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ABSTRACT

The structure and electronic properties of a molecule at an electrochemical interface are changed by interactions with the electrode surface and the electrolyte solution, which can be significantly modulated by an applied voltage. We present an efficient self-consistent quantum mechanics/molecular mechanics (QM/MM) approach to study a physisorbed molecule at a metal electrode–electrolyte interface under the constant-voltage condition. The approach employs a classical polarizable double electrode model, which enables us to study the QM/MM system in the constant-voltage ensemble. A mean-field embedding approximation is further introduced in order to overcome the difficulties associated with statistical sampling of the electrolyte configurations. The results of applying the method to a test system indicate that the adsorbed molecule is no less or slightly more polarized at the interface than in the bulk electrolyte solution. The geometry of the horizontally adsorbed molecule is modulated by their electrostatic interactions with the polarizable electrode surfaces and also the interactions with cations attracted toward the interface when the adsorbate is reduced. We also demonstrate that the approach can be used to quantitatively evaluate the reorganization energy of a one electron reduction reaction of a molecule in an electrochemical cell.

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I. INTRODUCTION

Modern technologies, such as rechargeable batteries, capacitors, fuel cells, and some nanodevices, such as chemical and biological sensors, have electrochemical interfaces.^{1–5} The functions and performance of such devices depend on the atomic structures and electronic states of adsorbates. They can differ from those in the gas phase and also in bulk solutions because of the heterogeneous interactions between the electrode surface and interfacial electrolyte solution. In order to study the geometries and electronic states of the adsorbates, computational approaches more efficient than the *ab initio* molecular dynamics (MD) method⁶ have been desired. Such methods are required to be capable of modeling

the image–charge interactions between the metal electrode and adsorbates and also the electrolyte solutions.

Considering its great success in treating a molecule interacting with a dielectric environment, it is natural to model a quantum mechanical molecule on a metal surface with the polarizable continuum model (PCM). It has been utilized not only to study optical properties of a chromophore on a metal nanoparticle⁷ but also to evaluate the reorganization energy of a heterogeneous electron transfer between an adsorbate molecule and a metal electrode.⁸ A similar strategy to incorporate the induction effects of metal electrodes was used to investigate the molecular electronic structure in the context of molecular electronics.⁹ Although these dielectric continuum approaches capture the essential physics, they lack

description of the interfacial inhomogeneity at an atomistic resolution, such as an electrode surface corrugation and an electric double layer.

In order to overcome this problem, approaches utilizing the quantum mechanics/molecular mechanics (QM/MM) idea^{10,11} have been developed in which metal nanoparticles or surfaces are modeled as a collection of classical polarizable atoms. Some approaches assign an atomic polarizability to each atom in metal clusters in their study of the effects on optical properties of an adsorbed molecule.^{12–14} Such an approach was extended to include also solvent molecules.¹⁵ In such studies, configurations of thermally fluctuating solvent molecules were sampled from purely classical MD simulations, followed by averaging of quantities evaluated by the QM/polarizable MM electronic structure calculations at selected configurations. A method especially oriented toward electrochemical interfaces, referred to as image–charge augmented QM/MM (IC-QM/MM), was developed by Golze *et al.*¹⁶ The method utilizes the constant-potential scheme proposed by Siepmann and Sprik¹⁷ to describe polarizable metal electrode surfaces and solves the coupled QM-polarizable electrode equations. The structure and electronic state of physisorbed molecules were obtained from IC-QM/MM molecular dynamics simulations of about 100 ps. The method successfully captures the effects of the image–charge interactions on the adsorbate structures and the electronic density rearrangement.

Since there is a strong coupling between the geometry and electronic state of an adsorbed molecule, the polarization of an electrode, the structure of a thermally fluctuating electrolyte solution, and the voltage in the electrochemical cell, an accurate modeling of an electrochemical interface requires a self-consistent treatment of all of these constituents. Although the above-mentioned QM/MM approaches could meet this requirement, it is quite difficult to sufficiently take into account the thermal fluctuation of the electrolyte solution due to demanding QM calculations at a lot of electrolyte configurations. The same problem related to how to carry out a proper statistical sampling of configurations of the environment has been discussed and tackled in QM/MM simulations for solutions and biological systems (for example, refer to Refs. 18–21 and those cited therein).

In this article, we propose such a self-consistent QM/MM method to treat molecules at electrochemical interfaces so that one can overcome this statistical sampling problem. This has the following two peculiarities that distinguish our approach from the previous QM/MM methods for adsorbates on metal surfaces. The first one is that the electronic polarization of metal electrodes is described with the method based on the chemical potential equalization principle.²² The voltage can be naturally applied to the electrochemical system as the difference between the electrochemical potentials of the working and counter electrodes. The second one comes from the introduction of the variational principle into the QM/MM Helmholtz free energy or the potential of mean force.^{19,23,24} This enables us to separate the quantum mechanical calculations and MD simulations for sampling configurations of the electrolyte solution so that the latter can be carried out quite efficiently to give a converged free energy. The structure of the physisorbed molecule can be optimized on the free energy surface. Note that this mean-field embedding QM/MM method is similar in spirit with the methods combining a QM calculation with

3D-RISM (3D-RISM-SCF^{25,26} or ESM-RISM²⁷) or classical DFT (e.g., JDFT²⁸). Our approach is expected to be more quantitative than those approaches since it introduces no further approximation into the classical description of molecules in solution or into the statistical averaging of the solvent degrees of freedom.

In Sec. II, we first give the formulation of our constant-voltage QM/MM (CV-QM/MM) method, in which a molecule in the electrolyte solution is treated quantum mechanically, based on our constant-voltage method originally developed for classical MD simulations of electrochemical cells.²² This is followed by the formulation of a variant (mean-field CV-QM/MM; MFCV-QM/MM) derived by a mean-field embedding that drastically accelerates statistical sampling of configurations of the electrolyte solution in the CV-QM/MM simulation. For demonstration purposes, we apply the method to a system composed of a quantum mechanical *p*-benzoquinone molecule and a classical mechanical electrolyte solution confined between two platinum electrodes. The *p*-benzoquinone/*p*-benzosemiquinone couple is a prototypical system and plays many important roles in electrochemistry.^{29,30} An electrochemically generated semiquinone is highly reactive with a molecular oxygen and utilized to control the ORR (oxygen reduction reaction) activity in the industrial synthesis of hydrogen peroxide.^{31,32} Furthermore, there are many reports on a *p*-benzoquinone molecule attached to an electrode surface as an electron transfer mediator. In this study, the electronic ground state and geometry of the neutral and reduced *p*-benzoquinone molecule are optimized at the electrode–electrolyte interface with and without an applied voltage. We also evaluate its reorganization energy quantum mechanically.

II. THEORY

A. Constant-voltage quantum mechanics/molecular mechanics method

The Hamiltonian of our CV-QM/MM method is derived by replacing the energy of a molecule of the electrolyte solution in the classical constant-voltage method described in Appendix with that of a quantum mechanical molecule. The system total energy can be written as

$$E[\Psi, \mathbf{q}^M; \mathbf{X}, \mathbf{x} | q_{\text{tot}}^M, \Delta q^M] = E^{\text{QM/MM}}[\Psi, \mathbf{q}^M; \mathbf{X}, \mathbf{x}] + E^{\text{MM}}(\mathbf{q}^M; \mathbf{r}^S) + U^{\text{nonele}}(\mathbf{X}, \mathbf{x}), \quad (1)$$

where Ψ is the wavefunction of the QM molecule. $\mathbf{q}^M = (q_1^M, q_2^M, \dots, q_{N_M}^M)$ denotes a collection of atomic charges of the electrodes, treated as dynamical variables and determined variationally at each configuration. q_{tot}^M and Δq^M are the sum of and the difference between the total charges of the left and right electrodes, respectively, as shown in Eq. (A7). A square bracket is used to indicate the functional dependence on the QM wavefunction. $\mathbf{X}$ collectively represents the internal coordinates of the QM molecule. $\mathbf{x}$ includes the coordinates of the electrolyte solution (other than the QM molecule and denoted as $\mathbf{r}^S$) and also the translational and rotational coordinates of the QM molecule. The first term on the right-hand side in Eq. (1) is the sum of the QM internal energy and the QM-MM electrostatic interaction energy

