

Three- versus four-coordinate phosphorus in the gas phase and in solution: Treacherous relative energies for phosphine oxide and phosphinous acid

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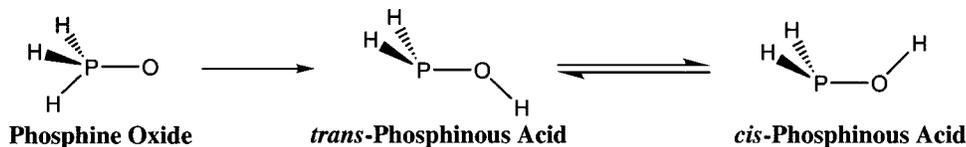
Previous *ab initio* studies have consistently predicted phosphine oxide (H_3PO) to be less stable than its nearly isoenergetic *cis*- and *trans*-phosphinous acid isomers (H_2POH). However, complete basis set extrapolations employing the coupled-cluster series show that phosphine oxide is actually ca. 1.0 kcal/mol *more* stable than its acid forms in the gas phase. Incorporation of tight *d* functions via Dunning's core-valence (cc-pCVXZ) or newly constructed "plus *d*" [cc-pV(X+d)Z] basis sets is essential for rapid convergence of core polarization effects which are evident even at the SCF level. The precision to which the phosphorus hybridization is described in the three- and four-coordinate environments ultimately determines the predicted gas-phase relative energy orderings. Focal-point analyses demonstrate that this system represents a disturbing case where use of a conventional valence quadruple- ζ quality basis set (cc-pVQZ)—even at the CCSD(T) level—fails to provide the correct relative energy ordering for simple closed-shell species which do not exhibit appreciable multireference character. Thus, we underscore the importance of using phosphorus basis sets which have the flexibility to describe core polarization adequately. In addition, Monte Carlo (MC) free-energy perturbation simulations in solution clearly demonstrate that the small energy gap significantly increases in favor of the oxide (10.0 kcal/mol) upon solvation due to stronger hydrogen bonding with the highly polar $\text{P}^{\delta+} \rightarrow \text{O}^{\delta-}$ bond. © 2002 American Institute of Physics.

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I. INTRODUCTION

Although the proper view of the P–O bond within phosphine oxide (H_3PO) has been vigorously debated over the last three decades,^{1–18} its *quantitative* electronic structure has not enjoyed the same level of attention. In general, accurate

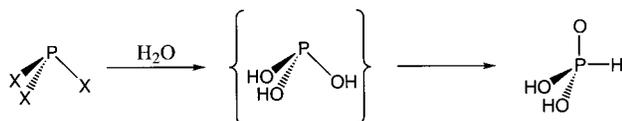
ab initio energy predictions of "hypervalent" phosphorus compounds have not been explored to the same extent as their qualitative bonding. For example, the gas-phase relative stabilities of even the simplest phosphine oxide and its acid isomers (*cis*- and *trans*- H_2POH) remain in question.



The rigorous examination of these prototype systems which undergo a change in phosphorus hybridization may provide useful guides for identifying and isolating sources of error in treatments of larger phosphorus-containing systems (e.g., Wittig olefination and phosphorylation of protein residues) that are currently limited to the use of very compact basis sets.

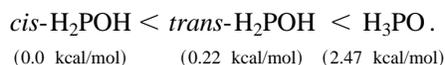
It is well known that phosphorus compounds often prefer four-coordinate species over three-coordinate forms.¹⁹ How-

ever, most *ab initio* computations have predicted the three-coordinate phosphinous acid to be more stable than its oxide by 3 to 7 kcal/mol.^{20–23} Indeed, the formation of dative $\text{P} \rightarrow \text{O}$ (or arguably $\text{P}=\text{O}$) bonds is considered to be a principal driving force within phosphorus chemistry and has been used to rationalize and predict a number of structures and reactions. For example, phosphorous acid has a four-coordinate structure despite being prepared by hydrolysis of three-coordinate phosphorus halides.



Similar arguments may be made for the Arbusov reaction with alkyl halides and the stability of phosphorus oxide cage molecules or phosphate esters in DNA. Therefore, the prediction that H_3PO is *less* stable than H_2POH is somewhat intriguing. Although the formation of four-coordinate phosphorus oxides from several tri-substituted organophosphines is well established,¹⁹ the trends are not as clear for unsubstituted phosphorus compounds.

The first optimized equilibrium and transition state structures between H_3PO and H_2POH were reported at the SCF/3-21G* level in 1987.²⁰ The *trans*- and *cis*- H_2POH isomers were found to be 6.8 kcal/mol and 6.5 kcal/mol more stable than H_3PO , respectively.²⁰ Single point energies using a truncated coupled-cluster approach (ACCD) and a TZP+ basis set indicated that the hydrogen shift isomerization barrier from H_3PO to *trans*- H_2POH is very large (68 kcal/mol).²¹ However, the subsequent internal rotation barrier leading to *cis*- H_2POH was only 3 kcal/mol.²¹ In later studies, Kwiatkowski and Leszczyński confirmed these structures and reported relative energies and thermochemical properties of $\text{H}_3\text{PO} \rightleftharpoons \text{H}_2\text{POH}$ using configuration interaction (CISD) and various levels of Møller–Plesset perturbation theory [MP2, MP3, MP4, MP4(SDQ)] with 6-31G** and 6-311G** basis sets.^{22,23} At their best level, the relative energetic ordering of the three isomers was



In opposition to the theoretically predicted energy orderings, Saito *et al.* have recently suggested that H_3PO may be intrinsically more stable than H_2POH .¹⁷ Since they do not observe the acid isomers in the microwave spectrum, Saito *et al.* conclude that the oxide is preferentially generated in their dc glow discharge of PH_3 , CO_2 and excess H_2 . While insights into the mechanism of formation may be gleaned from their study, the large kinetic barrier between the isomers (ca. 60 kcal/mol) prevents any conclusive evidence concerning relative stabilities of the oxide and acid forms. The relative energies are also clouded by the observation of the acid isomers via photolysis of phosphine/ozone mixtures in solid argon^{24,25} as well as by matrix isolation of PH_3 in a discharge of O_2 .²⁶

Recently, Chesnut reexamined the gas-phase stabilities of these compounds, as well as the effects of aqueous solvation.¹⁸ Density functional treatments (B3LYP) and various model chemistries (e.g., G3 and G3MP2) reduce the gas-phase energy differences to less than 1 kcal/mol favoring the acids, while the oxide is slightly favored using the CBS-Q method. Thus, the gas-phase relative energy ordering of these compounds remains in some doubt. However, Chesnut also used reaction field polarized continuum models and explicit computations of the oxide and acids hydrogen bonded to a single water molecule to estimate the effects of solvation. His results demonstrated that the oxide actually becomes the energetically favored isomer in solution.¹⁸

Model chemistries such as G3 have shown great promise in the prediction of thermodynamic values such as heats of formation and proton affinities.²⁷ However, energy differences of this magnitude (ca. 1 kcal/mol) are perhaps more reliably treated using an even more systematic complete basis set (CBS) and correlation extrapolation procedure. For example, so called “focal-point” analyses have provided highly accurate energy differences for several different systems (e.g., the torsional barrier of ethane,²⁸ the *E/Z* rotamer separation of formic acid,²⁸ and the barrier to linearity of water^{29,30}). On the other hand, there has also been recent concern of unacceptable errors (ca. 6 kcal/mol) for CBS limit predictions of dissociation energies involving second row atoms (e.g., SO_2 and SO)^{31,32} using the basis sets most commonly used for extrapolations [i.e., Dunning’s correlation-consistent (cc-pVXZ) basis sets].

