

Surface Enhanced **Raman** Scattering of Water Molecules
in Water-Ethanol Mixed Solution

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Stronger and narrower SERS bands of water molecules are observed in the water-ethanol mixed systems of 1M KBr/water-ethanol(1:1)/Ag electrode, 1 M NaBr/water-ethanol(1:1)/Ag electrode and 1M NaBr/water-ethanol(1:4 by volume)/Ag electrode. Due to the ethanol-assisted bandwidth reduction and intensity enhancement we have succeeded to observe in the water-ethanol(1:4) mixed system the two peak structure of the O-H bond stretching SERS band of water molecules with 1M electrolytic concentration of Na^+ ions which gives usually a very broad single peak structure of the SERS band in the purely water system. Ethanol seems to dilute hydrogen bonding between water molecules and thus enhance the stabilisation of the atomic surface complex of water molecules.

I. INTRODUCTION

Surface enhanced **Raman** scattering (SERS) of water molecules has been a great concern of many SERS people.¹⁻⁸ The SERS characteristics of water molecules have been found as follows:

- (1) SERS of water can be observed when the electrolytic concentration is greater than 1M and thus a very strong ORC (total charge transfer of $\sim 200\text{mC}/\text{cm}^2$) is given, while SERS of pyridine, for example, is obtained in the aqueous solution of 0.1 M KCl/0.05M pyridine with an ORC of $-20\text{mC}/\text{cm}^2$.¹
- (2) SERS of water can be observed for aqueous solutions of the electrolytes KCl, KBr, KI, NaN_3 , etc. but could not be observed for the electrolytes of KF, NaClO_4 , KNO_3 and K_2SO_4 . This anionic dependence is related to the solubility of the AgX-complex layer formed during the oxidation half cycle.³
- (3) SERS bandwidth of water also depends on the anions, becoming narrower in the order of Cl; Br^- and I^- .¹
- (4) Cations of Cs^+ , Rb^+ and K^+ lead to very narrow SERS bandwidth of water while broad bands are obtained for cations of Na^+ , Li^+ , Ba^{2+} , Sr^{2+} , Ca^{2+} and Mg^{2+} .⁹ The former cations have small hydration energy while large hydration energy for the latter.

- (5) O-H stretching band appears at higher frequencies in SERS spectra but H-O-H bending mode at lower frequencies in SERS as compared with the bulk water Raman spectra.”
- (6) Bulk signals of water can deteriorate the SERS spectra of water unless the distance between the electrode surface and the cell window is **greatly reduced**.²

We have studied on the SERS spectra of water in the ethanol/water mixed solution, where the bulk water signals are expected to be greatly reduced and we may hope to see the pyridine-like enhancement effect of ethanol associated with **Ag⁰ adatomic stabilization**” or the electromagnetic effect associated with the smaller dielectric constant of **ethanol**.⁷

II. EXPERIMENTALS

Polycrystalline silver plate was employed as a working electrode after polishing with alumina powder of $0.05\mu\text{m}$, cleaning with the $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ (1: 1 by volume) solution and rinsing with deionized water. One hour long purging the SERS solution with nitrogen gas was applied before the SERS experiment to reduce the oxygen and CO_2 contamination. The silver electrode of $1 \times 1 \text{ cm}^2$ area was separated from the cell window by $\sim 1\text{mm}$. Output power of the **Ar/Kr** mixed gas laser was adjusted to 140mW at 4880\AA before incident at the echelle grating-type tunable filter employed to block out the plasma fluorescence lines. Excitation was made using the cylindrical lens at an incidence angle of around 45° with respect to the electrode surface. Double grating spectrometer (Spex 1403) was used with a spectral bandwidth of about 10 cm^{-1} in the spectral region of the SERS spectra. All the electrode potentials quoted in this work are with respect to the saturated calomel reference electrode (SCE).

The SERS systems of our present work are: (1) 1M KBr/water/Ag electrode, (2) 1M KBr/water-ethanol (1: 1 by volume)/Ag electrode, (3) 1 M NaBr/water/Ag electrode, (4) 1 M NaBr/water-ethanol (1 : 1 by volume)/Ag electrode and (5) 1M NaBr/water-ethanol (1:4 by volume)/Ag electrode. Oxidation-reduction cycles (ORC) are applied through the potentiostat control with the triangular voltage cycle at 5mV/sec.

