Inverse-Photoemission Spectroscopy at the Metal-Electrolyte Interface

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The principle of the inverse photoelectric effect has been applied to the study of the metal-electrolyte interface. It is shown that charge-transfer-reaction inverse-photoemission spectroscopy is capable of investigating both empty and occupied electronic states in the interfacial region. Results for Au(111) electrodes in solutions of tetrapropylammonium tetrafluoroborate in acetonitrile, containing either electron-donor or electron-acceptor molecules, are presented. The spectra are shown to contain a wealth of detailed information about, for example, interfacial electronic states and molecular reorganization processes.

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Atomic or molecular electron donors and acceptors can undergo heterogeneous charge-transfer processes at the metal-electrolyte interface.[1] An intrinsic property of these solution species is the well-defined energy level of either the highest occupied (donor), or lowest unoccupied (acceptor), orbital. The ability to vary the energetic location of the Fermi level, with respect to the energy levels in solution, provides an opportunity to create excited states in the metal electrode. For inverse-photoemission spectroscopy[2] such excited states are created by injection of electrons from the vacuum and their radiative decay is utilized to probe empty electronic states of clean and adsorbate-covered metal surfaces. The purpose of this communication is to show that inverse photoelectric processes may be used to study both empty and occupied states at electrochemical interfaces. We have called this new technique charge-transfer-reaction inverse-photoemission spectroscopy (CTRIPS).[3]

Energy diagrams which schematically illustrate the relevant interfacial electronic levels associated with the injection and abstraction of electrons into and out of the metal are shown in Figs. 1(a) and 1(b), respectively. The levels of the oxidized (Ox) and reduced (Red) forms of the solution species are broadened by thermal fluctuations of the immediate environment and differ in energy as a result of reorganization phenomena.[1] A characteristic property of any such Red/Ox (redox) couple is the redox energy E_R, which is given by the intersection of the distribution curves for equal densities of states of both forms. The range of injection energies is related to the width of the level distributions, and for a particular injection energy radiative decay to the Fermi level E_F represents the maximum photon energy $h\nu_{max}$.

We have chosen the benzophenone radical anion as an example of an energetic donor species and the thianthrene radical cation as an energetic acceptor species. These two species may be generated electrochemically from the neutral molecules and their production can be monitored by the current recorded as a function of the voltage applied to the electrochemical cell. Usually, the applied voltage is scanned linearly with time in electrochemical investigations,[4] and typical current-voltage curves obtained in this manner for

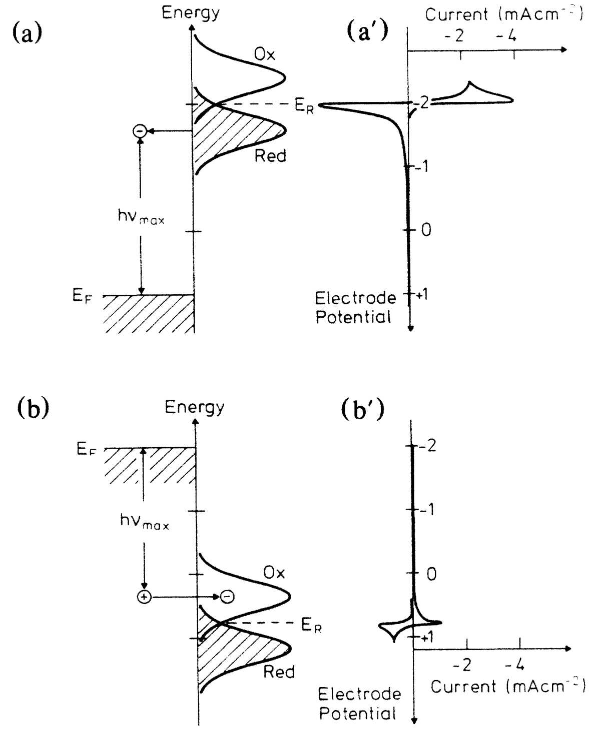

FIG. 1. (a) Energy level diagram showing electron injection from a highly reducing species with redox energy E_R into a positively biased metal. (a') Current-voltage curve (scan rate = 50 mV s^{-1}) for the acetonitrile/tetrapropylammonium tetrafluoroborate ($0.5M$)/benzophenone ($0.1M$) system at Au(111). (b) Energy level diagram showing hole injection from a highly oxidizing species into a negatively biased metal. (b') Current-voltage curve (scan rate = 50 mV s^{-1}) for the acetonitrile/tetrapropylammonium tetrafluoroborate ($0.5M$)/thianthrene ($0.02M$) system at Au(111).