Martin has examined the addition of high-exponent (i.e., “tight”) *d* and higher angular momentum functions to the cc-pVXZ basis sets for sulfur and found significant improvements in the extrapolated energies.³² He also demonstrated that the principal effect of the *d* functions is observed at the Hartree-Fock level and is largely a core polarization effect rather than a correlation effect.³² Furthermore, Martin and Uzan,³³ as well as Bauschlicher and Partridge,^{31,34} have shown that the core polarization problem may be more general and not restricted to sulfur. Prompted by these problematic cases, Dunning, Peterson and Wilson have reinvestigated the correlation-consistent basis sets for aluminum through argon.³⁵ Their new cc-pV(X+d)Z family of basis sets includes tight *d* functions as well as systematic expansion of the higher angular momentum functions to cover the valence and core regions. Their benchmark cases show a marked increase in the convergence of dissociation energies, as well as other molecular properties.³⁵

Considering the exceedingly small energy differences uncovered by the work of Chesnut,¹⁸ we have used high level *ab initio* methods including basis set and correlation limit extrapolations to predict the gas-phase relative energy ordering of the prototypical phosphine oxide H_3PO and its *cis*- and *trans*- H_2POH isomers. Systematic focal-point analyses including valence, core-valence, and the new cc-pV(X+d)Z correlation consistent basis sets were performed, and the convergence properties of each basis set were evaluated. Using these gas-phase structures, subsequent Monte Carlo (MC) free-energy perturbation (FEP) simulations were performed to quantify the relative stabilization of each isomer upon solvation and to compare with results from continuum solvent models.

II. THEORETICAL METHODS

A. Electronic structure

Electronic structure computations were carried out using three families of one-particle basis sets. The conventional correlation-consistent polarized valence sets of Dunning and co-workers^{36–39} (cc-pVXZ), as well as their core-valence counterparts⁴⁰ (cc-pCVXZ), were used throughout. In addition, the newly constructed cc-pV(X+d)Z basis sets of Dunning, Peterson and Wilson³⁵ were tested for this system. The

largest valence set (cc-pV6Z) includes basis functions with angular momentum up to i on phosphorus and oxygen and h on hydrogen. The cc-pVXZ basis sets range in size from 47 contracted Gaussian basis functions (cc-pVDZ) to 557 (cc-pV6Z). The corresponding core-valence sets range from 60 functions (cc-pCVDZ) to 491 functions (cc-pCV5Z). The valence plus d sets range from 52 [cc-pV(D+d)Z] to 356 functions [cc-pV(5+d)Z]. Spherical harmonic Gaussian functions were used throughout.

Reference electronic wave functions were computed using the spin-restricted Hartree–Fock (RHF) method.⁴¹ Dynamical correlation was incorporated using second-order Møller–Plesset perturbation theory⁴² (MP2), as well as the coupled-cluster series, including all single and double (CCSD)⁴³ and perturbatively estimated connected triple excitations [CCSD(T)].^{44,45} Explicit computation of the full set of triple excitations (CCSDT)^{46,47} was carried out where feasible. Geometry optimizations were performed using analytic gradient techniques at the coupled cluster with single and double excitations and perturbative triple excitations [CCSD(T)]^{48–50} level of theory until residual Cartesian coordinate gradients were less than 10^{-6} a.u. Harmonic vibrational frequencies were computed at the cc-pVTZ/CCSD(T) level via finite differences of analytic first derivatives and were used to estimate zero-point vibrational energies.

Reference geometries for the energy extrapolations were obtained at the cc-pVQZ CCSD(T) level. Focal-point analyses following the general prescription of Allen and co-workers^{51–53} were carried out via a two-dimensional extrapolation grid of single-point energies at the RHF, MP2, CCSD, CCSD(T), and CCSDT levels using Dunning’s hierarchical families of basis sets. RHF energies were extrapolated to the complete basis set limit (CBS)^{28,54–57} using the exponential form

$$E_X = E_{CBS} + a(e^{-bX}), \quad (1)$$

which effectively assumes that the incremental lowerings of total energy from cc-pVXZ \rightarrow cc-pV(X+1)Z lie in a geometric progression. The CBS limit of the correlation energies was estimated following the approach of Halkier *et al.*⁵⁸ The CBS correlation energy is estimated by

$$E_{CBS}(X, Y) = \frac{E^X X^3 - E^Y Y^3}{X^3 - Y^3}, \quad (2)$$

where E^X and E^Y denote correlation energies obtained from correlation-consistent basis sets with cardinal numbers X and Y .

First-order relativistic effects were included through the mass-velocity (MV) and one-electron Darwin (D) terms.^{59,60} All the electronic structure computations were carried out with the ACESII⁶¹ or PSI3.0⁶² program packages.

B. Monte Carlo free-energy perturbation

The free-energy change corresponding to the $\text{H}_3\text{PO} \rightarrow \text{trans-H}_2\text{POH}$ reaction was computed in water via Zwanzig’s⁶³ free-energy perturbation theory with Monte Carlo sampling.⁶⁴

TABLE I. CHELPG/cc-pV(Q+d)Z charges (e^-) and Lennard-Jones parameters (σ and ϵ) for each atom in the oxide and *trans*-acid solutes.

Atom	Charge	σ	ϵ
Phosphine oxide (H_3PO)			
P	0.923	3.74	0.20
O	-0.688	2.96	0.21
H	-0.078	2.46	0.03
H	-0.078	2.46	0.03
H	-0.078	2.46	0.03
<i>trans</i> -Phosphinous acid (H_2POH)			
P	-0.133	3.74	0.20
O	-0.473	2.96	0.21
H _a	0.104	2.46	0.03
H _a	0.104	2.46	0.03
H _b	0.398	0.00	0.00

$$\Delta G(A \rightarrow B) = -k_B T \ln \left\langle -\exp \left[\frac{E_B - E_A}{k_B T} \right] \right\rangle_A. \quad (3)$$

In Eq. (3), A and B denote the reference and perturbed states, and $\langle \rangle_A$ indicates sampling has been performed in the reference state. The coordinates and potential functions of molecule A are gradually mutated into those of B via a series of 20 steps that are coupled to a linear scaling parameter λ running from 0 to 1. Gas-phase cc-pVQZ CCSD(T) equilibrium structures were used as endpoints for the FEP calculations. Double-wide sampling was employed, yielding a step size $\Delta\lambda$ equal to 0.05. The simulations were performed in a $20 \times 20 \times 20 \text{ \AA}$ box with 265 TIP4P⁶⁵ water molecules. Each window consisted of 10×10^6 configurations of equilibration followed by 25×10^6 configurations of averaging for the oxide \rightarrow *trans* mutation. No internal degrees of freedom were sampled for the solute or solvent. Intermolecular nonbonded interactions were computed with a 10 \AA cutoff. All MC simulations were performed in the isothermal-isobaric (NPT) ensemble at 25 $^\circ\text{C}$ and 1 atm using the BOSS 4.2 program.⁶⁶ The solutes were described in the OPLS-AA format with one interaction site on each atom.⁶⁷ Standard Lennard-Jones parameters were used, as summarized in Table I.

