SOME PHYSICAL ASPECTS OF ATOMIC LINKAGES

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I. INTRODUCTION

Knowledge of the border-land between the realms of chemistry and physics has been widely extended in recent years. It is true that physical chemists have done much to bridge the gap between two branches of science which developed side by side and largely independently, but the approach is made mainly from the chemical standpoint, whilst developments on the physical side of the frontier have been so important and so numerous as to appear to justify the emergence of "chemical physics." To this field of study appropriately belong modern interpretations of atomic and molecular structure, viewed particularly in relation to inter-atomic linkages or valence bonds.

Science owes to the chemist the discovery of atoms and molecules, the conception of combining capacities of atoms represented in the elementary valence theory, and, above all, the classification of atoms in the periodic system. The physicist has appropriated these subjects one by one, making each peculiarly his own. It is wonderfully significant to find that spectroscopic measurements provide a basis for Mendeléeff's table, and that questions as to whether atoms shall combine to form stable molecules are reduced in the new quantum mechanics to matters of mathematical requirement. Further, the chemist's broad distinction between polar and homopolar substances, whilst admitting the existence of a continuous set of transitional stages between the ideal extremes, may also be very well approached from the physical angle.

Debye has familiarized the term "polar molecule" in a particular sense, as descriptive of cases where permanent electric moment is conferred by unsymmetrical distribution of positive and negative charge. Fajans has emphasized the importance of deformation in his studies of molecular refraction. In both theories, the conception of intermediate stages between polar and homopolar linkages is involved. Moreover, a given substance may contain different kinds of linkages in different physical states. Thus a homopolar linkage, H—Cl, may be attributed to hydrogen chloride as a gas or in the liquid state, whilst in aqueous solution this substance behaves as though polar. The question of state therefore becomes important in a discussion of linkages (1). Not only does no clear line of distinction exist, in general, between polar and homopolar, but also a particular kind of linkage may not be characteristic of a given molecule.

It may be still possible, though hardly practicable nowadays, to conceive atomic linkages as rigid bonds in space; the physical picture would be rather one of rapid oscillation, together with rotation. It is well known that the interpretation of band spectra requires that vibratory and rotatory motion, unlike translatory motion, shall be susceptible of discontinuous changes defined by quantization. The present paper is largely concerned with the characteristic frequencies of vibration of linkages as deduced from the spectra of diatomic molecules and from observations in the Raman effect. It is found that given linkages have more or less characteristic frequencies of vibration, at any rate so long as similar molecular types are being compared, and that these frequencies in ground states are often largely independent of whether the substance is examined as gas, liquid, or solid, in cases where the frequency considered persists on change of state. These characteristic frequencies prove of fundamental importance in the study of atomic linkages from the chemico-physical standpoint.

II. ATOMIC PERIODICITY

Schemes of electron distribution for atoms based upon spectroscopic evidence have been drawn up by McLennan, McLay, and Smith (2) and by Dushman (3). Whilst some of the suggested configurations may be open to question, the periods of elements containing 2, 8, 8, 18, 18, and 32 members, respectively, each ending with an inert gas, are entirely conformable with the chemical evidence, and may be readily accepted in general form. These schemes, however, are somewhat cumbersome, and also separate elements which the chemist would classify together in groups. The chemist is mainly concerned with electrons outside closed groups of electrons, and in comparing members of an atomic valency group it does not matter so very much that the electrons

TABLE 1

A spectroscopic classification of the elements (except the rare earths)

PERIODIC GROUP		ATOMIC QUANTUM NUMBERS			GROUND SPECTRAL TERM	ULTIMATE ELECTRONIC GROUP	PENULTIMATE GROUP									
		L	S	J				s^2	s^2p^6					$s^2p^6d^{10}$		
I	A	0	$\frac{1}{2}$	$\frac{1}{2}$	$^2S_{\frac{1}{2}}$	$,s$	H 1	Li 3	Na^1 11	K^2 19	Rb^3 37	Cs^4 55	(87)^6			
	B													Cu^2 29	Ag^3 47	Au^5 79
II	A	0	0	0	$^1S_0$	$,s^2$	He 2	Be 4	Mg^1 12	Ca^2 20	Sr^3 38	Ba^4 56	Ra^6 88			
	B													Zn^2 30	Cd^3 48	Hg^5 80
III	A	2	$\frac{1}{2}$	$\frac{3}{2}$	$^2D_{\frac{3}{2}}$	d,s^2				Sc^2 21	Y^3 39	La^4 57	Ac^6 89			
	B	1	$\frac{1}{2}$	$\frac{1}{2}$	$^2P_{\frac{1}{2}}$	$,s^2p$		B 5	Al^1 13					Ga^2 31	In^3 49	Tl^5 81
IV	A	3	1	2	$^3F_2$	d^2,s^2				Ti^2 22	Zr^3 40	Hf^5 72	(Th)^6 90			
	B	1	1	0	$^3P_0$	$,s^2p^2$		C 6	Si^1 14					Ge^2 32	Sn^3 50	Pb^5 82

V	A$_2$	3	$\frac{3}{2}$	$\frac{3}{2}$	$^4F_{\frac{3}{2}}$	d^3, s^2				V^2 23		Ta^5 73	(Pa)^6 91			
	A$_1$	2	$\frac{5}{2}$	$\frac{1}{2}$	$^6D_{\frac{1}{2}}$	d^4, s					Nb^3 41					
	B	0	$\frac{3}{2}$	$\frac{3}{2}$	$^4S_{\frac{3}{2}}$	$, s^2p^3$		N 7	P^1 15					As^2 33	Sb^3 51	Bi^5 83
VI	A$_2$	2	2	0	$^5D_0$	d^4, s^2						W^5 74	(U)^6 92			
	A$_1$	0	3	3	$^7S_3$	d^5, s				Cr^2 24	Mo^3 42					
	B	1	1	2	$^3P_2$	$, s^2p^4$		O 8	S^1 16					Se^2 34	Te^3 52	Po^5 84
VII	A$_2$	0	$\frac{5}{2}$	$\frac{5}{2}$	^6S	d^5, s^2				Mn^2 25		(Re)^5 75				
	A$_1$	2	$\frac{5}{2}$	$\frac{9}{2}$	$^6D_{\frac{9}{2}}$	d^6, s					Ma^3 43	(Re)^5 75				
	B	1	$\frac{1}{2}$	$\frac{3}{2}$	$^2P_{\frac{3}{2}}$	$, s^2p^5$		F 9	Cl^1 17					Br^2 35	I^3 53	(85)^5

TABLE 1—*Concluded*

PERIODIC GROUP		ATOMIC QUANTUM NUMBERS			GROUND SPECTRAL TERM	ULTIMATE ELECTRONIC GROUP	PENULTIMATE GROUP									
		L	S	J				s^2	s^2p^6					$s^2p^6d^{10}$		
VIII	C_2	2	2	4	$^5D_4$	d^6,s^2				Fe^2 26		$(Os)^5$ 76				
	C_1	3	2	5	$^5F_5$	d^7,s					Ru^3 44	$(Os)^5$ 76				
	D_2	3	$\frac{3}{2}$	$\frac{9}{2}$	$^4F_{\frac{9}{2}}$	d^7,s^2				Co^2 27		$(Ir)^5$ 77				
	D_1	3	$\frac{3}{2}$	$\frac{9}{2}$	$^4F_{\frac{9}{2}}$	d^8,s					Rh^3 45	$(Ir)^5$ 77				
	E_2	3	1	4	$^3F_4$	d^8,s^2				Ni^2 28		$(Pt)^5$ 78				
	E_1	2	1	3	$^3D_3$	d^9,s						$(Pt)^5$ 78				
	E_0	0	0	0	$^1S_0$	d^{10}					Pd^3 46^x	$(Pt)^5$ 78^y				
0		0	0	0	$^1S_0$	$,s^2p^6$		Ne 10	A^1 18					Kr^2 36	Xe^3 54	Nt^5 86
Highest quantum levels n........................							1	2	3	4	5	6	7	4	5	6
Order of completion of the vertical periods.......							1	2	3	4	6	8	10	5	7	9
Antepenultimate groups....................							$^1s^2,$	$^2s^2,s^2p^6,$			$^3s^2,s^2p^6,s^2p^6d^{10},$			$^4s^2,s^2p^6,s^2p^6d^{10},s^2p^6d^{10},$		
							$^5s^2,s^2p^6,s^2p^6d^{10},s^2p^6d^{10}f^{14},$						$^6s^2,s^2p^6,s^2p^6d^{10},s^2p^6d^{10}f^{14},s^2p^6d^{10},$			

[x] Highest quantum level $n = 4$. [y] Highest quantum level $n = 5$.

of incomplete groups are actually of different principal quantum number. The author (4) has therefore proposed a classification of the elements in which group as well as periodic relationships are shown, so that in representing configurations the principal quantum numbers are omitted, the quantum groups being separated by commas. This simple modification made possible the compilation of the scheme, here reproduced as table 1. Mulliken (5), in his latest paper on the electronic configurations of molecules in relation to those of their dissociation products, has adopted a similar plan in the description of molecules (see section III below). Thus both in atoms and in molecules it is possible, in general, to group electrons into completed closed groups with additional electrons of incomplete groups associated with chemical and spectroscopic behavior, although the distinction is not quite so clearly drawn in the molecular case. It appears therefore justifiable to bring together in systematic tabulation atomic systems whose electron configurations (in terms of s, p, d, f for atoms; σ, π, δ for molecules) are the same even where the appropriate principal quantum numbers are different. The intimate relation between spectroscopy and chemistry is further illustrated by new forms of the periodic table suggested by Gardner (6), Saha (7), and Mitra (8).

