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THE RAMAN EFFECT AND THE CARBON-HALOGEN BOND

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Abstract

By far the most intense line in the Raman spectra of (organic) aliphatic bromides exhibits a Raman wave number ($\Delta\bar{\nu}$) of about 600 cm^{-1} in the methyl derivative, of 564 cm^{-1} if from two to five carbon atoms are present in the normal chain, and of about 539 cm^{-1} if the chain is branched sufficiently close to the bromine atom. These frequencies are the most characteristic of the carbon-bromine bond. It is assumed that these Raman lines, and the corresponding most intense lines in the spectra of the chlorides and of the iodides, are produced by a decrease (or increase in anti-stokes lines) by unity in the vibrational quantum number. On the basis of this assumption the use in the calculations of this paper of only the first term in the brackets of the more general equation

$$\epsilon^v = hc[\bar{w}_e(v + \tfrac{1}{2}) - x_2(v + \tfrac{1}{2})^2 + \cdots]$$

may be considered to give only a small error, possibly of the order of one percent. Here w is the wave number, but the w used elsewhere in this paper gives the frequency, since for simplicity it includes the hc term. Although the fundamental frequency associated with the carbon-halogen bond in normal aliphatic compounds decreases by about 8 percent if the number of carbon atoms in the molecule is increased from one to two, a further increase in the length of the molecule up to 5 carbon atoms does not give any further decrease; that is, the frequency is independent of the length of the molecule. The fundamental frequencies which for the methyl halides are associated with this bond are 2.13×10^{13} for the chloride, 1.81×10^{13} for the bromide, and 1.60×10^{13} per second for the iodide. The value 1.81×10^{13} for the bromide with one carbon atom, is reduced to 1.69×10^{13} if three, four or five carbon atoms are present in the molecule. If it is assumed that the mechanical frequency (w_0) is, for a value of $\Delta v=\pm1$, related approximately by the equation

$$\Delta\nu = w_0(v'-v'') = \frac{1}{2\pi}\left(\frac{f}{\mu}\right)^{1/2}(v'-v'')$$

to the Raman frequency ($\Delta\epsilon$) which is associated with this bond, then the vibration of the bromine atom with respect to the adjacent part of the hydrocarbon chain, has a frequency which is independent of the length of the molecule, provided more than one carbon atom is present. The conclusion from these results is that the force constant which corresponds to the carbon-bromine bond, and therefore, presumably, the strength of the bond, either remains constant, or else increases only slightly as the length of the molecule increases. However, the force constant for methyl halides may be appreciably higher than those for the longer chain compounds. This indicates that the characteristic frequency of this bond corresponds to an inner vibration: that is, in general only a part of the rest of the organic molecule vibrates with respect to the halogen atom to give this frequency. The force constant characteristic of the carbon-halogen bond is found to have, for the methyl halides, values of about 3.0 for the chloride, 2.6 for the bromide, and 2.2×10^{-5} dynes per cm for the iodide. Thus the values decrease in the same order as the corresponding heats of dissociation. The values are much less than that (5×10^{-5} dynes per cm) previously found for single bonds (C·C, C·O, and C·N) in organic compounds. Another frequency, about 53 percent of that more distinctly characteristic, and with a value of about 300 cm^{-1} for the wave number, seems to be also associated with carbon-bromine bond, possibly with some type of transverse vibration. A not too distant branching of the chain of the aliphatic hydrocarbon causes a decrease of about 5 percent in the characteristic frequency associated with the carbon-bromine bond, and probably indicates a decrease in the strength of the bond. The value 1638 cm^{-1} is obtained for the wave number which is associated with the double bond of allyl bromide, while Dadieu and Kahlausch obtain 1639 cm^{-1} for the chloride and 1645 cm^{-1} for the alcohol. This illustrates the smallness of the effect of the change of mass of the substituted group upon the frequency at the double bond, which seems to indicate an inner and not an outer vibration. Experimental data are presented for the Raman spectra of nine (organic) aliphatic bromides. The spectra were taken by a large three prism Steinheil G. H. glass spectrograph, by the use of two constricted quartz mercury arcs. The ultraviolet light from these arcs was filtered out by special glass filters in order to prevent the appearance of a brown color in the liquid, and the resultant continuous fluorescence spectrum.

1. INTRODUCTION

WHILE very extensive researches have been carried out to determine the Raman frequencies most closely associated with various substituted radicals in organic compounds, there have been no investigations which show in a satisfactory way the effect of a change of length of the organic molecule upon any such frequency.[1] The work reported here was begun in 1929 to remedy this deficiency. In order to prevent the extra complication which arises when several atoms are present in the radical, it was decided to study the frequencies associated with a single halogen atom in the molecule.

2. EXPERIMENTAL METHOD

The Raman spectra were taken by the use of a large Steinheil three prism glass spectrograph. The Pyrex tube used to hold the liquid is similar in shape to that designed by Wood. The liquid, after purification by distillation, is put into a glass bulb (Fig. 1) which is kept sealed to the Raman tube. After evacuation of the tube, the liquid is distilled over into the Raman tube. This liquid is then poured back into the tube, and this process repeated several times to give an "optically empty" liquid.

