International Winter School

Molecules@Surfaces

Surfaces: structure, electronic states, defects
Molecules @ surfaces: foundations
Molecules & Surfaces at work
Molecules @ surfaces and quality of life

LECTURES
Book of Abstracts - Section 1

Edited by

Gabriele Ricchiardi **Giuseppe Spoto** **Bartolomeo Civalleri** **Domenica Scarano**

Department of Chemistry
University of Torino

Programme

January 31 – February 5 2016
Bardonecchia (Italy)
Olympic Village

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and with the sponsorship of the
Interdivisional Group of Catalysis of the Italian Chemical Society

with the participation and sponsoring of

Welcome to the "Molecules @ Surfaces" winter school!

Surfaces define the boundary of all kind of objects, made of both soft and hard matter, from the macro- to the nanoscale. Their "talking" with molecules from the surrounding environment often rules relevant functional properties. These functions are as diverse as in the case of devices for air and water purification, heterogeneous catalysts for the sustainable production of energy and chemicals, implanted biomaterials or injected nanocarriers of signals and drugs, or the origin of biomolecules in space. On such a basis, the importance of surfaces and of their interaction with molecules has been recognized since a long time as a central topic in many fields of chemistry and material science. The actual possibility to achieve new breakthroughs in many fields strategic to mankind, like food&water, health or sustainable growth, is based on advances in our knowledge and engineering of surface-molecule physical and chemical interactions.

This is the field targeted by the "Molecules@Surfaces" school, the 2016 winter edition of the series of courses organized by the Physical Chemistry Division of the Italian Society of Chemistry. This time featured also with an international character, including the auspices of the Physical Chemistry Division of the European Association for Chemical and Molecular Sciences (EuCheMS). The school will take place from January 31 to February 5 in Bardonecchia, near Torino (North-West Italy), one of the ski resorts of the 2006 Winter Olympic Games.

"Molecules@Surfaces" offers to PhD students and Post-Docs updated “tools” for acting as relevant scientific players in surface-related materials science and technology. Participants will be actively involved in lectures given by established experts, covering a comprehensive path from fundamental aspects to cutting-edge applications, based on both experimental and modeling approaches (with lab activities). Details can be found in the “Topics” section. The program includes the presence of industrial researchers, the possibility for participants to present their on-going research activities (also in an ISBN coded Abstract Book), an overview of relevant H2020 and complementary EC research funding actions, ...and specific sessions on the surfaces of the Bardonecchia ski-slopes!

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PROGRAMME
&
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20:00 *DINNER*

After Dinner

THE WINTER NIGHT SKY: STAR OBSERVATION

(Moon ephemeris are favourable, for a clear sky we can just hope…..)

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Time for ACTIVE PARTICIPATION of STUDENTS

(20.30-22.30)

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Presentation and Discussion

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Time for ACTIVE PARTICIPATION of STUDENTS

(20.30-22.30)

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14:00 – 19:00	S. Casassa, B. Civalleri, A.M. Ferrari, L. Maschio	Theoretical modeling hands-on session (including time for *coffee breaks*)

20.00 Departure for the
DINNER IN A MOUNTAIN CHALET

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AFTER DINNER, time for ACTIVE PARTICIPATION of STUDENTS
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13.00 LUNCH

ABSTRACTS

Opening lecture
OL1

SURFACE PHYSICO-CHEMICAL FEATURES FROM AN ASTROCHEMICAL PERSPECTIVE: CATALYSIS IN DEEP SPACE

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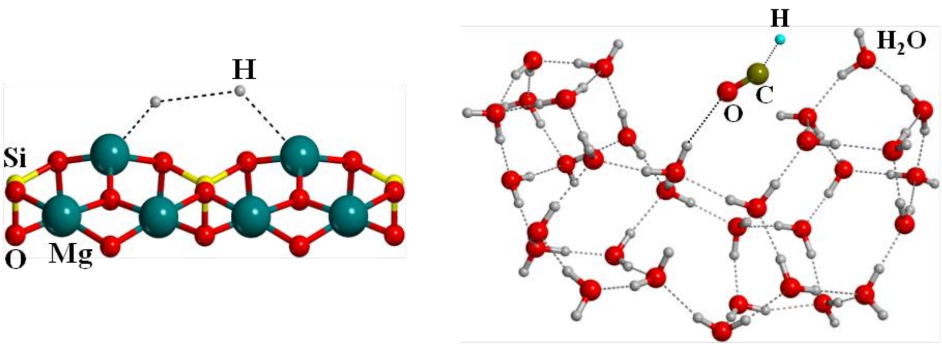
ABSTRACT

