255. *The Electronic Structures and Spectra of Some Molecules related to Oxygen.*

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The electronic structures and spectra of nitroso-compounds, nitrites, and azo-compounds are discussed in relation to those of the oxygen molecule. It is shown that the diamagnetism of these compounds and their spectra can be interpreted in terms of a simple perturbation treatment of the oxygen molecule.

Electronically, the nitroso-compounds and azo-compounds are closely related to oxygen. In this paper their spectra and electronic properties are discussed in the light of this relationship.

The ground state of oxygen is a $^3\Sigma_g^-$ state arising from the electronic configuration $(\sigma_g\, 2s)^2\, (\sigma_u\, 2s)^2\, (\sigma_g\, 2p)^2\, (\pi_u\, 2p)^4\, (\pi_g\, 2p)^2$. The other states arising from this configuration are $^1\Delta_g$ and $^1\Sigma_g^+$ located at 0·98 ev and 1·63 ev respectively above the ground state. The next observed states, about 4 ev above the ground state, are $^3\Sigma_u^+$ and $^3\Sigma_u^-$ arising from the configuration $(\pi_u\, 2p)^3\, (\pi_g\, 2p)^3$.

The wave-functions for the states arising from the lowest configuration are given by Moffitt (*Proc. Roy. Soc.*, 1951, **210**, *A*, 224). It is convenient to write them in a slightly different form. We define an *xz* plane containing the O–O axis, the latter being in the direction of the *x*-axis. If π_z and π_y are the components of the degenerate, antibonding π_g orbital which are parallel and perpendicular to the *xz* plane then, filled shells being neglected, the wave-functions are :

$$\Psi^{\prime\,3}\Sigma_g^-\ [\pi_z(1)\ \pi_y(2) - \pi_z(2)\ \pi_y(1)]\ \begin{cases}[\alpha(1)\ \alpha(2)]\\ [\alpha(1)\ \beta(2) + \alpha(2)\ \beta(1)]\\ [\beta(1)\ \beta(2)]\end{cases}$$

$$\left.\begin{array}{l}\Psi^{\prime\,1}\Delta_g\ [\pi_z(1)\ \pi_y(2) + \pi_z(2)\ \pi_y(1)]\\ \Psi^{\prime\prime\,1}\Delta_g\ [\pi_z(1)\ \pi_z(2) - \pi_y(1)\ \pi_y(2)]\end{array}\right\}[\alpha(1)\ \beta(2) - \alpha(2)\ \beta(1)]$$

$$\Psi^{\prime\,1}\Sigma_g^+\ [\pi_z(1)\ \pi_z(2) + \pi_y(1)\ \pi_y(2)]\quad [\alpha(1)\ \beta(2) - \alpha(2)\ \beta(1)]$$

where α and β are spin functions.

If we consider instead of O_2 the isolectronic molecule HNO we would expect changes in the intervals between the $^3\Sigma^-$, $^1\Delta_g$, and $^1\Sigma_g^+$ states, but no changes in the qualitative energy level scheme. The main changes in the π-electron system would come about through the mixing of the $(\pi_u\, 2p)^4\, (\pi_g\, 2p)^2$ with the $(\pi_u\, 2p)^3\, (\pi_g\, 2p)^3$ configurations. This, as may be seen by writing out the molecular-orbital functions explicitly, could lead to the concentration of charge at one end of the molecule.

If now we allow the hydrogen nucleus to move off the N–O axis, remaining in the *xz* plane, we find that the degenerate $^1\Delta_g$ level splits into two components. The $\Psi^{\prime\,1}\Sigma_g^+$ and $\Psi^{\prime\prime\,1}\Delta_g$ wave-functions are both symmetrical about the *xz* plane and hence will be mixed together by the non-axial perturbation of the hydrogen nucleus. A qualitative energy-level diagram showing the dependence of the levels on the displacement of the hydrogen nucleus from the N–O axis is given in the Figure. The $^3\Sigma_g^-$ and $^1\Delta_g$ levels have been drawn as parallel, straight lines. In fact these levels will be affected to different extents by the perturbation, so our procedure is not accurate. The important point is that the $^1\Delta_g$ level is split and may be displaced below the $^3\Sigma_g^-$ level.

