Linear and Non-linear Polarizabilities for $P_2\,(X^1\Sigma_g^+)$

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Electric polarizabilities and hyperpolarizabilities were calculated from accurate self-consistent field wavefunctions for P_2. The following values are reported, using the experimental bond length of 1.8934 Å: dipole polarizability $\alpha_{zz} = 69.83$ and $\alpha_{xx} = 41.20\ e^2 a_0^2 E_h^{-1}$, second dipole hyperpolarizability $\gamma_{zzzz} = 17\,040$, $\gamma_{xxxx} = 11\,581$ and $\gamma_{xxzz} = 4724\ e^4 a_0^4 E_h^{-3}$, quadrupole polarizability, $C_{zz,zz} = 276.14$, $C_{xz,xz} = 232.64$ and $C_{xx,xx} = 151.25\ e^2 a_0^4 E_h^{-1}$, dipole-octopole polarizability, $E_{z,zzz} = 331.00$ and $E_{x,xxx} = -154.66\ e^2 a_0^4 E_h^{-1}$ and for the dipole-dipole-quadrupole hyperpolarizability, $B_{zz,zz} = -2441$, $B_{xz,xz} = -1442$, $B_{xx,zz} = 866$ and $B_{xx,xx} = -1411\ e^3 a_0^4 E_h^{-2}$.

P_2 has been the subject of several theoretical studies recently [1–10]. Despite the interest in phosphorous clusters P_n [10], very little is known about the electric properties of this system. A numerical Hartree-Fock calculation of the quadrupole and hexadecapole moments has been reported by Pyykkö et al. [5], while theoretical values of the quadrupole moment and the dipole polarizability have been obtained by Glaser and et al. [9]. In this work we report self-consistent field (SCF) values of the linear and non-linear polarizabilities for all independent components of the electric multiple moment, polarizability and hyperpolarizability tensors up to the fourth rank. These include the quadrupole ($\Theta_{\alpha\beta}$) and hexadecapole ($\Phi_{\alpha\beta\gamma\delta}$) moment, the dipole ($\alpha_{\alpha\beta}$) quadrupole ($C_{\alpha\beta,\gamma\delta}$) and dipole-octopole ($E_{\alpha,\beta\gamma\delta}$) polarizability and the second dipole ($\gamma_{\alpha\beta\gamma\delta}$) and dipole-dipole-quadrupole ($B_{\alpha\beta,\gamma\delta}$) hyperpolarizability. The molecular properties are extracted from the induced multipole moments, an essentially finite-field approach [11]. We rely on a flexible, carefully optimized basis set of gaussian-type functions (GTF) for the calculation of the induced electric moments. We carried out our calculations with a (13s9p4d1f) [8s6p4d1f] basis set consisting of 148 primitive or 120 contracted GTF. This basis set was built upon a (11s7p) [6s4p] substrate [12]. The substrate was augmented to [8s6p] with diffuse s- and p-GTF with exponents chosen to form a geometric progression with the two most diffuse ones of the same symmetry. The addition of two d-GTF with exponents 0.4192 and 0.0871 (in units of a_0^{-2}) gave [8s6p2d]. The exponent of the tight GTF was chosen to minimize the energy of the free molecule. The exponent of the diffuse d-GTF was chosen to maximize the mean dipole polarizability. In a further step, an f-GTF was added and its exponent was chosen to maximize the mean quadrupole polarizability. Its value was found to be 0.0637. The construction of the basis set was completed with the addition of two d-GTF with exponents 0.91965 and 2.01755, where 2.01755 = 0.4192 K and 0.91965 = 0.4192 $K^{1/2}$ with $K = (0.4192)/(0.0871)$. Six-membered d-GTF and ten-membered GTF were used in all cases. All optimizations were performed for the experimental bond length of 1.8934 Å [13]. All calculations were performed with GAUSSIAN 86 [14].

