Calculation of NMR Chemical Shift for a $3d^1$ System in a Strong Crystal Field Environment of Tetrahedral Symmetry (1). Application of the Expansion Method for a Spherical Harmonics for Derivation of Overlap and the Dipole Moment Matrix Elements of |4p> Atomic Orbitals and Derivation of the Radial Integrals for the Hyperfine Interaction for |4p> Atomic Orbitals

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Master formulas for overlap integrals and the dipole moments involving |4p> atomic orbitals have been derived by the expansion method for spherical harmonics. The radial integrals for the hyperfine interaction have also been derived for |4p> atomic orbitals. The calculated values of the overlap integrals and dipole moment matrix elements by the expansion method for spherical harmonics for a hypothetical NO molecule are exactly in agreement with those of Mulliken's method. The radial integrals for the hyperfine interaction may be used to calculate the chemical shift for |4p> atomic orbitals.

Introduction

The expansion method for spherical harmonics has been developed to calculate the NMR chemical shift for a $3d^1$ system in a strong crystal field environment of octahedral, tetragonal and trigonal symmetries.[1] This method was applied to evaluate the hyperfine interaction tensor components, $A\alpha\beta$, and the higher order hyperfine terms in the hamiltonian.[2]

Recently the expansion method for spherical harmonics has been mainly adopted to calculate the NMR chemical shifts arising from the electron orbital angular momentum and the electron spin dipolar-nuclear spin angular momentum interaction for $3d^n$ [3,6], $4d^n$ [4,5,7] and $4f^n$ [8,9] systems in a strong crystal field environment of octahedral,[10,11] tetragonal[12] and trigonal[13] symmetries. Evaluation of two center overlap integrals has been performed using the spheroidal coordinate system by Mulliken, *et al.* In this spheroidal coordinate system, it is required to transform the spherical polar coordinate to the spheroidal coordinate for evaluation of two center integrals. Since, to evaluate two center integrals, two atoms must lie in one coordinate axis, namely the Z axis, a different coordinate transformation of each different overlap and the dipole moment matrix element, using Euler angle is required. To overcome such an inconvenience, the expansion method for spherical harmonics has been also applied to compute two center overlap integrals and the dipole moment matrix elements[15,16] in molecular systems. We found that the numerical values obtained by this method are in exact agreement with those of Mulliken's method. In the previous works,[14,15,16] the expansion method for spherical harmonics has been used to obtaine two center overlap matrix and the dipole moment matrix elements, but the formulas for expansion of |4p> orbital may not be given yet.

The purpose of this work is to derive the two center overlap and dipole moment matrix elements which are not given in the previous work.[14,15,16] The expansion formula is therefore applied to evaluate the radial part integrals for |4p> orbital. Here we adopt Slater type orbitals.

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Two Center Overlap Matrix Elements

Since we are interested in the |4p> atomic orbital centered at the reference point A, we may express the Slater type |4p> atomic orbitals as

$$
\begin{aligned}
|4p_x\rangle &= (\beta^9/105\pi)^{1/2} X r^2 \exp(-\beta r)\\
|4p_y\rangle &= (\beta^9/105\pi)^{1/2}\, y\, r^2 \exp(-\beta r)\\
|4p_z\rangle &= (\beta^9/105\pi)^{1/2}\, z\, r^2 \exp(-\beta r)
\end{aligned} \tag{1}
$$

For 4p atomic orbital, $|\phi\rangle = Nr^k \exp(-\beta r)\, Y_{lm}(\theta,\phi)$, located at arbitrary point B, the spherical harmonic part may be expressed in terms of the reference point A, using the following spherical harmonics part $Y_{lm}(\theta,\phi)$[19] and the exponential part which may also be translated into the following form.

$$
\begin{aligned}
& r^2 \exp(-\beta r)\\
&= 4\pi \sum_{n=0}^{\infty} h_n(R, r_N) \sum_{h=-n}^{n} Y^*_{nh}(\theta,\Phi)\, Y_{nh}(\theta_N,\phi_N)^{14-16,20}
\end{aligned} \tag{2}
$$

Here

$$
h_n(R, r_N) = (r_< r_>)^{-1/2} \sum_{i=0}^{3} H_i\, I_{n-\frac{1}{2}+i}(\beta r_<)\, K_{n-\frac{3}{2}+i}(\beta r_>) \tag{3}
$$

Where

$$H_0 = -\left(\frac{2n}{2n+1}\right) r_< r_>^2$$

$$H_1 = \left\{ r_>^3 + \left(\frac{4n+1}{2n+1}\right) r_<^2 r_> \right\}$$

$$H_2 = -\left\{ r_<^3 + \left(\frac{4n+3}{2n+1}\right) r_< r_>^2 \right\}$$

$H_3 = \left(\frac{2n+2}{2n+1}\right) r_<^2 r_>$, I_ν and K_ν are the modified Bessel functions. Combining the translated spherical harmonics part and the expressed radial part of the |4p> atomic orbitals into