The existence of matter in the form of gaseous molecules and grain particles in the interstellar media (ISM) has attracted the interest of astrophysicists, astrochemists and astronomers due to its relevance for the chemical evolution steps occurring in the deep space, which are ultimetaly relevant to the origin of life. On one hand, radio to near-infrared observations of the gaseous component detected rotational and vibrational transitions of over 185 different molecular species in the ISM. On the other hand, spectroscopic and photometric observations show that diffuse matter consisting of gas and submicron sized grains mixed together is also present in ISM. Such a matter is not distributed evenly but aggregates in clouds that settle in the disk of spiral galaxies. In clouds where the atomic densities are about 1-10 H atoms cm^{-3} (the so-called diffuse clouds) grains consist of dust of Mg/Fe-silicates and carbonaceous materials, whereas in clouds with atomic densities of about 10,000 cm^{-3} (the so-called dense clouds) dust grains are covered in ices of volatile species (i.e., mainly H_2O but also CO, NH_3, CH_4, etc.), thereby forming a core/mantle-type structure. The link between the grain particles and interstellar molecules is further extended as grain particles provide the surfaces where important chemical reactions can take place [1 – 5]. The present knowledge of this interstellar matter is mostly based on spectroscopic observational data, supported by the comparison with laboratory experiments and on results from numerical astrochemical models. The combination of these three approaches has provided important information such as the composition of grains and their chemical activity [6]. However, atomic-scale information such as the detailed structure of the grain particles or precise reaction mechanistic steps occurring on them is still lacking, which is a serious limitation to fully understand the basic physico-chemical steps leading to the increase of the chemical complexity in space. This information gap can partly be filled in by using theoretical calculations based on quantum mechanical approaches [7]. In this talk several examples on how these theoretical calculations can contribute to astrochemical studies by rationalizing both astronomical observations and puzzling experimental results will be presented. In particular, results obtained from simulations devoted to the formation of H_2 on bare silicate surfaces [8, 9], to the formation of H_2CO and CH_3OH through hydrogenation of CO on water ice surfaces [10], and to the formation of complex organic molecules from thermal activation of H_2O-dominated dirty ices [11, 12] will be shown.



Left: H_2 formation on a silicate surface; right: HCO formation on a water ice surface

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Notes

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Surface and Molecules@Surfaces: an experimental approach

OL2

The Langmuir-Blodgett approach to surface functionalisation: principles, techniques of characterisation and applications.

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ABSTRACT

The lesson will be centered on the multifarious aspects of the Langmuir-Blodgett (LB) technique.

The distinct aspects of the LB approach for the immobilization onto solid supports of organic substances, biomaterials, polymers, and composite materials will be described, from the theoretical basis of the method to the characterization of the deposited mono- and multi-layers and finally to the remarkable capability in diverse and disparate areas of applications.

The relevance of the Langmuir-Blodgett technique among the methods of immobilization of different materials establishes on its capacity of generating in the deposited multilayers organization at the molecular level even when structurally very complex compounds with significant sterical hindrance are employed. Furthermore the acknowledged potentiality of the fabrication of films with a predetermined thickness and architecture and an established composition has contributed to the recognition of the Langmuir-Blodgett technique as one of the frontier method in contemporary research fields such as molecular electronics, molecular engineering, optoelectronics, memory devices, drug delivery, etc.

Notes

Surface and Molecules@Surfaces: an experimental approach
OL3

SURFACES IN NANOPOROUS MATERIALS: ZEOLITES AND MOFs

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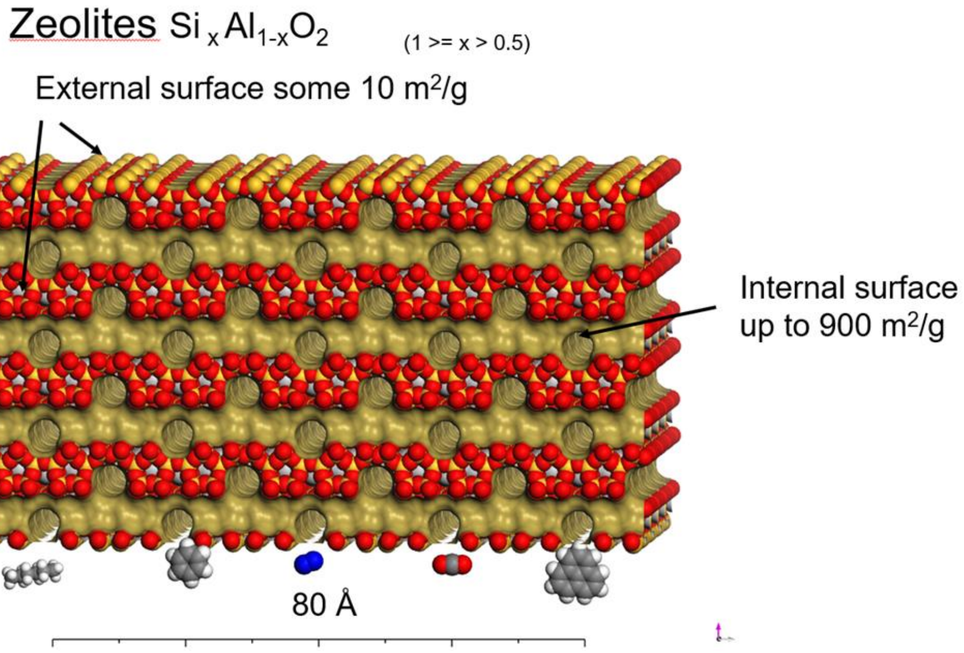
ABSTRACT

For normal materials are the surface where the regular part of the materials terminates. For crystalline materials is this were the periodicity found in the crystal is interrupted. This type of surface is therefore saturated with broken bonds that must be terminated, the property to the surface is normally very different from the bulk material.

