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SERS Detection of the Vibrational Stark Effect from Nitrile-Terminated SAMs to Probe Electric Fields in the Diffuse Double-Layer

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The vibrational Stark effect, a shift in vibrational frequency in response to an externally applied electric field,[1] is observed in the surface-enhanced Raman scattering spectra of self-assembled monolayers (SAMs) functionalized with pendant nitrile groups. The Stark tuning rate (dν/dE) of the nitrile stretching mode is used to characterize interfacial electric (E) fields. The results demonstrate the applicability of this experimental design for characterizing the diffuse region of the double layer.

The vibrational Stark effect requires extremely high fields for observation and is ideally suited for electrochemical interfaces where electric fields of $>10^8$ V m^{-1} are routinely generated due to the presence of small, mobile ions in solutions that organize at polarized interfaces.[2,3] These interfacial E fields act as the driving force for electrochemical reactions and depend on the concentration of ions and solvent structure immediately adjacent to metal surface.[4] Direct measurement of interfacial E fields is a challenging analytical measurement.[5−7] Korzeniewski and co-workers[1b,c,e] investigated interfacial structure of polycrystalline Pt surfaces using vibrational Stark tuning of the CO stretching mode. Interfacial E fields consistent with double-layer theory, $\sim 10^9$ V m^{-1}, were reported; however data interpretation is complicated by charge transfer between CO and the Pt surface.[1e−g] Buttry and co-workers avoided charge-transfer effects with the use thiol-derivatized hemicyanine dye molecules co-immobilized with alkanethiols on polycrystalline Ag and Au surfaces.[5,6] This technique serves to isolate the probe molecule from the metal surface and to restrain its orientation. Stark tuning of the electronic transition of the probe molecule exhibited a maximum interfacial E field of 3×10^7 V m^{-1}, which disagreed with theoretical predictions by an order of magnitude.[6]

The measurement approach presented here combines attributes of experiments performed by Korzeniewski and Buttry: vibrational Stark tuning rates of a neutral nitrile group pendant to alkanethiol are used to detect interfacial E fields. Nitrile was chosen as the pendant reporter group for its large dipole (~3 D) [8] in order to maximize the interaction with the applied field, which is the origin of the Stark effect.[1a] Mixed monolayers composed of 12-mercaptododecanenitrile[9] and 7-heptanethiol were assembled at Ag surfaces. Electrochemical and spectroscopic characterization of two component SAMs establish that mixed monolayers, similar to Ag−S(CH$_2$)$_6$CH$_3$/Ag−S(CH$_2$)$_{11}$CN, demonstrate insulating properties and high degree of order comparable to those associated with SAMs composed of a single alkanethiol.[10−13] In the experiment described here, the shorter alkane chain of the diluent was used to form a dielectric layer, which acts to isolate the nitrile probe molecule from the metal and force the probe molecule to maintain a fixed orientation.[6,13] The key concept in this design is that the shorter alkanethiol forms a barrier at which the aqueous double-layer forms;[6] the nitrile probe molecule, which terminates ~4−5 Å beyond the dielectric layer, is placed inside the double-layer and samples interfacial E field strength. Furthermore, the nitrile group, with a bond length of 1.15 Å,[8] is short relative to the decay length of the diffuse double-layer formed by even high ionic strength solutions and, accordingly, provides better spatial resolution than the electronic Stark effect, where the charge displacement associated with electronic absorption is ~3× longer.[6] The Raman scattering from the nitrile stretching mode, present in submonolayer coverage, receives electromagnetic enhancement from the highly polished Ag surface to provide detectable signal.[14−17a]

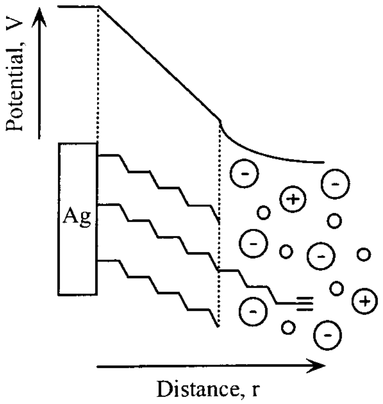

Figure 1. Schematic of the Ag/SAM/aqueous interfacial region.

Figure 1 shows a schematic diagram of the mixed-monolayer assembled on the surface, as well as the profile of the potential versus distance from the metal surface. Previous theoretical work predicts a potential decay within a homogeneous dielectric layer that is linear, which allows a significant fraction of the applied potential (~10%) to reach the aqueous region.[3] The methyl terminus of the diluent heptanethiol that is pictured here marks the boundary of the double-layer region where Gouy−Chapman theory predicts a fast potential decay at high electrolyte concentrations and results in large E fields within the diffuse double-layer.[1d,2] This diagram emphasizes the importance of employing a SAM with a high degree of structural integrity in order to prevent penetration of ions into the alkane chains and a subsequent loss of a well-defined diffuse double-layer boundary. These SAMs were allowed to assemble from 10 mM ethanolic solutions of [1:5] 12-mercaptododecanenitrile/7-heptanethiol onto highly polished Ag[16−17a] electrodes for 24−48 h, followed by a thorough rinse in ethanol.

