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Electric Quadrupole and Hexadecapole Moment, Dipole and Quadrupole Polarizability, Second Electric Dipole Hyperpolarizability for P_2, and a Comparative Study of Molecular Polarization in N_2, P_2, and As_2

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We have obtained electric properties of P≡P from finite-field Møller−Plesset perturbation theory, density functional theory and coupled cluster techniques. Reference, near-Hartree−Fock values have been obtained with a very large (20s15p10d5f) uncontracted basis set consisting of 300 Gaussian-type functions. At the experimental equilibrium bond length of $R_e = 1.8934$ Å we obtain self-consistent field values of 1.0682 ea_0^2 for the quadrupole moment (Θ), -41.68 ea_0^4 for the hexadecapole moment (Φ), 51.16 for the mean ($\bar{\alpha}$) and 28.58 $e^2a_0^2E_h^{-1}$ for the anisotropy of the dipole polarizability, and 16.5×10^3 $e^4a_0^4E_h^{-3}$ for the mean second dipole hyperpolarizability ($\bar{\gamma}$). Electron correlation reduces strongly the magnitude of the electric moments. Both components of the dipole polarizability are reduced by electron correlation, but a small increase is observed for the dipole hyperpolarizability. Our best post-Hartree−Fock values have been obtained with a [9s7p5d3f] basis set at the CCSD(T) level of theory: $\Theta = 0.4850$ ea_0^2, $\Phi = -31.25$ ea_0^4, $\bar{\alpha} = 49.20$ and $\Delta\alpha = 28.02$ $e^2a_0^2E_h^{-1}$, $\bar{\gamma} = 16.8 \times 10^3$ $e^4a_0^4E_h^{-3}$. The bond-length dependence around R_e has been obtained for all properties. Conventional density functional theory methods predict dipole polarizabilities close enough to the most accurate CCSD(T) values but overestimate the second dipole hyperpolarizability. The mean dipole polarizability changes as $\bar{\alpha}$(NaK) > $\bar{\alpha}$(AlCl) > $\bar{\alpha}$(SiS) > $\bar{\alpha}$(P_2) > $\bar{\alpha}$(Zn) for some isoelectronic, 30-electron systems. It is seen that the electric properties in the sequence $N_2 \rightarrow P_2 \rightarrow As_2$ display regular changes.

Introduction

Theoretical investigations of phosphorus clusters have brought forth many important aspects of the structure and bonding in these important systems.[1−5] Active interest in their molecular properties stems from current investigations in various fields. In a recent paper Bulgakov et al.[6] reported the synthesis by laser ablation of neutral (P_n, $n \leq 40$) and cationic (P_n^+, $n \leq 91$) clusters. Although nitrogen clusters have attracted more attention, because of their potential applications as high energy density materials,[7] many important applications and fundamental observations involving phosphorus systems have also been reported. Gingerich and Piacente[8] and Cocke et al.[9] reported experimental gas-phase studies of the diphosphides AlP_2 and RhP_2. Tast et al.[10] reported the preparation of fullerenes coated with phosphorus molecules. These systems have been identified as $C_{60}(P_4)_n$ and $C_{60}P_{4n+2}$, which suggests that the dominant building block is P_4 but P_2 is also present. Recently, Herms et al.[11] reported a Raman spectroscopic study of the composition of phosphorus vapor, a problem associated with the thermal treatment of GaAs and InP semiconductor compounds. The authors reported the temperature dependence of the P_2/P_4 ration and the first observation of the Raman mode of P_2 at 775 cm^{-1}. Boudon et al.[12] obtained an accurate estimate of the P−P bond length in P_4, a matter of some controversy in recent years.[13] A new field of importance for the chemistry of phosphorus concerns the use of P_n systems as ligands.[14] We also mention the theoretical investigation[15] of novel bonding effects between P_4 and Li^+. Last, in a very interesting paper, Kornath et al.[16] reported Raman spectroscopic studies of matrix isolated P_2 and P_4.

Surprisingly little is known about the electric properties of small phosphorus clusters. The only experimental studies reported so far concern exclusively P_4. Hohm and co-workers have deduced the dipole polarizability from refractivity measurements[17] and the dipole−quadrupole, dipole-octopole polarizability from collision-induced light scattering observations.[18] Few theoretical studies have been reported. Numerical Hartree−Fock values for the quadrupole and hexadecapole moment of P_2 were reported by Pyykkö et al.[19] For P_2, Glaser et al.[20] reported quadrupole moment and dipole polarizability values while de Brouckère and Feller[21] calculated the quadrupole moment for various electronic states. SCF values of the electric moments, polarizabilities, and hyperpolarizabilities of P_2 were reported by Maroulis.[22] The quadrupole moment of P_2 was also studied by Lawson and Harrison.[23] We are aware of only one study of the electric properties of P_4, a Møller−Plesset perturbation theory and coupled cluster calculation of the electric moments and dipole, dipole−quadrupole and dipole−octopole polarizability.[17]

In this work we report a systematic study of the electric properties of P_2. We aim at providing reliable values for this important diatomic, the smallest molecule with a triple phosphorus−phosphorus bond, P≡P. We rely on a finite-field method presented in sufficient detail in previous work.[24−27] We present self-consistent field (SCF) calculations with electron correlation effects obtained via Møller−Plesset perturbation theory (MP) and coupled-cluster techniques (CC). In addition to these conventional methods, we also report density functional theory (DFT) calculations performed with the widely used B3P86, P3PW91, and B3LYP methods. Our calculations employ carefully optimized, flexible basis sets of Gaussian-type func-

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tions (GTF). As there is little computational experience on the electric properties of P_2, we have added to our work a detailed investigation of basis set effects. We thus expect the constructed basis sets to be useful in further investigations on molecular interaction studies involving this important diatomic system.

Theory

The perturbed energy and electric multipole moments of an uncharged molecule interacting with a general, static electric field can be expanded in terms of the components of the field as[28,29]

$$\begin{aligned} E \equiv{}& E(F_\alpha, F_{\alpha\beta}, F_{\alpha\beta\gamma}, F_{\alpha\beta\gamma\delta}, ...) \\ ={}& E^0 - \mu_\alpha{}^0 F_\alpha - (1/3)\Theta_{\alpha\beta}{}^0 F_{\alpha\beta} - \\ & (1/15)\Omega_{\alpha\beta\gamma}{}^0 F_{\alpha\beta\gamma} - (1/105)\Phi_{\alpha\beta\gamma\delta}{}^0 F_{\alpha\beta\gamma\delta} + ... \\ & - (1/2)\alpha_{\alpha\beta}F_\alpha F_\beta - (1/3)A_{\alpha,\beta\gamma}\, F_\alpha F_{\beta\gamma} - (1/6)C_{\alpha\beta,\gamma\delta}\, F_{\alpha\beta}\, F_{\gamma\delta} \\ & - (1/15)E_{\alpha,\beta\gamma\delta}F_\alpha F_{\beta\gamma\delta} + ... \\ & - (1/6)\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - (1/6)B_{\alpha\beta,\gamma\delta}F_\alpha F_\beta F_{\gamma\delta} + ... \\ & - (1/24)\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta + ... \end{aligned} \tag{1}$$

