

## Supplementary information for

# First principles study of sulfuric acid anion adsorption on Pt(111) electrode

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## A. Mean field of static solvation medium

Within the Born-Oppenheimer approximation, a Hamiltonian of an interfacial system is described as follows,

$$H[\{\mathbf{P}_i\}, \{\mathbf{R}_i\}, \{\mathbf{P}_i^m\}, \{\mathbf{R}_i^m\}] = \sum_i \frac{|\mathbf{P}_i|^2}{2M_i} + \sum_i \frac{|\mathbf{P}_i^m|^2}{2M_i^m} + E[\{\mathbf{R}_i\}, \{\mathbf{R}_i^m\}], \quad (\text{A.1})$$

where  $\mathbf{P}_i$  and  $\mathbf{R}_i$  are momentums and positions of atoms in the region (i), and  $E$  is the potential energy of the system. The momentums and positions of atoms in the solvation medium (the region (ii)) are denoted using the superscript  $m$ . The partition function of the system is described as follows,

$$Q = \frac{1}{\prod_i h^{3N_i} \prod_i h^{3N_i^m}} \int \cdots \int \exp\left[-\frac{H[\{\mathbf{P}_i\}, \{\mathbf{R}_i\}, \{\mathbf{P}_i^m\}, \{\mathbf{R}_i^m\}]}{k_B T}\right] \prod_i d\mathbf{P}_i d\mathbf{R}_i \prod_i d\mathbf{P}_i^m d\mathbf{R}_i^m, \quad (\text{A.2})$$

where  $N_i$  and  $N_i^m$  are the numbers of atoms in the region (i) and region (ii), respectively. For simplifying the equation, all the atoms in the system are assumed to be non-identical in this section, but it is straightforward to extend equations to the system including identical atoms.

By using the Hamiltonian of the system without the region (ii) described as,

$$H_0[\{\mathbf{P}_i\}, \{\mathbf{R}_i\}] = \sum_i \frac{|\mathbf{P}_i|^2}{2M_i} + E_0[\{\mathbf{R}_i\}], \quad (\text{A.3})$$

eqn (A.2) can be rewritten as follows,

$$Q = \frac{1}{\prod_i h^{3N_i}} \int \cdots \int \exp\left[-\frac{H_0[\{\mathbf{P}_i\}, \{\mathbf{R}_i\}] + G_m[\{\mathbf{R}_i\}]}{k_B T}\right] \prod_i d\mathbf{P}_i d\mathbf{R}_i, \quad (\text{A.4})$$

where  $G_m$  is the mean field (or potential of mean force) of the region (ii) defined as follows,

$$G_m[\{\mathbf{R}_i\}] = k_B T \ln \frac{1}{\prod_i h^{3N_i^m}} \int \cdots \int \exp \left[ - \frac{\sum_i \frac{|\mathbf{P}_i^m|^2}{2M_i^m} + E[\{\mathbf{R}_i\}, \{\mathbf{R}_i^m\}] - E_0[\{\mathbf{R}_i\}]}{k_B T} \right] d\mathbf{P}_i^m d\mathbf{R}_i^m. \quad (\text{A.5})$$

On the basis of eqn (A.4), the system can be approximately regarded as the atoms in the region (i) moving on the effective potential energy surface described as follows,

$$E_1[\{\mathbf{R}_i\}] = E_0[\{\mathbf{R}_i\}] + G_m[\{\mathbf{R}_i\}]. \quad (\text{A.6})$$

This approximate picture is sometimes called as a static solvation<sup>48</sup> and has been successfully used in the self-consistent reaction field (SCRF) theory on isolated molecules and ions implemented in various well-established computational programs<sup>70</sup> for evaluating not only the static properties like solvation free energies<sup>38-44</sup> but also the dynamic properties like vibration frequencies.<sup>49, 50</sup>

## B. Continuum solvation model

As in the usual DFT,<sup>22, 23</sup> the kinetic and exchange-correlation energies of electrons in the region (i) are described as follows,

$$K = \sum_n f_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \left( -\frac{1}{2} \nabla^2 \right) \psi_n(\mathbf{r}), \quad (\text{B.1})$$

$$E_{xc} = E_{xc}[\rho_\uparrow, \rho_\downarrow] = \int d\mathbf{r} f_{xc}(\rho_\uparrow, \rho_\downarrow, \nabla\rho_\uparrow, \nabla\rho_\downarrow), \quad (\text{B.2})$$

where  $n$  denotes  $\mathbf{k}$ -point, spin and band indexes, and  $\rho_s$  ( $s = \uparrow$  or  $\downarrow$ ) is the electron density with a spin index  $s$ . In this study, two generalized gradient approximations (GGAs)<sup>64, 65</sup> were applied, and therefore,  $E_{xc}$  is described as a functional of the electron densities and those derivatives.

