Electronic effects in SERS by liquid water

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By exploiting the attenuated total reflection (ATR)–Otto configuration, surface-enhanced Raman scattering of water at monocrystalline copper and silver electrodes in 0.1M Na2SO4 was observed at cathodic electrode potentials with hydrogen evolution at a laser wavelength of 647.1 nm. The proposed enhancement model is based on the condition that the upshift of the Fermi level of the electrode and the absorption of one laser photon allow an electron of the electrode at the Fermi level to reach the lower level of the energy band of delocalized electrons in liquid water. The electron interaction with the water molecules in the first hydration shell of cations in the Helmholtz plane is so-called impulse scattering, which is the short-time, non-resonant excursion to the anionic ground state of molecules known for a long time in low-energy electron scattering from free molecules. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: surface-enhanced Raman scattering; water; copper; silver; impulse scattering

INTRODUCTION

Electrochemical research at electrode surfaces has been provided with a so-called non-traditional method by surface-enhanced Raman scattering (SERS) for metal electrodes in both aqueous and non-aqueous electrolytes.1 Whereas most of the early work was restricted to Au, Ag and Cu electrodes, it has become possible by confocal Raman microscopy and special surface roughening procedures2 to extend SERS by adsorbates to the transition metals Pt, Ni, Fe, Co, Ru, Rh and Pd.3,4 In aqueous electrodes, in the electrode potential range of the stability of water, the Raman signal from adsorbates is only slightly obscured by the bulk water signal. The first SERS spectra of pyridine on an oxidation–reduction cycle (OCR)-roughened silver electrode obtained by Jeanmaire and Van Duyne5 in a 0.1 M KCl × 0.05 M pyridine electrolyte showed only a comparatively weak bending band of bulk water, and the spectral range of the OH stretch band of bulk water was dominated by the CH stretch band of adsorbed pyridine. The confocal microscopy configuration suppresses the signal of bulk water (although not in any case completely, see Fig. 1 in Ref. 6), which renders SERS of adsorbates at rough transition metal surfaces possible. Even better suppression of the bulk water signal is possible by using the so-called Otto configuration of attenuated total reflection [see below (Fig. 7)].

In the first decade of SERS research, a puzzling phenomenon was the apparent lack of a ‘first layer’ signal of water on silver electrodes, for instance in the standard electrolyte 0.1 M KCl + 0.05 M pyridine. According to Blatchford et al.,7 for colloidal sols this was due to decreasing electromagnetic enhancement at the high wavenumber of the OH vibrations. This is an unlikely explanation at electrode surfaces, given the good signal of the C–H stretch vibration of pyridine (see above). A signal was only observed at rough silver surfaces in electrolytes of high halide concentration,8–13 but not in KF solutions,14 and on rough Cu9,15 and Au electrodes16 in solution with high halide concentrations.

The right-hand curves in Fig. 1(c) provide an example of SERS of an aqueous electrolyte with 1 M KBr at a roughened silver electrode.11 The loss of the low-wavenumber shoulder of the OH stretch band indicates that hydrogen-bonded H2O contributes less to the SERS spectra (the H–O–H and symmetric OH wavenumbers of the free water molecule are at 1595 and 3657 cm−1, respectively.) The H–O–H bending mode is at a lower wavenumber than in neat water, shifting from 1608 cm−1 at 0.3 V SCE to 1599 cm−1 at −0.85 V SCE. The SERS signals of water are irreversibly lost at potentials of and below −1.1 V SCE.

The SERS signal discussed above was attributed to water–halide–metal adatom complexes. Also, the addition of highly concentrated RbCl or NaCl solution (with 0.05 M pyridine) after an ORC in 0.1 M NaCl + 0.05 M pyridine would cause the SERS intensity of water to increase, which was not observed without pyridine.18 The stability of these complexes was also increased by KOH.19

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PREVIOUS RESULTS

Since 1990, Tian’s group has been pursuing systematic SERS studies on electrode/electrolyte interfacial water. The major findings are as follows:21,23

1. For the band wavenumber, shape and intensity, the present SERS spectra of water (Fig. 2) are quite different from the bulk [Fig. 1(b), left] and the previous SERS results of water in halide complex [Fig. 1(c)]; especially the bending and libration modes are abnormally enhanced.21,24 The enhancement factor \((G)\) for the bending and stretching modes of water has been calculated based on the SERS results; \(G\) for the bending mode is found to be two orders of magnitude higher than that of the stretching mode at Ag, Cu and Au electrodes (Table 1).23

2. The SERS band shape and peak wavenumber (especially the OH stretching mode) are found to be dependent on the electrolyte components of cations (e.g. Li\(^+\), Na\(^+\), K\(^+\) and Cs\(^+\))25,26 and anions (e.g. ClO\(_4\)^-, SO\(_4\)^2- and OH\(^-\)),25,27 although one may expect that the anion effect should be

![Figure 1. Comparison of the IR (a) and Raman (b) spectra of pure water\(^1^7\) with the SERS spectra of water (c) at a roughened Ag in 1 M KBr electrolyte at various negative electrode potentials (E\(_{SCE}\)). [Fig. 1c Reprinted from Ref. 11, with permission from Elsevier].](image)

The complexes (‘active sites’) are destroyed by sufficiently cathodic pulses, but preserve their stability even at an electrode potential of \(-1.5\) V, when the sample is cooled to 250 K.20 Further references may be found in Ref. 21.