benzophenone and thianthrene on Au(111) electrodes with a scan rate of 50 mV s^{-1} are shown in Figs. 1(a′) and 1(b′), respectively. The magnitudes of the currents are related to the different bulk concentrations of the respective molecules in solution. The close proximity of the oxidation and reduction peaks on the potential scale (~ 60 mV), in both current-voltage curves, is a well-known signature of a fully reversible charge-transfer reaction.[4] On this specific electrode potential scale, the values which correspond to the redox energies E_R for the benzophenone and thianthrene couples are -2.0 and $+0.8$ V, respectively. Since these couples are known to undergo outer-sphere charge transfer,[5] they do not chemically interact with the metal electrode and thus retain their well-defined energy levels.

Experiments were performed with a conventional three-electrode electrochemical system.[4] The solvent, acetonitrile,[6] the conducting salt, tetrapropylammonium tetrafluoroborate ($0.2M$),[6] the reference system, silver-silver ion ($AgNO_3$, $10^{-3}M$),[6] and the precursor molecules used to produce the radical ions, thianthrene[7] and benzophenone,[3] were rigorously purified by well-known procedures. The optical arrangement, consisting of focusing lenses, an interference-filter monochromator with spectral resolution $\lambda \simeq 20$ nm (Optical Coating Laboratory), a GaAs photomultiplier tube (RCA 31034), and a photon counter (Princeton Applied Research), is described in detail elsewhere.[7,8] The noise level did not exceed 5 counts per second. Single-crystal Au(111) electrodes (area = 1 cm^2), obtained by evaporation of gold onto mica at 250 °C,[9] were used to exploit the wide potential range accessible in aprotic solvent systems. All spectra were recorded with square-wave potential modulation, from either -2.1 V for the benzophenone system or $+0.9$ V for the thianthrene system, at a frequency of 25 Hz. The purpose of this modulation may be summarized as follows. During one half of the square-wave cycle neutral molecules are consumed at the surface, with concomitant diffusion from the bulk of the solution, to produce radical ions which in turn diffuse away from the electrode. During the other half of the cycle, when the CTRIPS events occur, these processes are reversed such that the radical ions inject their charge into the metal electrode and once again become neutral molecules (see Fig. 1). The concentration of the injecting species at the surface is therefore repetitively changing in a well-defined way and may be monitored by display of the current-time curve on an oscilloscope. One would expect the intensity of the emitted light to be proportional to the time integral of the injection current and this was confirmed experimentally. The thickness of the diffusion layer of the radical ions was estimated to be in the micron range such that absorption of light emitted from the electrode within this layer could be neglected. The spectra were not corrected for wavelength-dependent transmission efficiency of the monochromator and photomultiplier.

The CTRIPS data obtained by electron injection from the benzophenone radical anion into the single-crystal gold surface are shown in Fig. 2 for different energetic locations of the Fermi level relative to the injector energy. These changes in the position of the Fermi level were achieved by variation of the positive limit of the electrode-potential modulation. The observed spectral intensity and spectral distribution changed significantly with electrode potential. This behavior is consistent with the mechanism of the CTRIPS process. For low values of the modulation amplitude the spectral distribution is expected to be centered at longer wavelengths, beyond the accessible range of our detection system. With increasing modulation amplitude the energy of the excited electrons in the metal increases and consequently one would expect to observe the emission of higher-energy photons, again consistent with the observed trend shown in Fig. 2. At this stage we refrain from a detailed discussion of the structure seen in these spectra, but we will analyze later the systematic shift of the high-energy threshold of the light emission.

