The Radical Cation of Tetraphosphorus: ESR Spectra and Structure

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X- and Q-band ESR spectra were observed for $\cdot P_4^+$ cations prepared by exposing solid solutions of P_4 in Freon to X-rays or ^{60}Co γ-rays at 77 K; excellent agreement between the observed and simulated spectra revealed that the cations are formed in a D_{2d} 'butterfly' structure, resulting from the simultaneous cleavage of two bent chemical bonds in the tetrahedral P_4 molecule, induced by electron loss.

ESR studies have shown the occurrence of large Jahn–Teller distortions in radical cations formed from symmetrical precursors. For example, $CH_2D_2^+$ has C_{2v} symmetry,[1] $C_2H_6^+$ has C_{2v} symmetry,[2] benzene cations have D_{2h} symmetry,[3] and $\cdot SnH_4^+$ has two different distorted structures with C_{2v} and C_{3v} symmetries.[4]

According to ground-state calculations for P_4 molecules,[5] removal of an electron from the uppermost filled orbital leaves the $\cdot P_4^+$ cation in a degenerate ^2E state which is Jahn–Teller unstable. Group theoretically, however, the Jahn–Teller distorted configurations in this state are achieved via motion along the e normal co-ordinates.[5] Thus, it may be of interest to

detect the $\cdot P_4^+$ cations experimentally and to reveal Jahn–Teller distorted structures.

Exposure of a solid solution of $CFCl_3$ containing P_4 to X-rays or γ-rays at 77 K gave asymmetric and anisotropic ESR spectra, as shown in Figure 1(a). The lines in the highest and the next highest fields have a parallel form, whilst the signal in the lowest field, judging from the position, cannot seem to be interpreted as the lowest field component for the parallel features of a quintet containing these two lines. Moreover, features in an inner and lower field region are too complicated to be analysed from this spectrum alone, but they indicate large anisotropy in the g-tensor. Thus, measurements of Q-band ESR spectra were carried out at 95 K, at which temperature no significant change from the results obtained at 77 K occurs in X-band spectra. The observed spectrum, Figure 2(a), is composed largely of 'parallel' and 'perpendicular' components of the spectrum under consideration, a central
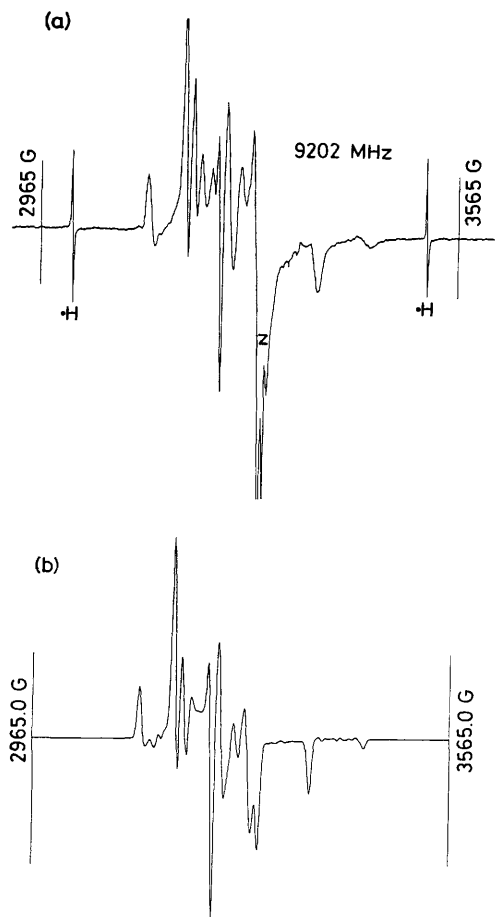

(a)

9202 MHz

2965 G   3565 G

·H   ·H

z

(b)

