

Ab Initio Ground-State Potential Energy Function and Vibration-Rotation Energy Levels of Imidogen, NH

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The accurate ground-state potential energy function of imidogen, NH, has been determined from *ab initio* calculations using the multireference averaged coupled-pair functional (MR-ACPF) method in conjunction with the correlation-consistent core-valence basis sets up to octuple-zeta quality. The importance of several effects, including electron correlation beyond the MR-ACPF level of approximation, the scalar relativistic, adia-

batic, and nonadiabatic corrections were discussed. Along with the large one-particle basis set, all of these effects were found to be crucial to attain "spectroscopic" accuracy of the theoretical predictions of vibration-rotation energy levels of NH. © 2015 Wiley Periodicals, Inc.

DOI: 10.1002/jcc.23931

Introduction

Imidogen, NH, is an important heteronuclear radical and its vibration-rotation spectrum has attracted significant interest by various experimentalists, see for example Refs. [1–3] and references therein. The vibration-rotation energy levels of the ground electronic state $X^3\Sigma^-$ of the two isotopologues, NH and ND, were experimentally characterized up to the sixth excited vibrational state, covering 3/5 of the potential energy well. Because the NH radical consists of only two nuclei and eight electrons, it is an attractive benchmark molecule for *ab initio* methods and, therefore, it has been the subject of numerous theoretical studies^[4–25]; and this list is by no means exhaustive.

In the calculation at the Hartree–Fock (HF) level of theory by Cade and Huo,^[4] the ground-state potential energy function of NH was determined. The binding energy D_e , the equilibrium internuclear distance r_e , and the vibrational fundamental wavenumber ν were calculated to be 16,900 cm^{-1} , 1.018 Å, and 3422 cm^{-1} , respectively. The electron correlation effects were then discussed by Bender and Davidson,^[5] Silver et al.,^[6] and O’Neil and Schaefer.^[7] In particular, the latter authors determined the values of D_e , r_e , and ν for the $X^3\Sigma^-$ state of NH using the configuration interaction approach with a modest double-zeta *spd* basis set to be 24,700 cm^{-1} , 1.041 Å, and 3060 cm^{-1} , respectively. These and the following theoretical studies^[8–25] showed clearly that electron correlation plays an important role in determining the electronic structure of NH. The most extensive calculations on the spectroscopic constants for the $X^3\Sigma^-$ state of NH, using the coupled-cluster approach with large correlation-consistent basis sets, were reported by Martin,^[20] Feller and Sordo,^[21] and Temelso et al.^[22] The equilibrium internuclear distance r_e was predicted in these studies to be 1.03635, 1.0369, and 1.03609 Å, respectively, whereas the fundamental wavenumber ν was predicted to be 3124.80, 3128.0, and 3125.25 cm^{-1} , respectively. The potential energy function for the $X^3\Sigma^-$ state of NH was determined using the multireference valence configuration interaction approach with large correlation-

consistent basis sets by Owono Owono et al.,^[23] Campbell et al.,^[24] and Srivastava and Sathyamurthy.^[25] In particular, the latter authors predicted the values of r_e and ν to be 1.0365 Å and 3127.9 cm^{-1} , respectively. The *ab initio* determined values of r_e and ν for the $X^3\Sigma^-$ state of NH are close to the corresponding experimental values of 1.03675 Å and 3125.5725 cm^{-1} .^[2,3] In contrast, the dissociation energy D_e for the $X^3\Sigma^-$ state of NH is still not well known both experimentally and theoretically. Previous experimental measurements and theoretical predictions of D_e were reviewed by Tarroni et al.^[19] and Owono Owono et al.^[23]

This work is a next step toward attaining "spectroscopic" accuracy in the *ab initio* calculation of vibration-rotation energy levels of imidogen. The goal is to provide the accurate state-of-the-art potential energy function for the ground electronic state of NH and to discuss the effects which should be taken into account to predict the vibration-rotation energy levels of NH with high accuracy.

Methodology

The molecular parameters of NH were determined in this work using the multireference averaged coupled-pair functional (MR-ACPF) method^[26,27] in conjunction with the augmented correlation-consistent core-valence basis sets up to octuple-zeta quality, aug-cc-pCVnZ ($n = D-8$). The MR-ACPF method is an approximately size-extensive variant of the multireference configuration interaction (MRCI) approach including single and double excitations. The calculations consisted of the complete-active-space self-consistent-field (CASSCF) step followed by the internally contracted^[28] MR-ACPF step. The usual full-valence active space, consisting of the 2s- and 2p-like orbitals of the nitrogen atom and the 1s-like orbital of the hydrogen atom, was extended with the 3s-, 3p-, and 3d-like orbitals of the

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nitrogen atom. The CASSCF wave function of NH included, thus, all excitations of six valence electrons in 14 molecular orbitals. In the generation of the CASSCF wave functions, the 1s-like (core) orbital of the nitrogen atom was optimized, but it was kept doubly occupied. The reference function for the MR-ACPF calculation consisted of the CASSCF orbitals, resulting in 15,840 reference configuration state functions for the $X^3\Sigma^-$ state of NH. In the MR-ACPF step, all of the electrons, including the core ones, were correlated through single and double excitations.

The one-particle basis sets for nitrogen consisted of the valence cc-pVnZ basis sets augmented with diffuse (aug) and tight (C) functions. The valence cc-pVnZ basis sets up to septuple-zeta quality were developed by Dunning,^[29] Wilson et al.,^[30] and Feller and Sordo.^[31] The largest basis set for nitrogen available in the literature, cc-pV7Z, contains the primitive (18s12p6d5f4g3h2i1k) functions contracted to [8s7p6d5f4g3h2i1k]. The cc-pV8Z basis set, containing only up to *i* functions (for the reason given below), was developed for this study. This basis set contains the primitive (24s16p7d6f5g4h3i) functions contracted to [9s8p7d6f5g4h3i]. The exponents of the *s* and *p* primitive functions were determined in the HF calculation for the nitrogen atom in its ground electronic state 4S . Using the uncontracted (24s16p) set, the HF total energy for the 4S state of N was calculated to be $-54.40093418 E_h$. This value is by just $0.03 \mu E_h$ larger than the numerical HF limit energy of $-54.40093421 E_h$.^[32] The exponents of the higher angular momentum functions were determined using the configuration interaction method, with single and double excitations (CISD), by minimizing the total CISD energy for the 4S state of N. The calculations were performed using the MOLPRO package of *ab initio* programs.^[33] Because the MOLPRO package cannot handle functions higher than *i*, these functions were omitted in all subsequent calculations. Only the spherical harmonic components of the *d* through *i* polarization functions were used.

