tion of the older conception of this bond demands that there be such lines. The observed state of affairs is to be expected on the basis of Pauling's suggestion. Furthermore, if the hydrogen ion is connected to the water molecule by means of a shared electron pair in the oxonium ion, we would expect a Raman spectrum characteristic of the latter ion. This would mean that all solutions of acids would have lines in common. An examination of the data for nitric, hydrochloric and sulfuric acids shows that this is not the case.

Another interesting example is the ammonium ion. In solution this ion has no observable Raman lines. This indicates not only that the hydrogen ion connects itself to the ammonia molecule through an ionic linkage, but that in doing so it causes the other bonds to become ionic. It is entirely possible that the case of the oxonium ion is parallel, and that each hydrogen is connected to the oxygen through an ionic linkage.

As investigations in solutions are inherently under adverse conditions, the bond may actually be intermediate in character. At least the evidence indicates quite strongly that it is not of the extreme electron pair type formerly assumed.

U. S. BUREAU OF STANDARDS   CHARLES KASPER
WASHINGTON, D. C.
RECEIVED MAY 20, 1931
PUBLISHED JUNE 8, 1931

THE CARBON–HALOGEN BOND AS RELATED TO RAMAN SPECTRA

Sir:

The purpose of the work described here was to determine the variation of the characteristics of the bond between carbon and another atom as the length and structure of the hydrocarbon chain is varied. The frequency which corresponds to the carbon–bromine bond in methyl bromide is 1.808×10^{13} per second, but in longer normal chains this is reduced to a constant value of 1.688×10^{13}. In an iso compound or in the presence of a double bond, this is reduced to about 1.61×10^{13}. These frequencies are of considerable interest, since in the simple theory they are supposed to be equal to the frequencies of the carbon–bromine bond in these compounds.

What is sometimes called the "strength of a bond" may be represented by the force constant, which for the carbon–carbon single bond is about 5×10^5 dynes per cm. The values for the carbon–halogen bond do not seem to have been calculated for monohalogens. They are given in Table I.

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 I

VALUES FOR THE CARBON–HALOGEN BOND

Compound	Wave number, cm.$^{-1}$	Frequency per second $\times 10^{-13}$	Force constant $\times 10^{-5}$ dynes		Amplitude $\times 10^{10}$ cm.	
			a	b	$n = 0$	$n = 1$
CH_3Cl^1	712	2.135	3.14	3.02	6.7	11.6
CH_3Br^2	603	1.808	2.70	2.60	6.65	11.5
CH_3I^2	534	1.601	2.25	2.17	6.9	11.9

The force constants decrease from the chloride to the iodide, in somewhat the same way as the corresponding energies of dissociation. Those given in Column (a) are much smaller than the values of the single bonds listed by Dadieu and Kohlrausch,[1] which are (in 10^5 dynes per cm.) equal to 4.31 for C–C in ethane, 4.96 for C–O in methyl alcohol, and 4.89 for C–N in methylamine.

That the frequencies chosen in Table I are those characteristic of the carbon–halogen bond is shown by work on various bromides. These are listed in Table II.

TABLE II

CHARACTERISTIC WAVE NUMBERS FOR THE CARBON–BROMINE BOND IN ORGANIC BROMIDES

CH_3Br	603 (2)	$(CH_3)_2CH(CH_2)_2Br$	564
C_2H_5Br	566 (2)	$(CH_3)_2CHBr$	540
n-C_3H_7Br	563	$C_2H_5CHBrCH_3$	537
n-C_4H_9Br	563	$(CH_3)_3CBr$	538
n-$C_5H_{11}Br$	564	$CH_2:CHCH_2Br$	535
		$(CH_2)_2CHCH_2Br$	572

The remarkable fact revealed by these data is that the frequency of the carbon–bromine bond is constant in normal compounds with the exception of methyl bromide, and that it is the same for an iso compound provided the side chain is sufficiently distant from the bromine. However, an adjacent side chain, attachment to a secondary or a tertiary carbon atom, or the double bond of an adjacent unsaturated group as in allyl bromide, in all the given cases lowers the wave number from 563.5 to about 537 cm.$^{-1}$. Thus the carbon–bromine bond seems considerably weaker in this latter class of compounds (with the exception of isobutyl bromide).

It is apparent from the constant value of the wave number for the 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 for the force constant.

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 $\times$ 10^5 dyne/cm.

[1] Wave number determined by Dadieu and Kohlrausch, *J. Opt. Soc. Am.*, **5**, 297 (1931).

[2] Wave number determined by Cleeton and Dufford, *Phys. Rev.*, **37**, 365 (1931).

(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 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, and is influenced by the vibration of this part of the molecule.

The writers have determined the frequencies of the Raman lines of nine organic bromides. These give a large number of characteristic frequency differences as, for example, 1639 cm.$^{-1}$ for the double bond of allyl bromide, but only the values characteristic of the carbon–bromine and other carbon–halogen bonds can be discussed here. The variation in the wave number corresponding to this bond is usually not more than one unit of wave number for any one compound, and the maximum variation for any compound is two units.

The equation for the force constant (k) is

$$\nu_0 = \omega_0 \, (n' - n'') = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{1/2} (n' - n'')$$

in which n represents a quantum number, μ the mutual mass, ν_0 the fundamental frequency of the radiation, and ω_0 the fundamental mechanical frequency. A further discussion will be presented in the final paper.

DEPARTMENT OF CHEMISTRY   WILLIAM D. HARKINS
UNIVERSITY OF CHICAGO   HAROLD E. BOWERS
CHICAGO, ILLINOIS
RECEIVED MAY 22, 1931
PUBLISHED JUNE 8, 1931

PREPARATION OF UNSYMMETRICAL DIALKYL ETHYLENE DERIVATIVES

Sir:

The recent description of the preparation of α,β-unsaturated ethers by Lauer and Spielman [THIS JOURNAL, **53**, 1533 (1931)] makes possible an extension of our nuclear synthesis of olefins [*ibid.*, **52**, 3396 (1930); **53**, 1505 (1931)] to include the unsymmetrical dialkyl derivatives of ethylene. The essential steps in the process are clearly represented by the scheme.

$$CH_2{=}C(R)OEt + Br_2 \longrightarrow CH_2Br{-}CBr(R)OEt \tag{1}$$
$$CH_2Br{-}CBr(R)OEt + R'MgBr \longrightarrow CH_2Br{-}C(R')(R)OEt + MgBr_2 \tag{2}$$
$$CH_2Br{-}C(R')(R)OEt + Zn(Alc.) \longrightarrow CH_2{=}C(R')R + EtOZnBr \tag{3}$$