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IR, Raman and SERS Spectra of 2-(Methoxycarbonylmethylsulfanyl)-3,5-dinitrobenzene Carboxylic Acid

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O ácido carboxílico 2-(metoxicarbonilmetilsulfanil)-3,5-dinitrobenzeno foi preparado por substituição nucleofílica. Seus espectros de infravermelho e Raman com transformada de Fourier foram obtidos e analisados. O espalhamento Raman intensificado pela superfície (SERS) foi obtido sobre prata coloidal. Os números de onda vibracionais foram computados pela teoria do funcional de densidade (DFT) com a base híbrida B3LYP/6-31G* e foram comparados com valores experimentais com boa concordância. Interações metal-molécula significativas foram substanciadas por um sinal Ag-O intenso nos espectros SERS, indicando a proximidade dos grupos nitro e carbonila à superfície de prata. Estudos SERS sugerem uma orientação inclinada da molécula sobre a superfície metálica.

2-(Methoxycarbonylmethylsulfanyl)-3,5-dinitrobenzenecarboxylic acid was prepared by nucleophilic substitution. FT-IR and FT-Raman spectra of 2-(methoxycarbonylmethylsulfanyl)-3,5-dinitrobenzenecarboxylic acid were recorded and analyzed. Surface enhanced Raman scattering (SERS) spectrum was recorded on a silver colloid. The vibrational wavenumbers were computed by density functional theoretical (DFT) computations at the B3LYP/6-31G* level and they were found to be in good agreement with the experimental values. Significant metal-molecule interaction has been substantiated by the appearance of intense Ag-O mode in the SERS spectrum and this is indicative of the nearness of nitro and carbonyl group to the silver surface. SERS studies suggest a tilted orientation of the molecule at the metal surface.

Keywords: nitro, FT-IR, FT-Raman, SERS, DFT, methoxy carbonyl

Introduction

The main characteristic of the surface enhanced Raman scattering (SERS) is the enormous enhancement of the Raman signal of a molecule when the spectrum is recorded in the neighbourhood of a metallic rough surface.[1,2] The nucleophilic substitution of *o*-nitrochlorobenzenes with substituted methanethiolates, catalyzed with triethylamine or pyridine, has been used to prepare a series of appropriately substituted methyl-*o*-nitrophenylsulfides.[3] Sulfenyl carbonyl compounds are an interesting family of molecules related to important biological systems and the anomeric and mesomeric effects in methoxycarbonylsulfenyl chloride is reported by Erben *et al*.[4] Vallejos *et al*.[5] reported the experimental investigation of the structure and vibrational properties of methoxycarbonylsulfenyl isocyanate. Nitro derivatives of salicylic acids as a donor in solid state coordination compounds have been studied by Lajumen *et al.*[6] and the study of metal complexes with 3,5-dinitrosalicylic acid is also reported.[7,8] Structural confirmation of the 3,5-dinitrosalicylate anion coordination ability to metal ions have been reported by Valigura *et al.*[9,10] and they have reported the characterization of complex by elemental micro analysis, electronic, IR and

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EPR spectra. 3,5-Dinitrosalicylic acid is an example of a proton donor having both carboxyl and hydroxyl groups, and provides one of the best chemical synthons for the construction of hydrogen-bonded structural motifs.[11] The acid has provided examples of polymorphism in which associations with solvent molecules such as water, dioxane and *tert*-butyl alcohol give a variety of hydrogen-bonded molecular assemblies.[12,13] Panicker *et al.*[14] reported the IR, Raman and SERS spectra of methyl(2-methyl-4,6-dinitrophenylsulfanyl)ethanoate. *Ab initio* quantum mechanical method is at present widely used for simulating IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable without involving them. So far, there is no report of the vibrational spectral analysis of the title compound. In the present study, the IR, Raman and surface enhanced Raman scattering spectra of 2-(methoxycarbonyl methylsulfanyl)-3,5-dinitrobenzenecarboxylic acid were investigated to get an idea regarding the orientation of the molecule on the silver surface. Theoretical calculations of the vibrational wavenumbers were made using Gaussian03 software package on a personal computer.[15]

Experimental

The title compound was prepared by the protocol given by Dudova *et al.*[3] Methyl sulfanylethanoate (4.46 g, 0.042 mol) was added drop wise to a stirred solution of 2-chloro-3,5-dinitrobenzoic acid (9.86 g, 0.04 mol) in 1,2-dimethoxy ethane (25 mL) to a 100 mL flask at room temperature under an inert atmosphere of Ar. Triethylamine (4.05 g, 0.04 mol) was added at once to neutralize the carboxy group. More triethylamine (4.05 g, 0.04 mol) was then added drop wise with stirring over a period of *ca.* 30 min. The mixture was stirred for an additional 10 min and then poured into dilute aqueous hydrochloric acid (1:1, 30 mL). The product was extracted with chloroform (3 × 50 mL), the organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was recrystallized from chloroform yielding 7.8 g (62%) of the product, mp 109-111 °C. The elemental analysis is: solvent for crystallization, chloroform; calculated/found (%) C 37.98/37.99, H 2.55/2.56, N 8.86/9.13, S 10.14/10.16. Chemical shifts (δ): solvent, DMSO-d_6 : H_7 8.69, H_{10} 8.94 (d, J 2.5 Hz), CH_2 3.92 s, OCH_3 3.60 s, ^{13}C NMR (δ): solvent DMSO- d_6 ; Ar-S-; 155.42 (C_4), 147.91 (C_6) 141.48 (C_3), 134.26 (C_1), 127.35 (C_5), 121.61 (C_5), COOH group: (169.27) (CO), 38.6 CH_2, 166.1, CO of $COOCH_3$, 53.44 CH_3. The ^1H and ^{13}C NMR spectra were measured at 25 °C with an AMX 360 Bruker spectrometer at the wavenumber of 360.14 and 90.57 MHz, respectively. For the measurements the substances were dissolved in $CDCl_3$ or $(CD_3)_2$ SO (5% solutions). The δ ^1H chemical shifts are referred to the signal of HMDSO in $CDCl_3$ solutions (δ ^1H: 0.05) and to the solvent signal in $(CD_3)_2$ SO solutions (δ ^1H: 2.55). The δ ^{13}C chemical shifts are referred to the signals of the two solvents (δ ^{13}C : 77.0 and 39.6, respectively). The analysis of the proton spectra was carried out according to the rules for the first-order splitting with the help of the integral intensities. The ^{13}C NMR spectra were measured with full decoupling from the protons, and the signals were assigned with the help of SCS. The quaternary carbon atoms and CH groups were differentiated by means of the APT pulse sequence. The elemental analyses were carried out on an automatic analyser EA 1108 (Fisons). The FT-IR spectrum (Figure 1) was recorded using a Perkin-Elmer spectrum one FT-IR spectrometer in the region 450-4000 cm^{-1} with the sample in standard KBr pellet technique. The spectral resolution was 2 cm^{-1}. Raman spectra (Figures 2 and 3) were recorded on a Bruker RFS 100/s FT instrument (Nd:YAG laser, 1064 nm excitation). The aqueous silver colloid used in the SERS experiments was prepared by reduction of silver nitrate by sodium citrate, using the Lee-Meisel method.[16] SERS of the title compound was obtained as previously described,[17] summarized next. Solution of the compound were made up in ethanol (0.1 mmol in 1 cm^3 of solvent) and transferred by a micro syringe into the silver colloid (10 µL in 1 mL of the colloid) such that the over all concentration was 10^{-3} mol L^{-1}. Colloid aggregation was induced by addition of an aqueous solution of $MgCl_2$ (1 drop of a 2 mol L^{-1} solution). Polyvinylpyrrolidone was then used to stabilize the colloid (1 drop of 0.1 g/10 mL aqueous solution). The final colloid mixture was placed in a glass tube and the Raman spectrum registered.