2965.0 G   3565.0 G

Figure 1. (a) First derivative X-band ESR spectrum for a dilute solution of P_4 in $CFCl_3$, recorded immediately after exposure to X-rays at 77 K. The sharp signals (z) and the central broad signal are attributable to defects formed in quartz and matrix radicals, respectively. (b) A simulation spectrum for the X-band, calculated using the ESR parameters shown in Figure 3 and line-widths of 6 G.
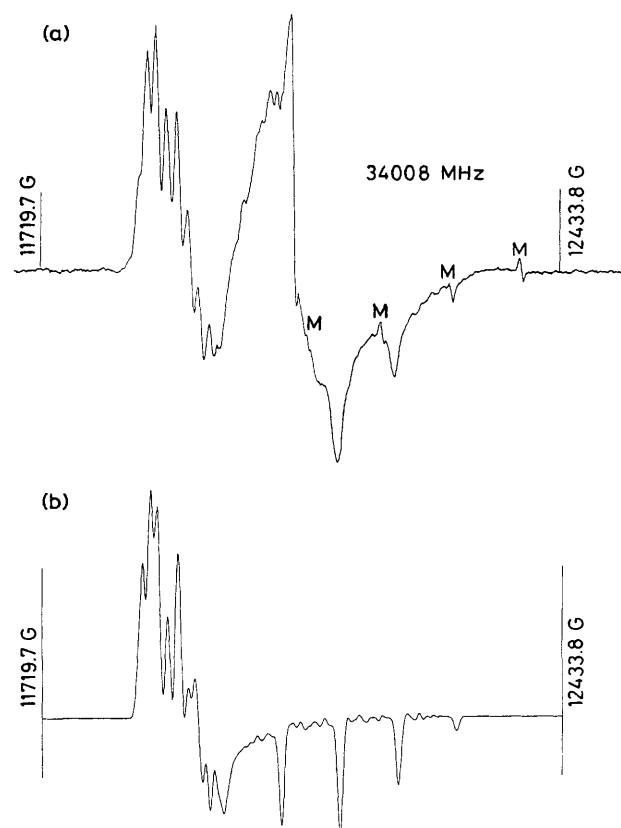

(a)

34008 MHz

11719.7 G   12433.8 G

M   M

M   M

(b)

11719.7 G   12433.8 G

Figure 2. (a) First derivative Q-band ESR spectrum for a dilute solution of P_4 in $CFCl_3$ recorded at 95 K immediately after exposure to γ-rays at 77 K. Refer to the text regarding the central broad signal and the lines indicated with 'M'. (b) A simulation spectrum for the Q-band, calculated using ESR parameters shown in Figure 3 and line-widths of 7 G.
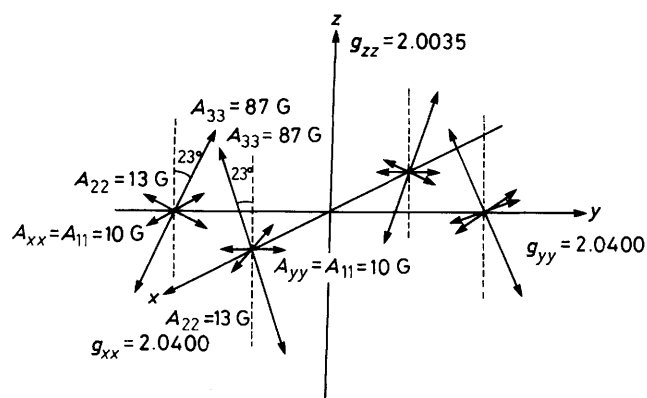
Figure 3. ESR parameters used for the calculation of the simulation spectrum for the $\cdot P_4{}^+$ cations, shown in Figure 1(b), the principal axes of the g-tensor and the hyperfine-tensors of four P nuclei being shown with their principal values.

