

RAMAN SPECTRUM OF C-DEUTERATED γ -GLYCINE ($\text{NH}_3^+\text{CD}_2\text{COO}^-$)

BY P. NEELAKANTHAN AND R. S. KRISHNAN, F.A.S.C.

(Department of Physics, Indian Institute of Science, Bangalore 12, India)

AND

YOICHI IITAKA

(Faculty of Pharmaceutical Science, The University of Tokyo, Hongo, Tokyo)

Received October 3, 1963

I. INTRODUCTION

A SYSTEMATIC study of the Raman effect in single crystals of glycine and its addition compounds was undertaken in the Department of Physics of the Indian Institute of Science, Bangalore, a few years ago. The Raman spectra of α -glycine (Krishnan and Balasubramanian, 1958) and of γ -glycine (Balasubramanian, Krishnan and Iitaka, 1962) have already been reported. Glycine could be deuterated to different extents, namely C-deuterated ($\text{NH}_3^+\text{CD}_2\text{COO}^-$), N-deuterated ($\text{ND}_3^+\text{CH}_2\text{COO}^-$) and C-N-deuterated ($\text{ND}_3^+\text{CD}_2\text{COO}^-$). A study of the Raman spectrum of the deuterated compound is of great interest. In the present study, the Raman spectrum of crystalline C-deuterated γ -glycine has been recorded and the results are given.

2. EXPERIMENTAL DETAILS

Samples of C-deuterated glycine (α -form) $\text{NH}_3^+\text{CD}_2\text{COO}^-$ was prepared in the following way: Two grams of glycine was dissolved in 10 c.c. of 4N NaOD solution, which was prepared from Na_2O_2 and D_2O . The solution was placed in a sealed vessel of stainless steel and kept at 100°C . for a few days (Gunther and Bonhoeffer, 1937). After the solution was neutralised with HCl, glycine was separated from NaCl by the use of ion exchange resin Amberlite XE-100. The whole procedure was repeated three times so that C-deuteration was brought to practical completion. The degree of C-deuteration was estimated by the decrease in the intensity of the 1334 cm^{-1} infra-red absorption band which is assigned to the CH_2 wagging vibration of the undeuterated glycine molecule.

Crystals of the γ form of the deuterated sample were grown by slow cooling of aqueous solution of α -deuterated glycine made acidic with acetic

acid. Crystals were extremely small in size. They exhibited strong piezoelectric property.

The Raman spectrum of C-deuterated γ -glycine in the crystal powder form was taken with λ 2536.5 excitation. As the sample was not in the form of a single crystal, heavily exposed photographs could not be taken due to the over-exposure of the mercury spectrum and the continuum accompanying it. The sample got coloured yellow on exposure to λ 2536.5 radiation.

3. RESULTS AND DISCUSSION

An enlarged photograph of the Raman spectrum of C-deuterated γ -glycine taken with a Hilger medium quartz spectrograph is reproduced in Fig. 1 (a). The corresponding microphotometer record is also reproduced in Fig. 1 (b). The recorded spectrum exhibits 26 Raman lines. The position and frequency shifts of these Raman lines are indicated in the microphotometer record. The frequency shifts are given in column (2) of Table I. The Raman frequency shifts of γ -glycine are also given in column (3) of Table I (Balasubramanian, Krishnan and Iitaka, 1962).

The sample exhibited a weak fluorescence on exposure to λ 2536.5 radiation. This fluorescence extends from λ 2625, the intensity increasing with increase in wavelength. The intensity of the fluorescence in the region of frequency shifts 2500–3000 cm^{-1} was such as to obliterate the hydrogen-bonded NH oscillations which should have appeared in this region. The authors were therefore unable to identify any Raman line in this region of the spectrum.

External Oscillations

In the low frequency spectrum of C-deuterated γ -glycine, only eight Raman lines could be identified. Of these, the lines at 188 and 221 cm^{-1} which also appear in the Raman spectrum of undeuterated γ -glycine should be attributed to the vibrations of hydrogen bond NH...O. One observes almost the same number of lattice lines in the spectra of C-deuterated and ordinary γ -glycine. As is to be expected, in the spectrum of deuterated specimen, the frequencies are slightly lower.

Internal Oscillations

The 18 Raman lines recorded in the region from 350 cm^{-1} to 2300 cm^{-1} are to be attributed to the internal oscillations. The lines at 2163 and 2249 cm^{-1} are due to the CD stretching vibrations. The absence of any

TABLE I
Raman frequencies of C-deuterated γ -glycine

Sl. No.	Raman frequencies of		Assignment
	C-deuterated γ -glycine	Undeuterated γ -glycine	
1	45	43	} Lattice
2	86	58	
3	106	89	
4	127	106	
5	147	137	
6	167	152	
7	188	170	
8	221	186	
9	358	217	
10	477	362	
11	532	503	
		686	
12	769		CD ₂ rocking
13	816		CD ₂ rocking
14	872	895	CCN sym. stretching
15	919	924	CD ₂ twisting
		1045	
16	1055	1049	CCN antisym. stretching
17	1138	1141	NH ₃ ⁺ rocking
		1165	
18	1213		CD ₂ wagging
19	1235		CD ₂ scissoring
20	1288		
		1326	CH ₂ wagging
		1341	CH ₂ wagging
		1348	CH ₂ wagging
21	1385	1391	COO ⁻ sym. stretching
		1405	
22	1414	1411	COO ⁻ sym. stretching
		1441	
23	1501	1500	NH ₃ ⁺ sym. deformation
24	1585	1586	NH ₃ ⁺ deg. deformation
		1607	
		1629	
		1682	
25	2163		C-D ₂ sym. stretching
26	2249		C-D ₂ antisym. stretching
		2546	
		2612	
		2663	
		2733	
		2788	
		2876	
	..	2964	C-H stretching
	..	2999	C-H stretching
	..	3120	

