

Surface-Enhanced Raman Scattering Study of Quinoxaline-2,3-dithiol and Disodium Bis(quinoxaline-2,3-dithiolato)nickelate(II) Adsorbed on Silver Surface

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Adsorption of quinoxaline-2,3-dithiol (H_2QS_2) and disodium bis(quinoxaline-2,3-dithiolato)nickelate(II) ($\text{Na}_2[\text{Ni}(\text{QS}_2)_2]$) on a silver surface has been studied by SERRS as well as FT-SERS techniques. The surface Raman spectra of H_2QS_2 are very similar to the corresponding normal Raman spectra of aqueous solutions of disodium quinoxaline-2,3-dithiolate, suggesting that H_2QS_2 dissociates on a silver surface to the quinoxaline-2,3-dithiolate ion. Normal-mode analysis based on the results of *ab initio* calculation shows that in-plane modes are selectively enhanced, indicating a perpendicular orientation for the adsorbed dithiolate ion with respect to the surface. The FT-SERS spectra of H_2QS_2 are found to be very weak on colloidal silver at all stages of aggregation, whereas intense spectra are observed when adsorbed on chemically deposited silver films, indicating that the surface Raman spectrum is mainly enhanced through electromagnetic mechanism for near-infrared excitation. The vibrational frequencies of $\text{Na}_2[\text{Ni}(\text{QS}_2)_2]$ are found to be virtually unaffected by adsorption, indicating only very weak interaction with silver surface.

Introduction

Since its discovery by Fleischmann, Hendra, and McQuillan,¹ surface-enhanced Raman scattering (SERS) has been widely used^{2–5} for the study of molecules adsorbed on metal surfaces at monolayer or submonolayer coverage. Detailed information on the structure, orientation, binding mechanism, etc. of the adsorbed species can be gained through a comparison of the SERS spectra with normal Raman spectra in the solution or solid form. Considerable amounts of theoretical and experimental investigations have been carried out to understand the origin of SERS. It is now generally accepted^{6–9} that at least two mechanisms, viz., electromagnetic and chemical, are contributing to the enhancement. The electromagnetic mechanism arises mainly from the enhancement of local electric fields at the metal surface due to the excitation of surface plasmon modes and modulation of metallic reflectance due to adsorbate vibrations. This model does not require specific bonds between the adsorbate and the metal. The chemical contribution is based on the overlap of the metal and adsorbate electronic wave functions, which lead to ground-state and light-induced charge-transfer processes. Direct proximity between the molecule and the metal surface is required for the charge-transfer mechanism. The orientation of molecules at metal surfaces is important for the understanding of metal–adsorbate binding and reactivity of adsorbed species. Creighton⁶ first derived a procedure for the evaluation of the orientation of molecules adsorbed on spherical particles. Moskovits^{7,8} expanded the analysis to both smooth and roughened SERS active substrates.

Quinoxaline-2,3-dithiol (H_2QS_2) was first prepared by Morrison and Furst¹⁰ and then used¹¹ mostly as a chelating agent in the qualitative and colorimetric analysis of transition metal ions. Recently, transition metal complexes of H_2QS_2 have been the

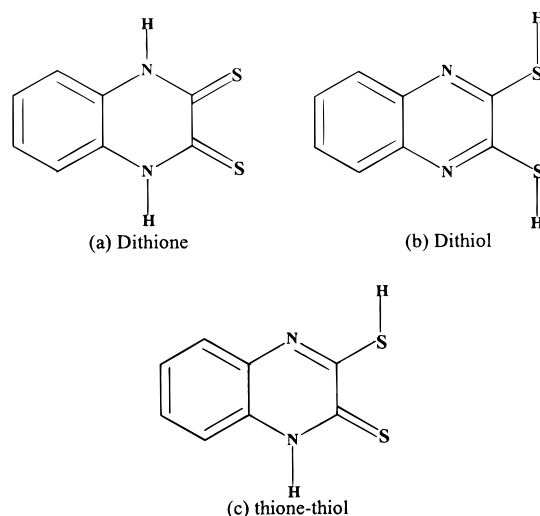


Figure 1. Tautomeric forms of H_2QS_2 .

topic of many investigations because of their luminescent properties and potential use of such materials as photocatalysts for light-to-chemical energy conversion.^{12,13} H_2QS_2 is capable of thione–thiol tautomerism and can exist in three limiting forms as shown in Figure 1. Pilipenko et al., from the studies¹⁴ of the electronic spectrum of H_2QS_2 in several solvents, concluded that the molecule exists as a dithione with strong H-bonding involving sulfur atoms. The dithione form should exhibit a $\nu(\text{NH})$, whereas the dithiol structure should reveal a SH stretching vibration in the IR spectrum. However, a study of the IR spectrum of H_2QS_2 by Ayers and McCrory¹⁵ did not lead to any definite conclusion of this thiol–thione tautomerism because neither $\nu(\text{SH})$ (near 2550 cm^{-1}) nor the $\nu(\text{NH})$ bands (near 3400 cm^{-1}) were observed. Peyronel et al.¹⁶ gave a complete vibrational assignment of H_2QS_2 based on a comparative study of the IR spectra of H_2QS_2 with those of other 2,3-

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disubstituted quinoxaline derivatives and concluded that H_2QS_2 exists predominantly in the dithione form in the solid state.