Table 1 lists the dependence of the electric quadrupole and hexadecapole moments and the quadrupole polarizability on the exponent for the f-GTF for the [8s6p2d1f] basis set. We have included the values of the electronic moments $\langle zz\rangle$, $\langle xx\rangle$, $\langle zzzz\rangle$, $\langle xxzz\rangle$, $\langle xxyy\rangle$ and $\langle xxxx\rangle$ as they represent more direct measures of the quality of the wavefunction than Θ_{zz} and Φ_{zzzz}. In Table 1 we give the values of all the molecular properties calculated with [8s6p4d1f] at three internuclear separations, $(R_e - 0.2)/a_0$, R_e/a_0, and $(R_e + 0.2)/a_0$.

It is obvious from Table 1 that the values of Θ_{zz} and Φ_{zzzz} are small compared to the electronic moments. Thus, both the electronic and nuclear part of Θ_{zz} are large and approximately equal. A small error in the electronic part of the quadrupole moment would result in substantial errors for the total value. Of all f-GTF exponents, extreme values for Θ_{zz} and Φ_{zzzz} are obtained for 0.025 and 0.25. From $\eta_f = 0.025$ to 0.25 the quadrupole moment changes by ≈ 15% and the hexadecapole moment by ≈ 32% (in absolute terms).

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Table 1. Dependence of the SCF molecular properties of P_2 on the exponent of the f-GTF for the (13s9p2d1f) [8s6p2d1f] basis set. Experimental bond length 3.5780072 a_0. All properties in atomic units.

Property	0.025	0.05	0.075	0.15	0.25	0.35
$\langle zz \rangle$	114.920	114.967	114.948	114.957	114.987	114.970
$\langle xx \rangle$	20.0530	19.9866	20.0017	19.9681	19.9514	19.9824
$\langle zzzz \rangle$	801.843	805.139	805.503	804.345	805.180	801.995
$\langle xxzz \rangle$	96.7369	96.5931	96.4648	95.5188	95.4790	95.6150
$\langle xxyy \rangle$	40.4921	40.3190	40.6062	40.4211	40.6335	40.1300
$\langle xxxx \rangle$	121.476	120.957	121.819	121.263	121.901	120.390
Θ_{zz}	1.149	1.036	1.084	1.027	0.981	1.029
Φ_{zzzz}	−35.60	−39.24	−41.23	−45.19	−46.90	−41.39
$C_{zz,zz}$	272.9	278.9	278.7	276.4	277.5	270.9
$C_{xz,xz}$	235.4	237.3	234.1	231.9	231.8	231.8
$C_{xx,xx}$	127.8	151.0	155.9	147.7	134.3	124.3
C [a]	317.8	338.5	339.9	331.3	320.6	312.0

[a] Mean quadrupole polarizability defined as $C = (C_{zz,zz} + 8\,C_{xz,xz} + 8\,C_{xx,xx})/10$.

Table 2. Bond length dependence of the electric properties of P_2. Basis set (13s9p4d1f) [8s6p4d1f]. Experimental bond length $R_e = 3.5780072\ a_0$. All properties in atomic units.

Property	$R_e - 0.2$	R_e	$R_e + 0.2$
$\langle zz \rangle$	104.649	114.788	125.537
$\langle xx \rangle$	19.6190	20.0232	20.4046
$\langle zzzz \rangle$	702.607	800.949	913.821
$\langle xxzz \rangle$	88.3661	95.6712	103.601
$\langle xxyy \rangle$	37.8101	39.7653	41.6862
$\langle xxxx \rangle$	113.43	119.296	125.059
Θ_{zz}	0.552	1.251	1.917
Φ_{zzzz}	−41.70	−38.92	−35.28
α_{zz}	63.29	69.83	76.79
α_{xx}	39.01	41.20	43.40
α [a]	47.10	50.74	54.53
$\Delta\alpha$ [a]	24.27	28.63	33.38
γ_{zzzz}	15772	17040	18752
γ_{xxxx}	9514	11581	13999
γ_{xxzz}	4030	4724	5632
γ [b]	11453	13364	15722
$C_{zz,zz}$	255.6	276.1	300.6
$C_{xz,xz}$	215.0	232.6	254.1
$C_{xx,xx}$	139.8	151.2	164.1
C	309.4	334.7	364.6
$E_{z,zzz}$	307.12	331.00	363.17
$E_{x,xxx}$	−146.76	−154.66	−166.95
$B_{zz,zz}$	−2256	−2441	−2672
$B_{xz,xz}$	−1275	−1442	−1647
$B_{xx,zz}$	715	866	1014
$B_{xx,xx}$	−1220	−1411	−1611
B [c]	−1536	−1732	−1959

