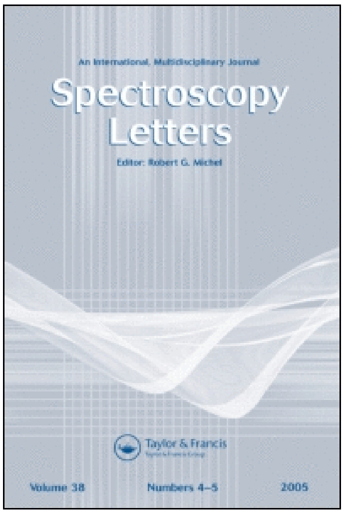

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FOURIER TRANSFORM SURFACE-ENHANCED RAMAN SPECTRA OF FULVIC AND HUMIC ACIDS ADSORBED ON AU ELECTRODES

Key words: fulvic acid, humic acid, Au electrode, FT-Raman, Surface-enhanced Raman scattering

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ABSTRACT

The Fourier transform Surface-enhanced Raman spectra of fulvic and humic acids from sea water adsorbed on an Au electrode were determined. At neutral and basic conditions, the humic acid was hung on the Au surface through its carbonyl groups, and the fulvic acid from the same source was adsorbed in both " end on " and " flat on " configurations. At acidic conditions, both of the fulvic and humic acids were adsorbed on the surfaces through their carboxylate and pyridine-like groups. The SERS behaviours of the humic and fulvic acids at different pH and potentials were from the difference of their chain sizes, charges and flexibility as well as the changes of their conformations. This preliminary study suggested that Fourier transform Surface-enhanced Raman spectroscopy could be used as a powerful probe with which to directly " see " humic substances at low concentrations.

INTRODUCTION

Our research to humic substances is addressed to understanding their roles in the environment. Since previous researches on these substances in aqueous media mainly rely upon some indirect methods and models which are estabilished on experimental data by these indirect methods (e.g., viscosity, surface tension, molecular determination, potentiometric titrations and various models), we can only indirect " analyze " their

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aggregation states and properties, and infer their structure and composition in refined experimental conditions hitherto. Our own effort, therefore, has been directed toward finding techniques that directly reveal valuable information about these substances at low concentrations typically found in natural environment.

This information can be obtained mainly by using advanced spectroscopic technologies rather than simply from the interpretation of normal molecular spectra of humic substances. Although the normal FT-IR-Raman and NMR spectra of humic substances can provide some important information, these methods are difficult to identify the samples at low concentrations because of their low sensitivity. On the other hand, the fluorescence and EPR spectra of humic substances at low concentrations reveal very limited information. The use of some spectroscopic probes and/or substrates, therefore, seem more attractive in further researches.

When organic species are adsorbed on the rough surfaces of some small metal particles such as Ag, Au and Cu, the surfaces can provide up to 10^3 - 10^7 folds enhancement of the Raman scattered intensity of the adsorbed species while scattering from the solvent and species in solution remains relatively weak. This effect is called Surface-enhanced Raman Scattering (SERS)[1]. This technique has been extensively used in many other fields because of its simplicity, surface - selectivity, sensitivity, the richness of the spectroscopic information and the ability which quenches fluorescence[1]. In previous researches[2-3], it had also been proved to be a powerful tool for trace detection of humic substances and co-existed organic species. Thus this paper further evaluates this technique as a tool with which to characterize humic substances at low concentrations by using an Au electrode as the substrate.

EXPERIMENTAL

The well-characterized fulvic and humic acids from sea water of Bohai Gulf, China were kindly provided by Ji et al [4]. The fulvic acid (FA) was directly dissolved in water and the humic acid (HA) was dissolved in water by adding freshly prepared 0.1 M KOH solution. The pH values were adjusted by using 0.1 M HCl and 0.1 M KOH solutions. The tested concentrations were 100 mg/L. Water is deionized and triply - distilled.

