RAMAN SPECTRA OF METHYL AND ETHYL ESTERS OF BENZOIC ACID

By T. A. Hariharan

(*Department of Physics, Indian Institute of Science, Bangalore-3*)

Received April 25, 1954

Abstract

The Raman spectra of methyl and ethyl benzoates have been recorded in the liquid state at room temperature and the frequency shifts are compared with those of earlier investigations. A new line at 140 cm.$^{-1}$ in methyl benzoate and three new lines at 377, 432 and 862 cm.$^{-1}$ in ethyl benzoate are reported. The lines 1720, 1110 and 670 cm.$^{-1}$ are assigned as the characteristic frequencies of the $-\overset{\overset{O}{\|}}{C}-O-$ group. The weak line at 850 cm.$^{-1}$ in methyl benzoate and the lines at 850 and 862 cm.$^{-1}$ in ethyl benzoate are ascribed to a mode of oscillation of the C–O–C chain and the frequencies below 200 cm.$^{-1}$ to intermolecular vibration in associated molecules.

1. Introduction

The Raman spectra of methyl and ethyl benzoates have been studied earlier by several investigators, particularly Ghosh and Kar (1931), Kohlrausch and Pongratz (1933), Matsuno and Han (1933), Murty and Seshadri (1939) and Herz Kahovec and Kohlrausch (1943). Matsuno and Han have given assignments to the various frequencies observed in a series of alkyl esters of benzoic acid and the results are compared with the values calculated using the method due to Lechner (1932). Since their assignments do not agree completely with later observations and more new lines have been reported, it is thought worthwhile to study the Raman spectra of the series of alkyl benzoates in detail. The present paper is a preliminary survey on two compounds of the series, *viz.*, methyl benzoate and ethyl benzoate.

2. Experimental Details

The conventional Wood's method for obtaining the Raman spectra of liquids is used in this investigation also. The substances studied were Kahlbaum's chemically pure products and they were distilled under reduced pressure directly into the experimental tube before use. The λ4358 of mercury arc was employed as the exciting radiation. The experimental tube was

surrounded by an outer jacket which contained a dilute solution of sodium nitrite to cut off radiation below 4,000 ÅU and thereby reduce the continuous background observed otherwise. The spectra were taken with a Hilger two prism spectrograph having a dispersion of 140 cm.$^{-1}$ in the 4358 region. The frequency measurements were made with the help of a superimposed iron arc comparison spectrum and also with a Hilger cross slide comparator.

3. RESULTS

The Raman spectra of methyl benzoate and ethyl benzoate and the direct mercury arc spectrum are reproduced in Figs. 1, 2 and 3 respectively in Plate XV and the frequency shifts are given in Table I. The visually estimated intensities are also given in brackets. For the sake of comparison the results of Herz, Kahovec and Kohlrausch for methyl benzoate and of Murty and Seshadri for ethyl benzoate are also included in Table I. It can be seen from Table I that there is good agreement with regard to the frequency shifts but discrepancies were observed in the relative intensities of some of the lines.

4. DISCUSSION

Of the 24 lines observed in methyl benzoate and 30 in ethyl benzoate, the low frequency line at 140 cm.$^{-1}$ in the former and the lines 377, 432 and 862 cm.$^{-1}$ in the latter are new lines not reported in the earlier investigations. The shifts at 615, 1001, 1025, 1158, 1177, 1595 and 3070 cm.$^{-1}$ are identified as the well-known characteristic frequencies of the phenyl group observed in good constance in several mono-substituted benzene compounds (Murray and Cleveland, 1941). The shifts due to the C-H valence and deformation oscillations of the aliphatic group are given by 2844, 2952, 1374, 1444, 1490 in methyl benzoate and 2933, 2980, 1370, 1393, 1453, 1492 in ethyl benzoate respectively.