The source of light was a set of vertical constricted 220 volt quartz mercury arcs. It was found that these arcs work smoothly if started on a 220 volt D.C. circuit, but the quartz of the capillary deteriorates rapidly when the arc is in operation. Thus the best Raman spectra are obtained if the capillary is replaced by a new one after each day of operation.

Organic bromides are changed chemically and colored brown by the action of ultraviolet light. The colored liquid thus produced gives rise in such work to a continuous fluorescence spectrum which obscures the Raman lines to some extent. To prevent this photochemical action various Corning glass filters were used to absorb wave-lengths below λ3650A.

When two 220 volt constricted arcs were used it was found that in the presence of the filters it was necessary to give an exposure of 10 to 12 hours

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[1] A. Dadieu and K. W. F. Kohlrausch, however, have (J. Opt. Soc. Am. **21**, 298 (1931)) published values for molecules up to 4 carbon atoms in length.

to obtain an entirely satisfactory Raman spectra. Without the filters the time is greatly reduced, but many lines are partly obscured by the continuous spectrum. With chlorides or hydrocarbons, the filters are not in general necessary.

3. Wave-Lengths and Shift of Frequency

The approximate wave-length of each line was obtained by direct comparison with the spectrum of an iron arc, but the final values were calculated by the use of the Hartmann formula, from the wave-lengths of adjacent well-known lines in the mercury spectrum.

Many of the Raman lines are broad and diffuse. This seems to be due in some cases to the overlapping of Raman lines, excited by two or more lines of the incident spectrum. The shift of frequency ($\Delta\nu$) was obtained by calculating all of the possible frequency shifts with reference to the strong mercury lines in the adjacent spectrum. The shifts selected as real were those which gave the same value if the Raman lines were caused by two or more exciting lines. In the relatively few cases in which there was no such coincidence in the values, the scattered line was assigned to the nearest mercury line of high intensity. A few doubtful selections are indicated by question marks. This is the usual method employed when the mercury arc, with its great number of lines, is used as the exciting source. Without doubt this method gives rise to the inclusion in tables of data, of frequency shifts which are not real, and to the omission of certain true shifts.

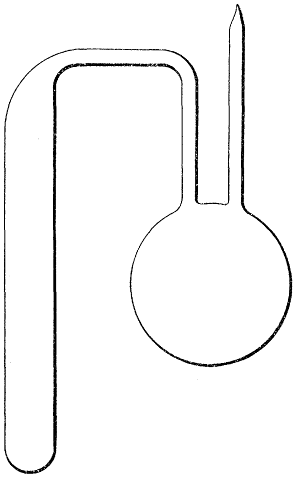

Fig. 1. Raman tube of the Wood type as modified by Langer and Meggers.

This is illustrated by Table I, which gives the Raman frequencies as determined by the writers (H.B.), by Dadieu and Kohlrausch[2] (D.K.), by Bhagavantam and Venkateswaren[3] (C.D.), and by Cleeton and Dufford[4]

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[2] A. Dadieu and K. W. F. Kohlrausch, J. Opt. Soc. Am. **5**, 286–322 (1931).

[3] S. Bhagavantam and S. Venkateswaren, Proc. Roy. Soc. **A127**, 360 (1930).

[4] Cleeton and Dufford, Phys. Rev.

(C.D.) for allyl bromide ($CH_2=CHCH_2Br$), and for n-propyl bromide ($CH_3CH_2CH_2Br$).

TABLE I. *Wave numbers of bromides.*

Allyl bromide H.B.	Allyl bromide D.K.	Allyl bromide B.V.	Propyl bromide H.B.	Propyl bromide D.K.	Propyl bromide C.D.
254 (3)	252	259	312 (2)	314	308
—	385	—	—	397	—
535 (2)	526	535	459 (2)	—	—
695 (2)	687	690	563 (1)	564	566
—	926	—	648 (2)	647	—
1000 (2)	—	—	778 (1)	773	—
1193 (2)	1190	—	—	836	—
1215 (2)	1212	1209	—	885	—
1296 (4)	1292	1301	—	—	968
1320 (2)	—	1321	1023 (2)	1024	—
1378 (2)	—	—	—	—	1079
1410 (2)	1406	1414	1143 (2)	1131	—
1638 (2)	1633	1641	1165 (2)	—	—
2157 (2)	—	—	1185 (2)	—	—
2986 (2)	2966	2975	1229 (2)	—	1254
—	3011	—	1435 (1)	1430	1456
—	3085	—	—	—	2736
			2896 (2)	2862	2875
			2933 (2)	2935	2923
			2965 (2)	2959	2976
			2993 (3)	3000	—