Atomic charges derived from the molecular electrostatic potential (CHELPG)⁶⁸ of each solute were computed using 6-31G*, cc-pVQZ, and cc-pV(Q+d)Z basis sets, and the relative solvation free-energy dependence on basis set was explicitly examined in a series of FEPs. The absolute average difference in charges computed for the oxide and acids with the 6-31G* and cc-pVQZ basis sets is rather small but noteworthy ($0.0485 e^-$). As the basis set size is increased from 6-31G* to cc-pVQZ, the relative solvation free energy in going from the oxide to the *trans* isomer is reduced by 2 kcal/mol. However, the addition of a further set of d functions via the cc-pV(Q+d)Z charges alters the relative ΔG by less than 0.2 kcal/mol. Further additions to the basis set are not expected to significantly change the electron distribution or the corresponding FEP results. The CHELPG/cc-pV(Q+d)Z charges were selected for all FEPs presented in this work, as listed in Table I. All CHELPG charges were computed using the GAUSSIAN 94 program package.⁶⁹

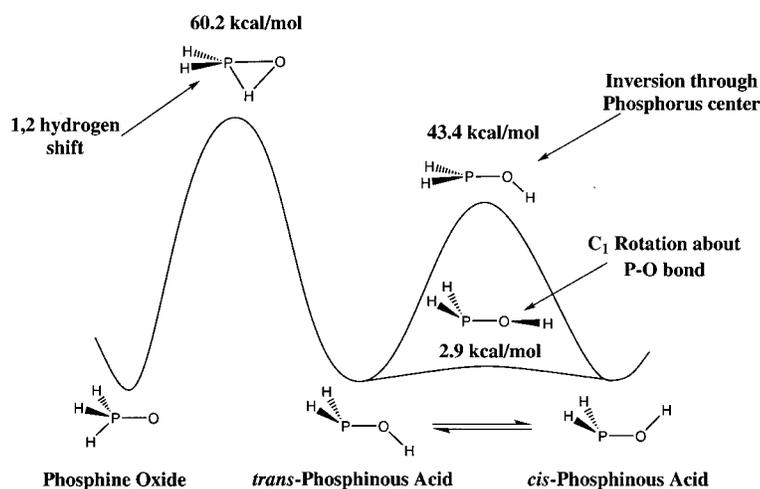


FIG. 1. Isomerization profile of phosphine oxide. Zero-point corrected barrier heights are given (in the forward direction) at the cc-pVTZ/CCSD(T) level of theory.

III. RESULTS AND DISCUSSION

A. Structures and isomerization pathway

The isomerization profile of phosphine oxide (Fig. 1) proceeds through a high-energy transition state to the *trans*-acid isomer followed by facile P–O bond rotation to the *cis*-acid isomer. The barriers computed at the cc-pVTZ/CCSD(T) level are in qualitative agreement with previous studies.²¹ Additionally, the phosphorus inversion barrier between the acid isomers is found to be very large (ca. 43 kcal/mol) and is not a viable alternate route to the *cis*-compound.

Structures of the minima at the cc-pVQZ/CCSD(T) level are provided in Fig. 2. The computed P–O bond distance for H₃PO is in excellent agreement (within 0.003 Å) with that deduced from the recent microwave analysis of Saito and co-workers.¹⁷ However, the remaining geometrical parameters which are not colinear with the C_{3v} axis deviate significantly ($\Delta r_{PH} = 0.04$ Å; $\Delta \theta_{HPO} = 2.6^\circ$). The differences in the P–H bond distances are comparable to those observed between high level *ab initio* r_e values and microwave r_0

values for the related H₂PO radical.^{70,71} The latter differences were reasonably attributed to a combination of two primary sources:⁷² (1) the experimental geometrical parameters were derived from vibrationally averaged structures and (2) structures were obtained via an incomplete isotopic substitution. While the r_e and r_0 structures are inherently different, the computed and experimentally derived P–O bond lengths which lie on the symmetric top axis are most directly comparable. The rotational constants provided in Table II illustrate that the cc-pVQZ CCSD(T) structure is consistent with the experimental B_0 rotational constants for H₃PO, D₃PO, and H₃P¹⁸O. Although only experimental B_0 values were reported, we estimated the A_0 value (corresponding to rotation about the C_{3v} axis) based on the experimental structure. The inferred experimental A_0 and computed A_e values for H₃PO differ by approximately 10 000 MHz, and further illustrate the sensitivity of the off-axis geometrical parameters.

Highly accurate structures are normally expected with the cc-pVQZ CCSD(T) method. However, optimizations using cc-pV(T+d)Z and cc-pCVTZ basis sets were also per-

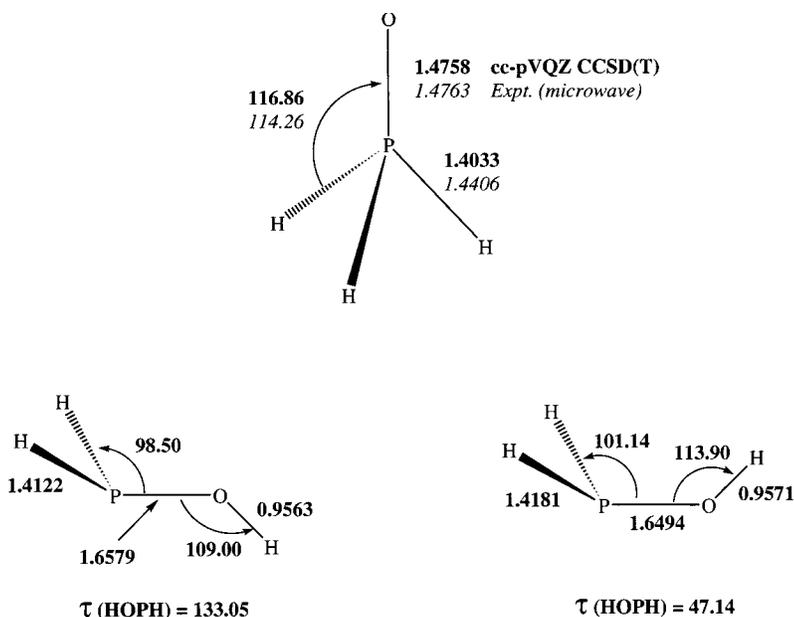


FIG. 2. Equilibrium structures of phosphine oxide and *cis*- and *trans*-phosphinous acid at the cc-pVQZ/CCSD(T) level of theory. Comparisons are made to the experimental r_0 structure where available. Bond lengths are in Å; bond angles are in degrees.

TABLE II. Comparison of experimental and *ab initio* rotational constants (in MHz) for H₃PO, D₃PO, and H₃P¹⁸O.

	H ₃ PO	D ₃ PO	H ₃ P ¹⁸ O
B_0^a	17 426.6	14 599.9	16 258.7
B_e^b	17 419.0	14 595.9	16 247.3
A_0^c	96 901.3	48 487.9	
A_e^b	106 651.5	53 366.8	

^aMicrowave spectroscopy results. See Ref. 17.

^bTheoretical results, from cc-pVQZ CCSD(T) optimized structure.

^cInferred from experimental structure. See Ref. 17.

formed to gauge the effect of additional tight functions on geometrical parameters. The differences between the cc-pVTZ, cc-pV(T+d)Z and cc-pCVTZ bond lengths and angles at the CCSD(T) level were fairly small (<0.008 Å and <0.1°, respectively). Thus, the cc-pVQZ CCSD(T) structures were chosen as reliable reference geometries for the energetic focal-point analyses.

B. Relative energetics and basis set convergence

Császár, Allen, and co-workers describe the guiding principles and assumptions of their general “focal-point” approach^{29,51–53} toward achieving the basis set and correlation limits as follows:

- Use of hierarchical families of basis sets which systematically approach completeness.
- Application of relatively low correlated levels of electronic structure theory with basis sets pushed to technical limits.
- Higher-order valence-only correlation treatments with the largest feasible basis sets.

- Layout of a two-dimensional extrapolation grid based on an assumed separability and additivity of correlation increments to the energy difference of concern.
- Inclusion of auxiliary corrections physically important for the problem.

The results of this specific approach applied to the energy differences between phosphine oxide and *cis/trans*-phosphinous acid are outlined below.

