59. *Binding in Some Diatomic Molecules.*

By J. W. LINNETT.

The electronic configurations of a number of states of C_2, N_2, N_2^+, O_2, and O_2^+ have been considered and it has been shown that it is possible, and in some ways convenient, to describe them in terms of a combination of atomic and molecular orbitals. On this basis the number of electrons having a high probability of being between the two nuclei has been assessed for the various states and it has been shown that, to a good approximation, the bond lengths, relative to the Pauling single-bond lengths, are dependent (*a*) on the number of bond electrons, and (*b*) on the way in which these are distributed between σ and π orbitals. A similar behaviour is found for the force constants. The molecules CN, CO, CO^+, and NO have been examined with analogous results. The electronic configurations of maximum probability have been derived, and those of O_2 and other molecules considered. The stability of NO and other odd-electron molecules has been discussed.

THE purpose of this paper is to consider the electron configuration of some of the ground and excited states of the diatomic molecules and molecular ions derived from carbon, nitrogen, and oxygen atoms; and to see how the binding, as assessed by the bond length and vibration frequency, is related to the configuration. The symmetric molecules and ions will be considered first, and then CN, CO, CO^+, and NO.

The lowest-lying orbitals of these diatomic molecules may be represented, in order of binding, by σ_1, σ_2, π_1, σ_3, π_2, σ_4, the two orbitals occupied by the *K*-electron pairs of each atom being omitted from this series. For symmetrical diatomic molecules these six orbitals have additional symmetry and are written as σ_g, σ_u, π_u, σ_g, π_g, σ_u. The first two, σ_1 and σ_2 (or σ_g and σ_u), may be regarded as being derived mainly from the 2*s* atomic orbitals of the component atoms (though see p. 284) and, for those states of the diatomic molecules derived from C, N, and O which are considered here, electrons in these molecular orbitals do not seem, from what follows, to affect the equilibrium bond lengths and force constants appreciably (see p. 285). Electrons in the next two orbitals, π_1 and σ_3 (π_u and σ_g), are bonding. These two orbitals may be regarded as being derived primarily from the $2p\pi$ and $2p\sigma$ atomic orbitals. Electrons in the last two orbitals, π_2 and σ_4 (π_g and σ_u), are anti-bonding. They are also derived primarily from the $2p\pi$ and $2p\sigma$ atomic orbitals.

Orbitals of the Diatomic Molecules.—Let us consider the orbitals π_1 and π_2 of the molecule AB. There are two degenerate π_1 orbitals, which may be designated by π_1^+ and π_1^-, the Φ part of the two functions being $e^{+i\phi}$ and $e^{-i\phi}$ respectively, where ϕ is the azimuthal angle. Similarly, there are π_2^+ and π_2^- orbitals. Now it is usual, to a first approximation, to suppose that the molecular orbitals π_1^+ and π_2^+ can be represented satisfactorily by combining together atomic orbitals in the following way

$$\pi_1^+ = a\,.\,2p\pi_A^+ + b\,.\,2p\pi_B^+$$

and

$$\pi_2^+ = a'\,.\,2p\pi_A^+ - b'\,.\,2p\pi_B^+ \qquad \ldots\ldots\ (1)$$

where *a*, *b*, *a'*, and *b'* are all positive. If the molecule is symmetrical and A is the same as B, then

$$a = b \text{ and } a' = b' \qquad \ldots\ldots\ (2)$$

Suppose two electrons with parallel spin occupy the orbitals $\pi_1{}^+$ and $\pi_2{}^+$ and, for the moment, that there are only two electrons in the molecule. The wave function describing this situation and satisfying the Pauli principle is

$$\begin{vmatrix} \pi_1{}^+(1)\,.\,\alpha(1) & \pi_2{}^+(1)\,.\,\alpha(1) \\ \pi_1{}^+(2)\,.\,\alpha(2) & \pi_2{}^+(2)\,.\,\alpha(2) \end{vmatrix} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

both electrons, 1 and 2, having the same spin wave function, represented by $\alpha(1)$ and $\alpha(2)$. By the usual methods of handling determinants it is easy to show that (3) is identical with

$$\begin{vmatrix} 2p\pi_A{}^+(1)\,.\,\alpha(1) & 2p\pi_B{}^+(1)\,.\,\alpha(1) \\ 2p\pi_A{}^+(2)\,.\,\alpha(2) & 2p\pi_B{}^+(2)\,.\,\alpha(2) \end{vmatrix} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Thus, to describe these two electrons as occupying the $2p\pi_A{}^+$ and $2p\pi_B{}^+$ atomic orbitals on the separate atoms is the same as saying that they occupy the $\pi_1{}^+$ and $\pi_2{}^+$ molecular orbitals, for, since (3) and (4) are equal, they represent the same spatial distribution. In fact, because the atomic orbitals are only of considerable magnitude in different regions of space whereas the two molecular orbitals probably have considerable (absolute) magnitude in the same regions, the atomic description in (4) brings out more clearly the actual spatial distribution, the configuration of high probability being that in which the two electrons are on separate atoms. The above provides an example of the way in which two electrons having parallel spins tend to separate as far from one another as is consistent with maintaining a low average potential energy (see Lennard-Jones, Hall, and Pople, *Proc. Roy. Soc.*, 1949, *A*, **198**, 1, 14; 1950, *A*, **202**, 155, 166, 323, 336). The above considerations enable one to see easily why the antibonding effect of an electron in the orbital $\pi_2{}^+$ cancels any bonding effect of an electron in the orbital $\pi_1{}^+$ for the two electrons "force" one another from the region between the two nuclei where it is necessary for their distribution function to have a high value if they are to contribute to the binding together of the two atoms.

Some States of Symmetric Molecules.—The electronic configurations of some of the known states of C_2, N_2, O_2, $N_2{}^+$, and $O_2{}^+$ will be considered. The states that have been examined are those for which the bond lengths and vibration frequencies (and, hence, force constants) are known with considerable certainty, and for which the electronic structures are fairly reliably known. Unfortunately, it is not possible to be as certain of the latter, in many cases, as of the former. Consideration has been restricted to the more low-lying states since, for those, interaction between different electronic states is not likely to be large (cf. Ross, *Trans. Faraday Soc.*, 1952, **48**, 973) for they are more widely separated on an energy scale than the more highly excited states. The results for seven states of C_2, five of N_2, two of $N_2{}^+$, five of O_2, and four of $O_2{}^+$ are listed in Table 1. Col. 1 lists the electronic state of the molecule; col. 2 gives the distribution of the electrons among the molecular orbitals; col. 3 gives a more detailed representation of the way in which the electrons may be regarded as being distributed among the various orbitals, each occupied state being listed individually. In col. 3 the conclusions of the last section have been adopted and the representation in terms of atomic orbitals is used wherever possible (*i.e.*, instead of writing $\pi_u{}^+\,.\,\pi_g{}^+$ for two electrons with parallel spins in these orbitals, this column gives $2p\pi_A{}^+\,.\,2p\pi_B{}^+$ which is completely equivalent to it). Also, in this column, the spins of the electrons occupying the various states are indicated. The presence of an electron in a $2s_A$ orbital with a β-spin function is represented by $\overline{2s_A}$, while if an electron in the same state is associated with an α-spin wave function the bar over the $2s_A$ is omitted. In some cases two or more representations would apply to a given state equally well, and the complete wave function is then a combination of the wave functions corresponding to these representations; for instance, for the $^1\Sigma_g{}^+$ state of O_2 a combination of

$$2s_A\,.\,\overline{2s_A}\,.\,2s_B\,.\,\overline{2s_B}\,.\,2p\pi_A{}^+\,.\,2p\pi_B{}^+\,.\,\overline{2p\pi_A{}^-}\,.\,\overline{2p\pi_B{}^-}\,.\,\overline{\pi_u{}^+}\,.\,\pi_u{}^-\,.\,\sigma_g\,.\,\overline{\sigma_g}$$

and

$$2s_A\,.\,\overline{2s_A}\,.\,2s_B\,.\,\overline{2s_B}\,.\,\overline{2p\pi_A{}^+}\,.\,\overline{2p\pi_B{}^+}\,.\,2p\pi_A{}^-\,.\,2p\pi_B{}^-\,.\,\pi_u{}^+\,.\,\overline{\pi_u{}^-}\,.\,\sigma_g\,.\,\overline{\sigma_g}$$

