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Is dodecahedral P_{20} special?*

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Summary. The laboratory study of phosphorus clusters by laser-based mass spectrometric methods indicates, tentatively, that P_{21}^+ may be special. A plausible interpretation might place a P^+ ion interior to a dodecahedral P_{20} molecule. *Ab initio* quantum mechanical methods have been applied to the P_{20} molecule using contracted gaussian basis sets as large as (9*s* 6*p* 4*d* 3*f*) on each phosphorus atom. At the highest level of theory, dodecahedral P_{20} is predicted to lie 23 kcal/mol above five separated P_4 molecules.

Key words: Phosphorus clusters – P_{20} – Dodecahedra

1 Introduction

As part of an ongoing search [1] for new high energy density molecular systems, we recently reported an *ab initio* quantum mechanical study [2] of the dodecahedral N_{20} molecule. In the final paragraph of that paper, we noted that dodecahedral P_{20} will be far more stable relative to 10 P_2 than N_{20} is relative to 10 N_2. The latter discussion [2] attracted the attention of Whetten [3], who was studying the formation of phosphorus clusters in the laboratory by laser-based mass spectrometric methods. Whetten's observations on positively charged clusters indicated, tentatively, that P_{21}^+ might be special. Whetten then suggested [3] "One possibility, related to your structures, is a pentagonal dodecahedron structure with an interior P^+ atom bonded to four surface atoms." This intriguing hint from experiment was sufficient to motivate us to carry out the present theoretical investigation of dodecahedral P_{20}, which is illustrated in Fig. 1.

Unknown to us at the start of this work was the excellent, very recent theoretical study of Häser, Schneider, and Ahlrichs [4] on a broad range of phosphorus clusters as large as P_{28}. Häser, Schneider, and Ahlrichs appear to show conclusively that P_{12} lies lower in energy with respect to P_4 than does P_{20}. They further suggest that P_{12} should be kinetically stable. In spite of this discouraging prognosis for P_{20}, we have taken the theory significantly farther than Ahlrichs. Thus it seemed appropriate to report these new P_{20} results here.

Our energetic results for P_{20} are summarized in Table 1. Due to the extraordinarily high symmetry of the dodecahedral P_{20}, the full geometry optimization

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* Dedicated to Professor Werner Kutzelnigg

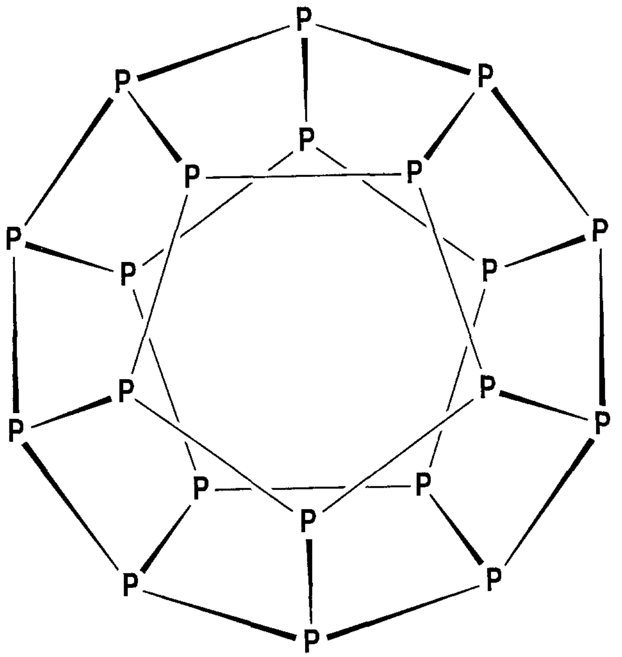

Fig. 1. The dodecahedral (I_h symmetry) P_{20} molecule. All phosphorus atoms are equivalent and all bonds are single P–P bonds

Table 1. Total energies of P_{20} in a.u., and relative energies in kcal/mol with respect to P_4 and bond distances in Å for P_{20}(dodecahedral), P_4(tetrahedral) and $P_2(^1\Sigma_g^+)$

