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MINDO/3 Study of Some Tetra-atomic Clusters

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MINDO/3 calculations have been made of the energies of tetra-atomic clusters $M_4^{\pm n}$ *(M = Si, P, S;* $|n| = 0, 2, 4$*) for a wide range of point groups, as well as for unconstrained geometries, in both singlet and triplet electronic configurations. The results are discussed in terms of the Jahn–Teller effect, in the first and second orders.*

Introduction

The Williams–Wade approach to molecular polyhedra [1–4] has successfully rationalised the structures of a wide range of cluster molecules containing between five and twelve cluster atoms, but the known tetra-atomic clusters do not fit into the *closo, nido, arachno* [1, 2], *hypho* [4, 5, 6] pattern of the Williams–Wade description. Symmetry arguments however have suggested that for a tetra-atomic cluster, a tetrahedral structure (*i.e. closo*) is favoured in the presence of sixteen or twenty valence electrons, whereas a square planar (*arachno* structure) is favoured in the presence of eighteen or twenty-two valence electrons [7]: no other geometries were considered explicitly but consideration of the second-order Jahn–Teller effect enabled predictions to be made of the possible distortions from tetrahedral or square planar geometries. In this paper we report MINDO/3 calculations of the structures and energies of the tetra-atomic clusters $M_4^{\pm n}$, where M = Si, P, or S and $|n| = 0, 2$ or 4.

Method

Calculations were made using the IBM version of MINDO/3 [8]. The most extensive study was made of $Si_4^{\pm n}$ species, with only a more restricted investigation of $P_4^{\pm n}$ and $S_4^{\pm n}$. For the silicon tetramers, the lowest singlets and triplets were investigated for n = 0, –2 and –4: for each value of n and each spin configuration, the molecular energy was calculated for D_{2h}, D_{4h} and T_d geometries, with optimisation of inter atomic distances in each case: free optimisations (without constraints) of the molecular geometry were then undertaken, for both singlet and triplet starting both from D_{4h} and T_d. The molecular states, enthalpies of formation and molecular geometries, expressed as a set of six interatomic distances, for silicon tetramers are given in Table I.

For the sulphur tetramers, species having n = 0 and +2 were investigated: singlet and triplet energies and structures were calculated in the restricted point groups D_{4h} and T_d together with free optimisations. Additionally, free optimisations were made of the structures and energies of S_8 and S_8^{+2}. Results for tetrameric sulphur species are in Table II. Only singlet species were investigated for P_4 species having n = 0, ±2: in addition free optimisations (from T_d) were made for P_4^+ and P_4^-. Computed results for tetrameric phosphorus species are recorded in Table III.

Electronic configurations of T_d and D_{4h} species are listed in Table V.

Results and Discussion

Tetrahedral versus *Square Planar Geometries*

The original symmetry-based discussion [7] of the structures of the homoatomic tetramers was in terms almost exclusively of the choice between tetrahedral and square planar configurations. The results recorded in Table I indicate that for the neutral sixteen electron species Si_4 the square planar geometry is of lower energy than the tetrahedral for both singlet and triplet spin configurations, by some 130 kJ mol^{-1} for the singlet and some 200 kJ mol^{-1} for the triplet: for the dinegative eighteen electron ion Si_4^{-2}, the energy differences between T_d and D_{4h} structures are very small in both spin configurations, and the tetrahedral geometry is marginally favoured for singlet Si_4^{-2}, while square planar geometry is favoured, even more marginally for triplet Si_4^{-2}. For the tetranegative twenty electrion ion Si_4^{-4}, the tetrahedral structure had the lower energy for the singlet configuration, but for the triplet, the square planar structure had the lower energy. So far as

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TABLE I. Computed Properties of Si_4^{+n}.

