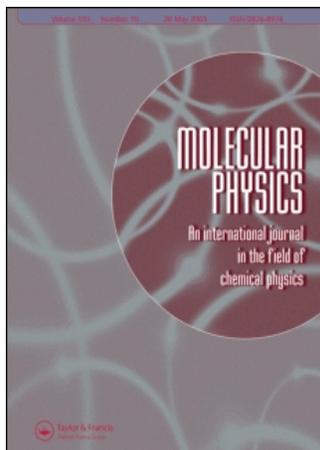


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Amir Karton^a; Jan M. L. Martin^a

^a Department of Organic Chemistry, Weizmann Institute of Science, IL-76100 Rehovot, Israel

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W4 thermochemistry of P₂ and P₄. Is the CODATA heat of formation of the phosphorus atom correct?

AMIR KARTON and JAN M. L. MARTIN*

Department of Organic Chemistry, Weizmann Institute of Science,
IL-76100 Rehovot, Israel

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The high-accuracy W4 computational thermochemistry protocol, and several post-W4 methods, have been applied to the P₂ and P₄ molecules. Contrary to previous studies, we find the experimental thermochemistry to be fundamentally sound. The reaction enthalpy for P₄ → 2P₂ has a very significant contribution from post-CCSD(T) correlation effects. We derive a gas-phase heat of formation for the phosphorus atom of $\Delta H_{f,0}^{\circ}[\text{P}(\text{g})] = 75.54 \pm 0.1 \text{ kcal mol}^{-1}$ and $\Delta H_{f,298}^{\circ}[\text{P}(\text{g})] = 75.74 \pm 0.1 \text{ kcal mol}^{-1}$, in the upper half of the CODATA uncertainty interval.

Keywords: Phosphorus; Atomic heat of formation; W4 theory

1. Introduction

The most important component of phosphorus vapour is tetrahedral P₄. It is also a building block of the most stable solid allotropes (white and red phosphorus), as well as an important component of the liquid phase [1].

P₄ is a challenging molecule to describe well in terms of both the one-particle basis set and *n*-particle space ('electron correlation treatment'). Its peculiar bonding pattern has been studied in some detail by Ahlrichs *et al.* [2]. Perhaps the most comprehensive *ab initio* study to date has been the work of Persson, Taylor, and Lee (PTL) [3], who studied the thermochemistry, geometry, and anharmonic force field of the molecule at the MP2 (second-order many-body perturbation theory) and CCSD(T) (coupled cluster with all singles and doubles plus quasiperturbative triples [4]) levels with basis sets of up to *spdfg* quality. Their work buttressed the earlier contention of Häser and Treutler [5] that the established bond distance [6] is considerably too long due to misassignment of the rotational fine structure of the Raman spectrum. Subsequent IR work [7] confirmed this conclusion.

In addition, the PTL anharmonic force field calculations showed implausibly large discrepancies with the experimental band origins, which were resolved by subsequent remeasurements [8].

Finally, PTL addressed the endothermicity of the reaction P₄ → 2P₂, and found a significant discrepancy with experiment, a substantial part of which resulted from a very large core–valence contribution. Haworth and Bacskay (HB) [9], in a later benchmark thermochemical study on a number of phosphorus compounds including P₂ and P₄, were able to rationalize the core–valence contribution as an artifact of the basis set used. However, despite their work being carried out near the CCSD(T) basis set limit and including both core–valence and scalar relativistic corrections, HB's best calculated total atomization energies (TAE₀ values) still imply a reaction energy for P₄ → 2P₂ that is almost 2 kcal mol⁻¹ more endothermic than experiment [10].

This is not a purely academic issue. This selfsame reaction represents the weakest link in the determination of the CODATA [11] gas-phase heat of formation of the phosphorus atom. (The other two links, namely the heat of vaporization of P₄ and the dissociation energy of P₂, are fairly precisely known [11, 12].) Said heat of formation enters the equation whenever one calculates the heat of formation of any phosphorus compound—be it by *ab initio*, semiempirical, or density functional techniques.

Very recently, we developed a next-generation, fully *ab initio*, computational thermochemistry method known as W4 theory [13], that was shown to be able to reproduce the best ATcT (active thermochemical tables [14–16]) atomization energies for several dozen small molecules with an RMS deviation of

*Corresponding author. Email: comartin@weizmann.ac.il

0.08 kcal mol⁻¹ (95% confidence interval of 0.16 kcal mol⁻¹). Among other things, this method was applied effectively in a recent revision [17] of the atomic heats of formation of boron, aluminum, and silicon. It would appear to be an appropriate tool for trying to resolve the P₄ issue. In the present paper, we will show that the experimental thermochemistry, in general, and the CODATA $\Delta H_{f,0}^{\circ}[\text{P}(\text{g})]$ value, in particular, are in fact fundamentally correct.