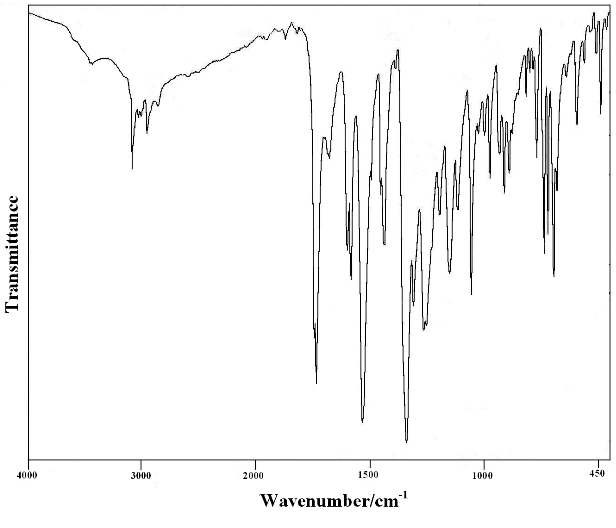

Figure 1. IR spectrum.

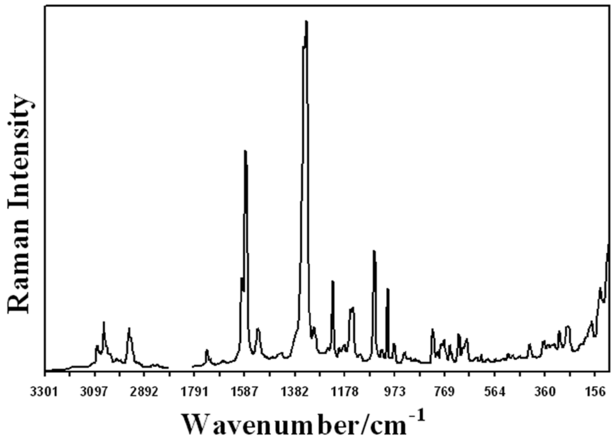

Figure 2. Normal Raman spectrum.

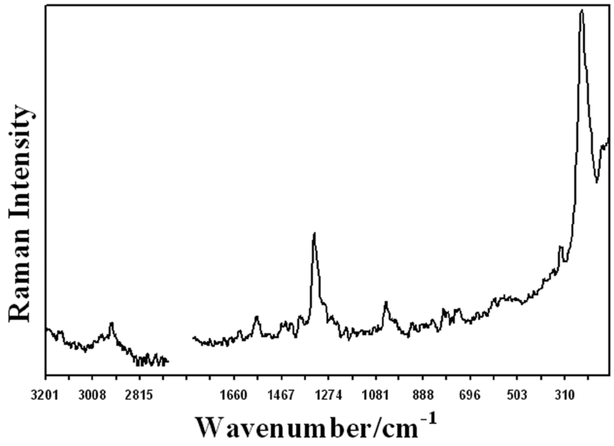

Figure 3. SERS spectrum.

Computational details

The density Functional Theory (DFT) computations were performed at the B3LYP/6-31G* level theory to get optimized geometry (Figure 4) and vibrational wavenumbers of normal modes of the title compound. DFT calculations were carried out with Becke's three parameters hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibratrional wavaenumbers were calculated using analytic second derivatives to confirm the convergence to minima in the potential surface. At the optimized structure of the examined species, no imaginary wavenumber modes were obtained, proving that a true minimum on the potential surface was found. The optimum geometry (Table S1, Supplementary Information) was determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. The DFT hybrid B3LYP functional tends also to overestimate the fundamental modes, therefore scaling factors have to be used for obtaining a considerable better agreement with experimental data.[18,19] Thus, a scaling factor of 0.9613 has been uniformly applied to the B3LYP calculated wavenumbers.[18] The observed disagreement between the theory and the experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry.[20] The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes.[21,22]

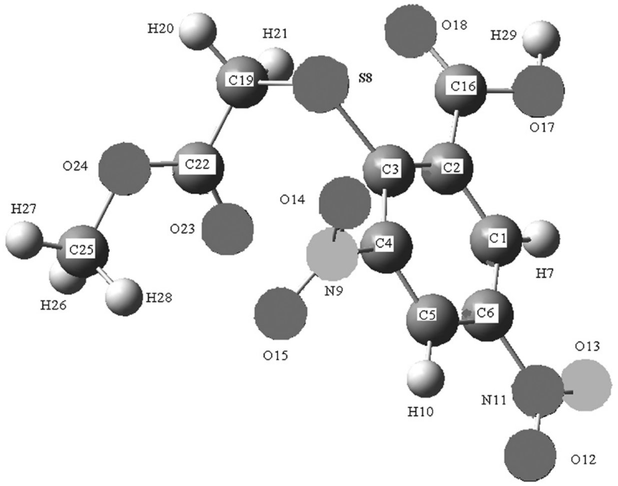

Figure 4. Optimized geometry of the molecule.

Results and Discussion

The observed Raman and IR bands with their relative intensities, calculated values and assignments are given in Table 1. The Raman of the solid and the SERS spectrum of 2-(methoxycarbonylmethylsulfanyl)-3,5-dinitrobenzenecarboxylic acid are presented in Figures 2 and 3, respectively.

