INFRARED ABSORPTION SPECTRA OF SINGLE CRYSTALS OF GLYCINE SILVER NITRATE AND MONOGLYCINE NITRATE

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ABSTRACT

The infrared absorption spectra of glycine silver nitrate ($GAgNO_3$) and glycine nitrate ($GHNO_3$) show that the glycine group exists completely in the zwitter ion form in the former and in both forms in the latter. The spectrum of $GAgNO_3$ at liquid air temperature did not reveal any striking change which can be attributed to a freezing of the rapid reorientation of the NH_3^+ group taking place at higher temperatures. The position of the COO^- stretching frequencies indicate that this group is co-ordinated only weakly to the Ag^+ ion. The summation frequencies reported by Schroeder, Wier and Lippincott (1962) for $AgNO_3$ were not observed in the present study on $GAgNO_3$. It shows however that ferroelectricity in $GAgNO_3$ is in all probability due to the motion of the Ag^+ ion in the oxygen co-ordination polyhedron and is not directly connected with the ordering of the hydrogen bonds below Curie point.

INTRODUCTION

FERROELECTRICITY in glycine silver nitrate ($NH_2CH_2COOH \cdot AgNO_3$) was reported by Pepinsky *et al.* (1957) and its Curie point lies at − 55° C. A recent investigation of the proton magnetic resonance in glycine silver nitrate (referred to hereafter as $GAgNO_3$) by Easwaran (1966) has shown that the glycine exists in the form of zwitter ions ($NH_3^+CH_2COO^-$) in this crystal and that there was a transition centred at 129° K. which could be explained as due to a freezing of the NH_3^+ group which was rotating at room temperature. Surprisingly no conclusive evidence of a change in the second moment at the ferroelectric transition temperature was found. Thus, contrary to what has been believed to be the case in other ferroelectric glycine addition compounds (Krishnan and Narayanan, 1963; Jona and Shirane, 1962) in $GAgNO_3$ the protons do not appear to play any part in the ferroelectric transition. In view of its interesting properties a detailed study of the infrared absorption spectrum of GAgNO$_3$ at room temperature and in the low temperature phase was undertaken. For the purpose of a definite identification of the frequencies, the related glycine compound, *viz.*, monoglycine nitrate (G.HNO$_3$) was also studied. On account of its coloration on prolonged irradiation with visible light, the Raman spectra of these crystals could not be obtained.

EXPERIMENTAL DETAILS

Single crystals of GAgNO$_3$ and GHNO$_3$ were grown by slow evaporation of the aqueous solutions containing glycine and silver nitrate and glycine and nitric acid in molar proportions. GAgNO$_3$ was grown in the dark and in both cases clear transparent crystals in the form of plates were obtained. The infrared spectra were recorded with single crystal sections as well as in the form of powder mulled in paraffin oil. GAgNO$_3$ exhibits perfect cleavage perpendicular to the *b*-axis. Easy cleavage directions reported earlier (*see* Jona and Shirane, 1962) are wrong. Therefore in this case the single crystals used were sections perpendicular to the *b*-axis. It was found that aqueous solutions of glycine and nitric acid yielded three types of crystals and these were identified to be γ-glycine, diglycine nitrate and monoglycine nitrate. Monoglycine nitrate was easily recognised since crystals of GHNO$_3$ grew mostly as near hexagonal plates with the crystallographic *c*-axis perpendicular to their plane (Vijayan, 1966). The crystals used for recording the infrared spectra were therefore plates perpendicular to the *c*-axis. Well polished specimens of suitable transmission characteristics were prepared as indicated in an earlier paper (Warrier and Narayanan, 1967). The cryostat for the study of the infrared absorption spectra at low temperature was of the conventional design (Lord, McDonald and Miller, 1952).

RESULTS AND DISCUSSION

The frequencies of the observed absorption maxima in GAgNO$_3$ and GHNO$_3$ are given in Table I along with absorption maxima of α-glycine (Khanna, 1961). The spectrum of GAgNO$_3$ at liquid air temperature did not reveal any spectacular change except for some minor changes in the width of the bands and alternations in relative intensity discussed below. The single crystal spectra of GAgNO$_3$ and GHNO$_3$ have been reproduced in Figs. 1 and 2 respectively. GAgNO$_3$ crystallises in the monoclinic space group $P2_1/a$ with the cell constants $a = 5 \cdot 53$, $b = 19 \cdot 58$, $c = 5 \cdot 51$ Å and $\beta = 100^\circ$ C. and $z = 4$ (Pepinsky *et al.*, 1957). A complete structure

