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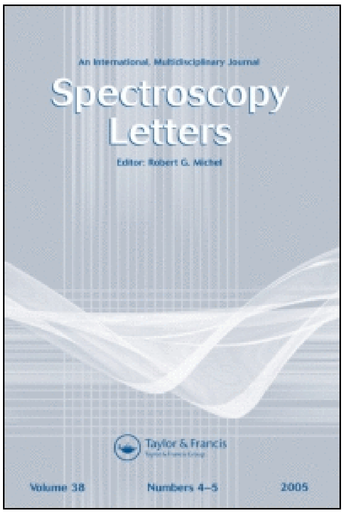

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Infrared and Raman Spectra of 1,4-Oxathiane-4-oxide

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INFRARED AND RAMAN SPECTRA OF 1,4-OXATHIANE-4-OXIDE

Key Words: IR and Raman spectra, 1,4-Oxathiane-4-oxide

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ABSTRACT

The IR and Raman spectra of 1,4-oxathiane-4-oxide have been studied for the solid and liquid samples. The observed bands have been assigned by comparison with the fundamental frequencies of 1,4-oxathiane and the band shifts have been discussed in terms of the mechanical coupling with the S=O vibrations. The C_s chair form with an axial conformation has been proposed for molecular structure.

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INTRODUCTION

Recently, we have reported the IR and Raman spectra of pentamethylene sulfoxide, PMSO, and the observed frequencies have been assigned tentatively (1). By comparison with the fundamental frequencies of pentamethylene sulfide (2), PMS, it has been observed that the CH_2 group vibrations and the skeletal stretching vibrations are not so influenced by the S=O bond formation, but the skeletal deformations are affected through the mechanical interactions.

In the present paper, the IR and Raman spectra of the solid and liquid phase 1,4-oxathiane-4-oxide, TSO, which have not yet been studied in detail, are reported and the band assignment is tentatively made, comparing with that of 1,4-oxathiane (3), TS. The influence of S=O bond formation to the skeletal vibrations are discussed considering the frequency shifts between TSO and TS and between PMSO and PMS. The molecular structure for TSO is proposed analising the observed fundamental frequencies.

EXPERIMENTAL

TSO was prepared from TS using the usual method written in literature (4) and distilled twice for the present IR and Raman study.

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The IR spectra of solid sample were recorded in the region from 4000 to 250 cm^{-1} at room and liquid nitrogen temperatures and those of liquid sample from 4000 to 160 cm^{-1} for the fused compound between two CsI or two polyethylene plates, using a Perkin-Elmer model 180 spectrophotometer.

The Raman spectra of solid and liquid phases were recorded in the region from 4000 to 40 cm^{-1} for the compound in a capillary cell, using a Jarrell-Ash model 25-300 spectrometer with an argon ion laser, 4880 and 5145 Å, for excitation.

RESULTS AND DISCUSSION

The observed IR and Raman frequencies for TSO are given in Table I, with the relative intensities and the tentative assignment. In Table II, the fundamental frequencies and the approximate descriptions of vibrational modes are given and compared with those for TS.

There are thirty-nine fundamental vibrations for TSO and they are classified into two symmetry species, on the assumption of C_s chair form, which seems to be reasonable by comparison with the structures of similar compounds (5-11). All vibrational modes, 21a' and 18a", are active in either IR and Raman spectra.

The vibrational assignment has been carried out, as follows, by comparison with that for TS and considering the Raman polarization measurements.

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TABLE I

Infrared and Raman frequencies for 1,4-oxathiane-4-oxide

infrared			Raman		assignment	
solid 298K	solid 77K	liquid	solid 298K	liquid		
			2976 m	2974 m,P	ν_1, ν_{22}	a', a"
2958 s	2960 s	2958 s	2964 s	2963 s,P	ν_2, ν_{23}	a', a"
2919 s	2918 s	2920 s	2930 s	2927 s,P	ν_3, ν_{24}	a', a"
2904 sh	2900 sh	2900 sh	2903 w	2904 vw,?	$\nu_5+\nu_{26}$	A"
2863 s	2863 s	2862 s	2866 m	2868 m,P	ν_4, ν_{25}	a', a"
2750 w	2752 w	2751 vw	2757 w		$\nu_{27}+\nu_{28}$	A'
2706 vw	2705 vw	2708 vw	2713 vw		$\nu_8+\nu_{27}$	A"
2686 w	2686 w	2689 vw	2694 w		$\nu_7+\nu_8$	A'
2197 vw		2200 vw			$2\nu_{32}$	A'
2080 vw	2078 vw	2084 vw			$\nu_{32}+\nu_{33}$	A'
2028 vw		2032 vw			$2\nu_{12}$	A'
1918 w	1919 w	1916 vw			$\nu_{15}+\nu_{33}$	A"
1462 m	1462 m	1461 m	1468 m	1467 m,P	ν_5	a'
1449 sh	1452 sh	1448 sh	1453 m	1452 m,D	ν_{26}	a"
1418 sh	1416 sh	1418 sh	1414 w	1413 w,?	ν_6	a'
1404 m	1406 m	1403 m	1400 m	1405 m,D	ν_{27}	a"
1384 m	1386 m	1383 m	1390 vw	1388 vw,?	ν_7	a'
1352 vw	1352 w	1350 vw	1357 w		ν_{28}	a"
1322 m	1326 m	1320 m	1328 m	1323 m,P	ν_8	a'
1288 m	1293 s	1287 m	1287 w	1285 w,D	ν_{29}	a"
1277 s	1277 s	1274 s	1275 vw	1278 vw,?	ν_9	a'
1259 m	1264 s	1258 m	1259 w	1253 vw,?	$2\nu_{16}$	A'
1213 s	1213 s	1210 s	1213 vw		ν_{30}	a"
1195 m	1192 m	1192 m	1195 m	1195 m,P	ν_{10}	a'
1159 sh	1158 m	1157 sh	1160 w	1162 w,?	ν_{31}	a"
1150 m	1152 sh	1149 m			$\nu_{18}+\nu_{36}$	A"