Point-group	Molecular state	$\Delta H_f^{\ominus}$/kJ mol^{-1}	Interatomic distances/Å
(a) n = 0			
D_{4h}	$^1A_{1g}$	645.1	2.137(×4), 3.023(×2)
D_{2h}	$^1A_{1g}$	591.8	2.310(×2), 2.003(×2), 3.058(×2)
T_d	$^1A_1$	774.3	2.373(×6)
D_{4h} } D_{2h} }	$^3A_{2g}$	614.2	2.143(×4), 3.031(×2)
T_d	$^3A_2$	814.6	2.352(×6)
D_2[a]	^1A	584.0	2.049(×2), 2.272(×2), 2.999(×2)
C_s[b] (~C_{2v})	^1A	528.6	2.218(×2), 2.232(×2), 2.396(×1), 3.750(×1)
D_2[a] (~D_{2d})	^3A	561.5	2.165(×2), 2.169(×2), 2.974(×2)
D_2[b]	$^3B_2$	630.0	2.055(×2), 2.407(×2), 2.836(×2)
(b) n = −2			
D_{4h} } D_{2h} }	$^1A_{1g}$	911.3	2.179(×4), 3.082(×2)
T_d	$^1A_1$	905.5	2.407(×6)
D_{4h}	$^3A_{2u}$	875.2	2.204(×4), 3.117(×2)
D_{2h}	$^3A_{1u}$	846.7	2.096(×2), 2.342(×2), 3.143(×2)
T_d	$^3A_2$	878.4	2.406(×6)
D_2[a] } (~D_{2d}) D_2[b] }	^1A	710.8	2.239(×2), 2.245(×2), 2.893(×2)
C_1[a]	^3A	743.9	2.255(×2), 2.257(×1), 2.260(×1), 2.526(×1), 2.643(×1)
C_1[b]	^3A	873.7	2.190(×1), 2.192(×1), 2.374(×1), 2.587(×2), 2.613(×1)
(c) n = −4			
D_{4h}	$^1A_{1g}$	3042.5	2.359(×4), 3.336(×2)
D_{2h}	$^1A_{1g}$	3026.7	2.262(×2), 2.503(×2), 3.374(×2)
T_d	$^1A_1$	2973.4	2.520(×6)
D_{4h} } D_{2h} }	$^3A_{2g}$	3005.8	2.361(×4), 3.339(×2)
T_d	$^3T_1$	3177.0	2.575(×6)
D_2[a]	$^1A_{1g}$	2933.5	2.235(×2), 2.689(×2), 3.495(×2)
C_{2v}[b]	$^1A_1$	2592.9	2.084(×1), 2.253(×1), 2.387(×2), 4.337(×2)

[a] Free optimisation from D_{4h}. [b] Free optimisation from T_d.

square planar/tetrahedral equilibria are concerned, the reduction $Si_4 \rightarrow Si_4^{-2} \rightarrow Si_4^{-4}$ causes a progressive destabilisation of the D_{4h} structure with respect to the tetrahedral. With exception of triplet Si_4 and singlet Si_4^{-2}, relaxation of the square planar geometry to rectangular planar effects a modest decrease in energy. In each instance the T_d species have M–M distances which are longer than the short distances in the D_{4h} and D_{2h} species, but shorter than the weighted mean interatomic distances in the planar species.

Of the sulphur species (Table II), for the neutral S_4 molecule having twenty four valence electrons D_{4h} is the lower energy configuration for the singlet, whereas T_d is somewhat the more stable for the triplet. In the twenty two electron ion S_4^{2+}, D_{4h} is again the stable configuration for the singlet, with the triplet more stable in T_d. The inter-atomic distances for D_{4h} and T_d species follow the same pattern as those in Si_4^{+n} species: in both Si_4^{+n} and S_4^{+n}, reduction increases the interatomic distances, as expected. Of the P_4^{+n} fragments having n = 0, ±2 (Table III), T_d is the more stable geometry for the twenty electron neutral P_4 (isoelectronic with Si_4^{-4}) and the eighteen electron ion P_4^{+2} (isoelectronic with Si_4^{-2}) while D_{4h} is the more favoured configuration for the twenty two electron ion P_4^{-2} (isoelectronic with S_4^{+2}).

TABLE II. Computed Properties of S_4^{+n}.

Point-group	Molecular state	ΔH_f^ϕ/kJ mol^{-1}	Interatomic distances/A
(a) n = 0			
D_{4h}[a]	$^1A_{1g}$	132.7	2.102(×4), 2.973(×2)
T_d	$^1A_1$	293.9	2.206(×6)
D_{4h}	$^3A_{2g}$	217.2	2.010(×4), 2.843(×2)
T_d[b]	$^3T_1$	200.1	2.015(×6)
(b) n = +2			
D_{4h}[c]	$^1A_{1g}$	2275.4	2.059(×4), 2.912(×2)
T_d	$^1A_1$	2350.6	2.128(×6)
D_{4h}	^3E_g	2337.9	2.065(×4), 2.921(×2)
T_d[c]	$^3T_1$	2233.4	2.074(×6)
C_{2v}[d]	$^1A_1$	2244.2	2.129(×4), 2.144(×1), 3.069(×1)
C_{2v}[e]	$^3A_1$	2274.3	2.076(×4), 2.586(×1), 3.019(×1)

[a] Free optimisation of singlet S_4 species starting from D_{4h} or T_d yields this minimum. [b] Free optimisation of triplet S_4 species starting from D_{4h} or T_d yields this minimum. [c] Free optimisation from this geometry effects no change. [d] Free optimisation from T_d. [e] Free optimisation from D_{4h}.

