

## The Raman Spectra of Some Compounds Containing CarbonBromine Bonds. Possible Changes of the Vibration Frequencies in Ionic Solutions

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## The Raman Spectra of Some Compounds Containing Carbon-Bromine Bonds. Possible Changes of the Vibration Frequencies in Ionic Solutions

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Raman spectra of methyl bromoacetate and methyl phenylbromoacetate are reported. The carbon-bromine bond line of the former is similar to that for ethyl bromide, while in the latter it does not appear in its normal position at all. The spectra of methyl alcohol and ethyl bromide have been accurately redetermined; some minor additions result. Shifts of the methyl bromoacetate and methyl alcohol lines in solutions of bromides are found.

KINETIC data suggest that in certain chemical systems at least a portion of the reacting molecules are associated. Association should affect the Raman spectra, either producing new lines or shifting old ones. An attempt to obtain such evidence of complex formation in reactions of the Finkelstein type, whose mechanisms have been discussed by Olson<sup>1</sup> and by Bergman, Polanyi and Szabo,<sup>2</sup> was made but the results were negative. However, as most of the compounds and solutions studied have not been previously observed, it is thought worth while to report the results.

### EXPERIMENTAL

Spectra were observed with a prism spectrograph of dispersion  $34\text{ cm}^{-1}/\text{mm}$  at  $4358\text{\AA}$  and  $54\text{ cm}^{-1}/\text{mm}$  at  $5025\text{\AA}$ . Three Pyrex mercury arcs with appropriate reflectors served as the source of illumination. Use of saturated aqueous  $\text{NaNO}_2$  or 4 percent *m*-dinitrobenzene in benzene as a filter restricted excitation to  $4358$  in most cases. The frequencies of all lines were obtained by linear interpolation between wave numbers of the nearest lines of an iron arc, photographed on the same plate. This procedure is liable to some error. Therefore the weak mercury lines appearing on the plates were measured in a manner identical to that used for the Raman lines, and a comparison with the known frequencies gave the desired correction. This correction ranged from 0

to  $2\text{ cm}^{-1}$ . The error in the values listed depends upon the nature of the individual lines, but is probably less than  $1\text{ cm}^{-1}$  for all definite lines.

### ETHYL BROMIDE

Eastman Kodak Company's product was refractionated from  $\text{P}_2\text{O}_5$ . An exposure of 25 hours with slit  $0.04\text{ mm}$  was made. The lines obtained were:  $290.5$  (4),  $560.3$  (10 *b*),  $959.4$  (2 *b*),  $1062.8$  (2),  $1244.7$  (2),  $1252.9$  (2 *b*),  $1444.0$  (2 *b*),  $2867.2$  (2),  $2924.4$  (4),  $2969.2$  (2 *bb* or *d*). Here *b*=broad, *d*=double. All these lines have been observed before<sup>3</sup> but the line at  $1245$  has been resolved into a doublet for the first time.

A 1:1 mole mixture of ethyl bromide and methyl alcohol showed only a superposition of the lines of the two components.

In a solution of anhydrous lithium bromide and ethyl bromide in methyl alcohol having the composition (mole fract.)  $\text{LiBr}$  0.072,  $\text{C}_2\text{H}_5\text{Br}$  0.301,  $\text{CH}_3\text{OH}$  0.627, no new lines appeared and it was found that the  $290$ ,  $560$ ,  $959$ ,  $1062$ ,  $1445$  and  $2924$  lines of ethyl bromide were unshifted within the limits  $\pm 1\text{ cm}^{-1}$ .

### METHYL BROMOACETATE

The Raman spectrum of methyl bromoacetate is given in Table I. It has not been observed before.\*

<sup>3</sup> Cleeton and Dufford, *Phys. Rev.* **37**, 362 (1931); Dadieu and Kohlrausch, *Monatshefte* **55**, 70 (1930).

\* Added in proof: The Raman spectrum of methyl bromoacetate has recently been published by Cheng (Hua-Chih Cheng, *Zeits. f. physik. Chemie* **B24**, 293 (1934)). The agreement with the values listed above is fairly good.

<sup>1</sup> Olson, *J. Chem. Phys.* **1**, 418 (1933).

<sup>2</sup> Bergman, Polanyi and Szabo, *Zeits. f. physik. Chemie* **B20**, 169 (1933).

TABLE I.  $\text{CH}_2\text{BrCOOCH}_3$  liquid. Prepared from bromoacetic acid and methyl alcohol by the method of Lepercq.<sup>4</sup>

Twice redistilled at 10–20 mm. Slit 0.07 mm. Exposure 48 hours.		
205.8 (2)	845.9 (2)	1404.8 (2)
278.4 (2)	882.4 (3)	1421.0 (3)
301.9 (2)	909.9 (2)	1454.3 (5)
374.1 (4 b and band to 420)	1003.2 (4 b)	1395 to (1 band)
550.3 (10 b)	1116.4 (2)	1465
670.2 (7)	1153.4 (2 b)	1739.7 (7) and band to 1762
710.5 (7)	1189.6 ? (3)	2845.9 (2)
766.5 (1 b)	1215.5 (2 b)	2956.9 (5)
	1287.8 (4)	2965 to 3050 (2 band)

A solution of methyl bromoacetate and lithium bromide in methyl alcohol with the composition (mole fractions) LiBr 0.123,  $\text{CH}_2\text{BrCOOCH}_3$  0.215,  $\text{CH}_3\text{OH}$  0.662 gave the following results. No new lines were observed. The lines 278, 374, 550, 710, 845, 882 and 1739 were unshifted within the limits  $\pm 1 \text{ cm}^{-1}$ , 670 increased by  $2 \text{ cm}^{-1}$ , 910 appeared to decrease 3.5, but as it is quite broad this is not certain.

