

Theoretical Interpretation of Vibration Frequencies of Paraffinic Hydrocarbons

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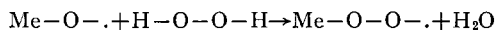
than in the other halogenides. The numbers given above in (b) and (c), as for As and Sb, are the electronegativities calculated from the heats of formation of the oxides.

The electronegativities of all elements which form per-compounds are generally smaller, rarely equal to 2.1, even in the oxide of the highest valency state.

From this statement and an examination of the numbers given above we can announce the following rule:

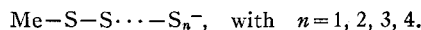
The elements whose electronegativities are smaller or at most equal to 2.1 form per-compounds; those whose whole electronegativities are greater than 2.1 do not form per-compounds. C (2.5), S (2.5), Hg (2.5), and N (3.0) are exceptions to this rule. Nitrogen presents another anomaly already mentioned (formation of a per-oxide of lower valency state).

The general rule can be easily accounted for if it is remembered that the electronegativity of hydrogen is 2.1. From the way in which the electronegativities have been calculated, it is to be expected that, for energetical reasons, the reaction



will not be carried out if $x_{\text{Me}} > x_{\text{H}}$.

The exceptions require a more detailed study. Note that sulfur has already a very marked tendency to form bridge bonds in the polysulfides and polythionates;



¹ We will, consequently, not consider here compounds which are called peroxides or per-acids, but which form with valency change, e.g., PbO_2 , MnO_2 , HMnO_4 , HIO_4 , etc.

² L. Pauling, *Nature of the Chemical Bond* (New York, 1944).

³ M. Haïssinsky, *J. Physique* 7, 7 (1946).

Selection Rules for Ionic Crystals

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February 2, 1947

IN the appendix of his article¹ Halford gives the standard symbol for the space group, followed by the symbols describing the various sites; each of those symbols is preceded by the number of distinct sets of this kind and followed by the number of equivalent sites per set. (The numbers are appended only when they differ from unity.)

But when the site group is one of the following: C_p , C_{pv} , C_s , with $p=1, 2, 3, \dots$, the number of distinct sets is infinite, for an axis or a plane of symmetry may contain several atoms belonging to different sets. Instead of $V_k^{16}:2C_i(4)$; $C_s(4)$, one should write: $V_k^{16}:2C_i(4)$; $\infty C_s(4)$.

In aragonite, the symmetry C_s for CO_3 ions does not exclude the symmetry C_s for Ca ions, which is the actual symmetry² instead of C_i . This will alter the theoretical conclusions: the lattice modes attributable to Ca ions are not forbidden in the Raman spectrum, and this, according to Halford's method, brings the number of lattice modes of aragonite up to nine.

I shall now discuss the validity of this method as applied to ionic crystals. In these crystals (in contrast to molecular crystals, e.g., organic crystals, rhombic sulfur) the number of Raman lines observed is often greater than the number deduced from Halford's method. For aragonite and cerussite this method permits 9 lattice modes in the Raman

spectrum; experimental data give more lines, 12 for aragonite, 17 for cerussite (the general theory permits 18 lines). For barites, Halford's method gives 9 Raman lines caused by internal vibrations; the Raman spectrum actually contains 13 lines, a close approximation to the number of lines given by general theory which predicts 18 lines, 4 of them being very weak.

Moreover, the coupling of like vibrations between different ions of one set gives rise to distinct Raman lines; their polarization shows that the symmetry of the corresponding vibration is related to the whole symmetry of the unit cell. For instance: $1363\text{--}1377\text{ cm}^{-1}$, Raman lines of internal vibrations for cerussite; $630\text{--}647\text{ cm}^{-1}$, etc. . . ., for barites³ $122.5\text{--}130\text{ cm}^{-1}$, Raman lines of rotational vibrations of ClO_3 ions in ClO_3Na ,⁴ even in some molecular crystals there appear separations caused by the coupling: $46\text{--}54$, $74\text{--}76$, $109\text{--}127\text{ cm}^{-1}$, in Raman spectrum of rotational vibrations for naphthalene.⁵

In the case of calcite, however, the selection rules obtained by Halford's method are in agreement with experimental data. This is due to the particular fact that the unit cell contains only two CO_3 ions which are symmetrical in relation to a center of symmetry. The theoretical conclusions are the same whether one takes the coupling into account or not. We have seen that this is not the general case.

