Surface enhanced Raman spectra of the organic nonlinear optic material: Methyl 3-(4-methoxy phenyl)prop-2-enoate

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Abstract. The surface geometry of methyl 3-(4-methoxy phenyl)prop-2-enoate molecule was studied by analysis of the SERS spectra adsorbed on silver colloid surfaces. For a reliable analysis of the SERS spectrum, we also performed density functional theoretical calculations. The absence of a C–H stretching vibrations and the observed C–H out-of-plane bending modes suggest that the MMP molecule may be adsorbed in a flat on orientation to the surface. The SERS spectral studies predict a tilted orientation of ethylenic bridge with respect to the phenyl ring.

Keywords. Adsorption behaviour; SERS; methyl 3-(4-methoxy phenyl)prop-2-enoate; silver nanoparticles; DFT.

1. Introduction

The elucidation of the adsorption mechanism of organic compounds on metal surfaces is of fundamental as well as practical interest.[1–2] An increased understanding of the interaction of the molecules with metal surfaces has been accompanied by a growing awareness that many surface-adsorbate interactions have their analogues in the field of organomettalic and co-ordination chemistry. Surface-enhanced Raman scattering (SERS), using silver, gold, or other noble metals as substrates,[3–5] is a powerful technique for studying the adsorption behaviour of molecules on substrates, revealing the molecules' orientation and the mechanism of interaction of the molecules with the surface of the substrate in which researchers are interested.[6–7] SERS is widely used to elucidate information about the behaviour of biomolecules adsorbed at the metal surfaces, orientation of adsorbed species and the changes in the orientation induced by external factors. In addition, the adsorption of molecules on metal particles reduces the fluorescence background and hence the technique is useful in the study of biological samples.[8–10] Most reported studies pertaining

to the adsorbate molecules, possessing one or more σ-donor atoms such as N, O and S, many of which possess potential π-donor systems such as an aromatic ring, which could compete for interaction with the surface. The enhancement of selective vibrational modes and band shifts observed in SERS have usually been explained in terms of the charge-transfer model, and are found to be sensitive to the orientation of the molecules with respect to the surface.[11–13] The technique is therefore expected to provide interesting information on the sites through which the interaction takes place and also the molecular orientation with respect to the metal surfaces. The present study reports the SERS spectral analysis of methyl 3-(4-methoxy phenyl)prop-2-enoate (MMP) supported by density functional computations (DFT) to derive information about the adsorption geometry and other molecular bonding features.

2. Experimental

Single crystals of methyl 3-(4-methoxyphenyl)prop-2-enoate (figure 1) were prepared in a methanol solution by a slow evaporation technique.[14] Colourless transparent crystals of title compound were obtained

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within 2 weeks. Repeated recrystallisation yielded good quality crystals. The single crystals of maximum size of around 0·6 mm were obtained.

2.1 *Preparation of silver colloid*

Silver colloid was prepared by reduction of silver nitrate by sodium citrate, using the Lee and Meisel's method.[15] In 500 ml of deionized water, 90 mg of silver nitrate was dissolved and the solution was heated to boiling. Then 10 ml of a 1% trisodium citrate aqueous solution was added into the boiling silver nitrate solution drop-wise, accompanied by vigorous stirring. The mixed solution was kept boiling for a further 10 min. Finally, a green–gray silver colloid was obtained, which was stable for several days or weeks. The stability of the colloid was ascertained using an Ocean Optics model S2000 fibre optic UV-visible-NIR spectrometer.

2.2 *Instrumentation*

The NIR FT-Raman spectrum (figure 2) was obtained on a RFS 100/s BRUKER spectrophotometer. Nd: YAG laser at 1064 nm with an output of 300 mW was used as the exciting source with liquid nitrogen cooled Ge-diode detector. 1000 scans were accumulated with a total registration time of about 30 min. The spectral resolution after apodization was 6 cm^{-1}. A correction according to the fourth power scattering factor was performed, but no correction to instrument was done. The upper limit for the Raman shift is 3500 cm^{-1} due to the detector sensitivity and the lower Raman shift is around 10 cm^{-1} due to the Raleigh line cut-off by a notch filter.

