

Electron Spin Resonance Study of ^{17}O -Containing Species Adsorbed on V_2O_5 Supported on Silica

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An attempt was made to identify the nature of the oxygen species adsorbed on V_2O_5 supported on silica gel using oxygen enriched with ^{17}O . $^{17}\text{O}_2$ adsorption at 77°K on samples containing $^{16}\text{O}_2^-$ and $^{16}\text{O}^-$ species resulted in the appearance of a new ESR signal with $g_1 = 2.007$, $g_2 = 2.002$ and $g_3 = 1.998$ with a hyperfine splitting of 78 ± 1 Oe about g_2 and in the disappearance of the O^- species. The same signal can be produced by $^{17}\text{O}_2$ adsorption at 77°K on the reduced samples. This signal is tentatively identified as an O_3^- type complex, formed by the interaction of O^- with an oxygen molecule. This assignment is in agreement with previous findings.

In the case of $^{17}\text{O}^-$ and $^{17}\text{O}_2^-$, the lack of detailed hyperfine structures prevented an unambiguous analysis of the corresponding ESR spectra.

Shvets and Kazansky (1) have shown that oxygen adsorption at room temperature on reduced V_2O_5 supported on silica leads to the appearance of ESR spectra which can be ascribed to O_2^- and O^- radicals, with hyperfine structures due to ^{51}V nuclei. The ESR spectrum of O_2^- was characterized by $g_1 = 2.023$, $g_2 = 2.011$ and $g_3 = 2.004$ with $a_1 = 9.7$, $a_2 = 6.8$ and $a_3 = 5.9$ Oe. In the case of the O^- species, it was concluded that $g_{\perp} = 2.026$, $A_{\perp} = 14$ Oe, $g_{\perp} > g_{\parallel}$ and $A_{\perp} \geq A_{\parallel}$.

More recently (2), it was reported that the lines belonging to O^- disappeared upon oxygen adsorption at 77°K leading to a new signal at $g_{\perp} = 2.001$ and $g_{\parallel} \approx 2.017$ without any hyperfine structure. It should be noted, however, that the parallel feature was not clearly seen in the spectrum because of the superposition of lines due to

O_2^- species. The reported g_{\parallel} value was derived in (2) by subtracting the two different spectra. This signal was tentatively assigned to O_3^- radicals. An increase in temperature from 77 to 150°K and simultaneous evacuation resulted in the disappearance of the new signal and restoration of the original spectra due to O^- and O_2^- radicals.

In the present work, ^{17}O has been used to investigate the nature of the oxygen species adsorbed on $\text{V}_2\text{O}_5/\text{SiO}_2$.

EXPERIMENTAL METHODS

Two sets of samples were used in this study:

a. Samples containing 1.5% by weight of V_2O_5 were prepared by impregnation of SiO_2 (Aerosil Degussa, specific surface area 200 m^2/g) with a VCl_4 solution in chloroform and dried at 100°C, in a manner similar to that described by Chien (3).

b. Samples containing 2.4 or 3% by weight of V_2O_5 were prepared by impreg-

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nation of SiO_2 (specific surface area $300 \text{ m}^2/\text{g}$) with NH_4VO_3 solutions of the proper concentration (1).

The samples were dried at $70\text{--}80^\circ\text{C}$ and then calcined in air for 3 hr at 500°C .

Before oxygen adsorption the samples were heated for 1 hr in oxygen (100 Torr) at 500°C , reduced by hydrogen (300 Torr) either for 3 hr (sample a) or for 0.5 hr (sample b) at 500°C and then evacuated to

