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THE OBSERVATION OF SERS OF WATER IN A WIDE POTENTIAL RANGE FROM THE Ag/NaClO$_4$ SYSTEM

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Abstract—The surface enhanced Raman scattering (SERS) of water adsorbed at silver electrodes in a wide potential range from −0.5 to −2.0 V was observed for the first time in a 8 M NaClO$_4$ solution. The significant changes in the SERS frequency and intensity at around −1.1 V may be due to orientation change of the adsorbed water.

Key words: surface enhanced Raman scattering, water, adsorption, silver electrode, molecular orientation.

INTRODUCTION

Water–electrode interaction is an important topic of research in electrochemistry. In order to obtain direct information at the molecular level about the adsorbed water, many studies on correlation of the SERS signals of water with the electrode potential[1], temperature[2], pH[3] and composition of electrolyte[4] have been carried out since the first observation of SERS of water in 1981[5, 6]. However, with only one exception[7], the previous studies have been restricted in the systems containing halide or pseudo-halide ions in the limited potential region and the potential dependencies of the SERS intensity of water and the (pseudo-) halide ions were found to be essentially parallel[1–6]. It may be inferred that these SERS signals are either from water molecules coadsorbed with these specifically adsorbed anions or from some special surface complexes[4, 8]. This communication is to report the first observation of SERS from water molecules adsorbed at silver electrodes in a 8 M NaClO$_4$ solution free of halide and pseudo-halide ions.

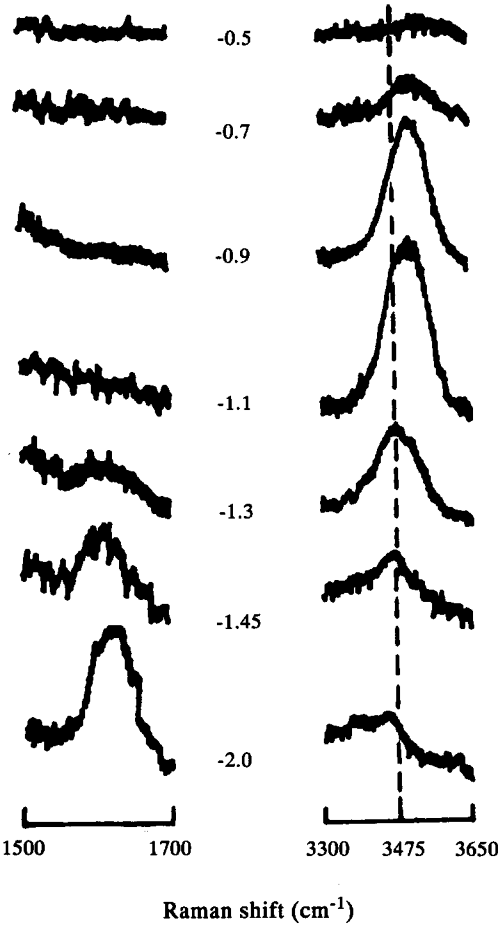
EXPERIMENTAL

Raman spectroscopic measurements were performed with a Jobin–Yvon Ramanor U1000 double monochromator with bandpass of 8 cm^{-1} and an Coherent Innova model 200 argon laser operated at 514.5 nm with about 100 mW at the sample. A silver electrode of 99.999% in purity was chemically polished until a mirror like appearance was obtained. Further roughening procedures and the SERS measurement conducted will be discussed in detail below. All potentials quoted here are relative to the saturated calomel electrode (*sce*).

