

Ab initio characterization of XH_3 ($X=N, P$). I. Ammonia, phosphine and their related ions and radicals: structure and thermochemistry

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Abstract Ammonia, phosphine and their related cations, anions and radicals have been investigated at a high level of accuracy. The singles and doubles coupled cluster method including a perturbational correction for connected triple excitations, CCSD(T), in conjunction with correlation consistent basis sets ranging in size from triple to sextuple zeta have been employed. Extrapolation to the complete basis set limit has been used with accurate treatments of core-valence correlation effects in order to accurately predict structures, ionization potentials, electron affinities as well as N–H and P–H bond dissociation energies. For all the species studied, harmonic vibrational frequencies have also been evaluated in order to obtain zero-point corrections.

Keywords Ab initio calculations · Equilibrium structure · Ammonia · Phosphine · Radicals and ions · Thermochemistry

1 Introduction

The structure and related properties of molecules containing second-row atoms are often different from their first-row analogues, making therefore their comparison interesting and of relevance to chemists. On this topic, ammonia, its second-row analogue phosphine, and their related ions and radicals are the subject of the present investigation. Since convergence and accuracy of ab initio computations are well known and tested for first-row-containing species, the structure and thermochemical properties calculated for ammonia and its

related ions and radicals may provide a calibration, allowing us to estimate the accuracy of our computed results for phosphine and related species.

The systems under consideration have a twofold interest: on one hand, as mentioned, they allowed us to compare structures and thermochemistry for first- and second-row analogues and, on the other hand, they play an important role in various fields of chemistry and physics. As well known, ammonia plays a major part in chemistry and, therefore, it is unnecessary to stress its importance. Furthermore, ammonia as well as phosphine are molecules of considerable spectroscopic and astronomical interest (see for example, Refs. [1–4] and references therein). In addition, NH_3 is a prototype pyramidal molecule which provides a good test case for theoretical spectroscopic models. As far as PH_3 is concerned, it is also worth to mention its technological importance. Phosphorous containing molecules may be potential catalysts thanks to their ability to accelerate a range of recombination reactions (see Ref. [5] and references therein). PH_3 is widely used as the source of phosphorous to produce high quality thin films (see Ref. [6] and references therein).

Finally, it deserves to be mentioned that radicals and radical cations are important intermediates in many reactions, in particular in many oxidative reactions of biological importance (see Ref. [7] and references therein). Similarly, protonated species are important as proton transfer reactions play a crucial role in many chemical transformations in chemistry and biochemistry (see for example, Ref. [8] and references therein).

2 Methodology

For all the species considered, a preliminary investigation at the multiconfiguration self consistent field (MCSCF) [9, 10]

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and coupled-cluster levels of theory with a basis of triple zeta quality has been performed in order to assess if the coupled-cluster model is adequate for studying these species and, in particular, the open-shell systems. On this subject, the coupled-cluster T_1 diagnostic [11, 12] has been found to be of the order of 0.005–0.014 for the closed-shell molecules and of the order of 0.015–0.021 for the open-shell ones. Additionally, the test computations carried out at the MCSCF level showed that all the ground states of the species considered are well described by a single reference wavefunction. Going into details, we have thoroughly investigated the electronic ground states of NH_3 (1A_1) and PH_3 (1A_1), and of their related cations NH_3^+ ($^2A_2''$) and PH_3^+ (2B_1), protonated species NH_4^+ (1A_1) and PH_4^+ (1A_1), anion NH_3^- (2A_1), and radicals NH_2 (2B_1) and PH_2 (2B_1). The PH_3^- anion has also been deeply studied, but no real minima have been found at any levels of theory considered.

The systematic study of the equilibrium structures and energies has been carried out at the coupled-cluster level of theory with single and double excitations, and a quasiperturbative account for triples substitutions [CCSD(T)]. More precisely, the CCSD(T) method [13–15] has been used for the closed-shell species, whereas for the open-shell molecules the variant denoted R/UCCSD(T) [16–18], which is based on restricted open-shell Hartree–Fock (ROHF) orbitals but spin unrestricted in the solution of the CCSD equations, has been employed.

Correlation consistent basis sets have been employed in the present investigation; more precisely, the d -augmented valence cc-pV($n+d$)Z basis sets ($n = Q, 5, 6$) [19] have been used for the phosphorus atom, whereas the standard cc-pV n Z sets ($n = Q, 5, 6$) [20] have been employed for hydrogen and nitrogen. On the whole, in the text we denote as cc-pVT($n+d$)Z the bases for phosphorous compounds and as cc-pV n Z those for the species containing nitrogen. The frozen core approximation has been adopted, i.e., only valence electrons have been correlated.

Geometry optimizations have been carried out with the MOLPRO suite of programs¹ and performed using numerical gradients [21, 22]. The step-sizes used were 0.0005 Å for bond lengths and 0.1° for bond angles. A convergence criterion stronger than the default one has been employed: both the maximum component of the gradient and the maximum component of the step have been constrained to be less than 1.0×10^{-6} a.u.

