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Theoretical insight into the vibrational spectra of metal–water interfaces from density functional theory based molecular dynamics†

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Understanding the structures of electrochemical interfaces at the atomic level is key to developing efficient electrochemical cells for energy storage and conversion. Spectroscopic techniques have been widely used to investigate the structures and vibrational properties of the interfaces. The interpretation of these spectra is however not straightforward. In this work, density functional theory based molecular dynamics simulations were performed to study the vibrational properties of the Pt(111)– and Au(111)–water interfaces.

It was found that the specific adsorption of some surface water on Pt(111) leads to a partial charge transfer to the metal, and strong hydrogen bonding with neighbouring water molecules, which resolves the interpretation of the elusive O–H stretching peak at around 3000 cm^{−1} observed in some experiments.

Interfacial water plays a vital role in electrochemical processes, and studying its structure is crucial for understanding electrochemical phenomena at the molecular level. A variety of experimental techniques have been developed to study the structure of interfacial water. The early work with X-ray scattering by Toney and co-workers¹ presented the density distribution of water along the surface normal of Ag(111), and recently, X-ray absorption spectroscopy² was employed to characterise the existence of a dangling O–H bond at the Au–water interface.

Vibrational spectroscopy (e.g. infrared, Raman and sum frequency generation (SFG)) is better suited to obtain information about the potential-dependent orientation and the degree of hydrogen bonding of interfacial water. Potential-dependent spectra measured from a variety of solid–electrolyte interfaces^{3–7} have been reported, but their interpretation is challenging and can be

controversial in some special cases. For example, Iwasita and Xia⁸ observed, using infrared reflection–absorption spectroscopy (IRRAS), that the O–H stretching frequency $\nu(\text{O–H})$ of water on the Pt(111) surface jumps from ~ 3000 to ~ 3150 cm^{−1} with a slight change in the potential around the potential of zero charge (PZC). The peak at ~ 3000 cm^{−1} was interpreted as an O–H...M vibrational mode based on measurements under ultrahigh vacuum (UHV) conditions.^{9–12}

Similarly, Osawa and co-workers⁴ obtained a broad band at ~ 3000 cm^{−1} at the Pt–water interface using surface-enhanced infrared absorption spectroscopy in the attenuated total reflection mode (ATR-SEIRAS). The signal of the surface water was extracted by employing the spectra measured from a CO-covered Pt electrode as the reference. Different from the interpretation of Iwasita and Xia, the band at ~ 3000 cm^{−1} was assigned to a strongly hydrogen bonded network between the water molecules. This assignment was supported by density functional theory based molecular dynamics (DFTMD) simulations of a gas phase water bilayer model on Pt(111) at 90 K by Meng and co-workers,¹³ who found a strongly hydrogen bonded O–H in the upper layer of the H-up ice-like bilayer model and estimated a $\nu(\text{O–H})$ frequency of 3104 cm^{−1}, similar to Osawa's experimental values.⁴

To further understand the structure of the interfacial water, the H–O–H bending mode $\delta(\text{HOH})$ must also be taken into account. Osawa *et al.*⁴ found a $\delta(\text{HOH})$ peak of water at 1600 cm^{−1} along with the emergence of a broad band at ~ 3000 cm^{−1} in the double layer region of the Pt–water interface, which was attributed to the water with partial electron donation to the Pt electrode *via* the 1b₁ orbital on the oxygen atom. Chemisorption of water molecules on transition metal surfaces can indeed lead to a partial charge transfer between the water and surfaces,^{9,14–16} and we have recently shown that the partial charge transfer from specifically adsorbed water to Pt(111) contributes more than 1 eV to the potential drop across the Pt(111)–electrolyte interface at PZC using DFTMD simulations.¹⁷ Another consequence of the specific adsorption of water is that the strength of the O–H bond of water will be weakened. However, this

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effect has often been overlooked when interpreting water vibrational spectra at interfaces.⁴ An exception is the work of the group of Gewirth,⁷ who observed a peak at 2970 cm^{-1} on the Ag(100) surface using SFG, and suggested that it may come from specifically adsorbed water. It was also proposed by Ibach and Lewald⁹ that the water peak at 2850 cm^{-1} measured on Pt(100) in UHV is probably due to a specific, surface induced form of the O–H...O bond.