For accurately describing electron distribution at large distances, the basis sets were augmented with diffuse functions. The diffuse functions for nitrogen, up to the basis set of septuple-zeta quality aug-cc-pV7Z, were taken from the literature.^[29–31] For the aug-cc-pV8Z basis set, the customary even-tempered exponents were calculated in this work by multiplying the exponent of the outermost primitive function of a given angular symmetry in the valence basis set by a factor of 0.4.

To account for the correlation effects of the 1s core electrons of the nitrogen atom, the basis sets were augmented with tight functions. Groups of the primitive tight functions were added to the valence cc-pVnZ basis set. The largest core-valence basis set of sextuple-zeta quality for nitrogen, cc-pCV6Z, available in the literature,^[34–36] was obtained by augmenting the cc-pV6Z basis set with the primitive (5s5p4d3f2g1h) functions. In this work, the cc-pV7Z basis set was augmented with the primitive (6s6p5d4f3g2h1i) functions to form the cc-pCV7Z basis set. The exponents of the tight functions were determined in the CISD calculations for the 4S state of N with either the valence active space or with all elec-

trons correlated, both calculations performed with the same core-valence basis set. The exponent values were adjusted to maximize the absolute sum of the calculated core–core and core-valence correlation energies. To reduce the problem of linear dependencies for the cc-pCV8Z basis set, a (7s7p6d5f4g3h2i) set of the tight functions was obtained in a different way. First, the valence part (24s16p)/[9s8p] of the cc-pV8Z basis set was recontracted to form the core-valence part (24s16p)/[16s15p]. Then, the polarization part (6d5f4g3h2i) was constructed in the way described above. The cc-pCV8Z(*i*) basis set thus obtained is given in the Supporting Information.

Using the MR-ACPF method with the active space described above and all electrons correlated, the total energy for the 4S state of N was calculated to be -54.587513 , -54.587963 , and $-54.588156 E_h$ for the aug-cc-pCV6Z, aug-cc-pCV7Z(*i*), and aug-cc-pCV8Z(*i*) basis set, respectively. The latter value can be compared with the total energy of $-54.58867(8) E_h$ obtained in the diffusion Monte Carlo calculations by Seth et al.^[37]

The one-particle basis sets for hydrogen consisted of the valence cc-pVnZ basis sets augmented with diffuse (aug) functions.^[29,35,36]

The vibration-rotation energy levels of two isotopologues, NH and ND, were calculated using the Numerov–Cooley method.^[38] The energy levels were calculated using the nuclear masses of nitrogen and hydrogen, 13.999233945 and 1.007276452 u, respectively. The spin-related interactions were not considered.

Results and Discussion

To determine the shape of the potential energy function of NH, the total energies were calculated at the MR-ACPF/aug-cc-pCVnZ ($n = Q - 8$) level of theory, with all electrons correlated, at 64 internuclear distances ranging from 0.5 to 50 Å. The molecular parameters for the $X^3\Sigma^-$ state of NH thus derived are given in Table 1. The parameters quoted include the equilibrium internuclear distance r_e , the total energy at minimum, the binding energy D_e , the vibrational fundamental wavenumber ν , and the ground-state vibrationally-averaged (effective) rotational constant B_0 . For a given vibrational state, the effective rotational constant B_v was determined by fitting the predicted rotation energies with a power series in $N(N + 1)$, where N is the rotational quantum number. The predicted values tend clearly to converge with enlargement of the basis set. Changes in the calculated equilibrium distance r_e and the binding energy D_e beyond the aug-cc-pCV8Z(*i*) basis set are estimated to be about 0.00005 Å and 10 cm^{-1} , respectively. The analogous changes in the vibrational fundamental wavenumber ν and the effective rotational constant B_0 are estimated to be about 0.2 and 0.001 cm^{-1} , respectively. The best potential energy function for the $X^3\Sigma^-$ state of NH, determined at the MR-ACPF/aug-cc-pCV8Z(*i*) level, is referred further to as “CV”.

To estimate the effects of electron correlation beyond the MR-ACPF level of approximation, full-configuration-interaction (FCI)^[39] calculations were performed. Even accounting only for valence electron correlation, only the correlation-consistent

Table 1. Molecular parameters for the $X^3\Sigma^-$ state of NH determined at the MR-ACPF/aug-cc-pCVnZ level of theory.

	$n = Q$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
$r_e^{[a]}$ (Å)	1.03687	1.03623	1.03611	1.03596	1.03591
$E + 55^{[b]}$ (hartree)	-0.213625	-0.217984	-0.219513	-0.220078	-0.220317
$D_e^{[c]}$ (cm^{-1})	28,760	28,907	28,962	28,988	28,997
$\nu^{[d]}$ (cm^{-1})	3122.76	3126.99	3128.47	3129.48	3129.64
$B_0^{[e]}$ (cm^{-1})	16.3597	16.3805	16.3853	16.3899	16.3912

[a] The equilibrium internuclear distance. [b] The total energy at a minimum. [c] The binding energy. [d] The vibrational fundamental wave-number. [e] The ground-state effective rotational constant.

basis sets of double- and triple-zeta quality could be applied. At each point of the potential energy function of NH, the total energy was calculated using either the FCI or MR-ACPF method with the aug-cc-pVTZ basis set and valence electrons correlated. Differences between the FCI and MR-ACPF total energies of NH were found to be small for all of the internuclear distances under consideration, steadily decreasing from about $-30 \mu E_h$ at the small distances to $-8 \mu E_h$ at the dissociation limit. The core-electron related effects were estimated in a similar way by calculating the sum of the core-core and core-valence correlation energies using either the FCI or MR-ACPF method with the aug-cc-pCVDZ basis set. Differences between the FCI and MR-ACPF energies were found again to be small, ranging from 6 to $-34 \mu E_h$. The valence correlation energy was calculated at the FCI/aug-cc-pVTZ level of theory to be about $-171 \text{ m}E_h$ in the vicinity of the equilibrium configuration of NH, whereas the difference between the FCI and MR-ACPF total energies was determined to be just about $-14 \mu E_h$. Therefore, the extensive CASSCF/MR-ACPF wave function used in this work accounts for about 99.99% of the valence correlation energy for the $X^3\Sigma^-$ state of NH. The potential energy function of NH was corrected for these effects by adding the differences between the FCI and MR-ACPF energies to the total energies of NH calculated previously at the MR-ACPF/aug-cc-pCV8Z(*i*) level. This function is referred further to as "CV+F".

