

Vibrational and surface-enhanced Raman spectra of vanillic acid

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The 3-methoxy-4-hydroxybenzoic acid or vanillic acid (VA) is a naturally occurring molecule important in winemaking. The spectral fingerprints of VA observed in the infrared and Raman spectra are assigned to fundamental vibrational wavenumbers supported by quantum chemical computations. The surface-enhanced Raman scattering (SERS) of the VA has been obtained in silver colloidal solutions making possible analytical applications for detection of VA at picomole concentrations. Copyright © 2008 John Wiley & Sons, Ltd.

KEYWORDS: absorption infrared spectroscopy; chemisorptions; surface-enhanced Raman scattering; vanillic acid

INTRODUCTION

Vanillic acid (VA) is a naturally occurring organic acid that has been isolated and characterized in rice,¹ as an end product of metabolic processes,² wine making³ among many other natural sources of VA. There are several reports on the separation of phenolic acids (including VA) and partial identification using Fourier transform infrared (FTIR) spectroscopy.⁴ VA has also been included as one of the phenolic acids tested in Fourier transform surface-enhanced Raman scattering (FT-SERS) studies.⁵ However, a detailed study of the vibrational fingerprints of VA is not available, and it is a necessary first step for its identification and development of a protocol for sensitive chemical analysis. The purpose of this work is to provide the vibrational infrared and Raman spectra to identify the fingerprints of VA, and show the results of surface-enhanced Raman scattering (SERS)⁶ on silver colloids.

EXPERIMENTAL

Analytical grade VA and silver nitrate were obtained from Sigma Aldrich and used without further purification. Raman spectra of the pure VA solid were obtained directly from the powder, while IR spectra were recorded from the powder dispersed in KBr pellets. All Raman spectra were collected

with a Renishaw research Ramanscope 1000, or a Renishaw in Via Raman microscope, both equipped with Peltier-cooled CCD detectors (-70°C), and Leica microscopes. The spectrographs use 1800 g/mm gratings with additional band-pass filter optics. Excitation lines of 442, 514.5, and 632.8 nm were used, and did not reveal any significant dispersion in relative intensities. SERS spectra in solution were recorded using the macro attachment and a 15 \times objective. All infrared absorption measurements were recorded with a Perkin Elmer FTIR spectrometer, System 2000, employing a DTGS detector. Each spectrum was measured with 300 scans, and 4 cm^{-1} resolution. Citrate and borohydride⁷ colloidal silver was prepared according to the procedure given in Ref. 6 pp. 144–146. The colloidal Ag was used as prepared without further dilution or aggregation with salts.

Computational methods

All reported calculations have been performed using the Gaussian 98 (Revision A.3) suite of programs,⁸ and employed Becke's three parameter functional including the correlational functional of Lee *et al.*,⁹ B3LYP. In order to calculate an optimized structure and vibrational spectra for VA, the 6-311G(d,p) basis set was employed using tight convergence criteria. All peaks in the presented calculated Raman and infrared spectra were scaled with a 0.9669 scaling factor,¹⁰ and artificially given a 7 cm^{-1} full width at half maximum. The calculated spectra (harmonic approximation for an isolated molecule) are to be seen as a guide to the assignment of vibrational modes where large differences between observed and calculated values should be expected since the experimental spectra

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correspond to solid samples with strong hydrogen bond interactions.