In view of the discrepancies in the assignments of the peaks at $\sim 3000\text{ cm}^{-1}$ in both experiments and calculations, we revisited the Pt(111)- and Au(111)-water interfaces using DFTMD simulations. Complementary to spectroscopic experiments, DFTMD methods have recently been used to study the water structure and vibrational properties at solid-liquid interfaces.^{18–21} In this work, DFTMD simulations were performed at 330 K using the freely available CP2K/QUICKSTEP package,²² and the detailed computational setup following our previous work^{17,23–27} can be found in the ESI† Fig. 1 shows a representative structure of the Pt(111)-water interface at the PZC from a DFTMD trajectory. Following the definitions in our recent publications,^{17,23} the water molecules inside the model are divided into three categories, namely, watA, watB and watC, based on their distance to the metal surfaces (see the population of surface water in Table S1 and the profiles of water density and dipole orientation in Fig. S1 in the ESI†). The three types of water are highlighted in different colors in Fig. 1. The closest to the surfaces are the watA molecules, mainly sitting on the top site of the metal surfaces (Pt and Au); they are chemisorbed on the surfaces *via* their oxygen atoms with dipoles (water bisector) pointing outwards, resulting in a partial electron transfer from watA to the metal surfaces. Estimated from the Mulliken population analysis, each watA molecule donates around 0.14 e^- to Pt(111) and 0.05 e^- to Au(111) at the PZC. Slightly above watA but still within the adsorption water layer are the watB molecules. In contrast to watA, the watB molecules interact weakly with the metal surfaces with dipoles pointing to the surfaces; they have no preferred adsorption site

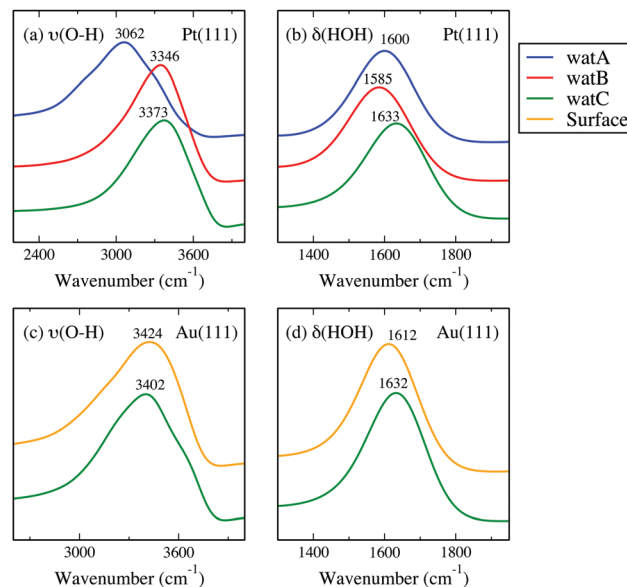


Fig. 2 Calculated vibrational density of states of different types of water at the Pt(111)- and Au(111)-water interfaces. WatA, watB and watC and surface water are represented by blue, red, green and orange curves, respectively. The O–H stretching modes are presented in (a and c), and the H–O–H bending modes are shown in (b and d).

and charge transfer to the metals is negligible. The watC molecules fall outside the water adsorption layer, having no direct interaction with the metal surfaces and thus serving as the ‘bulk’ reference in our study.

We calculated the vibrational density of states (VDOS) of watA, watB and watC at the Pt(111)- and Au(111)-water interfaces by using the Fourier transform of hydrogen-hydrogen velocity autocorrelation functions.²⁸ For the Au(111)-water interface, the watA molecules exchange very fast with the watB molecules as a result of weak adsorption (see Fig. S2 in the ESI†), and we therefore did not separate the VDOS of watA and watB. As shown in Fig. 2, the $\nu(\text{O-H})$ and $\delta(\text{HOH})$ of watC are peaked at ~ 3400 and $\sim 1630\text{ cm}^{-1}$, respectively, close to those of bulk water from the experiment^{8,29} (the libration peaks of water are shown in Fig. S3 of the ESI†). Compared to watC, the $\nu(\text{O-H})$ of watA at the Pt(111)-water interface at $\sim 3062\text{ cm}^{-1}$ (see Fig. 2(a)) is significantly red-shifted by over 300 cm^{-1} . Interestingly, it is comparable to the literature values around $\sim 3000\text{ cm}^{-1}$ that are assigned to water strongly adsorbed on metal surfaces in some experimental measurements.^{4,7,8} Concurrently, the $\delta(\text{HOH})$ of watA shows a red-shift to 1600 cm^{-1} , as would be expected due to the specific adsorption of watA. The red-shift of the $\delta(\text{HOH})$ was also observed experimentally on Pt, and a similar explanation of Pt–OH₂ charge transfer was proposed.⁴ In contrast, no noticeable shift of the $\nu(\text{O-H})$ of the surface water (watA and watB combined) at the Au(111)-water interface was found, and no apparent shoulder at $\sim 3000\text{ cm}^{-1}$ was observed, either, in line with the experimental results on Au electrodes. The difference between Au and Pt must be due to the fact that water binds much more weakly to the Au surface than to Pt.^{5,6,30}