line at 2864 and 2999 cm^{-1} in the spectrum of the deuterated sample clearly shows that the carbon-deuteration is complete. The lines at 1288, 1235, 1213, 816 and 769 cm^{-1} which are present in the spectrum of the deuterated γ -glycine are absent in the spectrum of undeuterated γ -glycine and therefore they have been assigned to the oscillations involving groups containing deuterium. Similarly, those lines which are due to oscillations of CH_2 groups, which are present in the spectrum of undeuterated γ -glycine, are absent in the spectrum of C-deuterated γ -glycine. As already indicated before, the N-H hydrogen-bonded oscillations which appear in the spectrum of undeuterated γ -glycine in the region 2500 to 3150 cm^{-1} are not recorded in the spectrum of the deuterated γ -glycine, due to the presence of weak fluorescence in this region.

4. SUMMARY

The Raman spectrum of C-deuterated γ -glycine ($\text{NH}_3^+\text{CD}_2\text{COO}^-$) in the crystal powder form was taken using $\lambda 2536.5$ excitation. 26 Raman lines were recorded. Of these, eight lines are attributed to the external oscillations and eighteen Raman lines to the internal oscillations. Proper assignments are given to the observed frequencies.

5. ACKNOWLEDGEMENT

The authors wish to thank Professor Masamichi Tsuboi for his interest in the work.

6. REFERENCES

- Balasubramanian, K.,
Krishnan, R. S. and
Iitaka, Y. *Bull. Chem. Soc. Japan*, 1962, **35**, 1303.
- Gunther, G. and Bonhoeffer,
K. F. *Z. Physik. Chem.*, 1937, **180 A**, 185.
- Krishnan, R. S. and Bala-
subramanian, K. *Proc. Ind. Acad. Sci.*, 1958, **48 A**, 55.

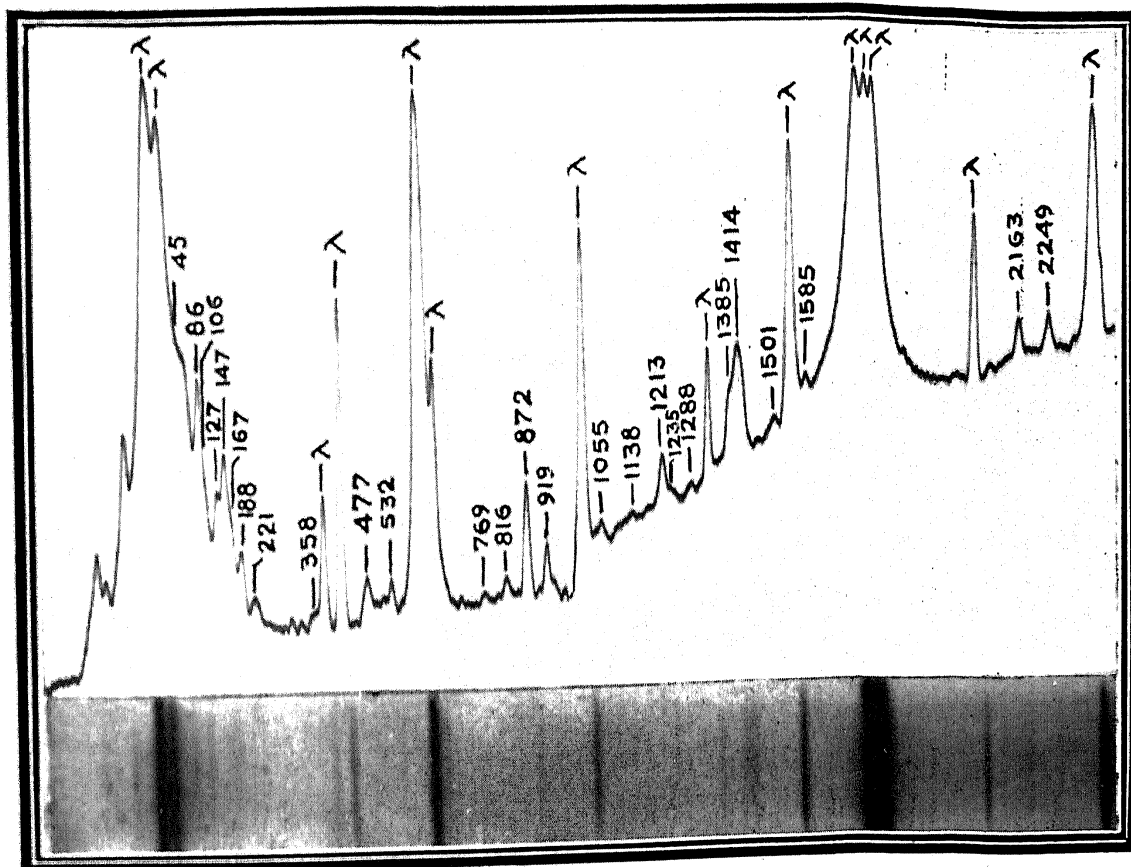


FIG. 1 (a). Raman Spectrum of $\text{NH}_3^+\text{CD}_2\text{COO}^-$ with λ 2536.5 excitation.

1 (b). Microphotometer Record of the Raman Spectrum of $\text{NH}_3^+\text{CD}_2\text{COO}^-$.