RAMAN STUDY OF THE PHOTOCHEMISTRY OF MALEIC ACID ADSORBED ON THE SURFACE OF COLLOIDAL SILVER

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ABSTRACT : *The surface- enhanced Raman scattering (SERS) spectra of maleic (cis; 2- butaneoic acid) and fumaric (trans; 2- butaneoic acid) acids adsorbed on aqueous silver sol particles are reported. These two acids form two groups of isomers which differ only in the relative positions of the two carboxylate groups.*

The photochemistry of maleic and fumaric acids adsorbed on the surface of silver colloids is investigated using SERS as a probe. The photochemical studies of these two acids adsorbed on colloidal silver surfaces show that the photoisomerization of maleic to fumaric acid has occured. We interpret our spectra as indicating that fumaric acid π bonds through a C=C double bond, while maleic acid σ bonds through lone pairs on the carboxylate groups.

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INTRODUCTION :

In the past 14 years, the spectroscopy of surface- enhanced Raman scattering has become a powerful tool for investigation of the vibrational spectra of adsorbed molecules [1-7]. SERS is a phenomenon in which the Raman scattering cross section of molecules adsorbed on the surfaces of certain metals is enhanced by as much as 10^6 compared to the cross section for normal Raman scattering.

The Raman intensity of adsorbed species on a metal surface may be considered as a product of molecular and electromagnetic effects. The first is related to the possibility of a change in the Raman polarizability of the adsorbed molecules by formation of charge- transfer complexes with the metal surfaces [8]. The second is associated with the enhanced electric fields that exist at the surface of metal particles with small radii of curvature and is only obtained for metals for which the complex part of the dielectric constant is small [8].

Enhanced surface photochemistry of molecules adsorbed on surfaces capable of surface-enhanced Raman was first considered by *Nitzan* and *Brus* [9], and expanded by *Metiu* [10] and *George* [11] and their co- workers.

The use of SERS makes it possible to study insitu the photochemistry of molecules adsorbed on the surface of colloids. Experimental and theoretical studies involving infrared [12] and visible [13] excitation of adsorbed molecules resulting both in photodesorption and in light-induced chemical transformation of the adsorbate have been reported.

In this paper, we present and discuss the geometry and photoisomerization of maleic acid adsorbed on colloidal silver surfaces. The photoisomerization studies are carried out by irradiating the adsorbates and interpreting the SERS spectra.

EXPERIMENTAL :

Silver sols were prepared as follows. A sodium borohydride solution (60mL of 2×10^{-3}M) was mixed with a silver nitrate solution (22 ± 2mL of 1×10^{-3}M) where both solutions were chilled to ice temperature. Silver ions are reduced to silver metal by the borohydride ions. Sodium borohydride is a strong reducing agent. At room temperature, it is hydrolyzed slowly with the evolution of hydrogen , $NaBH_4 + 2H_2O \longrightarrow NaBO_2 + 4H_2$. Therefore, chilling of both solutions to ice temperature may be necessary to avoid this reaction. When the two solutions were mixed immediately, yellow or orange yellow colloid solutions were produced. Aggregation of the yellow or orange yellow colloid took place one or two hours after mixing the two solutions. The pH of these colloid solutions was measured to be near 7.

The unaggregated colloid consists of fairly uniform silver spheres approximately 200Å in diameter. A simple calculation shows that the average distance between two colloid particles is about 10^4Å. There are about 5×10^{11} colloid particles/cm^3 of colloid solution. Aggregation does not produce coalescence into larger particles but rather assemblies of apparently randomly adhering spheres, each of about the original dimensions. These large-assemblies are presumably responsible for the color change of colloid solution from yellow to blue after adding absorbate. Maleic acid of purity 99.5% was used without further purification.

The adsorbates were introduced into the colloid by dissolving the acids in pure triply distilled water. A few measured drops of these aqueous solutions were added to approximately 3mL of colloid.