$$E^{\text{QM/MM}}[\Psi, \mathbf{q}^{\text{M}}; \mathbf{X}, \mathbf{x}] = \langle \Psi | \hat{H}_0 + \int d\mathbf{r} \hat{\rho}(\mathbf{r}) \mathcal{V}(\mathbf{r}) | \Psi \rangle, \quad (2)$$

where $\hat{\rho}(\mathbf{r})$ is the charge density operator of the QM region. $\mathcal{V}(\mathbf{r})$ is the effective electrostatic potential (ESP) created by the electrodes and the electrolyte solution

$$\mathcal{V}(\mathbf{r}) = \sum_i^{N^{\text{M}}} \frac{q_i^{\text{M}}}{|\mathbf{r} - \mathbf{r}_i^{\text{M}}|} + \sum_k^{N_{\text{mol}}^{\text{S}}} \sum_a^{N_k^{\text{S}}} \frac{q_{k,a}^{\text{S}}}{|\mathbf{r} - \mathbf{r}_{k,a}^{\text{S}}|}, \quad (3)$$

where k and a are indices for the molecules and their atoms in the electrolyte solution. In this study, we discretize the QM charge distribution and use atomic charges to efficiently evaluate the QM-MM electrostatic interactions

$$E^{\text{QM/MM}}[\Psi, \mathbf{q}^{\text{M}}; \mathbf{X}, \mathbf{x}] = \langle \Psi | \hat{H}_0 + \hat{\mathbf{Q}} \cdot \mathbf{V} | \Psi \rangle, \quad (4)$$

where $\hat{\mathbf{Q}} = (\hat{Q}_1, \hat{Q}_2, \dots, \hat{Q}_{N^{\text{QM}}})$ is a vector notation of partial charge operators, with N^{QM} being the number of the QM atoms. $\mathbf{V} = (\mathcal{V}_1, \mathcal{V}_2, \dots, \mathcal{V}_{N^{\text{QM}}})$ collectively denotes the ESP acting on the QM atoms evaluated as

$$\mathcal{V}_\gamma = \sum_i^{N^{\text{M}}} D_{\gamma,i}^{\text{QM-M}} q_i^{\text{M}} + \sum_k^{N_{\text{mol}}^{\text{S}}} \mathbf{D}_{\gamma,k}^{\text{QM-S}} \mathbf{q}_k^{\text{S}}, \quad (5)$$

where $D_{\gamma,i}^{\text{QM-M}}$ and $\mathbf{D}_{\gamma,k}^{\text{QM-S}}$ are the effective electrostatic interaction kernels between the QM-electrode atoms and the QM-electrolyte atoms, respectively. Previous studies suggest that this point-charge approximation into the QM charge distribution [using the restrained electrostatic potential (RESP) charge operator] works well, especially when no hydrogen bonds are formed between the QM and MM atoms.^{24,33} It is worth mentioning that approaches without introducing the point-charge approximation are also available for the mean-field embedding QM/MM calculations.^{24,34} The sum of the second and third terms on the right-hand side in Eq. (1) is the energy of the MM region, which has the same form as described in Eq. (A1). Note that $U^{\text{nonele}}(\mathbf{X}, \mathbf{x})$, the nonelectrostatic interaction energy of the system, includes the one between the QM and MM regions.

In order to perform a QM/MM simulation in the constant-voltage ensemble, a partial Legendre transformation is carried out to change one of the control variables Δq^{M} to ΔV as in Appendix. A partial grand potential for the QM/MM system is thus obtained as

$$\omega[\Psi, \mathbf{q}^{\text{M}}; \mathbf{X}, \mathbf{x} | q_{\text{tot}}^{\text{M}}, \Delta V] = E[\Psi, \mathbf{q}^{\text{M}}; \mathbf{X}, \mathbf{x} | q_{\text{tot}}^{\text{M}}, \Delta q^{\text{M}}] - \frac{1}{2} \Delta q^{\text{M}} \Delta V. \quad (6)$$

The following objective functional is introduced:

$$\begin{aligned} \mathcal{L}[\Psi, \mathbf{q}^{\text{M}}; \mathbf{X}, \mathbf{x} | q_{\text{tot}}^{\text{M}}, \Delta V] &= \omega[\Psi, \mathbf{q}^{\text{M}}; \mathbf{X}, \mathbf{x} | q_{\text{tot}}^{\text{M}}, \Delta V] \\ &+ \mu_{\text{c}} (Q_{\text{tot}} + q_{\text{tot}}^{\text{M}} + q_{\text{tot}}^{\text{S}}) - \mathcal{E}(\langle \Psi | \Psi \rangle - 1), \end{aligned} \quad (7)$$

where Q_{tot} is the total charge of the QM molecule treated as a constant in the simulation, and μ_{c} and $\mathcal{E}$ are Lagrange undetermined multipliers. The equation for the wavefunction is derived by minimizing the objective functional with respect to Ψ (the

variational variables Ψ and $\mathbf{q}^{\text{M}}$ should be treated independently) as

$$[\hat{H}_0 + \hat{\mathbf{Q}} \cdot \mathbf{V}] | \Psi \rangle = \mathcal{E} | \Psi \rangle. \quad (8)$$

As described in Appendix, minimization with respect to $\mathbf{q}^{\text{M}}$ results in the equations for $\mathbf{q}^{\text{M}}$ as

$$q_i^{\text{M}} = -\frac{1}{U^{\circ}} \left(v_i - \bar{v} \mp \frac{1}{2} \Delta V \right) - \frac{Q_{\text{tot}} + q_{\text{tot}}^{\text{S}}}{N^{\text{M}}}, \quad (9)$$

where the minus and plus signs are for the left and right electrode atomic charges, respectively. The effective ESP v_i acting on the i th electrode atom is

$$v_i = \sum_{j(\neq i)}^{N^{\text{M}}} J_{ij}^{\circ} q_j^{\text{M}} + \sum_k^{N_{\text{mol}}^{\text{S}}} \mathbf{D}_{i,k}^{\text{M-S}} \mathbf{q}_k^{\text{S}} + \sum_{\gamma}^{N^{\text{QM}}} D_{\gamma,i}^{\text{QM-M}} \langle \Psi | \hat{Q}_{\gamma} | \Psi \rangle. \quad (10)$$

We also obtain the electrochemical potentials of the left and right electrodes as

$$\mu_{\text{L}} = -\frac{\partial E}{\partial q_{i \in \text{L}}^{\text{M}}} = \mu_{\text{c}} - \frac{1}{2} \Delta V, \quad (11)$$

$$\mu_{\text{R}} = -\frac{\partial E}{\partial q_{i \in \text{R}}^{\text{M}}} = \mu_{\text{c}} + \frac{1}{2} \Delta V, \quad (12)$$

with

$$\mu_{\text{c}} = -\chi^{\circ} - \bar{v} + U^{\circ} \frac{Q_{\text{tot}} + q_{\text{tot}}^{\text{S}}}{N^{\text{M}}}. \quad (13)$$

The (adiabatic) QM/MM total energy and partial grand potential at each configuration $\{\mathbf{X}, \mathbf{x}\}$ in the constant-voltage ensemble are then obtained by substituting the solutions of the coupled Eqs. (8) and (9) so that

$$E[\Psi, \mathbf{q}^{\text{M}}; \mathbf{X}, \mathbf{x} | q_{\text{tot}}^{\text{M}}, \Delta q^{\text{M}}] \longrightarrow E_{\text{ad}}(\mathbf{X}, \mathbf{x} | q_{\text{tot}}^{\text{M}}, \Delta V), \quad (14)$$

$$\omega[\Psi, \mathbf{q}^{\text{M}}; \mathbf{X}, \mathbf{x} | q_{\text{tot}}^{\text{M}}, \Delta V] \longrightarrow \omega_{\text{ad}}(\mathbf{X}, \mathbf{x} | q_{\text{tot}}^{\text{M}}, \Delta V). \quad (15)$$