¹ MOLPRO is a package of ab initio programs written by H.-J. Werner and P.J. Knowles, with contributions of R.D. Amos, A. Bernhardsson, P. Celani, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A.W. Lloyd, S.J. McNicholas, F.R. Manby, W. Meyer, M.E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, H. Stoll, A.J. Stone, R. Tarroni, and T. Thorsteinsson.

Since a hierarchical sequence of bases has been considered, the systematic trend of geometrical parameters can be exploited to estimate the complete basis set (CBS) limit. Making use of the assumption that the convergence of the structural parameters has the same behavior as energy, the function used to describe the convergence for the correlation contribution is the consolidated $1/n^3$ extrapolation formula [23]:

$$\Delta r^{\text{corr}}(n) = \Delta r_{\infty}^{\text{corr}} + A n^{-3} \quad (1)$$

and it is applied to the case $n = 5$ and 6 . To obtain the extrapolated structure, the CBS limit value of the correlation contribution has then been added to the HF-SCF CBS limit, which is assumed to be reached at the HF-SCF/cc-pV6Z level:

$$r(\text{CBS}) = r_{\infty}^{\text{SCF}} + \Delta r_{\infty}^{\text{corr}}. \quad (2)$$

In the remainder of the text, the extrapolated structures will be denoted as $r(\text{CBS}, \text{valence})$ or even simply $r(\text{CBS})$.

Infinite valence basis set limits of the total energies have been obtained following two different extrapolation schemes. The first approach is similar to that employed for the extrapolation of the geometrical parameters, i.e., the CBS limit has been obtained by extrapolating the correlation contribution to the complete basis limit by n^{-3} [23, 24]:

$$\Delta E^{\text{corr}}(n) = \Delta E_{\infty}^{\text{corr}} + A' n^{-3} \quad (3)$$

and adding the Hartree–Fock complete basis limit, evaluated by the formula [25, 26]

$$E^{\text{SCF}}(n) = E_{\infty}^{\text{SCF}} + B' \exp(-C' n). \quad (4)$$

The second extrapolation has been performed using the mixed exponential/Gaussian extrapolation formula [27, 28]

$$E(n) = E_{\text{CBS}} + B'' e^{-(n-1)} + C'' e^{-(n-1)^2}. \quad (5)$$

The mean value from these two approaches has been taken as CBS limit for energy and thus employed in the evaluation of thermochemical properties.

Making use of the additivity approximation, corrections for taking into account core–valence correlation effects have then been added to the CBS geometries and energies. This involved carrying out geometry optimizations using the core–valence correlation consistent cc-pwCVQZ basis set [29] (cc-pwCV(Q+d)Z for P, obtained by adding the appropriate tight functions [29] to the cc-pV(Q+d)Z set). With regards to the geometrical parameters, the core correlation corrections have been added to the extrapolated structures as:

$$r_e(\text{CBS} + \text{CV}) \simeq r(\text{CBS}, \text{valence}) + r(\text{wCVQZ}, \text{all}) - r(\text{wCVQZ}, \text{valence}), \quad (6)$$

Table 1 Equilibrium geometries and energies of NH₃ and PH₃ computed at the coupled cluster level of theory employing different basis sets. Extrapolated geometries and energies to valence correlation limit (CBS) and best estimates of the equilibrium structure (CBS+CV) are also reported

	X–H (Å)	∠HXH (deg.)	Energy (hartree)	Ref.
NH ₃ (¹ A ₁) X = N				
CCSD(T)/CBS+CV+rel PES ^a	1.0103131 (59)	112.0966 (16)		[37]
CBS+CV+fT+fQ ^b	1.01094	106.815		[41]
cc-pVQZ	1.0125	106.18	–56.4930532	This work
cc-pV5Z	1.0121	106.51	–56.4994512	This work
cc-pV6Z	1.0121	106.59	–56.5014719	This work
cc-pwCVQZ (f.c.)	1.0125	106.19	–56.4941906	This work
cc-pwCVQZ (all)	1.0111	106.38	–56.5509285	This work
CBS-I ^c	1.0121	106.70	–56.5039378	This work
CBS-II ^d			–56.5026474	This work
CBS+CV ^e	1.0107	106.89	–56.5600304	This work
Experiment ^f	1.011 (6)	106.7		[43]
Experiment ^g	1.01139 (60)	107.17 (18)		[44]
PH ₃ (¹ A ₁) X = P				
(all)CCSD(T)/cc-pwCVQZ	1.411539	93.482		[39]
cc-pV(Q+d)Z	1.4147	93.55	–342.7096068	This work
cc-pV(5+d)Z	1.4145	93.56	–342.7137032	This work
cc-pV(6+d)Z	1.4144	93.56	–342.7152429	This work
cc-pwCV(Q+d)Z (f.c.)	1.4142	93.56	–342.7108210	This work
cc-pwCV(Q+d)Z (all)	1.4113	93.49	–343.0238612	This work
CBS-I ^c	1.4143	93.56	–342.7170474	This work
CBS-II ^d			–342.7161389	This work
CBS+CV ^e	1.4114	93.49	–343.0296333	This work
Experiment ^h	1.4116 (6)	93.33		[45]
Experiment ⁱ	1.411607 (83)	93.4184 (95)		[46]