Carboxylic group vibrations

Carboxylic acids are best characterized by the OH stretch, the C=O stretch and the OH out-of-plane deformation. The C=O stretching vibration in the spectra of carboxylic acids[23] give rise to a band in the region 1725 ± 65 cm^{-1}. In the present case, we have observed a band at 1750 cm^{-1} in the IR spectrum and 1756 cm^{-1} theoretically. Two bands arising from the C-O stretching and OH bending appear in the spectra of carboxylic acids near 1320-1210 cm^{-1} and 1440-1395 cm^{-1}, respectively.[24] Both of these bands involve some interaction between C-O stretching and in-plane C-O-H bending. The ν(C-O)$_c$ mode

Table 1. Infrared, Raman and SERS spectral data (wavenumbers in cm^{-1}), calculated data and band assignments for 2-(methoxycarbonylmethylsulfanyl)-3,5-nitrobenzenecarboxylicacid

Calculated/(cm^{-1})	IR/(KM/Mole)	IR/(cm^{-1})	Raman/(cm^{-1})	SERS/(cm^{-1})	Assignments
3553	104.96	-	-	-	νOH
3150	13.03	-	-	-	νCH
3138	14.74	-	-	3139 vw	νCH
3075	16.51	3086 m	3087 w	-	$\nu_{as}CH_2$
3068	15.06	-	3060 m	-	$\nu_{as}Me$
3038	4.72	3042 vw	-	-	$\nu_{as}Me$
2997	3.92	3000 vw	-	-	$\nu_{s}CH_2$
2962	24.40	2955 w	2958 m	2933 w	$\nu_{s}Me$
1756	294.05	1750 sh	-	-	νC=O carboxyl
1744	201.61	1733 vs	1741 w	-	νC=O methoxy
1609	183.04	1599 s	1600 s	1635 vw	$\nu_{as}NO_2$, νPh
1592	164.05	1583 s	1583 vs	-	$\nu_{as}NO_2$
1568	35.73	-	-	1567 w	$\nu_{as}NO_2$, νPh
1546	130.61	1533 vvs	1531 m	-	$\nu_{as}NO_2$
1464	6.43	-	-	1465 vw	$\delta_{as}Me$
1456	6.39	1453 m	-	1448 vw	$\delta_{as}Me$, νPh
1440	25.49	1439 m	-	1427 vw	$\delta_{s}Me$
1431	5.06	-	-	-	δCH_2
1410	37.62	-	-	-	δOH
1373	1.53	-	-	1383 vw	νPh
1365	92.86	-	-	-	$\nu_{s}NO_2$
1344	363.64	1341 vs	1345 sh	1332 s	$\nu_{s}NO_2$
1330	144.82	-	1336 vs	-	νC-O carboxyl
1285	153.10	1308 s	1303 m	-	ωCH_2
1278	235.82	1265 s	-	1254 vw	νC(=O)O
1209	37.85	1195 m	1228 s	-	ωCH_2
1179	118.03	-	-	1188 vw	δCH,
1173	4.68	-	-	1171 vw	δCH
1173	86.95	1152 s	1156 m	-	ρMe
1142	0.95	-	1145 m	-	ρMe
1121	148.83	1115 m	-	-	τCH_2
1107	192.66	-	-	-	τCH_2
1092	156.39	1056 s	1058 s	1041 m	δCH
1025	43.33	-	1004 s	-	Ring breathing
999	27.44	998 w	977 w	-	νO-C(Me)
928	10.53	933 w	935 vw	938 vw	γCH
922	4.65	-	-	-	γCH
913	22.62	912 w	-	-	νC-N
906	22.83	-	-	-	γCH
877	11.89	890 w	-	-	νC-N, νCC carboxyl
832	3.39	816 vw	819 w	-	ρCH_2
775	16.29	800 vw	784 w	804 m	δNO_2
772	19.01	770 w	775 w	-	δC=O carboxyl

Table 1. continuation

Calculated/(cm^{-1})	IR/(KM/Mole)	IR/(cm^{-1})	Raman/(cm^{-1})	SERS/(cm^{-1})	Assignments
765	1.05	-	748 w	-	δC=O methoxy
740	85.93	737 s	-	741 w	δNO$_2$
722	28.54	721 m	-	-	ωNO$_2$
720	29.56	-	-	-	ωNO$_2$
709	111.08	696 s	713 w	-	γPh
667	13.25	682 w	680 w	-	νC-S, γC=O methoxy
635	84.06	-	-	-	γC=O carboxyl
617	61.99	615 w	-	-	γOH
597	28.31	594 w	-	593 vw	δPh(X)
574	5.21	-	-	-	δPh(X)
561	17.41	562 w	-	554 vw	γPh
523	3.83	509 vw	-	-	ρNO$_2$
489	3.20	489 w	-	-	ρNO$_2$
477	8.47	-	-	-	γPh(X)
409	1.64	-	422 w	-	ρC(=O)-O
382	8.61	-	-	397 vw	γPh(X)
364	1.04	-	-	354 w	γPh(X)
335	2.88	-	-	327 m	Skel. C-O-C
313	0.45	-	302 w	-	γPh(X)
300	5.51	-	-	-	γPh(X)
283	9.53	-	-	-	δPh(X)
278	11.61	-	271 w	-	tMe
-	4.38	-	-	241 vs	νAg-O
232	0.31	-	-	-	tMe
207	0.60	-	-	-	tPh
168	0.50	-	169 w	-	tMe
162	2.38	-	-	-	tPh
157	2.88	-	-	-	tMe
145	0.78	-	-	-	tPh
139	3.68	-	134 m	-	tPh
121	3.03	-	-	-	tMe
108	0.78	-	110 m	-	tMe
63	0.18	-	-	-	tNO$_2$
59	0.203	-	-	-	tNO$_2$
52	0.86	-	-	-	tNO$_2$
45	0.56	-	-	-	tNO$_2$
35	1.70	-	-	-	tPh
29	0.48	-	-	-	tCH$_3$
18	0.78	-	-	-	tCH$_2$

ν-stretching; δ-in-plane deformation; γ-out-of-plane deformation; ρ-rocking; τ-twisting; ω-wagging; t-torsion; s-strong; b-broad; v-very; w-weak; Me-methyl; Ph-phenyl; X-substituent sensitive; m-medium.

is reported at 1377 cm^{-1} for sodium salicylate,[25] at 1391 cm^{-1} for 4-aminosalicylic acid[26] and at 1375 (IR), 1382 cm^{-1} (HF) for 3,5-dinitrosalicylic acid.[27] For the title compound, the band observed at 1330 cm^{-1}(DFT) and 1336 cm^{-1} (Raman) is assigned as ν(C-O)$_c$ mode.