B. Mean-field embedding into the constant-voltage QM/MM formulation

Because a CV-QM/MM simulation of an electrode–electrolyte system using the method described in Sec. II A needs to solve Eq. (8) coupled with Eq. (9) at each configuration as in the IC-QM/MM simulation,¹⁶ it is computationally demanding to move around the configuration space of the electrolyte solution for obtaining statistically converged free energy and interfacial structure of the electrolyte solution. This difficulty can be circumvented to introduce the mean-field approximation as in previous QM/MM simulations of bulk solution systems.¹⁹ We consider the canonical QM/MM potential of mean force (PMF) in the constant-voltage ensemble as a function of the internal coordinates of the QM region

$$A(\mathbf{X} | q_{\text{tot}}^{\text{M}}, \Delta V) = -\frac{1}{\beta} \ln \int d\mathbf{x} \exp[-\beta \omega_{\text{ad}}(\mathbf{X}, \mathbf{x} | q_{\text{tot}}^{\text{M}}, \Delta V)] \quad (16)$$

where evaluating the partial grand potential ω_{ad} in Eq. (15) requires the solution of Eq. (8) at each configuration of $\mathbf{x}$ as $\Psi(\mathbf{X}, \mathbf{x})$. Here, we define the following free energy functional by introducing a trial wavefunction $\tilde{\Psi}(\mathbf{X})$ independent of $\mathbf{x}$ as follows:

$$A[\tilde{\Psi}; \mathbf{X}|q_{\text{tot}}^{\text{M}}, \Delta V] = -\frac{1}{\beta} \ln \int d\mathbf{x} \exp[-\beta \omega_{\text{ad}}[\tilde{\Psi}; \mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta V]]. \quad (17)$$

Note that the partial grand potential functional

$$\omega_{\text{ad}}[\tilde{\Psi}; \mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta V] = E_{\text{ad}}[\tilde{\Psi}; \mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta q^{\text{M}}] - \frac{1}{2} \Delta q^{\text{M}} \Delta V \quad (18)$$

is obtained through the variational minimization of Eq. (6) with respect to only q^{M} at each $\mathbf{x}$. Since the following inequality for the partial grand potential holds at any $\{\mathbf{X}, \mathbf{x}\}$,

$$\omega_{\text{ad}}(\mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta V) \leq \omega_{\text{ad}}[\tilde{\Psi}; \mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta V], \quad (19)$$

the free energy functional, satisfies

$$A(\mathbf{X}|q_{\text{tot}}^{\text{M}}, \Delta V) \leq A[\tilde{\Psi}; \mathbf{X}|q_{\text{tot}}^{\text{M}}, \Delta V]. \quad (20)$$

The objective functional

$$\mathcal{L}[\tilde{\Psi}; \mathbf{X}|q_{\text{tot}}^{\text{M}}, \Delta V] = A[\tilde{\Psi}; \mathbf{X}|q_{\text{tot}}^{\text{M}}, \Delta V] - \mathcal{E}(\langle \tilde{\Psi} | \tilde{\Psi} \rangle - 1) \quad (21)$$

is thus minimized with respect to $\tilde{\Psi}$ to get the following equation for $\tilde{\Psi}$:

$$[\hat{H}_0 + \hat{\mathbf{Q}} \cdot \langle \mathbf{V} \rangle_{\tilde{\Psi}}] |\tilde{\Psi}\rangle = \mathcal{E} |\tilde{\Psi}\rangle. \quad (22)$$

Here, $\langle \dots \rangle_{\tilde{\Psi}}$ denotes the statistical average of a quantity in the constant-voltage ensemble

$$\langle \dots \rangle_{\tilde{\Psi}} = \frac{\int d\mathbf{x} \langle \dots \rangle \exp[-\beta \omega_{\text{ad}}[\tilde{\Psi}; \mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta V]]}{\int d\mathbf{x} \exp[-\beta \omega_{\text{ad}}[\tilde{\Psi}; \mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta V]]}. \quad (23)$$

Since $\langle \mathbf{V} \rangle_{\tilde{\Psi}}$ depends on $\tilde{\Psi}$, Eq. (22) has to be solved iteratively by sequentially performing a QM calculation and a molecular dynamics (or Monte Carlo) sampling based on Eq. (23). Hereafter, we denote the self-consistent solution of Eq. (22) as $\Psi_{\text{MF}}(\mathbf{X})$, with which the best approximate free energy is obtained as

$$\begin{aligned} A_{\text{MF}}(\mathbf{X}|q_{\text{tot}}^{\text{M}}, \Delta V) &= A[\Psi_{\text{MF}}; \mathbf{X}|q_{\text{tot}}^{\text{M}}, \Delta V] \\ &= -\frac{1}{\beta} \ln \int d\mathbf{x} \exp[-\beta \omega_{\text{ad, MF}}(\mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta V)], \end{aligned} \quad (24)$$

where $\omega_{\text{ad, MF}}(\mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta V) = \omega_{\text{ad}}[\Psi_{\text{MF}}; \mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta V]$. The following notations are also introduced for later use: $E_{\text{ad, MF}}(\mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta q^{\text{M}}) = E_{\text{ad}}[\Psi_{\text{MF}}; \mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta q^{\text{M}}]$, $\mathbf{Q}_{\text{MF}} = \langle \Psi_{\text{MF}} | \hat{\mathbf{Q}} | \Psi_{\text{MF}} \rangle$, and

$$\mathbf{V}_{\text{MF}} = \langle \mathbf{V} \rangle_{\Psi_{\text{MF}}} = \frac{\int d\mathbf{x} \mathbf{V} \exp[-\beta \omega_{\text{ad, MF}}(\mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta V)]}{\int d\mathbf{x} \exp[-\beta \omega_{\text{ad, MF}}(\mathbf{X}, \mathbf{x}|q_{\text{tot}}^{\text{M}}, \Delta V)]}. \quad (25)$$

This variational formulation of the method (referred to as the MFCV-QM/MM) allows us to derive the analytical derivative of the PMF with respect to the internal coordinates of the QM molecule

$$\frac{\partial A_{\text{MF}}}{\partial \mathbf{X}} = \left(\frac{\partial \mathcal{E}_{\text{MF}}}{\partial \mathbf{X}} \right)_{\mathbf{V}=\mathbf{V}_{\text{MF}}} + \left\langle \mathbf{Q}_{\text{MF}} \cdot \frac{\partial \mathbf{V}}{\partial \mathbf{X}} + \frac{\partial U^{\text{nonele}}}{\partial \mathbf{X}} \right\rangle_{\Psi_{\text{MF}}}, \quad (26)$$

where $\mathcal{E}_{\text{MF}}$ is defined as a function of $\mathbf{X}$ and $\mathbf{V}$ as follows:

$$\mathcal{E}_{\text{MF}}(\mathbf{X}, \mathbf{V}) = \langle \Psi_{\text{MF}} | \hat{H}_0 + \hat{\mathbf{Q}} \cdot \mathbf{V} | \Psi_{\text{MF}} \rangle. \quad (27)$$

The geometry of the QM molecule in an electrochemical system is optimized by using the free energy gradient in Eq. (26). For a system with a small QM region (e.g., a *p*-benzoquinone molecule as in this study), about five cycles, each of which consists of a QM geometry optimization calculation and a MD simulation to obtain averaged quantities like in Eqs. (25) and (26), are required to obtain a converged (self-consistent) result.

III. COMPUTATIONAL DETAILS

A. System and molecular dynamics sampling

The system is composed of a *p*-benzoquinone molecule treated quantum mechanically immersed in a (polarizable or non-polarizable) molecular mechanical electrolyte solution and a pair of polarizable Pt electrodes as shown in Fig. 1. The length of the simulation cell in the *x*, *y*, and *z* directions are 30.5, 28.8 and 100.0 Å, respectively. The *z* direction is normal to the surfaces of the two electrodes faced parallel to each other. The distance between the two electrode surfaces is set to 72.0 Å. Due to the use of the simulation cell of small distance between the electrodes, there are only a few ions in the bulk region. However, we confirmed by a calculation on another simulation cell of about twice as larger distance between the electrodes with the number of the electrolyte solution being doubled that the number of ions at the interface is independent of the cell size, and the ion concentration in the bulk region approaches the preset value (0.3 mol/l). The simulation cell is periodically replicated in three dimensions. The electrostatic interactions are evaluated by using the 3D-Ewald method with a correction to remove redundant interactions with the replicated images in the *z* direction.³⁵ The

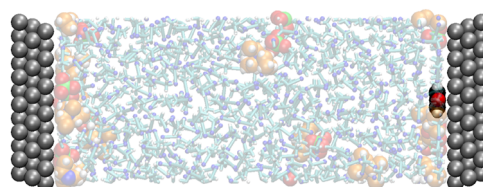


FIG. 1. A snapshot of the simulated system. The platinum electrode atoms are represented with silver balls. The *p*-benzoquinone physisorbed on the right electrode surface is depicted with balls in red for oxygen atoms, in black for carbon atoms, and in white for hydrogen atoms. The chlorine and oxygen atoms of perchlorate anions are displayed with green and red balls. The nitrogen, carbon, and hydrogen atoms of tetraethylammonium cations are shown with blue, orange, and small white balls, respectively. The acetonitrile molecules are drawn with sticks.

non-electrostatic interactions are modeled with the Lennard-Jones (LJ) potential functions.