It came as a surprise when SERS of surface water was detected in less concentrated aqueous solutions at cathodic Ag and Cu electrode potentials in the range of hydrogen evolution, where halide ions are desorbed from the electrode surface and the complexes discussed above are not present. Triggered by a publication by Funtikov et al.,22 the group of Tian started systematic work described in detail in Refs. 21 and 23 to understand the cause of SERS of water under the condition of hydrogen evolution. In the next section we describe some previous results and compare them to other spectra of water relevant for the further discussion. The following section gives the experimental details. We then present new results on Cu single crystals. Finally, a comprehensive interpretation of the results obtained so far is given.

![Figure 2. SERS spectra of water at roughened (a) Cu, (b) Ag and (c) Au electrodes in 1.0 M Na\(_2\)SO\(_4\) solution at negative potentials (E\(_{SCE}\)). \(\lambda = 632.8\) nm.](image)
Table 1. Enhancement factor of the bending ($G_b$) and stretching ($G_s$) of water at roughened Cu, Ag and Au electrodes (monolayer adsorption of H$_2$O is assumed; $\lambda = 632.8$ nm)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ag</th>
<th>Cu</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{SCE}/V$</td>
<td>-1.5</td>
<td>-1.6</td>
<td>-1.5</td>
</tr>
<tr>
<td>$G_b$</td>
<td>$4.2 \times 10^4$</td>
<td>$1.5 \times 10^5$</td>
<td>$3.6 \times 10^5$</td>
</tr>
<tr>
<td>$G_s$</td>
<td>$7.3 \times 10^4$</td>
<td>$1.5 \times 10^5$</td>
<td>$2.0 \times 10^4$</td>
</tr>
</tbody>
</table>

Figure 3. Dependence of SERS band intensity of the bending mode of water and cathodic current density at roughened Cu, Ag and Au electrodes in 1.0 M Na$_2$SO$_4$ or 0.1 M NaOH solution.

negligible since the electrode potential is too negative for anions to approach the electrode surface.

3. This kind of SERS by water was only observed in the relatively negative potential region ($<-1.0$ V$_{SCE}$) for Ag, Cu and Au (Fig. 2), which is not correlated with the potential of zero charge (PZC) of the corresponding metals (e.g. in 0.1 M Na$_2$SO$_4$, PZC of Au (ca. 0. 2–0.3 V), Cu ($-0.30$ V) and Ag ($-0.9$ V)), although one may expect that the SERS features should depend on the PZC of the electrodes, because water molecules change their orientations when the electrode potential goes across the PZC. Furthermore, the more negative is the electrode potential, the higher are the SERS bands intensities of water (Fig. 2).

4. SERS of water is only observed in neutral or basic solution (at least when pH > 4).$^{21,23}$

5. An approximately linear behaviour of Raman intensity and cathodic current density of the hydrogen evolution reaction (HER)$^{21,24}$ (by discharge of water: $e + H_2O \rightarrow H + OH^-$ but not by discharge of hydrated protons: $e + H^+ \rightarrow H$)$^{29}$ at Ag, Cu and Au electrodes is observed (Fig. 3).

6. At Ag electrodes, SERS of water has been observed at potentials below $-1.0$ V$_{SCE}$ with laser radiation of 514.5,$^{22,25,27}$ 632.8$^{21,23,24}$ and 647.1 nm (see later). No dependence of the onset potential of SERS by water with the laser frequency is observed [e.g. Figs 2(b) and 4].

7. For D$_2$O, SERS bands also appears at potentials below $-1.0$ V, there is no major difference of SERS band intensities between H$_2$O and D$_2$O at lower potential [$-1.0$ to $-1.4$ V, see Figs 2(b) and 5], but the D$_2$ evolution current is very mild at potentials below $-1.4$ V (see Fig. 6, where the relative band intensity and HER current are displayed).