In nanoporous materials on the other hand are surface a part of the regular crystal structure. The figure below illustrates the difference between this external and internal surface in a microporous material. The selected example is the zeolite ZSM-11.



The geometry is the first thing that distinguish this internal surface from regular external surfaces. The access and space are restricted and given by the crystal structure, this create the useful shape selectivity, se ref 1. In the figure above are normal small molecules drawn to the same scale as the porous solid. Illustrating the match in size between the channels and common molecules. The chemical property of these internal surface depends on the chemical composition of the porous material. Zeolites was the first class of these microporous materials. Zeolites are silico-alumino oxides with variable amount of aluminum substituting for silicon in the tetrahedraly coordinated structure. In the simplest case is the surface perfect SiO_2 which will be very inert and hydrophobic. Substituting silicon with an element with a different charge will create a charge defect this give rice to the useful properties; acidity and ion exchange. Se ref 2 for a thorough discussion of the origin and application of acidity. Substitution silicon for a red-oks active

elements like titanium create important red-oks catalyst like TS-1 (ref from Turin group?).
A relatively new family of micro-nano-porous materials are Metal Organic Frameworks. In these materials are the chemical composition both inorganic and organic. This is also reflected in the properties to the internal surface that can be tailored to a much larger extent compared to the oxide based microporous materials. These surfaces may be neutral like graphene, but functional groups both of organic, amines, amides, thiols, carboxylic acids etc. may be introduced. In addition, and in combination with these groups may most metals be incorporated. And for these materials my this be done in a controlled and planned way. The geometry for MOF surfaces vary more than what observed for oxide-based microporous materials. Measuring and calculating the surface area are therefore more challenging (ref 5,6).

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Surface and Molecules@Surfaces: an experimental approach

OL4

SPECTROSCOPIES FOR MOLECULES @ SURFACES

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ABSTRACT

Light-based spectroscopies are performed investigating the interaction between light and matter in the whole range of the electromagnetic spectrum: microwave (NMR and EPR), mid-infrared (IR), near-infrared (NIR), visible (Vis) and ultraviolet (UV) (Raman, optical and luminescence spectroscopies), far-UV (UPS) soft-X-ray (XPS) hard X-rays (XANES, EXAFS, XES), and γ (Mössbauer).

In this contribution the use of IR, Raman, UV-Vis-Nir, XANES, XES, and EXAFS spectroscopies will be introduced, highlighting their points of strength and weakness with the help of tutorial examples selected in the area of microporous materials and their interaction with simple molecules. In this context, heterogeneous catalysts and materials for selective adsorption (capture and storage) are the most strongly involved.

Molecular modelling, performed on clusters or on periodic structures, is commonly used in parallel with spectroscopies as it can give data that can be directly compared with some specific spectroscopic features, or can suggest structural model that can be used as starting point to describe a spectroscopic result.

Moreover, apart from the portion of the electromagnetic spectrum used for a specific study, nowadays, more and more we have the possibility to perform an experiment in controlled atmosphere, at different temperature and using time and space resolved techniques, thanks to enhanced sensitivity of the experimental apparatus and the combination of spectroscopies and microscopies, allowing to follow dynamic changes in the nature of active sites at the surfaces, such as their distribution and accessibility, that occur both between and within particles.

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Imaging of surfaces

Imaging of surfaces

OL5

SCANNING PROBE MICROSCOPIES BEYOND SURFACE IMAGING: UNRAVELLING THE NANOSCALE WORLD

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ABSTRACT

My lecture will review our recent results on the use of different Scanning Probe Microscopy approaches, relying on Scanning Tunneling Microscopy (STM) and Conducting – Atomic Force Microscopy (C-AFM) methods, to unveil physical and chemical processes in complex and multicomponent supramolecular systems.[1] Particular emphasis will be given to the sub-molecularly resolved STM mapping of the activity of light-responsive physisorbed and chemisorbed self-assembled monolayers [2,3] as well as to the on-surface reaction[4] for the unique case of dynamic covalent chemistry, i.e. operating under thermodynamic control[5]. On the other hand, examples of C-AFM explorations of low-dimensional architectures will be given,[6,7] with a particular focus on the fabrication of nanoscopic supramolecularly engineered 3-terminal devices (OFETs) and on the possibility of changing the electrical properties of nanostructures by photochemical generation of charge carriers.

Our findings will open new avenues towards the development of multifunctional materials and devices

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Surface and Molecules@Surfaces:
a theoretical approach

Surface and Molecules@Surfaces: a theoretical approach

OL6

OXIDE SURFACES IN CATALYSIS: FROM SIZE-SELECTED CLUSTERS, TO DEFECTS ENGINEERING AND TWO-DIMENSIONAL OXIDES

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ABSTRACT

Nanocatalysis deals with components of a solid catalysts at the nanoscale, a regime where neither quantum chemistry nor the classical laws of physics hold. The reactivity of metal clusters and nano-particlesis highly size- and shape dependent. This is at the basis of the development of methods to deposit size-selected clusters, i.e. collections of clusters all having the same size. Tuning the size of the metal clusters can lead to a tuning of the chemical reactivity.Size-selected nanoclusters are usually produced in gas-phase and then need to be deposited and stabilized at oxide surfaces. Here, the interaction with defects, structural and morphological irregularities, trapped electrons, etc. can significantly alter the properties of the supported cluster resulting in an enhanced chemical reactivity. The proper identification and the control on the type, nature, and concentration of surface defects at oxide surfaces (defects engineering) represents therefore aextraordinary opportunity to tune the activity of a supported catalyst (for a series of reviews on oxide surfaces and their properties see ref. [1]).

