On the Characteristic Frequencies of Radicals in Different Chemical Combinations.

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In a previous paper [1] on the Raman effect, we have pointed out how certain characteristic frequencies persist in the various compounds which possess one common radical or a certain type of bond. This fact has been mentioned by other workers and some [2] have even tried to calculate the frequencies from the mass of the constituents and the heat of dissociation. Some [3] have also tried to verify the formula by showing that the effect of increase of mass is in most cases a diminution of the frequency and have seen in this result an analogy with the usual dynamical result of the diminution of frequency with the load.

There is, however, a certain weakness in the argument which has not generally been pointed out. There is the assumption that the strength of the binding between the components of the radical responsible for the oscillation remains the same in all the various compounds. There is actually no experimental data which would justify this assumption and we have therefore thought it worth while to make an intensive study of one radical to clear up this point. We have chosen the CN group: the frequencies to be attri-

[1] Ind. Jour. Phys., Vol. V, Part I, 1980.

[2] Dadieu and Kohlrausch, Sitz. Akd. Wien., Vol. 138, p. 419, 1929.

[3]   ,,   Sitz. Akd. Wien., Vol. 138, pp. 424-428, 1929.

buted to CN in the different types of compounds are here collected for reference.

Compounds.	Frequency of CN	Investigators.
Organic :		
$N \equiv C - CH_2COOCH_3$	2266	[**]Petrikaln & Hochberg.
$N \equiv C - CH_2COOC_2H_5$	2258	[1]Dadieu and Kohlrausch
$CH_3 - C \equiv N$	2256	[2]Pal & Sen Gupta
$C_6H_5 - CH_2 - C \equiv N$	2248	Dadieu & Kohlrausch
$H_5C_2 - C \equiv N$	2246	,,
$C_6H_5 - C \equiv N$	2227	,,
Inorganic :		
$K - O - C \equiv N$	2183	Pal and Sen Gupta
Complex double cyanides		
K_2 Hg $(C \equiv N)_4$		
K_2 Zn $(C \equiv N)_4$	2150	Authors
K_2 Cd $(C \equiv N)_4$		
K Cu $(C \equiv N)_2$	2110	Authors
K Ag $(C \equiv N)_2$		
K $C \equiv N$	2080	Pal & Sen Gupta
$Na - S - C \equiv N$	2076	Dadieu & Kohlrausch
$K - S - C \equiv N$	2066	Pal & Sen Gupta
$N H_4 - S - C \equiv N$	2066	,,

It will be evident from the consideration of the data, that it is the nature of the bond which plays a predominant part in the determination of the frequency rather than the mass of the substituent radical.

Thus CN linked to an aliphatic carbon, seems to have a characteristic frequency which is but slightly changed by further substitution, in a different position in the chain, as

[**] Zeitschr. f. Phys. Chem. Abt. B, 3. 317, 1929 ; 4, 299, 1929.

[1] Sitz. Akd. Wien., Vol. 139, p. 167, 1930.

[2] Ind. Journ. Phys., Vol. V, Part I, 1930.

will be at once evident by looking at the table. When, however, CN is linked directly to an aromatic compound, that is to a carbon in the benzene ring the frequency is markedly changed.

A striking series of results have been obtained by the study of the complex metallic cyanides recently carried out by us. It has been found that the frequency remains practically the same when the valency of the complex—forming metal remains the same, so that the complex cyanides formed are of the same type. Here the change of the mass of the substituent seems to have absolutely no effect on the characteristic frequency, which is however at once changed when the valency of the metal is changed, thus:—zinc, cadmium and mercury cyanides have the same frequency, so also the cyanides of silver and copper.

It seems to us that a satisfactory explanation of these facts can be given, on the basis of the electron theory of valencies. The oscillation frequency of the CN radical is determined by the masses of C and N, and by the force of binding, to which both the charges of the nuclei, as well as the electronic configuration surrounding the atoms contribute. When the radical is attached to another atom, it is the electronic configuration surrounding the radical which is affected. According to the degree and strength of the bond, the effect on the electronic ring may vary from an actual increase in the number, due to sharing of electrons with other atoms, to a distortion of the electronic orbits, as will perhaps be evident from the change of the electronic moment, or both. It is then clearly understood how the same type of binding will give rise to the same characteristic frequency and how it will comparatively be unaffected by the mass of the rest of the molecule.

We are seeking for further experimental evidence which will support our ideas and we are studying at present the influence of crystal structure on the frequencies of different radicals like SO_4, NO_3, ClO_3, etc. as well as the influence of the rest of the molecules on the frequencies themselves.

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