The potential energy function of NH was further corrected for the scalar relativistic effects. These effects were investigated using the second-order Douglas-Kroll-Hess (DKH) one-electron Hamiltonian.^[40,41] The relativistic contributions to the total energy were calculated using the MR-ACPF method with the uncontracted aug-cc-pCVQZ basis set and all electrons correlated. At each point of the potential energy function of NH, the relativistic correction was determined as the difference in the total energy calculated using either the DKH or nonrelativistic Hamiltonian. The inclusion of the scalar relativistic effects lowers the total energy of NH by about $29.4 \text{ m}E_h$. The relativistic corrections were added to the CV+F potential energy function of NH, and this function is referred further to as "CV+F+R".

To account for the adiabatic effects, the diagonal Born-Oppenheimer correction (DBOC)^[42-44] was calculated for two isotopologues, NH and ND. The DBOC was determined using the

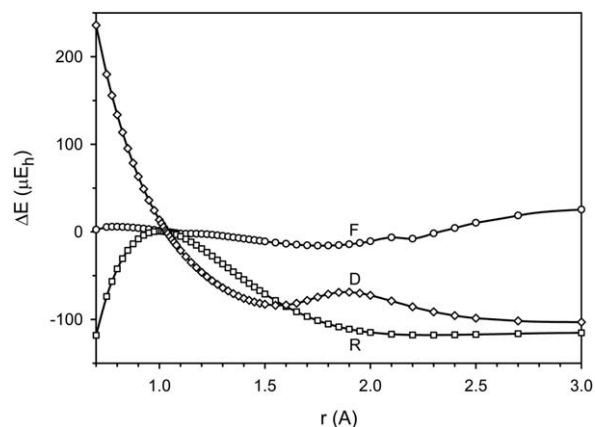


Figure 1. Changes in the total energy ΔE for the $X^3\Sigma^-$ state of NH due to electron correlation beyond the MR-ACPF level of approximation (F, circles), the scalar relativistic effects (R, squares), and the adiabatic effects (D, diamonds) as functions of the internuclear distance r . The relative values of ΔE are plotted, taking the absolute changes ΔE of $-36 \mu E_h$ (F), $-29,424 \mu E_h$ (R), and $2390 \mu E_h$ (D) calculated for $r = 1.035 \text{ Å}$ as the origin of the ΔE axis.

spin-unrestricted (UHF) and spin-restricted open-shell HF (ROHF) methods, as well as using the restricted-active-space configuration interaction (RAS CI)^[45] method, all in conjunction with the aug-cc-pCVTZ basis set. The calculations were performed using the PSI3 package of *ab initio* programs.^[46] The active space (RAS2) for the RAS CI wave function of NH consisted of five molecular valence orbitals: the 2s- and 2p-like orbitals of the nitrogen atom and the 1s-like orbital of the hydrogen atom. Only the six valence electrons of NH were correlated through single and double excitations. In the vicinity of the equilibrium configuration of NH, the DBOC was determined to be 516 cm^{-1} ($2.353 \text{ m}E_h$) with both UHF and ROHF methods. On the inclusion of electron correlation with the RAS CI method, the DBOC was determined to be 525 cm^{-1} . For the ND isotopologue, the corresponding DBOC was determined to be 484 cm^{-1} . The DBOC values determined with the ROHF method exhibit discontinuous behavior at the internuclear distances of about 1.6 and 2.2 Å. The rapid change in the DBOC value is related to similar discontinuous behavior of the ROHF wave function for the $X^3\Sigma^-$ state of NH. In contrast, a variation of the DBOC values determined with the RAS CI method is smooth, because the RAS CI wave function includes all excitations of the six valence electrons of NH within the active space. The DBOC values were calculated at the same set of points as the Born-Oppenheimer potential energy functions discussed above and were subsequently added to the CV+F+R total energies. The resulting mass-dependent adiabatic potential energy functions are referred further to as "CV+F+R+D".

Changes in the total energy for the $X^3\Sigma^-$ state of NH due to electron correlation beyond the MR-ACPF level of approximation (F), the scalar relativistic effects (R), and the adiabatic effects (D) with the internuclear distance are illustrated in Figure 1.

For each of the potential energy functions calculated for the $X^3\Sigma^-$ state of NH, the molecular parameters were then determined. The results are given in Table 2 and are compared with

Table 2. Molecular parameters^[a] for the $X^3\Sigma^-$ state of NH determined using various potential energy functions.

	CV ^[b]	CV+F ^[c]	CV+F+R ^[c]	CV+F+R+D ^[c]	Exp. ^[d]
r_e (Å)	1.03591	1.03594	1.03598	1.03625	1.03675 ^[47]
$E+55$ (hartree)	-0.220317	-0.220353	-0.249777	-0.247387	
D_e (cm ⁻¹)	28,997	29,004	28,979	28,957	29,200 ^[19]
ν (cm ⁻¹)	3129.64	3129.60	3127.80	3126.46	3125.5725 ^[2]
B_0 (cm ⁻¹)	16.3912	16.3906	16.3892	16.3808	16.3432753 ^[2]

[a] See Table 1. [b] The potential energy function was calculated at the MR-ACPF/aug-cc-pCV8Z(*i*) level of theory. [c] Including additionally the FCI (F), scalar relativistic (R), and diagonal Born–Oppenheimer (D) corrections (see the text). [d] The experimental values.