In table 1, the electron configuration assigned to any element (except the rare earths) may be readily found. Thus, for sodium, a small suffix number appears: Na^1. The suffixes refer in all cases to the corresponding antepenultimate groups at the foot of the table; to this must be added the penultimate group at the top of the column in which the element appears, together with the ultimate group given in heavy type at the left side of the group containing the element. Thus sodium is represented in the ground state by s^2,s^2p^6,s, or, in the older designation, by $1s^22s^2p^63s$, giving eleven electrons in all, corresponding to the atomic number $Z = 11$. Not only does the classification of table 1 show the elements in group relationship with the spectroscopic results, but also the elements having penultimate groups of s^2 (two electrons), s^2p^6 (eight electrons), and $s^2p^6d^{10}$ (eighteen electrons) are sharply separated. It is well known that the nature of the group of electrons underlying the outermost incomplete or valence group of electrons may greatly influence atomic and ionic properties. It is observed that Mendeléeff's subsidiary or "B" groups correspond with atoms having penultimate groups of electrons of $s^2p^6d^{10}$ instead of s^2p^6. The ground terms and the symbols *L*, *S*, *J* have their usual significance. The author has prepared in another connection (112) similar tables in which ions are classified according to the same principles.

III. THE PERIODICITY OF DIATOMIC MOLECULES

1. Classification of molecular electrons

In the approach to the study of the electronic structure of diatomic molecules, the tendency at first appeared to treat each molecular electron as though belonging to both nuclei. Against this method, Lennard-Jones (9) issued a timely warning. Even in relatively light molecules, such as N_2 and O_2, it seems necessary to suppose that the two K electrons belonging to the separated atoms must be regarded as belonging also to the individual nuclei when combination occurs. Mulliken (11) has done much to clarify the situation in his classification of molecular electrons as approximately non-bonding, bonding, or anti-bonding. The non-bonding electrons may, in general, be identified with closed K, L, M. . . . groups of electrons. Outside these systems, in homopolar linked molecular groups, there are other electrons which may be concerned in forming the linkages between the atoms, and others which, according to Mulliken, may tend to act repulsively between the atoms (anti-bonding electrons). It is necessarily to be understood that such classifications can be regarded only as approximations to the truth in such complex interacting systems as molecules actually form. The main point, however, for the present argument, is that such division of electrons into closed and unclosed groups must be made, and possesses fundamental importance in the understanding of molecular structure, particularly from the chemical point of view.

2. *Molecular types*

It would appear that three ideal types of molecular union must be distinguished. Typically polar union occurs perhaps in the vapor molecule of an alkali halide (in the case of the solid, the molecule disappears, or the crystal may be regarded as a giant polymerized molecule). The linkage would be classed as polar; the ions are separate distinct entities, and the electrostatic attraction is responsible for stability. It appears to be legitimate to retain the classical views of valence in such cases, but it should be remembered that even here the linkages may possess qualities leaning towards the homopolar type on account of deformation possibilities. If, for example, the electron sheath of the anion is drawn out towards the cation, certain electrons may be regarded as tending to become appropriated by both nuclei. The second type of union is exemplified by the hydrides, where the hydrogen nucleus may be supposed to have entered the electron system of a second atom, so that it is best to treat the corresponding molecules as single complexes composed of nuclei and electrons, where the normal idea of valence forces loses most of its meaning. Even in this case, however, in general, certain electrons of the second atom may be regarded as intimately associated with its nucleus and forming a closed group around it. The third type is provided by other cases of homopolar union, where some electrons are to be regarded as associated with both nuclei, as in the stable molecules N_2 and CO. In other less stable molecules, it becomes more nearly appropriate to treat them as if consisting of two separate atoms with the outer shells "incompletely shared" (Mulliken). In any case, it is perfectly clear that the gradations between the types are capable of continuous variation, so that it is often impossible to say exactly where one type begins and another ends. Still, it is desirable to recognize that individual molecules may conform approximately to one of the three ideal types of (*a*) separated-ions, (*b*) a united-atom, and (*c*) separated-atoms. The discussion is here mainly concerned with (*b*) and (*c*), where the necessary spectroscopic information is largely available.

The conception of complete and incomplete groups of electrons in molecules leads to a natural classification similar in many respects to that adopted for atoms, and definitely involves the further idea of molecular periodicity. A set of molecules whose outward incomplete electron groups are alike (except in respect of principal quantum number) but whose closed groups around the two nuclei are any pair in the series K, KL, KLM, KLMN . . . . ., K, KL, KLM, KLMN. . . . might logically be placed together in one group. It should be added that the word "incomplete" is here used by analogy with the atomic case, and really denotes no more than "electrons outside closed groups associated with individual nuclei."

3. Specification of molecular electrons

It seems undesirable to omit some reference, however brief, to the designations in use for molecular electrons. A few years ago, a molecular electron was generally specified by a symbol of the type $nl\lambda$, where n is the principal quantum number, and λ comes into existence when an atomic electron of serial quantum number l is brought into an electric field of suitable strength such as would be obtained by dividing the nucleus and separating the parts; it appears in much the same way for a diatomic molecule. It was early realized, however, that it was not generally possible to regard l and λ as corresponding accurately with components of angular momentum, this being particularly true of l (12). The assignment of appropriate l values to molecular electrons became often a matter of considerable doubt. The modern tendency is to retain this kind of specification (the "united-atom" designation) in the case of diatomic hydrides. In other cases, various types of symbolism have been suggested, in some of which electron promotion (increase of principal quantum number from atom to molecule) is designated by a dash or a star. An alternative practice, here adopted, is to use rather less committal symbolism for electrons outside closed groups, namely $z\sigma$, $y\sigma$, $x\sigma$, $w\pi$ . . . . ., the order in which the symbols are given denoting order of firmness of binding (5). Here principal quantum numbers are omitted, in conformity with a suggestion made by Dr. W. Weizel, and with the designation adopted for atoms by the present author. This type of specification would appear to possess special importance to the chemist, and enables the kind of classification proposed for atoms to be extended to molecules. It involves simplification in the treatment, and brings into relation molecules which are chemically of the same group.

IV. HYDRIDE DIATOMIC MOLECULES

1. Classification of diatomic hydrides

Hydrides are here classified on the united-atom basis of electron designation, principal quantum numbers being omitted. Molecular electrons in hydrides are designated by symbols of the type $l\lambda$, where the Greek letters σ, π, δ according as $\lambda = 0, 1, 2$, respectively, are used. Application of the Pauli principle leads to closed groups of electrons, in many ways analogous to those of atoms, as follows:

ATOMIC GROUP	K,	L,	M,	N.....
Atom........	s^2,	$s^2 \quad p^6$,	$s^2 \quad p^6 \qquad d^{10}$,	$s^2 \quad p^6 \qquad d^{10}$....
Molecule.....	$s\sigma^2$,	$s\sigma^2 p\sigma^2 p\pi^4$,	$s\sigma^2 p\sigma^2 p\pi^4 d\sigma^2 d\pi^4 d\delta^4$,	$s\sigma^2 p\sigma^2 p\pi^4 d\sigma^2 d\pi^4 d\delta^4$...
n............	1	2	3	4
Number of electrons...	2	8	18	18.....32

Table 2 is constructed in much the same form as table 1, and shows ultimate, penultimate, and antepenultimate electron groups.

In table 2, the electron configuration of a hydride is obtained as for atoms in table 1. The number in brackets after a molecular symbol is the number of electrons concerned, whilst the number below denotes the vibrational frequency at the ground state (ω_0) in cm.$^{-1}$ This number tends to decrease with increasing molecular weight of the hydrides in a period. The values for C—H, N—H and O—H may be compared with those of table 5 in connection with observations on the Raman effect.

