

## ADSORPTION AND REACTION OF *TRANS*-CINNAMONITRILE ON A SILVER SURFACE INVESTIGATED BY RAMAN SPECTROSCOPY

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### ABSTRACT

Adsorption of *trans*-cinnamitrile on the metal surface in silver sol has been investigated by the surface-enhanced Raman scattering technique. The molecule is found to adsorb on the surface via its nitrogen lone pair electrons. In the absence of coadsorbed chloride ions, the molecule is converted to *trans*-cinnamic acid by a surface reaction. When a small amount of sample is irradiated with a laser, a surface photoreaction of *trans*-cinnamitrile is observed.

### INTRODUCTION

Surface-enhanced Raman scattering (SERS) [1-5] has proved useful for the investigation of the first layer of adsorbates on metal surfaces. Using this vibrational spectroscopic technique, information on the molecular nature of the adsorbate and on the surface-adsorbate interaction mechanism can be made available.

Aromatic nitriles possess at least three coordination sites through which the molecules can adsorb onto the metal surfaces, namely the benzene ring  $\pi$  system, the CN  $\pi$  system, and the nitrogen lone pair electrons. In our previous SERS investigations [6-8] on the adsorption of benzonitrile and its methoxy derivatives on a silver surface, the molecules were found to adsorb via their nitrogen lone pair electrons. However, adsorption of hydrocinnamitrile [9] in which the CN group is not part of the conjugated system occurred through the CN  $\pi$  system. In the present work, adsorption of *trans*-cinnamitrile on a silver surface is investigated. In this molecule, the CN group is part of the conjugated system even though it is not directly attached to the benzene ring; the ethylene group of this molecule provides an additional coordination site.

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The surface reaction and surface photoreaction of adsorbed *trans*-cinnamionitrile which were observed in the course of this investigation will also be discussed.

## EXPERIMENTAL

The methods for silver sol preparation and the Raman scattering measurements have been previously reported [10]. A small amount ( $\sim 1 \mu\text{l}$ ) of neat *trans*-cinnamionitrile was added to 3 ml of silver sol solution, and KCl was added to a final concentration of  $10^{-3}$  M. To induce the aggregation of silver sol particles,  $20 \mu\text{l}$  of  $2 \times 10^{-2}$  M aqueous  $\text{NaBH}_4$  solution was added to the above solution. Finally,  $20 \mu\text{l}$  of 1% polyvinylpyrrolidone (mol.wt. 360 000) was added to stabilize the sol solution.

In order to minimize laser-induced reactions, a sample solution was circulated through a glass capillary using a peristaltic pump. A sample confined in a glass capillary (1 mm i.d.) was used to observe laser-induced reactions.

All the chemicals used in this work were reagent grade, and triply distilled water was used for the preparation of solutions.

## RESULTS AND DISCUSSION

The ordinary Raman spectrum of pure *trans*-cinnamionitrile is shown in Fig. 1(a). Even though aggregation of silver sol particles is a prerequisite for obtaining a good SER spectrum, *trans*-cinnamionitrile was not effective in inducing aggregation. It was found experimentally that addition of  $\text{NaBH}_4$  to the silver sol solution containing *trans*-cinnamionitrile induced the sol aggregation. Also, it was found that addition of  $\sim 10^{-3}$  M  $\text{Cl}^-$  ions was needed to obtain a good SER spectrum and that the sample solution had to be circulated through the glass capillary sample cell to minimize photoreaction. The SER spectrum thus obtained is shown in Fig. 1(b). Although some bands were more or less shifted in the SER-spectrum from those in the ordinary spectrum, the two spectra exhibit satisfactory correlation. Accordingly, the species in Fig. 1(b) is supposed to be adsorbed *trans*-cinnamionitrile. The major benzene ring modes [11,12] appeared at  $694(\nu_4)$ ,  $755(\nu_{11})$ ,  $830(\nu_1)$ ,  $847(\nu_{10a})$ ,  $972(\nu_5 \text{ or } \nu_{17a})$ ,  $1001(\nu_{12})$ ,  $1162(\nu_{9b})$ ,  $1183(\nu_{9a})$ ,  $1209(\nu_{13})$ ,  $1451(\nu_{19b})$ ,  $1496(\nu_{19a})$ ,  $1578(\nu_{8b})$ , and  $1600(\nu_{8a}) \text{ cm}^{-1}$  in the ordinary spectrum. The corresponding bands were observed in the SER spectrum at  $694$ ,  $753$ ,  $825$ ,  $847$ ,  $973$ ,  $1001$ ,  $1164$ ,  $1182$ ,  $1209$ ,  $1448$ ,  $1492$ ,  $1575$ , and  $1597 \text{ cm}^{-1}$ , respectively. Shifts in the benzene ring modes are thus insignificant as the cinnamionitrile molecule adsorbs on the silver surface. Furthermore, the bandwidths of the benzene ring modes were observed to be very similar for the two spectra. These observations suggest that the phenyl group of cinnamionitrile does not interact directly with the silver particle surface [13–15]. With this view, the spectral changes associated with the substituent group will now be considered.