the recent experimental data.^[2,19,47] The best Born–Oppenheimer potential energy function of NH (CV+F+R) has a minimum at 1.03598 ± 0.00005 Å and the well depth of $28,979 \pm 10$ cm⁻¹. The equilibrium distance r_e is predicted to lie in between the best theoretical estimates of 1.03635 Å by Martin^[20] and 1.03582 Å by Temelso et al.^[22] The binding energy D_e is close to the best theoretical estimates of 28,860 cm⁻¹ by Peterson et al.,^[16] 28,920 cm⁻¹ by Tarroni et al.,^[19] and 28,990 cm⁻¹ by Feller and Sordo.^[21] The best Born–Oppenheimer fundamental wavenumber ν is predicted in this work to be 3127.80 cm⁻¹, being noticeably larger than the best estimates of 3124.80 cm⁻¹ by Martin^[20] and 3125.25 cm⁻¹ by Temelso et al.^[22] For the NH and ND isotopologues, the adiabatic equilibrium internuclear distances are predicted to be longer than the Born–Oppenheimer equilibrium internuclear distance r_e by 0.00027 and 0.00014 Å, respectively. The adiabatic corrections to the Born–Oppenheimer binding energy D_e are predicted to be -22 and -11 cm⁻¹, respectively. The scalar relativistic and adiabatic corrections to the molecular parameters appeared to be essential for accurate describing the structure and dynamics of the NH radical. The total corrections F+R+D to r_e , D_e , ν , and B_0 amount to 0.00034 Å, -40 cm⁻¹, -3.18 cm⁻¹, and -0.0104 cm⁻¹, respectively. On the inclusion of the total corrections F+R+D, the experimental fundamental wavenumber ν and the ground-state effective rotational constant B_0 of the NH isotopologue^[2] were reproduced to 0.9 and 0.04 cm⁻¹, respectively. The adiabatic equilibrium distances r_e of 1.03625 and 1.03612 Å for the NH and ND isotopologues, respectively, are close to the corresponding values of 1.03675 and 1.03665 Å derived by Bernath and coworkers^[3,47] from the high-resolution vibration-rotation spectra. Using the adiabatic potential energy functions, the dissociation energies D_0 for the NH and ND isotopologues are determined to be 27,333 and 27,778 cm⁻¹, respectively. The former value is lower by about 250 cm⁻¹ than the lower bound to D_0 of $27,580 \pm 80$ cm⁻¹ derived by Tarroni et al.^[19] from the experimental data for the NH radical and its cation.

Relative energies of the predicted Born–Oppenheimer potential energy function for the $X^3\Sigma^-$ state of NH are given in Table 3. Relative energies of the predicted adiabatic potential energy functions for both isotopologues NH and ND are given in the Supporting Information.

The adiabatic potential energy functions CV+F+R+D were used to determine vibration-rotation energy levels for the $X^3\Sigma^-$ state of the NH and ND isotopologues. The calcu-

lated vibrational term values T_v and the effective rotational constants B_v and quartic centrifugal distortion constants D_v are given in Tables 4 and 5. The predicted values are compared with the experimental values reported by Ram and Bernath.^[2,3] The experimental data include seven vibrational energy levels for both NH and ND. The predicted vibrational term values T_v of the NH and ND isotopologues overestimate the corresponding experimental values by about 1.5 and 0.7 cm⁻¹, respectively. For all of the observed vibrational energy levels of NH and ND, the predicted effective rotational constants B_v overestimate the experimental values by about 0.03 and 0.01 cm⁻¹, respectively. The experimental

Table 3. Relative energies^[a] of the Born–Oppenheimer potential energy function (CV+F+R) for the $X^3\Sigma^-$ state of NH.

r (Å)	Energy	r (Å)	Energy
0.500	158,395.60	1.275	-23719.58
0.550	100,895.19	1.300	-22861.72
0.600	59,971.07	1.325	-21987.23
0.650	30,841.11	1.350	-21102.56
0.700	10,198.13	1.375	-20213.84
0.750	-4282.61	1.400	-19326.10
0.775	-9750.91	1.425	-18443.87
0.800	-14261.31	1.450	-17570.75
0.825	-17950.44	1.475	-16710.34
0.850	-20935.06	1.500	-15865.52
0.875	-23315.27	1.550	-14232.21
0.900	-25176.85	1.600	-12686.90
0.925	-26593.65	1.650	-11241.00
0.950	-27629.22	1.700	-9902.20
0.975	-28338.40	1.750	-8674.92
1.000	-28768.60	1.800	-7560.74
1.010	-28871.98	1.850	-6558.84
1.020	-28939.65	1.900	-5666.03
1.030	-28974.00	1.950	-4877.42
1.035	-28979.35	2.000	-4186.38
1.040	-28977.01	2.100	-3066.09
1.050	-28950.76	2.200	-2239.37
1.060	-28897.12	2.300	-1637.52
1.070	-28817.88	2.400	-1203.23
1.080	-28714.65	2.500	-890.17
1.100	-28442.68	2.700	-499.51
1.125	-27994.53	3.000	-223.70
1.150	-27444.93	4.000	-24.78
1.175	-26811.66	5.000	-5.01
1.200	-26109.89	10.00	-0.06
1.225	-25353.18	20.00	-0.00
1.250	-24552.95	50.00	0.00

[a] In cm⁻¹, relative to the total energy of NH at the internuclear distance of 50 Å.

Table 4. Vibrational term values (T_v) and the effective rotational (B_v) and quartic centrifugal distortion (D_v) constants (in cm^{-1}) for the $X^3\Sigma^-$ state of NH, calculated using the adiabatic potential energy function.

v	T_v			B_v			$D_v \times 10^3$		
	Exp. ^[a]	Calc. ^[b]	Δ ^[c]	Exp.	Calc.	Δ	Exp.	Calc.	Δ
0	0.0000	0.00		16.343275	16.3808	0.0375	1.70284	1.717	0.014
1	3125.5725	3126.46	0.89	15.696418	15.7320	0.0356	1.67936	1.694	0.015
2	6094.8749	6096.35	1.48	15.050471	15.0836	0.0331	1.66126	1.675	0.014
3	8907.5953	8909.35	1.75	14.402014	14.4328	0.0308	1.65061	1.664	0.013
4	11,562.3152	11,564.11	1.79	13.745925	13.7746	0.0287	1.64495	1.661	0.016
5	14,056.1527	14,057.81	1.66	13.076311	13.1027	0.0264	1.65406	1.672	0.018
6	16,384.3477	16,385.67	1.32	12.384084	12.4086	0.0245	1.67825	1.703	0.025

[a] The experimental values from Ref. [2]. [b] The calculated values, the zero-point energy is 1624.01 cm^{-1} . [c] A difference between the calculated and experimental values.

centrifugal distortion constants D_v are overestimated by about 0.016 and $0.003 \times 10^{-3} \text{ cm}^{-1}$, respectively. As shown below, the differences between the experimental and calculated values of the spectroscopic constants can be attributed to the neglected nonadiabatic effects.