In such circumstances only one has been given. The two exceptions to this are the $^3\Sigma_u{}^+$ and $^3\Sigma_u{}^-$ states of O_2 for which it is necessary to give the appropriate sum and difference

TABLE 1. *Values of the equilibrium bond lengths* (r_e) *and force constants* (k_e) *for different electronic states of some homopolar molecules with their electronic configurations. The scaling factors* r_1 (*Pauling's single-bond length*), r_2, k_1, *and* k_2 *are listed in Table* 3. *The spatial distribution of the electrons is indicated in col.* 10 (*see text*).

Electronic state	Electronic configuration		r_e	k_e	r_e/r_1	r_e/r_2	k_e/k_1	k_e/k_2	Electron pattern
	Summary	Detail							
C_2 molecule.									
d $^1\Sigma_u^+$	$\sigma_g^2.\sigma_u.\pi_u^4.\sigma_g$	$2s_A.2s_B.\overline{\sigma_g}(\pi_u^+.\overline{\pi_u^+}.\pi_u^-.\overline{\pi_u^-}.\overline{\sigma_g})$	1·2378	11·831	0·804	0·975	2·517	1·035	$sp^2(\pi^2)$; $s^{\frac{1}{2}}p^3(\sigma\pi^2)$
c $^1\Pi_g$	$\sigma_g^2.\sigma_u.\pi_u^3.\sigma_g^2$	$2s_A.2s_B.\overline{\sigma_g}(\pi_u^+.\overline{\pi_u^+}.\overline{\pi_u^-}.\sigma_g.\overline{\sigma_g})$	1·2730	11·568	0·827	1·003	2·461	1·012	$sp^2(\sigma\pi)$; $s^{\frac{1}{2}}p^3(\sigma\pi^2)$
b $^1\Pi_u$	$\sigma_g^2.\sigma_u^2.\pi_u^3.\sigma_g$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}(\pi_u^+.\overline{\pi_u^+}.\pi_u^-.\overline{\sigma_g})$	1·3180	9·143	0·856	1·038	1·945	0·800	$sp^2(\pi^2)$; $sp^2(\sigma\pi)$
a $^1\Sigma_g^+$	$\sigma_g^2.\sigma_u^2.\pi_u^4$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}(\pi_u^+.\overline{\pi_u^+}.\pi_u^-.\overline{\pi_u^-})$	1·2422	12·171	0·807	0·979	2·590	1·064	$sp^2(\pi^2)$; $sp^2(\pi^2)$
B $^3\Pi_g$	$\sigma_g^2.\sigma_u^2.\pi_u^2.\sigma_g.\pi_g$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+(\overline{\pi_u^-}\sigma_g)$	1·5350	4·328	0·997	1·209	0·921	0·378	$sp^2(\sigma)$; $sp(\pi)$
A $^3\Pi_g$	$\sigma_g^2.\sigma_u.\pi_u^3.\sigma_g^2$	$2s_A.2s_B.\overline{\sigma_g}(\pi_u^+.\overline{\pi_u^+}.\pi_u^-.\sigma_g.\overline{\sigma_g})$	1·2660	11·303	0·822	0·997	2·405	0·988	$sp^3(\sigma\pi^2)$; $s^{\frac{1}{2}}p^2(\sigma\pi)$
X $^3\Pi_u$	$\sigma_g^2.\sigma_u^2.\pi_u^3.\sigma_g$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}(\pi_u^+.\overline{\pi_u^+}.\pi_u^-.\sigma_g)$	1·3117	9·522	0·852	1·033	2·026	0·837	$sp^3(\sigma\pi^2)$; $sp(\pi)$
N_2 molecule.									
C $^3\Pi_u$	$\sigma_g^2.\sigma_u.\pi_u^4.\sigma_g^2.\pi_g$	$2s_A.2s_B.\overline{\sigma_g}.2p\pi_A^+.2p\pi_B^+(\overline{\pi_u^+}.\pi_u^-.\overline{\pi_u^-}.\sigma_g.\overline{\sigma_g})$	1·1482	17·082	0·820	1·000	2·847	1·000	$sp^3(\sigma\pi)$; $s^{\frac{1}{2}}p^3(\sigma\pi^2)$
B $^3\Pi_g$	$\sigma_g^2.\sigma_u^2.\pi_u^4.\sigma_g.\pi_g$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+(\overline{\pi_u^+}.\pi_u^-.\overline{\pi_u^-}.\sigma_g)$	1·2123	12·403	0·866	1·056	2·067	0·726	$sp^3(\sigma\pi)$; $sp^2(\pi^2)$
A $^3\Sigma_u^+$	$\sigma_g^2.\sigma_u^2.\pi_u^3.\sigma_g^2.\pi_g$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+(\pi_u^-.\overline{\pi_u^-}.\sigma_g.\overline{\sigma_g})$	1·293	8·796	0·924	1·126	1·466	0·515	$sp^3(\sigma\pi)$; $sp^2(\sigma\pi)$
a $^1\Pi_g$	$\sigma_g^2.\sigma_u^2.\pi_u^4.\sigma_g.\pi_g$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+(\overline{\pi_u^+}.\pi_u^-.\overline{\pi_u^-}.\overline{\sigma_g})$	1·213	11·808	0·866	1·057	1·968	0·691	$sp^3(\sigma\pi^2)$; $sp^2(\pi)$
