perger of Stanford University in the calculations for the classical case, and in the discussion applicable to that case.

[1] National Research Fellow.

[2] Rice, these Proceedings, **14**, 113 (1928). A joint paper treating this case will soon appear.[6b]

[3] Landolt, Börnstein, *Tabellen*, **1923**, p. 1275.

[4] See, e.g., Reiche, *Quantum Theory*, E. P. Dutton & Co., New York, p. 31. Zero point energy does not concern us.

[5] Ramsperger, *J. Amer. Chem. Soc.*, **49**, 1495 (1927).

[6] (*a*) Rice and Ramsperger, *J. Amer. Chem. Soc.*, **49**, 1617 (1927); (*b*) *Ibid.* (in press).

[7] We are using P's in this place instead of W's in order to avoid confusion.

[8] In later work it has been made more satisfactory. This calculation and the similar one made for the classical case (Ref. 6b) represent extreme differences in the assumptions as to the nature of the molecule, so it seems very probable that equation (1) needs no sensible modification.

[9] Ramsperger, *J. Amer. Chem. Soc.*, **50**, 131 (1928); *Proc. Nat. Acad. Sci.*, **13**, 849 (1927).

FUNDAMENTAL FREQUENCIES, INTERATOMIC FORCES AND MOLECULAR PROPERTIES

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During the past three or four years the study of the spectra of molecules has brought to light a large number of facts which have to do with the properties of the individual molecules as contrasted with the facts of chemistry which pertain to the properties of atoms and molecules in the aggregate. Of these specifically molecular properties, one of the most significant is the fundamental frequency, that is, the frequency of the vibration of an atom in the molecule when it moves with an amplitude which is small compared to its own dimensions. For this frequency there are now available quite accurate values covering a number of compounds. with the help of these values, we wish to point out some relations between the frequency and the force of binding on the one hand, and such macrochemical properties as heats of linkage, boiling points and directive influence on substitution.

In several fields different investigators have already met with considerable success in interpreting chemical behavior and physical properties with the help of the recently acquired knowledge of the behavior of individual atoms. Franck[2] has related the possibility of the photochemical decomposition of a molecule into atoms with the changes in binding and vibrational frequency which accompany electronic excitation. He and

his co-workers and Terenin made a series of very successful studies on this basis. Again in the study of the specific heats of solids it has long been recognized that frequencies, secured by optical observations and believed to be associated with the vibrations of atoms, are actually of the same order of magnitude as the empirical frequencies employed in calculating specific heats by the methods of the quantum theory. Recently Andrews[3] has shown that in the case of some compounds of carbon the observed frequencies in the infra-red, associated with the vibrations of carbon and hydrogen in the compound, can be used with the formulas of the quantum theory to obtain values of the specific heat which agree quite closely with the experimentally secured values. Salant[4] has also pointed out that such relations exist. Mecke[5] has made a study of the relation between frequencies and the positions of the elements in the periodic table.

The results of these different investigations tend to confirm the correctness and utility of regarding the basis of atomic motion in a molecule to be harmonic oscillation, that is, vibration of small amplitude with the frequency equal to the fundamental frequency, obeying the equations of mechanics for the harmonic oscillator. This treatment of atomic motion has indeed been employed recently in attempts to show relations between fundamental frequency and other properties, for example, by Eucken[6] in classifying heats of linkage with the values of the frequency secured from specific heat data; it promises to be especially useful as more and more accurate values of frequencies become available from the study of spectra. We, therefore, include a brief description of harmonic oscillation and the deviations from it which may be expected in real molecules, as a basis for discussing the relations we wish to point out between fundamental frequency and other properties.

For an atom vibrating harmonically in a crystal lattice the fundamental frequency of vibration is given by the expression

$$\nu = 1/\overline{2\pi} \sqrt{\frac{K}{M}} \tag{1}$$

where K is the force at unit displacement and M is the mass of the atom.

In the case of a diatomic molecule, however, the vibration of both atoms must be considered, and hence the equation connecting the frequency, ν, of such a harmonic oscillator with the force, K, is

$$\nu = 1/\overline{2\pi} \sqrt{\frac{K}{\mu}}, \tag{2}$$

where μ is the reduced mass of the two oscillators

$$\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}.$$

Letting r be the distance between the two nuclei, the value of the force is

proportional to the displacement $r - r_0$ from the point r_0 where the potential energy is equal to 0.