2. Computational methods

All calculations reported in the present work were performed on the Linux cluster of the Martin group. All SCF, CCSD and CCSD(T) calculations were carried out using MOLPRO 2006.1 [18]. Some CCSDT calculations were carried out using the Austin–Mainz–Budapest version of the ACES II [19] program system; the remaining post-CCSD(T) calculations were carried out using an OpenMP parallel version of Kállay's general coupled cluster code MRCC [20–22] interfaced to the Austin–Mainz–Budapest version of ACES II [19]. SCF and correlated DBOCs were obtained using the relevant module [23] of the PSI3 open source quantum chemistry code [24]. All basis sets employed belong to the correlation consistent family of Dunning and coworkers [25–28]. Convergence of iterative processes was accelerated by means of Pulay's direct inversion of the iterative subspace (DIIS) method [29].

The computational protocols for W4 theory, for the lower-cost methods W2.2, W3.2, and W4lite, and for the post-W4 methods W4.2, W4.3, and W4.4 have been documented in great detail elsewhere [13, 30], and will not be repeated here. For the sake of clarity in the following discussion, we note that the W4 energy consists of the following components (summarized in table 1): SCF, valence CCSD correlation, valence parenthetical triples (T), higher-order connected triples T_3 –(T), quasiperturbative connected quadruples (Q), higher-order connected quadruples T_4 –(Q), connected quintuples, CCSD(T) level inner-shell correlation, scalar relativistic effects (second-order Douglas–Kroll–Hess approximation [31]), first-order spin–orbit coupling, and diagonal Born–Oppenheimer correction (DBOC). W4.2 and higher add a contribution for core–valence higher-order triples, while W4.3 uses more extended basis sets in calculating and extrapolating the post-CCSD(T) correlation effects (besides adding a connected sextuples term). W4.4 theory [30] employs improved extrapolations, as well as core–valence parenthetical quadruples and a correlation correction to the DBOC.

3. Results and discussion

3.1. At the CCSD(T) limit

All relevant thermochemical data can be found in table 1. Convergence of various contributions as a function of basis set is summarized in table 2.

The valence-correlation-only CCSD(T)/cc-pV(Q+d)Z bond distance for P₄, 2.1987 Å, is nearly 0.01 Å longer than the all-electron CCSD(T)/cc-pwCVQZ bond distance, 2.1893 Å. Combining this with the computed $r_0 - r_e$ of PTL, 0.005 Å, this implies $r_0 = 2.194$ Å, in excellent agreement with the experimental value of Boudon *et al.* [7], $r_0 = 2.1958$ Å. (An earlier measurement [6] of 2.2228 ± 0.0005 Å was previously rejected by PTL on the basis of their calculations subsequent; Boudon *et al.* work confirmed their claim.)

The valence-only and all-electron calculated bond distances of P₂ are 1.9019 and 1.8941 Å, respectively. The latter value is in excellent agreement with the experimental value from Huber and Herzberg [12], $r_e = 1.8934$ Å.

It was recently noted, in the context of a basis set convergence study on higher-order correlation effects [30], that the use of valence-only correlated reference geometries has insignificant consequences for first-row systems, but has more noticeable effects for second-row compounds with strong bonds. In the present work, we find a small but non-negligible 0.05 kcal mol⁻¹ for P₂ and a whopping 0.13 kcal mol⁻¹ for P₄—the latter is not surprising in light of the significant geometry change.

The zero-point vibrational energy of P₄, 3.91 kcal mol⁻¹, was derived from combining the anharmonicity constants of PTL with the revised experimental fundamentals of [8]. That for P₂, 1.11 kcal mol⁻¹, derives from the spectroscopic constants given by Huber and Herzberg [12].

At the W4 level, the valence CCSD(T) contributions to TAE₀ add up to 116.09 kcal mol⁻¹ for P₂, and 289.32 kcal mol⁻¹ for P₄. These values are lower by 0.6–0.7 and 1.1–1.5 kcal mol⁻¹, respectively, than the corresponding limits of HB. (The ranges given refer to the spread among the various basis set combinations extrapolated from.) Of these respective discrepancies, 0.12 (P₂) and 0.24 kcal mol⁻¹ (P₄) reflect the different definitions of the restricted open-shell CCSD(T) energy used for the phosphorus atom: Watts–Gauss–Bartlett [32], a.k.a. RHF-UCCSD(T), in the present work, and Knowles–Hampel–Werner [33], a.k.a. RHF-RCCSD(T), in HB. The remainder may somewhat reflect the different reference geometries used (HB employed B3LYP/6-31G(2df) density