These results of a simple theoretical treatment can be explained qualitatively. The displacement of the hydrogen nucleus in the *xz* plane stabilises the π_z orbital relative to the π_y orbital. This does not greatly alter the energy levels in first-order perturbation theory, since in each case there is one electron in each orbital. However, in second-order perturbation theory the mixing of $\Psi^{\prime\prime\,1}\Delta_g$ and $\Psi^{\prime\,1}\Delta_g^+$ functions leads to a concentration of electrons in the *xz* plane. This is seen by forming the combination

$$\alpha\Psi^{\prime\prime\,1}\Delta_g + (1 - \alpha^2)^{\frac{1}{2}}\Psi^{\prime\,1}\Sigma_g^+$$

which can be written

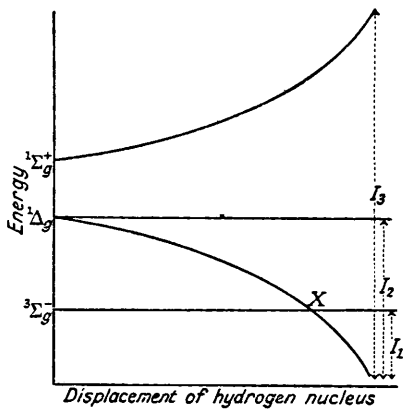
$$\{\alpha + (1 - \alpha^2)^{\frac{1}{2}}\}\pi_z(1)\ \pi_z(2) + \{(1 - \alpha^2)^{\frac{1}{2}} - \alpha\}\pi_y(1)\ \pi_y(2)$$

Clearly, if α increases to $1/\sqrt{2}$ we find both of the electrons in the π_z orbital. This crowding of electrons into the xz plane is opposed by the interelectronic repulsions. As the hydrogen nucleus is displaced from the N–O axis the perturbation becomes larger compared with the inter-electronic repulsions, and the electrons become more concentrated in the xz plane. Sooner or later the energy of the stabilised state becomes greater than that of the $^3\Sigma_g^-$ state and the energy levels cross. After this point the ground state is a singlet.

After the crossing point X (see Fig.), the $^3\Sigma_g^-$–$^1\Delta_g$ transition of oxygen should be replaced by a singlet–triplet transition shown as I_1, and a new singlet–singlet transition I_2 should appear. Of course the angular momentum about the N–O axis is no longer quantised, so descriptions such as Σ and Δ lose their significance. The considerations of the previous paragraph show that the upper states of these transitions have approximately equal densities of π-electrons in and perpendicular to the xz plane, while in the ground state both of the original π_g electrons are in the xz plane; *i.e.*, the $^3\Sigma_g^-$–$^1\Delta_g$ transition of oxygen is replaced by what is conventionally termed a σ–π transition, and also a new singlet–singlet σ–π transition I_2 appears. The transition I_3 becomes more and more like a two-electron transition and hence should be very weak.

If we make the reasonable assumption that the N–H group is less electronegative than the oxygen atom, we may expect the electron transferred in these transitions to come

Qualitative energy level diagram for the H–N–O *system, showing the effect of displacing the hydrogen atom from the* N–O *axis.*



largely from the nitrogen atom. Our final description of the transitions would be as unshared pair-antibonding orbital, σ–π transitions.