The complementary process, which is also associated

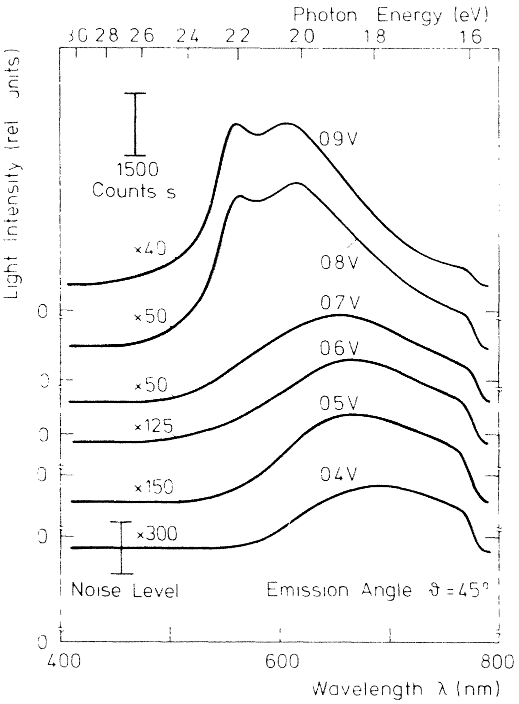

FIG. 2. CTRIPS spectra obtained for the Au(111) electrode in acetonitrile/tetrapropylammonium tetrafluoroborate ($0.5M$)/benzophenone ($0.1M$) system for different positive limits of potential modulation ($f = 25$ Hz). The negative limit of potential modulation was kept constant at -2.1 V.

with light emission, consists of hole injection by charge transfer from the metal to the thianthrene radical cation and data for this type of experiment are shown in Fig. 3(a). Again, with increasing modulation amplitude, higher counting rates and a blue shift of the spectral distribution were observed. We wish to emphasize that this effect, which may loosely be termed "inverse photohole emission," is very difficult to realize at the metal-vacuum interface.[10] To test that the generation of light originates from the single-crystal solid, CTRIPS spectra were also recorded at polar emission angles of 0° and 60° [see Fig. 3(b)]. For the three emission angles thus covered at −2.1 V, substantial structural variations of the photon energy dependence of the emitted light occurred. Such a variation is a well-known phenomenon in angle-resolved ultraviolet-photoelectron spectroscopy[11] as well as *k*-resolved inverse-photoemission spectroscopy.[2,12,13]

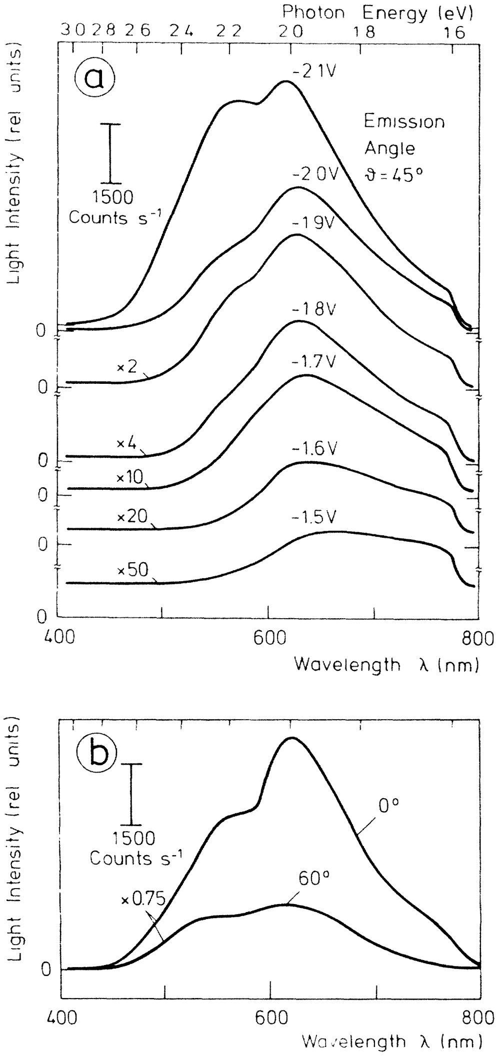

FIG. 3. (a) CTRIPS spectra obtained for the Au(111) electrode in acetonitrile/tetrapropylammonium tetrafluoroborate ($0.5M$)/thianthrene ($0.02M$) system for different negative limits of potential modulation ($f = 25$ Hz). The positive limit of potential modulation was kept constant at +0.9 V. (b) Emission-angle–dependent CTRIPS spectra for the system shown in (a) for a maximum negative limit of potential modulation of −2.1 V.

