SUPPORTING INFORMATION

Inhomogeneity of Interfacial Electric Fields at Vibrational Probes on Electrode Surfaces

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TABLE OF CONTENTS

Computational Methods .............................................................................................................. S2
Calculation of CN Stretch Frequency ..................................................................................... S6
Interfacial Solvation Reaction Field Model .............................................................................. S10
Differential Capacitance Calibrations ...................................................................................... S12
Additional CN Frequency Shifts with Applied Potential ....................................................... S16
Additional Electrostatic Potentials and Electric Fields .......................................................... S18
Charge Densities ....................................................................................................................... S20
Cartesian Coordinates and Sample Input Files of Model Systems ....................................... S22
References ................................................................................................................................ S30
Computational Methods

We performed periodic DFT calculations with Quantum ESPRESSO\textsuperscript{1,2} utilizing plane-wave basis functions, norm-conserving pseudopotentials,\textsuperscript{3} the PBE functional,\textsuperscript{4} and a wavefunction cutoff energy of 60 Ry. Calculations were performed on a model system consisting of a three-layer Au(111) slab with 4 atoms by 4 atoms in the surface-parallel dimensions. Only the gamma point of the Brillouin zone for the in-plane dimensions was computed given the duplication of the unit cell in these dimensions. This slab was constructed based on the bulk lattice constant of 4.176 Å, as determined from previous calculations of the fcc Au bulk crystal with a larger k-grid.\textsuperscript{5} The bottom two layers of the Au slab were frozen to the bulk geometry in all calculations. The sulfur atom of the 4-MBN molecule was placed above the top Au layer in an fcc chemisorption site (i.e., in between three Au atoms), which is known to be favorable for thiols on Au(111).\textsuperscript{6} Following geometry optimizations of the surface Au layer and the 4-MBN molecule, the S atom remained in this site, forming three bonds to Au atoms of approximately 2.48 Å in length. The tilt angle of the optimized probe molecule relative to the surface of gold was determined to be 5.8°. In all calculations, a unit cell height of 37.5 Å, much of which was filled with implicit solvent in all but the gas-phase calculations, was inserted above the 4-MBN molecule to separate adjacent periodic cells.

The effects of solvent were described via dielectric continuum solvation using the Environ module\textsuperscript{1} of the Quantum ESPRESSO code. In particular, the self-consistent continuum solvation (SCCS) method, in which the solute cavity is determined by the electronic density of the atomistic system, was used.\textsuperscript{7} In this approach, the solvation contribution to the electronic energy is determined by solving the Poisson equation self-consistently with the Kohn-Sham equations. Herein, the Poisson equation was solved with periodicity only in the two surface-parallel
dimensions so that unphysical solvation interactions between unit cells along the surface normal were excluded from the total energy.

Multiple schemes for including the effects of implicit solvent at the electrode interface were employed in this study. In all of these schemes, the dielectric constant was chosen to be unity on the back side of the Au slab (i.e., the side without the 4-MBN molecule). In principle, a virtually infinite Au electrode would have an effectively infinite dielectric constant in this region. However, given the limitations of a finite slab, imposing the lowest possible dielectric constant on the inactive side of the slab ensures the maximum amount of localization of excess charge on the active side. Although the 3-layer Au(111) slab model was chosen for computational efficiency, Figure 2B in the main text shows that the referenced electrostatic potentials are approximately constant in the interior of the slab.

Three different types of dielectric continuum solvent environments on the front of the Au slab were used. The simplest of these is a fully bulk solvation approach in which the environment’s dielectric constant is that of the bulk solvent everywhere beyond the Au slab. The other two types of calculations were performed with a low dielectric constant of 2.8 within a region near the surface of widths 3.5 Å or 6.3 Å and the bulk solvent dielectric constant beyond that region, providing a qualitative representation of the EDL at the interface. The regions were initiated at the surface-normal position z_{surf}, defined as the mean position of the surface-layer Au atoms plus one Au van der Waals radius of 1.66 Å. The choice of this interfacial dielectric constant was supported by calculations of the differential capacitance of the Au(111)/4-MBN system with different interfacial dielectric constants and region widths. However, the differential capacitance is also known to depend strongly on the parameterization of the solvent-solute interface in the SCCS method. The widths of these interfacial regions of the unit cell were chosen to be 3.5 Å and 6.3 Å to correspond
to the diameter of a water molecule and the approximate length of the probe molecule, respectively. The computational unit cell with such an interfacial region is illustrated in Figure 1 of the main text. The presence of this low dielectric interfacial region yielded better agreement with experimental data for the frequency shift versus the solvent dielectric constant. The z-dependence of the dielectric constants within each solvation scheme used are depicted in Figure S1.

The three solvation boundary conditions used herein exhibited different spatial dielectric profiles. At the solute-solvent interface (where solute refers to the entire Au(111)/4-MBN atomistic system), the environment dielectric constant approaches its prescribed value with an error function shape. The environment dielectric constant as a function of $z$ for the unit cell with each solvation boundary condition studied herein is given in Figure S1. When the low-dielectric interfacial region is present, the environment dielectric constant increases from 1 (corresponding to the absence of a dielectric environment) to 2.8 beyond the gold surface and then to 78.3 beyond the interfacial region width. Then the dielectric constant decays back to 1 due to periodicity.
Figure S1. Environment dielectric constant as a function of the slab-normal dimension, $z$, for an aqueous interfacial system. The $(x,y)$ coordinates chosen here represent a section of the unit cell that traverses the gold slab but not the 4-MBN molecule. For regions where the electronic density is sufficiently high, the environment dielectric constant is reported by Environ as 1. This region spans from about 5 Å to about 13 Å in this plot, corresponding to the Au slab. At distances beyond the Au surface (indicated by the yellow vertical dashed line), the environment dielectric constant increases to either 2.8 in the schemes with a low-dielectric interfacial region, or 78.3 in the bulk solvation case. In the former, the low dielectric constant persists for the prescribed width of the low-dielectric interfacial region. Beyond this region, the environment dielectric constant increases to 78.3. The dielectric constant changes with an error function shape.