$$\mu_\alpha = \mu_\alpha{}^0 + \alpha_{\alpha\beta}\, F_\beta + (1/3)A_{\alpha,\beta\gamma}\, F_{\beta\gamma} + (1/2)\beta_{\alpha\beta\gamma}\, F_\beta F_\gamma + (1/3)B_{\alpha\beta,\gamma\delta}F_\beta F_{\gamma\delta} + (1/6)\gamma_{\alpha\beta\gamma\delta}\, F_\beta F_\gamma F_\delta + ... \tag{2}$$

$$\Theta_{\alpha\beta} = \Theta_{\alpha\beta}{}^0 + A_{\gamma,\alpha\beta}E_\gamma + C_{\alpha\beta,\gamma\delta}F_{\gamma\delta} + (1/2)B_{\gamma\delta,\alpha\beta}\, F_\gamma F_\delta + ... \tag{3}$$

$$\Omega_{\alpha\beta\gamma} = \Omega_{\alpha\beta\gamma}{}^0 + E_{\delta,\alpha\beta\gamma}\, F_\delta + ... \tag{4}$$

where F_α, $F_{\alpha\beta}$, etc. are the field, field gradient, etc. at the origin. E^0, $\mu_\alpha{}^0$, $\Theta_{\alpha\beta}{}^0$, $\Omega_{\alpha\beta\gamma}{}^0$, and $\Phi_{\alpha\beta\gamma\delta}{}^0$ are the energy and the dipole, quadrupole, octopole, and hexadecapole moment of the free molecule. The electric (hyper)polarizabilities are $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$, $A_{\alpha,\beta\gamma}$, $C_{\alpha\beta,\gamma\delta}$, $E_{\alpha,\beta\gamma\delta}$, and $B_{\alpha\beta,\gamma\delta}$. The subscripts denote Cartesian components, and a repeated subscript implies summation over *x*, *y*, and *z*. For centrosymmetric molecules of $D_{\infty h}$ symmetry, such as P_2, $\mu_\alpha{}^0 = \Omega_{\alpha\beta\gamma}{}^0 = \beta_{\alpha\beta\gamma} = A_{\alpha,\beta\gamma} = 0$.[28] The number of independent components needed to specify the nonvanishing tensors is regulated by symmetry. The present choice is simply a convenient one.[30,31] There is only one independent component for all electric multipole moment tensors of a linear molecule.[28] Consequently, we drop the subscript to simplify notation and write $\Theta_{zz}{}^0 \equiv \Theta$ and $\Phi_{zzzz}{}^0 \equiv \Phi$. In addition to the Cartesian components of $\alpha_{\alpha\beta}$, $\gamma_{\alpha\beta\gamma\delta}$, $C_{\alpha\beta,\gamma\delta}$, and $B_{\alpha\beta,\gamma\delta}$, we also compute the following invariants:[28]

$$\begin{aligned} \bar{\alpha} &= (\alpha_{zz} + 2\alpha_{xx})/3 \\ \Delta\alpha &= \alpha_{zz} - \alpha_{xx} \\ \bar{\gamma} &= (3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz})/15 \\ \bar{C} &= (C_{zz,zz} + 8C_{xz,xz} + 8C_{xx,xx})/10 \\ \bar{B} &= (2/15)(B_{zz,zz} + 4B_{xz,xz} + B_{xx,zz} + 4B_{xx,xx}) \end{aligned} \tag{5}$$

Complete presentations of the post-Hartree−Fock methods used in this work are available in the literature.[32−38] The employed MP methods are the second- and fourth-order MP, MP2, and MP4, respectively. We lean heavily on the predictive capability of the CC methods for our concluding remarks on the size of the electric properties of P_2. The CC techniques used in this work are CCSD (single and double excitations CC) and CCSD(T), which includes an estimate of connected triple excitations obtained via a perturbational treatment. Electron correlation effects on Θ, Φ, $\alpha_{\alpha\beta}$, $\gamma_{\alpha\beta\gamma\delta}$, and $C_{\alpha\beta,\gamma\delta}$ were obtained from the perturbed molecular energies.[25] For $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$ we relied on the induced octopole and quadrupole moments obtained via the MP2 density.[39]

We have also included in our arsenal a number of DFT methods. The aim of this move is to enrich current knowledge on the predictive potential of DFT methods in electric (hyper)-polarizability calculations. The retained methods are B3LYP,[40,41] B3P86,[40,42] and B3PW91.[40,43]

Computational Details

Within the marked explosion of ab initio investigations of problems related to electronic structure determination, the choice of suitable basis sets has been widely recognized as a factor of primary importance in molecular property calculations.[44−46] The construction of the GTF basis sets used in this study follows a computational philosophy expanded paradigmatically in previous work.[25] Succinctly, in three steps: (i) the initial substrate is augmented with diffuse s- and p-GTF, (ii) a relatively tight d-GTF with exponent chosen to minimize E^0 is added, and (iii) a relatively diffuse d-GTF with exponent chosen to maximize $\bar{\alpha}$ is added. Subsequently, more GTF are then added even-temperedly. We have used three different substrates of primitive GTF. A sequence of basis sets was built on a TZV substrate (14s9p)[47] contracted to [5s4p] as {73211/6111}. A large Q ≡ [9s7p5d3f] set was built on a (12s9p)[6s5p] substrate.[48] Last, a very large, uncontracted basis set, PA ≡ (20s15p10d5f), was obtained from a (18s13p) primitive set.[49] The composition of the A0→A10 sequence, Q and PA basis sets is briefly given as

A0 ≡ [6s5p2d], from a [5s4p] TZV substrate[47]
+ s(0.041194037) + p(0.031996625) + d(0.4076, 0.0766)
A1 ≡ [6s5p3d], from A0 + d(0.0332)
A2 ≡ [6s5p3d1f], from A1 + f(0.0766)
A3 ≡ [6s5p3d1f], from A1 + f(0.0332)
A4 ≡ [6s5p4d2f], from A2 + d(0.1767) + f(0.0332)
A5 ≡ [6s5p4d3f], from A4 + f(0.1767)
A6 ≡ [6s5p5d2f], from A4 + d(0.9402)
A7 ≡ [6s5p5d2f], from A2 + d(0.9402, 0.1767) + f(0.4076)
A8 ≡ [6s5p5d3f], from A6 + f(0.1767)
A9 ≡ [6s5p5d3f], from A7 + f(0.0332)
A10 ≡ [6s5p5d4f], from A9 + f(0.1767)

Q ≡ [9s7p5d3f], from a [6s5p] substrate[48]
+ s(0.04497, 0.01643, 0.00600) + p(0.032951, 0.011126) +
d(0.9302, 0.4075, 0.1785, 0.0782) +
f(0.4075, 0.0782, 0.0343)

PA ≡ (20s15p10d5f), from a (18s13p) substrate[49]
+ s(0.037250, 0.015630) + p(0.026153, 0.010971) +
d(11.7258, 2.1977, 0.9514, 0.6260, 0.4119,
0.1783, 0.0772, 0.0334, 0.0145, 0.0063) +
f(0.9514, 0.4119, 0.1783, 0.0772, 0.0334)

5D and 7F GTF were used for all basis sets.

