Spectroscopic investigations and computational study of sulfur trioxide – pyridine complex

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The Fourier transform infrared (FT-IR) and FT-Raman spectra of sulfur trioxide-pyridine complex were recorded and analyzed. The potential-dependent surface-enhanced Raman scattering (SERS) was recorded from an electrochemically roughened silver electrode. The vibrational wave numbers of the compound were computed using the Hartree – Fock/6-31G* basis and compared with the experimental values. The presence of strong pyridine ring vibrations in the SERS spectrum reveals the interaction between the pyridine ring and the silver surface. The molecule is adsorbed on the silver surface with the pyridine ring in a tilted orientation. The direction of charge-transfer contribution to the SERS is discussed from the frontier orbital theory. The value of the calculated first hyperpolarizability is comparable to those reported for similar structures, which makes this molecule an attractive object for future studies of nonlinear optics. The optimized geometrical parameters of the title compound are in agreement with similar reported structures. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: sulfur trioxide – pyridine complex; FT-IR; FT-Raman; SERS; Hartree – Fock *ab initio* calculations; hyperpolarizability

Introduction

One of the most advanced and sensitive tools for investigating metal-adsorbate interactions and reactivity of adsorbed species is surface-enhanced Raman scattering (SERS).[1 – 10] Since the initial study by Fleischmann *et al.*,[1] extensive investigations are in progress on the theoretical and experimental aspects of SERS. The reason for the very large enhancement in intensity of SERS has been attributed to a combination of electromagnetic and chemical interactions between the adsorbed molecules and the metal surface. Surface plasmon resonance is one of the major electromagnetic effects contributing to the SERS phenomenon and involves the collective electron oscillation induced by the incident light on a rough metal surface. Pyridine has been extensively studied spectroscopically by normal Raman and SERS.[11] It is a very stable compound with a great deal of aromatic character. Compounds containing the pyridine ring systems are widely distributed in nature. Some examples are vitamin B6 and nicotinamide adenine, which are of great interest in the biochemical and pharmaceutical fields. The pyridine ring is also found in the structure of many drugs.[12] Sulfur trioxide is also a molecule of environmental and industrial importance and has been the subject of a number of infrared and coherent Raman studies.[13 – 15] It is one of the most potent oxidizing agents known, is important in the industrial synthesis of sufonic acid and is an intermediate in the oxidation of many sulfur-containing compounds.[16,17] It is believed to play a significant role in atmospheric chemistry since it contributes to the formation of acid rain.[18] Panicker *et al.*[19] reported the FT-IR, FT-Raman and SERS spectra of pyridine-3-sulfonic acid and suggested a perpendicular orientation of the molecule on the silver surface. Urena *et al.*[20] reported a complete vibrational analysis of pyridine

both experimentally and theoretically. However, there is no report on the IR, Raman and SERS spectra of the sulfur trioxide – pyridine complex. In the present study, we report the IR, Raman, SERS and theoretical calculations of the wavenumbers for the title compound. Many organic molecules containing conjugated π electrons and characterized by large values of molecular first hyperpolarizabilities have been analyzed by means of vibrational spectroscopy.[21] Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in frequency, phase or other physical properties.[22] Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing and dynamic

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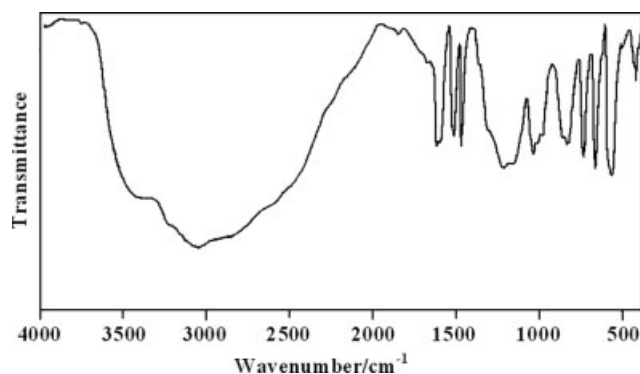f   Department of Chemistry, University of Victoria, Victoria, BC, Canada.

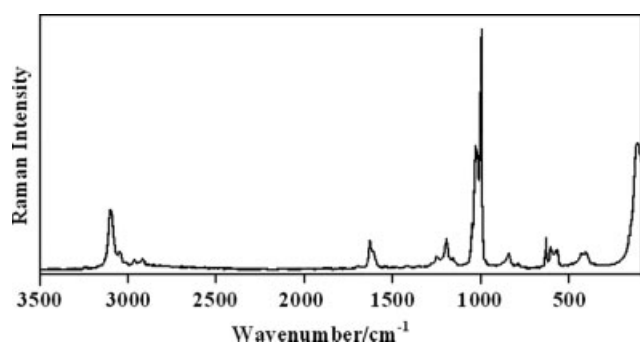**Figure 1.** IR spectrum of sulfur trioxide – pyridine complex.

Figure 2. Raman spectrum of sulfur trioxide – pyridine complex.

image processing.[23,24] In this context, the hyperpolarizability of the title compound is also calculated in the present study.

Figure 3. SERS spectra of sulfur trioxide – pyridine complex on an Ag electrode at the potentials indicated in the figure.

Experimental

The sulfur trioxide – pyridine complex was procured from Sigma – Aldrich, USA. The FT-IR and FT-Raman spectra (Figs 1 and 2) were recorded using a Bruker IFS 66v FT-IR/FT-Raman spectrometer. The FRA 106 module attached to the IFS66v FT-IR spectrometer extended the capabilities of the system to FT-Raman. A Nd : YAG laser operating at 1064 nm was used as the excitation source. The SERS spectra (Fig. 3) were obtained for the sulfur trioxide – pyridine complex adsorbed on an electrochemically roughened silver surface. The activation (roughening) procedure for the silver surface is described elsewhere.[25] The electrochemical potentials are reported *versus* an Ag wire quasi-reference electrode. The roughened silver surface was immersed in a 1 mM solution of sulfur trioxide – pyridine complex in 0.1 M KCl and the SERS was recorded *in situ*. The SERS spectra were acquired using a Renishaw InVia Raman micro-spectrometer. The objective used was a water-immersion one with 63× magnification. The laser line was the 632.8 nm of an He – Ne laser (Renishaw, 35 mV output).

