The Electronic Structure of Excited States of Simple Molecules

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An effort has been made to discuss the structure of excited states of diatomic molecules in terms of valence bonds. It has been found that the predicted valence-bond structures correspond in symmetry character and internuclear distance to the observed states, but that the attempt to develop a systematic treatment of dissociation energies on this basis is only partially successful.

In the last thirty years there has been developed a satisfactory theory of the electronic structure of molecules in their normal electronic states and normal nuclear configurations. This theory is ordinarily presented in one of two aspects: the first, the valence-bond aspect, treating molecules in terms of single, double and triple bonds, with the phenomenon of resonance among several electronic structures of the valence-bond type being also often of great importance; and the second, the molecular-orbital method, treating molecules primarily by the consideration of the motion of individual electrons among all of the nuclei. Each method has its own points of advantage.

There has not as yet been developed an extensive structural chemistry of molecules in excited states. The rates and mechanisms of chemical reactions, however, depend upon configurations and electronic structures of molecular systems that differ from the stable ones, and accordingly we cannot hope to obtain a complete understanding of chemical reactions without simultaneously developing the structural chemistry of excited states and configurations. In case that there is no change in multiplicity attending a reaction, the transition from the reactants through the activated complex to the products may not involve any electronic excitation, other than that attending the change in the nuclear configuration. When a hydroxide ion attacks a halogen-substituted methane, it begins to form a weak bond with the carbon atom through the face of the tetrahedron opposite to that occupied by the halogen atom; as the reaction progresses the weak bond becomes stronger and stronger, and the bond from the carbon atom to the halogen atom (halogen ion) becomes weaker and weaker, until at the configuration of minimum stability the carbon atom has as its coordination polyhedron a trigonal bipyramid: it forms three bonds in its equator with the three groups other than halogen originally attached to it, and two weak bonds (half-bonds) with the oxygen atom of the hydroxide ion and with the halogen ion. The reaction then proceeds to completion by the removal of the halogen ion from the carbon atom, the tetrahedron about the carbon atom having been inverted. The consideration of the stability of the activated complex requires a knowledge of the repulsive forces operating between the five groups attached to the carbon atom, and of the energies of the bonds from these five groups to the carbon atom. An important part of the latter quantity is the resonance energy of a single bond between two positions, corresponding to the formation of half-bonds with the hydroxide oxygen and the halogen.

In other reactions, especially in which there is a change in multiplicity, the activated complex may be related to an excited electronic state of a reactant molecule. I have felt that to begin an attack on the problem of the electronic structure of activated complexes it would be worth while to study the electronic structure of simple molecules in excited electronic states. In the past the discussion of excited states of simple molecules has been made mainly on the basis of the molecular-orbital method. In the following sections of this paper I shall discuss some of the experimental information available about excited states of diatomic molecules with use of the valence-bond method.

Internuclear Distance as a Criterion of Bond Type in Excited States of Molecules

I have assumed that in a diatomic molecule the two atoms may form with one another a single bond, a double bond, or a triple bond, with the strength of the bonds increasing regularly in this order, and that there may also be present, superimposed on one of these electron-pair bonds, one or two one-electron bonds or three-electron bonds, in case that the two atoms are identical or are not much different in electronegativity. In the hydrogen molecule-ion the one-electron bond has about sixty percent as much bond energy as the electron-pair bond in the hydrogen molecule; and the three-electron bond in the helium molecule-ion has also about the same energy as the one-electron bond in the hydrogen molecule-ion. I have accordingly assumed that in general a one-electron bond or a three-electron bond between two atoms is a little more than one half as strong as an electron-pair bond, when the two atoms have the same or nearly the same electronegativity.

Of the various molecular properties that can be determined from spectroscopic data, the internuclear distance r_e seems to provide the best reflection of bond type. The vibrational frequency ω_e is, of course, closely related to internuclear distance, and might be used just as satisfactorily, but the additivity relations for internuclear distances make their use simpler. The deviation from parabolic form of the electronic potential function, as expressed in the term $\omega_e x_e$, bears no relation to bond type. Moreover, the dissociation energy also bears no simple relation to bond type. Thus we shall later reach the conclusion that both the normal state $X^2\Sigma^+$ and the second excited state $B^2\Sigma^+$ of the cyanide molecule CN have essentially a triple-bonded structure. The internuclear distances are 1,148 and 1,169 Å, respectively (the values of ω_e being 2069 and 2164 cm^{-1}), whereas the dissociation energies are 7,6 and 4,4 v.e., and the values of $\omega_e x_e$ are 13,176 and 20,25, respectively*.

There are given in Table I values of the single-bond radii of electronegative atoms[1]. For nitrogen, oxygen and fluorine additional values are given in parentheses. These apply to bonds between light atoms (C, N, O, F), whereas the smaller values apply to bonds between these atoms and other atoms. It has been pointed out by Schomaker and Stevenson[2] that the difference in values is to be attributed to an effect of the partial ionic character of the bonds, this effect, presumably a general one, being especially important for bonds of the most electronegative atoms and other atoms.