While varying the total charge of the periodic atomistic system, a homogeneous background counter charge was employed to neutralize the cell and prevent a divergent Coulombic energy contribution. The contribution of this homogenous background counter charge is ultimately neglected from the total energy. Although this approach gives rise to a unit cell size dependence of the work function$^{11}$ and differential capacitance, for fixed cell sizes these spurious effects are negligible when considering the relative electrostatics, as in the present work. Alternative approaches such as the solvated Jellium method$^9$ introduce explicit counter charges within the dielectric continuum. However, we found the electrostatic potentials deep in the continuum solvent to be effectively constant (i.e., the electric fields were effectively zero) for the Au(111)/4-MBN system (see Figure 2 of the main text).
Furthermore, we computed the dependence of the differential capacitance on the presence of the nitrile probe molecule as well as the width and dielectric constant of the interfacial region (see below). The unit cell length was also found to weakly influence the calculated differential capacitance. Despite increases in the differential capacitance for smaller unit cells and smaller (or absent) low-dielectric interfacial regions, the computed nitrile frequency shifts with electrode potential were only minimally affected.

**Calculation of CN Stretch Frequency**

The CN stretch frequency was estimated for the various implicit solvation and biased electrode conditions from single-point electronic structure calculations characterizing the CN stretch potential energy curve, as inspired by previous computational work. First, a geometry optimization of the periodic Au(111)/4-MBN unit cell with the bulk solvent dielectric constant on the probe side of the metal slab was performed in Quantum ESPRESSO. Then, a gas-phase geometry optimization and Hessian calculation of isolated 4-MBN with the PBE functional using Gaussian 09 was performed. The same gas-phase calculations were also performed for the 4-MBN molecule hydrogen bonded to an explicit water molecule. The normal mode mass and coordinates corresponding to the CN stretch were obtained from the gas phase calculations and are given in Tables S1 and S2 for the cases without and with the added explicit water, respectively. The normal mode masses and coordinates were found to be the same to the required accuracy for the calculations of the isolated 4-MBN molecule performed in gas phase and in continuum solvent up to \( \varepsilon = 78.3 \). Moreover, while the atoms of the explicit water did not participate in the CN stretch normal mode, the reduced mass of the normal mode is slightly higher with explicit water.
**Table S1.** Normal Mode Mass and Coordinates for 4-MBN CN Stretch Mode Without Explicit Water Molecule

| Normal mode reduced mass: | 12.665 au |
|---------------------------|-----------|
| **Normal mode coordinates** |           |
| **Atom** | **X** | **Y** | **Z** |
| H | 0.00 | 0.00 | 0.00 |
| S | 0.00 | 0.00 | 0.00 |
| C | 0.00 | 0.00 | 0.01 |
| C | 0.00 | 0.00 | -0.01 |
| C | 0.00 | 0.00 | -0.01 |
| C | 0.00 | 0.00 | 0.01 |
| H | 0.00 | 0.00 | 0.00 |
| C | 0.00 | -0.01 | 0.01 |
| H | 0.00 | 0.01 | 0.00 |
| C | -0.02 | -0.01 | 0.12 |
| H | 0.00 | -0.01 | 0.00 |
| H | 0.00 | 0.01 | 0.00 |
| C | 0.13 | 0.04 | -0.79 |
| N | -0.10 | -0.03 | 0.57 |
Table S2. Normal Mode Mass and Coordinates for 4-MBN CN Stretch Mode With Explicit Water Molecule

| Atom | X    | Y    | Z    |
|------|------|------|------|
| H    | 0.00 | 0.00 | 0.00 |
| S    | 0.00 | 0.00 | 0.00 |
| C    | 0.00 | 0.00 | -0.01|
| C    | 0.00 | 0.00 | 0.01 |
| C    | 0.00 | 0.00 | 0.01 |
| C    | 0.00 | -0.01| -0.02|
| H    | 0.00 | 0.00 | 0.00 |
| C    | 0.00 | 0.01 | -0.02|
| H    | 0.00 | 0.00 | 0.00 |
| C    | 0.01 | 0.00 | -0.11|
| H    | 0.00 | 0.00 | 0.00 |
| H    | 0.00 | 0.00 | 0.00 |
| C    | -0.11| 0.00 | 0.79 |
| N    | 0.08 | 0.02 | -0.58|
| H    | 0.00 | 0.00 | 0.00 |
| O    | 0.00 | 0.00 | 0.00 |
| H    | 0.00 | 0.00 | 0.00 |

Starting with the optimized periodic unit cell of the Au(111)/4-MBN system, these normal mode coordinates were utilized to generate the CN stretch potential energy curve for the 4-MBN attached to Au. Specifically, the coordinates of the 4-MBN molecule in the periodic unit cell with the Au slab were propagated according to these normal mode coordinates, with magnitudes $-0.12$, $-0.08$, $-0.04$, $0.00$, $0.03$, $0.06$, $0.10$, $0.14$, and $0.17$. These values roughly evenly sampled CN bond lengths from 1.0 Å to 1.4 Å. Single-point energy calculations in Quantum ESPRESSO were performed for the Au(111)/4-MBN systems at each of these propagated coordinate values, and the CN stretch potential energy curve was generated by splining these points. The one-dimensional Schrödinger equation was then solved with the normal mode mass obtained from the isolated molecule Hessian calculations (Tables S1 and S2). The CN vibrational frequency was determined.
as the difference between the lowest two vibrational energy eigenvalues. The shortest and longest CN distances studied exhibited electronic energies roughly 50 kcal/mol higher than the energy at the equilibrium distance, whereas the higher eigenvalue used in the frequency determination was always between 9 and 10 kcal/mol. The computed absolute frequencies in air and water are given and compared to experiment in Table S3.