Table 1. Master Formulas for Two Center Overlap Matrix Elements

$\langle 1s \vert 4p_z\rangle = (16/105)^{1/2}$	$(\alpha/\beta)^{3/2}\cos\theta\,(K_1-\alpha G_0)$
$\langle 2s \vert 4p_z\rangle = (16/315)^{1/2}$	$(\alpha/\beta)^{5/2}\cos\theta\,(L_1-\alpha K_0)$
$\langle 2p_z \vert 4p_z\rangle = (16/945)^{1/2}$	$(\alpha/\beta)^{5/2}[L_0+(2\cos^2\theta-\sin^2\theta)L_2-(1+2\cos^2\theta-\sin^2\theta)\alpha K_1]$
$\langle 2p_x \vert 4p_z\rangle = (16/105)^{1/2}$	$(\alpha/\beta)^{5/2}\cos\theta\sin\theta\cos\phi\,(L_2-\alpha K_1)$
$\langle 2p_y \vert 4p_z\rangle = (16/105)^{1/2}$	$(\alpha/\beta)^{5/2}\cos\theta\sin\theta\sin\phi\,(L_2-\alpha K_1)$
$\langle 3s \vert 4p_z\rangle = (32/4725)^{1/2}$	$(\alpha/\beta)^{7/2}\cos\theta\,(M_1-\alpha L_0)$
$\langle 3p_z \vert 4p_z\rangle = (32/14175)^{1/2}$	$(\alpha/\beta)^{7/2}[M_0+(2\cos^2\theta-\sin^2\theta)M_2-(1+2\cos^2\theta-\sin^2\theta)\alpha L_1]$
$\langle 3p_x \vert 4p_z\rangle = (32/1575)^{1/2}$	$(\alpha/\beta)^{7/2}\cos\theta\sin\theta\cos\phi\,(M_2-\alpha L_1)$
$\langle 3p_y \vert 4p_z\rangle = (32/1575)^{1/2}$	$(\alpha/\beta)^{7/2}\cos\theta\sin\theta\sin\phi\,(M_2-\alpha L_1)$
$\langle 3d_{z^2} \vert 4p_z\rangle = (8/23625)^{1/2}$	$(\alpha/\beta)^{7/2}[4\cos\theta\,(M_1-\alpha L_2)+3(2\cos^3\theta-3\cos\theta\sin^2\theta)(M_3-\alpha L_2)]$
$\langle 3d_{zx} \vert 4p_z\rangle = (32/70875)^{1/2}$	$(\alpha/\beta)^{7/2}[\sin\theta\cos\phi\,(M_1-\alpha L_2)+(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi\,(M_3-\alpha L_2)]$
$\langle 3d_{yz} \vert 4p_z\rangle = (32/70875)^{1/2}$	$(\alpha/\beta)^{7/2}[\sin\theta\sin\phi\,(M_1-\alpha L_2)+(4\cos^2\theta\sin\theta-\sin^3\theta)\sin\phi\,(M_3-\alpha L_2)]$
$\langle 3d_{x^2-y^2} \vert 4p_z\rangle = (8/315)^{1/2}$	$(\alpha/\beta)^{7/2}\cos\theta\sin^2\theta\,(\cos^2\phi-\sin^2\phi)(M_3-\alpha L_2)$
$\langle 3d_{xy} \vert 4p_z\rangle = (32/315)^{1/2}$	$(\alpha/\beta)^{7/2}\cos\theta\sin^2\theta\sin\phi\cos\phi\,(M_3-\alpha L_2)$
$\langle 4s \vert 4p_z\rangle = (4/315)(3)^{1/2}$	$(\alpha/\beta)^{9/2}\cos\theta\,(Y_1-\alpha M_0)$
$\langle 4p_z \vert 4p_z\rangle = (4/315)$	$(\alpha/\beta)^{9/2}[Y_0+(2\cos^2\theta-\sin^2\theta)Y_2-(1+2\cos^2\theta-\sin^2\theta)\alpha M_1]$
$\langle 4p_x \vert 4p_z\rangle = (4/105)$	$(\alpha/\beta)^{9/2}\cos\theta\sin\theta\cos\phi\,(Y_2-\alpha M_1)$
$\langle 4p_y \vert 4p_z\rangle = (4/105)$	$(\alpha/\beta)^{9/2}\cos\theta\sin\theta\sin\phi\,(Y_2-\alpha M_1)$
$\langle 4d_{z^2} \vert 4p_z\rangle = (4/315)(3/20)^{1/2}$	$(\alpha/\beta)^{9/2}[4\cos\theta\,(Y_1-\alpha M_2)+3(2\cos^3\theta-3\cos\theta\sin^2\theta)(Y_3-\alpha M_2)]$
$\langle 1s \vert 4p_x\rangle = (16/105)^{1/2}$	$(\alpha/\beta)^{3/2}\sin\theta\cos\phi\,(K_1-\alpha G_0)$
$\langle 2s \vert 4p_x\rangle = (16/315)^{1/2}$	$(\alpha/\beta)^{5/2}\sin\theta\cos\phi\,(L_1-\alpha K_0)$
$\langle 2p_z \vert 4p_x\rangle = (16/105)^{1/2}$	$(\alpha/\beta)^{5/2}\cos\theta\sin\theta\cos\phi\,(L_2-\alpha K_1)$
$\langle 2p_x \vert 4p_x\rangle = (4/945)^{1/2}$	$(\alpha/\beta)^{5/2}\{2(L_0-\alpha K_1)-[2\cos^2\theta-\sin^2\theta-3\sin^2(\cos^2\phi-\sin^2\phi)](L_2-\alpha K_1)]\}$
$\langle 2p_y \vert 4p_x\rangle = (16/105)^{1/2}$	$(\alpha/\beta)^{5/2}\sin^2\theta\sin\phi\cos\phi\,(L_2-\alpha K_1)$
$\langle 3s \vert 4p_x\rangle = (32/4725)^{1/2}$	$(\alpha/\beta)^{7/2}\sin\theta\cos\phi\,(M_1-\alpha L_0)$
$\langle 3p_z \vert 4p_x\rangle = (32/1575)^{1/2}$	$(\alpha/\beta)^{7/2}\cos\theta\sin\theta\cos\phi\,(M_2-\alpha L_1)$
$\langle 3p_x \vert 4p_x\rangle = (8/14175)^{1/2}$	$(\alpha/\beta)^{7/2}\{2(M_0-\alpha L_1)-[2\cos^2\theta-\sin^2\theta-3\sin^2\theta(\cos^2\phi-\sin^2\phi)](M_2-\alpha L_1)\}$
$\langle 3p_y \vert 4p_x\rangle = (32/1575)^{1/2}$	$(\alpha/\beta)^{7/2}\sin^2\theta\sin\phi\cos\phi\,(M_2-\alpha L_1)$
$\langle 3d_{z^2} \vert 4p_x\rangle = (8/23625)^{1/2}$	$(\alpha/\beta)^{7/2}[3(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi\,(M_3-\alpha L_2)-2\sin\theta\cos\phi\,(M_1-\alpha L_2)]$
$\langle 3d_{zx} \vert 4p_x\rangle = (8/7875)^{1/2}$	$(\alpha/\beta)^{7/2}\{2\cos\theta\,(M_1-\alpha L_2)-[2\cos^3\theta-3\cos\theta\sin^2\theta-5\cos\theta\sin^2\theta(\cos^2\phi-\sin^2\phi)](M_3-\alpha L_2)\}$
$\langle 3d_{yz} \vert 4p_x\rangle = (32/315)^{1/2}$	$(\alpha/\beta)^{7/2}\cos\theta\sin^2\theta\sin\phi\cos\phi\,(M_3-\alpha L_2)$
$\langle 3d_{x^2-y^2} \vert 4p_x\rangle = (2/7875)^{1/2}$	$(\alpha/\beta)^{7/2}\{4\sin\theta\cos\phi\,(M_1-\alpha L_2)-[(4\cos^2\theta\sin^3\theta)\cos\phi+5\sin^3\theta(4\cos^3\phi-3\cos\phi)](M_3-\alpha L_2)\}$
$\langle 3d_{xy} \vert 4p_x\rangle = (2/7875)^{1/2}$	$(\alpha/\beta)^{7/2}\{4\sin\theta\sin\phi\,(M_1-\alpha L_2)-[(4\cos^2\theta\sin\theta-\sin^3\theta)\sin\phi+5\sin^3\theta(3\sin\phi-4\sin^3\phi)](M_3-\alpha L_2)\}$
$\langle 4s \vert 4p_x\rangle = (4/315)(3)^{1/2}$	$(\alpha/\beta)^{9/2}\sin\theta\cos\phi\,(Y_1-\alpha M_0)$
$\langle 4p_z \vert 4p_x\rangle = (4/105)$	$(\alpha/\beta)^{9/2}\cos\theta\sin\theta\cos\phi\,(Y_2-\alpha M_1)$
$\langle 4p_x \vert 4p_x\rangle = (2/315)$	$(\alpha/\beta)^{9/2}\{2(Y_0-\alpha M_1)-[2\cos^2\theta-\sin^2\theta-3\sin^2\theta(\cos^2\phi-\sin^2\phi)](Y_2-\alpha M_1)\}$
$\langle 4p_y \vert 4p_x\rangle = (4/105)$	$(\alpha/\beta)^{9/2}\sin^2\theta\sin\phi\cos\phi\,(Y_2-\alpha M_1)$
$\langle 4d_{zx} \vert 4p_x\rangle = (4/315)(9/20)^{1/2}$	$(\alpha/\beta)^{9/2}\{2\cos\theta\,(Y_1-\alpha L_2)-2\cos^3\theta-3\cos\theta\cos^2\theta-5\cos\theta\sin^2\theta(\cos^2\phi-\sin^2\phi)](Y_3-\alpha M_2)\}$
$\langle 1s \vert 4p_y\rangle = (16/105)^{1/2}$	$(\alpha/\beta)^{3/2}\sin\theta\sin\phi\,(K_1-\alpha G_0)$
$\langle 2s \vert 4p_y\rangle = (16/315)^{1/2}$	$(\alpha/\beta)^{5/2}\sin\theta\sin\phi\,(L_1-\alpha K_0)$
$\langle 2p_z \vert 4p_y\rangle = (16/105)^{1/2}$	$(\alpha/\beta)^{5/2}\cos\theta\sin\theta\sin\phi\,(L_2-\alpha K_1)$
$\langle 2p_x \vert 4p_y\rangle = (16/105)^{1/2}$	$(\alpha/\beta)^{5/2}\sin^2\theta\sin\phi\cos\phi\,(L_2-\alpha K_1)$
$\langle 2p_y \vert 4p_y\rangle = (4/945)^{1/2}$	$(\alpha/\beta)^{5/2}[2(L_0-\alpha K_1)-3\sin^2\theta\,(\cos\phi-\sin^2\phi)(L_2-\alpha K_1)+(2\cos^2\theta-\sin^2\theta)(L_2+\alpha K_1)]$
$\langle 3s \vert 4p_y\rangle = (32/4725)^{1/2}$	$(\alpha/\beta)^{7/2}\sin\theta\sin\phi\,(M_1-\alpha L_0)$
$\langle 3p_z \vert 4p_y\rangle = (32/1575)^{1/2}$	$(\alpha/\beta)^{7/2}\cos\theta\sin\theta\sin\phi\,(M_2-\alpha L_1)$
$\langle 3p_x \vert 4p_y\rangle = (32/1575)^{1/2}$	$(\alpha/\beta)^{7/2}\sin^2\theta\sin\phi\cos\phi\,(M_2-\alpha L_1)$
$\langle 3p_y \vert 4p_y\rangle = (8/14175)^{1/2}$	$(\alpha/\beta)^{7/2}[2(M_0-\alpha L_1)-3\sin^2\theta\,(\cos^2\phi-\sin^2\phi)(M_2-\alpha L_1)+(2\cos^2\theta-\sin^2\theta)(M_2+\alpha L_1)]$
$\langle 3d_{z^2} \vert 4p_y\rangle = (8/23625)^{1/2}$	$(\alpha/\beta)^{7/2}[3(4\cos^2\theta\sin\theta-\sin^3\theta)\sin\phi\,(M_3-\alpha L_2)-2\sin\theta\sin\phi\,(M_1-\alpha L_2)]$
$\langle 3d_{zx} \vert 4p_y\rangle = (32/315)^{1/2}$	$(\alpha/\beta)^{7/2}\cos\theta\sin^2\theta\sin\phi\cos\phi\,(M_3-\alpha L_2)$
$\langle 3d_{yz} \vert 4p_y\rangle = (8/7875)^{1/2}$	$(\alpha/\beta)^{7/2}\{2\cos\theta\,(M_1-\alpha L_2)-[(2\cos^3\theta-3\cos\theta\sin^2\theta+5\cos\theta\sin^2\theta(\cos^2\phi-\sin^2\phi)](M_3-\alpha L_2)\}$
$\langle 3d_{x^2-y^2} \vert 4p_y\rangle = (2/7875)^{1/2}$	$(\alpha/\beta)^{7/2}\{4\sin\theta\sin\phi\,(M_1-\alpha L_2)-[(4\cos^2\theta\sin\theta-\sin^3\theta)\sin\phi-5\sin^3\theta(3\sin\phi-4\sin^3\phi))(M_3-\alpha L_2)\}$
$\langle 3d_{xy} \vert 4p_y\rangle = (2/7875)^{1/2}$	$(\alpha/\beta)^{7/2}\{4\sin\theta\cos\phi\,(M_1-\alpha L_2)-[(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi-5\sin^3\theta(4\cos^3\phi-3\cos\phi)](M_3-\alpha L_2)\}$
$\langle 4s \vert 4p_y\rangle = (4/315)(3)^{1/2}$	$(\alpha/\beta)^{9/2}\sin\theta\sin\phi\,(Y_1-\alpha M_0)$
$\langle 4p_z \vert 4p_y\rangle = (4/105)$	$(\alpha/\beta)^{9/2}\cos\theta\sin\theta\sin\phi\,(Y_2-\alpha M_1)$
$\langle 4p_x \vert 4p_y\rangle = (4/105)$	$(\alpha/\beta)^{9/2}\sin^2\theta\sin\phi\cos\phi\,(Y_2-\alpha M_1)$
$\langle 4p_y \vert 4p_y\rangle = (2/315)$	$(\alpha/\beta)^{9/2}[2(Y_0-\alpha M_1)-3\sin^2\theta\,(\cos^2\phi-\sin^2\phi)(Y_2-\alpha M_1)+(2\cos^2\theta-\sin^2\theta)(Y_2+\alpha M_1)]$

