First-principles Simulation of Electrochemical Systems at Fixed Applied Voltage: Vibrational Stark Effect for CO on Platinum Electrodes

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Chemisorbed molecules at a fuel-cell electrode are a very sensitive probe of the surrounding electrochemical environment, and one that can be accurately monitored with different spectroscopic techniques. We develop a comprehensive electrochemical model to study molecular chemisorption at fixed applied voltage, and calculate from first principles the voltage dependence of vibrational frequencies (the vibrational Stark effect) for CO on platinum electrodes, finding excellent agreement with electrochemical spectroscopic experiments and resolving previous controversies.

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Rising sustainability concerns have revived strong interest in electrochemical electricity generation whose basic principle is to catalytically convert the energy stored in chemical bonds into usable electrical power. For any given electrochemical system (e.g., a fuel cell or a battery), the power generated is the product of two distinct contributions: (1) the electrode voltage difference, which is the thermodynamic variable that quantifies the energy per electron made available through the breaking and rearranging of chemical bonds (Nernst’s law), and (2) the current density, which is the kinetic observable that measures the rate at which these chemical processes take place (Arrhenius’ law). It should be emphasized, however, that these two factors are not completely independent, as one observes experimentally a systematic drop in voltage at high electrical current. This phenomenon, commonly known as activation voltage loss, represents one of the main limitations to the performance of electrochemical technologies.

Although the origins of the voltage dependence of the electrical current have long been conceptually understood, it is only recently that computational laboratories have applied first-principles calculations to study this effect with the difficult task of describing catalytic reactions at an electrode surface as a function of the applied voltage. The electrochemical free-energy correction introduced by Nørskov et al. represents a key successful step in this direction. In this approach, the influence of the electrode voltage $\mathcal{E}$ is included by adding a correction $-e\mathcal{E}$ to the energy of all reaction intermediates that involve an electron transferred to the metal. This zeroth-order correction has been shown to accurately predict the activation voltage of fundamental electrocatalytic processes, such as the oxygen reduction reaction at fuel-cell cathodes. However, this approach does not capture the self-consistent modifications of the electronic structure that arise from the applied potential. In particular, it does not consider the variation of the electrode charge as a function of the potential and the interaction of the induced surface electric field with chemisorbed molecules.

Several other authors have proposed to account for these important electronic effects using more representative electrochemical models. These calculations differ in key quantitative and qualitative details from the approach we present, and are generally carried out at constant electrode charge $q$, the voltage $\mathcal{E}$ being determined $a posteriori$ using various procedures to relate its value to the computed Fermi level $\varepsilon_F$. This is in clear contrast to most in-situ experiments, in which the state of the system is directly controlled via the electrode voltage and all relevant electrochemical properties are given in terms of this central intensive variable. Although the voltage dependencies of electrochemical properties can be recovered via an inverse Legendre transform, this indirect method entails repeated constant-charge calculations to invert the charge-to-voltage relation.

In this study, we introduce a practical computational model that allows to work directly at fixed electrode voltage while fully describing self-consistent changes in the electronic structure and taking into account realistic electrochemical conditions. A validation of the method is provided by the prediction of the voltage dependence of vibrational frequencies—the vibrational Stark effect—for CO on platinum electrodes, which offers a very sensitive spectroscopic probe of the electrochemical environment and surface electric field. Since the vibrational properties of chemisorbed molecules can be accurately described from first principles and precisely measured using various infrared techniques, the calculation of the Stark effect represents a stringent test for assessing the predictive ability of an electrochemical model. To date, very large discrepancies between first-principles predictions and Stark measurements have been reported, and their elucidation has been a long-standing question in surface science and electrochemistry.