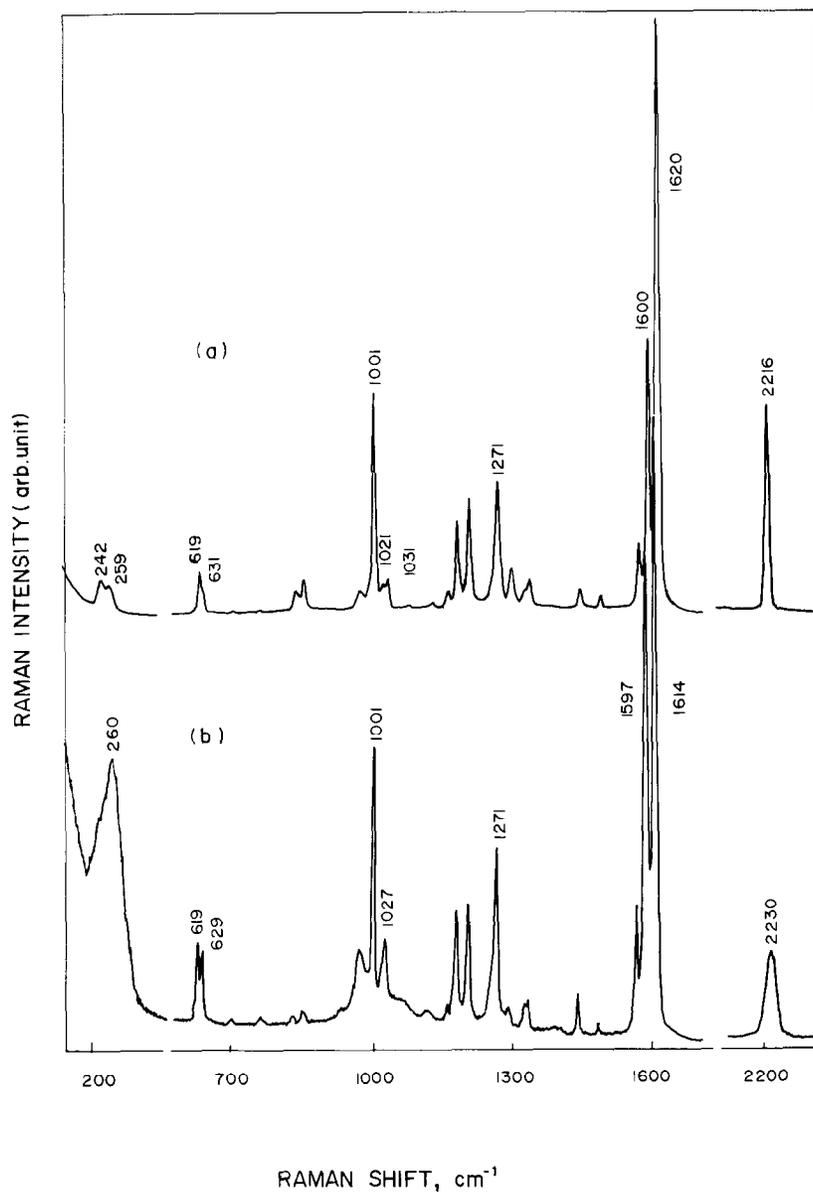


Fig. 1. (a) Ordinary Raman spectrum of pure *trans*-cinnamionitrile. (b) SER spectrum of  $10^{-3}$  M cinnamionitrile in silver sol recorded in the presence of  $10^{-3}$  M KCl. The sample was circulated through a glass capillary cell.

In the SER spectrum the  $\nu(\text{CN})$  mode appeared at  $2230 \text{ cm}^{-1}$  with  $24 \text{ cm}^{-1}$  bandwidth. The corresponding band occurred at  $2216 \text{ cm}^{-1}$  in the ordinary Raman spectrum with  $7 \text{ cm}^{-1}$  bandwidth. Hence, the  $\nu(\text{CN})$  band blue-shifted