The spectroscopic constants T_v and B_v for higher-excited vibrational states provide information about the structure and dynamics of the NH radical far from the equilibrium configuration. Therefore, it is also interesting to investigate the basis set convergence and "small" effects (F, R, D) on these constants.

The basis set convergence on the term values T_v is illustrated in Figure 2. For the smallest basis set used in this work, aug-cc-pCVQZ, the calculated term values underestimate the corresponding experimental values by 2.8 cm^{-1} for $v=1$ and by as much as 31.4 cm^{-1} for $v=6$. The enlargement of the basis set leads to a systematic increase of the calculated term values. For the largest basis set aug-cc-pCV8Z(i), the experimental term values are in turn overestimated by 4.1 cm^{-1} for $v=1$ and by as much as 20.2 cm^{-1} for $v=6$. Note that for the aug-cc-pCV5Z basis set, there is a seemingly good agreement between the calculated and experimental term values, the differences ΔT_v being 2.0 cm^{-1} on the average. Changes in the predicted term values beyond the aug-cc-pCV8Z(i) basis set are estimated to be about 0.2 and 2.3 cm^{-1} for $v=1$ and $v=6$, respectively. The basis set convergence on the effective rotational constants B_v is illustrated in Figure 3. There is a

seemingly good agreement between the experimental B_v values and those calculated using the smallest basis set aug-cc-pCVQZ, the differences ΔB_v being only 0.009 cm^{-1} on the average. On enlargement of the basis set, the calculated B_v values systematically overestimate the corresponding experimental values. The largest basis set aug-cc-pCV8Z(i) appears to be seemingly the worst in predicting the effective rotational constants of NH. In this case, the experimental B_v values are overestimated by 0.041 cm^{-1} on the average. Changes in the predicted rotational constants beyond the aug-cc-pCV8Z(i) basis set are estimated to be about 0.0013 and 0.0022 cm^{-1} for $v=0$ and $v=6$, respectively.

Changes in the term values T_v and the effective rotational constants B_v due to electron correlation beyond the MR-ACPF level of approximation (F), the scalar relativistic effects (R), and the adiabatic effects (D) are illustrated in Figures 4 and 5, respectively. As clearly shown in both the figures, the inclusion of these effects brings the theoretical predictions closer to the experimental data. The scalar relativistic and adiabatic effects appear to be more important than the higher-order correlation effects. For the term values T_v , all of the corrections F, R, and D increase with the vibrational quantum number v . The total correction F+R+D to T_v amounts to -3.2 cm^{-1} for $v=1$ and it increases to -18.8 cm^{-1} for $v=6$. On the inclusion of the total correction F+R+D, the experimental term values are reproduced to 1.5 cm^{-1} on the average. For the effective

Table 5. Vibrational term values (T_v) and the effective rotational (B_v) and quartic centrifugal distortion (D_v) constants (in cm^{-1}) for the $X^3\Sigma^-$ state of ND, calculated using the adiabatic potential energy function.

v	T_v			B_v			$D_v \times 10^3$		
	Exp. ^[a]	Calc. ^[b]	Δ ^[c]	Exp.	Calc.	Δ	Exp.	Calc.	Δ
0	0.0000	0.00		8.781588	8.7931	0.0115	0.48816	0.490	0.002
1	2315.2375	2315.64	0.40	8.528719	8.5398	0.0111	0.48292	0.485	0.002
2	4546.9759	4547.69	0.71	8.276445	8.2869	0.0105	0.47827	0.481	0.003
3	6695.2946	6696.12	0.83	8.024129	8.0341	0.0100	0.47450	0.477	0.003
4	8760.0036	8760.82	0.82	7.771022	7.7803	0.0093	0.47182	0.474	0.002
5	10,740.5915	10,741.31	0.72	7.516144	7.5249	0.0088	0.47038	0.474	0.004
6	12,636.1566	12,636.66	0.50	7.258347	7.2665	0.0082	0.47068	0.474	0.003

[a] The experimental values from Ref. [3]. [b] The calculated values, the zero-point energy is 1190.28 cm^{-1} . [c] A difference between the calculated and experimental values.

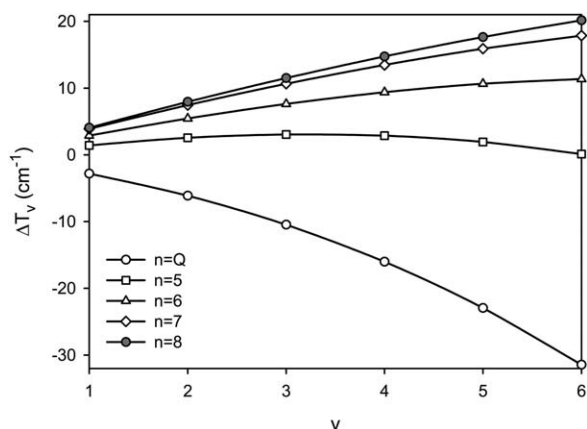


Figure 2. Changes in the vibrational term values T_v for the $X^3\Sigma^-$ state of NH on the basis set aug-cc-pCVnZ. Differences between the calculated and experimental values, ΔT_v (see Table 4), are plotted.

rotational constants B_v , all of the corrections F, R, and D are essentially constant in v . The total correction F+R+D to B_v amounts to -0.010 cm^{-1} on the average.