There seems to be some uncertainty regarding the frequencies to be assigned to the group $-\overset{O}{\overset{\|}{C}}-O-$. Matsuno and Han attribute the lines 1720, 1270 and 670 cm.$^{-1}$ as the characteristic vibrations of the above group whereas Herz, Kahovec and Kohlrausch have assigned the lines 1720, 1112, 966 and 828 to the inner vibrations of the $CO.OCH_3$ group in methyl benzoate. In a series of esters of fatty acids containing the group $-\overset{O}{\overset{\|}{C}}-O-$ Paranjpe and Savanur (1933) attribute the lines 1730, 1030 and 630 as characteristic of the same group.

TABLE I

Raman Spectrum of methyl benzoate		*Raman Spectrum of ethyl benzoate*	
Author	Herz, Kahovec and Kohlrausch (1943)	Author	Murty and Seshadri (1939)
140 (2)		187 (6)	193 (3)
171 (1)	170 (0)		214 (2)
212 (6)	213 (3 *b*)		
361 (6)	359 (3)	285 (1)	
623 (7)	616 (5)	326 (5)	326 (4)
678 (2)	676 (3)	377 (1)	..
810 (1)	808 (1)	397 (1)	395 (1)
826 (8)	825 (8)	432 (0)	..
850 (0)	853 (0)	493 (1)	488 (1)
967 (2)	966 (1)	556 (0)	558 (1)
..	994 (1)	613 (6)	619 (6)
1003 (12)	1003 (12)	672 (3)	677 (4)
1024 (5)	1027 (3)	785 (3)	783 (2)
1111 (4)	1112 (3)	808 (3)	809 (2)
1158 (4)	1159 (3)	850 (5)	852 (5)
1178 (4)	1177 (1)	862 (1)	..
1276 (8)	1276 (6 *sb*)	1000 (12)	1004 (10)
1311 (2)	1314 (2)	1024 (3)	1029 (3)
1444 (3 *b*)	1434 (1)	1108 (4)	1112 (3)
..	1449 (1)	1160 (2)	1160 (2)
1490 (2)	1493 ($\frac{1}{2}$)	1177 (2)	1178 (2)
1604 (12)	1600 (14)	1276 (6)	1277 (2)
1722 (8)	1722 (7 *sb*)	1304 (4)	1314 (2)
2844 (2)	2843 (1)	1370 (2)	1371 (2)
2952 (3)	2952 (4 *b*)	1393 (2)	1391 (2)
3075 (6)	3070 (8 *sb*)	1453 (4)	1453 (3)
		1492 (2)	1493 (1)
		1599 (15)	1602 (10)
		1718 (10)	1720 (8)
		2933 (3)	2935 (2)
		2980 (3)	2972 (2)
		3071 (6)	3076 (6)

It seems more probable that the lines 1720, 1110 and 670 cm.$^{-1}$ are the characteristic vibrations of the $-\overset{\overset{O}{\|}}{C}-O-$ group and the line 1270 cm.$^{-1}$ though fairly intense and occurring in all benzoates may be due to some form of deformation oscillation involving the hydrogen atoms in the attached aliphatic group. The frequency is too large to be ascribed to the valence oscillation

of the $-\overset{\overset{O}{\|}}{C}-O-$ group and more over acetophenone which does not contain this group gives an intense line at 1264 cm.$^{-1}$ [Murty and Seshadri (1942), Herz, Kahovec and Kohlrausch (1943)] and does not give the line at 1110 cm.$^{-1}$

The line at 814 cm^{-}.^{1} in methylbenzoate is attributed following Matsuno and Han to the vibration of the CH_3 group against the acid rest and the line at 846 cm.$^{-1}$ in ethyl benzoate to the vibration of the $-CH_2-$ radical adjacent to the oxygen atom against the acid rest. The weak line at 850 cm.$^{-1}$ in the methyl ester and the lines at 850 and 862 cm.$^{-1}$ in the ethyl ester were not observed by Matsuno and Han but the corresponding lines in *n*-propyl benzoate and *n*-butyl benzoate are ascribed as arising from the chain and ring forms of the carbon atoms due to free rotation. As these two forms are not possible in methyl and ethyl benzoates the lines are of different origin and they can be ascribed to a mode of vibration of the C–O–C chain.