An Au electrode was manufactured from Specpure - grade metal sealed into kel - F mountings. The electrochemical roughening required for the surface enhancement mechanisms was achieved in a 0.1 M KCl using a potential ramp from 0.1 to 1.1 V (all potentials were quoted *vs* SCE) at a ramp speed of 100 mW S^{-1}. Twenty - five cycles were used, and the electrode surface was kept in the horizontal plane during roughening to ensure that the enhancement was uniform over the electrode surface. The above electrode was rinsed using water and then immersed in the sample solution for SERS measurement. The surface potentials of the Au electrode were " in situ " changed. After a set of data at different potentials were obtained, the electrode was treated and rinsed again according to the above procedure and then used for further analysis.

The SER spectra were recorded by using a Bruker IFS - 66 spectrometer connected with a Raman module (Bruker, FRA - 106). Radiation of 1064 nm from an Nd : YAG laser was used for excitation with a laser power of 200 mW. The resolutions of the spectra were 4 cm^{-1}. 200 scans were co-added.

RESULTS

The SER spectra of the humic acid at neutral and basic conditions are observed only under positive surface potential. A representative result is shown in Figure 1.

The 1645 cm^{-1} band is unequivocally assigned to the stretch vibration of the carbonyl group(s). This peak is selectively enhanced because this kind of carbonyl groups directly bind with the Au surface. There are no peaks which are attributed to COO^- groups in this spectrum. Thus it is suggested that the humic acid is initially adsorbed in a neutral form rather than in an anionic form on the Au surface.

There is a few of high - resolved peaks in this spectrum. This phenomenon can be explained as follows. To almost all of the long polymer chain, only chemically and geometrically favoured groups or portions will be adsorbed on the surface, with the rest dangling in solution. Consequently, the spectrum will be simple and only one or a few of strong bands will be observed[5]. Rarely, more functional groups will be adsorbed closely on the surface so that their vibrations can be strongly enhanced. The in - plane aromatic ring stretch vibrations at 1537 cm^{-1} (ν_{19a}), 1297 cm^{-1} (ν_{14a}) and 1191 cm^{-1} (ν_{9a}) are from this kind of aromatic rings which directly connect with the carbonyl groups. Since the kind of rings are relatively far from the surface, the corresponding bands are weaker.

Clearly, the humic acid at neutral and basic conditions is hung on the surface through its C=O " bridge ".

The SER spectra of the fulvic acid from the same source are observed while the potential of the Au electrode lies between -0.8 V and -0.2 V. The typical results at neutral and basic conditions are shown in Figures 2 and 3.

The peaks in these spectra can be unequivocally assigned to two kinds of vibrational modes. The set of peaks at 1645 cm^{-1}, 1534 cm^{-1}, 1294 cm^{-1} and 1189 cm^{-1} clearly reveal that some FA aggregates are hung on the Au surface through the similar C=O " bridge ". The two broad and strong bands centred at 1290 cm^{-1} and 1589 cm^{-1} are assigned to the D

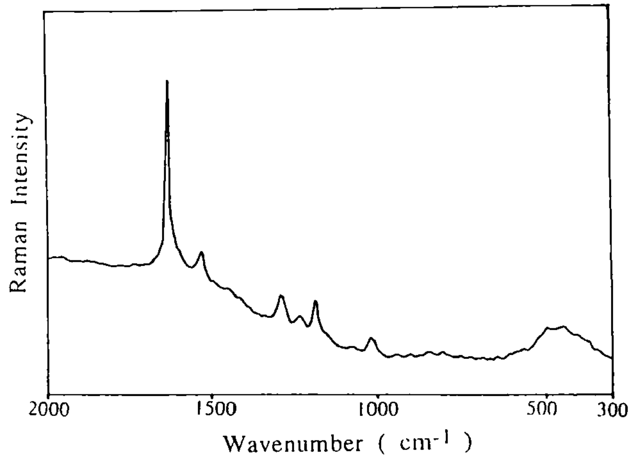

Figure 1. FT-Raman SER spectrum of the humic acid. Potential: + 0.2 V; pH: 7.