TABLE III. Computed Properties of P_4^{+n}.

n	Point-group	Molecular state	ΔH_f^ϕ/kJ mol^{-1}	Interatomic distances/A
0	T_d[a]	$^1A_1$	46.6	2.119(×6)
0	D_{4h}	$^1A_{1g}$	245.0	2.021(×4), 2.858(×2)
+2	T_d	$^1A_1$	2290.4	2.153(×6)
+2	D_{2d}[b]	$^1A_1$	2062.9	2.009(×4), 2.573(×2)
+2	D_{4h}	$^1A_{1g}$	2299.0	2.054(×4), 2.905(×2)
−2	D_{4h}[a]	$^1A_{1g}$	416.5	2.059(×4), 2.911(×2)
−2	T_d[c]	$^1A_1$	705.9	2.217(×6)
+1	D_{2d}[b]	$^2A_1$	815.5	2.042(×4), 2.353(×2)
−1	D_2[b]	^2A	27.5	1.982(×2), 2.079(×2), 2.861(×2)

[a] Free optimisation effects no change. [b] Free optimisation from T_d. [c] Free optimisation yields D_{4h} species exactly.

TABLE IV. Square Planar/Tetrahedral Energy Minima.

Number of Valence Electrons:	16	18	20	22	24
Examples:	Si_4	Si_4^{-2}/P_4^{+2}	Si_4^{-4}/P_4	P_4^{-2}/S_4^{+2}	S_4
Favoured Geometry:					
(a) Singlet	D_{4h}	T_d	T_d	D_{4h}	D_{4h}
(b) Triplet	D_{4h}	D_{4h}	D_{4h}	T_d	T_d

In summary (Table IV), for singlet species, the more stable configuration is D_{4h} for sixteen, twenty two, or twenty four valence electrons but T_d for eighteen or twenty electrons, while for the lowest triplet states, the stable configuration is D_{4h} (for sixteen, eighteen or twenty electrons, and T_d for twenty two or twenty four: in each case the result is independent of the element concerned. The species whose structures are known experimentally in the solid state (rather than as isolated gaseous fragments,

TABLE V. Electronic Configurations of D_{4h} and T_d Species.