SERS measurements were performed on a single stage imaging spectroscope (ISA Jobin-Yvon Spex HR-320, f/4.1) fitted with a liquid nitrogen cooled CCD det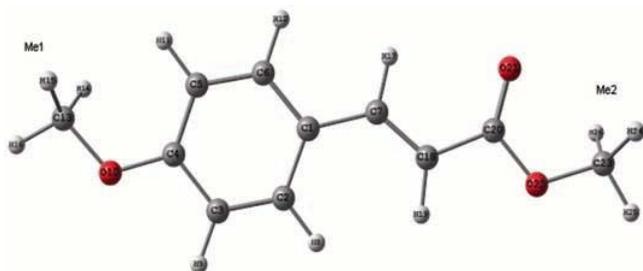ector (Spectrum one, 2000 × 800 pixels with an active area of 30 × 12 mm). The spectra were recorded with a 600 g/mm grating blazed at 1 μm (7 cm^{-1}). NIR laser excitation of 785 nm was provided by an SDL-8350 diode laser. To a 5 ml of silver colloid an equal volume of 10^{-4} M aqueous solution of MMP was added. The resultant solution having dark green colour was transferred to quartz cuvettes and the SERS spectra is recorded (figures 3 and 4).

3. Computational details

DFT calculations were carried out using the A.8 revision of the GAUSSIAN 98 program package.[16] All calculations, which include: geometry optimizations and vibrational spectra were performed on isolated systems using the Becke's three parameter B3LYP exchange-correlation functional.[17] The 6-31G (d) basis set[18] was chosen as a compromise between accuracy and applicability to large molecules. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. All optimized structures were confirmed to be minimum energy conformations. Harmonic vibrational wave numbers were calculated using analytic second derivatives to confirm the convergence to minima on the potential surface and to evaluate the zero-point vibrational energies. At the optimized structure of the examined species no imaginary frequency modes were obtained, proving that a true minimum on the potential energy surface was found. The optimum geometry was determined by minimizing the energy with respect to all geometrical parameters without
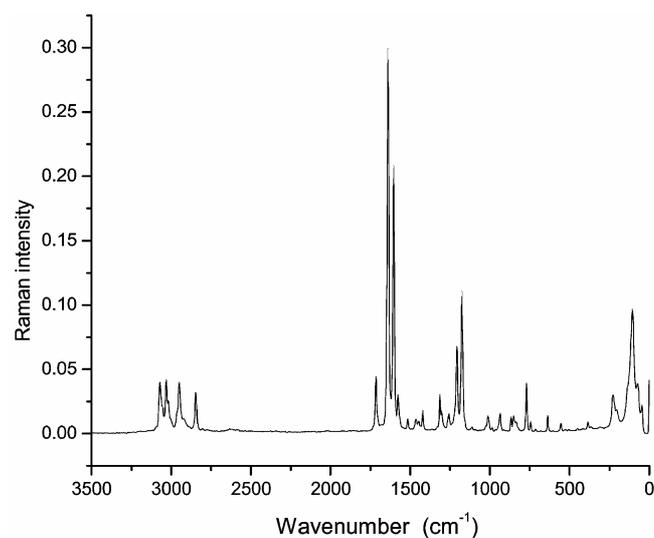