TABLE 1: Self-Consistent Field Values for the Electric Moments and Polarizabilities of P_2[a]

property	A0	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	Q	PA
Θ	1.1105	1.0510	1.0252	1.0502	1.0066	0.9543	1.1389	1.0235	1.0758	1.0234	1.0295	1.0176	1.0682
Φ	−38.92	−37.37	−42.95	−36.98	−41.58	−41.94	−39.89	−42.74	−41.02	−42.49	−42.21	−42.25	−41.68
α_{zz}	69.31	69.69	69.78	69.69	69.82	69.94	69.87	70.19	70.01	70.18	70.18	70.17	70.21
α_{xx}	41.31	41.20	41.21	41.22	41.40	41.41	41.55	41.54	41.55	41.57	41.57	41.56	41.63
$\bar{\alpha}$	50.64	50.70	50.74	50.71	50.87	50.92	50.99	51.09	51.04	51.10	51.11	51.09	51.16
$\Delta\alpha$	28.00	28.49	28.57	28.47	28.42	28.53	28.32	28.64	28.45	28.61	28.61	28.62	28.58
γ_{zzzz}	15.2	17.8	17.9	17.9	17.9	18.0	17.2	17.5	17.4	17.4	17.2	17.3	17.6
γ_{xxxx}	10.1	12.4	15.4	15.0	16.1	16.0	16.1	15.0	15.9	16.0	16.0	16.1	16.2
γ_{xxzz}	4.8	5.5	5.3	5.6	5.4	5.6	5.3	5.4	5.5	5.4	5.4	5.4	5.4
$\bar{\gamma}$	12.2	14.6	16.0	16.1	16.5	16.6	16.3	15.8	16.4	16.4	16.3	16.3	16.5
$C_{zz,zz}$	269.7	273.4	279.9	273.7	280.0	280.5	280.1	281.6	280.1	281.5	281.7	281.2	282.3
$C_{xz,xz}$	230.3	234.3	233.3	235.5	236.0	237.5	236.4	237.5	237.7	237.8	237.8	237.8	238.1
$C_{xx,xx}$	116.4	117.9	158.0	138.4	159.4	162.1	159.3	160.8	161.9	161.8	162.7	161.7	163.1
$\bar{C}$	304.3	309.1	341.1	326.5	344.3	347.7	344.5	346.8	347.6	347.9	348.6	347.7	349.2
$B_{zz,zz}$	−2351	−2523	−2586	−2520	−2552	−2544	−2513	−2540	−2505	−2526	−2520	−2522	−2540
$B_{xz,xz}$	−1518	−1644	−1608	−1675	−1627	−1656	−1619	−1624	−1652	−1642	−1636	−1640	−1646
$B_{xx,zz}$	883	961	1073	996	1053	1033	1050	1020	1027	1042	1045	1042	1042
$B_{xx,xx}$	−1253	−1355	−1729	−1609	−1733	−1717	−1727	−1672	−1709	−1724	−1723	−1724	−1727
$\bar{B}$	−1674	−1808	−1981	−1955	−1992	−2000	−1980	−1960	−1990	−1993	−1988	−1992	−1999
$E_{z,zzz}$	314.2	318.8	335.8	316.3	332.1	329.1	330.0	334.3	326.3	331.4	331.5	330.7	332.3
$E_{x,xxx}$	−153.6	−158.8	−146.3	−157.8	−151.6	−154.0	−152.9	−154.7	−155.0	−154.2	−154.0	−154.4	−154.4

[a] The second dipole hyperpolarizability is given as $10^{-3} \times \gamma_{\alpha\beta\gamma\delta}$.

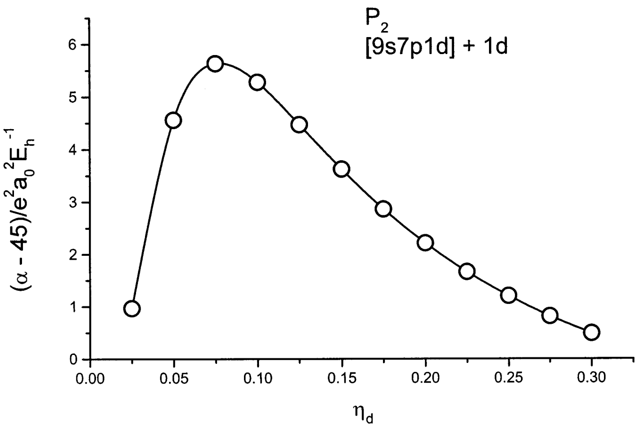

Figure 1. Dependence of the mean dipole polarizability on the exponent of the diffuse d-GTF exponent in the construction of the *Q* ≡ [9s7p5d3f] basis set (see text for details).

It is worth emphasizing the emergence of regular patterns in the construction of the basis sets. The most important aspect concerns the need for polarizability-optimized diffuse d-GTF. In Figure 1 we have traced the dependence of the mean polarizability on the exponent of the d-GTF in the construction of basis Q, $\bar{\alpha}(\eta_d)$. The optimal exponent is $\eta_d/a_0^{-2} = 0.0782$. The analogous exponent is 0.0766 for A0→A10 and 0.0772 for PA. What is more, the optimization of this exponent for A0 on the P_4 cluster[17] gives a value of 0.0745. This important result indicates that a value $\eta_d/a_0^{-2} \approx 0.075$ would be a judicious choice for subsequent calculations on phosphorus clusters.

Homogeneous fields of 0.005 $e^{-1}a_0^{-1}E_h$ were found suitable for the calculation of the dipole properties. For the calculation of the quadrupole properties and the hexadecapole moment we used strategically placed arrays of distant point charges that produce weak fields.[30,31] For the quadrupole moment we use arrays that produce $|Q/R^3| = 0.0000125\ e^{-1}a_0^{-2}E_h$ and $|Q/R^5| = 0.0000003125\ e^{-1}a_0^{-4}E_h$.

All optimizations and subsequent calculations were performed at the experimental bond length $R_e = 1.8934$ Å.[50] GAUSSIAN 92,[51] GAUSSIAN 94,[52] and GAUSSIAN 98[53] were used in this work.