by  $14\text{ cm}^{-1}$  and its bandwidth increased by  $17\text{ cm}^{-1}$  upon surface adsorption. These observations indicate direct interaction of the CN group with the silver surface. Surface adsorption of the molecule provides an additional channel for vibrational relaxation of the CN stretching mode resulting in band broadening. It has generally been accepted [16–21] that the linear coordination through the nitrogen lone pair electrons results in an increase in the  $\text{C}\equiv\text{N}$  stretching frequency from that of the free molecule. However, coordination through the  $\text{C}\equiv\text{N}$   $\pi$  system is known to result in a decrease in the  $\text{C}\equiv\text{N}$  stretching frequency from that of the free molecule. Hence, the experimental fact that the  $\nu(\text{CN})$  mode blue-shifts by  $14\text{ cm}^{-1}$  in the SER spectrum indicates that the *trans*-cinnamitrile molecule is adsorbed to the silver surface via its nitrogen lone pair electrons. Similar observations have been made in the SERS studies of benzonitrile [6,7] and its methoxy derivatives [8]. As mentioned previously it was found in our previous study on SERS of hydrocinnamitrile [9] that the molecule adsorbs on the silver surface via its CN  $\pi$  system. Hence, it seems that a nitrile adsorbs through the nitrogen lone pair electrons when the CN group is a part of a conjugation system, whilst coordination through the CN  $\pi$  system is favored when the group is not conjugated with the neighboring unsaturated moiety.

The stretching frequency of the  $\text{C}=\text{C}$  double bond which is in conjugation with the benzene ring has been a subject of great interest. Murray and Gallaway [22] assigned the bands at  $1635$  and  $1625\text{ cm}^{-1}$  in the vibrational spectra of *ortho*- and *para*-isopropenyltoluene, respectively, as the  $\text{C}=\text{C}$  stretching vibrations. They believed that the steric hindrance of the *ortho* methyl group gave rise to somewhat more conjugation, resulting in the higher frequency of this mode for the *ortho* compared to the *para* isomer. Murty and Seshadri [23] assigned the band at  $1624\text{ cm}^{-1}$  to the  $\text{C}=\text{C}$  stretching vibration of cinnamic acid. Gulse and Thoi [24] assigned the  $\text{C}=\text{C}$  stretching vibration of the conjugated double bond to the  $1631\text{ cm}^{-1}$  bands in the spectra of the two isomers of phenylbutene where the double bond is directly conjugated with the ring. One of the benzene ring modes appears in the  $\text{C}=\text{C}$  stretching frequency region, namely the  $\nu_{8a}$  mode. Katritzky and Lagowski [25] examined 85 different monosubstituted benzenes for the positions of the bands with stable frequencies. The bands belonging to vibration  $\nu_{8a}$  have been found in the region between  $1599$  and  $1611\text{ cm}^{-1}$ , which is the reason why the band at  $1600\text{ cm}^{-1}$  in Fig. 1 (a) has been assigned to the  $\nu_{8a}$  ring mode of *trans*-cinnamitrile. Then the remaining band at  $1620\text{ cm}^{-1}$  in this region in Fig. 1 (a) can be assigned to the  $\text{C}=\text{C}$  stretching mode of the olefinic substituent. In the SER spectrum the corresponding band appeared at  $1614\text{ cm}^{-1}$ , i.e. the  $\text{C}=\text{C}$  stretching band red-shifted by  $6\text{ cm}^{-1}$  upon the molecular adsorption of *trans*-cinnamitrile on the silver surface. It has been reported by Chong and Curthoys [26] that when acrylonitrile molecules undergo metal coordination through nitrogen lone pair electrons, the electron withdrawing power of the  $\text{C}=\text{C}$  bond in conjugation with

nitrile weakens. Similarly, Raman spectra of  $\text{CuL}_3\text{X}$  ( $L = \textit{trans}$ -cinnamionitrile;  $\text{X} = \text{Cl, Br}$ ) [27] were reported to indicate that coordination of the ligand ( $L$ ) to the metal occurred via the N atoms and that coordination induced a slight strengthening of the CN bond and weakening of the C=C bond. These reports are in agreement with the present observation.