A third way to exploit nanodimensionality in heterogeneous catalysis is related to the use of ultrathin films. Graphene is the prototype of two-dimensional materials, but is not the only one. SiO_2 films of few nanometers thickness grown on Si have been the basis of the microelectronics revolution in the second half of last century. In general, ultrathin oxide films grown on a metal, also called two-dimensional oxides, have a wide range of applications [2]. Oxides at the nanoscale may exhibit specific surface morphology, physical properties, chemical reactivity, thus providing new opportunities for the design of innovative materials. Here we will address in particular the role of two-dimensional oxides for heterogeneous catalysis [3,4].

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OL7

GAS ADSORPTION IN POROUS SOLIDS: MODELS, SPECIFIC SURFACES AND PORE DISTRIBUTIONS

Maurizio Cossi
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ABSTRACT

The lecture concerns the characterization of nanoporous materials with gas adsorption techniques. In particular, physisorption will be considered, i.e. processes in which the main interactions are “weak”, based on London or dispersion forces, and no covalent bonds are formed between gas and substrate.

The IUPAC classification of adsorption isotherms will be described and discussed, and the relationship between isotherm type and porous structure elucidated.

Different models will be presented to interpret the gas adsorption in terms of mono- and multi-layer processes, leading to Langmuir and Brunauer-Emmet-Teller (BET) theories of specific surface area.

The pore size distribution (PSD) analysis based on (older) thermodynamic theories will be briefly discussed, while modern Density Functional Theory (DFT) approaches will be presented in detail: the potentialities of this technique will be analysed with many examples of different nature.

Finally, we will discuss a case-study to illustrate how the atomistic structure of a disordered porous materials can be deduced with a combination of theoretical calculations (based on DFT and Monte-Carlo techniques) and experimental gas adsorption measures.

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Notes

Surface and Molecules@Surfaces: a theoretical approach

OL8

AB INITIO MODELING OF SURFACES AND ADSORPTION: MODELS AND STRATEGIES

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ABSTRACT

In the **lecture**, the basic concepts of ab initio modeling will be introduced with a concise syllabus of the main approximate quantum mechanical methods [1] used in solid-state chemistry to simulate periodic systems [2] (e.g. density functional methods [3]). The idea of computer experiments will be used to discuss the modeling of surfaces and adsorption there on. Different strategies to model surfaces will be presented with particular emphasis on the so-called slab model (i.e. a thin-film model of given thickness parallel to the (*hkl*) face of interest). The most relevant aspects related to the proper creation of a slab model will be discussed: how to create a slab model, selection of the Miller indexes, definition of the repeat unit, Tasker's classification of ionic surfaces, definition of the surface formation energy, relative stability of different faces. Adsorption on the external surfaces of solids and the inner surface of porous materials will be discussed with examples to relevant applications in surface science: from simple [4] to complex adsorbed molecules [5], from gas storage [4] to drug delivery [5]. Merits and limits of quantum mechanical methods in the prediction of the adsorption energy and related properties will be also discussed.

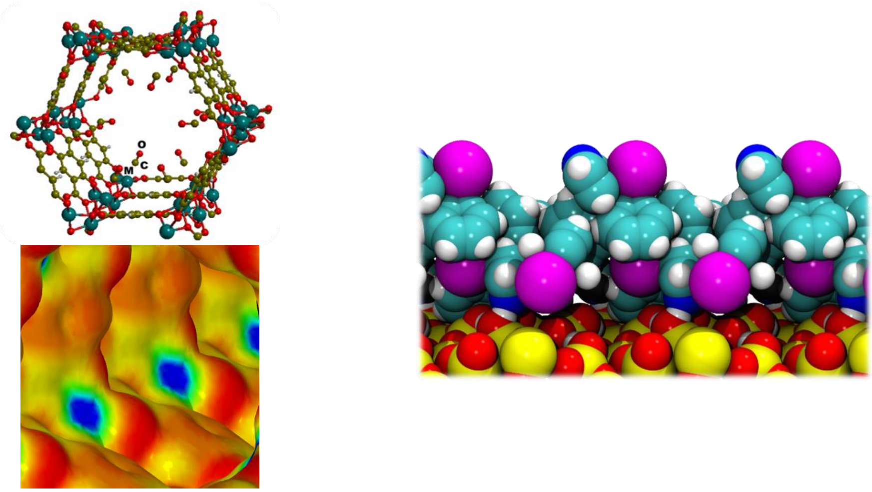

Figure. Left: Adsorption of CO within the pore of the CPO-27-Mg metal-organic framework, along with a picture of the electrostatic potential mapped on top of a charge density isosurface to highlight the location of the adsorption sites [4]. Right: Model of a monolayer of clotrimazole drug molecules adsorbed on an amorphous silica surface [5].

