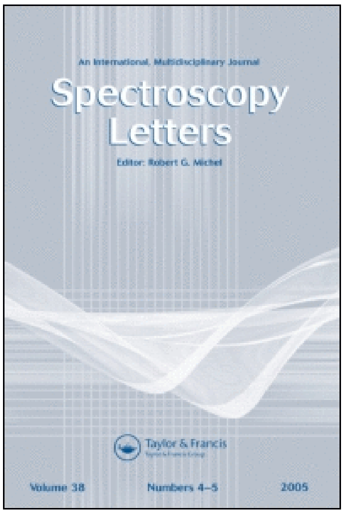

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Infrared and Raman Spectra of Pentamethylene Sulfoxide

Y. Hase[a]; Y. Kawano[b]
[a] Instituto de Química, Universidade Estadual de Campinas, Campinas, SP, Brazil [b] Instituto de Química, Universidade de SaTo Paulo, Sao Paulo, SP, Brazil

To cite this Article Hase, Y. and Kawano, Y.(1978) 'Infrared and Raman Spectra of Pentamethylene Sulfoxide', Spectroscopy Letters, 11: 3, 161 — 171
To link to this Article: DOI: 10.1080/00387017808067743
URL: http://dx.doi.org/10.1080/00387017808067743

SPECTROSCOPY LETTERS, 11(3), 161-171 (1978)

INFRARED AND RAMAN SPECTRA OF PENTAMETHYLENE SULFOXIDE

Key Words: IR and Raman spectra, Pentamethylene sulfoxide

Y. Hase,

Instituto de Química, Universidade Estadual de Campinas,
C. P. 1170, Campinas, SP, Brazil

Y. Kawano,

Instituto de Química, Universidade de São Paulo,
C. P. 20780, São Paulo, SP, Brazil

ABSTRACT

The IR spectra of pentamethylene sulfoxide were recorded in the frequency region from 4000 to 250 cm^{-1} in the solid phase. The Raman spectra were recorded from 4000 to 100 cm^{-1} in the solid and liquid phases and the polarization measurements were carried out in the liquid phase. The observed IR and Raman bands were assigned on the assumption of a C_s chair form and compared with the fundamental frequencies of pentamethylene sulfide.

INTRODUCTION

In the recent coordination chemistry studies, pentamethylene sulfoxide, $CH_2(CH_2CH_2)_2S{=}O$, henceforth called PMSO, has been used as a ligand and the vibrational frequency shifts from free ligand to coordinated PMSO, particularly the S=O stretching vibration, have been used to discuss the coordination effects. However, a detailed vibrational study of the IR and Raman spectra of free PMSO has not yet been carried out. Vedal et al. (1) studied, in 1975, the vibrational spectra of pentamethylene fulfide, PMS, which has the same skeletal ring system, and the observed bands were assigned on the assumption of a C_s molecular symmetry. The molecular symmetry of PMSO can also be assumed to be the C_s chair form and it is confirmed by comparison of the observed spectra of PMSO and PMS.

In the present paper, the IR and Raman spectra of PMSO are reported and the observed bands are assigned tentatively, by comparison with the fundamental frequencies of PMS, considering the Raman polarization ratios. The frequency differences between the fundamental vibrations of PMSO and PMS are discussed using terms of the mechanical coupling among the skeletal ring modes and the S=O modes.

EXPERIMENTAL

PMSO was obtained commercially and distilled twice for the present IR and Raman study.

The IR spectra were recorded in the frequency region from 4000 to 250 cm^{-1} with a Perkin-Elmer 180 spectrophotometer for the solid state sample, which was prepared by crystalization of the fused compound between two CsI plates.

The Raman spectra were recorded in the region from 4000 to 100 cm^{-1} with a Jarrell-Ash 25-300 spectrometer using the 4880 and 5145 Å lines of an argon ion laser for excitation. The solid PMSO was measured in the capillary cell by usual method and the liquid PMSO was measured for the fused compound in the capillary cell by heating system.