To put matters into perspective, a typical electrode-electrolyte interface is depicted in Fig. 1(a). The system consists of an adsorbate-covered metal surface in contact...
with an electrolyte solution. For this system, the electrode voltage $\mathcal{E}$ corresponds to the energy involved in displacing an electron from the metal electrode to the bulk of the ionic solvent \([14]\). Therefore, including voltage conditions requires to accurately describe the behavior of the screened electrostatic potential in the solvent region. It is important to note, however, that electrostatic screening in the electrolyte occurs on considerably large length scales—typically, $10^{-4}$–$10^{-1}$ molar/liter (M) \([15]\) for ionic concentrations in the range $10^{-4}$–$10^{-1}$ mol/liter (M) \([15]\), which renders the explicit first-principles representation of the electrolyte prohibitively expensive and practically inaccessible with current computational resources. Furthermore, quantitative errors in local and semilocal density-functional theory (DFT) descriptions of water \([16]\) have be reported. These errors result in overstructured representations of aqueous media and overestimated freezing temperatures \([17]\)—which translates into overevaluated dielectric responses for explicit solvation models.

To overcome these important limitations, we introduce an atom-continuum double layer model of the electrified electrode compound \([15]\). Within this implicit approach, the electrode voltage $\mathcal{E}$ can be simply expressed as

$$\mathcal{E} = \mathcal{V}_0 - \frac{1}{\varepsilon} \mathcal{E}_F = -\frac{1}{\varepsilon} \mathcal{E}_F,$$

where $\mathcal{V}_0 = 0$ V is the asymptotic value of the potential in the bulk of the electrolyte. With this physical picture in mind, it clearly appears that increasing the electrode voltage causes a depletion of surface electronic states compensated by an accumulation of negative counterions in the electrolyte \([\text{Fig. 1(b)}]\). The induced polarization enhances the double layer electric field, which interacts more strongly with the adsorbates and shifts their vibrational frequencies.

In this model, a smoothly varying dielectric permittivity $\varepsilon$ accounts for the water environment, and diffuse charge densities $c^+_{\text{d}}$ and $c^-_{\text{d}}$ represent the thermal distributions of the counterions of bulk concentration $c_0$, absolute charge $z_{\text{d}}$, and size $a_{\text{d}}$ (for the sake of simplicity, we restrict ourselves to the case of a $z_{\text{d}}$-$z_{\text{d}}$ symmetric ionic solution). The dielectric permittivity is calculated using the parametrization of Gygi and Fattebert that involves the static dielectric constant of water $\varepsilon_0 = 78$ \([19]\). This dielectric model properly captures the gradual transition of the permittivity across the solvation shell \([20]\) and yields accurate solvation energies for a broad range of molecular species \([21]\). The ionic concentrations $c^+_{\text{d}}$ and $c^-_{\text{d}}$ follow the modified Boltzmann statistics introduced by Borukhov, Andelman, and Orland \([22]\), which includes finite-size steric interactions between counterions. Note that the contribution from explicit water overlayers can always be included. However, due the weak chemical interactions between CO and the solvent \([23]\), we restrict here the explicit DFT treatment to the metal and to the chemisorbed molecules.

The ground state of the electrochemical system is that which minimizes the free energy functional

$$G = E' + \Delta E_{\text{corr}} + \Delta E_{\text{ion}} - \mathcal{E} q.$$  

(2)

The first contribution $E'$ corresponds to the DFT energy of the system within the supercell approximation (that is, for a periodically repeated metal slab in vacuum), as computed by standard plane-wave codes \([24]\). The corrective energy $\Delta E_{\text{corr}}$ equals the difference between the electrostatic energy of the isolated slab and that of the periodic slab in vacuum,

$$\Delta E_{\text{corr}} = \frac{1}{2} \int \rho(r) \mathcal{E}_F(r) dr,$$

(3)

where $\rho$ is the explicit charge density, and $\mathcal{E}_F = v - v'$ is a corrective potential defined as the difference between the Coulomb potential of the solvated system $v$ that satisfies a nonlinear modified Poisson-Boltzmann (MPB) equation

$$\nabla \cdot (\varepsilon(r) \nabla v(r)) = -4\pi [\rho(r) - z_0 c^+_{\text{d}}(r) + z_0 c^-_{\text{d}}(r)].$$