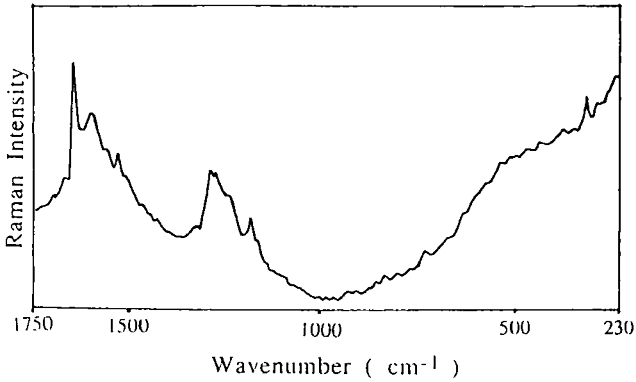

Figure 2. FT-Raman SER spectrum of the fulvic acid. Potential: - 0.2 V; pH: 7.

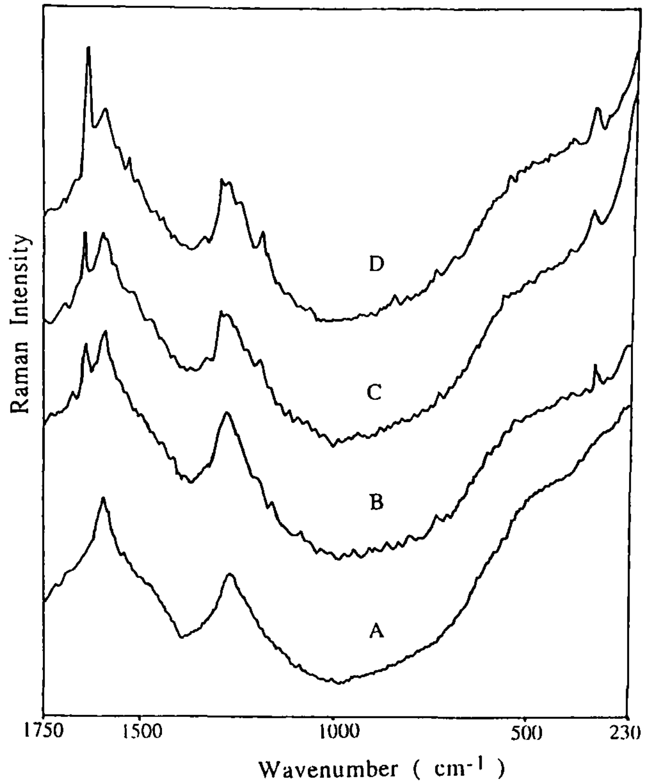

Figure 3. FT-Raman SER spectra of the fulvic acid at different potentials. pH: 9.
A: - 0.8 V; B: - 0.6 V; C: - 0.4 V; D: - 0.2 V.

and G bands of carbon-based materials[6-7]. When 1064 nm excitation line is used, it is proved[6] that the D band shifts toward 1320 - 1280 cm^{-1}. The D bands in the normal and SER FT-Raman spectra of humic substances generally show similar characteristics[8-9] and thus it has been proved that the building blocks of humic substances are low structurally disordered carbon networks[8-10]. The presence of the two peculiar bands here implies that the other FA aggregates lie on the Au surface.

As the changes of the potentials, the relative intensity ratios of the two peaks at 1645 cm^{-1} and 1589 cm^{-1} are different from each other (e.g., see Figure 3). It implies that the two kinds of adsorbed configuration compete with each other for the SERS - active sites of the surface. From Figure 3, it is found that the second configuration predominates at lower potentials. Besides, after a long of relax time, the ratio of the second configuration rises (Figure 4). This result suggests that this configuration is prefered although both of them are stable.

After changing the pH of the systems to acidic conditions, it is clearly observed that some HA suspensions are hung on the Au surface. The SER spectra of the FA and HA are observed at the same potentials as those under neutral and basic conditions, but they show very different characteristics.

Figure 5 and 6 are the SER spectra of the HA and FA at pH 1. Although the potentials are different, the SER spectra of the fulvic and humic acids at acidic conditions (pH < 5) are very similar to each other. It suggests that the same configurations are taken for both the FA and the HA.