Each electrode consisting of three atomic layers models a Pt(111) surface whose lattice constant is 3.924 Å, and the total number of Pt atoms in each electrode is 396. The coordinates of the Pt atoms are frozen during simulations. The LJ parameters of the Pt atoms are taken from the work of Heintz *et al.*³⁶ The parameters for the Pt electrodes, χ° and U° , are set to 5.6 eV/e and 21.9 eV/e², respectively, as in our previous studies.^{22,37} Note that we assume in this study that the Pt electrodes polarize as perfect conductors by setting $U^\circ \approx 20$ eV/e², though the electronic response of the Pt electrodes can be different from that of perfect conductors and $U^\circ \approx 9$ eV/e² may be more appropriate based on the discussion in a previous study.³⁸

The electrolyte solution contains 629 acetonitrile molecules as the solvent and 12 pairs of tetraethylammonium and perchlorate (TEAP) ions as the supporting electrolyte, whose molar concentration is about 0.3 mol/l. All of the molecules in the system (the *p*-benzoquinone molecule and those of the electrolyte solution) are treated as rigid bodies in molecular dynamics calculations. The internal geometry of the acetonitrile molecules and the LJ parameters are taken from the work of Böhm.³⁹ Note that we perform polarizable simulations unless otherwise noted in which the acetonitrile molecules are also electronically polarizable. The polarizable acetonitrile molecules are modeled with the charge response kernel (CRK),^{40–42} with which the *a*th atomic charge in the *k*th acetonitrile molecule is determined as

$$q_{k,a} = q_a^0 + \sum_b^N K_{a,b}^0 v_{k,b}. \quad (28)$$

q_a^0 and $K_{a,b}$ are the atomic charge and the CRK calculated at the LC-BOP/aug-cc-pVDZ level in the gas phase^{43,44} using a modified version of the GAMESS program.⁴⁵ $v_{k,b}$ is the ESP acting on the *b*th atom in the *k*th acetonitrile molecule. When we perform nonpolarizable simulations (for calculations of the reorganization energy for comparison), the atomic charges taken from the work of Böhm are used. The internal geometries of the supporting electrolyte molecules are the ones optimized at the B3LYP/6-31G(*d,p*) level^{46–48} combined with polarizable continuum model (solvent = acetonitrile) using the Gaussian16 package.⁴⁹ The LJ parameters are taken from the OPLS-AA force field.⁵⁰

All the interaction kernels, $\mathbf{J}^\circ$, $\mathbf{D}^{M-S}$, $\mathbf{D}^{S-S}$, $\mathbf{D}^{QM-M}$, and $\mathbf{D}^{QM-S}$, for the effective electrostatic interactions have the functional form

$$J_{ij}^\circ, D_{ij}^{X-Y} = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} f(|\mathbf{r}_i - \mathbf{r}_j|/s_{ij}). \quad (29)$$

Following the previous studies,^{22,37} we use the attenuation function^{41,42}

$$f(v) = \begin{cases} v^4 - 2v^3 + 2v & (v < 1) \\ 1 & (v \geq 1) \end{cases}. \quad (30)$$

The introduction of the attenuation function is to circumvent the problem of overpolarization that can occur in MD simulations for

polarizable systems if one uses the simple Coulomb interaction function. The attenuation distance between the Pt electrode atoms $s_{\text{Pt-Pt}}$ is set to 1.5 Å. The values between a Pt atom and an atom in the QM molecule or in the electrolyte solution are set to 1.1 Å. The other attenuation distances are determined from

$$s_{ij} = 2.6(\alpha_i \alpha_j)^{1/6}, \quad (31)$$

where α_i is the polarizability of the *i*th atomic species.^{41,42} The values used in this work are $\alpha_C = 1.405$, $\alpha_H = 0.514$, $\alpha_O = 0.862$, $\alpha_N = 1.105$, and $\alpha_{\text{Cl}} = 3.25$ Å³, respectively.^{23,51–53} Since our main focus in the present study is on developing a QM/MM method that can take into account the effects of the image-charge, an applied voltage, and the thermal fluctuation of an electrolyte solution self-consistently, we do not explicitly take into account the charge transfer and electronic repulsive short-range interactions between the electrode and the QM molecule (more generally, all the molecules) at the interface as in most of the previous studies cited earlier.

In order to get statistically converged results, ten independent simulations are performed and the results (including $\langle \mathbf{V} \rangle_{\bar{\psi}}$) are averaged. The uncorrelated initial configurations are extracted every 300 ps from 3.0 ns trajectory obtained from an MD simulation at 800 K. The systems are cooled down to 300 K over 5.0 ns. The data are then collected from ten production runs of 900 ps after 150 ps equilibration runs in the NVT ensemble. The use of rigid-body molecules and adiabatic determination of the electrode charges allow us to use 6 fs timestep. All the MD simulations are carried out by using our modified version of the DL_POLY package.⁵⁴

B. PMF calculation

The position of the center of mass (COM) of the *p*-benzoquinone molecule adsorbed on the cathode surface is estimated from the minimum position of its PMF profile evaluated by classical MD simulations with $\Delta V = 0$ V. In the calculation, the *p*-benzoquinone molecule is charge neutral and its internal geometry is fixed to the optimized one in the gas phase. The weighted histogram analysis method (WHAM)⁵⁵ is used to obtain the probability distribution of the *z* component of the COM coordinate. The *z* coordinate ranging from 3.00 to 10.00 Å away from the cathode surface is discretized every 0.25 Å (29 grid points). We apply a harmonic bias potential in the *z* direction, the spring constant of which is set to 80.0 kcal/mol Å^{−2} when the position of the grid point is $3.00 \leq z \leq 5.75$ and 40.0 kcal/mol Å^{−2} otherwise. The total trajectory length for the PMF calculation is thus 261 ns (0.9 ns × 10 trajectories × 29 grid points).

C. Electronic structure calculation and geometry optimization

The energy and geometry of the *p*-benzoquinone molecule are calculated at the B3LYP/6-31G(*d,p*) level unless otherwise noted. The symmetry of the *p*-benzoquinone molecule in the bulk electrolyte solution (far apart from the electrode surface) is assumed to be D_{2h} , while it is assumed to be C_{2v} at the electrode–electrolyte interface since the molecule is bended due to the interactions with the electrode surface. The restrained electrostatic potential (RESP) charge operator^{56,57} is employed for the QM/MM calculations. The

MFCV-QM/MM method requires the averaged ESP $\langle V \rangle_\Psi$ and mean forces to update the electronic structure and geometry of the QM molecule. They are calculated from constant-voltage MD simulations as described in Secs. II B and III A. During the MD simulations, the *p*-benzoquinone molecule can translate in the *x* and *y* directions and rotate, but with its COM *z* coordinate being fixed by using the RATTLE algorithm.⁵⁸ The residual small translational and rotational components in the mean forces due to imperfect statistical samplings are removed by projection.⁵⁹ In order to accelerate the geometry optimization, we employ the sequential sampling and optimization procedure,⁶⁰ in which the geometry of the *p*-benzoquinone molecule is completely relaxed without updating the mean forces for each step of the geometry optimization. This allows us to optimize the geometry of a small molecule within about five cycles of sequential MD and QM calculations as will be shown in Sec. IV B. The QM calculations in the MFCV-QM/MM simulations are performed by using our locally modified version of the GAMESS program. Since the QM region (a *p*-benzoquinone molecule) is small, the computational cost of the five QM geometry optimizations is negligible compared to that of the five MD simulations (each of 10 ns long in total as described in Sec. III A). In other words, most of the computational cost for this MFCV-QM/MM calculation comes from the classical constant-voltage MD simulations of 50 ns long in total.