(continued...)

TABLE I

(continued)

infrared			Raman		assignment	
solid 298K	solid 77K	liquid	solid 298K	liquid		
1126 w	1125 s	1125 m	1124 vw	1127 vw,D	$\nu_{16}+\nu_{37}$	A''
1098 vs	1097 vs	1097 vs	1095 m	1098 w,D	ν_{32}	a''
1062 vs	1060 vs	1060 vs	1057 m	1062 m,P	ν_{11}	a'
1039 w	1034 w	1037 w			$\nu_{36}+\nu_{38}$	A'
1019 vs	1016 vs	1018 vs	1012 s	1023 s,P	ν_{12}	a'
991 vs	995 s	990 vs	995 m	994 m,?	ν_{33}	a''
987 sh	987 sh		985 vw		ν_{13}	a'
961 m	963 m	960 m	968 vw	966 vw,?	ν_{14}	a'
942 vw	943 w	944 sh	944 m	944 w,D	ν_{34}	a''
854 w	854 w	851 w			$\nu_{17}+\nu_{20}$	A'
827 s	828 s	826 s	828 s	828 s,P	ν_{15}	a'
800 vw	800 w	802 vw	803 w		ν_{35}	a''
721 vw	721 w	716 vw	724 vw		$\nu_{18}+\nu_{20}$	A'
700 w	702 w	699 w	702 vw	702 m,D	ν_{36}	a''
676 sh	676 sh	676 sh	684 vw		$2\nu_{38}$	A'
666 w	667 w	664 w	665 vw	667 m,P	$\nu_{37}+\nu_{39}$	A'
632 w	637 w	631 w	631 vs	630 vs,P	ν_{16}	a'
629 sh	627 sh	627 sh	625 sh		$\nu_{20}+\nu_{38}$	A''
605 w	605 w	604 w	604 vw		$\nu_{19}+\nu_{39}$	A''
571 m	573 w	570 w	575 vw	573 m,P	ν_{17}	a'
503 w	503 m	505 w	502 vw	506 vw,?	$\nu_{21}+\nu_{38}$	A''
458 sh	460 sh	462 sh	468 s	462 m,D	ν_{37}	a''
450 s	452 s	451 s	454 m	453 m,?	ν_{18}	a'
438 sh	438 w	440 sh	440 vw	434 m,?	$\nu_{20}+\nu_{21}$	A'
418 w	418 vw	420 vw	418 vw	419 vw,?	$2\nu_{39}$	A'
394 w	394 vw	395 vw	401 w		ν_{19}	a'

(continued...)

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TABLE I

(continued)

infrared			Raman		assignment	
solid 298K	solid 77K	liquid	solid 298K	liquid		
			384 vw	379 vw,?	$\nu_{21}+\nu_{39}$	A"
345 w	349 w	345 w	354 s	347 m,D	ν_{38}	a"
315 w	320 vw	316 vw	318 vw	317 vw,?	$\nu_{12}-\nu_{36}$	A"
294 m	296 m	294 m	295 vw	295 vw,?	$\nu_{16}-\nu_{38}$	A"
278 m	285 m	280 w	279 s	280 m,?	ν_{20}	a'
		209 m	233 m	210 m,D	ν_{39}	a"
		167 m	188 m	168 m,?	ν_{21}	a'
			82 w		lattice vibration	
			61 m		lattice vibration	
			43 m		lattice vibration	