Atomic units are used throughout this paper. Conversion factors to SI units are: Energy, 1 $E_h = 4.3597482 \times 10^{-18}$ J, Length, 1 $a_0 = 0.529177249 \times 10^{-10}$ m, Θ, 1 $ea_0^2 = 4.486554 \times 10^{-40}$ Cm^2, Φ, 1 $ea_0^4 = 1.256363 \times 10^{-60}$ Cm^4, α, 1 $e^2a_0^2E_h^{-1} = 1.648778 \times 10^{-41}$ C^{2}m^{2}J^{-1}, γ, 1 $e^4a_0^4E_h^{-3} = 6.235378 \times 10^{-65}$ C^{4}m^{4}J^{-3}, C or E, 1 $e^2a_0^4E_h^{-1} = 4.617048 \times 10^{-62}$ C^{2}m^{4}J^{-1}, and B, 1 $e^3a_0^4E_h^{-2} = 1.696733 \times 10^{-63}$ C^{3}m^{4}J^{-2}.

Results and Discussion

SCF results for all properties and all basis sets are given in Table 1. Electron correlation effects obtained with A0, A6, A7, A9, and Q are shown in Table 2. Table 3 contains CCSD(T)/A9 data for the bond-length dependence of Θ, Φ, $\alpha_{\alpha\beta}$, $\gamma_{\alpha\beta\gamma\delta}$, and $C_{\alpha\beta,\gamma\delta}$, and Table 4 contains the calculated first derivatives at the SCF, MP2, MP4, CCSD, and CCSD(T) levels of theory. In Table 5, DFT data for the dipole (hyper)polarizability are compared to the presumably most accurate CCSD(T) values. Reference, near-Hartree−Fock values for N_2, P_2, and As_2 have been collected in Table 6. In Table 7 our predictions are compared to previous theoretical results. Last, in Table 8 we display $\bar{\alpha}$ and $\Delta\alpha$ values for the isoelectronic systems NaK, AlCl, SiS, P_2, and Zn.

Convergence to the Hartree−Fock Limit. We expect our largest basis set PA to provide near-Hartree−Fock results for all molecular properties. This basis yields $\alpha_{\alpha\beta}/e^2a_0^2E_h^{-1}$ values of $\bar{\alpha} = 51.16$ and $\Delta\alpha = 28.58$. The smallest basis used in this study, A0, gives $\bar{\alpha} = 50.64$ and $\Delta\alpha = 28.00$. These values are only 1.0 and 2.0% lower than the reference PA values. Thus, it is easily seen that all basis sets are nearly saturated with respect to this property. For the other properties, the sequence A0→A10 allows some systematic observations on basis set dependence. The SCF values of the quadrupole moment Θ/ea_0^2 are fairly stable: A0 gives $\Theta = 1.1105$, 4.0% above the reference PA value. For the hexadecapole moment $\Phi/ea_0{}^4$ A0 gives −38.92 or 6.6% lower than the PA result. To obtain reliable Φ values

TABLE 2: Electron Correlation Effects[a] on the Electric Properties of P_2

property	method	A0	A6	A7	A9	Q
Θ	SCF	1.1106	1.1390	1.0235	1.0234	1.0175
	MP2	0.2882	0.4220	0.3874	0.3889	0.3886
	MP4	0.3843	0.4880	0.3938	0.3948	0.3934
	CCSD	0.5994	0.7144	0.6278	0.6282	0.6273
	CCSD(T)	0.4470	0.5600	0.4851	0.4860	0.4850
Φ	SCF	−38.92	−39.89	−42.74	−42.49	−42.34
	MP2	−27.54	−27.64	−30.06	−29.87	−29.62
	MP4	−28.02	−27.99	−30.82	−30.66	−30.41
	CCSD	−30.13	−30.30	−33.40	−33.26	−33.05
	CCSD(T)	−28.87	−28.87	−31.64	−31.48	−31.25
α_{zz}	SCF	69.31	69.87	70.19	70.18	70.17
	MP2	67.38	68.05	67.80	67.80	67.77
	MP4	68.05	68.64	68.23	68.22	68.19
	CCSD	67.41	68.07	67.84	67.84	67.81
	CCSD(T)	67.71	68.31	67.91	67.91	67.88
α_{xx}	SCF	41.31	41.55	41.54	41.57	41.56
	MP2	39.84	40.38	40.08	40.12	40.10
	MP4	39.83	40.27	39.79	39.82	39.81
	CCSD	39.83	40.24	39.87	39.90	39.89
	CCSD(T)	39.88	40.30	39.84	39.87	39.86
$\bar{\alpha}$	SCF	50.64	50.99	51.09	51.10	51.09
	MP2	49.02	49.60	49.32	49.34	49.33
	MP4	49.24	49.73	49.27	49.29	49.27
	CCSD	49.02	49.51	49.20	49.21	49.19
	CCSD(T)	49.15	49.64	49.20	49.21	49.20
$\Delta\alpha$	SCF	28.00	28.32	28.64	28.61	28.62
	MP2	27.55	27.67	27.72	27.68	27.67
	MP4	28.21	28.37	28.44	28.40	28.39
	CCSD	27.58	27.83	27.97	27.94	27.92
	CCSD(T)	27.83	28.01	28.07	28.04	28.02
γ_{zzzz}	SCF	15.2	17.2	17.5	17.4	17.3
	MP2	22.4	24.0	23.8	23.9	23.6
	MP4	21.9	23.3	22.5	22.5	22.2
	CCSD	21.0	22.0	21.0	21.0	20.7
	CCSD(T)	22.6	23.6	22.4	22.4	22.2
γ_{xxxx}	SCF	10.1	16.1	15.0	16.0	16.1
	MP2	9.8	15.2	13.8	14.5	14.5
	MP4	10.3	15.4	13.7	14.3	14.3
	CCSD	10.3	15.2	13.6	14.3	14.3
	CCSD(T)	10.5	15.5	13.8	14.5	14.4
γ_{xxzz}	SCF	4.8	5.3	5.4	5.4	5.4
	MP2	5.7	6.2	6.0	6.1	6.1
	MP4	5.8	6.1	5.8	5.9	5.9
	CCSD	5.5	5.8	5.5	5.6	5.5
	CCSD(T)	5.8	6.1	5.7	5.8	5.8
$\bar{\gamma}$	SCF	12.2	16.3	15.8	16.4	16.4
	MP2	14.3	17.8	16.9	17.4	17.3
	MP4	14.5	17.7	16.4	16.9	16.8
	CCSD	14.1	17.1	15.8	16.3	16.2
	CCSD(T)	14.8	17.9	16.4	16.9	16.8
$C_{zz,zz}$	SCF	269.7	280.1	281.6	281.5	281.2
	MP2	281.6	292.4	291.0	290.9	290.5
	MP4	278.8	288.9	285.4	285.4	284.7
	CCSD	273.5	282.8	279.4	279.4	279.0
	CCSD(T)	277.2	286.8	282.5	282.4	282.0
$C_{xz,xz}$	SCF	230.3	236.4	237.5	237.8	237.8
	MP2	232.0	237.0	236.6	237.0	236.8
	MP4	228.1	233.0	231.7	232.2	232.0
	CCSD	224.4	229.4	229.1	229.5	229.3
	CCSD(T)	227.1	231.9	230.4	230.8	230.5
$C_{xx,xx}$	SCF	116.4	159.3	160.8	161.8	161.7
	MP2	119.1	158.4	157.6	158.4	158.1
	MP4	118.6	156.9	154.7	155.5	155.1
	CCSD	116.9	155.5	153.6	154.5	154.2
	CCSD(T)	118.3	156.5	154.1	154.9	154.7
$\bar{C}$	SCF	304.3	344.5	346.8	347.8	347.7
	MP2	309.0	345.6	344.5	345.4	345.0
	MP4	305.2	340.9	337.6	338.7	338.1
	CCSD	300.4	336.1	334.2	335.1	334.8
	CCSD(T)	304.0	339.4	335.8	336.8	336.4
$B_{zz,zz}$	SCF	−2351	−2513	−2540	−2526	−2522
	MP2	−2705	−2856	−2828	−2819	−2808
$B_{xz,xz}$	SCF	−1518	−1619	−1624	−1642	−1640
	MP2	−1698	−1794	−1745	−1764	−1762
$B_{xx,zz}$	SCF	883	1050	1020	1042	1042
	MP2	805	942	881	894	894
$B_{xx,xx}$	SCF	−1253	−1727	−1672	−1724	−1724
	MP2	−1191	−1610	−1508	−1544	−1542
$\bar{B}$	SCF	−1674	−1727	−1732	−1993	−1992
	MP2	−1794	−1914	−1862	−2021	−2017
$E_{z,zzz}$	SCF	314.2	330.0	334.3	331.4	330.7
	MP2	418.3	430.1	431.8	429.0	427.8
$E_{x,xxx}$	SCF	−154.6	−152.9	−154.7	−154.2	−154.4
	MP2	−179.5	−180.3	−183.1	−183.1	−183.1