(f.c.) and (all) denote calculations correlating only valence and all electrons, respectively

^a Minimum of the PES. Computation performed employing the CCSD(T) method in conjunction with the aug-cc-pVnZ (*n* = T, Q, 5) bases. Extrapolation to the CBS limit, CV and relativistic corrections have been considered

^b The gradient used in the geometry optimization has been obtained as sum of the following contributions: extrapolation to the complete basis set (CBS) limit, core–valence (CV) correlation effects, full triples (fT) and full quadruples (fQ) corrections

^c CBS geometries and energies evaluated using the *n*^{–3} extrapolation technique: see text

^d CBS energies evaluated using the mixed exponential/Gaussian function: see text

^e Best estimated equilibrium geometry employing Eq. (6): see text. For energies, CBS-I and CBS-II mean values have been used

^f Equilibrium structure

^g Empirical equilibrium structure: from a least-squares fit of the molecular structural parameters to equilibrium rotational constants derived from the experimental ground-state constants and the theoretical vibrational corrections (at the CCSD(T)/cc-pVQZ level)

^h Equilibrium structure

ⁱ Equilibrium structure

where $r(\text{wCVQZ}, \text{all})$ and $r(\text{wCVQZ}, \text{valence})$ are the geometries optimized at the (R/U)CCSD(T)/cc-pwCVQZ level correlating all and only valence electrons, respectively. The core–valence (CV) corrections to the total energies have been calculated as

$$\Delta E_{CV} = E_{\text{core+val}} - E_{\text{val}}, \quad (7)$$

where $E_{\text{core+val}}$ is the (R/U)CCSD(T) total energy obtained by correlating all electrons and E_{val} is the (R/U)CCSD(T)

total energy obtained in the frozen core approximation, both in the same cc-pwCVQZ basis set. (R/U) reported in parentheses indicates that the CCSD(T) and R/UCCSD(T) methods have been employed for closed-shell and open-shell molecules, respectively.

Finally, in order to estimate the inversion barrier of ammonia and phosphine, for both species the geometry of the transition state (TS) has also been optimized employing the series of correlation consistent bases previously mentioned as

Table 2 Equilibrium geometries and energies of NH_3^+ and PH_3^+ computed at the coupled cluster level of theory employing different basis sets. Extrapolated geometries and energies to valence correlation limit (CBS) and best estimates of the equilibrium structure (CBS+CV) are also reported

	X–H (Å)	$\angle\text{HXH}$ (deg.)	Energy (hartree)	Ref.
NH_3^+ (${}^2A_2'$) X = N				
RCCSD(T)/aug-cc-pVQZ PES ^a	1.0208	120.0		[34]
cc-pVQZ	1.0212	120.0	–56.1203681	This work
cc-pV5Z	1.0210	120.0	–56.1248204	This work
cc-pV6Z	1.0210	120.0	–56.1263109	This work
cc-pwCVQZ (f.c.)	1.0212	120.0	–56.1214125	This work
cc-pwCVQZ (all)	1.0203	120.0	–56.1780184	This work
CBS-I ^b	1.0210	120.0	–56.1281984	This work
CBS-II ^c			–56.1271781	This work
CBS+CV ^d	1.0201	120.0	–56.1842941	This work
Experiment ^e	1.014	120.0		[47]
PH_3^+ (2B_1) X = P				
MRCISD/G2	1.3940	114.41		[6]
cc-pV(Q+d)Z	1.3974	113.21	–342.3489762	This work
cc-pV(5+d)Z	1.3972	113.21	–342.3523126	This work
cc-pV(6+d)Z	1.3972	113.21	–342.3535524	This work
cc-pwCV(Q+d)Z (f.c.)	1.3969	113.21	–342.3500783	This work
cc-pwCV(Q+d)Z (all)	1.3943	113.24	–342.6622765	This work
CBS-I ^b	1.3972	113.21	–342.3549487	This work
CBS-II ^c			–342.3542740	This work
CBS+CV ^d	1.3946	113.24	–342.6668095	This work

(f.c.) and (all) denote calculations correlating only valence and all electrons, respectively

^a Minimum of the PES. Computation performed at the RCCSD(T)/aug-cc-pVQZ level

^b CBS geometries and energies evaluated using the n^{-3} extrapolation technique: see text

^c CBS energies evaluated using the mixed exponential/Gaussian function: see text

^d Best estimated equilibrium geometry employing Eq. (6): see text. For energies, CBS-I and CBS-II mean values have been used

^e Equilibrium structure: estimated value

well as the cc-pwCVQZ set for accounting for core correlation. Extrapolation procedures for structural parameters and energy have been carried out as previously described. The transition state distinctiveness has been checked by performing harmonic frequencies computations (at the CCSD(T)/cc-pVQZ level in the frozen core approximation); i.e., it has been confirmed that the hessian matrix evaluated at the optimized geometry contains one and only one imaginary frequency.