Where the radial part integrals are defined elsewhere.[15]

reference point, we may obtain the master formulas of |4p> atomic orbitals. The master formulas of overlap matrix elements for |4p> atomic orbitals are listed in Table 1.

Dipole Moment Matrix Elements

The dipole moment matrix elements may be obtained by combining the overlap matrix elements evaluated by the expansion method for spherical harmonics with the dipole moment operators expressed in terms of spherical harmonics,[21] the corresponding dipole moment matrix elements may be obtained. The master formulas of the dipole moment matrix element orbital involving $|4p\rangle$ atomic are listed in appendix.

Radial Integrals of $|4p\rangle$ Atomic Orbitals for the Hyperfine Interaction

To evaluate the hyperfine integrals of Slater type $|4p\rangle$ atomic orbitals expressed in equation (1), the integrand is expressed as a functioin or R and r_N and we introduce the following notation for $|4p\rangle$ atomic orbitals,[22]

$$R_n^{(L)}(t)=4\beta_1^{11}(-R)^L\int_0^\infty r_n^{5-L-4}\,h_n(R,r_N)dr_N \tag{4}$$

where $t=2\beta_1 R$, and further, for convenience

$$\begin{aligned} U_n(t)&=R_n^{(2)}(t)\\ V_n(t)&=R_n^{(1)}(t)\\ W_n(t)&=R_n^{(0)}(t) \end{aligned} \tag{5}$$

From the angular parts of the hyperfine integrals, selection rules may be obtained in n. The required radial integrals are listed in Table 2.

