

# Combined experimental and theoretical treatment of the dipole polarizability of P<sub>4</sub> clusters

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(Received 17 December 1999; published 14 April 2000)

The frequency dependence of the dipole polarizability  $\alpha(\omega)$  of P<sub>4</sub> is obtained from refractive index measurements on gaseous phosphorus by means of asymmetric white-light interferometry. The experimental results obtained in the range between 10 000 and 30 300 cm<sup>-1</sup> yield an extrapolated static value of  $\alpha = 91.71(92)e^2a_0^2E_H^{-1}$ . An extensive theoretical study, based on finite-field many-body perturbation theory and coupled cluster methods, leads to a theoretical estimate at zero frequency of  $\alpha \approx 93.2(0.9)e^2a_0^2E_H^{-1}$  at the experimental bond length  $R_0 = 2.1958 \text{ \AA}$ . For the symmetric stretch of the molecule the dipole polarizability of P<sub>4</sub> varies around  $R_0$  as  $[\alpha(R) - \alpha(R_0)]/e^2a_0^2E_H^{-1} = 34.02\Delta R + 3.68\Delta R^2 - 0.29\Delta R^3$  showing an essentially linear dependence on the change of the P–P bond distance  $\Delta R \equiv (R - R_0)/a_0$ . The dipole polarizability per atom is significantly smaller than that of the phosphorous atom  $25.22 e^2a_0^2E_H^{-1}$ . This differs from the corresponding change of  $\alpha$  in the homologous As<sub>4</sub> cluster, where the single atom value is very close to the polarizability per atom of the cluster.

PACS number(s): 36.40.Cg, 33.15.Kr

## I. INTRODUCTION

The structure of phosphorous clusters has attracted considerable attention in recent years [1–5]. Little is known about the electric properties of these systems. To our knowledge, only the properties of the dimer have been studied. Lawson and Harrison reported a study of the electric quadrupole moment [6], Glaser *et al.* [7] self-consistent field (SCF) values of the quadrupole moment and the dipole polarizability and Maroulis [8] SCF values of the electric moments, the dipole, and higher polarizabilities. In this paper we report a joint experimental and theoretical study of the dipole polarizability  $\alpha$  of the tetrahedral P<sub>4</sub> cluster. The experimental results of the frequency dependence of  $\alpha(\omega)$  are obtained from density-dependent gas-phase refractivity measurements on phosphorus vapor. To this end we use monochromatic measurements performed at four discrete wavelengths as well as quasicontinuous measurements with a broad-band radiation source. Our theoretical efforts rely on finite-field many-body perturbation (MP) theory and coupled cluster (CC) techniques. We have designed a sequence of large, flexible, carefully optimized basis sets of Gaussian-type functions (GTFs) for P<sub>4</sub>. This is an essential part of our study, as nothing is known about the electric properties of this system. An elucidation of the computational aspects of our calculations is expected to be of importance to future work on P<sub>4</sub> and related systems. In addition to the dipole polarizability  $\alpha$ , we have also calculated the electric octopole ( $\Omega$ ) and hexadecapole ( $\Phi$ ) moment, the dipole-quadrupole ( $A$ ), and dipole-octopole ( $E$ ) polarizability. The

electric moments are useful quantities as they are relevant to the analysis of interaction-induced far-infrared spectra of tetrahedral molecules [9]. There is also interest in the dipole-quadrupole ( $A$ ) and dipole-octopole ( $E$ ) polarizability of systems of this symmetry due to their importance for intermolecular interaction studies [10], collision- and interaction-induced spectroscopy [11], and, in particular, the very recent work on collision-induced light scattering in gaseous P<sub>4</sub> [12]. In addition we obtain very accurate values for the dipole polarizability of the phosphorous atom. We are interested in estimating the quantity  $\alpha(\text{P}_4) - 4\alpha(\text{P})$ , which may offer insight into the type of bonding in P<sub>4</sub>.