[a] Mean dipole polarizability and anisotropy defined as $\alpha = (\alpha_{zz} + 2\alpha_{xx})/3$ and $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$.

[b] Mean second dipole hyperpolarizability $\gamma = (3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz})/15$.

[c] Mean dipole-dipole-quadrupole hyperpolarizability $B = (2/15)(B_{zz,zz} + 4\,B_{xz,xz} + B_{xx,zz} + 4\,B_{xx,xx})$.

The component of $C_{\alpha\beta,\gamma\delta}$ most dependent on the f-GTF exponent is $C_{xx,xx}$. The mean quadrupole polarizability displays strong dependence on η_f, showing that the optimization of the latter is an essential part of the construction of the basis set.

With the notable exception of the electric moments and the dipole polarizability, all other properties listed in Table 2 are, to our knowledge, the first to be reported for P_2. At R_e we obtain $\Theta_{zz} = 1.125\ e a_0^2$ and $\Phi_{zzzz} = -38.92\ e a_0^4$. The numerical Hartree-Fock (NHF) [10] values are 1.064167 $e a_0^2$ and −41.7069 $e a_0^4$, respectively. It is more instructive to compare our $\langle zz \rangle$ and $\langle xx \rangle$ values with the numerical ones. We obtain $\langle zz \rangle = 114.788$ and $\langle xx \rangle = 20.0232\ e a_0^2$, to be compared with the NHF of 114.9060 and 19.8472 $e a_0^2$. Our $\langle xx \rangle$ is by less than 1% higher than the NHF value, but even such a small difference leads to a quadrupole moment 17.6% above the accurate one. Glaser et al. [9] obtained SCF dipole polarizability values of $\alpha_{zz} = 66.651$ and $\alpha_{xx} = 21.700\ e^2 a_0^2 E_h^{-1}$ with a small 6-31G* basis set. Our result for α_{zz} is 4.8% higher at 69.83 $e^2 a_0^2 E_h^{-1}$, but the difference is substantial for α_{xx} as our value is 41.20 $e^2 a_0^2 E_h^{-1}$ or 89.9% above theirs. The longitudinal components of $\alpha_{\alpha\beta}$ and $\gamma_{\alpha\beta\gamma\delta}$ are considerably larger than the transversal ones. Consequently, large anisotropies are calculated for both polarizabilities. The quadrupole moment varies considerably with the internuclear separation. The dependence is less strong for the other properties. From the values displayed in Table 2, we obtain, through a parabolic fit, estimates for the first and second derivatives of the molecular properties at R_e. Using experimental values [13] for the spectroscopic constants and our estimates for the derivatives we obtain for the electric moments and the dipole polarizability at the (v, J) rovibrational state [15, 16]

$$\Theta_{zz}(v,J) = 1.251 + 0.040\,(v + 1/2) + 0.000007\,J\,(J+1)\,,$$

$$\Phi_{zzzz}(v,J) = -38.92 + 0.31\,(v + 1/2) + 0.00003\,J\,(J+1)\,,$$

$$\alpha(v,J) = 50.74 + 0.26\,(v + 1/2) + 0.00004\,J\,(J+1)\,,$$

$$\Delta\alpha(v,J) = 28.63 + 0.34\,(v + 1/2) + 0.00005\,J\,(J+1)\,.$$

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