Results and Discussion

Using the analytical formulas listed in Table 2, the calculated overlap integrals for a hypothetical NO molecule are represented in Table 3 with Mulliken's results. As shown in Table 3, the numerical values of two center overlap integrals calculated, adopting the expansion method for spherical harmonics, are in exact agreement with those of Mulliken's method.

In Table 4, we represent the numerical values of the dipole moment matrix elements evaluated using the analytical formulas listed in appendix with the transformed overlap integrals for the dipole moment matrix elements[17] for a hypothetical NO molecule. As shown in Table 4, matrix elements evaluated by the expansion method for spherical harmonics are also in exact agreement with those for the transformed overlap in-

Table 2. The Required Radial Integrals for the 4P-Orbitals

$$U_2(t)=\beta_1^3\left[\frac{45}{t}-\left(\frac{t^6}{48}+\frac{t^5}{16}+\frac{3t^4}{8}+\frac{15t^3}{8}+\frac{15t^2}{2}+\frac{45t}{2}+45+\frac{45}{t}\right)e^{-t}\right]$$

$$V_1(t)=-\beta_1^3\left[\frac{45}{t}-\left(\frac{t^5}{16}+\frac{3t^4}{8}+\frac{15t^3}{8}+\frac{15t^2}{2}+\frac{45t}{2}+45+\frac{45}{t}\right)e^{-t}\right]$$

$$V_3(t)=-\beta_1^3\left[\left(\frac{45}{t}-\frac{4200}{t^3}\right)+\left(\frac{t^5}{24}+\frac{11t^4}{24}+\frac{95t^3}{24}+\frac{55t^2}{2}+\frac{305t}{2}+655+\frac{2055}{t}+\frac{4200}{t^2}+\frac{4200}{t^3}\right)e^{-t}\right]$$

$$W_0(t)=\beta_1^3\left[\frac{45}{t}-\left(\frac{t^4}{16}+\frac{5t^3}{8}+\frac{15t^2}{4}+15t+\frac{75}{2}+\frac{45}{t}\right)e^{-t}\right]$$

$$W_2(t)=\beta_1^3\left[\left(\frac{45}{t}-\frac{2520}{t^3}\right)+\left(\frac{t^4}{8}+\frac{13t^3}{8}+\frac{27t^2}{2}+\frac{165t}{2}+375+\frac{1215}{t}+\frac{2520}{t^2}+\frac{2520}{t^3}\right)e^{-t}\right]$$

$$W_4(t)=\beta_1^3\left[\left(\frac{45}{t}-\frac{8400}{t^3}+\frac{529200}{t^5}\right)-\left(\frac{t^4}{6}+\frac{10t^3}{3}+\frac{85t^2}{2}+\frac{815t}{2}+3055+\frac{17895}{t}+\frac{79800}{t^2}+\frac{256200}{t^3}+\frac{529200}{t^4}+\frac{529200}{t^5}\right)e^{-t}\right]$$

$^*t=2\beta_1 R$.

Table 3. The Numerical Values of Two Center Overlap Integrals for a Hypothetical NO Molecule ($\alpha=1.950$, $\beta=2.275$ and r = 1.50Å)

Overlap Integral	Numerical Value	
	This Method	Mulliken's Method
$\langle 1s\|4Pz\rangle$	0.326719	0.326719
$\langle 2s\|4Pz\rangle$	0.451562	0.451562
$\langle 3s\|4Pz\rangle$	0.481152	0.481152
$\langle 4s\|4Pz\rangle$	0.422939	0.422939
$\langle 2Pz\|4Pz\rangle$	0.342577	0.342577
$\langle 3Pz\|4Pz\rangle$	0.382617	0.382617
$\langle 4Pz\|4Pz\rangle$	0.327667	0.327667
$\langle 3dz^2\|4Pz\rangle$	0.123143	0.123143
$\langle 4dz^2\|4Pz\rangle$	0.063381	0.063381
$\langle 2Px\|4Pz\rangle$	0.200616	0.200616
$\langle 3Px\|4Px\rangle$	0.297287	0.297287
$\langle 4Px\|4Px\rangle$	0.370897	0.370897
$\langle 3dxz\|4Px\rangle$	0.355301	0.355301
$\langle 4dxz\|4Px\rangle$	0.472562	0.472562

Table 4. The Numerical Results for the Dipole Moment Matrix Element and the corresponding Transformed Overlap Integrals ($\alpha=1.950$, $\beta=2.275$ and r = 1.50Å)

Dipole moment matrix elements	Numerical value	Transformed overlap integrals	Numerical value
$\langle 1s\|z\|4p_z\rangle$	0.175681	$(1/\alpha)\langle 2p_z\|4p_z\rangle$	0.175681
$\langle 2s\|z\|4p_z\rangle$	0.310241	$(5/2)/\alpha\langle 3p_z\|4p_z\rangle$	0.310241
$\langle 3s\|z\|4p_z\rangle$	0.362996	$(14/3)^{1/2}/\alpha\langle 4p_z\|4p_z\rangle$	0.363098
$\langle 4s\|z\|4p_z\rangle$	0.287369	$(15/2)^{1/2}/\alpha\langle 5p_z\|4p_z\rangle$	0.287755
$\langle 2p_z\|z\|4p_z\rangle$	0.479445	$(5/2)^{1/2}/\alpha\langle 3s\|4p_z\rangle$ $+(2)^{1/2}/\alpha\langle 3d_{z^2}\|4p_z\rangle$	0.287755 0.479445
$\langle 3p_z\|z\|4p_z\rangle$	0.531341	$(14/3)^{1/2}/\alpha\langle 4s\|4p_z\rangle$ $+(56/15)^{1/2}/\alpha\langle 4dz^2\|4P_z\rangle$	0.531341
$\langle 4p_z\|z\|4p_z\rangle$	0.385697	$(15/2)^{1/2}/\alpha\langle 5s\|4p_z\rangle$ $+(6)^{1/2}/\alpha\langle 5d_z^2\|4p_z\rangle$	0.385437
$\langle 2p_x\|z\|4p_x\rangle$	0.223156	$(3/2)^{1/2}/\alpha > 3d_{xz}\|4p_x\rangle$	0.223156
$\langle 3p_x\|z\|4p_x\rangle$	0.405511	$(15/5)^{1/2}/\alpha\langle 4d_{xz}\|4p_x\rangle$	0.405511
$\langle 4p_x\|z\|4p_x\rangle$	0.595415	$(9/2)^{1/2}/\alpha\langle 5d_{xz}\|4p_x\rangle$	0.595415

tegrals for the dipole moment matrix elements. Such results indicate that we may use to calculate two center integrals such as the overlap integrals and the dipole moment matrix elements involving |4p> atomic orbitals without coordinate transformations into spheroidal coordinate.

