THE RAMAN SPECTRA OF CERTAIN ORGANIC LIQUIDS

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Abstract

The Raman spectra of nineteen organic compounds chosen from different chemical series have been measured. Frequency shifts are given and a relationship is shown between certain frequency shifts and molecular structure. In particular the frequency shift $\Delta\nu = 1024$ cm^{-1} recurs with the $C-C$ structure, likewise $\Delta\nu = 1613$ cm^{-1} is associated with $C=C$, $\Delta\nu = 1446$ cm^{-1} with $-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-$, $\Delta\nu = 2929$ cm^{-1} with $H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-C$ and $\Delta\nu = 3054$ cm^{-1} with $H-\hexagon$. It is suggested that anti-Stokes lines may have slightly greater frequency shifts than the corresponding Stokes lines. A comparison between Raman frequency shifts and infrared absorption data is made.

Introduction

DATA on the incoherent scattering of light, as first observed by Raman,[1] give information about the energies associated with different states of vibration and rotation of molecules. It is evident, therefore, that a study of the scattering of light by organic molecules affords one means of advancing our knolwedge of the structure of these molecules. The possibility of correlating structural characteristics of organic molecules with frequency shifts observed in the Raman effect has been made highly probable by the work of Dadieu and Kohlrausch.[2] Certain special atomic groupings in the molecule, for example hydrogen bound to carbon or two carbons bound by a double bond, appear to have definite frequency shifts associated with them. The assignment of certain frequency shifts to definite types of molecular structure is further strengthened by the results obtained by Kettering, Shutts, and Andrews[3] in their investigations of the vibrations executed by mechanical models of various types of molecular structure. The mechanical vibrations produced in the models are in good agreement with those which would be postulated on the basis of observed frequency changes in the Raman effect.

Experimental

A high speed glass spectrograph was used, consisting of two 60° glass prisms 4×2.5 in, and two achromatic lenses of 6 in focal length and 2.5 in aperture. The dispersion obtained was 54A per mm at 4000A, 95A per mm at 4500A, and 145A per mm at 5000A. The slit width used was 0.1 mm.

[1] Raman, Ind. Jour. Phys. **2**, 387 (1928).

[2] Dadieu and Kohlrausch, Ber. d. Deut. Chem. Ges. **63**, II, 251 (1930).

[3] Kettering, Shutts, and Andrews, Phys. Rev. **36**, 531 (1930).

The source of radiation was a horizontal Cooper-Hewitt quartz mercury arc lamp. It was operated in a vertical position from a 125 volt d.c. generator in series with suitable inductances and resistances to give a steady current of about 2.2 amperes. The tube containing the liquid to be studied had the form indicated in Fig. 1. The exposed length of the column of liquid from A to B was 11 cm and the diameter of this portion of the tube 2.5 cm. This tube and the arc were surrounded by a cylindrical reflector. The bottom end of the tube was flattened and ground plane, care being taken to get this plane perpendicular to the axis of the tube. This precaution together with the fact that the index of refraction of the liquids used did not differ widely from that of the tube reduced to a minimum stray reflection from the walls of the tube into the spectrograph. The tube was painted with flat black paint at A and for about 10 cm at B to prevent undesirable reflections. The scattered light
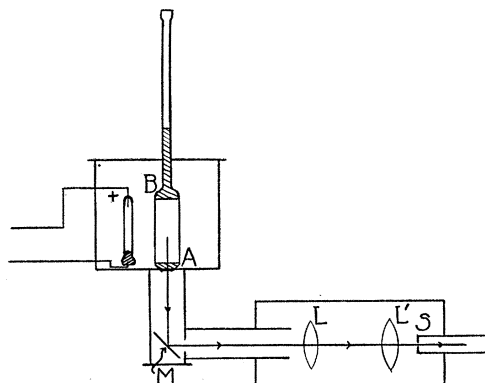

Fig. 1. Diagram of apparatus.

passed through the bottom end of the tube was reflected by the mirror, M, and focussed by means of the convex lenses L and L' on the slit of the spectrograph, S. Suitable shields and diaphragms were provided to prevent stray illumination from reaching the spectrograph. The mercury arc and the observation tube were cooled by blowing air against them. The temperature of the tube was kept at about 45° C.

