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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.

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 evanescence 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
Vibrational				
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
Electronic, Acoustic				
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
X-ray, neutron				
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
Other spectroscopies				
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
Microscopies				
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 the opening of multiple synchrotrons around the world in recent years, some insightful reports have been coming out on the characterization of liquid/solid interfaces with NEXAFS to address problems of catalysis [43], electrochemistry [44], corrosion [45], crystal growth [46], and mineral chemistry [47]. Electronic spectra are in general less informative than vibrational data, but can still be used to follow adsorption and reaction kinetics as well as chemical changes at liquid/solid interfaces.

The availability of intense X-ray sources has also afforded the development of scattering and diffraction techniques to provide structural information, mostly about the solid surface but in some instances also about adsorbates. Surface sensitivity in those cases is attained by measuring X-ray reflectivity or by using small scattering arrangements. For instance, information about surface bonding has been extracted from in-situ X-ray reflectivity and X-ray standing-wave measurements on the adsorption of small cations from aqueous solutions onto titania [48]. X-ray scattering has been used to follow self-assembly dynamics [49] and weight fluctuations [50] in lipid bilayers, and also the growth of nanoparticles from solution [51]. Surface X-ray diffraction (SXRD) studies have proven useful in dynamic measurements of electrochemical reactions [52]. Additional local structural information can be extracted from extended X-ray absorption fine structure (EXAFS) experiments [53]. Neutron scattering can in principle be used to characterize buried interfaces as well, but those experiments are much more difficult to carry out, and require access to one of only a limited number of neutron sources available worldwide. The study of lipid/polymer assemblies to understand hydrocarbon chain packing, structural changes due to head group modification, and water penetration [54] provides a nice example of the potential of neutron scattering for structural characterizations in liquid/solid interfaces.

Other optical techniques can be used to follow the thermodynamic and kinetic behavior of adsorption processes, even if they may not provide the type of detailed molecular information available with the spectroscopies discussed above. One often-used technique in this category is surface plasmon resonance (SPR), which has been incorporated in the design of multiple bioassays [55–58]. Another common optical technique used for the characterization of liquid/solid interfaces is ellipsometry, typically as a way to follow adsorption kinetics and film thicknesses with surfactants [59] and biological systems [60]. Both SPR and ellipsometry monitor the refractive index of the phases involved, and can also yield information on other interfacial properties such as morphology, crystallinity, chemical composition, and electrical conductivity. A new development in ellipsometry is the use of infrared light to improve contrast and to add molecular specificity [61].

Adsorption uptake information can also be obtained by using instruments based on mass-sensitive resonators that work with acoustic waves. The best known of these devices is the quartz crystal microbalance (QCM). QCM has a long history in other fields, but their use to characterize liquid/solid interfaces had to wait for the development of the high-gain oscillator circuits needed to overcome the damping of oscillation due to the extra load from the liquid phase. There are nice reviews available already on the use of QCM for the study of the uptake of polymers [62] and biological molecules [63,64] on surfaces from liquid phase. The performance of QCM is comparable, and sometimes complementary, to that of SPR [65].

Other techniques may in principle be amenable to the study of liquid/solid interfaces even if they have not been fully developed for this purpose yet. The particular case of nuclear magnetic resonance (NMR) comes to mind. NMR is not intrinsically surface-sensitive and also quite insensitive in general, but it is also very versatile, and has been adapted to studies in many other areas of chemical research [66]. A few examples do exist on the use of NMR to issues of adsorption at liquid/solid interfaces [67–70], but much more should be possible. There have even been reports where NMR has been used in imaging mode (MRI) to follow the spatial distribution of reactions inside the pores of high-surface-area catalysts [71]. A cousin of NMR, electron spin resonance (ESR, also known as electron paramagnetic spectroscopy, EPR), is significantly less common in general, but has also been employed to look at the structural changes of surfactants during adsorption [72], the behavior of polymer surfaces [73], the dynamics of bilayers and membranes in biologically relevant systems [74,75], and in catalysis [76]. ESR does require the presence of paramagnetic centers, which are often added purposely as labels to the functionality being studied.

Some surface-sensitive techniques are not naturally suited for the investigation of liquid/solid interfaces but can be made useful by proper adaptation. These include the electron-based spectroscopies that have been so powerful in modern surface science [77–80] and that have been recently modified to sustain non-vacuum environments. Those modifications are mainly being implemented to study gas/solid interfaces, but may, in particular cases, be extended to liquids as well. For instance, in a recent study, the segregation of anions toward the surface of solid ionic salts upon their contact with water was nicely established using X-ray photoelectron spectroscopy (XPS) [81]. Transmission electron microscopy has also been used to follow the growth of solids from the liquid phase [82]. These developments are promising, and may entice others to design equally clever arrangements to address other liquid/solid interfaces.