X $^1\Sigma_g^+$	$\sigma_g^2.\sigma_u^2.\pi_u^4.\sigma_g^2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}(\pi_u^+.\overline{\pi_u^+}.\pi_u^-.\overline{\pi_u^-}.\sigma_g.\overline{\sigma_g})$	1·094	22·964	0·781	0·953	3·827	1·344	$sp^3(\sigma\pi^2)$; $sp^3(\sigma\pi^2)$
N_2^+ ion.									
B $^2\Sigma_u^+$	$\sigma_g^2.\sigma_u.\pi_u^4.\sigma_g^2$	$2s_A.2s_B.\overline{\sigma_g}(\pi_u^+.\overline{\pi_u^+}.\pi_u^-.\overline{\pi_u^-}.\sigma_g.\overline{\sigma_g})$	1·075	24·151	0·767	0·936	4·025	1·414	$sp^3(\sigma\pi^2)$; $s^{\frac{1}{2}}p^3(\sigma\pi^2)$
X $^2\Sigma_g^+$	$\sigma_g^2.\sigma_u^2.\pi_u^4.\sigma$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}(\pi_u^+.\overline{\pi_u^+}.\pi_u^-.\overline{\pi_u^-}.\sigma_g)$	1·1162	20·093	0·797	0·972	3·349	1·176	$sp^3(\sigma\pi^2)$; $sp^2(\sigma\pi)$
O_2 molecule.									
B $^3\Sigma_u^-$	$\sigma_g^2.\sigma_u^2.\pi_u^3.\sigma_g^2.\pi_g^3$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+.2p\pi_A^-.2p\pi_B^-[\overline{\pi_u^+}.\overline{\pi_g^-} - \overline{\pi_u^-}.\overline{\pi_g^+}](\sigma_g.\overline{\sigma_g})$	1·604	2·311	1·215	1·429	0·308	0·139	$sp^3(\sigma)$; $sp(p^2)^{\frac{1}{2}}(\sigma)$
A $^3\Sigma_u^+$	$\sigma_g^2.\sigma_u^2.\pi_u^3.\sigma_g^2.\pi_g^3$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+.2p\pi_A^-.2p\pi_B^-[\overline{\pi_u^+}.\overline{\pi_g^-} + \overline{\pi_u^-}.\overline{\pi_g^+}](\sigma_g.\overline{\sigma_g})$	1·42	3·160	1·076	1·265	0·421	0·191	$sp^3(\sigma)$; $sp^2(\sigma)$
b $^1\Sigma_g^+$	$\sigma_g^2.\sigma_u^2.\pi_u^4.\sigma_g^2.\pi_g^2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+.\overline{2p\pi_A^-}.\overline{2p\pi_B^-}(\overline{\pi_u^+}.\pi_u^-.\sigma_g.\overline{\sigma_g})$	1·2268	9·670	0·929	1·094	1·289	0·583	$sp^3(\sigma\pi)$; $sp^3(\sigma\pi)$
a $^1\Delta_g$	$\sigma_g^2.\sigma_u^2.\pi_u^4.\sigma_g^2.\pi_g^2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.\overline{2p\pi_A^+}.2p\pi_B^+.\overline{2p\pi_B^+}(\pi_u^-.\overline{\pi_u^-}.\sigma_g.\overline{\sigma_g})$	1·2155	10·732	0·921	1·083	1·431	0·647	$sp^3(\sigma\pi)$; $sp^3(\sigma\pi)$
X $^3\Sigma_g^-$	$\sigma_g^2.\sigma_u^2.\pi_u^4.\sigma_g^2.\pi_g^2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+.2p\pi_A^-.2p\pi_B^-(\overline{\pi_u^+}.\overline{\pi_u^-}.\sigma_g.\overline{\sigma_g})$	1·2074	11·766	0·915	1·075	1·569	0·709	$sp^3(\sigma\pi^2)$; $sp^3(\sigma)$
O_2^+ ion.									
b $^4\Sigma_g^-$	$\sigma_g^2.\sigma_u^2.\pi_u^4.\sigma_g.\pi_g^2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+.2p\pi_A^-.2p\pi_B^-(\overline{\pi_u^+}.\overline{\pi_u^-}.\sigma_g)$	1·2795	6·748	0·969	1·140	0·900	0·407	$sp^3(\sigma)$; $sp^2(\pi^2)$
A $^2\Pi_u$	$\sigma_g^2.\sigma_u^2.\pi_u^3.\sigma_g^2.\pi_g^2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+.\overline{2p\pi_A^-}.\overline{2p\pi_B^-}(\overline{\pi_u^+}.\sigma_g.\overline{\sigma_g})$	1·4089	3·816	1·067	1·255	0·509	0·230	$sp^3(\sigma\pi)$; $sp^2(\sigma)$
a $^4\Pi_u$	$\sigma_g^2.\sigma_u^2.\pi_u^3.\sigma_g^2.\pi_g^2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+.2p\pi_A^-.2p\pi_B^-(\overline{\pi_u^+}.\sigma_g.\overline{\sigma_g})$	1·3813	5·053	1·046	1·230	0·674	0·305	$sp^3(\sigma)$; $sp^2(\sigma\pi)$
X $^2\Pi_g$	$\sigma_g^2.\sigma_u^2.\pi_u^4.\sigma_g^2.\pi_g$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+(\overline{\pi_u^+}.\pi_u^-.\overline{\pi_u^-}.\sigma_g.\overline{\sigma_g})$	1·1227	16·587	0·851	1·000	2·212	1·000	$sp^3(\sigma\pi^2)$; $sp^3(\sigma\pi)$

