Surface-enhanced Raman Scattering of SCN⁻ in Ag Sol

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The surface enhanced Raman scattering (SERS) of SCN⁻ was investigated in silver sol. The addition of pyridine significantly increased SERS by as large as 70. The role of pyridine was interpreted based on the model of plasma resonance-enhanced Raman scattering.

Introduction

Since Fleischmann *et al*[1]. reported the surface Raman spectrum of pyridine adsorbed on a silver electrode, the search for new systems to study this phenomenon has been extensive. Surface enhanced Raman scattering (SERS) is now a well established technique for the investigation of molecules adsorbed on surfaces and continuing research in the area is producing further developments[2].

Recently, we have reported the possibility to increase further the surface enhancement for molecules which displayed rather weak SERS effect[3]. Pyridine was observed in that work to serve as a promoter of SERS effect, increasing the enhancement factor of Ag(CN)₂⁻ from *ca.* 3×10^3 to as large as 5×10^5. The role of pyridine was adequately interpreted as due to its surface conditioning effect based on the surface plasmon resonance theory[4-6] for SERS.

The purpose of this work is to present another example of pyridine to serve as a promoter of SERS effect. Here we report the SERS of SCN⁻ in silver sol. Small molecules like SCN⁻, capable of complexation with silver atoms, are interesting systems for the investigation of SERS phenomenon since their Raman spectra tend to be simple and more easily characterized. The spectra were obtained under the similar conditions at which the SERS of Ag(CN)₂⁻ has been observed, which points out the importance of surface plasmon resonance in SERS effect.

Experiment

Experimental method is similar to that in the previous report[3]. Aqueous silver sol was prepared following a procedure described by Creighton *et al*[7]. Briefly, 10 m*l* of 10^{-3} *M* AgNO₃ solution was added dropwise to 30 m*l* of 2×10^{-3} *M* NaBH₄ solution. The latter solution was maintained at ice cold temperature and the mixture was stirred vigorously during preparation. The resulting sol which was stable for several weeks was yellowish in tint with UV/VIS absorption spectrum displaying a single peak near 392 nm as reported previously[3]. All the chemicals used in this work were reagent grade and triply distilled water was used for preparation of solutions. Raman spectra were obtained with Japan Spectroscopic Company model R-300 laser Raman spectrophotometer using 514.5 nm line of an Ar⁺ laser (Spectra physics model 164–06) as an exciting source. Glass capillary tube was used as sampling device and Raman scatter-

ing was observed with 90° geometry. Raman signal was detected using a commercial photon counting system. In a typical experiment, laser power was 100 mw and spectral slit width was 6.4 cm⁻¹.

Results and Discussion

In the Raman spectrum of 1 *M* aqueous solution of SCN⁻, three distinct peaks at 750, 515 and 2070 cm⁻¹ were observed consistent with previously assigned v_1, v_2 and v_3 modes of solid KSCN, respectively[8]. The Raman spectrum of 1.7×10^{-4} *M* SCN⁻ solution containing Ag sol is shown in Figure 1 (A). There appeared a broad intense band at 2114 cm⁻¹ (v_3) and a weak band at 445 cm⁻¹ (v_2). The v_1 band was too weak to be unequivocally observable in the SERS spectrum. Nevertheless, shifts in the peak positions of v_2 and v_3 bands clearly indicate the adsorption of SCN⁻ onto the surfaces of Ag particles.

Thiocyanate can bind to metal surfaces or metal cations in two ways, through either the sulfur or the nitrogen atom. Generally the former is preferred for "soft" polarizable cations in low oxidation state. There is strong evidence that metal surfaces such as silver behave as "soft" acceptors so that thiocyanate attachment *via* the sulfur atom should be strongly favored[9]. For example, thiocyanate ions are more strongly adsorbed at silver and mercury surfaces than are azide anions[10], even though surface attachment through nitrogen is expected to yield comparable adsorption thermodynamics on account of the similar coordination properties of —N₃ and —SCN⁻[11]. Also isothiocyanato chromium (III) complexes, in which the thiocyanate nitrogen is unavailable for surface binding, adsorb much more strongly than the corresponding azide complexes at silver electrodes[12].

The SERS spectrum for SCN⁻ provides strong evidence that the Raman active thiocyanate anions are more preferably adsorbed *via* the sulfur atom. This assignment relies on the documented differences in the frequencies of the various vibrational modes between *S*- and *N*-bound thiocyanate ligands. As shown in Figure 1 (A), the peak of v_3 mode appears at 2114 cm⁻¹ as found for various *S*-bound thiocyanates (2100 – 2140 cm⁻¹), but at a noticeably higher frequency than found for N-bound thiocyanates (2050–2070 cm⁻¹)[13]. This frequency difference probably arises from the expected increase in C—N bond order caused by coordinate bond formation between the silver surface and sulfur lone pair[14].