## II. EXPERIMENT

The dipole polarizability  $\alpha(\omega)$  of P<sub>4</sub> is obtained from gas-phase refractive index measurements as a function of gas density  $\rho$ , temperature  $T$ , and frequency  $\omega$ . The apparatus used consists mainly of an evacuated Michelson twin interferometer which is described in detail elsewhere [13,14]. This interferometer is specially designed for working at higher temperatures. Two types of refractive index measurements are performed. Monochromatic measurements are performed at four different vacuum wavelengths of  $\lambda_1 = 632.99 \text{ nm}$ ,  $\lambda_2 = 543.516 \text{ nm}$  (both HeNe lasers)  $\lambda_3 = 441.686 \text{ nm}$ , and  $\lambda_4 = 325.130 \text{ nm}$  (both HeCd lasers). The corresponding frequencies  $\omega$  are 0.07 198 12, 0.083 830 7, 0.103 1578, and 0.140 138 9 (all in atomic units [15]). In this case an amount  $m$  of red phosphorus (purity >99.999%) is filled into the cylindrical sample cells. These cells are evacuated and fused off. After putting one cell into one arm of the interferometer the cell is heated by means of a pipe furnace. The evaporating sample causes an interference fringe shift  $\Delta N(T, \lambda)$ . The refractivity  $[n(\lambda, T_0, \rho) - 1]$  at temperature  $T_0$  where complete evaporation has been achieved is related to the totally recorded interference fringe shift  $\Delta N(T_0, \lambda)$  via

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TABLE I. Experimental conditions and measured refractivities  $n-1$  of phosphorus vapor.

$\varrho$ (mol m <sup>-3</sup> )	$T$ (K) <sup>a</sup>	$10^5[n(\lambda_1)-1]$	$10^5[n(\lambda_2)-1]$	$10^5[n(\lambda_3)-1]$	$10^5[n(\lambda_4)-1]$
8.369(32)	798.65			47.746(48)	
	515.55	45.385(45)	46.090(46)		
	516.65	45.259(45)	45.982(46)		
	513.15	45.259(45)	45.982(45)		
	513.55			46.995(47)	51.338(96)
11.465(47)	514.95				51.241(32)
	543.65	61.337(61)	62.287(63)		
	544.45	61.084(61)	62.070(62)		
	540.25	61.020(61)	61.961(62)		
	545.15			63.603(44)	
15.806(63)	546.65			63.426(44)	
	806.45	84.732(63)	86.057(57)		
	537.65	83.657(63)	84.971(57)		
	541.65	83.024(63)	84.428(57)		
	542.40	83.783(63)	85.080(57)		
	540.15	83.783(63)	85.080(57)		

<sup>a</sup>The uncertainty in  $T$  is less than 1 K.

$$n(\lambda, T_0, \varrho) - 1 = \frac{\Delta N(T_0, \lambda) \lambda}{2\mathcal{L}(T_0)} \quad (1)$$

$\mathcal{L}(T_0)$  is the length of the sample cell at  $T_0$ . These non-isothermal measurements are performed at three different densities  $\varrho = m/V$ , where  $V$  is the volume of the sample cell. The experimental conditions and measured refractivities are given in Table I. After complete evaporation of the sample isothermal measurements at  $T_0, \varrho(T_0)$  of the frequency dependence of the refractivity are performed by means of asymmetric white light interferometry. This special technique yields a quasicontinuous refractivity spectrum in the range between 400 and 1000 nm with a resolution of about  $3.7 \text{ cm}^{-1}$  [13,14]. Asymmetric white-light interferometry only yields a relative dispersion curve. The obtained refractivity, therefore, is fixed to the two measured values at  $\lambda_1$  and  $\lambda_2$ .