The light source was the 488nm line of an Ar ion laser (*Spectra- Physics* Model 165, Ontario, Canada). The spectra were recorded using a SPEX 1400 series monochromator equipped with a *Hamamatsu* R955 phototube (Ontario, Canada) and a *Princeton Applied Research* 1140A photon counter. All were interfaced to a *Tektronix* 4052 computer. Typical running conditions for the surface- enhanced Raman

spectra are as follows:

$5 cm^{-1}$ slit width, $3 cm^{-1}$ step size, laser at a power level of 200mW, 0.5S counting time per step. The alignment of the scrambler was checked by measuring depolarization data for pure CCl_4.

RESULTS AND DISCUSSION :

The SERS spectra of maleic and fumaric acids adsorbed on aqueous silver sol particles are shown in Figs. (1-3). When fumaric acid was added the yellow colloidal solution changed color to deeper red then to blue over a period of several seconds. In the case of maleic acid the yellow color changed to blue over a period of several minutes. The SERS spectra of maleic and fumaric acids adsorbed on silver are much more intense than their ordinary solution Raman counter- parts.

The band assignments were taken from the work of *Maillois* et al [14]. The strongest band in the spectrum of maleic acid is at $1400 cm^{-1}$ and that of fumaric acid at $1648 cm^{-1}$ (A_{1g} mode). The former is unequivocally assigned to the symmetric stretching vibration of the carboxylate group (A_1 mode), indicating simultaneously, that maleic- acid binds to the surface as an anion and the $-COO^-$ group is almost certainly on the surface and forms the surface bond, while the latter is assigned to the symmetric stretching vibration of the $C=C$ bond (A_g mode) indicating that fumaric acid π bonds to the surface via the ethylenic double bond.