(a)	Si_4	
	D_{4h} ($^1A_{1g}$):	$(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1a_{2u})(1b_{2g})^2(2a_{1g})^2(1e_g)^2 \| (2e_u)^0(1b_{2u})^0(3e_u)^0(2b_{1g})^0(1a_{2g})^0$
	D_{4h} ($^3A_{2g}$):	
	T_d ($^1A_1$):	$(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6 \| (1e)^0(1t_1)^0(3t_2)^0$
	T_d ($^3A_2$):	$(1a_1)^2(1t_2)^6(2t_2)^6(1e)_2^2 \| (2a_1)^0(1t_1)^0(3t_2)^0$
(B)	Si_4^{-2}	
	D_{4h} ($^1A_{1g}$):	$(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1a_{2u})^2(1b_{2g})^2(2a_{1g})^2(1e_g)^4 \| (2e_u)^0(1b_{2u})^0(3e_u)^0(2b_{1g})^0(1a_{2g})^0$
	D_{4h} (^3E_u):	$(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1a_{2u})^2(1b_{2g})^2(2a_{1g})^2(1e_g)^3(1b_{2u})^1 \| (2e_u)^0(3e_u)^0(2b_{1g})^0(1a_{2g})^0$
	T_d ($^1A_1$):	$(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^2 \| (1t_1)^0(3t_2)^0$
	T_d ($^3A_2$):	
(c)	Si_4^{-4}	
	D_{4h} ($^1A_{1g}$):	$(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1a_{2u})^2(1b_{2g})^2(2a_{1g})^2(1b_{2u})^2(1e_g)^4 \| (2e_u)^0(3e_u)^0(2b_{1g})^0(1a_{2g})^0$
	D_{4h} ($^3A_{2g}$):	$(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1a_{2u})^2(1b_{2g})^2(2a_{1g})^2(1e_g)^4(2e_u)^2 \| (1b_{2u})^0(3e_u)^0(2b_{1g})^0(1a_{2g})^0$
	T_d ($^1A_1$):	$(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^4 \| (1t_1)^0(3t_2)^0$
	T_d ($^3T_1$):	$(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1t_1)^4 \| (1e)^0(3t_2)^0$
(d)	S_4	
	D_{4h} ($^1A_{1g}$):	$(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1a_{2u})^2(1b_{2g})^2(2a_{1g})^2(1e_g)^4(2e_u)^4(1b_{2u})^2 \| (3e_u)^0(2b_{1g})^0(1a_{2g})^0$
	D_{4h} ($^3A_{2g}$):	$(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1a_{2u})^2(1b_{2g})^2(2a_{1g})^2(1e_g)^4(2e_u)^4(3e_u)^2 \| (1b_{2u})^0(2b_{1g})^0(1a_{2g})^0$
	T_d ($^1A_1$):	$(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^4(1t_1)^4 \| (3t_2)^0$
	T_d ($^3T_1$):	
(e)	S_4^{+2}	
	D_{4h} ($^1A_{1g}$):	$(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1a_{2u})^2(1b_{2g})^2(2a_{1g})^2(1e_g)^4(2e_u)^4 \| (1b_{2u})^0(3e_u)^0(2b_{1g})^0(1a_{2g})^0$
	D_{4h} (^3E_g):	$(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1a_{2u})^2(1b_{2g})^2(2a_{1g})^2(1e_g)^4(2e_u)^3(1b_{2u})^1 \| (3e_u)^0(2b_{1g})^0(1a_{2g})^0$
	T_d ($^1T_1$):	$(1a_1)^2(1t_2)^6(1a_1)^2(2t_2)^6(1e)^4(1t_1)^2 \| (3t_2)^0$
	T_d ($^3T_1$):	
(f)	P_4	
	D_{4h} ($^1A_{1g}$):	$(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1a_{2u})^2(1b_{2g})^2(2a_{1g})^2(2e_u)^4(1e_g)^2 \| (1b_{2u})^0(3e_u)^0(2b_{1g})^0(1a_{2g})^0$
	T_d ($^1A_1$):	$(1a_1)^2(1t_2)^6(2t_2)^6(2a_1)^2(1e)^4 \| (1t_1)^0(3t_2)^0$
(g)	P_4^{+2}	
	D_{4h} ($^1A_{1g}$):	$(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1a_{2u})^2(1b_{2g})^2(2a_{1g})^2(2e_u)^4 \| (1e_g)^0(1b_{2u})^0(3e_u)^0(2b_{1g})^0(1a_{2g})^0$
	T_d ($^1A_1$):	$(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^2 \| (1t_1)^0(3t_2)^0$
(h)	P_4^{-2}	
	D_{4h} ($^1A_{1g}$):	$(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1a_{2u})^2(1b_{2g})^2(2a_{1g})^2(2e_u)^4(2e_g)^4 \| (1b_{2u})^0(3e_u)^0(2b_{1g})^0(1a_{2g})^0$
	T_d ($^1A_1$):	$(1a_1)^2(1t_2)^6(2t_2)^6(2a_1)^2(1e)^4(1t_1)^2 \| (3t_2)^0$
(i)	P_4^{+}	
	T_d (^2E):	$(1a_1)^2(1t_2)^6(2t_2)^6(2a_1)^2(1e)^3 \| (1t_1)^0(3t_2)^0$
(j)	P_4^{-}	
	T_d ($^2T_1$):	$(1a_1)^2(1t_2)^2(2t_2)^6(2a_1)^2(1e)^4(1t_1)^1 \| (3t_2)^0$

to which the present calculations refer) are the singlets Si_4^{-4} [9, 10], S_4^{+2} [11], and P_4 [12]: of these, Si_4^{-4} and P_4 are tetrahedral, and S_4^{+2} is square planar (*cf.* Table IV).

Electronic Configurations

The electronic configurations of square planar and tetrahedral species listed in Table V show a number of common features. The lowest levels of the T_d

TABLE VI. Direct Products in T_d Yielding Symmetry Class E.