Computational Details

The vibrational wave numbers were calculated using Guassian'03 software package on a personal computer.[26] The geometry of sulfur trioxide – pyridine complex was fully optimized without imposing external symmetry constraints using the 6-31G* basis set at the Hartree – Fock level of theory. Since, normally, the errors
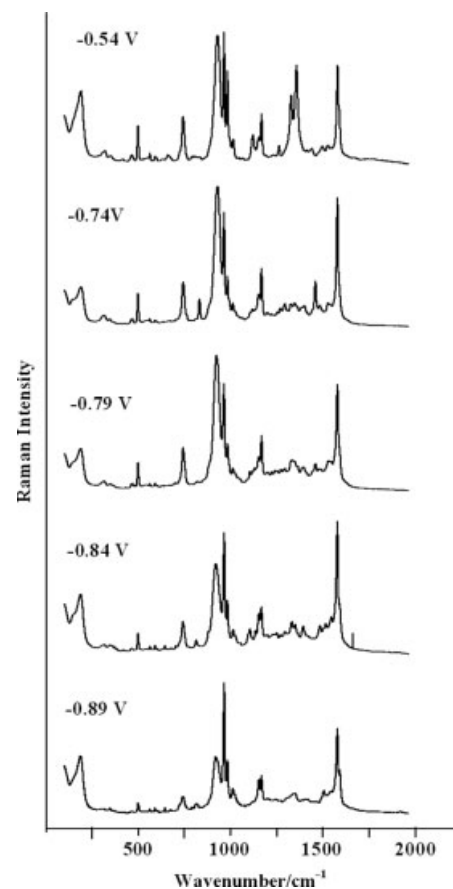

Figure 4. Optimized geometry of sulfur trioxide – pyridine complex.

within this type of calculation are systematic, it is common practice to use empirical correction factors.[27] In this study, a unique scale factor of 0.8929 was employed for the final wavenumbers. Parameters corresponding to the optimized geometry of sulfur trioxide – pyridine (Fig. 4) are given in Table 1. The calculated

Table 1. Optimized geometrical parameters of sulfur trioxide pyridine complex

Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)	
C_1-C_2	1.3764	A(2,1,6)	120.8	D(6,1,2,3)	−0.1
C_1-N_6	1.3290	A(2,1,8)	123.3	D(6,1,2,9)	−179.5
C_1-H_8	1.0712	A(6,1,8)	115.8	D(8,1,2,3)	179.3
C_2-C_3	1.3859	A(1,2,3)	118.5	D(8,1,2,9)	−0.5
C_2-H_9	1.0725	A(1,2,9)	119.8	D(2,1,6,5)	0.2
C_3-C_4	1.3859	A(3,2,9)	121.6	D(2,1,6,12)	−176.6
C_3-H_7	1.0744	A(2,3,4)	119.7	D(8,1,6,5)	−179.2
C_4-C_5	1.3764	A(2,3,7)	120.2	D(8,1,6,12)	4.0
C_4-H_{10}	1.0725	A(4,3,7)	120.2	D(1,2,3,4)	−0.1
C_5-N_6	1.3290	A(3,4,5)	118.5	D(1,2,3,7)	−179.9
C_5-H_{11}	1.0712	A(3,4,10)	121.6	D(9,2,3,4)	179.7
N_6-S_{12}	1.8943	A(5,4,10)	119.8	D(9,2,3,7)	−0.1
$S_{12}-O_{13}$	1.4235	A(4,5,6)	120.8	D(2,3,4,5)	0.13
$S_{12}-O_{14}$	1.4218	A(4,5,11)	123.3	D(2,3,4,10)	−179.7
$S_{12}-O_{15}$	1.4235	A(6,5,11)	115.8	D(7,3,4,5)	179.9
		A(1,6,5)	121.5	D(7,3,4,10)	0.1
		A(1,6,12)	119.2	D(3,4,5,6)	0.1
		A(5,6,12)	119.2	D(3,4,5,11)	−179.3
		A(6,12,13)	98.8	D(10,4,5,6)	179.9
		A(6,12,14)	99.7	D(10,4,5,11)	0.5
		A(6,12,15)	98.8	D(4,5,6,1)	−0.2
		A(13,12,14)	17.4	D(4,5,6,12)	176.6
		A(13,12,15)	18.0	D(11,5,6,1)	179.1
		A(14,12,15)	17.4	D(11,5,6,12)	−4.0
				D(1,6,12,13)	−31.4
				D(1,6,12,14)	88.5
				D(1,6,12,15)	−151.7
				D(5,6,12,13)	151.6
				D(5,6,12,14)	−88.5
				D(5,6,12,15)	31.4

The atom labeling is according to Fig. 4.

vibrational spectrum had no imaginary wave numbers, which confirms that the structure of the title compound deduced following optimization corresponds to the energy minimum. The assignment of the calculated wave numbers was aided by the animation option of the MOLEKEL program, which gives a visual presentation of the vibrational modes.[28,29]