To account for the effects beyond the adiabatic approximation,^[48–50] the vibrational and rotational g -factors, g_v and g_r , were determined for both isotopologues NH and ND. The g -factors were included by means of second-order perturbational corrections to the vibrational and rotational terms of the effective vibration-rotation Hamiltonian of a diatomic molecule. The reduced nuclear mass μ in the vibrational term was replaced by the effective vibrational reduced mass μ_v defined as $\mu_v = \mu/(1+\beta)$, whereas that in the rotational term was replaced by the effective rotational reduced mass μ_r defined as $\mu_r = \mu/(1+\alpha)$.^[48–50] The parameters β and α are related to the electronic contributions to the vibrational and rotational g -factors, respectively, as follows: $\beta = (m_e/m_p)g_v^{\text{el}}$ and $\alpha = (m_e/m_p)g_r^{\text{el}}$, where m_e/m_p is the electron–proton mass ratio. For both isotopologues NH and ND, the vibrational and rotational g -factors were calculated at various internuclear distances using the CASSCF method with the aug-cc-pVQZ basis set and the active space consisting of 14 molecular orbitals (described

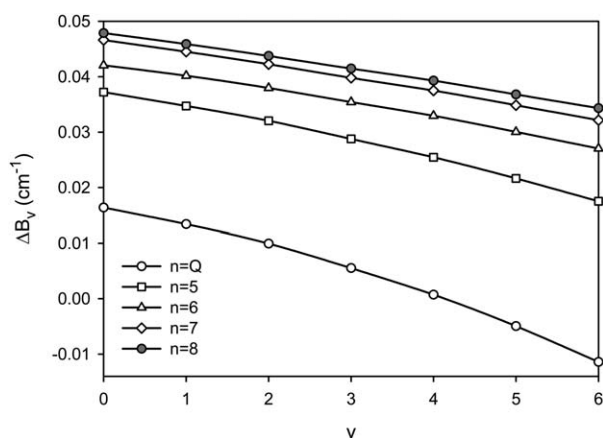


Figure 3. Changes in the effective rotational constants B_v for the $X^3\Sigma^-$ state of NH on the basis set aug-cc-pCVnZ. Differences between the calculated and experimental values, ΔB_v (see Table 4), are plotted.

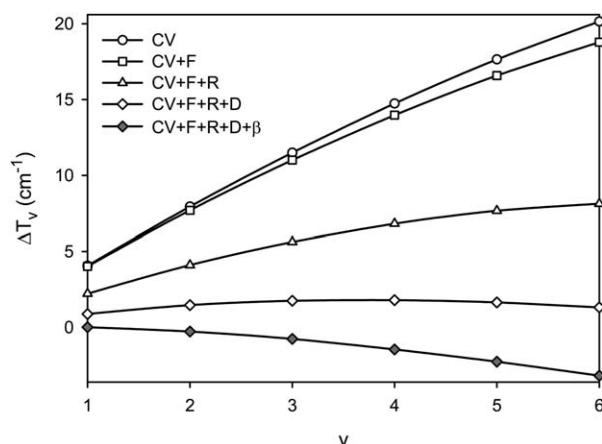


Figure 4. Changes in the vibrational term values T_v for the $X^3\Sigma^-$ state of NH on the effects F, R, D, and β (see the text). Differences between the calculated and experimental values, ΔT_v , are plotted.

above). For general theoretical and computational details of these calculations, the reader is referred to Refs. [51–53]. The calculations were performed using the DALTON package of *ab initio* programs.^[54] The nonadiabatic parameters α and β determined for the main isotopologue NH are shown in Figure 6.

It is interesting to analyze individual contributions of the excited electronic states of NH to the nonadiabatic parameters α and β , see eqs. 16 and 17 of Ref. [52]. For the parameter α , the sum over excited states consists of terms including the transition matrix elements of the total angular momentum operators \hat{L}_x and \hat{L}_y (with the N and H nuclei located at the z axis) and the excitation energies. In the vicinity of the equilibrium configuration of NH, the largest contribution to the sum over excited states arises from the lowest-energy $^3\Pi$ state A. Contributions from the higher-energy $^3\Pi$ states are by two orders of magnitude smaller. Over a wide range about the equilibrium configuration of NH, the sum over excited states is calculated to be nearly constant. Therefore, the dependence of the nonadiabatic parameter α on the internuclear distance r is largely due to the multiplicative factor $1/r^2$. For the parameter β , the sum over excited states consists of terms including the

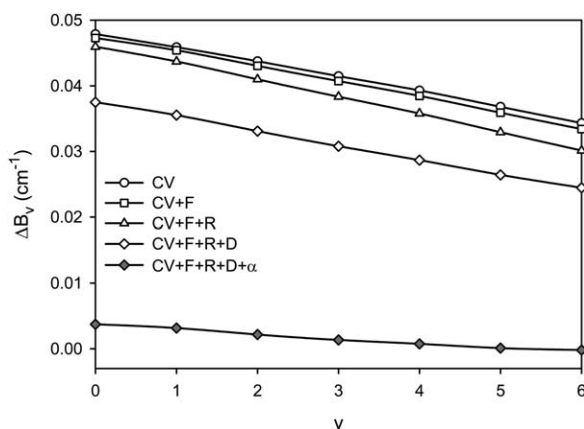


Figure 5. Changes in the effective rotational constants B_v for the $X^3\Sigma^-$ state of NH on the effects F, R, D, and α (see the text). Differences between the calculated and experimental values, ΔB_v , are plotted.

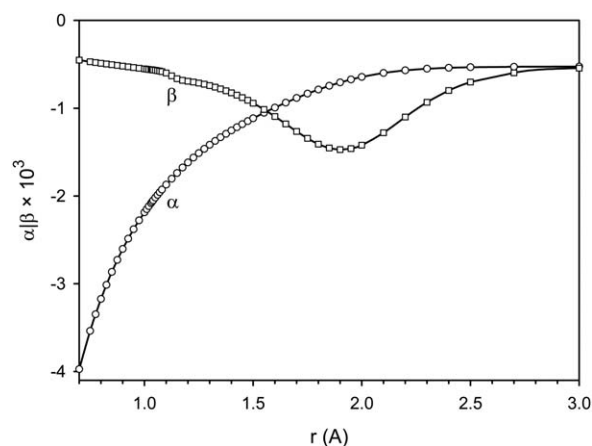


Figure 6. Nonadiabatic parameters α (circles) and β (squares) for the $X^3\Sigma^-$ state of NH as functions of the internuclear distance r .

transition matrix elements of the momentum operator $-i\hbar\partial/\partial r$ and the excitation energies. In the vicinity of the equilibrium configuration of NH, the largest contribution to the sum over excited states arises from the first excited $3^3\Sigma^-$ state 2. The transition matrix element (the absolute value) for this state has a maximum at the internuclear distance of about 1.8 Å, thus leading to a minimum in the nonadiabatic parameter β shown clearly in Figure 6. Because the excitation energy to the $2^3\Sigma^-$ state decreases with the increasing internuclear distance, this minimum is shifted toward a slightly larger internuclear distance. The shape of the function $\beta(r)$ is also somewhat influenced by the higher-excited $3^3\Sigma^-$ states.