Previous SERS studies^{17,18} on quinoxaline adsorbed at silver surfaces have shown that it exhibits two kinds of adsorption geometries depending on the surface concentration of the adsorbed species. In concentrated solutions quinoxaline molecules were found to preferentially adsorb through the N atom with a perpendicular orientation, whereas in dilute solutions a binding through a π -system with a flat orientation was observed. If H_2QS_2 adsorbs via σ -donation of N lone pair, it would mean that the aromatic rings are oriented perpendicular to the surface for maximum overlap with the metal surface. In such an adsorption mechanism, the charge distribution around the C atoms is not affected much and frequencies of the internal modes in the SERS spectrum should show only minor variations compared with the bulk phase spectrum. On the other hand, if adsorption occurs via π -donation of electrons, then change in the charge distribution upon π -adsorption would be large, and this will result in a significant shift of ring modes. Thus, the possibility of the existence of several tautomeric forms, each form having different potential adsorption sites, makes the SERS investigation of H_2QS_2 very interesting and worthwhile.

Experimental Section

H_2QS_2 and $\text{Na}_2[\text{Ni}(\text{QS}_2)_2]$ were prepared according to the procedures reported^{10,11,19} in the literature. The silver colloid was prepared by a chemical reduction method as reported by Creighton et al.²⁰ Samples for SERRS were prepared by mixing 5 volumes of the colloid with 1 volume of methanolic solution of H_2QS_2 so that final concentrations were in the range 10^{-4} – 10^{-6} M. The color of the colloidal solutions was found to change from yellow to brown upon addition of the substrate. Resonance Raman and SERRS spectra were recorded using a Z-24 Raman spectrometer. The 488 nm line of an Ar ion laser with a power of 80 mW at the sample was used for excitation. The scattered light was collected at a 90° scattering geometry. Samples for resonance Raman and SERRS were circulated through a capillary tube at a rate of 100 mL/min to avoid photodecomposition.

Chemically deposited silver films were prepared according to the procedure reported by Ni and Cotton.²¹ For recording the FT-SERS spectra, silver-deposited glass slides were dipped in methanolic solutions of adsorbates for about 30 min. Films were then taken out and dried in air. FT-Raman spectra were recorded with a laser power of 200 mW and a spectral resolution of 2 cm^{-1} . The scattered light was collected at 180° scattering geometry. Three-hundred scans were averaged to obtain each spectrum. No concentration-dependent changes were observed for the compounds reported in this work.

Results and Discussion

The normal FT-Raman spectra of H_2QS_2 (solid) and Na_2QS_2 (solid) and the FT-SERS spectrum of H_2QS_2 adsorbed on a chemically deposited silver film from a 10^{-5} M methanol solution are shown in Figure 2. The FT-SERS spectrum of H_2QS_2 adsorbed on colloidal silver is found to be extremely weak. H_2QS_2 shows an electronic absorption of moderate intensity in the visible region¹⁶ with a λ_{max} around 450 nm. The resonance Raman spectrum of an aqueous solution of H_2QS_2 could not be obtained with 488 nm excitation because of its very poor solubility. The SERRS spectrum of H_2QS_2 adsorbed on Ag colloid (10^{-6} M) and the resonance Raman spectrum of Na_2QS_2 (10^{-3} M) in aqueous medium, both obtained with the 488 nm exciting laser line, are shown in Figure 3. The 488 nm

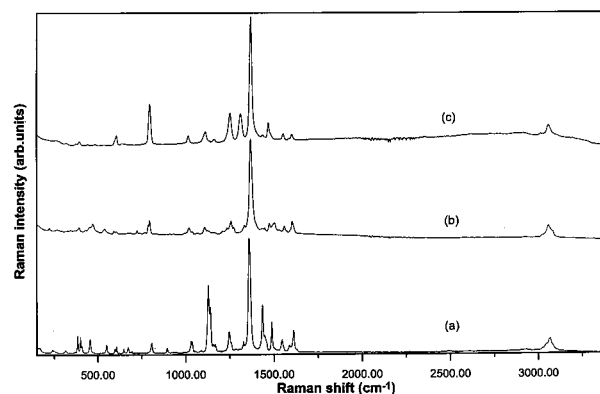


Figure 2. (a) Normal FT-Raman spectrum of H_2QS_2 (solid). (b) Normal FT-Raman spectrum of Na_2QS_2 (solid). (c) FT-SERS spectrum of H_2QS_2 (adsorbed on Ag film from 10^{-5} M methanol solution).