D. Calculation of reorganization energy and driving force of reduction reaction

The kinetics of the reduction reaction of a *p*-benzoquinone molecule can be characterized with the reorganization energy λ . Also, its reduction potential is related to the driving force ΔA . Our previous study³⁷ and preliminary calculation indicate that the nonadiabatic electron transfer between the *p*-benzoquinone molecule and the cathode at the electrode–electrolyte interface⁶¹ occurs in the linear response regime. The λ and ΔA are thus calculated as⁶²

$$\lambda = \frac{\langle \Delta E_{\text{ox}} \rangle_{\Psi_{\text{ox, MF}}} - \langle \Delta E_{\text{red}} \rangle_{\Psi_{\text{red, MF}}}}{2}, \quad (32)$$

$$\Delta A = \frac{\langle \Delta E_{\text{ox}} \rangle_{\Psi_{\text{ox, MF}}} + \langle \Delta E_{\text{red}} \rangle_{\Psi_{\text{red, MF}}}}{2}. \quad (33)$$

The meaning of the angle brackets is the same as in Eq. (23). $\Psi_{i, \text{MF}}$ is the self-consistent solution of Eq. (22) for the *i* [oxidized (charge neutral) or reduced] state. ΔE_i is the vertical energy gap between the reduced state and the oxidized state at the optimized QM geometry $\mathbf{X}_i$ for the *i* state

$$\Delta E_i = E_{\text{ad}}[\Psi_i^{\text{red}}(\mathbf{X}_i); \mathbf{X}_i, \mathbf{x} | q_{\text{tot}}^{\text{M}}, \Delta V] - E_{\text{ad}}[\Psi_i^{\text{ox}}(\mathbf{X}_i); \mathbf{X}_i, \mathbf{x} | q_{\text{tot}}^{\text{M}}, \Delta V], \quad (34)$$

with the total energies sampled from a constant-voltage MD simulation. $\Psi_i^j(\mathbf{X}_i)$ (*i, j* are “red” or “ox”) is the wavefunction determined from

$$[\hat{H}_0 + \hat{\mathbf{Q}} \cdot \mathbf{V}_{i, \text{MF}}] \Psi_i^j = \mathcal{E} \Psi_i^j \quad (35)$$

for the *j* state at the geometry $\mathbf{X}_i$, where $\mathbf{V}_{i, \text{MF}}$ is the averaged ESP given in Eq. (25) obtained from the MFCV-QM/MM calculation for the *i* state. Note that the energy gap Eq. (34) includes the contributions from the change in not only the interactions with the electrodes and electrolyte solution but also the internal energy of the QM molecule.

Since the accuracy of the calculated electron affinity (EA) significantly depends on the level of the QM calculation, a correction is made for the vertical energy gap in Eq. (34) by adding the difference between the gas-phase adiabatic EA obtained from a high-level QM calculation and that evaluated at the B3LYP/6-31G(*d, p*) level. We employ the G3(MP2) method⁶³ implemented in the Gaussian16 package for that purpose because it gives 1.92 eV for the adiabatic EA of a *p*-benzoquinone molecule in the gas phase, in quantitative agreement with the experimental estimate of 1.85 eV.⁶⁴ The correction to the energy gap is 0.42 eV.

As has been pointed out in previous studies of constant-voltage MD simulations,^{37,65} a hole transfers from the *p*-benzoquinone molecule not only to the cathode (right electrode) but also partly to the anode (left electrode). The amount of hole transferred to the anode depends on the distance of the *p*-benzoquinone molecule from the cathode surface and also on the distance between the two electrodes. This problem arises from performing a constant-voltage simulation with two electrodes whose distance is not so large, and is irrelevant from how to describe the system (quantum mechanically or classical mechanically). We thus need to correct the calculated energy gap by adding

$$\Delta E^{\text{corr}} = -\delta q_{\text{L}}^{\text{M}} \cdot \Delta V, \quad (36)$$

where $\delta q_{\text{L}}^{\text{M}}$ is the change in the total charge on the anode (left electrode).⁶⁵ This correction term can be derived in terms of the electrochemical potentials of the electrodes.³⁷

IV. RESULTS AND DISCUSSION

In the following, we will describe in detail the results of PMF profile calculation of the *p*-benzoquinone molecule approaching the electrode surface, geometry optimizations in the bulk electrolyte solution and at the electrode–electrolyte interface, and free energy changes associated with the reduction reaction. The averaged atomic structures of the electrolyte solution at the interface obtained from the MFCV-QM/MM calculations are given in the [supplementary material](#).

A. Potential of mean force profile to locate adsorption position

In our simulations, the neutral *p*-benzoquinone molecule adsorbs nearly horizontally the Pt electrode surface mainly due to the attractive van der Waals (vdW) interaction evaluated to be around 55 kcal/mol. The calculated PMF profile shown in Fig. 2 has its minimum at 3.2 Å distance from the electrode surface. This minimum position is used in the MFCV-QM/MM calculations at the interface with the COM *z* coordinate of the *p*-benzoquinone molecule being fixed. The PMF is expected to increase exponentially in the region within 3.0 Å distance from the electrode surface because of the strong repulsive interaction (via the LJ potential). The well depth of the PMF profile is about 19 kcal/mol, much smaller

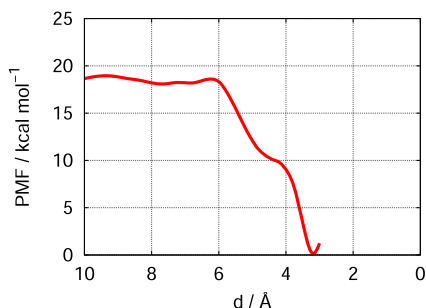


FIG. 2. Potential of mean force (PMF) profile for the center of mass (COM) of the neutral *p*-benzoquinone molecule immersed in the electrolyte solution to approach the right Pt electrode, whose surface is located at $d = 0$ Å (d is the distance between the right electrode surface and the COM of the *p*-benzoquinone molecule). This PMF profile is calculated from a constant-voltage MD simulation with $\Delta V = 0$ V.

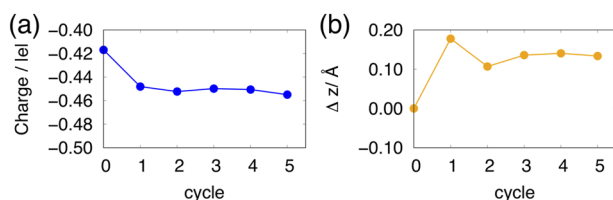


FIG. 3. Convergence behavior of (a) the atomic charge and (b) the displacement in the z direction of the oxygen atoms of the *p*-benzoquinone molecule physisorbed on the Pt electrode surface. The horizontal axis is the cycle number of the MFCV-QM/MM calculation. One cycle consists of MD simulations (composed of ten uncorrelated 1.05 ns simulations) and one QM calculation (geometry optimization with external mean electrostatic potentials and mean forces).

than the energy of the vdW interaction with the electrode surface. This difference mainly comes from taking into account in the PMF calculation the thermal motion of the *p*-benzoquinone molecule in directions parallel to the surface (loss of the entropic contribution due to the adsorption), and the loss of adsorption energies of acetonitrile molecules pushed aside due to the adsorption of the quinone molecule.

B. Effects of interface and applied voltage on electronic state and geometry

We shall then show that the MFCV-QM/MM calculations can determine the optimized electronic state and geometry at the interface. Figure 3 displays the atomic charge on an oxygen atom and the displacement of the atom in the direction normal to the molecular plane as functions of cycle number of the MFCV-QM/MM calculation on the neutral *p*-benzoquinone molecule under $\Delta V = 0$ V condition. Similar convergence behavior is observed for the other atoms not only in the neutral form but also in the reduced form and with $\Delta V = 2$ V. The results indicate that the geometry optimization and the self-consistent calculations are completed within five cycles.