The spectroscopic constants calculated for the NH and ND isotopologues are given in Tables 6 and 7, respectively, under the heading "Variable β ". A comparison of these constants

Table 6. Vibrational term values (T_v) and the effective rotational (B_v) and quartic centrifugal distortion (D_v) constants (in cm^{-1}) for the $X^3\Sigma^-$ state of NH, calculated including the nonadiabatic effects.

v	T_v		B_v		$D_v \times 10^3$	
	Calc.[a]	Δ [b]	Calc.	Δ	Calc.	Δ
Variable β						
0	0.00		16.3471	0.0038	1.704	0.001
1	3125.59	0.02	15.6998	0.0034	1.681	0.002
2	6094.60	-0.27	15.0529	0.0024	1.663	0.002
3	8906.84	-0.76	14.4037	0.0017	1.651	0.000
4	11,560.87	-1.45	13.7472	0.0013	1.649	0.004
5	14,053.89	-2.26	13.0770	0.0007	1.660	0.006
6	16,381.17	-3.18	12.3847	0.0006	1.690	0.012
Constant $\beta \equiv$ atomic masses						
0	0.00		16.3471	0.0038	1.704	0.001
1	3125.68	0.11	15.6999	0.0035	1.681	0.002
2	6094.87	0.00	15.0531	0.0026	1.663	0.002
3	8907.26	-0.34	14.4040	0.0020	1.651	0.000
4	11,561.49	-0.83	13.7475	0.0016	1.649	0.004
5	14,054.74	-1.41	13.0774	0.0011	1.660	0.006
6	16,382.25	-2.10	12.3851	0.0010	1.690	0.012

[a] The calculated values, the zero-point energy is 1623.53 and 1623.59 cm^{-1} for the variable and constant β , respectively. [b] A difference between the calculated and experimental values, see Table 4.

Table 7. Vibrational term values (T_v) and the effective rotational (B_v) and quartic centrifugal distortion (D_v) constants (in cm^{-1}) for the $X^3\Sigma^-$ state of ND, calculated including the nonadiabatic effects.

v	T_v		B_v		$D_v \times 10^3$	
	Calc.[a]	Δ [b]	Calc.	Δ	Calc.	Δ
Variable β						
0	0.00		8.7834	0.0018	0.488	0.000
1	2315.31	0.07	8.5305	0.0018	0.483	0.000
2	4547.02	0.04	8.2779	0.0015	0.479	0.001
3	6695.15	-0.14	8.0255	0.0014	0.475	0.000
4	8759.56	-0.44	7.7721	0.0011	0.473	0.001
5	10,739.78	-0.81	7.5170	0.0009	0.472	0.002
6	12,634.86	-1.30	7.2591	0.0008	0.472	0.001
Constant $\beta \equiv$ atomic masses						
0	0.00		8.7834	0.0018	0.488	0.000
1	2315.33	0.09	8.5304	0.0017	0.483	0.000
2	4547.10	0.12	8.2779	0.0015	0.479	0.001
3	6695.28	-0.01	8.0254	0.0013	0.475	0.000
4	8759.74	-0.26	7.7720	0.0010	0.473	0.001
5	10,740.02	-0.57	7.5169	0.0008	0.472	0.002
6	12,635.18	-0.98	7.2589	0.0006	0.472	0.001

[a] The calculated values, the zero-point energy is 1190.02 and 1190.12 cm^{-1} for the variable and constant β , respectively. [b] A difference between the calculated and experimental values, see Table 5.

with those given in corresponding Tables 4 and 5 shows that the use of the effective vibrational reduced mass μ_v leads to a systematic decrease of the term values T_v . For the NH isotopologue, the term value T_1 decreases by 0.9 cm^{-1} , whereas the term value T_6 decreases by as much as 4.5 cm^{-1} . This is also illustrated in Figure 4. For the ND isotopologue, the corresponding changes are smaller, amounting to -0.3 and -1.8 cm^{-1} for the term values T_1 and T_6 , respectively. On accounting for this nonadiabatic effect, the experimental fundamental wavenumber ν of both isotopologues NH and ND is reproduced to just 0.05 cm^{-1} on the average. At this level of theory, the term values for the higher-excited vibrational states are underestimated by 2–4 cm^{-1} . Note, however, that this error will be compensated by further enlarging of the one-particle basis set toward the complete basis set limit, compare Figure 2. The use of the effective rotational reduced mass μ_r leads also to a systematic decrease of the effective rotational constants B_v . As illustrated in Figure 5, these changes are quite spectacular. In fact, changes in the B_v values due to the nonadiabatic effect are by a factor of 3 larger than those due to the total correction F+R+D. As a result, the experimental effective rotational constants of both isotopologues NH and ND are reproduced to 0.002 cm^{-1} on the average.

For the ground vibrational state of the NH and ND isotopologues, the electronic contribution of the averaged vibrational g -factor $\langle g_v^{\text{el}} \rangle$ was calculated to be -1.073 and -0.541, respectively. By adding the corresponding nuclear contribution, the averaged vibrational g -factor $\langle g_v \rangle$ was thus obtained to be -0.106 and -0.040, respectively. The electronic contribution of the averaged rotational g -factor $\langle g_r^{\text{el}} \rangle$ was calculated for the NH and ND isotopologues to be -3.721 and -2.002, respectively. The averaged rotational g -factor $\langle g_r \rangle$ was obtained to be -2.755 and -1.502, respectively.