C	N	O	F
0,77	0,70 (0,74)	0,66 (0,73)	0,64 (0,72)
Si	P	S	Cl
1,17	1,10	1,04	0,99

$$r\,(A \overset{\cdot}{-} B)^* = r\,(A \overset{\cdots}{-} B)^* = r\,(A - B) - 0{,}14$$

$$r\,(A = B) = r\,(A - B) - 0{,}21$$

$$r\,(A \genfrac{}{}{0pt}{}{\cdots}{\cdots} B)^* = r\,(A - B) - 0{,}24$$

$$r\,(A \overset{\cdot}{=} B)^* = r\,(A \overset{\cdots}{=} B)^* = r\,(A - B) - 0{,}29$$

$$r\,(A \equiv B) = r\,(A - B) - 0{,}34$$

* For A and B closely similar in electronegativity

Table I. Single-bond Radii of Electronegative Atoms

The interatomic distance corresponding to a double bond is approximately 0,21 Å less than that for a single bond, and the distance for a triple bond is approximately 0,34 Å less than that for a single bond. Corrections for bonds involving one-electron or three-electron bonds also are given in Table I; these have been interpolated logarithmically on the assumption that a one-electron or three-electron bond is equal to 60% of a single bond. Thus we would predict for an oxygen molecule containing a single bond plus two three-electron bonds the internuclear distance 1,46 — 0,24, or 1,22 Å. The equation

$$r\,(n) = r\,(1) - 0{,}70 \log_{10} n \tag{1}$$

may be used to change from the single-bond distance $r\,(1)$ to the distance for bond number n.

In the use of the large radii for nitrogen, oxygen, and fluorine the correction for difference in electronegativity of the two bonded atoms suggested by Schomaker and Stevenson involves subtracting $0{,}08\,(x_A \rightarrow x_B)$, where x_A and x_B are the electronegativity values for the elements (Schomaker and Stevenson used the factor 0,09). The electronegativities of C, N, O and F are 2,5, 3,0, 3,5, and 4,0, respectively[1]. Hence for N—O the electronegativity correction is 0,04 Å, and the single-bond distance would be expected to be 1,47—0,04=1,43 Å. The bond in this molecule is a double bond plus a

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* Spectroscopic data quoted in this paper are taken mainly from H. Sponer, Molekülspektren, J. Springer, Berlin 1935.

[1] L. Pauling, The Nature of the Chemical Bond, Cornell University Press, 2nd Edition, 1940.

[2] V. Schomaker and D. P. Stevenson, J. Amer. chem. Soc. **63**, 37 [1941].

		A_0 v. e.	Bond structure	$r_{\text{predicted}}$ Å	$r_{e\,\text{obs.}}$ Å	ω_e cm^{-1}	$\omega_e x_e$	$D_{\text{extrap.}}$ v. e.	$D_{\text{extrap.}} + A_0$ v. e.
O_2	$X\,^3\Sigma_g^-$	0	$:\mathrm{O}\overset{\cdot\cdot\uparrow}{\underset{\cdot\cdot\uparrow}{-}}\mathrm{O}:$	1,22	1,204	1580	11,99	6,36	6,36
	$a\,^1\Delta_g$	0,98	$:\underset{\cdot\cdot}{\mathrm{O}}=\underset{\cdot\cdot}{\mathrm{O}}:$	1,25	1,22	1509	12,9	5,38	6,36
	$A\,^1\Sigma_g^+$	1,62	$:\mathrm{O}\overset{\cdot\cdot\uparrow}{\underset{\cdot\cdot\downarrow}{-}}\mathrm{O}:$	1,22	1,223	1433	13,92	4,49	6,12
	$C\,^3\Sigma_u^+$	4,71	$:\overset{\cdot\cdot}{\mathrm{O}}\underset{\cdots}{-}\overset{\cdot}{\mathrm{O}}:$	1,46	1,58	—	—	—	—
	$B\,^3\Sigma_u^-$	6,11	$:\underset{\cdot\cdot}{\mathrm{O}}\overset{\cdots}{-}\underset{\cdot}{\mathrm{O}}:$	1,46	1,599	710	10,71	1,42	7,53
O_2^+	$X\,^2\Pi_g$	0	$:\mathrm{O}\overset{\cdots}{=}\mathrm{O}:$	1,17	1,14	1876	16,53	6,51	6,51
	$A\,^2\Pi_u$	4,75	$:\overset{\cdot\cdot}{\mathrm{O}}=\overset{\cdot}{\mathrm{O}}:$	1,36	1,41	899	13,7	1,77	6,53
N_2	$X\,^1\Sigma_g^+$	0	$:\mathrm{N}\equiv\mathrm{N}:$	1,14	1,094	2360	14,44	11,80	11,80
	$A\,^3\Sigma_u^+$	6,17	$:\dot{\mathrm{N}}=\dot{\mathrm{N}}:$	1,27	1,290	1460	13,93	4,75	10,92
	$B\,^3\Pi_g$	7,34	$\cdot\mathrm{N}\overset{\cdots}{=}\mathrm{N}:$	1,19	1,207	1733	14,44	6,68	14,02
	$a\,^1\Pi_u$	8,53	$\cdot\mathrm{N}\overset{\cdots}{=}\mathrm{N}:$	1,19	1,207	1692	13,32	6,56	15,09
	$C\,^3\Pi_u$	11,01	$\cdot\mathrm{N}\overset{\cdots}{=}\mathrm{N}:$	1,19	1,144	2046	26,40	4,79	15,80
N_2^+	$X\,^2\Sigma_g^+$	0	$\cdot\mathrm{N}\equiv\mathrm{N}:$	1,14	1,113	2207	16,04	9,27	9,27
	$B\,^2\Sigma_u^+$	3,18	$\cdot\mathrm{N}\equiv\mathrm{N}:$	1,14	1,071	2418	20,95	8,56	11,74
C_2	$A\,^3\Pi_u$	0	$:\mathrm{C}\doteq\mathrm{C}\cdot$	1,25	1,308	1642	11,67	7,05	7,05
	$b\,^1\Pi_u$	(1,70)	$:\mathrm{C}\doteq\mathrm{C}\cdot$	1,25	1,315	1608	12,10	6,55	8,25
	$B\,^3\Pi_g$	2,40	$:\mathrm{C}\doteq\mathrm{C}\cdot$	1,25	1,261	1793	19,35	5,04	7,45
	$d\,^1\Pi_g$	(4,91)	$:\mathrm{C}\doteq\mathrm{C}\cdot$	1,25	1,251	1832	34,01	3,03	7,94

Table II. Diatomic Molecule

three-electron bond, for which the correction is 0,29 Å. We hence predict the internuclear distance 1,14 Å, which is practically equal to the observed value 1,146 Å.