8. So far, no SERS of water has been observed on other transition metal electrodes (Ni, Pt, Rh, Ru, etc.) in the whole potential region where water is stable (Z. Q. Tian, personal communication). In previous SERS studies on roughened metal electrodes, one uncertainty is whether the change in the SERS intensity of water in the negative potential region is partly due to the change of the surface roughness. As we know, superatomic surface roughness is one of the prerequisites for providing surface enhancement in most electrochemical SERS studies, but the complexities of the surface roughness and its changes with external environment, e.g. changes with electrode potential, temperature,
etc., cause great problems in studying the origins of the surface Raman enhancement effect, and consequently result in uncertainties in the correlation of the Raman signal with surface concentration and adsorption configuration of the detected species. In order to surmount these difficulties, the attenuated total reflection (ATR)–Raman method, which yields electromagnetic enhancement on smooth metal surfaces, was set up. In this way the detection of Raman signals of adsorbates on both smooth and single-crystalline metal surfaces becomes possible. Here we present some of our further results on ATR–Raman spectroscopic studies of water at Cu(111), Cu(110), Cu(110) and Ag(111) electrode/electrolyte interfaces.

**EXPERIMENTAL**

For the present experiments on SERS of water, the crystal faces produced by Bruckbauer were used. Originally a copper single-crystal rod with a diameter of 8 mm was cut by spark erosion perpendicular to the chosen crystallographic axis, oriented with a precision ±0.5° by Laue back-reflection, and was then sealed in a Teflon holder. After mechanical polishing with SiC paper of decreasing grades, it was mechanically polished with diamond spray from 1 to 0.25 μm to a mirror-like face. Then the Cu(111) and Cu(100) faces were electrochemically polished for 30 s in a solution of 60% H₃PO₄ in water at 2.0 V and rinsed thoroughly with Milli-Q water. The crystal was finally transferred with a drop of water on its surface and inserted into the electrochemical ATR–Raman cell (see Fig. 7) for measurement.

A solution of 0.1 M Na₂SO₄ prepared with Milli-Q water was used as electrolyte and deaerated before and during the experiment with N₂. The potential of the working electrode was measured with respect to the Hg/Hg₂SO₄/0.5 M Na₂SO₄ reference electrode [−420 mV vs a saturated calomel reference electrode (SCE)] and controlled by a potentiostat using an Au counter ring electrode. The potentials are scaled to the SCE reference electrode. Raman spectra were excited with 647.1 nm radiation (100 mW). A Weierstrass prism (WP) made of ZnSe (radius r = 5 mm, refractive index n = 2.6 at 647.1 nm), which is longer by r/n than a hemispherical prism, is mounted in the bottom of the electrochemical cell (see Fig. 7). The electrode surface is carefully pressed against the prism with a micrometer and a spring so that the optimized gap size (ca half a wavelength) can be adjusted. With exact adjustment of the angle of the incident laser line with a triangular prism and of the distance between electrode surface and the WP, the optimum conditions for surface plasmon polariton excitation are reached, when a bright cone of scattered light is emitted and appears as a sharp ring behind the 1:1 collection objective (see Fig. 7). The intensity of the reflected light goes nearly to zero and the Raman intensity reaches a maximum

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**Figure 6.** Potential-dependent hydrogen and deuterium evolution current density (top) and band intensities of the bending modes of H₂O and D₂O (bottom) on Ag electrodes in 1.0 M Na₂SO₄.

**Figure 7.** Schematic diagram of the electrochemical ATR cell. WE working electrode of Cu crystals, about half a wavelength distant from the Weierstrass prism (WP), collection objective O, mirror M, movable prism P changing the angle of incidence α. Black ring S signifies scattered light from surface plasma polaritons.
under these optimum conditions. The scattered signal was recorded with a laboratory-built Raman spectrometer, which has a crossed Czerny–Turner design.

RESULTS

Cu(111)

Figure 8 reconfirms the SERS results from the copper electrodes roughened by OCR (Fig. 2) in the water bending mode spectral region. Figure 8 shows the relatively small background and the strong increase in the SERS intensity of water at potentials between −0.7 and −1.9 V vs. SCE. The comparison with the Raman spectrum from the same bulk electrolyte in Fig. 8 (bottom) shows an 18 cm$^{-1}$ downshift of the SERS band of the water bending mode in the same electrolyte. Apparently the water molecules contributing to SERS have fewer hydrogen bonds than those outside the Helmholtz plane.

Cu(100)

Figure 9 shows the cyclic voltammogram in the HER range of the Cu(100) crystal in 0.1 M Na$_2$SO$_4$ aqueous electrolyte.