In the **hands-on session**, some practical work will be carried out to show how modern computational tools presented in the lecture can be applied to the study of surfaces and adsorption. Some calculations

will be performed to predict the surface formation energy and the relative stability of different faces of simple solids (e.g. MgO, TiO_2, …). The adsorption of small molecules will then be modeled and the adsorption energy computed. Outputs from calculations on more complex systems will be provided and analyzed to show how to extract relevant information.
All calculations will be carried out by means of the ab initio periodic code CRYSTAL14 [6,7].

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Molecules, surfaces and spectroscopy: the point of view of instruments makers

OL9

THE IMPORTANCE OF SURFACES IN RAMAN SPECTROSCOPY: SERS AND TERS, STATE OF THE ART AND PERSPECTIVES

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ABSTRACT

Surface-enhanced Raman spectroscopy (SERS)[1,2] and (2) TIP-enhanced Raman spectroscopies (TERS)[3,4] are surface-sensitive techniques that enhance Raman scattering by different orders of magnitude, via nano-structured noble metal surfaces (silver or gold) either by (1) depositing the sample on particular substrate (noble metal nanoparticles, nanostructured metal surfaces, etc.) or (2) combining metallized STM sub-micron tips to simultaneously achieve near-field high spatial resolution effects. In contrast to SERS, where the sample is coated onto a rough metal surface that provides enhancement of the electromagnetic (EM) field and of the Raman signals, in tip-enhanced Raman spectroscopy (TERS) the enhancing metal structure is brought into close contact with the sample from outside by a sharp full-metal or metal-coated tip.

In this lesson we will give a brief introduction to Raman spectroscopy, explain the SERS effect and detail the different substrates, explain the TERS effect and illustrate the different tip typologies and show examples for both the techniques.

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OL10

NEW ADVANCED MULTI-CHANNEL SPECTROFLUOROMETER ENHANCE SPEED AND SENSITIVITY FROM UV TO NIR

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ABSTRACT

Multi-channel CCD camera for spectroscopy represents an established detector technique to record weak photoluminescence &raman emission. Recently, Horiba Scientific develop new spectrofluorometers based on new CCD camera detector to overcome the limits of PMT single-channel acquisition. Thanks to strong collaboration with academic and research centers Horiba Scientific develop optimized multi-channel instrumentation as the AquaLog™ spectrofluorometer for monitoring chromophoric dissolved organic matter (CDOM) in water quality analysis, or the modular NanoLog® to study the electronic properties of single-walled carbon nanotubes (SWNTs) using photoluminescence spectroscopy. I here describe the development of the modern spectrofluorometers over the years and I introduce the key features of the multi-channel technique in terms of speed, sensitivity and wavelength range.

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Molecules@Surfaces at work: adsorption, self-assembly

Molecules@Surfaces at work: adsorption, self-assembly

OL11

TRANSPORT PHENOMENA IN GAS-SELECTIVE SILICA MEMBRANES

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ABSTRACT

Upcoming technology platforms for green fuel production require the development of advanced molecular separation processes for recovering dry liquid biofuels [1,2], biomethane [2] and hydrogen [3]. Replacement of extractive distillation, cryodistillation and adsorption processes by membrane units may lead to vast energy savings [2,3]. In this context, ultramicroporous silica membranes, that is, silica membranes with pores smaller than 1 nm [4], appear to be able to play a determinant role. Indeed, in reason of their extremely small pore size, these membranes can be used as sieves to recover, for instance, pure hydrogen from gaseous mixtures, or to dehydrate ethanol and other fuels produced in biological processes. Moreover, they can be fabricated by a facile procedure, they are more thermally, chemically and mechanically stable than their organic counterparts and they commonly show higher permeate fluxes than zeolite membranes.

Ultramicroporous silica membranes typical typically an asymmetric structure, consisting of few millimeters thick macroporous tubes or disks, which confer mechanical strength to the membrane, and one or more mesoporous intermediate layers with subsequently smaller pore sizes to provide a smooth deposition surface for the final ultramicroporous selective layer.This asymmetric structure has been developed in order to minimize the membrane thickness and thus to reduce the resistance of the membrane to the permeate flow.

This lecture will review the methods for the fabrication of ultramicroporous silica membranes [5-6] and the transport mechanisms occurring in the different membrane layers [5-7] including viscous flow, Knudsen diffusion and activated transport.

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OL12

MAGNETIC MOLECULES @ SURFACES

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ABSTRACT

Due to the wealth and the tuneability of their properties, molecular materials stand out as a possible answer to the needs for innovative technologies. The ensemble of magnetic molecules constitutes a rich playground for chemists and physicists toward the development of novel molecular based devices also because of this possibility to finely tune the device properties through proper design of the molecular structure and the assembling of established building blocks following a rational design. This idea explains the huge efforts of *molecular magnetism*[1] community in the exploration of the use of magnetic molecules for the development of novel devices for the information and computation technologies including spintronics and quantum computation. However a migration from classical materials to future molecular-based devices requires a careful evaluation of the chemical and physical properties of those *fragile* magnetic systems after that nanostructuration processes have been attempted. A multi-technique approach including X-rays absorption-based spectroscopies become fundamental for the verification that chemistry of molecules and their magnetic features survives to the extreme conditions occurring in single-molecule-device-like environments. Going beyond a morphological characterization allowing to “see” isolated molecular objects, intactness of molecules can be evaluated by using surface sensitive techniques including mass spectrometry and photoelectron spectroscopies that provide a complete overview of the chemical and electronic properties of those systems. X-ray circular magnetic dichroism (XMCD) experiments lead to fundamental steps forward in this demanding exploration by directly accessing to static and dynamic magnetic properties of those systems down to the nanoscale.
Molecules showing slow relaxation of the magnetisation, known as single molecule magnets (SMMs) [2–4], and temperature and light switchable molecular systems like Valence Tautomers (VT) [5]and Spin Crossover compounds (SCO) [6] can be assembled on surfaces by adopting wet-chemistry approaches or sublimating them using high vacuum compatible techniques. Only the combination of several characterization tools allows to demonstrate that their magnetic behavior can be maintained, lost or enhanced by the interaction with surfaces.