The Stark effect observed at surfaces immersed in 10 mM NaClO$_4$ is shown in Figure 2; the nitrile stretching mode increases in frequency with increasingly positive applied potential. The direction of the Stark shift agrees with expectations: E fields associated with a positively charged metal are opposite that of the nitrile dipole and, as a result, the stretching frequency of the nitrile bond increases because the E field acts to “compress” the nitrile bond. The potential of zero charge (PZC) for polycrystalline Ag in

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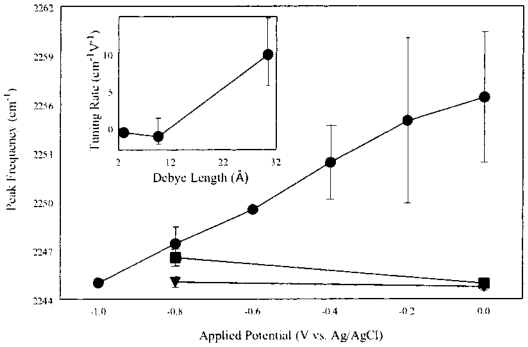

Figure 2. Peak frequency of nitrile stretching mode as a function of ionic strength: (●) 10 mM $NaClO_4$ (■) 100 mM $NaClO_4$ and (▼) 1000 mM $NaClO_4$. Inset shows the dependence of Stark tuning rate of the nitrile stretching mode on the Debye length.

the absence of specifically absorbing ions is −0.9 V (vs Ag/AgCl).[17] This value is expected to shift further negative upon adsorption of thiols. As the applied potential approaches the PZC, E fields are predicted to vanish and the nitrile stretching frequency should approach its isotropic value (2243 cm^{-1}).[18] All three plots in Figure 2, representing a broad range of ionic strengths, converge on this frequency at negative potentials. From these results, the CN stretching frequency appears to be a direct measure of the local E field, which can be used to provide an estimate of the PZC (∼−1V vs Ag/AgCl).

The Stark tuning rate, dν/dE, observed for surfaces immersed in 10 mM $NaClO_4$ is 9.8 ± 3.5 cm^{-1} V^{-1}. Comparison of this value with those determined by Boxer et al., where large E fields applied to aliphatic alkanenitriles trapped in glass were used to observe Stark tuning of the nitrile stretching frequency, shows that our observed values are very reasonable.[19] Furthermore, nitrile Stark tuning rates reported by Boxer suggest that our interfacial probe experiences an E field on the order of 10^9 V m^{-1}, consistent with Gouy−Chapman theory.[1e,2]

The inset of Figure 2 demonstrates the sensitivity of this experiment to detect changes in the diffuse double-layer: the Stark tuning rate of the nitrile probe changes with Debye length (κ^{-1}) of the double layer. Stark tuning rates will reflect the interfacial E field that is present at the nitrile probe position. For long Debye lengths (∼10 mM $NaClO_4$), double-layer structure produces interfacial E fields that persist for tens of angstroms into solution from the dielectric interface, resulting in measurable Stark tuning of the nitrile probe molecules. For short Debye lengths (≥1000 mM $NaClO_4$), Stark tuning rates are expected to be negligible because the double layer is tightly compressed, resulting in a field that fully decays before reaching the nitrile molecule. This result establishes that Stark tuning rates of the nitrile molecule respond to changes in the field distribution at the interface. While Stark tuning rates measured for both extremely low and high ionic strengths reflect predicted interfacial E fields, the negligible Stark tuning rate for a Debye length of 12 Å (100 mM $NaClO_4$) is unexpected because large interfacial E fields are predicted to exist well beyond the position of the nitrile probe.

This result may indicate that ions penetrate into the underlying SAM causing a premature decay in potential and E field or other perturbations in double-layer structure. This observation is consistent with the behavior of self-assembled monolayers, particularly those formed on polycrystalline Ag surfaces, where surface morphology is well-known to influence the degree of order of alkanethiol SAMs, as well as the susceptibility of these SAMs to penetration by electrolyte and redox species.[14−15,17,19]

This communication presents a method for the observation of E field within the diffuse double-layer at SAM-modified Ag electrode surfaces using Stark tuning rates of a small, isolated vibrational probe molecule. The magnitude of these interfacial E fields measured using this method provides a highly localized probe of the diffuse double-layer region adjacent to the dielectric SAM interface. Future work will include use of this system to interrogate double-layer structure as a function of distance into the aqueous phase, the effects of substrate morphology, and SAM order.

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