Little is known about the molecule HNO, but all our considerations should apply with little change to the systems RNO, where R is an aliphatic, aromatic, or other univalent radical. The physical properties of aliphatic and aromatic nitroso-compounds have been studied. The monomeric molecules are diamagnetic, showing that the singlet state has been displaced beneath the lowest triplet. Their blue or green colours are found to result from rather weak absorption bands which extend some way into the infra-red (Lewis and Kasha, *J. Amer. Chem. Soc.*, 1945, **67**, 997). Lewis and Kasha claim that this band, which in typical cases begins at about 1·7 ev, is a singlet–triplet transition. If this is true it may be identified with the transition I_1 of the figure. In view of the rather high intensity, however, it seems quite possible that it is in fact the transition I_2, an assignment which is not ruled out by Lewis and Kasha's evidence. In either case the displacement of the singlet level is not less than 1·7 ev compared with the 0·65 ev separating the $^1\Delta_g$ and $^1\Sigma_g^+$ states of oxygen. This shows that the structure with both electrons in the RNO plane does predominate. Rough calculations suggest that the configuration with two electrons in the antibonding orbital cannot contribute more than a few units % to the wave-function or more than 1% in weight to the final structure.

The absorption spectra of a number of compounds in which the N–O group is attached to a univalent radical have been measured. The aliphatic and aromatic nitroso-compounds have bands in the visible and near infra-red beginning at about 14,500 cm.$^{-1}$ and 12,000 cm.$^{-1}$, respectively. The corresponding values of $\varepsilon_{max.}$ are about 10 and 50 (Kortum,

Z. Electrochem., 1941, **47**, 55; Hertel and Lebok, *Z. phys. Chem.*, 1940, **47**, *B*, 315). The nitrites and nitrosamines absorb at about 25,000 cm.$^{-1}$ with $\varepsilon_{max.}$ values of 50—70 (Kortum, *ibid.*, 1941, **50**, *B*, 361). Nitrosyl chloride has a very weak absorption with $\varepsilon_{max.} < 1$ at 15,500—17,500 cm.$^{-1}$, followed by a very broad absorption band with a maximum at 30,000 cm.$^{-1}$ and a value of 32 for $\varepsilon_{max.}$ (Goodeve and Katz, *Proc. Roy. Soc.*, 1939, **172**, *A*, 432). It seems probable that all the bands with $\varepsilon_{max.}$ between 10 and 100 arise from the same fundamental transition and this, in the author's view, is likely to be the singlet–singlet σ–π transition. If this is correct the weak band in nitrosyl chloride must be the singlet–triplet transition. Its appearance in this compound can be understood, since the heavy chlorine atom will facilitate multiplicity-forbidden transitions. We would expect that in nitrosyl bromide the corresponding transition would be in much the same position but several times more intense.

The displacement to longer wave-lengths of the main transition in nitrosobenzene is probably due to the conjugation of the excited π-electron with the aromatic system in the upper state. The much larger shift to shorter wave-lengths in the nitrites, etc., is due to the extensive donation of electrons into the antibonding π-orbital from the oxygen unshared pairs which takes place in the ground state. This partial occupation of the antibonding π-orbital is much less favoured in the upper states since it then already contains one electron. Consequently, the ground state is stabilised relative to the excited state and the transition moves to shorter wave-lengths.

If we now replace the oxygen atom of the nitroso-compounds by a second N–R group we obtain an azo-compound. Azomethane vapour has a weak absorption with a maximum at about 25,000 cm.$^{-1}$ and $\varepsilon_{max.}$ 16 (Kirkbride and Norrish, *J.*, 1933, 122). In the aromatic azo-compounds the absorption in this region is often more intense, presumably owing to interactions with the nearby aromatic absorptions. In some of the simpler compounds the absorption is normal, *e.g.* in phenylazomethane $\varepsilon_{max.} = 87$ (Burawoy, *J.*, 1937, 122). These characteristic azo-bands are probably due to the same σ–π transition displaced to shorter wave-lengths by the extra stabilisation of the π-electrons in the plane of the molecule.

If the azo-molecule is deformed until the N–R bonds lie in perpendicular planes containing the N–N axis, then we would expect the ground state to be a triplet. This should be compared with the similar situation in ethylene.

Formally, we can treat the molecules $CH_2{:}O$, $CH_2{:}NR$, and $CH_2{:}CH_2$ in the same way. Although the σ–π transitions can be detected spectroscopically, the molecules are now so different from oxygen that it seems unlikely that this method can be applied profitably.

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