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Introduction to Vibrational Spectroscopy

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By spectroscopically probing vibrational states one can obtain valuable information on the molecular structure of a sample. Not only vibrational states are sensibly dependent on the chemical composition of the sample, but also on molecular conformation and possible environmental interactions of the sample molecule with e.g., the surrounding solvent.

The interpretation of vibrational spectra has its historical roots in well-established empirical correlations (see for instance [1,2]). Nowadays, such basic information is greatly corroborated by the use of Density Functional Theory (DFT) based calculations, which have been showing an excellent performance in terms of reliability and chemical-physical insights (i.e., the explanation of experimental observations in terms of conformers, inter-and intra-molecular interactions, etc.) [3].

In this introductory lecture, I will cover the fundamental theory of vibrational states at the harmonic approximation, and I will introduce the most popular experimental techniques which probe vibrational states, namely IR absorption and Raman scattering (also covering resonance Raman). Due to its current widespread, my concluding remarks will be devoted to Surface Enhanced Raman Spectroscopy (SERS). This is a notable variant of Raman spectroscopy, where the signal produced by the molecules of interest that are in proximity to noble metal nanostructures increases by many orders of magnitude.

References
Introduction to SERS and TERS

Surface and Tip- Enhanced Raman Spectroscopy: from basics to state-of-the-art applications

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Surface Enhanced Raman Spectroscopy (SERS) that takes advantage of the huge signal amplification, up to $10^8 - 10^{10}$, due to the electromagnetic field localization and amplification experienced by molecules adsorbed at the hot spots of nanoscale particles. Localized surface plasmon resonances are largely responsible of this phenomenon when metal nanoparticles are involved. SERS is nowadays a well recognized technique for ultrasensitive molecular detection, with sensitivity that reaches the single molecule. In this talk I will review the basics and applications of SERS in the light of the most recent advances in this field. Tip Enhanced Raman Spectroscopy (TERS) is a nanoscopy technique that exploits the highly confined electromagnetic field at the edge a metal tip to scan and image the surface of samples. TERS is usually implemented by coupling an AFM/STM setup with a Raman spectrometer and allows for simultaneous topographic and chemical imaging with a spatial resolution of few nm, that can reach the atomic scale in specific conditions. In this talk I will review the experimental basics of this technique, together with the most recent applications in Nanospectroscopy of materials and biological macromolecules.
Emerging trends in Enhanced Raman Scattering

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Conventional SERS relies on the exploitation of surface-plasmon polaritons, which are excited upon interaction of a laser source with coinage metals (Ag, Au, Cu) in form of nanoparticles, nanostructures or electrochemically roughened surface. In parallel, borrowing strategies, based on coating of coinage metals with ultrathin metal or metal-oxide layers to form core/shell nanostructures, are also utilized to impart SERS activity to a variety of substrates.

On the other hand, SERS in all-dielectric materials has received so far much less attention in comparison to the metal counterpart. This is quite surprising, because the engineering community has realized for a long time that dielectric materials provide unique capabilities for manipulating light at the nano-scale, as demonstrated, for example, by vibrant research on nano-lasers, optical waveguides and all-dielectric optical nanoantennas.

Dielectrics represent a new frontier for Surface Enhanced Raman Scattering. They can serve either as a complement or an alternative to conventional, metal-based SERS, offering key advantages in terms of low invasiveness, reproducibility, versatility and recyclability. In comparison to metals, dielectric systems and, in particular, semiconductors, are characterized by a much greater variety of parameters and properties that can be tailored to achieve enhanced Raman scattering or related effects. Light trapping and sub-wavelength focusing capabilities, morphology-dependent resonances, control of band gap and stoichiometry, size-dependent plasmons and excitons, charge transfer between semiconductors and molecules and vice-versa are a few examples of the manifold opportunities associated to use of semiconductors as SERS-active materials. This lecture provides a broad analysis of SERS with dielectrics, encompassing different optical phenomena at the basis of the Raman scattering enhancement and introducing future challenges for light harvesting, vibrational spectroscopy, imaging and sensing. [1-7]