2. Comparison of diatomic hydrides with atoms of related constitution

Grimm (13), in his "hydride displacement law," called attention to the resemblance in physical properties between hydride molecular groups and the corresponding atoms with the same number of electrons. This has been found in accordance with spectroscopic facts, and the following pairs may be considered together: C, BH; N, CH; O, NH; F, OH; Ne, FH. Thus the fluorine atom ($s^2,s^2p^5;{}^2P$) resembles the molecular group OH ($s\sigma^2,s\sigma^2p\sigma^2p\pi^3;{}^2\Pi$). Pearse (14) noted resemblances between the energy levels of Na and MgH (see figure 1, reproduced from the paper). Such correspondence may be anticipated, although the numbers of electrons are not the same, from the assigned electronic configurations: Na ($s^2,s^2p^6,s;{}^2S$) and MgH ($s\sigma^2,s\sigma^2p\sigma^2p\pi^4,s\sigma^2p\sigma;{}^2\Sigma$), since there is one electron outside closed groups in each case, and the remainders are approximately alike. Thus analogies may be discerned between the atom whose atomic

TABLE 2

Suggested configurations of diatomic hydrides in ground states

GROUND TERM TYPE	ULTIMATE GROUP	PENULTIMATE GROUP OF ELECTRONS			
			$s\sigma^2$,	$s\sigma^2\,p\sigma^2\,p\pi^4$,	$s\sigma^2\,p\sigma^2\,p\pi^4\,d\sigma^2\,d\pi^4\,d\delta^4$
${}^1\Sigma$	$s\sigma^2$	H_2 (2) 4375	LiH (4) 1406	NaH (12)[1] 1171	CuH (30)[2] (1904)
			BeH^+ (4) 2222	MgH^+ (12)[1] 1702	ZnH^+ (30)[2] 1915
${}^2\Sigma$	$s\sigma^2p\sigma$		BeH (5) (2106)	MgH (13)[1] 1494	ZnH (31)[2] (1614)
${}^1\Sigma$	$s\sigma^2p\sigma^2$		BH (6) (2230)	AlH (14)[1] 1681	
${}^2\Pi$	$s\sigma^2p\sigma^2p\pi$		CH (7) (2930)	SiH (15)[1] (2012)	
${}^3\Sigma$	$s\sigma^2p\sigma^2p\pi^2$		NH (8) (3270)	PH (16)[1] (2600)	
${}^2\Pi$	$s\sigma^2p\sigma^2p\pi^3$		OH (9) (3660)	HCl^+ (17)[1] 2608	
Antepenultimate groups..................				${}^1s\sigma^2$,	${}^2s\sigma^2,s\sigma^2p\sigma^2p\pi^4$,

number is Z and the hydrides of atoms of atomic numbers $Z - 1$ and $Z + 1$ in certain cases. It may also be noted that Mecke (15) traced resemblances between hydrides of similar chemical composition, though not from the standpoint of electron configuration.

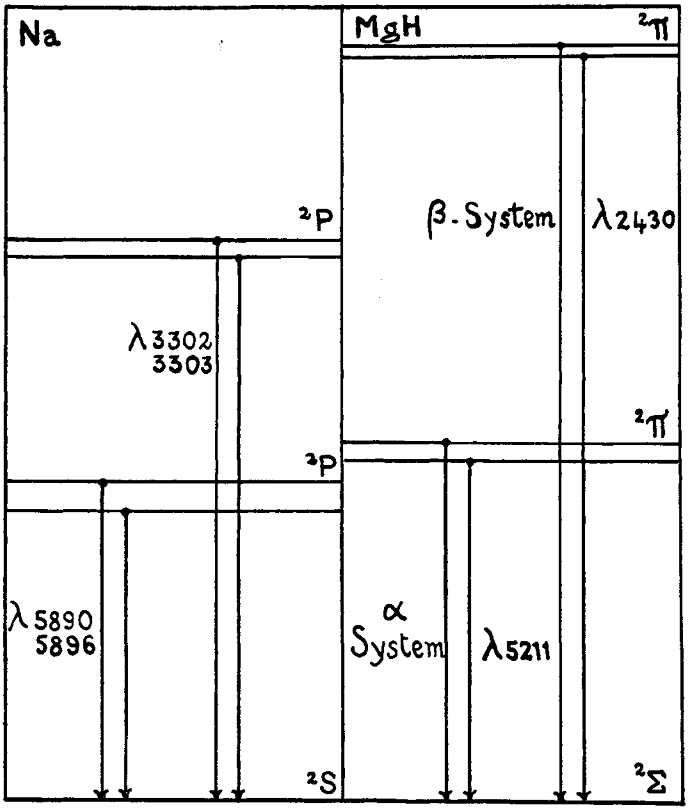


FIG. 1. ELECTRONIC LEVELS OF THE Na ATOM AND THE MgH MOLECULE
The diagrams are approximately to scale, except for the doublet separations, which are increased about one hundred times. See Pearse (14).

V. NON-HYDRIDE DIATOMIC MOLECULES

1. Numbers of valence bonds

In accordance with London and Heitler's theory of valence in terms of paired electrons ("neutralized" spins), the multiplicities of two uniting atoms, M_1, M_2 respectively, and the multiplicity of the resulting molecule M give the number, V, of homopolar valence bonds by means of the relation

$$V = \tfrac{1}{2}\,(M_1 + M_2 - M - 1) \qquad (1)$$

As is well known, this theory accounts in a simple way for the formation of many diatomic molecules, but Mulliken (11) has given another interpretation in terms of the bonding power of electrons, which in many cases leads to different values of V. In what follows, both systems are given and placed side by side for comparison. Mulliken's system follows that of Herzberg (18) in defining the number of bonds as equal to one-half of the number of bonding electrons minus one-half of the number of anti-bonding electrons, and admits the possibility of half-integers. According to the system of designation here adopted, outside closed shells of electrons, the following approximate classification is made as a basis for calculation: $z\sigma$, $x\sigma$, $w\pi$ are bonding, and $y\sigma$ and $v\pi$ are anti-bonding electrons. In table 3, the number of bonds obtained by the two methods are compared for molecules composed of pairs of atoms, like or unlike, in the first period from Li to F. The values of V are calculated by the above equation from the assumed dissociation products, and would be different if these are substituted for others with different multiplicity. (Multiplicity is shown by the upper prefix in front of the symbol denoting a ground term). The number of bonds calculated on the basis of bonding and anti-bonding electrons is shown in the column headed V_1 (anti-bonding electrons in heavy type).

In table 3, Mulliken's assignments of numbers of valence bonds agree for like configurations of a given number of molecular electrons, that is, for "isoteric" groups. The older assignment, depending on the sum of the multiplicities of the dissociation products, may be different for groups which must be classed together chemically and spectroscopically. It must be noted that the data in the table for the molecule Be_2 is theoretical only. Both systems give no bonds, suggesting instability. On the other hand, if the assigned dissociation products are correct, BeO should be in the same unstable class on the older system, whereas its spectrum has been observed. The difference in the assignments of bonds for CO, NO and O_2 is noteworthy. The new theory gives O_2 a "double" bond. Some of the above results are further considered in section XII in relation to the Raman effect.

TABLE 3

Valency bonds of non-hydride diatomic molecules in ground states on the basis of suggested electronic configurations and atomic or ionic dissociation products

ATOM 1		s, s p	ATOM 2		s, s p	MOLECULE	V	ELECTRONS OUTSIDE K^2K^2					$2V_1$	V_1
								$z\sigma$	$y\sigma$	$w\pi$	$x\sigma$	$v\pi$		
Li	^2S	2 1	Li	^2S	2 1	Li_2 (6) $^1\Sigma$	1	2					2	1
Be	^1S	2 2	Be	^1S	2 2	Be_2 (8) $^1\Sigma$	0	2	**2**				0	0
Be	^1S	2 2	O	^1D	2 2 4	BeO (12) $^1\Sigma$	0	2	**2**	4			4	2
C	^3P	2 2 2	C	^3P	2 2 2	C_2 (12) $^3\Pi$	1	2	**2**	3	1		4	2
Be	^1S	2 2	F	^2P	2 2 5	BeF (13) $^2\Sigma$	0	2	**2**	4	1		5	2½
B	^2P	2 2 1	O	^3P	2 2 4	BO (13) $^2\Sigma$	1	2	**2**	4	1		5	2½
C^+	^2P	2 2 1	O	^3P	2 2 4	CO^+ (13) $^2\Sigma$	1	2	**2**	4	1		5	2½
C	^3P	2 2 2	N	^4S	2 2 3	CN (13) $^2\Sigma$	2	2	**2**	4	1		5	2½
N^+	^3P	2 2 2	N	^4S	2 2 3	N_2^+ (13) $^2\Sigma$	2	2	**2**	4	1		5	2½
C	^3P	2 2 2	O	^3P	2 2 4	CO (14) $^1\Sigma$	2	2	**2**	4	2		6	3
N	^4S	2 2 3	O^+	^4S	2 2 3	NO^+ (14) $^1\Sigma$	3	2	**2**	4	2		6	3
N	^4S	2 2 3	N	^4S	2 2 3	N_2 (14) $^1\Sigma$	3	2	**2**	4	2		6	3
										$x\sigma$	$w\pi$			
N	^4S	2 2 3	O	^3P	2 2 4	NO (15) $^2\Pi$	2	2	**2**	2	4	**1**	5	2½
O^+	^4S	2 2 3	O	^3P	2 2 4	O_2^+ (15) $^2\Pi$	2	2	**2**	2	4	**1**	5	2½
O	^3P	2 2 4	O	^3P	2 2 4	O_2 (16) $^3\Sigma$	1	2	**2**	2	4	**2**	4	2
F	^2P	2 2 5	F	^2P	2 2 5	F_2 (18) $^1\Sigma$	1	2	**2**	2	4	**4**	2	1