The fumarate and maleate ions are the trans and cis forms of the ions of ethylene dicarboxylic acid. The former is planar, (C_{2h}) while the latter is nonplanar (C_{2v}) [15] implying that the plane of the carboxylate group is rotated 90° relative to the plane formed by the two hydrogens and the $C=C$ bond. It is suggested that the maleate ion "stands up" on the surface, bonding through the carboxylate group while the fumarate π bonds via the $C=C$ bond.
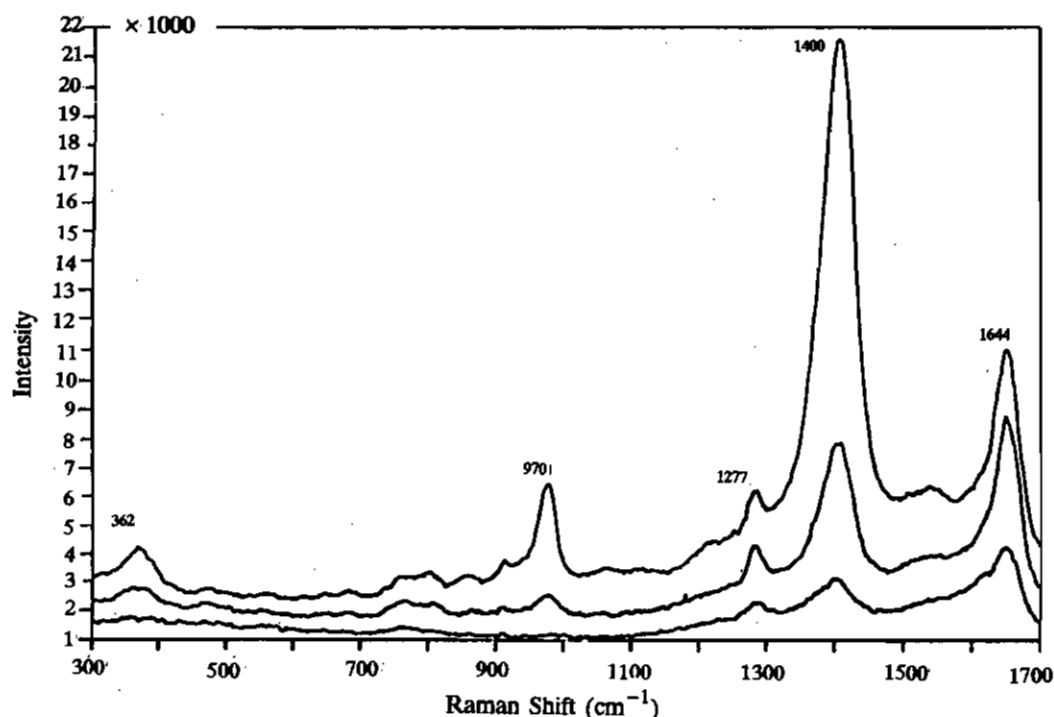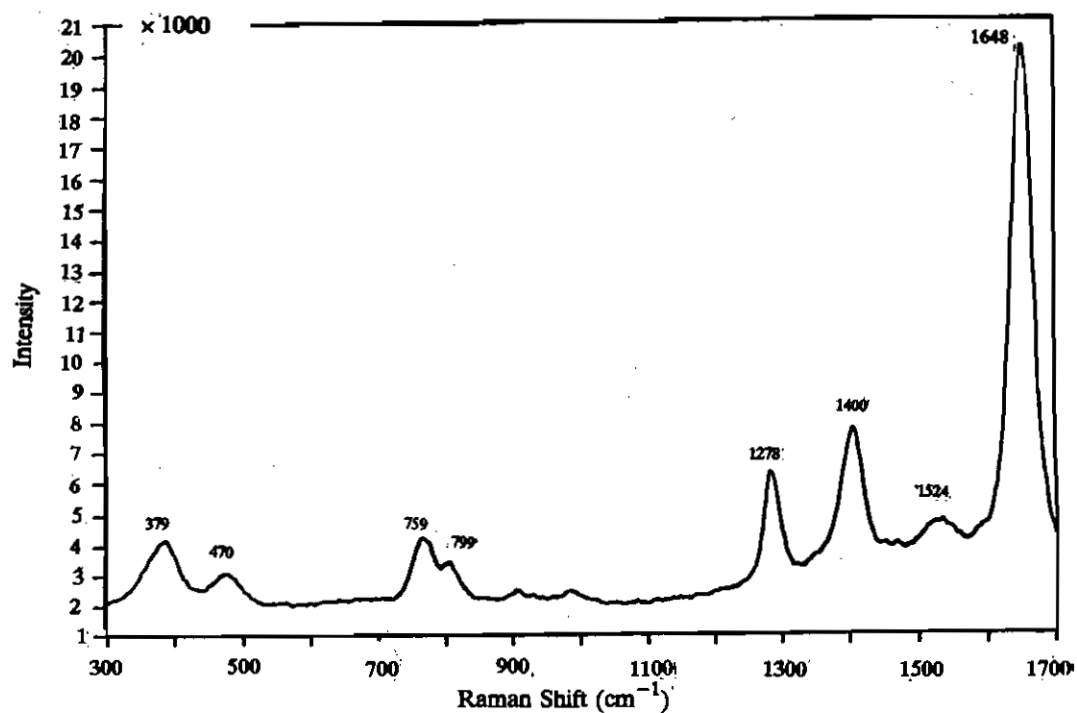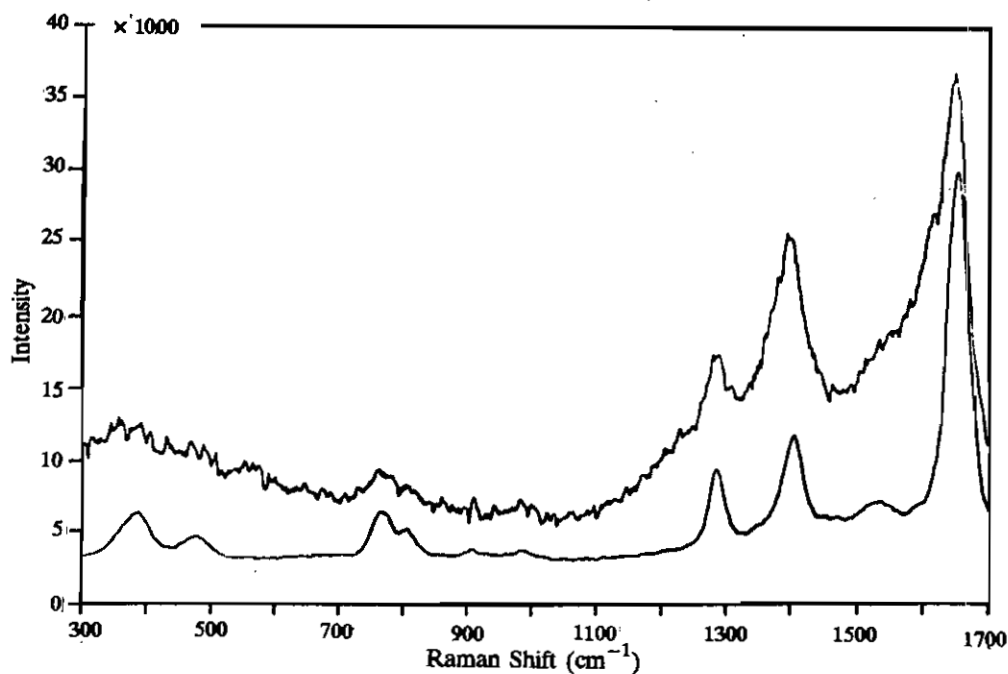

