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$$T_{\sigma_i, l}^{(K)} = \begin{cases} -R_l, & K=0 \\ \sum_{p \neq l} \frac{R_p}{(\sigma_l - \sigma_p)^K}, & K \neq 0 \end{cases} \quad (12)$$

For concreteness, Eq. (7) yields for the zeroth-order term in γ ,

$$\gamma^{(0)} = - \sum_i S_{\sigma_i, l}^{(0)} \quad (13)$$

If $G(z)$ is expressed in terms of the eigenfunctions of the unperturbed Hamiltonian, Eqs. (13) and (9) yield the familiar independent particle approximation for γ ; γ is diagonal in this basis with occupied orbital occupation numbers of unity and virtual orbital occupation numbers of zero. The first Born correction¹ $\gamma^{(1)}$ is given by

$$\gamma^{(1)} = - \sum_i [S_{\sigma_i, l}^{(1)} T_{\sigma_i, l}^{(0)} S_{\sigma_i, l}^{(0)} + S_{\sigma_i, l}^{(0)} T_{\sigma_i, l}^{(1)} S_{\sigma_i, l}^{(0)} + S_{\sigma_i, l}^{(0)} T_{\sigma_i, l}^{(0)} S_{\sigma_i, l}^{(1)}] - \sum_i S_{\sigma_i, l}^{(0)} T_{\sigma_i, l}^{(0)} S_{\sigma_i, l}^{(0)} \quad (14)$$

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¹J. D. Doll and W. P. Reinhardt, J. Chem. Phys. 57, 1169 (1972).

²J. Simons [J. Chem. Phys. 59, 2436 (1973)] carries out the analysis through third order.

³See A. Messiah, *Quantum Mechanics* (Wiley, New York, 1966), pp. 712-717.

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⁵We are assuming that a finite basis has been used to represent $G(z)$ and $\Sigma(z)$, which then have no cuts; see the discussion of Ref. 1.

The ESR spectrum of PH_4 *

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There is considerable evidence¹⁻⁴ that the basic structure of free radicals derived from tetravalent phosphorus (phosphoranyl radicals) is that of a distorted trigonal bipyramid in which two ligand sites, apical and equatorial, are distinguished. ESR hyperfine interactions show a striking disparity between the unpaired spin densities at the two positions, and theoretical arguments^{4,5} favor the apical position as having the higher spin density. Thus the two fluorine interactions in PF_4 (259 and 59 G) have been attributed to apical and equatorial ^{19}F nuclei, respectively.⁵

In the face of mounting evidence that all phosphoranyl radicals have a similar structure, the reported⁶ ESR spectrum (four equivalent protons, 21 G) of PH_4 is rather anomalous, unless the possibility of rapid intramolecular proton exchange is invoked. The unexpectedly large ^{31}P hyperfine interaction has also drawn adverse comment and the suggestion of a possible misidentification.⁷ INDO calculations⁸ which we have carried out for PH_4 models having bipyramidal, tetrahedral, and square-planar geometries predict the bipyramidal structure to be more stable than the other two by several kcal/mole. They furthermore predict, for the energy-optimized geometry, hyperfine interactions for the apical and equatorial protons of 245 and 2 G, respectively. These values imply an average proton interaction of ~120 G should rapid intramolecular proton exchange occur.

We therefore sought a method of preparing the radical PH_4 which would yield an isotropic ESR spectrum susceptible to unequivocal interpretation. A neopentane matrix was chosen since (a) it generates hydrogen atoms upon radiolysis and (b) small radicals generated therein exhibit isotropic ESR spectra. By γ irradiation at 77 °K of a matrix consisting of 5% PH_3 in neopentane, we have been able to generate and subsequently detect an ESR spectrum which we attribute to PH_4 radicals.

Phosphine (Matheson) and neopentane (Phillips) were used as received. Deuterophosphine, PD_3 , was prepared⁹ from Ca_3P_2 and D_2O ; neopentane- d_{12} (99%) was obtained from Merck, Sharp, and Dohme Ltd. A gaseous mixture of 5% phosphine and neopentane was condensed into a quartz ESR tube and γ -irradiated at 77 °K for 1 h in a 9000 Curie ^{60}Co source. ESR spectra were subsequently recorded and measured at 100 °K using a Varian E-12 spectrometer.³

The spectrum which we ascribe to PH_4 consisted of eight 6.0 G, 1:2:1 triplets (Table I and Fig. 1). It was conclusively shown by experiments with PD_3 and neopentane- d_{12} that a large interaction of ~500 G was due to a ^{31}P nucleus, and that smaller (~6 and 200 G) interactions were due to pairs of equivalent protons. The characteristic second-order splitting associated with the 200 G interaction was readily resolved. The spectrum of PD_4 , obtained from PD_3 and neopentane-

FIG. 1. ESR spectrum of γ -irradiated 5% PH_3 in neopentane at 100°K. Field measurements of the centers of the 6 G triplets in the spectrum attributed to PH_4 (lower stick spectrum) are given in Table I.

d_{12} , consisted of a pair of 30 G, 1:2:3:2:1 quintets arising from hyperfine interactions with a ^{31}P nucleus and two equivalent deuterons.

