Equilibrium Inversion Barrier of NH_3 from Extrapolated Coupled-Cluster Pair Energies

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Dedicated to Professor Paul von R. Schleyer

ABSTRACT: The basis-set convergence of singlet and triplet pair energies of coupled-cluster theory including single and double excitations is accelerated by means of extrapolations based on the distinct convergence behaviors of these pairs. The new extrapolation procedure predicts a nonrelativistic Born–Oppenheimer inversion barrier of $1767 \pm 12\ \mathrm{cm}^{-1}$ for NH_3. An effective one-dimensional, vibrationally averaged barrier of $2021 \pm 20\ \mathrm{cm}^{-1}$ is obtained when relativistic effects ($+20\ \mathrm{cm}^{-1}$), Born–Oppenheimer diagonal corrections ($-10\ \mathrm{cm}^{-1}$), and zero-point vibrations ($+244\ \mathrm{cm}^{-1}$) are accounted for. © 2001 John Wiley & Sons, Inc. J Comput Chem 22: 1306–1314, 2001

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Introduction

A wealth of empirical and theoretical data is available for the inversion barrier associated with the ν_2 umbrella mode in NH_3.[1−21] Here, it suffices to say that the best empirical procedures predict *effective* one-dimensional, vibrationally averaged barriers in the 2018 ± 10 cm^{-1} range. More problems are encountered in the empirical analyses when attempting to include the effects of zero-point vibrations (ZPV). Due to these difficulties, the inferred bare electronic (i.e., equilibrium) inversion barriers (B_e) scatter between 1794 and 1885 cm^{-1}.

The highest quality *ab initio* results for the equilibrium inversion barrier of NH_3 have been obtained by Császár, Allen, and Schaefer.[21] Using the focal-point technique,[21, 22] these authors determined $B_e = 1810$ cm^{-1} for the barrier at the extrapolated nonrelativistic valence-only level. These focal-point studies indicated that the greatest computational difficulty in assessing the equilibrium inversion barrier of NH_3 lies in the relatively protracted basis-set convergence, a case similar to water.[23, 24] Therefore, we decided to extend the previous investigations with a set of CCSD(T) and CCSD(T)-R12/B calculations that decompose the correlation energy into singlet and triplet pair energies. The new coupled-cluster calculations (a) allow extrapolations based on the pair energies obtained in various correlation-consistent basis sets, and thus provide a new and interesting way to arrive at the basis-set limit;[25] and (b) extend the range of directly computed values for the focal-point analysis, and thus can help checking an intrinsic approximation of the focal-point scheme, namely, the neglect of the basis-set dependence of higher order correlation increments and thus their additivity.

Computational Methods

EXTRAPOLATION OF CCSD PAIR ENERGIES

Reference electronic wave functions were determined by the one-determinant restricted Hartree–Fock (RHF) method. Dynamical electron correlation was accounted for by coupled-cluster methods (see, e.g., refs. 26 and 27), including single and double excitations (CCSD), and in cases also a noniterative perturbative correction for connected triple excitations (e.g., CCSD(T)[28] or CCSD[T][29]).

The correlation energy of the CCSD model for a closed-shell system can be written as a sum of singlet ($s = 0$) and triplet ($s = 1$) pair energies, both including contributions from single (S) and connected double (D) excitations,

$$E_{\mathrm{CCSD}} = E_{\mathrm{Hartree\text{–}Fock}} + E^{\mathrm{S}}_{\mathrm{CCSD}} + E^{\mathrm{D}}_{\mathrm{CCSD}}, \tag{1}$$

with

$$E^{\mathrm{S}}_{\mathrm{CCSD}} = \sum_{aibj} t^a_i t^b_j L_{iajb}, \qquad E^{\mathrm{D}}_{\mathrm{CCSD}} = \sum_{aibj} t^{ab}_{ij} L_{iajb}. \tag{2}$$

Here, t^a_i and t^{ab}_{ij} are the coupled-cluster amplitudes while $L_{iajb} = 2g_{iajb} - g_{ibja}$ is a linear combination of electronic repulsion integrals.[27] The reason for decomposing the correlation energy into singlet and triplet contributions is that this will enable us to apply extrapolation schemes that take into account the characteristic convergence behaviors of principal expansions of the singlet and triplet energies, which converge as X^{-3} and X^{-5}, respectively, with the cardinal number X of the basis set.[30, 31]