The atomic charges derived from the optimized electronic state of the neutral and reduced *p*-benzoquinone molecule are listed in Figs. 4(a) and 4(b), respectively. For comparison, we also show the atomic charges in the gas phase, in the bulk electrolyte solution, at the interface with $\Delta V = 0$ V, and at the cathode (negatively charged) interface with $\Delta V = 2$ V. The oxygen atoms are more negatively charged both in the bulk electrolyte solution and at the interface regardless of its charged state, reflecting the change in the electronic state from that in the gas phase. The results of the atomic charges especially in the neutral form indicate that the polarity of the electrode–electrolyte interface is not so different from that of the bulk solution. Applying $\Delta V = 2$ V seems to slightly modulate but not significantly affect the electronic state of the *p*-benzoquinone molecule.

The change in the bond lengths of the *p*-benzoquinone molecule from the gas phase is small (less than 0.01 Å, see the [supplementary material](#)) both in the bulk electrolyte solution and at the interface. However, a modest geometrical variation appears at the interface as the molecular plane bent to or away from the electrode surface as shown in Fig. 5. We also display in Fig. 6 the external component of the mean force [the terms in bracket in the right side of Eq. (26)] and their LJ and electrostatic contributions in the z direction acting on the atoms in order to find out which interaction serves to distort the structure of the *p*-benzoquinone molecule. In the neutral state under $\Delta V = 0$ V condition, the oxygen atoms are attracted toward the electrode surface. This is due to the vdW interaction between the oxygen atoms and the electrode surface as can be seen from Fig. 6(a), which is related to an observation in the MD simulations that the oxygen atoms tend to reside on hollow sites as shown in Fig. 5(e). On the other hand, the carbon

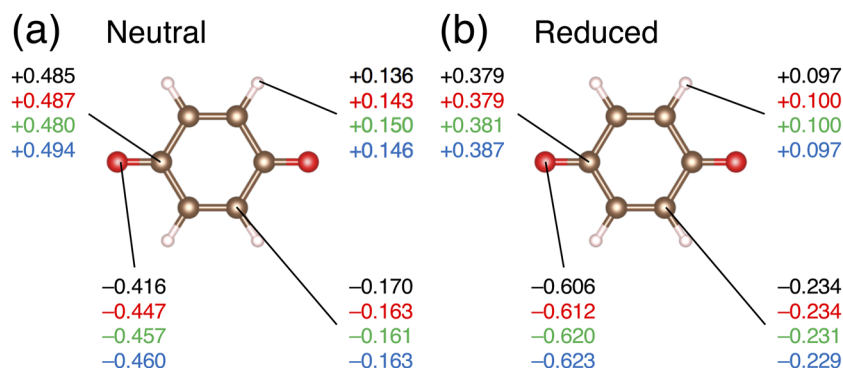


FIG. 4. Restrained electrostatic potential charges (in unit of e) of *p*-benzoquinone in (a) the neutral form and (b) the reduced form. The values obtained in the gas phase, in the bulk electrolyte solution, on the electrode surface with $\Delta V = 0$ V, and on the cathode surface with $\Delta V = 2$ V are shown in black, red, green, and blue, respectively.

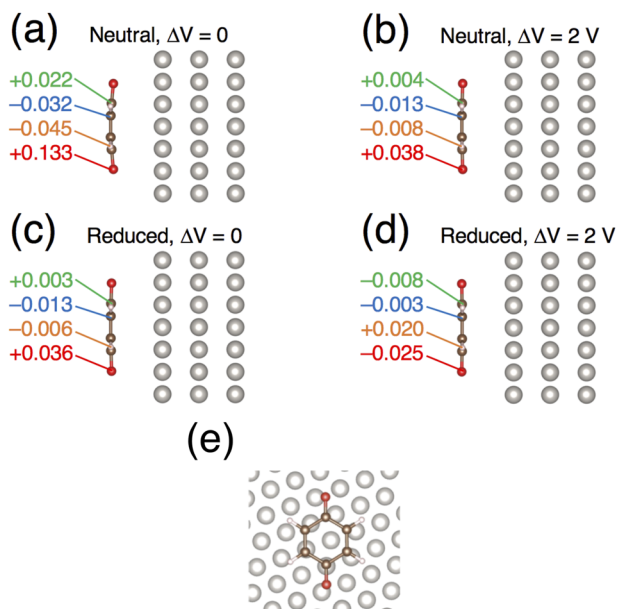


FIG. 5. Side views of the optimized structures of the *p*-benzoquinone molecule physisorbed on the Pt electrode surface (a) in the neutral form with $\Delta V = 0$ V, (b) in the neutral form with $\Delta V = 2$ V, (c) in the reduced form with $\Delta V = 0$ V, and (d) in the reduced form with $\Delta V = 2$ V, respectively. The values in the figures are the displacements (in Å) from the plane normal to the *z* axis (parallel with the electrode surface) that passes the geometric center of the *p*-benzoquinone molecule. The values shown in green, blue, orange, red are for the carbonyl carbon atoms, the other carbon atoms, the hydrogen atoms, and the oxygen atoms, respectively. A representative conformation of the physisorbed *p*-benzoquinone molecule in MD simulations are shown in (e), which is viewed from above the electrode surface.

atoms bonded to the oxygen atoms tend to get too close to electrode atoms and repel each other due to the repulsive interaction of the LJ potential. The electrostatic forces acting on the atoms are small when the *p*-benzoquinone molecule is in the neutral form and $\Delta V = 0$ V.

Applying $\Delta V = 2$ V induces negative charge on the cathode surface that interacts with the charge distribution of the adsorbed *p*-benzoquinone molecule and clearly modulates its bent structure. The displacements of the *p*-benzoquinone atoms become smaller. Focusing on the oxygen atoms, this is mainly because the repulsive electrostatic interaction between the negative charge on the oxygen atoms and the negative charge induced on the cathode surface works to partially cancel out their attractive vdW interaction. On the other hand, the attractive electrostatic force acts on the positively charged carbon atoms next to the oxygen atoms, which works in the opposite direction to that of the LJ repulsive force.

The bending of the molecular plane is smaller in the case of the reduced *p*-benzoquinone molecule under $\Delta V = 0$ V condition than that in the case of the neutral form. Comparison of the mean force components acting on each atom in Figs. 6(a) and 6(c) indicates that the LJ forces are similar regardless of the charged state of the *p*-benzoquinone molecule as expected. A clear difference emerges as the repulsive and attractive electrostatic forces acting on the oxygen atoms and their bonded carbon atoms. Considering that an attractive image force works between the reduced *p*-benzoquinone molecule and the platinum electrode surface, the repulsive electrostatic force acting on the oxygen atoms is counterintuitive. This is possibly because of the attractive interaction between the reduced *p*-benzoquinone molecule and an electrolyte cation attracted from the direction opposite to the cathode surface, indicated from an analysis of the trajectories and the distribution of atoms of the electrolyte solution at the interface.

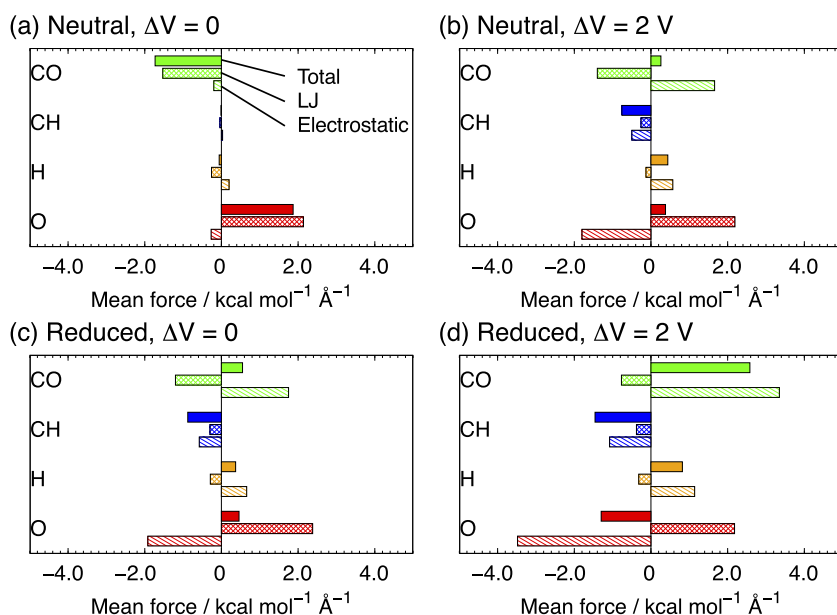


FIG. 6. The *z* components of the external mean force [the second and third terms on the right-hand side of Eq. (26)] acting on the atoms of the *p*-benzoquinone molecule physisorbed on the electrode surface. The LJ and electrostatic contributions and their sum are represented for the carbon atoms next to the oxygen atoms (CO) with green bars, for the carbon atoms next to the hydrogen atoms (CH) with blue bars, for the hydrogen atoms (H) with orange bars, and for the oxygen atoms (O) with red bars, respectively. The results are for the *p*-benzoquinone molecule and the applied voltage being (a) in the neutral form and $\Delta V = 0$ V, (b) in the neutral form and $\Delta V = 2$ V, (c) in the reduced form and $\Delta V = 0$ V, and (d) in the reduced form and $\Delta V = 2$ V, respectively.