| Environment | Type | $\nu$ (cm$^{-1}$) |
|-------------|------|------------------|
| Air         | Calculated$^a$ | 2264.3 |
|             | Experiment$^b$ | 2230.0 |
|             | Bulk solvent   | 2250.8 |
|             | 3.5 Å region   | 2254.4 |
|             | 6.3 Å region   | 2257.5 |
|             | 6.3 Å region w/ explicit H$_2$O$^c$ | 2261.4 |
|             | Experiment$^b$ | 2232.5 |

$^a$No implicit solvation utilized, corresponding to vacuum environment.  
$^b$Experimental values obtained from Dawlaty and coworkers.$^{16}$  
$^c$One explicit water molecule hydrogen-bonded to N was added to unit cell

The calculated nitrile stretching frequencies in the gas phase are in fair agreement with the experimental value considering the underlying approximations and the level of theory. The calculated frequencies in water are in similarly fair agreement with experiment. However, the calculated aqueous frequencies are lower than those in air, while the experimental frequencies demonstrate the opposite trend. The blue-shift of the aqueous nitrile stretching frequency in the experimental data was ascribed to an effect of hydrogen bonding,$^{16}$ which is not captured by the fully implicit solvent used here. To test the effect of hydrogen bonding, we also performed these calculations using one explicit water molecule hydrogen-bonded to the nitrile N and found that the absolute frequency increased by 4 cm$^{-1}$ relative to the value with the same dielectric solvation
environment, consistent with the experimentally observed increase albeit still not greater than the calculated gas-phase frequency. However, we did not observe a significant difference in the vibrational Stark frequency shifts with the explicit water molecule hydrogen-bonded to the nitrile N (see below). We emphasize that the absolute CN frequencies are not important for this study, but rather only the changes in CN frequency with solvent dielectric constant and applied potential are relevant. Thus, for the purposes of this study, we calculated the differences in the CN frequency \( \Delta \nu \) with changes in the solvent dielectric constant as well as with applied potential using the fully implicit solvent model.

**Interfacial Solvation Reaction Field Model**

The Onsager-like interfacial solvation reaction field model used to fit the calculated data in Figure 3 in the main text was developed by Dawlaty and coworkers. Here, we briefly introduce the model and define its terms. The change in frequency \( \Delta \nu \) (in wavenumbers) as a function of solvent dielectric constant \( \varepsilon_{\text{solv}} \) is expressed as follows:

\[
\Delta \nu(\varepsilon_{\text{solv}}) = \left( \frac{\mu \Delta \mu}{4 \pi \varepsilon_0 a^3} \right) \left( \frac{4(n^2+2)^2 \zeta(\varepsilon_{\text{solv}})}{3(n^2+3)(n^2-1)\zeta(\varepsilon_{\text{solv}})-3n^2-9} \right)
\]

(S1)

where \( \mu \) is the permanent dipole moment, \( \Delta \mu \) is the difference in dipole moments between the first excited and ground vibrational states, \( \varepsilon_0 \) is the permittivity of free space, \( a \) is the radius of the solute cavity, and \( n \) is the bulk solvent refractive index. Moreover, \( \zeta \) is an infinite sum that is written as

\[
\zeta(\varepsilon_{\text{solv}}) = \sum_j A(\varepsilon_{\text{solv}})^j \left( \frac{128j^6 + 12j^2 - 1}{4j^3(4j^2-1)^3} \right)
\]

(S2)
where

\[ A(\varepsilon_{\text{solv}}) = \frac{\varepsilon_{\text{solv}} - 1}{\varepsilon_{\text{solv}} + 1}. \]  

(S3)

The infinite sum in \( j \) was found to be convergent for all solvent dielectric constants used herein and was computed numerically. The prefactor term in Eq. (S1), \( \frac{\mu \Delta \mu}{4\pi\varepsilon_0 a^3} \), was used in the experimental work as the lone fitting parameter to the data.\(^{16}\) The values of this parameter used in each fit in Figure 4 of the main text are given in Table S4.

Table S4. Interfacial Solvation Reaction Field Model Prefactors Used to Fit Data in Figure 3.

| Model               | \( \frac{\mu \Delta \mu}{4\pi\varepsilon_0 a^3} \) (cm\(^{-1}\)) |
|---------------------|---------------------------------------------------------------|
| Expt.\(^{16}\)      | 15                                                            |
| Bulk solvent        | 27                                                            |
| 3.5 Å layer\(^{a}\) | 21                                                            |
| 6.3 Å layer\(^{a}\) | 13                                                            |

\(^{a}\)This interfacial layer has a dielectric constant of 2.8.
**Differential Capacitance Calibrations**

The differential capacitance was obtained for the bare Au(111) slab and for the Au(111) slab with 4-MBN appended using interfacial solvation schemes that vary in the width and dielectric constant of the low-dielectric interfacial region. The width of the low-dielectric interfacial region was defined as starting one Au van der Waals radius (1.66 Å) above the mean $z$ coordinate of the surface Au atoms, denoted $z_{\text{surf}}$. Beyond the low-dielectric interfacial region, the dielectric constant was set to 78.3 to represent bulk water for these benchmarking calculations. Periodic DFT calculations were performed with electrode charges of zero and +1, and the electrode potential for the latter system versus PZC, $\Delta \Phi_e$, was determined for each interfacial solvation scheme using the procedure outlined in the main text. For simplicity, only one non-zero electrode charge was utilized in this benchmarking, as justified by the virtually linear charge-potential relationship observed for this system. The differential capacitance was estimated from $\Delta \Phi_e$ by converting units from elementary charge per V per unit cell area to the more standard $\mu$F/cm$^2$. The plots of differential capacitance versus low-dielectric region width for different dielectric constants are shown in Figures S2 and S3. The relationship between the low-dielectric region width and the dielectric constant of this region corresponding to a constant differential capacitance of 11 $\mu$F/cm$^2$ for the Au(111)/4-MBN system is shown in Figure S4.
Figure S2. Differential capacitances of a $4 \times 4 \times 3$ atom Au(111) slab with vacuum on one side and a low-dielectric interfacial region followed by bulk water on the other side. Four dielectric constants for the low-dielectric interfacial region were utilized with varying widths up to 10 Å.