Symmetrical Diatomic Molecules Formed by First-Row Elements

The Oxygen Molecule. There are given in Table II data for molecules such as O_2, O_2^+, etc. Let us first discuss the structure of the oxygen molecule. The number of electrons is such that this molecule could use all of its L-shell orbitals in holding unshared electron pairs and forming a double bond between the two oxygen atoms. However, instead of using one pair of the π orbitals for the π-half of a double bond and the other pair of π orbitals, one on each oxygen atom, for holding two unshared electron pairs, the π orbitals could instead be used for the formation of two three-electron bonds. Inasmuch as two three-electron bonds are somewhat more stable than a single bond, the three-electron-bond structure would be expected to represent the normal state. Moreover, each three-electron bond contains one odd electron, and the spins of the odd electrons for the two bonds could place themselves parallel, giving a $^3\Sigma_g^-$ state, or antiparallel, giving a $^1\Sigma_g^+$ state. We can predict that the triplet state would be more stable than the singlet state, by the following argument: a three-electron bond involves the resonance

		A_0 v. e.	Bond structure	$r_{\text{predicted}}$ Å	r_e obs. Å	ω_e cm^{-1}	$\omega_e x_e$	$D_{\text{extrap.}}$ v. e.	$D_{\text{extrap.}} + A_0$ v. e.
NO	$X\,^2\Pi$	0	$:\mathrm{N}\overset{\cdots}{=}\mathrm{O}:$	1,14	1,146	1906	14,42	7,69	7,69
	$A\,^2\Sigma^+$	5,47	$(:\mathrm{N}\equiv\mathrm{O}:)\cdot$	1,09	1,06	2374	16,3	10,55	16,03
	$B\,^2\Pi$	5,65	$:\dot{\mathrm{N}}=\ddot{\mathrm{O}}:$	1,33	1,413	1038	7,45	4,45	10,10
	$C\,^2\Sigma^+$	6,47	$(:\mathrm{N}\equiv\mathrm{O}:)\cdot$	1,09	1,07	—	—	—	—
	$D\,^2\Sigma^+$	6,58	$(:\mathrm{N}\equiv\mathrm{O}:)\cdot$	1,09	1,06	2351	27	6,23	12,81
CN	$X\,^2\Sigma^+$	0	$\cdot\mathrm{C}\equiv\mathrm{N}:$	1,13	1,148	2069	13,18	10,00	10,00
	$A\,^2\Pi_{\text{verk}}$	1,35	$:\mathrm{C}\overset{\cdot}{=}\mathrm{N}:$	1,18	1,236	1789	12,88	7,62	8,97
	$B\,^2\Sigma^+$	3,22	$:\mathrm{C}\equiv\mathrm{N}\cdot$	1,13	1,169	2164	20,25	6,92	10,14
CO	$X\,^1\Sigma^+$	0	$:\mathrm{C}\equiv\mathrm{O}:$	1,08	1,13	2169	13,28	10,85	10,85
	$a\,^3\Pi$	6,01	$\cdot\dot{\mathrm{C}}=\ddot{\mathrm{O}}:$	1,21	1,205	1739	14,5	6,38	12,39
	$a'\,^3\Sigma$	7,15	$:\dot{\mathrm{C}}=\dot{\mathrm{O}}:$	1,21	(1,33)	1182	9	4,8	12,0
	$A\,^1\Pi$	8,04	$\cdot\dot{\mathrm{C}}=\ddot{\mathrm{O}}:$	1,21	1,232	1515	17,18	4,07	12,11
	$b\,^3\Sigma$	10,35	$(\cdot\mathrm{C}\equiv\mathrm{O}:)\cdot$	1,08	1,086	(2109)	—	—	—
CO$^+$	$X\,^2\Sigma^+$	0	$\cdot\mathrm{C}\overset{\lceil\!\rightarrow}{\equiv}\mathrm{O}:$	1,08	1,114	2211	15,12	9,95	9,95
	$A\,^2\Pi_{\text{verk}}$	2,53	$:\mathrm{C}=\dot{\mathrm{O}}:$	1,21	1,212	1565	14,07	5,30	7,83
	$B\,^2\Sigma^+$	5,67	$\cdot\mathrm{C}\overset{\overline{\downarrow}}{=}\ddot{\mathrm{O}}:$	1,21	1,168	1720	24,25	3,67	9,34

Formed by First-row Elements.

of an electron pair and a single electron between the two atoms, and in the aspect of the resonating structure for the oxygen molecule, when the odd electrons from each of the two three-electron bonds are on the same oxygen atom, the energy quantities leading to stabilization would be the same as those that cause Hunds rule of maximum multiplicity to hold for atoms. Accordingly the triplet state should be stabilized, and the singlet state destabilized, by an appropriate amount.