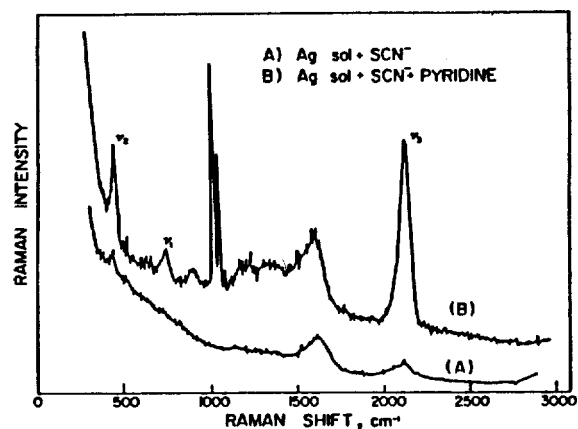We may not, however, completely exclude the possibility of

Figure 1. Raman spectra of SCN⁻ in silver sol with 514.5 nm excitation (100 mw): (A) $1.7 \times 10^{-4} M$ solution. (B) $1.7 \times 10^{-4} M$ together with $9 \times 10^{-2} M$ pyridine. Bands other than v_1, v_2 and v_3 of SCN⁻ are due to pyridine and water.

Figure 2. UV/VIS spectra of silver sol solutions with different concentration of pyridine: Cell path-length 1 cm.

the formation of N-bound thiocyanate. As can be seen in Figure 1(A), the v_3 band is somewhat asymmetric, being significantly wider on the low frequency side in agreement with the previously reported SERS spectra of SCN⁻ on Ag electrode[15]. Usually, such broad peaks occur for the SERS of chemisorbed anions. Inhomogeneous line broadening probably arising from a distribution of adsorption site environments on metal surfaces and from long range coulombic interactions between ions are responsible for the broad band width. On the other hand, the asymmetry of v_3 band many occur partially from the contribution of N-bound thiocyanate. The low frequency side of v_3 band clearly covers the region (2050-2070 cm⁻¹) corresponding to those in N-bound thiocyanates or free SCN⁻. Nevertheless, the amount of N-bound thiocyanate, if present, is believed to be negligibly small compared with that of S-bound ones.

The Raman spectrum of a silver sol solution containing $1.7 \times 10^{-4} M$ SCN⁻ together with $9 \times 10^{-2} M$ pyridine is shown in Figure 1(B). No significant shift has occurred in the peak positions of v_2 and v_3 bands of thiocyanate. However, in the presence of pyridine, formerly unobservable v_1 band of thiocyanate appeared at 738 cm⁻¹ indicating that addition of pyridine increases the band intensities of SCN⁻. Enhancement factors for the v_3 band of $1.7 \times 10^{-4} M$ SCN⁻ in sol solution with and without pyridine were evaluated using the method of Kerker et al[16]. Average particle radius was estimated to be ~5 nm based on Henglein's work[17], and each ion of SCN⁻ was assumed to occupy an area of 30Å². Enhancement factor thus estimated was ~3 × 10³ in the absence of pyridine. For the solution containing pyridine, enhancement factor of ~2 × 10⁵ was obtained assuming that all the surface sites were occupied by SCN⁻ ions. Considering that some of the surface sites may be occupied by pyridine, actual enhancement factor for SCN⁻ can be larger than this value. Thus, addition of pyridine has provided an additional enhancement of ~70 or larger to the SERS effect of SCN⁻.

As in our previous work[3], it appears then that the role of pyridine might be to change the state of aggregation of Ag sol particles. Figure 2 shows the UV/VIS spectra of Ag sol solution with different concentration of pyridine. As reported by Blatchford et al[18]., addition of pyridine to Ag sol solution results
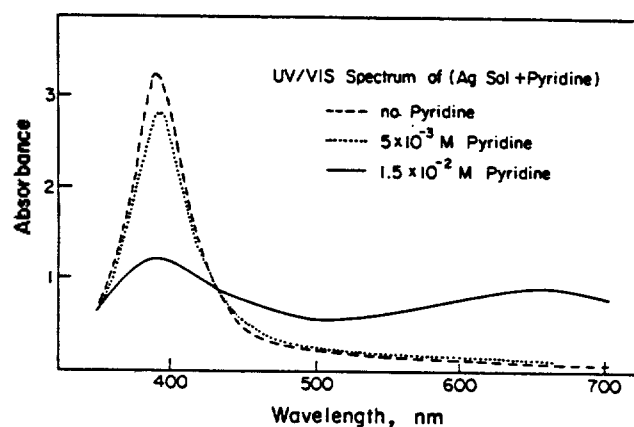
in appearance of new absorption band in the red. Based on the report of Blatchford et al., pyridine may cause the formation of string—shaped aggregates of Ag sol particles. Linear strings, then, have anisotropic polarizability on account of coupling between the plasma modes of the individual spherical Ag sol particles constituting the string. It has been known that there are two plasma modes in the string, perpendicular and parallel to the string axis. The transverse mode remains at roughly the same wavelength as the sphere (unaggregated) resonance wavelength while the longitudinal mode moves toward the red as the string gets longer. In Figure 2, the band moving toward longer wavelength is then identified as the longitudinal dipole resonance of linear aggregates of Ag sol particles, while the band near 392 nm is due to the transverse resonance of linear aggregates. Thus, it now appears that the SERS of SCN⁻ in the presence of pyridine is closely related to the longitudinal plasma resonance of the aggregated silver sol particles. Above argument was confirmed further from the Raman excitation profiles. Ranging from 457.9 to 514.5 nm, the enhancement factor for the v_3 band of SCN⁻ increased as the excitation wavelengths got close to the envelope of the longitudinal resonance while enhancement got reduced as the excitation wavelength approached the transverse aggregate/single particle excitation band.

