

# THE STRUCTURE OF OZONE—AN INTERPRETATION OF ITS MAGNETIC SUSCEPTIBILITY

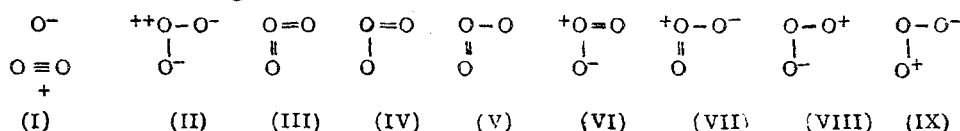
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THE structure of the ozone molecule has provided material for so many investigations that an addition to the literature may seem superfluous. The present communication is an attempt to correlate the various resonance structures with the observed magnetic susceptibility.

Using the method of electron diffraction, Shand and Spurr<sup>7</sup> obtained for the O—O bond distances and the O—O—O bond angle values consistent with the observations of Penney and Sutherland<sup>5</sup> that the molecule has a symmetrical angular form. The possible electronic structures consistent with this isosceles triangle form are



Of these structures I and II are unlikely as ozone does not show the characteristic properties of a highly polar substance. Penney and Sutherland consider that the O—O bonds have about 30% double-bond character with structures VI, VII, VIII and IX as the most important among the resonance structures.

It has been shown earlier<sup>1</sup> that in the case of carbon compounds, following the method of Gray,<sup>2</sup> bond depression values could be calculated for various bond types and an empirical curve correlating these bond depressions with bond orders could be obtained for C—C bonds. One may reasonably expect a similar relationship with other elements as well. A direct evaluation of bond depression values for O—O bonds is not feasible as the simplest molecule O<sub>2</sub> does not have a covalent double bond and the structure of hydrogen peroxide eliminates that compound as a standard for a single bond. Both values have consequently to be obtained by some form of extrapolation. This is possible if one were to assume that the paramagnetic contribution of a bond can be treated as a periodic property. The values for C—C bonds have been calculated (Anantakrishnan, *loc. cit.*) and by similar methods using hydrazo and azo benzene as standards, the bond depressions of the N—N bonds, single and double, can be obtained. As a first approximation, the difference between the carbon bonds and the nitrogen

bonds can be taken as the difference between the latter and the oxygen bonds. The values will then be as in Table I.

TABLE I

Nature of Bond	Bond depression value		
	Carbon-Carbon	Nitrogen-Nitrogen	Oxygen-Oxygen
Single bond ..	2.08	1.80	1.52
Double bond ..	7.68	5.0	2.3

Using these bond depression values and Slater's values for the atomic susceptibility of oxygen, the molar susceptibility of the different valence bond structures may be evaluated. The results are summarised in Table II.

TABLE II

All susceptibility values are in units of  $10^{-6}$

Structure	Susceptibility
IV and V ..	- 17.46
VI and VII ..	- 18.09
VIII and IX ..	- 18.89
III ..	- 16.66

All the possible valence structures thus appear to indicate that ozone should be diamagnetic. The careful work of Laine<sup>3</sup> makes out that the compound is a feebly paramagnetic substance with a susceptibility of  $6.72 \pm 0.96 \times 10^{-6}$  (one experiment, however, appears to give a diamagnetic value). Wulf<sup>9</sup> and Vaidyanathan<sup>8</sup> working with ozonised oxygen make it out to be a diamagnetic compound. One obvious explanation for the discrepancy is the possible presence of molecular oxygen in the ozone studied. Also, it is necessary to consider possible deviations when considering measurements in liquids at the low temperatures used by Laine. In his experiments, Laine allows for the temperature dependent paramagnetism of oxygen and the key to the problem lies in a consideration of the high frequency paramagnetism of the two molecules, oxygen and ozone.

Van Vleck has shown that the molar susceptibility of oxygen can be calculated on the assumption that the multiplet structures are small compared to  $kT$  making the matrix elements of the spin essentially of the low frequency type. Rough calculation of  $h^2/8 \pi L$  using existing spectroscopic data on ozone shows that this is much larger than  $T$  and the multiplet structure of ozone is also not of negligible width. Even with oxygen, where

these complications are relatively unimportant, the Leiden observations<sup>6</sup> have been shown by Van Vleck to require a consideration of high frequency elements. The position with ozone then becomes even more complex. A further difficulty in taking the observations in a liquid has also to be mentioned. Even with non-polar liquids, highly discrete spectra are rarely-obtained and forbidden transitions often make their appearance, presumably involving a modification of the selection rules. Ellis and Kneser have found this to be the case with liquid oxygen. A small but definite dipole moment has been observed for the ozone molecule<sup>4</sup> and the polar nature of the liquid can be expected to modify to an even greater extent the spectroscopic behaviour. This will naturally be reflected in the matrix elements of the high frequency term. The possibility of differences between the liquid and gaseous states together with the difficulties involved in the accurate measurements can account for the range of values reported by different authors or even by the same worker.

The magnetic susceptibility value then does not enable any unequivocal decision about the contributing valence bond structures. At the same time, it is obvious that structures IV and V cannot be excluded, nor even structure III which gives the lowest diamagnetic susceptibility value. Lewis and Smyth<sup>4</sup> observe for ozone a dipole moment of  $0.49 \times 10^{-18}$  e.s.u. and this is consistent with appreciable contributions by the three structures mentioned. Susceptibility values may then be considered to conform to what may be expected from other physical measurements.

#### SUMMARY

Calculation of magnetic susceptibility for the different valence bond structures indicate that ozone should be diamagnetic, the susceptibility being about  $-18 \times 10^{-6}$  while reported experimental values show that it is feebly paramagnetic in the liquid state, diamagnetic values being reported for the gaseous state. The possible causes of the discrepancy and a comparison with oxygen are discussed. The magnetic behaviour may be considered to conform to what may be expected from other physical properties of ozone.

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