VIBRATIONAL STUDY AND SPECTRA-STRUCTURE CORRELATIONS IN MAGNESIUM DISACCHARINATE HEPTAHYDRATE, Mg(sac)$_2$·7H$_2$O*

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Infrared and Raman vibrational spectra of magnesium disaccharinate heptahydrate, Mg(sac)$_2$·7H$_2$O, in the 4000–380 cm^{-1} region (for infrared) and 4000–100 cm^{-1} region (for Raman) were studied. The assignment of the spectra was based on the experimental data for the previously studied metal saccharinates as well as the literature data for the *ab initio* calculations on the free deprotonated saccharinato species. Special attention was paid to the analysis of the H$_2$O, CO and SO$_2$ stretching modes. The spectral picture in the regions of the water, carbonyl and sulfonyl stretches is correlated with the number of the crystallographically determined non-equivalent H$_2$O, CO and SO$_2$ structural units. It was found that the presence of seven crystallographically different water molecules in the structure (fourteen different O$_w$···O and O$_w$···N distances) is not reflected in the appearance of the expected fourteen IR bands in the region of the OD stretching vibrations of the isotopically isolated HDO molecules. This must be due to the existence in the structure of several O$_w$···O or O$_w$···N hydrogen bonds with very similar strengths causing an overlap of the corresponding bands in the spectrum. Despite the presence of two carbonyl groups with practically identical C–O distances [124.2(3) and 124.0(3) pm], two clearly separated bands are registered in the carbonyl stretching region of the IR (1660 and 1627 cm^{-1}) and Raman spectrum (1648 and 1620 cm^{-1}). On the other hand, although two non-equivalent SO$_2$ groups are present in the structure of Mg(sac)$_2$·7H$_2$O, only one pair of bands due to SO$_2$ stretchings [ν_{as}(SO$_2$) and ν_s(SO$_2$) modes] is registered in the IR spectrum.

Key words: magnesium disaccharinate heptahydrate; IR spectrum; Raman spectrum; spectra-structure correlations

ВИБРАЦИОНА СТУДИЈА И СПЕКТАР-СТРУКТУРНИ КОРЕЛАЦИИ КАЈ МАГНЕЗИУМ ДИСАХАРИНАТ ХЕПТАХИДРАТ, Mg(sac)$_2$·7H$_2$O*

Изучувани се инфрацрвените и раманските вибрациони спектри на магнезиум дисахаринат хептахидрат, Mg(sac)$_2$·7H$_2$O, во подрачјето 4000–380 cm^{-1} (за инфрацрвените) и 4000–100 cm^{-1} (за раманските). Асигнацијата на спектрите е заснована на експерименталните податоци за претходно изучуваните метални сахаринати, како и на литературните податоци од *ab initio* пресметките за слободен депротониран сахаринатен примерок. Специјално внимание е обрнато на анализата на валентните модови на H$_2$O, CO и SO$_2$. Изгледот на спектарот во подрачјето на валентните вибрации на молекулите вода, карбонилната и сулфонилната група е корелиран со бројот на кристалографски определените нееквивалентни H$_2$O, CO и SO$_2$ групи во кристалната структура. Најдено е дека постоењето на седум кристалографски различни молекули вода во структурата (четиринаесет различни O$_w$···O односно O$_w$···N растојанија) не е одразено во појава на очекуваните четиринаесет инфрацрвени ленти во подрачјето на OD валентните вибрации на изотопски изолираните HDO молекули. Тоа секако се должи на постоењето, во структурата, на неколку O$_w$···O или O$_w$···N водородни врски со многу слични

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* Sac stands for deprotonated saccharin.

јачини, што доведува до препокривање на соодветните ленти во спектарот. Наспроти постоењето, во структурата на ова соединение, на две карбонилни групи со многу блиски C–O растојанија [124.2(3) и 124.0(3) pm], во инфрацрвениот спектар (1660 и 1627 cm^{-1}) и во раманскиот спектар (1648 и 1620 cm^{-1}) се регистрирани по две јасно раздвоени ленти во подрачјето на карбонилните валентни вибрации. Од друга страна, и покрај постоењето на две нееквивалентни SO$_2$-групи во структурата на Mg(sac)$_2$·7H$_2$O, инфрацрвениот спектар во подрачјето на SO$_2$-валентните вибрации [ν$_{as}$(SO$_2$ и ν$_s$(SO$_2$) модови] се појавува само еден пар ленти.