TABLE I. Reorganization energies and driving forces (in eV) calculated from Eqs. (32) and (33) under various conditions: the *p*-benzoquinone molecule is in the bulk electrolyte solution (bulk), or on the electrode (cathode) surface (Interface; the center of mass of the *p*-benzoquinone being fixed at 3.2 Å away from the electrode surface), with applied voltage $\Delta V = 0$ or 2 V. The values in parentheses are those obtained from simulations in which the acetonitrile molecules are modeled with a nonpolarizable force field.

ΔV	Bulk		Interface	
	0 V	2 V	0 V	2 V
λ	2.18 (2.96)	2.18 (2.98)	0.91 (0.99)	0.90 (1.00)
ΔA	1.70 (1.70)	0.71 (0.69)	1.97 (1.85)	1.28 (1.10)

Application of $\Delta V = 2$ V induces negative charge on the cathode surface. The changes in the electrostatic forces on the atoms of the reduced *p*-benzoquinone molecule are in line with our intuition that larger attractive forces act on the positively charged carbon atoms bonded to the oxygen atoms and the larger repulsive forces act on the negatively charged oxygen atoms. Further approach of cations to the reduced *p*-benzoquinone molecule due to their attraction toward the negatively charged cathode may also play a role.

C. Reorganization energy

The Marcus theory for electron transfer between a metal electrode and a redox species in an electrolyte solution suggests that the reorganization energy λ is strongly dependent on the image-charge interaction with the electrode and the equilibrium and nonequilibrium electrostatic interactions with the surrounding electrolyte via the Pekar factor.⁶⁶ Our method enables us to take into account these factors explicitly in the MD simulation by using the polarizable metal electrodes and electrolyte solution (acetonitrile molecules). Moreover, the contribution of the geometric change of the redox species to λ can be included in the QM calculation part through the geometry optimization in each redox state. The reorganization energies calculated at the interface are 0.91 and 0.90 eV with $\Delta V = 0$ and 2 V, respectively, in quantitative agreement with both a previous theoretical calculation (0.95 eV)⁸ and experimental estimates (0.94 and 1.0 eV).^{67–69} For reference, Table I lists λ and also ΔA values evaluated under different conditions: the *p*-benzoquinone molecule being located in the bulk electrolyte solution, the use of a non-polarizable force field for the acetonitrile molecules, and application of 0 or 2 V voltages. The applied voltages have small effect on λ . The close proximity to the electrode surface and then the image-charge interaction dominantly serve to decrease λ . Although the nonequilibrium solvation effect due to electronic polarization of the acetonitrile molecules plays a significant role in the bulk electrolyte solution, the effect is marginal at the interface as discussed in our previous work.³⁷

V. CONCLUSIONS

In this work, we have proposed a novel QM/MM method and its variant to study the electronic state and geometry of a physisorbed molecule at an electrode–electrolyte interface under the constant voltage condition. The induction effects of metal electrodes or the

image-charge interactions are described by the method based on the chemical potential equalization principle, which naturally gives the electrochemical potential of the electrode electrons. The charges on the electrode atoms are determined at each MD timestep so that the difference between the electrochemical potentials of the working and counter electrodes becomes a prescribed value. Thus, various quantities including the electronic state and geometry of the adsorbate can be calculated at the QM/MM level in the constant voltage ensemble. By virtue of the mean-field embedding in the variant of the constant-voltage QM/MM (MFCV-QM/MM) method, the electronic structure calculations for the adsorbate and the classical molecular dynamics simulations to sample the system configurations are completely separated. This enables us to access the wide range of configuration space of the thermally fluctuating electrolyte solution in order to correctly evaluate thermodynamic quantities such as the potential of mean force.

The MFCV-QM/MM method was applied to a typical example of an electrochemical system, *p*-benzoquinone immersed in an electrolyte solution in contact with platinum electrodes. The calculations show that the polarization of the *p*-benzoquinone physisorbed horizontally on the platinum electrode surface is not so different from that in the bulk electrolyte solution. The planar structure of *p*-benzoquinone is distorted mainly because of the strong vdW interaction between the oxygen atoms and the platinum atoms. The distorted structure is further modulated by the interactions due to the polarization of the metal electrode, which can be enhanced by charging the *p*-benzoquinone by reduction or the electrode by applying a voltage. The analysis of the mean force and the MD trajectories imply that the interactions with cations approaching from above may play a role to modulate the structure of the physisorbed *p*-benzoquinone. We also demonstrated the calculations of thermodynamic quantities, the reorganization energy, of the one-electron reduction of *p*-benzoquinone. The result is in reasonable agreement with previous theoretical and experimental values. The calculations show that taking into account the image-charge interaction with the metal electrode surface is essential for quantitative evaluation of the reorganization energy. In a future study, we will show how to evaluate the reduction potential using the results obtained from the MFCV-QM/MM calculation. We hope the present method facilitates further studies on a molecule at an interface between a metal surface (of a semi-infinite or nanoparticle electrode) and a solution, and electrochemical processes in an electrochemical cell.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for the profiles of number density and running integration number of the atoms of acetonitrile molecules and electrolyte ions along the direction perpendicular to the electrode surfaces, a snapshot of the electrode–electrolyte interface, and the bond lengths of the *p*-benzoquinone molecule optimized in the gas phase, in the bulk electrolyte, at the interface on the cathode surface with $\Delta V = 0$ and 2 V.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Ken Takahashi: Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (equal); Software (equal); Visualization (lead); Writing – original draft (equal); Writing – review & editing (supporting). **Hiroshi Nakano:** Conceptualization (lead); Formal analysis (supporting); Funding acquisition (equal); Investigation (supporting); Methodology (equal); Project administration (lead); Resources (lead); Software (equal); Supervision (equal); Validation (lead); Writing – original draft (equal); Writing – review & editing (lead). **Hirofumi Sato:** Funding acquisition (equal); Project administration (supporting); Resources (supporting); Supervision (equal); Writing – review & editing (supporting).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

APPENDIX: CLASSICAL CONSTANT-VOLTAGE SIMULATIONS BASED ON THE CHEMICAL POTENTIAL EQUALIZATION PRINCIPLE

In this [Appendix](#), the method that realizes the constant-voltage classical simulations of electrochemical systems will be presented. The most part of the following formulation follows that described in our previous work²² but is more systematic due to the use of a partial Legendre transformation.³⁸ The electrode atoms are assumed to be fixed in position during simulations. Also, the electrolyte solution is assumed to be modeled with a nonpolarizable force field. Note, however, that the corresponding formulation for a polarizable electrolyte solution is straightforward,³⁷ because it only adds additional independent variational variables and the procedure described below remains the same.