It has generally been observed [28–30] that two strong bands appear in the ordinary Raman spectra of olefinic derivatives. One is due to the C=C stretching vibration and the other is due to the CH symmetric in-plane wagging (=C–H bending) vibration. The  $1620\text{ cm}^{-1}$  band in Fig. 1(a) has already been assigned to the C=C stretching mode. In the ordinary Raman spectra of 1-butene and *trans*-2-butene [28–30], the CH symmetric in-plane wagging modes were reported to appear at  $1296$  and  $1305\text{ cm}^{-1}$ , respectively. Based on these assignments, one may attempt to assign the band at  $1302\text{ cm}^{-1}$  in Fig. 1(a) as the CH symmetric in-plane wagging mode of *trans*-cinnamionitrile. It is preferred, however, to assign the  $1271\text{ cm}^{-1}$  band in Fig. 1(a) as the CH symmetric in-plane wagging mode. Such an assignment is based on the following argument. It is a well-known fact [11,12] that, in the benzene derivatives with mono “light” substituents, the normal vibrations,  $\nu_3$  and  $\nu_{14}$ , which are the CH in-plane bending and the carbon–carbon stretching vibrations of benzene ring, respectively, appear in the spectral regions  $1270$ – $1330$  and  $1300$ – $1350\text{ cm}^{-1}$ , respectively. In Fig. 1(a), four bands are observed in these regions, namely at  $1271$ ,  $1302$ ,  $1333$  and  $1340\text{ cm}^{-1}$ . However, it has been observed in the ordinary Raman spectrum of hydrocinnamionitrile [9] that two distinct bands appear in the above regions, namely at  $1308$  and  $1343\text{ cm}^{-1}$ . No band was observed in the spectral region of  $1250$ – $1300\text{ cm}^{-1}$ . The  $1308\text{ cm}^{-1}$  peak could be ascribed to the composite of the vibration  $\nu_3$  of benzene and the  $\text{CH}_2$  wagging mode of the *trans* conformer. The  $1343\text{ cm}^{-1}$  peak could be ascribed to the composite of the vibration  $\nu_{14}$  of benzene and the  $\text{CH}_2$  wagging mode of the *gauche* conformer. The fact that there appears one rather strong peak at  $1271\text{ cm}^{-1}$  in the ordinary Raman spectrum of *trans*-cinnamionitrile while no band appears in the  $1250$ – $1300\text{ cm}^{-1}$  spectral region in the ordinary Raman spectrum of hydrocinnamionitrile suggests that the peak at  $1271\text{ cm}^{-1}$  in Fig. 1(a) is due to the olefinic CH symmetric in-plane wagging vibration. Based on this assignment, the  $1302\text{ cm}^{-1}$  peak in Fig. 1(a) is assigned to the normal vibration  $\nu_3$  of the benzene ring. In addition to the  $\nu_{14}$  vibration of benzene ring, the olefinic CH asymmetric in-plane wagging vibration may also appear in the  $1300$ – $1350\text{ cm}^{-1}$  spectral region. In the Raman spectrum of *trans*-2-butene [28], the CH asymmetric in-plane wagging band was known to appear at  $1364\text{ cm}^{-1}$  with very weak intensity. Considering that the CH symmetric in-plane wagging vibration appears for *trans*-2-butene and cinnamionitrile at  $1304$  and  $1271\text{ cm}^{-1}$ , respectively, the CH asymmetric in-plane wagging band of cinnamionitrile is expected to appear at  $\sim 1331\text{ cm}^{-1}$ . Based on this argument, the  $1333\text{ cm}^{-1}$  peak in Fig. 1(a) is tentatively assigned to the olefinic CH asymmetric in-plane

wagging mode and the  $1340\text{ cm}^{-1}$  peak to the normal vibration  $\nu_{14}$  of benzene. Nevertheless, no significant band shift was observed for the bands considered above in the SER spectrum, i.e. the bands centered at  $1271$ ,  $1302$ ,  $1333$  and  $1340\text{ cm}^{-1}$  peaks in Fig. 1 (a) correspond respectively to the  $1271$ ,  $1300$ ,  $1334$ , and  $1339\text{ cm}^{-1}$  peaks in Fig. (b). Bandwidths were also observed to be very similar in the two spectra.

Another noticeable feature in the Raman spectra of cinnamionitrile and hydrocinnamionitrile is that in the spectrum of the latter molecule the bands due to the vibration  $\nu_{6b}$  and  $\nu_{18a}$  of benzene could be unambiguously assigned while in the spectrum of the former molecule the corresponding bands are more or less overlapped with other bands. The  $\nu_{6b}$  and  $\nu_{18a}$  peaks appeared distinctly for hydrocinnamionitrile at  $621$  and  $1031\text{ cm}^{-1}$ , respectively, in the ordinary Raman spectrum, and the corresponding peaks were observed at  $621$  and  $1028\text{ cm}^{-1}$  in its SER spectrum. However, in the ordinary Raman spectrum of *trans*-cinnamionitrile the  $619\text{ cm}^{-1}$  peak is overlapped with a shoulder peak centered at  $631\text{ cm}^{-1}$ , and the  $1031\text{ cm}^{-1}$  peak is partially overlapped with a peak centered at  $1020\text{ cm}^{-1}$ . The latter two peaks merged into one peak in the SER spectrum, appearing at  $1027\text{ cm}^{-1}$ . However, the shoulder peak at  $631\text{ cm}^{-1}$  in the ordinary Raman spectrum became distinct in the SER spectrum appearing at  $629\text{ cm}^{-1}$ . Based on the assignment of hydrocinnamionitrile, the  $619$  and  $1031\text{ cm}^{-1}$  peaks in Fig. 1 (a) may be assigned respectively to the  $\nu_{6b}$  and  $\nu_{18a}$  vibrations of benzene in cinnamionitrile. Considering that the HC=CH *cis* and *trans* wagging modes in gaseous 1-butene [28,29] with the *gauche* conformation have been reported to appear at  $634$  and  $993\text{ cm}^{-1}$ , respectively, the bands at  $631$  and  $1020\text{ cm}^{-1}$  in Fig. 1 (a) will be assigned respectively to the olefinic HC=CH *cis* and *trans* wagging vibrations of cinnamionitrile. Although the latter peak may also be attributed to the C-C stretching vibration of the substituent in *trans*-cinnamionitrile, it is preferable to assign the weak peak at  $1126\text{ cm}^{-1}$  in Fig. 1 (a) to the C-C stretching mode, based on the report that the C-C stretching band appears at  $1138\text{ cm}^{-1}$  in the ordinary Raman spectrum of *trans*-2-butene. The vibrational assignments for *trans*-cinnamionitrile in the spectral region  $500$ - $2300\text{ cm}^{-1}$  are listed in Table 1.