$\Gamma_i \times \Gamma_j$	$\Gamma_i \times \Gamma_i$
$A_1 \times E$	$E \times E$
$A_2 \times E$	$T_1 \times T_1$
$T_1 \times E$	$T_2 \times T_2$
$T_2 \times E$	
$T_1 \times T_2$	

TABLE VII. Direct Products in D_{4h} Yielding Symmetry Classes B_{2u}, B_{2g} and B_{1g}.

	$\Gamma_i \times \Gamma_j$	$\Gamma_i \times \Gamma_i$
(a) B_{2u}	$A_{1g} \times B_{2u}$	NONE
	$A_{2g} \times B_{1u}$	
	$A_{1u} \times B_{2g}$	
	$A_{2u} \times B_{1g}$	
	$E_g \times E_u$	
(b) B_{2g}	$A_{1g} \times B_{2g}$	$E_g \times E_g$
	$A_{2g} \times B_{1g}$	$E_u \times E_u$
	$A_{1u} \times B_{2u}$	
	$A_{2u} \times B_{1u}$	
(c) B_{1g}	$A_{1g} \times B_{1g}$	$E_g \times E_g$
	$A_{2g} \times B_{2g}$	$E_u \times E_u$
	$A_{1u} \times B_{1u}$	
	$A_{2u} \times B_{2u}$	

TABLE VIII. HOMO and LUMO Symmetry Classes, and Energy Gaps for Species Sensitive to the Second Order Jahn–Teller Effect.

	Molecule	HOMO	LUMO	Energy gap/eV
(a) T_d	Si_4	t_2	e	5.61
	Si_4^{-4}	e	t_1	7.23
	P_4	e	t_1	9.05
(b) D_{4h}	Si_4^{-2}	e_g	e_u	4.78
	Si_4^{-4}	e_g	e_u	4.42
	S_4	b_{2u}	e_u	6.51
	S_4^{+2}	e_u	b_{2u}	6.88
	P_4^{+2}	e_u	e_g	5.59
	P_4^{-2}	e_g	b_{2u}	6.85

species are always $(1a_1)^2(1t_2)^6$ and those of the D_{4h} species are always $(1a_{1g})^2(1e_u)^4(1b_{1g})^2$: these levels correspond mainly to s-orbital combinations, and justify the original choice [7] of a p-orbital basis set upon which to base the discussion of these structures. The next six levels in the singlet D_{4h} species are $(1a_{2u})(1b_{2g})(2a_{1g})(1e_g)(2e_u)(1b_{2u})$, although the order of the last three varies slightly from species to species: the first five are, with an alternative choice of axes interchanging the designation b_{2g} and b_{1g}, identical with those derived [7] solely on grounds of symmetry. The remaining levels in singlet T_d species are usually $(2a_1)(2t_2)(1e)(1t_1)(3t_2)$; in Si_4 ($^3A_2$) the $2a_1$ level is between 1e and $1t_1$, and in both P4 ($^1A_1$) and P_4^{-2}($^1A_1$) this level is between $2t_2$ and 1e: again this ordering is identical with that deduced earlier.

It is interesting to note that for the triplet configurations there is often a subtle change in the ordering of the energy levels from that found in the corresponding singlet. For example in tetrahedral Si_4, the singlet configuration has the levels in the order expected intuitively namely $(1a_1)(1t_2)(2a_1)(2t_2)\|(1e)(1t_1)(3t_2)$, whereas in the triplet the $2a_1$ level is between 1e and $1t_1$ to give the configuration $(1a_1)^2(1t_2)^6(2t_2)^6(1e)^2\|(2a_1)^0(1t_1)^0(3t_2)^0$, ideal for a triplet state. Similar changes in order may be found (Table 5) for Si_4^{-2} (D_{4h}), Si_4^{-4} (D_{4h} and T_d), and S_4(D_{4h}).

Of the singlet T_d species listed in Table V, the following may be expected, by virtue of their electronic degeneracy, to be sensitive to first order Jahn–Teller distortions: Si_4^{-2}, S_4, S_4^{+2}, P_4^{+2}, and P_4^{-2}: the first order disortions will be discussed after the second order Jahn–Teller effect has been dealt with. The only singlet D_{4h} species in Table V, which are sensitive to first order distortions are Si_4 and P_4.