We accordingly predict that the normal state of the oxygen molecule should be $^3\Sigma_g^-$, with two three-electron bonds with parallel spins, that the first excited state should be the double-bonded state $^1\Delta_g$, and that the next state should be another state with two three-electron bonds, $^1\Sigma_g^+$. Three states with these term symbols are in fact observed to be the low-lying states of the oxygen molecule. The difference in energy of $^1\Sigma_g^+$ and $^3\Sigma_g^-$ is 1,62 v.e., indicating that the interaction of the spins is for each of these states about 0,81 v.e. It may be pointed out that this value is not unreasonable in comparison with the separation of the Russell-Saunders states for the normal configuration of the oxygen atom. The ^1D level of the atom lies 1,97 v.e. above the normal ^3P state, and the ^1S level lies 4,19 v.e. above the normal state. Reference to Slaters treatment of atomic states[3] shows that the ^1D—^3P separation is equal

[3] J. C. Slater, Physic. Rev. 34, 1293 [1929].

to 6/25 F^2 (F^2 being a resonance integral for two p-electrons), and that the ${}^1S$—${}^3P$ separation is equal to 15/25 F^2. The resonance energy for a $p\pi_+$ and a $p\pi_-$ electron is $\pm 6/25\ F^2$, and hence the splitting of ${}^3\Sigma$ and ${}^1\Sigma$ would be predicted to be ± 1,97 v.e. (from ${}^1D$—${}^3P$) or ± 1,67 e.v. (from ${}^1S$—${}^3P$), the average being ± 1,82 e.v. But the two odd electrons of the two three-electron bonds would be on the same oxygen atom only half the time if resonance occurred independently in the bonds, and hence the splitting is predicted to be equal to ± 0,91 e.v. The experimental value ± 0,81 e.v. agrees very well with the predicted value, and even the small difference may be accounted for as resulting from a slight preference for the structures $:\underset{\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}\!-\!\underset{\cdot\cdot}{\overset{\cdot}{\mathrm{O}}}:$ and $:\underset{\cdot\cdot}{\overset{\cdot}{\mathrm{O}}}\!-\!\underset{\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:$, with neutral atoms, over the structures $:\underset{\cdot\cdot}{\overset{-\,\cdot\cdot}{\mathrm{O}}}\!-\!\underset{\cdot}{\overset{\cdot\,+}{\mathrm{O}}}:$ and $:\underset{\cdot}{\overset{+\,\cdot}{\mathrm{O}}}\!-\!\underset{\cdot\cdot}{\overset{\cdot\cdot\,-}{\mathrm{O}}}:$, involving a separation of charge.

The average energy of the two three-electron-bonded states is 0,81 v.e. above the normal state, and the energy of the double-bonded state is 0,98 v.e. Hence we see that two three-electron bonds are somewhat more stable (by 0,17 v.e.) than a single bond, as we have assumed.

Without promoting an electron into another atomic orbital, we may form two more bond structures for the oxygen molecule, by having one of the sets of three π electrons be in an anti-bonding relation, the electron pair and the single electron resonating between the two atoms in a destabilizing manner. Inasmuch as the three-electron anti-bond could occupy either π_+ or π_-, the other being occupied by a three-electron bond, there would be two structures of this sort, and for each of them a triplet state and a singlet state, with the triplet state lying lower, for the reason discussed above. Hence we anticipate that two ${}^3\Sigma$ states will occur next. These are shown in the table, as C and B. Their difference in energy results from the effect of the symmetrical and anti-symmetrical interchange of the anti-bonding and bonding groups of three electrons between the orbitals π_+ and π_-. Their close similarity in nature is shown by the closeness of their values of r_e. The large values of r_e for C and B, 1,58 and 1,60 Å, as compared with 1,46 for a single bond between the two oxygen atoms, indicate that the anti-bonding set of three electrons has more than enough destabilizing effect to counteract the three-electron bond.

The Oxygen Molecule-ion. There are two well-defined low-lying states of the oxygen molecule-ion reported in the literature, $X^2\Pi_g$ and $A^2\Pi_u$. We would predict for the normal state of this molecule the structure with a double bond and a three-electron bond. Its term symbol would be ${}^2\Pi_g$. The prediction of the first excited state cannot be made with confidence, but a low-lying state would have a structure in which there is a double bond between the two oxygen atoms and a three-electron anti-bond. The probability that these electronic structures are to be assigned to states X and A is shown by the approximate agreement of the predicted values of internuclear distances and the observed values. It may be mentioned that the uncertainty about the proper atomic radii to use amounts to a few hundredths of an Angström, and that exact agreement is not to be expected. The fact that $r_{e\ \mathrm{obs.}}$ for the state A is 0,05 Å larger than the predicted value indicates that the anti-bonding effect of three electrons is somewhat greater than the bonding effect.

A word may be said about the symmetry-character symbols g and u. Analysis of the significance of these symbols shows that two σ electrons or two π electrons combining symmetrically (to form a bond) lead to an even state, with symbol g. One σ electron forming a bond leads to an even state, and three σ electrons forming a bond to an odd state. One π electron forming a bond leads to an odd state, and three π electrons forming a bond to an even state. The formation of an anti-bond by one or three electrons reverses the state. Thus the three electrons forming a three-electron bond in the normal state of the oxygen molecule-ion cause this to be an even state, whereas the three-electron anti-bond in the state A causes it to be an odd state, with symbol u.