In comparing the results of these two complementary inverse-photoelectric effects we would like to draw attention to the dramatic difference of light intensity for comparable modulation amplitudes (see Figs. 2 and 3). An inspection of the band structure of gold, previously carried out in conjunction with photoelectron-emission studies at the metal-electrolyte interface,[9] offers an explanation for this difference. Light emission is expected to be most intense when the excited electronic states in the metal can decay via direct transitions.[12] In our experiments electrons are injected from the benzophenone radical cation at energies of less than 3 eV above the Fermi level. In this energy range neither direct nor any other type of interband transitions can take place in gold. In addition, in the direction normal to the (111) surface, where tunneling from the injecting species is most likely to occur, there are no bulk states available to accept electrons because of a band gap of at least[14] 3 eV in the vicinity of the Γ-L direction in the band structure. However, when holes are injected into a Au(111) crystal, with excess energies exceeding −2.3 eV (see Fig. 3), both of these restrictions are lifted and instead a multitude of direct transitions, resulting in increased light emission, can occur between intrinsically occupied electronic bulk states. These interband processes involve transitions of electrons from the *sp* band to holes created in the

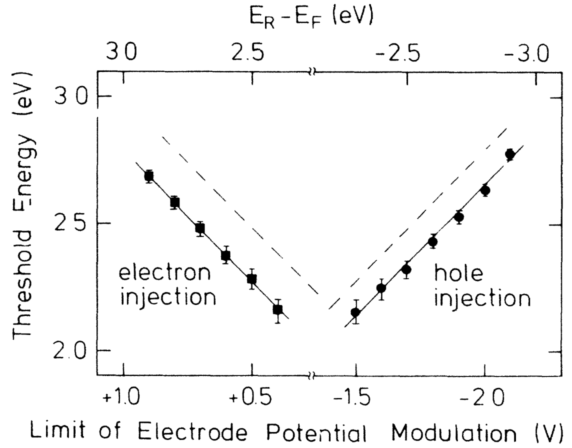

FIG. 4. Dependence of the high-energy threshold of the light emission due to electron and hole injection as a function of the limit of electrode potential modulation. The dashed lines represent threshold energies equal to the absolute difference between the redox energy E_R and the Fermi level E_F.

high density of d-band states. The direction of the electrons tunneling from the metal to the acceptors may also be less critical in this case. The difference in light emission for these two inverse-photoelectric effects can be understood in this way.

A crucial aspect of identifying, unequivocally, the origin of the observed light is the shift in the position of the high-energy threshold of the emitted radiation. In Fig. 4 the variation of the threshold energy with respect to the electrode potential is shown for both electron and hole injection. These values were determined by measurements in a narrow spectral region with increased sensitivity and larger periods of data accumulation. In accordance with the CTRIPS mechanism, a slope of unity was obtained for the relationship between threshold energy and electrode potential for both electron and hole injection. The dashed lines in Fig. 4 would be expected if the onset of injection were to take place at the respective redox energies E_R (see Fig. 1). In both cases the experimental threshold energies are lower than the absolute values of $E_R - E_\mathrm{F}$, namely ~ 200 mV for electron injection and ~ 130 mV for hole injection. Clearly, these lower values reflect the energy level distributions of the injecting species and thus contain important information about the reorganization energies of these systems.[1] More detailed studies are, however, required to establish the significance of the observed difference of ~ 70 mV for the two different organic injectors.

We note in passing that prior to our work there existed some confusion about the origin of light emission observed under experimental conditions comparable to ours.[15] At that time, one was unaware of the possibility of observing radiative transitions taking place in the metal electrode, and explanations were sought solely on the basis of radiative decay of excited molecular states in solution. Clearly, our results do not agree with any such mechanism, with regard to either the angle dependence of the light emission[16] or the spectral composition.[17] We shall elaborate on this point in a forthcoming publication.[18]

In conclusion, we feel we have demonstrated the simplicity, versatility, and compatibility with surface physics concepts and methods of charge-transfer-reaction inverse-photoemission spectroscopy.

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