Results and Discussion

IR and Raman spectra

The IR and normal Raman spectra of the sulfur trioxide – pyridine complex are presented in Figs 1 and 2, respectively. The positions of the vibrational bands and their relative intensities are shown in Table 2. Table 2 also shows the calculated (scaled) wavenumbers and assignments. The asymmetric and symmetric stretching of SO_3 in the sulfur trioxide – pyridine complex are observed at 1295 (IR), 1314 (Raman) and 1041 (Raman) cm^{-1}. These are in good agreement with the calculated values at 1311, 1308 ($\upsilon_a SO_3$) and 1036 cm^{-1} ($\upsilon_s SO_3$). Usually, the SO_2 deformation[30] absorbs with a weak to moderate intensity. The SO_2 scissoring is expected in the region $565 \pm 35\ cm^{-1}$. The deformation bands of SO_3 are observed at 581 and 530 cm^{-1} in the IR and at 583 and 124 cm^{-1} in the Raman spectrum. The HF calculations yield the

wavenumber for these modes at 572, 542 and 105 cm^{-1}. Varghese *et al.*[31] reported the bands at 1257 and 1231 cm^{-1} as $\upsilon_a SO_3$ and the band at 1007 cm^{-1} as υSO_3 modes for 2,6-dimethyl-pyridine-3-sulfonic acid. In sodium benzene sulfonate,[32] the band at 1035 cm^{-1} is assigned as the υSO_3 stretching mode, which also appears in the spectra of benzene sulfonic acid, phenol sulfonic acid and *p*-toluene sulfonic acid. Marzotto *et al.*[33] have reported the asymmetric and symmetric stretching of SO_3 at 1300 and 1150 cm^{-1}, respectively, for sodium 5-sulfosalicylate dihydrate. The deformation bands[32] of SO_2 are reported at 643 and 620 cm^{-1}. For sulfur trioxide, the stretching vibrations of SO_3 are reported at 1065 and 1391 cm^{-1} and the deformation modes at 530 and 493 cm^{-1}, respectively.[34] Bonner and Torres[35] adopted the assignments of earlier workers and assumed that the strongest band in Raman spectra of *p*-toluene sulfonic acid solutions at 1125 cm^{-1} was the υSO_3 symmetric stretching band, largely because earlier works had concluded that this was so because of 'complete ionization' of the polymer sulfonic acid. Then the weaker band near 1030 cm^{-1} was assigned to the υSO_2 mode of un-ionized species, despite the observation that the strongest Raman band in the solutions of sodium 2,5-dimethylbenzene sulfonate was observed at 1025 cm^{-1}. The wave number shift of 95 cm^{-1} from 1125 to 1030 cm^{-1} was attributed to methyl substitution effects in the benzene ring. Clearly, a much more reasonable scenario would be provided by the assignment of the approximately 1030 cm^{-1} band in the sulfonate salt, which contains only the SO_3 group, to the υSO_3 mode. Kurokawa *et al.*[36] reported the SO_3 symmetric stretching vibrations at 920 cm^{-1} and bending deformations at 620 cm^{-1} by comparing them with the vibrational wavenumbers of sulfito complexes. In the free-ion state, band at 1093 cm^{-1} is assigned to υSO_3. In the IR study of sulfur trioxide, Chrysostom *et al.*[37] reported the SO_3 vibration at 1392, 1364, 1044, 527, 516 and 494 cm^{-1}. For sulfanilic acid, the bands at 1157, 1124, 1034, 682 and 558 cm^{-1} in the Raman spectrum are due to the presence of SO_3 group.[38,39] The pyridine C–H vibrations[37] are usually observed in the range 3000–3100 cm^{-1}. In the present case, the bands observed at 3125 and 3074 cm^{-1} in the IR spectrum and at 3109, 3050 and 3020 cm^{-1} in the Raman spectrum are assigned to the υCH modes of the pyridine ring. The calculated values of these modes are 3081, 3079, 3053, 3049 and 3029 cm^{-1}, respectively. Ring stretching vibrations[40] of pyridine occur in the spectral region 1600–1300 cm^{-1}. Theses vibrations involve stretching and contraction of all the bonds in the ring as well as interaction between the stretching modes. The bands at 1632, 1602, 1486 and 1433 cm^{-1} in the IR spectrum and 1637, 1610 and 1480 cm^{-1} in the Raman spectrum are assigned as the υPy modes. These results are in agreement with the previously reported values.[41] The ring breathing mode[20] is observed as a strong band at 995 cm^{-1} in the Raman spectrum, and the calculated value is 990 cm^{-1}. The out-of-plane CH deformation vibrations are observed at 1027, 1000, 880 and 752 cm^{-1} in the IR spectrum and at 1028, 850 cm^{-1} in the Raman spectrum, while the calculated values are 1028, 1017, 997, 877 and 777 cm^{-1}, respectively.[20,30] Panicker *et al.*[19] reported the ring breathing mode of pyridine-3-sulfonic acid at 1022 cm^{-1} in the IR spectrum and at 1020 cm^{-1} in the Raman spectrum. The out-of-plane CH deformation vibrations[20,30] of the pyridine ring are observed in the range 1010-820 cm^{-1}.

The N–S stretching vibration[30,42] provides a weak to moderate band in the region $905 \pm 70\ cm^{-1}$. The $\upsilon N–S$ stretching exhibits a strong band at 880 cm^{-1} in the IR spectrum and a weak band in the Raman spectrum at 850 cm^{-1}. The calculated value is 877 cm^{-1};

Table 2. Calculated vibrational wavenumbers, measured IR and Raman band positions and assignments of sulfur trioxide pyridine complex