RESULTS AND DISCUSSION

Infrared and Raman spectra

There are 54 fundamental vibrational modes in 3-methoxy-4-hydroxy benzoic acid. The molecule has a C_1 symmetry point group and the calculated dipole moment is 4.07 debye. The high wavenumber region contains characteristic wavenumbers of the OH stretchings that are observed in one broad band in the IR (Fig. 1) and also in the Raman spectrum, where a deconvolution provides two overlapping bands at 3487 and 3476 cm^{-1} . The observed OH wavenumbers are much lower than the calculated ones (3699 and 3649 cm^{-1}) due to hydrogen bonding. The observation of close OH-stretching bands is similar to previous findings for salicylic acid.¹¹ The CH-stretching region encompasses six CH stretching; three from the aromatic ring and three from the CH_3 moiety. The Raman spectra and the corresponding calculated spectra are shown in Fig. 2. In the high wavenumber region of the spectra, the anharmonicity along can explain substantial differences between calculated and observed wavenumbers. Although in the calculated spectrum only four wavenumbers have high relative intensity, in the experimental spectrum, all the six CHs are observed. The Raman spectra of VA cannot be detected in the dilute water solutions (10^{-3} M); but it can be seen from a saturated solution and long integration times. Notably the observed Raman scattering of the saturated solution at 514.5 nm is identical with the Raman scattering at 442 nm excitation and they are shown in Fig. 3. The vibrational wavenumbers, intensities, and assignments are given in Table 1. In the infrared spectrum, the CHs are observed with relatively weak intensity. The infrared spectrum shown in Fig. 1 is in full agreement with the FTIR spectrum given as part of a comprehensive study on the spectroscopy and photophysics of VA acid in different solvents,¹² and also with the spectral region between 1000–1800 cm^{-1} shown in Ref. 13.

The carbonyl stretching is calculated at 1739 cm^{-1} ; but due to hydrogen bonding is observed at 1680 cm^{-1} in the FTIR spectrum, as can be seen in Fig. 1. The same red shift was seen in salicylic acid.¹¹ The $\text{C}=\text{O}$ is not a characteristic vibration in the Raman spectrum. The ring stretching vibration at 1601 cm^{-1} is the most intense band in the Raman spectra as can be seen in Fig. 3. Ring-stretching modes and CH bending dominate the 1500–1000 cm^{-1} region of the Raman spectrum. Vibrational modes in the low wavenumber region of the spectrum contain contributions of several internal coordinates and their assignment is a reduction approximation to one of two of the internal coordinates.

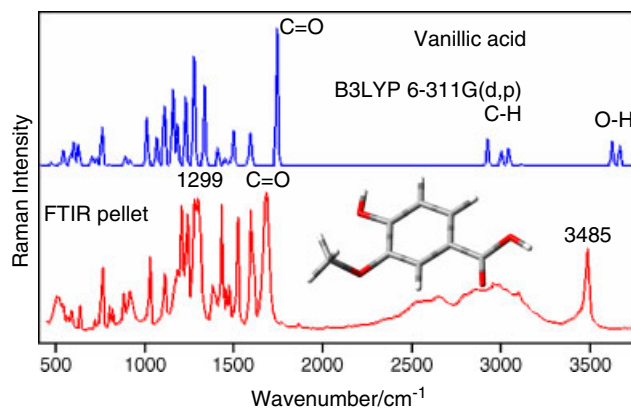


Figure 1. Calculated and experimental infrared spectra of VA in a KBr pellet. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

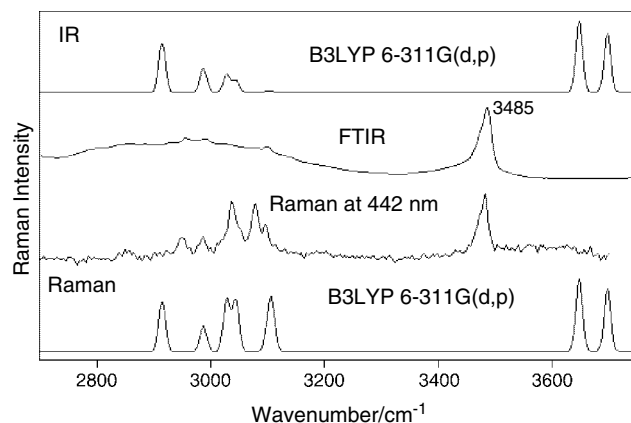


Figure 2. High wavenumber region of the Raman and infrared spectra of VA and the corresponding calculated wavenumbers.