TABLE 2. *Values of the equilibrium bond lengths* (r_e) *and force constants* (k_e) *for different electronic states of some heteropolar molecules with their electronic configurations. The scaling factors* r_1, r_2, k_1, *and* k_2 *are listed in Table* 3. *The spatial distribution of the electrons is indicated in col.* 10 (*see text*).

Electronic state	Electronic configuration		r_e	k_e	r_e/r_1	r_e/r_2	k_e/k_1	k_e/k_2	Electron pattern
	Summary	Detail							
CN molecule.									
B ${}^2\Sigma^+$	$\sigma_1^2.\sigma_2.\pi_1^4.\sigma_3^2$	$2s_A.2s_B.\overline{\sigma_2}(\pi_1^+.\overline{\pi_1^+}.\pi_1^-.\overline{\pi_1^-}.\sigma_3.\overline{\sigma_3})$	1·1506	17·829	0·777	0·933	3·639	1·423	$sp^3(\sigma\pi^2)$; $s^{\frac{1}{2}}p^3(\sigma\pi^2)$
A ${}^2\Pi_i$	$\sigma_1^2.\sigma_2^2.\pi_1^3.\sigma_3^2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}(\pi_1^+.\overline{\pi_1^+}.\pi_1^-.\sigma_3.\overline{\sigma_3})$	1·2327	12·533	0·832	1·000	2·558	1·000	$sp^3(\sigma\pi^2)$; $sp^2(\sigma\pi)$
X ${}^2\Sigma^+$	$\sigma_1^2.\sigma_2^2.\pi_1^4.\sigma_3$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}(\pi_1^+.\overline{\pi_1^+}.\pi_1^-.\overline{\pi_1^-}.\sigma_3)$	1·1718	16·291	0·792	0·951	3·325	1·300	$sp^3(\sigma\pi^2)$; $sp^2(\pi^2)$
CO molecule.									
a′ ${}^3\Sigma^+$	$\sigma_1^2.\sigma_2^2.\pi_1^3.\sigma_3^2.\pi_2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+(\pi_1^-.\overline{\pi_1^-}.\sigma_3.\overline{\sigma_3})$	1·359	5·992	0·924	1·106	1·362	0·573	$sp^3(\sigma\pi)$; $sp^2(\sigma\pi)$
a ${}^3\Pi_r$	$\sigma_1^2.\sigma_2.\pi_1^4.\sigma_3^2.\pi_2$	$2s_A.2s_B.\overline{\sigma_2}.2p\pi_A^+.2p\pi_B^+(\overline{\pi_1^+}.\pi_1^-.\overline{\pi_1^-}.\sigma_3.\overline{\sigma_3})$	1·2093	12·218	0·823	0·984	2·777	1·169	$sp^3(\sigma\pi)$; $s^{\frac{1}{2}}p^3(\sigma\pi^2)$
A ${}^1\Pi$	$\sigma_1^2.\sigma_2.\pi_1^4.\sigma_3^2.\pi_2$	$2s_A.2s_B.\overline{\sigma_2}.\overline{2p\pi_A^+}.\overline{2p\pi_B^+}(\pi_1^+.\pi_1^-.\overline{\pi_1^-}.\sigma_3.\overline{\sigma_3})$	1·2351	9·278	0·840	1·005	2·109	0·888	$sp^3(\sigma\pi^2)$; $s^{\frac{1}{2}}p^3(\sigma\pi)$
X ${}^1\Sigma^+$	$\sigma_1^2.\sigma_2^2.\pi_1^4.\sigma_3^2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}(\pi_1^+.\overline{\pi_1^+}.\pi_1^-.\overline{\pi_1^-}.\sigma_3.\overline{\sigma_3})$	1·1282	19·023	0·767	0·918	4·323	1·820	$sp^3(\sigma\pi^2)$; $sp^3(\sigma\pi^2)$
CO⁺ ion.									
B ${}^2\Sigma^+$	$\sigma_1^2.\sigma_2^2.\pi_1^4.\sigma_3$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}(\pi_1^+.\overline{\pi_1^+}.\pi_1^-.\overline{\pi_1}{}^-\sigma_3)$	1·1687	12·146	0·795	0·951	2·761	1·162	$sp^3(\sigma\pi^2)$; $sp^2(\pi^2)$
A ${}^2\Pi_i$	$\sigma_1^2.\sigma_2^2.\pi_1^3.\sigma_3^2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}(\pi_1^+.\overline{\pi_1^+}.\pi_1^-.\sigma_3.\overline{\sigma_3})$	1·2437	9·855	0·846	1·012	2·240	0·943	$sp^3(\sigma\pi^2)$; $sp^2(\sigma\pi)$
X ${}^2\Sigma^+$	$\sigma_1^2.\sigma_2.\pi_1^4.\sigma_3^2$	$2s_A.2s_B.\overline{\sigma_2}(\pi_1^+.\overline{\pi_1^+}.\pi_1^-.\overline{\pi_1^-}.\sigma_3.\overline{\sigma_3})$	1·1151	19·802	0·759	0·907	4·500	1·895	$sp^3(\sigma\pi^2)$; $s^{\frac{1}{2}}p^3(\sigma\pi^2)$
NO molecule.									
B ${}^2\Pi_r$	$\sigma_1^2.\sigma_2^2.\pi_1^3.\sigma_3^2.\pi_2^2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+.\overline{2p\pi_A^-}.\overline{2p\pi_B^-}(\overline{\pi_1^+}.\sigma_3.\overline{\sigma_3})$	1·385 1·448	4·743 4·730	1·011 1·057	1·204 1·258	0·753 0·751	0·297 0·297	$sp^3(\sigma\pi)$; $sp^2(\sigma)$ —
X ${}^2\Pi_{\frac{3}{2}}$ ${}^2\Pi_{\frac{1}{2}}$	$\sigma_1^2.\sigma_2^2.\pi_1^4.\sigma_3^2.\pi_2$	$2s_A.\overline{2s_A}.2s_B.\overline{2s_B}.2p\pi_A^+.2p\pi_B^+(\overline{\pi_1^+}.\pi_1^-.\overline{\pi_1^-}.\sigma_3.\overline{\sigma_3})$	1·1508 —	15·940 15·946	0·840 —	1·000 —	2·530 2·531	1·000 1·000	$sp^3(\sigma\pi^2)$; $sp^3(\sigma\pi)$ —

combinations of the wave functions corresponding to the basic representations (see p. 280). In Table 1 the occupied orbitals having large values in the region between the atoms, the electrons in which are therefore bonding, are enclosed in parentheses. In col. 4 of Table 1 the observed equilibrium internuclear distances r_e are listed. These are taken from Herzberg (" Molecular Spectra and Molecular Structure of Diatomic Molecules," Van Nostrand Co. Inc., 1950). Col. 5 gives the force constants k_e derived from the observed vibration frequencies which are also taken from Herzberg (*op. cit.*). In col. 6 the bond lengths listed in col. 4 are divided by the C–C, N–N, and O–O single-bond lengths r_1

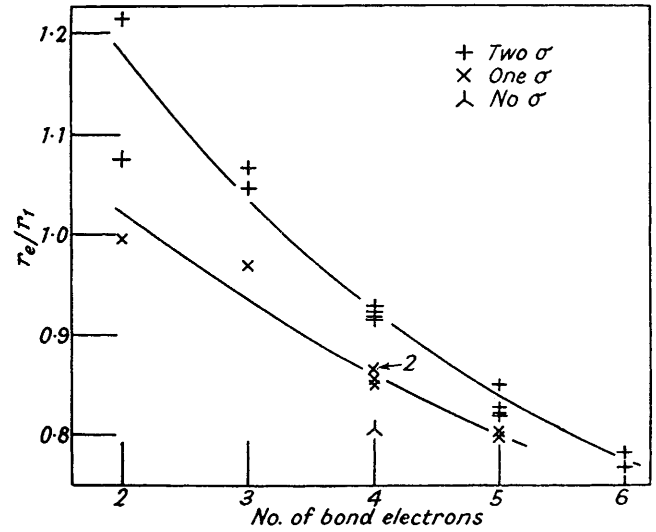


FIG. 1. *Graph of r_e/r_1 against the number of bond electrons for C_2, N_2, N_2^+, O_2, and O_2^+, when r_1 (Pauling's single-bond length) has the values listed in Table 3.*

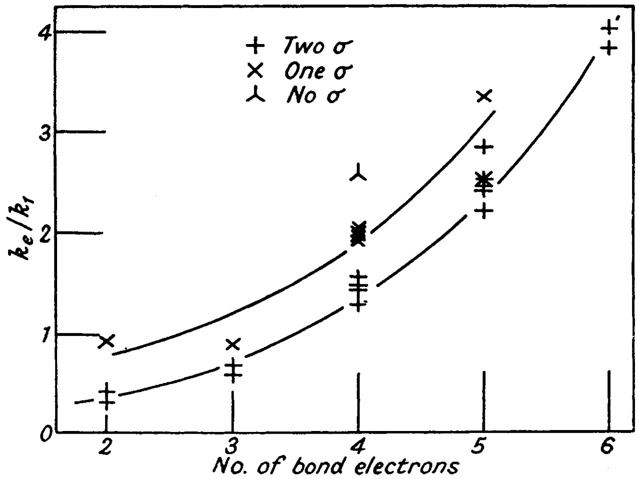


FIG. 2. *Graph of k_e/k_1 against the number of bond electrons for C_2, N_2, N_2^+, O_2,* and *O_2^+, when k_1 has the values listed in Table 3.*

given by Pauling (1·54, 1·40, and 1·52 Å, respectively; " Nature of the Chemical Bond," Cornell Univ. Press, 1939, p. 167). In col. 7 another scaling procedure has been carried out on the bond lengths by using as standards the bond lengths (or mean of several) for those structures in which bonding is by two σ_g and three π_u electrons * [for CC, NN, and OO, these are 1·2695 (mean of two values), 1·1482, and 1·1227 Å respectively]. In col. 8 a procedure analogous to that in col. 6 has been carried out for the force constants of col 5. The scaling constants, arbitrarily chosen (see p. 280), are 4·7, 6·0, and 7·2 × 10^5 dynes cm.$^{-1}$

---

* The sole reason for choosing this group of bonding electrons is that it alone is to be found in some state binding together CC, NN, OO, CN, CO, and NO.

for CC, NN, and OO. In col. 9 a procedure similar to that in col. 7 has been carried out on the force constants, the three scaling constants being 11·435, 17·082, and 16·587 × 10^5 dynes cm.$^{-1}$. Col. 10 is explained in the Discussion (p. 283).

