

VIBRATIONAL SPECTROSCOPY AT SURFACES AND INTERFACES USING SYNCHROTRON SOURCES AND FREE ELECTRON LASERS

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1. INTRODUCTION

A detailed description of the inter-atomic interaction determining the structure and dynamics at clean and adsorbate-covered surfaces is one of the most fundamental topics in surface science. It is of paramount importance in any attempt to understand the many microscopic scale phenomena involving interfacial processes such as adsorption, desorption, diffusion, friction, lubrication, epitaxial growth, catalysis and electronic properties. Among key understanding are the bonding characteristics between molecules and surfaces, the structure of the adsorbed layer, and the dynamical aspect of the interaction between the adsorbate and the substrate. Such information is now attainable by using a variety of different experimental tools with sensitivities on the order of a fraction of a monolayer ($\sim 10^{14}$ atoms/cm²).

Vibrational spectroscopy has been widely employed for the last 15 years for the determination of surface interaction and reactivity. It relies, primarily, on the fact that any molecule can be easily identified through its vibrational signature (often referred as its "fingerprint"). Indeed, surface chemical analysis has benefited greatly from the determination of the internal vibrational structure of adsorbate species. Most recently, these studies have been extended, using non-linear vibrational techniques, to encompass high pressure environments and even liquid

interfacial systems, allowing direct observation of chemical reaction pathways in environments of practical interest.

Notably, the majority of vibrational studies to date have been confined to the mid-infrared region ($\geq 600\text{ cm}^{-1}$), due to limitations in source intensity, detector sensitivity or the optical response of the substrate and other optical components (e.g. salt windows). Consequently, the low frequency substrate-adsorbate modes that contain a wealth of information about the potential energy surface of the molecule bound to the surface have not been studied in detail. The effective mass involved in the motion of the so-called "external" modes is usually significantly larger than for the intra-molecular vibrations, and the binding energy is usually less than the chemical bonds within the molecule, so that the frequency of these modes is generally much smaller than that of the internal modes, and typically spans the $20\text{-}1000\text{ cm}^{-1}$ spectral region.

Optical methods are, furthermore, of non-destructive character, and are capable of *in situ* remote sensing with high temporal and spatial resolution. One of the particularly unique aspects of optical techniques is the possibility of probing buried interfaces.

Recent advances in laser technology, and detectors [in particular the development of detector arrays of Charge-Coupled Devices (CCD) for Sum-Frequency Generation (SFG)] have allowed such techniques to reach the required sensitivity for surface studies. Similarly, for InfraRed Absorption Spectroscopy (IRAS), the use of synchrotron infrared sources and improvements in Fourier transform infrared (IR) instrumentation, have also afforded increased potentialities. As a result of these experimental advances, complex surfaces and interfaces (often close to those found in technologically relevant systems), can now be investigated over a wide spectral range, yielding unprecedented insight into the formation and thermal evolution of these systems.

This article is intended to focus on one hand on the description of laser-based and synchrotron vibrational-based spectroscopy techniques applied to surface and interface analysis, and on the other hand, on selected examples demonstrating the new scientific opportunities offered by these new sources.