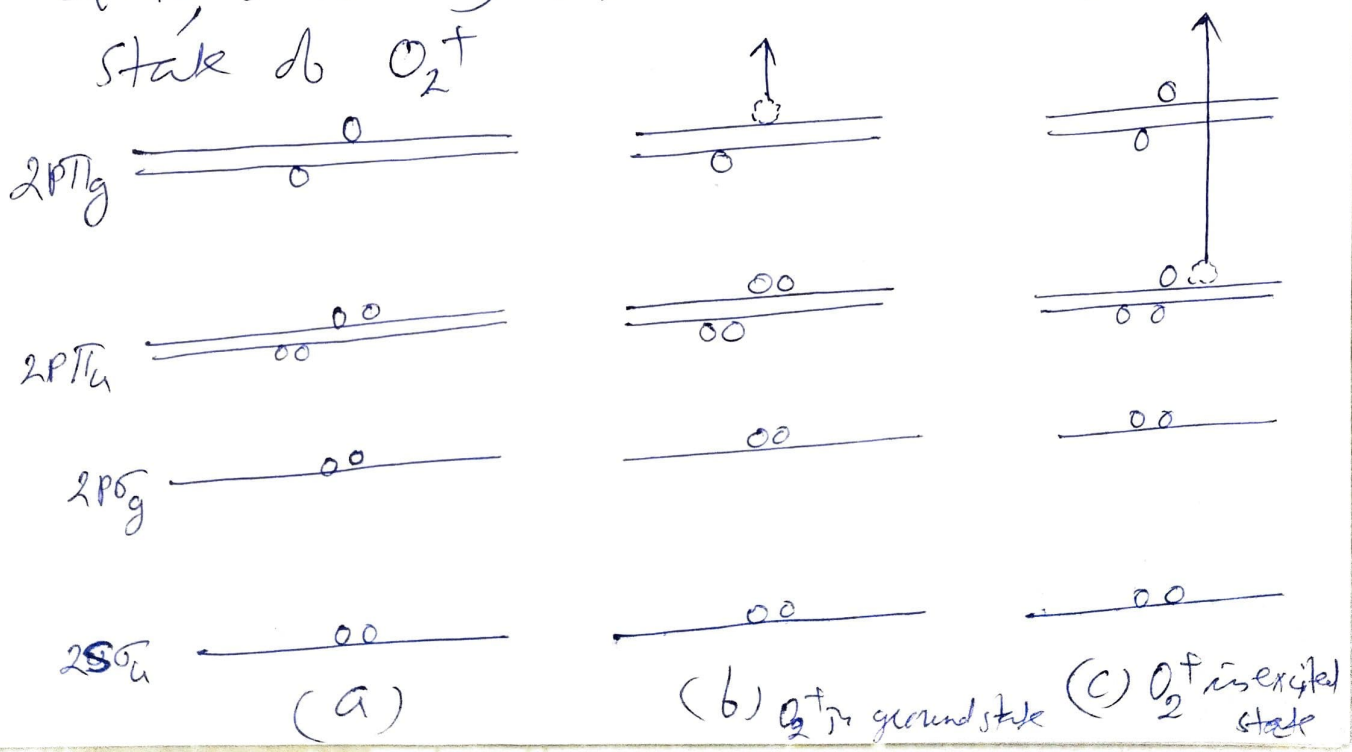


Molecular Photoelectron Spectroscopy

Here we discuss the information which this technique can give us about diatomic molecule. We use the oxygen molecule as an example.

photoelectron spectroscopy relies on the ejection of an electron, and consequent formation of an ion, under the influence of a beam of radiation; Two ways in which this can happen for O_2 . Part (a) shows the upper four energy levels of the O_2 molecule, and the way in which they are filled in the ground state. The ionization process requiring least energy is the removal of an electron from the $2p\pi_g$ level (an antibonding electron); the resulting O_2^+ is in its lowest possible energy state, so we may refer to it as the ground state of O_2^+



Part (c), shows the removal of a bonding $2p\pi_u$ electron, requiring somewhat more energy, and resulting in the formation of an excited O_2^+ . Other more highly excited states can be formed by the ejection of more firmly bound electrons (e.g. the $2p\sigma_g$ or the $2s\sigma_u$).