RESULTS AND DISCUSSION

The observed IR and Raman frequencies for PMSO are given in Table I, with the assignment tentatively made. In Table II, the fundamental frequencies of PMSO and PMS are compared, using the approximate descriptions for vibrational modes.

Forty-five fundamental vibrations can be devided into two symmetry species, 25a' and 20a", and all of them are active in the

TABLE I

Vibrational spectral data for pentamethylene sulfoxide

infrared	Raman			assignment	
solid	solid	liquid			
2957 sh	2960 s	2952 sh	P	ν_1, ν_{26}	a', a"
2932 vs	2934 s	2933 s	P	$\nu_2, \nu_3, {}_{27}$	a', a', a"
2915 sh	2916 s	2914 vs	P	ν_4	a'
2899 sh	2898 vw			ν_{28}	a"
2873 sh	2876 vw			ν_5, ν_{29}	a', a"
2860 s	2855 w	2855 w	P	ν_6	a'
2827 sh				$2\nu_9=2836$	A'
2808 sh				$2\nu_{31}=2816$	A'
1457 vw	1453 vw			ν_7	a'
1440 vs	1442 m	1444 m	P	ν_8	a'
1422 m				ν_{30}	a"
1418 s	1415 m	1414 m	P	ν_9	a'
1408 vw				ν_{31}	a"
1378 vw				$2\nu_{42}=1388$	A'
1367 vw				$\nu_{39}+\nu_{43}=1369$	A'
1352 vw	1350 w	1350 w	?	ν_{10}	a'
1337 m				ν_{32}	a"
1310 m	1310 w	1309 w	P	$\nu_{11}, {}_{33}$	a', a"
1283 vw	1287 vw			$\nu_{17}+\nu_{23}=1283$	A'
1279 vw				ν_{34}	a"
1260 vw	1262 w	1263 vw	?	ν_{35}	a"
1246 m	1242 w	1245 w	P	ν_{12}	a'
1231 w	1233 w			$2\nu_{20}=1238$	A'
1209 m	1214 w	1203 w	P	ν_{13}	a'
1192 sh	1190 sh			$\nu_{15}+\nu_{25}=1190$	A'
1171 vw				$\nu_{18}+\nu_{44}=1173$	A"

(continued...)

TABLE I

(continued)

infrared	Raman			assignment	
solid	solid	liquid			
1141 m	1139 w	1140 w	?	ν_{36}	a"
1110 vw	1119 vw			$\nu_{41}+\nu_{44}=1110$	A'
1092 vw	1092 vw			ν_{37}	a"
1072 s	1066 m	1067 m	P	ν_{14}	a'
1041 vw				$\nu_{20}+\nu_{43}=1051$	A"
1032 vs	1024 s	1034 s	P	ν_{15}, ν_{38}	a', a"
993 vs	997 s	999 s	P	$\nu_{20}+\nu_{23}=1020$	A'
954 s	956 w	957 w	P	ν_{16}	a'
937 vw	944 m	936 w	D	ν_{39}	a"
882 s	887 w	888 w	?	ν_{17}, ν_{40}	a', a"
843 m	843 w			ν_{18}	a'
814 sh	815 s	815 s	P	ν_{19}	a'
803 w				$2\nu_{23}=802$	A'
780 w	782 w			ν_{41}	a"
694 s	694 m	692 m	D	ν_{42}	a"
652 m	653 s	652 s	P	$2\nu_{44}=660$	A'
633 s	632 vs	630 sh	?	$\nu_{43}+\nu_{45}=634$	A'
619 w	618 vs	614 vs	P	ν_{20}	a'
552 s	554 w	558 w	?	$2\nu_{24}=564$	A'
513 m	514 w	513 m	P	ν_{21}	a'
444 vs	445 w	445 w	?	ν_{22}	a'
432 s	434 m	430 w	?	ν_{43}	a"
401 w	401 s	400 s	P	ν_{23}	a'
358 vw	362 vw			$\nu_{14}-\nu_{42}=378$	A"
347 w	347 w	348 w	?	$\nu_{25}+\nu_{45}=360$	A"
330 m	331 s	330 m	?	ν_{44}	a"

(continued...)