functional calculations): stretching or compressing bonds causes a redistribution of binding energy between valence and core–valence contributions that is much more significant than the overall change in the sum of these parts. A more important component of the difference probably results from the fact that while HB extrapolated the total valence CCSD(T) energy, the present authors carried out separate extrapolations of the SCF, valence CCSD correlation, and (T) contributions, and, in addition, extrapolated singlet- and triplet-coupled pair correlation energies separately as advocated by Klopper [34]. Furthermore, we use more extended aug-cc-pV(5+d)Z and aug-cc-pV(6+d)Z basis sets. Using smaller basis sets with our procedure—as is done in W2.2 and W3.2 theory—changes the atomization energies of P_2 and P_4 by just -0.07 and $+0.08$ kcal mol $^{-1}$, respectively, suggesting that our W4-level extrapolation should be close to Nature.

Likewise, our core–valence contributions differ somewhat from those of HB: for P_4 we obtain 1.76 kcal mol $^{-1}$ extrapolated from CCSD(T)/aug-cc-pwCVTZ and aug-cc-pwCVQZ basis sets, while their result with the rather small cc-pCVTZ basis set is 2.2 kcal mol $^{-1}$ without counterpoise correction, and 1.4 kcal mol $^{-1}$ with counterpoise correction. HB’s core–valence contributions for P_2 likewise bracket ours.

Our scalar relativistic contributions, -0.28 (P_2) and -0.72 (P_4) kcal mol $^{-1}$, are somewhat larger in absolute value than those of HB (-0.2 and -0.5 kcal mol $^{-1}$, respectively): while they employ first-order Darwin and mass–velocity corrections [35] from a CASPT2 [36] wave function with the G3large basis set [37], we use the second-order Douglas–Kroll–Hess [31] approximation from a CCSD(T) wave function with a relativistically contracted aug-cc-pVQZ basis set [38]. The latter approximation should normally be the more rigorous one.

3.2. Beyond the CCSD(T) limit

We now consider post-CCSD(T) contributions. The %[(T)] diagnostic [13] for P_2 , 8.4%, indicates a system with moderate, bordering on severe, non-dynamical correlation. (The largest T_2 amplitude in the CCSD calculation, 0.10 per degenerate component, is related to the $\pi \rightarrow \pi^*$ excitation. For additional diagnostics, see table 3.) As a result, error compensation between higher-order triples (-1.00 kcal mol $^{-1}$ at the W4 level) and connected higher-order excitations ($+1.46$ kcal mol $^{-1}$ connected quadruples, $+0.10$ kcal mol $^{-1}$ connected quintuples) is less than perfect, and any CCSD(T)-based thermochemistry protocol would significantly underestimate D_0 . In fact,

the difference between W4 and the higher-level W4.3 protocol, 0.20 kcal mol $^{-1}$, is the largest we have thus far encountered. The difference breaks down as 0.06 kcal mol $^{-1}$ higher-order triples, 0.06 kcal mol $^{-1}$ connected quadruples, 0.03 kcal mol $^{-1}$ connected quintuples, 0.03 kcal mol $^{-1}$ from the newly introduced connected sextuples term, and 0.03 kcal mol $^{-1}$ from higher-order triples in the inner shell correlation term. Applying our highest-level protocol, W4.4 theory, only causes an additional 0.02 kcal mol $^{-1}$ change in D_0 : decreases in the CCSD and (T) extrapolated contributions are compensated by a 0.11 kcal mol $^{-1}$ contribution from core–valence connected quadruples.

Our W4.4 D_0 , 116.22 ± 0.10 kcal mol $^{-1}$ at the CCSD(T)/cc-pV(Q+d)Z geometry and 116.27 ± 0.10 kcal mol $^{-1}$ at the CCSD(T)/cc-pwCVQZ geometry, at first sight seem significantly higher than the spectroscopic value of 116.06 ± 0.09 kcal mol $^{-1}$. The latter (from a 1932 Herzberg paper [39]) derives from a predissociation limit in the $C^1\Sigma_u^+$ state to $P(^4S) + P(^2D)$, where it is not clear whether the latter is in the $J = 3/2$ or $J = 5/2$ fine structure level. Taking the fine structure data from the NIST database, we obtain 116.10 ± 0.07 kcal mol $^{-1}$ in the former, and 116.06 ± 0.07 in the latter case. The $J = 3/2$ case, in particular, agrees to within overlapping uncertainties with our calculations.