![Figure 9. Cyclic voltammogram of Cu(100)/0.1 M Na$_2$SO$_4$. Scan rate, 20 mV s$^{-1}$.](image)

Figure 10(a) gives the SERS spectrum of water on Cu(100) in the ATR configuration. For comparison, a SERS spectrum of weakly roughened Cu(100) surface (indicated by the survival of the surface plasmon polariton ring, see Fig. 7) is given in Fig. 10(b). Although the signal of the water bending mode is stronger, there is no signal outside the potential range of the HER at −0.9 V. This will be discussed below. The differences in intensities of the water bending mode SERS from Cu(111) (Fig 8) and Ag(111) (Fig 11) may occur because the Ag(111) crystal surface, which was very carefully prepared, has minimal roughness.

DISCUSSION

Contribution of electromagnetic enhancement

In previous SERS measurements using a highly sensitive confocal micro-Raman spectrometer, Chen et al.$^{21}$ did not observe any SERS of water on smooth polycrystalline Cu, Ag and Au. In our present ATR–Raman study on a single-crystalline Cu electrode, an EM enhancement of ca 70-fold is provided by the ATR–Raman configuration.$^{30,31}$ We also tried to change the distance between the Cu single-crystalline electrode and the ZnSe prism to adjust the SPP excitation on or off. When the distance is not optimized for SPP excitation, no SERS signal of water is observed in the whole potential region investigated. This suggests that although the EM enhancement factor is small in the ATR configuration, it is a prerequisite for the appearance of SERS of water at Cu or Ag single-crystalline electrodes, but not sufficient.

SERS active sites and impulse mechanism of SERS at ‘normal sites’

For the following discussion it is necessary to discuss the influence of the surface morphology on the electronic contribution to SERS.

Bruckbauer and Otto$^{31}$ observed in the Raman spectra of pyridine adsorbed at single-crystal copper electrodes with
the ATR configuration, irrespective of the surface orientation, always the same wavenumbers of the low-intensity pyridine bands, which therefore was assigned to species at SERS active sites of low surface concentration. At single-crystal copper surfaces in perchlorate solution, the SERS active sites are not quenched by the application of a cathodic potential.\textsuperscript{32} As shown, for instance, in Fig. 10, the intensity of SERS by liquid water is not quenched at intentionally roughened Cu(100) electrodes at an electrode potential of \(-1.9\) V. The important role of SERS active sites has recently been highlighted by a comparison of the Raman and IR spectra of NO, N\(_2\)O and CO\(_2\) adsorbed at cold-deposited copper films (M. Lust, A. Pucci and A. Otto, in preparation). Whereas the surface-enhanced Raman spectra display only the reaction products of the molecules at the active sites, the IR spectra show a large majority of the unreacted molecules adsorbed on the smooth micro-terraces. The state of our theoretical knowledge of active sites and ‘normal sites’ was given in Ref. 33:

1. The interaction zone of the electromagnetic radiation with the metal electrons, which bring the adsorbed molecule

\(\text{Figure 10.} \) Spectra of water at Cu(100) in the ATR configuration in 0.1 M Na\(_2\)SO\(_4\) (a) and (b) mild roughened Cu(100) (see text) and (c) in 0.5 M KOH at negative electrode potentials (\(E_{\text{SCE}}\)).

\(\text{Figure 11.} \) ATR–Raman spectra of the bending and stretching modes of water on Ag(111) in 0.1 M Na\(_2\)SO\(_4\), at negative electrode potentials (\(E_{\text{SCE}}\)) background spectrum taken at \(-0.9\) V.
with low-lying $\pi^*$ state for a few seconds ($1 \text{ fs} = 10^{-15} \text{ s}$) into the anionic state of adsorbates (so-called photon-driven charge transfer) is confined to the narrow transition range from full interior electron density to zero intensity.

2. C–H stretch modes of molecules with $\pi^*$ states and all vibrations of molecules without $\pi^*$ states are only non-resonantly excited by an electron impact mechanism, which is an excursion for times below 0.5 fs to higher anionic $\sigma^*$-type states.

3. Electron–hole pair excitation, in addition to vibrational excitation, is detrimental for electronic SERS. This cannot be avoided at smooth facets in the case of electron resonance.\textsuperscript{34}

4. SERS active sites are sites of weaker coupling of electrons to bulk electronic states, with electronic residence times of the order of the lifetime of the anionic state of the adsorbate. These sites are of atomic dimensions, but their configuration is still unknown.

5. Owing to the time in states below 0.5 fs, electron–hole pair excitation is not a likely effect in the impact mechanism. Therefore, this non-resonant electronic mechanism is possible for all adsorbates, not only those adsorbed at SERS active sites.