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Molecules@Surfaces at work:
reactivity

Molecules@Surfaces at work: reactivity

OL13

HETEROGENEOUS CATALYSIS: SURFACE REACTIONS INVESTIGATED BY IR SPECTROSCOPY

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ABSTRACT

The nature and main aspects of *operando* infrared spectroscopy will first be summarized. Relevant reviews are in refs [1-3]. An example of spectroscopy inside a working catalytic monolith will be presented., showing the ultimate way for real operando, but also showing that similar results can be obtained with a self supporting wafer in the reactor-cell [4].

The detection of reaction intermediates might need very special ways to approach the catalytic reaction. By using conditions halfway between static *in situ* and *operando* spectroscopy, short-lived intermediates can be monitored at the nanosecond with step-scan Fourier transform infrared spectroscopy, triggering the reaction with ultra fast lasers [5].

Infrared spectroscopy is very versatile, and the technique can fairly easily be applied to various experimental conditions and to various types of heterogeneous catalysis. A new setup for looking at the surface of the catalyst during photocatalytic reactions will be presented [6-7]. The way the reactor can be used to study the influence of the reaction conditions will be shown. Surface species monitoring during the reaction shows the complexity of the reaction mechanism. Isotope transients kinetic analysis (SSITKA) evidenced the detailed surface reactions, and the role of the various formates and methoxy species in methanol photo-oxidation [8,9].

High time-resolved FTIR can be applied to electronically controlled surface reactions, such as in cold plasma assisted heterogeneous catalysis [10]. Cold plasma can be used for the preparation or post-treatment of the catalyst [11,12], and operando FTIR gave the clue about the real active species in plasma assisted processes [13]. FTIR gave the first evidence for the real role of the solid catalyst in such plasma-assisted reactions, and showed the details of the VOC plasma-assisted oxidation on alumina [14].

In the second part of the lecture, a new experimental tool for in situ measurement of the sample mass in the *operando* IR catalytic reactor-cell will be shown (AGIR, for Analysis by Gravimetry and IR) [15]. It showed the intermolecular perturbations between adsorbed probe molecules (water and ammonia) in the pores of zeolites. AGIR is the ultimate answer for the quantitative question in IR spectroscopy of adsorbed species on powders. It was used to check the influence of pelletisation on the quantitative measurements, and to assess the validity of Beert-Lambert law for adsorbed species on self-supporting wafers of catalysts [16]. The sensitivity and power of the new approach allowed the differentiation and determination of adsorption energies of small alkanes in zeolites, separating van der Waals and H-bonding inside the pores [17].

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OL14

BIOMOLECULES, SMALL AND LARGE: CONSEQUENCES OF ADSORPTION ON REACTIVITY

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ABSTRACT

Many studies have been devoted to the adsorption of biomolecules on solid surfaces and the topic has been treated in a previous course in this School. The next question one is naturally led to ask is whether biomolecules can be made to "work" in this strange environment, so different from the intracellular conditions.

Several attempts have indeed been made to investigate this possibility. First, enzymes, which are the workhorses of cellular machinery, have been immobilized on both flat surfaces and porous materials, in the aim of combining the advantages of heterogeneous and homogeneous catalysis. [1]

Second, the highly specific molecular recognition by molecules of the immune system, namely antibodies, has also been transferred to the realm of surfaces. Antibodies have a very high specificity for the corresponding antigen, and may therefore be used as highly sensitive sensors for the antigen molecule if they are integrated in a detection device. [2]

These two domains of application have many common points since both enzymes and antigens are based on proteic chains. Efficient pathways have been devised to chemically anchor these chains on a surface previously modified by functionalization: in both cases the molecule of interest is "tethered" to the surface by a chemical rope, and its working environment is an aqueous solution.