We considered yet larger basis sets for calculating the post-CCSD(T) corrections, namely cc-pV5Z for T_3 –(T) and (Q), cc-pVQZ for T_4 –(Q), and cc-pVTZ for T_5 . Results can be found in table 2. The higher-order triples contribution would change by -0.01 kcal mol $^{-1}$ relative to W4.3 but by $+0.01$ kcal mol $^{-1}$ relative to W4.4. The combined quadruples contributions would decrease by 0.04 kcal mol $^{-1}$, but in our experience [30], this basis set expansion tends to be mostly cancelled by the effect of expanding the basis set for the core–valence higher-order triples—which, incidentally, is the reason (besides computational intractability) why all three expansions are neglected in W4.4 theory. Unfortunately, a CCSDT/cc-pwCVQZ calculation is not feasible (yet) for a molecule with two second-row atoms. Finally, the quintuples contribution would go up by 0.03 kcal mol $^{-1}$.

Let us now turn to P_4 . The highest-level calculation we were able to perform was W4 theory, and even that stretched our computational resources (8-core AMD Opteron and Intel Cloverton machines with 16 to 32 GB of RAM and 2 TB of striped disk space each) to the limit. With a %[(T)] diagnostic of 7.5%, the CCSD(T) method is significantly in error here too; yet, we note that no single T_2 amplitude is larger than 0.05 for P_4 . We find a whopping -3.28 kcal mol $^{-1}$

Table 1. Component breakdown of total atomization energies of P₂ and P₄, as well as the reverse dimerization reaction. Computed and CODATA heats of formation at absolute zero of the phosphorus atom. All data in kcal mol⁻¹.

			P ₂ → 2P	P ₄ → 4P	P ₄ → 2P ₂	ΔH _{f,0} ^o [P(g)]
SCF	aug-cc-pV({5,6} + d)Z ^a	W4 and W4.x	38.93	121.40	43.54	
CCSD	aug-cc-pV({5,6} + d)Z ^b	W4, W4.2, W4.3	67.45	146.17	11.27	
	aug-cc-pV({5,6} + d)Z ^c	W4.4	67.43	146.12	11.27	
(T)	aug-cc-pV({Q,5} + d)Z ^d	W4, W4.2, W4.3	9.71	21.82	2.40	
	aug-cc-pV({Q,5} + d)Z ^e	W4.4	9.67	21.70	2.36	
$\hat{T}_3 - (T)$	cc-pV{D,T}Z ^f	W4, W4.2, W4.3	-1.00	-3.28	-1.29	
	cc-pV{T,Q}Z ^f	W4.3	-0.94			
	cc-pV{T,Q}Z ^g	W4.4	-0.96			
\hat{T}_4	1.1 × cc-pVTZ ^h	W4, W4.2	1.46	2.57	-0.34	
	cc-pV{T,Q}Z ⁱ	W4.3, W4.4	1.52			
\hat{T}_5	cc-pVDZ(no d)	W4, W4.2	0.10	0.13 ^j	-0.07	
	cc-pVDZ	W4.3, W4.4	0.13			
\hat{T}_6	cc-pVDZ(no d)	W4.3, W4.4	0.03			
Inner shell	CCSD(T)/aug-cc-pwCV{T,Q}Z	W4	0.73	1.76	0.31	
	+ΔCCSDT/cc-pwCVTZ	W4.2,3	0.76			
	+{Q}/cc-pwCVTZ	W4.4	0.87			
Relativ. DBOC ^k	DK-CCSD(T)/aug-cc-pVQZ	W4 and W4.x	-0.28	-0.72	-0.17	
	HF/aug-cc-pVTZ	W4, W4.2, W4.3	0.01	0.02	0.00	
	+CISD/cc-pVDZ	W4.4	0.01			
A-M ^l		W4 only	0.02	0.04	0.00	
ZPVE	See text	W4	1.11	3.91	-1.68	
ΔE _{r,0}		W2.2	115.36	286.60	55.87	75.61 ^m
		W3.2	115.41	285.11	54.28	75.23
		W4lite	115.48	285.03	54.07	75.22
		W4	116.00	285.96	53.97	75.45
		W4.2	116.02			
		W4.3	116.20			[75.55] ⁿ
		W4.4	116.22			[75.56] ⁿ
Δgeom.		All	0.05	0.13	0.03	0.03
ΔE _{r,0}		Best	116.27 ± 0.10	[286.32 ± 0.22] ^o		[75.54 ± 0.1] ⁿ
Experiment		CODATA	116.0 ± 0.7	285.9 ± 1.0	53.87 ± 0.7	75.45 ± 0.24 ^q
		Gurvich	116.06 ± 0.09 ^p		53.83 ± 1	75.45 ± 0.24 ^q

The notation cc-pV{X, Y}Z, for instance, indicates extrapolation from the cc-pVXZ and cc-pVYZ basis sets.

^aExtrapolated using the Karton–Martin [41] modification of Jensen’s extrapolation formula [42].

^b \hat{T}_1 term from largest basis set, singlet- and triplet-coupled pair energies are extrapolated using the two-point $A + B/L^\alpha$ expression of Halkier *et al.* [43] with $\alpha = 3$ and 5, respectively.