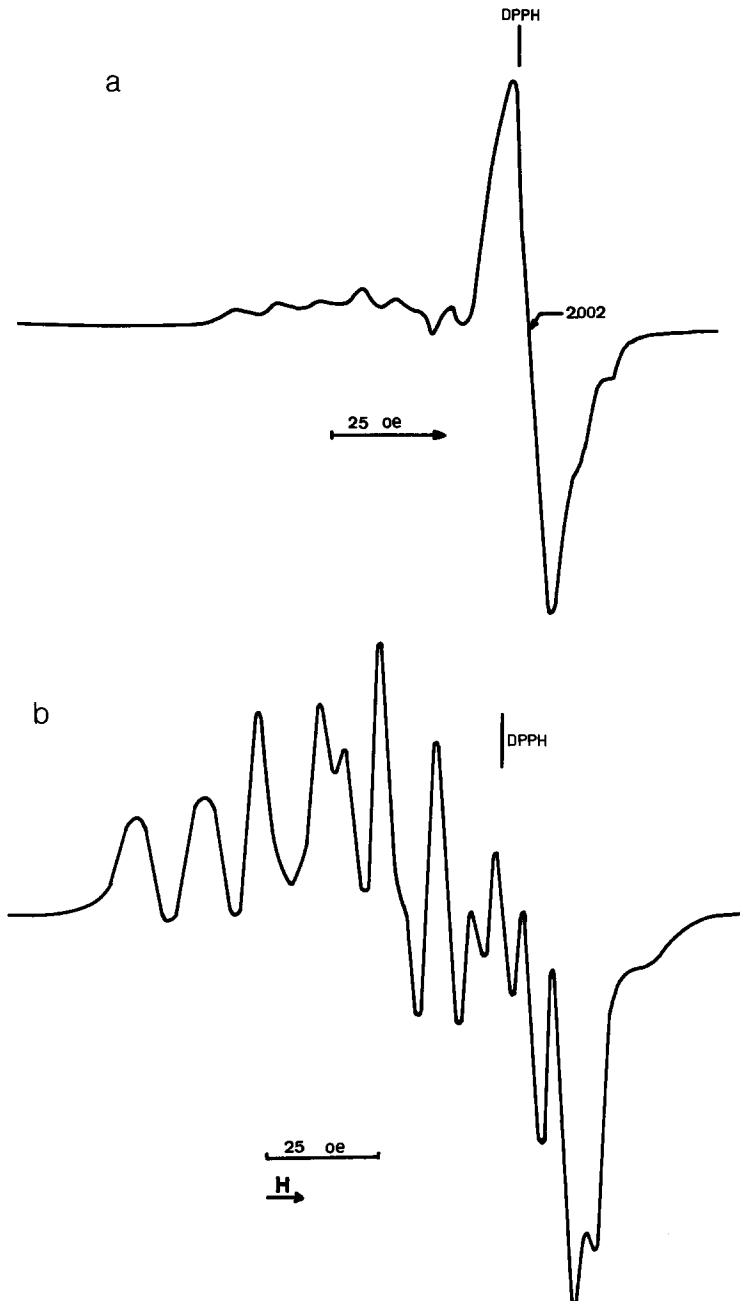


FIG. 1a. ESR spectrum after $^{16}\text{O}_2$ adsorption at 77°K on a reduced $\text{V}_2\text{O}_5/\text{SiO}_2$ sample; (b) ESR spectrum of the previous sample after $^{16}\text{O}_2$ evacuation at 300°K .

10^{-4} – 10^{-5} Torr at the same temperature. Similar results were obtained for both sets of samples except that oxygen species were less stable on samples a.

Oxygen was adsorbed at pressures ranging from 10^{-1} to 10^{-2} Torr at 77°K using $^{16}O_2$ and isotopically enriched O_2 of the following composition: 15% $^{16}O^{16}O$, 50% $^{16}O^{17}O$ and 35% $^{17}O^{17}O$.

ESR measurements were carried out on a Varian V 4502 spectrometer at 9.5 GHz (X-band) or 35 GHz (Q-band). ESR spectra were taken at 77°K.

DPPH and Mn^{2+} in SrO powder were used for g and sweep calibration, respectively (4).

