Theor Chem Account (2008) 121:1–10
DOI 10.1007/s00214-008-0409-8

REGULAR ARTICLE

Ab initio characterization of XH_3 ($X = N,P$). Part II. Electric, magnetic and spectroscopic properties of ammonia and phosphine

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Received: 18 November 2007 / Accepted: 4 January 2008 / Published online: 29 January 2008

Abstract The coupled cluster theory in conjunction with core valence triple and quadruple zeta basis sets has been employed for investigating electric, magnetic and spectroscopic properties of ammonia and phosphine. Namely molecular dipole and quadrupole moments, NMR shielding and spin-rotation constants, as well as spectroscopic properties such as rotational and centrifugal distortion constants as well as harmonic and anharmonic frequencies of NH_3 and PH_3 have been determined at a high level of accuracy. To obtain parameters directly comparable to experiment, vibrational effects have also been taken into account. In addition, the basis set convergence has been investigated for the molecular dipole moment.

Keywords Ammonia · Phosphine · Ab initio calculation · Dipole and quadrupole moment · Magnetic shielding · Spin-rotation constants · Spectroscopic parameters

1 Introduction

In view of investigating the difference between molecules containing second-row atoms and their first-row analogs, as a continuation of the study on structure and thermochemistry carried out in Ref. [1], some electric and magnetic as well as spectroscopic properties of ammonia and phosphine have been investigated. To have a meaningful comparison, high-level ab initio methods should be employed. The most accurate non-relativistic methods presently used to study a variety of molecular properties are based on the coupled cluster wavefunction (see for instance Ref. [2–7] and references therein). In addition, errors due to core correlation effects as well as incompleteness of the basis set cannot be neglected. Furthermore, to obtain results suitable for a direct comparison with experiment, one has also to take into account vibrational corrections.

Rotational and NMR spectroscopy are important experimental tools for probing molecular structure and properties. To analyze and understand such spectroscopic information, quantum chemical calculations of spectroscopic as well as NMR parameters are very helpful. In this view the choice of the properties investigated in this work can be understood. Going into details, we decided to study the electric molecular dipole and quadrupole moments, the nitrogen quadrupole coupling constant (of course, only for ammonia), as well as the NMR shielding and spin-rotation constants. As far as spectroscopic parameters are concerned, rotational, centrifugal distortion and vibro-rotation interaction constants as well as harmonic and anharmonic frequencies have been considered.

2 Methodology and theoretical details

The coupled-cluster level of theory with single and double excitations, and a quasiperturbative account for triples substitutions [CCSD(T)] [8] has been employed throughout in conjunction with correlation consistent basis sets. This level of theory has been chosen as it is proved to provide very accurate results for molecular and spectroscopic properties. In fact, the CCSD(T) method in conjunction with large basis sets is able to give almost quantitative results, when core correlation effects are also taken into account (see for instance Refs. [4,5,9–15]).

First of all, the molecular dipole moment has been deeply investigated. This has been evaluated as a first derivative

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of the total energy with respect to a homogeneous electric field at zero field strength. More precisely, the results have been obtained from computations in which finite perturbations with electric field strengths of ±0.0001 a.u. have been applied and then the dipole moment has been calculated from central-differences numerical differentiation of the energy. Since inclusion of diffuse functions in the basis set is particularly important for an accurate evaluation of this property, the calculations have been carried out with the aug-cc-pV(n+d)Z (n = Q,5,6) series of bases for P [16] and the aug-cc-pVnZ (n = Q,5,6) basis sets for H and C [17] (frozen core), and with the aug-cc-pwCVQZ (aug-cc-pwCV(Q+d)Z for P) basis set for accounting for core-valence effects (frozen core and all electrons). The augmented aug-cc-pwCVQZ sets have been obtained by adding the opportune diffuse functions [17] to the corresponding core-valence set [18], whereas the aug-cc-pwCV(Q+d)Z for P has been obtained by adding the appropriate tight [18] functions to the aug-cc-pV(Q+d)Z set [16]. As suggested in Ref. [18], the 1s electrons of P have not been correlated in any computations. All computations have been carried out at the corresponding best estimated geometry from Ref. [1] employing the MOLPRO package [19].

Since we have used hierarchical sequences of bases and μ exhibited a monotonic trend, the dipole moment has been extrapolated to the complete basis set (CBS) limit using the $1/n^3$ extrapolation form [20]:

$$\Delta\mu^{\mathrm{corr}}(n) = \Delta\mu^{\mathrm{corr}}_{\infty} + A\,n^{-3} \tag{1}$$

and it is applied to the case $n = 5$ and 6. To obtain the extrapolated dipole moment, 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/aug-cc-pV6Z level:

$$\mu(\mathrm{CBS}) = \mu^{\mathrm{SCF}}_{\infty} + \Delta\mu^{\mathrm{corr}}_{\infty}. \tag{2}$$

The best estimate of the dipole moment has then been obtained by adding to the CBS limit the core-valence (CV) correction determined using the aug-cc-pwCVQZ basis set:

$$\begin{aligned}\mu_e(\mathrm{CBS}+\mathrm{CV}) \simeq \mu(\mathrm{CBS, valence}) + \mu(\mathrm{awCVQZ, all})\\ -\mu(\mathrm{awCVQZ, valence}),\end{aligned} \tag{3}$$

where μ(awCVQZ, all) and μ(awCVQZ, valence) are the molecular dipole moment computed at the CCSD(T)/aug-cc-pwCVQZ level correlating all and only valence electrons, respectively.