2. Classification of non-hydride diatomic molecules

It becomes possible to construct a tentative table showing molecules containing two atoms and of like structure and chemical characteristics in groups. In table 4, the classification shows the inner, practically non-bonding groups of electrons, as well as the ultimate group, which is the same for members of a kindred

TABLE 4

Classification of diatomic molecules on the basis of suggested configurations in ground states

TERM TYPE	ULTIMATE GROUP	PENULTIMATE ELECTRONIC GROUP (NON-BONDING)			
		K^2K^2	$K^2L^8K^2L^8$	$\frac{K^2L^8M^8K^2L^8M^8}{K^2L^8M^{18}K^2L^8M^{18}}$	Various
$^1\Sigma$	$z\sigma^2$	Li_2 (6) 351	Na_2 (22) 159	K_2 (38) 93	
$^1\Sigma$	$z\sigma^2 y\sigma^2$	Be_2 (8)			Zn_2, Cd_2, Hg_2
$^1\Sigma$	$z\sigma^2 y\sigma^2 w\pi^4$	BeO (12) 1371			
$^3\Pi$	$z\sigma^2 y\sigma^2 w\pi^3 x\sigma$	C_2 (12) 1642			
$^2\Sigma$	$z\sigma^2 y\sigma^2 w\pi^4 x\sigma$	BeF (13) 1266			AlO, SiN, CP, ScO, YO, LaO
		BO (13) 1885			
		CO^+ (13) 2212			
		CN (13) 2069			
		N_2^+ (13) 2208			
$^1\Sigma$	$z\sigma^2 y\sigma^2 w\pi^4 x\sigma^2$	CO (14) 2167			CS, SiO, TiO, SnO, PbO
		N_2 (14) 2360			
$^2\Pi$	$z\sigma^2 y\sigma^2 x\sigma^2 w\pi^4 v\pi$	NO (15) 1906			PO, SbO, BiO, VO, SnCl (?)
		O_2^+ (15) 1876			
$^3\Sigma$	$z\sigma^2 y\sigma^2 x\sigma^2 w\pi^4 v\pi^2$	O_2 (16) 1585			S_2, Se_2, Te_2, SO
$^1\Sigma$	$z\sigma^2 y\sigma^2 x\sigma^2 w\pi^4 v\pi^4$	F_2 (18)	Cl_2 (34) 565	Br_2 (70) 324	I_2, ICl

type within a group of molecules. This classification would be easily capable of extension. For the present, a number of molecules believed to possess the named ultimate groups of electrons are listed together (see last column), without detailed specification of their non-bonding systems. Except in these cases the ω_0 values are also given.

In the tables here presented, the idea of completed groups or closed shells of electrons finds a place for molecules in much the same way as for atoms. Whilst the configuration results are partly tentative, the theory in its application to molecular groups of similar constitution seems well grounded. The cautious beginning offers the prospect of further advance in a subject of fundamental chemical significance.

VI. CHARACTERISTIC MOLECULAR FREQUENCIES

1. Determination of characteristic frequencies

Characteristic molecular frequencies in the infra-red may be estimated by various methods, the results of which appear to find reasonably good general agreement. Apart from direct absorption measurements, the following methods may be noted: (*a*) dispersion measurement, with application of suitable formulas; (*b*) use of reflection and of residual rays; (*c*) measurement of frequency of light scattered by molecules with change of frequency (Raman effect). There exist also a number of independent methods whereby characteristic frequencies may be calculated in terms of other molecular constants, such as dielectric constants, elastic constants, compressibilities, melting-points, and coefficients of expansion. The present discussion takes some account of (*b*) and (*c*) above only. Recent results in connection with the Raman effect are considered, and, finally, the bearing of these and of other results mentioned in the paper on the general interpretation of atomic linkages is discussed.

With regard to (*b*), it is found that reflection by a crystal increases very much, in general, in the neighborhood of a strong characteristic vibration within the lattice, so that the maxima of reflection gives the approximate corresponding wave-lengths.

By repetition of the reflection process from successive crystal surfaces, it is possible to isolate very long infra-red rays (Rubens' residual rays).

It may be noted that, according to the theory of Born (19), the number of characteristic infra-red vibrations of crystals increases with decreasing symmetry. Thus crystals of alkali halide type give one fundamental vibration; uniaxial sulfates give double lines, whilst biaxial sulfates show tripling. The theory is applicable to cases where the vibrations can be treated as strictly harmonic. It is a characteristic feature of most observed vibrations that they are decidedly anharmonic, and, in consequence, give overtones at wave-lengths which are approximately integral multiples of the fundamental.

2. Internal and external vibrations

Fundamental frequencies may be classified as associated with internal or external vibrations. The internal vibrations, with which this paper is concerned, occur within molecular or radical groups, by oscillations of the constituent atoms in various ways, and correspond with frequencies in the near infra-red region of the spectrum. Internal vibrations may be further subdivided as active or inactive, according as a corresponding variation of electric moment takes place or not. Thus oscillation of the carbon atom of a CO_2 molecule would constitute an active vibration, whilst symmetrical oscillations of the two oxygen atoms along the line joining them to the nuclei, or the symmetrical "breathing" of the CO_3 radical would be classed as inactive vibrations, which do not appear directly in absorption or reflection spectra, but may produce frequencies capable of observation by combination with active frequencies. A combination frequency ω may be expressed in terms of fundamental frequencies $\omega_1, \omega_2 \ldots.$ by means of a relation of the type

$$\omega = \omega_1 n_1 + \omega_2 n_2 + \ldots\ldots \qquad (2)$$

where $n_1, n_2 \ldots.$ are whole numbers (20). Inactive fundamentals appear in the Raman effect, and, where they cannot be directly detected, can often be deduced from observed frequencies by means of the above equation.

On the other hand, external vibrations correspond, for example, with relative motion in lattices between whole cation and anion frameworks, regarded as approximately rigid bodies. Such vibrations, on account of the relatively large masses and small forces generally involved, belong to the far infra-red region of the spectrum.

3. *Valence and deformation vibrations*

The characteristic frequencies of molecules may be subdivided as associated with "valence" and "deformation" vibrations (94). Valence oscillations occur along the valence directions, and are equal in number to the number of linkages, that is, there are n-1 valence oscillations for a molecule having n atoms; deformation oscillations are associated with movements which alter the angles between valence directions, such as the vibration of the carbon atom in CO_2 at right angles to the line connecting the two oxygen atoms.

VII. REFLECTION SPECTRA OF CRYSTALS

The reflection method of examining crystals has the advantage that it reveals only the strongest vibrations, and was used by Rubens to determine the external vibration wave-lengths of crystals of the alkali halide type. The leading task of Schaefer (21) and coworkers has been to ascertain the fundamental infra-red vibrations of oxygenated negative radicals by this method. The general effect of this work is to indicate that vibrations characteristic of groups such as SO_4 and CO_3 are largely independent of the positive ion with which they may be associated. The resemblance between the carbonate and nitrate radicals, already suggested by the crystalline resemblance of $NaNO_3$ and $CaCO_3$, was also borne out in this work and in observations on the Raman effect (see table 9).

Other results may be briefly summarized as follows. Sulfates (22) give two characteristic fundamentals at λ = about 9μ and 16μ. On the assumption that the atoms constituting groups of the type XO_4 are arranged tetrahedrally about the central atom and are completely ionized, Rolan (23) solved the necessary potential function and found that two frequencies may be expected for SO_4 in accordance with this observation. The shorter wave-length (inactive) may be associated with oscillations of the oxygen atoms along the medians of the tetrahedron, and the longer wave-length (active) with vibration of the central sulfur ion S^{--}. Carbonates (22) also show characteristic vibrations at 9μ (inactive) and at 7μ, 11μ, and 15μ (active). Theoretical interpretation has been provided by Kornfeld (24) and Brester (25). Kornfeld assumed an ionized structure of the carbonate group, but made allowance for the deformability of O^{--}. The observed wave-lengths are found capable of interpretation in terms of corresponding frequencies of vibration of the ions within the group in characteristic ways.