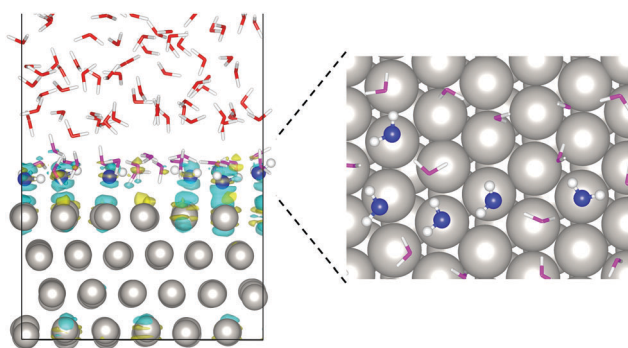


Fig. 1 Side (left) and top (right) views of a snapshot of the Pt(111)-water interface from a DFTMD trajectory. Pt, watA, watB and watC are colored in grey, blue, magenta and red, respectively. The isosurfaces represent the electron density difference profile of the interface before and after water interacts with the metal surface electronically, and the regions colored in cyan and yellow indicate electron depletion and accumulation, respectively.

Table 1 Calculated vibrational modes of a water molecule adsorbed on Pt(111) and in the gas phase. d_{OH} , $\delta(\text{HOH})$ and $\nu(\text{O-H})$ represent the O-H bond length, H-O-H bending and O-H stretching vibration frequency of water, respectively. The experimental data is taken from ref. 8 and references therein

Water monomer	$d_{\text{OH}}/\text{\AA}$	$\delta(\text{HOH})/\text{cm}^{-1}$	$\nu(\text{O-H})/\text{cm}^{-1}$
Pt(111)	0.979	1552	3613, 3727
Gas	0.972	1586	3728, 3840
Exp.		1595	3657, 3756

To confirm the charge transfer effect on the vibrational frequency of watA, we calculated a water monomer adsorbed on the top site of the Pt(111) surface (see Fig. S4 in the ESI†) and in the gas phase for comparison. Our previous study²³ has shown that the structure of watA at the interface is indeed similar to the preferred configuration of the water monomer on Pt(111), and therefore it should be informative for investigating the charge transfer effect of the water monomer, thereby excluding the effect of hydrogen bonding. As expected, we observed that a fraction of the electron on the water monomer is transferred to the metal surface, which induces an elongation of the O-H bonds compared to water in the gas phase. Also note that the $\delta(\text{HOH})$ is red-shifted by 34 cm^{-1} due to the surface adsorption (see Table 1), almost the same as the $\delta(\text{HOH})$ shift of watA. In the $\nu(\text{O-H})$ mode, the charge transfer effect causes a red-shift of $\sim 110\text{ cm}^{-1}$ for both the symmetric and asymmetric vibrations of the water monomer. This appears insufficient to account for the $\sim 300\text{ cm}^{-1}$ red-shift of watA at the Pt(111)-water interface compared to that of watC, indicating that some other factors may play a role.

As suggested by Ibach and Lehwald⁹ that the O-H...O hydrogen bonds between interfacial water may be distorted due to surface adsorption, we studied the structures of hydrogen bonding of watA, watB and watC at the Pt(111)-water interface, following a geometric definition of hydrogen bonds often used in the literature^{2,23} that the O...O distance is within 3.5 \AA and the $\angle\text{OOH}$ is within 35° . As summarised in Table 2, each watA at the Pt(111)-water interface donates ~ 2 H atoms on average for the formation of hydrogen bonds, similar to watC, whereas the O...O separation ($D_{\text{O-O}}$) between watA and the corresponding hydrogen bond acceptor is apparently shortened to 2.71 \AA compared to that of watC (2.85 \AA). As reported by Feibelman,³¹ there exists a good correlation between $\nu(\text{O-H})$ and

Table 2 Results of the hydrogen bonds and vibrational frequencies of different kinds of water at the Pt(111)- and Au(111)-water interfaces. N_{donor} denotes the number of hydrogen bond donors, and $D_{\text{O-O}}$ corresponds to the O...O distance of the hydrogen bonds. $\delta(\text{HOH})$ and $\nu(\text{O-H})$ are the bending and stretching frequencies of water. Water labels are defined in the main text. On Au, surfwat indicates watA and watB combined

	N_{donor}	$D_{\text{O-O}}/\text{\AA}$	$\delta(\text{HOH})/\text{cm}^{-1}$	$\nu(\text{O-H})/\text{cm}^{-1}$
watA@Pt(111)	1.97	2.714	1600	3062
watB@Pt(111)	1.38	2.817	1585	3346
watC@Pt(111)	1.91	2.847	1633	3373
surfwat@Au(111)	1.62	2.840	1612	3424
watC@Au(111)	1.85	2.857	1632	3402

$D_{\text{O-O}}$, and the contraction of $D_{\text{O-O}}$ is associated with a red-shift of $\nu(\text{O-H})$. Therefore, we propose that the O-H bonds of watA form strong hydrogen bonds with neighbouring water, contributing to the extra red-shift of the $\nu(\text{O-H})$ of watA. Note that such strengthening of the hydrogen bonds of watA is a consequence of its specific adsorption on the metal surface that leads to the polarisation of watA.