It is interesting to observe that the *trans*-cinnamionitrile molecule adsorbs on silver via the nitrogen lone pair electrons of its nitrile group, whilst hydrocinnamionitrile adsorbs through its C $\equiv$ N  $\pi$  system. For the case of hydrocinnamionitrile, its SER spectra could be obtained in the presence of either  $\text{Cl}^-$  or  $\text{BH}_4^-$ . In the SER spectrum taken with additional  $\text{BH}_4^-$ , vibrational bands characteristic of  $\text{BH}_4^-$  were distinctly observed. On the other hand, the SER spectrum taken in the presence of  $\text{Cl}^-$  showed a prominent band at  $240\text{ cm}^{-1}$  assignable to the Ag-Cl stretching vibration. Even though adsorption of hydrocinnamionitrile occurred via its C $\equiv$ N  $\pi$  system regardless of the coadsorbed species, two SER spectra, one taken with additional  $\text{BH}_4^-$  in the sample and the other with  $\text{Cl}^-$ , were noticeably different. This difference was attributed

TABLE 1

Vibrational assignments for *trans*-cinnamitrile

| Frequency (cm <sup>-1</sup> ) |      | Assignment             |
|-------------------------------|------|------------------------|
| ORS                           | SERS |                        |
| 619                           | 619  | 6b                     |
| 631                           | 629  | HC=CH <i>cis</i> wag   |
| 694                           | 694  | 4                      |
| 755                           | 753  | 11                     |
| 830                           | 825  | 1                      |
| 847                           | 847  | 10a                    |
| 972                           | 973  | 5 or 17a               |
| 1001                          | 1001 | 12                     |
| 1020                          |      | HC=CH <i>trans</i> wag |
| 1031                          | 1027 | 18a                    |
| 1126                          | 1118 | C-C stretch            |
| 1162                          | 1164 | 15                     |
| 1183                          | 1182 | 9a                     |
| 1209                          | 1209 | 13                     |
| 1271                          | 1271 | CH sym wag             |
| 1302                          | 1300 | 3                      |
| 1333                          | 1334 | CH asym wag            |
| 1340                          | 1339 | 14                     |
| 1451                          | 1448 | 19b                    |
| 1496                          | 1492 | 19a                    |
| 1578                          | 1575 | 8b                     |
| 1600                          | 1597 | 8a                     |
| 1620                          | 1614 | C=C stretch            |
| 2216                          | 2230 | C≡N stretch            |

to difference in conformation of adsorbates in two cases. Experimentally, the spectral change was found to be related to the change in surface potential which was affected by the concentration of  $\text{BH}_4^-$ . In the case of *trans*-cinnamitrile, its SER spectrum could be obtained when  $\text{Cl}^-$  was present in the sample. As mentioned previously, a small amount of additional  $\text{BH}_4^-$  was needed to obtain a SER spectrum. However, this was mostly for the aggregation of silver sol particles and did not have anything to do with the surface potential. For example, even though the effective concentration of  $\text{BH}_4^-$  and hence the surface potential changed with the lapse of time after the addition of  $\text{BH}_4^-$ , the SER spectrum of *trans*-cinnamitrile hardly changed. In addition, the bands due to  $\text{BH}_4^-$  were either very weak or absent in the SER spectrum. The above observations indicate that the role of  $\text{BH}_4^-$  is simply in aggregating the silver sol particles in SERS of *trans*-cinnamitrile unlike the case for hydrocinnamitrile.

The intense band at  $260\text{ cm}^{-1}$  in Fig. 1(b) may be assigned to the Ag-Cl stretching vibration. However, considering that the corresponding band appeared at  $240\text{ cm}^{-1}$  in the SER spectrum of hydrocinnamionitrile, only the shoulder peak at  $240\text{ cm}^{-1}$  in Fig. 1(b) may be due to the Ag-Cl stretching vibration. Then, the broad band at  $260\text{ cm}^{-1}$  in Fig. 1(b) may contain the Ag-Cl stretching, Ag-N stretching, and C=C bending vibrations of the olefinic substituent, altogether [28,31,32]. In that case, the Ag-Cl stretching band is much weaker in the SER spectrum of *trans*-cinnamionitrile than in that of hydrocinnamionitrile.