Another field of application is the prevention of biofouling of materials: indeed living organisms, e.g. animals and plants, have developed efficient strategies to prevent the colonization of their surfaces by pathogens and/or destroy them if they do reach the surface. They can be mimicked to protect inorganic materials surfaces, for instance in order to insure asepsis of medical devices. [3]

All of the previous threads of research attempt to transpose existing biochemistry by using well-known molecule, the role of the surface being mainly structural (to provide an attachment point). One may wonder if surfaces can act by themselves as a source of quasi-biological structuring. This line of investigation is more exploratory, and often connected to studies of the Origins of Life, where "surface scenarios" for complexity building have been proposed for a long time. [4]

In particular, it has been observed that oxide and clay surfaces are able to promote the condensation of biological monomers (amino acids, nucleotides) to the corresponding polymers (proteins, and RNA respectively), [5, 6] which might solve a major problem in the emergence of life from simple molecules. The role of the mineral surface is both thermodynamical and kinetical (catalysis and condensation reactions), and can be investigated from a "surface science" perspective. Furthermore, some substrates seem to be able to promote the formation of higher-level structures such as sheets and helices in peptidic chains. [7]

In addition, adsorption can also promote the formation of supramolecular assemblies of amino acids and peptides. [8]

Each one of these applications is crucially dependent on the details of the biomolecule adsorption mechanism and progress in surface biochemistry hinges on the development and refinement of *in situ* surface characterization techniques for both planar surfaces and divided matter (nanoparticles).

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OL15

WHEN SOLIDS MEET LIVING MATTER: THE COMPLEX INTERPLAY BETWEEN WEAK AND STRONG MOLECULE-SURFACE INTERACTION

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ABSTRACT

Blood cells on a glass container, lichens on a rock, osteoblasts on a hip replacement prosthesis, quartz particles in body fluids, fungi and bacteria on a graphene sheet, asbestos fibers within the lung, nanoparticles delivering drugs in defined body compartments, cell adhesion to crystal faces, … Just a few cases in which some very relevant and specific “chemistry” takes place at the biointerface between the surface of a solid and fluids, cells, tissues.

In all cases Van der Waals forces will be established between the two entity, mainly involving dispersion forces, but often also hydrogen bonding. Because of the aqueous environment of any living organism, water molecules will always be present at the surface, at least on the hydrophilic parts of it. Sometimes chemical bonds may develop linking biomolecules to the solid surface where surface reactions may take place, with consequent modification of the biomolecule features or release of potentially toxic moieties. All the molecules free to move at the interface will compete with the others, including water, for surface bonding. Bigger molecules will eventually displace the smaller ones. At the end a complex interplay will be established with the solid surface partially irreversibly covered by fluids components and other small and large biomolecules in dynamic equilibrium. In the specific case of nanoparticles in body fluids such equilibriums has been defined as protein corona.

We will describe some of the cases listed above and will discuss in detail the following points

- oxidative stress caused by a foreign body
- adsorption of proteins from body fluids
- coordination chemistry at the basis of lichen colonization of rocks
- red blood cells haemolysis and the specific role of surface functionalities

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Molecules@Surfaces at work:

Heterogeneous catalysis at industrial level

OL16

PROBING CATALYSIS ON SUPPORTED METAL NANOPARTICLES

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ABSTRACT

Catalysis is an important phenomenon for the chemical industry [1, 2]. In particular, heterogeneous catalysis allows to convert raw materials into valuable chemicals and fuels and to treat pollutants.During catalyst development as well as during catalyst production, catalytic performance has to be evaluated. Chemisorption [3, 4, 5], representing the bases of catalysis, is the first method to be used to assess the metal surface area available to reactants for catalytic process to take place. Moreover, the real catalytic effect of metal nanoparticles can be evaluated through a proper catalytic test [6, 7, 8]. This can almost strictly reproduce or just mimic a real industrial catalytic reaction. In any case a catalytic test allows to determine the reaction rate (activity) as well as selectivity towards the wanted product. A relationship exists between catalytic activity and metal surface area or dispersion in that the higher the latter, the higher the former. When this relation is violated it means that some phenomena is taking place such as pore diffusion, modification of active sites (e.g. poisoning), etc. A convenient method in comparing catalytic performances of different catalysts is to use the turnover frequency (TOF) [9] which combines catalytic activity and chemisorption results.

Examples of chemisorption and catalytic test (liquid-phase hydrogenation) will be given for supported metal nanoparticles and in particular for Pd [10, 11] and Pt supported catalysts.

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OL17

MOLECULES @ INDUSTRIAL SURFACES…
…MOLECULAR DYNAMICS IN CATALYSTS FOR SULFUR CHEMISTRY

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ABSTRACT

Two examples of highly complex and dynamic catalyst systems for sulfur chemistry will be discussed: the first example concerns the structural transformations occurring during the generation of active MoS_2-based hydrotreating catalysts, while in the second part of the lecture we will shed some light on the chemistry of V_2O_5-based SO_2 oxidation catalysts.

As a catalyst producer, Topsøe is continuously striving to extend the competencies and fundamental understanding within environmental catalysis. This knowledge enables us to rationally design new, improved catalysts and to move the boundaries for industrial hydrotreating and sulfuric acid catalyst performance, in order to aid the industry in meeting increasingly more stringent regulations for SO_2 emissions.

In order to look directly at the state of the working catalysts, we have recently introduced new advanced in situ techniques including e.g. Raman, infrared and electron energy-loss spectroscopy as well as high resolution electron microscopy to directly resolve the dynamic state of catalyst samples interacting with reactive gas mixture at temperatures up to 600°C.

Such in situ observations are of vital importance because catalysis is a surface phenomenon and because surfaces tend to restructure to adapt to the surrounding gas environment. Strictly speaking, the catalytic active state is only present during catalysis. Information about surface structures and dynamics under conditions mimicking those encountered during catalysis is therefore utmost important to further improve the understanding of structure-sensitive functionality and properties in catalysis.