1. Valence *ab initio* limits

The effects of valence basis set size and electron correlation on the relative energies of phosphine oxide and *cis*- and *trans*-phosphinous acid are collected in Table III. The results for the H₃PO/*trans*-H₂POH energy difference are also presented graphically (in kcal/mol) in Fig. 3. Systematic expansion of the basis set lowers the oxide/*trans*-energy difference, eventually favoring the oxide; the most dramatic changes occur at the RHF and MP2 levels. The successive corrections at the MP2 and CCSD levels largely cancel one another, and the addition of the CCSD(T) correction fortuitously brings the total energy difference near that of the original RHF value. Although the correlation limit converges rapidly, the basis set convergence for the oxide/*trans*-difference is quite poor. This is the opposite of the convergence trends recently observed for the T_e of the disilaethynyl radical (Si₂H) where significant rehybridization does not occur.⁷³ In the present case, quintuple- ζ (cc-pV5Z) basis sets are required to achieve the correct energy ordering for these isomers—even at the CCSD(T) level.

The very small change in relative energy from CCSD(T) to CCSDT ($\delta[\text{CCSDT}] = 14 \text{ cm}^{-1}$) is an indication of the excellent performance of the CCSD(T) method. However, the T_1 diagnostic of Lee and Schaefer⁷⁴ was also computed for each isomer at the cc-pVQZ/CCSD(T) level to assess the

TABLE III. Effects of valence basis set size and electron correlation on the relative energies between phosphine oxide (H₃PO), *cis*- and *trans*-phosphinous acid (H₂POH). All energies are given in cm⁻¹.^a

Basis set	$\Delta E_e(\text{RHF})$	$\delta[\text{MP2}]$	$\delta[\text{CCSD}]$	$\delta[\text{CCSD(T)}]$	$\delta[\text{CCSDT}]$	$\Delta E_e(\text{total})$
$E_e(\text{H}_3\text{PO}) - E_e(\text{trans-H}_2\text{POH})$						
cc-pVDZ (47)	4322	-1194	1150	-264	-17	3997
cc-pVTZ (106)	1147	-784	1240	-176	14	1441
cc-pVQZ (204)	321	-925	1224	-171	[14]	[463]
cc-pV5Z (351)	-195	-1023	1221	-170	[14]	[-153]
cc-pV6Z (557)	-306	-1078	[1221]	[-170]	[14]	[-319]
CBS limit (∞)	-337	-1156	[1221]	[-170]	[14]	[-428]
$E_e(\text{trans-H}_2\text{POH}) - E_e(\text{cis-H}_2\text{POH})$						
cc-pVDZ (47)	106	-161	33	-22	-2	-46
cc-pVTZ (106)	125	-140	32	-27	-2	-12
cc-pVQZ (204)	89	-137	41	-26	[-2]	[-35]
cc-pV5Z (351)	69	-138	49	-26	[-2]	[-48]
cc-pV6Z (557)	62	-140	[49]	[-26]	[-2]	[-57]
CBS limit (∞)	60	-141	[49]	[-26]	[-2]	[-60]

^aEnergies are computed at the optimized unfrozen core cc-pVQZ CCSD(T) geometries. For each basis set the total number of contracted Gaussian functions is given in parentheses. For correlated calculations the symbol δ denotes the increment in the relative energy (ΔE_e) with respect to the preceding level of theory as given by the hierarchy RHF→MP2→CCSD→CCSD(T)→CCSDT. Brackets signify assumed increments from smaller basis set results. Complete basis set (CBS) RHF ΔE_e values are obtained by extrapolation of the absolute cc-pV{Q,5,6}Z energies using Eq. (1). The CBS MP2 increments are obtained by extrapolation of cc-pV{5,6}Z results using Eq. (2).

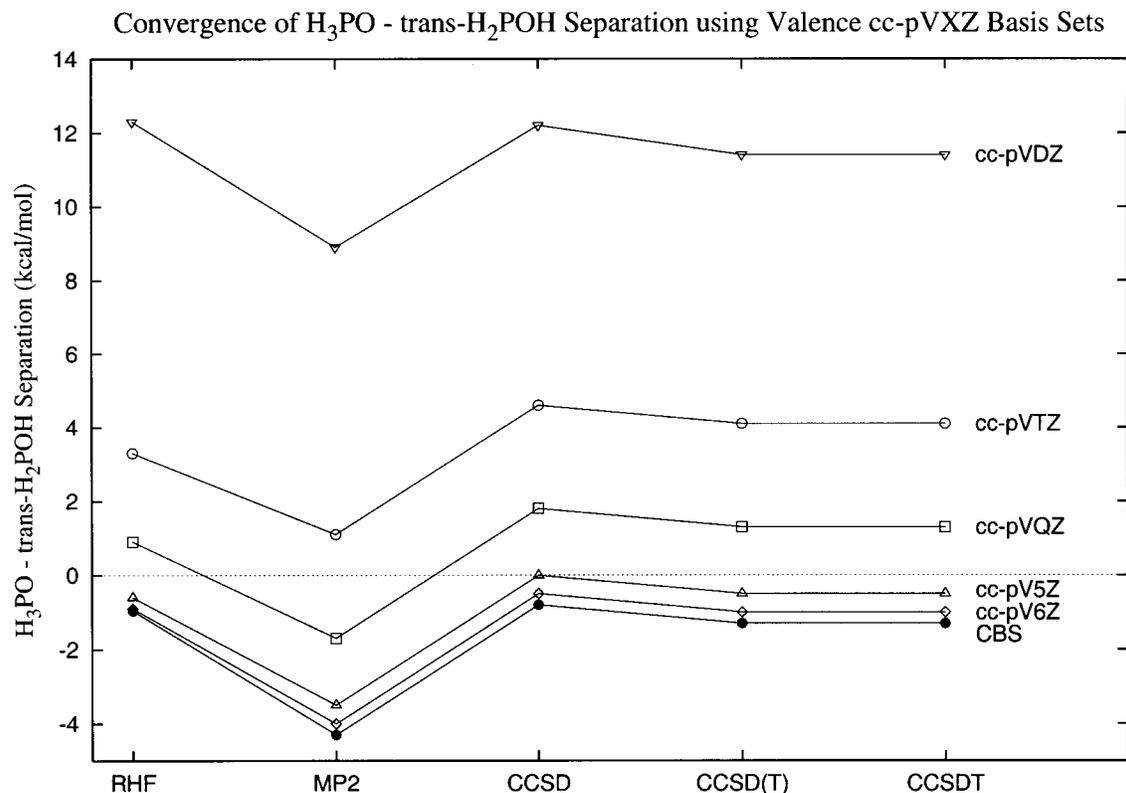


FIG. 3. Effects of valence basis set size and electron correlation on the relative energies between phosphine oxide and *trans*-phosphinous acid. See footnote of Table I for details.

suitability of a single-reference coupled-cluster approach to this problem. The T_1 diagnostics are 0.011, 0.009, and 0.009 for the oxide, *cis*-, and *trans*- isomers, respectively. These diminutive T_1 diagnostics as well as the small magnitudes of the largest individual T_2 amplitudes (-0.023 , -0.046 , and -0.043 , respectively) are indications that these systems do not exhibit appreciable multireference character, and the CCSD(T) approach should produce highly accurate energetics with suitable basis sets. The final extrapolated valence limit for the oxide-*trans* energy difference using the coupled-cluster series is -428 cm^{-1} (-1.22 kcal/mol).

The *trans/cis* energy difference is smaller in magnitude and converges more rapidly in both basis set and correlation energy. This energy separation is similar to the previously studied *E/Z* rotamer separation of formic acid for which convergence is also rapid.²⁸ However, due to the exceedingly small magnitude of the *trans/cis* separation (ca. 0.15 kcal/mol), further extensions may still be required to definitively predict the more stable isomer.