### III. EXPERIMENTAL RESULTS

The monochromatic measurements are evaluated according to the relation

$$n(\lambda, T, \varrho) - 1 = 2\pi N_A \varrho a_0^3 \alpha(\lambda, T). \quad (2)$$

$N_A = 6.022 136 7 \times 10^{23} \text{ mol m}^{-3}$  is the Avogadro constant. We use a constraint fit which ensures  $n \equiv 1$  at  $\varrho = 0$ . For the four monochromatic wavelengths used we obtain the dipole polarizabilities  $\alpha(\lambda_1) = 95.08(25) e^2 a_0^2 E_H^{-1}$ ,  $\alpha(\lambda_2) = 96.57(25) e^2 a_0^2 E_H^{-1}$ ,  $\alpha(\lambda_3) = 99.75(57) e^2 a_0^2 E_H^{-1}$ , and  $\alpha(\lambda_4) = 109.29(10) e^2 a_0^2 E_H^{-1}$ , respectively. In all cases a linear dependence of  $n-1$  on  $\varrho$  according to Eq. (2) is observed which means that collision-induced effects are not detectable at the densities used in our experiments. Moreover, we do not observe a systematic temperature dependence of  $\alpha(\lambda, T)$ . We conclude, that in our range of tempera-

ture a possibly small temperature dependence of the dipole polarizability on account of rotational and vibrational excitation is not detectable. In our experiments the maximum temperature used was 806.45 K. At this temperature the partial pressure of  $P_2$  is absolutely negligible [17,18]. Therefore, all experimental results refer to the  $P_4$  cluster. In Fig. 1, our experimental results are displayed. The full curve is the mean of three independent white-light measurements of the refractivity spectrum of gaseous  $P_4$ . These measurements are carried out at the three different densities given in Table I. It can be seen that the experimental point recorded at  $\lambda_3 = 441.686 \text{ nm}$  ( $\omega_3 = 0.103 157 8 E_H \hbar^{-1}$ ) is in perfect agreement with the quasicontinuous measurements. This strengthens the quality of our white-light interferometric technique. In order to obtain the polarizability at wavelengths not used in our experiments we have to extrapolate our results. This has been done according to a three term Cauchy formula

$$\alpha(\omega) = S(-2) + S(-4)\omega^2 + S(-6)\omega^4. \quad (3)$$

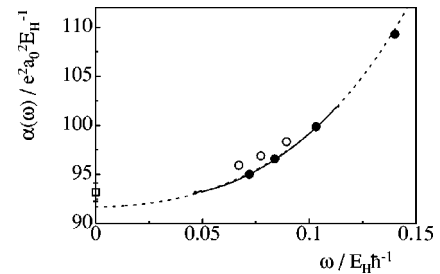


FIG. 1. Frequency dependence of the dipole polarizability  $\alpha(\omega)$  of  $P_4$  clusters. Full curve, quasicontinuous results obtained by means of asymmetric white-light interferometry; dashed curve, fit according to Eq. (3); ●, monochromatic measurements, this work; ○, monochromatic measurements Ref. [16]; □, *ab initio* result, this work.

TABLE II. Basis sets designed for  $P_4$  and used in this work.

Basis set	No. CGTF	Description
A0≡[6s5p2d]	124	From (14s9p)/[5s4p] + s(0.041 194 037) + p(0.031 9966 25) + d(0.4013,0.0745)
A1≡[6s5p3d]	144	From A0 + d(0.1729)
A2≡[6s5p3d]	144	From A0 + d(0.0321)
A3≡[6s5p3d1f]	172	From A0 + d(0.0321) + f(0.0745)
A4≡[6s5p4d2f]	220	From A1 + d(0.0321) + f(0.0745,0.0321)
A5≡[6s5p4d2f]	220	From A1 + d(0.0321) + f(0.4013,0.0745)

A least squares fit yields the Cauchy moments  $S(-2) = 91.71(2)$ ,  $S(-4) = 567(4)$ , and  $S(-6) = 1.814(27) \times 10^4$ . Taking into account the uncertainty of the two absolute values  $\alpha(\lambda_1)$  and  $\alpha(\lambda_2)$  we deduce an experimental value of the static dipole polarizability of  $\alpha(0) \equiv S(-2) = 91.71(92) e^2 a_0^2 E_H^{-1}$ .