(4)
(in a.u.) with boundary conditions \( v = 0 \) V at infinity, and the periodic potential \( \nu' \) calculated in the reciprocal space representation using fast Fourier transform techniques. Heuristically, \( \nu^\text{corr} \) can be identified as the electrolyte reaction field \([20]\), which self-consistently accounts for the influence of the applied electrode voltage. The remaining contribution \( \Delta E^\text{ion} \) is that from the counterions in solution, including steric repulsion \([22]\):

\[
\Delta E^\text{ion} = \int d\mathbf{r} \left[ \frac{1}{2} z_d (c_d^- - c_d^+ v - (c_d^+ + c_d^- - 2c_0) \mu) \right]
- T \int d\mathbf{r} \left[ s^\text{ion}(c_d^+ + c_d^- + c_d^0) \right.

\left. - s^\text{ion}(c_0, c_0, a_d^{-3}) \right],
\]

(5)

where \( \mu = -k_B T \ln(a_d^{-3} c_0^{-1} - 2) \) is the ionic potential, \( s^\text{ion} \) is the local ionic entropy, and \( c_d^0 \) is the saturated (maximum packing) ionic concentration that smoothly goes from 0 to \( a_d^{-3} \) at a distance \( \lambda_H \) from the metal surface. The entropy density \( s^\text{ion} \) can be expressed as

\[
s^\text{ion}(c_d^+ + c_d^- + c_d^0) = -k_B \left[ c_d^+ \ln \left( \frac{c_d^+}{c_d^0} \right) + c_d^- \ln \left( \frac{c_d^-}{c_d^0} \right) \right]

+ (c_d^0 - c_d^+ - c_d^- \ln \left( 1 - \frac{c_d^+}{c_d^0} - \frac{c_d^-}{c_d^0} \right)),
\]

(6)

and the maximal concentration \( c_d^0(\mathbf{r}) \) is parametrized as

\[
c_d^0(\mathbf{r}) = \frac{1}{a_d^3} \prod_I \Theta \left( |\mathbf{r} - \mathbf{R}_I| - \lambda_H \right),
\]

(7)

where the index \( I \) runs exclusively over the metal layer atoms (at position \( \mathbf{R}_I \)), and the counterion exclusion region is defined by a smooth step function \( \Theta \) (smeared over a few grid points for numerical convergence). Consequently, the equilibrium ionic concentrations read

\[
c_d^0(\mathbf{r}) = c_d^0 \exp \left( \pm \frac{z_d v(\mathbf{r})}{k_B T} \right)

\times \left\{ c_0 a_d^{-3} + 2 \left[ \cosh \left( \frac{z_d v(\mathbf{r})}{k_B T} \right) - 1 \right] \right\}^{-1}.
\]

(8)

This ionic model directly involves the Helmholtz thickness \( \lambda_H \) through the prefactor \( c_d^0 \) and provides a simple representation of the diffuse distributions in direct connection to the Stern picture \([14]\).

The implementation of this electrochemical model raises three main difficulties. First, solving the MPB electrostatic problem in a finite simulation cell with, e.g., periodic or homogeneous boundary conditions results in significant errors in the electrode voltage. To correctly extrapolate the slowly vanishing electrostatic potential, we choose to impose fictitious electrochemical boundary conditions obtained from the long-range integration of the MPB equation in the planar-average approximation:

\[
\nabla_n v \cdot \mathbf{n}_z = -\sqrt{\frac{2\pi c_0 k_B T}{e_0}} \sinh \frac{z_d v}{2ek_B T} (\text{where } \mathbf{n}_z \text{ denotes the external surface vector}).
\]

Additionally, the solution of the MPB equation is expensive due to the fine grids required in discretizing the charge density. To reduce this computational burden, we exploit the fact that the corrective potential \( \nu^\text{corr} \) varies smoothly over space, which allows for its direct and inexpensive computation on coarse-grained meshes in the spirit of the density-countercharge method \([25]\). Last, constant-potential simulations require fixing the Fermi energy while readjusting the electron number during the electronic-structure optimization. In the course of such calculations, large charge oscillations occur, which results in systematic energy divergence. To eliminate these instabilities without resorting to artificial charge compensations, we employ a generalization of the ensemble density-functional theory scheme \([26]\) and optimal damping algorithm \([27]\), which ensures that the free energy converges monotonically.