The CCSD singlet ($\varepsilon^{\mathrm{SD},0}_{ij}$) and triplet ($\varepsilon^{\mathrm{SD},1}_{ij}$) pair energies are given by

$$\varepsilon^{\mathrm{SD},s}_{ij} = \varepsilon^{\mathrm{S},s}_{ij} + \varepsilon^{\mathrm{D},s}_{ij}, \tag{3}$$

with

$$\varepsilon^{\mathrm{S},s}_{ij} = \sum_{ab} t^a_i t^b_j L^s_{iajb}, \qquad \varepsilon^{\mathrm{D},s}_{ij} = \sum_{ab} t^{ab}_{ij} L^s_{iajb}, \tag{4}$$

and

$$L^s_{iajb} = \frac{2s+1}{2}\{g_{iajb} + (-1)^s g_{ibja}\}. \tag{5}$$

In our new extrapolation procedure (cf. ref. 25), which is a small modification of the two-point extrapolation technique proposed by Helgaker et al.,[32−34] the calculated doubles pair energies $\varepsilon^{\mathrm{D},s}_{ij}$ are replaced by the corresponding extrapolated values while the computed singles pair energies $\varepsilon^{\mathrm{S},s}_{ij}$ remain unchanged. When triples contributions are calculated—as in the CCSD(T) model, for example—they also remain unchanged.

The extrapolated doubles pair energies are given by

$$\varepsilon^{\mathrm{D},s}_{ij}(X-1,X) = \frac{X^{2s+3}\varepsilon^{\mathrm{D},s}_{ij}(X) - (X-1)^{2s+3}\varepsilon^{\mathrm{D},s}_{ij}(X-1)}{X^{2s+3} - (X-1)^{2s+3}}, \tag{6}$$

where $\varepsilon^{\mathrm{D},s}_{ij}(X)$ is the value of the pair energy contribution computed with the cc-pVXZ basis and $\varepsilon^{\mathrm{D},s}_{ij}(X-1)$ the corresponding value from the cc-pV($X-1$)Z basis. At the CCSD/cc-pV($X-1,X$)Z extrapolated level, we add the CCSD/cc-pVXZ computed singles contributions to the extrapolated doubles pair energies,

$$\varepsilon^{\mathrm{SD},s}_{ij}(X-1,X) = \varepsilon^{\mathrm{S},s}_{ij}(X) + \varepsilon^{\mathrm{D},s}_{ij}(X-1,X). \tag{7}$$

Similarly, we define CCSD(T)/cc-pV($X-1,X$)Z energies as the ones obtained by replacing solely the CCSD(T)/cc-pVXZ doubles energy contributions by their CCSD/cc-pV($X-1,X$)Z extrapolated counterparts.

The same extrapolation procedure is used for valence-only (frozen-core approximation, FC) and all-electron (FU) correlated calculations as well as for extensions of the correlation-consistent basis sets such as aug-cc-pVXZ or (aug)-cc-pCVXZ.

GEOMETRIES, BASIS SETS, AND PROGRAMS

The reference pyramidal(C_{3v})/planar(C_{3h}) geometries of NH_3 were optimized at the CCSD(T)(FU)/cc-pCVQZ level of theory to r(N—H) = 101.12/99.40 pm and ∠(H—N—H) = 106.36/120.0 degrees. The decrease in the r(N—H) bond length at the planar geometry is due to the increased s character of the bonding. The following is perhaps the most accurate estimate of the equilibrium geometry of pyramidal NH_3: r_e(N—H) = 101.1 pm and $\angle_e$(H—N—H) = 106.7 degrees.[1] Consequently, just as expected, all-electron correlated *ab initio* equilibrium geometries obtained using a CCSD(T)(FU) wave function with a large basis set are very accurate.[27,35] The optimized reference geometries were kept fixed throughout the present computational study.

We employed the (aug)-cc-p(C)VXZ correlation-consistent basis sets of Dunning and coworkers,[36–38] because these sets approach basis-set completeness in a systematic fashion, thus providing opportunities for extrapolations to the limit of a complete basis.