The line at 785 cm.$^{-1}$ in ethyl benzoate can be assigned to the C–C valence oscillation in the ethyl group. The lines between 200 and 400 cm.$^{-1}$ may be due to the bending motion of the C–O–C chain. The lines below 200 cm.$^{-1}$ may be due to some form of intermolecular vibration in associated molecules similar to the line at 162 cm.$^{-1}$ observed in benzoyl chloride and which was found to diminish in intensity with dilution in benzene (Hariharan, 1952).

ACKNOWLEDGEMENT

The author wishes to express his grateful thanks to Prof. R. S. Krishnan for his kind encouragement and guidance during the progress of the work.

REFERENCES

1. Ghosh and Kar .. *J. Phys. Chem.*, 1931, **35**, 1735.
2. Hariharan .. *Indian J. Phys.*, 1952, **26**, 115.
3. Herz, Kahovec and Kohlrausch .. *Monatsh.*, 1943, **74**, 253.
4. Kohlrausch and Pongratz .. *Ibid.*, 1933, **63**, 427.
5. Lechner .. *Ibid.*, 1932, **61**, 385.
6. Matsuno and Han .. *Bull. Chem. Soc.*, Japan, 1933, **8**, 333.
7. Murty and Seshadri .. *Proc. Ind. Acad. Sci.*, 1939, **10**, 307.
8. ———— .. *Ibid.*, 1942, **15**, 154.
9. Murray and Cleveland .. *J. Chem. Phys.*, 1941, **9**, 129.
10. Paranjpe and Savanur .. *Indian J. Phys.*, 1933. **8**, 503.

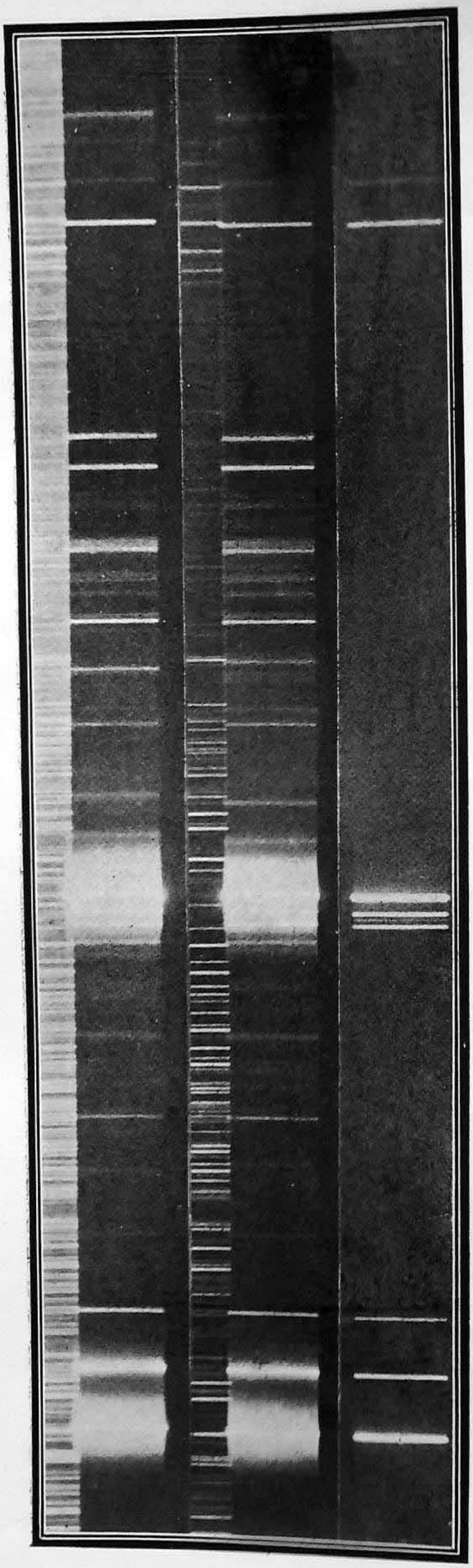

FIG. 1 Raman spectrum of methyl benzoate at 28° C.

FIG. 2. Raman spectrum of ethyl benzoate at 28° C

FIG. 3. Direct mercury arc spectrum.