Figure 4. The D_{2d} 'butterfly' structure proposed for the $\cdot P_4{}^+$ cation. The p orbitals possessing the spin densities of 0.25 are shown, but the s and p orbitals with the spin densities of 0.1 are omitted, the latter p orbitals lying along the bisectors of $\angle$ PPP angles.

broad signal originating from the matrix, and four lines, indicated with 'M', which are attributable to four of six lines due to Mn^{2+} in the quartz tube used. The next highest field line of the four lines is superimposed on the highest field line with a parallel feature. Three equally spaced lines, with parallel features and binomial intensity ratios, suggest that they are three lines of a quintet for $g_{zz} = 2.0035$ and a coupling constant of $ca.$ 79 G ($1\ G = 10^{-4}$ T). The quintet means that cations of P_4 were formed, and suggests that the lowest field line in the X-band spectrum may be an abnormal divergence peak appearing at a fortuitous turning point.[6] The true parallel feature appears as a shoulder on the lowest field line. The form of the observed Q-band spectrum also shows that $g_{xx} \simeq g_{yy} \simeq 2.04$. This suggests a near planar structure for the $\cdot P_4{}^+$ cations.

Accordingly, simulations were performed in order to reproduce the observed X- and Q-band spectra, on the assumption of a planar configuration. It was impossible to obtain simulated spectra to fit the observed X- and Q-band spectra, using one set of ESR parameters. Thus, it was supposed that there is a small distortion from a planar structure. In that case, the major principal axis for the g-tensor is not parallel to the axes of the individual hyperfine-tensor on the four P nuclei, and they will not be parallel to each other.

According to this assumption, simulations were performed with a program containing the nuclear Zeeman terms for four P nuclei, which are necessary for the simulation of Q-band spectra.[7] The simulation spectrum, Figure 1(b), obtained for the ESR parameters shown in Figure 3, is in complete agreement with the observed X-band spectrum, as shown in Figure 1. Using the same ESR parameters, a satisfactory simulation spectrum, Figure 2(b), was also obtained for the Q-band if account was taken of a lot of 'allowed' and 'forbidden' lines in the Q-band, appearing in the directions of the magnetic field nearly perpendicular to the symmetry axis of the hyperfine-tensor of each P nucleus.[7] It was confirmed that agreement is unique, in particular for the X-band spectra, and such an excellent fit for X- and Q-band spectra could not be obtained for four P nuclei in any other symmetry.

The major principal axes of the hyperfine tensors for the four P nuclei incline alternately by $\pm 23°$ from the g_{zz} axis (the molecular axis), as shown in Figure 3. Accordingly, the 'parallel' and 'perpendicular' features are not real but apparent, although they are real for the g-tensor. Being used together with hyperfine coupling constants for a P atom,[8] the
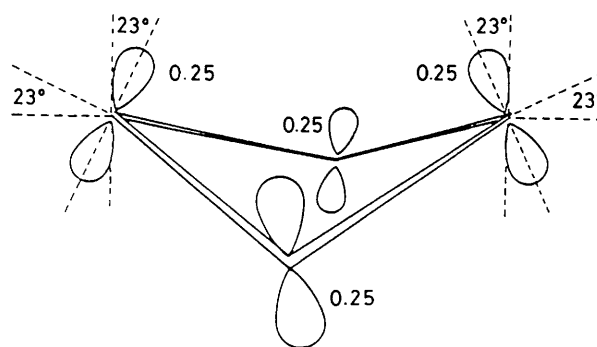
principal values of the hyperfine tensors indicate spin densities of 0.01, 0.25, and 0.01 in 3s and two 3p orbitals, respectively, on each P nucleus. This means that the unpaired electron is largely shared in a 3p orbital, reasonably equally on each P nucleus. The other p orbitals, possessing low spin density, are perpendicular to the p orbital with the spin density of 0.25 and in the plane containing the latter p orbital and the g_{zz} axis. They can be thought of as sp-hybrids which experience some spin polarization. The large shift for g can be ascribed to coupling to these 'lone-pair' orbitals. These results suggest that $\cdot P_4{}^+$ cations have a D_{2d} 'butterfly' structure, as shown in Figure 4, where the orbitals with major spin densities on the P nuclei were included. We conclude that capture of a positive-hole causes the simultaneous cleavage of two bent chemical bonds in the tetrahedral P_4 molecule, resulting in a drastic, but very reasonable, deformation to this butterfly structure of the $\cdot P_4{}^+$ cation. This structure is similar to the zigzag ring structure of S_8 molecules, but constrasts with the proposed linear structure of $\cdot N_4{}^+$ cations.[9]

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