[a] The 10 innermost MO were kept frozen in all post-Hartree−Fock calculations. In addition, for the Q basis, excitations were not allowed to the two highest unoccupied MO. The second dipole hyperpolarizability is given as $10^{-3} \times \gamma_{\alpha\beta\gamma\delta}$. All values in atomic units.

one needs more complete basis sets. Adding a relatively diffuse f-GTF on A1 (basis A2) improves both Θ and Φ. If a more diffuse f-GTF is chosen (basis A3), the value of Θ improves but the agreement of Φ with the reference PA value worsens. In some cases the change is not obvious. Basis A4 gives Θ and Φ in very good agreement with PA, but the addition of another f-GTF (basis A5) leads to a lower Θ value. To rationalize the basis set dependence of the SCF electric multipole moments, one should emphasize the fact that Θ and Φ are calculated as differences of fairly larger quantities. For PA $\Theta = 1.0682$ ea_0^2, but this quantity is calculated as $\Theta = \langle zz \rangle - \langle xx \rangle$, where the second moments are $\langle zz \rangle = -18.8213$ and $\langle xx \rangle = -19.8896$ ea_0^2. A small error in $\langle zz \rangle$ or $\langle xx \rangle$ may result in a sizable one for Θ. An analogous situation is obvious for $\Phi = -41.68$ ea_0^4: $\langle zzzz \rangle = -495.89$ ea_0,[4] more than an order of magnitude larger. The second hyperpolarizability values, $10^{-3} \times \gamma_{\alpha\beta\gamma\delta}/e^4a_0^4E_h^{-3}$, obtained with A0 are $\gamma_{zzzz} = 15.2$, $\gamma_{xxxx} = 10.1$, $\gamma_{xxzz} = 4.8$, and $\bar{\gamma} = 12.2$. These values are significantly lower than the reference PA results $\gamma_{zzzz} = 17.6$, $\gamma_{xxxx} = 16.2$, $\gamma_{xxzz} = 5.4$, and 16.5 (PA). Adding more d- and f-GTF to A0 increases the transversal component γ_{xxxx} and brings $\bar{\gamma}$ close to the reference value. We observe, more or less, the same pattern for the higher properties $C_{\alpha\beta,\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$. The transversal components $C_{xx,xx}$ and $B_{xx,xx}$ increase rapidly with basis set size. The mean values obtained with A0, $\bar{C} = 304.3$ $e^2a_0^4E_h^{-1}$ and $\bar{B} = -1674$ $e^3a_0^4E_h^{-2}$, are 12.9 and 16.3% smaller in magnitude than the respective reference PA results. From basis set A4 onward, these mean values are quite close to the reference PA values $\bar{C} = 349.2$ $e^2a_0^4E_h^{-1}$ and $\bar{B} = -1999$ $e^3a_0^4E_h^{-2}$. Last, for the dipole−octopole polarizability we observe again that for A4→A10 and Q, agreement with the PA values is very good.

Overall, the large basis sets A8, A9, A10, Q, and PA are in close agreement for all molecular properties.

Electron Correlation Effects. Electron correlation affects strongly the SCF values of Θ/ea_0^2 and Φ/ea_0^4. For both properties, MP2 and MP4 seem to overestimate the magnitude of the electron correlation correction. Our best values are the CCSD(T)/Q results of $\Theta = 0.4850$ and $\Phi = -31.25$, which correspond to a reduction of 52.3 and 26.2%, respectively, of

TABLE 3: Bond Length, $\Delta R/a_0 \equiv (R - R_e)$ Dependence of the Electric Properties of P_2 Calculated with Basis Set A9 ≡ [6s5p5d3f] at the CCSD(T) Level of Theory[a]

property	−0.2	−0.1	0	0.1	0.2
Θ	0.0278	0.2634	0.4860	0.6957	0.8923
Φ	−34.27	−32.96	−31.48	−29.82	−27.98
α_{zz}	62.70	65.28	67.91	70.55	73.20
α_{xx}	38.22	39.05	39.87	40.67	41.45
$\bar{\alpha}$	46.38	47.79	49.21	50.63	52.04
$\Delta\alpha$	24.48	26.24	28.04	29.88	31.75
γ_{zzzz}	20.9	21.6	22.4	23.3	24.5
γ_{xxxx}	12.4	13.4	14.5	15.5	16.7
γ_{xxzz}	5.2	5.5	5.8	6.2	6.6
$\bar{\gamma}$	14.9	15.9	16.9	17.9	19.1
$C_{zz,zz}$	261.7	271.6	282.4	294.0	306.1
$C_{xz,xz}$	215.2	222.6	230.8	239.3	248.2
$C_{xx,xx}$	145.7	150.1	154.9	159.8	164.8
$\bar{C}$	314.9	325.4	336.8	348.7	361.0

[a] The 10 innermost MO were kept frozen in all calculations. The second dipole hyperpolarizability is given as $10^{-3} \times \gamma_{\alpha\beta\gamma\delta}$. All values in atomic units.