The data in cols. 6 and 8 of Table 1 are presented graphically in Figs. 1 and 2, in both of which the points for states in which two, one, or none of the bonding electrons are σ_g electrons are represented differently. In obtaining the results presented in Fig. 1 it was not unnatural to attempt to scale the data for the different molecules according to Pauling's values for single-bond lengths (the exact values used would not be critical). For the force-constant results in Fig. 2 an effort was made to treat them in an analogous manner. The standard values chosen (4·7, 6·0, and 7·5 × 10^5) were selected after an examination of the force constants and electronic structure for which there are four bonding electrons and, unlike the normal single-bond lengths used for Fig. 1, these three figures are arbitrary. The results in both Figures will be considered in the Discussion.

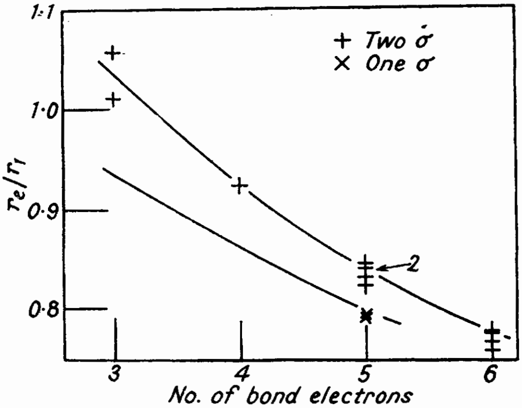
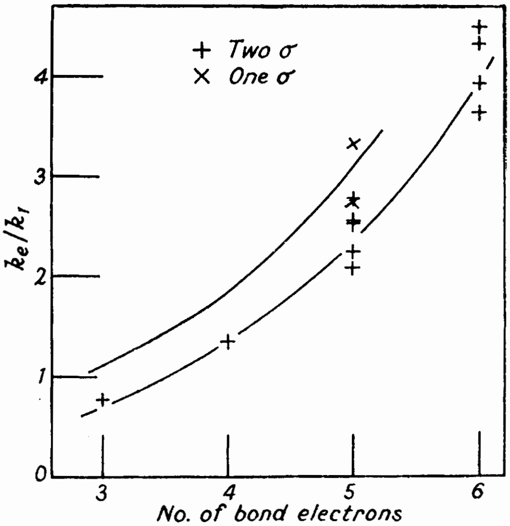


FIG. 3. *Graph of r_e/r_1 against the number of bond electrons for* CN, CO, CO$^+$, *and* NO *when r_1 has the values listed in Table* 3. (The lines are the same as in Fig. 1.)

FIG. 4. *Graph of k_e/k_1 against the number of bond electrons for* CN, CO, CO$^+$, *and* NO *when k_1 has the values listed in Table* 3. (The lines are the same as in Fig. 2.)



In Table 1 it will be seen that the $^3\Sigma_u^+$ and $^3\Sigma_u^-$ states of O_2 are described as having two bonding electrons. The reason for this is as follows. If the combination $(\pi_u^+ . \pi_g^- - \pi_u^- . \pi_g^+)$ is multiplied out, it is found to be equal to $[2p\pi_A(i) . 2p\pi_A(j) - 2p\pi_B(i) . 2p\pi_B(j)]\sin(\phi_i - \phi_j)$, while $(\pi_u^+ . \pi_g^- + \pi_u^- . \pi_g^+)$ equals $[2p\pi_A(i) . 2p\pi_B(j) - 2p\pi_A(j) . 2p\pi_B(i)]\cos(\phi_i - \phi_j)$, where i and j are the two electrons and $2p\pi_A$ is that part of $2p\pi_A^+$ and $2p\pi_A^-$ which is independent of ϕ. The electrons in these orbitals do not contribute to the bond, and therefore the only bond electrons are the two in the σ_g orbital.

The $^3\Sigma_u^-$ state involves a combination of ionic states, so it is not surprising that it has a higher energy than the $^3\Sigma_u^+$ state in which the pair of electrons in these orbitals have a high probability of being on the separate atoms.

Some States of Heteropolar Molecules.—Data for some states of CN, CO, CO$^+$, and NO are given in Table 2, the same columns being used as in Table 1. The results in cols. 6 and 8 are shown graphically in Figs. 3 and 4, the lines being drawn in these graphs to be identical with those of Figs. 1 and 2 respectively. The single-bond lengths used for scaling (1·48 for CN, 1·47 for CO and CO$^+$, and 1·37 for NO) were chosen to bring the results for these molecules in Fig. 3 most closely in line with those for the symmetric molecules in Fig. 1. The force constant scaling factors in col. 8 of Table 2 (graph in Fig. 4) were chosen in the same way relative to the results in Fig. 2.

The data listed in cols. 7 and 9 of Tables 1 and 2 are shown graphically in Figs. 5 and 6, the representation being similar to that used in Figs. 1—4.

DISCUSSION

The results shown in Fig. 1 are perhaps the most interesting. Consider the nine states involving four bonding electrons. The four for which there are two σ and two π electrons in the bond all have a bond length relative to the single bond length which is close to 0·92 (three for O_2 and one for N_2). The four which have one σ and three π electrons in the bond have a relative bond length of about 0·86 [two are for N_2 (superimposed) and two for C_2]. The state of C_2 with four π but no σ electrons in the bond region has the relative bond length of about 0·81. The same type of behaviour is apparent for the states having five electrons in the bond (*i.e.*, those having two σ electrons form one group having a relative bond length greater than the two having one σ electron in the bond). The situation is the same when there are two and three electrons in the bond though fewer such states are known with these molecules.

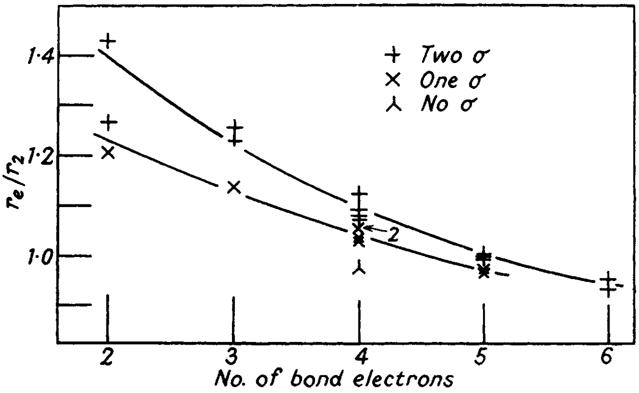


FIG. 5*a*. *Graph of* r_e/r_2 *against the number of bond electrons for* C_2, N_2, N_2^+, O_2, *and* O_2^+ *when* r_2 *has the values listed in Table* 3.