III. RESULTS AND DISCUSSION

III-1. Voltammograms

In Fig. 1. we show the voltammograms as obtained in the 1M KBr/water/Ag system(1 a) and the 1M KBr/water-ethanol (1: 1 by volume)/Ag system(1 b). Fig. 2. shows the voltammograms for the 1 M NaBr/water/Ag system(2a) and the 1 M NaBr/water-ethanol (1: 1 by volume)/Ag system(2b). In both Fig. 1. and Fig. 2. we can see that total ORC current is increased in the 3rd ORC (solid line) as compared with the 1st ORC (dotted line). Roughness created by precedent ORC may thus help the succeeding ORC. From the voltammograms the total charge transfer by ORC is estimated to be about 200 mC/cm^2 for both the water and the water-ethanol mixed system, which corresponds to about 1000 surface

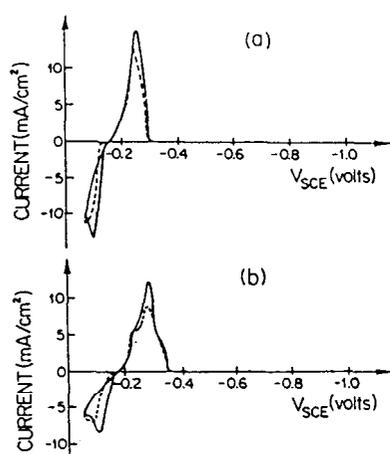


FIG. 1 Voltammogram of the ORC process in **KBr** solutions: (a) **1M KBr/water/Ag**, (b) **1M KBr/water-ethanol(1:1)/Ag**. Dotted line represents 1st ORC and solid line represents 3rd ORC.

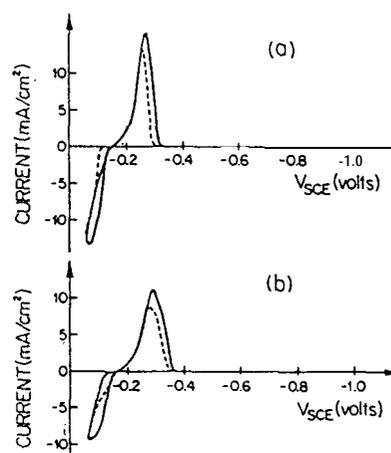


FIG. 2 Voltammogram of the ORC process in **NaBr** solutions: (a) **1M NaBr/water/Ag**, (b) **1M NaBr/water-ethanol(1:1)/Ag**. Dotted line represents 1st ORC and solid line represents 3rd ORC.

layers of silver atoms involved in the ORC process. However, the starting potential of oxidation current and the completing potential of reduction current are more negative in the water-ethanol mixed solution and also for the **NaBr** electrolytes as compared with the ethanol-free water and the **KBr** electrolytes respectively. This difference may be due to the fact that the dielectric constant is smaller and thus stronger Coulomb interactions between ions or between the charged electrode surface and ions in the ethanol and **NaBr** solutions.¹²

111-2. SERS in **1M KBr/water-ethanol(1:1)/Ag** system

For the comparison's purpose we show the SERS spectra of the **1M KBr/water/Ag** system in Fig. 3. Fig. 4. represents the SERS spectra of the **1M KBr/water-ethanol(1:1)/Ag** system. We can see, as expected, the lower background of bulk water Raman band in the water-ethanol system. Concerning the spectrum observed at $-0.4 V_{SCE}$ we can locate a weak shoulder band at around 3550 cm^{-1} and also a very weak band at around 3240 cm^{-1} . The 3550 cm^{-1} band has been assigned as corresponding to asymmetric O-H stretching mode,¹³ or O-H stretching band of the hydration shell water molecules around the metal cation,¹⁴ or different orientations and interfacial environments of the surface adsorbed water molecules.¹³ The 3240 cm^{-1} band was assigned to an overtone band of O-H bending vibration.³ Maximum SERS intensity is obtained at $-0.4 V_{SCE}$ in the water-ethanol system as compared to $-0.6 V_{SCE}$ of the ethanol free water system. But minimum SERS intensity is observed at the same $-0.8 V_{SCE}$ for both systems. This potential dependence of the SERS intensity is more elaborated for the O-H stretching band at 3500 cm^{-1} , as shown in Fig. 5. In addition to the maximum at $-0.4 V_{SCE}$ and the minimum at $-0.8 V_{SCE}$ this diagram of Fig. 5. also shows that there is a secondary maximum at around $-1.1 V_{SCE}$ before the irreversible loss of SERS intensity below around $-1.2 V_{SCE}$. This secondary maximum at

$-1.1V_{SCE}$ instead of the continuous decrease after the principal maximum at $-0.4V_{SCE}$ may be attributed to the reorientation of the interfacial water molecules at the electrode surface. that is, at the potential more positive than PZC the electrode surface will be