The electrostatic energy  $E_{es}$  is described as follows,

$$E_{es} = \int d\mathbf{r} [\rho_\uparrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r}) + \rho_c(\mathbf{r}) + \rho_+(\mathbf{r}) + \rho_-(\mathbf{r})] \phi(\mathbf{r}) - \int d\mathbf{r} \frac{\varepsilon(\mathbf{r})}{8\pi} |\nabla\phi(\mathbf{r})|^2, \quad (\text{B.3})$$

where  $\rho_c$  is the charge density of the nuclei in the region (i), and  $\varepsilon$  is the dielectric permittivity. Similarly to the polarizable continuum model,  $\varepsilon$  is 1 near the atoms in the region (i) and is  $\varepsilon_b$  ( $= 78.36$ ) far from the atoms. At the intermediate region,  $\varepsilon$  smoothly changes from 1 to  $\varepsilon_b$ . Details of the function form of  $\varepsilon$  is described elsewhere.<sup>29</sup>

The non-electrostatic free energy  $G_{ss,nes}$  is a summation of cavitation, dispersion and repulsion free energies, which are denoted as  $G_{ss,cav}$ ,  $G_{ss,dr}$  and  $G_{ss,rep}$ . The cavitation free energy  $G_{ss,cav}$  is described as a product of a total surface area  $S$  of the atoms in the region (i) by a surface tension  $\gamma_b$  ( $= 71.99$  mN/m) of the solvent as follows,

$$G_{ss,cav} = \gamma_b S. \quad (\text{B.4})$$

The surface area  $S$  is obtained by a methodology<sup>29</sup> similar to that suggested by Scherlis et al.<sup>43</sup> The dispersion and repulsion free energies are obtained as a linear function of atomic surface areas  $\{S_\alpha\}$  as follows,

$$G_{ss,dr} + G_{ss,rep} = \sum_{\alpha} (a_{\alpha} S_{\alpha} + b_{\alpha}). \quad (\text{B.5})$$

$S_{\alpha}$  is obtained by partitioning  $S$  using a methodology described in Ref. 29. Parameters  $a_{\alpha}$  and  $b_{\alpha}$  were determined to reproduce the dispersion and repulsion free energies of molecules and ions in a homogeneous solution given by the polarizable continuum model implemented in Gaussian03.<sup>70</sup>

The non-electrostatic interaction energy  $G_{is,nel}$  is described as follows,

$$G_{is,nel} = \int d\mathbf{r} (|\rho_{-}(\mathbf{r})| + |\rho_{+}(\mathbf{r})|) \phi_{rep}(\mathbf{r}). \quad (\text{B.6})$$

$\phi_{rep}$  describes non-electrostatic repulsive potentials between atoms in the region (i) and ions in the region (ii). The repulsive interaction avoids that ions in the region (ii) approach to atoms in the region (i) too closely. A similar repulsive potential was introduced by Otani and Sugino<sup>26</sup> for describing a Stern layer, and the methodology was extended to an adaptive form in a variationally consistent manner by Jinnouchi and Anderson.<sup>29</sup>

The entropy  $S_i$  is described using a lattice gas model as follows,

$$S_i = -\frac{k_B}{a^3} \int d\mathbf{r} [|\rho_{+}(\mathbf{r})| a^3 \ln(|\rho_{+}(\mathbf{r})| a^3) + |\rho_{-}(\mathbf{r})| a^3 \ln(|\rho_{-}(\mathbf{r})| a^3) + (1 - |\rho_{+}(\mathbf{r})| a^3 - |\rho_{-}(\mathbf{r})| a^3) \ln(1 - |\rho_{+}(\mathbf{r})| a^3 - |\rho_{-}(\mathbf{r})| a^3)]. \quad (\text{B.7})$$

This term was introduced by Borukhov et al.<sup>46, 47</sup> to describe steric effects of ion in a solution.