The Nitrogen Molecule. The nitrogen atom in its normal state is able to form three bonds, and it is not surprising that the normal state of the nitrogen molecule is the triple-bonded state, $X^1\Sigma_g^+$. We now ask what is the easiest way of exciting this molecule. To transfer one of the s electrons of the atom to a p orbital would require a good bit of energy. An easier way of exciting the molecule might be to destroy one of the bonds constituting the triple bond by unpairing two π electrons in the molecule, thus producing a ${}^3\Sigma_u^+$ state. This would give to the molecule a structure involving a double bond, with each nitrogen atom also possessing an unshared pair of electrons and an unshared single electron. The two unshared electrons on the two nitrogen atoms would not give rise to an anti-bond, but rather would produce no bonding effect at all. The argument supporting this conclusion can be conveniently based on the molecular-orbital viewpoint. A single electron may occupy a bonding molecular orbital or an anti-bonding molecular orbital. There are then four states possible for two electrons: a singlet state in which the two electrons occupy the bonding orbital, producing an electron-pair bond; a singlet state and a triplet state in which one of the two electrons occupies the bonding orbital and the other an anti-bonding orbital; and a singlet state in which the two electrons occupy the anti-bonding orbital. Thus in the triplet state we would expect the bonding and anti-bonding effects approximately to cancel one another. We identify this double-bonded structure with the first excited level, $A\,^3\Sigma_u^+$, of the nitrogen molecule, and predict the internuclear distance 1,27 Å, which is in approximate agreement with the observed value 1,290 Å.

If an s electron of one of the nitrogen atoms is promoted to the p orbital, it is possible to form between the two nitrogen atoms a double bond plus two three-electron bonds one of which, due to the outer σ electrons, should be relatively weak. This bond structure gives rise to four states, $^3\Pi_g$, $^3\Pi_u$, $^1\Pi_g$, and $^1\Pi_u$. A number of Π states have been observed; those for which the internuclear distance is known are given in the table. We predict this distance to be 1,19 Å for these states, in good agreement with the experimental value 1,207 Å for B and a, but somewhat larger than the value 1,144 Å for C, which may hence be presumed to have a somewhat different bond structure.

The Nitrogen Molecule-ion. The states $X\,^2\Sigma_g^+$ and $B\,^2\Sigma_u^+$ of the nitrogen molecule-ion are shown by the small values of their internuclear distances to be triple-bonded states. A triple bond can be formed between a nitrogen atom and a nitrogen ion in their normal configuration ($2s^2 2p^3$ and $2s^2 2p^2$, respectively): thus the nitrogen atom may be considered to present its $2s\sigma$ electron pair to a $p\sigma$ unoccupied orbital of the nitrogen ion, for formation of the σ bond, and the two π bonds required for the triple bond are then formed by pairing of odd electrons in p orbitals of the atom and ion. The normal state and the first excited state, at 3,18 v.e., correspond respectively to the stabilizing and destabilizing mode of resonance of the outer σ electron pair and odd electron. It is interesting to note that for the outer electrons the antisymmetric mode of combination is more stable than the symmetric mode. This effect may be the result of a more favorable aspect of the bonding σ electrons when the outer σ electrons are related in the antisymmetric way than when they are related in the symmetric way, and may well be associated with the phenomenon of ferromagnetism in the transition metals and similar substances.

The Carbon Molecule. Two carbon atoms in their normal configuration $2s^2 2p^2$ can form many kinds of bonds. Of these the most stable is a double bond plus a one-electron bond, formed by the use of the pair of $s\sigma$ electrons of one carbon atom in forming a single bond with the $p\sigma$ orbital at the other atom, leaving an outer electron pair on the first atom and an outer single σ electron on the other carbon atom. The π electrons of the two atoms then form the second half of a double bond and a one-electron bond. Four Π states containing this sort of bond can be constructed, $^3\Pi_u$, $^1\Pi_u$, $^3\Pi_g$, and $^1\Pi_g$. The stabilizing effect and maximum multiplicity when two odd electrons are on the same atom would cause the triplet state to be somewhat more stable than the singlet, and the interaction of the outer electron pair and odd electron would cause the odd state (even for these three electrons) to be more stable than the even state, the latter effect being greater than the effect of multiplicity. Hence we predict the $^3\Pi_u$ state to be the normal one, with the others following in the above order. This is presumably the order observed, although there is some uncertainty about the location of the singlet states relative to the triplet states. The internuclear distances for all four states correspond approximately to the value expected for a double bond plus a one-electron bond, with the distance somewhat larger for the antisymmetric resonance of the outer electrons than for the symmetric resonance, as is observed also for the nitrogen molecule and the nitrogen molecule-ion.

Diatomic Compound Molecules of First-Row Elements

Nitric Oxide. The normal state of the nitric oxide molecule is expected to be a $^2\Pi$ state containing a double bond and a three-electron bond. The predicted internuclear distance, 1,14 Å, agrees well with the observed distance, 1,146 Å.

The only other predicted low-lying state based on the same configuration is a $^2\Pi$ state in which there is a three-electron anti-bond. This is without doubt the state B, lying 5,65 e.v. above the normal state. The observed internuclear distance, 1,413 Å, is somewhat larger than that predicted, 1,33 Å, on the assumption that a three-electron anti-bond decreases the bond number by 0,6. This comparison increases the evidence that the effect of an anti-bond on internuclear distance is somewhat greater than the effect in the opposite direction of the corresponding bond.

The other three states, A, C, and D, are clearly shown by the observed internuclear distance 1,06 to 1,07 Å to be triple-bonded states. A triple bond can be formed in nitric oxide only by exciting one electron to an atomic orbital with total quantum number 3. The lowest states of this sort to be expected are four doublet states, three of which have been reported.

The Cyanide Molecule. For the cyanide molecule CN we expect two low-lying $^2\Sigma$ states, each corresponding to a triple bond, and one with a stabilizing and the other with a destabilizing resonance of the outer electron pair and odd electron. These states are observed—they are designated X and B—, the internuclear distance being close to the expected value 1,13 Å. A remaining low-lying state, intermediate between them in energy, is $A^2\Pi$, with internuclear distance 1,236 Å suggesting a double bond plus a one-electron bond. This sort of bond could be formed by the transfer of a π electron to an outer σ orbital, the loss of bond energy being partially compensated for by the gain in atomic energy resulting from the s character of the σ orbital.