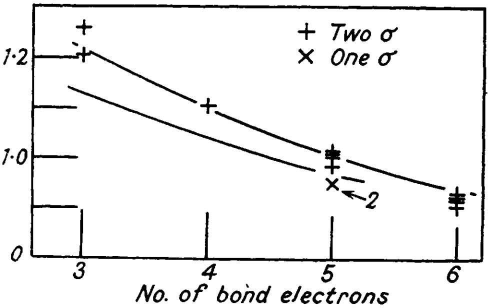


FIG. 5*b*. *Graph of* r_e/r_2 *against the number of bond electrons for* CN, CO, CO$^+$, *and* NO *when* r_2 *has the values listed in Table* 3. (The lines are the same as in Fig. 5*a*.)

In Fig. 1 a smooth curve has been drawn which passes near the points for states involving two σ bonding electrons, and another line, below it, which passes near the points for states involving only one σ bonding electron. The figure shows that, for a given number of σ electrons in the bond, the length (relative to the Pauling single-bond length) is governed quite closely by the number of electrons in the bond. The variation, for a given electron grouping, seems to become greater the smaller the number of electrons in the bond (cf. the two states of O_2 involving only two bonding electrons). So, as regards equilibrium bond length (relative), there appear to be two main effects. The first, and more important, is the number of electrons in the bond region. The second is that the length depends on the number of σ electrons. The effect of this is quite considerable and is that the bonds are longer, for a given number of bonding electrons, the more of these that are σ electrons (in Fig. 1 there is no exception to this).

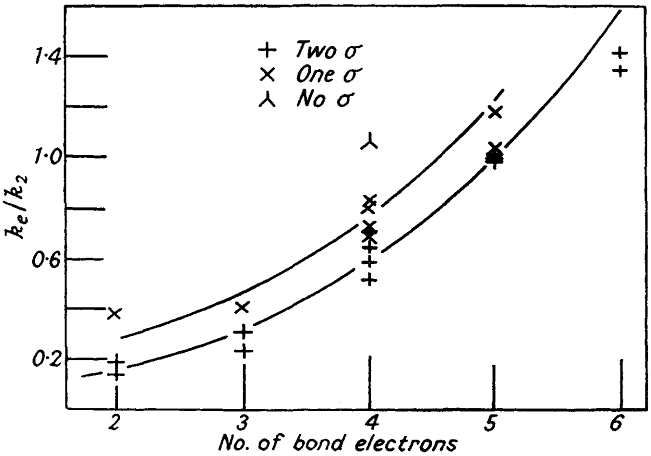


FIG. 6a. *Graph of k_e/k_2 against the number of bond electrons for* C_2, N_2, N_2^+, O_2, *and* O_2^+ *when* k_2 *has the values listed in Table* 3.

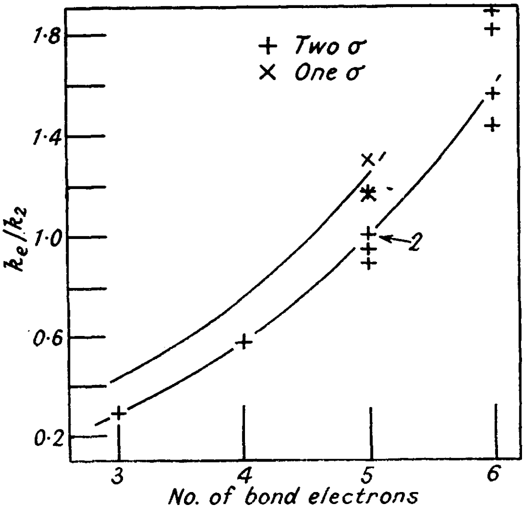


FIG. 6b. *Graph of k_e/k_2 against the number of bond electrons for* CN, CO, CO^+, *and* NO *when* k_2 *has the values listed in Table* 3. (The lines are the same as in Fig. 6*a*.)

The results in Fig. 3 show that the data for heteropolar molecules are in good agreement with the above, though it must be remembered that arbitrary single-bond lengths were chosen for these molecules. The results in Fig. 5 are also of the same type and are presented here because, for these results, no arbitrary choice was made for the scaling factor for the heteropolar molecules. All scaling factors were chosen in the same way, being the bond length (or mean of several) when two σ and three π electrons are involved in the bond. The disadvantage of this treatment is that it places particular importance on the bond lengths of a few states (*i.e.*, those used as standards).

The analogous data for force constants are presented in Figs. 2, 4, and 6. The general form of these results is the same as that obtained for bond lengths, though the spread of values for a given electron grouping is greater than for the bond lengths. The scaling constants used in obtaining the data for Figs. 2 and 4 were arbitrarily chosen.

The scaling factors used in the previous sections are summarised in Table 3. As regards the bond lengths, the standard value for AB is, in all instances, greater than the mean of those for AA and BB. This is true for the approach summarised in Figs. 1 and 3, and also for that of Fig. 5. Moreover, the results for the force constants show the same behaviour since the standard force constant for AB is, in all cases, less than the mean of those for AA and BB. Further, in every column of Table 2, the difference from the mean is greater for CO than for CN and NO. This would be expected if it arises from the difference between the two nuclear charges in the heteropolar molecules. This result appears to be different from that generally accepted for polyatomic molecules. For example, Stevenson and Schomaker (*J. Amer. Chem. Soc.*, 1941, **63**, 37), in modifying Pauling's scale of normal single-bond lengths, suggested that the length of the bond A–B would be *less* than the mean of those of A–A and B–B, the difference from the mean being greater the greater the electronegativity difference between A and B. Also, Pauling (*loc. cit.*), when formulating his scale of electronegativities, reached the conclusion that the bond energy of AB was greater than the mean of the bond energies of AA and BB, the difference again being greater the greater the electronegativity difference. The reason for the reverse conclusion found here is not easy to see, but it may arise because Pauling and Stevenson and Schomaker were concerned mainly with single bonds in polyatomic molecules in which electrons not in the bond under consideration were often shared with other atoms. The results given in this paper are largely for bonds stronger and shorter than single bonds and the electrons not in the bond are always unshared.

TABLE 3. *The scaling factors r_1, r_2, k_1, and k_2 used in Tables* 1 *and* 2, *cols.* 6—9; *data are shown graphically in Figs.* 1—6; *r_1 and r_2 are in* Å, *and k_1 and k_2 in units of* 10^5 *dynes cm.$^{-1}$.*

	Bond lengths		Force constants	
Atom pair	Figs. 1 & 3 Col. 6 (r_1)	Fig. 5 Col. 7 (r_2)	Figs 2 & 4 Col. 8 (k_1)	Fig. 6 Col. 9 (k_2)
CC	1·54	1·27	4·7	11·4
NN	1·40	1·15	6·0	17·1
OO	1·32	1·12	7·5	16·6
CN	1·48	1·23	4·9	12·5
CO	1·47	1·23	4·4	10·5
NO	1·37	1·15	6·3	15·9

To the extent that the chemist tends to regard σ bonds as stronger than π bonds the results presented in Figs. 1—6 are surprising. However, it has only been shown that the presence of a σ electron rather than a π electron in a bond containing a given number of electrons causes the bond to be longer and to have a lower force constant. There has been no consideration of heats of dissociation. The reason for the results obtained here must lie in the spatial distribution of the electrons and these will now be considered.