$G_{mc}$  is described as follows,

$$G_{mc} = -\varepsilon_F N - \mu_{+} N_{+} - \mu_{-} N_{-}, \quad (\text{B.8})$$

where  $N_{\pm}$  are the numbers of cation and anion:

$$N_{\pm} = \int \rho_{\pm}(\mathbf{r}) d\mathbf{r}, \quad (\text{B.9})$$

The chemical potentials  $\mu_{\pm}$  of ions are the same as those in the bulk electrolyte in contact with the system. Those are obtained using a lattice gas model of the bulk electrolyte<sup>46,47</sup> as follows,

$$\mu_{\pm} = k_B T \ln \frac{c_b a^3}{1 - 2c_b a^3}. \quad (\text{B.10})$$

## C. Enthalpies and entropies of chemical species

Adsorbed species are assumed to be rigidly bounded to the surface, and those enthalpies  $H_n$  and entropies  $S_n$  based on the motions of nuclei are described using a harmonic oscillator model as follows,

$$H_n = H_{vib} = \frac{1}{2} \sum_i h \nu_i + \sum_i \frac{h \nu_i}{e^{h \nu_i / k_B T} - 1}, \quad (\text{C.1})$$

$$S_n = S_{vib} = k_B \sum_i \left( \frac{h \nu_i / k_B T}{e^{h \nu_i / k_B T} - 1} - \ln(1 - e^{-h \nu_i / k_B T}) \right), \quad (\text{C.2})$$

where  $h$  is the Planck constant, and  $\nu_i$  is the frequency of  $i$ th vibration mode. For the chemical species in a homogeneous gas phase or aqueous phase, translation, rotation, and vibration motions are taken into account as follows,

$$H_n = H_{trans} + H_{rot} + H_{vib}, \quad (\text{C.3})$$

$$S_n = S_{trans} + S_{rot} + S_{vib}, \quad (\text{C.4})$$

$$H_{trans} = \frac{3}{2} k_B T, \quad (\text{C.5})$$

$$H_{rot} = \begin{cases} k_B T, & \text{for linear molecules} \\ \frac{3}{2} k_B T, & \text{for nonlinear molecules} \end{cases}, \quad (\text{C.6})$$

$$S_{trans} = k_B \left( \ln \left( \frac{2 \pi m k_B T}{h^2} \right)^{3/2} \frac{k_B T}{p} + 1 + \frac{3}{2} \right), \quad (\text{C.7})$$

$$S_{rot} = \begin{cases} k_B \ln \left( \frac{T}{\sigma \Theta_z} + 1 \right), & \text{for linear molecules} \\ k_B \ln \left( \frac{\pi^{1/2} T^{3/2}}{\sigma_{rot} \sqrt{\Theta_x \Theta_y \Theta_z}} + \frac{3}{2} \right), & \text{for nonlinear molecules} \end{cases}, \quad (\text{C.8})$$

$$\Theta_{x,y,z} = \frac{h^2}{8\pi^2 I_{x,y,z} k_B}. \quad (\text{C.9})$$

where  $m$  is the mass of the specie,  $p$  is the pressure,  $\sigma_{rot}$  is the rotational symmetry number, and  $I_{x,y,z}$  are the momentum inertia.

All the enthalpies and entropies are compiled in Table S1.



**Table S1**  $H_n$  and  $TS_n$  ( $T = 298.15$  K). For species in gas phase, the pressure is set at 1 atm.  $H_2O(aq)$  corresponds to  $H_2O(g)$  with a vapor pressure of 0.035 atm. The unit of energy is eV. The data for the adsorbates were obtained by using the partial Hessian matrices.

	$H_n$	$TS_n$
$H_2O(aq)$	0.665	0.673
$H_2O(ads)$	0.724	0.086
$H^+(g)$	0.064	0.337
$HSO_4^-(g)$	0.821	0.909
$SO_4(ads)+H_2O(ads)$	1.321	0.372
$HSO_4(ads)+H_2O(ads)$	1.620	0.440
$H_3O-SO_4(ads)$	1.570	0.354
$H(ads)$	0.141	0.016
$OH(ads)$	0.400	0.130
$O(ads)$	0.098	0.041

## **D. Results of preliminary calculations on small clusters**

Results of preliminary calculations on small clusters are compiled in Table S2-S7. Details of the calculation method are described in the section 2.6.