2. Core correlation and flexibility of *d* space

Core correlation effects on the oxide/acid energy separation are largely the result of the rehybridization of electron lone pairs which results in changes in core penetration and radial correlation. The effects of core correlation were assessed using core-valence basis sets designed by Dunning and co-workers⁴⁰ (Table IV). The adjustment to the oxide/*trans* relative energy is approximately 0.75 kcal/mol at the MP2 level and plays a significant role in predicting an energy difference so close to zero. However, the more highly corre-

lated methods with the two larger basis sets reduce the correction by a factor of five. The corrections for the *trans/cis* separation are minuscule ($+4 \text{ cm}^{-1}$); there is essentially no rehybridization of the heavy atoms between these isomers.

While the core correlation correction is rather small at the cc-pCVQZ/CCSD(T) level, core polarization is more evident in the comparison of SCF convergence for the cc-pVXZ, cc-pCVXZ and cc-pV(X+d)Z families of basis sets, especially early in the series (Fig. 4). While all three basis set families ultimately reach essentially the same asymptotic limit, the cc-pVXZ series converges the slowest. The new cc-pV(X+d)Z basis sets appear to be on par with the cc-pCVXZ basis sets at the SCF level and clearly outperform their cc-pVXZ predecessors. For example, the cc-pVTZ energy difference is 4.2 kcal/mol above the CBS limit, while the addition of a single set of tight *d* functions via the

TABLE IV. Contribution of core correlation to the relative energies between phosphine oxide (H₃PO), *cis*- and *trans*-phosphinous acid (H₂POH). All energies are given in cm^{-1} .^a

Basis set	MP2	CCSD	CCSD(T)
$E_e(\text{H}_3\text{PO}) - E_e(\text{trans-H}_2\text{POH})$			
cc-pCVTZ (144)	+258	+69	+74
cc-pCVQZ (204)	+244	+47	+53
$E_e(\text{trans-H}_2\text{POH}) - E_e(\text{cis-H}_2\text{POH})$			
cc-pCVTZ (144)	+3	+2	+3
cc-pCVQZ (204)	+4	+3	+4

^aEach contribution is computed as the change in relative energy between the frozen core computation ($1s$, $2s$, $2p$ orbitals on phosphorus and $1s$ orbital on oxygen) and the analogous all electron computation.

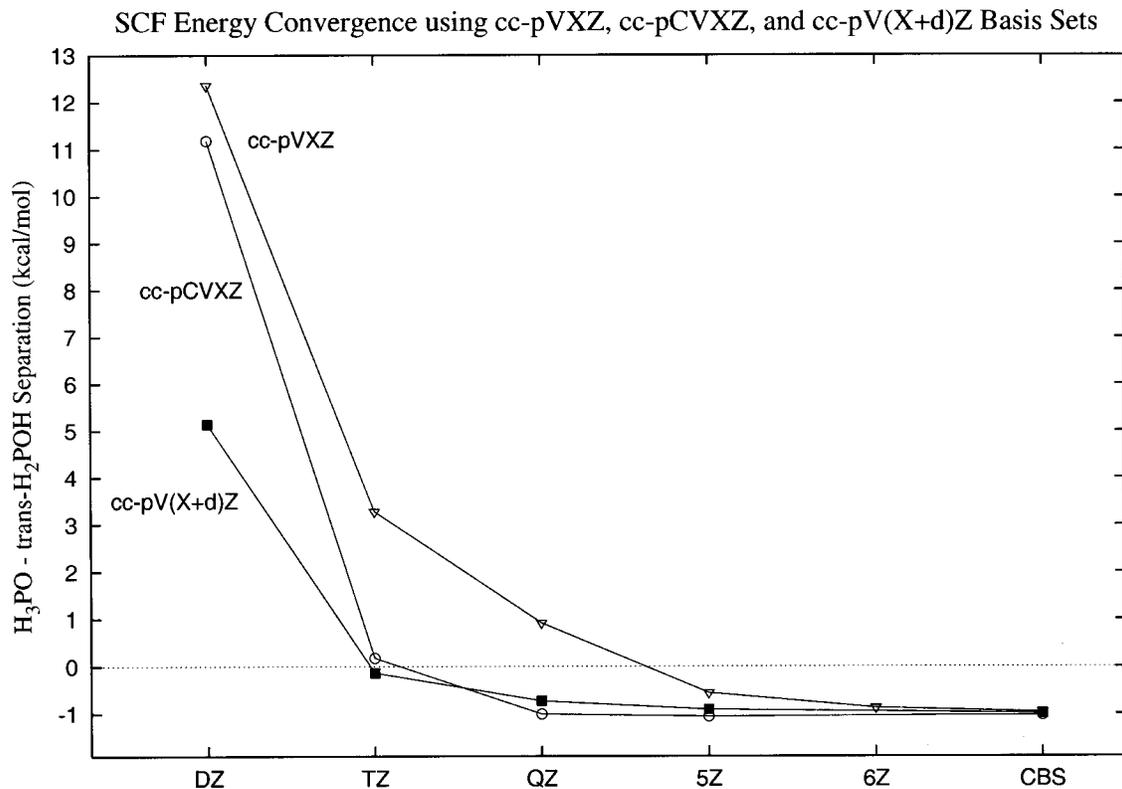


FIG. 4. Convergence of SCF $\text{H}_3\text{PO}/\text{trans-H}_2\text{POH}$ energy separation using three families of correlation consistent basis sets. The RHF separations and CBS limit for the cc-pVXZ sets are given in Table I. The corresponding values for the cc-pCVXZ sets are 3911, 62, -353 , and -370 cm^{-1} for X=D, T, Q, and 5, respectively. The corresponding values for the cc-pV(X+d)Z basis sets are 1797, -47 , -255 , and -319 cm^{-1} for X=D, T, Q, and 5, respectively. The RHF CBS {T, Q, 5} limits for the cc-pCVXZ and cc-pV(X+d)Z basis sets are -360 and -346 cm^{-1} , respectively.

cc-pV(T+d)Z set reduces the error to 0.9 kcal/mol. Thus, we underscore the importance of using second row atom basis sets which have the flexibility to describe core polarization adequately.

3. Relativistic effects and zero-point corrections

Relativistic effects on the energies were approximated at the cc-pVQZ/CCSD(T) level. Only the two components expected to make the largest contributions were considered. The mass-velocity (MV) term corrects the kinetic energy of

the system while the one-electron Darwin (D1) term corrects the Coulomb attraction.⁵⁹ The individual components and their summed contributions are collected in Table V. As expected, relativistic effects for the *cis/trans* pair are quite fungible and almost precisely cancel. However, the difference in phosphorus hybridization is apparent between the three- and four-coordinate forms as the relativistic correction to the oxide/*trans* energy separation is a notable 124 cm^{-1} (0.35 kcal/mol) at the cc-pVQZ/CCSD(T) level. The relativistic adjustments are slightly affected by basis set size, core-

TABLE V. Relativistic corrections to the oxide/*trans*-acid and *trans/cis*-acid energy differences. All values are given in cm^{-1} .^a

Basis set	RHF			CCSD(T)		
	D1	MV	Sum	D1	MV	Sum
(H_3PO)-(<i>trans</i> - H_2POH)						
cc-pVTZ (106)	-284	+416	+132	-255	+370	+115
cc-pV(T+d)Z (111)	-295	+439	+144	-270	+397	+127
cc-pCVTZ (144)	-307	+460	+153	-282	+416	+132
cc-pVQZ (204)	-288	+421	+133	-266	+390	+124
(<i>trans</i> - H_2POH)-(<i>cis</i> - H_2POH)						
cc-pVTZ (106)	-29	+37	+8	-33	+42	+9
cc-pV(T+d)Z (111)	-29	+36	+7	-33	+43	+10
cc-pCVTZ (144)	-31	+41	+10	-36	+47	+11
cc-pVQZ (204)	-28	+34	+6	-32	+40	+8

^aObtained with all electrons correlated. D1 denotes one-electron Darwin term; MV denotes one-electron mass-velocity term.