### Missing resonant Raman effect by charge transfer

There might be a resonance Raman-like process which determines the behaviour of the Raman signal of water at negative potential, in which the metal electron is first transferred into a molecular orbital of a water molecule and then back to the metal state. However, this resonant charge-transfer mechanism of SERS\textsuperscript{35} is impossible in the present case. The free $\text{H}_2\text{O}$ molecule has two empty molecular orbitals\textsuperscript{36} with representations $4a_1$ and $2b_2$, when water is adsorbed on Cu(110) at 90 K. Its valence orbitals $1b_2$, $3a_1$ and $1b_1$ are $-17.1$, $-13.3$ and $-11.3$ eV, respectively, which are slightly below the gas-phase values of $-18.5$, $-14.7$ and $-12.6$ eV. This implies that in electrochemical systems the changes of the energy levels of the water molecules are also small.

This is corroborated by the following observations. In inverse photoemission from Ag(100), the intrinsic surface state and the image state were quenched by exposure to water, but no structure which might be assigned to the anionic states of adsorbed water was observed.\textsuperscript{37} For the free molecule, the splitting by dissociative attachment of an electron starts only at a 6.5 eV electron energy.\textsuperscript{38,39} in amorphous ice at 5.5 eV.\textsuperscript{40} Below these energies, the vibrational excitation cross-sections by electron impact do not show a pronounced dependence on electron energy.\textsuperscript{41} For Cu electrodes the Fermi energy level at $-1.5$ eV is about $-3.4$ eV and all these energy levels are out of range for a resonance with incident photons of 1.93–2.41 eV.

The approximate linear relationship between integrated intensity of Raman bands of water and the cathodic current density (see Fig. 3), may imply an important role of the process of the electrochemical dissociation of water molecules in the hydrogen evolution reaction (HER) in SERS by liquid water.

Reference 21 proposes the possibility: ‘The incident photon may be just equal to the excitation energy of the charge transferring from the metal to a special intermediate energy level of water molecules to be dissociated’. Some other less likely mechanisms are also discussed in Ref. 24. In the present paper we try to substantiate the statement above.

First, the Raman scattering is observed from ‘molecules to be dissociated’ rather than from molecules during dissociation. This becomes evident by a rough estimate: the electrode current of 20 mA cm\textsuperscript{-2} during HER in a neutral electrolyte corresponds to a splitting rate of water molecules of $\sim 1.25 \times 10^{17}$ cm\textsuperscript{-2} s\textsuperscript{-1}. Assuming a surface density of water in the inner Helmholtz plane of $1.25 \times 10^{14}$–$1.25 \times 10^{15}$ cm\textsuperscript{-2}, the average survival time of a surface water molecule before dissociation is $10^{-2}$–$10^{-3}$ s. The ‘splitting time’ is given by the time of nuclear motions during dissociation, which is certainly smaller than $10^4$ times the vibrational time of the OH stretch mode, yielding $10^{-10}$ s as upper limit of the ‘splitting time’. Therefore, the chances of meeting a water molecule during splitting are not better than $10^{-7}$–$10^{-8}$.

There is a further reason why cw-Raman scattering ‘during splitting’ is not possible, which is discussed below.

### Energy levels of electrons in liquid water

What is ‘the special intermediate energy level’ for resonance, or what are the energy levels of an extra electron in liquid water, and what is the ‘first layer’ electronic Raman enhancement in this case? Photoemission of electrons from solid metals with poor hydrogen adsorption properties (In, Bi, Pb, Hg)\textsuperscript{42,43} into aqueous electrolytes shows a common threshold of 3.39 V versus H\textsuperscript{+}/H\textsubscript{2}. At a silver electrode potential of 0 V\textsubscript{SCE}, the photon threshold energies have been measured as 3.4,\textsuperscript{44} 3.3,\textsuperscript{45} 3.26,\textsuperscript{46} 3.48\textsuperscript{40} and 3.48 eV\textsuperscript{47} above the Fermi level within the liquid mercury drop of the SCE. This is called the PE-threshold in Fig. 12. Note that this level is not the vacuum level of the metals, given by the energy $E_F + \text{work function}$. Neither is this level related to the potential of zero charge, which is important in the theory of the HER.\textsuperscript{48} The PE-threshold is the lowest state of the continuum of delocalized states of the electron before solvation.\textsuperscript{49} This figure also gives the energetic position of the fully hydrated electron in the energetically broad and short-lived (300 fs according to Ref. 49) so-called p-state and in the s-ground state, which survives some hundreds of nanoseconds depending on the concentration of quencher molecules.\textsuperscript{49} The reaction of the electron in the s-state with water, $e(s) + \text{H}_2\text{O(l)} \rightarrow \text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq})$, was studied in Ref. 50 as a function of temperature in hydrogen-saturated water, yielding a rate constant at 25 °C of 1040 s\textsuperscript{-1} and an activation energy of ca 0.32 eV. The shape of the s-state is
given in Ref. 51. The energy difference between the s- and p-states is known² from the optical absorption band, centred at 1.72 eV with an FWHM of 0.84 eV; the position of the s-state is 3.3⁵³ or 3.1 eV⁵⁴ below the continuum states according to experiment and 3.2⁵⁰ or 3.4 eV⁵⁶ according to theory.