From the radial integrals for the hyperfine interaction of the |4p> atomic orbitals, we may calculate tne NMR chemical shift for |4p> atomic orbital, but it was reported that the correct 3d wave functions to use in the construction of the tetrahedral state are then given by first-order perturbation theory as.[23]

$$\Psi(3d) = \Psi^{\circ}(3d) - \sum_{p} \frac{\langle \Psi^{\circ}(3d) | v | \Psi^{\circ}(4p) \rangle}{E_p^{\circ} - E_d^{\circ}} 4p \qquad (6)$$

Here v = kxyz in cartesian coordinates where k is a constant.[24]

APPENDIX: Master Formulas for Dipole Moment Matrix Elements involving |4p> Atomic Orbitals

$$\langle 1s |z| 4p_z\rangle = (16/945)^{1/2} \quad (\alpha/\beta)^{3/2}\{(L_4 - aK_1) + (2\cos^2\theta - \sin^2\theta)(L_2 - aK_1)\}/\beta$$

$$\langle 2s |z| 4p_z\rangle = (16/2835)^{1/2} \quad (\alpha/\beta)^{5/2}[(M_4 - aL_1) + (2\cos^2\theta - \sin^2\theta)(M_2 - aL_1)]/\beta$$

$$\langle 2p_z |z| 4p_z\rangle = (16/23625)^{1/2} \quad (\alpha/\beta)^{5/2}[\cos\theta\,(9M_1 - 5aL_4 - 4aL_2) + 3(2\cos^3\theta - 3\cos\theta\sin^2\theta)(M_3 - aL_3)]/\beta$$

$$\langle 2p_x |z| 4p_z\rangle = (16/2625)^{1/2} \quad (\alpha/\beta)^{5/2}[\sin\theta\cos\phi\,(M_1 - aL_2) + (4\cos^2\theta\sin\theta - \sin^3\theta)\cos\phi\,(M_3 - aL_3)/\beta$$

$$\langle 3s |z| 4p_z\rangle = (32/42525)^{1/2} \quad (\alpha/\beta)^{7/2}[(Y_0 - aM_1) + (2\cos^2\theta - \sin^2\theta)(Y_2 - aM_1)]/\beta$$

$$\langle 3p_z |z| 4p_z\rangle = (4/225)(2/7)^{1/2} \quad (\alpha/\beta)^{7/2}[\cos\theta\,(9Y_1 - 5aM_4 - 4aM_2) + 3(2\cos^3\theta - 3\cos\theta\sin^2\theta)(Y_3 - aM_3)]/\beta$$

$$\langle 3p_x |z| 4p_z\rangle = (32/39375)^{1/2} \quad (\alpha/\beta)^{7/2}[\sin\theta\cos\phi\,(Y_1 - aM_2) + (4\cos^2\theta\sin\theta - \sin^3\theta)\cos\phi\,(Y_3 - aM_2)]/\beta$$

$$\langle 3d_z2 |z| 4p_z\rangle = (1/315)(8/105)^{1/2} \quad (\alpha/\beta)^{7/2}[28(Y_0 - aM_1) + (2\cos^2\theta) - \sin^2\theta\,(55Y_2 - 28aM_1 - 27aM_3) + 9(35\cos^4\theta - 30\cos^2\theta + 3)(Y_4 - aM_3)]/\beta$$

$$\langle 3d_{xz} |z| 4p_z\rangle = (4/315)(2/35)^{1/2} \quad (\alpha/\beta)^{7/2}[3\cos\theta\sin\theta\cos\phi\,(15Y_2 - 7aM_1 - 8aM_3) + 15\sin\theta\,(7\cos^2\theta - 3\cos\theta)\cos\phi\,(Y_4 - aM_3)]/\beta$$

$$\langle 4s |z| 4p_z\rangle = (4/315)(1/3)^{1/2} \quad (\alpha/\beta)^{9/2}[(\Delta_0 - aY_1) + (2\cos^2\theta - \sin^2\theta)(\Delta_2 - aY_1)]/\beta$$

$$\langle 4p_z |z| 4p_z\rangle = (4/1575) \quad (\alpha/\beta)^{9/2}[\cos\theta\,(9\Delta_1 - 5aY_4 - 4aY_2) + 3(2\cos^3\theta - 3\cos\theta\sin^2\theta)(\Delta_3 - aY_2)]/\beta$$

$$\langle 4p_x |z| 4p_z\rangle = (4/525) \quad (\alpha/\beta)^{9/2}[\sin\theta\cos\phi\,(\Delta_1 - aY_2) + (4\cos^2\theta\sin\theta - \sin^3\theta)\cos\phi\,(\Delta_3 - aY_2)]/\beta$$

$$\langle 4d_z2 |z| 4p_z\rangle = (2/2205)(1/7)^{1/2} \quad (\alpha/\beta)^{9/2}[28(\Delta_0 - aY_1) + (2\cos^2\theta - \sin^2\theta)(55\Delta_2 - 28aY_1 - 27aY_3) + 9(35\cos^4\theta - 30\cos^2\theta + 3)\Delta_4 - a\Delta_3]/\beta$$

$$\langle 2p_x |z| 4p_x\rangle = (4/2625)^{1/2} \quad (\alpha/\beta)^{5/2}[2\cos\theta M_1 - (2\cos^3\theta - 3\cos\theta\sin^2\theta)M_3 - \{2\cos\theta - (2\cos^3\theta - 3\cos\theta\sin^2\theta)\}aL_2 + 10\cos\theta\sin^2\theta\,(\cos^2\phi - \sin^2\phi)(M_3 - aL_3)]/\beta$$

$$\langle 3p_x |z| 4p_x\rangle = (8/39375)^{1/2} \quad (\alpha/\beta)^{7/2}[2\cos\theta Y_1 - (2\cos^3\theta - 3\cos\theta\sin^2\theta)Y_3 - \{2\cos\theta - (2\cos^3\theta - 3\cos\theta\sin^2\theta)\}aM_2 + 10\cos\theta\sin^2\theta\,(\cos^2\phi - \sin^2\phi)(Y_3 - aM_3)]/\beta$$

$$\langle 3d_{xz} |z| 4p_x\rangle = (2/315)(2/35)^{1/2} \quad (\alpha/\beta)^{7/2}[14(Y_0 - aM_1) + (2\cos^2\theta - \sin^2\theta)(5Y_2 + 7aM_1 - 12aM_3) + 3\sin^2\theta\,(\cos^2\phi - \sin^2\phi)(5Y_2 - 7aM_1 + 2aM_3) - 3\{(35\cos^4\theta - 30\cos^2\theta + 3) + 5\sin^2\theta\,(7\cos^2\theta - 1)(\cos^2\phi - \sin^2\phi)\}(Y_4 - aM_3)]/\beta$$

$$\langle 4p_x |z| 4p_x\rangle = (2/525) \quad (\alpha/\beta)^{9/2}[2\cos\theta\,\Delta_1 - (2\cos^3\theta - 3\cos\theta\sin^2\theta)\Delta_3 - \{2\cos\theta - (2\cos^3\theta - 3\cos\theta\sin^2\theta)\}aY_2 + 10\cos\theta\sin^2\theta\,(\cos^2\phi - \sin^2\phi)(\Delta_3 - aY_3)]/\beta$$

$$\langle 2p_y |z| 4p_y\rangle = (4/2625)^{1/2} \quad (\alpha/\beta)^{5/2}(2\cos\theta\,(M_1 - aL_2) - (2\cos^3\theta - 3\cos\theta\sin^2\theta)(M_3 - aL_2) - 5\cos\theta\sin^2\theta\,(\cos^2\phi - \sin^2\phi)(M_3 - aL_3)]/\beta$$