Spatial Distribution of Electrons.—An attempt has been made to give some indication of the spatial distribution of the electrons in the various states in the last column of Tables 1 and 2. In the symmetrical molecules the spatial distribution of electrons is symmetrical for all states in the sense that the dipole moment is zero for all states. In the last column of Table 1 the electrons of each spin are described separately. For each spin the distribution at each atom is given for both shared and unshared electrons which are members of this set. For example $sp^3(\sigma\pi)$ means that round each atom there is a group of four electrons, the contributing atomic orbitals being the 2*s* and three 2*p*. Of these electrons two are shared with the other atom, one occupying a σ orbital and the other a π orbital (this is half an ordinary double bond). The description $sp^2(\pi)$, which involves five electrons in all, means that the grouping at each atom is sp^2 and that one electron is shared, two being unshared; the one shared is in a π orbital. This is a binding configuration not encountered in polyatomic molecules. Finally, the symbol $s^{\frac{1}{2}}p^3(\sigma\pi^2)$ (see ${}^1\Sigma_u{}^+$ state of C_2) means that there is a $\sigma_g 2s$ non-bonding electron shared between the two atoms, that, in addition, each atom is employing three $2p$ orbitals, and that there are three shared electrons in a σ and two π orbitals. Four electrons, in all, are involved in this grouping. The situation is that, at any instant, one atom has three bonding electrons associated with it while the other has three bonding and one lone electron. However, there is an equal probability of each having three and each having four. The mode of representation used in col. 10 of Tables 1 and 2 does not give a complete description of the electron distribution even within its own limitations. For instance, the $^1\Sigma_g^+$ and $^1\Delta_g$ states of O_2 are both described as $sp^3(\sigma\pi)$; $sp^3(\sigma\pi)$, though they involve different distributions. The difference lies in the relation of the electrons of one spin to those of the other. Nevertheless they are of help in visualising the distribution.

Lennard-Jones *et al.* (*loc. cit.*) have shown that the system of two electrons with parallel spin in σ and π bonding orbitals can be described equally well by the equivalent orbitals which are the sum and difference of the more usual σ and π molecular orbitals. The use of equivalent orbitals brings out more clearly the actual spatial arrangement of the electrons, for the most probable configuration is that in which the two bonding electrons are disposed symmetrically each side of the line joining the two atoms and, for symmetrical molecules, half way between them. Similarly, for the triple bond grouping $\sigma\pi^2$ of three electrons having parallel spins the most probable configuration is that in which the three electrons are symmetrically disposed in the form of an equilateral triangle round the line joining the two atoms. Again, Lennard-Jones *et al.* give the appropriate equivalent orbitals. These representations of the double and triple bonds come close to the older representations (*e.g.*, that of Baeyer). Consequently, in the group of six electrons $sp^3(\sigma\pi)$ the most probable configuration is that in which each atom has four electrons of the particular spin under consideration around it, these being arranged at the corners of a tetrahedron which is not far from being regular; of these there are two electrons on each atom which are unshared and two which are shared. For the group $sp^3(\sigma\pi^2)$ each atom has a tetrahedral group of four but one is unshared and three are shared. For $sp^2(\sigma)$ each atom has a group of three disposed, in the configuration of maximum probability, in the form of a triangle round it with two unshared on each atom and one shared between the two atoms. Other arrangements can be visualised on similar lines. The arrangements $sp(\pi)$, $sp^2(\pi)$, and $sp^2(\pi^2)$ (cf. states of N_2 and C_2) are more difficult to describe. In the first there are two electrons of a particular spin round each atom, one of which is shared and one unshared. From the known configuration of maximum probability of two electrons with parallel spins in $2s$ and $2p$ orbitals it would seem that the pair on each atom will be approximately on opposite sides of the nucleus but that the line joining them will be at an angle to the line joining the two atoms, the shared electron being away from the internuclear line in the most probable configuration. The overall, time average, distribution will, of course, be axially symmetrical. The other two arrangements are similar but each involves three electrons round each atom.

On the basis of the above treatment the two σ orbitals (σ_g and σ_u or σ_1 and σ_2) are presumably best described in terms of combinations of $2s$ and $2p\sigma$ atomic hybrids rather than as combinations of the $2s$ atomic orbitals. There is no objection on the basis of symmetry to this, since combination of the $2s$ orbitals leads to σ_g and σ_u orbitals, as does the combination of the $2p\sigma$ atomic orbitals. The hybrids for these two σ orbitals are then those in which the electrons occupying them are located with highest probability on the far side of the atom from the other atom. Being outside the bond region they would not be expected to affect the equilibrium bond length and force constant greatly. That this is so is indicated by the results in Tables 1 and 2. For example, the $^1\Sigma_u^+$ state of C_2 and the $^2\Sigma_g^+$ state of N_2^+ both have the bonding group ($\pi_u^4\sigma_g$), and the relative bond lengths (col. 6) are 0·804 and 0·797 even though they have different numbers of electrons (3 and 4 respectively) in the lower-lying σ orbitals. Comparison may also be made for the nine states having the bonding group ($\pi^3\sigma^2$). There are four states for which the σ_1 and σ_2 orbitals (or σ_g and σ_u) are filled and the mean bond length (col. 6) is 0·84. There are five states for which there are three electrons in these two σ orbitals and the mean figure for these is 0·83. The difference is therefore small, though it may indicate that electrons in these orbitals do exert a small effect on the bond length. However, it is small, being less than other variations considered in this paper and less than variations with other groupings of bonding electrons.

It should perhaps be pointed out that, in all the states considered in Tables 1 and 2 in which the grouping $(\sigma_1{}^2\sigma_2)$ exists, there is also present at least one electron in the σ_3 orbital; and moreover that, if only one electron is present in the σ_3 orbital, the resultant spin of the group of four electrons is zero. So, for all states examined one electron in the σ_1 orbital has its spin parallel to that of the electron in the σ_2 orbital, while the other has the same spin as the electron in the σ_3 orbital.

It follows from the above that the other σ_g orbital (σ_3) is then constructed from hybrids more concentrated in the bond region. No state has been considered in this paper in which there is an electron in the high-energy σ_u (or σ_4) orbital.

On the basis of the above, the ground states of N_2 and CO are ordinary triple bonds, there being three electrons of each spin concentrated in the bond region, each set of three having a similar configuration. However, the ground state of O_2, on this interpretation, is to be regarded as involving a distribution of electrons such that those of one spin form half a triple bond $(\sigma\pi^2)$, while those of the other spin form half a single (σ) bond. The distribution of electrons in the configuration of maximum probability can be described in the following way. Seven electrons of one spin are arranged at the corners of two tetrahedra with a common apex between the nuclei which are located inside the two tetrahedra; five electrons of the other spin are at the corners of two tetrahedra with a common base between the nuclei which are located inside the two tetrahedra. There are therefore four electrons between the two nuclei.

The first and the second excited state of O_2 involve the more normal double $(\sigma\pi)$ bonds. The difference between these two states has already been considered. All three states involve a concentration of four electrons in the bond region, and their equilibrium bond lengths are very nearly the same. The reason why the configuration involved in the $^3\Sigma_g{}^-$ state leads to the lowest energy is possibly that, in this state, the electrons concentrated in the bond region (and also the lone electrons) are, by the effect of the Pauli principle, separated spatially in the configuration of maximum probability so that the mean inter-electronic repulsion energy is less than for the other two states. The description of the binding in the ground state of O_2 as resulting from one single bond and two three-electron bonds is very close to the above if it is realised that the group of three electrons in a three-electron bond is distributed so that one electron (of one spin) has a high probability of being in the bond region while the other two (of the opposite spin) have a high probability of being on the two atoms, being " forced " out of the bond region because two electrons of the same spin tend to separate widely from one another. The present treatment therefore provides a bridge between the molecular-orbital and valence-bond descriptions.

