OPTICAL PROPERTIES OF SURFACES: RECENT ADVANCES

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The calculation of the spectroscopic response of solids to external electromagnetic fields may be decomposed into three steps: (1) the evaluation of the elementary excitation spectra described by Maxwell's equations plus the constitutive equations characteristic of linear media; (2) the computation of the interaction of these excitations with the incident fields; and (3) the solution of the boundary-value problem appropriate to the description of a given experimental apparatus. The presence and properties of interfaces in a system exerts only an indirect influence on spectroscopic responses associated with optical properties (e.g., reflectance and transmission spectroscopies, ellipsometry, Raman spectroscopy, plasma radiation excited by light). This influence is described by the theoretical models utilized in steps 1 and 3. Consequently, the optical properties of surfaces per se are inferred quantities which depend upon the model selected to analyze a particular set of observations.

Step (1) is the center of attention in our considerations. First, a brief review of the textbook description [1] of the electrodynamics of continuous media is presented. This is used as the basis for introducing the concept of a bulk polariton [2], i.e., an elementary excitation described by a transverse solution to Maxwell's equations in continuous media for which the energy in the electromagnetic wave is shared between the electromagnetic field and the polarization of the medium. Second, the influence of an interface on the polariton spectrum is illustrated for a planar interface between two dielectric media [1, 4]. New surface branches of the polariton spectrum appear. These branches are the dispersion relations of polaritons propagating along the interface but for which the electromagnetic fields are localized in the vicinity of the interface. Specifically, they are the bound state analogues of Brewster modes in the continuum [1, 5].

Consideration of the planar three-medium (sandwich) geometry is motivated by four recent developments: (1) the advent of integrated optics [6, 7], (2) the measurement of surface-polariton dispersion by attenuated total reflection [3, 5], (3) the reflection spectroscopy of adsorbed monolayers [8], and (4) the theory of Van-der-Waals forces in continuous media [9]. All of these areas of investigation require the evaluation of the polariton excitation spectra for asymmetric three-medium sandwiches. We review the salient features of these spectra and their utilization in these four areas [3-9].

An important extension of the three-medium sandwich is that in which one of the boundaries becomes diffuse as, for example, at the surface of an inhomogeneously doped semiconductor [10]. Thus, we present a brief discussion of the polariton spectra for an inhomogeneously doped polar semiconductor in contact with an inert dielectric medium at a planar boundary. A special limiting case of this model is the metal-vacuum interface [11, 12]. We conclude by examining the present status [13] of analyses of surface plasmon dispersion as a measure of the diffuseness of the electronic charge density at metal surfaces.

References

DISCUSSION

YEAGER. — We recognize the limited specificity of optical measurements to the interface and their dependence principally on bulk phase properties. Electrochemists, however, are pressed to find techniques with specificity to the surface and hence turn to optical methods. We are able to modulate the potential across the interface and should be able to make use of this to gain some surface specificity in optical studies of electrochemical interfaces.

DUKE. — In my judgement one must distinguish between two rather different types of application of optical measurements for surface characterization. In the first, these measurements are used as a fingerprint to identify surface species (or even structures) on a strictly empirical basis. The desired identification is based upon empirical correlations between a particular spectral feature (e. g. Raman line) and a property of the interface (e. g. the presence of an adsorbed ion). An analogue in surface science is the use of Auger spectroscopy as a measure of surface composition. In this sense, there is little doubt that electrochemical interfaces (see, e. g. Dr. Kruger's lecture in this colloque). In my lecture, however, I addressed a rather different topic: the use of optical techniques to yield a microscopic characterization of physical phenomena in the interfacial region of solid-liquid boundaries. This is a rather more difficult task for optical methods, because of the long wavelength of light (\( \lambda \approx 5 \text{ 000 } \text{Å} \)), relative to the thickness of a microscopic surface region (\( d \approx 5 \text{ Å} \)). Moreover, it is fraught with ambiguities because of the necessity of distinguishing manifestations of bulk and surface phenomena in any particular measurement. Given the long wavelength and generally large (\( d_{\text{opt}} \approx 500 \text{ Å} \)) penetration depth of electromagnetic radiation, the resultant lack of specific sensitivity to surface phenomena relative to bulk (or space-charge) phenomena is a serious and intrinsic barrier to the use of optical phenomena as a primary probe of surface properties (see, e. g. DUKE, C. B., Adv. Chem. Phys. 27 (1974) 1 for a more detailed discussion of this topic). It is this fact, plus the ambiguities intrinsic in subtraction procedures to separate surface from bulk optical phenomena, which I emphasized in my lecture. It seems worth noting in this context that no paper presented at this colloque provided a counter example to the conclusions stated on the final vu-graph of my lecture (the closest approach to achieving this objective being the lecture of H. Luth).