	Number of basis functions in P_{20}	Total energy	Relative energy			Bond distance		
			P_{20}	$5P_4$	$10P_2$	P_{20}	P_4	P_2
DZ SCF	360	– 6813.736765	– 165	0	– 36	2.352	2.399	1.929
DZP SCF	460	– 6814.391880	7	0	126	2.235	2.167	1.855
TZ2P SCF	620	– 6814.991759	64	0	199	2.248	2.186	1.857
TZ2Pf SCF	760	– 6815.053303	65	0	215	2.240	2.176	1.854
(9*s*6*p*4*d*3*f*) SCF	1340	– 6815.094877	70	0	207	2.238	2.173	1.850
DZ MP2	360	– 6815.106346	– 98	0	– 104	2.434	2.508	2.088
DZP MP2	460	– 6816.569856	– 10	0	111	2.243	2.182	1.929
TZ2P MP2	620	– 6817.512056	23	0	259	–	–	–
Experiment			–	0	269[a]	–	2.21[b]	1.894[c]

[a] Chase MW Jr., Davies CA, Downey JR Jr., Frurip DJ, McDonald RA, Syverud AN (1985) JANAF thermal chemical tables. Dow Chemical Corp, Midland, Michigan

[b] Maxwell LR, Hendrichs SB, Mosley V (1935) J Chem Phys 3:699

[c] Huber KPH, Herzberg G (1979) Constants of diatomic molecules. Van Nostrand, NY

involves the variation of only a single P–P bond distance. Accordingly, this structural optimization was completed at all but one level of theory. The largest basis set considered by Häser, Schneider, and Ahlrichs [4] was their own P(12*s* 9*p* 2*d*/7*s* 5*p* 2*d*) set [5], designated triple zeta plus double polarization (TZ2P). With their TZ2P SCF method, Häser and coworkers predict that dodecahedral P_{20} lies 268 kJ/mol (64 kcal/mol) above five separated P_4 molecules. The present TZ2P basis set is slightly different, P(12*s* 9*p* 2*d*/6*s* 5*p* 2*d*), and is taken from the work of McLean and Chandler [6], with polarization function orbital exponents $\alpha_d(\mathrm{P}) = 1.2, 0.3$. Although the two TZ2P basis sets are by no means identical, our predicted TZ2P SCF binding energy T_e for the process:

$$P_{20} \rightarrow 5\,P_4 \tag{1}$$

is also 64 kcal/mol.

The addition of a set of *f* functions $[\alpha_f(\mathrm{P}) = 0.45]$ to our TZ2P basis set changes ΔE for reaction (1) by only 1 kcal, to 65 kcal/mol. However, the addition of one set of *f* functions to each phosphorus atom does decrease the P–P bond distances by 0.008 Å. Häser and coworkers [4] do not report the equilibrium geometry of P_{20}.

To explore the Hartree-Fock limit, we have utilized a much larger basis set, designated:

P(12*s* 9*p* 5*d* 4*f*/9*s* 6*p* 4*d* 3*f*).

This extended basis set uses the original Huzinaga [7] P(12*s* 9*p*) primitive gaussian set, contracting it to provide maximum flexibility in the valence region, i.e. 411111111 for the *s* functions and 411111 for the *p* functions. The *d* and *f* functions in this extended basis set were contracted using the atomic natural orbitals (ANO's) of Widmark, Persson, and Roos [8]. Compared to the TZ2Pf basis set the (9*s* 6*p* 4*d* 3*f*) basis lowers the SCF energy of 5 P_4 more than the energy of dodecahedral P_{20}. Specifically, P_{20} is predicted to lie 70 kcal/mol above 5 P_4 at the (9*s* 6*p* 4*d* 3*f*) SCF level of theory, an increase of 5 kcal/mol compared to the TZ2Pf result. The P–P bond distance is decreased by 0.002 Å from TZ2Pf to (9*s* 6*p* 4*d* 3*f*). To summarize, one may say that pressing on from Ahlrichs SCF results [4] toward the Hartree-Fock limit results in only modest changes in the P_{20} dissociation energy.