$v_{(HF)}$ (cm^{-1})	IR v (cm^{-1})	Raman v (cm^{-1})	SERS (−0.54 V)	SERS (−0.74 V)	SERS (−0.79 V)	SERS (−0.84 V)	SERS (−0.89 V)	Assignments
3081	3125 s	3109 m						vCH
3079	3074 sbr							vCH
3053								vCH
3049		3050 w						vCH
3029		3020 w						vCH
1629	1632 m	1637 m				1661 m		vPy
1594	1602 m	1610 w	1579 vs	1578 vs	1578 vs	1578 vs	1578 s	vPy
1479	1486 s	1480 vw	1497 w		1489 vw	1484 w		vPy
1453	1433 vw		1442 w	1459 m	1460 w			vPy
1347	1336 sbr		1358 vs	1397 w	1396 w	1393 w	1407 w	δCH
1311			1328 s	1346 w	1331 w	1333 w	1349 w	v_aSO$_3$
1308	1295 s	1314 vw	1264 w	1292 w	1293 w	1294 w		v_aSO$_3$
1194	1230 sbr	1203 w	1228 vw	1200 w		1199 vw	1199 vw	δCH
1186		1180 vw	1168 m	1167 m	1168 m	1167 m	1167 m	δCH
1073			1120 m	1140 m	1105 w	1105 w		δCH
1071								δCH
1058	1055 sbr	1052 w						δCH
1036		1041 s	1029 vw	1020 m				v_sSO$_3$
1030								δPy
1028	1027 mbr	1028 s						γCH
1017			1010 m			1013 w	1012 w	γCH
997	1000 m							γCH
990		995 vs	965 vs	964 vs	964 vs	965 vs	965 vs	Ring breathing
877	880 s	850 w	929 vs	928 vs	922 vs	920 s	918 m	γCH, vNS
777	752 s		743 m	743 m	742 m	742 m	739 w	γCH
671	680 s		660 vw			676 w	674 vw	γPy
645						643 w	643 vw	δPy
633		612 w						δPy
572	581 vs	583 w	591 w	590 vw	590 w	590 vw	590 vw	ωSO$_3$
542	530 w		499 m	498 m	499 m	499 m	499 w	ωSO$_3$
454	444 m	430 w	465 w	466 w	466 w	463 w		γPy
394		412 w	412 w					γPy
341			316 w	314 w	314 w	344 w	346 w	γPy
285								τPy, τSO$_3$
221								τPy, τSO$_3$
186								τPy, τSO$_3$
105		124 s						τPy, τSO$_3$
11								τSO$_3$

v, stretching; δ, in-plane bending; γ, out-of-plane bending; τ, torsion; s, strong; m, medium; w, weak; v, very; br, broad; Py, pyridine; subscript: a, asymmetric; s, symmetric.

this mode is not pure but contains contributions from the out-of-plane CH vibration. The torsional modes of pyridine complexes are reported to be below 400 cm^{-1}, by Barczynski et al.,[43] Erdogu et al.,[44] and Baran et al.[45] Arenas et al.[46] reported 200, 195, 42 and 39 cm^{-1} for 2,6-dimethylpyridine, Green et al.[47] reported 130, 128 and 126 cm^{-1} for formylpyridine and Varghese et al.[41] reported in the range 25–184 cm^{-1} for pyridine-3-sulfonic acid, as torsional modes of pyridine. In the present case, the calculated values in the range 285–105 cm^{-1} are assigned to the torsional modes of the pyridine ring, which are not pure but contain significant contributions from SO$_3$ also.

Surface-enhanced Raman scattering (SERS)

The relative intensities of the bands from the SERS spectra are expected to differ significantly from those of normal Raman spectrum owing to the specific selection rules.[48] Moreover, the relative intensities are also potential-dependent.[25,48] Surface selection rules suggest that, for a molecule adsorbed flat on the silver surface, its out-of-plane bending modes will be more enhanced when compared to its in-plane bending modes, and vice versa when it is adsorbed perpendicular to the silver surface.[49,50] It is further seen that vibrations involving atoms that are closer to the silver surface will be more enhanced. For the SO$_3$ group, the v_aSO$_3$ vibrations observed as a very weak band at 1314 cm^{-1} in the Raman spectrum is shifted to 1264, 1292, 1293 and 1294 cm^{-1} in the SERS spectrum as weak bands at different potentials −0.54, −0.74, −0.79 and −0.84 V, respectively which indicates the presence of the SO$_3$ moiety near the metal surface. Moreover, the SO$_3$ bands at 499, 591 and 1328 cm^{-1} are also present in the SERS spectrum. In the case of sulfanilic acid,[38] the v_sSO$_3$ vibration

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that is observed as a strong band at 1035 cm^{-1} in the normal Raman spectrum is shifted to 1024 cm^{-1} in the SERS spectrum, which indicates the nearness of the SO bond to the silver surface. In the present case, υ_sSO$_3$ vibration is observed at 1041 cm^{-1} in the normal Raman spectrum and shifted to 1029 and 1020 cm^{-1} at potentials −0.54 and −0.74 V and absent for other potential values in the SERS spectrum, which reveals a change in orientation of the SO$_3$ group with respect to the silver surface as a function of the applied potential.

The in-plane bending modes δCH of the pyridine ring are observed at 1358, 1228, 1168, 1120 cm^{-1} (−0.54 V); 1397, 1200, 1167, 1140 cm^{-1} (−0.74 V); 1396, 1168, 1105 cm^{-1} (−0.79 V); 1393, 1199, 1167, 1105 cm^{-1} (−0.84 V); and 1407, 1199, 1167 cm^{-1} (−0.89 V) in the SERS spectra of the sulfur trioxide pyridine complex presented in Fig. 3. According to the surface selection rules,[51,52] the presence of in-plane vibrational modes δCH in addition to the out-of-plane vibrational modes γCH vibrations of pyridine ring at around 1010 and 742 cm^{-1} in the potential range −0.54 to −0.89 V in the SERS spectra of the title compound suggest that there is an angle between the pyridine ring and the metal surface.[48,49] The δCH vibrational modes are reported at 1077, 1115, 1152 and 1222 cm^{-1} for chloropyridine complex adsorption on oxides,[53] at 1288, 1249, 1200, 1080 and 1044 cm^{-1} for some pyridine complex SERS study[54] and at 1212 cm^{-1} for the SERS study of pyridine adsorbed on platinum and nickel electrodes.[55] In the case pyridine adsorbed on silver, Muniz-Miranda *et al.*[56] has reported the strong SERS band of pyridine at 1025 cm^{-1} corresponding to the 1036 cm^{-1} band in the normal Raman spectrum. When the wavenumber difference between the Raman bands in the normal and SERS spectrum is not more than 5 cm^{-1}, the molecular plane will be perpendicular to the silver surface.[57] Thus, the stretching modes υCC of pyridine ring vibrations observed at 1579, 1497, 1442 cm^{-1} (−0.54 V); 1578, 1459 cm^{-1} (−0.74 V); 1578, 1489, 1460 cm^{-1} (−0.79 V); 1661, 1578, 1484 cm^{-1} (−0.84 V); and 1578 cm^{-1} (−0.89 V) in the SERS spectrum support the tilted orientation of the pyridine ring. Ma and Wu[58] assigned the pyridine ring stretching vibrations at 1595 and 1375 cm^{-1} for pyridine–iodine complex. Dines *et al.*[53] have reported bands at 1589, 1570, 1460 and 1426 cm^{-1} for the pyridine complex adsorbed on SiO$_2$, at 1596, 1578, 1568, 1454 and 1421 cm^{-1} for pyridine complex adsorbed on TiO$_2$, at 1583, 1567, 1455 and 1422 cm^{-1} for pyridine complex adsorbed on ZrO$_2$ and at 1609, 1591, 1568, 1563, 1539, 1468, 1456, 1427 and 1423 cm^{-1} for the pyridine complex on SiO$_2$–Al$_2$O$_3$ and assigned these bands to υCC pyridine ring modes.