Клучни зборови: магнезиум дисахаринат хептахидрат; инфрацрвен спектар; рамански спектар; спектар-структурни корелации

INTRODUCTION

Saccharin (1,2-benzisothiazole-3(2*H*)-one 1,1-dioxide) (Fig. 1) is about 500 times sweeter than sugar but is practically insoluble in the water at room temperature. Therefore its water-soluble sodium salt is the most frequently used artificial sweetener for diabetics as well as a dietetic food additive. Due to the presence of three different functional groups (imino, carbonyl and sulfonyl) in the structure of saccharin, its deprotonated form serves as a versatile polyfunctional ligand forming complexes with various metals [1]. The versatile ligation properties of saccharin [e.g. 2–16] and the physiological activity [e.g. 17] of saccharin and its metal complexes have been widely studied mainly due to its proven cancerous nature in rats [e.g. 18]. Consequently, in 1977 saccharin joined the list of human potential cancer-causing substances in USA, the products containing saccharin carrying a special warning label [1, 19]. Since in the meantime numerous epidemiological studies did not provide a clear evidence that saccharin indeed causes cancer in humans, in 2001 the use of the warning label on saccharin-containing products was discontinued [20, 21].

Fig. 1. Structural formula of saccharin with the atom labeling

Continuing our systematic study of the coordination properties of saccharin in various metal saccharinates, in addition to the numerous structural and spectroscopic studies of other saccharinate compounds, we have undertaken a study of the structural and/or spectroscopic characteristics of saccharin compounds with metals of group 2 (Mg, Ca, Sr and Ba). Aside of this study, the reported structural and vibrational spectroscopic data on Mg and earth metal (Ca, Sr and Ba) saccharinates are rather scarce. Thus, the crystal structure of magnesium disacchari-

nate heptahydrate has been reported [4] and the infrared spectra of the saccharinates of Ca, Sr and Ba in the regions of the OH, OD, CO and SO$_2$ stretching modes (together with their X-ray powder diagrams) have been studied [22].

Here we report the results of vibrational investigations and complete assignment of the infrared and Raman spectra of magnesium disaccharinate heptahydrate, Mg(sac)$_2$·7H$_2$O, as well as the correlation of the spectroscopic data with the previously published (by us) structural data for this compound. Special attention is paid to the discussion concerning the H$_2$O, HOD, CO and SO$_2$ stretching vibrations.

EXPERIMENTAL

The studied compound was synthesized from warm aqueous solution of saccharin and MgCO$_3$. Partially deuterated analogues were obtained by recrystallization of the protiated sample from D$_2$O.

The room temperature (RT) and liquid nitrogen temperature (LNT) infrared spectra in the 4000–380 cm^{-1} region were recorded on a Perkin-Elmer 580 infrared spectrophotometer using KBr pellets. A variable temperature cell (RIIC VLT-2) was used for the LNT measurements. The room-temperature Raman spectra in the 4000–100 cm^{-1} region were recorded on a micro-Raman multichannel spectrometer – Horiba JobinYvon LabRam Infinity (*f* × 100) operating at 532 nm YAG laser line. The GRAMS/32 software package was applied for the spectral manipulations.

STRUCTURAL DATA

The results of the crystal structure determination of magnesium disaccharinate heptahydrate, Mg(sac)$_2$·7H$_2$O, have already been published [4]. Here, only some important general characteristics of the structure as well as details concerning the H$_2$O, CO and SO$_2$ groups are mentioned.

The crystals of the title compound belong to the triclinic system, space group $P\bar{1}$, $Z = 2$. The structure consists of two crystallographically different saccharinate anions, one type of magnesium cations and seven independent types of water molecules. Each magnesium ion is octahedrally coordinated by six oxygen atoms, one of them belonging to the carbonyl group of the saccharinate anion [labeled O(13) in [4]] and the remaining five to the water molecules. The remaining two water molecules are non-coordinated to the metal atom. The Mg–O distances range from 203.0 to 211.3 pm.

Only one of the two independent saccharinate ions is coordinated to the magnesium cation, the second one being at a distance from Mg larger than 340 pm. The carbonyl oxygen of the non-coordinated saccharinate anion, {labeled O(23) in [4]}, is a proton acceptor involved in hydrogen bonding with the neighboring water molecules. The two C–O distances of the non-coordinated and the coordinated carbonyl group are very close to each other (124.2 and 124.0 pm, respectively). Both O–S–O angles in the two crystallographically different sulfonyl groups are practically identical (114.4 and 114.7 °), whereas the S–O distances are 144.5 and 144.9 pm in the first and 142.2 and 144.5 pm in the second SO₂ group.