Electron emission into a basic electrolyte was also achieved by emitting hot electrons from metal–insulator–silver⁵⁷ and – gold junctions⁵⁸ at and above the PE-threshold. When the top silver electrode of the metal–insulator–Ag junction was ‘activated’ by an ORC process, an HER by hot electrons was already observed below this threshold, increasing in yield when approaching the PE-threshold at a smooth Ag surface.⁵⁹ This is indicated schematically on the right side of Fig. 12.

Direct electron emission into the p- and s-states is not possible, because these states involve a strong rearrangement of the water molecule to accommodate the electron, which would take 300 ± 50 and 1000 ± 200 fs, respectively,⁴⁹ much longer than the lifetime of hot electrons of 1.3–3.2 eV in Cu (dephasing within 10 fs, thermalization within about 50 fs).⁶⁰

At the cathodic onset of hydrogen evolution from water, hydrated cations settle in the outer Helmholtz layer, with water molecules of the first hydration shell in the inner Helmholtz plane (IHP). The surface concentration of the hydrated cations increases with the cathodic potential. With decreasing E (increasing cathodic potential), the Fermi level $E_F$ of the metal electrode is energetically shifted upwards with respect to electronic levels in bulk water (see the left side of Fig. 12). The water molecules in the IHP see only an unknown fraction of this shift. Phenomenologically this is described by the transfer coefficient $\alpha$, defined via the relative change of the Gibbs activation energy $A$ of the HER by water splitting with respect to the change of the electrode potential $E$ via $\Delta A = \alpha e \times \Delta E$.⁶¹

HER by dissociation of water is caused by electron transfer to a water molecule in the inner Helmholzt layer, probably leading to a hydrogen atom and an OH⁻ anion. The measured HER by water splitting sets in exponentially (linear Tafel plot) when the Fermi level is already about 1 eV above the s level (see Fig. 12). In HER the potential of zero charge plays a role in the value of the so-called overpotential of the HER.⁴⁸ Electron transfer at metal electrodes accompanied by bond breaking was studied by molecular dynamics simulation⁶²–⁶⁴ and may be used also for water splitting (W. Schmickler, personal communication).

In the sense of the Born–Openheimer model, HER is a process of first the quantized movement of the electron in a multi-dimensional energy potential, shaped by the internal and external movement of the water molecules in the neighbourhood⁶⁵ (the so-called bath) and the vibrational phases, the distortions and the eventual dissociation of a given water molecule. The electron itself exerts changes in the water structure, which is on the picosecond time scale (see above). According to Ref. 56, fluctuation energies of electronic levels in water are large, exceeding thermal energies (0.025 eV) by more than an order of magnitude. Second, the nuclear motion of this water molecule evolves under the influence of the tunnelling electron and the bath, leading eventually to splitting. The potential for the electron is fluctuating in space and time owing to the bath and the nuclear movement of the given water molecule. Only for short moments do the fluctuating potential barriers and the nuclear configuration of the given water molecule allow for splitting; this is in line with the estimation of the average survival time of a water molecule in the inner Helmholzt plane of the order of $10^{-2}–10^{-3}$ s (see above).

Any photo-excited metal electron influenced by the fluctuations cannot yield cw-laser excited Raman scattering by the target molecule, because the coherence necessary for Raman spectroscopy is broken by dephasing when the electron interacts with the fluctuating bath. Therefore, it is not possible to infer along which normal coordinate the H₂O molecule splits. However, intramolecular Raman scattering by enhanced local laser fields is possible in principle. This channel is too weak even for the majority species and it is not observed. However, if a transient intramolecular electronic optical absorption does exist during the process of water splitting, a cathodic pulse for HER of the order of a $10^{-3}$ s with a strong resonant laser pulse during this period could perhaps deliver information on the vibrations of the species present in the transition state. Here one should mention...
the picosecond time-resolved pump probe resonance Raman experiments on solvated electrons in bulk water.66

**Electron propagation in the direction of the electrolyte**

Figure 13 shows that hot electrons starting at $E_F$ excited by a laser photon (energy 1.91 eV at 647.1 nm wavelength) may reach the level for injection into the electrolyte ($L$ reaching asymptotically infinity) at an electrode potential of ca $-1.2$ V, corresponding to the beginning HER.