Finally, there are techniques available already to obtain spatial resolution on the chemistry of reactions occurring at liquid/solid interfaces. These include optical microscopies, which can be used to image liquid/solid interfaces [83,84]. The resolution available in regular optical microscopies is limited by the wavelength of the light used, which is on the order of tens of nanometers at best; that is too low to provide molecular resolution. Nevertheless, isolation of individual events can be accomplished via dilution of the adsorbed layer. Many lab-in-a-chip and other sensors have been designed based on this approach [85]. Fluorescence microscopy has also been extended to studies in catalysis [86,87]. In fact, the establishment of structure sensitivity of particular reactions and the identification of single sites for catalysis has been possible using an optical microscopy approach [88–90]. Other regular optical techniques mentioned above, including Raman scattering and SPR, can also be implemented in microscopy mode. An example with SFG is that where spatial variations of the reaction of cyanide ions were followed across a gold surface [91], and a second case using SHG involved the study of image membrane potentials in neurons [92].

Higher spatial resolution can be obtained with scanning probes. By scanning a tip in close proximity to the surface, at distance a few tens of nanometers away, scanning near-field optical microscopy (SNOM) can increase resolution to values on the order of ~50 nm in diameter [93]. An apertureless version of SNOM can even identify features of sizes around 10 Å [94]. Scanning tunneling microscopy (STM) provides an even higher resolution, all the way to the detection of individual atomic features at the interface, and has been used for the study of several liquid/solid systems, mostly in connection with the formation of nanoporous networks on surfaces [95,96] but also for catalysis [97] and electrochemistry [98]. An added advantage with STM is that the tip can be used as an electrode to perform scanning electrochemical microscopy (SECM) [99], or to carry out chemical manipulations on adsorbed molecules [100]. It should be noted that STM maps electronic, not atomic, distributions, and require the use of conductive solids. It is also more difficult to obtain atomic resolution with STM when a liquid is present in contact with the solid. An alternative to STM is atomic force microscopy (AFM), where forces instead of tunneling currents are used to obtain topographic images of the interface. It has been in general much more difficult to obtain atomic resolution with AFM than with STM, but that is starting to change [101]. AFM can also be used to measure forces down to the magnitude of individual molecular interactions, and with that to characterize individual molecular interactions such as hydrogen bonding [102].

In summary, there are a number of techniques already available for the characterization of liquid/solid interfaces. They range from spectroscopies able to provide detailed vibrational and electronic information on adsorbates to scattering and diffraction techniques to extract structural information on the interface itself and other techniques capable of providing means to quantitatively follow changes in adsorption and surface composition. Moreover, both optical and scanning microscopies can add spatial information to the behavior of heterogeneous interfaces. Nevertheless, in most cases, these techniques can only offer a limited picture of the chemical processes that occur at liquid/solid interfaces. For one, not all techniques are suitable to address all problems. In addition, a preference seems to have developed over time for the use of certain analytical tools in the study of liquid/solid interfaces associated with specific areas of chemistry. For instance, RAIRS was initially extended to liquid/solid interfaces by the electrochemistry community, but have been rarely used in the characterization of other liquid/solid systems. SPR and QCM have been particularly popular in the design of bioassays, but are not as commonly used for other areas where the measurement of adsorption isotherms and kinetics is needed. Most of the STM work published to date involving liquid/solid interfaces focuses on supramolecular self-assembled monolayers. X-ray diffraction has primarily been used for studies in electrochemistry and in nanotechnology. Perhaps research in liquid/solid interfaces could benefit from a greater interaction across these and other subdisciplines.

There is also ample room for the development of additional instrumentation and techniques for liquid/solid interface characterization. The particular example of NMR, a spectroscopy that is extremely useful in other areas of research but has not yet made a significant impact in the characterization of liquid/solid interfaces, is quite telling. Also, the recent extension of the ultrahigh vacuum-based surface-sensitive techniques to uses in non-vacuum environments is encouraging, and will hopefully be extended to address liquid/solid interfaces in the near future. Liquid/solid systems can certainly benefit from the incorporation of more young scientists into the relevant fields of research.

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