As already mentioned in the Introduction, the quadrupole moment, the nuclear quadrupole coupling tensor, as well as the NMR shielding and spin-rotation constants have been evaluated at the CCSD(T) level of theory. Since for all these properties theoretically justified extrapolation formula to the CBS limit are not available in the literature, we restrict our discussion to the results obtained with a basis set as large as the core-valence cc-pwCVQZ. In some cases, the cc-pwCVTZ basis has also been considered. In all cases only all electrons calculations have been performed and, since weighted core-valence sets have been used, the 1s electrons of P have not been correlated in any computations. Furthermore, for magnetic properties the rotational London Atomic Orbitals [21] have been used to avoid unphysical gauge-origin dependence of the properties investigated as well as to improve basis-set convergence. For these computations the Mainz-Austin-Budapest (MAB) development version of the ACESII program package [22] has been employed.

The permanent multiple moments characterize the charge distribution in a molecule. The zeroth (monopole) moment corresponds to the total charge, the first moment to the dipole, the second moment to the quadrupole, etc. Therefore, they can be computed as the average values of the corresponding multipole moment operator. In particular, the molecular quadrupole moment operator, as defined by Buckingham [23], is given by

$$\mathbf{\Theta}_{\alpha,\beta} = \mathbf{\Theta}_{\beta,\alpha} = \frac{1}{2}\sum_i e_i(3r_{i\alpha}r_{i\beta} - r_i^2\delta_{\alpha,\beta}) \tag{4}$$

with e_i being the ith element of charge at location r_i relative to some fixed origin in the molecule and $\delta_{\alpha,\beta}$ denoting Kroneckers delta.

For nuclei with a quadrupole moment, the interaction of the latter (defined for nucleus K as $-eQ_K$) with the electric field gradient at that nucleus $\boldsymbol{V}^K$ is given by [24]

$$H_{\mathrm{Q}} = \frac{1}{2}\sum_K \frac{-eQ_K}{I_K(2I_K-1)}\boldsymbol{I}_K \cdot \boldsymbol{V}^K \cdot \boldsymbol{I}_K, \tag{5}$$

where $\boldsymbol{I}_K$ denotes the nuclear spin and the sum runs over all the K nuclei. The elements of the nuclear quadrupole coupling tensor for the nucleus K are then defined as

$$\chi_{ij} = -eQ_K V^K_{ij}/\hbar, \tag{6}$$

where i, j refer to the inertial axes a, b, or c. Since, in order to have a nuclear quadrupole moment the nuclear spin quantum number I_K must be ≥1, we have such an interaction only for nitrogen in NH_3.

The nuclear magnetic shielding tensor σ is a second-order response property with magnetic field and nuclear magnetic moment as the corresponding perturbations. Accordingly, it is defined by the second derivative of the electronic energy with respect to the nuclear magnetic moment $\mathbf{m}_N$ and to the external magnetic field $\mathbf{B}$ (see for example the general discussion in Ref. [2]):

$$\sigma = \left.\frac{\partial^2 E^{\mathrm{el}}}{\partial\mathbf{m}_N\partial\mathbf{B}}\right|_{\mathbf{m}_N,\mathbf{B}=0}. \tag{7}$$

Therefore, this is efficiently computed using analytic second derivative techniques nowadays available for coupled-cluster methods [25,26].

To describe the interaction between the nuclear magnetic dipole and the effective magnetic field of a rotating molecule, Flygare derived a formulation in terms of a second rank tensor **C** coupled with the rotational **J** and nuclear spin **I** momenta [27]:

$$H_{\rm SR} = \sum_K \boldsymbol{I}_K \cdot \boldsymbol{C}_K \cdot \boldsymbol{J}, \tag{8}$$

where the sum runs over the K nuclei of the molecule. Each element of the spin-rotation tensor has an electronic and a nuclear contribution. The electronic contribution can be theoretically defined as the second derivative of the electronic energy with respect to the rotational angular momentum $\boldsymbol{J}$ and the nuclear spin $\boldsymbol{I}_K$ [28]

$$\mathbf{C}_K^{\rm el} = \left.\frac{\partial^2 E^{\rm el}}{\partial \mathbf{I}_K \partial \mathbf{J}}\right|_{\mathbf{I}_K,\mathbf{J}=0}, \tag{9}$$

and therefore it is efficiently computed using analytic second derivatives [21]. On the other hand, the nuclear contribution $\boldsymbol{C}_K^{\rm nucl}$ depends only on the molecular geometry, on g_K (which is the nuclear g-value of nucleus K), and μ_N (the Bohr magneton):

$$\mathbf{C}_K^{\rm nucl} = -\alpha^2 \mu_N g_K \times \sum_{L\neq K} Z_L \frac{(\mathbf{R}_L-\mathbf{R}_K)\cdot(\mathbf{R}_L-\mathbf{R}_K)\mathbf{1}-(\mathbf{R}_L-\mathbf{R}_K)(\mathbf{R}_L-\mathbf{R}_K)}{|\mathbf{R}_L-\mathbf{R}_K|^3}\mathbf{I}^{-1}. \tag{10}$$