Hu *et al.*[54] have reported the pyridine ring stretching modes (υPy) at 1612, 1604, 1478, 1457 and 1394 cm^{-1} in the SERS study of pyridine complex on silver foil. The ring breathing mode of pyridine at 1014 cm^{-1} has been reported for the pyridine complex adsorbed on some oxides.[53] Similarly, Muniz-Miranda *et al.*[59] have assigned the ring breathing mode as a very strong band at 1008 cm^{-1} from the SERS spectra of pyridine; the intensity corresponding to the prominent bands calculated for the Py/Ag$^+$ complex also falls almost in the same range. Chambers and Buck[60] have reported weak and very strong bands at 1014 and 1005 cm^{-1}, respectively, for the ring breathing mode of ruthenium–pyridyl complexes. Cao *et al.*[55] have assigned the ring breathing mode of pyridine adsorbed on platinum and nickel electrodes at 1021 and 1035 cm^{-1}, while these two modes correspond to strong bands at 991 and 1030 cm^{-1} for pure liquid pyridine. Similar results were observed for pyridine adsorbed on iron and cobalt.[61] Hu *et al.*[54] reported pH-dependent SERS spectral changes on silver colloids

for some pyridine complexes and assigned the ring breathing modes at 1006, 998 and 998 cm^{-1} for three different structures of 4-mercaptopyridine surface complex.

It has been documented in the literature[62] that, when a benzene ring moiety interacts directly with a metal surface, the ring breathing mode is red-shifted by 10 cm^{-1} along with substantial band broadening in the SERS spectrum. In the present case, the ring breathing mode of the pyridine ring is observed in the SERS spectrum as a very strong band at 965 cm^{-1}, which is present in the normal Raman spectrum at 995 cm^{-1}. This band is red-shifted by 35 cm^{-1} with significant band broadening, which indicates a direct interaction of the pyridine ring and the metal surface. As the potential increases from −0.54 to −0.89 V, the intensity of the δCH mode 1358 and 1120 cm^{-1} decreases. The out-of-plane (γCH) vibration at 929 cm^{-1} (−0.54 V) shows the same behavior. These changes in intensities and wavenumber values show a potential-dependent change in the surface orientation of the sulfur trioxide–pyridine complex. When the potential changes from −0.54 V to −0.84 V, significant intensity changes are observed for the bands 1358 cm^{-1} (in-plane CH bending vibration) and 1328 cm^{-1} (asymmetric SO$_3$ stretching vibration). This indicates the change of orientation of the molecule with respect to the silver surface and the change in the interaction between SO$_3$ group and silver. We have reported a similar behavior previously.[38]

Apart from the interaction of the pyridine ring in the adsorption process, the SO$_3$ group of the molecule can also bind to the silver surface through the oxygen atom. A more favored adsorption site can be postulated theoretically by estimating the partial atomic charges on each of the probable active sites.[63,64] The more the negative charge density on the atom, the higher the probability of it acting as an adsorptive site for the silver substrate. Theoretical results estimated from HF *ab initio* calculations show that the partial atomic charges on the nitrogen, sulfur, oxygen (O13), oxygen (O14), and oxygen (O15) atoms determined by natural population analysis are −0.755, 1.7, −0.665, −0.647 and −0.665, respectively (for atom numbering, see Fig. 4). The negative charge density is thus observed to be more on the nitrogen atom than others, thereby indicating the active involvement of the pyridine ring on the adsorption process.

The charge transfer mechanism of SERS can be explained by a resonant Raman mechanism, in which charge transfer excitations from the metal to the absorbed molecule or vice versa occur at the energy of the incident laser frequency.[10,25,65–68] The frontier orbital theory plays a significant role in the understanding of the charge transfer mechanisms of SERS.[69,70] Two types of charge transfer mechanisms are predicted. One is molecule to metal and the other is metal to molecule. Molecule to metal charge transfer excitations occur when an electron is transferred from the highest occupied molecular orbital (HOMO) of the adsorbate to the Fermi level of the metal. Conversely, transfer of an electron from the Fermi level of the metal to the lowest unoccupied molecular orbit results in metal to molecule charge transfer.[69,71–73] SERS spectra show reduced intensity for bands around 1400–1200 cm^{-1} when the reduction potential applied is made high, i.e. from −0.54 to −0.74 V. This can be attributed to the effect of the charge transfer from molecule to metal involved in the system. The position of the Fermi level of the metal is related to the electrode potential.[65] As the potential increases, charge transfer from the molecule to the metal decreases and that from the metal to the molecule increases. Thus the transition from the HOMO of the substrate to the Fermi level of metal becomes less significant and the intensity
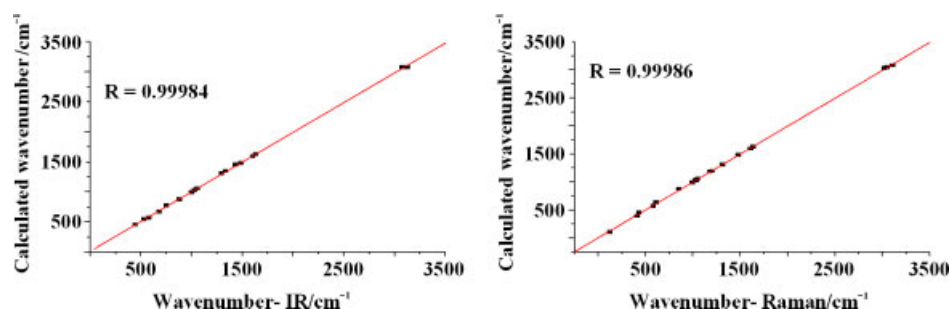
Figure 5. Correlation graph between experimental and calculated wavenumebrs.