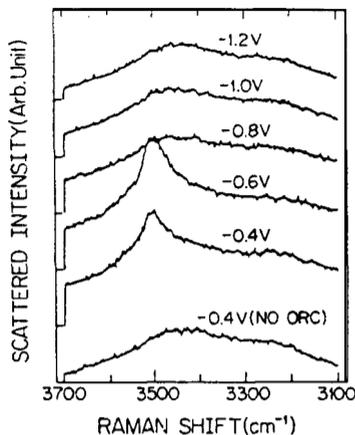


FIG. 3. SERS spectra of water in 1MKBr/water/Ag system at various electrode potentials. Spectrum shown at the bottom is recorded before ORC is applied.

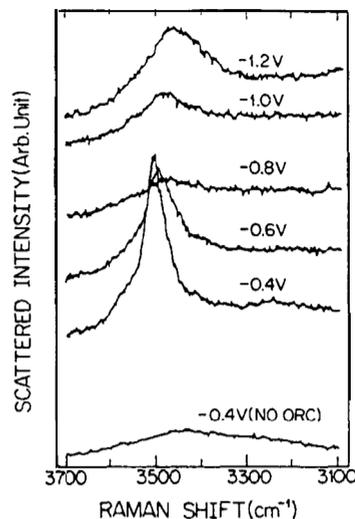


FIG. 4. SERS spectra of water in 1MKBr/water-ethanol(1:1)/Ag system at various electrode potentials. Spectrum shown at the bottom is recorded before ORC is applied.

positively charged and the surface water molecules in the Helmholtz double layer will turn their oxygen heads toward the electrode surface, while at the potential more negative than PZC the hydrogen tails of the surface water molecules will be directed toward the electrode surface.¹³ We can see indeed a distinct frequency shift of the O-H stretching band to lower frequency as the electrode potential falls below $V_{SCE} = -0.8V$.

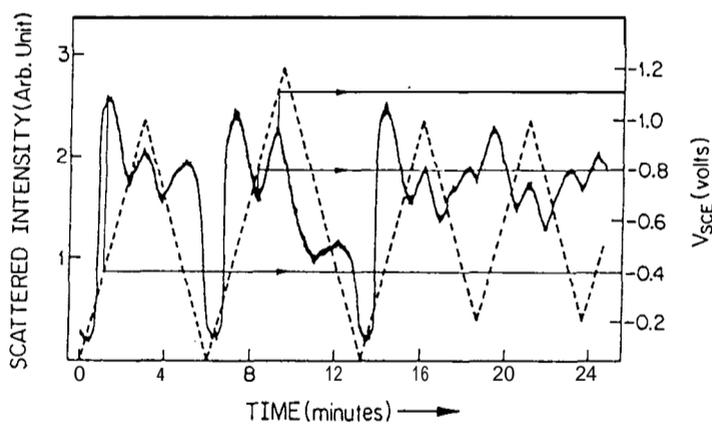


FIG. 5. SERS intensity variations (solid line) in the cyclic electrode potential changes (dotted line) for the 3500 cm^{-1} water band of 1MKBr/water-ethanol(1:1)/Ag system. Potentials of the primary and secondary maxima and also the minimum SERS intensity in the reversible range are guided by arrow lines.

111-3. SERS in 1M NaBr/water-ethanol(1:1)/Ag system

In Fig. 6, we show the SERS spectra of 1M NaBr/water/Ag system as a reference to which we will compare the SERS spectra of 1M NaBr/water-ethanol(1:1)/Ag system shown in Fig. 7. As for the previous KBr system we find additional enhancement of SERS intensity by a factor of over 2 in the NaBr system by mixing ethanol into water. In the potential dependence of the SERS spectra we have the maximum SERS intensity at $-1.0V_{SCE}$ for the ethanol-water mixed system as compared with the maximum at $-0.9V_{SCE}$

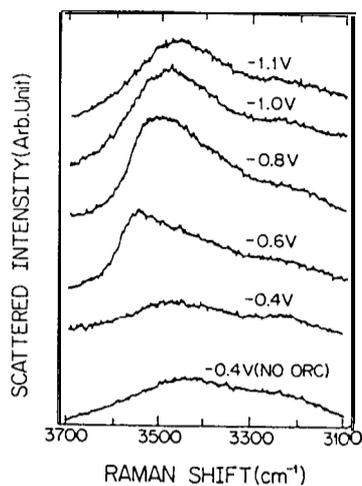


FIG. 6. SERS spectra of adsorbed water in 1M NaBr/water/Ag electrode system. Bottom spectra is recorded before ORC process.