3 Results and discussion

3.1 Molecular structures

The equilibrium geometries and energies of the species investigated, obtained at the CCSD(T) level employing different basis sets, are summarized in Tables 1, 2, 3, 4 and 5. The

extrapolation to the CBS limit of both geometries and energies has been carried out for all the molecules considered as explained in the methodology section and the results are also listed in Tables 1, 2, 3, 4 and 5. Furthermore, the inclusion of the core correlation corrections, performed as previously explained, provided the best estimated values.

From the results of Tables 1, 2, 3, 4 and 5, it is first observed that the valence correlation limit is nearly reached at the (R/U)CCSD(T)/cc-pV5Z level; in fact, the discrepancies between $r(\text{V5Z})$ and $r(\text{CBS})$ are usually lower than 0.0002 Å for bonds and 0.1° for angles. The largest deviations are presented by the NH_3^- anion: 0.003 Å for the N–H bond and 0.3° for the $\angle\text{HNH}$ even when $r(\text{V6Z})$ is considered. This may be ascribed to the negative charge not so well described by the correlation consistent bases used. For this reason computations employing the aug-cc-pVnZ ($n = \text{T, Q, 5}$) bases [30] have also been performed. The results, collected in Table 3, show a faster convergence to the CBS limit when augmented

Table 3 Equilibrium geometries and energies of NH_3^- computed at the coupled cluster level of theory employing different basis sets. Extrapolated geometries and energies to valence correlation limit (CBS) and best estimates of the equilibrium structure (CBS+CV) are also reported

	N–H (Å)	$\angle\text{HNH}$ (deg.)	Energy (hartree)
$\text{NH}_3^- (^2A_1)$			
aug-cc-pVTZ	1.0214	104.97	–56.4568157
aug-cc-pVQZ	1.0187	105.15	–56.4739223
aug-cc-pV5Z	1.0175	105.24	–56.4808625
aug-cc-pV6Z	1.0168	105.30	–56.4861991
cc-pVQZ	1.0369	102.09	–56.4043095
cc-pV5Z	1.0328	102.98	–56.4275621
cc-pV6Z	1.0291	103.29	–56.4444754
cc-pwCVQZ (f.c.)	1.0370	102.09	–56.4055270
cc-pwCVQZ (all)	1.0356	102.20	–56.4620375
CBS-I ^a	1.0162	105.34	–56.4872394
CBS-II ^b			–56.4882064
CBS+CV ^c	1.0148	105.45	–56.5442334

(f.c.) and (all) denote calculations correlating only valence and all electrons, respectively

^a CBS geometries and energies evaluated using the n^{-3} extrapolation technique: see text

^b CBS energies evaluated using the mixed exponential/Gaussian function: see text

^c Best estimated equilibrium geometry (Eq. 6) employing the aug-cc-pVnZ bases. For energies, CBS-I and CBS-II mean values have been used

sets are employed. It is also worth noting that largely shorter bond lengths have been obtained when diffuse functions are included: for a given n value, bond distances are shorter by about 0.02 Å.

It is well known that from the literature that the convergence to the CBS limit for the first-row species is expected to be faster than that for the second-row analogues. Actually, the conclusion that can be drawn from this study is that very similar convergence rates can be obtained for first- and second-row analogues when d -augmented sets are employed for the latter. Anyway, it is important to stress that this result may be too optimistic because an atom as light as hydrogen is involved in the geometrical parameters.

As far as core–valence corrections are concerned, they are small but not negligible, i.e., they are of the order of 0.001–0.003 Å for bond lengths and 0.1°–0.2° for angles. What is more interesting is that, as expected, core correlation effects are larger for bond distances involving the phosphorous atom. More precisely, they are about 2–3 times larger.

In the view of a comparison between first- and second-row analogues, it is of particular interest to discuss how structural parameters change from one species to another. The N–H bond distance increases by about 0.01 Å when going from NH_3 to either an ionic (NH_3^+ , NH_3^- , NH_4^+) or radical (NH_2) species, whereas the P–H bond length decreases by about 0.02 Å from PH_3 to the PH_3^+ and PH_4^+ cationic species. On the contrary, P–H remains almost unchanged when going from PH_3 to the PH_2 radical. With respect bond angles,

it should be noted that the $\angle\text{HNH}$ angle varies just a little (1–2°) from NH_3 to NH_3^- , while $\angle\text{HPH}$ enlarges by about 20° from PH_3 to PH_3^+ . It is also worth of mention that, whereas NH_3^+ is planar, PH_3^+ has a pyramidal minimum structure. Another difference between N- and P-containing species that should be stressed is that, when considering negative ions, only for NH_3^- a real minimum has been found.

Some previous theoretical investigations on ammonia, phosphine and their ionic and radical species are available in the literature [6, 31, 32, 34–41]. The most recent and accurate data are reported in Tables 1, 2, 3, 4 and 5. First of all, one can notice an overall agreement. As far as nitrogen-containing species are concerned, some benchmark results are available, in particular for ammonia. The comparison to them allows us to calibrate the accuracy of the computations performed for the compounds which contain phosphorous. Concerning this, we are confident that we are able to get equilibrium distances with an accuracy better than 0.001 Å. As concerns the comparison to experiment, a good agreement is noticed, further confirming the quality of the approach followed. Then, the recommendation that can be derived from the results given in Tables 1, 2, 3, 4 and 5 and from what reported above is that a basis set of at least quintuple-zeta quality should be used and core valence effects should be taken into account if accurate results are required.