If the vibration remained perfectly harmonic through all values of r, no dissociation could occur. So some assumption must be made as to how the force changes for larger values of r. The simplest of these would be that the vibration remains very close to harmonic until a value of r is reached, practically that at dissociation, at which point the restoring force suddenly becomes very small. As a matter of fact the theory of the vibrational quantum states in band spectra shows that the vibration is anharmonic. When the atoms move apart the force does not increase
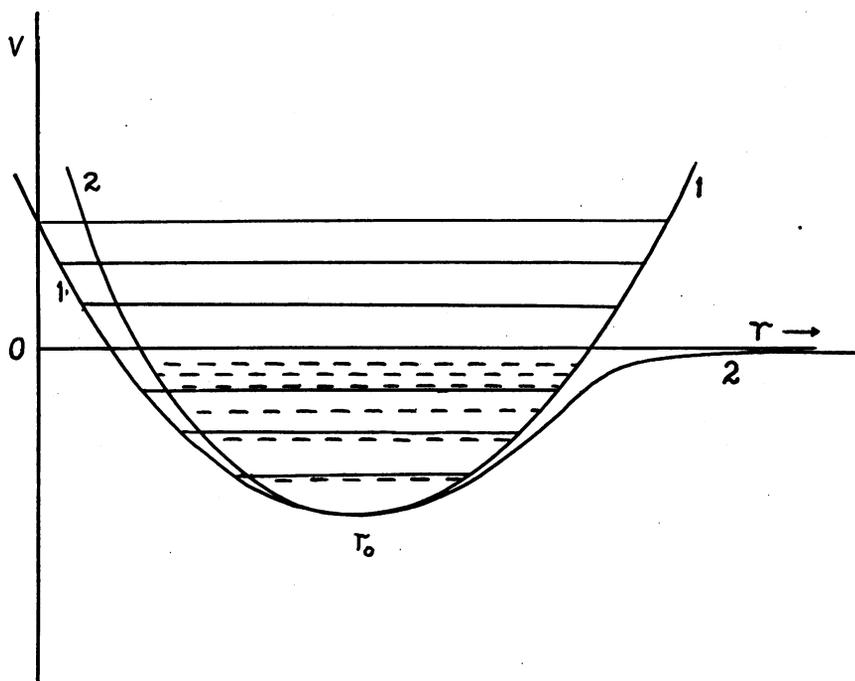

FIGURE 1

as rapidly as it would were the vibration harmonic. Thus for a harmonic oscillator the term value of the various quantum states would be

$$\nu = \nu_0 n$$

where ν_0 is the fundamental frequency and n is the quantum number. In the case of an anharmonic vibration this becomes

$$\nu = \nu_0 n - b n^2$$

where b is a constant for any series of vibrational levels. This can be seen from an examination of figure 1, in which the potential energy[7] is plotted

as a function of r. The parabola (1) and the evenly spaced energy levels represent a harmonic oscillator, while curve (2) is that of an actual molecule and the series of levels with decreasing separation is that of an anharmonic oscillator.

The distance $r_D - r_0$ for the harmonic oscillator represents the distance the atoms must be pulled apart from the position of equilibrium in order that the work done shall be equal to the heat of dissociation. In other words, the atoms should fly apart without further work when this point is reached. In the case of the anharmonic oscillator, since the force does not increase as rapidly with the distance the atoms are apart, the displacement for dissociation $r_D - r_0$, will be somewhat greater than in the previous case, provided we assume the same work must be done in both cases. Unfortunately, we do not know how the force varies near the point of dissociation except for the case of electronically excited molecules.

The energy necessary to dissociate the normal molecule can be shown to be

$$E = \int_{r_0}^{r_D} K(r - r_0)dr = \frac{K}{2}(r_D - r_0)^2$$

now if for E we take $\dfrac{-\Delta H \cdot 10^7}{N \cdot J}$ where $-\Delta H$ is the heat of linkage, i.e., heat of dissociation into normal atoms, J is the Joule, and N Avogadro's number, and for K the values calculated from equation (2) are used, then a value of $r_D - r_0$ is obtained which is equal to the amplitude of vibration necessary for decomposition of two atoms. assuming their vibrations to remain harmonic until r reaches a value close to r_D. This will, of course, be a minimum value and in all actual cases r_D will be somewhat larger than that calculated for the harmonic oscillation.

Eucken[8] in determining heats of dissociation by similar considerations tacitly made two assumptions; first that $r_D - r_0$ was equal for different types of molecules, and second that K was harmonic throughout. His very high values for the heats of dissociation of oxygen and nitrogen were probably due to this, and to the uncertainty of the frequency values then to be obtained.

