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A large variety of techniques are now being used to characterize many different interface/surface properties. Among them, the observation of vibrational spectra of chemical species provides one of the most incisive methods for understanding chemical and physical phenomena at interfaces and on surfaces. The fact that the vibrational modes of the molecule at interface and on surface retain much of their free space character permits species identification. The small deviations from free space behavior, such as in transition energies, linewidths, and split degeneracies, are the measured quantities that are used to ascertain both the local environment such as bond site or molecular orientation and the characteristics of the adsorbate-substrate interaction.

The most widespread surface vibrational spectroscopic techniques are infrared absorption spectroscopy, surface-enhanced Raman spectroscopy, electron energy loss spectroscopy, inelastic tunneling spectroscopy, neutron inelastic scattering, and atomic inelastic scattering. The purpose of this presentation is to review how FT-IR spectroscopy can be applied to the catalytic/interfacial and surface science research, referring to the spectra obtained in the author's laboratory.

**2. Instrumental**

The spectra were obtained by using the Bruker IFS 113v FT-IR spectrometer, equipped with global light source and liquid nitrogen cooled mercury cadmium telluride detector.

**3. Illustration of Spectral Measurement**

Depending on the sampling condition, four different methods, i.e. TR (transmission), ATR (attenuated total reflection), DR (diffuse reflection), and RA (reflection-absorption), were adopted in recording the infrared spectra of chemical species at interfaces and on surfaces.

**TR Spectra** : Essentially self-supporting materials such as films, fibers, rods, tapes, and pressed powdered-substances can be observed directly by the TR method. Based on this, we have investigated the adsorption behavior of acetonitrile on a silica-supported nickel surface.<sup>1</sup> It could be concluded that acetonitrile was adsorbed on the nickel surface by forming a  $\sigma$  bond via the nitrogen lone-pair electrons, but on the nickel oxide surface by forming di- $\sigma$  bonds with the nitrile carbon and nitrogen atoms following a parallel dehydrogenation of the methyl group of acetonitrile.

**ATR Spectra** : For internal reflection spectroscopy, it is only necessary to bring the sample in contact with or in close proximity to the surface of the internal reflection element (IRE) where the light is totally internally reflected and where the sample interacts with the evanescent wave. Based

on this, we have investigated the interaction of indolicidin, an antimicrobial tridecapeptide, with reconstituted model membranes anchored on an IRE.<sup>2</sup> The conformation of peptides in lipid membranes was concluded to change from a  $\beta$ -sheet to an  $\alpha$ -helix with admixed random coil structure.

**DR Spectra** : Diffuse reflectance describes light reflected from a matte surface. Diffuse reflectance spectrometry has several advantages over TR absorption spectrometry for characterizing species adsorbed on powdered adsorbent. Most importantly, loose powders can be sampled without the need for pressing them into pellets. Based on this, we have investigated the pyrolysis of lignite coal.<sup>3</sup> The increase of aromaticity factor with temperature was clearly evidenced from the C-H stretching region, demonstrating that the temperature and atmospheric effects on the physicochemical properties of powdered materials could be readily studied by interfacing the reflectance optics with a controlled environment reaction chamber.

**RA Spectra** : When light is reflected from a surface the electric vector of the incident light suffers a phase change on reflection which depends on the angle of incidence and the state of polarization of the incident light. Since the phase change of the perpendicularly polarized light on reflection from a typical metal is near  $180^\circ$  for all angles of incidence, the incident and reflected electric vectors very nearly cancel each other resulting in only a very small net electric field parallel to the metal. At small angles of incidence the phase change for the parallel light is near  $0^\circ$  and again the two electric vectors very nearly cancel. However, at larger angles of incidence, i.e. near  $90^\circ$ , the vector addition of the two electric vectors results in an electric field with a substantial component perpendicular to the metal. Based on the latter, we have obtained the infrared spectra of various organic molecules self-assembled on gold and silver surfaces. The adsorbed structures of 4-methoxy benzyl cyanide<sup>4</sup> and 1,2-benzenedithiol,<sup>5</sup> for instance, were evidenced to depend greatly on the kind of adsorbing metal substrates. In an electrochemical environment, the potential dependence of adsorbate structure could be examined also by the external reflection spectroscopy.<sup>4,6</sup>

#### 4. Concluding Remark

Besides the four methods described above, the photothermal spectrometry (photoacoustic spectrometry) and emission spectrometry can be applied also to the measurements of the infrared spectra of adsorbed species. In the standpoint of surface scientist, the RA infrared spectroscopy is the most effective tool to elucidate the molecular adsorption on clean annealed polycrystalline and ultimately well-defined single crystalline metal surfaces prepared under UHV conditions. Finally, the author hopes to emphasize that infrared photons do not exhibit the destructive nature of many other surface analytical techniques and more importantly do not require an ultrahigh vacuum.

#### References

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