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BOOK REVIEW

R. Aroca: Surface-enhanced vibrational spectroscopy:

Wiley, Chichester, 2006, 233 + XXV pp, 70.00£; ISBN 0-471-60731-1

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Spectroscopic studies of interfaces between adjacent phases are of the utmost importance in understanding structures and dynamics at these interfaces and within the adjacent interphases. Besides numerous other methods less frequently used (and, in most cases, more demanding in terms of equipment and know-hows) employing nonlinear optical effects (sum and difference frequency generation, second harmonic generation), the basic vibrational spectroscopies, infrared and Raman spectroscopies, have been the most frequently applied ones. This comes somewhat surprisingly, because both methods have inherent drawbacks particularly inconvenient during in situ investigations in electrochemical cells: Infrared spectroscopy is seriously hampered by the strong infrared absorption of most electrolyte solution constituents, in particular, of solvents like water, and Raman spectroscopy employs the inelastic scattering of light, which already has a very low yield (10^{-6}) with standard liquid or solid samples. Investigations of surfaces or interfaces deal with much smaller numbers of scattering species, further limiting the amount of scattered light, making the detecting very difficult. Despite these inherent limitations, both spectroscopies have been applied frequently with great success. In the case of surface Raman spectroscopy, this is mostly due to the surface enhancement observed with rough surfaces, and this is particularly strong with coinage metals (Cu, Ag, and Au). The method thus described has been established years ago as surface-enhanced Raman spectroscopy (SERS).

In recent years, surface-enhanced infrared spectroscopy (SEIRAS) has emerged as a powerful and widely applicable spectroelectrochemical method beyond the already firmly established SERS. Although the enhancement mechanisms of the latter method still seem to be the subject of further discussion, SERS (the author quite nicely calls it a moving target) has apparently moved into the family (this term appears most appropriately in the introductory section of the book reviewed here) of well-established methods, as it is not the subject of annual reviews anymore. Nevertheless, a critical report of these vibrational spectroscopies is certainly timely. The state of the art of SEIRAS has not been reviewed comprehensively so far. As both spectroscopies are closely related (in undergraduate education, both are treated almost as twins or as the two sides of a single coin), a book covering both methods seems to be a particularly rewarding approach, providing the possibility of highlighting common features associated with the surface-enhancement mechanisms.

The book reviewed here was prepared by an expert who is well known for his numerous contributions in dealing with these vibrational spectroscopies in their various forms. Obviously, it is this expertise that made the author start with a glossary of terms—quite helpful to avoid confusion in spectroscopists terminology.

The first chapter deals with the theory of molecular vibrations. Besides the already well known contents of students' textbooks, some details of calculations of vibration spectra are presented. These aspects are enhanced with respect to smooth surfaces and nanoscopic particles in the following chapter for both spectroscopies. The following part deals with the electromagnetic enhancement, somewhat misleadingly, it is named, simply, SERS. The second part of this moving target—the chemical enhancement effect—is treated in the next chapter. Details of SERS suggesting a molecular specificity are treated in a short chapter with respect to conceivable interdependencies between the type

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of molecule, surface, and wavelength of illuminating light. Not surprisingly, with respect to the author's background, the following larger part describes applications of surface Raman spectroscopies in chemical analysis. Despite the author's optimistic approach, the broader application in general analysis will depend strongly on the availability of affordable instruments. Recent advances in laser technology, small and rugged spectrometers and improved solid-state light detectors, are promising. The final chapter is dedicated to SEIRAS. A brief look back is followed by descriptions of all relevant details including numerous examples like those in the preceding chapters. This part looks somewhat short at first glance; taking into account the vast amount of literature on Raman spectroscopies, the relations are correct.

The book is well written, easy to read, and richly illustrated. Presumably, inappropriate software use has resulted in numerous rather fuzzy plots showing numerous types of gray instead of clear lines. This might have been avoided easily; it is, nevertheless, no argument that should keep anybody interested in surface-enhanced vibrational spectroscopies from buying the book. It is a must for all libraries associated with educational and research institutions dealing with interfacial spectroscopies, and the price makes it accessible even for the personal library of a researcher.