We thus proceed to calculate the vibrational properties of CO-covered platinum interfaces under electrochemical conditions \([31]\). In carrying out these calculations, the solvation parameters are set to the values determined and used in Ref. \([21]\). The electrode voltage range, counterion concentration and ionic temperature are selected to be \( \mathcal{E} = 5.0-5.2 \) V, \( c_0 = 0.1 \) M and \( T = 300 \) K, respectively, corresponding to experimental conditions. We reference the absolute potential of the half cell to that of the normal hydrogen electrode (NHE) by matching the electrode voltage calculated at the point of zero charge \( \mathcal{E}_{\text{pzc}} = 5.07 \) V to the referenced experimental potential \( \mathcal{E}(\text{exp}) - \mathcal{E}^\circ = 0.33 \) V \([28]\). This corresponds to shifting the absolute electrode potential by \( \mathcal{E}^\circ = 4.74 \) V in our calculations. The thickness of the double layer \( \lambda_H \) equals 4 Å, that is, in the middle of the experimental range 3–5 Å. The size and charge of the counterions are chosen to be \( a_d = 2 \) Å and \( z_d = 1 \) for a typical monovalent electrolyte. We compute stretching frequencies using a frozen-phonon method—the calculated frozen-phonon frequencies agree

![FIG. 2: Vibrational frequency \( \nu \) as a function of the NHE-referenced electrode voltage \( \mathcal{E} = \mathcal{E}^\circ \) for 1/4 ML and 3/4 ML of CO on Pt(111). The absolute electrode potential \( \mathcal{E} \) is also indicated. The experimental Stark tuning rates \( d\nu/d\mathcal{E} \) are given in parentheses.](image-url)
The vibrational Stark slope is calculated to be 43.2 cm$^{-1}$/V, whereas at 3/4 ML, $d\nu/dE$ equals 28.4 cm$^{-1}$/V [22]. Despite this marked dependency as a function of monolayer coverage, the Stark rates are found to be in remarkable accordance with their experimental counterparts $d\nu/dE = 40$ cm$^{-1}$/V at 1/4 ML [23] and 28 cm$^{-1}$/V at 3/4 ML [11,12]. Thus, in variance with previously reported large discrepancies, the calculated Stark tuning rates are found here to deviate by less than 8% from experimental spectroscopic measurements in both the low- and high-coverage regimes, providing an important illustration of the predictive performance of the present electrochemical model.

In summary, we have developed a practical and comprehensive electrochemical model to study quantum-mechanical systems as a direct function of the fixed applied voltage. We used this model to calculate voltage-induced Stark shifts, finding excellent agreement with spectroscopic experiments at low and high surface coverage, and resolving long-standing inconsistencies in the interpretation of electrochemical spectroscopic measurements. These results open promising perspectives for the first-principles description of electrochemical systems and electrocatalytic reactions under realistic voltage conditions.

The calculations in this work have been performed using the Quantum-Espresso package [30]. The authors acknowledge support from the MURI grant DAAD 19-03-1-0169 and Sire grant ANR 06-CIS6-014. We thank Andrzej Wieckowski for his help in providing and in interpreting spectroscopic data. Helpful suggestions and comments from Gerbrand Ceder, Stefano de Gironcoli, Damian Scherlis, Nicéphore Bonnet, Jean-Sébastien Filhol, and Eduardo Lamas are gratefully acknowledged.

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[31] We employ the Perdew-Burke-Ernzerhof approximation and ultrasoft pseudopotentials. The Brillouin zone is sampled with a shifted 4×4×1 supercell.

[32] By performing a sensitivity analysis, we find the Stark slopes to be altered by less than 3 cm$^{-1}$/V when varying the main experimental parameter $\lambda_H$ by ±1 Å.