Frequency and Directly Related Quantities as Observed for Diatomic Molecules.—In table 1 are given the fundamental frequencies and heats of linkage as secured from the best available values in the literature for a number of diatomic molecules, arranged in the order of magnitude of frequency. The parallelism between frequencies and heats is striking. From the frequency (ν) and the reduced mass (μ) the force constant[9] (K) has been calculated for each type of linkage by means of equation (2). From the force constants and the heats of linkage the values of $r_D - r_0$ have been calculated.

TABLE 1

BOND	FREQUENCY $\times 10^{-13}$ SEC.$^{-1}$	HEAT OF LINKAGE KG. CAL.	FORCE CONSTANT $\times 10^{-3}$ DYNES/CM.	REDUCED MASS $\times$ 6.06 $\times 10^{23}$ G.	$r_D - r_0$ $\times 10^{-8}$ CM.
		Non-Polar Bonds			
H—H	14.6[1]	101.0[10]	695	0.5	1.00
H—N	10.0[2]	98.0[11]	562	0.93	1.06
H—C	8.95[3]	90.0[11]	478	0.92	1.14
C—C	3.03[4]	81.6[11]	(359)[13]	6.0	1.25
C—Cl	1.79[5]	81.0[11]	188	9.0	1.72
C—Br	1.74[5]	39.7[11]	189	9.6	1.20
C—I	1.71[5]	40.0[11]	208	10.9	1.39
Cl—Cl	1.70[6]	58.5[6]	330	17.5	1.10
I—Cl	1.146[7]	49.6[7]	236	27.4	1.20
Br—Br	0.975[6]	45.2[6]	248	40.0	1.12
I—I	0.639[12]	35.2[12]	168	63.5	1.20
		Polar Bonds			
H—F[8]	11.82	153–173[11]	865	0.98	
H—Cl[8]	8.67	99.5[11]	486	0.95	
H—Br[9]	7.56	78.3[11]	369	0.99	

[1] J. H. Van Vleck, *Bull. Nat. Res. Council*, No. **54**, p. 101 (1926).

[2] J. W. Ellis, prelim. abstract No. **52**, meeting of *Amer. Phys. Soc.*, Dec. 28–30, 1927; E. O. Salant, *Proc. Nat. Acad. Sci.*, **12**, 74 (1926).

[3] J. W. Ellis, prelim. abstract No. **36**, meeting of *Amer. Phys. Soc.*, Dec. 28–30, 1927.

[4] Andrews, loc. cit.

[5] J. W. Ellis, *Phys. Rev.*, **28**, 25 (1926). Observations on CH_2Cl_2, $CHCl_3$, CH_2Br_2, $CHBr_3$, CH_3I, CH_2I_2.

[6] H. Kuhn, *Z. Physik*, **39**, 77 (1926).

[7] G. E. Gibson and H. C. Ramsperger, *Phys. Rev.*, **30**, 598 (1927).

[8] Hund, *Z. Physik*, **32**, 1 (1925).

[9] Brinsmade and Kemble, *Proc. Nat. Acad. Sci.*, **3**, 422 (1917).

[10] Diecke and Hopfield, *Z. Physik*, **40**, 299 (1927).

[11] Calculated from the best thermal data available.

[12] Dymond, *Z. Physik*, **34**, 553 (1925).

[13] The value for the total force acting on a carbon atom in a —C—C—C— chain, due to bonds from two adjacent carbon atoms.

It is to be noted that the forces in non-polar molecules have values much closer together than we would expect from the values of the frequencies, the former varying only four-fold while the latter vary twenty-three-fold. The similarity of the values of $r_D - r_0$ is also very striking, especially among related types of linkage such as for hydrogen compounds and the halogens. This suggests the great similarity of all non-polar bindings.

The frequencies of the polar molecules HF, HCl, HBr, give values for K which vary, as can be seen, over a large range. Any value of $r_D - r_0$ would, of course, in the case of these molecules which are apparently built up of ions, be meaningless as far as decomposition into atoms is concerned. Such a decomposition, if it occurred monomolecularly, would

involve a building up of energy in the vibration of the ions until it equaled or exceeded the energy of the electron transition giving an atomic binding. At this point a transfer of energy from vibration to electron jump would take place.

The values as calculated from the best thermal data obtainable for C—Br and C—I were very uncertain. Bowen[10] gives 40 K cal. as a value for C—I and certainly C—Br is no higher than this. If these values are at all correct it would appear that the values of the fundamental frequencies of these linkages as given by Ellis may in reality be the first harmonics. This would also be more in accord with the decrease in K observed as we go down through —Cl, —Br, —I.