## METHYL PHENYLBROMOACETATE

The ester was prepared from phenylbromoacetic acid (melting point  $81^\circ\text{--}82^\circ$ . Kindly furnished by Miss M. J. Young) and methyl alcohol in the presence of sulfuric acid. Exposures of 15 to 48 hours were made on methyl alcohol solutions with slit widths of 0.05 to 0.07 mm. The lines obtained, averages over four exposures, are given in Table II. *bd*=band.

TABLE II.  $\text{C}_6\text{H}_5\text{CHBrCOOCH}_3$  in  $\text{CH}_3\text{OH}$ .

246.1 (1)	616.2 (3)	1003.3 (7)
272.1 (1)	675 $\pm$ 15 (1 <i>bd</i> )	1156.3 (2 <i>b</i> )
292.7 (1)	707.8 (1 <i>b</i> )	1184.5 (3 <i>bb</i> )
371.1 (1)	782.1 (3)	1218.3 (4)
403.0 ( $\frac{1}{2}$ )	846.9 (2 <i>b</i> )	1602.4 (7)
486.5 (2)	898.5 (2)	3064.7 (3)
566 $\pm$ 18 (2 <i>bd</i> )		

Notable in the spectrum of methyl phenylbromoacetate is the absence of the C-Br line from its usual position at 550, where it has been found for all other aliphatic bromo compounds.<sup>5</sup>

In view of the thorough investigation of vibration spectra of carbonyl compounds now

being carried out by Kohlrausch and his co-workers no attempt had been made to interpret the spectra of methyl bromoacetate and methyl phenylbromoacetate, observed for the first time in this work.

## METHYL ALCOHOL

Methyl alcohol, used as a solvent, was rather carefully investigated. The interpretation given its spectrum is shown in Table III together with the results of others. The alcohol used was a commercial product twice fractionated with retention of only the center third. No lines of the common impurities were observed. The values listed are means from three plates with a slit of 0.05 mm and exposures to 41 hours.

TABLE III.  $\text{CH}_3\text{OH}$ .

Observed	Kohlrausch in <i>Der Smekal-Raman Effekt</i> <sup>6</sup>	Wood and Collins <sup>7</sup>
1032.3 (6 <i>b</i> )	1034 (5)	1028 (10)
1062.7 ? (1)		
1109.8 (1 <i>b</i> )		1107 (2)
1166 (1 <i>b</i> )		
	1362 (0)	
1452.2 (4 <i>b</i> ) and 1430 to 1490 band center=1470	1462 (5 <i>b</i> )	1457 (10)
		2729 (1)
2834.4 (5 <i>b</i> )	2835 (6 <i>b</i> )	2831 (10)
2919 (2 side band)		
2943.7 (4 <i>b</i> )	2943 (5 <i>b</i> )	2942 (10)
2980 (2 side band)		
	3388 $\pm$ 85 (band)	

In an exposure at low dispersion 1360 was positively identified. 1063 is doubtful as it may possibly have been 2834 excited by the 4047A mercury line. The unsymmetric band at 1460 has been rather arbitrarily interpreted as a combination of line and band.

TABLE IV. Shifts of the  $\text{CH}_3\text{OH}$  lines.

Solu- tion	7 mol % LiBr	13 mol % HBr	24 mol % LiBr
Line			
1032.3	+0.1	-1.7	-3.8
2834.4	+2.1	-0.3	+4.3
2943.7	+1.9	+1.1	+7.1

<sup>4</sup> Lepercq, Bull. Soc. Chim. (3) 11, 297 (1894).<sup>5</sup> Dadiou, Pongratz and Kohlrausch, Monatshefte 61, 409 (1932).<sup>6</sup> Kohlrausch, *Der Smekal-Raman Effekt*, p. 309.<sup>7</sup> Wood and Collins, Phys. Rev. 42, 386 (1932).

The methyl alcohol lines were slightly displaced in concentrated LiBr and HBr solutions. The changes are shown in Table IV and agree in direction with those observed by Hibben<sup>8</sup> for ZnCl<sub>2</sub> solutions, and by Goubeau<sup>9</sup> for LiClO<sub>4</sub> solutions. The alterations of the methyl alcohol lines are roughly proportional to concentration. They indicate a weakening of the C—O bond (1032 line) and a strengthening of the C—H bond (2900 lines). LiBr and HBr form complexes with

methyl alcohol<sup>10, 11</sup> and it is to be expected that the intermolecular forces involved will effect the binding forces. The weakening of the C—O bond is in accord with the important part played by the oxygen in compound formation.<sup>12, 13</sup>

In conclusion I wish to thank Professor A. R. Olson for suggesting this topic.

<sup>8</sup> Hibben, Proc. Nat. Acad. Sci. **18**, 523 (1932).

<sup>9</sup> Goubeau, Naturwiss. **21**, 468 (1933).

<sup>10</sup> Turner and Bissett, J. Chem. Soc. **105**, 1777 (1914).

<sup>11</sup> Maas and McIntosh, J. Am. Chem. Soc. **34**, 1284 (1912).

<sup>12</sup> McIntosh, J. Am. Chem. Soc. **28**, 588 (1906).

<sup>13</sup> Archibald and McIntosh, J. Chem. Soc. **85**, 919 (1904).