It is not certain why  $\text{Cl}^-$  needs to be present in the Ag sol solution to obtain the SER spectrum of *trans*-cinnamionitrile. Nevertheless, it has been generally agreed [31,33-38] that the role of adsorbed  $\text{Cl}^-$  is to stabilize the co-adsorbed species providing SERS active sites. The argument that the role of  $\text{Cl}^-$  is to stabilize the adsorbed *trans*-cinnamionitrile may be supported by looking at the SER spectrum of the molecule taken in the absence of  $\text{Cl}^-$ . Figure 2(a) represents the SER spectrum of *trans*-cinnamionitrile obtained after adding  $10^{-4}\text{ M BH}_4^-$  alone. Other than the absence of  $\text{Cl}^-$  ions, the experimental conditions under which Fig. 2(a) was obtained were identical to those for Fig. 1(b). It can be seen immediately that the spectral features of Fig. 2(a) are completely different from that of Fig. 1(b). Moreover the peaks appearing in Fig. 2(a) hardly correlate with those in the ordinary Raman spectrum of cinnamionitrile shown in Fig. 1(a). Hence, the species responsible for Fig. 2(a) is believed not to be *trans*-cinnamionitrile adsorbed on silver. Since no peak appears in Fig. 2(a) which can be related to the CN group, the adsorbed species responsible for Fig. 2(a) does not seem to contain this group. One may wonder whether the species responsible for Fig. 2(a) may be a certain impurity originating from the reagent used. Such a possibility could be removed, however, based on gas chromatographic/mass spectrometric analysis. Hence, the species responsible for Fig. 2(a) is likely to be a reaction product of *trans*-cinnamionitrile. In this respect, the role of  $\text{Cl}^-$  seems indeed to be stabilization of the adsorbed *trans*-cinnamionitrile. In the absence of  $\text{Cl}^-$ , the adsorbed *trans*-cinnamionitrile is very likely to produce a new chemical species.

It is well known [39] that organonitriles can be converted to acids in the presence of acid catalyst. Since silver sol particles can function as a soft Lewis acid, such a nitrile-to-acid reaction may also occur in the present system. In this regard, the SER spectrum of *trans*-cinnamic acid has been recorded (Fig. 2(b)). It can be noticed immediately that the spectra shown in Fig. 2(a) and (b) are almost identical. The two spectra exhibit strict correlation in both the peak positions and the relative intensities. The peaks at  $1639$  and  $1394\text{ cm}^{-1}$  in Fig. 2(a) can be ascribed respectively to the olefinic CC stretching vibration and the carboxylate stretching vibration of the *trans*-cinnamic acid molecule [12,23].

It has been argued earlier that the  $\text{Cl}^-$  ions stabilize the adsorbed *trans*-