Eastman Speedway plates were used with the time of exposure ranging from 1 to 4 hours. In most cases an exposure of 1 hour was sufficient to bring out all the lines which could be obtained. The plates were measured on a Zeiss comparator. The probable error of the sharper lines is approximately 0.5A at 4500A but for the more diffuse lines it reaches about 1.5A.

RESULTS

In Table I are given the data for the nineteen organic compounds studied in this investigation. The Raman frequency shifts are expressed in vacuum wave-numbers, followed in each case by the average estimated intensity in parenthesis, and this in turn by the exciting line also in parenthesis. The estimated intensities are expressed on a 1 to 5 scale with 5 the greatest in-

TABLE I.

Substance Formula	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
ter-Amyl Chloride $(CH_3)-CH_2(CH_3)_2CCl$	378(4)(ad)	566(5)(ae)	618(1)(ae)	788(3)(ae)	922(2)(ae)	1150(4)(ae)	1207(3)(ade)	1451(3)(ace)	2929(3)(aegi)	2983(4)(aei)	
Benzyl Acetate $CH_3COOCH_2C_6H_5$	364(1)(d)	479(1)(e)	633(1)(d)	998(4)(ae)	1022(2)(def)	1602(1)(e)	2933(2)(ae)	3046(2)(ae)			
Benzyl Chloroacetate $CH_2ClCOOCH_2C_6H_5$	490(2)(e)	618(3)(ade)	808(2)(ae)	1009(3)(adef)	1150(1)(a)	1614(2)(ae)	3061(1)(acde)				
n-Butyl Acetate $CH_3COOC_4H_9$	629(1)(e)	1031(1)(e)	1440(1)(ae)	1686(1)(a)	2916(3)(ade)						
n-Butyl Formate $HCOOC_4H_9$	832(1)(ae)	912(1)(e)	1065(1)(e)	1314(1)(e)	1452(2)(ae)	1710(1)(a)	2734(3)(de)	2926(4)(aeh)			
-Butyraldehyde $CH_3(CH_2)_2CHO$	983(1)(a)	2915(1)(a)	3032(1)(a)								
o-Chlorophenol ClC_6H_4OH	168(1)(a)	254(1)(a)	559(1)(ae)	680(1)(ae)	829(1)(ae)	890(1)(e)	1022(2)(ae)	1155(1)(a)	1585(1)(ae)	2138(1)(de)	3061(1)(adeg)
Cyclohexanol $(CH_2)_5CHOH$	783(3)(ae)	832(1)(de)	1080(4)(a)	1256(2)(de)	2887(3)(a)	2935(3)(ei)					
Cyclohexene C_6H_{10}	814(3)(ae)	1068(2)(ae)	1212(2)(e)	1254(2)(ae)	1426(2)(ae)	1643(2)(a)	2908(2)(adeg)	3005(2)(ad)			
p-Cymene $CH_3C_6H_4CH(CH_3)_2$	619(1)(de)	808(1)(a)	1195(1)(e)	1617(1)(a)	2720(1)(de)	2975(1)(ad)	3020(1)(ad)				
Dichloroacetic acid $CHCl_2COOH$	421(1)(a)	779(1)(a)	3025(1)(a)								
Ethyl Chloroacetate $CH_2ClCOOC_2H_5$	788(2)(e)	863(2)(e)	1186(1)(b)	2953(2)(ah)							
Ethylene Glycol $HOCH_2CH_2OH$	860(1)(ae)	1042(1)(e)	1225(1)(e)	1444(1)(e)	2873(3)(e)	2907(2)(a)					
Isoamyl Propionate $CH_3CH_2COOC_5H_{11}$	272(1)(a)	412(1)(a)	605(1)(a)	770(2)(ade)	827(2)(ae)	989(1)(a)	1078(1)(e)	1151(3)(ae)	1456(2)(ae)	1738(1)(a)	2925(4)(adeh)
n-Propyl n-Propionate $C_2H_5COOC_3H_7$	1077(1)(d)	1435(2)(e)	2924(3)(ae)								
Propylene Glycol $CH_3CHOHCH_2OH$	830(1)(ae)	919(1)(e)	1050(1)(e)	2918(2)(ae)							
Safrol $C_{10}H_{10}O_2$	594(1)(ade)	721(2)(ade)	816(2)(ade)	1107(1)(de)	1174(1)(d)	1248(1)(ade)	1303(1)(ae)	1624(1)(a)	2911(1)(ae)	3072(1)(ade)	
†Tetrachloroethylene $CCl_2{:}CCl_2$	239(4)(a)	347(2)(ae)	450(4)(ade)	513(2)(ae)	1575(5)(ae)						
1,2,4 Trichlorobenzene $C_6H_3Cl_3$	188(1)(a)	319(1)(a)	392(1)(a)	816(1)(a)	1030(1)(a)	1144(2)(a)	1229(2)(ad)	1573(2)(a)	1882(1)(e)	2235(1)(e)	3067(2)(ae)