RESULTS

$^{16}O_2$ adsorption at 77°K on a reduced sample gave rise to the ESR spectrum shown in Fig. 1a due to the superposition of the O_2^- radical spectrum and a singlet at $g = 2.002$ previously assigned to O_3^- radicals. The Q-band spectrum of the same sample given in Fig. 2 demonstrates that the singlet of Fig. 1 is in fact a weakly anisotropic line with $g_1 = 2.007$, $g_2 = 2.002$

and $g_3 = 1.998$. After pumping off the excess oxygen at room temperature for a short time the O^- species appeared in the ESR spectrum (Fig. 1b). A further adsorption of oxygen enriched with ^{17}O on the same sample at 77°K gave rise to the spectrum shown in Fig. 3. It is possible to distinguish two sets of hyperfine patterns with 6 and 11 lines, respectively, separated by $A = 78 \pm 1$ Oe. Both sets of lines are centered about $g_2 = 2.002$. A similar spectrum was obtained after $^{17}O_2$ adsorption on reduced V_2O_5/SiO_2 samples at 77°K. After evacuation of these samples at room temperature for a short time the spectrum of Fig. 4 was obtained which is very similar to that of $^{16}O_2^- + ^{16}O^-$ species, except that there are additional weak lines on the wings (they are marked by an asterisk in Fig. 4). Presumably these lines are due to $^{17}O^{16}O^-$ or $^{17}O^{17}O^-$ species, for they remained unchanged after admission at 77°K of H_2 or O_2 (under low pressure), gases which are known to react very rapidly with O^- radicals. The spectrum obtained after $^{16}O_2$ adsorption again exhibited the singlet at $g = 2.002$. No new hyperfine structure due to ^{17}O appears in this spectrum.

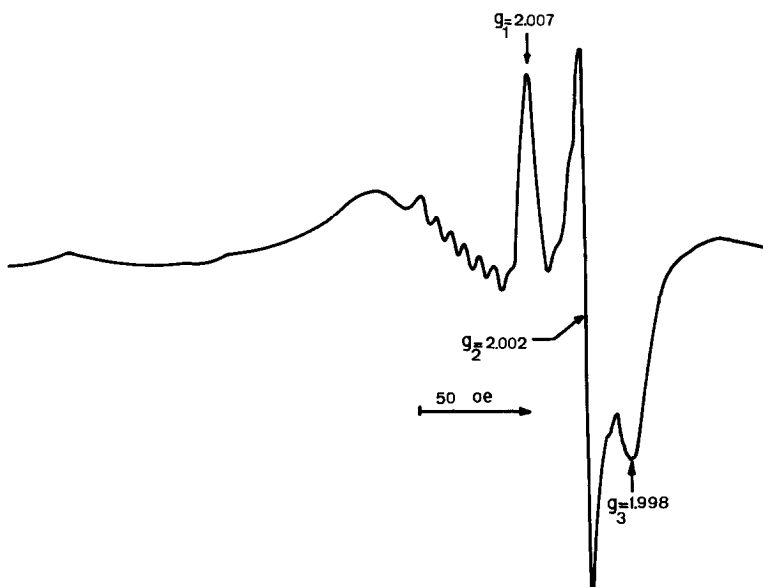


FIG. 2. Q-band ESR spectrum of the sample of Fig. 1a.