Methoxycarbonyl group vibrations

In the spectra of methyl esters the overlap of the regions in which both asymmetric stretching[23] ν_{as}Me absorb with a weak to strongly (3020 ± 30 and 2990 ± 40 cm^{-1}) is not large and regularly seen above 3000 cm^{-1}. The computed wavenumbers of modes corresponding to the ν_{as}Me group are 3068 and 3038 cm^{-1}. For the title compound, bands observed at 3060 cm^{-1} in the Raman spectrum and 3042 cm^{-1} in the IR spectrum are assigned as asymmetric methyl stretching vibrations. The symmetric stretching mode ν_sMe is expected in the range 2920 ± 80 cm^{-1} in which all the CH bonds extend and contract in phase.[23] The bands at 2955 (IR), 2958 (Raman) and 2962 cm^{-1} (DFT) are assigned as this mode. Panicker *et al.*[14] reported the stretching vibrations of methyl group at 3068, 3038, 2963 (DFT), 2961 (IR) and 2962 cm^{-1} (Raman) for methyl stretching vibrations. The stretching vibrations of the methyl group are reported at 3016, 2967, 2857 cm^{-1} (IR), 3046, 2962, 2842 cm^{-1} (Raman), 3171, 3137, 3058 cm^{-1} (DFT) for methoxycarbonylsulfenyl isocyanate[5] and at 3014, 2966, 2850 cm^{-1} (IR), 3039, 2959, 2840 cm^{-1} (Raman), 3191, 3159, 3073 cm^{-1} (DFT) for methoxycarbonylsulfenyl chloride.[4]

Two bending vibrations can occur within a methyl group. The first of these, the symmetric bending vibration δ_sMe involves the in-phase bending of the C-H bonds. The second, the asymmetrical bending mode δ_{as}Me involves out-of-phase bending of the C-H bonds.[24] The asymmetric bending vibrations of the methoxy group[23] normally appears in the regions 1460 ± 25 and 1450 ± 15 cm^{-1} and the symmetric vibrations mostly displayed in the range 1435 ± 15 cm^{-1}. The intensity of these vibrations is only weak to moderate. In the spectra of $H_2NC(=O)OMe$ and $Cl_2NC(=O)OMe$, the symmetric deformation δ_sMe is reported at 1369 and 1386 cm^{-1}, respectively.[23] The DFT calculations give 1464, 1456 and 1440 cm^{-1} as δ_{as}Me and δ_sMe, respectively, for the title compound. The bands observed at 1453 and 1439 cm^{-1} in the IR spectrum are assigned to these modes. For methyl (2-methyl-4,6-dinitrophenyl sulfanyl) ethanoate[14] the bending vibrations of the methyl group are reported at 1464, 1455, 1375 (DFT), 1376 (Raman) and 1371 cm^{-1} (IR). For methoxycarbonylsulfenyl compounds, the bending modes of the methyl group are reported at 1465, 1454, 1453, 1450, 1437, 1436, 1435, 1428, 1302 cm^{-1} in IR, 1452, 1329 cm^{-1} in Raman, 1499, 1488, 1470 cm^{-1} (DFT)[4] and at 1443, 1436, 1368 cm^{-1} in IR, 1450, 1410 cm^{-1} in Raman, 1495, 1484, 1468 cm^{-1} (DFT).[5]

The methyl rock ρMe has been observed at 1185 ± 35 cm^{-1} often as a shoulder on the low wavenumber wing of νC(=O)O absorption.[23] In *i*-PrC(=O)O-OMe this mode (1194 cm^{-1}) is next to νC(=O)O (1202 cm^{-1}) but *t*-BuC(=O)-OMe both absorptions[23] coincide at 1193 cm^{-1}. The second methyl rock[23] absorbs at 1155 ± 35 cm^{-1}. The bands calculated at 1173 and 1142 cm^{-1} are assigned as rocking modes of the methyl group. Experimentally the bands observed at 1152 cm^{-1} in the IR spectrum and at 1156, 1145 cm^{-1} in the Raman spectrum are assigned rocking modes of the methyl group. The methyl rocking modes are reported at 1195, 1171 cm^{-1} in IR, 1193, 1148 cm^{-1} in Raman, 1212, 1181, 1167 cm^{-1} (DFT)[5] and at 1194, 1190 cm^{-1} in IR, 1196 cm^{-1} in Raman, 1211 cm^{-1} (DFT).[4]

The most characteristic bands of esters arising from the C=O stretching vibration occurring at 1750 ± 50 cm^{-1} with a strong to very strong intensity.[23] Methyl esters of α-unsaturated and aromatic carboxylic acids[23] show the νC=O at 1725 ± 25 cm^{-1}. Seth Paul and Van Duyse[28] identified the region 1730 ± 15 cm^{-1} for mono- and di-substituted methyl benzoates and Nyquist[29] proposed 1733 ± 5 cm^{-1} for *o*-phtalic esters. The intensity of the carbonyl stretching band can increase owing to conjugation, or formation of hydrogen bonds. The increase in conjugation, therefore leads the intensification of the Raman lines and increase IR band intensities. The stretching modes of the carbonyl group of the ester part may be lowered to around 1720 cm^{-1} in the presence of conjugation.[30] In the present study the νC=O mode is seen at 1733 cm^{-1} in IR, 1741 cm^{-1} in Raman and 1744 cm^{-1} theoretically. For methoxycarbonylsulfenyl compounds, νC=O is reported at 1772 (DFT), 1779 (IR), 1756 cm^{-1} (Raman)[4] and at 1788 (DFT), 1750 (IR), 1734 cm^{-1} (Raman).[5]

The C(=O)O stretching vibration, often considered as the C-O-C asymmetric stretch, appears strongly at 1255 ± 60 cm^{-1}, a region in good agreement with that of the νC-O in carboxylic acids (1250 ± 80 cm^{-1}).[23] The band at 1265 cm^{-1} in IR spectrum is assigned as the νC-O-C mode and the calculated value of this mode is 1278 cm^{-1}. The O-C stretching vibration of the O-CH_3 group, coupled with the methyl rock, appears in the wide region 975 ± 125 cm^{-1} with an intensity varying from weak to strong.[23] This vibration is often called the symmetric COC stretching vibration. The band at 999 cm^{-1} given by DFT calculation is assigned as this mode. Erban *et al.*[4] reported the νOC stretching mode at 963 (DFT), 977 cm^{-1} (IR), 937 cm^{-1} (Raman) and Vallejos *et al.*[5] reported this mode at 940 (Raman), 959 cm^{-1} (DFT).

The δC=O deformation[23] has been found in the region 710 ± 80 cm^{-1} and the band at 748 (Raman), 765 cm^{-1}

(DFT) is assigned as this mode. The γC=O absorption[23] is in the range 625 ± 75 cm^{-1} and the DFT calculation give this mode at 667 cm^{-1}. The C-C(=O)-O deformation[23] rock absorbs weakly to moderately in the region 435 ± 95 cm^{-1}. For most of the methyl esters give the region 445 ± 60 cm^{-1} for this rock. Methyl acetate absorbs at 435 cm^{-1} and methyl propanoate at 440 cm^{-1}.[23] Saunders *et al.*[31] found 445 ± 10 cm^{-1} as C-C(=O)-O deformation for a series of fourteen aliphatic methyl esters. The DFT calculations give this mode at 409 cm^{-1} and a weak band is observed at 422 cm^{-1} in the Raman spectrum. The skeletal C-O-C deformation[23] appears in the region 325 ± 40 cm^{-1}. For methyl formate and methyl acetate this mode is at 330 and 318 cm^{-1}, respectively.[23] Saunders *et al.*[31] found 330 ± 15 cm^{-1} for a series of aliphatic methyl esters. For the title compound this C-O-C deformation is found at 335 cm^{-1}.