Second Order Jahn–Teller Effect

The electronic configurations listed in Table V are of importance in assessing the usefullness of the approach used previously [1], *via* the second order Jahn–Teller effect, to the question of whether square planar or tetrahedral geometry would be favoured for a particular species. For an M_4 cluster of T_d symmetry, the e vibration (ν_2) distorts the geometry ultimately to D_{4h}: the two components of ν_2 distort the structure in different ways one *via* D_{2d} intermediates and the other via D_2 intermediates, but in the limit both components yield D_{4h}. For a D_{4h} cluster M_4, the b_{2u} vibration (ν_4) distorts the geometry *via* D_{2d} intermediates giving ultimately a T_d geometry: on the other hand the b_{2g} vibration (ν_3) distorts the geometry to rectangular D_{2h}, while b_{1g} (ν_2) distorts the geometry to rhomboidal D_{2h}. The direct products $\Gamma_i \times \Gamma_j$ of relevance to the second order Jahn–Teller interconversion of D_{4h} and T_d are given in Tables VI and VII, along with those relevant to in-plane distortions of D_{4h}, together with the direct products $\Gamma_i \times \Gamma_i$ of relevance to the first order Jahn–Teller effect (see below).

The singlet T_d species in this study which are not subject to the first order Jahn–Teller effect are Si_4, Si_4^{-4}, and P_4, while those not so subject in D_{4h} are Si_4^{-2}, Si_4^{-4}, S_4, S_4^{+2}, P_4^{+2}, and P_4^{-2} and to all these species the second order effect is relevant. Table VIII lists the symmetry classes of the HOMO and LUMO of species sensitive to the second order effect, together with the corresponding energy gaps. Of the T_d species, all generate a HOMO/LUMO direct product containing the symmetry class E (Table VI), as required as a necessary but not sufficient condition for distortion along ν_2 towards D_{4h}: as well as the direct product, the magnitude of the energy gap is also important. Pearson [13] has suggested that an energy gap less than *ca.* 4 eV is required for distortion to occur: although the energies of unoccupied orbitals are generally calculated by MINDO/3 to be somewhat too positive it is noteworthy that of the T_d species in Table VIII, Si_4 with the smallest HOMO/LUMO gap of 5.61 eV is less stable as a tetrahedral than as a square planar molecule, while Si_4^{-4} and P_4 with energy gaps of 7.23 eV and 9.04 eV are calculated to be more stable in T_d than in D_{4h}, in accord not only with experimental observation but with the predictions of the second order Jahn–Teller effect also.

Of the square planar singlets in Table VIII, both Si_4^{-2} and Si_4^{-4} generate a direct product which contains the symmetry class B_{2u}, and for both these ions the HOMO/LUMO gap is small: neither is stable in D_{4h} (Table IV) and both distort towards T_d. Neither of S_4 and S_4^{+2} generates the symmetry class B_{2u} from the direct product of the symmetry classes of its HOMO and LUMO and the energy gaps are 6.51 eV and 6.88 eV. For each of these fragments, the only orbital combinations (1 occupied, 1 unoccupied) which gave the appropriate direct product (*cf.* Tables V and VII) are $a_{2u} \times b_{1g}$ for each, and in addition $a_{1g} \times b_{2u}$ for S_4^{+2}; in each instance the energy gap greatly exceeds the possible value so that no distortion along ν_4 (b_{2u}) is expected. Table IV records that each of these species is more stable in D_{4h} than in T_d.

First Order Jahn–Teller Effect

The conditions for a first order distortion of a T_d fragment towards D_{4h} are given in Table VI; reference to Table V shows that these conditions are fulfilled in all the cases where degeneracy occurs. The conditions for first order distortion of a D_{4h} fragment towards T_d or D_{2h} are given in Table VII: there is no first order effect which can give a distortion along b_{2u} since $g \times g = u \times u \neq u$: however both Si_4 and P_4 are sensitive to distortion along both $\nu_2(b_{1g})$ and $\nu_3(b_{2g})$.

Of the T_d species, Si_4^{-2} and P_4^{+2} are sensitive to distortion along no other coordinate but S_4, S_4^{+2}, and P_4^{-2} are also sensitive to distortion along the t_2 vibration ν_3: with the possibility that one, two or three components of ν_3 could be activated, the number of possible structures, all of rather low symmetry, which could arise from such distortion is large.