† Numerical data given in part by Pringsheim and Rosen, Zeits. f. Physik **50**, 741(1928).
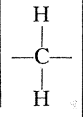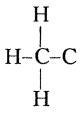
tensity. The intensity of the Hg line 4916A is assumed arbitrarily to have an intensity of 5 units on this scale. The wave-lengths of the exciting lines corresponding to each of the letters used in Table I are as follows,

	wave-length in A.U.	wave-number in cm^{-1}
a	4358	22938
b	4348	22994
c	4339	23038
d	4078	24516
e	4047	24705
f	3984	25093
g	3663	27290
h	3655	27354
i	3650	27388

Where the Raman frequency shift as tabulated in Table I is followed by two or more letters in parentheses, as (a, d, e), the meaning is that this Raman frequency shift was observed for the three exciting lines designated by the letters a, d, e, that is, for $\lambda = 4358$A, $\lambda = 4078$A and $\lambda = 4047$A. In such cases the frequency shift recorded is the mean of the values obtained from each of the exciting lines. Where only one letter in parentheses follows a Raman frequency shift this frequency shift was observed for this exciting line only.

Table II classifies certain frequency shifts as suggested by Dadieu and Kohlrausch.[2] The average values of frequency shifts here listed for particular structural characteristics are in close agreement with those given in the reference cited. In the case of n-butyl acetate the $C = C$ structure does not occur, but there is however in this case an unexplained frequency shift of 1686 cm^{-1}

TABLE II.

Substance	Δν C—C	Δν H–C–H	Δν C=C	Δν H–C–C	Δν H—⟨⟩
ter-Amyl Chloride $(CH_3) - CH_2(CH_3)_2CCl$		1451(3)		2929(3)	
Benzyl Acetate $CH_3COOCH_2C_6H_5$	998(4) 1022(2)		1602(1)	2933(2)	3046(2)
Benzyl Chloroacetate $CH_2ClCOOCH_2C_6H_5$	1009(3)		1614(2)		3061(1)
n-Butyl Acetate $CH_3COOC_4H_9$		1440(1)	1686(1)	2918(2)	
n-Butyl Formate $HCOOC_4H_9$		1452(2)		2926(4)	
n-Butyraldehyde $CH_3(CH_2)_2CHO$	983(1)			2915(2)	
o-Chlorophenol ClC_6H_4OH	1022(2)		1585(1)		3061(1)
Cyclohexanol $(CH^2)_5CHOH$	1080(4)			*2935(3)	
Cyclohexene C_6H_{10}	1068(2)		1643(2)	*2908(2)	
p-Cymene $CH_3C_6H_4CH(CH_3)_2$			1617(1)	2975(1)	3020(1)
Ethyl Chloroacetate $CH_2ClCOOC_2H_5$				2953(2)	
Ethylene Glycol $HOCH_2CH_2OH$	1042(1)	1444(1)		*2907(2)	
Isoamyl Propionate $CH_3CH_2COOC_5H_{11}$	989(1)	1456(2)		2925(4)	
n-Propyl n-Propionate $C_2H_5COOC_3H_7$		1435(2)		2924(3)	
Propylene Glycol $CH_3CHOHCH_2OH$				2918(2)	
Safrol $C_{10}H_{10}O_2$			1624(1)	*2911(1)	3072(1)
Tetrachloroethylene $CCl_2:CCl_2$			1575(5)		
1·2·4 Trichlorobenzene $C_6H_3Cl_3$	1030(1)		1573(2)		3067(2)
Average	1024	1446	1613	2929	3054