Figure S3. Differential capacitances of the Au(111)/4-MBN system with vacuum on one side and a low-dielectric interfacial region followed by bulk water on the other side. Four dielectric constants for the low-dielectric interfacial region were utilized with varying widths up to 10 Å.
Figure S4. Relationship between the low-dielectric interfacial region width and the dielectric constant of this region corresponding to a constant differential capacitance of 11 μF/cm² for the Au(111)/4-MBN system based on the data in Figure S3.

These data, combined with Figure 3 in the main text, demonstrate the difficulty in simultaneously reproducing the experimentally measured dependence of the CN vibrational frequency on solvent dielectric constant and a sufficiently high differential capacitance with the current methods. As mentioned in the main paper, the differential capacitance of the Au(111)-aqueous electrolyte interface has been measured to be 11‒40 μF/cm², depending considerably on experimental conditions such as the identity and concentration of the electrolyte. The low-dielectric interfacial region that reproduces the experimental CN vibrational frequency shifts with solvent dielectric constant (Figure 3A) is wider and has a lower dielectric constant than the parameters required to obtain a differential capacitance of at least 11 μF/cm² (Figure S4). In addition, the following section demonstrates that the low-dielectric region required to obtain this differential capacitance does not reproduce the experimentally measured vibrational Stark shifts either. Furthermore, the experimentally measured differential capacitance depends strongly on the electrolyte, and the ionic strength (i.e., the effect of electrolyte ions) is not included in our calculations, preventing a clear comparison of the calculated and measured differential
capacitance. Thus, the calculations with an electrified Au slab in the main text were performed using solvation conditions that reproduce the experimentally measured dependence of the CN vibrational frequency on solvent polarity.

The choice of computational conditions such as unit cell size, solvation scheme, and inclusion of an explicit water modestly affected the electrode charge-potential relationship and ultimately the calculated response of the CN frequency to applied bias. The calculated differential capacitances with various computational parameters are given in Table S5. These data show that the cell size weakly affects the differential capacitance, which is a known consequence of using a homogeneous, non-local Jellium-like countercharge. The cell size used for the data presented in the main paper was 37.5 Å. The smaller unit cell used herein generally yielded larger differential capacitances. In particular, with the smaller unit cell and in the absence of any low dielectric interfacial region, the differential capacitance was 16.2 μF/cm², which is within the range of experimental values. However, Figure 3A of the main text demonstrates the inability of this solvation scheme to reproduce the experimental dependence of the CN frequency on solvent polarity, so this approach cannot necessarily be considered a more physically accurate description of the interface. Table S5 also shows the very small impact the inclusion of one explicit water molecule had on the differential capacitance of the Au(111)/4-MBN system.
Table S5. Calculated Differential Capacitances, $C_d$, of the Au(111)/4-MBN System with Different Computational Models.

| Model                               | $C_d$ (μF/cm²) |
|-------------------------------------|----------------|
| 6.3 Å region$^a$                    | 5.8            |
| Explicit H$_2$O, 6.3 Å region$^{a,b}$ | 5.9            |
| 6.3 Å region$^c$                    | 6.2            |
| 3.5 Å region$^c$                    | 8.2            |
| Bulk solvent$^c$                     | 16.2           |

$^a$Unit cell height (in z) of 37.5 Å.
$^b$One explicit water molecule hydrogen bonded to N added to the unit cell.
$^c$Unit cell height (in z) of 23.5 Å.

Additional CN Frequency Shifts with Applied Potential

The choices of computational schemes furthermore affected the calculated frequency shifts with applied potential, albeit modestly. In addition to Figure 3B of the main text, these data are shown in Figure S5, and the slopes of their linear fits are given in Table S6. Figure S5 and Table S6 demonstrate that the differences in the vibrational Stark effect on the CN frequency for the various solvation schemes used are relatively small. For the three sets of data obtained with the smaller unit cell, the bulk solvation approach demonstrated a slope corresponding to the frequency shift versus applied electrode potential of 9.4 cm$^{-1}$/V, while the approaches with low dielectric interfacial regions of 3.5 Å and 6.3 Å produced slopes of 9.3 cm$^{-1}$/V and 9.6 cm$^{-1}$/V, respectively. The Stark shift calculations performed with the larger unit cell, namely those presented in the main text, generally exhibited larger slopes, specifically 10.7 cm$^{-1}$/V and 12.1 cm$^{-1}$/V without and with explicit water. The presence of the explicit water increased the slope compared to the fully implicit solvent. All of the frequency shifts in Figures 3B and S5 demonstrate various degrees of non-linearity, especially over wider ranges of applied potentials.
Figure S5. Aqueous CN stretching frequencies as a function of applied electrode potential for the 6.3 Å low-dielectric interfacial region and the smaller unit cell (purple circles), 3.5 Å low-dielectric interfacial region and the smaller unit cell (red squares), bulk solvent and the smaller unit cell (green diamonds), and with one explicit water molecule, a 6.3 Å low-dielectric interfacial region, and the larger unit cell (blue triangles).