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From the assignment of TS (3), it is found that only four bands are expected for eight CH_2 stretching vibrations with the accidental degeneracy on each them. The relatively intense bands at 2976, 2958, 2919 and 2863 cm^{-1}, in which the frequencies except for the first one are coincident in the IR and Raman spectra, are assigned no doubtfully to these CH_2 stretching vibrations. On the other hand, for the CH_2 scissoring, wagging, twisting and rocking vibrations, the accidental degeneracies are not expected. The depolarized bands at 1449 and 1404 cm^{-1} are assigned to the scissor-

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TABLE II

Fundamental frequencies of TSO

			TSO*	TS**				TSO*	TS**
a':	ν_1	νCH_2	2976	2966	a":	ν_{22}	νCH_2	2976	2966
	ν_2	νCH_2	2958	2953		ν_{23}	νCH_2	2958	2953
	ν_3	νCH_2	2919	2923		ν_{24}	νCH_2	2919	2923
	ν_4	νCH_2	2863	2864		ν_{25}	νCH_2	2863	2864
	ν_5	δCH_2	1462	1460		ν_{26}	δCH_2	1449	1444
	ν_6	δCH_2	1418	1424		ν_{27}	δCH_2	1404	1410
	ν_7	ωCH_2	1384	1385		ν_{28}	ωCH_2	1352	1355
	ν_8	ωCH_2	1322	1319		ν_{29}	ωCH_2	1288	1286
	ν_9	τCH_2	1277	1269		ν_{30}	τCH_2	1213	1212
	ν_{10}	τCH_2	1195	1200		ν_{31}	τCH_2	1159	1169
	ν_{11}	$\nu C-C$	1062	1047		ν_{32}	$\nu C-O$	1098	1113
	ν_{12}	$\nu S=O$	1019	——		ν_{33}	ρCH_2	991	1005
	ν_{13}	ρCH_2	987	1009		ν_{34}	$\nu C-C$	942	951
	ν_{14}	ρCH_2	961	969		ν_{35}	ρCH_2	800	806
	ν_{15}	$\nu C-O$	827	830		ν_{36}	$\nu C-S$	700	691
	ν_{16}	$\nu C-S$	632	666		ν_{37}	δring	458	430
	ν_{17}	δring	571	552		ν_{38}	$\rho S=O$	345	——
	ν_{18}	δring	450	397		ν_{39}	δring	209	252
	ν_{19}	$\omega S=O$	394	——					
	ν_{20}	δring	278	341					
	ν_{21}	δring	167	206					

* This work.

** Reference 3.

ing vibrations of a" species and the bands at 1462 and 1418 cm^{-1} to those of a' species. Four bands at 1384, 1352, 1322 and 1288 cm^{-1} and four bands at 1277, 1213, 1195 and 1159 cm^{-1} are assigned to the wagging and twisting vibrations, respectively. These frequencies are very closed to those of TS. For the rocking vibrations, a slight frequency shift may be considered (1) and the four bands at 991, 987, 961 and 800 cm^{-1} can be attributed to these vibrational modes.

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An intense band at 1062 cm^{-1}, which is the polarized one in the liquid Raman spectra, is assigned to the C-C stretching vibration of a' species, and this mode of a" species gives rise to a weak band at 942 cm^{-1}. The band at 1098 cm^{-1} is assigned to the C-O stretching vibration of a" species which is coupled by Fermi resonance with a combination band at 1126 cm^{-1}. The corrected frequency of this vibration is comparable to the same mode of TS. At 827 cm^{-1}, a Raman polarized band is observed and assigned directly to the C-O stretching vibration of a' species. As already discussed for PMSO and PMS (1), the interaction by the potencial energy is not expected on the C-S stretching vibrations, though the a' mode is mechanically coupled with the S=O stretching vibration. The polarized band at 630 cm^{-1} and the depolarized band at 702 cm^{-1} are respectively assigned to the characteristic C-S stretching vibrations of a' and a" species.

The Raman polarized band at 1019 cm^{-1}, which is one of the most characteristic band for TSO, is directly assigned to the S=O stretching vibration and this value observed indicates that the axial conformation of S=O bond is more adequate as the molecular structure of TSO (7).

The skeletal ring deformations are considerably coupled among them and also with the S=O deformations and the band assignment is rather tentative. Five bands can be taken into consideration for a' species, at 571, 450, 394, 278 and 167 cm^{-1}, and they can be observed to be the polarized bands or, at least, the non-depolarized bands in the liquid Raman spectra. Three bands at 458, 345 and 209 cm^{-1} are relatively intense and assigned to the skeletal deformations of a" species.

In the lower frequency region, three bands are observed, at 82, 61 and 43 cm^{-1}, in the solid Raman spectra, but these bands disappear in the liquid Raman spectra. Therefore, they are probably attributable to the lattice vibrations of TSO. Assuming the mechanical coupling among the internal and external fundamental vibrations, the band shifts from the solid to the liquid phase spectra at 209 and 167 cm^{-1} may be explained.

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