Therefore, I conclude that, in ionic crystals, coupling of vibrations between the ions of a set cannot be neglected and that Halford's method, which is applicable to molecular crystals, cannot be applied to ionic crystals, even as a first approximation.

¹ R. S. Halford, *J. Chem. Phys.* 14, 8 (1946).

² W. L. Bragg, *Proc. Roy. Soc. London* A105, 16 (1924).

³ L. Couture, *Comptes rendus* 218, 669 (1944); 220, 87 (1945); 222, 495 (1945); and also a paper which will shortly appear in *Ann. de physique*.

⁴ A. Rousset, *Comptes rendus* 216, 886 (1943).

⁵ A. Kastler and A. Roussett, *J. Phys.* 2, 49 (1941).

Theoretical Interpretation of Vibration Frequencies of Paraffinic Hydrocarbons

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IN a recent paper Ahonen¹ has calculated the normal frequencies of vibration for a number of octanes on the assumption of a valency force field. The values obtained are compared with the experimental data and although some degree of correlation is obtained, it would be difficult to apply these results to the discussion of the spectra of other paraffins. The purpose of the present note is to report briefly some calculations made during the war as part of a program of research² on the vibration spectra of hydrocarbons (primarily for analytical purposes), since these deal with certain skeletal frequencies common to many branched hydrocarbons and have therefore a wider application than the results of Ahonen.

Instead of attempting to calculate the frequencies of an isomeric series of hydrocarbons, we have concentrated on calculating the skeletal frequencies of certain structural units which are common to many paraffins. The particular

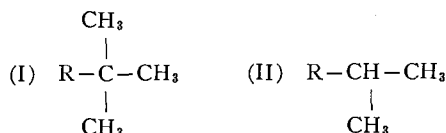
TABLE I. 2,2-dimethyl grouping.

Hydrocarbon		Characteristic frequencies in cm^{-1}		
Mass of Z	Name	Formula	Observed	Calculated
15	neopentane	$\text{CH}_3 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_3$	1250	1288
29	2,2-dimethyl propane	$\text{CH}_3 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}_2\text{H}_5$	1214 1252	1225 1265
43	2,2-dimethyl butane	$\text{CH}_3 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}_3\text{H}_7$	1206 1250	1211 1261
57	2,2-dimethyl pentane	$\text{CH}_3 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}_4\text{H}_9$	1202 1250	1203 1257
71	2,2-dimethyl hexane	$\text{CH}_3 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}_5\text{H}_{11}$	1201 1250	1197 1254
85	2,2-dimethyl heptane	$\text{CH}_3 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}_6\text{H}_{13}$	— —	1194 1252
99	2,2-dimethyl octane	$\text{CH}_3 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}_7\text{H}_{15}$	— —	1191 1249
∞	2,2-dimethyl <i>n</i> -ane	$\text{CH}_3 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}_n\text{H}_{2n+1}$	— —	1177 1240
			ν_8 ν_2	ν_8 ν_2

TABLE II. 2-methyl grouping.

Hydrocarbon		Characteristic frequencies in cm^{-1}		
Mass of Z	Name	Formula	Observed	Calculated
15	isobutane	$\text{CH}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_3$	1170	1182
29	2-methyl propane	$\text{CH}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{C}_2\text{H}_5$	1170 1150	1180 1125
43	2-methyl butane	$\text{CH}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{C}_3\text{H}_7$	1170 1145	1180 1116
57	2-methyl pentane	$\text{CH}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{C}_4\text{H}_9$	1170 1145	1180 1108
71	2-methyl hexane	$\text{CH}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{C}_5\text{H}_{11}$	1172 1145	1180 1101
85	2-methyl heptane	$\text{CH}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{C}_6\text{H}_{13}$	1171 1143	1180 1095
∞	2-methyl <i>n</i> -ane	$\text{CH}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{C}_n\text{H}_{2n+1}$	— —	1179 1085
			ν_2 ν_5	ν_2 ν_5