TABLE I

Infrared absorption spectra of α-glycine, glycine silver nitrate and monoglycine nitrate (frquencies in cm.$^{-1}$)

α-G	$GAgNO_3$	$GHNO_3$	Assignment
		3263 m	O—H....O
3170	3180 s 3100 s	3180 s 3100 s	N—H Stretch of NH_3^+
2860	2982 s	2980 m	C—H Stretch
2780 2685	2620 m	2723 m	N^+—H....O
2200 2100	2259 w 1980 m	.. 1980 w	NH_3^+ deformation + NH_3^+ torsion (?)
..	1782 w	..	
..	..	1758 w	C=O of COOH
1615 1590	1629 s	1649 s	COO^- Antisymmetric stretch
1505	1536 1486 s	1534 s 1479 s s	NH_3^+ bending
1405	1379 s	1389 m	COO^- Symmetric stretch and $\nu_3 (NO_3^-)$
1335	1345 s	1349 s	CH_2 twisting
..	..	1266 m	C—O Stretch of COOH
1135 1110	1105 s	1133 s	NH_3^+ rocking
1032	1049 s	1049 m	C—N Stretch
916	..	916 m	CH_2 rocking
896	907 s	899 m	C—C Stretching (also COO^- scissoring
..	..	875 m	C—OH out of plane bending.
..	826 s 780 w	822 m	$\nu_2 (NO_3^-)$
..	722 s 704 w	731 s	$\nu_4 (NO_3^-)$
688	676 s	667 m	COO^- bending
609	602 s	580 w	COO^- wagging
505	538 w	514 w	NH_3^+ torsion

s = Strong, m = medium, w = weak.

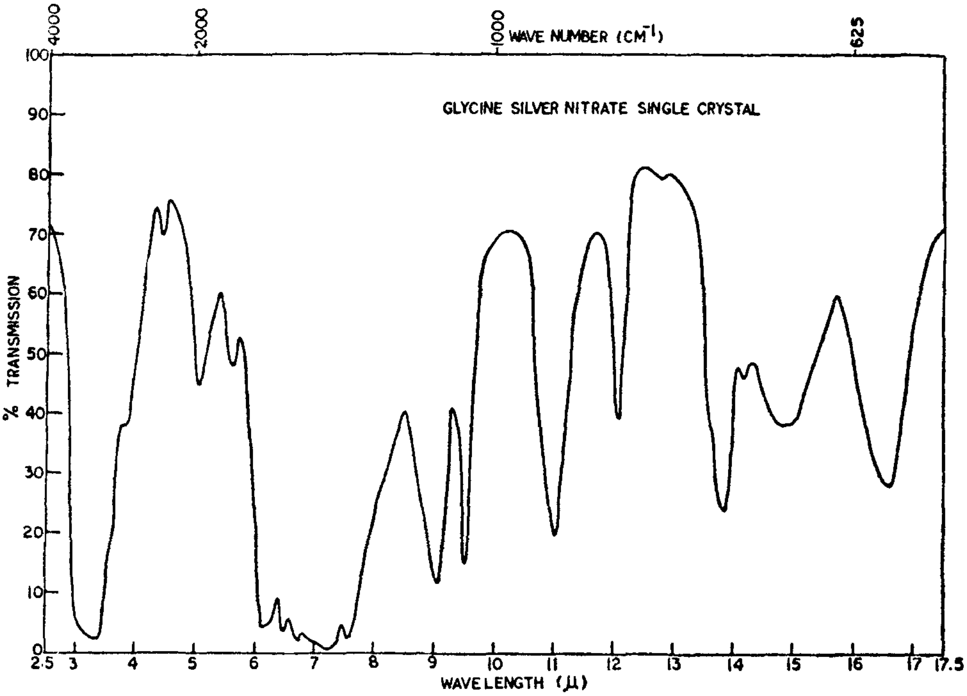
GLYCINE SILVER NITRATE SINGLE CRYSTAL
WAVE NUMBER (CM⁻¹)
4000
2000
1000
625
% TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
WAVELENGTH (μ)
2.5
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
17.5

FIG. 1.