$$\langle 3p_y |z| 4p_y\rangle = (8/39375)^{1/2} \quad (\alpha/\beta)^{7/2}(2\cos\theta\,(Y_1 - aM_2) - (2\cos^3\theta - 3\cos\theta\sin^2\theta)(Y_3 - aM_2) - 5\cos\theta\sin^2\theta\,(\cos^2\phi - \sin^2\phi)(Y_3 - aM_3)]/\beta$$

$$\langle 3d_{yz} |z| 4p_y\rangle = (2/315)(2/35)^{1/2} \quad (\alpha/\beta)^{7/2}[14(Y_0 - aM_1) + (2\cos^2\theta - \sin^2\theta)(5Y_2 + 7aM_1 - 12aM_3) - 3\sin^2\theta\,(\cos^2\phi - \sin^2\phi)(5Y_2 - 7aM_1 + 2aM_3) + 3\{(35\cos^4\theta - 30\cos^2\theta + 3) - 5\sin^2\theta\,(7\cos^2\theta - 1)(\cos^2\phi - \sin^2\phi)\}(Y_4 - aM_3)]/\beta$$

$$\langle 4p_y |z| 4p_y\rangle = (2/525) \quad (\alpha/\beta)^{9/2}\{2\cos\theta\,(\Delta_1 - aY_2) - (2\cos^3\theta - 3\cos\theta\sin^2\theta)(\Delta_3 - aY_2) - 5\cos\theta\sin^2\theta\,(\cos^2\phi - \sin^2\phi)(\Delta_3 - aY_3)]/\beta$$

$$\langle 1s |x| 4p_z\rangle = (16/105)^{1/2} \quad (\alpha/\beta)^{3/2}\cos\theta\sin\theta\cos\phi\,(L_2 - aK_1)/\beta$$

$$\langle 2s |x| 4p_z\rangle = (16/315)^{1/2} \quad (\alpha/\beta)^{5/2}\cos\theta\sin\theta\cos\phi\,(M_2 - aL_1)/\beta$$

$$\langle 2p_z |x| 4p_z\rangle = (16/2625)^{1/2} \quad (\alpha/\beta)^{5/2}[\sin\theta\cos\phi\,(M_1 - aL_2) + (4\cos^2\theta\sin\theta - \sin^3\theta)\cos\phi\,(M_3 - aL_2)]/\beta$$

$$\langle 2p_x |x| 4p_z\rangle = (4/23625)^{1/2} \quad (\alpha/\beta)^{5/2}[2\cos\theta\,(3M_1 - 5aL_4 + 2aL_2) - 3\{(2\cos^3\theta - 3\cos\theta\sin^2\theta) - 5\cos\theta\sin^2\theta\,(\cos^2\phi - \sin^2\phi)\}(M_3 - aL_2)]/\beta$$

$$\langle 3s |x| 4p_z\rangle = (32/4725)^{1/2} \quad (\alpha/\beta)^{7/2}\cos\theta\sin\theta\cos\phi\,(Y_2 - aM_1)/\beta$$

$$\langle 3_z |x| 4p_z\rangle = (32/39375)^{1/2} \quad (\alpha/\beta)^{7/2}[\sin\theta\cos\phi\,(Y_1 - aM_2) + (4\cos^2\theta\sin\theta - \sin^3\theta)\cos\phi\,(Y_3 - aM_2)]/\beta$$

$$\langle 3p_z |x| 4p_z\rangle = (2/225)(2/7)^{1/2} \quad (\alpha/\beta)^{7/2}[2\cos\theta\,(3Y_1 - 5aM_4 + 2aM_2) - 3\{(2\cos^3\theta - 3\cos\theta\sin^2\theta) - 5\cos\theta\sin^2\theta\,(\cos^2\phi - \sin^2\phi)\}(Y_3 - aL_2)]/\beta$$

$$\langle 3d_{xz} |x| 4p_z\rangle = (2/315)(2/105)^{1/2} \quad (\alpha/\beta)^{7/2}[14(Y_0 - aM_1) + (2\cos^2\theta - \sin^2\theta)(5Y_2 - 14aM_1 + 9aM_3) + 15\sin^2\theta\,(\cos^2\phi - \sin^2\phi)(Y_2 - aM_1) - 3\{(35\cos^4\theta - 30\cos^2\theta + 3) - 5\sin^2\theta\,(\cos^2\theta - 1)(\cos^2\phi - \sin^2\phi)\}(Y_4 - aM_3)]/\beta$$

$$\langle 4s |x| 4p_z\rangle = (4/315)(3)^{1/2} \quad (\alpha/\beta)^{9/2}\cos\theta\sin\theta\cos\phi\,(\Delta_2 - aY_1)/\beta$$

$$\langle 4p_x |x| 4p_z\rangle = (4/525) \quad (\alpha/\beta)^{9/2}[\sin\theta\cos\phi\,(\Delta_1 - aY_2) + (4\cos^2\theta\sin\theta - \sin^3\theta)\cos\phi\,(\Delta_3 - aY_2)]/\beta$$

$$\langle 4p_z |x| 4p_z\rangle = (2/1575) \quad (\alpha/\beta)^{9/2}[2\cos\theta\,(3\Delta_1 - 5aY_4 + 2aY_2) - 3\{(2\cos^3\theta - 3\cos\theta\sin^2\theta) - 5\cos\theta\sin^2\theta\,(\cos^2\phi - \sin^2\phi)\}(\Delta_3 - aY_2)]/\beta$$

$$\langle 1s |x| 4p_x\rangle = (4/945)^{1/2} \quad (\alpha/\beta)^{3/2}[2(L_0 - aK_1) + \{3\sin^2\theta\,(\cos^2\phi - \sin^2\phi) - (2\cos^2\theta - \sin^2\theta)\}(L_2 - aK_1)]/\beta$$

$$\langle 2s |x| 4p_x\rangle = (4/2835)^{1/2} \quad (\alpha/\beta)^{5/2}[2(M_0 - aL_1) + \{3\sin^2\theta\,(\cos^2\phi - \sin^2\phi) - (2\cos^2\theta - \sin^2\theta)\}(M_2 - aL_1)]/\beta$$

$$\langle 2p_x |x| 4p_x\rangle = (1/23625)^{1/2} \quad (\alpha/\beta)^{5/2}[4\sin\theta\cos\phi\,(9M_1 - 5aL_4 - 4aL_2) - 3\{3(4\cos^2\theta\sin\theta - \sin^3\theta)\cos\phi - 5\sin^3\theta\,(4\cos^3\phi - 3\cos\phi)(M_3 - aL_3)]/\beta$$

$$<3s\,||x|4p_x> = (8/42525)^{1/2} \quad (\alpha/\beta)^{7/2}\{2(Y_4 - aM_1) + \{3\sin^2\theta(\cos^2\phi - \sin^2\phi) - (2\cos^2\theta - \sin^2\theta)\}(Y_2 - aM_1)\}/\beta$$

