields or elimination of static charge and others.

The methodology for the detection of small Cr(VI) concentrations with the use of RS is developed. Trivalent and hexavalent chromium compounds are produced in large quantities and are accessible to most of the population. However, Cr(VI) is a carcinogenic substance and may cause health risks. There is a possibility of conversion of Cr (III) into Cr (VI). It is already proved that RS can distinguish Cr (III) from Cr (VI) (Kikuchi et al., 2005) (Fig. 2). Temporary results

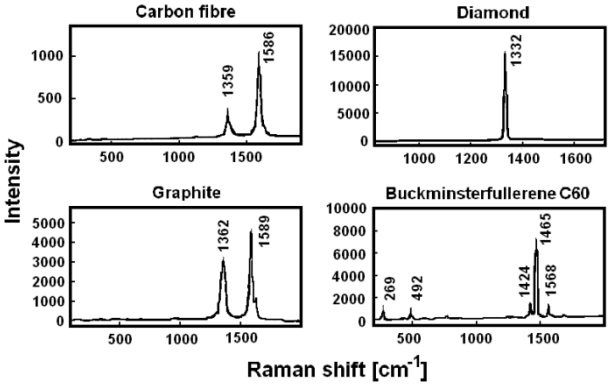

Fig. 1. Raman spectra of different modifications of carbon

show the complication with luminescence (Fig. 2) that masks the Raman spectra of natural polymers containing Cr compounds. This situation should be feasibly solved by changing visible wavelength laser by another suitable NIR excitation laser.

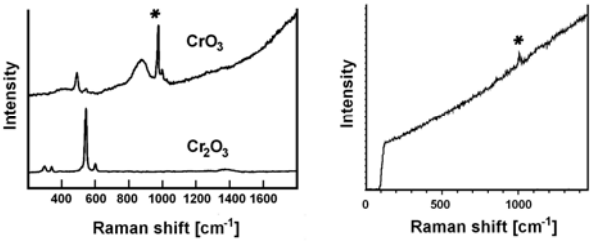

Fig. 2. Raman spectrum of trivalent and hexavalent chromium; a specrum of Cr(VI) masked by fluorescence

4. CONCLUSION

Raman spectroscopic technique was studied as an innovative method for obtaining information about a structure and properties of a wide range of materials, which can be used in almost all technical and industrial branches. Measurements on a concrete device InVia Basis Raman Microscope were realized. Possibilities of both a structure and properties of selected materials were verified. Laboratory program for forensic applications, mechanical properties and aging of solids is preparing at the present time.

5. ACKNOWLEDGEMENT

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