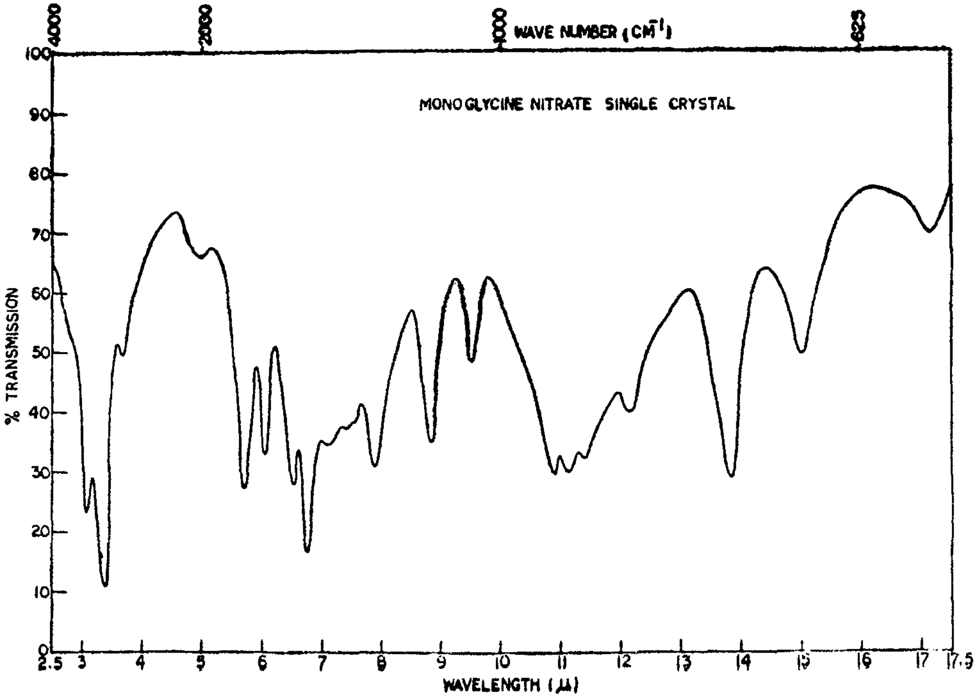
MONOGLYCINE NITRATE SINGLE CRYSTAL
WAVE NUMBER (CM⁻¹)
4000
2000
1000
625
% TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
WAVELENGTH (μ)
2.5
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
17.5

FIG. 2.

analysis of $GAgNO_3$ is in progress in this laboratory (J. K. Mohana Rao and Mani). The preliminary data confirm the space group and cell dimension but show that the cleavage planes are as indicated by us earlier. The dielectric studies (Pepinsky *et al.*, 1957; Mitani, 1964) show the existence of a ferroelectric phase below – 55° C. and the spontaneous polarisation was found to take place along the *b*-axis. The preliminary results on the structure of $GHNO_3$ (Vijayan, *loc. cit.*) show that it belongs to the orthorhombic space group $P2_12_12_1$ with the cell dimensions $a = 5 \cdot 59$, $b = 6 \cdot 10$ and $c = 16 \cdot 35$ A and there are four molecules in the unit cell.

The absorption maxima at 3180 and 3100 $cm.^{-1}$ which occur in $GAgNO_3$ and also in $GHNO_3$ obviously arise from the N—H stretching vibrations of the NH_3^+ group. The absorption at 2621 $cm.^{-1}$ in $GAgNO_3$ and at 2723 $cm.^{-1}$ in $GHNO_3$ must on the other hand be due to the hydrogen bonded vibrations of the $N^+H \ldots O$ group. From the correlation curve given recently by Krishnan and Krishnan (1964) one finds that for 2621 $cm.^{-1}$ the estimated (N—H...O) distance is about 2·76 Å. In the case of $GHNO_3$ the distance will be slightly larger. It may therefore be concluded that in both cases the NH_3^+ groups form N^+–H...O bonds of varying strengths, the corresponding distances ranging from about 3·0 Å to 2·76 Å. No significant change either in intensity or width of the bands in this region was found even at about 90° K., well below the Curie point of 218° K. Therefore the rapid reorientation of the NH_3^+ groups or alignment of the hydrogen bonds may not play any direct role in the ferroelectric behaviour. The band at 3263 $cm.^{-1}$ observed in $GHNO_3$ is to be assigned to the hydrogen bonded vibrations of the O–H group of the COOH. This fact combined with the spectral features in other regions discussed below indicate beyond doubt that in $GAgNO_3$ the glycine units exist only in the zwitter ion configuration. On the other hand in $GHNO_3$ the evidence is in favour of the existence of both zwitter ions and "glycinium" ions or ($NH_3^+CH_2COOH$).