All seven independent water molecules (five coordinated and two non-coordinated) are involved in the hydrogen bonding with the neighboring water molecules and/or with the electron-donor atoms from the saccharinate anions (N, O_{CO}, O_{SO_2}), except the coordinated carbonyl oxygen [O(13)] (see Table 1).

RESULTS AND DISCUSSION

The RT and LNT infrared spectra of the protiated and the partially deuterated forms of the studied compound are presented in Figs 2 and 3 respectively, whereas the RT Raman spectrum of the protiated compound is given in Fig. 4. The O–D stretching region in the RT and LNT infrared spectrum of the partially deuterated sample is shown in Fig. 5, and Fig. 6 gives the infrared spectral appearance in the region of the SO₂ stretching vibrations. The assignment of the experimental frequencies in the infrared and Raman spectra of magnesium disaccharinate heptahydrate in the 4000–100 cm⁻¹ region is presented in Table 2.

T a b l e   1

Scheme of the hydrogen bonding in the Mg(sac)₂·7H₂O

Hydrogen bond	Distance/pm
$O_w(1)\cdots N(2)$	292.6(3)
$O_w(1)\cdots O_w(5)^{ii}$	304.6(3)
$O_w(2)\cdots O(22)$	277.2(3)
$O_w(2)\cdots O(21)^{i}$	281.8(2)
$O_w(3)\cdots O_w(6)$	271.4(3)
$O_w(3)\cdots O_w(7)$	273.2(3)
$O_w(4)\cdots O_w(6)^{i}$	285.2(3)
$O_w(4)\cdots N(1)^{iii}$	293.9(3)
$O_w(5)\cdots O(23)^{ii}$	275.4(2)
$O_w(5)\cdots N(2)^{i}$	289.8(3)
$O_w(6)\cdots O(23)^{iv}$	275.7(4)
$O_w(6)\cdots O_w(7)^{v}$	276.3(3)
$O_w(7)\cdots O(12)^{iii}$	277.0(3)
$O_w(7)\cdots O(11)^{v}$	283.2(3)

$^{i} = x, y, z - 1;$ $^{ii} = 1 - x, -y, -z;$ $^{iii} = 1 - x, 1 - y, -z;$
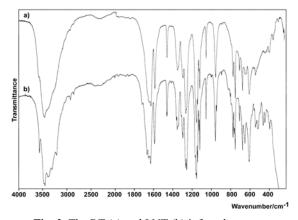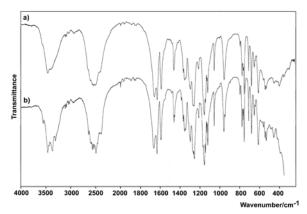$^{iv} = 1 - x, -y, 1 - z;$ $^{v} = 1 - x, 1 - y, 1 - z$

Fig. 2. The RT (a) and LNT (b) infrared spectra of Mg(sac)₂·7H₂O

Fig. 3. The RT (a) and LNT (b) infrared spectra of highly deuterated (*ca.* 60 % deuterium content) Mg(sac)₂·7H₂O

T a b l e 2

Assignment[*] of the experimental frequencies in the infrared and Raman spectra of $Mg(sac)_2 \cdot 7H_2O^a$