Finally, as mentioned in the computational section, the transition states for the inversion motion of ammonia as well as phosphine have been optimized at the coupled cluster level

Table 4 Equilibrium geometries (T_d symmetry) and energies of NH_4^+ and PH_4^+ computed at the coupled cluster level of theory employing different basis sets. Extrapolated geometries and energies to valence

correlation limit (CBS) and best estimates of the equilibrium structure (CBS+CV) are also reported

	X–H (Å)	Energy (hartree)	Ref.
NH_4^+ (1A_1) X=N			
CCSD(T)/aug-cc-pVQZ	1.0217	–56.833285	[32]
CCSD(T)/CBS+CV ^a	1.0203		[48]
cc-pVQZ	1.0214	–56.8323728	This work
cc-pV5Z	1.0212	–56.8374099	This work
cc-pV6Z	1.0211	–56.8391381	This work
cc-pwCVQZ (f.c.)	1.0214	–56.8334290	This work
cc-pwCVQZ (all)	1.0205	–56.8903849	This work
CBS-I ^b	1.0211	–56.8413388	This work
CBS-II ^c		–56.8401437	This work
CBS+CV ^d	1.0202	–56.8976971	This work
Experiment ^e	1.0208		[49]
PH_4^+ (1A_1) X=P			
CCSD(T)/aug-cc-pVTZ	1.3972		[38]
cc-pV(Q+d)Z	1.3937	–343.0181897	This work
cc-pV(5+d)Z	1.3935	–343.0220795	This work
cc-pV(6+d)Z	1.3935	–343.0235350	This work
cc-pwCV(Q+d)Z (f.c.)	1.3933	–343.0194454	This work
cc-pwCV(Q+d)Z (all)	1.3905	–343.3319064	This work
CBS-I ^b	1.3935	–343.0251736	This work
CBS-II ^c		–343.0243820	This work
CBS+CV ^d	1.3907	–343.3372387	This work

(f.c.) and (all) denote calculations correlating only valence and all electrons, respectively

^a CBS from CCSD(T)/cc-pV(Q,5)Z results. CV correction at the CCSD(T)/cc-pwCVQZ level^b CBS geometries and energies evaluated using the n^{-3} extrapolation technique: see text^c CBS energies evaluated using the mixed exponential/Gaussian function: see text^d Best estimated equilibrium geometry employing Eq. 6: see text. For energies, CBS-I and CBS-II mean values have been used^e Equilibrium structure derived by employing vibrational corrections from CH_4

employing different basis sets. As well known from the literature, for both species the transition state has planar structure. The results, given in Table 6, show that the convergence is smooth even if, somewhat surprisingly, the N–H distance increases by enlarging the basis. The extent of the CV corrections are similar to those already observed for the minima. Consequently, similar conclusions can be drawn and the best estimated geometries, also reported in Table 6, are expected to have similar accuracy.

3.2 Thermochemical properties

Adiabatic ionization potentials

$$IP_{\text{ad}}^{\text{e}} = E_{\text{e}}(\text{cation}) - E_{\text{e}}(\text{neutral}) \quad (8)$$

have been obtained at the coupled-cluster level by using equilibrium total energies E_{e} of the neutral and cationic species. Analogously, adiabatic electron affinities have been derived by the following expression:

$$EA_{\text{ad}}^{\text{e}} = E_{\text{e}}(\text{neutral}) - E_{\text{e}}(\text{anion}), \quad (9)$$

thus employing total energies of neutral and anionic species. From the energies computed so far, the N–H equilibrium dissociation energies corresponding to the following reactions can be evaluated:



where the third reaction essentially defines the proton affinity (PA) of ammonia at $T = 0$ K. Analogously, the P–H

Table 5 Equilibrium geometries and energies of NH₂ and PH₂ computed at the coupled cluster level of theory employing different basis sets. Extrapolated geometries and energies to valence correlation limit (CBS) and best estimates of the equilibrium structure (CBS+CV) are also reported

	X–H (Å)	∠HXH (deg.)	Energy (hartree)	Ref.
NH ₂ (² B ₁) X = N				
CCSD(T)/aug-cc-pCV5Z	1.0236	103.152		[35]
cc-pVQZ	1.0250	102.72	–55.8107785	This work
cc-pV5Z	1.0248	102.95	–55.8162743	This work
cc-pV6Z	1.0247	103.01	–55.8180641	This work
cc-pwCVQZ (f.c.)	1.0251	102.72	–55.8119225	This work
cc-pwCVQZ (all)	1.0238	102.85	–55.8681679	This work
CBS-I ^a	1.0246	103.08	–55.8202149	This work
CBS-II ^b			–55.8191054	This work
CBS+CV ^c	1.0233	103.21	–55.8759055	This work
Experiment ^d	1.0254 (12)	102.85 (14)		[50]
Experiment ^e	1.039	103.105		[35]
PH ₂ (² B ₁) X = P				
CCSD(T)/cc-pV5Z PES ^f	1.4183	91.81		[40]
cc-pV(Q+d)Z	1.4186	91.87	–342.0709623	This work
cc-pV(5+d)Z	1.4183	91.88	–342.0745014	This work
cc-pV(6+d)Z	1.4183	91.88	–342.0758489	This work
cc-pwCV(Q+d)Z (f.c.)	1.4181	91.88	–342.0720407	This work
cc-pwCV(Q+d)Z (all)	1.4153	91.81	–342.3849110	This work
CBS-I ^a	1.4183	91.88	–342.0774387	This work
CBS-II ^b			–342.0766332	This work
CBS+CV ^c	1.4155	91.81	–342.3899063	This work