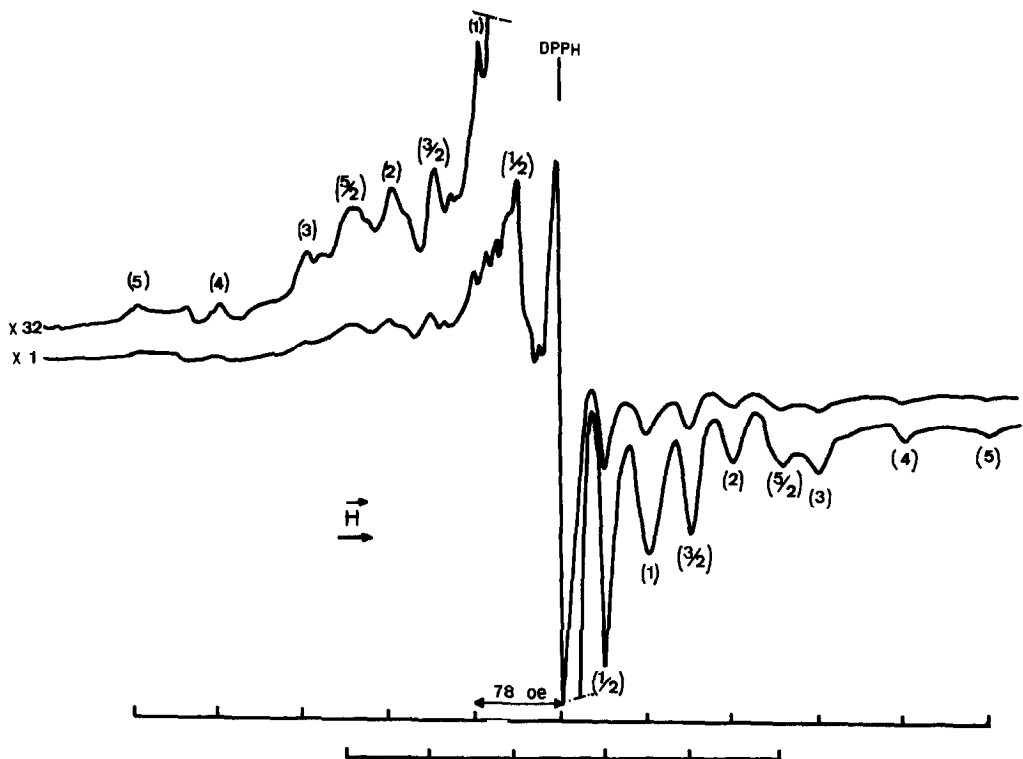


FIG. 3. ESR spectrum after $^{17}\text{O}_2$ adsorption at 77°K on a reduced $\text{V}_2\text{O}_5/\text{SiO}_2$ sample.

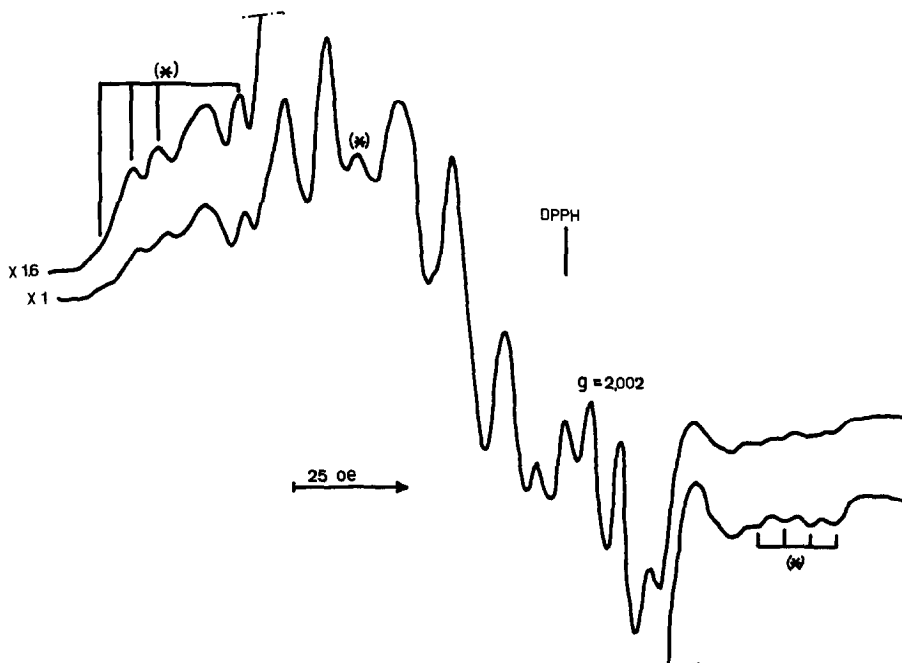


FIG. 4. ESR spectrum of the sample of Fig. 3 after evacuation for a short time at room temperature.