As described in the section 4.1, the GGA-PBE results on the extended slabs in the modeled continuum electrolyte shown in the section 4.2 were corrected through eqn (31). In this correction, the results by MP2/6-311++G(2df,2pd) and GGA-PBE/6-311++G(2df,2pd) in Tables S4 and S5 were used.

**Table S2** Frequencies of a D<sub>2</sub>SO<sub>4</sub> molecule in vacuum. All the calculations were performed by using the GGA-PBE functional.  $\Delta\nu$  is the average error from the experimental results. The unit is cm<sup>-1</sup>.

	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$	$\nu_7$	$\nu_8$	$\Delta\nu$
Exp. <sup>a</sup>	547	565	820	834	883	1223	1446	2663	–
FEM <sup>b</sup>	509	537	818	835	881	1164	1400	2649	–24
aug-cc-pVQZ <sup>c</sup>	497	507	801	827	873	1157	1389	2656	–34
aug-cc-pVTZ <sup>c</sup>	487	497	791	828	873	1141	1370	2651	–43
aug-cc-pVDZ <sup>c</sup>	464	696	753	828	868	1084	1305	2638	–43
6-311++G(2df,2pd) <sup>c</sup>	495	506	802	830	875	1156	1390	2666	–33
DZDP+f <sup>d</sup>	503	507	779	823	863	1163	1398	2662	–35
DZP <sup>e</sup>	483	491	763	833	870	1131	1368	2665	–47

a. Experimental results from Ref. S1.

b. Theoretical results from Ref. S2 obtained by using a finite-element basis set.

c Theoretical results by Gaussian 03 (Ref. 70).

d Theoretical results by the methodology used in this study.

e Theoretical results by using the basis set without the second polarization and the f-orbital.

**Table S3** Frequencies of a  $\text{SO}_4^{2-}(\text{H}_2\text{O})_3$  cluster in vacuum.  $\Delta\nu$  is the average error from the experimental results. Partial hess. means that the frequencies are obtained by using partial Hessian matrices of  $\text{SO}_4$ . The unit is  $\text{cm}^{-1}$ .

	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$	$\nu_7$	$\Delta\nu$
Exp. <sup>a</sup>	613	862	943	1052	1080	1102	1735	–
MP2/TZP <sup>b</sup>	589	869	913	1058	1016	1094	1746	–15
MP2/6-311++G(2df,2pd) <sup>c</sup>	611	851	950	1091	1056	1121	1719	2
B3LYP/TZP <sup>b</sup>	569	837	866	1008	971	1040	1722	–53
B3LYP/6-311++G(2df,2pd) <sup>c</sup>	601	831	915	1055	1023	1083	1736	–20
GGA-PBE/6-311++G(2df,2pd) <sup>c</sup>	571	817	872	1014	980	1045	1689	–57
GGA-PBE/DZDP+f <sup>d</sup>	573	824	875	1017	973	1050	1683	–56
GGA-PBE/DZDP+f (partial hess.) <sup>d</sup>	576	–	875	1021	976	1055	–	–57
GGA-RPBE/DZDP+f (partial hess.) <sup>d</sup>	570	–	861	1000	959	1031	–	–74

a Experimental results from Ref. S3.

b. Theoretical results from Ref. 87.

c Theoretical results by Gaussian 03 (Ref. 70).

d. Theoretical results by our program.

**Table S4** Frequencies of a sulfate on a Pt<sub>3</sub> cluster in vacuum. The structure of the sulfate on the Pt<sub>3</sub> cluster is similar to the one shown in Fig. 5 (C). Partial hess. means that the frequencies were obtained by using the partial Hessian matrices of SO<sub>4</sub>. The unit is cm<sup>-1</sup>.

	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$	$\nu_7$
MP2/6-311++G(2df,2pd) <sup>a</sup>	613	614	628	918	977	979	1361
B3LYP/6-311++G(2df,2pd) <sup>a</sup>	574	574	600	870	886	887	1303
GGA-PBE/6-311++G(2df,2pd) <sup>a</sup>	534	535	557	807	846	848	1240
GGA-PBE/DZDP+f <sup>b</sup>	541	542	570	797	834	837	1238
GGA-PBE/DZDP+f (partial hess.) <sup>b</sup>	539	540	569	797	834	836	1238
GGA-RPBE/DZDP+f (partial hess.) <sup>b</sup>	534	535	563	785	821	824	1219

a Theoretical results by Gaussian 03 (Ref. 70).

b. Theoretical results by our program.