Fig. 1 : *SERS spectra of maleic acid adsorbed on the surface of silver colloid excited with 488nm argon ion laser light (top: before irradiation; middle: after irradiating with xenon arc- lamp for 30 seconds; botton: after irradiating for 60 seconds).*

Fig. 2 : SERS spectrum of fumaric acid adsorbed on the surface of silver colloid excited with 488nm argon ion laser light (after irradiating with xenon arc- lamp for 60 seconds).

Fig. 3 : SERS spectra of maleic and fumaric acids adsorbed on the surface of silver colloid excited with 488nm argon ion laser light. (top: maleic acid after irradiating with xenon arc-lamp for 60 seconds; bottom: fumaric acid- before irradiation).

There are three other groups of spectral features in our SERS spectra which aid us in determining the structure of the molecule and its disposition with respect to the surface. These are as follows: In the SERS spectrum of fumarate, the C=C vibration should be the most prominent, the C-H stretching modes should be weak, and no metal- adsorbate vibration should be seen; while in SERS spectrum of maleate we expect to see more intense C-H stretching, a greater representation in the spectrum of -COO⁻ vibrations, and a higher frequency metal-adsorbate vibration. In fact our spectra are in accord with a maleic acid molecule bonded to the metal surface through the COO⁻ groups and a fumaric acid molecule π bonded to the surface via the C=C bond. The C-COO⁻ vibration is also intense in the SERS spectrum of adsorbed maleic acid , which is not unexpected on the basis of its having a rather large component normal to the metal surface. The surface geometry of the maleate and fumarate ions is shown in Fig. 4.

Extensive band assignment for potassium maleate and fumarate in aqueous solutions have been reported by *Maillios* et al [14] based on infrared and Raman studies. Fortunately adsorption onto silver produces sufficiently small frequency shifts to allow the assignment of the surface enhanced Raman spectra directly on the basis of ref.14. The observed frequencies and
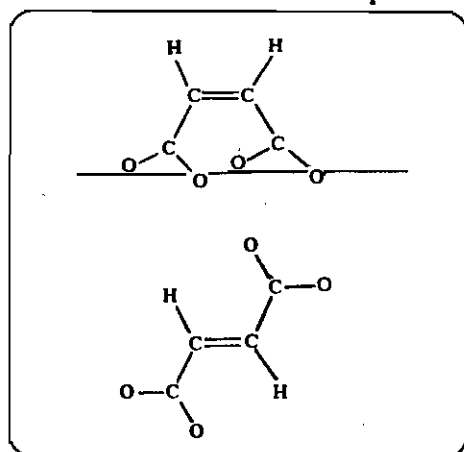

Fig. 4 : The proposed surface geometries of the maleate (upper) and fumarate (lower) ions bonded to the surface.

band assignment are summarized in Tables 1 and 2).