^cSame expressions, but using Schwenke’s extrapolation [44], which is equivalent to $\alpha = 3.06967$ for singlet pairs and $\alpha = 4.62528$ for triplet pairs.

^dExtrapolated using the two-point $A + B/L^3$ expression of Halkier *et al.* [43].

^eSame expression, but using Schwenke’s extrapolation [44], which is equivalent to $\alpha = 3.22788$.

^fExtrapolated from PVnZ basis sets using the two-point $A + B/L^3$ expression of Halkier *et al.* [43].

^gExtrapolated using empirical $A + B/L^{5/2}$ found in [30].

^hApproximated as $1.1 \times (Q)/cc-pVTZ + 1.1 \times [Q-(Q)]/cc-pVDZ$, as proposed in [13].

ⁱ{Q} contribution extrapolated cc-pV{T, Q}Z, Q-(Q) contribution obtained as difference between CCSDTQ and CCSDT(Q) calculations with the cc-pVTZ basis set.

^jValue for P₄ is approximated by CCSDTQ_{5,4}-CCSDTQ.

^kPost-Hartree–Fock corrections to the DBOC as obtained at the CISD/cc-pVDZ level are found to be +0.003 kcal mol⁻¹ for P₂ and +0.001 kcal mol⁻¹ for P₄. This correction exhibits very weak basis set sensitivity: A. Karton, B. Ruscic, and J. M. L. Martin, *J. Molec. Struct. (THEOCHEM)* **811**, 345 (2007).

^lDifferences between ACES II and MOLPRO definitions of the valence CCSD(T), extrapolated from PVDZ and PVTZ basis sets using the two-point $A + B/L^3$ expression of Halkier *et al.* [43].

^mComputed $\Delta H_{f,0}^o[P(g)]$ values are derived as $(1/4)(\Delta H_{f,0}^o[P_4(g)] + TAE_0[P_4(g)])$, where the experimental $\Delta H_{f,0}^o[P_4(g)] = 15.83 \pm 0.07$ kcal mol⁻¹ is obtained from CODATA $\Delta H_{f,298}^o[P_4(g)] = 58.9 \pm 0.3$ kJ mol⁻¹, $[H_{298} - H_0][P_4(g)] = 14.10 \pm 0.20$ kJ mol⁻¹, and $[H_{298} - H_0][P(\text{cr, white})] = 5.360 \pm 0.015$ kJ mol⁻¹. Note that using the best currently available fundamental frequencies [8] for P₄, the rigid rotor-harmonic oscillator $[H_{298} - H_0][P_4(g)] = 14.046$ kJ mol⁻¹.

Footnote continued

Table 2. Basis set convergence of various contributions to the total atomization energy (kcal mol⁻¹).

	P ₂				P ₄			
	AV(T+d)Z	AV(Q+d)Z	AV(5+d)Z	AV(6+d)Z	AV(T+d)Z	AV(Q+d)Z	AV(5+d)Z	AV(6+d)Z
SCF	38.35	38.72	38.83	38.91	120.24	120.83	121.17	121.36
CCSD T-pair	23.86	24.45	24.58	24.61	66.64	68.94	69.50	69.66
CCSD S-pair	36.07	40.27	41.73	42.32	59.95	69.79	73.54	75.01
CCSD T ₁	-0.29	-0.30	-0.31	-0.31	-0.58	-0.60	-0.62	-0.62
CCSD total	59.65	64.42	66.01	66.62	126.01	138.13	142.43	144.05
(T)	9.09	9.36	9.53	9.59	19.79	20.82	21.31	
	PVDZ	PVTZ	PVQZ	PV5Z	PVDZ	PVTZ	PVQZ	PV5Z
T ₃ -(T)	-0.07	-0.72	-0.85	-0.90	-0.78	-2.54	—	—
(Q)	1.04	1.43	1.57	1.61	1.77	2.66	—	—
T ₄ -(Q)	-0.11	-0.15	-0.17	—	-0.32	—	—	—
T ₅	0.13 ^a	0.16	—	—	(a)	—	—	—
	ACVTZ	ACVQZ			ACVTZ	ACVQZ		
Core-valence	0.67	0.70			2.00	1.86		

^aWith PVDZ (no d) basis set: 0.10 kcal mol⁻¹ for P₂, 0.13 kcal mol⁻¹ for P₄.

Table 3. Diagnostics for importance of non-dynamical correlation.