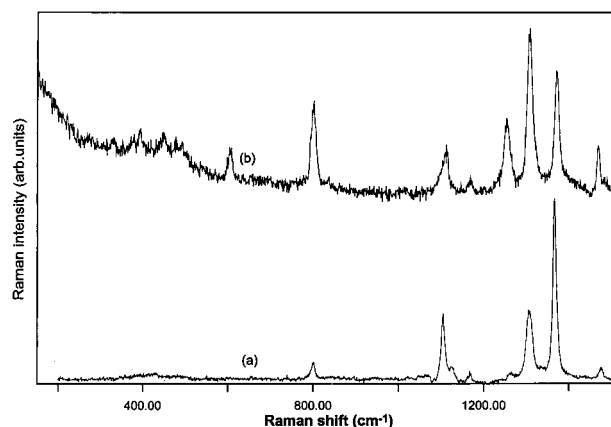


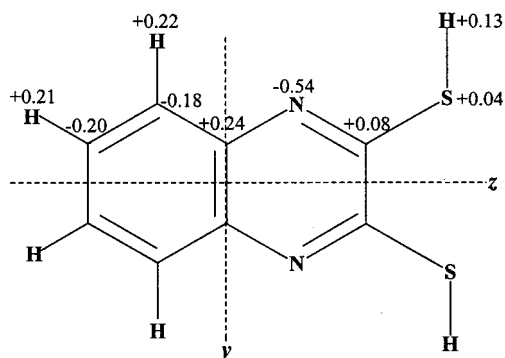
Figure 3. (a) Resonance Raman spectrum of Na_2QS_2 (10^{-3} M in H_2O , 488 nm). (b) SERRS spectrum of H_2QS_2 adsorbed on Ag colloid (10^{-6} M, 488 nm).

excitation is within the long-wavelength side of the visible absorption band of Na_2QS_2 . The frequencies and assignment of vibrational bands are given in Table 1. The frequency positions of vibrational bands in the SERRS spectrum are very similar to those in the FT-SERS spectrum, indicating that the adsorption mechanisms of H_2QS_2 on Ag colloids and chemically deposited silver films are identical.

The frequencies and symmetries of various normal modes of the dithiol form of H_2QS_2 have been computed by ab initio calculation using the Gaussian 92 program at the HF/6-31G** level. The calculations are done by restricting the molecule to a planar C_{2v} geometry. The atomic charges and the optimized geometry obtained from the calculations are presented in Figure 4. A comparison of the normal FT-Raman spectrum of H_2QS_2 with its FT-SERS spectrum shows that the band around 807 cm^{-1} in the former, assigned¹⁶ to $\nu(\text{CS})$, is found to be shifted to 797 cm^{-1} in the FT-SERS spectrum. Such a downshift in frequency of this mode has also been observed¹⁹ on coordination through sulfur atoms in the transition metal complexes of quinoxaline-2,3-dithiol. The presence of only one band in this region indicates that the H_2QS_2 binds to the surface through both sulfur atoms. Such a binding would reduce the double bond character of the CS bond. It is also notable that the peaks due to both $\nu(\text{NH})$ and $\nu(\text{SH})$ are completely absent in the SERS spectra. Therefore, it is reasonably concluded that the dithione form of H_2QS_2 tautomerises to the dithiol form on the surface and subsequently dissociates to dithiolate ion by the rupture of both S–H bonds. This is in accordance with the results of previous SERS studies^{22,23} on many aromatic and aliphatic

TABLE 1: Frequencies and Assignments for Vibrational Bands in the IR, Normal FT-Raman, and FT-SERS Spectra of H₂QS₂

H ₂ QS ₂		Na ₂ QS ₂	H ₂ QS ₂	H ₂ QS ₂	assignments ^a
IR (solid) ^a	normal FT-Raman (solid)	normal FT-Raman (in H ₂ O)	(dithiol, ab initio)	FT-SERS, Ag film	
3150, br					$\nu(\text{NH})$
1621, m	1625, vw		1620 (B ₂)		ring stretch
1601, s	1611, m	1601, m	1597 (B ₂)	1603, w	ring stretch
1550, m	1546, m	1564, m	1585 (A ₁)	1554, w	$\nu(\text{NCS})_{\text{asym}}$
1477, vs	1487, m	1477, m	1485 (A ₁)	1470, m	ring stretch
1452, w	1435, s	1434, w	1450 (B ₂)		$\delta(\text{C-H})$
1354, vs	1360, vs	1367, vs	1362 (A ₁)	1370, vs	ring stretch
1320, vs	1328, w	1306, m	1330 (A ₁)	1310, s	(2,3-R)
1248, m	1247, m	1263, m	1231 (A ₁)	1253, s	ring stretch
1130, vs	1130, s	1105, m	1153 (A ₁)	1114, m	$\nu(\text{NCS})_{\text{sym}}$
1027, m	1030, m	1023, m	1040 (A ₁)	1016, m	skel dist
810, w	807, w	801, m	773 (A ₁)	797, s	$\nu(\text{CS})$
618, vs	606, w	605, vw	613 (A ₁)	606, w	$\delta(\text{NCS})$

^a From ref 16.**Figure 4.** Atomic charges and the optimized geometry of quinoxaline-2,3-dithiol.