To study photochemical reactions of maleic and fumaric acids on the surface, we have irradiated these molecules by employing the total output of an xenon arc- lamp. To reduce thermal effects, a pure water filter was used. it is clear that the SERS spectrum of maleic acid is dramatically changed upon irradiation (Fig. 1).

The dominant band at 1400cm⁻¹ and the band at 970cm⁻¹ (C-COO⁻ vibration) become much less intense due to irradiation. In the case of fumaric acid the SERS spectra, before and after irradiation, are identical and no major changes were observed. These experimental evidences indicates that upon irradiation,fumaric acid was not photoisomerized.Infact, the SERS spectra of maleic (after irradiation) and those of fumaric acid (either before or after irradiation) are almost identical. This leads us to the conclusion that the photoisomerization of maleic acid molecules adsorbed on the silver surface has occured.

In order to find the suitable wavelengths which could cause the isomerization of maleic acid the xenon arc- lamp was equipped with a monochromator. By irradiating the adsorbate molecules at wavelenghths 400, 488 and 600nm, we have observed similar spectral changes to those seen for the total output of xenon arc- lamp. It should be noted that the spectral changes at 600nm were slower than those of 400 and 488nm. Further experiments are underway to study the kinetics of the photoisomerization reaction.

As was mentioned in the experimental section the purity of maleic acid used in our experiments was 99.5%. To clarify that the isomerization was not due to impurities in the maleic acid, we performed SERS experiments with mixtures of 99% maleic and 1% of fumaric acid. The resulting spectra were exactly the same as those of the original samples of maleic acid, indicating that photoisomerization was not due to minute amount of impurities in the original maleic acid.

Table 1 : observed frequencies (cm^{-1}) and assignments for maleic acid.

Raman (aqueous solution) (Ref. 14)		SERS		Types of Vibrational modes	Assignments (Ref.14)
1641	(vs)	1644	(s)	A_1	ν(C-C)
1398	(vs)	1400	(vs)	A_1	ν_I(C=O)
1306	(m)	1277	(m)	A_1	δ(CH) plane deformation
977	(m)	970	(m)	B_1	ν(C-COO$^-$)
900	(vs)	903	(w)	A_1	ν(C-COO$^-$)
850	(w)	797	(w)	B_1	δ(CO$_2^-$)
750	(w)	757	(w)	A_1	δ(CO$_2^-$)
334	(m)	362		A_2	γ(C-COO$^-$) out of plane deformation

Table 2 : observed frequencies (cm^{-1}) and assignments for fumaric acid.

Raman (aqueous solution) (Ref. 14)		SERS		Types of Vibrational modes	Assignments (Ref.14)
1655	(vs)	1648	(s)	A_g	ν(C=C)
1565		1524	(w)	A_g	ν_{iv}(C=O)
1403	(vs)	1400	(s)	A_g	ν_1(C=O)
1280	(vs)	1278	(s)	A_g	δ(CH) plane deformation
980	(s)	980	(w)	A_g	ν(C-COO$^-$)
905	(s)	901	(w)	B_g	γ(CH) out of plane deformation
768	(m)	799	(w)	A_g	δ(CO$_2^-$)
-		754	(m)	-	-
432	(m)	470	(w)	A_g	r(CO$_2^-$) rotation
-		379	(m)	-	-

We thus, propose that a photo-induced, charge-transfer reaction on the silver surface is probably responsible for the photoisomerization process. The C=C double bond absorbs photons to go to the excited states and subsequently the excited electron is transferred to the silver metal. This charge-transfer process leaves the adsorbate to be a C-C single bond, which can rotate freely.

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