TABLE II. *Raman wave numbers for bromides. Average* $\Delta\bar{\nu}$ *values.*

iso-propyl bromide	n-butyl bromide		Secondary butyl bromide	iso-butyl bromide	Tertiary butyl bromide	n-amyl bromide	iso-amyl bromide
	H.B.	D.K.					
172 (1)	280 (2)	279	291 (4)	303 (4)	301 (6)	219 (1)	288 (2)
297 (3)	457 (2)		317 (1)	421 (2)	515 (5)	436 (1)	564 (2)
353 (2)	563 (2)	557	347 (2)	470 (2)	538 (2)	473 (1)	619 (2)
409 (2)	642 (3)	637	455 (2)	495 (2)	615 (2)	564 (3)	636 (2)
423 (1)	702 (2)	—	482 (2)	517 (2)	803 (2)	642 (3)	648 (2)
540 (4)	745 (2)	—	533 (2)	572 (2)	954 (2)	703 (2)	749 (2)
882 (2)	798 (3)	794	612 (1)	622 (3)	1141 (2)	747 (2)	822 (2)
964 (1)	867 (3)	853	635 (2)	653 (4)	1260 (2)	780 (2)	1297 (2)
1040 (3)	893 (2)	—	840 (2)	796 (1)	1456 (1)	1057 (2)	2872 (2)
	—	1057					
1096 (2)	1103 (3)		956 (1)	812 (2)	2923 (3)	1113 (2)	2932 (3)
	—	1139					
1227 (3)	1170 (2)		1077 (1)	1144 (2)	2970 (2)	1208 (2)	2962 (2)
	—	1257					
1284 (2)	1299 (2)	—	1103 (1)	1198 (2)	3025 (2)	1248 (3)	
1441 (2)	1362 (2)	—	1212 (2)	1234 (2)		1302 (3)	
	—	1440					
2927 (2)	1491 (2)	—	1263 (2)	1313 (1)		1436 (2)	
2958 (3)	2874 (2)	2865	1451 (2)	1454 (1)		1491 (2)	
2983 (2)	2935 (4)	2930	2877 (2)	2871 (2)		2824 (2)	
2993 (2)	2964 (4)	2962	2922 (3)	2962 (3)		2877 (2)	
			2974 (2)			2936 (2)	
						2968 (4)	
						3013 (2)	
						3068 (2)	

NOTE: The figures in parentheses give the number of values from which the average value was obtained.

For allyl bromide the values of Dadieu and Kohlrausch are from 2 to 9 wave numbers smaller than ours, while those of Bhagavantam and Venkateswaren vary from ours by from +5 to −6. Where the differences are much greater it is possible that the same lines were not measured.

The Raman wave number 459 for n-propyl bromide was found only by ourselves, and not by the two other workers. That it may correspond to a real frequency is indicated by its occurrence with the value 457 in n-butyl bromide and 455 in secondary butyl bromide. A vibration of about this wave number is attributed by Andrews to a transverse vibration in the -C-C-C- chain.

The wave numbers which correspond to the Raman shifts for other organic bromides are listed in Table II and Fig. 2. It may be seen that n-amyl bromide gives a surprisingly large number of values, but it is possible that some of them do not correspond to real shifts. One difficulty, which is not sufficiently recognized in connection with the Raman spectra of such compounds, is that it is exceedingly difficult to obtain such organic liquids free from isomers or other compounds similar in properties.

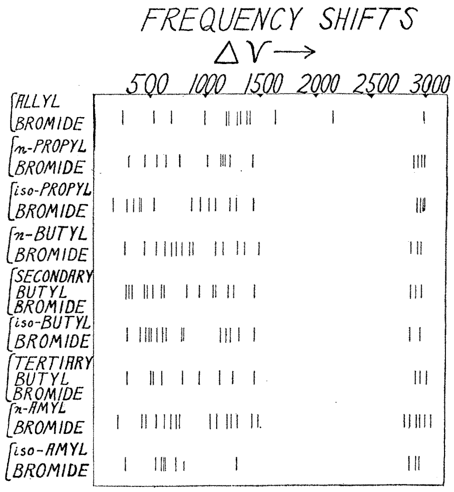

Fig. 2.

The data from which the mean values of the Raman shifts given in Tables I and II have been obtained, are given in Table III. The few anti-Stokes lines are designated by a negative $\Delta\bar{\nu}$. In general the variation in the value of $\Delta\bar{\nu}$ for what seems to be the same Raman shift is not more than 3 units.

4. The Carbon-Halogen Bond with a Single Carbon Atom

As is indicated in Table IV the frequency which corresponds to the carbon-chlorine bond is 2.13×10^{13}, to the carbon-bromine bond, 1.81×10^{13}, and to the carbon-iodine bond 1.60×10^{13} per second, when only one carbon atom is present. If more than one carbon atom is in the molecule these characteristic frequencies are reduced by from 6 to 11 percent for bromides and probably somewhat more for chlorides, as is shown in the next section.