groupings we wish to discuss here are



where R is any alkyl radical $\text{C}_n\text{H}_{2n+1}$, so that the molecules represented by I and II are 2,2-dimethyl and 2-methyl paraffins, respectively. It was found from data on infra-red spectra accumulated at Oxford and Cambridge that all hydrocarbons containing these structural units had strong, highly characteristic bands which appeared to be virtually unaffected by the remainder of the molecule. It seemed reasonable, therefore, to isolate such groups from the rest of the molecule and consider their internal vibrations as a separate problem, representing the remainder of the molecule R by a large mass. A simple valency force field was applied to these isolated units, the CH_3 and CH groups being treated as nuclei of mass 15 and 13, respectively. The most striking results are summarized in Tables I and II which give the frequencies of infra-red bands we found characteristic of the 2,2-dimethyl and 2-methyl groupings together with our calculated values. It should be emphasized that the pair of frequencies at 1250 and 1200 cm^{-1} is found in all the more complex paraffins containing the 2,2-dimethyl grouping, e.g., 2,2,3- and 2,2,4-trimethyl pentane. Our main aim was indeed to establish the reason for the constancy of these characteristic frequencies rather than to give a complete interpretation of the vibration spectrum.

In the case of the 2,2-dimethyl compounds the model used was the ZYX_3 molecule in which X is a mass of 15 (CH_3), Y of 12 (C), and Z a mass of $14n+1$ ($\text{C}_n\text{H}_{2n+1}$). The six fundamental frequencies of such a molecule are conventionally numbered so that ν_1 , ν_3 , and ν_5 are single parallel vibrations, while ν_2 , ν_4 , and ν_6 are doubly degenerate perpendicular vibrations. Using this notation, the pair of frequencies at 1250 and 1200 cm^{-1} are, respectively, ν_2 and ν_8 , being derived from one of the triply degenerate frequencies of the symmetrical tetrahedral YX_4 molecule. This explains why these two frequencies coalesce into one in the case of neopentane. It will be noticed that the calculated values of the perpendicular frequency ν_2 change by only 16 cm^{-1} in going from 2,2-dimethyl butane to 2,2-dimethyl nonane whereas the parallel frequency ν_8 is

predicted to show a shift of 34 cm^{-1} over the same range. Experimentally, ν_2 appears to be virtually constant but ν_8 exhibits a shift of 13 cm^{-1} in going from 2,2-dimethyl butane to 2,2-dimethyl heptane. The calculations also suggest that there should be another characteristic frequency (ν_6) near 420 cm^{-1} . Such Raman data as are available give some indication that this prediction is justified. The force constants employed were 4.65×10^5 dynes/cm for C—C stretching, and 0.45×10^6 dynes/cm for C—C—C bending. These clearly give too high a value for the triply degenerate frequency in neopentane and it seems probable, from this and other considerations, that both these constants should be somewhat lower in this particular molecule.

In the case of the 2-methyl compounds, the model employed was the ZYX_2 molecule (with X, Y, Z defined as above). This molecule has six non-degenerate fundamental skeletal frequencies, of which ν_1 and ν_3 may be regarded as being derived from the parallel frequencies (ν_1^5 and ν_3^5) in the more symmetrical pyramidal molecule YX_3 , while ν_2 , ν_5 and ν_4 , ν_6 arise from the splitting of the doubly degenerate pair which (following the usual conventional numbering) we may refer to as ν_2^5 and ν_4^5 . Using this notation, the two frequencies near 1170 and 1140 cm^{-1} are to be interpreted as ν_2 and ν_5 , respectively, and correspond to the single frequency ν_2^5 in isobutane. It will be noticed that, while the calculated value of ν_2 stays virtually constant over the whole range of molecules considered, ν_5 decreases slowly but steadily as the mass Z is increased. On the experimental side ν_2 is constant, while ν_5 seems to show a slight decrease as Z increases. No doubt a more exact theory would give better agreement on this point. In addition we find that there should be another characteristic constant frequency (ν_6) near 400 cm^{-1} , but more experimental work is required to confirm this assignment. The force constants used were, for C—C stretching 4.5×10^5 dynes/cm, and for C—C—C bending 0.40×10^5 dynes/cm, i.e., somewhat less than those used for the 2,2-dimethyl paraffins. In view of the entire neglect of interaction terms we do not think these differences should be regarded as significant without further investigation.

¹ C. O. Ahonen, J. Chem. Phys. 14, 625 (1946).

² This work which involved the spectroscopic examination of more than 200 hydrocarbons in the infra-red and ultraviolet was undertaken for the Ministry of Aircraft Production and the Institute of Petroleum by groups of workers at Oxford (under Dr. H. W. Thompson) and Cambridge (under Dr. G. B. B. M. Sutherland). The experimental results are now being prepared for general publication.