Nitro group vibrations

The most characteristic bands in the spectra of nitro compounds are due to the NO_2 stretching vibrations, which are the two most useful group wavenumbers, not only because of their spectral positions but also for their strong intensities.[23] Nitrobenzene derivatives display $\nu_{as}NO_2$ in the regions 1535 ± 30 cm^{-1} and 3-nitropyridines at 1530 ± 20 cm^{-1}.[23,32] The authors have reported bands at 1604, 1583, 1538 cm^{-1} (Raman), 1604, 1582, 1532 (IR) and 1605, 1588, 1565, 1544 cm^{-1} (DFT) as $\nu_{as}NO_2$ modes.[14] The bands seen at 1583, 1531 cm^{-1} in the Raman spectrum and 1599, 1583, 1533 cm^{-1} in the IR spectrum are assigned as $\nu_{as}NO_2$ for the title compound. The calculated values for these modes are 1609, 1592, 1568 and 1546 $cm^{-1.}$ In substituted nitrobenzenes[23,32] ν_sNO2 appears strongly at 1345 ± 30 cm^{-1}, in 3-nitropyridine at 1350 ± 20 cm^{-1}, and in conjugated nitroalkenes[33] at 1345 ± 15 cm^{-1}. Panicker *et al.*[14] reported 1346 (Raman) , 1344 (IR) and 1348, 1339 cm^{-1} (DFT) as ν_sNO_2 modes .The band at 1341 cm^{-1} in IR spectrum, 1345 cm^{-1} in Raman spectrum and 1365, 1344 cm^{-1} (calculated) are assigned as ν_sNO_2 modes. The NO_2 scissors occur at higher wavaenumbers (850 ± 60 cm^{-1}) when conjugated to C=C or aromatic molecules.[34,35] In aromatic compounds the wagging mode ωNO_2 is assigned at 740 ± 50 cm^{-1} with a moderate to strong intensity.[23] The bands at 784 cm^{-1} in the Raman spectrum, 800, 737 cm^{-1} in the IR spectrum and 775, 740 cm^{-1} (DFT) are assigned as the deformation bands of nitro groups. The DFT calculations give the wagging modes ωNO_2 at 722 and 720 cm^{-1}. The rocking mode ρNO_2 is active in the region 540 ± 70 cm^{-1} in aromatic nitro compounds.[23] Varsanyi *et al.*[36] found 70 ± 20 cm^{-1} and Suryanarayana *et al.*[37] found 65 ± 10 cm^{-1} as the torsion of the NO_2 for aromatic compounds.

CH_2 group vibrations

The vibrations of the CH_2 group, the asymmetric stretch $\nu_{as}CH_2$, symmetric stretch ν_sCH_2, scissoring vibration δCH_2 and wagging vibration ωCH_2 appear in the regions 3000 ± 50, 2965 ± 30, 1455 ± 55 and 1350± 85 cm^{-1}, respectively.[23,38] The DFT calculation give $\nu_{as}CH_2$ at 3075 and ν_sCH_2 at 2997 cm^{-1}. The CH_2 deformation band which comes near 1463 cm^{-1} in alkenes[39] is lowered to about 1440 cm^{-1} when the CH_2 group is next to a double or triple bond. A carbonyl, nitrile or nitro group each lowers the wavenumber of the adjacent CH_2 group[38] to about 1425 cm^{-1}. For the title compound the DFT calculation give 1431, 1209, 1121 and 1107 cm^{-1} as the deformation bands of CH_2 group. The rocking mode[23] ρCH_2 is expected in the range 895 ± 85 cm^{-1} and the band at 832 (DFT), 816 (IR) and 819 cm^{-1} (Raman) are assigned as ρCH_2 modes. The torsional modes of methyl, CH_2 and nitro group are seen in the low wavenumber region.[23]

Phenyl ring and other vibrations

In poly substituted benzenes, the aromatic CH stretching vibrations[23,40] absorb weakly to moderately between 3000 and 3120 cm^{-1}. The DFT calculations give bands at 3150 and 3138 cm^{-1}. The aromatic CH out-of-plane deformation[23] are observed in the range 720-1000 cm^{-1}. The spectral positions of the weaker γCH near 900 cm^{-1} correlates well with electron donating or electron attracting properties of the substituent. The CH in-plane deformations δCH are obtained at 1056 cm^{-1} in the IR spectrum and at 1058 cm^{-1} in the Raman spectrum. The DFT calculation gave 1179, 1173 and 1092 cm^{-1} as these modes. The out-of-plane deformations and in-plane deformation of the phenyl ring[23] are observed below 1000 cm^{-1} and these modes are not pure but contain a significant contribution from other modes and are substituent sensitive. The ring breathing mode appears as a weak band near 1000 cm^{-1}, in mono-, 1,3-di- and 1,3,5-tri substituted benzenes.[23] In the otherwise substituted benzenes however, this vibration is substituent sensitive and difficult to distinguish from the ring in-plane deformation.[23] For the title compound the ring breathing mode appears as a strong band at 1004 cm^{-1} in the Raman spectrum, and at 1025 cm^{-1} theoretically. Aromatic nitro compounds show a C-N stretching vibration[24,41] near 870 cm^{-1}. In the present study, the νCN is 890 and 912 cm^{-1} in the IR spectrum.

For the title compound the bond lengths C_{22}-O_{23}, C_{22}-O_{24}, and C_{25}-O_{24} are found to be 1.2139, 1.3429 and 1.4418 Å, respectively. For methoxycarbonylsulfenyl compounds, the reported values of bond lengths are C_{22}-O_{23}= 1.1962 (XRD), 1.2 (DFT), 1.215 Å (MP2),[5] 1.19(XRD), 1.202

