cays by another route to the ground state (eq 4). Bond scission in (DA)* must be too slow to compete with rapid decay of this species (eq 4) but it may occur from the free ion $A\cdot^-$ (eq 5) at a rate competitive with slower diffusion controlled ion pair annihilation (eq 6).

$$(DA)^* \rightarrow D\cdot^+ + A\cdot^- \tag{3}$$

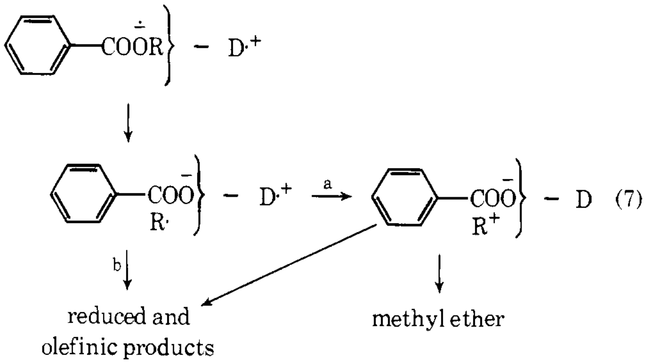
$$(DA)^* \rightarrow D + A \tag{4}$$

$$A\cdot^- \rightarrow \text{products} \tag{5}$$

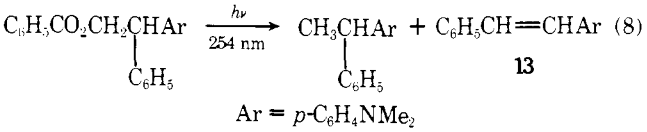
$$D\cdot^+ + A\cdot^- \rightarrow D + A \tag{6}$$

The singlet *N,N*-dimethylaminophenyl group has ample energy (88 kcal/mol)[7] to yield free ions. Thus the difference in the half wave oxidation and reduction potentials of *N,N*-dimethylaniline and methyl benzoate (+0.88 and −2.32 V, respectively) suggest that electron transfer requires only about 74 kcal/mol.[8,9] The occurrence of intramolecular sensitization with 254-nm light suggests that this may produce a higher C-T state having sufficient energy that bond scission competes effectively with decay.

The ratios of methyl ether to total nonacidic products (Table I) are consistent with the proposed mechanism (eq 7). For a given compound this ether ratio should be proportional to the fraction of products formed from carbonium ions. Unlike **7**, direct excitation of **2** and **12** yield ether ratios that are substantially higher than in the sensitized reactions. Equation 7 suggests that electron transfer (step a) should occur more rapidly upon direct excitation of **2** and **12** because the donor is attached to the incipient carbonium ion center R·, and carbonium ion formation can thus compete more effectively with formation of radical-derived products (step b).[10]



It is of interest that when carbonium ion formation is energetically unfavorable no ether is formed (eq 8).[11]



$$C_6H_5CO_2CH_2CH(C_6H_5)Ar \xrightarrow[254\ nm]{h\nu} CH_3CH(C_6H_5)Ar + \underset{\mathbf{13}}{C_6H_5CH{=}CHAr} \tag{8}$$

$$Ar = p\text{-}C_6H_4NMe_2$$

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Internal Reflection Resonance Raman Spectroscopy for Studies of Adsorbed Dye Layers at Electrode–Solution Interface[1]

Sir:

The in situ observation of species adsorbed at or formed in the vicinity of the electrode-solution interface during electrolysis has been one of the most exciting fields in electrochemistry and has been the subject of a number of studies in recent years.[2-4] Although a variety of methods involving internal reflection spectroscopy (IRS) using visible radiation have been developed during the course of these investigations, there have been only a few applications of Raman spectroscopy to electrochemical systems.[5-10] Fleischmann, Hendra, and McQuillan[5] were the first to demonstrate that Raman spectroscopy has a bright prospect in the study of electrode surfaces and often is a more convenient method than infrared[11,12] in such a solvent as water which gives only very weak Raman scattering. While the present work was in progress, Van Duyne and co-workers[8-10] demonstrated that vibrational spectra of electrogenerated species can be readily obtained from solutions originally ca. 1 × 10^{-3} M in electroactive substrate by utilizing the resonance Raman effect. Although IRS[3] has been a powerful tool for the study of electrode surfaces because of its capability of observation of the region within about one wavelength of the interface,[13,14] as yet no Raman spectra from the interface except that of a solvent[15] excited with laser beam in the internal reflection mode have been observed. In the present case the Raman spectra of adsorbed methylene blue (MB) at quartz-aqueous solution and at SnO_2 electrode-aqueous solution interfaces were obtained by utilizing the resonance Raman effect and using an Ar ion laser beam totally reflected in the optically denser solid phase side. The change in the Raman intensity as a function of electrode potential was also studied.

The Raman spectra were recorded using a Narumi double monochromater with standard photon counting detection and a CRL Ar ion laser for excitation. The resonance Raman spectra of aqueous MB solution were obtained using a rotating cell similar to that reported by Kiefer and Bernstein.[16] The cell design used for the internal reflection mode is shown in Figure 1. A quartz prism and a SnO_2 optically transparent electrode (OTE) were assembled into the cell using a silicon rubber gasket and a fluid with refractive index close to that of the optical elements. The quartz prism itself was employed as an adsorbent for the study of adsorbed MB at the quartz–aqueous solution interface. The electrical contact to the working electrode was similar to that previously described using a peripheral copper ring.[17] The auxiliary electrode was a Pt gauze and the electrode potential was referred to a saturated calomel electrode (SCE) with a Luggin capillary. The electrochemical perturbation was applied with a conventional potentiostat.