No.	Infrared	Raman	A^b		Approximate assignment[c]
	Experimental		Ab initio [8]		
1.	3570 sh				$\nu(H_2O)$
2.	3450 vs	3459 w			$\nu(H_2O)$
3.	3380 sh	3389 vw			$\nu(H_2O)$
4.	3240 sh				$\nu(H_2O)$
5.		3099 m			$\nu(CH)$
6.		3075 s			$\nu(CH)$
7.		3061 m			$\nu(CH)$
8.		3040 w			$\nu(CH)$
9.	1660 sh	1648 w	1700	495.6	$\nu(CO) + \nu(CN)$
10.	1645 s				$\delta(H_2O)^d$
11.	1627 vs	1620 vw			$\nu(CO)+\nu(CN)$
12.	1587 s	1589 m	1596	17.7	$\nu(CC)+ \delta(CCC)$
13.	1462 m	1460 w	1468	4.5	$\delta(HCC)+ \nu(CC)$
14.	1458 m	1454 sh	1459	13.2	$\delta(HCC)+ \nu(CC)$
15.	1414 vw	1415 vw			
16.	1360 sh	1359 m			
17.	1350 m	1352 sh			
18.	1338 sh	1338 sh			
19.	1300 sh	1303 sh			
20.	1293 m	1293 m	1285	9.5	$\delta(HCC)+\delta(SCC)+\nu(CC)$
21.	1265 vs	1268 w	1289	297.6	$\nu_{as}(SO_2)$
22.	1258 s	1251 w	1246	46.2	$\delta(HCC)+ \nu(CC)$
23.	1217 sh	1216 vw			
24.	1168 sh	1171 m			
25.	1160 sh		1201	450.3	$\nu(CN)+\nu(PhC)+\delta(CSN)$
26.	1155 vs	1146 vs	1160	349.4	$\nu_s(SO_2)+ \delta(CSN)+\nu(CC)$
27.	1142 s		1135	2.4	$\nu(CC)+\delta(HCC)$
28.	1130 m		1127	0.6	$\nu(CC)+\delta(SCC)+\delta(HCC)$
29.	1121 m	1119 vw	1117	40.9	$\delta(CCC)+\delta(HCC)$
30.	1054 m	1055 vw			$\nu(CS)$
31.	1015 vw	1017 m			$\delta(CCC)$
32	1000 vw				
33.	958 s	961 vw			$\nu_{as}(CNS)$
34.	890 vw	888 vw			
35.	795 sh	801 vw			
36.	775 m	776 vw			$\delta(CO)$
37.	753 s				
38.	708 m	707 vs			$\delta(CCC)$
39.	678 m				$\delta(CCC)$
40.	647 w				
41.	610 m	609 w			$\delta(SO_2)$
42.	560 vw	553 sh			

No.	Experimental		Ab initio [8] A^b	Approximate assignment^c
	Infrared	Raman		
43.	543 w	539 m		δ(CNS)
44.	532 vw			δ(CCC)
45.	440 w	446 vw		
46.	393 w	396 m		ρ(SO$_2$)
47.	355 w	355 w		
48.	300 vw	299 vw		τ(SO$_2$)
49.	257 w			
50.	243 w			
51.	156 sh			Lattice vibrations
52.	142 sh			Lattice vibrations
53.	131 vs			Lattice vibrations
54.	117 s			Lattice vibrations

* Based on the literature theoretical infrared data for the deprotonated saccharin (saccharin anion) and the literature data for the earlier empirical assignments of the vibrational spectra of various metal saccharinates.

^{a} Except for column denoted by A, the data are given in cm^{-1}; vw – very weak; w – weak; m – medium; s – strong; vs – very strong; sh – shoulder.

^{b} IR intensities (in km mol^{-1}) for saccharin anion.

^{c} Vibrational modes: ν, stretching; δ, bending (all kinds of); ρ, rocking; subscripts: as, antisymmetric; s, symmetric.

^{d} Assignment based on the band intensity decreasing in the IR spectrum of the deuterated sample (see Fig. 6).

General considerations

The assignment of the bands in the RT and LNT IR and RT Raman spectra of the studied compound was based on the earlier theoretical HF/3-21G(d) results for the free deprotonated saccharin species and the experimental values for its DMSO solution [8], as well as the literature data for the earlier empirical assignments of vibrational spectra of various saccharinates [e.g. 1, 11, 14, 23–27]. Here, the characteristic OH and OD stretching vibrations of the water molecules as well as the CO and SO$_2$ stretching modes are discussed and correlated with the crystallographic values of the corresponding interatomic distances.
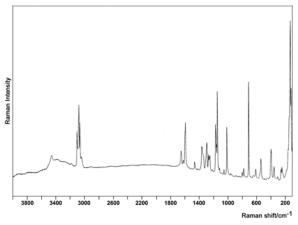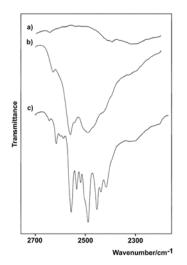

Fig. 4. The RT Raman spectrum of Mg(sac)$_2$·7H$_2$O

The O–H and O–D stretchings

As it was already mentioned, all seven crystallographically non-equivalent water molecules in the structure of Mg(sac)$_2$·7H$_2$O are involved in hydrogen bonding with carbonyl and sulfonyl oxygens or with nitrogen atoms from the saccharinate anions [4]. The O$_w$···O and O$_w$···N distances range from 271.4 to 304.6 pm and from 289.8 to 293.9 pm, respectively (Table 1). Some of the distances are very close (practically equal) to each other [e.g. 275.4(2) and 275.7(2) pm, or 277.0(3) and 277.2(3) pm].