Interest attaches to the assumption of polar structure within oxygenated radical groups. Chemists have generally preferred a model involving linkages of the shared-electron type between a central atom and the oxygen atoms round it. It is noteworthy in this connection that Slater (26) finds a "valence model" for the groups NO_3 and ClO_3 energetically more stable than that containing purely ionic linkages. Further discussion is postponed to section XII.

VIII. THE RAMAN EFFECT

1. *Historical and general*

The phenomenon of the scattering of light with change of frequency has provided a new and valuable method of ascertaining characteristic molecular frequencies. The effect was reported by Raman in the spring of 1928. The literature dealing with the subject is, however, already very large, and it is fortunate that able summarizing papers are available, by Raman (27), Smekal (28), Dadieu and Kohlrausch (29), and Kohlrausch (30).

Smekal (31), in 1923, extended arguments of Compton and Epstein (on the alteration in size of x-ray quanta on endowing free electrons with kinetic energy) to include collisions between quanta of visible light and atomic or molecular systems with attendant energy changes. To put the idea in its simplest form, if ω represents a characteristic frequency of a molecule in wave-numbers (cm.$^{-1}$), sometimes written ω_0, and ν_0 that of an incident light quantum in cycles per second, then if energy $hc\omega$ is expended on a molecular system, energy $h\nu_0 - hc\omega$ will remain, the scattered light containing the red-shifted frequency $\nu = \nu_0 - c\omega$. "Anti-Stokes" lines corresponding to a blue-shifted frequency $\nu = \nu_0 + c\omega$ may also be predicted, by excited molecules parting with a quantum $h\omega$ to the light quantum, which is, however, likely to be a rarer event and to give weaker lines. This is entirely in accord with observation. Similar results appear in the dispersion theory of Kramers and Heisenberg (32), and in the new quantum mechanics (33, 34, 35, 36). The effect is that of "combination scattering." For further explanation, see papers by Herzfeld (37), Smekal (38, 39), and Kohlrausch (30). Now a simple calculation shows that if changes as described are to be wrought in electronic systems by visible quanta, the energy levels concerned in the frequency shift must not differ by more than about 1.5 equivalent volts, if the scattered light is also in the visible region (113). Such relatively small energy differences are often found in the rotational and vibrational levels of molecules, which are therefore in general better suited for observation than the energy levels of atoms, which are usually more widely separated. Electronic transitions in molecules tend to be excluded on this account. Continuous spectra may be expected in scattering where the changes involve energy of translatory motion, which is not quantized. The frequencies quoted in the paper are given in wave-numbers $\omega = \nu/c$ cm.$^{-1}$ where c is the velocity of light *in vacuo.*

2. Raman scattering and infra-red absorption

The investigation of the Raman effect of benzene showed that characteristic vibrations could be associated with molecular infrared frequencies, whilst in the case of toluene, additional vibrations could be assigned to the methyl group. Considerable progress has been made in the classification of frequencies as associated with particular linkages within molecules. A very large number of substances, mainly organic liquids, have been examined.

The observation that Raman shifts sometimes find no corresponding infra-red bands led Langer (40) and Dieke (41) to the conclusion that modified frequencies may differ from incident frequency by differences between frequencies observed in absorption. This was applied by the authors with success in the interpretation of the Raman spectrum of carbon tetrachloride. This possibility must be borne in mind in interpreting Raman results. It is claimed by workers in the field that the technique of these experiments is simpler than that of infra-red absorption, and indeed this may be expected to be the case, since measurements are made upon visible light. A few of the more typical results are considered below.

IX. THE RAMAN EFFECT OF GASES

Gases have been investigated at high pressures in order to increase the intensity of the scattered light. The Raman spectra of hydrogen, nitrogen, and oxygen were examined by Rasetti (42, 43, 44). In hydrogen, the odd-numbered rotational levels have greater statistical weight, in accordance with the suggestion that two gases are present in the ratio 1:3, with even and odd rotational levels respectively. In nitrogen, even-numbered levels have greater weight, whilst in oxygen, where the numbers of nuclear protons and electrons are even, so that there is no resultant nuclear spin, alternate lines corresponding with transitions between odd-numbered levels are alone observed. These results are in accordance with the new quantum mechanics. Kemble and Hill (45) deduced that for a diatomic molecule in a Σ state, the Raman spectrum for a vibration-rotation band should contain a Q branch as a single intense line, although absent in infra-red absorption, together with double P and R branches. These results were found in agreement with the observations of Wood (46, 47, 48) on hydrogen chloride. A considerable number of other gases have been studied.

X. THE RAMAN EFFECT OF LIQUIDS

1. Liquefied gases

McLennan (49) examined the Raman effect of liquid hydrogen, and found evidence of the existence of ortho- and para-hydrogen. Daure (50, 51) worked also on liquefied gases, and found that linkages between a "metalloid" atom (e.g., Cl, N, C) and H involve relatively high frequencies, ranging from wave-numbers 2780 to 3380 cm.$^{-1}$, whilst shifts of lower frequencies, which moved in the direction of higher wave-numbers from single to double, and from double to triple bonds (see table 5) were associated with linkages between metalloid atoms. The spectrum of liquid ammonia is more complex than that of the gas, which seems to be due to formation of new linkages in the liquid by molecular association. Other liquefied gases have been examined. It is often very difficult to interpret the observed results in the present stage of the investigations.

2. *General results on liquids*

The Raman effect was discovered in benzene (53, 54), and a large number of liquids have been since examined. Dadieu and Kohlrausch (29, 30, 52) have described and discussed the results obtained with over one hundred organic liquids. Some leading results may be mentioned. The general characteristic of H atoms attached to carbon atoms having double linkages to other carbon atoms, as in benzene, is an increase of frequency as compared with aliphatic C—H: 3050 cm.$^{-1}$ (aromatic), 2930 cm.$^{-1}$ (aliphatic). Strangely enough, in view of this conclusion, benzene shows also a shift of 2930 cm.$^{-1}$. It is possible that this frequency is associated with the complete symmetry of the molecule, the agreement with the aliphatic linkage being accidental, though this remains undecided. Tautomerism has been detected in ethyl acetoacetate: CO (keto) 1714 cm.$^{-1}$, CO (enol) 1740 cm.$^{-1}$. In conjugated systems, it is found that there is no reason to suppose that the C=C linkage behaves differently from the usual double bond, as in molecules of the allyl type. In organic liquid binary mixtures (55), the Raman spectra are in general like those which would be obtained by superposition of the spectra of the components, but in certain cases there is a small shift in the C=O vibration where acids form one of the constituents (benzene–acetic acid, benzene–benzoic acid) which has been attributed to molecular association. Studies of the Raman effect of mixed liquids, as well as the comparison between the spectra of liquids and of the same substances in other states of aggregation, promises to throw light on the problem of association in liquids. In contrast with liquid ammonia and water, Ramdas (56, 57) found agreement between the characteristic frequencies of ethyl ether in the liquid and vapor states. On the whole, polar liquids tend to give higher frequencies in the gaseous state, whilst non-polar liquids show relatively small changes. Corresponding with the infra-red absorption band near 3.0μ, water gives three Raman frequencies, one component of which disappears at about 80°C., possibly owing to the breaking-up of complexes, $(H_2O)_n$. Water consequently undergoes characteristic changes in intensities and wave-numbers of characteristic frequencies with changing temperature (58, 59, 60, 61). Weaker bands in the region of this absorption band of water are shown by methyl and ethyl alcohols. Castler (62) has recently suggested that the doublets and triplets observed in Raman spectra provide evidence of quantized rotation in liquids. It has been found that the oxygen atoms are bound differently in oxygen and in hydrogen peroxide (63).

3. *Characteristic frequencies of various linkages*

Considerable progress is to be reported in the task of assignment of particular vibration frequencies to specific atomic linkages. There are four leading frequency regions, shown in table 5 below, where linkages of the respective types X—X, X=X, X≡X, X—H are considered (X is C, N, O, or S).

TABLE 5

Characteristic frequency regions of linkage types $(cm.^{-1})$

REGION	100–1000		1300–1800		1900–2400		2800–3400
Linkage	Frequency	Linkage	Frequency	Linkage	Frequency	Linkage	Frequency
S—S	510	N=O	1350	C≡C	1960	C—H (al)	2930
C—S	690	O=O	1550	CO	2155	C—H (ar)	3050
C—C	990	C=C	1600	C≡N	2200	N—H	3330
C—O	1030	C=O (keto)	1700	N≡N	2330	O—H	3390
C—N	1040	C=O (enol)	1740				

It is clear from the table that the approximate classification into frequency regions finds adequate justification, and that a definite increase of frequency occurs from single → double → triple bonds, at least for linkages involving the approximately equally heavy atoms C, N, and O. The characteristic frequencies involving S are definitely smaller (64). The molecule CO appears in the region characteristic of triple bonds, a point to which further reference is made.