In a simple model of the electrode/electrolyte interface given as a sharp boundary with continuous free electron state above $E_F$ in the metal and above the PE-threshold (see Fig. 12), one can derive a simple relation for the penetration depth $L$ of the photo-excited electrons of energy $\hbar \omega$ into the electrolyte:

$$L = \frac{\hbar}{2m} \frac{1}{\sqrt{P(E_{\text{threshold}})} - (-E_{\text{SCE}} + \hbar \omega)}$$

The wavefunction decays as $\exp(-z/L)$, where $z$ is the coordinate perpendicular to the surface. For a position of $P(E_{\text{threshold}})$ 3.3 eV above 0 V$_{\text{SCE}}$, the value of $L$ is plotted as function of the electrode potential for two photon energies in Fig. 13. The approximate position of the oxygen atoms within the water molecules of the IHP at $z \approx 3.5$ Å is indicated, according to x-ray scattering at $E = -0.23$ V$^6$ and to modelling of the interface.$^6$ In the electrode potential range from about $-1.0$ to $-1.2$ V$_{\text{SCE}}$, the hot electron wavefunctions can reach the water molecules with amplitude diminished by $e^{-1}$. It is possible that the cathodic onset potential is somewhat lowered by surface roughness, as indicated schematically in Fig. 12.

![Figure 13. Mean penetration length $L$ of photo-excited electrons, starting at the Fermi level of the Cu electrode with excess energy $\hbar \omega_{\text{laser}}$, into the electrolyte. The position of oxygen atoms of water molecules in the IHP is given at 3.5 Å in front of the metal edge.](image)

Before discussing the interaction mechanism of hot electrons with water, the point has been reached where we should explain why one does not observe SERS by water in acidic aqueous electrolytes. During the HER at low pH, the electron is transferred to the hydrated proton and not to a water molecule, although of course in acidic electrolytes there are plenty of water molecules around. This must mean that the electrons at the Fermi level of the electrode do reach the protons easier than the water molecules. This is also indicated by the difference of $\sim 0.28$ V between the plots of the onset potentials of the HER at low and at high pH (see Fig. 14) (Reprinted from Diesing D, Winkes H, Otto A. *Phys. Status Solidi A* 1997; 159: 243, Copyright © 1997 WILEY-VCH Verlag GmbH & CO. KGaA, Weinheim). We propose tentatively that also hot electrons do reach protons better than water molecules and that at potentials of HER water molecules have a larger distance from the surface at low than at high pH. This is not unlikely, because in acidic media at cathodic potentials protons contribute to the charge in the IHP, whereas at higher pH the charges on the electrolyte side are given by the solvated cations in the outer Helmholtz plane, separated from the metal by the water molecules in the IHP.

**Electron–water interaction in the impulse approximation**

Electron–water interaction at relatively low kinetic electron energy (without resonance) has been measured in the gas phase; see, for example, Fig. 15 (from Ref. 41).

Compared with the Raman spectra of neat liquid water (see Fig. 1), the bending mode intensity is enhanced with respect to the stretch mode intensity in electron energy loss spectra (EELS), as in the SERS spectra in Fig. 2. Excitation of librations of molecules adsorbed in the tunnelling area of scanning tunnelling microscopes by the tunnelling electrons
Energy potential of H2O gas, yielding high intensity for the bending and libration modes (see Fig. 15). These excitations are not caused by long-range electromagnetic interactions with the vibrational electric dipoles of the water molecules, because this would not lead to the observed large scattering angles.

Most likely, the water Raman signals originate from the H2O molecules in the first hydration shell of the cations (here K+), which are in the first Helmholtz plane. Maybe the sensitivity to the chemical nature of the cations (see above) can be explained in this way. Those molecules have less chance of hydrogen bonding than others, which explains qualitatively the relative high wavenumber of the OH stretch band and the low wavenumber of the bending mode. Probably the libration modes observed in SERS are also those of the H2O molecules situated between K+ and Cu. The increase in their wavenumber with respect to liquid water cannot, of course, be assigned to an increase in hydrogen bonding as in the case of solid water. Rather, it seems that the position between the cation and the metal increases the wavenumber of the libration modes. One may also expect that the kind of anion influences the stretch wavenumber of the water molecules delivering the SERS signal. Such delicate effects have indeed been observed and should be reconsidered again.

With decreasing electrode potential, the accessible density of states of delocalized electrons increases. However, the Raman channel (weak in comparison with the channel of quasi-permanent electron emission into the electrolyte) will certainly only contain electronic excursions to one water molecule in the IHP and back to the initial state in the metal. If it meets on its path more than one water molecule, it probably becomes dephased and the Raman channel is closed. Accordingly, in agreement with Fig. 12, one may expect for decreasing electrode potential increasing SERS intensity, but it would be premature to make a more quantitative statement.