The Force Constant (K) and the Boiling Point.—A very curious relation exists between the force constant K and the boiling point in the case of the halogens as shown in table 2. It is difficult to say just what connection we should expect to exist between these properties, whether connected with the steepness of the potential energy curve on the compressional side of equilibrium, or with some saturation of the field of force around the molecule. It would appear to be an indication of a relation between the forces within the molecule and the field of force around it.

TABLE 2

BOILING POINTS AND FORCE CONSTANTS

	$T°K$	$K \times 10^3$	$T \times K \times 10^{-6}$
H_2	20.4	695	1.4
Cl_2	238.5	330	7.9
Br_2	331.8	248	8.2
ICl	370.0 circa	236	8.7
I_2	457.0	168	7.7

Hydrogen is also given to show that a larger force does make for a lower boiling point, even when not included in a homologous series. No close proportionality could be expected between the others and hydrogen, since the potential energy curve would be probably of an entirely different character there.

Fundamental Frequency and Directive Influence on Substitution.—The relation which appears to exist between the fundamental frequency and the boiling point suggested to us that a relation might also be found between the fundamental frequency of the bond C.R or R.R and the directive influence which the atom or radical (R) exerts on substitution in the benzene ring, since the parallelism between this influence and the boiling point of HR and C_6H_5R has recently been pointed out by Francis, Andrews, and Johnston.[11] Of the nine radicals for which the directive influence is very definitely established, we know the frequency associated with the R—C bond for only the four ortho-para orienting radicals I, Br, Cl and CH_3, and for hydrogen which considered as such a radical, appears to lie

between the ortho-para and the meta orienting groups. Table 3 gives for these five radicals the data which might be related to the directive influence, namely the boiling points of C_6H_5R, HR, and RR, and the frequencies and force of binding for C—R and R—R. There appears to be a parallelism in the values for this rather restricted group, so that there is at least an indication that force of binding and directive influence are both related to the same factors, probably involved in the electronic configuration of the molecule. Any direct connection between these two quantities appears doubtful.

TABLE 3

	BOILING POINTS °C.			FREQUENCY $\times 10^{-13}\ \frac{1}{\text{SEC.}}$		$K \times 10^3$ DYNES/CM.	
R	C₆H₅R	HR	RR	R.R	C.R	RR	CR
I	188.6		184.3	0.639	1.71	168	208
Br	156.0	— 69	58.7	0.975	1.74	248	189
Cl	132.0	— 83	— 34.6	1.70	1.79	330	188
CH₃	110.0	—153	— 88.3	3.03	3.03	359	(175)*
H	80.0	—258	—258.0	14.6	4.59	695	126

* Approximate value calculated from value for carbon in a chain.

Summary.—It has been shown that relations appear to exist between the fundamental frequency and force of binding in non-polar molecules and such properties as heats of linkage, boiling points and directive influence. Assuming the molecule acts as a harmonic oscillator, the displacement, at which the potential energy of the oscillator equals the heat of linkage, has about the same value for all non-polar linkages.

[1] NATIONAL RESEARCH FELLOW.

[2] *Trans. Far. Soc.*, **21**, 536 (1925).

[3] Donald H. Andrews, *Verslag. Konink. Akad. Wetens. Amsterdam*, **29**, 744 (1926); *Comm. Phys. Lab. Leiden, Suppl.*, **56**, 15 (1926).

[4] E. O. Salant, *Proc. Nat. Acad. Sci.*, **12**, 334, 370 (1926).

[5] R. Mecke, *Z. Physik*, **42**, 390 (1927).

[6] A. Eucken, *Liebig's Annalen*, **440**, 111 (1924); see also H. G. Grimm, *Atombau und Chemie, Handbuch der Physik*, Band, **24**, 520–545 (1927).

[7] For further discussion of this diagram, see J. Franck, loc. cit.

[8] Loc. cit.

[9] This constant is the value of the force of restitution between the two atoms when pulled apart to the distance of one centimeter, provided that the force has increased proportionally to the distance separating the atoms. This condition is, of course, quite hypothetical. It is obvious, however, that for displacements say of one-half Ångstrom, the forces of restitution for different linkages will be proportional to the corresponding force constants.

[10] *Trans Far. Soc.*, **21**, 543 (1926).

[11] *J. Amer. Chem. Soc.*, **48**, 1624 (1926).