Table 8. Predicted vibrational term values (T_v) and the effective rotational (B_v) and quartic centrifugal distortion (D_v) constants (in cm^{-1}) for the $X^3\Sigma^-$ state of NH and ND.

v	NH			ND		
	T_v^a	B_v	$D_v \times 10^3$	T_v	B_v	$D_v \times 10^3$
0	0.00	16.3471	1.704	0.00	8.7834	0.488
1	3125.68	15.6999	1.681	2315.33	8.5304	0.483
2	6094.87	15.0531	1.663	4547.10	8.2779	0.479
3	8907.26	14.4040	1.651	6695.28	8.0254	0.475
4	11,561.49	13.7475	1.649	8759.74	7.7720	0.473
5	14,054.74	13.0774	1.660	10,740.02	7.5169	0.472
6	16,382.25	12.3851	1.690	12,635.18	7.2589	0.472
7	18,536.73	11.6583	1.749	14,443.88	6.9965	0.475
8	20,507.38	10.8790	1.851	16,164.14	6.7277	0.480
9	22,278.74	10.0222	2.020	17,793.36	6.4503	0.490
10	23,829.50	9.0525	2.295	19,327.92	6.1611	0.504
11	25,131.52	7.9198	2.746	20,763.18	5.8561	0.526
12	26,150.45	6.5641	3.468	22,093.08	5.5299	0.557
13	26,853.84	4.9277	4.696	23,309.97	5.1759	0.601
14	27,232.35	3.0272	7.197	24,404.31	4.7854	0.665
15				25,364.44	4.3467	0.757
16				26,176.76	3.8475	0.885
17				26,827.77	3.2759	1.071
18				27,306.01	2.6190	1.347
19				27,609.20	1.8923	1.702

[a] The zero-point energies are 1623.59 and 1190.12 cm^{-1} for NH and ND, respectively.

In the context of the nonadiabatic effects, it is interesting to investigate the effect of using atomic masses instead of nuclear masses for calculating the vibration energy levels, as advocated by Handy and Lee.^[43] This can be performed here by holding the nonadiabatic parameter β fixed at the negative nuclear contribution to the vibrational g -factor, $\beta = -(m_e/m_p)g_v^{\text{nu}}$. The results of such calculations are given in Tables 6 and 7 under the heading "Constant $\beta \equiv$ atomic masses." The use of atomic masses reproduces indeed a large fraction of the nonadiabatic effects related to the vibrational g -factor. It has a negligible effect on the effective rotational constants B_v , because these constants are largely influenced by the nonadiabatic parameter α . As shown in Figure 6, the nonadiabatic parameter β is nearly constant and close to the value of $-(m_e/m_p)g_v^{\text{nu}} = -0.526 \times 10^{-3}$ in the vicinity of the equilibrium configuration of the NH isotopologue.

The spectroscopic constants predicted for all bound vibration-rotation energy levels for the $X^3\Sigma^-$ state of the NH and ND isotopologues are given in Table 8. These were calculated using the corresponding adiabatic potential energy functions and the nonadiabatic parameters, with β held fixed. The results can assist future experimental detection of highly-excited states of imidogen by high-resolution vibration-rotation spectroscopy.

Finally, it is interesting to address the issue of the electric dipole moment of NH. The dipole moment function for the $X^3\Sigma^-$ state of NH was recently calculated by Campbell et al.^[24] and Brooke et al.^[1] using the expectation value formula and the MRCI method with the aug-cc-pV6Z basis set. In this work, it was determined using the finite field approach. As for the potential energy function, the total energy of the NH

Table 9. Predicted vibrationally averaged electric dipole moments (μ) (in D) for the $X^3\Sigma^-$ state of NH and ND, calculated using the adiabatic vibrational wave functions.

v	NH	ND
0	1.5150	1.5207
1	1.4718	1.4900
2	1.4233	1.4567
3	1.3692	1.4205
4	1.3090	1.3814
5	1.2422	1.3390
6	1.1679	1.2933

radical in a static homogeneous electric field was calculated using the MR-ACPF method with the aug-cc-pCV6Z basis set. The dipole moment was then calculated using the five-point central difference formula. Changes in the electric dipole moment of NH beyond the aug-cc-pCV6Z basis set are estimated to be about 0.0003 D. Because the CASSCF/MR-ACPF wave function used in this work appeared to be close to the FCI wave function, the dipole moment function of NH was corrected only for the scalar relativistic effects. The corrections, calculated at the MR-ACPF/aug-cc-pCVQZ(uncontracted) level of theory, were found to amount to as much as -0.005 D. The dipole moment function of NH determined in this way is given in the Supporting Information. In the vicinity of the equilibrium configuration of NH, the dipole moment values determined using the expectation value formula and the finite field approach differ by about 0.0002 D. However, these differences increase significantly at both shorter and longer internuclear distances, reaching as much as 0.01 D at the distance of about 1.8 Å. Predicted vibrationally-averaged (effective) electric dipole moments (μ) for the $X^3\Sigma^-$ state of NH and ND, calculated using the adiabatic vibrational wave functions, are given in Table 9. For lower-energy vibrational states of both the isotopologues, changes due to the nonadiabatic effects are negligible. For the ground vibrational state of NH, the effective dipole moment is predicted in this work to be 1.5150 D, slightly smaller than that of 1.5246 D calculated by Campbell et al.^[24] and Brooke et al.^[1] Both the theoretical predictions are substantially larger than the experimental value of 1.389 ± 0.075 D obtained by Scarl and Dalby.^[55]

Conclusions

In conclusion, the accurate potential energy function of imidogen in its ground electronic state $X^3\Sigma^-$ was determined in the state-of-the-art *ab initio* calculations. The vibration-rotation energy levels of the NH and ND isotopologues were predicted to near "spectroscopic" accuracy. In particular, the experimental fundamental wavenumber ν and effective rotational constants B_v of both the isotopologues were reproduced to about 0.1 and 0.002 cm^{-1} , respectively, resulting in a relative error of 10^{-4} . To attain this accuracy, all the scalar relativistic, adiabatic, and nonadiabatic effects should be taken into account. Somewhat pessimistic conclusion is that despite the very large basis sets and the extensive treatment of electron correlation used

in this work, the calculated term values T_v for the higher-excited vibrational states of NH and ND are still underestimated by 2–4 cm⁻¹. Apparently, even for such a simple radical as imidogen, it is not a pedestrian task to calculate all of the vibrational term values to sub-cm⁻¹ accuracy.

Keywords: imidogen · potential energy function · spectroscopic constants

How to cite this article: J. Koput. *J. Comput. Chem.* **2015**, *36*, 1286–1294. DOI: 10.1002/jcc.23931



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Received: 10 February 2015

Revised: 7 April 2015

Accepted: 10 April 2015

Published online on 28 April 2015