TABLE 4: Convergence of Electric Property Derivatives at Post-Hartree−Fock Levels of Theory[a]

property	SCF	MP2	MP4	CCSD	CCSD(T)
$(d\Theta/dR)_e$	3.3321	1.7468	1.9077	2.3850	2.1616
$(d\Phi/dR)_e$	15.79	18.57	16.57	15.66	15.69
$(d\bar{\alpha}/dR)_e$	19.15	12.68	14.45	14.57	14.22
$(d\Delta\alpha/dR)_e$	22.34	16.53	19.99	18.01	18.21
$(d\bar{\gamma}/dR)_e$	15.7	9.5	9.0	11.1	9.8
$(d\bar{C}/dR)_e$	143.3	111.8	114.6	118.6	116.9

[a] Basis set A9 ≡ [6s5p5d3f]. The 10 innermost MO were kept frozen in all post-Hartree−Fock calculations. The second dipole hyperpolarizability is given as $10^{-3} \times (d^k\bar{\gamma}/dR^k)_e$, $k = 1, 2$. All values in atomic units.

TABLE 5: Comparison of DFT and CCSD(T) Polarizabilities Obtained with the $Q \equiv$ [9s7p5d3f] Basis Set[a]

property	B3P86	B3PW91	B3LYP	CCSD(T)
α_{zz}	69.07	69.02	70.04	67.88
α_{xx}	40.36	40.36	41.06	39.86
$\bar{\alpha}$	49.93	49.91	50.72	49.20
$\Delta\alpha$	28.70	28.66	28.98	28.02
γ_{zzzz}	23.4	24.0	26.3	22.2
γ_{xxxx}	15.6	16.2	18.2	14.4
γ_{xxzz}	6.3	6.4	7.1	5.8
$\bar{\gamma}$	18.0	18.6	20.7	16.8

[a] The second dipole hyperpolarizability is given as $10^{-3} \times \gamma_{\alpha\beta\gamma\delta}$. All values in atomic units.

the magnitude of the SCF values. Correlated values obtained with basis sets A7, A9, and Q are in close agreement. It is worth noticing that the only difference between the A6 and A7 basis sets is the relatively tight f-GTF exponent on A7.

Both components of $\alpha_{\alpha\beta}/e^2a_0^2E_h^{-1}$ are slightly reduced by electron correlation. This results in an overall small reduction of both invariants: CCSD(T)/Q gives (SCF/Q values in parentheses) $\bar{\alpha} = 49.20$ (51.09) and $\Delta\alpha = 28.02$ (28.62). The effect is only 3.7 and 2.1%, respectively. All basis sets perform well in the prediction of the dipole polarizability.

The effect is not uniform on the components of $10^{-3} \times \gamma_{\alpha\beta\gamma\delta}/e^4a_0^4E_h^{-3}$. The longitudinal component increases while the transversal one decreases. For CCSD(T)/Q we have (SCF/Q values in parentheses): $\gamma_{zzzz} = 22.2$ (17.3), $\gamma_{xxxx} = 16.1$ (14.4), and $\gamma_{xxzz} = 5.4$ (5.8). Overall, $\bar{\gamma} = 16.8$ (16.4) or an increase of only 2.4%. We note the very good agreement of the A9 and Q values. We also note that MP2 exaggerates somewhat the electron correlation effect but MP4 seems to predict values reasonably close to the higher CCSD(T) method.

Electron correlation has a non uniform effect on the quadrupole polarizability $C_{\alpha\beta,\gamma\delta}/e^2a_0^4E_h^{-1}$. The CCSD(T)/Q results suggest a slight increase for the longitudinal component but a decrease for the other two. Overall, the mean SCF/Q value of $\bar{C} = 347.7$ reduces to 336.4 or by 3.2%. The decrease is very small for the minimal basis A0 but is more or less stably predicted by the larger A6, A7, A9, and Q. We also note the good agreement for the MP4, CCSD and CCSD(T) methods.

Very much as in the case of $\gamma_{\alpha\beta\gamma\delta}$ and $C_{\alpha\beta,\gamma\delta}$, a non uniform change is brought upon the components of $B_{\alpha\beta,\gamma\delta}/e^3a_0^4E_h^{-2}$. The

TABLE 6: Reference Near-Hartree−Fock Results for the Electric Properties of N_2, P_2, and As_2[a]

property	N_2[b]	P_2[c]	As_2[d]
Θ	−0.9302	1.0682	1.4569
Φ	−7.40	−41.68	−52.42
α_{zz}	15.03	70.21	91.87
α_{xx}	9.83	41.63	51.49
$\bar{\alpha}$	11.57	51.16	64.95
$\Delta\alpha$	5.20	28.58	40.37
γ_{zzzz}	799	17.6	29.4
γ_{xxxx}	666	16.2	28.6
γ_{xxzz}	250	5.4	9.3
$\bar{\gamma}$	715	16.5	28.5
$\Delta_1\gamma$	482	4.2	1.5
$\Delta_2\gamma$	−35	1.3	2.4
$C_{zz,zz}$	31.43	282.3	394.5
$C_{xz,xz}$	24.33	238.1	342.7
$C_{xx,xx}$	19.36	163.1	225.7
$\bar{C}$	38.10	349.2	494.2
$B_{zz,zz}$	−175	−2540	−3813
$B_{xz,xz}$	−105	−1646	−2669
$B_{xx,zz}$	65	1042	1662
$B_{xx,xx}$	−117	−1727	−2665
$\bar{B}$	−133	−1999	−3131
$E_{z,zzz}$	28.76	332.3	500.4
$E_{x,xxx}$	−18.40	−154.4	−212.2

[a] The second dipole hyperpolarizability for P_2 and As_2 is given as $10^{-3} \times \gamma_{\alpha\beta\gamma\delta}$. All values in atomic units. [b] Basis set [15s12p9d7f], 290 CGTF (Maroulis, unpublished results). [c] Basis set PA ≡ (20s15p10d5f), 300 GTF, present investigation. [d] Basis set (20s15p12d4f), 314 GTF (Maroulis, unpublished results).

TABLE 7: Present and Previous Theoretical Values for the Electric Properties of P_2[a]

property	NHF[b]	SCF[c]	MP2[d]	SCF[e]	CCSD(T)[f]
Θ	1.064167	1.251		1.0682	0.4850
Φ	−41.7069	−38.92		−41.68	−31.25
$\bar{\alpha}$		50.74	35.290	51.16	49.20
$\Delta\alpha$		28.63	41.163	28.58	28.02
$\bar{\gamma}$		13364		16.5×10^3	16.8×10^3
$\bar{C}$		334.7		349.2	336.4

[a] All values in atomic units. [b] Numerical Hartree−Fock values.[19] [c] Basis set [8s6p4d1f], Maroulis.[22] [d] 6-31G* basis set, Glaser et al.[20] [e] Present investigation, basis set PA ≡ (20s15p10d5f). [f] Present investigation, basis set Q ≡ [9s7p5d3f].