Dadieu and Kohlrausch (29, 30) have studied the influence of substituent groups replacing H attached to C of the linkages C—H and C=O in respect to characteristic frequencies. It is found, for instance, that OH increases the frequency of C—H in HCOOH, whilst the C=O frequency is decreased. Halogen substituents act in the opposite way in both cases. A few results are collected in table 6.

TABLE 6

Influence of substituents on the characteristic frequencies of C—H and C=O (cm.$^{-1}$)

LINKAGE	C—H	C=O
HCOOH	2951	1647
$HCOC_6H_5$	2922	1696
$HCONH_2$	2882	1670

It would appear undesirable to omit reference to the more complicated cases where linkages may exhibit more than one frequency. In the case of a molecule of the type RX, where R is an alkyl group and X is a halogen, there are two sets of frequencies to be considered, which may be classified as inner and outer frequencies. The inner frequencies occur within the alkyl group (e.g., CH_3), and are relatively large and more or less constant in a homologous series. The outer frequencies, between R and X, are smaller, and are displaced in the direction of lower frequencies with increasing molecular weight of the halogen. With regard to the halogen derivatives of methane, if the groups CH_3, CH_2, and CH are treated as mass-points, one outer frequency is derived for mono-, three for di-, and four for tri-derivatives, on the assumption that CH_3Cl is linear, CH_2Cl_2 symmetrical and plane triangular, and $CHCl_3$ symmetrical pyramidal (65). This has been confirmed experimentally (66). Calculation indicates that the valence bonds maintain a constant strength in order of magnitude, and that the angles between the valence directions connecting C and H are in close agreement with the requirements of the tetrahedral model of the carbon atom. The models are depicted in figure 2. Dennison (67, 68) found that four fundamental frequencies should be observed for symmetrical pyramidal and tetrahedral models, the vibrating atoms being treated as mass-points. Experiment (50, 51, 69) shows observations on tri- and tetra-halides in agreement with this result. In series such as PCl_3, $AsCl_3$, $SbCl_3$, $BiCl_3$; CCl_4, $SiCl_4$, $TiCl_4$, $SiCl_4$; there occurs a frequency decrease in each of the four fundamentals progressively with increasing molecular weight. There is a

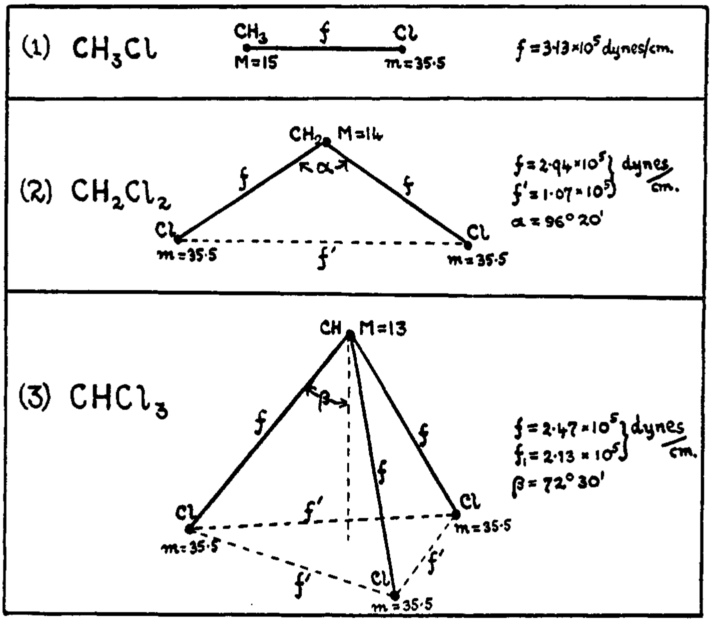


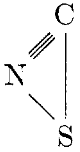
FIG. 2. STRUCTURAL MODELS OF CH_3Cl, CH_2Cl_2 AND $CHCl_3$
See Kohlrausch (65)

similar drop from PCl_3 to PBr_3, and from $SnCl_4$ to $SnBr_4$ (70). Apparently comparison of the Raman spectra of $SiBr_4$ and of $SnBr_4$ is in agreement with the assumption of tetrahedral models for both molecules (71). On the other hand, the existence of definite dipole moment for $SnCl_4$ ($\mu = 0.8 \times 10^{-18}$ C. G. S. units) has been held to suggest a pyramidal model (72). $SiCl_4$ has no moment; perhaps the right model for $SnCl_4$ is a deformed tetrahedron. $SiCl_4$ and $SnCl_4$ when mixed together give the lines of the components; PCl_3 and PBr_3 give new lines in addition, which have been attributed to the formation of new complexes PCl_2Br and $PClBr_2$. Such interchanges of halogen atoms, if this interpretation is correct, would appear as examples of an isolated type of phenomenon. Langseth (73) has found evidence of isotope effects; the Raman displacement at 458 cm.$^{-1}$ in CCl_4 is found to be a triplet on this account.

The fundamental frequencies of CH_3Cl, CH_3Br, and CH_3I near 725, 600, and 510 cm.$^{-1}$, respectively, agree well with work in the infra-red (74, 75). Harkins and Bowers (76) find that the fundamental frequency C—Br in CH_3Br is displaced in the direction of lower frequencies ($\approx$ 563 cm.$^{-1}$) in the case of longer normal chains. It seems reasonable to suppose, with these authors, that the effective mass of CH_2 increases by constraints due to union with a hydrocarbon chain.

Raman frequencies may be used to deduce the shapes of molecules other than those containing carbon. For example, it is found that S_2Cl_2 and $SOCl_2$ are Y-shaped molecules with sulfur atoms at the centers (95).

4. Mean restoring force: measure of linkage strength

It appears that the fundamental frequencies of molecular linkages may be used to provide information not only as to what types of link are present, but also as to the relative strengths of the links. As an example of the first named kind of deduction, Dadieu (77) found that in the case of the mustard oils (thiocarbimides) two frequencies occur in the region characteristic of triple linkages; hence the structure R.  is assigned, instead of the R.N:C:O of carbimides. With regard to the second point, when allowance is made for changes of mass of the vibrating particles from one compound to another of similar type, a decrease of frequency may be taken to indicate weaker binding, and *vice versa.* Dadieu and Kohlrausch (78) have attempted to calculate the "mean restoring forces" of linkages with the aid of a formula of the pendulum type, in the following way. The frequency ν is expressed by means of the relation

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}} \tag{3}$$

where f is the elastic force and μ is the "reduced" mass. (Strictly, ν refers to infinitely small displacements, and is sometimes written ν_0). If ω is the wave-number corresponding to ν, then $\omega = \nu/c$, where c is the velocity of light; introducing this relation into equation 3, and using

$$\mu = \frac{mM}{(m+M)N} \tag{4}$$

where m, M are the masses of the vibrating parts on the scale $O = 16$, and N is the Avogadro number, it follows that

$$f = 4\pi^2c^2\frac{mM}{(m+M)N}\omega^2 \tag{5a}$$

whence, inserting $\pi = 3.1416$, $c = 2.998 \times 10^{10}$ cms. per sec., and $N = 6.064 \times 10^{23}$,

$$f = 5.842 \times 10^{-2}\frac{mM\omega^2}{m+M}\text{ dyne per cm.} \tag{5b}$$

If now the mean restoring force K is put equal to $\frac{1}{2}af$, where a is the amplitude of vibration, the energy $\frac{1}{2}fa^2$ may be equated to $h\omega$, so that $a = \sqrt{2h\omega/f}$, whence, using equation 5a,

$$a = \sqrt{\frac{hN(m+M)}{2\pi^2c\omega mM}} \tag{6a}$$

from which, inserting $h = 6.547 \times 10^{-27}$ erg secs.,

$$a = 8.193 \times 10^{-8} \sqrt{\frac{m + M}{mM\omega}} \text{ cm.} \tag{6b}$$

whence $K = \frac{1}{2}af$ may be found. As an example, consider the fundamental frequency $\omega = 990$ cm.$^{-1}$ of ethane, $CH_3.CH_3$. Here $m = M = 15$, and $mM/(m + M) = 7.5$; hence, by equation 5b, $f = 4.301 \times 10^5$ dynes per centimeter, and, by equation 6b, $a = 9.51 \times 10^{-10}$ cm. From this, the mean restoring force $K = 2.045 \times 10^{-4}$ dyne. Some results calculated by Dadieu and Kohlrausch by this method are shown in table 7.