	CCSD(T)/cc-pVTZ								
	%TAE				Diagnostic		NO occupations		
	%TAE[SCF] ^a	%TAE[(T)] ^a	[post-CCSD(T)] ^a	%TAE[T ₄ + T ₅] ^a	T ₁ [46]	D ₁ [47]	Largest T ₂ amplitudes	HOMO ^b	LUMO
P ₂	33.2	8.29	-0.48	1.33	0.018	0.033	0.118 (×2)	1.899	0.085
P ₄	41.9	7.53	-0.20	0.93	0.018	0.037	0.048	1.916	0.061

^aPercentages of the total atomization energy relate to non-relativistic, clamped-nuclei values with inner shell electrons constrained to be doubly occupied (from W4 theory).

^bHighest doubly occupied molecular orbital.

from higher-order triples, 2.57 kcal mol⁻¹ from connected quadruples, and 0.13 kcal mol⁻¹ from connected quintuples. The computed TAE₀ of 285.96 ± 0.16 kcal mol⁻¹ at the standard W4 reference geometry, and 286.09 ± 0.16 kcal mol⁻¹ at the core-valence reference geometry, agree well with the Gurvich TAE₀ of 285.9 ± 1 kcal mol⁻¹, but this is a rather hollow victory in light of the stated uncertainty.

We expect that the computed TAE₀ would go up significantly if we were able to perform W4.3 or W4.4 calculations.

Interestingly, for P₄, CCSD(T) errs on the opposite side from the case of D₀(P₂), such that the error on the reaction energy P₄ → 2P₂ actually becomes *amplified*: overall, CCSD(T) overestimates the full CI limit by 1.70 kcal mol⁻¹ for this reaction.

Footnote continued

ⁿAssuming that ΔE_{r,0} for the dimerization reaction, 2P₂ → P₄, is converged at the W4 level. Further basis set effects then amount to (1/2)ΔD₀(P₂).

^oSee text.

^pSpectroscopic value extracted from Herzberg [39]. Value derives from predissociation of the C¹Σ_u⁺ state to P(4S_{3/2}) + P(2D_x), where x ∈ {3/2, 5/2}. Combining Herzberg's predissociation limit of 51 969 ± 24 cm⁻¹ with the latest atomic excitation energy data from the NIST database [45] (²D_{3/2}: 11 361.02 cm⁻¹ and ²D_{5/2}: 113 76.63 cm⁻¹), we obtain 116.10 ± 0.07 kcal mol⁻¹ if ²D_{3/2} and 116.06 ± 0.07 kcal mol⁻¹ if ²D_{5/2}.

^qFrom CODATA ΔH_{f,298}^o[P(g)] = 316.5 ± 1 kJ mol⁻¹, [H₂₉₈ - H₀][P(g)] = 6.197 ± 0.001 kJ mol⁻¹, and [H₂₉₈ - H₀][P(cr,white)] = 5.360 ± 0.015 kJ mol⁻¹.

The experimental value actually derives from $D_0(\text{P}_2)$ and the rather uncertain measured enthalpy for $\text{P}_4 \rightarrow 2\text{P}_2$, evaluated by Gurvich *et al.* [10] as $53.83 \pm 1 \text{ kcal mol}^{-1}$. As can be seen in table 1, our computed reaction energy for $\text{P}_4 \rightarrow 2\text{P}_2$ converges fairly rapidly with the level of theory, and it can reasonably be assumed that the W4 value, $53.97 \text{ kcal mol}^{-1}$ at the standard reference geometry and $54.00 \text{ kcal mol}^{-1}$ at the core-valence geometry, is not far from Nature. Combining the latter with our W4.4 $D_0(\text{P}_2)$ would suggest that W4 and W4.4 TAE₀ values differ by about $0.4 \text{ kcal mol}^{-1}$, which is not impossible but does seem excessive; $286.53 \pm 0.10 \text{ kcal mol}^{-1}$ would seem to be a plausible upper limit, and 286.10 ± 0.16 a plausible lower limit. Intermediate values of 286.12 and $286.20 \text{ kcal mol}^{-1}$ are obtained by combining the computed reaction energy with the two possible experimental $D_0(\text{P}_2)$ values. Our best estimate, $286.32 \pm 0.22 \text{ kcal mol}^{-1}$, splits the difference between our estimated upper and lower limits.

Combining one-quarter of our best estimated TAE₀[P₄(g)] with one-quarter of the quite precisely known [10, 11] $\Delta H_{f,0}^\circ[\text{P}_4(\text{g})] = 15.83 \pm 0.07 \text{ kcal mol}^{-1}$, we obtain an estimated gas-phase heat of formation of the phosphorus atom, $\Delta H_{f,0}^\circ[\text{P}(\text{g})] = 75.54 \pm 0.1 \text{ kcal mol}^{-1}$. Using the CODATA heat content functions of P(g) and white phosphorus (see footnotes to table 1), we obtain $\Delta H_{f,298}^\circ[\text{P}(\text{g})] = 75.74 \pm 0.1 \text{ kcal mol}^{-1}$, which is in excellent agreement with the CODATA reference value of $75.65 \pm 0.24 \text{ kcal mol}^{-1}$, but carries a much smaller uncertainty. Our calculations do seem to suggest that the true value is in the upper half of the CODATA uncertainty interval.

