

Note The Electronic Configuration of Molecules and Their Electron Affinity

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Note

The Electronic Configuration of Molecules and Their Electron Affinity

IT is well known that the probability of formation of negative ions by electron attachment varies widely for different gases. The cause of this variation, however, has been very obscure. Attempts have been made to relate the electron affinity of a molecule to its dipole moment, but such a hypothesis almost universally breaks down. It is generally held that negative ions may be formed in the so-called "electronegative" gases, but this is largely an ad hoc explanation. It is obvious that the real factor which determines whether or not a molecule will be able to hold a stable additional electron must be closely related to the electronic configuration of the normal molecular state. Heretofore, the data on electron attachment have been of so limited extent that no relation between the electronic structure of a molecule and its electronic affinity could be determined. With the additional evidence which is now available,¹ however, it is possible to point out some extremely interesting relations which appear to exist between the electronic configurations of molecules and their ability to form stable negative ions.

The data which are available for diatomic gas molecules relative to their structure and their electron affinity are given in Table I.

It is seen that the diatomic molecules which are characterized by ${}^1\Sigma$ configurations (1S_0 for the monatomic gases) do not form stable negative diatomic ions. It is true that

negative ions exist in several of these gases, but in such cases they are formed in a dissociation process, one of the products of which attaches the electron. The ${}^1\Sigma$ state is characterized by having no resultant spin or angular momentum, the electrons all forming entirely closed λ groups. Such a configuration at once makes evident the relative inertness of the molecule with respect to an extra-molecular electron, and negative ions would not be expected to be formed. On the other hand, those molecules which possess uncombined spin or orbital momenta can form stable negative ions by adding an extra electron whose momentum can add to that already present. This rule apparently holds for all diatomic molecules which are available for experiment. It also suggests that certain molecules might tend to form negative ions by attaching electrons in an excited state, providing the life of that state were long enough. Some evidence to this effect has been presented by da Silva³ for N_2 .

It is possible to extend the reasoning in a limited fashion to polyatomic molecules. It would be expected that highly symmetrical molecules would not form negative ions. This is borne out by experiments in NH_3 and probably by experiments in CH_4 . Two particularly interesting cases are presented by CO_2 and N_2O . According to Mulliken⁴ these are both linear molecules and have electronic states analogous to the ${}^1\Sigma$ case for diatomic molecules. The prediction that such molecules would possess no electron affinity is borne out by experiment.¹ The electronic configuration of acetylene, C_2H_2 , is of the ${}^1\Sigma$ type according to Hedfeld and Mecke.⁵ It is probable that C_2H_2 has no electron affinity since Loeb found a probability of attachment of the order of 10^{-7} or less, and Tate and Smith⁶ in electron bombardment experiments observed negative ions in the gas which were definitely *not* $C_2H_2^-$.

It therefore seems possible that one can predict the qualitative character of the electron affinity of a molecule if the electronic configuration is known. On the other hand, it may be possible to obtain knowledge of the normal state of a molecule from the character of the electron attachment in the gas. This should prove of particular value in studying the electronic structure of polyatomic molecules.

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Molecule	Ground state ²	Negative ion exists
He	1S_0	No
A, Kr, Ne	1S_0	No
H_2	${}^1\Sigma$	No
N_2	${}^1\Sigma$	No
CO	${}^1\Sigma$	No
Cl_2 , Br_2 , I_2	${}^1\Sigma$	No—probably dissociates into Cl^- , etc.
HCl	${}^1\Sigma$	No—dissociates into Cl^-
O'_2 (1.62 v)	${}^1\Sigma$	No—(probably not)
O_2	${}^3\Sigma$	Yes
NH	${}^2\Sigma$	Yes
NO	${}^2\Pi$	Yes
OH	${}^2\Pi$	Yes
CN	${}^2\Sigma$	Yes
SO	${}^2\Sigma$	Yes

¹ N. E. Bradbury, Phys. Rev. **44**, 883 (1933). N. E. Bradbury, J. Chem. Phys. **2**, 827 (1934). N. E. Bradbury and H. Tatel, J. Chem. Phys. **2**, 835 (1934). V. A. Bailey and W. E. Duncanson, Phil. Mag. **10**, 144 (1930).

² Jevons, Report on Band Spectra of Diatomic Molecules, p. 272. University Press, Cambridge, 1932.

³ M. A. da Silva, Ann. d. Physik **12**, 100 (1929).

⁴ R. S. Mulliken, Phys. Rev. **40**, 60 (1932).

⁵ Hedfeld and Mecke, Zeits. f. Physik **64**, 151 (1930).

⁶ J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

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