Anharmonic force field calculations have been carried out for the main isotopic species of ammonia and phosphine, i.e., $^{14}NH_3$ and $^{31}PH_3$. The cubic force fields have been evaluated at the CCSD(T)/cc-pwCVTZ and CCSD(T)/cc-pwCVQZ levels correlating all electrons but 1s of P. More precisely, the quadratic (f_{ij}), cubic (f_{ijk}) and semidiagonal quartic (f_{ijkk}) normal coordinates force constants have been computed. The harmonic part of the force field has been obtained using analytic second derivatives of the energy [29], and the corresponding cubic force field has been determined in a normal coordinate representation via numerical differentiation of the analytically evaluated force constants as described in Refs. [30,31]. Subsequently, the force field has been used to compute spectroscopic constants by means of the vibrational second-order perturbation theory [32]. The MAB development version of the ACESII program package [22] has been employed.

The force field evaluations also allowed the determination of the zero-point vibrational (ZPV) corrections to the molecular properties investigated. The perturbational approach followed is that described in Ref. [5] for NMR shielding tensors and can be automatically performed in the MAB development version of ACESII. Shortly, the procedure consists in expanding the expectation value of the generic property X over the vibrational wavefunction in a Taylor series around the equilibrium value with respect to normal-coordinate displacements

$$\langle \mathbf{X}\rangle = \mathbf{X}_{\rm eq} + \sum_r \left(\frac{\partial \mathbf{X}}{\partial Q_r}\right)_{Q=0}\langle Q_r\rangle + \frac{1}{2}\sum_{r,s}\left(\frac{\partial^2 \mathbf{X}}{\partial Q_r \partial Q_s}\right)_{Q=0}\langle Q_r Q_s\rangle + \cdots, \tag{11}$$

where the expansion is truncated after the quadratic term. The expectation values over Q_r and $Q_r Q_s$ are evaluated using a perturbation theory treatment starting from the rigid-rotator harmonic-oscillator approximation [32]. The corresponding expressions are in lowest order

$$\langle Q_r\rangle = -\frac{\hbar}{4\omega_r^2}\sum_s \frac{k_{rss}}{\omega_s} \tag{12}$$

and

$$\langle Q_r Q_s\rangle = \delta_{rs}\frac{\hbar}{2\omega_r}, \tag{13}$$

where ω_r denotes the harmonic frequency of the rth normal mode and k_{rss} the cubic force constants within a normal-coordinate representation. The expansion of Eq. (11) has been already successfully employed to investigate vibrational effects on various molecular properties (see, as examples, Refs. [5,11,12,14]). In the case of the dipole moment, the vibrational correction, defined as the difference between the equilibrium and vibrationally averaged values, has been added to the best estimate (CBS+CV) for obtaining the corresponding zero-point corrected parameter that can be directly compared to the available experimental data.

3 Results and discussion

The only non-vanishing dipole moment component is along the z inertial axis, i.e., along the C_3 axis. The values obtained employing different basis sets are given in Table 1. As expected, the dipole moment of ammonia is larger than that of phosphine: this is surely ascribed to the decreasing electronegativity from nitrogen to phosphorous. From Table 1 one can notice that for both NH_3 and PH_3 there is a systematic trend, i.e., the absolute value of the dipole moment increases by enlarging the basis set. Anyway, even if basis sets containing additional diffuse functions have been employed for phosphorous, the convergence is faster in the case of ammonia. For both molecules the CV correction is relevant but in the opposite direction: for NH_3 it increases the absolute value of the dipole moment, while for PH_3 it decreases it.

In regard to the comparison with the literature, an overall good agreement is observed. In particular, it deserves a brief

Table 1 Dipole moment (debye) of ammonia and phosphine evaluated at the coupled cluster level employing different basis sets. Extrapolated and best estimated values are also reported