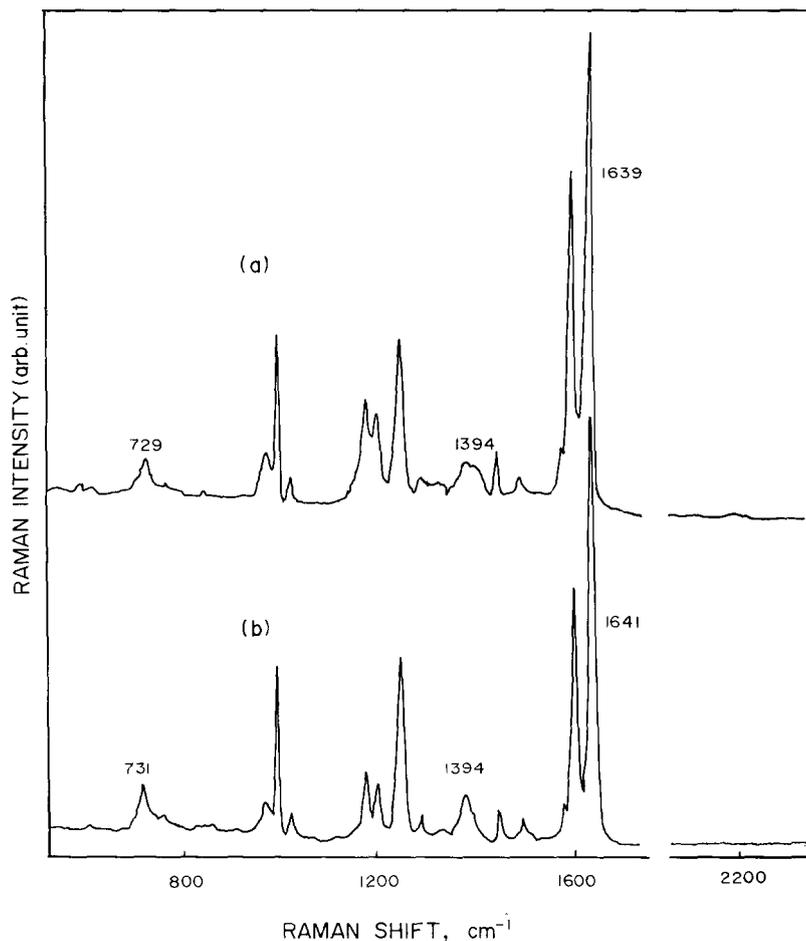


Fig. 2. (a) SER spectrum of  $10^{-3}$  M cinnamionitrile in silver sol without  $\text{Cl}^-$  ions. The sample was circulated through a glass capillary cell. (b) SER spectrum of  $10^{-3}$  M cinnamic acid in silver sol.

cinnamionitrile. The above observation also suggests that the presence of  $\text{Cl}^-$  could be viewed as reducing the Lewis acidity of the silver sol particle so that the nitrile-to-acid reaction is suppressed. However, the presence of  $\text{Cl}^-$  would change the adsorption strength of *trans*-cinnamic acid. The competitive adsorption onto a silver surface of citrate and pyridine [40] has been reported to be strongly influenced by the presence of  $\text{Cl}^-$ . The  $\text{Cl}^-$  ion would similarly enhance the adsorption capability of nitrile while that of its corresponding acid would be lowered. Nevertheless, it may be worth mentioning that a similar observation of nitrile-to-acid conversion was made in the SERS study of *trans*-4-methoxycinnamionitrile in silver sol [41].

The question naturally arises as to whether the nitrile-to-acid conversion is a pure surface reaction or a laser-induced surface photoreaction. In this regard, a SER spectrum of *trans*-cinnamitrile has been obtained without circulating silver sol. The spectrum taken in the absence of  $\text{Cl}^-$  is shown in Fig. 3(a). If the nitrile-to-acid conversion is mainly a surface photoreaction, the SER spec-

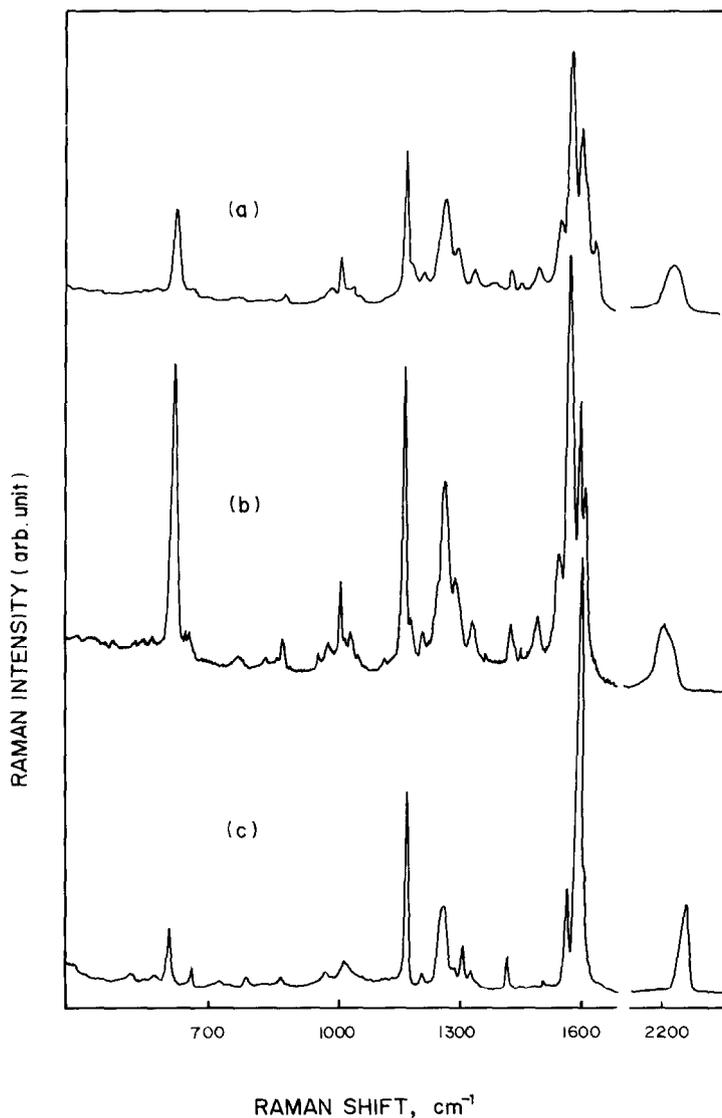


Fig. 3. SER spectrum of  $10^{-3}$  M cinnamitrile in silver sol recorded with sample confined in a narrow (1 mm i.d.) capillary: (a) containing  $10^{-3}$  M KCl; and (b) without added anions. (c) SER spectrum of  $10^{-3}$  M *trans*-4-methoxycinnamic acid.