thiols. It is also pertinent to note that quinoxaline-2,3-dithiol has two different dissociation constants¹⁶ ($\text{p}K_1 = 6.84$, $\text{p}K_2 = 9.95$). Thus, judging solely from the $\text{p}K_a$ values, quinoxaline-2,3-dithiol is likely to adsorb on the metal surface as the monothiolate ion at neutral pH, as the dithiolate ion at basic pH, and as the dithiol itself at acidic pH. However, a lowering of $\text{p}K_a$ values of thiols on metal surfaces has been reported²⁴ and can be attributed to strong “soft–soft” interactions; silver being a “soft” metal will predominantly interact with sulfur, which is known to be a “soft” base. Another vibrational mode, which shows appreciable change upon adsorption, is the band due to $\nu(\text{NCS})$. It is seen that the band at 1130 cm^{-1} in the normal FT-Raman spectra of H₂QS₂ is lowered to 1105 cm^{-1} in the FT-SERS spectrum and to 1114 cm^{-1} in the normal FT-Raman spectrum of Na₂QS₂. The FT-SERS spectra of H₂QS₂ show a good correlation with the normal FT-Raman spectrum of Na₂QS₂. The FT-SERS spectra of H₂QS₂ at different concentrations (10^{-4} – 10^{-6} M) are found to be almost invariant except for some slight changes in the intensity and peak positions. This indicates that the adsorbed species does not undergo any change in the binding mechanism or orientation with changes in concentration.

Previous SERS studies on benzene and some monosubstituted benzenes^{25,26} have shown that for adsorption via the substituent atoms, ring mode frequencies and bandwidths do not show much change upon adsorption, whereas substituent vibrations exhibit frequency shifts and band broadening. On the other hand, the opposite trend is observed in the case of adsorption via the aromatic π -system. The bandwidths of all ring modes in the FT-SERS spectrum are very similar to those of the corresponding bands in the normal FT-Raman spectrum. This suggests that aromatic rings of the adsorbed dithiolate ion does not interact

directly with the silver surface, and hence, it is not oriented parallel to the surface.

The process by which an ion or molecule adsorbs on the surface has been described by the perturbation theory or frontier orbital theory.^{27,28} In this approach when two species interact, the change in energy of the system, ΔE , is the energy gained or lost when the metal orbitals, with energy E_r , and adsorbate orbitals, with energy E_s , overlap. A pair of metal and adsorbate orbitals with very similar energies (smallest value of $E_r - E_s$) will contribute most to ΔE . The adsorbate molecule can donate electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied or partially occupied molecular orbital (LUMO or conduction band) of the substrate. When $E_r - E_s$ is small, charge transfer from the adsorbate molecule to the substrate will be more and the reaction will be under “orbital control”. The closer the energies of the adsorbate HOMO and substrate LUMO orbitals, the larger is the magnitude of the charge-transfer interaction. When $E_r - E_s$ is large, the charge-transfer contribution is small and the reaction is governed by Coulombic interaction. The adsorbate molecules with higher HOMO energies (“softer” bases) adsorb more readily on metals such as silver, mercury, and gold. They achieve greater stabilization upon adsorption than the adsorbate molecules with lower HOMO energies because of stronger charge-transfer interactions. The atomic charges on the dithiol form of H₂QS₂ indicate that most of the negative charge is on the nitrogen atom (-0.54 on each atom). Thus, if the Coulombic interaction is the dominant factor determining the adsorption, then an interaction through the nitrogen atoms is expected. On the other hand, if charge-transfer interaction is the dominant factor, then an adsorption through sulfur atoms is more likely because the HOMO will have a major contribution from atomic orbitals on sulfur atoms. A preferential interaction through the sulfur atoms of quinoxaline-2,3-dithiol with subsequent deprotonation shows that the charge-transfer interaction is the driving force for the adsorption of quinoxaline-2,3-dithiol on the silver surface. The HOMO energies of the quinoxaline-2,3-dithiol and its dithiolate ion, as given by the ab initio results, are -8.5 and 1.02 eV , respectively. Thus, the HOMO of the dithiolate ion is situated at a considerably high energy compared to the dithiol, making charge-transfer interaction of the substrate more feasible with the former than with the latter.

It is widely accepted that^{7,29} the enhancement of the electromagnetic field near the rough surface and the surface resonance Raman effect are the main causes for SERS. For the first layer of adsorbate, both mechanisms are thought to operate but with varying degrees depending on the adsorbate and the surface.

No general rule has been proposed so far to predict the orientation of the adsorbed molecule on the surface based on the enhancement of the intensities of the bands in the SERS spectrum compared to those in the normal Raman spectrum.

Assuming that the source of enhancement is primarily electromagnetic in origin, a successful basis for analyzing SERS spectra with regard to the orientation of the adsorbates has been worked out in the form of surface selection rules by Creighton⁶ and later expanded by Moskovits et al.^{7,8} Different vibrations of a molecule belong to different irreducible representations of the point group to which it belongs. The Raman active modes are those that possess nonzero components of the Raman polarizability tensor. The relative intensities of normal modes in the Raman spectrum of a molecule may dramatically change when it is placed near a metal surface. On the basis of the relative enhancement of bands in the SERS spectra, the normal modes of an adsorbed molecule can be classified into three groups in terms of their polarizability tensor elements. The normal modes associated with α_{33} are most enhanced, those associated with α_{13} or α_{23} are less enhanced, and the modes associated with α_{11} , α_{12} , or α_{22} are least enhanced. Here, the subscripts 1–3 refers to the orthogonal axes parallel (1, 2) and perpendicular (3) to the surface.