Table S6. Slopes of Linear Fits to Computed CN Frequency Shifts Versus Applied Electrode Potential with Different Computational Models.

| Model                        | Slope$^d$ (cm$^{-1}$/V) |
|------------------------------|--------------------------|
| 6.3 Å region$^a$             | 10.7                     |
| Explicit H$_2$O, 6.3 Å region$^{a,b}$ | 12.1                     |
| 6.3 Å region$^c$             | 9.6                      |
| 3.5 Å region$^c$             | 9.3                      |
| Bulk solvent$^c$             | 9.4                      |

$^a$Unit cell height (in $z$) of 37.5 Å.
$^b$One explicit water molecule hydrogen bonded to N added to the unit cell.
$^c$Unit cell height (in $z$) of 23.5 Å.
$^d$Linear fits are for the entire potential range despite significant non-linearity.
Additional Electrostatic Potentials and Electric Fields

This section contains additional contour plots of electrostatic potentials and electric fields relative to those at the PZC. The qualitative analyses of these data are the same as those for $\Delta \Phi_e = \pm 0.5$ V shown in Figures 5 and 6 of the main text. Figures S6 and S7 depict computational PZC-referenced electrostatic potentials and Figures S8 and S9 depict the corresponding referenced surface-normal electric fields.

**Figure S6.** Contour plots of the computational PZC-referenced electrostatic potentials, $\Delta \varphi$, in roughly the plane of the 4-MBN molecule near the Au(111) surface at electrode potentials $-0.75$ V (left) and $-0.25$ V (right). The vertical axes have been shifted by the position of the Au(111) surface, $z_{surf}$, and the structure of the 4-MBN molecule has been transparently overlaid based on its coordinates.
Figure S7. Contour plots of the computational PZC-referenced electrostatic potentials, \( \Delta \varphi \), in roughly the plane of the 4-MBN molecule near the Au(111) surface at electrode potentials 0.25 V (left) and 0.75 V (right). The vertical axes have been shifted by the position of the Au(111) surface, \( z_{\text{surf}} \), and the structure of the 4-MBN molecule has been transparently overlaid based on its coordinates.

Figure S8. Contour plots of the surface-normal electric field relative to the field at the PZC, \( \Delta F \), in roughly the plane of the 4-MBN molecule near the Au(111) surface at electrode potentials \(-0.75\) V (left) and \(-0.25\) V (right). The vertical axes have been shifted by the position of the Au(111) surface, \( z_{\text{surf}} \), and the structure for the 4-MBN molecule has been transparently overlaid based on its coordinates.
Figure S9. Contour plots of the surface-normal electric field relative to the field at the PZC, $\Delta F$, in roughly the plane of the 4-MBN molecule near the Au(111) surface at electrode potentials 0.25 V (left) and 0.75 V (right). The vertical axes have been shifted by the position of the Au(111) surface, $z_{surf}$, and the structure for the 4-MBN molecule has been transparently overlaid based on its coordinates.

Charge Densities

In addition to the electrostatic potentials and electric fields, we investigated the charge densities in the interfacial region versus those at PZC, $\Delta \rho$. Figure S10 presents two different one-dimensional (along the surface-normal z) slices of the three-dimensional differential charge densities for $\Delta \Phi_e = \pm 0.5$ V: one through the 4-MBN probe and another through only the dielectric continuum away from the probe.
Figure S10. Charge densities $\Delta \rho$ relative to the charge density at the computational PZC as a function of $z - z_{\text{surf}}$ at $\Delta \Phi_e = \pm 0.5 \text{ V}$ through A) the center of the 4-MBN molecule and B) a region of the unit cell away from 4-MBN molecule, where the electrode interfaces only with the dielectric continuum. Note that the vertical axes are scaled differently by an order of magnitude.

The scales of these differential charge densities differ by over an order of magnitude. Therefore, the changes in charge density inside and near the probe molecule are significantly larger than the nearly isotropic accumulation of charge elsewhere on the surface. Figure S10B shows that excess charge of the same sign as the applied electrode potential accumulates around $z - z_{\text{surf}} = 0 \text{ Å}$ at the Au(111)-dielectric continuum interface. The accumulation of excess charge through the center of the 4-MBN probe (Figure S10A) is a qualitatively different situation. The expected accumulated charge of the same sign as the electrode potential near $z - z_{\text{surf}} = 0 \text{ Å}$ is still observed, but $\Delta \rho$ oscillates and changes signs through 4-MBN. Thus, Figure S10A clearly demonstrates the
polarization of the probe molecule, with charge of the same sign as the electrode potential accumulating near the S and CN ($z - z_{surf} \approx 0 \, \text{Å}$ and $z - z_{surf} \approx 7 \, \text{Å}$, respectively) and charge of the opposite sign as the electrode potential accumulating in parts of the benzene ring ($z - z_{surf} \approx 2-5 \, \text{Å}$). These charge densities serve as further evidence of the inhomogeneity of the electrostatic environment at the electrode/probe/solution interface. Furthermore, the significant electric field inhomogeneity and intramolecular polarization of 4-MBN in response to the applied potential may be related to the challenges in designing empirical electrostatic potential-frequency correlation maps for nitrile groups compared to other chromophores in vibrational spectroscopy calculations.\textsuperscript{17}