TABLE I

(continued)

infrared	Raman			assignment	
solid	solid	liquid			
304 w				$2\nu_{25}=316$	A'
282 s	276 m	278 m	P	ν_{24}	a'
	202 m	200 m	D	ν_{45}	a"
	158 m	152 m	P	ν_{25}	a'

both IR and Raman spectra. The a' Raman bands are expected to be polarized in the liquid phase spectra.

There are ten CH_2 stretching modes, in which five are the symmetric vibrations and other five the asymmetric ones, and they are expected in the range from 2960 to 2850 cm^{-1}. These modes are assigned to the bands at 2957, 2932, 2915, 2899, 2873 and 2860 cm^{-1} by some accidental degeneracies. The frequencies assigned are comparable with those of PMS.

For the CH_2 deformations, there are five scissoring, five wagging, five twisting and five rocking vibrations and they can be easily assigned by comparison with PMS, but it is notable that some frequency differences between the rocking modes of PMSO and PMS are not so slight because of the mechanical coupling with the skeletal ring deformations (1-5). The CH_2 scissoring vibrations of

TABLE II

Fundamental frequencies of PMSO

			PMSO*	PMS**				PMSO*	PMS**
a':	ν_1	νCH_2	2957	2948	a":	ν_{26}	νCH_2	2957	2948
	ν_2	νCH_2	2932	2929		ν_{27}	νCH_2	2932	2929
	ν_3	νCH_2	2932	2929		ν_{28}	νCH_2	2899	2892
	ν_4	νCH_2	2915	2904		ν_{29}	νCH_2	2873	2878
	ν_5	νCH_2	2873	2878		ν_{30}	δCH_2	1422	1433
	ν_6	νCH_2	2860	2849		ν_{31}	δCH_2	1408	1405
	ν_7	δCH_2	1457	1451		ν_{32}	ωCH_2	1337	1338
	ν_8	δCH_2	1440	1440		ν_{33}	ωCH_2	1310	1313
	ν_9	δCH_2	1418	1426		ν_{34}	ωCH_2	1279	1269
	ν_{10}	ωCH_2	1352	1348		ν_{35}	τCH_2	1260	1259
	ν_{11}	ωCH_2	1310	1299		ν_{36}	τCH_2	1141	1141
	ν_{12}	τCH_2	1246	1237		ν_{37}	τCH_2	1092	1090
	ν_{13}	τCH_2	1209	1215		ν_{38}	$\nu C-C$	1032	1013
	ν_{14}	$\nu C-C$	1072	1061		ν_{39}	$\nu C-C$	937	929
	ν_{15}	$\nu S=O$	1032	——		ν_{40}	ρCH_2	882	905
	ν_{16}	ρCH_2	954	965		ν_{41}	ρCH_2	780	791
	ν_{17}	ρCH_2	882	897		ν_{42}	$\nu C-S$	694	688
	ν_{18}	ρCH_2	843	826		ν_{43}	δring	432	398
	ν_{19}	$\nu C-C$	814	813		ν_{44}	$\rho S=O$	330	——
	ν_{20}	$\nu C-S$	619	656		ν_{45}	δring	202	242
	ν_{21}	δring	513	504					
	ν_{22}	δring	444	359					
	ν_{23}	$\omega S=O$	401	——					
	ν_{24}	δring	282	344					
	ν_{25}	δring	158	194					

* This work. ** Reference 1.

a' species are assigned to bands at 1440 and 1418 cm^{-1} which are polarized and the remaining one to the very weak band at 1457 cm^{-1}. Those of a" species are at 1422 and 1408 cm^{-1}. Two a' and three a" wagging vibrations are assigned at 1352, 1310, 1337, 1310 and 1279 cm^{-1}, respectively, and ν_{11} and ν_{33} are accidentally degenerate. Two polarized Raman bands at 1245 and 1203 cm^{-1} are attributed to the twisting vibrations of a' species, and other twisting vibrations of a" species are at 1260, 1141 and 1092 cm^{-1}. The rocking vibrations are expected below 1000 cm^{-1} and attributed to bands at 954, 882, 843 and 780 cm^{-1}.