$$<3p_x\,|x|4p_x> = (1/225)(2/7)^{1/2} \quad (\alpha/\beta)^{7/2}[4\sin\theta\cos\phi(9Y_1 - 5aM_0 - 4aM_2) - 3\{3(4\cos^2\theta\sin\theta - \sin^3\theta)\cos\phi - 5\sin^3\theta (4\cos^3\phi - 3\cos\phi)\}(Y_3 - aM_2)]/\beta$$

$$<3d_{zx}|x|4p_x> = (1/105)(2/35)^{1/2} \quad [4\cos\theta\sin\theta\cos\phi(15Y_2 - 7aM_1 - 8aM_3) - 5\{3\sin\theta(7\cos^3\theta - 3\cos\theta)\cos\phi - 7\sin^3\theta\cos\theta(4\cos^3\phi - 3\cos\phi)\}(Y_4 - aM_3)]/\beta$$

$$<4s\,|x|4p_x> = (4/945)(1/3)^{1/2} \quad (\alpha/\beta)^{9/2}[2(\Delta_0 - aY_1) + \{3\sin^2\theta(\cos^2\phi - \sin^2\phi) - (2\cos^2\theta - \sin^2\theta)\}(\Delta_2 - aY_1)]/\beta$$

$$<4p_x\,|x|4p_x> = (1/1575)^{1/2} \quad (\alpha/\beta)^{9/2}[4\sin\theta\cos\phi(9\Delta_1 - 5aY_0 - 4aY_2) - 3\{3(4\cos^2\theta\sin\theta - \sin^3\theta)\cos\phi - 5\sin^3\theta (4\cos^3\phi - 3\cos\phi)\}(\Delta_3 - aY_2)]/\beta$$

$$<2p_y\,|x|4p_y> = (1/2625)^{1/2} \quad (\alpha/\beta)^{5/2}[4\sin\theta\cos\phi(M_1 + aL_2) - \{(4\cos^2\theta\sin\theta - \sin^3\theta)\cos\phi + 5\sin^3\theta(4\cos^3\phi - 3\cos\phi)\}(M_3 - aL_2)]/\beta$$

$$<3p_y\,|x|4p_y> = (2/39375)^{1/2} \quad (\alpha/\beta)^{7/2}[4\sin\theta\cos\phi(Y_1 + aM_2) - \{(4\cos^2\theta\sin\theta - \sin^3\theta)\cos\phi + 5\sin^3\theta(4\cos^3\phi - 3\cos\phi)\}(Y_3 - aM_2)]/\beta$$

$$<3d_{yz}|x|4p_y> = (1/21)(2/35)^{1/2} \quad (\alpha/\beta)^{7/2}[4\cos\theta\sin\theta\cos\phi(Y_2 - aM_1) - \{\sin\theta(7\cos^3\theta - 3\cos\theta)\cos\phi + \sin^3\theta(4\cos^3\phi - 3\cos\phi)\}(Y_4 - aM_3)]/\beta$$

$$<4p_y\,|y|4p_y> = (1/525)^{1/2} \quad (\alpha/\beta)^{9/2}[4\sin\theta\cos\phi(\Delta_1 + aY_1) - \{(4\cos^2\theta\sin\theta - \sin^3\theta)\cos\phi + 5\sin^3\theta(4\cos^3\phi - 3\cos\phi)\}(\Delta_3 - aY_2)\}/\beta$$

$$<2p_y|y|4p_z> = (4/23625)^{1/2} \quad (\alpha/\beta)^{5/2}[2\cos\theta(M_1 - 5aL_0 + 2aL_2) - 3\{(2\cos^3\theta - 3\cos\theta\sin^2\theta) + 5\cos\theta\sin^2\theta(\cos^2\phi - \sin^2\phi)(M_3 - aL_2)]/\beta$$

$$<3p_y\,|y|4p_z> = (2/225)(2/7)^{1/2} \quad (\alpha/\beta)^{7/2}[2\cos\theta(3Y_1 - 5aM_0 + 2aM_2) - 3\{(2\cos^3\theta - 3\cos\theta\sin^2\theta) + 5\cos\theta\sin^2\theta(\cos^2\phi - \sin^2\phi)\}(Y_3 - aM_2)]/\beta$$

$$<3d_{yz}|y|4p_z> = (2/315)(2/35)^{1/2} \quad (\alpha/\beta)^{7/2}[14(Y_0 - aM_1) + (2\cos^2\theta - \sin^2\theta)(15Y_2 - 14aM_1 + 9aM_3) - 15\sin^2\theta\cos^2\theta(\cos^2\phi - \sin^2\phi)(Y_2 - aM_3) - 3\{(35\cos^4\theta - 30\cos^2\theta + 3) + 5\sin^2\theta(7\cos^2\theta - 1)(\cos^2\phi - \sin^2\phi)\}(Y_4 - aM_3)]/\beta$$

$$<4p_y\,|y|4p_z> = (2/1575) \quad (\alpha/\beta)^{9/2}(2\cos\theta(3\Delta_1 - 5aY_0 + 2aY_2) - 3\{(2\cos^3\theta - 3\cos\theta\sin^2\theta) + 5\cos\theta\sin^2\theta(\cos^2\phi - \sin^2\phi)\}(\Delta_3 - aY_2)\}/\beta$$

$$<2p_x\,|y|4p_x> = (1/2625)^{1/2} \quad (\alpha/\beta)^{5/2}[4\sin\theta\sin\phi(M_1 - aL_2) - \{(4\cos^2\theta\sin\theta - \sin^3\theta)\sin\phi - 5\sin^3\theta(3\sin\phi - 4\sin^3\phi)\}(M_3 - aL_2)]/\beta$$

$$<3p_x\,|y|4p_x> = (2/39375)^{1/2} \quad (\alpha/\beta)^{7/2}[4\sin\theta\sin\phi(Y_1 - aM_2) - \{(4\cos^2\theta\sin\theta - \sin^3\theta)\sin\phi - 5\sin^3\theta(3\sin\phi - 4\sin^3\phi)\}(Y_3 - aM_2)]/\beta$$

$$<3d_{zx}|y|4p_x> = (2/15435)^{1/2} \quad (\alpha/\beta)^{7/2}[4\cos\theta\sin\theta\sin\phi(Y_2 - aM_1) - \{\sin\theta(7\cos^3\theta - 3\cos\theta)\sin\phi - 7\sin^3\theta\cos\theta(3\sin\phi - 4\sin^3\phi)\}(Y_4 - aM_3)]/\beta$$

$$<4p_x\,|y|4p_x> = (1/525)^{1/2} \quad (\alpha/\beta)^{9/2}[4\sin\theta\sin\phi(\Delta_1 - aY_2) - \{(4\cos^2\theta\sin\theta - \sin^3\theta)\sin\phi - 5\sin^3\theta(3\sin\phi - 4\sin^3\phi)(\Delta_3 - aY_2)]/\beta$$

