VIBRATIONAL SPECTRA OF THIOGLYCOLLIC ACID

P. G. PURANIK, K. VENKATA RAMIAH AND VIJAY KUMAR

DEPARTMENT OF PHYSICS, UNIVERSITY COLLEGE OF SCIENCE
OSMANIA UNIVERSITY, HYDERABAD 7

ABSTRACT. The infrared and Raman spectra of thioglycollic acid and its solutions in different solvents have been recorded and the assignments of some of the frequencies have been proposed.

INTRODUCTION

The Raman spectrum of thioglyclollic acid has been earlier reported by Thatte and Ganesan (1933), but these authors have not recorded any line in the region of 2500 cm^{-1} corresponding to S-H stretching vibrations. Hibben (1936) while discussing the Raman spectra of thioacids, interpreted the absence of a line in the region of 2500 cm^{-1} in these compounds, as due to the absence of S-H group. There appears to be no mention in literature regarding the studies of infrared spectrum of thioglycollic acid. The authors have studied the infrared and Raman spectra of the acid and in various solvents in order (a) to assign the various vibrational frequencies of the monomer and associated molecules and (b) to study the effects of the solvents on the frequencies of the O-H, S-H and C = O stretching absorption bands.

EXPERIMENTAL

A Perkin-Elmer Model 21 Infrared Spectrophotometer with NaCl optics was used to obtain the infrared spectra. The infrared spectrum of the pure liquid was obtained by pressing a drop of the liquid between two NaCl plates, along with an NaCl plate of equivalent thickness inserted into the reference beam. The spectra in solutions were obtained with a pair of matching cells of 0.1 and 1 mm thickness.

The Raman spectra were obtained by using a Fuess glass spectrograph having a dispersion of 19 cm^{-1} in the λ4358 region along with a Hilger Raman source unit. λ4358 was the exciting radiation.

Thioglycollic acid (*E.* Merck) was distilled under reduced pressure and the fraction collected at 123°C and 29 mm pressure was used for the investigation. The fact that this acid forms an aqueous mixture of constant boiling point has been noted and absolutely anhydrous acid was used in the investigations.

RESULTS

The Raman and infrared frequencies of thioglycollic acid as recorded by the authors are given in Table I.   The Raman spectrum reported by Thatte and Ganesan is given for comparison.   The microphotometric trace of the Ramna spectrum is given in Fig. 1.   The infrared spectrum of thioglycollic acid has broad absorption band in the 3μ region, but this band could be resolved into three peaks in solutions of chloroform and carbon tetrachloride.   The Raman spectrum of thioglycollic acid has a sharp and intense line in the region of 2500 cm ^{1} while the corresponding infrared band is weak.   The authors could record a number of Raman lines which have not been reported earlier (Thatte and Ganesan, 1933).
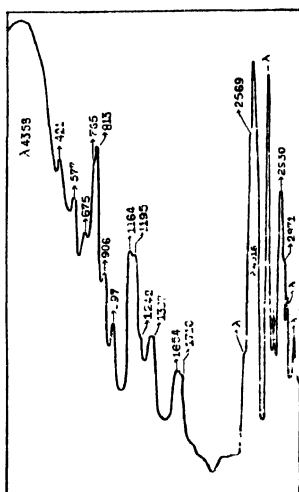

Fig. 1.   Microphotometric trace of the Raman spectrum of thioglycollic acid.

DISCUSSION

Assignments :

The infrared spectrum of thioglycollic acid has a broad absorption band extending from 3125 cm^{-1} to 2900 cm^{-1}, but in solutions of chloroform it could be resolved into three distinct peaks at 3495, 3125 and 2900 cm^{-1}.   With increasing dilution, the intensity of the band at 3125 cm^{-1} becomes less and at 0.02 molar concentrations, this band becomes very feeble while the one at 3495 cm^{-1} is prominent.   A characteristic feature of carboxylic acids is their dimeric manifestation, with the result that the intermolecular associations break up progressively with increasing dilution of these substances in chloroform or carbon tetrachloride.   Therefore the authors assign the band at 3495 cm^{-1} to the free O-H stretching vibrations of the monomers and the one at 3125 cm^{-1} to the same mode of vibrations of the associated molecules.   The Raman line which is assigned

to the bonded O-H stretch, has a banded structure extending from 2926 to 2971 cm^{-1}. A sharp intense Raman line appears at 2930 cm^{-1} superposed on the hydroxyl band. The band at 2900 cm^{-1} in the infrared or the one at 2930 cm^{-1} in the Raman spectrum is assigned to C-H stretching vibrations.

The C = O stretching absorption of thioglycollic acid has two peaks at 1717 and 1730 cm^{-1}, the former being a weak shoulder. The carbonyl frequency in the Raman spectrum appears as a band at 1654 cm^{-1} along with a sharp, faint line at 1710 cm^{-1}. These results indicate that the thioglycollic acid is not a completely associated liquid. With increasing dilution of the acid in chloroform, the peak at 1730 cm^{-1} becomes more prominent in the infrared spectrum and the band at 1717 cm^{-1} becomes a shoulder. At a molar concentration of 0.02 in solution of chloroform, only the band at 1730 cm^{-1} could be recorded. Therefore the infrared frequency at 1717 cm^{-1} or the Raman line at 1654 cm^{-1} is assigned to the C = O stretching of the associated molecules and the frequency at 1730 cm^{-1} in the infrared or the one at 1710 cm^{-1} in Raman spectrum to the same mode of vibrations of the monomers. The large differences in the infrared and Raman frequencies of the C — O stretch of the thioglycollic acid are in agreement with similar results obtained by Davies and Sutherland (1938) in their investigations of carboxylic acids.