**Table S5** Frequencies of a bisulfate on a Pt<sub>2</sub> cluster in vacuum. Partial hess. means that the frequencies were obtained by using the partial Hessian matrices of HSO<sub>4</sub>. The unit is cm<sup>-1</sup>.

	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$	$\nu_7$
MP2/6-311++G(2df,2pd) <sup>a</sup>	592	594	813	1027	1101	1179	1371
B3LYP/6-311++G(2df,2pd) <sup>a</sup>	563	574	796	985	1034	1160	1323
GGA-PBE/6-311++G(2df,2pd) <sup>a</sup>	532	535	752	922	981	1127	1272
GGA-PBE/DZDP+f <sup>b</sup>	536	543	748	909	967	1119	1273
GGA-PBE/DZDP+f (partial hess.) <sup>b</sup>	535	542	748	910	967	1119	1273
GGA-RPBE/DZDP+f (partial hess.) <sup>b</sup>	529	537	730	899	956	1122	1255

a Theoretical results by Gaussian 03 (Ref. 70).

b. Theoretical results by our program.

**Table S6** Frequencies of a sulfate on a Pt<sub>3</sub> cluster and Pt(111) slab. Both results were obtained by using the GGA-PBE functional, DZDP+f basis set and the partial Hessian matrices of SO<sub>4</sub>. The unit is cm<sup>-1</sup>.

	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$	$\nu_7$
Sulfate on Pt <sub>3</sub> cluster	539	540	569	797	834	836	1238
Sulfate on Pt(111) slab	553	554	569	805	823	826	1238

**Table S7** Frequencies of a bisulfate on a Pt<sub>2</sub> cluster and Pt(111) slab. Both results were obtained by using the GGA-PBE functional, DZDP+f basis set and the partial Hessian matrices of HSO<sub>4</sub>. The unit is cm<sup>-1</sup>.

	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$	$\nu_7$
Bisulfate on Pt <sub>2</sub> cluster	535	542	748	910	967	1119	1273
Bisulfate on Pt(111) slab	533	560	752	923	936	1096	1260

## E. Displacement vectors of vibrational modes

The displacement vectors of vibrational modes for sulfate, bisulfate and hydronium-sulfate ion pair are summarized in Figs. S1, S2 and S3, respectively. Vibration frequencies and the corresponding squares of dynamic dipole moments are also shown in these figures.

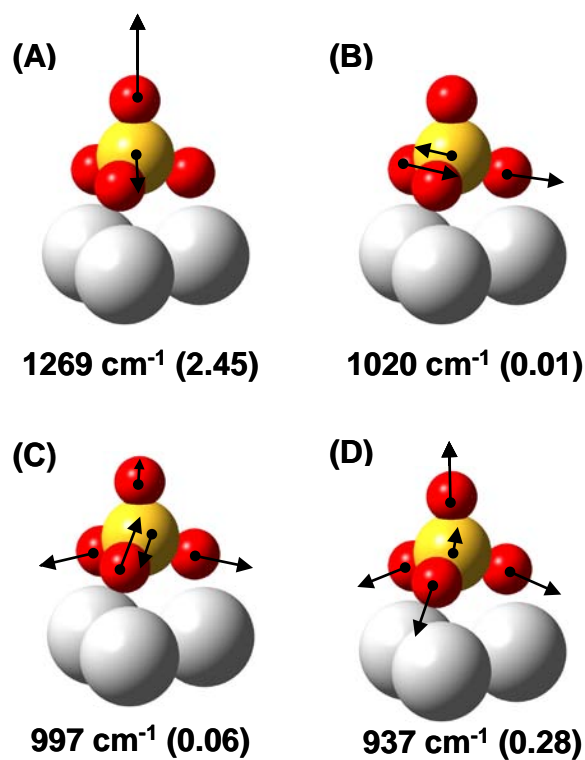


Figure S1 Displacement vectors of vibration modes for sulfate at 0.63 V (RHE). Values in the parenthesis are the squares of the dipole moments along the surface normal, the unit of which is  $e^2$ .