TABLE 8: Electric Polarizability for Some 30-electron Systems[a]

property	NaK[b]	AlCl[c]	SiS[d]	P_2[e]	Zn[f]
$\bar{\alpha}$	365.08	53.25	49.76	49.20	39.2 ± 0.8
$\Delta\alpha$	257.79	11.95	20.31	28.02	0

[a] All values in atomic units [b] Urban and Sadlej.[60] [c] Maroulis, unpublished results. [d] Maroulis et al.[61] [e] Present investigation. [f] Goebel et al.,[62] recommended theoretical value.

MP2/Q results show that the effect, MP2 − SCF, on the magnitude of the components is positive for $B_{zz,zz}$ and $B_{xz,xz}$ and negative for $B_{xx,zz}$ and $B_{xx,xx}$. Consequently, the effect on the mean value $\bar{B}$ is very small: an increase of magnitude of 1.3%.

For the dipole−octopole polarizability $E_{\alpha,\beta\gamma\delta}/e^2a_0^4E_h^{-1}$ we observe a strong increase of the magnitude of both components. For MP2/Q (SCF/Q values in parentheses) we obtain $E_{z,zzz}$ = 427.8 (330.7) and −183.1 (−154.4), an increase in magnitude of 29.4 and 18.6%. It is interesting to notice that this trend is present for all other basis sets.

Bond-Length Dependence of the Electric Properties. The CCSD(T)/A9 values of Θ, Φ, $\bar{\alpha}$, $\Delta\alpha$, $\bar{\gamma}$, and $\bar{C}$ shown in Table 3 may be used to obtain accurate estimates of the first derivatives $(dP/dR)_e$. The dependence of the first derivative values on the level of theory may be gleaned from the contents of Table 4.

The electric moments vary strongly around R_e. We observe a rapid increase of the magnitude of the quadrupole moment while the opposite trend is obvious for the hexadecapole. A third-degree polynomial was found to represent adequately the R-dependence for $-0.2 \le R/a_0 \le 0.2$. At the SCF and CCSD(T) levels of theory Θ and Φ vary as

$$\text{SCF:}\quad \Theta(R)/ea_0^2 = 1.0234 + 3.3321(R-R_e) - 0.3743(R-R_e)^2 - 0.0083(R-R_e)^3$$

$$\text{CCSD(T):}\quad \Theta(R)/ea_0^2 = 0.4860 + 2.1616(R-R_e) - 0.6493(R-R_e)^2 - 0.0083(R-R_e)^3 \quad (6)$$

and

$$\text{SCF:}\quad \Phi(R)/ea_0^2 = -42.49 + 15.79(R-R_e) + 12.57(R-R_e)^2 + 0.83(R-R_e)^3$$

$$\text{CCSD(T):}\quad \Phi(R)/ea_0^2 = -31.48 + 15.69(R-R_e) + 8.86(R-R_e)^2 + 0.83(R-R_e)^3 \quad (7)$$

The SCF/A9 values for the first derivatives of the dipole polarizability invariants are $(d\bar{\alpha}/dR)_e = 19.15$ and $(d\Delta\alpha/dR)_e = 22.34\ e^2a_0E_h^{-1}$. Electron correlation lowers both values. The higher order methods MP4, CCSD, and CCSD(T) predict values in good agreement for these two properties. Predicting reliable values for the second derivatives appears less obvious. The values pertaining to the mean show strong method dependence. The SCF value is $(d^2\bar{\alpha}/dR^2)_e = 2.21\ e^2E_h^{-1}$, whereas for the CCSD(T) value $(d^2\bar{\alpha}/dR^2)_e \approx 0$. For the anisotropy the situation is not much different. We obtain $(d^2\Delta\alpha/dR^2)_e = 9.72$ and 3.71 $e^2E_h^{-1}$ at the SCF and CCSD(T) levels, respectively.

For the second dipole hyperpolarizability we calculate a SCF value $(d\bar{\gamma}/dR)_e = 15.7 \times 10^3\ e^4a_0^3E_h^{-3}$. Electron correlation almost halves this value. The post-Hartree−Fock methods predict rather stable values for this first derivative. At the highest level of theory, we obtain the CCSD(T) value of $(d\bar{\gamma}/dR)_e = 9.8 \times 10^3\ e^4a_0^3E_h^{-3}$. The second derivative is also reduced by electron correlation. We obtain $(d^2\bar{\gamma}/dR^2)_e = 15.7 \times 10^3$ and $5.7 \times 10^3\ e^4a_0^2E_h^{-3}$ at the SCF and CCSD(T) levels, respectively.

For the mean quadrupole polarizability we calculate a SCF value of $(d\bar{C}/dR)_e = 144.3\ e^2a_0^3E_h^{-1}$. Electron correlation reduces significantly this value, but the stability of the post-Hartree−Fock values is very satisfactory. This is not the case for the second derivative. The SCF value $(d^2\bar{C}/dR^2)_e = 115.7$ reduces to 19.7 $e^2a_0^2E_h^{-1}$ at the MP2 level. MP4, CCSD, and CCSD(T) predict values in good agreement. Our CCSD(T) value is 58.6 $e^2a_0^2E_h^{-1}$.

Last, we obtained SCF and MP2 values for the R-dependence of dipole−octopole polarizability and the dipole−dipole−quadrupole polarizability.[54] At the SCF level the R-dependence of the two components of $E_{\alpha,\beta\gamma\delta}$ is well represented by

$$E_{z,zzz}(R)/e^2a_0^4E_h^{-1} = 331.4 + 130.9(R-R_e) + 95.7(R-R_e)^2 + 8.3(R-R_e)^3$$

$$E_{x,xxx}(R)/e^2a_0^4E_h^{-1} = -154.2 - 47.4(R-R_e) - 53.6(R-R_e)^2 - 8.3(R-R_e)^3 \quad (8)$$

The magnitude of the first-derivative increases considerably at the MP2 level. The corresponding curves are

$$E_{z,zzz}(R)/e^2a_0^4E_h^{-1} = 429.0 + 315.0(R-R_e) + 249.4(R-R_e)^2 + 97.5(R-R_e)^3$$

$$E_{x,xxx}(R)/e^2a_0^4E_h^{-1} = -183.1 - 93.4(R-R_e) - 68.6(R-R_e)^2 + 1.7(R-R_e)^3 \quad (9)$$

For the mean value of $B_{\alpha\beta,\gamma\delta}$ we find that a parabola reproduces quite well the calculated values. Subsequently, we expand this property as

$$\text{SCF:}\quad \bar{B}(R)/e^3a_0^4E_h^{-2} = -1993 - 1404(R-R_e) - 614(R-R_e)^2$$

$$\text{MP2:}\quad \bar{B}(R)/e^3a_0^4E_h^{-2} = -2021 - 860(R-R_e) - 6(R-R_e)^2 \quad (10)$$