There are unequivocally pyridine - like molecules or fragments in the two samples. The peaks at 1014 cm^{-1} and 1039 cm^{-1} are assigned to the in - plane bending vibration of the pyridine - like rings and the peaks in the ranges of 1600 - 1700 cm^{-1} are from ring stretch vibrations[11-12]. The selective enhancement of these peaks are because the pyridine - like rings are adsorbed on the Au surface through the " end on " configuration[11-12].

The most enhanced bands at 1600 - 1300 cm^{-1} can be assigned to the asymmetric and symmetric stretch vibrations of the carboxylate groups, indicating simultaneously that the samples bind to the Au surface as anions and the $-COO^-$ groups are almost certain on the surface[13-16]. When carboxylic acids bind to metal surfaces, their pK_a values are enhanced up to ca. 10^8 folds[17]. Both single " bridge " and bidentate bonding of $-COO^-$ groups to the Au surface possibly exist[13-16].

The dependence of the SERS peaks on the potentials (e.g., see Figure 5) indicates that there are at least two possibly adsorbed configurations through the lone pairs of pyridine - like rings and/or carboxylate groups.

DISCUSSION

The SERS characteristics of the fulvic and humic acids at different pH and potentials are well consistent with the difference of their conformations and physico-chemical properties which have been concluded by other methods[17-18].

At neutral and basic conditions, the fulvic and humic acids behave as polyelectrolytes with a number of negative charges[17-18]. The chains of the HA aggregates are rigid and their sizes are large[17-18], thus the HA aggregates can not lie on the Au surface at lower potentials and only the " end on " configuration through its C=O bridge is taken at higher potentials.

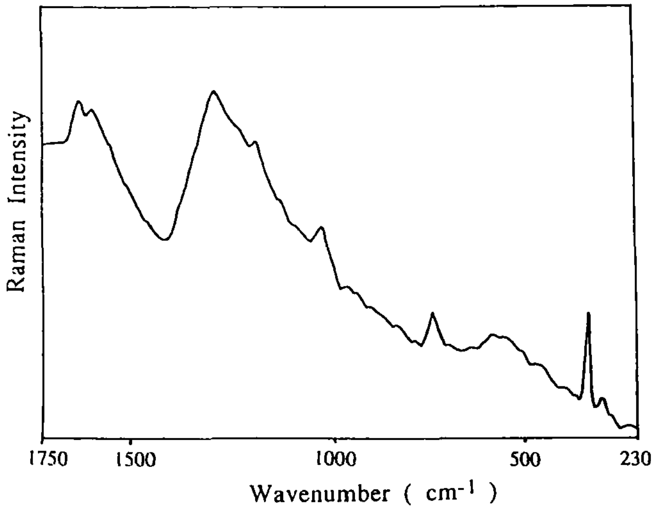

Figure 4. FT-Raman SER spectrum of the fulvic acid adsorbed on the Au surface for eight hours. Potential: - 0.2 V; pH: 7.

Different from the behaviour of the HA, besides the same " end on " configuration, the FA from the same source can also lie on the surface. It indicates the flexibility of the chains and the small sizes of the FA aggregates[17-18]. This phenomenon that the adsorption of the humic acid occurs at higher potentials than that of the corresponding fulvic acid implies that the HA chains possess higher negative charges.

At neutral and basic conditions, the carboxyl groups and other polar groups in the humic and fulvic acids dissociate and/or hydrate, prefer to stay in the aqueous phase[17-18]. Since they are far from the surface, the corresponding SERS signals are too weak to be observed. When the pH of the above systems are lowered by adding acids, the negative charges of the HA and FA chains are reduced to a large extent[17-18]. Thus the acidic groups protonate and run into the inner space of the micelles and the polymer chains coil[1,17-18]. Hence their adsorption on the Au surface become favourable owing to a reduced hydration energy. The SER spectra here unequivocally characterize the " turn over " change of the conformation. The only difference from the bulk suspensions without Au electrode is the dissociation of the carboxyl groups on the Au surface and its strong binding with the surface instead of the self - assembly among the groups. Therefore, the SERS characteristics of the carboxylate and pyridine-like groups which bind to the surface are clearly revealed. At the same time, the SERS signals of the carbonyl groups and the carbon skeletons which appear in neutral