References
Introduction to SEIRA

Introduction to surface-enhanced infrared absorption

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Infrared absorption spectroscopy is a powerful tool to study molecules. However, because of the difference of more than three orders of magnitude between the wavelength of light and the typical size of a molecule, light-matter coupling is weak in this frequency range. Resonant plasmonic antennas can be exploited to circumvent this limitation since they act as a powerful tool to couple non-propagating near fields with propagating far fields and vice versa. In this context, the coupling between the electromagnetic resonance of the plasmonic nanoantenna and the vibrational resonance of the molecule gives rise to a rich phenomenology that is typical of coupled oscillators, such as the appearance of asymmetric Fano-like lineshapes or electromagnetically-induced transparency. Experimentally, surface-enhanced infrared absorption has been mainly performed with Au antennas that sustain localized surface plasmon modes in resonance with the molecular vibrations, exploiting either a single rod geometry [2-4], a double-rod geometry [5-7], or more advanced designs allowing for an even better funneling of the light into a small gap [8,9]. Recently, also heavily-doped semiconductors have been employed [10,11]. In this lecture we will review the fundamentals of surface-enhanced infrared absorption, covering the basics of plasmonic nanoantennas and how they couple to the vibrational molecular resonances and assessing some of the most recent and representative experimental results.

References
Raman spectroscopy possesses an enormous potentiality in unfolding basic and applicative issues of biomaterials and biomedical science with both large economic benefits and promising developments into preventive healthcare. The Raman method comprehensively suites a number of technological needs for spatially resolved and quantitative assessments of crystal structures, domain textures, crystallographic alignments, chemical drifts, and mechanical stresses in synthetic and natural biomaterials. However, the physics underlying the Raman effect represents an issue of deep complexity and, in a yet conspicuous lack of working algorithms, its applicative development to biomaterial structures could yet be considered in its infancy. This lecture revisits basic issues and puts forward some applicative aspects of the physics governing the Raman emission in both synthetic/natural biomaterials and biomolecules. Its ultimate aim is to disentangle the convoluted dependences of Raman spectra on crystal orientation, chemical/stoichiometric alterations, and mechanical stress. Working algorithms are shown in an explicit form, in order to quantitatively extract structural, chemical, and mechanical information from experimentally collected confocal/polarized Raman spectra. As an additional task, it is also shown that the Raman spectrum of selected biomolecules could be used to monitor the metabolism of cells and bacteria and its environmentally driven structural dependences. In situ Raman assessments of living neuronal cells and various types of bacteria are shown as vivid examples of the potential of this vibrational method.
Resonance Raman spectroscopy: techniques and applications in life sciences

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Resonance Raman (RR) spectroscopy is of particular interest in the analysis of biomolecules containing a chromophore, as it permits the intensification of the Raman bands specific to the chromophore. In fact, the coincidence of the incident laser excitation wavelength with the electronic transition energy of the chromophore (resonance effect) leads to a considerable intensity enhancement of the Raman vibrational modes of the chromophore of interest (about 10^2–10^6 fold). RR spectroscopy has a number of characteristics that have been advantageous in its application in life sciences: (i) it requires only very small quantities of sample (~40 μL, 30–50 mM); (ii) it can be used easily in aqueous media, hence reflecting physiological conditions, since the Raman water spectrum is very weak; (iii) it is able to enhance only the vibrational modes of a chosen chromophore in a multiple chromophore molecule.

Heme proteins represent one of the classes of molecules most studied in the last 20 years with the RR technique. The first RR spectra were obtained on hemoglobin in 1972 [1]. The enhancement mechanism of Raman scattering by heme proteins has been reported in many reviews [2,3]. The technique has been demonstrated to be extremely informative in probing heme protein active site structures and many studies today are aimed at understanding the relationships existing between the spectra and the structure and consequently the activity of the proteins [4,5]. Moreover, in combination with site-directed mutagenesis, the marked sensitivity of the technique to small structural changes in the heme pocket has provided considerable insight into the roles of active site amino acids and furnished important information on protein function, flexibility and stability [6-9]. A general introduction to the technique, with particular attention to the information that RR can provide on the study of heme proteins will be given spanning from UV to visible excitations. Moreover, applications of RR microscopy on protein single crystals will be presented. The RR data will highlight the artifacts induced by the crystallization process [10], or the conformational alteration induced by cooling [11-12]. In addition, our recent results will show how the combined spectroscopic/crystallographic approach is a powerful new weapon in the structural biologist’s armamentarium [13].

References
Surface enhanced Raman scattering is a powerful technique with potential application in many fields, since it allows detecting vibrational fingerprint of molecules with huge intensity signals. In the biotechnology field one of the most used optical signal is fluorescence which, however, suffers from many problems, among which the bleaching of signals, which is not an issue for SERS. Moreover, fluorescence shows very large bandwidths, being of electronic origin, whereas SERS, which is of vibrational origin, shows very narrow resonances. This allows obtaining multiplexing measurements with SERS also using one single exciting laser line, which is not possible with fluorescence.