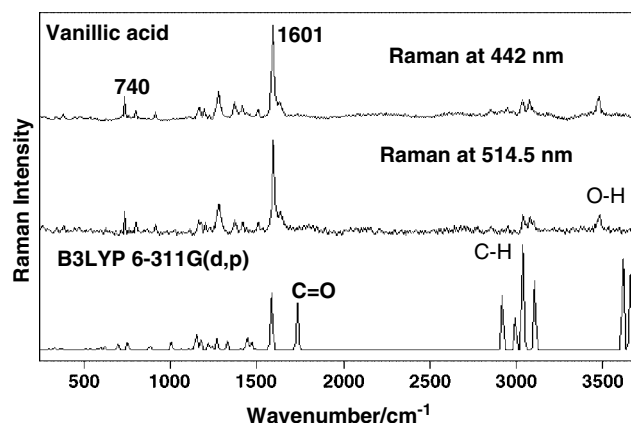


Figure 3. Raman scattering of solid VA excited at 442 nm, and that of a saturated VA solution excited at 514.5 nm. The bottom traces are the calculated spectrum.

Table 1. Calculated and observed fundamental vibrational wavenumbers of vanillic acid

Calculated cm ⁻¹	Infrared Km/mol	Raman Å ⁴ /amu	Raman Observed	Infrared Observed	Assignment
62	1.6	0.3			COOH twisting
67	3.2	1.0			Torsion
110	0.2	0.6			Ring wagging
141	2.3	2.5			CH ₃ torsion
155	1.2	1.1			Skeletal rocking
191	0.5	0.5	205 (6)		COOH rocking
260	1.5	1.0	276 (4)		Ring twisting
300	2.6	1.6			COH rocking n
333	10.6	3.9			Ring deformation
347	67.7	2.3	343 (14)		OH wagging
360	27.1	1.5			Ring twisting
393	6.5	1.0	383 (15)		Ring deformation
474	7.0	1.1	450 (6)		Ring wagging
517	10.8	2.8	482 (7)		Ring deformation
534	40.8	3.1	543 (7)	541 m	Ring deformation
577	29.0	2.5	566 (2)	565 w	CO rocking
600	59.4	4.6		589 m	scissors (COOH)
612	31.0	3.7	635 (12)	640 m	Ring deformation
700	20.6	10.7	722 (6)	722 w	Ring deformation
721	13.1	1.0	740 (55)		Ring twisting
752	69.7	1.4		758 s	CH wagging
757	23.4	12.7	765 (8)	766 s	Ring breathing
796	3.3	0.4	807 (24)	806 m	CH twisting
886	22.3	6.7			COCH ₃ stretch
909	8.7	0.8	917(19)	918 m	CH wagging
921	4.4	0.5	929 (6)		CH twisting
1005	119.9	14.9			OCH ₃ stretch
1060	75.6	1.5	1030 (8)	1029 s	CH bend + ring st.
1101	159.6	3.0			CH bending
1133	9.2	4.6		1113 s	CH ₃ deformation
1144	134.7	24.5	1118 (6)		CO stretch (COOH)
1149	51.9	5.3	1167 (21)	1169 m	CH bending
1170	86.7	15.7	1181 (22)	1187 m	CH ₃ deformation
1221	156.9	12.8	1205 (20)	1205 s	CO(CH ₃) stretch
1242	3.9	4.2	1235 (6)	1240 s	CH bending
1272	263.3	22.9	1286 (40)	1282 vs	COH + CO(CH ₃) st.
1327	216.0	21.0	1299 (19)	1299 vs	OH bending
1329	0.1	0.3			OH bend + ring st.
1404	45.2	3.2	1379 (14)	1378 m	CH ₃ bend + ring st.
1437	21.7	15.1	1426 (14)		Ring stretch + CH ₃ bend
1438	8.4	14.1		1435 s	CH ₃ bend + ring st.
1460	7.7	13.1		1457 m	CH ₃ bending
1491	93.4	1.4		1475 m	Ring stretch
1574	15.3	8.0	1520 (9)	1525 s	Ring stretch
1590	85.5	110.3	1601 (100)	1600 s	Ring stretch
1739	344.8	91.5		1680 vs	C=O stretch
2915	64.1	114.6	2854 (2)	2857 vw	CH stretch (CH ₃)
2988	32.3	58.8	2953 (4)	2954 w	CH stretch (CH ₃)

(continued overleaf)

Table 1. (Continued)

Calculated cm ⁻¹	Infrared Km/mol	Raman Å ⁴ /amu	Raman Observed	Infrared Observed	Assignment
3029	24.0	120.2	2988 (3)	2989 w	CH stretch (CH ₃)
3045	16.0	116.8	3038 (9)		CH ring stretch
3103	2.1	54.1	3080 (8)		CH ring stretch
3109	0.7	89.4	3097 (4)	3098 w	CH ring stretch
3649	93.0	165.5	3476 (4)		OH stretching(COOH)
3699	77.3	143.5	3487 (5)	3485 s	OH stretching

Relative intensities for Raman are given in parenthesis.