**Cartesian Coordinates and Sample Input Files of Model Systems**

*Au(111)/4-MBN in vacuum:*

\[
\begin{align*}
\text{Au} & \quad 5.113349030 \quad 0.000000000 \quad 6.410455850 \\
\text{Au} & \quad 7.670023550 \quad 1.476096720 \quad 6.410455850 \\
\text{Au} & \quad 5.113349030 \quad 2.952193440 \quad 6.410455850 \\
\text{Au} & \quad 7.670023550 \quad 4.428290160 \quad 6.410455850 \\
\text{Au} & \quad 5.113349030 \quad 5.904386880 \quad 6.410455850 \\
\text{Au} & \quad 7.670023550 \quad 7.380483600 \quad 6.410455850 \\
\text{Au} & \quad 5.113349030 \quad 8.856580320 \quad 6.410455850 \\
\text{Au} & \quad 7.670023550 \quad 10.332677040 \quad 6.410455850 \\
\text{Au} & \quad 0.000000000 \quad 0.000000000 \quad 6.410455850 \\
\text{Au} & \quad 2.556674520 \quad 1.476096720 \quad 6.410455850 \\
\text{Au} & \quad 0.000000000 \quad 2.952193440 \quad 6.410455850 \\
\text{Au} & \quad 2.556674520 \quad 4.428290160 \quad 6.410455850 \\
\text{Au} & \quad 0.000000000 \quad 5.904386880 \quad 6.410455850 \\
\text{Au} & \quad 2.556674520 \quad 7.380483600 \quad 6.410455850 \\
\text{Au} & \quad 0.000000000 \quad 8.856580320 \quad 6.410455850 \\
\text{Au} & \quad 2.556674520 \quad 10.332677040 \quad 6.410455850 \\
\text{Au} & \quad 6.817798710 \quad 0.000000000 \quad 8.820911700 \\
\text{Au} & \quad 9.374473220 \quad 1.476096720 \quad 8.820911700 \\
\text{Au} & \quad 6.817798710 \quad 2.952193440 \quad 8.820911700 \\
\text{Au} & \quad 9.374473220 \quad 4.428290160 \quad 8.820911700 \\
\text{Au} & \quad 6.817798710 \quad 5.904386880 \quad 8.820911700 \\
\text{Au} & \quad 9.374473220 \quad 7.380483600 \quad 8.820911700 \\
\text{Au} & \quad 6.817798710 \quad 8.856580320 \quad 8.820911700 \\
\text{Au} & \quad 9.374473220 \quad 10.332677040 \quad 8.820911700
\end{align*}
\]
%  
|  |  |  |  |
|---|---|---|---|
| Au | 1.704449680 | 0.000000000 | 8.820911700 |
| Au | 4.261124190 | 1.476096720 | 8.820911700 |
| Au | 1.704449680 | 2.952193440 | 8.820911700 |
| Au | 4.261124190 | 4.428290160 | 8.820911700 |
| Au | 1.704449680 | 5.904386880 | 8.820911700 |
| Au | 4.261124190 | 7.380483600 | 8.820911700 |
| Au | 1.704449680 | 8.856580320 | 8.820911700 |
| Au | 4.261124190 | 10.332677040 | 8.820911700 |
| Au | 8.523619705 | -0.000704455 | 11.266281710 |
| Au | 5.906101083 | 1.366103880 | 11.249867277 |
| Au | 8.586101083 | 2.879282211 | 11.341012611 |
| Au | 6.069272220 | 4.097546970 | 11.365497194 |
| Au | 8.493041248 | 5.904042556 | 11.162938548 |
| Au | 6.070161923 | 7.709695269 | 11.359437621 |
| Au | 8.587261553 | 8.929220283 | 11.341958735 |
| Au | 5.904803639 | 10.44256628 | 11.251464068 |
| Au | 3.56364655 | 0.000024949 | 11.339770760 |
| Au | 0.849495731 | 1.435034423 | 11.349300534 |
| Au | 3.381912392 | 2.911312131 | 11.220630045 |
| Au | 0.741197009 | 4.316311703 | 11.293067257 |
| Au | 3.068140173 | 5.903933490 | 11.262361870 |
| Au | 0.741856820 | 7.492608584 | 11.292603966 |
| Au | 3.381770310 | 8.897626279 | 11.220891642 |
| Au | 0.849541221 | 10.374143899 | 11.349961365 |
| S  | 5.063136993 | 5.905099886 | 12.741747837 |
| C  | 4.882688132 | 5.904244324 | 14.516048559 |
| C  | 4.807639635 | 4.686999776 | 15.20439082 |
| C  | 4.802486972 | 7.121041635 | 15.20423086 |
| C  | 4.664563737 | 4.687627769 | 16.584123693 |
| H  | 4.863268680 | 3.745520377 | 14.65872638 |
| C  | 4.659329417 | 7.119490910 | 16.584508995 |
| H  | 4.853872089 | 8.062783577 | 14.659074768 |
| C  | 4.592708759 | 5.903262407 | 17.286034340 |
| H  | 4.610901963 | 3.746800196 | 17.128886703 |
| H  | 4.601383876 | 8.059847581 | 17.129311186 |
| C  | 4.455616436 | 5.902983747 | 18.704281353 |
| N  | 4.341362415 | 5.902831433 | 19.862469241 |

\textit{Au(111)/4-MBN in water:}

| Au  | 5.113349030 | 0.000000000 | 6.410455850 |
| Au  | 7.670023550 | 1.476096720 | 6.410455850 |
| Au  | 5.113349030 | 2.952193440 | 6.410455850 |
| Au  | 7.670023550 | 4.428290160 | 6.410455850 |
| Au  | 5.113349030 | 5.904386880 | 6.410455850 |
| Au  | 7.670023550 | 7.380483600 | 6.410455850 |
| Au  | 5.113349030 | 8.856580320 | 6.410455850 |

