



Surface Science Prospectives

Surface chemistry at the liquid/solid interface

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ABSTRACT

In this Prospective, a critical overview is provided on the status and future of the analytical techniques available for the study of chemistry at liquid/solid interfaces. A number of spectroscopies already available are identified, including infrared absorption, surface-enhanced Raman (SERS) and sum frequency generation (SFG) to obtain vibrational information, and second harmonic generation (SHG) and X-ray absorption (XAS) to provide electronic details of surfaces and adsorbates. X-ray scattering and X-ray diffraction techniques are also used for structural characterization, and surface plasmon resonance (SPR) and quartz crystal microbalance (QCM) to follow adsorption uptakes and kinetics. Finally, optical and scanning microscopies add a spatial dimension to these studies. Overall, a number of surface-sensitive techniques do already exist to address chemical issues at liquid/solid interfaces, but those are still limited, and have perhaps not been exploited to their fullest yet. There is also a need for more cross collaboration among different research communities, and for new and clever developments to augment the toolbox of liquid/solid interface characterization.

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The development of new ways to investigate liquid/solid interfaces at a molecular level is perhaps the next big challenge for the surface-science community. Liquid/solid interfaces are prevalent in nature, and central in many chemical processes, in catalysis, electrochemistry, corrosion, lubrication, environmental science, mineral chemistry, materials science, analytical chemistry, and biological systems, among others. Because they involve two condensed phases, liquid/solid interfaces are in general difficult to interrogate. Many of the modern surface-sensitive techniques available for the study of vacuum/solid, or even gas/solid, interfaces, rely on the use of particles, mainly electrons, ions and atoms, and the strong interactions of those particles with liquids and solids, what makes these techniques surface-sensitive, prevent them from been useful in liquid/solid systems. The alternative is to use spectroscopies based on electromagnetic radiation, light in particular. However, those are, in general, not surface-sensitive; the challenge in this case is to extract information about the minority of atoms or molecules at the interface from the much larger signals originating from the bulk liquid and solid phases. Stated this way, the problem may seem hopeless. Nevertheless, much progress has already been made on developing ways to study chemistry at liquid/solid interfaces. The state-of-the-art of this field is briefly surveyed below. A summary of the main spectroscopic techniques used for the characterization of liquid/solid interfaces is also provided in [Table 1](#).

Perhaps the most common technique used for the characterization of molecules at liquid/solid interfaces is infrared (IR) absorption

spectroscopy. IR absorption spectroscopy is quite versatile and cheap to implement, and provides vibrational information, which is very sensitive to bonding, to local chemical environments, and to structural details at a molecular level. Most IR studies of liquid/solid interfaces have been carried out in attenuated total reflection (ATR) mode, where surface sensitivity is defined by the penetration depth of the evanescent wave that projects into the environment outside the ATR prism, about 1–2 μm [1,2]. Many investigations of liquid/solid interfaces using ATR have involved the surface of the prism itself, but extensions to other thin films, typically of metals, deposited on that surface, and to powders or nanoparticles placed in liquid suspensions in contact with the prism, have also been implemented. The use of ATR infrared absorption spectroscopy for the study of liquid/solid interfaces has a long history already [3], during which that technique has provided valuable insights into problems related to adsorption [4], catalysis [5], reactions on mineral surfaces [6], environmental issues [7], materials science [8], and the development of biosensors [9].

Although less popular, other arrangements have also proven to be viable for the use of IR spectroscopy to probe liquid/solid interfaces. For instance, reflection–absorption IR (RAIRS, or IRRAS) cells were developed some time ago for the characterization of adsorbed species on electrodes [10–13]. Surface discrimination in these setups can be obtained by either modulating the applied voltage to the surface or the polarization of the incident light. Surprisingly, though, only simple adsorbates have been studied this way to date, perhaps because of difficulties associated with the sensitivity of the technique. We [14–22] and others [23] have recently extended the use of RAIRS to problems involving liquid/solid interfaces of relevance to catalysis. IR

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Table 1
Summary of spectroscopic techniques available for the characterization of liquid/solid interfaces.