DISCUSSION

Comparison with Well-Characterized Oxygen Species

Superoxide Ion

It is tempting in view of the similarity of the hyperfine constants observed in O₂⁻ adsorbed on oxides (5) (75–80 Oe) to ascribe the new species to O₂⁻. However, it is difficult to reconcile this with the g_{zz} value, whose shift from the free electron g value has been shown to be proportional to the charge of the cation acting as the adsorption site (6). Känzig and Cohen (7) have derived the g tensor expressions for O₂⁻ and the g_{zz} component is expressed as:

$$g_{zz} = g_e + 2\lambda/\delta,$$

where λ is the spin-orbit coupling constant and δ is the separation between levels as indicated in Fig. 5. Taking $g_1 = g_{zz}$ and 0.014 eV for λ (6), we calculate δ to be 5.96 eV, in contrast to the value 1.33 eV calculated from the value $g_{zz} = 2.023$ reported for the V⁵⁺O₂⁻ system (1). Thus the presence of more than one V⁵⁺ ion at the adsorption site is required in order to reconcile the observed g_1 value. This can be ruled out for the following reasons: (i) the absence of any corresponding hyperfine structure in the experimental spectrum, (ii) the low concentration of surface vanadium (1.5–3% by weight of V₂O₅) used in the present experiments and (iii)

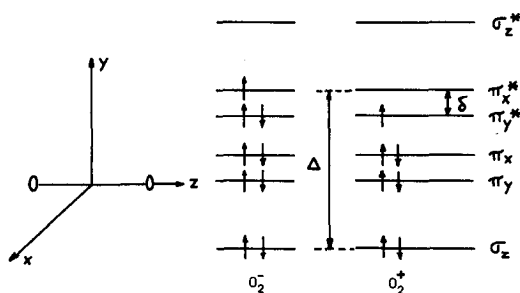


FIG. 5. Energy level diagram and coordinate system for O₂⁻ and O₂⁺.

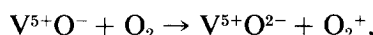
the presence of only 8 hyperfine lines (interaction with only *one* ⁵¹V nucleus with $I = 7/2$) in the spectrum of the O⁻ species which leads to the new oxygen species.

The thermal stability of O₂⁻ adsorbed on V₂O₅/SiO₂ does not agree with that observed for the species under consideration.

Clearly the O₂⁻ ion is not responsible for the new ESR signal.

O₂⁺ Species

Alternatively the spectrum of Fig. 3 could be assigned to O₂⁺ species formed by the reaction,



since, by analogy with O₂⁻, one might expect that the unpaired electron would interact equally with the two oxygen nuclei in these radicals, giving rise to the hyperfine constant of 78 Oe.

However, the g values observed are inconsistent with this assignment. The g tensor components for O₂⁺ have been derived from the g shift tensors expressed as (8):

$$\Delta g_{ij} = 2\lambda \sum \frac{\langle 0|L_i|k\rangle \langle k|L_j|0\rangle}{E_0 - E_k}$$

and are found to be, to the first order with λ positive:

$$\begin{aligned} g_{xx} &= 2.0023 + 2\lambda/(\Delta - \delta), \\ g_{yy} &= 2.0023, \\ g_{zz} &= 2.0023 - 2\lambda/\delta, \end{aligned}$$

where λ has the same meaning as previously.

The energy separations δ and Δ and the coordinate system used above are given in Fig. 5.

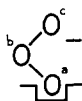
These expressions differ appreciably from those obtained earlier by Iyengar *et al.* (9). Taking $g_{xx} = 2.007$, $g_{yy} = 2.002$ and $g_{zz} = 1.998$ and the above g tensor equations, δ was found to be 6.5 eV, as compared to the value 1.33 eV calculated for the system V⁵⁺O₂⁻. Assuming the same adsorption site, one would expect a δ value

similar for O_2^+ and O_2^- ions. Alternatively a much stronger crystal field would explain the experimental g_{zz} value of 2.007 but again the presence of more than one V^{5+} ion is ruled out for the same reasons as given above. Clearly the discrepancy by a factor of 5 leads to the conclusion that the spectrum of Fig. 3 cannot be due to the O_2^+ species. Also the thermal instability of the species at $g = 2.002$ is inconsistent with the suggestion of O_2^+ formation. Furthermore, the species thought to be O_2^+ adsorbed on TiO_2 was shown later to be due to NO_2^{2-} and NO radicals (10,11) and so far no conclusive ESR evidence of the presence of O_2^+ on surfaces exists.