Figure 1. Molecular structure of MMP.
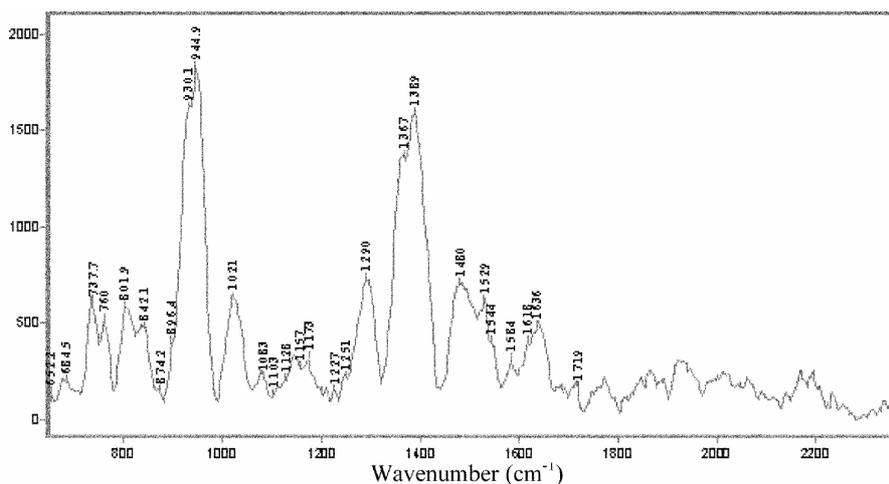

Figure 2. NIR–FT Raman spectrum of MMP.

Figure 3. NIR–FT SERS spectrum of MMP (2400–600 cm^{-1}).

imposing molecular symmetry constraints. The calculated harmonic vibrational wavenumbers were scaled down uniformly by a factor of 0·96 as recommended by Scott and Radom.[19]

4. Results and discussions

The SERS spectrum of MMP has been recorded and the vibrational analysis is performed by comparing it with the normal Raman spectrum. The vibrational spectrum calculated at B3LYP/6-311G (d, p) is used to determine the vibrational modes unambiguously. The calculated vibrational wavenumbers, measured SERS and Raman band positions and their tentative assignments are given in table 1. The adsorption mechanism of an adsorbate can be deduced from its SERS spectrum. The orientation of the adsorbate on the metal surface will depend on the active sites through which the interaction takes place. The chemically possible orientations of the MMP molecular ion with respect to the silver surface can be envisaged: 'flat' or lying down on the metal surface through bonding with the ring system or 'standing up' (end-on) with bonding through the lone pair of the oxygen atom with silver.[20–23] The orientation of the molecule on the silver surface can be inferred from aromatic C–H stretching vibrations, ring stretching vibrations, the ring breathing mode, in plane and out-of-plane vibrations and the SERS surface selection rule.

The ring stretching vibrational modes of the phenyl ring with vibration numbers 14, 19a, 19b, 8a and 8b among which the degenerate vibrations are observed around 1600 cm^{-1}.[23–25] The vibrational mode corre-

sponding to the band at a wavenumber of 1618 cm^{-1} and 1585 cm^{-1} in SERS is also observed in normal Raman spectrum at 1604 cm^{-1} and 1577 cm^{-1} as a strong band. Here the ring mode is blue shifted by around 10 cm^{-1} along with the substantial band broadening in SER spectrum. This indicates the direct interaction of benzene ring moiety with the metal surface, as well documented in literature[5–7] and the probability of direct ring π orbital to metal interaction should be high.[23–25] This can be interpreted as the bond weakening in the benzene ring system caused by the back donation of the metal d electrons to the benzene ring antibonding π^* orbitals.[25] The modes corresponding to 19a can be found at 1516 cm^{-1} in Raman spectrum are down-shifted in SERS spectrum at 1529 cm^{-1} and their bandwidths are hardly affected. The SERS band at 1389 cm^{-1} is up-shifted by about 30 cm^{-1} and the band width is decreased with respect to the corresponding band at 1419 cm^{-1} in Raman spectrum. From the observed both down-shifted and up-shifted peaks, it is difficult to make an unambiguous orientation of the absorbed molecules using ring stretching vibrations.