trum recorded without circulating silver sol is expected to exhibit more intense bands due to the *trans*-cinnamic acid compared with the case recorded under conditions of silver sol circulation. It is seen that the species responsible for Fig. 3(a) is not *trans*-cinnamic acid. Although small amount of acid may be present on the silver surface, the appearance of the  $\nu(\text{CN})$  band in Fig. 3(a) indicates the presence of an adsorbate containing nitrile group on the silver surface. However, the adsorbed species does not seem to be *trans*-cinnamionitrile, because the peaks in Fig. 3(a) hardly correlate with those in the ordinary Raman spectrum (Fig. 1(a)) of the molecule. It is thought that the major species exhibiting Fig. 3(a) is a certain nitrile compound produced by surface photoreaction. Although its exact identity is not known, it is apparent that the photoreaction product is not formed via *trans*-cinnamic acid, otherwise the peak assignable to the  $\nu(\text{CN})$  mode would be absent in Fig. 3(a).

It has been mentioned earlier that the SER spectrum of *trans*-cinnamionitrile recorded in the absence of  $\text{Cl}^-$  with the Ag sol circulation is due to the *trans*-cinnamic acid produced on the silver surface. This may be in conflict with the above argument that the species responsible for Fig. 3(a) is neither *trans*-cinnamic acid nor its derivative, but a certain nitrile compound formed from *trans*-cinnamionitrile. One of the possible explanations for these seemingly conflicting observations is to assume that under the experimental conditions giving Fig. 2(a) a considerable amount of *trans*-cinnamionitrile exists on the Ag surface as a multilayer species above the first layer of *trans*-cinnamic acid. In other words, the *trans*-cinnamionitrile molecule is converted to its conjugate acid by the catalytic action of silver, and as the laser power increases the overlying *trans*-cinnamionitrile molecule is transformed to a certain nitrile derivative, which replaces the *trans*-cinnamic acid species already present on the silver surface.

When the silver sol circulation was stopped, the SER spectrum of photoreaction products similar to that shown in Fig. 3(a) was immediately obtained even in the presence of  $\text{Cl}^-$ . A typical spectrum is shown in Fig. 3(b). It can be seen that the spectral features of Fig. 3(b) are completely different from those of Fig. 1(b), but rather similar to those of Fig. 3(a). The peaks in Fig. 3(b) are much more intense than those in Fig. 3(a). One noticeable feature is that a small amount of *trans*-cinnamionitrile also appears to be present on the silver surface when spectra like that shown in Fig. 3(b) are obtained. These observations indicate that the photoreaction product giving Fig. 3(a) is formed directly from *trans*-cinnamionitrile. It should also be mentioned that the peak assignable to the Ag-Cl stretching mode is very weak in Fig. 3(b) compared with the case of Fig. 1(b). This may suggest that the adsorption strength of the unknown photo product is greater than that of  $\text{Cl}^-$ .

The identities of the photo products showing SER spectra in Fig. 3(a) and (b) are not certain. An increasing amount of attention has recently been given to the photochemistry of cinnamionitrile. Typically, cinnamionitrile [42-46]

has been known to undergo *cis-trans* isomerization, reduction to hydrocinnamitrile, polymerization, hydrodimerization and cycloaddition. So far efforts to explain the SER spectra shown in Fig. 3(a) and (b) based on these reactions have been fruitless. However, it may be worth mentioning that the spectra shown in Fig. 3(a) and (b) are quite similar to the SER spectrum of *trans*-4-methoxycinnamitrile shown in Fig. 3(c). Hence, it may be supposed that the species responsible for Fig. 3(a) and (b) is a kind of *para*-disubstituted benzene with a nitrile group. If this is true, the photochemistry of cinnamitrile should be of great concern from the synthetic point of view. In this respect further studies on the surface photochemistry of cinnamitrile need to be carried out.

In summary, it has been observed that *trans*-cinnamitrile exhibits relatively large Raman enhancement when both  $\text{Cl}^-$  and  $\text{BH}_4^-$  ions were present in aqueous silver sol. The molecule was found to adsorb on the silver surface via its nitrogen lone pair electrons. In the absence of coadsorbed chloride ions, the molecule was converted to *trans*-cinnamic acid by a surface reaction. In the course of interpreting the SER spectra, the vibrational assignment has been made for the *trans*-cinnamitrile molecule in the liquid state.

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