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Charge Transfer Reaction Inverse Photoemission Spectroscopy (CTRIPS) at a Gold/Acetonitrile Solution Interface.
Evidence for Photon Emission via Surface States

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The emission of light caused by electron transfer reaction at a gold electrode in acetonitrile solution containing one of three aromatic redox compounds (benzophenone, t-stilbene and benzonitrile) was studied. From the potential dependence of the spectrum, we proposed that the emission is due to charge transfer reaction inverse photoemission (CTRIP) process which takes place via surface states.

It is well known that surface states play a very important role in semiconductor devices as well as in semiconductor electrochemistry. Surface states of metals have been also observed under UHV by inverse photoemission spectroscopy (IPS)$^{1)}$ and in electrolyte solution by electroreflectance (ER) spectroscopy.$^{2)}$ In this paper we demonstrate that charge transfer reaction inverse photoemission spectroscopy (CTRIPS) proposed by McIntyre and Sass$^{3-6)}$ is useful to probe energy distribution of surface states of metal in solution.

Acetonitrile used as a solvent, tetrabutylammonium tetrafluoroborate ($(C_4H_9)_4NBF_4$) used as a supporting electrolyte and electron injection reagents (benzophenone, t-stilbene and benzonitrile) were rigorously purified.$^{7)}$ Gold electrode was prepared by vacuum deposition on clean glass or cleaved mica under 10^{-5} Torr. The temperature of the substrate and the deposition rate were controlled to obtain the smooth (111) face.$^{8)}$

In CTRIPS spectrum measurement,$^{9)}$ the electrode potential was stepped first to a negative potential where the anion radical of the species is generated and then to various positive potentials (U_f = -0.5 - 0.7 V vs. Ag/Ag^+) where the anion radical is oxidized. Light is observed while the electrode is kept at U_f. The negative potential limit at CTRIPS spectrum measurement was restricted to 0.1 V more positive than the redox potential, U^{o}, of each species[10)] to avoid the decomposition of the solvent and the polymerization of the aromatic species.

Figure 1 shows the emission spectra at various U_f obtained in a solution containing benzonitrile as a redox species. As pointed out by McIntyre and Sass, the high energy threshold of the CTRIPS spectrum, E_{th}, corresponds to the maximum radiative energy due to the decay from the electron injected state to the Fermi level and is, therefore, determined by the difference between the redox potential of the chemical species and the electrode potential (Fig. 2). The energy of injected electron, E_{inj}, with respect to the Fermi level may be represented by the difference between U^{o} and U_f ($E_{inj}/e=-(U^{o}-U_f)$). Figure 1 shows that E_{th} decreases linearly as U_f becomes more negative, i.e., the energy difference between E_{inj} and E_{th} is almost constant at each spectrum. The linear relations between E_{th} and U_f were found in all cases investigated in the present study. These results support that the emission observed in the present study is due to CTRIP process. If the relaxation of injected electrons to the bulk unoccupied states is the only cause of this emission, not only ($E_{th}-E_{inj}$) but also the shape of the spectrum should be independent of U_f. The difference between E_{inj} and the spectral peak energy, E_p, however, becomes larger when U_f becomes more positive as shown in Fig. 1. The values of ($E_{inj}-E_p$) obtained for the three redox species are plotted against U_f in Fig. 3. The data of not only the present study but also the results by McIntyre et al.[3,6)] are shown. It seems that there is a linear relation between ($E_{inj}-E_p$) and U_f with the positive slope of 0.5 eV/V, although there is some deviation from the linear line at relatively positive potentials. It must be also noted that there is no clear effect of electron injecting species on this relation. These results presented here suggest that the distribution of the unoccupied electronic states of gold, which is responsible for the CTRIP

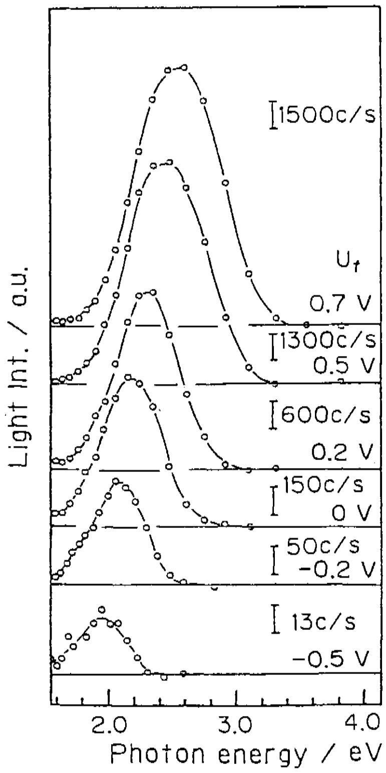

Fig. 1. Emission spectra of gold at various electrode potential, U_f, in acetonitrile solution containing 50 mM benzonitrile and 0.2 M $(C_4H_9)_4NBF_4$.