Our experimental results can be compared to refractive index measurements reported by Cuthbertson and Metcalfe [16]. Their results are also displayed in Fig. 1. The three values are higher by approximately 1.3%. The frequency-dependence obtained by Cuthbertson and Metcalfe is smaller than the results reported in this work. Extrapolation to zero frequency yields a static polarizability of  $\alpha(0) = 93.0(0.1) e^2 a_0^2 E_H^{-1}$ , a value which is also slightly higher than our experimental estimate.

#### IV. THEORY AND COMPUTATIONAL STRATEGY

There is only one independent component for the octopole and the hexadecapole moment of a system of tetrahedral symmetry as  $P_4$  [19]. There is also only one independent component for the dipole ( $\alpha_{\alpha\beta}$ ), dipole-quadrupole ( $A_{\alpha,\beta\gamma}$ ), and dipole-octopole ( $E_{\alpha,\beta\gamma\delta}$ ) polarizability tensors [19,20]. The computational strategy for the extraction of these molecular properties from finite-field calculations has been presented in detail in previous work on  $CH_4$  [21,22],  $CF_4$  [22,23], and  $SF_6$  [24]. We rely on many-body Møller-Plesset (MP) perturbation theory [25,26] and coupled cluster (CC) techniques [27–29] for our post-Hartree-Fock calculations. Extensive presentations of the computational aspects of the application of these methods may be found in previous work [30–34]. The MP levels of theory employed in this work are second order (MP2), fourth order with contributions from single, double, and quadruple substitutions from the reference wave function (SDQ-MP4) and complete fourth order (MP4). The CC techniques are CCSD, single and double, excitation coupled cluster theory and CCSD(T), which includes an estimate of connected triple excitations by a perturbational treatment.

*Basis set construction and computational details.* We have designed a very large basis set for our calculations on the phosphorous atom. We have used as starting point a very large, uncontracted basis set consisting of (18s13p) GTFs [35]. We augmented the initial substrate to (21s16p10d3f) by adding diffuse  $s$  and  $p$  GTFs,  $d$  GTF chosen to maximize

the dipole polarizability  $\alpha$  and  $f$  GTF chosen to maximize the quadrupole polarizability  $A$ . We have followed a computational philosophy developed in previous work [36]. Details of the construction are available from the corresponding author [37]. For  $P_4$  we have used a (14s9p)[5s4p] substrate [38]. This initial set was augmented by diffuse GTF to [6s5p]. Furthermore, we added in succession one  $d$  GTF with exponent chosen to minimize the energy of the free molecule and one diffuse  $d$  GTF with exponent chosen to maximize the dipole polarizability. The resulting basis set [6s5p2d], hereafter A0, was systematically increased to obtain the remaining sets used in this work. Their composition is given in detail in Table II. All optimizations on  $P_4$  were carried out at the experimental bond length  $R_0 = 2.2228 \text{ \AA}$  [39]. Our knowledge of this fundamental quantity was improved by more recent experimental work [40]. All subsequent calculations for the dipole polarizability were performed at the new value of 2.1958  $\text{\AA}$  while electric multipole moments, dipole-quadrupole and dipole-octopole polarizabilities, by-products of our investigation, are reported for the old bond length. The GAUSSIAN 94 set of programs was used in all calculations [41].

#### V. RESULTS AND DISCUSSION

Table III lists the dipole polarizability values for  $P_4$ . The smallest basis set used on  $P_4$ , A0, yields a SCF value of 91.11 for  $\alpha/e^2 a_0^2 E_H^{-1}$ . The two largest sets A4 and A5 give 91.38 and 91.53, or 0.3 and 0.5% above the A0 value. Thus, our SCF values are quite stable. We have obtained MP and CC results with sets A0, A1, and A2, MP4 values with sets A3, A4, and A5. The total electron correlation correction (ECC) for the dipole polarizability is surprisingly small. What is more, the MP4 and CCSD(T) results are quite close. For sets A0, A1, and A2 the total electron correlation correction,  $ECC = CCSD(T) - SCF$ , barely exceeds 1% of the SCF value. Let us concentrate on the correction  $ECC = MP4 - SCF$  obtained with A3, A4, and A5. We observe that the respective absolute differences are 2.08 (A3), 1.86 (A4), and 0.88 (A5). Thus, for the three largest basis sets the predicted electron correlation effect is in the range of 1–2%. A4 and A5 are of the same size, but A4 is more diffuse than A5 (see Table II). The stability of our results leads to an estimate of  $\alpha = 93.2(0.9) e^2 a_0^2 E_H^{-1}$  for the dipole polarizability of  $P_4$ . Within the uncertainty limits this theo-