(f.c.) and (all) denote calculations correlating only valence and all electrons, respectively

^a CBS geometries and energies evaluated using the n^{-3} extrapolation technique: see text

^b CBS energies evaluated using the mixed exponential/Gaussian function: see text

^c Best estimated equilibrium geometry employing Eq. 6: see text. For energies, CBS-I and CBS-II mean values have been used

^d Equilibrium structure

^e Empirical equilibrium structure: from a least-squares fit of the molecular structural parameters to equilibrium rotational constants derived from the experimental ground-state constants and the theoretical vibrational corrections (at the RCCSD(T)/(aug)-cc-pCVQZ level)

^f Minimum of the PES

equilibrium dissociation energies corresponding to the following reactions can be evaluated:



where the third reaction essentially defines the proton affinity (PA) of phosphine at $T = 0$ K. More precisely, the equilibrium dissociation energies, D_e , have been determined as the difference between the minimum energy of the reactant and the sum of the energy of the separated fragments at their equilibrium geometry.

Ionization potentials and electron affinities computed at the CCSD(T) level employing different basis sets are summa-

rized in Table 7, whereas the results for dissociation energies and proton affinities are given in Table 8.

From Table 7 it is evident that the convergence to the infinite basis set limit is smooth and the CV corrections are small for both ammonia and phosphine. Going in detail, as already noticed for structural parameters, the convergence to the CBS limit of IP_{ad}^e of phosphine is as fast as that of ammonia. Again, the core correlation effects are larger for the second-row analogue. It may be interesting to note that, as expected, IP of PH₃ is smaller than that of NH₃. It is also worth of mention the overall good agreement between the present results and those previously reported.

With respect to Table 8, first of all, it should be noted that for both N- and P-containing species the dissociation energy increases by enlarging the basis set for neutral species, while it decreases when cations are involved. As previously seen

Table 6 Transition state (TS) geometries (planar: D_{3h}), energies and barrier height for inversion motion of NH_3 and PH_3 computed at the coupled cluster level of theory employing different basis sets. Extrapolated

geometries and energies to valence correlation limit (CBS) and best estimates of the equilibrium structure (CBS+CV) are also reported

	X–H (Å)	Energy (hartree)	ΔE^a (kcal/mol)	Ref.
NH_3 (X=N)				
CCSD(T)/aug-cc-pVQZ	0.99598		5.34	[51]
CCSD(T)/aug-cc-pVQZ	0.994		5.20	[52]
cc-pVQZ	0.9949	−56.4838236	5.79	This work
cc-pV5Z	0.9952	−56.4908220	5.41	This work
cc-pV6Z	0.9954	−56.4930196	5.30	This work
cc-pwCVQZ (f.c.)	0.9949	−56.4849787	5.78	This work
cc-pwCVQZ (all)	0.9940	−56.5420149	5.59	This work
CBS-I ^b	0.9955	−56.4956462	5.20	This work
CBS-II ^c		−56.4942980	5.24	This work
CBS+CV ^d	0.9946	−56.5520083	5.03	This work
CBS+CV+ZPV ^e			5.42	This work
Experiment			5.39	[53]
PH_3 (X=P)				
MP2/aug-cc-pV5Z	1.367		32.43	[52]
B3LYP/aug-cc-pV5Z	1.379		33.45	[52]
cc-pV(Q+d)Z	1.3792	−342.6547834	34.40	This work
cc-pV(5+d)Z	1.3784	−342.6606261	33.31	This work
cc-pV(6+d)Z	1.3783	−342.6622927	33.23	This work
cc-pwCV(Q+d)Z (f.c.)	1.3779	−342.6574841	33.47	This work
cc-pwCV(Q+d)Z (all)	1.3749	−342.9703220	33.60	This work
CBS-I ^b	1.3783	−342.6641734	33.18	This work
CBS-II ^c		−342.6632632	33.18	This work
CBS+CV ^d	1.3753	−342.9765562	33.31	This work
CBS+CV+ZPV ^e			34.07	This work
QCISD(T)/6-311+G(2d,p) + ZPE(MP2)			33.8	[54]

(f.c.) and (all) denote calculations correlating only valence and all electrons, respectively

^a Inversion barrier: $\Delta E = E_{TS} - E_{\min}$ (total energies from this Tables 1 and 6)^b CBS geometries and energies evaluated using the n^{-3} extrapolation technique: see text^c CBS energies evaluated using the mixed exponential/Gaussian function: see text^d Best estimated equilibrium geometry employing Eq. (6): see text. For energies, CBS-I and CBS-II mean values have been used^e Zero point vibrational corrections added to the best estimated equilibrium value

for IP and EA , the convergence to the infinite basis set limit is smooth, and the convergence behavior and rate for the first- and second-row analogues are similar. In regard to the CV corrections, they are small but not entirely negligible, and, as already noticed, they are larger for the phosphorous-containing species. As expected, the dissociation energies of bonds involving P are lower (by about 20–30 kcal/mol) than that of the corresponding N analogues.