Carbon Monoxide. A number of states of the carbon monoxide molecule have been reported. The five most stable states for which data are available (there are two others of undetermined energy that might lie rather low) are given in the table. For the normal state we expect a resonating bond with some triple-bond and some double-bond character. The observed internuclear distance 1,13 Å corresponds to bond number 2,6, calculated from the single-bond distance 1,42 Å. A much less stable orthogonal $^1\Sigma^+$ state can be predicted to exist, with bond number about 2,4 and internuclear distance about 1,16 Å.

A $^3\Sigma$ and a $^1\Sigma$ excited structure can be formulated by having an odd σ electron, presumably on the carbon atom. This would permit a double bond and a three-electron bond to be formed between the two atoms, except that the considerable difference in electronegativity of the atoms would cause the three-electron bond to be of little significance. We accordingly show in the table two structures, $a\,^3\Pi$ and $A^1\Pi$, with a double bond represented between the two atoms, and with two odd electrons, a σ electron and a π electron, on the carbon atom. The observed internuclear distances are very close to those expected for a double bond. Between these two states there lies a state $a'\,^3\Sigma$, to which the structure represented can be assigned, involving two unpaired π electrons. If these π electrons were to produce no repulsion the internuclear distance would be 1,21 Å, and it would be increased by an amount reflecting the magnitude of the repulsion caused by them. The observed vibrational frequency suggests a value for the internuclear distance of about 1,33, indicating a significant amount of repulsion.

The last state shown in the table, $b\,^3\Sigma$, has internuclear distance corresponding to a triple bond. We assign to it a structure in which an outer electron, with total quantum number greater than 2, moves in the field of a carbon monoxide cation, with a triple bond.

The Carbon Monoxide Molecule-ion. The carbon monoxide ion in its normal state is expected to resonate between the double bonded structure $\cdot C{=}\ddot{O}:$ and the triple bonded structure $\cdot C{\equiv}O:$, and its observed internuclear distance, 1,114 Å, agrees moderately well with the expected value, somewhat larger than 1,08 Å. The orthogonal resonating state would be expected to have internuclear distance somewhat smaller than the double-bond value 1,21 Å ; the observed value, for $B\,^2\Sigma^+$, is 1,168 Å. It is interesting that the bond numbers calculated by Equation (1) are 2,73 and 2,29 for $X\,^2\Sigma^+$ and $B\,^2\Sigma^+$, respectively, indicating the ratios 72 : 28 and 28 : 72 of the contributions of the triple-bonded and double-bonded structures. These ratios and the observed energy difference of the two states are compatible with the energies 1,54 e.v. (above $X^2\Sigma^+$) for the structure $\cdot C{\equiv}O:$ and 4,13 e.v. for the structure $\cdot C{=}\ddot{O}:$, and the

		A_0 v. e.	Bond structure	$r_{\text{predicted}}$ Å	r_e obs. Å	ω_e cm^{-1}	$\omega_e x_e$	$D_{\text{extrap.}}$ v. e.	$D_{\text{extrap.}} + A_0$ v. e.
S_2	$X\,^3\Sigma_g^-$	0	$:\mathrm{S}\overset{\cdot\cdot\uparrow}{\underset{\cdot\cdot\uparrow}{-}}\mathrm{S}:$	1,84	1,88	727	2,75	5,90	5,90
	$B\,^3\Sigma_u^-$	3,92	$:\underset{\cdot\cdot}{\mathrm{S}}\overset{\cdots}{-}\underset{\cdot}{\mathrm{S}}:$	2,08	2,19	435	2,75	2,09	6,01
SO	$X\,^3\Sigma^-$	0	$:\mathrm{S}\overset{\cdot\cdot\uparrow}{\underset{\cdot\cdot\uparrow}{-}}\mathrm{O}:$	1,46	1,489	1124	6,12	6,34	6,34
	$B\,^3\Sigma^-$	4,83	$:\underset{\cdot}{\mathrm{S}}\overset{\cdots}{-}\underset{\cdot\cdot}{\mathrm{O}}:$	1,70	1,769	629	5,65	2,08	6,91
P_2	$X\,^1\Sigma_g^+$	0	$:\mathrm{P}\equiv\mathrm{P}:$	1,86	1,88	780	2,812	6,66	6,66
	$a\,^1\Sigma_u^+$	5,80	$:\dot{\mathrm{P}}=\dot{\mathrm{P}}:$	1,99	2,12	475	2,60	2,66	8,46
SC	$X\,^1\Sigma$	0	$:\mathrm{S}\equiv\mathrm{C}:$	1,47	1,532	1285	6,5	7,82	7,82
	$A\,^1\Pi$	4,80	$:\mathrm{S}\overset{\cdots}{=}\mathrm{C}\cdot$	1,52	1,559	1072	10,3	3,38	8,18
PN	$A\,^1\Sigma$	0	$:\mathrm{P}\equiv\mathrm{N}:$	1,46	1,487	1337	6,98	7,85	7,85
	$B\,^1\Pi$	4,45	$\cdot\mathrm{P}\overset{\cdots}{=}\mathrm{N}:$	1,51	1,542	1103	7,22	5,24	9,69
SiO	$X\,^1\Sigma$	0	$:\mathrm{Si}\equiv\mathrm{O}:$	1,49	1,506	1242	6,05	7,84	7,84
	$A\,^1\Pi$	5,29	$\cdot\dot{\mathrm{Si}}=\ddot{\mathrm{O}}:$	1,62	1,617	852	6,14	3,60	8,89
PO	$X\,^2\Pi$	0	$:\mathrm{P}\overset{\cdots}{=}\mathrm{O}:$	1,47	1,443	1231	6,52	7,15	7,15
	$B\,^2\Pi$	3,78	$:\dot{\mathrm{P}}=\ddot{\mathrm{O}}:$	1,66	(1,46)*	1158	6,6	6,26	10,04
	$A\,^2\Sigma$	5,01	$(:\mathrm{P}\equiv\mathrm{O}:)\cdot$	1,42	1,402	1391	7,65	7,79	12,80
SN	$X\,^2\Pi$	0	$:\mathrm{S}\overset{\cdots}{=}\mathrm{N}:$	1,45	(1,44)*	1220	7,75	5,91	5,91
	$B\,^2\Pi$	4,93	$:\dot{\mathrm{S}}=\ddot{\mathrm{N}}:$	1,64	—	—	—	—	—
	$A\,^2\Sigma$	5,36	$(:\mathrm{S}\equiv\mathrm{N}:)\cdot$	1,40	—	—	—	—	—
SiN	$X\,^2\Sigma^+$	0	$\cdot\mathrm{Si}\equiv\mathrm{N}:$	1,53	1,568	1152	6,56	6,21	6,21
	$A\,^2\Pi$	—	$:\mathrm{Si}\doteq\mathrm{N}:$	1,58	(1,59)*	1031	16,74	1,91	—
	$B\,^2\Sigma^+$	3,00	$:\mathrm{Si}\equiv\mathrm{N}\cdot$	1,53	1,576	1034	18,39	1,75	4,75
PC	$X\,^2\Sigma$	0	$:\mathrm{P}\equiv\mathrm{C}\cdot$	1,53	1,558	1240	6,86	6,90	6,90
	$A\,^2\Pi$	0,84	$:\mathrm{P}\doteq\mathrm{C}:$	1,58	1,667	1062	6,04	5,74	6,58
	$B\,^2\Sigma$	3,58	$\cdot\mathrm{P}\equiv\mathrm{C}:$	1,53	1,685	836	5,92	3,62	7,20