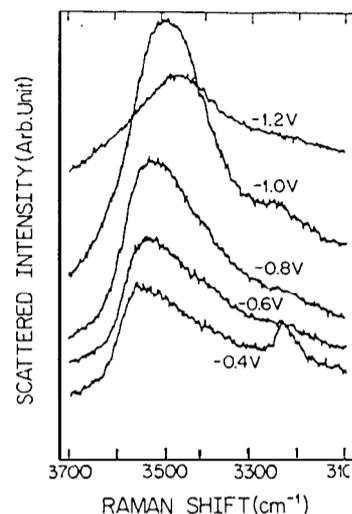


FIG. 7. SERS spectra of adsorbed water in 1M NaBr/water-ethanol(1:1)/Ag electrode system.

for the ethanol-free water system. At $-0.4V_{SCE}$ we see a very strong and asymmetric SERS band with the peak at 3550 cm^{-1} for the ethanol-water mixed system while a very weak and symmetric band with a peak at 3500 cm^{-1} for the ethanol-free water system of Fig. 6. However, in both the ethanol-water mixed system and the ethanol-free water system we can observe at the same potential of $-0.8V_{SCE}$ a band shape change from higher frequency asymmetric to lower frequency symmetric band. In contrast to the case of the KBr systems we do not see a secondary maximum behaviour in the SERS intensity dependence on the electrode potential with the NaBr systems. The NaBr systems show broader SERS bands and a larger potential dependence of frequency shift as depicted in Fig. 8. This difference between K^+ and Na^+ in the SERS effects has been understood as due to the difference in the hydration energy of the respective metal cation bringing about different adsorption geometry of water molecules at the electrode-electrolyte interface.^{1,2} Also more distinct with the 1M NaBr/water-ethanol/Ag system there is the O-H bending overtone SERS band at around 3240 cm^{-1} , popping up strong only at $V_{SCE} = -0.4V$ as can be seen in Fig. 7. The fundamental band of the O-H bending mode, however, hardly appears at $V_{SCE} = -0.4V$ in the NaBr system as can be seen from Fig. 9. We can see, however, that the overall

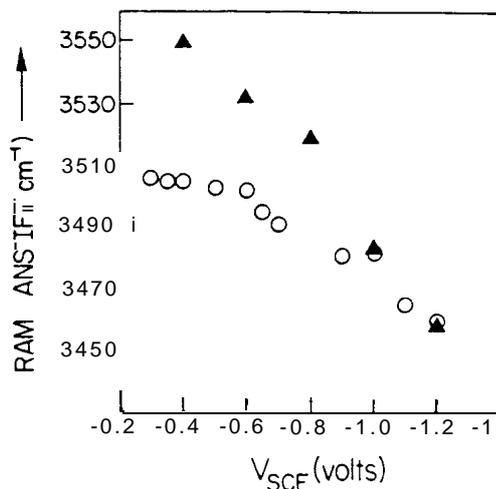


FIG. 8. Frequency dependence on the electrode potential for the O-H stretching band of adsorbed water in 1 M KBr/water-ethanol(1:1)/Ag electrode (○) and 1 M NaBr/water-ethanol(1:1)/Ag electrode (▲).

potential dependence of the SERS intensity are similar between the O-H stretching and the O-H bending bands in both the 1 M NaBr/water-ethanol(1:1)/Ag system (see Fig. 7. and Fig. 9.(b)) and the 1 M KBr/water-ethanol(1:1)/Ag system (see Fig. 4. and Fig. 9.(a)).

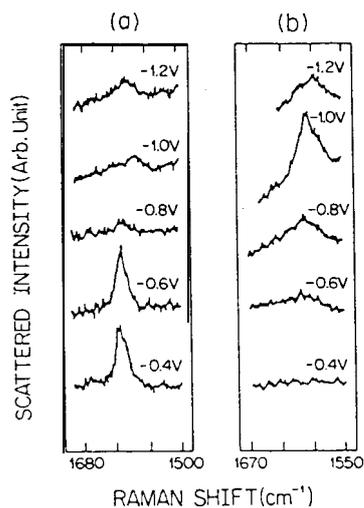


FIG. 9. SERS spectra of O-H bending mode at various electrode potentials: (a) 1 M KBr/water-ethanol (1:1)/Ag electrode and (b) 1 M NaBr/water-ethanol(1:1)/Ag electrode.