The C=C stretching, observed as a strong characteristic band in cinnamic acid derivatives, can be seen in MMP at 1639 cm^{-1} in Raman spectrum as a strong band. This band is blue-shifted to 1647 cm^{-1} in SERS spectrum followed by an intensity reduction, which predicts a tilted orientation of the ethylenic bridge with respect to the phenyl ring. The ethylenic bridge is slightly out of the plane with the O–Me bond of CH$_3$ on the metal surface, favoured by π orbital metal surface interaction.[23–25] The CH$_3$ asym-
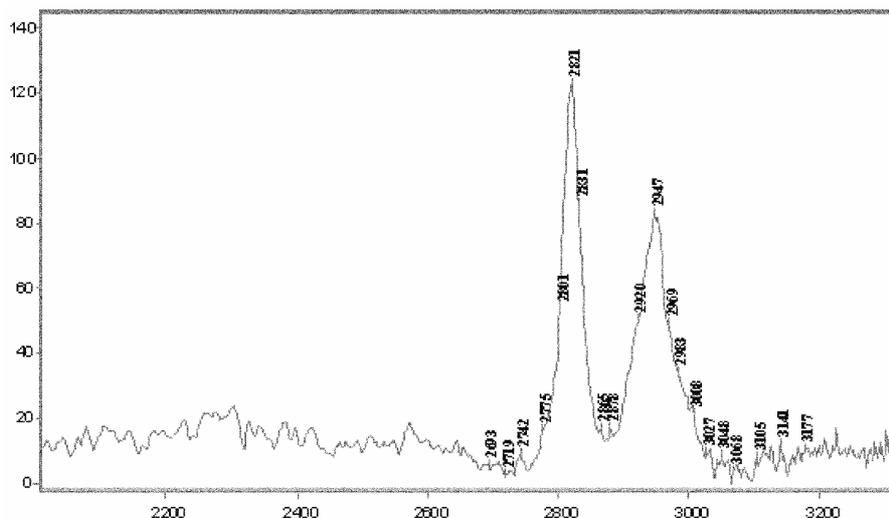
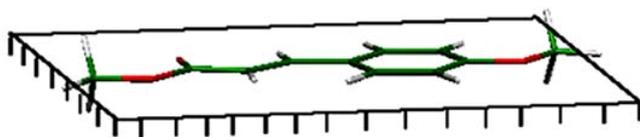**Figure 4.** NIR–FT SERS spectrum of MMP (2200–3200 cm⁻¹).

Figure 5. Schematic model for the adsorption geometry of MPP on a colloidal sliver surface.

metric bending mode can be observed as a medium intense in MMP at 1480 cm⁻¹ in SERS, which confirms a flat orientation of the CH₃ in the adsorbed molecule with respect to the metal surface. Moreover, the medium intense band at 1716 cm⁻¹ in the NIR–FT Raman spectrum assigned to the carbonyl stretching vibration is not observed in the SERS spectrum and this also supports the above assumption. The carbonyl stretching appears only as a very weak band at 1719 cm⁻¹ in the SERS spectrum. The weakening of this carbonyl stretching vibration indicates that the C=O is not in direct interaction with the silver surface.

In the case of aromatic molecules, the intensity of out-of-plane vibrational modes increases substantially relative to the in-plane vibrational modes when the absorbate orientation is altered from vertical to flat on orientation.[20–25] The in-plane vibrational modes occur both in Raman spectrum and SERS spectra in the region 1300–1000 cm⁻¹. Some of the in-plane vibrational modes are not observed in the SERS spectrum. The intensity of the SERS band is less than

that of the band in Raman spectrum. Similarly, aromatic out-of-plane C–H bands with respect to the in-plane bending mode increases as the molecule is adsorbed on almost flat to the silver surface.[23–25] The absence of some of the in-plane bending modes also indicates that the probability of the absorption of the MMP molecule in a flat on orientation is greater.