The total energy of the system consisting of an electrolyte and two (left and right) electrodes can be written as follows:

$$E(\mathbf{q}^M; \mathbf{r}^S | q_L^M, q_R^M) = E^M(\mathbf{q}^M; \mathbf{r}^S) + E^{S-M}(\mathbf{q}^M; \mathbf{r}^S) + E^S(\mathbf{r}^S) + U^{\text{nonele}}(\mathbf{r}^S), \quad (\text{A1})$$

where E^M , E^{S-M} , and E^S are the internal energy of the electrodes, the electrostatic interactions between the electrodes and the electrolyte, and the internal and electrostatic interactions of the electrolyte solution, respectively. $\mathbf{q}^M$ denotes a collection of atomic charges of the electrodes. They are treated as dynamical variables and determined variationally so that the total energy of the system is

minimized at each electrolyte configuration $\mathbf{r}^S$ with the following constraint conditions:

$$\sum_{i \in L}^{N_L^M} q_i^M = q_L^M, \quad \sum_{i \in R}^{N_R^M} q_i^M = q_R^M. \quad (\text{A2})$$

q_L^M and q_R^M are the total charges of the left and right electrodes, respectively, and treated as control variables in constant-charge simulations⁷⁰ Note that in this article, in parentheses, we list variational variables first, variables, such as $\mathbf{r}^S$, on which the function parametrically depend second, and control variables third. We also separate them with a semicolon and a vertical bar.

Here, we restrict ourselves to consider metallic electrodes composed of only one element (e.g., platinum electrodes) in the following. A combination of different electrodes, such as platinum and graphene electrodes, can be handled straightforwardly. The internal energy of the polarizable electrodes are approximately given by

$$E^M(\mathbf{q}^M; \mathbf{r}^S) \approx E_0^M + \chi^\circ \mathbf{1} \cdot \mathbf{q}^M + \frac{1}{2} \mathbf{q}^M \cdot \mathbf{J}^\circ \mathbf{q}^M, \quad (\text{A3})$$

where $\mathbf{1}$ is a vector whose all elements are equal to 1, χ° is the electronegativity of an atom of the electrodes, and $\mathbf{J}^\circ$ is the interaction kernel between electrode atomic charges. The diagonal element of $\mathbf{J}_{ii}^\circ = U^\circ$ corresponds to the chemical hardness of the electrode atom. The electrostatic interactions between the electrodes and the electrolyte solution can be written as

$$E^{S-M}(\mathbf{q}^M; \mathbf{r}^S) = \sum_k^{N_{\text{mol}}^S} \mathbf{q}^M \cdot \mathbf{D}_k^{M-S} \mathbf{q}_k^S, \quad (\text{A4})$$

where N_{mol}^S is the number of molecules in the electrolyte solution, $\mathbf{D}_k^{M-S}$ is a matrix notation of the interaction kernel between charges of the electrodes and the electrolyte solution, and $\mathbf{q}_k^S$ is a vector notation of atomic charges in the k th molecule in the electrolyte solution. The internal and electrostatic interaction energies of the electrolyte solution are written as

$$E^S(\mathbf{r}^S) = \sum_k^{N_{\text{mol}}^S} \mathcal{E}_k(\mathbf{r}^S) + \frac{1}{2} \sum_{k \neq l}^{N_{\text{mol}}^S} \mathbf{q}_k^S \cdot \mathbf{D}_{k,l}^{S-S} \mathbf{q}_l^S, \quad (\text{A5})$$

where $\mathbf{D}_{k,l}^{S-S}$ is a matrix notation of the interaction kernel between atomic charges of the electrolyte solution. The internal energy functions $\{\mathcal{E}_k(\mathbf{r}^S)\}$ are assumed to be modeled with a classical force field. We can perform a constant-charge simulation by using the electrode atomic charges obtained by minimizing Eq. (A1) with respect to $\mathbf{q}^M$ at each $\mathbf{r}^S$ under the constraint conditions in Eq. (A2).⁷⁰

We will then show how to achieve the constant-voltage condition in simulations. The system total energy E in Eq. (A1) is a function of the control variables q_L^M and q_R^M . The total differential with respect to the variables thus becomes

$$dE(q_L^M, q_R^M) = -\mu_L dq_L^M - \mu_R dq_R^M, \quad (\text{A6})$$

where μ_L and μ_R are the chemical potentials of electrons in the left and right electrodes, respectively. Note that $dq_L^M = -dn_L^M$ and

$dq_R^M = -dn_R^M$, where n_L^M and n_R^M are the number of electrons in the left and right electrodes. The variables q_L^M and q_R^M are transformed to q_{tot}^M and Δq^M defined as follows:

$$q_{\text{tot}}^M = q_L^M + q_R^M, \quad \Delta q^M = q_L^M - q_R^M, \quad (\text{A7})$$

and then the total differential becomes

$$dE(q_{\text{tot}}^M, \Delta q^M) = -\mu_c dq_{\text{tot}}^M - \frac{1}{2} \Delta \mu d\Delta q^M, \quad (\text{A8})$$

with $\mu_c = (\mu_L + \mu_R)/2$ and $\Delta \mu = \mu_L - \mu_R$. In order to change the control variables from $(q_{\text{tot}}^M, \Delta q^M)$ to $(q_{\text{tot}}^M, \Delta V)$ with $\Delta V = -\Delta \mu$, a partial Legendre transformation is carried out to introduce a new quantity called as the partial grand potential hereafter as follows:

$$\omega(\mathbf{q}^M; \mathbf{r}^S | q_{\text{tot}}^M, \Delta V) = E(\mathbf{q}^M; \mathbf{r}^S | q_{\text{tot}}^M, \Delta q^M) - \frac{1}{2} \Delta q^M \cdot \Delta V. \quad (\text{A9})$$

The charges of the polarizable electrode atoms are determined by minimizing this partial grand potential with respect to $\mathbf{q}^M$ under the constraint condition on the total charge

$$\sum_i^{N^M} q_i^M = q_{\text{tot}}^M, \quad (\text{A10})$$

where $N^M = N_L^M + N_R^M$ is the total number of the electrode atoms. For that purpose, the following objective function is introduced:

$$\mathcal{L}(\mathbf{q}^M; \mathbf{r}^S | q_{\text{tot}}^M, \Delta V) = \omega(\mathbf{q}^M; \mathbf{r}^S | q_{\text{tot}}^M, \Delta V) + \mu_c (q_{\text{tot}}^M + q_{\text{tot}}^S). \quad (\text{A11})$$

μ_c is a Lagrange undetermined multiplier and q_{tot}^S is the total charge of the electrolyte solution given by

$$q_{\text{tot}}^S = \sum_k^{N_{\text{mol}}^S} \sum_a^{N_k^S} q_{k,a}^S, \quad (\text{A12})$$

where N_k^S is the number of atoms in the k th molecule and the $q_{k,a}^S$ is the charge of the a th atom in the k th molecule in the electrolyte solution. The variational equations $\partial \mathcal{L} / \partial q_i^M = 0$ ($i = 1, 2, \dots, N^M$) lead to

$$q_i^M = -\frac{1}{U^\circ} (\chi^\circ + v_i \mp \frac{1}{2} \Delta V + \mu_c), \quad (\text{A13})$$

with the minus and plus signs for the left and right electrode charges, respectively. v_i is the ESP acting on the i th electrode atom

$$v_i = \sum_{j(i \neq j)}^{N^M} J_{ij}^\circ q_j^M + \sum_k^{N_{\text{mol}}^S} \mathbf{D}_{i,k}^{M-S} \mathbf{q}_k^S. \quad (\text{A14})$$

By combining Eqs. (A10) and (A13), and assuming $N_L^M = N_R^M$, μ_c can be determined as

$$\mu_c = -\chi^\circ - \bar{v} + U^\circ \frac{q_{\text{tot}}^S}{N^M}, \quad (\text{A15})$$

where $\bar{v} = \sum_i^{N^M} v_i / N^M$ is the averaged effective ESP on the electrode atoms. The electrode atomic charges can then be written as

$$q_i^M = -\frac{1}{U^\circ} (v_i - \bar{v} \mp \frac{1}{2} \Delta V) - \frac{q_{\text{tot}}^S}{N^M}. \quad (\text{A16})$$

In brief, from Eqs. (A15) and (A16), the chemical potential of the left electrode can be written as

$$\mu_L = -\frac{\partial E}{\partial q_{i \in L}^M} = \mu_c - \frac{1}{2} \Delta V \quad (\text{A17})$$

and that of the right electrode as

$$\mu_R = -\frac{\partial E}{\partial q_{i \in R}^M} = \mu_c + \frac{1}{2} \Delta V, \quad (\text{A18})$$

which means that we can perform constant-voltage simulations by using the electrode charges determined as Eq. (A16). Note that v_i depends on all the other q_j^M , then the coupled equations for the electrode charges are solved iteratively or by a matrix inversion procedure.²²

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