which does not differ greatly from the mean value of 1613 cm^{-1} attributed to C = C bond. A few cases were noted in which frequency shifts are missing for structural characteristics that do occur. It is probable that in these cases the corresponding Raman lines were produced but with intensity too weak to detect. In a few instances, as indicated by an asterisk in the table, frequency shifts are found without the corresponding molecular structure occurring. However in the great majority of cases similar frequency shifts are noted with the recurrence of similar molecular structures.

Table III gives a comparison of Raman frequency shifts with infrared absorption data for isoamyl-propionate and safrol. The column headed $\Delta\nu$ gives the average Raman frequency shifts, the column headed μ_λ gives the corresponding wave-lengths calculated from these frequency shifts, and the column headed μ_I gives the wave-lengths from observations on infrared

TABLE III.

Isoamyl Propionate			Safrol		
$\Delta\nu$	μ_λ	μ_I*	$\Delta\nu$	μ_λ	μ_I†
272	36.8		594	16.8	
412	24.3		721	13.9	13.9s
605	16.5				12.9s
770	13.0	13.2s	816	12.3	12.36s
827	12.1	12.3			11.67s
989	10.1				10.85s
		9.5s			10.06s
					9.62s
1078	9.27				
1151	8.69	8.6s	1107	9.03	9.12s
		7.5s			8.4s
		7.0	1174	8.52	
1456	6.87				8.15s
		5.9	1248	8.01	
1738	5.57		1303	7.67	
2925	3.42	3.5s			7.43
					6.82s
			1624	6.16	6.07
					5.78
			2911	3.43	3.42s
			3072	3.25	
					2.90
					2.58

* Weniger, Phys. Rev. [1] **31**, 388 (1910).

† Coblentz, Investigation of Infrared Spectra, Carnegie Institution of Washington, Pub. No. 35 (1905).

absorption. The letter *s* is used to indicate particularly strong infrared absorption. As has been noted by many observers a direct correspondence does not exist between Raman frequency shifts and infrared absorption data. This table gives a sample of results obtained in this investigation in which only an occasional near approach of values exists. This is in accord with theoretical considerations as has been shown by Langer and Meggers[4] and others.

An observation that seems worthy of mention is the appearance in the case of tetrachloroethylene of three anti-Stokes lines of frequency shifts -448 cm^{-1}, -349 cm^{-1}, -240 cm^{-1} with corresponding Stokes lines of frequency shifts 447 cm^{-1}, 348 cm^{-1}, 238 cm^{-1}. The shift of the anti-Stokes lines

[4] Langer and Meggers, B S. Jour. Research **4**, 711 (1930).

thus average slightly greater than the coresponding Stokes lines. In the accurate work of Langer and Meggers[4] a similar difference appears in the data on carbon tetrachloride and chloroform. These small differences by which the negative shifts exceed the positive may be due to a systematic error in measurement. However, the suggestion is here offered that perhaps we are observing a true difference such as might be expected to exist if a double electron shift takes place when the molecule is removed from its excited state to its normal state. More data accurately taken with high dispersion will need to be secured before final statement can be made on this point.

In conclusion the author wishes to express his appreciation to Professor Alpheus W. Smith for suggesting the problem and for his assistance in the work. He is also indebted to Dr. M. L. Pool for advice and helpful discussion as the work progressed.