In conclusion, pyridine was observed again to serve as a promoter of SERS effect, increasing the enhancement factor of SCN⁻ from ~3 × 10³ to as large as ~2 × 10⁵. Based on the surface plasmon resonance theory for SERS, role of pyridine was interpreted as due to its surface conditioning effect. Along with the previous result, we believe that it is possible to obtain strong SERS effect for many adsorber-adsorbate system by properly adjusting the experimental conditions such as in situ chemical treatment.

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Calculation of the NMR Chemical Shift for a 3d² System in a Strong Crystal Field of Octahedral Symmetry

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The NMR chemical shift arising from 3d electron spin dipolar nuclear spin angular momentum interactions for a 3d² system in a strong crystal field environment of octahedral symmetry has been investigated when the fourfold axis is chosen to be our axis of quantization. The NMR shift is separated into the contribution of $1/R^5$ and $1/R^7$ terms. A comparision of the multipolar terms with nonmultipolar results shows that the $1/R^5$ term contributes dominantly to the NMR shift and there is in good agreement between the exact solution and the multipolar results when $R \geqslant 0.25$. A temperature dependence analysis may lead to the results that the $1/T^2$ term has the dominant contribution to the NMR shift for a paramagnetic 3d² system but the contribution of the $1/T$ term may not be negligible.

1. Introduction

Since our interest is centered on the NMR chemical shift arising from the electron angular momentum and the electron spin diploar-nuclear spin angular momentum interactions for a 3d² system in a strong crystal field environment of octahedral symmetry, it is necessary to examine the NMR chemical shift in a 3d² paramagnetic system. The effects of paramagnetism on the characteristics of nuclear magnetic resonances have been investigated by the various methods.[1-3] The NMR shift in a 3dⁿ and a 4fⁿ systems has been interpreted as arising through the Fermic contact interaction between the electron bearing nucleus and the NMR nucleus.[4,5] In other cases,[6,7] the NMR shift has been interpreted as arising dominantly through pseudo contact interaction.

In this paper we investigate in detail the pseudo contact contribution of a 3d² system to the NMR shift for a 3d² system in a strong crystal field environment of octahedral symmetry.

The pseudo contact NMR shift, B, was first given by McConell and Robertson[8] in the form

$$\frac{\Delta B}{B} = - \mu_B^2 \frac{S(S+1)}{3kT} \frac{(3\cos^2\theta - 1)}{R^3} F(g) \qquad (1)$$

where R is the distance between the paramagnetic center and

the NMR nucleus and θ is the angle between the pricipal asix of the complex and the vector between the paramagnetic center and the NMR nucleus. $F(g)$ is a function of the principal g-values. Kurland and McGravey[9] extended this expression and showed that the pseudo contact shift may be expressed in terms of the magnetic susceptiblity components, X_{aa}, namely,

$$\frac{\Delta B}{B} - \frac{1}{3R^3} \left[\{X_{zz} - \frac{1}{2}(X_{xx} + X_{yy})\}(3\cos^2\theta - 1) + \frac{3}{2}(X_{xx} - X_{yy})\sin^2\theta\ \cos^2\phi \right] \qquad (2)$$

This expression has extensively been used in interpreting the pseudo contact shift in paramagnetic 3dⁿ and 4fⁿ systems.[10] Thereafter, attention has been focused on the higher multipolar terms[11-13] and the NMR shift may be expressed as

$$\frac{\Delta B}{B} = \sum_{L=2}^{K} \sum_{M=0}^{L} \frac{\{A_{LM}\cos M\phi + B_{LM}\sin M\phi\} P_L^M(\cos\theta)}{R^{L+1}} \qquad (3)$$

where $K = 2(\ell + 1)$ for a specific ℓ-electron, $P_L^M(\cos\theta)$, the associated Legendre polynomials and the coefficients A_{LM} and B_{LM} measure the anisotropy in the multipolar magnetic susceptibilities of the molecule. Recently, nonmultipole expansion method has been developed by Golding and Stubbs[14] and this method was applied to investigate the NMR chemical shift