process, shift to the high energy direction against the Fermi energy, E_F, when U_f becomes more positive. In Fig. 2, the distributions of the unoccupied states at U_f = -0.5 V (E_{inj} = 2.2 eV)(a) and 0.5 V (E_{inj} = 3.2 eV)(b) were shown schematically. This type of shift may occur if the states locate at the surface, i.e., surface states. In CTRIPS measurement, the mean free path of the injected electron is so short that one can expect that the spectrum reflects the distribution of the energy states closer to the metal surface rather than the bulk.11) Similar potential dependence of peak position was observed in ER spectroscopy which measures the optical transition from occupied states to unoccupied states. It was proposed that the peak shift occurs because the transition is from occupied bulk states to unoccupied surface states. Since surface states are localized at the metal/ electrolyte interface, the energy position of the states is affected by the field within the electric double layer.12) When the electrode potential becomes positive, the energy position shift to higher energy with respect to E_F. The result that the potential dependences of the peak position of

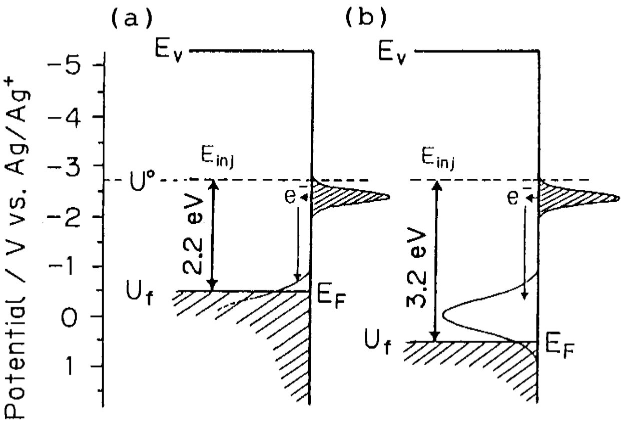

Fig. 2. Schematic energy diagram of gold electrode during the oxidation of the benzonitrile anion radical. (a) U_f = -0.5 V. (b) 0.5 V.

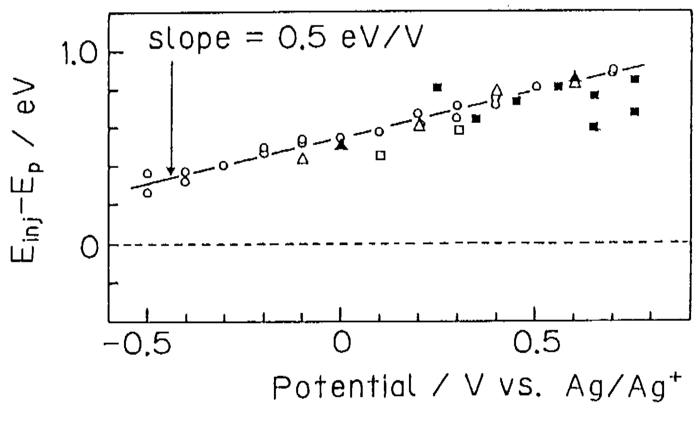

Fig. 3. Relation between (E_{inj}-E_p) and U_f. (○): benzonitrile, present results. (△): t-stilbene, present results. (▲): t-stilbene, results of McIntyre et al.6) (□): benzophenone, present results. (■): benzophenone, results of McIntyre et al.3)

the CTRIPS and ER spectra are similar in both cases supports that the surface states are also involved in the CTRIP process. The fact that $(E_{inj}-E_p)$ at a given potential is not affected by electron injecting species means that the states involved are intrinsic. The detailed analysis of the spectra which should provide the information of energy distribution of surface states is under way.

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7) Spectro-grade acetonitrile was purified by repeating the vacuum transfer and stirring with P_2O_5 for 3 h for three times. Reagent-grade tetrabutylammonium tetrafluoroborate, benzophenone and t-stilebene were recrystallized three times from ethyl acetate, hexane and methanol, respectively. Reagend-grade benzonitrile was dried with $MgSO_4$ and distilled from P_2O_5 under reduced pressure.
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9) Optical window of a spectroelectrochemical cell was placed in front of an entrance slit of a monochromator. A PMT and a photon counter were used to detect the light intensity. The PMT response was averaged for four times at each wavelength.
10) U^o of benzophenon, t-stilbene and benzonitrile were determined as the average of the cathodic and anodic peak potentials of cyclic voltammograms in acetonitrile solution and are -2.15, -2.5 and -2.7 V, respectively.
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