	μ
NH_3	
B3LYP/d-aug-cc-pVTZ[a]	−1.4961
B3PW91/d-aug-cc-pVTZ[a]	−1.5101
CI/cc-pVTZ[a]	−1.6178
MRSD-CI/$5s3p2d-3s2p$[b]	−1.5123
CCSD(T)/aug-cc-pVQZ[c]	−1.521
CCSD(T)/aug-cc-pCVQZ[d,1]	−1.5217
CCSD(T)/aug-cc-pCVQZ[d,2]	−1.5372
CCSD(T)/aug-cc-pVQZ	−1.5061
CCSD(T)/aug-cc-pV5Z	−1.5087
CCSD(T)/aug-cc-pV6Z	−1.5095
CBS	−1.5099
CBS+CV[e]	−1.5157
Zero-point corrected[f]	−1.4764
Best estimate[g]	−1.4762
Experiment[h]	1.471932 (7)
PH_3	
B3LYP/aug-cc-pVTZ[a]	−0.5899
B3PW91/aug-cc-pVTZ[a]	−0.6431
CI/cc-pVTZ[a]	−0.6657
MP2/$11s8p3d2f1g$[i]	−0.648
BD(T)/TZP+ZPV(MP2/TZP)[j]	−0.5566
CCSD(T)/aug-cc-pV(Q+d)Z	−0.6177
CCSD(T)/aug-cc-pV(5+d)Z	−0.6217
CCSD(T)/aug-cc-pV(6+d)Z	−0.6232
CBS	−0.6238
CBS+CV[e]	−0.6151
Zero-point corrected[f]	−0.5879
Best estimate[g]	−0.5878
Experiment[k]	0.57395 (30)

[a] Ref. [41]

[b] Ref. [42]

[c] Ref. [34]: calculated correlating all electrons at the (all)CCSD(T)/aug-cc-pVQZ optimized geometry

[d] Ref. [33]: calculated (1) at the experimental equilibrium structure, (2) at the (all)CCSD(T)/cc-pCVQZ optimized geometry

[e] CV corrections added to the CBS extrapolated values: see text

[f] ZPV correction added to the CBS+CV values (see text)

[g] Full triples corrections added to the zero-point corrected values (see text)

[h] Ref. [43]: absolute value

[i] Ref. [44]

[j] Ref. [36]

[k] Ref. [45]: absolute value

comment the comparison of the various CCSD(T) results obtained for ammonia in conjunction with quadrupole bases and reported in Table 1 (Refs. [33,34] and this work). The main differences consist in slightly different basis sets (aug-cc-pVQZ or aug-cc-pCVQZ), numbers of electrons correlated (frozen core or all electrons) and different reference geometries used in the calculations. It is, therefore, difficult to draw a clear conclusion, but it is evident a strong effect of the equilibrium structure chosen as reference.

To our knowledge, full configuration interaction (FCI) calculations of the dipole moment of either ammonia or phosphine are not available in the literature. Anyway, on the basis of the FCI benchmark calculations of first-order one-electron properties carried out by Halkier et al. for BH and HF [35], we are confident that even for the systems under investigations the CCSD(T) model is a very good approximation of the full CCSDT one and that the error due to the approximate description of triple excitations is comparable in size to that due to the neglect of higher-order excitations. Full triples corrections computed employing the cc-pVTZ basis have been found entirely negligible for both ammonia and phosphine (see Table 1).

Also interesting is how the theoretical values compare with experiment: the agreement is within 0.3% for ammonia and within 2.4% for phosphine. Therefore, for both species a very good agreement is observed. On the one hand, vibrational corrections are essential for getting such a good agreement since they are fairly large, being of the order of 3–5%, and, on the other hand, the faster convergence to the CBS limit for NH_3 is very likely responsible for the better agreement observed. For both species the vibrational corrections decrease the absolute value of the dipole moment.

Equilibrium and vibrationally averaged values of other electric and some magnetic properties are summarized in Tables 2 and 3, respectively. More in detail, the molecular quadrupole moment and nitrogen quadrupole coupling constant are reported in the former table, whereas NMR shielding and spin-rotation constants are collected in the latter. In both tables the results obtained in the present work are also compared to the theoretical and experimental data available in the literature. In the first place, a general good agreement has to be noted for all the properties investigated, and the main conclusion that can be drawn is that the CCSD(T)/cc-pwCVQZ level of theory is able to provide accurate results for both ammonia and phosphine. Furthermore, it should be pointed out that vibrational corrections have to be taken into account in order to improve the agreement with experiment.

Concerning electric properties (Table 2), the molecular quadrupole tensor as well as the nuclear quadrupole coupling one are traceless. In our particular case, since ammonia and phosphine belongs to the C_{3v} symmetry group, these tensors are diagonal, and

$$\Theta_{xx} = \Theta_{yy} = -1/2\Theta_{zz},$$

$$\chi_{xx} = \chi_{yy} = -1/2\chi_{zz}.$$

The traceless quadrupole moment describes the deviation from an isotropic charge distribution, vanishing with a spher-

Table 2 Electric properties of ammonia and phosphine evaluated at the coupled cluster level[a]: quadrupole moment and quadrupole coupling constant of nitrogen

