

# INFRARED AND RAMAN SPECTROSCOPY AS AN EFFICIENT PROBER OF PHOTOCATALYTIC REACTION AT Ag SURFACE

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In the past decade, adsorption of molecular monolayers on metal surfaces has attracted tremendous research interest [1]. In addition to the fundamental interest in such metal adsorbate systems, practical considerations such as the modification of metal surfaces and the preparation of organic thin films have increased research activity in this area. On the other hand, organic molecule-derivatized metal nanoparticles have also attracted great research interest recently since particles with sizes in nanometers range may possess properties which are quite different from those of bulk material [2,3]. In particular, organic molecule-derivatized substances are readily soluble, isolable, and amenable to further functionalization so that applications for their use can be found in many areas of science and technology, including optoelectronics, chemical and biosensors, drug delivery, and catalysis.

In order to develop efficient, functional molecular devices by virtue of molecular monolayers on metal surfaces as well as organic molecule-derivatized metal nanoparticles, it is of prerequisite to build up our capability to analyze the adsorption and reaction characteristics of organic molecules on metal surfaces. In this respect, a large variety of techniques are now being used to characterize many different surface/interface properties. Among the several spectroscopic techniques developed for this purpose, vibrational spectroscopic techniques such as reflection-absorption infrared spectroscopy (RAIRS) and surface-enhanced Raman scattering (SERS) are most frequently used for obtaining information on structural details of adsorbates [4]. The sensitivity of SERS is remarkable, enabling routine investigation of adsorbates even at submonolayer coverages. SERS has, however, two noticeable disadvantages, namely that its applicability is limited to a few metals and that its unequivocal surface selection rule has not been established yet. On the other hand, the sensitivity of RAIRS is inferior to that of SERS, but the applicability of RAIRS is not limited to a few metals. Moreover, its metal surface selection rule demands that only those vibrational modes with a component of dynamic dipole moment perpendicular to the surface can be observed. Hence, the combination of SERS and RAIRS will be very useful in investigating the molecular adsorption on metal surfaces.

It is desirable that SER and RAIR spectra are taken for the same adsorbate/substrate system. However, RAIR spectra are usually taken for adsorbates adsorbed on flat metal surfaces while SER spectra are obtained either in metal-colloidal media or at roughened-metal electrodes. We have previously prepared a vacuum-evaporated silver film that enabled us to get the RAIR and SER spectra of 4-cyanobenzoic acid (4CBA) on silver simultaneously [5]; such a film was obtained by evaporating silver rapidly at  $10^{-3}$  torr on the chromium-coated glass slide. Recently we could obtain very high SNR infrared spectrum of 4CBA adsorbed on fine silver particles by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [6,7]. The