The applications of SERS probes will be shown for different biotechnology applications, with both in vitro and in vivo experiments. It will be shown how efficient SERS nanosystems can be obtained starting from laser ablated nanoparticles which also allow quick functionalizations with targeting units for recognizing for example antigens on cancer cells.

Simulations of extinctions spectra of the localized plasmon resonances of the nanostructures, used for SERS applications, will allow understanding which are the best situations for obtaining strong signals useful also with very low concentrations, usually in the nano- to pico-molar region, of the plasmonic nanostructures.

Examples of multimodal SERS nanostructures and their use for imaging and for other applications like photothermal ablation will be recalled.

Some recent works, produced within the NOL group, follow and could be discussed during the seminar.

References
Vibrational Optical Activity: Vibrational Spectroscopy for Chiral Systems

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Vibrational Circular Dichroism (VCD) and Raman Optical Activity (ROA) are the two forms of Vibrational Optical Activity (VOA) spectroscopies. [1,2] Together with the corresponding absorption and scattering counterparts, namely IR absorption and Raman scattering spectroscopies, they have been employed successfully, through the last 40 years, to help define the absolute configuration and conformational properties of natural products and of chiral organic molecules with potential both biological and material science applications. Most of these measurements are carried out in solutions and, as such, they reveal complementary and in some instances, superior to the ultimate technique for structural determination, namely X-ray diffraction. They have also been applied to investigate, in water solution, natural biopolymers, encompassing peptides and proteins, nucleic acids, carbohydrates and model systems for lipids and membranes. In the recent years a big step forward was taken due to the advent of ab-initio (in particular DFT) methods to reliably predict spectra. [3,4] Nowadays further steps are taken to appropriately model the chiroptical response, by also accounting effects from the solvent, beyond the Polarizable Continuum Model (PCM), and to consider solute-solute interactions. To this instance Molecular Dynamics (MD) and ancillary methods thereof are under scrutiny, use and investigation.

In this lecture the principles and the functioning of the main apparatuses for measuring VCD and ROA will be reviewed and practical information about the interpretation of the data will be provided. Illustrative examples in the field of biological molecules, of natural products and of small organic systems for electronics will be discussed.

References
The world in which we live is multivariate.
In everyday life we think multivariate, i.e. we elaborate the information we get from the real world by taking into account all the different variables at the same time.
Unfortunately, in scientific life people are used to forget the natural way of thinking and to work by taking into account just one variable at a time. This is completely wrong, because by doing that all the correlations (or interactions) among variables are totally lost.
In this short course the bases of multivariate thinking will be shown and taught, both for analysing data (Multivariate Analysis) and for performing optimally planned experiments (Experimental Design).
It is really unbelievable that this way of thinking is not yet commonly used and taught, in spite of the fact that the basic techniques shown date back to 1901 (Principal Component Analysis) and 1935 (Factorial Design).
In the afternoon the use of a free software will be shown, possibly on data set brought by the participants.
Raman Metrology - Towards Traceable and Quantitative Measurements

Andrea Mario Rossi¹, Li-Lin Tay², Angela Hight Walker³, Erlon Ferreira⁴ and The International Raman Metrology Team

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Raman spectroscopy/microscopy is a powerful surface analytical technique for rapid, non-destructive characterization of materials. It works under ambient conditions, often without requirement of any sample preparation. Its applications span biomedical, microelectronics, pharmaceutical, security and fundamental investigations of nanomaterials such as the novel 2D and nanocarbon materials. More recently, miniaturized hand-held Raman instruments enable an even broader range of measurement capabilities, such as environmental monitoring, screening of explosives and analysis of illicit drugs, to be brought into field and increasingly these measurements are carried out by non-experts of the scientific or spectroscopic community. Despite nearly a century of development, Raman spectroscopy remains a qualitative analytical technique. A major obstacle in the use of Raman data in regulatory applications is the lack of traceable quantification and the absence of certified reference and documentary standards. This talk summarizes activities under development by the international Raman Metrology Team (iRMT) to develop traceable and quantitative measurements for various Raman measurands. The iRMT is composed of Raman experts from 15 National Measurements Institutes (NMIs) throughout the world that collaborate through monthly meetings on the development of quantitative and traceable Raman measurements as well as standards relevant to Raman spectroscopy. This presentation covers the CCQM-SAWG pre-pilot study on the Raman confocal volume measurements and strategy towards traceable and quantitative Raman measurements; Raman shift calibration interlaboratory comparison carried out under VAMAS TWA42; Structural characterization of CVD-grown graphene under VAMAS TWA 41 and Raman spectroscopy for the quantification of phases within TiO₂ nanoparticle mixtures.
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