* Estimated from ω_e by Badgers rule.

Table III. Other Diatomic Molecules.

value 2,56 e.v. for the resonance integral between the two structures.

Other Diatomic Molecules

Data for some other diatomic molecules are given in Table III. The bond structures assigned (column 4) are similar to those for corresponding molecules in Table II, and the predicted interatomic distances are those calculated with use of the ordinary radii in Table I, without the electronegativity correction.

It is seen that in general there is reasonably good agreement between the predicted and observed interatomic distances. Some of the differences may be eliminated by a refinement of the proposed structures; for example, the structures $:\mathrm{P} \overset{\cdots}{=} \mathrm{O}:$ for $X^2\Pi$ and $:\dot{\mathrm{P}} = \ddot{\mathrm{O}}:$ for $B^2\Pi$ may both be in resonance with structures involving a triple-bonded ion and an outer $4p\pi$ electron, $(:\mathrm{P} \equiv \mathrm{O}:)\cdot {}^2\Pi$.

With a few exceptions, such as the foregoing, the calculated distances are about 0,03 Å too small; presumably the system of radii and corrections summarized in Table I contains an error of this magnitude.

The state $A^1\Pi$ of SiO shows the effect of a large difference in electronegativity (1,7 units) in inhibiting three-electron-bond resonance. Whereas the values of r_e for the corresponding states of SC and PN (with electronegativity differences only 0,0 and 0,9, respectively) agree with those predicted for a structure with a double bond plus a three-electron bond, disagreement is found for SiO, the bond instead being essentially a double bond only.

Dissociation Energies and Bond Energies

It would be expected that if the assignments of valence-bond structures in Tables II and III are reliable they would be reflected in a systematic way in the dissociation energies of the molecules. However, the observed values of D_0 might well not make existent regularities apparent, because of the perturbing effect of the energy of stabilization of the normal states of the atoms into which the molecules dissociate. Thus the normal oxygen molecule, in which the bond may be said to be formed by bivalent oxygen atoms $:\underset{\cdot\cdot}{\dot{\mathrm{O}}}\cdot$, with configuration $2s^2 2p^4$, dissociates into oxygen atoms in the state $2s^2 2p^4\,{}^3P$, which is not identical with the valence state $2s^2 2p^4$ $:\underset{\cdot\cdot}{\dot{\mathrm{O}}}\cdot$; and for other elements also the atoms into which molecules dissociate have normal states differing in energy from their valence states by amounts characteristic of the element.

Application of the Slater theory[3] leads to the energy $-11/100\,F^2$ for the valence state of oxygen, the spectroscopic states ${}^3P$, ${}^1D$, and ${}^1S$ having energies $-5/25\,F^2$, $1/25\,F^2$, and $10/25\,F^2$, respectively. The ${}^1D$—${}^3P$ and ${}^1S$—${}^3P$ separations 1,967 and 4,190 v.e. then lead to 0,74 v.e. and 0,63 v.e., respectively, with weighted mean 0,66 v.e., for the energy of the valence state of oxygen relative to the ${}^3P$ ground state.

It seems not unreasonable that the potential energy function for the oxygen molecule in the neighbourhood of its minimum should be dependent only on the nature of the bond in the molecule, and in particular that it should not reflect the special interactions of the state ${}^3P$ of the atoms into which dissociation ultimately may occur. Hence a value of the dissociation energy obtained by extrapolation, $D_{\text{extrap.}}$, would be the energy required to dissociate the molecule into atoms in the valence state discussed above. The Morse function leads to the Birge-Sponer equation

$$D_{\text{extrap.}} = \frac{\omega_e^{\,2}}{4\,\omega_e x_e} - \frac{1}{2}\,\omega_e \qquad (2)$$

for this dissociation energy in cm^{-1}. The value found for O_2 $X^3\Sigma_g^-$ is 6,36 v.e.; when corrected by $2 \cdot 0{,}66$ v.e. this gives 5,04 v.e. for the energy of dissociation into normal oxygen atoms, in good agreement with the observed value $D_0 = 5{,}084$ v.e.