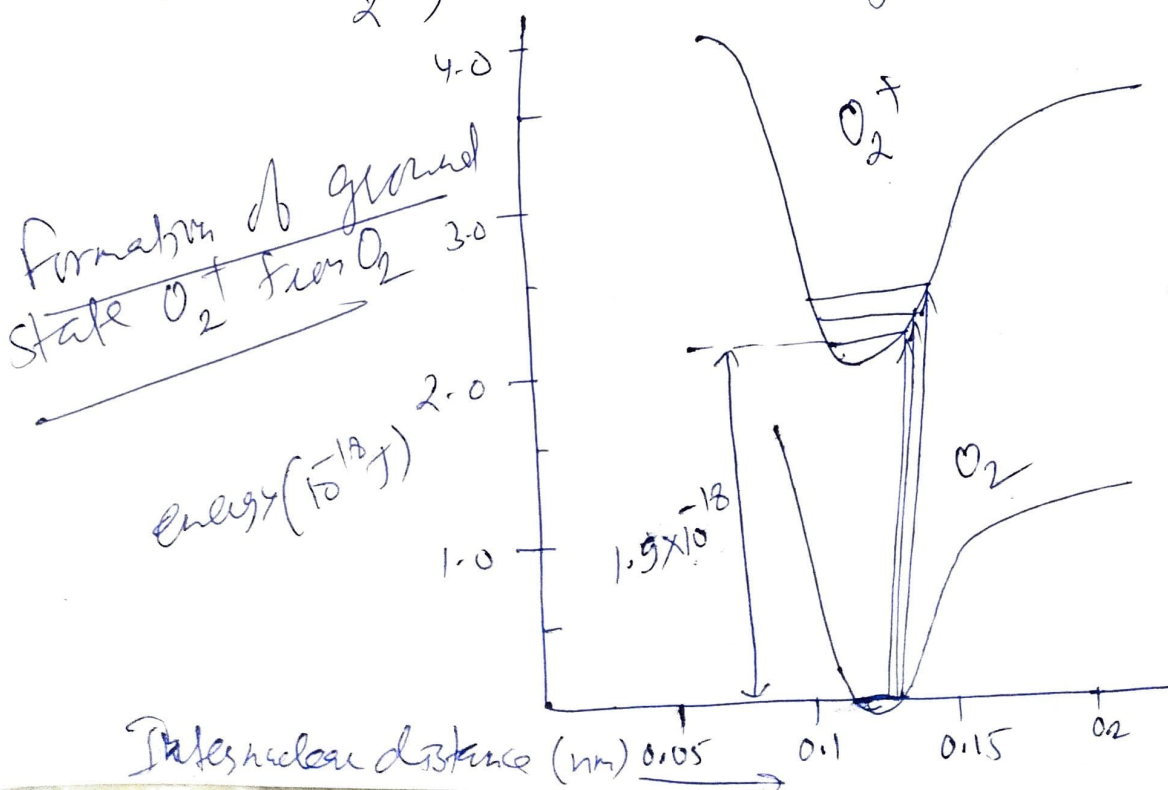
The usual notation for O_2 and its ions describes the ground state molecule as ${}^3\Sigma_g^-$ (triplet, since $s = \frac{1}{2} + \frac{1}{2} = 1$, and since the electrons' angular momenta are opposed so $\Lambda = \lambda_1 + \lambda_2 = 1 - 1 = 0$), while the ground state of O_2^+ is ${}^4\Pi_g$ (three unpaired spins, hence quartet).

The observed photoelectron spectrum of O_2 confirms this pattern of energy levels, since it indicates electrons having an ionization potential of about $1.9 \times 10^{-18} \text{ J}$ (12.1 eV) and twice as many electrons with an ionization potential of about $2.6 \times 10^{-18} \text{ J}$ (16.2 eV) - clearly this corresponds to the two $2p\pi_g$ electrons and the four $2p\pi_u$ electrons respectively.

Higher ionization potentials are found for the (2) more firmly held electrons.

Thus, photoelectron spectroscopy immediately gives us a quantitative estimate of the relative energies of the various molecular orbitals in the oxygen molecule, or of any other diatomic molecule which can be studied by this technique.

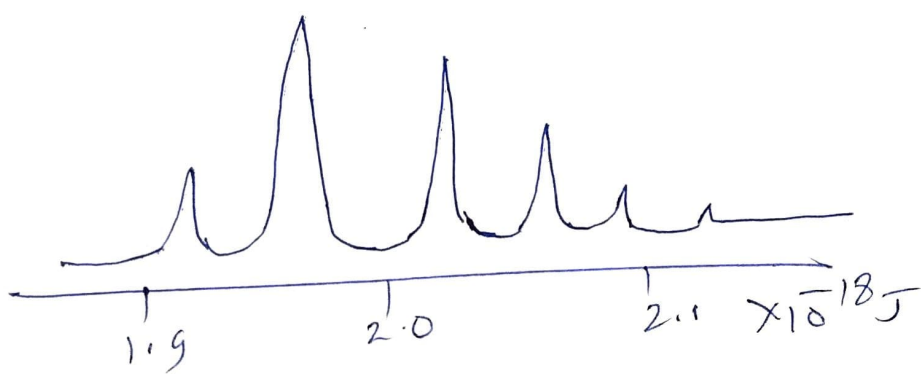
The O_2^+ ions formed in this way are stable, but short-lived molecules. In the absence of electron capture (when they react to O_2) they have ~~no~~ tendency to dissociate into O and O^+ , but behave like ordinary diatomic molecules. In particular they vibrate and rotate. We show the situation for O_2 and O_2^+ , both in their ground states in following figure



(22)

UV-Visible spectroscopy shows that the equilibrium bond lengths of these two molecules are 0.121 nm for O_2 and 0.112 nm for O_2^+ . If we take the $v=0$ state of O_2 as the arbitrary zero of energy, then the $v=0$ state of O_2^+ is some $\frac{1.9 \times 10^{-18} \text{ J}}{\text{I.P.}}$ above this.

Because of the differences in the equilibrium internuclear distances, the Franck-Condon rule indicates that a jump from the ground vibrational state of O_2 will produce several vibrational states of O_2^+ ; this behavior is corroborated by the high-resolution photoelectron spectrum, which shows a set of discrete ionization potentials, each corresponding to a particular vibrational state of O_2^+ .



Resulting fine structure of the photoelectron spectrum