S23
| Au    | 7.67023550 | 10.332677040 | 6.410455850 |
|-------|------------|--------------|-------------|
| Au    | 0.000000000 | 0.000000000 | 6.410455850 |
| Au    | 2.556674520 | 1.476096720 | 6.410455850 |
| Au    | 0.000000000 | 2.952193440 | 6.410455850 |
| Au    | 2.556674520 | 4.428290160 | 6.410455850 |
| Au    | 0.000000000 | 5.904386880 | 6.410455850 |
| Au    | 2.556674520 | 7.380483600 | 6.410455850 |
| Au    | 0.000000000 | 8.856580320 | 6.410455850 |
| Au    | 2.556674520 | 10.332677040 | 6.410455850 |
| Au    | 6.817798710 | 0.000000000 | 8.820911700 |
| Au    | 9.374473220 | 1.476096720 | 8.820911700 |
| Au    | 6.817798710 | 2.952193440 | 8.820911700 |
| Au    | 9.374473220 | 4.428290160 | 8.820911700 |
| Au    | 6.817798710 | 5.904386880 | 8.820911700 |
| Au    | 9.374473220 | 7.380483600 | 8.820911700 |
| Au    | 6.817798710 | 8.856580320 | 8.820911700 |
| Au    | 9.374473220 | 10.332677040 | 8.820911700 |
| Au    | 1.704449680 | 0.000000000 | 8.820911700 |
| Au    | 4.261124190 | 1.476096720 | 8.820911700 |
| Au    | 1.704449680 | 2.952193440 | 8.820911700 |
| Au    | 4.261124190 | 4.428290160 | 8.820911700 |
| Au    | 1.704449680 | 5.904386880 | 8.820911700 |
| Au    | 4.261124190 | 7.380483600 | 8.820911700 |
| Au    | 1.704449680 | 8.856580320 | 8.820911700 |
| Au    | 4.261124190 | 10.332677040 | 8.820911700 |
| Au    | 8.523908719 | -0.000675456 | 11.265387265 |
| Au    | 5.908677517 | 1.366886002 | 11.250850202 |
| Au    | 8.588351071 | 2.878473146 | 11.341973370 |
| Au    | 6.069502468 | 4.100247745 | 11.366382724 |
| Au    | 8.491865353 | 5.904038876 | 11.162094060 |
| Au    | 6.070412372 | 7.706871246 | 11.360442442 |
| Au    | 8.588972780 | 8.929962627 | 11.342942811 |
| Au    | 5.907383288 | 10.441712923 | 11.252467074 |
| Au    | 3.356038396 | 0.000089500 | 11.37071324 |
| Au    | 0.848890112 | 1.437224127 | 11.348920195 |
| Au    | 3.382284242 | 2.912431106 | 11.218281176 |
| Au    | 0.741537710 | 4.315625572 | 11.293533793 |
| Au    | 3.070833801 | 5.903953570 | 11.263593345 |
| Au    | 0.742163835 | 7.493253482 | 11.293061022 |
| Au    | 3.382171621 | 8.896411488 | 11.218544501 |
| Au    | 0.848944979 | 10.371987222 | 11.349599844 |
| S     | 5.059785996 | 5.905152278 | 12.741821063 |
| C     | 4.882401361 | 5.904236514 | 14.520835089 |
| C     | 4.809258037 | 4.684801561 | 15.204286377 |
| C     | 4.804070898 | 7.123175459 | 15.204574859 |
| C     | 4.665428126 | 4.683661922 | 16.585595700 |
| H     | 4.864621400 | 3.742721929 | 14.662426765 |
|   |   |   |   |
|---|---|---|---|
| C | 4.660162037 | 7.123371740 | 16.585792722 |
| H | 4.855262529 | 8.065652288 | 14.662903108 |
| C | 4.593426406 | 5.903326329 | 17.281080178 |
| H | 4.610714221 | 3.742618861 | 17.127811612 |
| H | 4.601229646 | 8.064074060 | 17.128274544 |
| C | 4.454913644 | 5.902974569 | 18.698877226 |
| N | 4.341872040 | 5.902778800 | 19.857950934 |

**Au(111)/4-MBN with Explicit H2O in water:**

|   |   |   |   |
|---|---|---|---|
| Au | 5.113349030 | 0.000000000 | 6.410455850 |
| Au | 7.670023550 | 1.476096720 | 6.410455850 |
| Au | 5.113349030 | 2.952193440 | 6.410455850 |
| Au | 7.670023550 | 4.428290160 | 6.410455850 |
| Au | 5.113349030 | 5.904386880 | 6.410455850 |
| Au | 7.670023550 | 7.380483600 | 6.410455850 |
| Au | 5.113349030 | 8.856580320 | 6.410455850 |
| Au | 7.670023550 | 10.32677040 | 6.410455850 |
| Au | 0.000000000 | 0.000000000 | 6.410455850 |
| Au | 2.556674520 | 1.476096720 | 6.410455850 |
| Au | 0.000000000 | 2.952193440 | 6.410455850 |
| Au | 2.556674520 | 4.428290160 | 6.410455850 |
| Au | 0.000000000 | 5.904386880 | 6.410455850 |
| Au | 2.556674520 | 7.380483600 | 6.410455850 |
| Au | 0.000000000 | 8.856580320 | 6.410455850 |
| Au | 2.556674520 | 10.32677040 | 6.410455850 |
| Au | 6.817798710 | 0.000000000 | 8.820911700 |
| Au | 9.374473220 | 1.476096720 | 8.820911700 |
| Au | 6.817798710 | 2.952193440 | 8.820911700 |
| Au | 9.374473220 | 4.428290160 | 8.820911700 |
| Au | 6.817798710 | 5.904386880 | 8.820911700 |
| Au | 9.374473220 | 7.380483600 | 8.820911700 |
| Au | 6.817798710 | 8.856580320 | 8.820911700 |
| Au | 9.374473220 | 10.32677040 | 8.820911700 |
| Au | 1.704449680 | 0.000000000 | 8.820911700 |
| Au | 4.261124190 | 1.476096720 | 8.820911700 |
| Au | 1.704449680 | 2.952193440 | 8.820911700 |
| Au | 4.261124190 | 4.428290160 | 8.820911700 |
| Au | 1.704449680 | 5.904386880 | 8.820911700 |
| Au | 4.261124190 | 7.380483600 | 8.820911700 |
| Au | 1.704449680 | 8.856580320 | 8.820911700 |
| Au | 4.261124190 | 10.32677040 | 8.820911700 |
| Au | 8.542181218 | 0.000115709 | 11.258202363 |
| Au | 5.923806703 | 1.364731117 | 11.246920402 |
| Au | 8.611858868 | 2.871353113 | 11.363188914 |
| Au | 6.095091045 | 4.086484429 | 11.366865877 |
| Au | 8.502003879 | 5.904636667 | 11.149069926 |
Sample Quantum-ESPRESSO input - 6.3 Å layer, +0.25 V