	Θ^{b}_{zz} (a.u.)	χ^{c}_{zz} (MHz)
NH_3		
B3LYP/d-aug-cc-pVTZ[d]	−2.3236	
B3PW91/d-aug-cc-pVTZ[d]	−2.3031	
aug-cc-pCVQZ-equilibrium	−2.184	
cc-pwCVQZ-equilibrium	−2.066	−4.163
cc-pwCVQZ-vibrationally averaged	−2.086	−4.181
Best estimate[e]	−2.204	
Experiment	−2.42 (4)[f]	−4.0915[g]
PH_3		
B3LYP/d-aug-cc-pVTZ[d]	−1.6674	
B3PW91/d-aug-cc-pVTZ[d]	−1.6386	
MP2/11$s8p3d2f1g$[h]	−1.683	
BD(T)/TZP+ZPV(MP2/TZP)[i]	−1.5566	
aug-cc-pCVQZ-equilibrium	−1.596	
cc-pwCVQZ-equilibrium	−1.583	
cc-pwCVQZ-vibrationally averaged	−1.540	
Best estimate[e]	−1.553	
Experiment[j]	−1.56 (70)	

[a] Computations performed correlating all electrons (but 1s of P)

[b] For molecules belonging to the C_{3v} symmetry group: $\Theta_{xx} = \Theta_{yy} = -1/2\Theta_{zz}$. See text

[c] The nitrogen quadrupole coupling constant χ_{zz} is derived from the values of the corresponding electric field gradient V_{zz} at the N nucleus: $\chi_{ij} = -eQ_K V^K_{ij}/\hbar$. See text

[d] Ref. [41]

[e] Vibrational correction added to (all)CCSD(T)/aug-cc-pCVQZ equilibrium value, see text

[f] Ref. [46]

[g] Ref. [47]

[h] Ref. [44]

[i] Ref. [36]

[j] Ref. [48]

ical charge distribution. Therefore, from the results reported in Table 2 we can deduce that this deviation is larger for ammonia than for phosphine. By comparing our results to experiment, we note that vibrational corrections are in the right direction, i.e., they make theoretical values closer to experiment, even if, as expected [36], they are relative small: ∼1% for ammonia and about 3% for phosphine. More in detail, they increase the absolute value for NH_3, whereas they decrease it for PH_3. Furthermore, as already observed for the dipole moment, the absolute value decrease going from ammonia to phosphine. It is worthwhile noting that the results for phosphine seems to be more accurate than those for nitrogen. In particular, by comparing theory to experiment for NH_3 a discrepancy of about 14% is observed, whereas for phosphine the agreement is within ∼1%. Since there is no reason for the latter being more accurate, but at least the opposite is expected, we believe that the experimental value for ammonia is not as accurate as claimed by the given uncertainty. This conclusion is also supported by the more favorable comparison noticed for the nitrogen quadrupole coupling constant: it agrees with experiment within 2%. In order to improve even more the description of this property, calculations of the equilibrium value employing the aug-cc-pCVQZ have also been carried out. Assuming the additivity of the vibrational corrections, these, computed at the (all)CCSD(T)/cc-pwCVQZ level as the difference between the equilibrium and vibrationally averaged values, have then been added to the (all)CCSD(T)/aug-cc-pCVQZ equilibrium values giving our best estimates. While the improvement is small for phosphine (i.e., lower than 1%), that for ammonia is relevant reducing the discrepancy to ∼9%. Without further investigating this issue, we attribute the remaining difference between our best estimate and the experimental value to inaccuracy of experiment as well as to errors inherent in the convergence to the basis set limit and in neglecting higher-order excitations. Nevertheless, on the basis of the FCI benchmark calculations performed by Halkier et al. [35], the latest ones are expected to be small, i.e., largely lower than 0.01 a.u. We also checked the error due to the neglect of full treatment of triples excitations by comparing CCSDT/cc-pVTZ and CCSD(T)/cc-pVTZ calculations; this error was found negligible, being lower than 1×10^{-5} a.u. for ammonia and about 0.002 a.u. for phosphine.

For magnetic properties (Table 3), the agreement between theory and experiment is very good, especially when vibrationally averaged values are considered. Actually, for these properties vibrational corrections result to be relevant as they range from ∼2% to about 10%. Vibrational corrections decrease the equilibrium values for all the parameters but the spin-rotation constants of nitrogen as well as phosphorous. The good agreement obtained for phosphine with the very accurate, nearly benchmark, results reported in Ref. [37] has to be noted. As far as the comparison between the CCSD(T)/cc-pwCVTZ and CCSD(T)/cc-pwCVQZ results is concerned, the employment of the larger basis set improves the values by about 5–20% for ammonia properties, while the improvement is smaller, i.e., about 0.2–5%, for phosphine. In contrast improvements due to inclusion of full triples corrections (computed employing the cc-pVTZ basis) have been found mostly negligible.