Häser, Schneider, and Ahlrichs [4] also reported the energy of P_{20} using second-order perturbation theory (MP2) in conjunction with a basis set [5] that they designate split-valence plus polarization (SVP). At the SVP MP2 level of theory, Häser reports that P_{20} lies 81 kJ/mol (19 kcal/mol) above 5 P_4. In this work we first extended the MP2 studies to the double zeta plus polarization (DZP) basis set of Huzinaga, Dunning, and Hay [7, 9]. The predicted DZP MP2 bond distance is $r_e(\mathrm{P{-}P}) = 2.243$ Å, only 0.008 Å longer than the analogous SCF result. The DZP MP2 method actually places P_{20} *below* 5 P_4 by 10 kcal/mol.

Since the above result disagreed with Ahlrichs' SVP MP2 prediction, it was deemed necessary to press on to the TZ2P MP2 method. In the latter case only, the geometry was assumed (rather than optimized) to be the TZ2P SCF structure. In this manner P_{20} is predicted to lie 23 kcal/mol above 5 P_4. Inspection of the SCF results (apparent convergence to within 6 kcal/mol with the TZ2P basis set) in Table 1 suggests that this result from second-order perturbation theory may be within 10 kcal/mol of the basis set limit. The good agreement with Häser's result [4] of 19 kcal/mol must be considered somewhat fortuitous in light of the DZP MP2 prediction of the opposite sign.

Table 2. Vibrational frequencies (cm^{-1}) and infrared intensities (km/mol, in parentheses) for dodecahedral P_{20}

Symmetry	Degeneracy	DZ SCF
H_g	5	458
H_u	5	456
G_g	4	397
T_{2u}	3	387
G_u	4	374
H_g	5	328
T_{2u}	3	305
G_g	4	292
T_{1u}	3	291(1.0)
A_g	1	257
G_u	4	219
T_{2g}	3	197
H_g	5	170
H_u	5	148

Table 3. Valence electron orbital energies (in eV) for the dodecahedral P_{20} molecule

Symmetry		DZP SCF	TZ2P SCF	TZ2Pf SCF	$(9s6p4d3f)$ SCF
LUMO	$7t_{1u}$	− 0.93	− 0.58	− 0.54	− 0.56
HOMO	$6g_g$	− 9.12	− 8.83	− 8.79	− 8.74
	$6g_u$	− 9.30	− 8.91	− 8.96	− 8.91
	$8h_g$	− 11.04	− 10.60	− 10.68	− 10.65
	$6t_{2u}$	− 11.28	− 10.99	− 10.95	− 10.91
	$6t_{1u}$	− 13.25	− 12.79	− 12.88	− 12.85
	$3h_u$	− 13.47	− 13.01	− 13.03	− 12.99
	$5a_g$	− 14.49	− 14.01	− 14.11	− 14.08
	$7h_g$	− 14.69	− 14.22	− 14.24	− 14.21

In Tables 2 and 3 are reported harmonic vibrational frequencies and valence electron orbital energies for dodecahedral P_{20}. Due to the molecule's high symmetry only the T_{1u} fundamental is allowed in the infrared. The single A_g and three H_g fundamentals are Raman allowed.

The present research confirms the earlier study of Häser, Schneider, and Ahlrichs [4] that dodecahedral P_{20} is not "special". That is, P_{20} is not the most favored energetically among phosphorus clusters. This result does not, of course, exclude the possibility proposed by Whetten [3] that a P_{21}^{+} ion, with one phosphorus atom internal to the P_{20} cage, might be "special". Also, since P_{20} lies only slightly higher in energy than 5 P_4, the possibility that dodecahedral As_{20}, Sb_{20}, or Bi_{20} might be special remains open.

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