The increase in the SERS signal of water by moderate roughening (see Fig. 10) might have two reasons: increased electromagnetic enhancement (which, however, is not strong enough to yield SERS of water at potentials above −1.1 V), but also by SERS active sites within the increased atomic scale roughness, in the following sense. The validity of SERS by the impulse mechanism at all surface sites rests on the fast return (<1 fs) of the electron to the metal after impact with the adsorbate. SERS active sites with larger retention times of holes (ca 5–10 fs) are needed for the resonant mechanism. The SERS active sites may also allow for the impact mechanism with water molecules in the outer Helmholtz plane with higher roundtrip times. These additional channels for SERS will increase the intensity.

Relation of the HER and SERS by water
Finally, the relation between this theory of the electronic effect of the SERS by water and the hydrogen evolution reaction (HER) must be reconsidered. The scheme in Fig. 12,
may be checked by using different laser frequencies. The onset of the SERS intensity of water should be about 0.4 V more cathodic for a laser wavelength of 632.8 nm (photon energy 1.96 eV) compared with a laser wavelength of 514.7 nm (2.41 eV). This is not observed (see Fig. 4). The onset of the SERS intensity of liquid water is within the error of the measurements the same for the two values of wavelength.

The onset of the deuterium evolution is considerably more cathodic than the hydrogen evolution (see Fig. 6, top), whereas the integrated intensities of the bending bands of H2O at ca. 1610 cm\(^{-1}\) and of D2O at ca. 1188 cm\(^{-1}\) develop about in the same way (see Fig. 6, bottom). This can be rationalized as follows.

The positions of the electronic levels in water do not depend on the pH, and the band of delocalized electronic states in H2O and D2O should be the same, because in the delocalized state the water molecules have not yet been rotated or displaced to form the hydration shell of the electron. But also the energy of the maximum optical absorption of an electron solvated in H2O and D2O is within a margin of 0.03 eV the same.\(^5\)\(^2\) Therefore, one would expect the development of the SERS intensity of water independent of the isotopes H and D. Here, an approximate agreement with the experiment in Fig. 6 (bottom) does exist.

In the discussions above we have assumed, that the impact mechanism works on the water molecules in the IHP, which belong to the solvation shell of the cations. This implies a certain orientation and distance from the surface of these water molecules. Probably the effectiveness of the impulse mechanism, where these water molecules are for a time of the order of 1 fs in an anionic state, depends on this spatial configuration. This configuration may be reached at the potentials where the water molecules are in the ‘waiting state’ for the HER. Of course, we know nothing about these details. However, if this orientation is important, we would expect the potential-dependent SERS signal intensity to be independent of both the laser wavelength and also the isotope species, as is approximately observed.

CONCLUSION

This paper reviews the efforts to obtain a SERS spectrum of water. About 15 years ago, SERS of water was observed at roughened Ag, Cu and Au electrodes in neutral aqueous electrolytes at cathodic potentials during hydrogen evolution, when no anions are contact adsorbed. It was not possible to assign this SERS signal exclusively to local laser field enhancement, but the ‘chemical’ mechanism of the enhancement remained elusive.

Here we report further experiments on SERS of water at single-crystalline Cu surfaces, using as electromagnetic enhancement the resonance of surface plasmon polaritons in an ATR configuration, allowing total suppression of the Raman signal of bulk water. A clear onset and potential dependence of the intensity of the water bending mode were observed, corroborating the previous results. Small intentional roughening of a Cu(100) crystal further increases the SERS intensity.

The signal cannot be assigned to water molecules undergoing splitting, because first their surface concentration is far too low and second a metal electron inducing the water dissociation reaction loses phase and cannot deliver a Raman signal, because returning to the initial state in the metal and keeping the coherence are necessary conditions for the Raman process by electron transfer.

We propose a mechanism based on the present knowledge of electronic states in liquid water, which is reviewed in this paper. When the Fermi level of the electrode is raised by the negative electrode potential to a sufficient energetic height, an electron from this Fermi level can reach the energy of delocalized electrons in liquid water by absorbing a laser photon. This is the onset potential of SERS of water. The interaction of the electron with water is the short-time (<10\(^{-15}\) s) residence in the unoccupied orbitals of water, allowed by Heisenberg’s uncertainty principle. This mechanism has been known as the impulse approximation for about 40 years in electron scattering by molecules. It is a non-resonant electronic SERS mechanism.\(^3\)\(^3\) According to this model, the common onset of the hydrogen evolution and SERS by water is fortuitous. However, when the local configuration of the water molecules in non-acid aqueous electrolytes at the SERS active sites is necessary for the impulse process, this configuration may only exist for H2O molecules ‘waiting’ to be split. Although we do not know this configuration, we would expect that the SERS signal intensity is independent of the laser wavelength but also of the isotope species (H or D), as is approximately observed.

Given the present state, further experiments, focusing on the hypothesis of SERS from water outlined in this paper, should be performed.

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REFERENCES