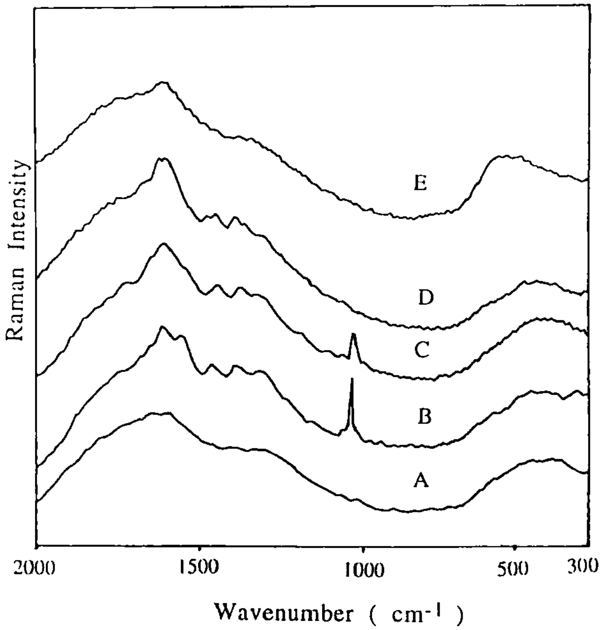

Figure 5. FT-Raman SER spectra of the humic acid at different potentials. pH: 1. A: 0 V; B: + 0.3 V; C: + 0.5 V; D: + 0.8 V; E: + 1.0 V.

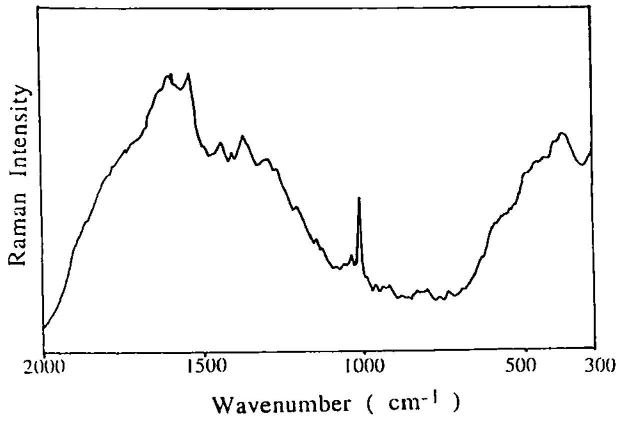

Figure 6. FT-Raman SER spectrum of the fulvic acid. Potential: - 0.2 V; pH: 1.

and basic conditions are not observed because these structural fragments and/or portions are now far from the Au surface.

In the normal FT-Raman spectra of the humic acid at different degrees of neutralization[8], there are only two broad D and G bands characteristic of low structurally disordered carbon networks. In the corresponding spectra of the fulvic acid, the stretch and bending vibrations of the aliphatic fragments or portions are also observed[8,10]. Unfortunately, no further informations can be extracted[8,10]. The SER spectra here shows obvious differences from the normal ones. Clearly, the SER spectra here are more specific and rich of valuable information due to the surface-selectivity of the SER spectroscopy[1]. For instance, the vibrations of the aliphatic fragments or portions are not observed here and it indicates that the structural parts of the fulvic and humic acids are far from the Au surface. The presence of the pyridine-like rings in the structures of the fulvic and humic acids are also clear and this information is very difficult to be obtained by the current methods in this field.

To the best of our knowledge, none of the methods in this field can give such a clear and specific " picture " about the binding sites, the structural fragments and so on of humic substances like the data here. Clearly, the SER spectra here are also enough sensitive and realistic to reflect the changes of the conformations. Since the interactions of the adsorbates with gold are generally weak and little denaturation will be encountered[19], it is not unreasonable to expect that the SER spectroscopy by using Au electrodes as the substrates can be used as a window with which to directly " see " humic substances at low concentrations typically found in real environment.

CONCLUSION

The SER spectrocscopy can reveal invaluable and specific information about the binding sites, adsorded configurations, conformations, compositions and structures of humic substances when an Au electrode is used.

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