Ozonide Ion

The formation of the species at $g = 2.002$ produced by reaction between O^- and oxygen and the thermal dissociation of the species leading again to the original O^- species strongly suggest that it is triatomic.

On MgO , it has been shown that ozonide ions can be formed upon reaction of O^- ions with molecular oxygen $^{17}O_2$. Starting with $^{17}O^-$, Lunsford obtained the following parameters: $g_1 = 2.0172$, $g_2 = 2.0100$ and $g_3 = 2.0014$ with the hyperfine splittings $A_3^a = 26$ Oe, $A_3^b = 82$ Oe and $A_3^c = 65$ Oe (12). Tench (13), using $^{16}O^-$, obtained a different g tensor, namely, $g_1 = 2.0148$, $g_2 = 2.0121$ and $g_3 = 2.0020$ and was able to resolve the hyperfine tensors for oxygens b and c as follows: 108, 15, 15 Oe and 70, 10, 10 Oe, respectively. These values were explained in terms of the following model:



It is evident, however, that the g values, the hyperfine splitting constants and the thermal stability of the species under consideration are quite different from those of the ozonide ion.

Peroxy Radical

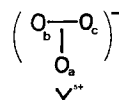
It has been found recently (14) that peroxy radicals labeled with ^{17}O and stabilized on polytetrafluoroethylene (PTFE) exhibit a very strong nonequivalence of the oxygen nuclei and a pronounced and reversible temperature dependence. The magnetic parameters were found to be: $g_{\perp} = 2.022$, $g_{\parallel} = 2.006$ with $a_{\parallel 1} = 40 \pm 1$ Oe, $a_{\parallel 2} = 89 \pm 1$ Oe at 300°K and $g_{zz} = 2.038$, $g_{xx} \cong g_{yy} = 2.003$ with $a_{xx1} = 46 \pm 1$ Oe, $a_{xx2} = 107 \pm 1$ Oe at 77°K. The peroxy radicals were very stable at room temperature and the parent radicals $-CF_2-CF-CF_2-$ were regenerated from the peroxy radicals only at higher temperatures (about 200°C).

These results, i.e., the magnitude of the g and A tensors showing nonequivalent oxygen nuclei as well as the thermal behavior, demonstrate that the peroxy radicals are not responsible for the new ESR signal.

This comparison of our data and existing data in the literature confirms that we are dealing with a new type of species.

The Structure of the New Oxygen Species

It is clear that the disappearance of O^- and the appearance of a new signal when oxygen is present at low temperatures strongly suggest the formation of a O_3^- type complex. The spectrum in Fig. 3 can be explained assuming that a weak covalent bonding between π -electrons of the oxygen molecule and the free electron in O^- radical takes place, i.e., a species



is formed after adsorption of oxygen. The unpaired electron in this species interacts with the two equivalent oxygen nuclei giving rise to the two sets of 6 and 11 lines with the same splitting of 78 ± 1 Oe corre-

sponding to ¹⁶O¹⁷O or ¹⁷O¹⁷O adsorption, respectively.

Assuming a value of $A_1 \approx A_3 \approx 0$ for the hyperfine constant along g_1 and g_3 , the isotropic part of the hyperfine interaction is 25.7 Oe for oxygens O_b and O_c. This corresponds to a s -orbital spin density of 0.015 using A_0 (¹⁷O) = 1660 Oe (15). The components of the dipolar tensor are 51.3, -25.7, -25.7 Oe and correspond to a spin density of 0.99 using a value of $2 B_0 = 104$ Oe (15).