Rovibrational Corrections. We have used a well-tested approach[55] and experimental spectroscopic constants[50] for P_2 in order to estimate the rovibrational correction to the calculated molecular properties. We find that the value of property P at υJ rovibrational state is given as

$$P_{\upsilon J} - P_e = \left(0.012954\left(\frac{dP}{dR}\right)_e + 0.004978\left(\frac{d^2P}{dR^2}\right)_e\right) \times \left(\upsilon + \frac{1}{2}\right) + 0.000002\left(\frac{dP}{dR}\right)_e J(J+1) \quad (11)$$

Inserting the calculated derivatives into eq 11 we obtain the desired corrections. The zero-point vibrational correction (ZPVC), defined as ZPVC $\equiv P_{00} - P_e$, is found to be small for all properties. For Θ, Φ, $\alpha_{\alpha\beta}$, $\gamma_{\alpha\beta\gamma\delta}$, and $C_{\alpha\beta,\gamma\delta}$ we have used CCSD(T)/A9 values for $(d^kP/dR^k)_e$, k = 1,2. The calculated ZPVC is 0.0108 ea_0^2 for Θ, 0.15 ea_0^4 for Φ, 0.09 and 0.13 $e^2a_0^2E_h^{-1}$ for $\bar{\alpha}$ and $\Delta\alpha$, 0.08 × $10^3\ e^4a_0^4E_h^{-3}$ for $\bar{\gamma}$, and 0.9 $C^2m^4J^{-1}$ for $\bar{C}$. Using MP2/A9 values, we calculated a ZPVC of 3.3 and −0.9 $C^2m^4J^{-1}$ for $E_{z,zzz}$ and $E_{x,xxx}$ and $-6e^3a_0^4E_h^{-2}$ for $\bar{B}$.

DFT Results. As the development of new DFT methods for the reliable prediction of electric properties has been intensely pursued in recent years,[56,57] we have considered it instructive to add to our study on P_2 a series of calculations with widely used and easily accessible DFT methods. These B3P86, B3PW91, and B3LYP dipole (hyper)polarizabilities have been obtained with basis set Q and are compared in Table 5 to our accurate CCSD(T)/KT values. The DFT values slightly overestimate the mean and the anisotropy of the dipole polarizability. This trend is also present in the calculated $\gamma_{\alpha\beta\gamma\delta}$ components. Overall, P3B86 and B3PW91 perform better than the B3LYP method. The B3LYP $\bar{\gamma} = 20.7 \times 10^3$ $e^4a_0^4E_h^{-3}$, 23.2% larger than the CCSD(T)/KT result.

Electric Moments and (Hyper)polarizabilities of N_2, P_2, and As_2. In Table 6 we show the evolution of the electric properties with increasing size in N_2, P_2, and As_2. Although we do not belabor the point, we think it both useful and instructive to add a few comments on the emerging patterns. The reference near-Hartree−Fock values for these three homonuclear diatomics show a regular increase of the electric (hyper)-polarizability. The hexadecapole moment is negative for all three. Most important, the quadrupole moments are comparable in magnitude. The quadrupole moment is negative for N_2 and positive for P_2 and As_2. Thus, while the electrostatic part of eq 1 will make comparable contributions to the total interaction energy for the three diatomics, the inductive part will be increasingly more important in the order $N_2 \rightarrow P_2 \rightarrow As_2$. From an induction point of view, these molecules become increasingly “softer” in the above order.

Comparison of Theoretical Predictions for the Electric Properties of P_2. The numerical Hartree−Fock calculations of Pyykkö et al.[19] yielded $\Theta = 1.064167$ ea_0^2 and $\Phi = -41.7069$ ea_0.[4] Our SCF/PA values are remarkably close to these values. We are also aware of two previous papers that have reported polarizability values. Maroulis[22] obtained SCF electric moments and (hyper)polarizabilities with a [8s6p4d1f] basis sets. With the exception of the second dipole hyperpolarizability his values are in fair agreement with the present results. Glaser et al.[20] reported MP2/6-31G* values for the dipole polarizability. As the basis set used in their work is rather small, their values are understandably different than ours: the mean $\bar{\alpha}$ is lower and the anisotropy higher than our respective results. Lawson and Harrison[23] reported an exhaustive study of the quadrupole moment of P_2. Their best value for $\Theta = 0.4759$ ea_0^2, obtained from multireference configuration interaction calculations (MRCI) with a very large basis set, agrees quite well with our CCSD(T)/Q value. They have also reported first and second derivative values $(d^k\Theta/dR^k)_e$, $k = 1, 2$, calculated with the complete active space self-consistent field (CASSCF) method. Their values (CASSCF+1+2 results, Table 4 in their paper) are 2.0972 ea_0 for the first and −1.6068 e for the second derivative. Both are in agreement with our CCSD(T)/A9 values (see eq 6). Last, we mention a MRCI quadrupole moment value of 0.424 ea_0^2 calculated by de Brouckère and Feller.[21]

Electric Polarizability of 30-Electron Systems. Isoelectronic sequences of atoms/molecules constitute a favorite ground for systematic observations on the evolution of atomic/molecular properties.[58,59] We show in Table 8 mean ($\bar{\alpha}$) and anisotropy ($\Delta\alpha$) values for a series of 30-electron systems. The displayed values represent simply a selection. For instance, the reliability of the given value[62] of the dipole polarizability of Zn has been confirmed by the findings of a recent study by Ellingsen et al.[63] The NaK molecule is by far the more polarizable of the series. It is worth noticing that for the AlCl, SiS, and P_2 molecules we have $\bar{\alpha}(\text{AlCl}) > \bar{\alpha}(\text{SiS}) > \bar{\alpha}(P_2)$ and $\Delta\alpha(\text{AlCl}) < \Delta\alpha(\text{SiS}) < \Delta\alpha(P_2)$, although the variation of the anisotropy is more important than that of the mean.

Conclusions

We have reported an exhaustive study of the electric properties of P_2. We have obtained reference near-Hartree−Fock values for all properties. Electron correlation effects have also been estimated. The electron correlation correction is strong for the quadrupole and the hexadecapole moment but rather small for the dipole polarizability and hyperpolarizability. The dependence of the properties on the bond length has been examined in some depth.

Our best values for the electric moments and the dipole (hyper)polarizability are $\Theta = 0.4850$ ea_0^2, $\Phi = -31.25$ ea_0^4, $\bar{\alpha} = 39.86$, and $\Delta\alpha = 28.02$ $e^2a_0^2E_h^{-1}$ and $\bar{\gamma} = 16.8 \times 10^3$ $e^4a_0^4E_h^{-3}$.

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