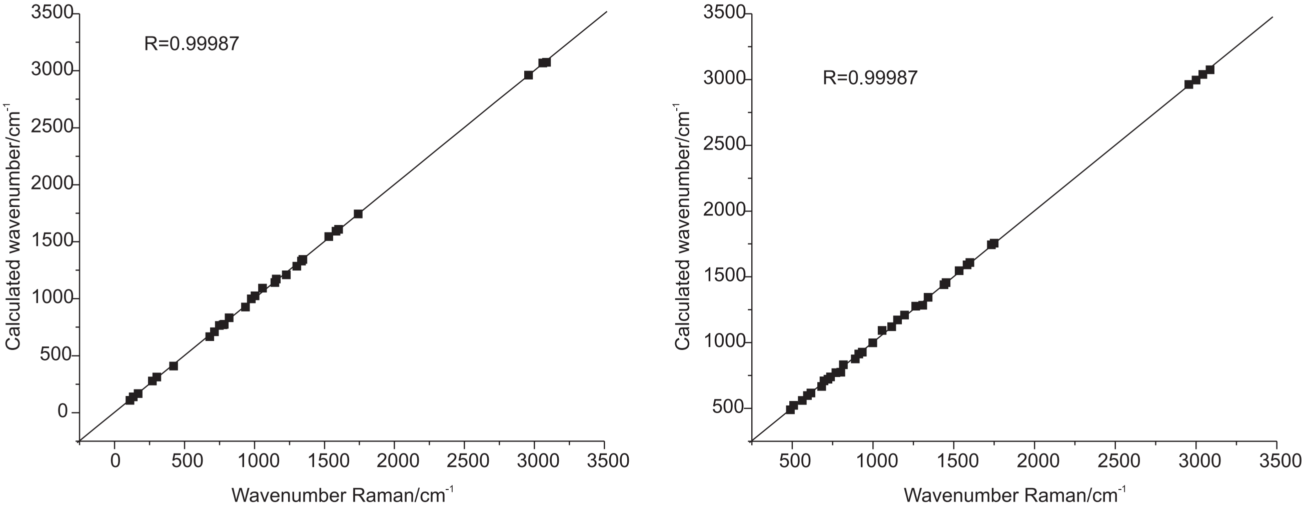

Figure 5. Correlation graphs.

(DFT), 1.199 Å (MP2)[4] and C_{22}-O_{24} = 1.3249 (XRD), 1.341(DFT), 1.34 Å (MP2) and C_{22}-O_{24} = 1.4587 (XRD), 1.449 Å (DFT, MP2).[4] For the title compound, the bond angles O_{23}-C_{22}-O_{24}, C_{22}-O_{24}-C_{25} are 124.5 and 115.3°, respectively, while the reported values are 127.3 and 115.8°, respectively.[4] In the present case, the carbon-sulfur bond lengths C_3-S_8 = 1.7949 and C_{19}-S_8 = 1.8493 Å while the reported values are 1.7846 (XRD), 1.792 (MP2) 1.811 Å (DFT)[4] and 1.771 (XRD), 1.803 (DFT), 1.783 Å (MP2).[5] The carbon-oxygen distances unambiguously define the single and double bonds in the carboxylate group (C_{16}-O_{17} = 1.3546 and C_{16}-O_{18} = 1.2119 Å) and are in agreement with the values given by Ng *et al.*[42] The aromatic ring of the title compound is somewhat irregular and the spread of bond distances is 1.3865-1.4199 Å, which is similar to the spread reported by Smith *et al.*[12]

The DFT calculation gives shortening of angle C_4-C_3-S_8 by 1.6° and increase of angle C_2-C_3-S_8 by 5° from 120° at C_3 position and this asymmetry of exocyclic angles reveal the repulsion between carboxylic group and the phenyl ring.[43] The reduction in the angle C_{19}-C_{22}-O_{24} to 111.8° from 120° is associated with repulsive interactions, repulsion between methyl and O_{23}, which is evident from the enlargement in the angle O_{23}-C_{22}-O_{24} by 4.5°. Similar repulsion leads to enlargement of C_{19}-C_{22}-O_{23} by 3.6°. The angle C_{22}-O_{24}-C_{25} is reduced by 4.7° due to the repulsion between the two lone pairs of O_{24} and the neighboring atoms. DFT calculations give the shortening of the angle C_5-C_4-N_9 by 4.8° and the increase of angle C_3-C_4-N_9 by 1.1° from 120° at C_4 position and this asymmetry of exocyclic angle, reveal the hydrogen bonding with H_{10}, which is evident from the enlargement in the angle C_5-C_4-C_3 by 3.8°. At C_6 position the exocylic angles are nearly the same. For a molecule containing a methoxy group, electronic charge is back-donated from the lone pair of oxygen atom to the σ^* orbital of C-H bonds, causing a weakening of the C-H bonds.[44] This is followed by the increase in C-H bond distance and the decrease in C-H force constants and can result in the enhancement of IR band intensities of the C-H stretching modes.[45] Another electronic effect, induction, produces stronger polarization of C-H bonds along with an increase in C-H force constant and charge on the hydrogen atom and with a decrease in C-H bond length.[45] In the title compound, the methoxy hydrogen atoms are subjected to induction, which cause a decrease in the C-H bond length.

In order to investigate the performance and vibrational wavenumbers of the title compound, root mean square (RMS) and correlation coefficient between calculated (Figure 5) and observed vibrational wavenumbers were calculated. RMS values of wavenumbers were calculated using the following expression.[46]

$$RMS = \sqrt{\frac{1}{n-1}\sum_{i}^{n}\left(\nu_i^{calc} - \nu_i^{\exp}\right)^2}$$

The RMS errors between the observed and scaled wavenumbers are found to be 12.41 and 13.19 for IR and Raman wavenumbers. The small differences between experimental and calculated vibrational modes are observed. It must be due to the fact that hydrogen bond vibrations present in the crystal lead to strong perturbation of the infrared wavenumbers and intensities of many other modes. Also, we state that experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

SERS spectrum

The relative intensities from SERS spectra are expected to differ significantly from normal Raman spectrum owing to specific surface selection rules.[47] The surface selection rule suggest that for a molecule adsorbed flat on the silver surface, its out-of-plane bending modes will be more enhanced when compared with its in-plane bending modes and *vice-versa* when it is adsorbed perpendicular to the surface.[47,48] It is further seen that vibrations involving atoms that are close to the silver surface will be enhanced. When the wavenumber difference between Raman bands in the normal and SERS spectra is not more than 5 cm^{-1}, then the molecular plane will be perpendicular to the silver surface.[49] In the case of the SERS spectrum of methyl(2-methyl-4,6-dinitro phenylsulfanyl)ethanoate[14] the CH stretching mode of the methyl group in the methoxy carbonyl group appears at 2936 cm^{-1} shifted from 2962 cm^{-1} in the normal Raman spectrum. In the present study the methyl stretching vibration is observed at 2933 cm^{-1} in the SERS spectrum as a broad band shifted from 2958 cm^{-1} from the normal Raman spectrum. It should be related to the closeness of the methyl group to the silver surface. This is justifiable because the modes in groups directly interacting with the metal surface will be prominent in the SERS spectrum and undergo a wavenumber shift.[50] Further, the methyl bands at 1465, 1448, 1427 cm^{-1} are also observed in the SERS spectrum thereby supporting the above argument. In our previous studies[14] the symmetric stretching mode of NO_2 is reported at 1346 cm^{-1} in the normal Raman spectrum and at 1319 cm^{-1} in the SERS spectrum. For 2-amino,5-nitropyrimidine[51] the symmetric NO_2 stretching mode corresponds to the most intense band, which appears broad and significantly downshifted from 1344 cm^{-1} (Raman) to 1326 cm^{-1} (SERS), suggesting a binding to silver surface through the lone pairs of oxygen atom. Carrasco *et al.*[52] observed $\nu_{as}NO_2$ band in the SERS spectrum at *ca.* 1500 cm^{-1} with medium intensity which demonstrates the importance of nitro group in regard to the interaction with the metal. Further, they observed the enhancement of νPh modes revealing that the molecule is oriented perpendicular to the metal surface where as the changes that occur in the nitro group indicates that the interaction occurs through O atoms of the nitro moiety. The interaction induces a π electronic redistribution primarily around both the nitro group and the aromatic portion in the vicinity of substituent site. Also Gao and Weaver[53] observed broadening and downshift of the corresponding band of nitrobenzene, adsorbed on gold via nitro group. For the title compound, the symmetric stretching mode of nitro group seen at 1345 cm^{-1} in the normal Raman spectrum appears at 1332 cm^{-1} in the SERS spectrum. A charge transfer from the oxygen atoms of the nitro group to the metal is evidenced by the marked downshift of the symmetric stretching mode of the nitro group as detected by SERS.[51-53] Interaction through the nitro group was also supported by the presence of modes at 1635, 1567, 804, 741 cm^{-1} in the SERS spectrum. According to surface selection rules, vibrations involving atoms that are close to the silver surface will be enhanced.[47,48]