The equation for the Raman frequency ($\Delta\nu$) may be written in a simple approximate form as

$$\Delta\nu = \omega_0(v' - v'') = \frac{1}{2\pi}\left(\frac{f}{\mu}\right)^{1/2}(v' - v'')$$

TABLE III. *Wave-lengths of Raman and exciting lines.*

Raman line	Exciting line			Raman line	Exciting line		
$\bar{\nu}$	λ	$\bar{\nu}$	$\Delta\bar{\nu}$	$\bar{\nu}$	λ	$\bar{\nu}$	$\Delta\bar{\nu}$
			Allyl bromide				
24451	4046.56	24705	254	21997	4347.50	22995	998
24174	4046.56	24705	531	21744	4339.24	23039	1295
24010	4046.56	24705	695	21744	4358.34	22938	1194
23514	4046.56	24705	1191	21721	4046.56	24705	2984
23514	4077.84	24516	1002	21721	4339.24	23039	1318
23492	4046.56	24705	1213	21721	4358.34	22938	1217
23408	4046.56	24705	1297	21699	4347.50	22995	1296
23328	4046.56	24705	1377	21642	4358.34	22938	1296
23296	4046.56	24705	1409	21617	4358.34	22938	1321
23068	4046.56	24705	1637	21617	4347.50	22995	1378
22786	4339.24	23039	253	21528	4077.84	24516	2988
22682	4358.34	22938	256	21528	4358.34	22938	1410
22546	4046.56?	24705	2159	21299	4358.34	22938	1639
22400	4358.34	22938	538	20885	4339.24?	23039	2154
22243	4358.34	22938	695				
			n-propyl bromide				
24394	3663.27	27290	2896	21830	4347.50	22995	1165
24394	3650.14	27388	2994	21809	4046.56	24705	2896
24394	4046.56	24705	311	21809	4339.24	23039	1230
24057	4046.56	24705	648	21809	4347.50	22995	1186
24057	4077.84	24516	459	21793	4358.34	22938	1145
22626	4358.34	22938	312	21774	4046.56	24705	2931
22536	4347.50	22995	459	21774	4358.34	22938	1164
22375	4358.34	22938	563	21742	4046.56	24705	2963
22291	4358.34	22938	647	21711	4046.56	24705	2994
22160	4358.34	22938	778	21711	4358.34	22938	1227
21970	4347.50	22995	1025	21503	4358.34	22938	1435
21918	4358.34	22938	1020	20003	4347.50	22995	2992
21855	4339.24	23039	1184	20003	4358.34	22938	2935
21855	4347.50	22995	1140	19972	4358.34	22938	2966
			iso-propyl bromide				
24407	3650.14	27388	2981	21897	4358.34	22938	1041
24407	4046.56	24705	298	21844	4358.34	22938	1094
24298	3663.27	27290	2992	21812	4339.24	23039	1227
24298	4046.56	24705	407	21778	4046.56	24705	2927
24165	4046.56	24705	540	21749	4046.56	24705	2956
24165	4077.84	24516	351	21711	4046.56	24705	2994
23975	4077.84	24516	541	21711	4347.50	22995	1284
23824	4046.56	24705	881	21711	4358.34	22938	1227
23664	4046.56	24705	1041	21556	4077.84	24516	2960
23477	4046.56	24705	1228	21556	4347.50	22995	1439
23477	4077.84	24516	1039	21495	4358.34	22938	1443
23232	4077.84	24516	1284	20011	4347.50	22995	2984
22641	4347.50	22995	354	20011	4358.34	22938	2927
22641	4358.34	22938	297	19980	4358.34	22938	2958
22528	4358.34	22938	410	18135	5460.74	18307	172
22399	4358.34	22938	539	18010	5460.74	18307	297
22056	4358.34	22938	882	17884	5460.74	18307	423
21974	4358.34	22938	964	17768	5460.74	18307	539
21897	4347 50	22995	1098				

TABLE III. (*Continued*)