RESULTS AND DISCUSSION

The idea to conduct the present work of the SERS study on adsorbed water molecules by using a special electrode roughening procedure in a 8 M NaClO$_4$ solution arose from the previous work carried out in our two laboratories[7, 9]. Funtikov *et al.* have designed a special oxidation reduction cycle (ORC) of roughening procedure to the Ag electrode, *ie* after the oxidation of about 100 monolayer of silver, the applied potential was stepped to −1.3 V that is negative of the potential of zero charge (PZC), by which the SERS signal from the bending vibration of water in 0.1 M Na$_2$SO$_4$ or NaF systems was obtained for the first time[7]. Surprisingly, they were not able to detect any SERS signals from the stretching mode of water. Even so, the SERS signal was obtained only in the potential region from −1.1 to −1.5 V and it was quenched irreversibly as the potential was moved to the region positive of the PZC. On the other hand, Tian *et al.*[9] have made an attempt to conduct the SERS study by using 8 M NaClO$_4$ as the main supporting electrolyte. It has been shown that SERS of water can be observed using much lower halide concentrations. This indicates that the highly concentrated ClO$_4^-$ may play a key role in the system because the measuring condition and the ORC roughing procedure were the same as those systems containing only halide ions. The marked effect of ClO$_4^-$ ions was attributed to that ClO$_4^-$ having a large radius and little deformation can break the hydrogen-bond structure in the solution very effectively. Therefore, water molecules with less and weak hydrogen bonds are dominant in the highly concentrated ClO$_4^-$ solution including electrode/solution interphase[10]. In the present work, the electrode was subjected to a special ORC procedure mentioned above[7] in 8 M NaClO$_4$, it was then pressed against the cell window to avoid interference by Raman signals from the bulk water.

With such a thin layer cell configuration the hydrogen gas evoluted with strong but very fine bubbles so that neither the incident nor the scattered light intensities would be altered due to vigorous hydrogen evolution. The SERS spectra of water shown in Fig. 1 demonstrate the advantages of combining our two previous proaches[7, 9]. The potential region where the SERS of water are observed has been extended to a much wide potential range from -2.0 to -0.5 V. The potential dependences of intensities for both the stretching and bending vibrations are found to be considerably different (see Figs 1 and 2). For the stretching vibration, the intensity reaches the maximum at around -1.1 V and the dramatic frequency change with the rate of $149\,\mathrm{cm^{-1}\,V^{-1}}$ occurs in the same potential region while an overall frequency change rate is only $79\,\mathrm{cm^{-1}\,V^{-1}}$ in the whole region studied. The significant changes in the SERS intensity and frequency in the potential region around -1.1 V could be considered as an evidence for orientation change of the adsorbed water molecules. It is well known that the bond formed between the water molecule and the electrode surface is through the oxygen with higher stretching vibration frequency at potentials positive of the PZC and through the hydrogen with lower frequency at potentials negative of the PZC. In the potential region around the PZC, the coverage of the adsorbed water is higher than that in the other regions, which may be correlated to the SERS intensity change shown in Fig. 2. It should be emphasized that in the very negative potential region, the SERS intensity of the bending vibration is higher than that of the stretching one. This is in contrast to the fact that the Raman intensity of the stretching band is about 20 times higher than that of the bending band for the bulk water. A more detailed investigation has being carried out on this abnormal phenomenon, which may be beneficial to fully understand the nature of adsorbed water molecules and the SERS mechanisms.



(a) (b)

Fig. 1. SERS spectra of water at silver electrodes for the region (a) 1500–$1700\,\mathrm{cm^{-1}}$ and (b) 3300–$3650\,\mathrm{cm^{-1}}$ in 8 M $NaClO_4$ at various potentials with the value in volts indicated in the figure.

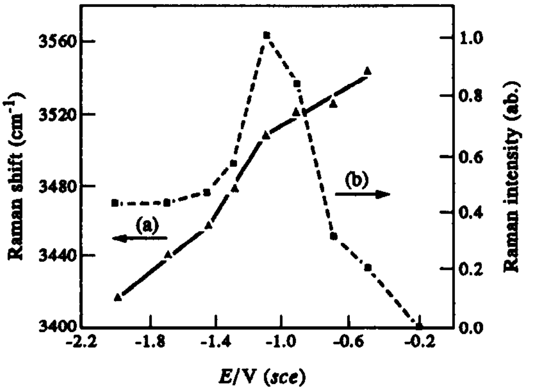


Fig. 2. SERS frequency (a) and intensity (b) of the OH stretching band of water as functions of potential in 8 M $NaClO_4$.

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