In Table 3 the isotropic shielding and anisotropy are given. It could be useful to recall that, since the shielding tensor is a non-symmetric tensor of rank two, in the principal axis system an isotropic part as well as an anisotropy can be defined. The isotropic shielding of a nucleus is the average of the diagonal elements of the shielding tensor

$$\sigma_{\mathrm{iso}} = \frac{1}{3}\mathrm{Tr}(\sigma), \tag{14}$$

Table 3 Magnetic properties of ammonia and phosphine evaluated at the CCSD(T) level

	σ_{iso} (ppm)	$\Delta\sigma$ (ppm)	C_{xx} (kHz)	C_{yy} (kHz)	$(C_{xx} + C_{yy})/2$ (kHz)	C_{zz} (kHz)	C_{xz} (kHz)	C_{zx} (kHz)
NH_3/N								
GIAO-EMPI/TZ2P[a]	278.3							
WAH/IGLO IV[b]	265.2	24.3						
Scaled DFT[c]	263.3	23.2						
GIAO-CCSD(T)/$pz3d2f/pz3p$[d]	270.7	21.9						
SOPPA[e]			6.648	6.648		6.759		
cc-pwCVTZ-equilibrium	275.489	29.074	5.070	5.070		6.470		
cc-pwCVTZ-vibrat. averag.	268.527	27.039	5.877	5.877		6.584		
cc-pwCVQZ-equilibrium	272.701	22.489	5.558	5.558		6.560		
cc-pwCVQZ-vibrat. averag.	265.981	20.524	6.328	6.328		6.663		
Best estimate[f]	265.356	20.205	6.218	6.218		6.679		
Experiment[g]	264.50 (5)[d]	20[d]	6.764	6.764		6.695		
NH_3/H								
GIAO-CCSD(T)/$pz3d2f/pz3p$[f]	31.6	16.2						
SOPPA[f]			−4.243	−38.772		−22.140		
cc-pwCVTZ-equilibrium	31.924	16.396	−5.667	−33.573		−20.158	7.498	12.781
cc-pwCVTZ-vibrat. averag.	31.283	15.515	−4.946	−32.073		−18.991	7.023	12.146
cc-pwCVQZ-equilibrium	31.612	16.442	−4.936	−33.279		−19.960	7.245	12.435
cc-pwCVQZ-vibrat. averag.	30.986	15.592	−4.246	−31.831		−18.820	6.762	11.782
Best estimate[f]	30.984	15.546	−4.188	−31.864		−18.821	6.767	11.812
Experiment[g]	30.68[d]		−3.28	−32.26		−18.97		
PH_3/P								
GIAO-EMPI/TZ2P[a]	597.4							
Scaled DFT[c]	596.1	27.3						
GIAO-MP2/IGLOIII(uncontr.)[h]	610.3							
GIAO-SVWN5/6-31+G(d)[i]	598.2 (589.0)							

Table 3 continued

	σ_{iso} (ppm)	$\Delta\sigma$ (ppm)	C_{xx} (kHz)	C_{yy} (kHz)	$(C_{xx}+C_{yy})/2$ (kHz)	C_{zz} (kHz)	C_{xz} (kHz)	C_{zx} (kHz)
CCSD(T)/CVQZ+ZPV(CVTZ)[j]	596.898				113.508[k]			
cc-pwCVTZ-equilibrium	604.449	27.520	113.269	113.269		114.727		
cc-pwCVTZ-vibrat. averag.	595.303	25.440	114.564	114.564		114.127		
cc-pwCVQZ-equilibrium	605.002	28.429	113.034	113.034		114.986		
cc-pwCVQZ-vibrat. averag.	596.182	26.347	114.386	114.386		115.369		
Best estimate[f]	592.374	24.337	115.103	115.103		115.699		
Experiment	599.93[l]	28[c]	114.90 (13)[m]	114.90 (13)[m]		116.38 (32)[m]		
PH_3/H								
CCSD(T)/CVQZ+ZPV(CVTZ)[j]	29.240				−7.812[k]			
cc-pwCVTZ-equilibrium	29.634	10.924	−1.905	−14.747	−8.326	−8.112	7.035	8.321
cc-pwCVTZ-vibrat. averag.	29.213	10.604	−1.739	−14.082	−7.911	−7.687	6.721	7.969
cc-pwCVQZ-equilibrium	29.558	10.896	−1.862	−14.688	−8.275	−8.076	7.003	8.307
cc-pwCVQZ-vibrat. averag.	29.126	10.572	−1.678	−14.026	−7.852	−7.655	6.687	7.970
Best estimate[f]	29.108	10.500	−1.625	−14.036	−7.831	−7.651	6.694	7.994
Experiment[m]					−8.01 (8)	−7.69 (19)		

Computations performed correlating all electrons (but 1*s* of P)

[a] Ref. [49]. For details on EMPI approach see Ref. [49]

[b] Ref. [50]

[c] Ref. [51]. Experimental values as reported in Ref. [51]

[d] Ref. [26]. Results for $^{15}NH_3$ are given. Experimental values as reported in Ref. [26]

[e] Property surfaces were computed; a 68 CGTOs basis set has been employed in the calculations. For details see Ref. [52]

[f] Full triples corrections (CCSDT/cc-pVTZ-CCSD(T)/cc-pVTZ) added to vibrational averaged values at the (all)CCSD(T)/cc-pwCVQZ level: see text

[g] Ref. [53]

[h] Ref. [54]

[i] Ref. [55]. In parenthesis the vibrational corrected data is given

[j] Ref. [37]

[k] Ref. [37]; isotropic values of spin-rotation constants, $(C_{xx}+C_{yy}+C_{zz})/3$, are reported

[l] Ref. [56]