It has been well established that the presence or absence of the benzene ring CH stretching vibration is a reliable probe for the perpendicular or parallel orientation, respectively, of the benzene ring with respect to the metal surface.[54,55] In the SERS spectrum of the title compound the aromatic CH stretching vibration is observed as a weak broad band at 3139 cm^{-1} which is absent in the normal Raman spectrum, which suggests that the phenyl ring may be in a position close to the perpendicular to the silver surface[49,54,55] possibly a tilted position since it is a weak band. It has also been documented in literature[56] when a benzene ring moiety interacts directly with a metal surface, the ring breathing mode has to be red shifted by ca. 10 cm^{-1} along with substantial band broadening in the SERS spectrum. Neither a substantial red shift nor significant band broadening was identified in the SERS spectrum of the title compound implying that the possibility of a direct ring π-orbital to metal interaction should be low, in accordance to a tilted position of the ring. Also, the in-plane CH vibrations of the phenyl ring are present in the SERS spectrum at 1188, 1171 cm^{-1} as very weak bands and at 1041 cm^{-1} as a medium band. The out-of-plane CH mode is also present at 938 cm^{-1} in the SERS spectrum. This suggests that the benzene ring is oriented in a tilted position. The νPh vibrational modes corresponding to the bands at 1635, 1567, 1448, 1383 cm^{-1} are weak in intensity in the SERS spectrum. Correspondingly, in the normal Raman spectrum, only a single strong band is observed at 1600 cm^{-1}. This indicates an interaction between the phenyl ring and the metal surface. The presence of a sensitive substituent in-plane and out-of-plane modes, at 593, 554, 397, 354 cm^{-1} supports the tilted orientation of the molecule on the metal surface.

The C=O stretching band is absent in the SERS spectrum while the band of νC(=O)O is present at 1254 cm^{-1} in the SERS spectrum. The presence of methyl group modes in the SERS spectrum indicates the closeness of the methyl group with the metal surface and a possible interaction of the silver surface with the carbonyl group. This is supported by the strong band at 241 cm^{-1} which may be due to Ag-O stretching vibration.[50,57,58] This band may be due to Ag-O/Ag-S stretching vibration. But in the SERS spectrum, nitro and carbonyl group vibrations are affected and the absence of the sulfur group vibration indicates that the 241 cm^{-1} band is due to Ag-O stretch. We have reported similar strong band at *ca.* 240 cm^{-1} for the Ag-O stretching vibration in earlier studies.[14,57]

Conclusions

SERS spectroscopy is a good technique for studying adsorption of molecules on metal surface. From the SERS spectrum we have deduced that the title compound has a tilted orientation on the silver surface. Significant metal-molecule interaction has been substantiated by the appearance of intense Ag-O mode in the SERS spectrum and this is indicative of the nearness of nitro and carbonyl group to the silver surface. The presence of methyl modes in the SERS spectrum shows the nearness of the methyl group to the metal surface and it affects the orientation and metal molecule interaction. The calculated vibrational wavenumbers obtained on theoretical method are in good agreement with the experimental values obtained for the investigated molecule.

Supplementary Information

Supplementary data, optimized geometry of the molecule are available free of charge at http://jbcs.sbq.org.br, as PDF file.