Therefore, from the results collected in Tables 7 and 8, we may conclude that a similar accuracy can be obtained for first- and second-row atoms containing molecules.

For all the species investigated, calculations of the harmonic frequencies have been performed, allowing the evaluation of the zero-point vibrational (ZPV) energy corrections in the harmonic approximation:

$$E_{ZPV}^{\text{harm}} = \frac{1}{2} \sum_i d_i \omega_i, \quad (16)$$

where d_i and ω_i are the degeneracy and the harmonic frequency of the i th vibrational mode, respectively. The computations have been performed employing the (R/U)CCSD(T) method in conjunction with the cc-pVQZ basis set (cc-pV

Table 7 Adiabatic ionization potentials of ammonia and phosphine and adiabatic electron affinity of ammonia evaluated at the coupled cluster level. Extrapolated values to the infinite basis limit (CBS), best estimates (CBS+CV) and zero-point corrected values are also reported

	IP_{ad} (eV)	EA_{ad} (eV)
NH ₃		
G2(MP2) ^a	10.19	
B3LYP/6-31G* ^b	10.829	-2.302
cc-pVQZ	10.14	-2.41
cc-pV5Z	10.19	-1.96
cc-pV6Z	10.21	-1.55
cc-pwCVQZ (f.c.)	10.14	-2.41
cc-pwCVQZ (all)	10.15	-2.42
CBS ^c	10.22	-1.49
CBS+CV ^d	10.22	-1.50
Zero-point corrected ^e	10.18	-1.41
CBS+CV+SR+FCI+ZPV ^f	10.171 (3)	
W3 ^g	10.184	
Experiment ^h	10.07 (2)	
PH ₃		
G2(MP2) ^a	9.84	
cc-pVQZ	9.81	
cc-pV5Z	9.83	
cc-pV6Z	9.84	
cc-pwCVQZ (f.c.)	9.82	
cc-pwCVQZ (all)	9.84	
CBS ^c	9.85	
CBS+CV ^d	9.87	
Zero-point corrected ^e	9.86	
W3 ^g	9.881	
Experiment ^h	9.869 (2)	

(f.c.) and (all) denote calculations correlating only valence and all electrons, respectively

^a Ref. [55]

^b Ref. [56]

^c From mean CBS energy values. See text

^d CV corrections added to mean CBS energy values. See text

^e Vibrational corrections added to the CBS+CV values

^f Ref. [32]: CBS from CCSD(T)/aug-cc-pVnZ, with $n = Q, 5, 6$, computations; CV corrections at the CCSD(T)/cc-pCVQZ level; scalar relativistic (SR) corrections at the CISD/cc-pVQZ level; full-CI (FCI) corrections at the FCI/cc-pVTZ level; ZPV corrections from the empirically corrected potentials of Martin et al. For details see Ref. [32]

^g Ref. [33]: W3 theory

^h NIST Database, 2004 (<http://webbook.nist.gov>)

(Q+d)Z for P). The (R/U)CCSD(T)/cc-pVQZ harmonic force fields have been evaluated in a cartesian coordinate representation at the corresponding optimized geometry using the MOLPRO package (See footnote 1). As for the energy gradients, the hessian matrix was calculated numerically by finite differences [21, 22]. Then, IP_0 , EA_0 and D_0 have been derived from the corresponding equilibrium IP_e , EA_e and D_e values by adding the appropriate zero-point energy differences. These results, collected in Tables 7 and 8, allow

the comparison to experimental data, which are vibrational ground state data.

From Table 7 it can be pointed out that the vibrational corrections are small but not negligible. In particular, they allow to get an IP_0 value in very good agreement with the highly accurate benchmark results of Refs. [32, 33] for ammonia and of Ref. [33] for phosphine. It also has to be noted the very good agreement with experiment. As far as dissociation energies are concerned, the ZPV corrections are clearly relevant,

Table 8 N-H and P-H dissociation energies and proton affinities of ammonia and phosphine evaluated at the coupled cluster level. Extrapolated values to the infinite basis limit (CBS), best estimates (CBS+CV) and zero-point corrected values are also reported