[m] Ref. [45]

whereas the shielding anisotropy is defined as

$$\Delta\sigma = \sigma_{33} - \frac{1}{2}(\sigma_{22} + \sigma_{11}), \qquad (15)$$

where $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$. It is therefore clear that errors in calculations of isotropic shielding often tend to cancel each other, while it is more difficult to calculate anisotropy accurately. Consequently, its evaluation may provide a test for theory. From Table 3 we may conclude that the CCSD(T)/cc-pwCVQZ level of theory is able to well reproduce isotropic as well as anisotropic shielding. This conclusion was somehow expected: for instance, in Refs. [9,26,38] Gauss and coworkers yielded clear evidence for the high accuracy of CCSD(T) computations and their proximity to FCI limit. In Ref. [9] CCSDT calculations confirmed the good performance of the CCSD(T) approach. It was also shown that the error due to the neglect of full triples is usually lower than 1 ppm and that, by comparing with FCI results of Ref. [38] for the BH molecule, the higher-order corrections are very small as well. As briefly mentioned before, we personally checked the error due to the neglect of full triples for ammonia and phosphine by comparing CCSDT/cc-pVTZ and CCSD(T)/cc-pVTZ calculations; this error was found negligible being corrections generally lower than 1 ppm (only for σ_{iso}(P) it is 3.8 ppm, but it is anyway a very small correction: $\sim$0.6%). Best estimated values including such corrections are also reported in Table 3.

The spin-rotation tensor is non-vanishing only for nuclei with $I_K \geq 1/2$. Therefore, in the present case all nuclei present such an interaction. The number of non-vanishing tensor elements depends on the so-called site symmetry—that is, the actual symmetry seen by the given nucleus in its position. For C_{3v} molecules, as ammonia and phosphine, the nuclear spin-rotation tensor of the atoms lying on the C_3 axis (i.e., N and P) is diagonal with $C_{xx} = C_{yy}$. The spin-rotation tensor of the H_1 nucleus has five non-vanishing components: the diagonal elements C_{xx}, C_{yy}, C_{zz} (with $C_{xx} \neq C_{yy}$) and the off-diagonal C_{xz} and C_{zx}; where x, y and z are the inertial axes and xz is the plane on which H_1 and the C_3 axis lie. The $\mathbf{C}(H_1)$ tensor is not symmetric, that is $C_{xz} \neq C_{zx}$. For symmetry reasons, the spin-rotation tensors of the other hydrogen atoms (H_2 and H_3) can be obtained by rotation of $\mathbf{C}(H_1)$: $\mathbf{C}(H_2) = \mathbf{R}_2{}^{-1}\,\mathbf{C}\,(H_1)\,\mathbf{R}_2$ and $\mathbf{C}(H_3) = \mathbf{R}_3{}^{-1}\,\mathbf{C}(H_1)\,\mathbf{R}_3$; where $\mathbf{R}_2 = \mathbf{R}_3{}^{-1}$. From the results collected in Table 3 it can be pointed out that all the spin-rotation constants are small, ranging on an average from 6 to 20 kHz, with the only exception of P for which they are as large as $\sim$115 kHz.

It deserves to briefly recall that nuclear magnetic shielding and spin-rotation constants are strongly connected. In fact, accordingly to Ramsey's formulation [39], σ can be decomposed into two contributions: the paramagnetic contribution (σ^p) and the diamagnetic one (σ^d), where the former can be determined from spin-rotation constant [27]. Additionally, while σ^d, which depends on the ground state of the molecule, can be accurately calculated by means of standard quantum chemical methods, σ^p is more difficult to calculate accurately. Therefore, when establishing absolute magnetic shielding scale, highly precise experimental determinations of spin-rotation constants are employed for evaluating σ^p.

The evaluation of the anharmonic force field allowed the derivation of various spectroscopic parameters: rotational and centrifugal distortion constants, vibration–rotation interaction constants, harmonic and anharmonic frequencies. Harmonic and anharmonic force constants are not reported here, but they are available from the author upon request. The experimental and computed spectroscopic parameters are compared in Table 4. Once again, as expected, the values for PH_3 are smaller with respect the corresponding ones of NH_3. From this table it is also evident that the discrepancies between the experimental and ab initio values are only a few percent. In particular, the agreement between computed and experimental ground-state rotational constants is excellent as the deviations are largely lower than 0.5%. As far as the quartic centrifugal distortion constants are concerned, even if ground-state experimental data are compared to the equilibrium theoretical ones, one can notice a rather good agreement, being 12% the largest discrepancy. The good agreement between the calculated and experimental vibrational frequencies ν_i has to be noted: the deviations are of the order of 0.2–0.5%, with the exception of the ν_2 of NH_3 for which a discrepancy of $\sim$7% is observed. This is clearly related to the fact that ν_2 is the frequency of the inversion motion, which is not so well described by a cubic force field evaluated in normal coordinates. Going from CCSD(T)/cc-pwCVTZ to the CCSD(T)/cc-pwCVQZ level of theory a small but evident improvement is observed. Furthermore, from this comparison it comes out that the spectroscopic properties computed at the same level of theory for both ammonia and phosphine seem to have the same accuracy. The error due to the neglect of higher-order excitations is expected to be small even for spectroscopic constants. For instance, the benchmark calculations of harmonic and anharmonic frequencies of BH and HF reported in Ref. [40] pointed out that CCSD(T) results are very closed to the FCI limit (i.e., discrepancy largely lower than 0.5%).