The SERS spectrum of the molecules, which are flat on the metal surface, would contain strong out-of-plane vibrations. For a benzene molecule lying flat on the surface, the intensity of the C–H stretching mode would be almost zero, since the C–H stretching vibrations do not have contributions from α_{zz}, α_{xz} and α_{yz} Raman polarizability components which would result in strong SERS intensity.[24] However, the out-of-plane vibrations do have large contributions from these Raman polarizability components. In MMP shows four C–H out-of-plane vibrations at 930 cm⁻¹, 896 cm⁻¹, 842 cm⁻¹ and 760 cm⁻¹ in SERS spectrum having medium intensity. However, it does not show any C–H stretching vibrations. The entire C–H out-of-plane bending modes belong to an 'A' species, which has the polarizability components α_{xz} and α_{yz}. The observed C–H out-of-plane bending modes, obtain their SERS intensity from these Raman polarizability components. The absence of a C–H stretching vibrations and the observed C–H out-of-plane bending modes suggest that the MMP molecule may be adsorbed in a flat on orientation to the surface (figure 5). The enhancement methyl asymmetric (2947 cm⁻¹), symmetric stretch-

Table 1. Calculated vibrational wavenumbers, measured SERS and Raman band positions (cm^{-1}) and assignments for methyl 3(4-methoxy phenyl) prop-2-enoate.

B3LYP/6311G(d, p) V_{cal}	ν_{SERS}	ν_{Raman}	Assignments
2971	2960 sh	2947 m	CH$_3$ asym. stretch
2910	2846 m	2821 s	CH$_3$ sym. stretch
1727	1716 m	1719 w	C=O stretch
1632	1639 vvs	1636 m	C$_7$=C$_8$ stretch
1602	1604 vs	1618 sh	8a ring stretch
1558	1577 w	1584 w	8b ring stretch
1504	1513 vw	1529 m	19a ring stretch
1462		1480 m	CH$_3$ asym. bend
1415	1419 vw	1389 s	19b ring stretch
1340		1367 s	CH$_3$ sym. bend
1303	1304 vvw	1290 m	3, C–H i.p bend
1171	1176 m	1173 w	CH$_3$ rock
1155		1157 w	9b, C–H i.p bend
1099		1083 w	18b, C–H i.p bend
1016	1024 w	1021 m	C$_{18}$–H$_{19}$ i.p bend
931		945 vs	C–O=O i.p bend
926	935 w	930 s	C$_{18}$–H$_{19}$ o.p bend
915		896 sh	17b, C–H o.p bend
831	840 vvw	842 m	10a, C–H o.p bend
792		801 m	1 ring breadth
755	769 m	760 m	C–H o.p bend
732	744 vvw	738 w	C–H o.p bend
678		683 w	C$_{18}$–H$_{19}$ i.p bend
2971	2960 sh	2947 m	CH$_3$ asym. stretch
2910	2846 m	2821 s	CH$_3$ sym. stretch
1727	1716 m	1719 w	C=O stretch
1632	1639 vvs	1636 m	C$_7$=C$_8$ stretch
1602	1604 vs	1618 sh	8a ring stretch
1558	1577 w	1584 w	8b ring stretch
1504	1513 vw	1529 m	19a ring stretch
1462		1480 m	CH$_3$ asym. bend
1415	1419 vw	1389 s	19b ring stretch
1340		1367 s	CH$_3$ sym. bend
1303	1304 vvw	1290 m	3, C–H i.p bend
1171	1176 m	1173 w	CH$_3$ rock
1155		1157 w	9b, C–H i.p bend
1099		1083 w	18b, C–H i.p bend
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732	744 vvw	738 w	C–H o.p bend
678		683 w	C$_{18}$–H$_{19}$ i.p bend

ing (2821 cm^{-1}), asymmetric bending (1480 cm^{-1}) umbrella (1367 cm^{-1}) and rocking mode (1173 cm^{-1}) further support the orientation of MMP on a silver surface is flat on orientation of the benzene ring moiety on a silver substrate.

5. Conclusion

The comparative study of normal Raman spectrum with the SERS along with the scaled DFT calculations predicts the adsorption geometry of MMP on

silver surface. The SERS spectral analysis indicated that the MMP molecules should be bound to silver as flat on orientation of the benzene ring moiety on a silver substrate. The absence of a C–H stretching vibrations and the observed C–H out-of-plane bending modes suggest that the MMP molecule may be adsorbed in a flat on orientation to the surface. The SERS spectral studies predict a tilted orientation of ethylenic bridge with respect to the phenyl ring.

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