Raman line $\bar{\nu}$	Exciting line λ	 $\bar{\nu}$	$\Delta\bar{\nu}$	Raman line $\bar{\nu}$	Exciting line λ	 $\bar{\nu}$	$\Delta\bar{\nu}$
n-butyl bromide							
24425	3650.14	27388	2963	22197	4347.50	22995	798
24425	4046.56	24705	280	22139	4358.34	22938	799
24143	4046.56	24705	562	22070	4358.34	22938	868
24061	4046.56	24705	644	22045	4358.34	22938	893
24061	4077.84	24516	455	21891	4347.50	22995	1104
23961	4046.56	24705	744	21870	4339.24	23039	1169
23907	4046.56	24705	798	21836	4358.34	22938	1102
23877	4077 84	24516	639	21768	4046.56	24705	2937
23838	4046.56	24705	867	21768	4358.34	22938	1170
23813	4046.56	24705	892	21741	4046.56	24705	2964
23813	4077.84	24516	703	21741	4339.24	23039	1298
23650	4077.84	24516	866	21676	4339.24	23039	1363
23603	4046.56	24705	1102	21643	4077.84	24516	2873
23216	4046.56	24705	1489	21577	4077.84	24516	2939
23216	4077.84	24516	1300	21577	4358.34	22938	1361
22659	4358.34	22938	279	21553	4077.84	24516	2963
22480	4358.34	22938	458	21503	4347.50	22995	1492
22375	4358.34	22938	563	20064	4347.50	22995	2931
22294	4339.24	23039	745	20064	4358.34	22938	2874
22294	4347.50	22995	701	20004	4358.34	22938	2934
22294	4358.34	22938	644	19974	4358.34	22938	2964
Secondary butyl bromide							
24414	3650.14	27388	2974	22406	4358.34	22938	532
24414	3663.27	27290	2876	22359	4347.50	22995	636
24414	4046.56	24705	291	22326	4358.34	22938	612
24224	4046.56	24705	481	22154	4347.50	22995	841
24224	4077.84	24516	292	22099	4358.34	22938	839
24171	4046.56	24705	534	21982	4358.34	22938	956
24171	4077.84	24516	345	21892	4347.50	22995	1103
23253	4046.56	24705	1452	21861	4358.34	22938	1077
23253	4077.84	24516	1263	21828	4046.56	24705	2877
23229	4358.34	22938	−291	21828	4339.24	23039	1211
22647	4347.50	22995	348	21783	4046.56	24705	2922
22647	4358.34	22938	291	21783	4347.50	22995	1212
22621	4358.34	2293	317	21732	4046.56	24705	2973
22586	4339.24	23039	453	21732	4347.50	22995	1263
22482	4358.34	22938	456	21593	4077.84	24516	2923
22455	4358.34	22938	483	21488	4358.34	22938	1450
22406	4339.24	23039	633	20018	4358.34	22938	2920
iso-butyl bromide							
24401	4046.56	24705	304	22518	4358.34	22938	420
24283	4046.56	24705	422	22469	4339.24	23039	570
24235	4046.56	24705	470	22469	4358.34	22938	469
24212	4046.56	24705	493	22421	4347.50	22995	574
24212	4077.84	24516	304	22421	4358.34	22938	517
24189	4046.56	24705	516	22316	4358.34	22938	622
24083	4046.56	24705	622	22285	4358.34	22938	653
24052	4046.56	24705	653	22142	4358.34	22938	796
23893	4046.56	24705	812	22126	4358.34	22938	812
23893	4077.84	24516	623	21833	4046.56	24705	2872
23861	4077.84	24516	655	21796	4347.50	22995	1199
23590	4358.34	22938	−652	21796	4358.34	22938	1142
23560	4046.56	24705	1145	21741	4046.56	24705	2964
23470	4046.56	24705	1235	21741	4358.34	22938	1197
23392	4046.56	24705	1313	21705	4358.34	22938	1233
23239	4358.34	22938	−301	21555	4077.84	24516	2961
22634	4358.34	22938	304	21484	4358.34	22938	1454
22542	4339.24	23039	497	20068	4358.34	22938	2870
				19976	4358.34	22938	2962

Table III. (*Continued*).

Raman line	Exciting line			Raman line	Exciting line		
$\bar{\nu}$	λ	$\bar{\nu}$	$\Delta\bar{\nu}$	$\bar{\nu}$	λ	$\bar{\nu}$	$\Delta\bar{\nu}$
			Tertiary butyl bromide				
25005	4046.56	24705	−300	22134	4358.34	22938	804
24403	4046.56	24705	302	21982	4358.34	22938	956
24214	4077.84	24516	302	21797	4358.34	22938	1141
24189	4046.56	24705	516	21781	4046.56	24705	2924
24167	4046.56	24705	538	21781	4339.24	23039	1258
24000	4077.84	24516	516	21734	4046.56	24705	2971
23903	4046.56	24705	802	21734	4347.50	22995	1261
23903	4077.84	24516	613	21594	4077.84	24516	2922
23564	4046.56	24705	1141	21482	4358.34	22938	1456
23564	4077.84	24516	952	20015	4339.24	23039	3024
23453	4358.34	22938	−515	20015	4358.34	22938	2923
23240	4358.34	22938	−302	19970	4347.50	22995	3025
22635	4358.34	22938	303	19970	4358.34	22938	2968
22422	4339.24	23039	617	18008	5460.74	18307	299
22422	4358.34	22938	516	17793	5460.74	18307	514
22400	4358.34	22938	538				
			n-amyl bromide				
24141	4046.56	24705	564	21882	4347.50	22995	1113
24062	4046.56	24705	643	21882	4358.34	22938	1056
23956	4046.56	24705	749	21830	4046.56	24705	2875
23923	4046.56	24705	782	21830	4339.24	23039	1209
23877	4077.84	24516	639	21768	4046.56	24705	2937
23811	4077.84	24516	705	21739	4046.56	24705	2966
23739	4077.84	24516	777	21739	4339.24	23039	1300
23647	4046.56	24705	1058	21692	4046.56	24705	3013
23499	4046.56	24705	1206	21692	4077.84	24516	2824
23454	4046.56	24705	1251	21692	4347.50	22995	1303
23403	4046.56	24705	1302	21692	4358.34	22938	1246
23403	4077.84	24516	1113	21637	4046.56	24705	3068
23269	4046.56	24705	1436	21637	4077.84	24516	2879
23269	4077.84	24516	1247	21637	4358.34	22938	1301
22719	4358.34	22938	219	21549	4077.84	24516	2967
22502	4358.34	22938	436	21549	4339.24	23039	1490
22465	4358.34	22938	473	21503	4077.84	24516	3013
22430	4347.50	22995	565	21503	4347.50	22995	1492
22375	4358.34	22938	563	21503	4358.34	22938	1435
22294	4339.24	23039	745	20068	4339.24	23039	2971
22294	4347.50	22995	701	20004	4358.34	22938	2934
22294	4358.34	22938	644	19971	4339.24	23039	3068
21882	4046.56	24705	2823	19971	4358.34	22938	2967
			iso-amyl bromide				
24142	4046.56	24705	563	22190	4358.34	22938	748
24055	4046.56	24705	650	22116	4358.34	22938	822
23955	4046.56	24705	750	21834	4046.56	24705	2871
23883	4046.56	24705	822	21768	4046.56	24705	2937
23883	4077.84	24516	633	21743	4046.56	24705	2962
22707	4347.50	22995	288	21743	4339.24	23039	1296
22651	4358.34	22938	287	21641	4358.34	22938	1297
22400	4339.24	23039	639	20065	4347.50	22995	2930
22374	4347.50	22995	621	20065	4358.34	22938	2873
22374	4358.34	22938	564	20008	4358.34	22938	2930
223 2	4358.34	22938	616	19976	4358.34	22938	2962
22292	4358.34	22938	646				