The appearance of only *eight* bands in the region of the OD stretching vibrations of the isotopically isolated HDO molecules (Fig. 5), instead of the *fourteen* expected based on the structural characteristics (Table 1) obviously results from the overlap of the bands due to the existence of some very close O$_w$···O distances in the structure. The non-equal intensity of the bands in the O–D stretching region (Fig. 5) is in line with such a conclusion. All together, it is evident that the existence of a considerable number of expected bands in a relatively narrow spectral region makes the spectra–structure correlation rather difficult.

Fig. 5. The O–D stretching region in the RT (b) and LNT (c) infrared spectrum of partially deuterated (*ca*. 3 % deuterium content) Mg(sac)$_2$·7H$_2$O. Curve (a) corresponds to the LNT spectrum of the protiated form of the studied compound

The C=O stretchings

The stretching vibrations of the carbonyl group are considered as characteristic vibrational modes and are manifested by very strong bands in the vibrational Raman and, especially, infrared spectra of the corresponding compounds including the metal saccharinates [e.g. 1, 8, 26]. Therefore they are very often used to correlate the predicted and the experimentally observed spectroscopic evidence for the carbonyl stretches with the corresponding data obtained by structure determination.

The assignment of the carbonyl stretching bands in magnesium disaccharinate heptahydrate is not straightforward since the bands due to vibrations are localized mainly in the six-membered aromatic ring [ν(CC)+ δ(CCC)] and the bands originating from the bending vibrations of the water molecules [δ(H$_2$O)] are found in the same spectral region [1, 23, 26, 28]. The former bands, however, are usually sharper and appear at somewhat lower frequencies (Figs 2 and 3, Table 2), whereas the latter bands can be eliminated almost completely by recording the spectra of highly deuterated compounds (Fig. 3), or can be recognized by decreasing of their intensity in the spectra of the partially deuterated samples.

Two well separated bands (1645 and 1627 cm^{-1}) and one shoulder (1660 cm^{-1}) are registered in the RT infrared spectrum of Mg(sac)$_2$·7H$_2$O in the region where the stretching C=O modes are

expected to appear (Fig. 2a, Table 2). The number of the observed bands in the corresponding region of the RT Raman spectrum is also two (1648 and 1620 cm^{-1}) (Fig. 4, Table 2). By lowering the temperature, the number of IR bands in this region increases to five (1718, 1668, 1653, 1641 and 1630 cm^{-1}) (Fig. 2b). Finally, only two bands (at 1660 and 1627 cm^{-1}) are observed in the RT and LNT IR spectrum of the highly deuterated analogue (*ca*. 60 % deuterium content) of the studied compound (Fig. 3a and 3b, respectively). Having in mind that the bands which disappear (1718, 1653 and 1641 cm^{-1}) belong to the δ(HOH) modes, whereas the lower-frequency band at 1586 cm^{-1} (IR) and at 1589 cm^{-1} (Raman) is due to the [ν(CC)+ δ(CCC)] mode, obviously the two remaining bands at 1660 and 1627 cm^{-1} are due to the carbonyl stretching modes. This observation shows that, despite the fact that both carbonyl distances [C–O(13) and C–O(23)] in the structure of Mg(sac)$_2$·7H$_2$O are practically the same (124.2 and 124.0 pm, respectively) [4], two well resolved ν(C=O) bands appear in its IR (and Raman) spectrum. Here, it should be mentioned that few new bands were observed in the 1480–1380 cm^{-1} region where the δ(HOD) vibrations are expected to take place in the spectrum of the highly deuterated analogue (Fig. 2 and Fig. 3).