The lines at 1298 and 1397 cm^{-1} in the Raman and the corresponding frequencies at 1286 and 1412 cm^{-1} in the infrared can be assigned to C-O stretch and $C\diagdown^{\diagup O}_{OH}$ deformation. Such assignments have been made by Hadzi and Sheppard (1953) in case of carboxylic acids and by Puranik (1955) in case of esters.

The Raman spectrum of thioglycollic acid has a sharp and intense line at 2569 cm^{-1} and the corresponding frequency in the infrared is a weak absorption at 2565 cm^{-1}. The authors assign this band to S-H stretching vibrations. The frequency remains unchanged even in dilute solutions of chloroform. This invariance of the frequency indicates that S-H linkage is a free linkage in thioglycollic acid. The intermolecular associations in this compounds, may therefore be concluded, as of O-H......O = C type.

The S-H in-plane deformation frequency has been identified by Sheppard (1949) with a Raman line at 832 cm^{-1} and therefore the Raman line at 813 cm^{-1} in the thioglycollic acid may be assigned to this mode of vibration. The C-SH stretch is known to appear in the region of 600-700 cm^{-1} as a strong line in The Raman spectrum (Sheppard, 1950) and therefore a fairly intense Raman line at 675 cm^{-1} may be assigned to C—SH stretching vibrations.

The 220 cm^{-1} in the Raman spectrum corresponds to the symmetrical vibrations of the two acid molecules of the dimer through the stretching of the hydrogen bond.

TABLE I

Raman and infrared frequencies of thioglycollic acid
(in cm^{-1})

Raman		Infrared
Present authors	Thatte and Ganesan	Present authors
220 (0)	—	—
421 (2)	433 (1d)	—
—	511 (1)	—
577 (2)	580 (1)	—
675 (3)	686 (0)	—
765 (4)	—	755 (w)
813 (6)	818 (4)	—
906 (4)	914 (2)	897 (w)
997 (4)	1004 (0)	990 (vw)
1164 (5)	—	1149 (m)
1195 (3)	—	1199 (m)
1242 (3)	—	—
1298 (0)	—	1286 (s)
1397 (3)	1409 (2d)	1412 (s)
—	1563 (1d)	—
1654 (3d)	—	1717 (s)
1710 (1)	1707 (1d)	1730 (sh)
—	—	2336 (w)
2459 (2)	—	—
2569 (8)	—	2565 (w)
2678 (2)	—	2680 (sh)
2930 (9)	2950 (1d)	—
2926 to 2971	—	2930 to 3125

TABLE II

O—H, S—H and C = O stretching frequencies of thioglycollic acid in different solvents

Solvents	O-H stretch	S-H stretch	C-O stretch
Liquid	2930 to 3125	2565	1717 1730
Carbon totrachloride	3510	2575	1718 1731
Chloroform	3500	2565	1717 1730
Acetonitrile	3450	2565	1742
Dioxane	3450	2535	1745
Pyridine	3225	2440	1717 (sh) 1730
α-picoline	—	2440	1709 1724
β-picoline	—	2440	1717 1730

Solvent effect.

The infrared spectrum of thioglycollic acid has been recorded in various solvents and the OH, SH and C — O stretching frequencies in those solvents are given in Table II and the traces are given in Figs. 2 and 3.
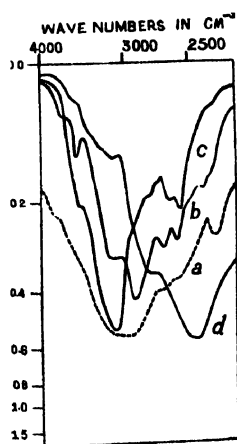

Fig. 2. The O–H, and S–H stretching frequencies in (a) pure liquid (b) chloroform (c) dioxane and (d) pyridine.
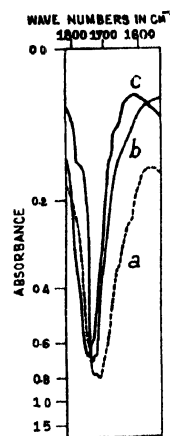
Fig. 3. The C—O stretching frequencies in (a) pure liquid (b) chloroform and (1) dioxane.

The absorption band at 3495 cm^{-1} in chloroform or at 3510 cm^{-1} in carbon tetra-chloride, which is assigned to the O—H stretch of the monomers, does not appear in the donor solvents. Instead it appears at 3450 cm^{-1} in dioxane and acetonitrile and at 3225 cm^{-1} in solutions of pyridine. At these concentrations the carbonyl frequency is at 1743 cm^{-1} in both dioxane and acetonitrile. In pyridine it is at 1730 cm^{-1} with a weak shoulder at 1717 cm^{-1} Similar results are obtained in solutions of picolines.

The appearance of a single C — O absorption in the donor solvents corres-ponding to the monomer frequency is an indication that the intermolecula associations have broken up considerably in these solvents. Then the simulta-neous reduction in the O-H stretching frequency compared to the monomer frequency in solutions of chloroform or carbon tetrachloride is due to the hydrogen bond formation between the donor groups of the solvent and the O—H group of the monomers of the acid by the OH...N and OH...O bonds. The shift in the O—H stretching frequency is maximum in solutions of pyridine.

The S-H stretching frequency, which has the same value in pure liquid and in dilute solutions of chloroform, decreases to the extent of 125 cm^{-1} in solutions of pyridine and picolines and becomes broad. In solutions of dioxane this band shifts only to the extent of only 25 cm^{-1}. The large shifts in S-H stretching frequency in solutions of pyridine and picolines, may be concluded as due to the associations by way of S-H...N bonding.

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