of the corresponding peaks becomes weak, and these values are given in Table 2.

First hyperpolarizability and geometrical parameters

The reported values of C–N bond lengths of pyridine complexes are 1.338–1.313 Å,[74] 1.336–1.329 Å,[75] and 1.338–1.36 Å.[76] In the present study, the C–N bond length is calculated as 1.329 Å. For the title compound, the HF calculation gives the C–C bond length in the range 1.3859–1.3764 Å. This is in agreement with the reported values of the C–C bond lengths of similar pyridine complexes.[74–76] The C–H bond length is reported as 1.086 Å for thiocarbamoyl pyridine complex[76] and the calculated value of the C–H bond length for the sulfur trioxide–pyridine complex is between 1.0744 and 1.0712 Å. For the sulfur trioxide–pyridine complex, the HF calculations give the C–C–C and C–C–N bond angles as 119.691–118.5° and 120.8°. The reported values are 122.4–117.5°,[74] 119–117.4°[76] for C–C–C and 122.4–120.2°.[74] Zhuang et al.[75] reported the C–C–H bond angle between 121.6 and 116.7° for the pyridine complex and, in the present study of sulfur trioxide–pyridine complex, the *ab initio* calculations give the values in the range 121.6–115.8°. According to the literature, the S=O bond lengths are 1.386 Å for the pyridine–sulfuric acid complex,[45] 1.448–1.446 Å for sulfuric acid[77] and 1.472–1.448 Å for some monohydrated sulfuric acid.[78] In the present case, from *ab initio* calculations, the S=O bond length ranges between 1.4235 and 1.4218 Å. Givan et al.[79] have reported the S=O bond length for sulfuric acid and deuterated sulfuric acid by the X-ray, microwave and *ab initio* study as 1.426, 1.422 and 1.429 Å and the O=S=O angle as 123.3, 124.8° (experimental) 124.9° (*ab initio*), respectively.

Analysis of organic molecules having conjugated π-electron systems and large hyperpolarizability using IR and Raman spectroscopy has evolved as a subject of research.[80] The potential application of the title compound in the field of nonlinear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using the IR and Raman spectra. The ring stretching bands at 1632 and 1602 cm^{-1} observed in IR have their counterparts in the Raman spectrum at 1637, 1610 cm^{-1}, respectively, and their relative intensities in the IR and Raman spectra are comparable. The first hyperpolarizability (β_0) of this novel molecular system is calculated using the density functional theory (DFT) method, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first hyperpolarizability is a third-rank tensor that can be described by a 3 × 3 × 3 matrix. The 27 components of the three-dimensional matrix can be reduced to 10 components due to the Kleinman symmetry.[81] The components

of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2}\sum_{ij}\alpha_{ij}F^iF^j - \frac{1}{6}\sum_{ijk}\beta_{ijk}F^iF^jF^k$$
$$- \frac{1}{24}\sum_{ijkl}\gamma_{ijkl}F^iF^jF^kF^l + \cdots \quad (1)$$

where E_0 is the energy of the unperturbed molecule, F^i is the field at the origin, μ_i, α_{ij}, β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability, the first hyper polarizabilities, and second hyperpolarizibilites, respectively. The calculated first hyperpolarizability of the title compound is 80.04×10^{-30} esu, which is comparable to the reported values of similar derivatives,[82] but experimental evaluation of this data is not readily available. We conclude that the title compound is an attractive object for future studies of nonlinear optical properties.

In order to investigate the performance and vibrational wavenumbers of the title compound, the root mean square (RMS) value and the correlation coefficients between the calculated and observed wavenumbers were calculated (Fig. 5). The RMS values of wavenumbers were evaluated using the following expression[83]:

$$\mathrm{RMS} = \sqrt{\frac{1}{n-1}\sum_i^n (\upsilon_i^{\mathrm{calc}} - \upsilon_i^{\mathrm{exp}})^2} \quad (2)$$

The RMS error of the observed Raman bands and IR bands are found to be 14.91 and 16.78. Small differences between experimental and calculated vibrational modes are observed. It must be due to the fact that the hydrogen bond vibrations present in the crystal lead to strong perturbation of the IR wavenumbers and intensities of many other modes. Also, we note that the experimental results are from the solid phase and theoretical calculations pertain to the gaseous phase.

Conclusion

The FT-IR, FT-Raman and SERS spectra of the sulfur trioxide–pyridine complex were studied. From the comparison of SERS and normal Raman spectra, it could be concluded that the title compound is adsorbed in the metal surface and that it interacts with silver via SO_3 and the pyridine ring. The molecular plane assumes a tilted orientation with respect to the silver surface. The molecular geometry and wavenumbers were calculated theoretically. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives, which shows that the

molecule is an attractive object for further studies of nonlinear optics.

References

[1] M. Fleischmann, P. J. Hendra, A. J. McQuillan, *Chem. Phys. Lett.* **1974**, *26*, 163.

[2] D. L. Jeanmaire, R. P. Van Duyne, *J. Electroanal. Chem.* **1977**, *84*, 1.