TABLE 7

Mean restoring forces for single, double, and triple linkages

SUBSTANCE	LINKAGE	FUNDAMENTAL FREQUENCY ω	MEAN RESTORING FORCE K	MEAN VALUES OF K
		cm.$^{-1}$	10^{-4} *dyne*	
CH_3CH_3	C—C	990	2.05	2.18
CH_3OH	C—O	1031	2.27	
CH_3NH_2	C—N	1038	2.23	
C_2H_4	C═C	1620	4.13	4.22
Ketones	C═O	1700	4.40	
O_2	O═O	1552	4.14	
C_2H_2	C≡C	1960	5.30	6.30
CO	C≡O	2155	6.28	
Nitriles	C≡N	2246	6.48	
N_2	N≡N	2329	7.14	

The results show the means of mean restoring forces of single, double, and triple linkages in the examples chosen to be almost exactly in the ratio 1:2:3, a very pretty and significant result. In this connection, it should be noted that the heat of dissociation per bond is found constant in the molecules from C_2 to F_2 (11). Moreover, the K values in table 7 fall into three well-defined groups and are more or less constant within each group, although the frequencies show no such regularity. Andrews (79, 80) has made calculations of fundamental frequencies of single homopolar bonds, on the assumption that frequency variations in different cases are to be attributed to variations in the masses of the vibrating particles rather than to differences in bonding strength. Frequencies calculated on the assumption of an elastic constant of 4×10^5 dynes per cm. were found to be in good general agreement with observation. An attempt to calculate specific heats from Raman results may also be noted (81). The conclusion that bonding strength is more or less constant for given types of homopolar linkages (single, double, or triple) is of interest, and is further considered in the concluding section XII.

5. *Raman effect of solutions*

It is only possible to touch very lightly upon the Raman effect of solutions. In cases where a characteristic frequency is preserved when solution of a substance occurs, there is generally a shift in the direction of lower wave-numbers, and with dilution, the lines suffer decreased sharpness and intensity and often displacement in frequency. Interest attaches to changes of intensity of the water bands in aqueous solutions of HNO_3, $NaNO_3$, and $NaClO_3$ (82), which appear to be due to changes in the degree of polymerization of H_2O. The nitrate ion is apparently effective in favoring the depolymerization of water (83). Sometimes lines characteristic of the undissolved substances disappear in solutions in water, suggesting fission of linkages in ionic dissociation. Thus HCl (84) and KCl (85) in certain dilutions do not give the characteristic lines of the undissociated solutes. Hg_2Cl_2, on the other hand, shows displacements due to the undissociated molecule. The characteristic frequencies of oxygenated anions are generally preserved in solution, with reduced wave-numbers in the case of NO_3^- (86) and of ions of the AO_4^{--} type (87). A given frequency of SO_4^{--} is further reduced by the removal of water and addition of hydrogen ions to form undissociated H_2SO_4 (88). This effect is probably to be associated with entry of the hydrogen ions within the outer electronic shell of the SO_4 group. By comparison with the Raman spectra of alkyl and aryl nitrates and nitrites, evidence is found of the presence of the ψ-acid $HO \cdot NO_2$ in 64 per cent solutions of nitric acid, whilst pure nitric acid is found to consist entirely of molecules of this constitution (89). The study of complex ammines in solution shows that coördinated linkages give rise to characteristic displacements (90, 91), whilst investigation of complex halides and cyanides provides evidence of the presence or absence of dissociation of the complex anions (92). The weaker "associated" linkages give no characteristic lines (90, 93).

XI. THE RAMAN EFFECT OF CRYSTALS

The Raman effect of crystals was discovered independently of the Indian school of physicists by Landsberg and Mandelstam (96, 97). Comparison of substances in different physical states shows that, in general, more frequencies are observed with gases, but that where the same frequency persists there is a small wave-number rise from solid to liquid and from liquid to gas. Raman (53) and Rao (98, 99) found that the bands of ice were sharper and somewhat raised in wave-length as compared with corresponding bands of water. In the region $\lambda = 3\mu$, very nearly equal frequencies are observed for ice, water, and the water of crystallization of selenite ($CaSO_4 \cdot 2H_2O$), as in table 8 (30, 100).

TABLE 8

Raman frequencies of H_2O in different states ($cm.^{-1}$)

	CHARACTERISTIC FREQUENCIES		
Water	3220	3440	3580
Ice	3190	3390	3550
Water of crystallization	3240	3400	3494

Quartz and calcite have received very thorough examination both in infra-red absorption and in Raman scattering. The inactive vibration of calcite at 9.2μ appears in the Raman effect, though not in infra-red absorption. In view of the isosterism and crystalline resemblance between calcite and sodium nitrate, it becomes of interest to observe that the characteristic fundamental vibrations of NO_3^- and CO_3^{--} in these compounds are also closely alike (101, 102, 103, 104). The middle vibration shown in each series in table 9 is inactive and differently polarized from the other two. The ions ClO_3^-, BrO_3^-, and IO_3^- show a principal frequency decreasing with increasing weight of the group, whilst ClO_4^- resembles SO_4^{--} (105).

It is noteworthy that residual ray frequencies of typically polar crystals as NaCl do not appear in the Raman effect, but show a region of continuous absorption which does not correspond with the infra-red fundamental. Thus it is found that NaCl shows a weak continuous displacement extending from 165 to 365 cm.$^{-1}$ (106, 108). The intensity of lines rises from zero for typically polar substances to a maximum for homopolar substances (107). Fluorite is reported to show a line at 321 cm.$^{-1}$, corresponding with the infra-red vibration at 31.1μ. Calcite and fluorite also give high frequencies in the regions between 7270 and 7455, and between 7256 and 7298 cm.$^{-1}$, respectively (108).

TABLE 9

Fundamental vibrations of calcite and sodium nitrate (cm.$^{-1}$)

	FUNDAMENTAL VIBRATIONS		
Sodium nitrate, $NaNO_3$	1391	1074	730
Calcite, $CaCO_3$	1437	1087	712

TABLE 10

Characteristic frequencies of gypsum, barytes, and an ammonium sulfate solution (cm.$^{-1}$)

	CHARACTERISTIC FREQUENCIES					
Gypsum, $CaSO_4 \cdot 2H_2O$	414.2,492.9	620.0	670.4	1008.4	1135.5	3403.0,3491.5
Barytes, $BaSO_4$	452	622		984	1148	
Solution, $(NH_4)_2SO_4 + nH_2O$	451	620		980.3	1113	3430 (not dissolved)

With regard to the relation between the behavior of groups in the solid state and in solution, Dickinson and Dillon (109) compared the Raman spectra of gypsum and an ammonium sulfate solution. The figures, including frequencies of barytes reported by Nisi, are recorded in table 10. The frequencies attributed to water of crystallization are absent in anhydrous barium sulfate in accordance with anticipation (28). Differences between the characteristic frequencies of barytes and of gypsum may be attributed to the hydration of gypsum or to the effect of the cation. Examination of the inactive Raman frequencies in a series of nitrates with and without water of crystallization shows the nature of these influences (86). The results presented in table 11 (to the nearest 0.5 cm.$^{-1}$) show that the characteristic frequency is greater the smaller the atomic number of the cation for a given valence, that is, the smaller the interionic distance and the greater the deforming power of the cation. Comparison of the figures for KNO_3 and $Ca(NO_3)_2$, where the atomic numbers, masses, and electron configurations do not differ very greatly, shows that an increase of charge (valence) of the cation involves an increase in frequency. The progressive increase of number of water molecules in hydrating $Sr(NO_3)_2$ is accompanied by falling frequency, so that the effect of the double charge on the strontium ion becomes wholly or partly compensated. The effect of solution, in the case of $NaNO_3$, as previously noticed, is to depress the characteristic frequency, which further decreases on dilution. It is found that a lower limit is reached, which is approximately that of the nitrate with large cation and double charge (Ba^{++} or Pb^{++} $\approx$ 1046 cm.$^{-1}$).

TABLE 11

Inactive Raman frequencies of crystallized nitrates (cm.$^{-1}$)

$LiNO_3$	1086	$Ca(NO_3)_2$	1064	Hydrated	$Sr(NO_3)_2$
$NaNO_3$	1074*	$Sr(NO_3)_2$	1054.5	$+4H_2O$	1053.5
KNO_3	1048.5	$Ba(NO_3)_2$	1046.5	$+6H_2O$	1053
$AgNO_3$	1045	$Pb(NO_3)_2$	1045	$+9H_2O$	1044.5

* Taken from reference 103.

XII. GENERAL DISCUSSION

The present paper is concerned, as far as section V, with the electronic configurations of atoms and diatomic molecules, and afterwards with the characteristic frequencies of molecules, mainly from the standpoint of the Raman effect. The treatment in sections VIII to XI is in some detail, because it seems desirable to state the present position as adequately as possible, at least in the leading features, in connection with a discovery which is still recent but has had considerable influence in molecular physics. There remains the task of a general consideration of the results on electronic configurations and characteristic frequencies in relation to each other.