If the quinoxaline-2,3-dithiolate ion is adsorbed through the two sulfur atoms, with its C_2 axis (z -axis) perpendicular to the surface. Then

$$\begin{array}{ll} \alpha_{11} \rightarrow \alpha_{xx} & \alpha_{12} \rightarrow \alpha_{xy} \\ \alpha_{22} \rightarrow \alpha_{yy} & \alpha_{13} \rightarrow \alpha_{xz} \\ \alpha_{33} \rightarrow \alpha_{zz} & \alpha_{23} \rightarrow \alpha_{yz} \end{array}$$

For a molecule with C_{2v} symmetry, the α_{xx} , α_{yy} , and α_{zz} components of the molecular polarizability tensor belong to A_1 symmetry, α_{xy} belongs to A_2 , α_{xz} belongs to B_1 , and α_{yz} belong to B_2 . Then, according to electromagnetic surface selection rules, the A_1 modes that derive their intensities mainly from the α_{zz} component of polarizability tensor, will be the most intense in the SERS spectra. The next intense bands will be those that derive intensity from α_{xz} or α_{yz} and correspond to B_1 and B_2 modes, respectively. The least enhanced bands are those that derive intensity from α_{xy} , and they are the A_2 modes. On the other hand, if the dianion is adsorbed parallel to the surface, then its x axis will be perpendicular to the surface and

$$\begin{array}{ll} \alpha_{11} \rightarrow \alpha_{zz} & \alpha_{12} \rightarrow \alpha_{yz} \\ \alpha_{22} \rightarrow \alpha_{yy} & \alpha_{13} \rightarrow \alpha_{xz} \\ \alpha_{33} \rightarrow \alpha_{xx} & \alpha_{23} \rightarrow \alpha_{xy} \end{array}$$

Thus, for a flat orientation, the A_1 modes having a large α_{xx} component will be the most enhanced, A_2 and B_1 modes will be less enhanced, and B_2 modes will be the least enhanced. Creighton⁶ has shown that for molecules with C_{2v} symmetry, the relative enhancement factors for A_1 , A_2 , B_1 , and B_2 modes respectively would be 1–16, 1, 4, and 4 for edge-on orientation whereas these would be 1–16, 4, 4, and 1 for face-on orientation.

The A_2 and B_1 modes of H_2QS_2 in the normal FT-Raman and FT-SERS spectra are very weak. This is due to the relatively small polarization changes for out-of-plane ring bending modes. This trend is generally observed in all aromatic ring systems. Since H_2QS_2 exists as a dithiolate ion on the silver surface, it would be more appropriate to compare the FT-SERS spectrum of H_2QS_2 with the normal FT-Raman spectrum of Na_2QS_2 to

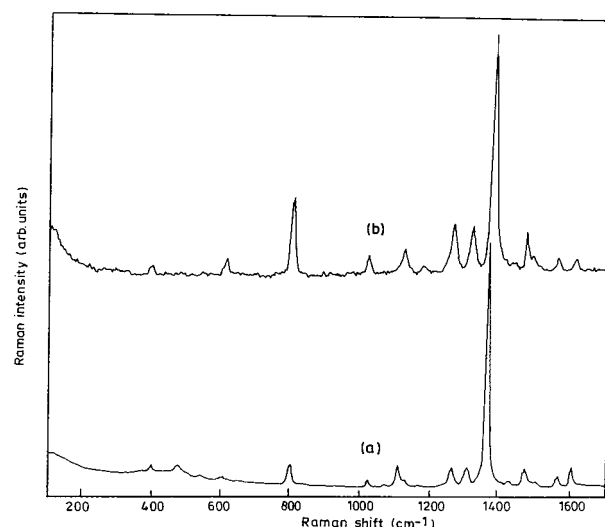


Figure 5. (a) FT-SERS spectrum of H_2QS_2 (Ag film, 10^{-5} M in methanol). (b) Normal FT-Raman spectrum of Na_2QS_2 (10^{-2} M in H_2O).