Odd-electron Molecules.—The ground state of NO (and of $O_2{}^+$) has the electron distribution represented by $sp^3(\sigma\pi^2);sp^3(\sigma\pi)$ so that each atom is surrounded by a quartet of electrons of each spin but those of one spin contribute half a triple bond while those of the other contribute half a double bond, there being, in all, five electrons in the bond region. It is interesting to consider the dimerisation of NO on the present basis. One NO molecule involves three lone electrons on each atom and five in the bond region. If the dimer is to be produced it must be O=N–N=O. This structure involves twelve unshared electrons and ten shared electrons, which is the same as for two NO molecules. So, if there is any lowering of energy on dimerisation it is likely to be small. Though NO has an odd electron it cannot be said to have a free valency because, if an extra electron is brought on to the nitrogen (as must happen if the nitrogen is to form a two-electron covalent bond to another atom) the extra electron must be of such spin as to make two electron pairs on the nitrogen atom which are unshared with the oxygen atom, and thus the additional electron must have the same spin as the group of three in the bond region. Therefore, because in the first short period five electrons of parallel spin have a very low probability of being near one atom simultaneously, the addition of this extra electron must force one electron out of the NO bond region (in ONNO this would happen for both NO bonds). Therefore, the formation of the additional N–N bond must lead to a weakening of the two NO bonds from 2½-bonds to double bonds. There can therefore be little lowering of energy on association to counter the increase of entropy resulting from dissociation. The situation bears no resemblance at all to the association of halogen atoms or of free radicals like methyl which also contain an odd number of electrons.

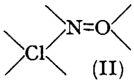
But why is NO so stable compared with other possible diatomic odd-electron molecules involving elements of the first short period? The molecule CN is also formed from elements in adjacent groups of the Periodic Table; but it readily dimerises at ordinary temperatures to NCCN which has, in all, seven bonds. For there to be no increase in the total number of bonding electrons on association (this being the case for NO) the bond in CN would have to involve seven electrons. That is, four electrons of the same spin would have to be in the bond region. This is impossible because four valency shell electrons near an atom of the first short period must tend to distribute themselves tetrahedrally round the atom if they have the same spin. Consequently, there cannot be more than three electrons of the same spin serving to bind one atom to another. Hence the association of two CN molecules must lead to an increase in the number of bonding electrons and therefore association is much favoured energetically, and resembles the combination of halogen atoms and methyl radicals.

The molecule FO would also have an odd number of electrons and might resemble NO in existing as a monomer. However, the dimer F_2O_2 undergoes thermal decomposition at temperatures little greater than −100° to O_2 and F_2. Nitric oxide is also unstable at room temperature with respect to N_2 and O_2, but the conversion involves a high energy of activation possibly because the change necessitates a considerable rearrangement of the electrons. The oxide KO_2 contains a paramagnetic ion O_2^- which contains 17 electrons (as would OF). It is tentatively suggested that this ion possesses stability with respect to dimerisation, analogous to that of NO, because on association two bonds involving three electrons in the bond region would be converted into three two-electron bonds. For this reason the association of this ion to O_4^{2-} would be expected to bear more resemblance to that of NO than to that of CN.

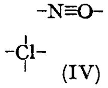
The low tendency of NO_2 and ClO_2 to dimerise may be accounted for in the same terms as for NO.

In the nitrosyl halides, XNO, the X–N bond lengths are much greater than the normal single-bond lengths while the N–O bond has approximately the same length (1·12 Å) as in nitric oxide (Ketelaar and Palmer, *J. Amer. Chem. Soc.*, 1937, **59**, 2629). This suggests that the N–O bond remains a five-electron bond while the X–N bond is weaker than a two-electron bond. Pauling (*loc. cit.*) accounted for this by suggesting that the electronic structure could be described best in terms of resonance between, *e.g.*, Cl–N=O and Cl^- $N{\equiv}O^+$. By analogy with the conclusions of this paper for diatomic molecules, the system may alternatively be described by supposing that the nine electrons of one spin have a configuration which may be represented by the first of Pauling's resonance structures (I) or (II),

Cl–N=O
(I)


(II)

Cl^- $N{\equiv}O^+$
(III)


$\begin{array}{c} -N{\equiv}O- \\ | \\ -Cl- \\ | \end{array}$
(IV)

each line in (II) representing one electron, while the nine of the other spin have a configuration corresponding to the second, (III) or (IV). On this basis, the complete wave function would be formulated so that the electrons of one spin occupied different orbitals from those of the other. The wave function would therefore differ from that corresponding to the resonance description. On the basis of this single structure the NO and NCl bonds are five-electron and one-electron bonds respectively. Similarly the nitrosyl compounds of the metals [*e.g.*, $Fe(CO)_2(NO)_2$] may perhaps have structures in which the NO retains its five-electron bond, the three electrons on the nitrogen all being shared with the metal atom. According to this description, the electrons of one spin would again occupy a different set of orbitals from those of the other spin.

It will be noted that the electronic structure ascribed in Table 2 to the ground state of CO^+ is not the same as that ascribed in Table 1 to the ground state of the isoelectronic N_2^+. In fact, the structures of the ground and excited $^2\Sigma$ states have been reversed for the two molecular ions. This has been done on the basis of the observed bond lengths and force constants, and would appear to be justified by the way in which the data for these states then fall into line with the values for the other molecules as summarised in the graphs of Figs. 1—6. The electron in the σ_2 non-bonding orbital of CO^+ (ground state) has presumably a greater probability of being near the oxygen than near the carbon atom because of the higher nuclear charge of the former. Therefore, it would appear that the difference between the changes in bond length and vibration frequency ceased by the ionisation of N_2 and CO (originally stressed by Long and Walsh, *Trans. Faraday Soc.*, 1947, **43**, 342) is a consequence of the fact that with N_2 one of the bonding electrons is lost, leaving a five-electron bond which is only a little weaker than the six-electron bond of N_2 (for a $\sigma^2\pi^4$ bond is replaced by a $\sigma\pi^4$ bond), whereas with CO a non-bonding electron is lost and this is probably one mainly associated with the carbon atom since that has a lower nuclear charge. The small increase in binding is then probably a consequence of the increase in the effective nuclear charge of the carbon atom.

Conclusion.—It has been shown by using a description that employs simultaneously atomic and molecular orbitals, that the relative bond lengths and force constants for various states of the nine known diatomic molecules and ions derived from C, N, and O are, to a good approximation, related solely to the number of bonding electrons and to their distribution between σ and π bonding orbitals.

The spatial configuration of maximum probability of the electrons in these diatomic molecules has been considered on the same basis. In many excited states, and in some ground states, the configurations for the electrons of opposed spins are different from one another. Some consequences of this have been discussed.

I thank the Royal Society and Imperial Chemical Industries Limited for providing calculating machines.

INORGANIC CHEMISTRY LABORATORY, OXFORD. [*Received, February* 16*th*, 1955.]