Although these values are necessarily approximate owing to the unobserved hyperfine constants along g_1 and g_3 , they show nevertheless that the spin density on the third oxygen (O_a) is small, that is, the free electron is largely localized on the two oxygen nuclei of the original O₂ molecule. This could explain both the nonobservance of hyperfine structure from ⁵¹V of the V⁵⁺O₃⁻ complex and the absence of any

¹⁷O hyperfine lines for the V⁵⁺ $\begin{pmatrix} \text{O}^{16} \\ \text{O}^{17} - | \\ \text{O}^{16} \end{pmatrix}$

complex. This is consistent with the fact that the negative charge of the V⁵⁺O₃⁻ complex moves towards the V⁵⁺ adsorption site while the spin density of the unpaired electron moves in the opposite direction towards O_b and O_c. The thermal instability of the O₃⁻ complex is also in agreement with the model proposed.

Distribution of the spin density, surprising at first, is encountered in a number of radicals. In large radicals such as S₂O₈⁻ (16) it is quite remarkable that the wave function of the unpaired electron is equally and highly peaked at just 2 (out of 10) atoms and is essentially zero elsewhere. A value of 75.7 Oe was found for the hyperfine constant which is very close to the situation in O₂⁻ ions. In O₃SOO⁻ (16), the unpaired electron is localized in a π -type orbital on the peroxy group with a spin distribution of about 1:2 between the bridge and terminal oxygen atoms with a zero spin density elsewhere. In smaller radicals,

like CO₃⁻ (17), the unpaired electron is again predominantly distributed over two oxygen atoms (2/3 and 1/3, respectively) with very little left for the rest of the radical.

The analysis of the g tensor of the new O₃⁻ species turns out to be more difficult.

As expected for a 19-electron molecule, the odd electron occupies the $2b_1$ MO which has the form

$$|2b_1\rangle = -c_1(2p_x^0) + c_2(2p_x^{01} + 2p_x^{02})/2^{1/2},$$

with the $2p_x$ AO's perpendicular to the molecular plane.

Thus with a ²B₁ ground state, $(1a_2)^2(2b_2)^2(3a_1)^2(2b_1)^1$, and neglecting the effect of d -orbitals, the Δg 's are as follows (18):

$$\begin{aligned} \Delta g_{xx} &= 0, \\ \Delta g_{yy} &= 2\lambda^0(c_1c_3 + c_2c_4)^2/(E_{(2b_1)} - E_{(4a_1)}), \\ \Delta g_{zz} &= 2\lambda^0c_2^2c_8^2/(E_{(2b_1)} - E_{(3b_2)}), \end{aligned}$$

where λ^0 is the spin-orbit coupling constant for oxygen. The c_i 's are the MO coefficients used by Schlick (18). The coordinate system is the following:



The c_i 's show very little variation for an apex angle in the range 114–126° (18). Walsh's diagram (19) for AB₂ molecules indicates that both energies $E_{(2b_1)} - E_{(4a_1)}$ and $E_{(2b_1)} - E_{(3b_2)}$ increase when the angle decreases down to 90°. Assuming that the coefficients do not vary appreciably in the range 126–90°, one would expect the g tensor to become more isotropic. Using Schlick's values for O₃⁻ at site C, and a 120° angle, one can roughly estimate from Walsh's diagram the g tensor for a 90° angle. One obtains: $g_{yy} \approx 2.011$, $g_{zz} \approx 2.009$, while g_{xx} is theoretically equal to 2.0023. This suggests that the angle of the new O₃⁻ complex is far smaller than the angle of the normal

ozonide ion which lies between $110 \pm 5^\circ$ (20) and $120 \pm 7^\circ$ (18). However, this qualitative discussion is restricted to angles larger than 90° and does not explain the negative shift observed for the g_3 value and the anomalous spin density distribution.

Evidently, the novelty of the model based on the experimental results for the new species requires further theoretical calculations to be made in order to derive the g and A tensors. This might prove to be difficult because of the likely participation of vanadium d -orbitals.

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