assess the relative enhancements. Figure 5 shows the FT-SERS spectrum of H_2QS_2 and normal FT-Raman spectrum of an aqueous solution of Na_2QS_2 . The FT-SERS spectrum of H_2QS_2 is very similar to the normal FT-Raman spectrum of Na_2QS_2 . In the FT-SERS spectrum of H_2QS_2 , all the modes that show enhancement are either A_1 or B_2 modes. All these vibrations involve displacements of the atoms along both z and y axes of the molecular system. This suggests that the quinoxaline-2,3-dithiolate ions are oriented perpendicular to the silver surface, and this results in the selective enhancement of those A_1 modes that have a large contribution from α_{zz} . Thus, it is reasonably concluded that the electromagnetic mechanism is the main contributing factor to the SERS of quinoxaline-2,3-dithiolate on the silver surface for near-infrared excitation. The tangential field at the surface is much smaller than the normal field for near-infrared excitations, and only those modes having atomic displacements normal to the surface will show enhancement.^{6,7} This is the case with A_1 , B_1 , or B_2 modes in C_{2v} symmetry. However, B_1 modes are out-of-plane modes, and these modes are generally weak in the bulk phase spectrum of H_2QS_2 and in the FT-SERS spectra. For a perpendicular orientation of adsorbed quinoxaline-2,3-dithiolate ions, the A_1 modes having a significant contribution from the α_{zz} component of the polarizability tensor would be preferentially enhanced. The cancellation of the tangential field^{6,7} results in a much simpler surface spectrum for near-infrared excitations compared with visible excitations. Thus, all these observations suggest that the FT-SERS spectrum of H_2QS_2 is mainly enhanced through an electromagnetic mechanism.

SERS intensities of aromatic C–H vibrations provide the most specific evidence of the orientation of the adsorbed molecules on the silver surface,^{3,8} since C–H stretching coordinates do not mix significantly with other vibrations of the aromatic ring and the polarizability of C–H bond lies along the bond axis. The SERS intensity associated with a specific C–H bond will depend on the angle at which the bond lies in relation to the surface. Maximum intensity will be expected when the C–H bond is normal to the surface (90° angle from the surface). The intensity will fall off as the angle is reduced to 0° . If the dithiolate ion interacts with the surface through both the sulfur atoms and has a perpendicular orientation with respect to the surface, then two C–H bonds will be parallel to the silver surface and the other two hydrogen atoms will make an angle of 60° to the surface. The presence of a band at 3030

cm^{-1} of moderate intensity corresponding to the C–H stretch in the FT-SERS spectrum (Figure 2) further supports the view that the adsorbed quinoxaline-2,3-dithiolate ion has a perpendicular orientation with respect to the silver surface. If the ion is oriented parallel to the silver surface, then all four C–H bonds would be parallel to the surface and the band corresponding to the C–H stretch should be very weak in the FT-SERS spectrum.

Takahashi et al. observed overtones and combination bands in the SERS spectra of quinoxaline^{17,18} and concluded that these arise from the charge-transfer contribution to SERS. However, such bands are not observed in the FT-SERS spectra of H_2QS_2 under any conditions. Further, we have seen that the FT-SERS spectrum of H_2QS_2 adsorbed on colloidal silver particles is extremely weak, whereas for the same colloidal solutions strong SERS signals are observed with visible excitations. Electromagnetic theoretical calculations³⁰ have shown that the wavelength for optimal enhancement shifts to longer wavelengths with increasing particle size. Thus, a strong enhancement on chemically deposited silver films compared to that on silver colloids probably arises from the larger particle size of the former arising from larger degree of aggregation.^{31–33} Since only the electromagnetic enhancement mechanism is critically dependent on the size and shape of the particles,^{30,32} a strong enhancement on silver films suggests that the electromagnetic mechanism is the dominant enhancement factor contributing to the FT-SERS spectrum of H_2QS_2 for near-infrared excitation.

The intensities of bands in the SERRS spectrum of H_2QS_2 , however, is found to be dramatically different compared with those in the RR spectrum of Na_2QS_2 (Figure 3). The band at 1366 cm^{-1} is stronger than the band at 1326 cm^{-1} in the RR spectrum of Na_2QS_2 , and these bands are found to be shifted to 1372 and 1306 cm^{-1} , respectively, in the SERRS spectrum, the band at 1306 cm^{-1} being stronger than that at 1372 cm^{-1} . This may be due to the charge-transfer contribution to surface enhancement when excited with 488 nm compared to that with near-infrared excitation. However, it may be noted that this may also result from the increased contribution from the tangential component of the surface electric field,⁷ since for excitations close to the surface plasmon frequency, the magnitude of the tangential component becomes comparable to that of the normal component. This makes the selection rules less rigorous^{6,7} for visible excitations (488 nm). Thus, the drastic changes in the intensities of the bands in the SERRS spectrum relative to its bulk phase spectra may be accounted for in the framework of the electromagnetic mechanism itself.

In the disodium bis(quinoxaline-2,3-dithiolato)nickelate(II) complex, the terminal sulfur atoms of both ligands are coordinated to Ni and it is likely that the complex may bind to the silver surface through some site other than sulfur atoms, for example, the aromatic π -system or nitrogen atom. It is also possible that it may undergo surface-induced dissociation to the quinoxaline-2,3-dithiolate. The $\text{Na}_2\text{Ni}[\text{QS}_2]_2$ possesses three intense electronic absorption bands in the visible region¹⁹ with λ_{max} around 562 , 520 , and 482 nm . Figure 6a shows the resonance Raman spectrum of aqueous $\text{Na}_2\text{Ni}[\text{QS}_2]_2$ obtained with the 488 nm laser line, which is within the contour of the 482 nm electronic absorption band, and Figure 6b shows the SERRS spectrum of $\text{Na}_2\text{Ni}[\text{QS}_2]_2$ on Ag colloid with 488 nm excitation. Curves a and b of Figure 7 are the normal FT-Raman spectrum of $\text{Na}_2\text{Ni}[\text{QS}_2]_2$ (powder) and FT-SERS spectrum of $\text{Na}_2\text{Ni}[\text{QS}_2]_2$ (on silver film), respectively. The presence of a band at 344 cm^{-1} in the resonance Raman spectrum, assigned to the Ni–S stretch, indicates that the 482 nm band in the electronic spectrum arises from charge-transfer excitation