Finally, it deserves to be noted that the cubic force fields initially obtained for the main isotopic species can be transformed to the normal-coordinate representations of other isotopic species and used to compute spectroscopic parameters, such as vibration–rotation interaction constants and centrifugal distortion constants, using the usual second-order perturbation treatment of the rovibrational problem [32].

4 Conclusions

Using the highly accurate ab initio approach CCSD(T), a theoretical investigation of some electric and magnetic

Table 4 Spectroscopic constants of $^{14}NH_3$ and $^{31}PH_3$

Parameters	(all)CCSD(T)/ cc-pwCVTZ	(all)CCSD(T)/ cc-pwCVQZ	Experiment
NH_3			
B_0 (MHz)	297600.17[a]	297989.26[a]	298117.06[b]
C_0 (MHz)	186680.77[a]	186576.70[a]	186726.36[b]
B_0–B_e (MHz)	−2627.17	−2238.08	
C_0–C_e (MHz)	−3509.23	−3613.30	
D_J (MHz)	26.68	27.61	25.4662 (12)[c]
D_{JK} (MHz)	−45.43	−47.46	−47.3100 (29)[c]
D_K (MHz)	25.26	26.89	27.3959 (33)[c]
ω_1 (cm^{-1})	3482.4	3489.2	
ω_2 (cm^{-1})	1105.2	1076.3	
ω_3 (cm^{-1})	3607.7	3618.9	
ω_4 (cm^{-1})	1689.1	1679.8	
ν_1 (cm^{-1})	3368.3	3342.4	3336.11[d]
ν_2 (cm^{-1})	1033.3	1000.9	932.43[e]
ν_3 (cm^{-1})	3455.9	3444.0	3443.68[f]
ν_4 (cm^{-1})	1648.9	1634.9	1626.28[g]
PH_3			
B_0 (MHz)	133629.13[a]	133694.77[a]	133480.128989 (95)[h]
C_0 (MHz)	117404.20[a]	117361.19[a]	117489.436 (10)[i]
B_0–B_e (MHz)	−1634.43	−1568.79	
C_0–C_e (MHz)	−1237.66	−1280.67	
D_J (MHz)	3.88	3.98	3.936901 (36)[h]
D_{JK} (MHz)	−1.03	−1.07	−1.237 (85)[h]
D_K (MHz)	1.46	1.49	1.34 (27)[h]
ω_1 (cm^{-1})	2425.8	2429.3	
ω_2 (cm^{-1})	1025.7	1016.6	
ω_3 (cm^{-1})	2433.3	2437.1	
ω_4 (cm^{-1})	1150.8	1147.3	
ν_1 (cm^{-1})	2326.9	2331.1	2321.124 (3)[j]
ν_2 (cm^{-1})	1003.9	996.8	992.13477 (1)[k]
ν_3 (cm^{-1})	2330.5	2336.0	2326.505 (9)[j]
ν_4 (cm^{-1})	1124.5	1122.4	1118.30639 (2)[k]

[a] Obtained by adding to the best estimated equilibrium rotational constants (derived from r_e obtained from Eq. (6) of Ref. [1]) the vibrational corrections at the (all)CCSD(T)/cc-pwCVnZ level. See text

[b] JPL catalog

[c] Ref. [57]

[d] Ref. [58]

[e] Ref. [59]

[f] Ref. [60]

[g] Ref. [61]

[h] Ref. [62]

[i] Ref. [63]

[j] Ref. [64]

[k] Ref. [65]

properties of ammonia as well as phosphine has been performed. In particular, molecular dipole and quadrupole moments, as well as NMR shielding and spin-rotation constants have been investigated. Theoretical results, obtained employing a basis set as large as the cc-pwCVQZ to account for core correlation effects, also include estimates for zero-point vibrational effects. As far as dipole moment is concerned, a deeper investigation has been carried out also accounting for basis set truncation error. In addition, the cubic force fields of ammonia and phosphine have been evaluated at the CCSD(T)/cc-pwCVTZ as well as CCSD(T)/cc-pwCVQZ levels of theory allowing the derivation of various spectroscopic parameters: rotational and centrifugal distortion constants, vibration–rotation interaction constants, harmonic and anharmonic frequencies.

On the whole, the present results are in excellent agreement with experiment. On this purpose, it deserves to be noted that vibrational effects have to be taken into account for such a comparison.

Acknowledgments This work has been supported by “PRIN 2005” funds (project “Trasferimenti di energia e di carica a livello molecolare”), and by University of Bologna (RFO funds). The author gratefully thanks Prof. J. Gauss for providing the MAB development version of ACESII. The author thanks the CINECA supercomputing center for a grant of computer time on the IBM SP5 machine.

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