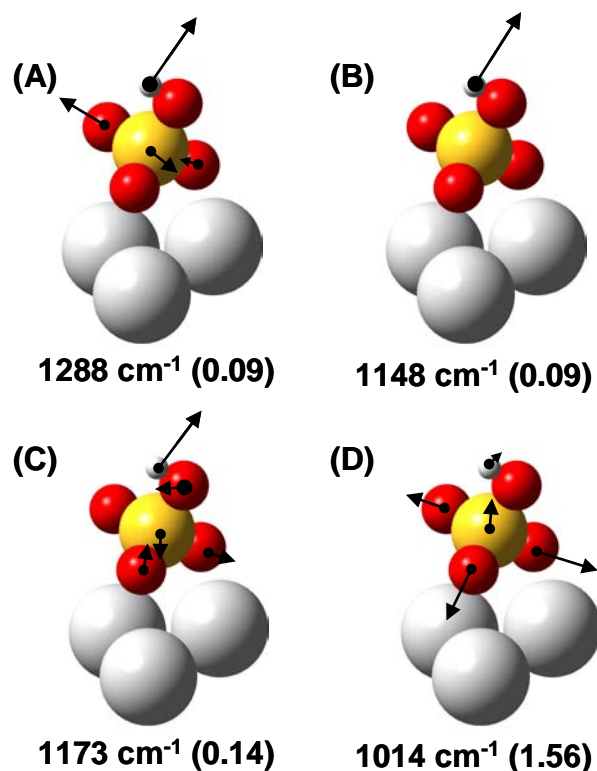


Figure S2 Displacement vectors of vibration modes for bisulfate at 0.50 V (RHE). Values in the parenthesis are the squares of the dipole moments along the surface normal, the unit of which is  $e^2$ .

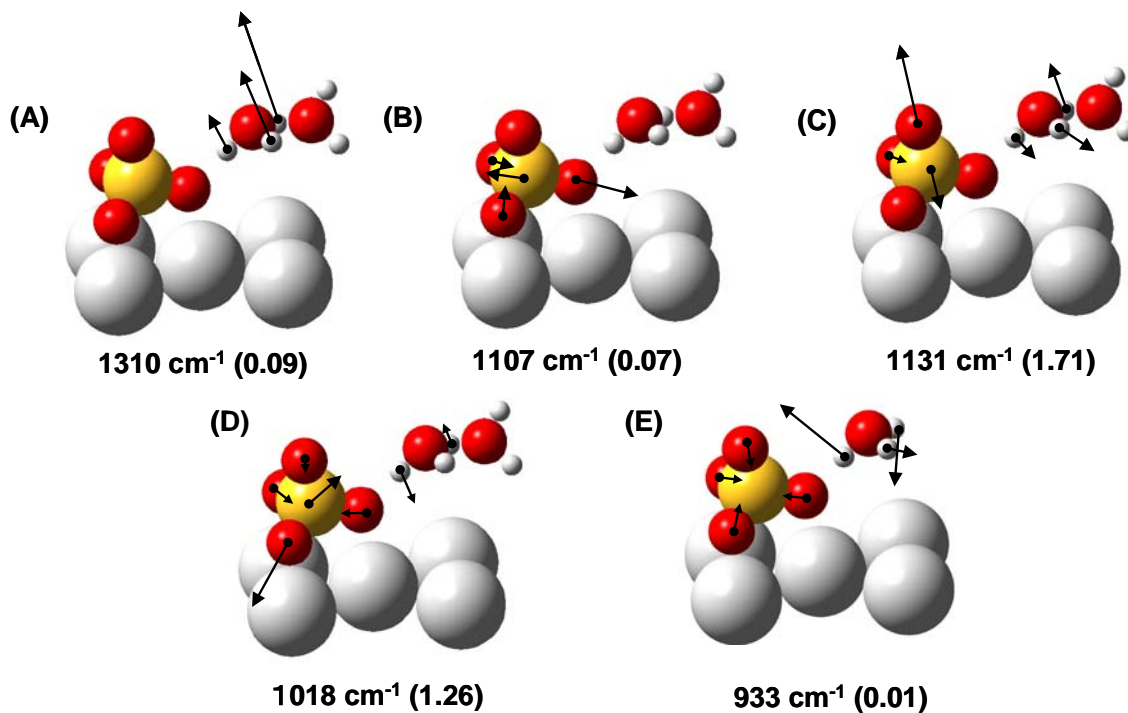


Figure S3 Displacement vectors of vibration modes for hydronium-sulfate ion pair at 0.46 V (RHE). Values in the parenthesis are the squares of the dipole moments along the surface normal, the unit of which is  $e^2$ .

## References

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