Removal of a single electron from tetrahedral P_4 yields P_4^+ whose electronic configuration is in Table V: similarly addition of a single electron yields P_4^-. These ions are both subject to first order Jahn–Teller distortion, in the case of P_4^+ along $\nu_2(e)$ and in the case of P_4^- along $\nu_2(e)$ or $\nu_3(t_2)$. Free optimisation of the geometry (Table III) shows that they both distort along ν_2, but along different components as P_4^+ adopts a structure of D_{2d} symmetry, while P_4^- adopts a D_2 structure; both are intermediate along different pathways between T_d and D_{4h}.

Free Optimisations

In addition to a comparison of T_d and D_{4h} structures, a number of free optimisations were undertaken, where the energy was minimised without geometrical constraints: the results of these optimisations are given in Tables I–III. The majority of the freely optimised geometries of are D_2 symmetry: of the D_2 species, ^3A of Si_4 is virtually D_{2d} ($^3A_1$) as is ^1A of Si_4^{-2}; similarly the C_s species $^1A'$ of Si_4 is very close to $C_{2v}(^1A_1)$.

Free optimisations of Si_4^{+n} generally lead to $D_2(D_{2d})$ species for singlet electronic configurations: none of these represents a substantial geometrical change from the structure of Table IV. The C_{2v} (or near C_{2v}) structure observed are not planar, but are of 'butterfly' configuration resulting from the distortion of a tetrahedron along one of its edges (*i.e.* a distortion along any one component of ν_3). The D_2 structures can arise by distortion from T_d along ν_2, as can D_{2d}, which may also arise by distortion from D_{4h} along $\nu_4(b_{2u})$.

In singlet tetrahedral Si_4 the HOMO and LUMO are, respectively, t_2 and e, whose direct product contains $t_1 + t_2$; so that although a second order distortion along $\nu_2(e)$ is not possible, such a distortion along $\nu_3(t_2)$ is possible to yield a C_{2v} geometry. In singlet tetrahedral Si_4^{-2}, the ion is subject to a first order distortion along $\nu_2(e)$, which can give the $D_2(D_{2d})$ geometry found in the free optimisation. Tetrahedral singlet Si_4^{-4} has HOMO and LUMO of symmetry classes e and t_1 respectively whose direct product contains $t_1 + t_2$: second order distortion along $\nu_2(e)$ towards D_{4h} is not therefore possible, but distortion is possible along $\nu_3(t_2)$ to give the C_{2v} structure resulting from the free optimisation.

For neutral singlet S_4, free optimisation yields an exactly D_{4h} structure; a first order distortion of the tetrahedral molecule is expected along a coordinate contained in $[t_1]^2$ *i.e.* along either $\nu_2(e)$ or $\nu_3(t_2)$: distortion ν_2 can give the square planar geometry calculated in the free optimisation. The distortion of tetrahedral singlet S_4^{+2} can again be along ν_2 or ν_3: ν_2 gives the square planar geometry observed experimentally [11] while ν_3 can give rise to the C_{2v} structure calculated without constraints. It should be emphasised in this instance that the energy difference between D_{4h} and C_{2v} is very modest.

In tetrahedral singlet P_4^{+2}, a first order distortion along the ν_2 vibration is to be expected: the freely optimised geometry is of D_{2d} symmetry in accord with this: the structures of P_4^{+} and P_4^{-} have been discussed above. In P_4^{-2}, the tetrahedral singlet is subject to a first order distortion along a coordinate contained in $[t_1]^2$ *i.e.*, along ν_2 or ν_3: the freely optimised geometry has D_{4h} symmetry corresponding to distortion along ν_2.

In the singlet square planar molecule Si_4, the system is subject to a first order distortion along a coordinate contained in $[eg]^2$, *i.e.* along b_{1g} or b_{2g}: the geometry calculated by free optimisation starting from D_{4h} has only D_2 symmetry, whereas only planar species could be obtained by b_{1g} or b_{2g} distortions. Si_4^{-2} and Si_4^{-4} are both subject, as D_{4h} singlets, to second order distortion along b_{2u}: both give D_2 geometries on free optimisation from D_{4h}, corresponding closely but not identically to a b_{2u} distortion. In both S_4 and S_4^{+2} the free optimisations from D_{4h} yield no change in structure, consistent with the large HOMO/LUMO gaps (Table VIII). No free optimisations starting from D_{4h} were undertaken for P_4^{+n} species.

Overall the free optimisations starting from T_d gave results entirely consistent with the predictions of the first and second order Jahn–Teller effects, although those starting from D_{4h} were rather less satisfactory: that for Si_4, in particular, is wholly inconsistent.

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