The resonance Raman spectrum of a 5 × 10^{-4} M aqueous MB solution excited at 514.5 nm contains the strong bands at 449, 503, 775, 861, and 1625 cm^{-1}, medium intensity bands at 957, 1073, and 1400 cm^{-1}, and weak bands at 595, 673,

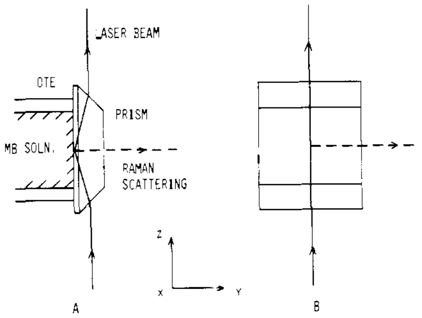

Figure 1. Raman cell for the internal reflection mode. The incident angle which depends on the geometry was ca. 74° and greater than the critical angle in the present geometry where the interface was parallel to the laser beam propagating in air (*z* axis). Raman scattering was observed in the direction along the *y* axis and perpendicular to the electrode surface (arrangement A) or perpendicular to the plane of incidence by rotating the cell 90° around the *z* axis (arrangement B). The electric vector of the incident laser beam was parallel to the interface in A and parallel to the plane of incidence in B.

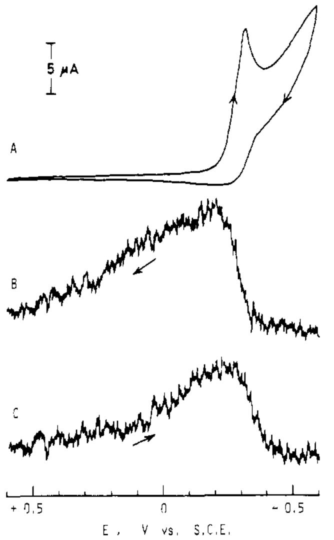

Figure 2. Current-potential curve (A) and the change in the internal reflection resonance Raman intensity at 1625 cm^{-1} of the adsorbed MB at SnO_2 electrode-aqueous solution interface as a function of the applied potential for the cyclic linear sweep mode (scan rate 4.8 mV s^{-1}) on anodic sweep (B) and on cathodic sweep (C). 1×10^{-4} M MB in 1×10^{-2} M aqueous KCl solution. Raman scattering was observed with the arrangement B in Figure 1.

1042, 1167, 1187, 1302, 1365, and 1472 cm^{-1}. The relative intensities of these bands were different from those observed in the spectrum excited at 488.0 nm. Observation of the internal reflection resonance Raman spectra of the adsorbed MB at the quartz-aqueous and at the SnO_2 electrode-aqueous solution interfaces in the wavenumber region less than 1250 cm^{-1} was not easy because of interference of the high background Raman scattering from quartz or glass substrate of OTE. Although the spectra obtained at both interfaces are very similar to that of solution, the observed spectra can be considered to be due to the adsorbed MB because of the presence of a negligibly slight amount of MB solute within the penetration depth compared with the adsorbed MB at the concentration measured.[3,18]

The change in Raman intensity at 1625 cm^{-1} of adsorbed MB as a function of the applied potential is shown in Figure 2 for the cyclic linear sweep mode. The internal reflection resonance Raman spectra of adsorbed MB disappeared as expected when the adsorbed MB was reduced to leuco-MB at more cathodic potential than −0.4 V vs. SCE. The decrease of the Raman intensity observed with increase of anodic potential can be interpreted by the decrease of the amount of adsorbed MB due to the repulsion of adsorbed MB cation with increasing positive charge of the electrode surface. This potential dependence of adsorption and the decrease of the amount of adsorbed MB due to the change in the surface charge with lowering pH of the aqueous solution in contact with the quartz surface have been confirmed previously[18,19] using IRS in the visible region.

In conclusion, Raman spectra of the adsorbed submonolayer at solid-solution interface were obtained without interference from species in bulk solution using internal reflection resonance Raman spectroscopy. Reabsorption of Raman scattering troublesome in resonance Raman spectroscopy can be neglected in this mode. This method can be applicable widely for the study of a variety of interfaces[20] in situ involving electrode-solution interfaces with OTE.

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Direct Observation of a Sulfurane Intermediate in the Neighboring-Sulfide-Assisted Thermolysis of a Perester[1]

Sir:

The anchimeric acceleration of O–O homolysis in perester **1a** in chlorobenzene at 60 °C amounts to a factor of 2.45×10^4 relative to **1b.**[2] Peresters **1c–f** and **2** also exhibit substantial rate enhancements mediated by neighboring group participation in reactions leading primarily to free radicals.[2-6]

In 1962, sulfurane **3** was postulated as a logical albeit unprecedented intermediate in the thermolysis of **1a.**[2] The recent