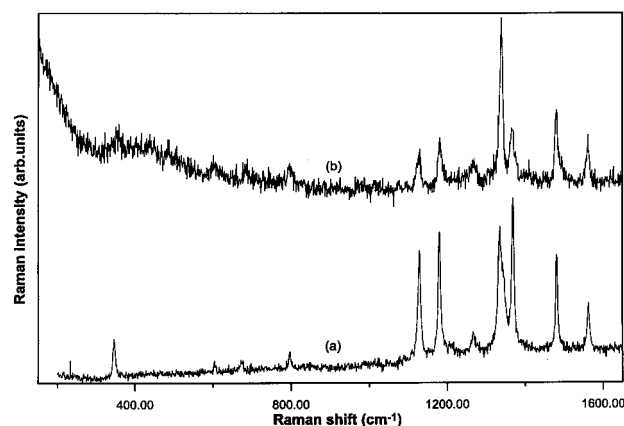


Figure 6. (a) Resonance Raman spectrum of $\text{Na}_2\text{Ni}(\text{QS}_2)_2$ (10^{-4} M in H_2O , 488 nm). (b) SERRS spectrum of $\text{Na}_2\text{Ni}(\text{QS}_2)_2$ (on Ag colloid, 10^{-6} M , 488 nm).

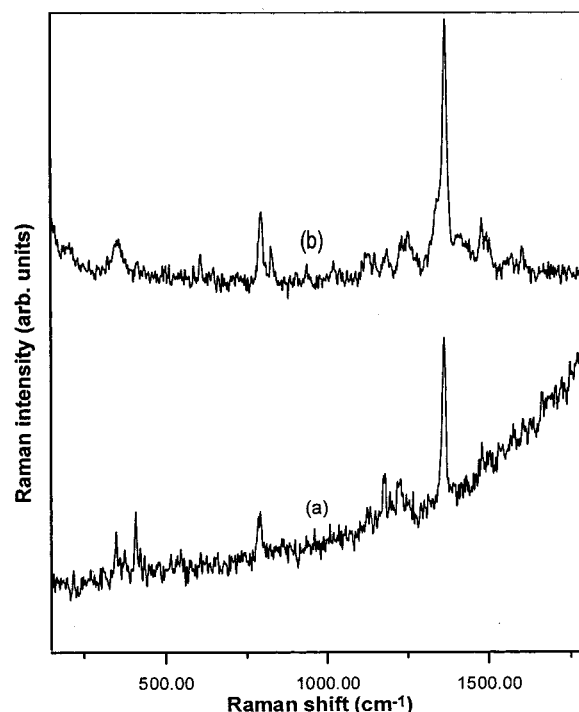


Figure 7. (a) Normal FT-Raman spectrum of $\text{Na}_2\text{Ni}(\text{QS}_2)_2$ (powder). (b) FT-SERS spectrum of $\text{Na}_2\text{Ni}(\text{QS}_2)_2$ (Ag film, 10^{-4} M in H_2O).

between the Ni and quinoxaline-2,3-dithiolate. In the resonance Raman spectrum of $\text{Na}_2\text{Ni}[\text{QS}_2]_2$ all the bands, which show enhancement, are A_{1g} modes of the complex, and these modes correspond to the A_1 modes of the ligand. This shows that these bands are enhanced through the A-term resonance Raman enhancement mechanism. It is seen that the frequencies of bands in the SERRS spectrum are very similar to those in the resonance Raman spectrum, indicating that the complex is very stable on the silver surface. This also suggests that the $\text{Ni}[\text{QS}_2]_2^{2-}$ ions are only physisorbed or that there is only very weak chemical interaction. It is notable, however, that the intensities of the bands in the SERRS spectrum are dramatically changed compared to that of the resonance Raman spectrum. On the other hand, it is seen from Figure 7 that the intensities of bands in the FT-SERS spectrum are very similar to those in the normal FT-Raman spectrum of $\text{Na}_2\text{Ni}[\text{QS}_2]_2$. Since charge-transfer contribution to surface enhancement can only arise if there is chemical interaction of the adsorbate with the surface, the above observation suggests that the SERRS spectrum of $\text{Na}_2\text{Ni}[\text{QS}_2]_2$ is mainly

enhanced through the electromagnetic mechanism, with visible excitation (488 nm) as well as with near-infrared excitation (1064 nm). Thus, even when electromagnetic enhancement is the major contributing mechanism to the surface enhancement, there are strong changes in the relative intensities of bands of the same symmetry (A_{1g} in the present case) when the sample is excited in different wavelength regions. This may be due to the changes in the contributions for A_1 modes from the α_{xx} , α_{yy} , and α_{zz} components of the polarizability tensor when exciting wavelengths are different. It is difficult to predict the adsorbate orientation on the basis of the relative enhancement of A_1 modes, since they are composed of a linear combination of α_{xx} , α_{yy} , and α_{zz} .