NH ₃	NH ₃ → NH ₂ + H (kcal/mol)	NH ₃ ⁺ → NH ₂ + H ⁺ (kcal/mol)	NH ₄ ⁺ → NH ₃ + H ⁺ (kcal/mol)
BP86/QZ4P//BP86/TZ2P ^a			203.2
cc-pVQZ	114.41	194.27	212.93
cc-pV5Z	114.95	193.62	212.07
cc-pV6Z	115.09	193.43	211.89
cc-pwCVQZ (f.c.)	114.41	194.21	212.88
cc-pwCVQZ (all)	114.72	194.43	213.01
CBS ^b	115.23	193.29	211.75
CBS+CV ^c	115.54	193.52	211.89
Zero-point corrected ^d	105.90	184.85	202.26
CBS+CV+SR+FCI+ZPV ^e		202.43	
CBS+fT+fQ+Rel+ZPV+DBOC ^f	106.02		
CCSD(T)/6-311++G(3df/2pd) ^g	103.7	185.0	
Experiment	106.1 (3) ^h		202.5 (10) ⁱ
PH ₃	PH ₃ → PH ₂ + H (kcal/mol)	PH ₃ ⁺ → PH ₂ + H ⁺ (kcal/mol)	PH ₄ ⁺ → PH ₃ + H ⁺ (kcal/mol)
BP86/QZ4P//BP86/TZ2P ^a			185.3
B3LYP/6311+G** ^j			187.4
cc-pVQZ	87.03	174.46	193.64
cc-pV5Z	87.35	174.33	193.51
cc-pV6Z	87.47	174.26	193.46
cc-pwCVQZ (f.c.)	87.12	174.47	193.66
cc-pwCVQZ (all)	87.23	174.05	193.30
CBS ^b	87.57	174.18	193.39
CBS+CV ^c	87.68	173.76	193.03
Zero-point corrected ^d	81.03	167.25	185.85
CCSD(T)/6-311++G(3df/2pd) ^g	79.5	168.5	
Experiment ^h	82.44	168.31	188 ^k

(f.c.) and (all) denote calculations correlating only valence and all electrons, respectively

^a Ref. [57]

^b From mean CBS energy values. See text

^c CV corrections added to mean CBS energy values. See text

^d Vibrational corrections added to the CBS+CV values

^e Ref. [32]: CBS from CCSD(T)/aug-cc-pVnZ, with $n = Q, 5, 6$, computations; CV corrections at the CCSD(T)/cc-pCVQZ level; SR corrections at the CISD/cc-pVQZ level; ZPV corrections from the empirically corrected potentials of Martin et al. For details see Ref. [32]

^f Ref. [42]: CBS [(all)CCSD(T)/aug-cc-pCV∞Z] + full-T corrections [CCSDT-CCSD(T)/cc-pV(T,Q)Z] + full-Q corrections [CCSDTQ-CCSDT/cc-pVDZ] + Scalar relativistic effects [CCSD(T)/aug-cc-pCVTZ] + vibrational corrections [CCSD(T)/cc-pVQZ] + DBOC corrections (HF-SCF)

^g Ref. [7]: D_0 values. Energy calculations performed at the B3LYP/6-31++G(d,P) optimized geometries. Vibrational corrections computed at the B3LYP level

^h Value derived from the experimental data at 298 K: 108.2(3) kcal/mol [58,59]

ⁱ Value derived from the experimental data at 298 K: 204(1) kcal/mol [60,61]

^j Ref. [62]

^k NIST Database, 2004 (<http://webbook.nist.gov>)

i.e., of the order of 5–10%, and thus they are important in order to get a good agreement with the available experimental values. It is also worth of mention to note how well our zero-point corrected data agree with the benchmark results reported in Ref. [42] for D_0 of NH₃ and in Ref. [32] for PA of

NH₃. Therefore, the conclusion that can be drawn is that the approach followed allow us to get results of nearly benchmark quality for nitrogen-containing compounds. Since the properties of the second-row analogues show the same behavior, we can assume for them the same accuracy.

One spectroscopic peculiarity of pyramidal molecules is the inversion motion. The energy difference between the TS and minimum structures provides the barrier height for it. The results for ammonia as well as phosphine are collected in Table 6. From this table, in the first place, it is clear why ammonia has a marked inversion motion, whereas this is not experimentally observable for phosphine. It has also to be noted that for both NH_3 and PH_3 the barrier decreases by enlarging the basis set, whereas the CV correction is positive for phosphine and negative for ammonia. Finally, a good agreement with previous results, both theoretical and experimental, is observed.

4 Conclusions

The structural and thermochemical properties of ammonia, phosphine, and related radicals, cations and anions have been accurately investigated using the CCSD(T) method with systematic treatments of basis set truncation errors and core–valence correlation effects. Where available the present results are in excellent agreement with experiment and benchmark calculations. As far as molecular structures are concerned, the accuracy reached in the present study is estimated to be better than 0.001 Å for bonds and 0.1° for angles. The CCSD(T) ionization potentials, electron affinity and dissociation energy presented in this work are estimated to be accurate within about 0.01–0.02 eV and 0.5–1 kcal/mol, respectively.

On the whole, we are confident that all the properties studied in this investigation are useful for improving the knowledge and for a better understanding of the differences between the structure and thermochemistry of the molecules containing nitrogen and those involving its second-row analogue P. In addition, we have shown that the approach followed is able to provide results of nearly benchmark quality not only for the nitrogen-containing compounds but also for the second-row analogues.

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