[3] M. G. Albrecht, J. A. Creighton, *J. Am. Chem. Soc.* **1977**, *99*, 5215.

[4] R. P. Van Duyne, in *Chemical and Biological Applications of Lasers*, vol.4 (Ed.: C. B. Moore), Academic Press: New York, **1979**, pp 101.

[5] R. K. Chang, T. E. Furtak (Eds), *Surface Enhanced Raman Scattering*, Plenum Press: New York, **1982**, pp 423.

[6] M. Moskovits, *Rev. Mod. Phys.* **1985**, *57*, 783.

[7] A. Otto, I. Mrozek, H. Grabhorn, W. Akemann, *J. Phys: Condens. Matter.* **1992**, *4*, 1143.

[8] T. Vo-Dinh, in *Photonic Probes of Surfaces*, (Ed.: P. Halevi), Elsevier: Amsterdam, **1995**, pp 65.

[9] T. M. Cotton, in *Spectroscopy of Surface*, (Eds: R. J. H. Clark, R.E. Hester), Wiley: New York, Chichester, **1988**, pp 91.

[10] A. Campion, P. Kambhampati, *Chem. Soc. Rev.* **1998**, *27*, 241.

[11] A. R. Katrizky C. W. Rees E.F.V. Scriven (Eds), *Comprehensive Heterocyclic Chemistry II*, vol. 6, Pergamon: Oxford, UK, **1996**, 507.

[12] V. Krishnakumar, R. J. Xavier, *Spectrochim. Acta* **2005**, *61A*, 253.

[13] A. Kaldor, A. G. Maki, *J. Mol. Struct.* **1973**, *15*, 123.

[14] N. F. Henfrey, B. A. Thrush, *Chem. Phys. Lett.* **1983**, *102*, 135.

[15] J. Ortigoso, R. Escribano, A. G. Maki, *J. Mol. Spectrosc.* **1989**, *138*, 602.

[16] J. G. Calvert, A. Lazrus, G. L. Kok, B. G. Heikes, J. G. Walege, J. Lind, C. A. Cantrell, *Nature* **1985**, *317*, 27.

[17] J. G. Calvert W. R. Stockwell, *SO_2, NO and NO_2 Oxidation Mechanisms: Atmospheric Considerations*, Butterworth: Boston, **1984**.

[18] R. P. Wayne, *Chemistry of Atmospheres*, Oxford University Press: Oxford, **2000**.

[19] C. Y. Panicker, H. T. Varghese, D. Philip, H. I. S. Nogueira, *Spectrochim. Acta* **2006**, *64A*, 744.

[20] F. P. Urena, M. F. Gomez, J. J. L. Gonzalez, E. M. Torres, *Spectrochim. Acta* **2003**, *59A*, 2815.

[21] P. L. Anto, R. J. Anto, H. T. Varghese, C. Y. Panicker, D. Philip, *J. Raman Spectrosc.* **2009**, *41*, 113.

[22] Y. R. Shen, *The Principles of Nonlinear Optics*, Wiley: New York, **1984**.

[23] P. V. Kolinsky, *Opt. Eng.* **1992**, *31*, 1676.

[24] D. F. Eaton, *Science* **1991**, *253*, 281.

[25] A. G. Brolo, D. E. Irish, B. D. Smith, *J. Mol. Struct.* **1997**, *405*, 29.

[26] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Peterson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegava, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. U. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Daapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Ragavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Cliffor, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision C.02*, Gaussian Inc: Wallingford, **2004**.

[27] J. B. Foresman, in *Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian* (Ed.: E. Frisch), Gaussian Inc: Pittsburg, PA, **1996**.

[28] P. Flukiger, H. P. Luthi, S. Portmann, J. Weber, *MOLKEL 4.3*, Swiss Centre for Scientific Computing: Manno, Switzerland, **2000–2002**.

[29] S. Portman, H. P. Luthi, *Chimia* **2000**, *54*, 766.

[30] N. P. G. Roeges, *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, Wiley: New York, **1994**.

[31] H. T. Varghese, C. Y. Panicker, P. L. Anto, D. Philip, *Int. J. Chem. Sci.* **2006**, *4*, 512.

[32] H. G. M. Edwards, D. R. Brown, J. R. Dale, S. Plant, *J. Mol. Struct.* **2001**, *595*, 111.

[33] A. Marzotto, D. A. Clemente, T. Gerola, G. Valle, *Polyhedron* **2001**, *20*, 1079.

[34] S. W. Sharpe, T. A. Blake, R. L. Sams, A. Maki, T. Mesiello, J. Barber, N. Vulpanovici, J. W. Nibler, A. Weber, *J. Mol. Spectrosc.* **2003**, *222*, 142.

[35] O. D. Bonner, A. L. Torres, *J. Phys. Chem.* **1965**, *69*, 4109.

[36] Y. Kurokawa, Y. Imai, Y. Sasaki, T. Maeda, *Anal. Biochem.* **1993**, *209*, 247.

[37] E. T. H. Chrysostom, N. Vulpanovici, T. Masiello, J. Barber, J. W. Nibler, A. Weber, A. Maki, T. A. Blake, *J. Mol. Spectrosc.* **2001**, *210*, 233.

[38] C. Y. Panicker, H. T. Varghese, P. L. Anto, D. Philip, *J. Raman Spectrosc.* **2006**, *37*, 853.

[39] L. Ganguly, C. I. Jose, A. B. Biswas, *Spectrochim. Acta* **1968**, *24A*, 215.

[40] R. M. Silverstein F. X. Webster, *Spectrometric Identification of Organic Compound* (6th edn), Wiley: New York, **2003**.

[41] H. T. Varghese, C. Y. Panicker, P. L. Anto, D. Philip, *Asian J. Chem.* **2007**, *19*, 2627.

[42] H. T. Varghese, C. Y. Panicker, D. Philip, *Spectrochim. Acta* **2006**, *65A*, 155.

[43] P. Barczynski, A. Katrusiak, J. Koput, M. Szafran, *J. Mol. Struct.* **2008**, *889*, 394.