TABLE III. Theoretical values (the 20 innermost MO were kept frozen in all post-Hartree-Fock calculations) of the dipole polarizability of  $P_4$  at the experimental P—P bond length of 2.1958 Å.

Basis set	No. CGTF	Method	$\alpha/e^2a_0^2E_H^{-1}$
A0≡[6s5p2d]	124	SCF	91.11
		MP2	93.47
		SDQ-MP4	91.89
		MP4	93.09
		CCSD	91.71
		CCSD(T)	92.45
A1≡[6s5p3d]	144	SCF	91.29
		MP2	93.47
		SDQ-MP4	91.87
		MP4	92.87
		CCSD	91.77
		CCSD(T)	92.32
A2≡[6s5p3d]	144	SCF	91.18
		MP2	93.50
		SDQ-MP4	91.78
		MP4	92.90
		CCSD	91.78
		CCSD(T)	92.52
A3≡[6s5p3d1f]	172	SCF	91.23
		MP2	93.71
		SDQ-MP4	92.11
		MP4	93.31
A4≡[6s5p4d2f]	220	SCF	91.38
		MP2	93.86
		SDQ-MP4	92.24
		MP4	93.24
A5≡[6s5p4d2f]	220	SCF	91.53
		MP2	93.23
		SDQ-MP4	91.41
		MP4	92.41

retical result is in good agreement with our experimental value of  $\alpha=91.71(92) e^2a_0^2E_H^{-1}$ .

We have used the A3 basis set to obtain the dependence of  $\alpha$  on the P—P bond length for the symmetric distortion of the system. We find

$$[\alpha(R) - \alpha(R_0)]/e^2a_0^2E_H^{-1} = 34.02\Delta R + 3.68\Delta R^2 - 0.29\Delta R^3, \quad (4)$$

where  $\Delta R \equiv (R - R_0)/a_0$ . This curve shows an essentially linear dependence on the change of the P—P bond length. It is noteworthy, that by using the pre-1999 P—P bond length of 2.2228 Å, the *ab initio* value of the dipole-polarizability will be  $\alpha=95.0(0.9)e^2a_0^2E_H^{-1}$ . The error bars of the experimental and theoretical  $\alpha$  do not overlap in this case, indicating that the old P—P bond length in the  $P_4$  cluster is too large. We find that precise experimental results and high-level *ab initio* calculations of the dipole-polarizability give a hint to an erroneous value of the bond length reported in the literature [39].

TABLE IV. Dipole polarizability of the phosphorous atom obtained in this work [basis set (uncontracted) 21s16p10d3f, 140 CGTF; the innermost AO was kept frozen in the post-Hartree-Fock calculation].

Method	$\alpha/e^2a_0^2E_H^{-1}$
SCF	25.42
MP2	25.10
MP4	25.09
CCSD	25.11
CCSD(T)	25.22
NHF <sup>a</sup>	25.469
Estimate <sup>b</sup>	24.4–24.8

<sup>a</sup>Numerical Hartree-Fock value by Stiehler and Hinze [42].

<sup>b</sup>From relation between bond dissociation energy and dipole polarizability [43].