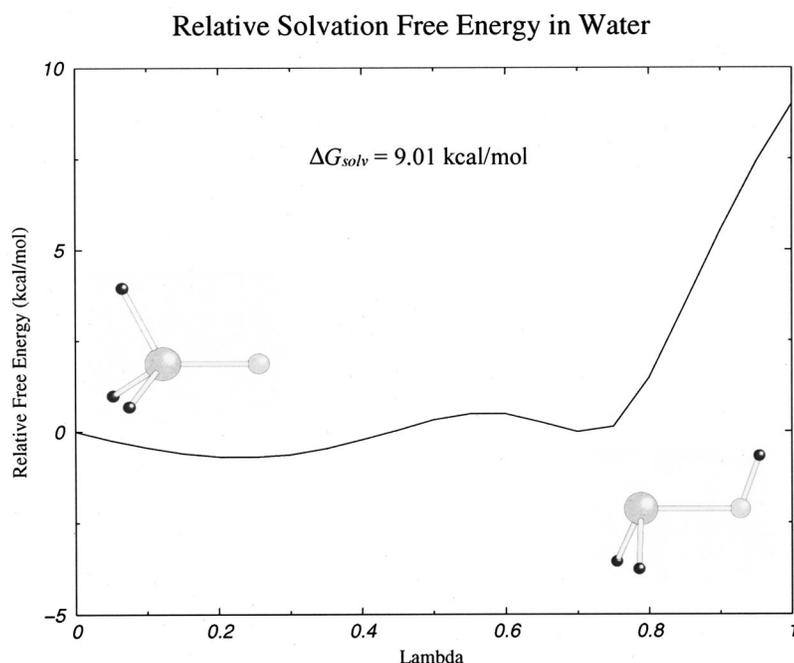


FIG. 5. Free-energy perturbation from phosphine oxide to *trans*-phosphinous acid in water. Optimized cc-pVQZ/CCSD(T) structures were used as endpoints, and only intermolecular degrees of freedom were sampled.

polarization and electron correlation as shown with the triple- ζ basis set family (see Table V). However, based on the triple- ζ trends, the correction is not expected to increase by more than ca. 20 cm^{-1} (0.06 kcal/mol) upon addition of further core functions via the cc-pCVQZ basis set.

The net vibrationless energy differences were further adjusted using harmonic zero-point vibrational energy corrections (ZPVE) at the cc-pVTZ/CCSD(T) level. The ZPVE corrections (*vide infra*) are of nearly the same magnitude and *opposite* sign as the one-electron MVD relativistic corrections, and the two effects largely cancel. While improvements to the zero-point energy may be made via anharmonic force fields, the refinements are unlikely to change the energetic ordering of the oxide and acid isomers.

4. Gas-phase relative energies

The final gas-phase relative energy predictions are obtained from the sum of the valence *ab initio* limit, the core correlation correction, estimates of relativistic effects, and a harmonic zero-point vibrational energy correction. The components for the oxide/*trans* and the *trans*/*cis* energy separations are

$$\begin{aligned}
 & \text{(H}_3\text{PO)} - \text{(trans-H}_2\text{POH)} \\
 & \underbrace{-428}_{\text{valence limit}} + \underbrace{+53}_{\text{core correlation}} + \underbrace{+124}_{\text{relativistic effects}} \\
 & \quad + \underbrace{-94}_{\text{ZPVE}} = -345 \text{ cm}^{-1} \text{ (-1.0 kcal/mol)} \\
 & \text{(trans-H}_2\text{POH)} - \text{(cis-H}_2\text{POH)} \\
 & \underbrace{-60}_{\text{valence limit}} + \underbrace{+4}_{\text{core correlation}} + \underbrace{+8}_{\text{relativistic effects}} \\
 & \quad + \underbrace{-3}_{\text{ZPVE}} = -51 \text{ cm}^{-1} \text{ (-0.15 kcal/mol)}.
 \end{aligned}$$

Our focal-point prediction that the oxide is ca. 345 cm^{-1} (1.0 kcal/mol) *more* stable than the *trans* isomer is in contrast to nearly every previous gas-phase prediction of ΔE . Previous G3 and G3MP2 place the oxide higher in energy than the *trans* compound by 0.25 and 0.26 kcal/mol, respectively.¹⁸ Density functional (B3LYP) treatments with a 6-311++G(3df,2p) basis set predict the oxide to be less stable by 0.19 kcal/mol.¹⁸ Of the four model chemistries previously tested by Chesnut,¹⁸ only the CBS-Q method of Petersson and co-workers^{75,76} predicts a value consistent with our focal-point analysis (oxide-*trans* = -1.11 kcal/mol).

C. Solvent effects: Monte Carlo FEP in water

The effect of solvent on the relative energies was examined using Monte Carlo free-energy perturbations in water. The smooth transformation of phosphine oxide to *trans*-phosphinous acid is shown in Fig. 5. The computed relative solvation ΔG of $9.01 \pm 0.12 \text{ kcal/mol}$ clearly establishes the oxide as the more stable isomer in solution. The different charge distributions in the oxide and acid provide a clear rationale for the solvation free-energy difference. The oxygen atom in the oxide isomer has a significantly larger negative charge relative to the oxygen within the acids, and it is capable of forming stronger hydrogen bonds with the solvent. Strongly polar $\text{P}^{\delta+} \rightarrow \text{O}^{\delta-}$ bonds are typical for phosphine oxides and would be expected to be more effectively solvated.

The relative strengths of the hydrogen bonds to the oxide and *trans*-acid isomers are illustrated by the energy pair distribution (EPD) in Fig. 6. The strong negative charge on the oxygen of the oxide serves as a hydrogen bond acceptor to three water molecules. The acid isomer also forms three hydrogen bonds: the oxygen atom accepts two hydrogen bonds, while the acid hydrogen is a donor to the solvent. While the average number of hydrogen bonds is roughly the same, the