SASS. — Could you comment on the influence of the electrode potential, i. e. of the surface charge, and in particular the two opposite cases where the electrode is positively and negatively charged, on the tail of the electron concentration near the surface and are there possible consequences for the guided modes that you said should be present at the metal-electrolyte interface.

DUKE. — To answer this question one must distinguish between true charge accumulation at a surface and the termination of external electric fields by an effective charge. The qualitative influences of electric field termination are known from field emission and field ionization spectroscopy. The positive charge termination of a field which would accelerate positive charges away from the surface suppresses the microscopic electron leakage out of a metal surface. Conversely, the negative charge termination of an effective electron-accelerating field enhances the electron leakage. This latter effect has been inferred directly from field emission experiments, but strong fields (\( E \approx 10^7 \text{ \text{V/cm}} \)) are required to achieve an observable effect. In the case of true charge transfer upon adsorption, the situation is more complex because such adsorption changes the surface charge density in a microscopic fashion. (See, e. g. DUKE, C. B., J. Vac. Sci. Technol. 6 (1969) 152.) As noted in my talk, for such thin (\( d \approx 2 \text{ Å} \)) depletion regions, optical techniques like the observation of extra guided waves are ill suited to examine the surface electronic structure. The comments in my lecture pertain to guided modes trapped in the diffuse space charge region of a metal-electrolyte interface rather than to modifications of the microscopic electronic structure at the surface of the metal electrode. Such modifications would influence the value of the potential right at the metal surface (i. e. the inner boundary of the inner Helmholtz layer) and hence would play the role of boundary conditions in the electromagnetic mode problem.

HANSEN. — You seem to imply that it is difficult or impossible to obtain direct information concerning the nature of thin layers or chemical species within a surface region by means of optics and spectroscopy. If this is true, would you explain the difficulty?

DUKE. — See my response to Pr. Yeager's question. Empirical information about thin layers is readily obtained by optical techniques. These methods do not, however, give microscopic information without the aid of a detailed microscopic model, and many models usually are consistent with any given set of data. Thus, experimentalists should distinguish between empirical structure-property relationships (which can be both useful and reliable) and inferences which are drawn from some particular microscopic model (which often are neither).

HANSEN. — Consider a system with phase 1 glass, phase 2 a thin (200 Å) metal film, and third phase an aqueous solution of an absorbing chemical species.
Light is incident on the boundaries from phase 1 and detected after reflection. From your analysis, do you expect meaningful spectral to result? What are problems that might be involved?

Duke. — Yes. I would expect the selection of a specific set of materials properties and concomitant experimental parameters to observe pronounced effects (e.g., extra guided waves at the metal-electrolyte interface) to be the major design problem. One needs an electrolyte with strong changes in optical properties in the surface and diffusion layers to achieve unambiguous surface-wave phenomena.

Luth. — I want to comment to the point that optical results on surfaces are ambiguous in general: To my opinion transition energies between occupied and empty surface states can very well be evaluated from optical surface spectroscopy even though there is considerable ambiguity concerning absolute values of the dielectric constants, line shape details, etc. A great number of converging results obtained by different methods including optical ones on Si, Ge, GaAs, etc. support this statement. The same, by the way, is true for low-energy electron loss spectroscopy.

Duke. — In my experience, good agreement of the optical and electron-loss measurements with theoretical models occurs for the bulk properties of semi-conductors and certain metals (e.g., Cu). I am not aware of correspondingly adequate and tested theoretical models of those features of the optical and energy loss experiments which are thought to be associated with specifically surface phenomena. The fact that several spectroscopics give (nearly) the same transition energies does not imply that the microscopic origin of these transitions is well understood. This is true even for the Silicon and GaAs surfaces discussed in your talk, for which exciton correlations are still poorly understood, and the atomic geometries of the surfaces are in doubt.