The two radicals PH_4 and PD_4 had quite different stabilities in their respective matrices. At 122°K, the extrapolated half-life of PH_4 in neopentane was ~ 1.7 s, whereas the half-life of PD_4 in neopentane- d_{12} was ~ 100 s. This surprisingly large isotope effect is probably indicative of hydrogen-atom transfer between PH_4 and trapped alkyl radicals, effectively healing the radiation damage.

We were also able to detect certain intermediate species in the series $\text{PH}_n\text{D}_{4-n}$ by radiolysis of PH_3 in a neopentane- d_{12} matrix, or PD_3 in a neopentane matrix. The ESR parameters obtained from our spectra are collected in Table II. It will be noted that there are small changes in the ^{31}P and H_{ap} hyperfine interactions upon deuteration in the apical position. These changes are probably

due to slight differences between the amplitude of anti-symmetric vibrations in the different isotopic species.¹⁰

As is apparent from Table II, we have detected PH_3D radicals in which the deuteron was either in the apical or the equatorial position. From the relative intensities of the two spectra, the ratio $[\text{PH}_3\text{D}_{\text{eq}}]/[\text{PH}_3\text{D}_{\text{ap}}]$ was estimated to be 15 ± 5 at 77°K. This preference of the deuteron for the equatorial position is to be expected on thermodynamic grounds. An equatorial P-D bond, being shorter than an apical P-D bond, will have a higher (stretching) vibrational frequency. A difference of about 800 cm^{-1} would account for the observed intensity ratio because of a greater zero-point energy depression (from

TABLE I. ESR spectrum^a of PH_4 at 100°K.

MU_{P}	$ 1,1\rangle^b$	$ 1,0\rangle$	$ 0,0\rangle$	$ 1,-1\rangle$
+0.5	2776.00 ^c	2966.84	2980.86	3171.97
-0.5	d	3492.73	3502.61	3696.29

^aThe spectrum consisted of eight 6.0 G triplets. Microwave frequency 9147.05 ± 0.05 MHz.

^b $|I_{\text{H}_{\text{ap}}}, M(I_{\text{H}_{\text{ap}}})\rangle$.

^cGauss, ± 0.25 G.

^dOverlapped by signal from matrix.

TABLE II. ESR parameters^a of $\text{PH}_n\text{D}_{4-n}$ radicals at 100°K.

Radical	^{31}P	Hyperfine interactions (Gauss)	
		Apical	Equatorial
PH_4	519.3 ^b	198.7 ^b	6.0 ^c
$\text{PH}_3\text{D}_{\text{eq}}$	520.7	198.3	6.0(H) <1.0(D)
$\text{PH}_3\text{D}_{\text{ap}}$	518.1	203.7(H) 30.2(D)	6.0
$\text{PD}_3\text{H}_{\text{ap}}$	517.0	204.2(H) 30.3(D)	<1.0
PD_4	516.0	30.2	<1.0

^aAll g values were 2.0030 ± 0.0002 .

^b ± 0.3 G; shown to have the same sign by best-fit procedures [R. W. Fessenden, *J. Mag. Reson.* 1, 277 (1969)].

^c ± 0.2 G.

that of PH_4) for $\text{PH}_3\text{D}_{\text{eq}}$ than for $\text{PH}_3\text{D}_{\text{ap}}$.

The proton and phosphorus hyperfine interactions in PH_4 are consistent with those of a series of phosphoranyl radicals reported by Krusic *et al.*,² and quite different from those of McDowell *et al.*⁶ We are therefore forced to conclude that the latter authors had not detected PH_4 but another species, possibly containing two phosphorus nuclei.

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Primary radiation products in x-irradiated dihydromethyluracil*

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The primary radicals produced by ionizing radiation in uracil derivatives are of interest in that related species may be produced in irradiated nucleic acids.¹ ESR and ENDOR measurements have been made on single crystals of 5,6-dihydro-6-methyluracil, (I), x-irradiated at 4.2 °K. The effect of low temperature is to stabilize the primary radiation products:

The ESR spectrum obtained with the magnetic field applied parallel to the c' axis is shown in Fig. 1(a).² In partially deuterated crystals in which the exchangeable N-H protons are replaced by deuterons, the spectrum is changed to that shown in Fig. 1(b). One component of the absorption is due to the oxidation product (II). A large hyperfine coupling occurs in this radical between the unpaired electron and the proton of the non-exchangeable hydrogen atom attached to C_6 . The coupling tensor derived from ENDOR measurements is described in Table I. The unpaired electron also interacts with the ^{14}N nucleus, but the ENDOR resonance could not be observed. The ^{14}N coupling tensor given in Table I had to be deduced from ESR measurements. This coupling indicates that the unpaired electron is localized essentially in a $2p\pi$ orbital on N_1 .³ The coupling is nearly axially symmetric and the direction of

axial symmetry approximately coincides with the direction normal to the planar part of the molecule.² The g tensor for the oxidation product absorption is also given in Table I. The direction of maximum g value is approximately parallel to the plane defined by the molecule and perpendicular to the direction of the $\text{N}_1\text{--H}$ bond in the undamaged molecule.² This is also expected theoretically for a nitrogen π -electron radical.³ In nondeuterated crystals the oxidation product absorption exhibits an additional proton hyperfine splitting owing to an exchangeable proton. The characteristics of this proton coupling, as determined from ENDOR measurements, are unlike

FIG. 1. ESR spectra with the magnetic field parallel to the c' axis: (a) normal crystal, (b) partially deuterated crystal.