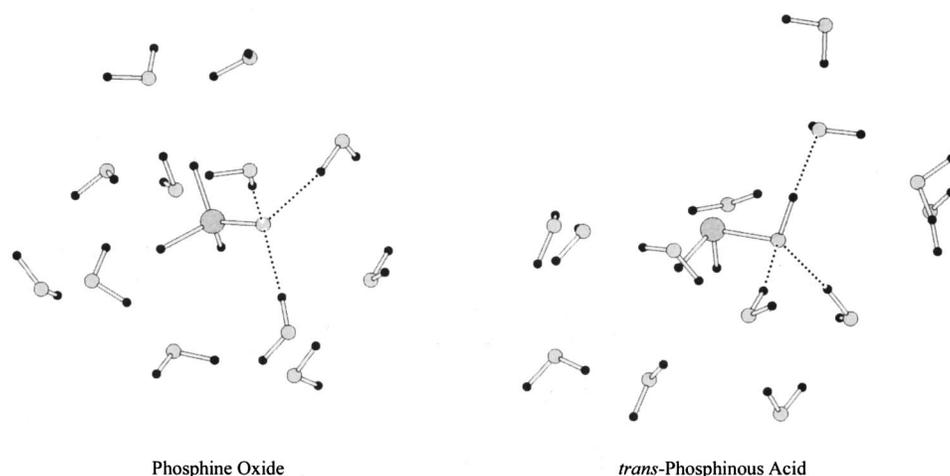
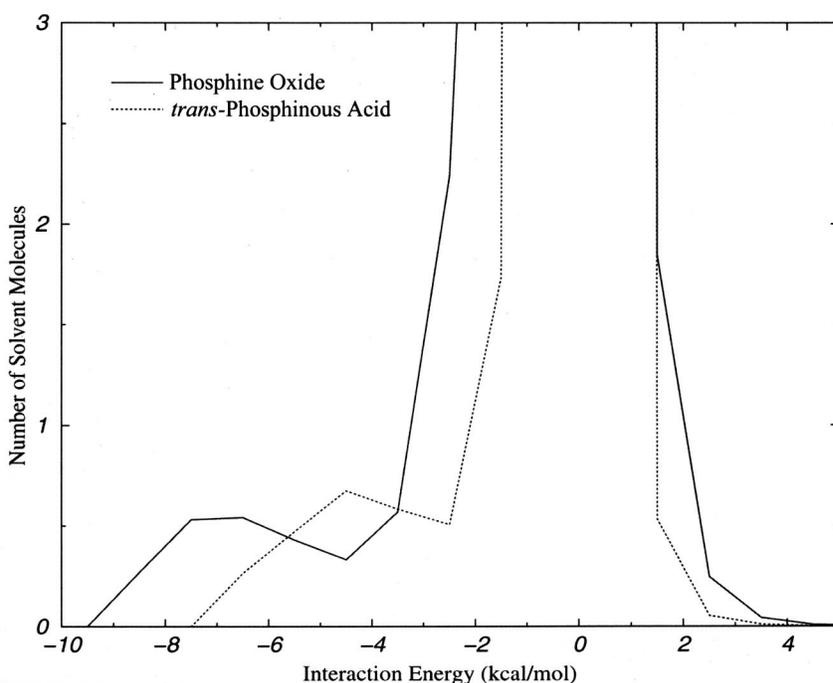


FIG. 6. Solute-solvent energy pair distributions for H_3PO and *trans*- H_2POH . While both isomers participate in approximately three hydrogen bonds, those associated with the oxide are decidedly stronger.



hydrogen bonds in the oxide are clearly stronger as shown by the maximum of the energy pair distribution at ca. -7 kcal/mol. The weaker hydrogen bonding of the acid isomer appears in the EPD at a notably higher energy (ca. -4.5). The steeper shoulders in the EPD of both the oxide (ca. -3 kcal/mol) and acid (ca. -2 kcal/mol) represent less oriented interactions and would account for the bulk of the solvent effect likely to be recovered by continuum models. The energy associated with the oxide is also lower for these more random interactions and increases the differential solvation effect further.

As a first approximation, the change in free energy of isomerization upon solvation ($\Delta\Delta G$) might be taken as the difference between the relative free energy of solvation and the gas-phase *ab initio* focal-point limit for the oxide/*trans* separation. This approximate $\Delta\Delta G$ of -10.0 kcal/mol is more than twice the size of those predicted using continuum solvent models. For example, the self-consistent isodensity

polarized continuum model (SCIPCM)⁷⁷ yields a $\Delta\Delta E$ of -3.29 kcal/mol at the B3LYP/6-311++G(2d,p) level.¹⁸ Approximate accounting of differential solvation effects using B3LYP energy differences of the monohydrated oxide and *trans* isomer give a similar value ($\Delta\Delta E = -4.00$ kcal/mol).¹⁸ However, when explicit hydrogen bonding between the solute and solvent is present, the polarized continuum models often underestimate differential solvation effects.⁷⁸ For example, SCIPCM results were recently found to only yield half of the observed differential solvation effects on the acidities of haloacetic acids upon transfer from the gas phase to aqueous solution, while corresponding MC results were in close accord with experiment.⁷⁹ The free-energy perturbation treatments incorporating explicit water molecules, both at and beyond the first solvation sphere (Fig. 6), likely provide a more quantitative account of the hydrogen bonding for the different isomers.

IV. CONCLUSIONS

Three principal conclusions are drawn in this study.

- Based on several complete basis set extrapolations employing correlation consistent valence (cc-pVXZ), core-valence (cc-pCVXZ) and the recently developed cc-pV(X+d)Z basis sets, phosphine oxide is ca. 1.0 kcal/mol more stable in the gas phase than its *trans*-acid isomer. The *trans*-acid is nearly isoenergetic with its *cis*-isomer. Our best estimate places the *trans*-compound 0.15 kcal/mol lower than the *cis*-isomer.
- The energy differences computed using the cc-pCVXZ and new cc-pV(X+d)Z basis sets converge much more rapidly than the original cc-pVXZ series. While the energy differences between the *cis*- and *trans*-acids maintain the proper sign even with double-zeta quality basis sets, cc-pV5Z quality basis sets are required to achieve the correct relative energy when comparing the oxide to the acid isomers. While the behavior of phosphates or substituted phosphine oxides might not be as pronounced, extreme care should be taken when comparing phosphorus compounds having different hybridizations. Basis sets capable of describing core polarization effects should be employed even at the SCF level.
- Monte Carlo free-energy perturbation (FEP) computations of phosphine oxide \rightarrow *trans*-phosphinous acid in water reveal that the oxide is stabilized significantly more than the acid (9.01 ± 0.12 kcal/mol) and confirm the oxide as the energetically favored isomer in solution as first predicted by Chesnut.¹⁸ While the average number of hydrogen bonds is similar, the highly polar P–O bond in phosphine oxide makes stronger solvent interactions relative to those of the *trans*-acid isomer. Estimates of relative solvation free energy using explicit solvation within the Monte Carlo approach are nearly twice those from continuum models due to accurate accounting of the strong (anisotropic) hydrogen bonds.

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¹J. Demuynck and A. Veillard, *J. Chem. Soc. Chem. Commun.* **1970**, 873.

²I. H. Hillier and V. R. Saunders, *J. Chem. Soc. A* **1970**, 2475.

³H. Marsmann, L. C. D. Groenmweghe, L. J. Schaad, and J. R. VanWazer, *J. Am. Chem. Soc.* **92**, 6107 (1970).

⁴M. F. Guest, I. H. Hillier, and V. R. Saunders, *J. Chem. Soc., Faraday Trans. 2* **68**, 867 (1972).

⁵W. Kutzelnigg, *Pure Appl. Chem.* **49**, 981 (1977).

⁶H. Wallmeier and W. Kutzelnigg, *J. Am. Chem. Soc.* **101**, 2804 (1979).

⁷M. W. Schmidt, S. Yabushita, and M. S. Gordon, *J. Phys. Chem.* **88**, 382 (1984).

⁸M. W. Schmidt and M. S. Gordon, *J. Am. Chem. Soc.* **107**, 1922 (1985).

⁹A. E. Reed and P. v. R. Schleyer, *J. Am. Chem. Soc.* **112**, 1434 (1990).

¹⁰E. Magnusson, *J. Am. Chem. Soc.* **112**, 7940 (1990).

¹¹E. Magnusson, *J. Am. Chem. Soc.* **115**, 1051 (1993).

¹²R. P. Messmer, *J. Am. Chem. Soc.* **113**, 433 (1991).

¹³J. Cioslowski and S. T. Mixon, *J. Am. Chem. Soc.* **113**, 4142 (1991).

¹⁴D. G. Gilheany, *Chem. Rev.* **94**, 1339 (1994).

¹⁵H. Dobado, H. Martinez-Garcia, J. M. Molina, and M. R. Sundberg, *J. Am. Chem. Soc.* **120**, 8461 (1998).

¹⁶D. B. Chesnut and A. Savin, *J. Am. Chem. Soc.* **121**, 2335 (1999).

¹⁷I. K. Ahmad, H. Ozeki, and S. Saito, *J. Chem. Phys.* **110**, 912 (1999).

¹⁸D. B. Chesnut, *Heteroat. Chem.* **11**, 73 (2000).