The pronounced frequency lowering of the two IR carbonyl stretching bands (from 1725 cm^{-1} in the spectrum of saccharin [27] down to 1660 cm^{-1}; Δν = 65 cm^{-1} and to 1627 cm^{-1}; Δν = 95 cm^{-1}) in the IR spectrum of Mg(sac)$_2$·7H$_2$O agrees well with the previously determined ionic character of the magnesium-to-deprotonated saccharin bonding in the studied compound [4]. Similar spectral behavior is observed in the case of the ionic saccharinates of sodium, potassium and lead [1, 11, 28]. This is in line with the earlier conclusions [1] that the extent of the frequency lowering of the ν(C=O) mode depends on the character of the metal-to-deprotonated saccharin bonding, and it is more pronounced in the ionic than in the covalent saccharinates.

It is worth mentioning that significant frequency difference is also observed in the case of the Raman active ν(C=O) modes observed in the spectrum of saccharin [27] as compared with the corresponding modes in the Raman spectrum of the presently studied compound which appear at 1648 cm^{-1} (Δν = 49 cm^{-1}) and 1620 cm^{-1} (Δν = 77 cm^{-1}) (Fig. 4, Table 2).
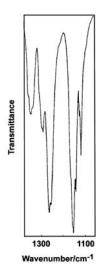
The SO₂ vibrations

The theoretical and empirical analysis of the SO_2 stretching vibrations in various compounds containing SO_2 groups has shown that, similarly to CO group, the SO_2 group can also be considered as a characteristic group vibration [1, 8, 25, 29, 30]. The situation is complicated by the fact that four bands originating from the saccharinate ring vibrations are expected in the region (1335–1130 cm^{-1}) where the antisymmetric, $\nu_{as}(SO_2)$, and symmetric, $\nu_s(SO_2)$ sulfonyl stretches are predicted to appear [8] or are experimentally observed [1, 25, Table 2]. The saccharinate ring bands are found to be sharper and less intense than those arising from the sulfonyl stretching vibrations.

Two strong bands in the RT infrared (at 1265 and 1258 cm^{-1}) and also two weaker bands in the RT Raman spectrum (at 1268 and 1251 cm^{-1}) of the studied compound are registered in the $\nu_{as}(SO_2)$ region (Figs. 4 and 6, Table 2). Taking into account the results of the theoretical analysis [8] as well as the empirical results for the series of metal saccharinates [25], the bands at 1265 cm^{-1} in RT infrared spectrum and at 1268 cm^{-1} in the Raman spectrum are attributed to the antisymmetric SO_2 stretching vibrations.

The assignment of the band arising from the symmetric SO_2 stretches is much easier. Namely, only one strong band (at 1155 cm^{-1}) accompanied by a shoulder at the high-frequency side (at 1160 cm^{-1}) is present in the RT infrared spectrum of Mg(sac)₂·7H₂O in the region where this type of vibrations are expected to appear (Fig. 6). Similarly, one strong band (at 1146 cm^{-1}) is observed in the RT Raman spectrum in the same spectral region (Fig. 4). Undoubtedly they originate from the symmetric SO_2 stretching mode (Table 2).

The presence of a single pair of $\nu(SO_2)$ bands in the vibrational (infrared and Raman) spectra of the studied compound is consistent with the crystallographic data for the studied Mg(sac)₂·7H₂O [4] as well as with the detailed analysis of the SO_2 stretches in metal saccharinates [25] which has shown that the $\nu(SO_2)$ frequencies are dependent on the O–S–O angle values rather than on the S–O distances or on the type of the metal-to-deprotonated saccharin type of bonding. Namely, as it was previously mentioned, the O–S–O angles (114.4 and 114.7°) in both crystallographically different sulfonyl groups are practically the same.

Fig. 6. The region of the SO₂ stretching vibrations in the infrared spectrum of Mg(sac)₂·7H₂O

In the compounds containing SO_2 groups, in addition to the SO_2 stretches, the bands due to the $\delta(SO_2)$ as well as to $\rho(SO_2)$, $\omega(SO_2)$ and $\tau(SO_2)$ modes are expected in the region below 610 cm^{-1}. Following Quinzani et al. [31], the bands at 610 cm^{-1} (infrared) and at 609 cm^{-1} (Raman) are attributed to the $\delta(SO_2)$ mode, those at 393 cm^{-1} (infrared) and at 396 cm^{-1} (Raman) to the $\rho(SO_2)$ librational mode, whereas the bands at 300 cm^{-1} (infrared) and at 299 cm^{-1} (Raman) are assigned to the $\tau(SO_2)$ librational modes (Figs. 2, 3 and 4).

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