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Molecules@Surfaces and quality of life

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OL18

SURFACE SCIENCE AND TRANSLATIONAL MEDICINE

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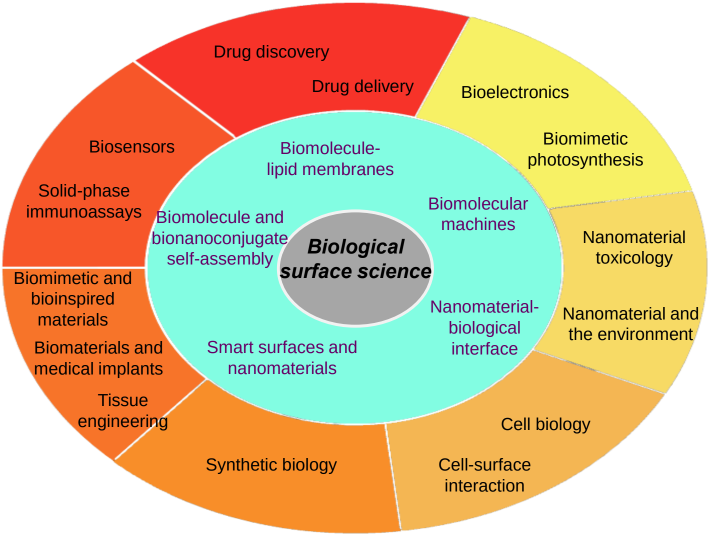
ABSTRACT

Less than fifteen years ago Bengt Kasemo hinted: “It is likely that the symbiosis with biology/medicine will be as important for surface science for the coming thirty years as the symbiosis with semiconductor technology, catalysis and materials science have been in the past thirty years” [1]. His vision appears more prophetic than ever today, when life science is among the most lively and promising fields of surface science (and vice versa). One may name this area biological surface science and think about it as the branch that deals with “pure” biological surface systems as well as “hybrid” biological-inorganic interfaces, on the typical length scales of molecules, membranes and cells.

The primary basic and applied subjects that orbit biological surface science can be framed in the “galaxy” reported in the figure [2]. The lecture proposes a walk along two paths across such galaxy (and a bit beyond), which show how fundamental research in surface science can be translated into effective applications in biomedicine. By the first path we will see how some vintage thermodynamics of colloids and interfaces [3] offers a simple and effective platform for general understanding of energetics of surface confined biomolecules, which can be put into action (for example) to better understand cell signaling [4], to realize universal probes for designer drugs [5] or to contribute to epigenetic research.

The second, narrower path starts from basic research on the multiscale interaction of inorganic nanoparticles with model membranes [6] and goes straight to its application in purification of exosomes [7] and subsequent clinical exploitation in Multiple Myeloma assessment [8] (exosomes are nanovesiclesof 30-150 nm in size which are secreted by cells for intercellular communication). Hope you will enjoy the trip.



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SOFT MATTER AND COLLOIDS FOR THE CONSERVATION OF CULTURAL HERITAGE

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ABSTRACT

Works of art and artifacts that constitute our cultural heritage are subject to deterioration. Their surfaces interacting with the environment are the most prone to aging and decay; accordingly, soiling is a prime factor in the degradation of surfaces, chemical and mechanical degradation are often associated to soiling and lead to the disfigurement of a piece of art. The effects of these processes are usually strongly amplified in the presence of protective coatings (mainly acrylic and vinyl polymers), applied in previous restoration treatments. We pioneered the synthesis and the application of several advanced systems for the consolidation and the cleaning of works of art, as hydroxides nanoparticles, microemulsions and chemical/physical gels. All these systems constitute a new platform for Conservation of Cultural Heritage and are characterized by scale lengths below 100 nm in one or more dimensions, making neutrons and x-rays the primary tool for the investigation and the tailoring of these systems to the final application. Scattering techniques played a major role in the development of new palette of materials for the conservation, as microemulsions, physical and chemical gels, magnetic gels and microemulsion confined in responsive gels. In this talk examples from self assembled systems for the cleaning or the removal of coatings from pictorial surfaces will be highlighted. Micellar solutions and microemulsions constitute very efficient systems for the removal of acrylic, vinyl and alkyd polymers or grime/soil. These systems (as well as neat solvents used in "traditional" conservation) can be confined into chemical and physical gels having proper nano-domains for the upload or the delivery of compounds from/to the work of art. For example, a fine control of the cleaning procedure can be obtained even for challenging cleanings as water sensitive works of art, where the cleaning can be achieved by using water confined into gels, leaving no residues on the works of art.

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OL20

BUILDING CAREER AND FUNDING OPPORTUNITIES FOR YOUNG SCIENTISTS

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ABSTRACT

The course is designed to provide young researchers with practical tips about how to raise the academic profile and where to find research funding opportunities.

It will focus on:

1) Career management
    a) Planning the professional development post-PhD life (skills to be acquired or improved to be ready for the next step)
    b) Building-up the career opportunities (scientific networks, teaching activities, awards, visiting abroad etc.)
    c) Creating effective CVs to apply to research positions (e.g. ERC Starting template)
2) Finding career opportunities
    a) Where to find a Post Doc
    b) How to propose you own project idea
    c) How to apply for a Post Doc

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