in which v represents a quantum number, μ the mutual mass, w_0 is sometimes considered as the fundamental mechanical frequency, and f as the force constant. The values of f for the methyl halides are given in Table IV. It is assumed that in the emission of these intense Raman lines $v' - v'' = \pm 1$.

The force constant (a) is calculated in the ordinary way, and it is considered that the methyl group vibrates as a unit with respect to the halogen atom. In (b) a slight, somewhat arbitrary allowance has been made for the fact that this is not strictly true.

TABLE IV. *Values for the carbon-halogen bond.*

Compound	Wave Number cm^{-1}	ν Frequency per Second $\times 10^{-13}$	Force Constant f $\times 10^5$ dynes		Amplitude $\times 10$ cm		$\frac{1}{2}fa \times 10$	
			a	b	$v=\frac{1}{2}$	$v=1\frac{1}{2}$	$v=\frac{1}{2}$	$v=1\frac{1}{2}$
CH_3Cl	712	2.135	3.136	3.02	6.7	11.6	2.0	3.5
CH_3Br	603	1.808	2.695	2.60	6.65	11.5	1.7	3.0
CH_3I	534	1.601	2.246	2.17	6.9	11.9	1.5	2.6

The force constant decreases from the chloride to the iodide. The values are much smaller than those of the single bonds listed by Dadieu and Kohlrausch which are, in 10^5 dynes per cm, equal to 4.31 for C·C in ethane, 4.96 for C·C in methyl alcohol, and 4.89 for C·N in methyl amine.

Thus if f represents the strength of the bond, the carbon-halogen bond seems to be much weaker than the most common of the other single bonds found in organic compounds. That the strength of the bond decreases rapidly from chloride to bromide to iodide, is in agreement, not only with the heats of dissociation, but also with the other known relations.

The meaning of the amplitude a' is definite in the classical quantum theory, but loses this definiteness in the newer quantum mechanics.

Since $\epsilon = fa^2/2 = (v + \frac{1}{2})w_0 h$

$$a = \left(\frac{2\epsilon}{f}\right)^{1/2} = \left(\frac{(2v + 1)hw_0}{f}\right)^{1/2}$$

in which (ϵ) is the energy and w_0 is the mechanical frequency. The values for this amplitude for $v = \frac{1}{2}$ and $v = 3/2$ are given in Table IV.

Dadieu and Kohlrausch give the mean value of the force as $\frac{1}{2}fa$, and consider this to be more characteristic of the bond than the force constant.

For $v = \frac{1}{2}$ the values of $\frac{1}{2}fa$ in 10^{-4} dyne cm are 2.0, 1.7, and 1.5 for methyl chloride, bromide, and iodide, respectively, while Dadieu and Kohlrausch give 2.04 for the C·C bond in methane, 2.27 for the C·O bond in methyl alcohol, 2.23 for the C·N bond in methyl amine, 4.13 for the double bond in ethylene, 4.4 for the carbonyl C·O bond, 4.14 for the oxygen bond in O_2, and 6.28 for the bond in carbon monoxide.

5. THE EFFECT OF A LENGTHENING OF THE CHAIN UPON THE CARBON-HALOGEN BOND

The effect of a lengthening of the hydrocarbon chain upon the characteristic carbon-bromine frequency is exhibited in Table V.

This is the most intense line in the Raman spectrum of the bromides.

The remarkable fact revealed by our data is that while the carbon-bromine frequency is reduced by about 6 percent if the number of carbon atoms in the chain is increased from one to two, a further increase from two to five carbon atoms produces no appreciable effect.

TABLE V. *Characteristic wave numbers for the carbon-bromine bond in organic bromides* .