1. Bonding power and valence

Mulliken (11) has recently stated that it is really not necessary to think of valence bonds as existing in the molecule. From the physical standpoint, this author has shown that electrons act in different ways, and that it is better to think of molecules as a whole, as assemblages of constituent protons and electrons. Whilst the cogency of this standpoint must be admitted, it would appear that, at least until the mechanism of the bonding and anti-bonding of electrons is more clearly defined, and especially in more purely chemical discussions, it is desirable to retain a large part of the older symbolism of valence. Indeed, Mulliken finds that the constitution of the nitrogen molecule, for example, is such that on the whole it behaves as if there were approximately three bonding pairs of electrons, or six bonding electrons.

If a pair of electrons may be considered as corresponding with one valence bond, then for practical purposes the bond in the nitrogen molecule may still be considered as triple, into which class it falls according to the evidence of its characteristic frequency and behavior in the Raman effect. Similarly, the conception of single and double bonds in hydrogen and oxygen, respectively, may be retained. On the other hand, the proved existence of single electron bonds would seem to indicate that the natural unit of valence on the ordinary scale would be equal to $\frac{1}{2}$ instead of 1. It seems a little confusing to regard a single bonding electron as the "natural unit bond," and yet to obtain the "number of bonds" by halving the number of (effective) bonding electrons. Mulliken's numbers of bonds in diatomic molecules could be obtained by treating each bonding electron as of value

$+\frac{1}{2}$ and each anti-bonding electron as of value $-\frac{1}{2}$. Reference to table 3 will show this. Even though it is true that bonding power must be treated as a continuous variable from the physical angle, there are reasons why the conception of number of bonds should be retained, and the chemist will be tempted to equate this number to what he calls the valence in question, although the idea of half a bond does not enter into any of the ordinary definitions of valence. In spite of this anomaly, the chemists' conception of single, double, and triple valence bonds has so many practical advantages that it must be retained, even if a new definition of valence is required to meet the cases where half values are required. The discussion need not be prolonged here, but the author hopes to take up the subject again in a later paper.

2. Apparent difficulties in the spin theory of valence

If the assigned dissociation products of diatomic molecules shown in table 3 are correct, it appears that the spin theory of homopolar union possesses several weaknesses. According to the formulation there shown, the molecules BeO and BeF should be incapable of existence, since the beryllium atom has no electron of unneutralized spin in its normal ground state. Further, the isosteric groups of similar electronic configurations have different valence numbers in many cases, as is seen from a comparison of the numbers shown in the column headed V. The numbers in the last column headed V_1 calculated independently of the spin theory of homopolar valence are free from this disadvantage. The spin theory also fails in the case of certain hydrides, and offers no ready explanation of the coördinate linkage, which appears as a definite type in the complex ammines, for example, giving rise to characteristic Raman bands. Whatever electrons are concerned in bonding in these cases, it would appear necessary to assume that both come from the same atom, where their spins are already paired. The theory further makes O_2 like F_2 with a single bond.

It may be alleged against the argument used concerning isosteres in the preceding paragraph that such molecules tend to resemble each other more in physical than in chemical properties, so that good chemical reasons may exist why different numbers of bonds should be postulated in the comparison of some molecules to which are assigned the same outward electronic configuration. For example, the configurations of CO and N_2 are alike, and the characteristic frequencies of the two linkages fall together in the region of triple bonds (table 5). CO has the frequency 2155 corresponding to the infra-red bond at 4.66μ; the ketone linkage C:O has the lower value 1700 $cm.^{-1}$ Yet CO forms addition compounds of the type of $COCl_2$, in which the Cl atoms are both attached to C, so that the chemist may prefer the structure :C:O, which makes the linkage double and thus in accordance with the interpretation of Heitler and London. Again, a close resemblance exists between the characteristic frequency of N_2O (1282 $cm.^{-1}$) and that of CO_2 (1285 $cm.^{-1}$), and the two gases resemble each other in general physical character. The gases are not very alike in chemical behavior, however, and it seems difficult to believe that their linkages really resemble one another as much as the physical evidence might suggest.

3. Oxygenated negative radicals and complex ammines

The question of the structure of oxygenated anions is raised at the end of section VII. On the one hand, work in the infra-red suggests a polar structure, whilst chemists have generally treated the linkages between the central atom of the group and oxygen as of the shared electron type. According to Taylor (110), the seemingly discordant results indicate that the electrons concerned are more effective in screening the oxygen atoms than the central atom, so that the linkages are "approximately electrostatic." Zachariasen (111) states that up to the present the application of the principle of shared electron pairs in the atomic arrangement of inorganic crystals has proved unsuccessful, and suggests that the constitution of an ion of the ClO_3^- type should be treated primarily as ionic, taking account of deformation of the oxygen anions. The continuity of the transition between polar and homopolar types of linkages is illustrated by this intermediate state. It may be said that a similar difficulty, if such it may be called, appears in the interpretation of coördinated linkages in compounds of the amine type. It is possible to regard the linkage between the central atom of a group and an outer coördinated molecule, such as H_2O or NH_3, either as (*a*) associated with the dipole moment of the attached group, electrostatic force holding it to the central atom, regarded as an ion, or (*b*) linked with the sharing of electrons both provided by the coördinated group. But in the nature of things, according to (*b*), the linkage must be at least partly electrostatic, since the central atom becomes endowed with a share of negative charge it did not previously possess. Such cases seem to be adequately described as semipolar.

4. Mean restoring forces and calculated characteristic frequencies

The idea that given types of bonds between atoms (single, double, or triple) have more or less constant bonding forces (mentioned in section X) seems to accord best with the electronic configurations shown in table 3. It does not agree so well with the different numbers of valence bonds assigned by the spin theory for molecules assumed (on the Raman and other physical grounds) to possess the same types of bonds. The assumption, of course, can be only approximately true, but it seems to have some fundamental significance when orders of magnitude rather than actual values are taken into account. This seems to be well illustrated by the following method of calculation. Consideration of the relations given in section X shows that the characteristic wave-number, ω, of a linkage may be expressed in terms of the mean restoring force K as follows:

$$\omega^3 = K^2 \cdot \frac{N}{2\pi^2 hc^3} \cdot \frac{m + M}{mM} \tag{7a}$$

which gives, inserting the values of the constants,

$$\omega = (5.584 \times 10^5 K^{\frac{2}{3}}) \cdot \sqrt[3]{\frac{m + M}{mM}} \text{ cm.}^{-1} \tag{7b}$$

Now inserting the mean values of K for single, double, and triple bonds shown in table 7, the part within the bracket in equation 7b is found to assume the values 2022, 3142, 4102 in the three cases respectively, the numbers being approximately in the ratio 2:3:4. The characteristic frequency of a linkage of one of the three types should then be obtained by multiplying the appropriate value of the bracketted term in equation 7b by $1/\mu_a^{\frac{1}{3}}$, where

$$1/\mu_a = (m + M)/mM$$

the values of m and M being expressed on the ordinary atomic weight scale. The extent to which this expectation is fulfilled is shown in table 12, for the cases previously considered in table 7.

TABLE 12

Calculation of characteristic frequencies from mean restoring forces

SUBSTANCE	LINK	M	m	$\sqrt[3]{\frac{m+M}{mM}}$	CHARACTERISTIC FREQUENCY Calculated	CHARACTERISTIC FREQUENCY Observed
C_2H_6	C—C	15	15	0.5109	1033	990
CH_3OH	C—O	15	17	0.5006	1013	1031
CH_3NH_2	C—N	15	16	0.5055	1022	1038
CH_2:CH_2	C=C	14	14	0.5228	1643	1620
Ketones	C=O	12	16	0.5264	1657	1700
O_2	O=O	16	16	0.5000	1571	1552
CH⋮CH	C≡C	13	13	0.5358	2198	1960
CO	C≡O	12	16	0.5264	2159	2155
Nitriles	C≡N	12	14	0.5369	2203	2246
N_2	N≡N	14	14	0.5228	2144	2329

It seems probable that the discrepancies observable in certain cases in table 12 between calculated and observed frequencies might be lessened if account were taken of the anharmonic nature of the vibrations.

5. Conclusion

The exposition of the inward nature of the periodicity of the elements, first formally revealed by the labors of chemists, and its interpretation in the light of the work of Moseley and others and of the Pauli principle, is surely one of the very great achievements of physical science. Yet a long road lies ahead. The chemist has also provided, in a wealth of detail, description of a complex group of phenomena, remarkable alike in its manifold variety and often in its lack of agreement with anticipation, connected with the behavior of atoms in relation to each other and in actual combination. Modern physics is making important contributions to the understanding of many problems raised in this way, and perhaps offers the surest prospect of further advance.

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