4. Conclusions

Summing up, the high-accuracy W4 computational thermochemistry protocol, and several post-W4 methods, have been applied to the P₂ and P₄ molecules. Contrary to previous studies, we find the experimental thermochemistry to be fundamentally sound. The quite significant contribution of post-CCSD(T) correlation effects to the reaction enthalpy for $\text{P}_4 \rightarrow 2\text{P}_2$ illustrates the importance of their proper treatment in accurate computational thermochemistry work. We derive a gas-phase heat of formation for the phosphorus atom of $75.54 \pm 0.1 \text{ kcal mol}^{-1}$, in the upper half of the CODATA uncertainty interval.

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References

- [1] See, e.g., R. O. Jones and D. Hohl, *J. Chem. Phys.* **92**, 6710 (1990) and references therein.
- [2] R. Ahlrichs, S. Brode, and C. Ehrhardt, *J. Am. Chem. Soc.* **107**, 7260 (1985).
- [3] B. J. Persson, P. R. Taylor, and T. J. Lee, *J. Chem. Phys.* **107**, 5051 (1997).
- [4] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- [5] M. Häser and O. Treutler, *J. Chem. Phys.* **102**, 3703 (1997).
- [6] N. Brassington, H. J. Edwards, and D. Long, *J. Raman Spectrosc.* **11**, 346 (1981).
- [7] V. Boudon, E. B. Mkadmi, H. Bürger, and G. Pierre, *Chem. Phys. Lett.* **305**, 21 (1999).
- [8] A. Kornath, A. Kaufmann, and M. Torheyden, *J. Chem. Phys.* **116**, 3323 (2002).
- [9] N. Haworth and G. B. Bacskay, *J. Chem. Phys.* **117**, 11175 (2002).
- [10] L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere Publishing, New York, 1989).
- [11] J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere Publishing, New York, 1989) (see also <http://www.codata.org/resources/databases/key1.html>).
- [12] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979). Available online at: <http://webbook.nist.gov/chemistry>
- [13] A. Karton, E. Rabinovich, J. M. L. Martin, and B. Ruscic, *J. Chem. Phys.* **125**, 144108 (2006).
- [14] B. Ruscic, R. E. Pinzon, M. L. Morton, G. von Laszewski, S. Bittner, S. G. Nijsure, K. A. Amin, M. Minkoff, and A. F. Wagner, *J. Phys. Chem. A* **108**, 9979 (2004).
- [15] B. Ruscic, in *2005 Yearbook of Science and Technology* (annual update to McGraw-Hill Encyclopedia of Science and Technology) (McGraw-Hill, New York, 2004), p. 3.
- [16] B. Ruscic, R. E. Pinzon, G. von Laszewski, D. Kodeboyina, A. Burcat, D. Leahy, D. Montoya, and A. F. Wagner, *J. Phys. Conf. Ser.* **16**, 561 (2005).
- [17] A. Karton and J. M. L. Martin, *J. Phys. Chem. A*, **111**, 5936 (2007).
- [18] MOLPRO is a package of *ab initio* programs written by H.-J. Werner, P. J. Knowles, M. Schtz, R. Lindh, P. Celani, T. Korona, G. Rauhut, F. R. Manby,