CH_3Br	603 (C.D.)	594 (D.K.)
C_2H_5Br	566 (C.D.)	557 (D.K.)
$n-C_3H_7Br$	563 (H.B.)	564 (D.K.)
n C_4H_9Br	563 (H.B.)	557 (D.K.)
$C_5H_{11}Br$	564 (H.B.)	
$(CH_3)_2CH\ (CH_2)_2Br$	564 (H.B.)	

If an attempt is now made to apply Eq. (1) to determine the value of the force constant f and thus, presumably, the strength of the bond, it is apparent that the equation cannot be solved without additional knowledge or an additional assumption. It seems to have been customary to assume that all of the hydrocarbon chain vibrates with respect to the bromine atom: —or more complicated equations are used which indicate a change of the single fundamental frequency into two values.

The constancy of the fundamental carbon-bromine frequency seems to suggest that neither of these assumptions is valid in this case.

Thus it seems apparent from the constant value of the frequency for normal compounds that *the organic radical cannot vibrate as a whole with respect to the bromine atom*, for such an assumption leads to an absurd value of the force constant for very long chains.

Thus, on the basis of the assumption that the effective mass of the methyl group with respect to the vibration toward bromine is 14.4 atomic weight units, the force constant for methyl bromide is 2.60×10^5 dyne/cm (or 2.70 if CH_3 vibrates as a single unit of mass 15). If now the amyl group vibrates as a unit the force constant for amyl bromide would be 7.0×10^5 dyne/cm, or more than two and a half times larger than for methyl bromide. This is much too large.

If the force constant in all of the normal bromides is assumed to be constant and equal to 2.60×10^5 dyne/cm, the effective mass of the portion of the hydrocarbon chain of two or more carbon atoms, which vibrates (with respect to the bromine) is 17. This indicates that the CH_2 group adjacent to the bromine possesses most of the mass which is effective. That is the CH_2 group vibrates, but its effective mass is increased by the constraint due to its union with the rest of the hydrocarbon chain.

If it is assumed that the force constant decreases with the length of the chain, then the amount of mass in the radical R which vibrates, also decreases with increase of mass of the radical, which seems to be improbable, except for the increase from one to two carbon atoms. Thus these facts, together with the equation $\nu=1/2\pi(f/\mu)^{1/2}(v'-v'')$, lead to the idea that (1) the force constant remains constant as the length of the chain increases, or

(2) the force constant increases as the length of the chain increases, and at the same rate as the mutual mass (μ) of the vibrating parts increases.

From what is known from the standpoint of organic chemistry, it seems that the strength of the carbon-halogen bond does not increase rapidly with the length of the chain.

Thus the final conclusions reached are: (1) The force constant either remains constant, or else it increases only slightly with an increase in length and mass of the normal hydrocarbon chain. (2) As indicated before, only a part of the radical R vibrates with respect to the halogen atom in the process in which the characteristic frequency is emitted.

The values of Dadieu and Kohlrausch suggest that the characteristic frequency of this bond may be higher if an odd number of carbon atoms is present in the molecule than if this number is even. The variation in value is, however, very small, and is not exhibited by our data.

The data of a recent paper by West and Farnsworth[5] indicates the probability that the chlorides exhibit the same relations as the bromides. Unfortunately for the purpose of the present paper, their work does not extend to chains of more than 3 carbon atoms.

TABLE VI. *Characteristic wave numbers for the carbon-halogen bond.*

1.	2. Cl	3. Br	4. I	5. Cl-Br	6. Br-I	7. Cl^2-Br^2 $\times 10^{-3}$	8. Br^2-I^2 $\times 10^{-3}$	9. $\frac{Br^2-I^2}{Cl^2-Br^2}$
Methyl	711 (W.F.)	603 (C.D.)	522 (D.K.)	108	81	142	91	.64
Ethyl	655 (W.F.)	556 (C.D.)	499 (D.K.)	89	67	109	71	.65
n-Propyl	650 (W.F.)	563 (H.B.)	—	87	—	105	—	—
n-Butyl		563 (H.B.)						
n-Amyl		564 (H.B.)						

Since, with a constant mutual mass, the force constant varies as the square of the frequency, it is apparent from column 9 of Table VI, that the decrease in the value of the force constant is only 65 percent as great between the bromide and iodide as it is between the chloride and bromide.

6. THE EFFECT OF A BRANCHING OF THE CHAIN UPON THE FUNDAMENTAL FREQUENCY ASSOCIATED WITH THE CARBON-HALOGEN BOND

The branching of the hydrocarbon chain seems to have no effect upon the fundamental frequency associated with the carbon-halogen bond, provided the branching occurs sufficiently distant from the halogen atom. Thus isoamyl bromide ($(CH_3)_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot Br$) gives the wave number 564, which is the same as that associated with n-amyl, n-butyl, and n-propyl bromides. However, if the branching is considerably less distant, the frequency is reduced considerably. Thus with iso-compounds, or if the halogen atom is attached to a secondary or tertiary carbon atom, the wave number is reduced from 564 to about 537 cm^{-1} (Table VII).