In several amino-acids and primary and secondary amine compounds, (Koegel *et al.*, 1957; Chenon and Sandorfy, 1958), and also in lithium hydrazinium sulphate (Warrier and Narayanan, 1966) and the addition compounds of glycine (Krishnan and Narayanan, 1963) one finds infrared absorption maxima between 2000–2100 $cm.^{-1}$ whose origin is not quite certain. While Leifer and Lippincott (1957) favour the view that they arise from a bending mode raised in frequency by hydrogen bonding, Chenon and Sandorfy (*loc. cit.*) believe that the band in the region may be due to an unusually strong combination of a deformation mode around 1600 cm.$^{-1}$ and some torsional frequency of about 500 cm.$^{-1}$ We find that in both $GAgNO_3$ and $GHNO_3$ a fairly strong band occurs at 1,980 cm.$^{-1}$ and in $GAgNO_3$ it shows no change in intensity at all at low temperature. If this band is due to an unharmonic coupling either electrical or mechanical then it should exhibit an appreciable temperature dependence. Possibly an investigation of the spectra at liquid helium temperature may serve to clarify this point (Schroeder, Weir and Lippincott, 1962).

In the spectral region where absorption due to the carboxyl vibrations is to be expected one finds a strong band at 1629 cm.$^{-1}$ in $GAgNO_3$ and a similar band at 1649 cm.$^{-1}$ in $GHNO_3$ which can be assigned to the antisymmetric vibration of the ionized carboxyl group, *viz.*, (COO^-). The corresponding absorption bands due to the symmetric vibration are found at 1379 and 1389 cm.$^{-1}$ respectively. However in $GHNO_3$ we find in addition to these, an absorption band at 1,758 cm.$^{-1}$ usually assigned to the $C = O$ vibration of the (COOH) group. This is in agreement with our earlier conclusions based on the features in the 3000 cm.$^{-1}$ region. From the fact that the COO^- symmetric stretching frequency is diminished (1405 to 1379) and the antisymmetric stretching frequency is increased (1615 to 1629) in going from α-glycine to $GAgNO_3$ one may reasonably conclude that the hydrogen band system of the oxygen atoms of any ionized carboxyl group gets altered. Further one of the oxygen atoms can be co-ordinated with the Ag atom and this may alter the force constants in such a manner as to increase the antisymmetric frequency. The influence of co-ordination on the carboxylate ion frequencies has been discussed by Nakamoto (1963). The other absorption bands in the region 1600–1100 cm.$^{-1}$ may be offered a satisfactory assignment by a comparison with the spectrum of α-glycine, as indicated in Table 1. The frequencies at 1049 and 899 cm.$^{-1}$ in $GHNO_3$ may be assigned the C–N stretching and C–C stretching vibrations of the skeleton, in agreement with the normal co-ordinate analysis of the vibrations of the glycine and deuterated glycine molecules by Suzuki, Shimanouchi and Tsuboi (1963). But Pinchas and Laulicht (1965) have questioned the assignment of the band at 894 cm.$^{-1}$ in normal glycine to a C—C stretching since a vibration of this type must show an isotopic shift of about 1% only of its frequency, *i.e.*, not bigger than about 10 cm.$^{-1}$ and they found experimentally a shift of 24 cm.$^{-1}$ with O^{18} labelled glycine. They therefore assigned the band at 894 cm.$^{-1}$ to a CO_2 scissoring vibration which can be expected to show an isotopic shift of about 25 cm.$^{-1}$ in analogy to the *ca.* 30 cm.$^{-1}$ isotopic shift observed for the similar 914 cm.$^{-1}$ NO_2 bending of nitromethane. It may be pointed out that the latter authors do not appear to have taken cognizance of the fact that the C—C stretching vibration may in reality be a complicated vibration to which C—C stretching, CO_2 symmetric stretching and CH_2 wagging can contribute in varying proportions, as can be readily seen from Table VII giving the potential energy distribution, in the paper referred to (Suzuki *et al.*, *loc. cit.*). The absorption bands in the region 690–500 cm.$^{-1}$ are easily analysed by a comparison with the spectrum of α-glycine and the assignments are indicated in the table.

The free NO_3^- ion has the symmetry D_{3h}. The six possible vibrations are distributed among the different symmetry species of this group as $A_1' + A_2'' + 2E'$ with the A_1' vibration being active only in Raman effect, A_2'' being active only in infrared, the E' vibrations being active in both. The observed values of these frequencies are:

$$\nu_1 (A_1') \sim 1050 \text{ cm.}^{-1}, \ \nu_2 (A_2'') \sim 830 \text{ cm.}^{-1}, \ \nu_3 (E') \sim 1370 \text{ and}$$
$$\nu_4 (E') \sim 720 \text{ cm.}^{-1} \text{ (Lecomte, 1958).}$$