- R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, A. W. Lloyd, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson.
- [19] ACES II (Austin–Mainz–Budapest version) is an electronic structure program system written by J. F. Stanton, J. Gauss, J. D. Watts, P. G. Szalay, and R. J. Bartlett, with contributions from A. A. Auer, D. B. Bernholdt, O. Christiansen, M. E. Harding, M. Heckert, O. Heun, C. Huber, D. Jonsson, J. Jusélius, W. J. Lauderdale, T. Metzroth, and K. Ruud.
- [20] MRCC, a string-based general coupled cluster program suite written by M. Kállay. See also M. Kállay and P. R. Surján, *J. Chem. Phys.* **115**, 2945 (2001) (also <http://www.mrcc.hu>).
- [21] M. Kállay and J. Gauss, *J. Chem. Phys.* **123**, 214105 (2005).
- [22] See also: Y. J. Bomble, J. F. Stanton, M. Kállay, and J. Gauss, *J. Chem. Phys.* **123**, 054101 (2005). Approximate CCSDT(Q) methods relying on approximate factorization were earlier proposed by Bartlett and coworkers: S. A. Kucharski and R. J. Bartlett, *Chem. Phys. Lett.* **158**, 550 (1989); R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, *Chem. Phys. Lett.* **165**, 513 (1990); S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **108**, 9221 (1998); S. Hirata, M. Nooijen, I. Grabowski, and R. J. Bartlett, *J. Chem. Phys.* **114**, 3919 (2001); S. Hirata, P. D. Fan, A. A. Auer, M. Nooijen, and P. Piecuch, *J. Chem. Phys.* **121**, 12197 (2004); S. A. Kucharski, M. Kolaski, and R. J. Bartlett, *J. Chem. Phys.* **114**, 692 (2001).
- [23] E. F. Valeev and C. D. Sherrill, *J. Chem. Phys.* **118**, 3921 (2003).
- [24] T. D. Crawford, C. D. Sherrill, E. F. Valeev, J. T. Fermann, R. A. King, M. L. Leininger, S. T. Brown, C. L. Janssen, E. T. Seidl, J. P. Kenny, and W. D. Allen, PSI 3.2, 2003 (see also: <http://www.psicode.org>).
- [25] T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- [26] R. A. Kendall, T. H. Dunning, and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- [27] T. H. Dunning, Jr., K. A. Peterson, and A. K. Wilson, *J. Chem. Phys.* **114**, 9244 (2001).
- [28] K. A. Peterson and T. H. Dunning, Jr., *J. Chem. Phys.* **117**, 10548 (2002).
- [29] P. Pulay, *Chem. Phys. Lett.* **73**, 393 (1980); *J. Comput. Chem.* **3**, 556 (1982).
- [30] A. Karton, P. R. Taylor, and J. M. L. Martin, *J. Chem. Phys.*, submitted.
- [31] M. Douglas and N. M. Kroll, *Ann. Phys. (NY)* **82**, 89 (1974); B. A. Hess, *Phys. Rev. A* **33**, 3742 (1986).
- [32] J. D. Watts, J. Gauss, and R. J. Bartlett, *J. Chem. Phys.* **98**, 8718 (1993).
- [33] P. J. Knowles, C. Hampel, and H. J. Werner, *J. Chem. Phys.* **99**, 5219 (1993); Erratum **112**, 3106 (2000).
- [34] W. Klopper, *Molec. Phys.* **99**, 481 (2001).
- [35] R. D. Cowan and M. Griffin, *J. Opt. Soc. Am.* **66**, 1010 (1976); R. L. Martin, *J. Phys. Chem.* **87**, 750 (1983).
- [36] K. Andersson, P.-Å. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, *J. Phys. Chem.* **94**, 5483 (1990); K. Andersson, P.-Å. Malmqvist, and B. O. Roos, *J. Phys. Chem.* **96**, 1218 (1992).
- [37] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- [38] W. A. de Jong, R. J. Harrison, and D. A. Dixon, *J. Chem. Phys.* **114**, 48 (2001). These basis sets were obtained from the EMSL Basis Set Exchange, <http://purl.oclc.org/NET/EMSL/BSE>, which is documented in: K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, and T. L. Windus, *J. Chem. Inf. Model.* **47**, 1045 (2007).
- [39] G. Herzberg, *Ann. Phys.* **407**, 677 (1932).
- [40] B. Ruscic, J. E. Boggs, A. Burcat, A. G. Csaszar, J. Demaison, R. Janoschek, J. M. L. Martin, M. L. Morton, M. J. Rossi, J. F. Stanton, P. G. Szalay, P. R. Westmoreland, F. Zabel, and T. Berces, *J. Phys. Chem. Ref. Data* **34**, 573–656 (2005) (see also <http://www.iupac.org/projects/2003/2003-024-1-100.html>).
- [41] A. Karton and J. M. L. Martin, *Theor. Chem. Acc.* **115**, 330 (2006).
- [42] F. Jensen, *Theor. Chem. Acc.* **113**, 267 (2005).
- [43] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, *Chem. Phys. Lett.* **286**, 243 (1998).
- [44] D. W. Schwenke, *J. Chem. Phys.* **122**, 014107 (2005).
- [45] NIST Atomic Spectral Database, Version 3.1.2 (National Institute for Standards and Technology, Gaithersburg, MD) (<http://physics.nist.gov/PhysRefData/ASD/index.html>).
- [46] T. J. Lee and P. R. Taylor, *Int. J. quant. Chem. Symp.* **23**, 199 (1989).
- [47] M. L. Leininger, I. M. B. Nielsen, T. D. Crawford, and C. L. Janssen, *Chem. Phys. Lett.* **328**, 431 (2000); C. L. Janssen and I. M. B. Nielsen, *Chem. Phys. Lett.* **290**, 423 (1998); I. M. B. Nielsen and C. L. Janssen, *Chem. Phys. Lett.* **310**, 568 (1999).
- [48] N. C. Handy, Y. Yamaguchi, and H. F. Schaefer, *J. Chem. Phys.* **84**, 4481 (1986).