[44] Y. Erdogu, M. T. Gulluoglu, M. Kurt, *Spectrochim. Acta* **2008**, *71A*, 377.

[45] J. Baran, Z. Dega-Szafran, M. Jaskolski, M. K. Marchewka, H. Ratajczak, M. Szafran, *J. Mol. Struct.* **1997**, *406*, 127.

[46] J. F. Arenas, J. C. Otero, S. P. Senteno, I. L. Tocon, J. Soto, *Surf. Sci.* **2002**, *511*, 163.

[47] J. H. S. Green, D. J. Harrsion, *Spectrochim. Acta* **1977**, *33A*, 75.

[48] J. A. Creighton, *Spectroscopy of Surfaces – Advances in Spectroscopy*, vol. 16, Wiley: New York, **1988**, p 37, Chapt. 2.

[49] X. Gao, J. P. Davies, M. J. Weaver, *J. Phys. Chem.* **1990**, *94*, 6858.

[50] J. A. Creighton, *Adv. Spectrosc.* **1988**, *19*, 37.

[51] M. Moskovits, J. S. Suh, *J. Phys. Chem.* **1984**, *88*, 5526.

[52] M. Moskovits, J. S. Suh, *J. Phys.Chem.* **1988**, *92*, 6327.

[53] T. J. Dines, L. D. MacGregor, C. H. Rochester, *Spectrochim. Acta* **2003**, *59A*, 3205.

[54] J. Hu, B. Zhao, W. Xu, B. Li, Y. Fan, *Spectrochim. Acta* **2002**, *58A*, 2827.

[55] P. Cao, R. Gu, B. Ren, Z. Tian, *Chem. Phys. Lett.* **2002**, *366*, 440.

[56] M. Muniz-Miranda, G. Cardini, M. Pagliai, V. Schettino, *Chem. Phys. Lett.* **2007**, *436*, 179.

[57] G. Levi, J. Patigny, J. P. Massault, J. Aubard, Thirteenth international conference on Raman spectroscopy, Wurzburg, **1992**.

[58] S. Ma, G. Wu, *J. Mol. Sturct.* **1995**, *372*, 127.

[59] M. Muniz-Miranda, G. Cardini, V. Schettino, *Theor. Chem. Acc.* **2004**, *111*, 264.

[60] J. A. Chambers, R. P. Buck, *J. Raman Spectrosc.* **1984**, *15*, 160.

[61] G. F. S. Andrade, M. L. A. Temperini, *J. Raman. Spectrosc.* **2009**, *40*, 1989.

[62] P. Cao, M. J. Weaver, *J. Phys. Chem.* **1989**, *93A*, 6205.

[63] J. Chowdhury, M. Ghosh, T. N. Misra, *Specctrochim. Acta* **2000**, *56A*, 2107.

[64] J. Chowdhury, K. M. Mukherjee, T. N. Misra, *J. Raman Spectrosc.* **2000**, *31*, 427.

[65] J. F. Arenas, J. Soto, I. Lopez-Tocon, D. J. Fernandez, J. C. Otero, J. I. Marcos, *J. Chem. Phys.* **2002**, *116*, 7207.

[66] J. R. Lombardi, R. L. Brike, T. H. Lu, J. Xu, *J. Chem. Phys.* **1986**, *84*, 4174.

[67] J. C. Rubim, P. Corio, M. C. C. Ribeiro, M. Matz, *J. Phys. Chem.* **1995**, *99*, 15765.

[68] J. R. Lombardi, R. L. Brike, *J. Chem. Phys.* **2007**, *126*, 244709.

[69] J. Sarkar, J. Chowdhury, P. Pal, G. B. Talapatra, *Vib. Spectrosc.* **2006**, *41*, 90.

[70] R. L. Garell, J. E. Chadwick, D. L. Severance, N. A. McDonald, D. C. Myles, *J. Am. Chem. Soc.* **1995**, *117*, 11563.

[71] J. Sarkar, J. Chowdhury, M. Ghosh, R. De, G. B. Talapatra, *J. Phys. Chem.* **2005**, *109B*, 22536.

[72] A. R. Bizzarri, S. Cannistraro, *Chem. Phys.* **2003**, *290*, 297.

[73] A. R. Bizzarri, S. Cannistraro, *Chem. Phys. Lett.* **2004**, *395*, 222.

[74] B. Raimondi, G. L. Manna, *Spectrochim. Acta* **2008**, *69A*, 933.

[75] Z. Zhuang, J. Cheng, H. Jia, J. Zeng, X. Han, B. Zhao, H. Zhang, G. Zhang, W. Zhao, *Vib. Spectrosc.* **2007**, *43*, 306.

[76] R. Wysokinski, D. Michalska, D. C. Bienko, S. Ilakiamani, N. Sundaraganesan, K. Ramalingam, *J. Mol. Struct.* **2006**, *791*, 70.

[77] Y. Miller, G. M. Chaban, R. B. Gerber, *J. Phys. Chem.* **2005**, *109A*, 6565.

[78] S. Re, Y. Osamura, K. Morokuma, *J. Phys. Chem.* **1999**, *103A*, 3535.

[79] A. Givan, L. A. Larsen, A. Loewenschuss, C. J. Nielsen, *J. Mol. Struct.* **1999**, *509*, 35.

[80] M. Tommasini, C. Castiglioni, M. D. Zoppo, G. Zerbi, *J. Mol. Struct.* **1999**, *480*, 179.

[81] D. A. Kleinman, *Phys. Rev.* **1962**, *126*, 1777.

[82] V. B. Jothy, T. Vijayakumar, V. S. Jayakumar, K. Udayalekshmi, K. Ramamoorthy, I. H. Joe, *J. Raman Spectrosc.* **2007**, *38*, 1148.

[83] V. Krishnakumar, S. Dheivamalar, R. J. Xavier, V. Balachandran, *Spectrochim. Acta* **2006**, *65A*, 147.

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