References

1. Fleischmann, M.; Hendra, P. J.; McQuillan, A. J.; *Chem. Phys. Lett.* **1974**, *26*, 163.
2. JeanMaire, D. L.; Van Duyne, R. R.; *J. Electroanal. Chem.* **1977**, *84*, 1.
3. Dudova, K.; Castek, F.; Machacek, V.; Simunek, P.; *Molecules* **2002**, *7*, 7.
4. Erben, M. F.; Della Vedova, C. O.; Romano, R. M.; Boese, R.; Oberhammer, H.; Willner, H.; Sala, O.; *Inorg. Chem.* **2002**, *41*, 1064.
5. Vallejos, S. T.; Erben, M. F.; Willner, H.; Boese, R.; Della Vedova, C. O.; *J. Org. Chem.* **2007**, *72*, 9074.
6. Lajumen, L. H. J.; Kokkonen, P.; Nissi, A.; Ruotsalainen, H.; *Thermochim. Acta* **1984**, *72*, 219.
7. Anjaneyulu, Y.; Rao, N. V. S.; Rao, P. R.; Murthy, L. N.; Pisipati, V. G. K. M.; *Indian J. Pure Appl. Phys.* **1986**, *24*, 256.
8. Ranford, J. D.; Sadler, P. J.; Tocher, D. A.; *J. Chem. Soc., Dalton Trans.* **1993**, *22*, 3393.
9. Valigura, D.; Melnik, M.; Komen, M.; Martiska, L.; Korabik, M.; Mrozinsky, J.; Glowiak, T.; *Polyhedron* **2004**, *23*, 2447.
10. Valigura, D.; Melnik, M.; Komen, M.; Martiska, L.; Korabik, M.; Glowiak, T.; *Inorg. Chem. Commun.* **2004**, *7*, 548.
11. Smith, G.; Wermuth, U. D.; White, J. M.; *Acta Crystallogr.* **2001**, *E57*, 1036.
12. Smith, G.; Lyncy, D. E.; Byriel, K. A.; Kennard, C. H. L.; *Aust. J. Chem.* **1995**, *48*, 1133.
13. Kumar, V. S. S.; Kuduva, S. S.; Desiraju, G.R.; *J. Chem. Soc., Perkin Trans.* **1999**, *2*, 1069.
14. Panicker, C. Y.; Varghese, H. T.; Philip, D.; Nogueira, H. I. S.; Castkova. K.; *Spectrochim. Acta Part A* **2007**, *67*, 1313.
15. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr. J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; *Gaussian 03, Revision C.02* Gaussian, Inc.: Wallingford, CT, **2004**.
16. Lee, P. C.; Meisel, D. J.; *J. Phys. Chem.* **1982**, *86*, 3391.
17. Nogueira, H. I. S.; *Spectrochim. Acta Part A* **1998**, *54*, 1461.
18. Foresman, J. B.; Frisch, E.; *Exploring Chemistry with Electronic Structure Methods: A Guide to using Gaussian*; Gaussian Inc: Pittsburg, PA, 1996.
19. Scott, A. P.; Radom, L.; *J. Phys. Chem. A* **1996**, *100*, 16502.
20. Rauhut, G.; Pulay, P.; *J. Phys. Chem.* **1995**, *99*, 3093.
21. Flukiger, P.; Luthi, H. P.; Portmann S, Weber, J.; *MOLEKEL 4.3*; Swiss Centre for Scientific Computing, Manno, Switzerland, 2000-2002.
22. Portmann, S.; Luthi, H. P.; *Chimia* **2000**, *54*, 766.
23. Roeges, N. P. G.; *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, Wiley: New York, 1994.
24. Silverstein, R. M.; Bassler, G. C.; Morril, T. C.; *Spectrometic Identification of Organic Compounds,* 5th ed., John Wiley and Sons Inc.: Singapore, 1991.
25. Philip, D.; John, A.; Panicker, C. Y.; Varghese, H. T.; *Spectrochim. Acta Part A* **2001**, *57*, 1561.
26. Panicker, C. Y.; Varghese, H. T.; John, A.; Philip, D.; Istvan, K.; Keresztury, G.; *Spectrochim. Acta Part A* **2002**, *58*, 281.
27. Varghese, H. T.; Panicker, C. Y.; Philip, D.; Chowdhury, J.; Ghosh, M.; *J. Raman Spectrosc.* **2007**, *38*, 323.
28. Seth Paul, W. A.; Van Duyse, A.; *Spectrochim. Acta Part A* **1972**, *28*, 211.
29. Nyquist, R. A.; *Appl. Spectrosc.* **1972**, *26*, 81.
30. Sajan, D.; Binoy, J.; Joe, I. H.; Jayakumar, V. S.; Zaleski, J.; *J. Raman Spectrosc.* **2005**, *36*, 221.

31. Saunders, J. E.; Lucier, J. J.; Bentley, F. F.; *Appl. Spectrosc*. **1968**, *22*, 697.
32. Prejessy, A.; Rasala, D.; Tomasik, P.; Gawinecki, R.; *Collect. Czech. Chem. Commun*. **1985**, *50*, 2443.
33. Brown Jr, J. F.; *J. Am. Chem. Soc*. **1955**, *77*, 6341.
34. Exner, O.; Kovac, S.; Solcaniovas, E.; *Collect. Czech. Chem. Commun*. **1972**, *37*, 2156.
35. Ranga Rao, D. S.; Thyagarajan, G.; *Indian J. Pure Appl. Phys*. **1978**, *16*, 941.
36. Varsanyi, G.; Molner-Paal, E.; Kosa, K.; Keresztury, G.; *Acta Chim. Acad. Sci. Hung*. **1979**, *106*, 481.
37. Suryanaranaya ,V.; Kumar, A. P.; Rao, G. R.; Pandey, G. C.; *Spectrochim Acta Part A* **1992**, *48*, 1481.
38. Colthup, N. B.; Daly, L. H.; Wiberly, S. E.; *Introduction to Infrared and Raman Spectroscopy,* 2nd ed., Academic Press: New York, 1985.
39. McMurry, H. L.; Thornton, V.; *Anal. Chem.* **1952**, *24*, 318.
40. Varsanyi. G.; *Assignments of Vibrational Spectra of Seven Hundred Benzene Derivatives,* Wiley: New York, 1974.
41. Socrates. G.; *Infrared and Raman characteristic Group frequencies,* Wiley: Middlesex, UK, 2001.
42. Ng, S. W.; Naumov, P.; Drew, M. G. B.; Wojciechowski, G.; Brzezinski, B.; *J. Mol. Struct*. **2001**, *595*, 29.
43. Bujak, M.; Zaleski, J.; Preszhdo, V.; Uspienskij, B.; *Acta Crystallogr*. **2002**, *58C*, 76.
44. Rumi, M.; Zerbi, G.; *J. Mol. Struct*. **1999**, *509*, 11.
45. Kurtz, S. K.; Perry, T. T.; *J. Appl. Phys*. **1968**, *39*, 3798.
46. Krishnakumar, V.; Dheivamalar, S.; Xavier, R. J.; Balachandran, V.; *Spectrochim. Acta Part A* **2006**, *65*, 147.
47. Creighton, J. A.; *Spectroscopy of Surfaces - Advances in Spectroscopy*, Wiley: New York, 1988, vol. 16, p. 37 (Chapter 2).
48. Gao, X.; Davies, J. P.; Weaver, M. J.; *J. Phys. Chem. A* **1990**, *94*, 6858.
49. Levi, G.; Patigny, J.; Massault, J. A.; Aubard J.; *13th International Conference on Raman Spectroscopy,* Wurzburg, 1992, p. 652.
50. Kai, S.; Chaozhi, W.; Guangzhi, X.; *Spectrochim. Acta Part A* **1989**, *45*, 1029.
51. Muniz-Miranda, M.; *Vib. Spectrosc*. **2002**, *29*, 229.
52. Carrasco, E. A.; Campos-Vallett, M.; Leyton, P.; Diaz, G.; Clavijo, R. E.; Garcia-Ramos, J. V.; Inostroza, N.; Domingo, C.; Sanchez-Cortes, S.; Koch, R.; *J. Phys. Chem. A* **2003**, *107*, 9611.
53. Gao, P.; Weaver, M. J.; *J. Phys. Chem*. 1985, *89*, 5040.
54. Suh, J. S.; Moskovits, M.; *J. Am. Chem. Soc*. **1986**, *108*, 4711**.**
55. Creighton, J. A.; *Surf. Sci*. **1983**, *124*, 209.
56. Gao, P.; Weaver, M. J.; *J. Phys. Chem. A* **1989**, *93*, 6205.
57. Panicker, C. Y.; Varghese, H. T.; Philip, D.; Nogueira, H. I. S.; *Spectrochim. Acta* **2006**, *64A*, 744.
58. Greaves, S. J.; Griffith, W. P.; *J. Raman Spectrosc*. **1988**, *19*, 503.

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