As for watB, we can see from Fig. 2 that the $\nu(\text{O-H})$ at the Pt(111)-water interface is very similar to the 'bulk' reference watC that indeed corresponds to liquid-like water as interpreted in the experiment.^{6,30} As watA is indistinguishable from watB at the Au(111)-water interface, the $\nu(\text{O-H})$ of all the surface water was calculated and also found to be close to that of watC. Meanwhile, the corresponding $\delta(\text{HOH})$ on both the metal surfaces were found to be red-shifted, in particular, by $\sim 50\text{ cm}^{-1}$ for watB on Pt. As indicated in the charge analysis above, the charge transfer effects for watB on Pt and surface water on Au are much smaller than that for watA on Pt, which is also consistent with the finding that their hydrogen bond distances $D_{\text{O-O}}$ are only slightly decreased (see Table 2). We therefore regard the charge transfer effects to be small on the vibrational modes of watB on Pt and surface water on Au. More important is the structure of hydrogen bonding. As listed in Table 2, the number of hydrogen bond donors (N_{donor}) is considerably decreased, from 1.91 to 1.38 for watB on Pt(111), to which the red-shift of $\delta(\text{HOH})$ can be attributed. Note that the effect of reduced hydrogen bonding can be compensated by the small charge transfer effect, giving rise to hardly altered $\nu(\text{O-H})$ on Pt.

Finally, we present the following assignments of the peaks often observed in the vibrational spectra of interfacial water on Pt, based on the structure of surface water on Pt(111) at the PZC proposed in our recent publication,²³ as illustrated in Fig. 3. Part of the highest occupied molecular orbital (HOMO) was clearly made from the $1b_1$ orbital of watA, indicating the chemisorption of watA on Pt. We assign the peaks at $\sim 3000\text{ cm}^{-1}$ observed in the

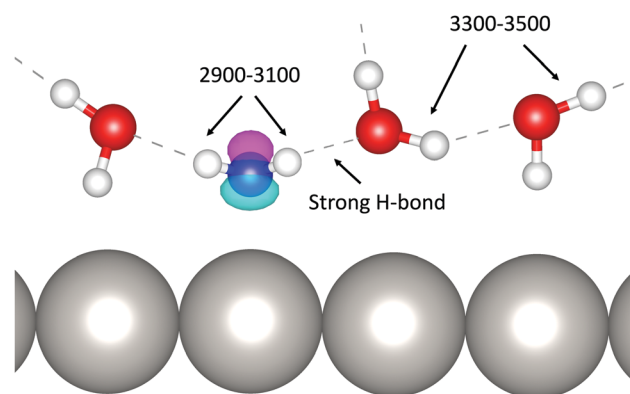


Fig. 3 Illustration of the structure of surface water on Pt(111) at the potential of zero charge. The Pt and oxygen atoms in watA and watB are colored in grey, blue and red, respectively. The O-H stretching frequencies of surface water are indicated. The HOMO of the interface is partially located on watA, as represented with pink and cyan isosurfaces (those on Pt are not shown).

experiment on Pt⁴ to the O–H stretching of watA, which donates electrons to the metal electrode and forms strong O–H···O hydrogen bonds with the neighbouring water molecules, giving rise to the significantly red-shifted peaks. The angle between the molecular plane of watA and the Pt(111) surface is $\sim 30^\circ$ at the PZC. This suggests that, although not prohibited in IRRAS, ATR-SEIRAS or SFG by the surface selection rule, the intensity of this vibrational mode would be predictably small, and in some cases it may not even be observed due to the strong noise from bulk water. We attribute the peaks at $\sim 3400\text{ cm}^{-1}$ often observed at the metal–water interfaces^{6,7} to the watB molecules. They hardly interact with the metal surfaces electronically, while the degree of hydrogen bonding decreases in the vicinity of the surfaces.

In conclusion, according to DFTMD simulations, we propose that the controversial peak at $\sim 3000\text{ cm}^{-1}$ often observed in the vibrational spectra of the Pt(111)–electrolyte interface corresponds to some specifically adsorbed water, and that the significant red-shift, as compared to bulk water, is due to the combined effects of charge transfer and strong O–H···O hydrogen bonds. This assignment provides new chemical insight into the interpretation of the vibrational spectra of interface water and a molecular level understanding of electrochemical interfaces.

Conflicts of interest

There are no conflicts to declare.

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