The S=O stretching vibration is expected at about 1000 cm^{-1}. The observed spectra show two strong bands at 1032 and 993 cm^{-1} and both bands are polarized in the liquid Raman spectra. Considering the S=O stretching frequency of 1,4-thioxan oxide (6), this mode is assigned at 1032 cm^{-1} and it is coupled by Fermi resonance with the band at 993 cm^{-1}.

PMSO has four C-C stretching vibrations and it is easy to assign these modes by comparison with those of PMS. Two a' modes are assigned to bands at 1072 and 814 cm^{-1} which are the polarized Raman bands, and two a" modes at 1032 and 937 cm^{-1}.

The C-S stretching vibrations of a' and a" species are assigned to bands at 619 and 694 cm^{-1}, respectively. The a' mode is coupled with two bands at 652 and 633 cm^{-1} by Fermi resonance. The a' mode shows the low frequency shift from that of PMS, though the a" mode gives almost the same frequency. It may be explained by the mechanical coupling with the S=O stretching vibration.

Five skeletal deformations of a' species are expected in the frequency region below 600 cm^{-1}. The comparison with those of PMS is not adequate in this case because of the different degrees of mechanical coupling among them. The Raman polarization shows that the bands at 513, 400, 278 and 152 cm^{-1} can be considered to be a' species and they may be the fundamental bands because of relative strong intensities. The remaining one of a' species is at 444 cm^{-1} Three skeletal deformations of a" species are assigned to the intense bands which have not yet been attributed to a' species. They are at 432, 330 and 202 cm^{-1}.

Comparing the observed fundamental frequencies of PMSO and PMS, it is notable that the S=O bond making influences the vibrations in terms of the mechanical coupling and the kinetic energy adjustment, but the potencial energy distributions on the skeletal ring are not so perturbed. The slight frequency shifts only for the CH_2 vibrations and ring stretching vibrations, from PMS to PMSO, suggests the C_s chair form may be proposed for the molecular structure

For the conformation analysis, axial or equatorial, it is already known that the S=O stretching frequency of axial form is lower than that of equatorial form (7). The former is expected in the region about 1020 cm^{-1}, and the later in the region about 1040

cm^{-1}. The S=O stretching frequency for PMSO is 1032 cm^{-1} and it is difficult to determine the conformation directly. When the Fermi resonance is considered between the bands at 1032 and 993 cm^{-1}, the frequency corrected is lowered and the axial conformation may be suggested. The conformation changing between the solid and liquid phases can not be observed on the frequency ou intensity shifts in the observed Raman spectra.

ACKNOWLEDGEMENTS

The authors are grateful to V. K. L. Osório for preparing the sample and to O. Sala for permission to use the spectrometers.

REFERENCES

1. D. Vedal, O. H. Ellestad, P. Klaboe and G. Hagen, Spectrochim. Acta, 31A, 355 (1975).
2. P. Klaboe, Spectrochim. Acta, 25A, 1437 (1969).
3. O. H. Ellestad, P. Klaboe and G. Hagen, Spectrochim. Acta, 28A, 137 (1972).
4. O. H. Ellestad, P. Klaboe, G. Hagen and T. S. Hausen, Spectrochim. Acta, 28A, 149 (1972).
5. D. Vedal, O. H. Ellestad, P. Klaboe and G. Hagen, Spectrochim. Acta, 31A, 339 (1975).

6. Y. Hase and Y. Kawano, *to be published.*

7. P. B. D. De la Mare, D. J. Millen, J. G. Tillett and D. Watson, *J. Chem. Soc.*, *1963*, 1619.