Our unrestricted Hartree-Fock (UHF) values for the dipole polarizability  $\alpha/e^2a_0^2E_H^{-1}$  of the phosphorous atom are given in Table IV. Our SCF value is 25.42, very close to the numerical Hartree-Fock result of 25.469 [42]. Clearly, the basis set employed in our calculations is of Hartree-Fock quality. We expect the post-Hartree-Fock values in Table IV to be of high accuracy as well. At the highest level of theory we obtain a CCSD(T) value of 25.22, barely 0.20 below the SCF one. All other methods predict values quite close to the above. Several years ago we have observed a linear relationship between the bond dissociation energy  $D_0$  and the change of the polarizability  $\delta\alpha$  during the course of a chemical reaction according to  $D_0 = a + b\delta\alpha$  [43].  $\delta\alpha$  is the difference between the polarizability of the products and that of the reactants, the parameters being  $a=0.2137$  a.u. and  $b=0.0405$  a.u. Using the dissociation energy  $D_0 = 0.4527 E_H$  for the reaction  $P_4 \rightarrow 4 P$  [17,44] we obtain  $\alpha = (24.4 - 24.8) e^2a_0^2E_H^{-1}$  for the polarizability of the phosphorus atom. This estimated value is also in reasonable agreement with the *ab initio* calculations. It turns out that the polarizability of the isolated phosphorus atom is higher by  $\approx 9\%$  than that of a P atom inside a  $P_4$  cluster. This result should be compared to the higher homologue  $As_4$ , where the observed change in the polarizability is negligibly small and in the order of 1% [33]. In Table V we show electric moment and higher polarizability values of the  $P_4$  cluster calculated at the SCF and MP2 levels of theory. The SCF results display remarkable stability for such high order properties. Surprisingly enough, electron correlation effects are very important for  $\Omega$  and  $\Phi$ , but less so for the dipole-quadrupole and dipole-octopole polarizability. These results are a by-product of our present investigation, but nevertheless we expect our MP2/A3 values to represent a fairly accurate prediction for all properties. The theoretical results for the dipole-quadrupole and dipole-octopole polarizability may be compared to recent experimental results obtained from depolarized collision-induced light scattering measurements [12]. The experimental results  $A = 77(26)e^2a_0^3E_H^{-1}$  and  $|E| = 3.06(41) \times 10^3 e^2a_0^4E_H^{-1}$  are obtained at  $T = 1000$  K and  $\lambda = 514.5$  nm. Our MP2 value of  $A = 85.1 e^2a_0^3E_H^{-1}$  is in

TABLE V. Octopole ( $\Omega$ ) and hexadecapole ( $\Phi$ ) moment, dipole-quadrupole ( $A$ ), and dipole-octopole ( $E$ ) polarizability of  $P_4$  at a P—P bond length of 2.2228 Å.

Basis set	No. CGTF	Method <sup>a</sup>	$\Omega$	$\Phi$	$A$	$E$
[6s5p2d] <sup>b</sup>	124	SCF	-6.66	-18.1	87.0	-157.1
		MP2	1.30	-33.5	83.6	-156.7
[6s5p3d] <sup>c</sup>	144	SCF	-6.95	-15.8	87.9	-164.5
		MP2	0.91	-32.3	85.4	-162.4
[6s5p3d1f] <sup>d</sup>	172	SCF	-7.43	-14.5	88.9	-165.8
		MP2	1.04	-31.6	85.1	-159.0

<sup>a</sup>The 20 innermost MO were kept frozen in all MP2 calculations.

<sup>b</sup>Same as A0.

<sup>c</sup>[6s5p2d]+d(0.0321). Same as A2.

<sup>d</sup>A2+f(0.0745). Same as A3.

good agreement with the experimental findings, however, the predicted  $E = -159.0 e^2 a_0^4 E_H^{-1}$  is much lower than reported in Ref. [12]. However, the latter discrepancy is to be expected due to the severe difficulties in evaluating the  $E$  tensor from the collision-induced light scattering measurements [12,24].

## VI. CONCLUSIONS

Our combined accurate experimental and theoretical treatment of the dipole-polarizability of the  $P_4$  cluster yields a static value  $\alpha(0)$  from which even bounds on the P—P bond

length can be estimated. Additionally we have shown, that the polarizability of a single P atom is higher by 9% than the corresponding  $\alpha$  of a P atom inside the cluster. This strong change of the polarizability is due to the high bond-energy of the atoms inside the cluster.

## ACKNOWLEDGMENT

Financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged by Uwe Hohm and Achim Loose.

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