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[5] W. West and M. Farnsworth, Trans. Faraday Soc. **27**, 145 (1931).

Thus a branching of the chain sufficiently close to the substituted halogen atom either lowers the force constant and presumably weakens the bond, or else it lowers the effective mass of the part of the hydrocarbon chain which vibrates. The former of these seems the more probable.

The frequency for iso-butyl bromide (wave number 572 cm^{-1}) seems exceptional in that it is higher than for the normal compound. However, a lower frequency also appears.

TABLE VII. *Characteristic wave numbers for the carbon-halogen bond with branched chains.*

(Normal)	711	(564)
ISO propyl $(CH_3)_2CH X$	616 (W.F.)	540
Secondary butyl $CH_3CH_2CHX CH_3$	—	537
Tertiary butyl $(CH_3)_3C X$	564 (D.K.)	538
ISO amyl $(CH_3)_2CH CH_2CH_2 X$		(564)
ISO butyl $(CH_3)_2CH CH_2 Br$		(572) and (517)

7. A LOWER CHARACTERISTIC FREQUENCY SEEMINGLY ASSOCIATED WITH THE CARBON-BROMIDE BOND

A wave number of about 300 cm^{-1} has been found for all of the organic monobromides investigated by us, with the exception of allyl bromide, in which a double carbon bond is present. A similar value of about 330 cm^{-1} has been found for chlorides by West and Farnsworth, and with ethyl iodide a value of 260 cm^{-1} was found by Dadieu and Kohlrausch.

Table VIII gives a list of these wave numbers for different chlorides and bromides, and a single value for an iodide.

The values for the bromides (in the upper part of Table VIII) may be associated with some type of transverse vibration at the carbon-bromine bond. Unlike the frequency which the writers have associated with a longitudinal vibration at this bond, the values for iso- or secondary compounds do not exhibit any general differentiation from those of the normal compounds. A few examples are listed to show that if two or more halogen atoms are present the frequencies due to carbon-halogen bonds are greatly modified. Thus, according to Dadieu and Kohlrausch, carbon tetrachloride is represented by the wave numbers 216 (4), 313 (4), 455 (4), 755 (2), 782 (2), in which the numbers in parenthesis represent the intensities. The more intense lines have wave numbers which are smaller than the most characteristic of the carbon-halogen bond in aliphatic compounds. This is probably due in part at least to a greater mutual mass of the vibrating parts of the molecule.

8. WAVE NUMBERS BETWEEN 1400 AND 1460 CM^{-1}

Almost all of the hydrocarbons of the paraffin series and their derivatives exhibit a Raman wave number between 1400 and 1460 cm^{-1}.

This has been attributed by Dadieu and Kohlrausch to a transverse vibration of the hydrogen atoms in the CH_2 group, and by Daure to the single carbon-carbon bond. There seems to be much evidence which indicates the probability that one of these points of view is correct, and certain different details of evidence which seem to speak against each of these ideas. Present opinion seems on the whole more in favor of the former of these conclusions. Table IX lists frequencies in this range as found in monobromides.

TABLE VIII. *Lower wave numbers presumably characteristic of the carbon-halogen bond.*

	Cl	Br	I
Methyl	372 (W.F.)		
Ethyl	327 (W.F.)	290	260 (D.K.)
n-propyl	333 (W.F.)	312	
n-butyl	—	280	
Isopropyl	330 (W.F.)	297	
Isobutyl	—	303	
Isoamyl	—	288	
Secondary butyl	—	291	
β Chloropropylene	337 (W.F.)		
The above values are changed considerably if more than one halogen atom is present.			
CX_4	216–313 (D.K.)		
CHX_3	259–364 (D.K.)	154–221 (D.K.)	
CH_2X_2	283 (D.K.)	178 (D.K.)	119 (D.K.)
XH_2C-CH_2X	295 (D.K.)	188 (D.K.)	
$X_2HC-CHX_2$	287–351 (D.K.)	218 (D.K.)	
1–3 dibromopropane		371 (D.K.)	

TABLE IX. *Wave numbers of about 1450 cm^{-1} for monobromides.*

ethyl bromide	1439 (D.K.)		
n-propyl bromide	1435 (H.B.)	isopropyl bromide	1441
n-butyl bromide	1440 (D.K.)	isobutyl bromide	1454
	1491 (H.B.)	secondary butyl bromide	1451
n-amyl bromide	1436 (H.B.)	tertiary butyl bromide	1456
	1491 (H.B.)	allyl bromide	1410

9. FREQUENCY CHARACTERISTIC OF THE DOUBLE BOND BETWEEN CARBON ATOMS

Dadieu and Kohlrausch have found 1639 cm^{-1} as the wave number characteristic of the double carbon bond in allyl chloride. The writers obtain the value 1638 for the bromide, so the increase of mass of the halogen has little effect upon the frequency. Dadieu and Kohlrausch point out that the frequency, characteristic of the double bond, is moderately constant. Thus their values for di-chlor, tri-chlor, and tetra-chlor ethylene indicate values of 1583, 1585, and 1569, respectively.

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