&CONTROL
  restart_mode = 'from_scratch',
  calculation = 'scf',
  prefix       = 'AuSPhCN',
  outdir       = './',
  pseudo_dir   = './',
  etot_conv_thr = 1.0D-4,
  forc_conv_thr = 1.0D-3,
  nstep = 200,
/

&SYSTEM
  ibrav       = 0,
  !   celldm(1) = 7.89223,
  nspin       = 1,
  tot_charge  = 0.11,
  nat         = 61,
  ntyp        = 5,
ecutwfc = 60,
occupations = 'smearing', smearing = 'cold', degauss = 0.01,

&ELECTRONS
  conv_thr = 1.D-5,
  mixing_beta = 0.7D0,
  startingwfc = 'atomic',
  startingpot = 'atomic+random',

/K_POINTS { automatic }
  1 1 1 0 0 0

ATOMIC_SPECIES
Au  196.96657  Au_ONCV_PBE-1.0.UPF
H  1.00  H_ONCV_PBE-1.0.UPF
S  32.065  S_ONCV_PBE-1.1.UPF
C  12.0107  C_ONCV_PBE-1.0.UPF
N  14.0067  N_ONCV_PBE-1.0.UPF

CELL_PARAMETERS (angstrom)
  10.226698060  0.000000000  0.000000000
  0.000000000  11.808773755  0.000000000
  0.000000000  0.000000000  37.462735094

ATOMIC_POSITIONS (angstrom)
Au  5.113349030  0.000000000  6.410455850  0  0  0
Au  7.670023550  1.476096720  6.410455850  0  0  0
Au  5.113349030  2.952193440  6.410455850  0  0  0
Au  7.670023550  4.428290160  6.410455850  0  0  0
Au  5.113349030  5.904386880  6.410455850  0  0  0
Au  7.670023550  7.380483600  6.410455850  0  0  0
Au  5.113349030  8.856580320  6.410455850  0  0  0
Au  7.670023550 10.332677040  6.410455850  0  0  0
Au  0.000000000  0.000000000  6.410455850  0  0  0
Au  2.556674520  1.476096720  6.410455850  0  0  0
Au  0.000000000  2.952193440  6.410455850  0  0  0
Au  2.556674520  4.428290160  6.410455850  0  0  0
Au  0.000000000  5.904386880  6.410455850  0  0  0
Au  2.556674520  7.380483600  6.410455850  0  0  0
Au  0.000000000  8.856580320  6.410455850  0  0  0
Au  2.556674520 10.332677040  6.410455850  0  0  0
Au  6.817798710  0.000000000  8.820911700  0  0  0
Au  9.374473220  1.476096720  8.820911700  0  0  0
Au  6.817798710  2.952193440  8.820911700  0  0  0
Au  9.374473220  4.428290160  8.820911700  0  0  0
Au  6.817798710  5.904386880  8.820911700  0  0  0
Au       9.374473220  7.380483600  8.820911700  0   0   0
Au       6.817798710  8.856580320  8.820911700  0   0   0
Au       9.374473220 10.332677040  8.820911700  0   0   0
Au       1.704449680  0.000000000  8.820911700  0   0   0
Au       4.261124190  1.476096720  8.820911700  0   0   0
Au       1.704449680  2.952193440  8.820911700  0   0   0
Au       4.261124190  4.428290160  8.820911700  0   0   0
Au       8.523908719 -0.000675456 11.265387265
Au       5.908677517  1.366886002 11.250850202
Au       8.588351071  2.878473146 11.341973370
Au       6.069502468  4.100247745 11.366382724
Au       8.491868535  5.904038876 11.162094060
Au       6.070412372  7.706871246 11.360442442
Au       8.588972780  8.929962627 11.342942811
Au       5.907383288 10.441712923 11.252467074
Au       3.356038396  0.000895000 11.337071324
Au       0.848890112  1.437224127 11.34920195
Au       3.382284242  2.912431106 11.218281176
Au       0.741537710  4.315625572 11.293533793
Au       0.742168385  7.493253482 11.293061022
Au       3.382171621  8.926411488 11.218544501
Au       0.848944979 10.371987222 11.349599844
S        5.059785996  5.905152278 12.741821063
C        4.882401361  5.904236514 14.520835089
C        4.809258037  4.684801561 15.20426377
C        4.804070898  7.123175459 15.204574859
C        4.665428126  4.683661922 16.585595700
H        4.864621400  3.742721929 14.662426765
C        4.660162037  7.12371740 16.585792722
H        4.855262529  8.065652288 14.662903108
C        4.593426406  5.903326329 17.281080178
H        4.610714221  3.742618861 17.127811612
H        4.601229646  8.064074060 17.128274544
C        4.454913644  5.902974569 18.698877226
N        4.341872040  5.902778800 19.857950934

Sample Environ input, 6.3 Å layer

&ENVIRON
!  
  verbose = 2
  environ_thr = 1.d-1
environ_type = 'input'
env_electrostatic = .true.
env_static_permittivity = 78.3D0
env_dielectric_regions = 2
!
/ &BOUNDARY
  solvent_mode = 'electronic'
/
&ELECTROSTATIC
!
  pbc_correction = 'none'
  pbc_dim = 2
  pbc_axis = 3
!
  tol = 1.d-11
  mix = 0.6
  solver = 'iterative'
  auxiliary = 'full'
!
/ DIELECTRIC_REGIONS {angstrom}
  2.8 1.0 5.5 5.5 12.9586 6.32 0.5 2 3
  1.0 1.0 5.5 5.5 4.7435 4.7435 0.5 2 3
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