Conclusions

H_2QS_2 is found to decompose on the silver surface to the dithiolate ion, which binds to the surface through its sulfur atoms. The adsorbed dithiolate ion has a perpendicular orientation on the silver surface. The intensities of bands in the FT-SERS spectrum of H_2QS_2 are found to be very similar to those in the normal Raman spectrum of an aqueous solution of Na_2QS_2 , suggesting that the electromagnetic mechanism is the main factor contributing to SERS intensities for near-infrared excitation (1064 nm). Only very weak interaction with the silver surface is observed for $Na_2Ni[QS_2]_2$.

References and Notes

- (1) Fleischmann, M.; Hendra, P. J.; McQuillan, A. J. *Chem. Phys. Lett.* **1974**, *26*, 163.
- (2) Chang, R. K.; Furtak, T. E., Eds. *Surface Enhanced Raman Scattering*; Plenum Press: New York, 1982.
- (3) Strekas, T. C.; Diamandopoulos, P. S. *J. Phys. Chem.* **1990**, *94*, 1986.
- (4) Neto, N.; Muniz-Miranda, M.; Sbrana, G. *J. Phys. Chem.* **1996**, *100*, 9911.
- (5) Garrel, R. L. *Anal. Chem.* **1989**, *61*, 401A.
- (6) Creighton, J. A. *Surf. Sci.* **1983**, *124*, 209.
- (7) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.
- (8) Moskovits, M.; Suh, J. S. *J. Phys. Chem.* **1988**, *92*, 6327.
- (9) Otto, A. *J. Raman Spectrosc.* **1991**, *22*, 743.
- (10) Morrison, D. C.; Furst, A. *J. Org. Chem.* **1956**, *21*, 470.
- (11) Theriot, L. J.; Ganguli, K. K.; Kavarnos, S. J. *Inorg. Nucl. Chem.* **1969**, *31*, 3133.
- (12) Cummings, S. D.; Eisenberg, R. *Inorg. Chem.* **1995**, *34*, 2007.
- (13) Cummings, S. D.; Eisenberg, R. *Inorg. Chem.* **1995**, *34*, 3396.
- (14) Pilipenko, A. T.; Savranski, L. I.; Ryabushko, O. P.; Krivokhizina, L. A. *Chem. Abstr.* **1974**, *81*, 62915h.
- (15) Ayers, G. H.; McCrory, R. W. *Anal. Chem.* **1964**, *36*, 133.
- (16) Peyronel, G.; Pignedoli, A.; Malawasi, W. *Spectrochim. Acta* **1976**, *32A*, 1015.
- (17) Takahashi, M.; Ito, M. *Chem. Phys. Lett.* **1984**, *103*, 512.
- (18) Takahashi, M.; Sakai, Y.; Fujita, M.; Ito, M. *Surf. Sci.* **1986**, *176*, 351.
- (19) Mukhopadhyay, S.; Day, D. J. *Chem. Soc., Dalton Trans.* **1993**, 1159.
- (20) Creighton, J. A.; Blatchford, C. G.; Albrecht, M. G. *J. Chem. Soc., Faraday Trans. II* **1979**, *75*, 790.
- (21) Ni, F.; Cotton, T. M. *Anal. Chem.* **1986**, *58*, 3159.
- (22) Cho, S. H.; Han, H. S.; Hang, D. J.; Kim, K.; King, M. S. *J. Phys. Chem.* **1995**, *99*, 10594.
- (23) Lee, T. G.; Kim, K.; Kim, M. S. *J. Phys. Chem.* **1991**, *95*, 9950.
- (24) Lee, S. B.; Kim, K.; Kim, M. S. *J. Raman Spectrosc.* **1991**, *22*, 811.
- (25) Gao, P.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 5040.
- (26) Gao, P.; Davies, J. P.; Weaver, M. J. *J. Phys. Chem.* **1990**, *94*, 6858.
- (27) Garrel, R. L.; Chadwick, J. E.; Severance, D. L.; McDonald, N. A.; Myles, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 11563.
- (28) Anderson, A. B. *J. Electroanal. Chem.* **1990**, *280*, 37.
- (29) Kudelski, A.; Bukowska, J. *Chem. Phys. Lett.* **1996**, *253*, 246.
- (30) Zeman, E. J.; Schatz, G. C. *J. Phys. Chem.* **1987**, *91*, 634.
- (31) Pan, D.; Phillips, D. L. *Chem. Phys. Lett.* **1997**, *275*, 227.
- (32) Chase, B.; Parkinson, B. *J. Phys. Chem.* **1991**, *95*, 7810.
- (33) Joy, V. T.; George, L.; Srinivasan, T. K. *Chem. Phys. Lett.* **1999**, *302*, 517.