¹⁹D. E. C. Corbridge, *Phosphorus: An Outline of Its Chemistry, Biochemistry and Technology* (Elsevier Science, Portland, OR, 1980).

²⁰J. A. Boatz, M. W. Schmidt, and M. S. Gordon, *J. Phys. Chem.* **91**, 1743 (1987).

²¹C. J. Cramer, C. E. Dykstra, and S. E. Denmark, *Chem. Phys. Lett.* **136**, 17 (1987).

²²J. S. Kwiatkowski and J. Leszczyński, *Mol. Phys.* **76**, 475 (1992).

²³J. S. Kwiatkowski and J. Leszczyński, *J. Phys. Chem.* **96**, 6636 (1992).

²⁴R. Withnall, M. Hawkins, and L. Andrews, *J. Phys. Chem.* **90**, 575 (1986).

²⁵R. Withnall and L. Andrews, *J. Phys. Chem.* **91**, 784 (1987).

²⁶R. Withnall and L. Andrews, *J. Phys. Chem.* **92**, 4610 (1988).

²⁷L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **112**, 7374 (2000).

²⁸A. G. Császár, W. D. Allen, and H. F. Schaefer, *J. Chem. Phys.* **108**, 9751 (1998).

²⁹G. Tarczay, A. G. Császár, W. Klopper, V. Szalay, W. D. Allen, and H. F. Schaefer, *J. Chem. Phys.* **110**, 11971 (1999).

³⁰E. F. Valeev, W. D. Allen, H. F. Schaefer, and A. G. Császár, *J. Chem. Phys.* **114**, 2875 (2001).

³¹C. W. Bauschlicher and H. Partridge, *Chem. Phys. Lett.* **240**, 533 (1995).

³²J. M. L. Martin, *J. Chem. Phys.* **108**, 2791 (1998).

³³J. M. L. Martin and O. Uzan, *Chem. Phys. Lett.* **282**, 16 (1998).

³⁴C. W. Bauschlicher, *J. Phys. Chem. A* **103**, 11126 (1999).

³⁵T. H. Dunning, K. A. Peterson, and A. K. Wilson, *J. Chem. Phys.* **114**, 9244 (2001).

³⁶T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).

³⁷D. E. Woon and T. H. Dunning, *J. Chem. Phys.* **98**, 1358 (1993).

³⁸A. K. Wilson, T. van Mourik, and T. H. Dunning, *THEOCHEM* **388**, 339 (1996).

³⁹T. van Mourik and T. H. Dunning, *Int. J. Quantum Chem.* **76**, 205 (2000).

⁴⁰D. E. Woon and T. H. Dunning, *J. Chem. Phys.* **103**, 4572 (1995).

⁴¹C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951).

⁴²C. Møller and M. S. Plesset, *Phys. Rev.* **46**, 618 (1934).

⁴³G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).

⁴⁴K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).

⁴⁵R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, *Chem. Phys. Lett.* **165**, 513 (1990); erratum: **167**, 609 (1990).

⁴⁶J. Noga and R. J. Bartlett, *J. Chem. Phys.* **86**, 7041 (1987); erratum: **89**, 3401 (1988).

⁴⁷G. E. Scuseria and H. F. Schaefer, *Chem. Phys. Lett.* **152**, 382 (1988).

⁴⁸M. Rittby and R. J. Bartlett, *J. Phys. Chem.* **92**, 3033 (1988).

⁴⁹J. D. Watts, J. Gauss, and R. J. Bartlett, *Chem. Phys. Lett.* **200**, 1 (1992).

⁵⁰J. D. Watts, J. Gauss, and R. J. Bartlett, *J. Chem. Phys.* **98**, 8718 (1993).

⁵¹W. D. Allen, A. L. L. East, and A. G. Császár, in *Structures and Conformations of Non-Rigid Molecules*, edited by J. Laane, M. Dakkouri, B. van der Veken, and H. Oberhammer (Kluwer, Dordrecht, 1993).

⁵²A. L. L. East and W. D. Allen, *J. Chem. Phys.* **99**, 4638 (1993).

⁵³B. D. Wladkowski, W. D. Allen, and J. I. Brauman, *J. Phys. Chem.* **98**, 13532 (1994).

⁵⁴D. Feller, *J. Chem. Phys.* **96**, 6104 (1992).

⁵⁵D. Feller, *J. Chem. Phys.* **98**, 7059 (1993).

⁵⁶H. Partridge and D. W. Schwenke, *J. Chem. Phys.* **106**, 4618 (1997).

⁵⁷T. Helgaker, W. Klopper, H. Koch, and J. Noga, *J. Chem. Phys.* **106**, 9639 (1997).

⁵⁸A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, *Chem. Phys. Lett.* **286**, 243 (1998).

⁵⁹K. Balasubramanian, *Relativistic Effects in Chemistry, Part A: Theory and Techniques* (Wiley, New York, 1997).

⁶⁰W. Klopper, *J. Comput. Chem.* **18**, 20 (1997).

⁶¹J. F. Stanton, J. Gauss, J. D. Watts *et al.*, ACES II, a program product of the Quantum Theory Project, University of Florida. Integral packages in-

- cluded are VMOL (J. Almlöf and P. R. Taylor); VPROPS (P. R. Taylor); ABACUS (T. Helgaker, H. J. A. Jensen, P. Jørgensen, J. Olsen, and P. R. Taylor).
- ⁶²T. D. Crawford, C. D. Sherrill, E. F. Valeev *et al.*, PSI 3.0, PSITECH, Inc., Watkinsville, GA, 2000.
- ⁶³R. W. Zwanzig, *J. Chem. Phys.* **22**, 1420 (1954).
- ⁶⁴W. L. Jorgensen, in *Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer, Vol. 3, p. 1754 (Wiley, New York, 1998).
- ⁶⁵W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.* **79**, 926 (1983).
- ⁶⁶W. L. Jorgensen, BOSS, Version 4.2; Yale University, New Haven, CT, 2000.
- ⁶⁷W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, *J. Am. Chem. Soc.* **118**, 11225 (1996).
- ⁶⁸C. M. Breneman and K. B. Wiberg, *J. Comput. Chem.* **11**, 361 (1990).
- ⁶⁹M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 94, Revision C.3, Gaussian, Inc., Pittsburgh, PA, 1995.
- ⁷⁰S. S. Wesolowski, E. M. Johnson, M. L. Leininger, T. D. Crawford, and H. F. Schaefer, *J. Chem. Phys.* **109**, 2694 (1998).
- ⁷¹T. Hirao, S. Saito, and H. Ozeki, *J. Chem. Phys.* **105**, 3450 (1996).
- ⁷²S. Saito (private communication).
- ⁷³C. Pak, S. S. Wesolowski, J. C. Rienstra-Kiracofe, Y. Yamaguchi, and H. F. Schaefer, *J. Chem. Phys.* **115**, 2157 (2001).
- ⁷⁴T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem., Symp.* **23**, 199 (1989).
- ⁷⁵J. A. Montgomery, J. W. Ochterski, and G. A. Petersson, *J. Chem. Phys.* **101**, 5900 (1994).
- ⁷⁶J. W. Ochterski, G. A. Petersson, and J. A. Montgomery, *J. Chem. Phys.* **104**, 2598 (1996).
- ⁷⁷J. B. Foresman, T. A. Keith, K. B. Wiberg, J. Snoonian, and M. J. Frisch, *J. Phys. Chem.* **100**, 16098 (1996).
- ⁷⁸H. Castejon, K. B. Wiberg, S. Sklenak, and W. Hinz, *J. Am. Chem. Soc.* **123**, 6092 (2001).
- ⁷⁹K. B. Wiberg, S. Clifford, W. L. Jorgensen, and M. J. Frisch, *J. Phys. Chem. A* **104**, 7625 (2000).