$$<1s\,|y|4p_y> = (4/945)^{1/2} \quad (\alpha/\beta)^{5/2}[2(L_0 - aK_1) - \{(2\cos^2\theta - \sin^2\theta) + 3\sin^2\theta(\cos^2\phi - \sin^2\phi)\}(L_2 - aK_1)]/\beta$$

$$<2s\,|y|4p_y> = (4/2835)^{1/2} \quad (\alpha/\beta)^{5/2}[2(M_0 - aL_1) - \{(2\cos^2\theta - \sin^2\theta) + 3\sin^2\theta(\cos^2\phi - \sin^2\phi)\}(M_2 - aL_1)]/\beta$$

$$<2p_y|y|4p_y> = (1/23625)^{1/2} \quad (\alpha/\beta)^{5/2}[4\sin\theta\sin\phi(9M_1 - 5aL_0 - aL_2) - 3\{3(4\cos^2\theta\sin\theta - \sin^3\theta)\sin\phi + 5\sin^3\theta(3\sin\phi - 4\sin^3\phi)\}(M_3 - aL_2)]/\beta$$

$$<3s|y|4p_y> = (8/42525)^{1/2} \quad (\alpha/\beta)^{7/2}[2(Y_0 - aM_1) - \{(2\cos^2\theta - \sin^2\theta) + 3\sin^2\theta(\cos^2\phi - \sin^2\phi)\}(Y_2 - aM_1)]/\beta$$

$$<3p_y|y|4p_y> = (1/225)(2/7)^{1/2} \quad (\alpha/\beta)^{7/2}[4\sin\theta\sin\phi(9Y_1 - 5aM_0 - 4aM_2) - 3\{3(4\cos^2\theta\sin\theta - \sin^3\theta)\sin\phi + 5\sin^3\theta(3\sin\phi - 4\sin^3\phi)\}(Y_3 - aM_2)]/\beta$$

$$<3d_{yz}|y|5p_y> = (1/105)(2/35)^{1/2} \quad (\alpha/\beta)^{7/2}[4\cos\theta\sin\theta\sin\phi(15Y_2 - 7aM_1 - 8aM_3) - 5\{\sin\theta(7\cos^3\theta - 3\cos\theta)\sin\phi + 7\sin^3\theta\cos\theta(3\sin\phi - 4\sin^3\phi)\}(Y_4 - aM_3)]/\beta$$

$$<4s|y|4p_y> = (2/315)(1/3)^{1/2} \quad (\alpha/\beta)^{9/2}[2(\Delta_0 - aY_1) - \{(2\cos^2\theta - \sin^2\theta) + 3\sin\theta(\cos^2\phi - \sin^2\phi)\}(\Delta_2 - aY_1)]/\beta$$

$$<4p_z|y|4p_y> = (2/525)(\alpha/\beta)^{9/2}[2\cos\theta(\Delta_1 - aY_2) - \{(2\cos^3\theta - 3\cos\theta\sin^2\theta) + 5\sin^2\theta(\cos^2\phi - \sin^2\phi)\}(\Delta_3 - aY_2)]/\beta$$

$$<4p_y|y|4p_y> = (1/1575)(\alpha/\beta)^{9/2}[4\sin\theta\sin\phi(9\Delta_1 - 5aY_0 - 4aY_2) - 3\{3(4\cos^2\theta\sin\theta - \sin^3\theta)\sin\phi + 5\sin\phi - 4\sin^3\phi)\}(\Delta_3 - aY_2)]/\beta$$

Therefore we may write the t_2 correct 3d wave functions in a T_d symmetry as

$$|\Psi_{xy}> = |3d_{xy}> - b|4p_z>$$

$$|\Psi_{xz}> = |3d_{xz}> - b|4p_y>$$

$$|\Psi_{yz}> = |3d_{yz}> - b|4p_x>$$

Where $b = \frac{k}{E_p^\circ - E_d^\circ} <3d_{xy}|xyz|4p_z>$

It was also reported that using a point-charge model,[24] the value of b is about 8×10^{-2}. The intermixing of |3d> and |4p> atomic orbitals is thus the about 10 percent in this approximation.

In a strong crystal field environment of tetrahedral symmetry, the contribution of the NMR chemical shift for |4p> system is needed to calculate the NMR chemical shift for the correct $3d^1$ system. The radial integrals of |4p> atomic orbitals for the hyperfine interaction is required to calculate the NMR chemical shift for $4p^n$ systems. In this work b is chosen to be a parameter.

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Photoreaction of 1,6-Disubstituted-1,3,5-hexatriynes with Some Olefins

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When the two conjugated poly-ynes, 1-phenyl-6-methyl- and 1,6-diphenyl-1,3,5-hexatriynes, were irradiated with UVA in deaerated 2,3-dimethyl-2-butene solution, 1:2 photoadducts, 1-(1′-phenylethynyl-2′,2′,3′,3′-tetramethylcyclopropyl)-2-(1″,2″,2″,3″,3″-pentamethylcyclopropyl) acetylene and 1-(1′- phenylethynyl-2′,2′,3′,3′ -tetramethylcyclopropyl)-2-(1″-phenyl-2″,2″,3″,3″-tetramethylcyclopropyl) acetylene, were obtained, respectively. No photoadduct was formed with aerated 2,3-dimethyl-2-butene, or deaerated solutions of dimethyl fumarate, methyl crotonate, dimethyl maleate, and trans-1,2-dichloroethylene. The results suggest that the reactions proceed from the triplet state only with electron rich olefins such as 2,3-dimethyl-2-butene.

Introduction

A naturally occurring conjugated polyacetylene, 1-phenyl-1,3,5-heptatriyne (PHT), is phototoxic to a variety of micro organisms, bacteriophages, animal viruses, human erythrocytes, algae, nematodes, cercariae, and the larvae.[1-10] Previous report shows that the phototoxicity of PHT exerts influence to viruses but only to those with membranes.[10] It was also reported that murine cytomegalovirus, which has been rendered non-infectious by treatment with PHT-UVA, is incapable of synthesizing viral DNA and viral RNA and proteins, in spite of the fact that the treated viral genome and virion proteins can penetrate susceptible cells and nuclei in a normal manner.[11] Furthermore the viral genome remains essentially intact and no cross-links formation is observed but the base sensitive cross-links such as protein-DNA etc. are not ruled out because cross-links were tested through the treatment of base. It was reported previously that PHT can produce PHT radical cation and anion via one electron transfer reaction with electron donor or acceptor such as methylviologen(electron acceptor) or triethylamine(electron donor).[12] In addition it was suggested that PHT radical cation is likely to be the phototoxic species responsible for the non-oxidative process. Until now, however, no information on photoreactions of PHT and reactive site for phototoxicity is available. For this reason, the photoreaction of 1,6-diphenyl-1,3,5-hexatriyne (DPH) and PHT with some olefins are investigated as a model reaction for the PHT phototoxicity and to elucidate the molecular mechanism for the PHT phototoxicity.

Results and Discussion

Photoreaction of PHT and DPH with some olefins. PHT and DPH were photolyzed in deaerated solutions of several olefins. No photoproduct was obtained from dimethyl fumarate, methyl crotonate, dimethyl maleate, and *trans*-1,2-dichloroethylene while 1:2 photoadducts were obtained