It may be seen from the values of $D_{\text{extrap.}} + A_0$ in the last column of Table II that the Morse extrapolation leads to exactly the same atomic energy level for the first excited state, $a^1\Delta_g$, of the oxygen molecule as for the normal state, and that essentially the same value (only 0,24 v.e. lower) is obtained for the next state, $A^1\Sigma_g^+$.

The spectroscopic data for sulfur indicate that the bivalent structure $:\underset{\cdot\cdot}{\dot{\mathrm{S}}}\cdot$ has energy 0,37 v.e. greater than the normal state S $3s^2 3p^4\,{}^3P$. Hence the value $D_{\text{extrap.}} = 5{,}90$ v.e. suggests that D_0 for S_2 $X^3\Sigma_g^-$ should be 5,16 v.e. The experimental value is uncertain; Gaydon[4] has suggested 4,4 + 0,1 v.e.

The value 6,34 v.e. for $D_{\text{extrap.}}$ for SO leads on correction by 0,37 + 0,66 for the valence states of the two atoms to $D_0 \cong 5{,}31$ v.e., in approximate agreement with the precisely known value 5,184 v.e.

The valence state for nitrogen, at 27/100 F^2 (with ^2D at 9/25 F^2 and ^2P at 3/5 F^2), is calculated to lie about 1,67 v.e. above the normal state, ^4S, that for the iso-electronic oxygen ion O^+ is 2,34 v.e., and that for phosphorus is 1,05 v.e. above their normal states. Similarly the bivalent states of carbon, $:\dot{\text{C}}\cdot$, the nitrogen ion, $:\dot{\text{N}}\cdot^+$, and silicon, $:\underset{\cdot}{\dot{\text{Si}}}\cdot$, are 0,44 v.e., 0,64 v.e., and 0,28 v.e., respectively, above the ^3P normal states. The valence corrections together with the values of $D_{\text{extrap.}}$ lead to values of the dissociation energy in rough agreement with the directly determined values for many molecules.

It is interesting to consider the nitrogen molecule and the carbon monoxide molecule, the dissociation energies of which remain uncertain despite much work and discussion. Values of D_0 for N_2 between 5,2 and 11,9 v.e. have been suggested in recent years, the most likely[4] being 7,383, 8,573, and 9,764 v.e. We note that $D_{\text{extrap.}}$ diminished by the valence correction for two nitrogen atoms is 8,46 v.e., supporting the value 8,573 v.e. Similarly the value 9,75 v.e. is found for carbon monoxide, which supports the predissociation value[5] 9,847 v.e., rather than the alternatives 11,11, 9,14, and 6,92 v.e. that have been proposed. However, the values of $D_{\text{extrap.}} + A_0$ for the first three excited states indicate 11,1 v.e. for D_0.

A rough correlation between $D_{\text{extrap.}}$ and bond type is evident for the more stable states of the diatomic molecules. Thus the bonds $\text{A} \overset{\cdots}{=} \text{A}$ and $\text{A} \dot{=} \text{A}$ between elements of the first short period tend to have dissociation energy to the atomic valence state equal to about 6,6 v.e. Examples are O_2^+ *X*, 6,51; N_2 *B*, 6,68; N_2 *a'*, 6,56; C_2 *A*, 7,05; C_2 *b*, 6,55 v.e. An increase, presumably due to the stabilizing effect of the partial ionic character of the double bond, is observed when the atoms differ by 0,5 in electronegativity: NO *X*, 7,69; CN *A*, 7,62 v.e.

There is striking agreement, at 7,84 ± 0,02 v.e., among the values of $D_{\text{extrap.}}$ for the normal states of SC, PN, and SiO, with the structures $:\text{A} \equiv \text{B}:$. The agreement extends even to the excited state $A\,^2\Sigma$ of PO, with a promoted outer electron, $(:\text{P} \equiv \text{O}:)\cdot$. The presence of two outer σ electron pairs is seen to stabilize the molecule, since $D_{\text{extrap.}}$ is smaller for triple-bonded structures with an odd outer σ electron — 6,90 for PC *X*, and 6,21 for SiN *X*. This is surprising; the resonance of the outer odd electron and electron pair, $\{\cdot\text{A} \equiv \text{B}:,\ :\text{A} \equiv \text{B}\cdot\}$, might be expected to contribute to the stabilization of the normal state, and to make such a bond stronger than the ordinary triple bond.

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[4] A. G. Gaydon, Dissociation Energies, Chapmann and Hall, Ltd., London 1947.

[5] H. D. Hagstrum and J. T. Tate, Physic. Rev. **59**, 354 [1941], have stated that 9,6 ± 0,2 v.e. is the only value which yields a consistent interpretation of all of the electron-impact observations made on carbon monoxide.

Polyhedral Harmonics

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It is a familiar fact and one which is frequently referred too in books on the methods of theoretical physics that solutions of the wave equation are possible in closed form only for domains of a very limited number of shapes. In the sequel, a solution for a region is meant to be a solution, which either vanishes itself or whose normal derivative vanishes on the boundary of that region. The limitation just referred to may concern both the shape of the bounding surface and the range of the curvilinear coordinates, which vary along the surface. As an example of the first type of restriction we note that solutions of the wave equations are known only for domains bounded