Infrared: vs, very strong; s, strong; m, medium; w, weak and vw, very weak.

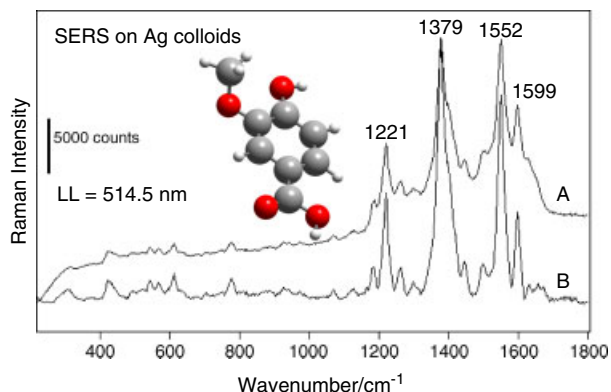


Figure 4. SERS spectrum of VA on Ag colloids. (A) Raw spectrum and (B) baseline corrected spectrum excited with the 514.5 nm laser line. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

Surface-enhanced Raman scattering

Reproducible and stable SERS spectra of VA were obtained in both the citrate and borohydride sols. The results for borohydride colloids obtained using the macro attachment and 15× objective are shown in Fig. 4. The raw spectrum carries the ubiquitous background observed in the SERS spectra,¹⁴ and the baseline corrected spectrum is also shown in Fig. 4. The stock solution of VA was 10⁻³ M. 300 μl of the solution were added to 3 ml of the colloidal solution as prepared (pH ca 7.3). The incident excitation line was the 514.5 nm of the argon-ion laser. Under identical conditions no Raman signal could be detected from the stock solution. The same SERS spectrum shown in Fig. 4 was also obtained from cast colloidal solution, containing VA, on glass. The SERS spectra are quite different from that of the solid VA presented in Fig. 3. These differences in relative intensities and wavenumbers can only be explained in terms of chemical adsorption of the VA to the silver surface. A close examination reveals that the characteristic vibration of the COO⁻ moiety at 1379 cm⁻¹ is the most intense band in the spectrum.¹⁵ Therefore it is reasonable to conclude that VA is chemically adsorbed forming a complex through the carboxylic group. There are four

main characteristic bands in the SERS spectrum: the symmetric COO⁻ stretching at 1379 cm⁻¹, the antisymmetric COO⁻ stretching at 1552 cm⁻¹, the ring stretching at 1599 cm⁻¹ and the CH bending at 1221 cm⁻¹.

In an early report⁵ on Fourier transform SERS (FT-SERS) of VA on Ag colloids (at pH = 4.1) excited at 1064 nm was also found that the VA was chemisorbed and the COO stretching mode was the most intense band in the observed SERS spectrum. Since the spectrum shown in Fig. 4 is reproducible under several conditions (in liquid, cast on glass), we assigned the observation to the chemisorbed species of VA. When photodissociation (burning) of the sample is caused by high energy density on the sample under the microscope, the typical carbon spectra are recorded. From the SERS spectra obtained from cast colloids, it can be estimated that picomole quantities of VA may be detected by SERS on colloidal silver. The group of phenolic acids related to VA is the *p*-hydroxybenzoic acid, the gallic and the syringic acids. The SERS of *p*-hydroxybenzoic acid is also due to chemisorbed species showing the strong symmetric COO stretching mode.¹⁶ However, there are some subtle differences with the results shown here for VA. These phenolic acids are easily photodissociated on the Ag surface and their SERS is elusive. Finding the appropriate SERS substrate that may allow their identification in mixtures is the next step in this work.

CONCLUSIONS

SERS spectra of VA, a phenolic acid, in the visible (514.5 nm) are reported here for the first time. The infrared and Raman spectra of VA have been revisited and assigned.

Acknowledgements

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