In the spectra of $GAgNO_3$ and $GHNO_3$ strong absorption bands are found corresponding to the ν_2 and ν_4 frequencies of the NO_3 ion. At the temperature of liquid air, no sharpening or splitting of these bands was found in $GAgNO_3$. Since the region of ν_3 coincides with the vibrations of NH_3^+ and COO^- groups it was not possible to separate them. Similarly, the activation of the vibration ν_1 in the crystal due to the lower site symmetry could not also be investigated since at this position, *viz.*, 1047 cm.$^{-1}$ there occurs the C—N stretching vibration of the glycine unit. But a comparison with the spectrum of silver nitrate (Schroeder, Weir and Lippincott, 1962) reveals certain interesting features. They found absorption bands at 711 cm.$^{-1}$ and 806 cm.$^{-1}$ corresponding to the ν_4 and ν_2 vibrations of the NO_3 ions in addition to a sharp band at 1046 cm.$^{-1}$ due to the originally inactive mode ν_1. At room temperature they found other broad absorption bands which on cooling the crystal to liquid helium temperature resolved into a series of a large number of bands not attributable to fundamentals or combinations of fundamental frequencies of the anions. They were interpreted by them as summational bands of fundamental frequencies with successive levels of an oscillator librating about the threefold axis with a spacing of about 20–30 cm.$^{-1}$ We find that in $GAgNO_3$ there is no appreciable absorption between 910 and 1047 cm.$^{-1}$ and the two broad bands noticed by them in this region in $AgNO_3$ are absent in $GAgNO_3$. But weak absorption bands were found at 780 and 704 cm.$^{-1}$ and these were interpreted by them as summations. The intensity of the bands at 704, 780 and 1,785 were dependent on the orientation of the crystal.

Thus only a small enhancement of the frequencies of the NO_3^- ions from their value in $AgNO_3$ and the changes in the frequencies of the carboxyl groups and the influence of temperature on spectrum of $GAgNO_3$ suggest that even if there is a "freezing" of the motion of the NH_3^+ it does not contribute to the ferroelectric transition. In fact it is the position of the silver ions and its oxygen co-ordination that appears to play an important role.

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REFERENCES

Pepinsky, R., O Kaya, Y., Eastman, D. P. and Mitsui, T.	*Phys. Rev.*, 1957, **107**, 1938.
Easwaran, K. R. K. ..	*J. Phys. Soc., Japan*, 1966, **21**, 1614.
Krishnan, R. S. and Narayanan, P. S.	*Crystallography and Crystal Perfection*, edited by G. N. Ramachandran, 1963, pp. 329–46.
Jona, F. and Shirane, G. ..	*Ferroelectric Crystals*, Pergamon Press, 1962.
Vijayan, M. ..	*Ind. Jour. of Pure and Appl. Phys.*, 1966, **4**, 251.
Warrier, A. V. R. and Narayanan, P. S.	*Proc. Ind. Acad. Sci.*, 1966 **64**, 254.
Lord, R. C., McDonald, R. S. and Miller, F. A.	*J. Opt. Soc. Am.*, 1952, **42**, 149.
Khanna, R. K. ..	*Ph.D. Thesis*, I.I.Sc., 1961.
Mohana Rao, J. K. and Mani, N. V.	Private communication.
Mitani, S. ..	*J. Phys. Soc., Japan*, 1961, **19**, 481.
Krishnan, R. S. and Krishnan, K.	*Proc. Ind. Acad. Sci.*, 1964, **60**, 11.
Koegel, R. J., MaCallun, R. A., Wintz, M., Greenstein, J. P. and Birnbaun, S.	*Natl. Acad. Sci., N.Y.*, 1957, **69**, 94.
Chenon, B. and Sandorfy, C.	*Can. J. Chem.*, 1958, **36**, 1181.
Leifer, A. and Lippincott, E. R.	*J. Am. Chem. Soc.*, 1959, **79**, 5807.

Schroeder, R. A., Weir, C. E. and Lippincott, E. R. *J. Res., NBS.*, 1962, **66 A**, 407.

Nakamoto, K. .. *Infrared Spectra of Inorganic and Co-ordination Compounds*, John Wiley, New York, 1963, p. 198.

Suzuki, S., Shimanouchi, T. and Tsuboi, M. *Spectrochim. Acta*, 1963, **19**, 1195.

Pinchas, S. and Laulicht, I. .. 8*th European Congress on Molecular Spectroscopy*, Copenhagen, 1965.

Lecomte, J. .. *Handbuch der Physik*, Vol. XXVI/2, Light and Matter, Springer-Verlag, 1958.