Technique	Main information	Typical sample	Highlights	Limitations
<i>Vibrational</i>				
IR absorption	Vibrational, mostly on adsorbates	Various	Quite versatile; cheap; extensively used	Non-zero background; limited sensitivity
Raman scattering	Vibrational, mostly on adsorbates	Rough; requires Ag, Au	Complementary to IR; widely available	Weak signal, better with surface enhancement
Sum frequency generation (SFG)	Vibrational, mostly on adsorbates	Flat; reflective	Surface discrimination; high sensitivity	Difficult; quantification not straightforward; limited frequency range
<i>Electronic, Acoustic</i>				
UV-Visible absorption	Electronic	High surface area solids	Easy to quantify, follows Beer's Law	Low resolution; interference from bulk
Fluorescence emission	Electronic	Requires fluorophore	Potential for time resolution	Limited information
SHG	Electronic; adsorbate coverage	Flat; reflective	Surface discrimination; high sensitivity	Difficult; quantification not straightforward
Surface plasmon resonance (SPR)	Adsorbate coverage	Flat, requires metal film with strong plasmons	Easily extended for spatial resolution	Limited information
Ellipsometry	Film thickness	Flat	Fast; easy	Quantification requires modeling
Quartz crystal microbalance (QCM)	Mass changes; adsorbate coverage	Flat; quartz crystal surface	Easy	Viscous damping by liquid phase
<i>X-ray, neutron</i>				
X-ray absorption (XAS); emission (XES)	Electronic; local structure	Varied; high surface area	Information for each individual element	Requires synchrotron source; No surface discrimination
X-ray scattering; diffraction	Structural, typically for the solid	Crystalline; flat	Surface sensitive	Very difficult; requires synchrotron source
Neutron scattering	Structural; vibrational	High surface area	Detects hydrogen	Very difficult; requires neutron source
<i>Other spectroscopies</i>				
X-ray photoelectron spectroscopy (XPS)	Electronic, chemical (oxidation states)	Various	Surface sensitive	Not easily adaptable to liquid/solid interfaces
Nuclear magnetic resonance (NMR)	Chemical; structural	Various	Quite versatile, many elements and pulse sequences available	Low sensitivity; not surface sensitive; low resolution in MAS mode
Electron spin resonance (ESR, EPR)	Chemical	Paramagnetic	Sensitive to radicals and solid defects	Difficult; no surface sensitivity
<i>Microscopies</i>				
Optical	Spatial inhomogeneities	Flat; thin	Useful for bio-assays	Low resolution; no molecular information
Scanning (STM; AFM; SECS)	Structural; topography	Flat; conductive for STM	Atomic resolution; possible local electronic information	No elemental information; interpretation not straightforward
Optical scanning (near-field, NSOM)	Spatial inhomogeneities	Flat; thin	Useful for bio-assays; possible single molecule detection	Low resolution; no molecular information
Electron; added energy dispersive X-ray spectroscopy (EDX)	Shape; structure element distribution	Varied	Straightforward	Not easily adaptable to liquid/solid interfaces

spectroscopy can also be performed in transmission mode, but such arrangement is not as well suited for liquid/solid interfaces; only a few examples of this approach are available to date [24,25].

Vibrational data on chemical species at liquid/solid interfaces can also be obtained by other optical spectroscopies, surface-enhanced Raman (SERS) and sum-frequency generation (SFG) in particular. Both those techniques use powerful lasers, which may damage the samples, but rely on visible or ultraviolet light, which allows for single-photon counting, a way to increase sensitivity. In the case of SERS, surface enhancement requires the use of rough surfaces and either gold or silver, the reason why most of the initial work with that technique was on the adsorption of organic molecules on those metals [26–28]. Nevertheless, by electrodepositing other metals on top, it has been possible to extend the use of SERS to other systems [29,30].

SFG is a more sophisticated technique that relies on the up-conversion of IR photons with a second laser into the visible energy range. Because SFG is dependent on the second-order susceptibility of the sample, signal is only generated from non-centrosymmetric media such as interfaces, a fact that leads to exquisite discrimination against any interfering signals from the isotropic bulks. SFG experiments are non-trivial to setup and can only cover the frequency

range available to IR lasers, but can provide rich information on both the nature and the geometrical orientation of adsorbed species complementary to that from IR and/or Raman. Interesting reports can already be found in the literature on the molecular characterization by SFG of liquid/solid interfaces relevant to electrochemistry [31,32], the adsorption of surfactants [33,34], chemistry on mineral surfaces [35], and biological systems [36,37]. By using specific light polarizations, geometrical information can be extracted from SFG data as well [38].

Information about the electronic structure of molecules can be extracted from optical spectroscopies reliant on the use of high-energy photons, from the visible to the X-ray range. For instance, second harmonic generation (SHG), a simplified version of SFG where both photons are provided by the same visible-light laser [39], can be used to probe electronic transitions in situ at liquid/solid interfaces [40] and to extract chemical properties such as acidity [41] and interfacial potentials [42]. X-ray absorption around the energies of core-level electrons can also be used to identify specific electronic states on interfacial atoms. This latter technique, known as either X-ray absorption near-edge spectroscopy (XANES) or near-edge X-ray absorption fine structure (NEXAFS), is not intrinsically surface-sensitive, and also requires the use of tunable X-rays. Nevertheless, with

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