III-4. SERS in 1 M NaBr/water-ethanol(1:4)/Ag system

SERS spectra of the 1 M NaBr/water-ethanol(1:4 by volume)/Ag electrode system are shown in Fig. 10. The SERS bands of water are seen to be much stronger in this system as compared with the ethanol-free water system of Fig. 6. even though the bulk concentration of water molecules is greatly reduced. In Fig. 10. we can also see the separated two band

structure of the O-H stretching mode in the SERS spectra of water. Below the electrode potential of $V_{\text{SCE}} = -0.8\text{V}$ the higher frequency ($\sim 3550\text{ cm}^{-1}$) band obtains stronger intensity but the lower frequency ($\sim 3500\text{ cm}^{-1}$) band becomes stronger at and above $V_{\text{SCE}} = -0.8\text{V}$. This double peak structure of the O-H SERS band was previously observed for K^+ , Rb^+ and Cs^+ ions but one broad band structure for Na^+ and Li^+ ions.¹⁰ Our observation of double peak structure for Na^+ in the ethanol-water(4:1 by volume) system may be partly due to the reduced hydrogen bond interactions between surface water molecules, that is, the

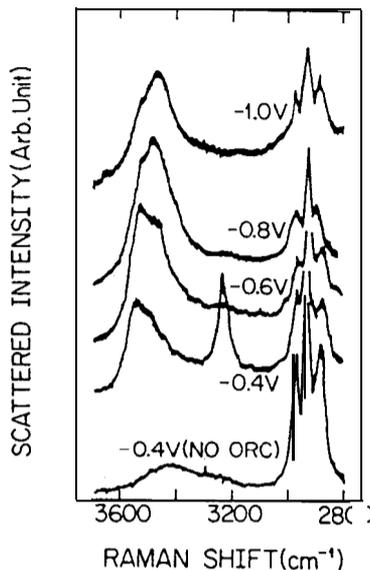


FIG. 10. SERS spectra of 1M NaBr/water-ethanol(1:4)/Ag electrode. Bottom spectra is recorded before ORC application.

hydration shells of Na^+ ions separated by ethanol molecules and thus the narrower band width. At higher concentration of Na^+ ions (2M NaCl) D_2O was found to give even three peaks in the region of the O-D stretching SERS bands associated with interfacial DOD and OD^- ions.¹³ The 3240 cm^{-1} band is observed to appear very strong and narrow at a particular potential of $V_{\text{SCE}} = -0.4\text{V}$ in both the 1M NaBr/water-ethanol(1:1)/Ag system and the 1 M NaBr/water-ethanol(1:4)/Ag system. This band may correspond to the overtone band of O-H bending mode.³ We find, however, very weak fundamental band of the O-H bending mode at this potential of $V_{\text{SCE}} = -0.4$ (Fig. 9(b)). The strong Raman bands in the region between 2850 cm^{-1} and 3000 cm^{-1} corresponding to the C-H stretching modes of ethanol or other organic impurities created from dissolved CO_2 , etc, at the electrode surface.^{6,9} This C-H band appears most strong before any ORC is applied and depends very little on the electrode potential with intensities rather reduced after ORC application as can be seen in Fig. 10.

IV. SUMMARY AND CONCLUSION

SERS bands of water molecules are observed to be further enhanced by ethanol mixing in both 1M KBr and 1M NaBr aqueous solutions. SERS bands in NaBr solutions are much broader than those of KBr solutions with peaks at -3550 cm^{-1} in NaBr but at -3500 cm^{-1} in KBr solutions, both of which shift to lower frequencies as the electrode potential is lowered (more negative). When ethanol concentration is increased as for the 1M NaBr/water-ethanol (1:4 by volume)/Ag electrode system, the SERS bands of water show two peaks at both -3500 cm^{-1} and -3550 cm^{-1} with each band reduced in bandwidth. This bandwidth reduction is seen already in the water-ethanol (1: 1 by volume) system of lower ethanol concentration. The band at 3240 cm^{-1} shows a transient SERS behavior with a very strong intensity at $V_{\text{SCE}} = -0.4\text{V}$ in the water-ethanol (1:4 by volume) system of 1M NaBr solution. The C-H bands of the water-ethanol system observed in the region of 2850 cm^{-1} to 3000 cm^{-1} are strongest before ORC application but hardly dependent on the electrode potential and reduced in intensity after the ORC application. In conclusion the SERS bands of water molecules become stronger and narrower with ethanol mixing in the aqueous SERS solution. This change of SERS behaviour of surface water molecules may be attributed to the enhanced stabilisation of adatomic surface complex and hydrogen bond dilution effects derived from ethanol mixing as for the case of pyridine addition.”

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