R12/B computations necessitate the use of basis sets designed differently from the (aug)-cc-p(C)VXZ basis sets.[39] Therefore, a [N/H] = [19s14p8d6f4g3h/9s6p4d3f] basis set—taken from ref. 25—was employed for the R12/B calculations.

The two geometry optimizations were carried out with the program package Gaussian 98,[40] while all (standard) single-point energy calculations were performed with the Dalton program.[41] Nonstandard R12/B calculations were performed with the DIRCCR12-95 program.[42]

Calculations of relativistic energies, utilizing the direct perturbation theory (DPT) approach of Kutzelnigg[43,44] in the framework of the Dirac–Coulomb Hamiltonian, were performed with a modified[45] version of the program package Dalton.[41] Gaunt and Breit energy corrections[46] were determined perturbationally by the MOLFDIR[47,48] and BERTHA[49,50] program packages, respectively, using four-component relativistic Dirac–Hartree–Fock wave functions. Uncontracted correlation-consistent basis sets (denoted as u-cc-pCVXZ with X = D and T) were used for the large component and kinetic balance[48,51] was used to generate the small-component basis functions.

The calculations were performed on SGI Origin 2000 R12000 computers at Utrecht University and at the Academic Computing Services Amsterdam (SARA).

Results and Discussion

The calculated and extrapolated energies of the C_{3v} and D_{3h} geometries of NH_3 are collected in Tables I–V. Table I contains the R12/B energies, while Tables II and III display the standard CCSD(FC) pair energies as obtained from calculations and extrapolations in the cc-pVXZ basis sets, in comparision with the R12/B results. The final CCSD(T)(FC) results are shown in Table IV, leading to the valence-shell correlation contributions to the inversion barrier shown in Table V.

TABLE I.
R12/B Energies (in E_h) as Obtained in the [N/H] = [19s14p8d6f4g3h/9s6p4d3f] Basis with the DIRCCR12-95 Program at the CCSD(T)(FU)/cc-pCVQZ Optimized Geometries of the Pyramidal C_{3v} and Planar D_{3h} Structures of NH_3.

	Valence-Shell Correlation (FC)		All-Electron Correlation (FU)	
	C_{3v}	D_{3h}	C_{3v}	D_{3h}
Hartree–Fock	−56.224967	−56.217617	−56.224967	−56.217617
CCSD-R12/B	−56.494225	−56.486043	−56.553677	−56.545796
CCSD(T)-R12/B	−56.503634	−56.495230	−56.563574	−56.555462
CCSD[T]-R12/B[a]	−56.503385	−56.495021	−56.563269	−56.555203

[a] CCSD[T] was originally denoted CCSD+T(CCSD), see ref. 29.

TABLE II.

Basis-Set Dependence of the Valence-Shell CCSD(FC) Pair Energies (in mE_h) of the C_{3v} Structure of NH_3.

Pair	D	T	Q	5	6	(56)[a]	R12/B
			Singlet pairs				
$(2a_1)^2$	−9.89	−11.94	−12.74	−13.00	−13.11	−13.26	−13.25
$1e2a_1$	−29.72	−38.52	−41.37	−42.32	−42.70	−43.23	−43.16
$(1e)^2$	−53.85	−61.13	−63.66	−64.49	−64.82	−65.28	−65.21
$1a_22a_1$	−10.51	−14.89	−16.25	−16.70	−16.89	−17.16	−17.14
$1a_21e$	−20.62	−25.66	−27.52	−28.18	−28.43	−28.77	−28.72
$(1a_2)^2$	−19.57	−24.19	−25.62	−26.09	−26.29	−26.55	−26.54
Total	−144.15	−176.33	−187.16	−190.77	−192.24	−194.25	−194.02
$\bar{\Delta}_{abs}$	4.99	1.77	0.69	0.32	0.18	0.02	
Δ_{max}	6.97	2.34	0.92	0.45	0.25	0.03	
			Triplet pairs				
$1e2a_1$	−8.83	−11.33	−11.91	−12.08	−12.12	−12.15	−12.16
$(1e)^2$	−13.36	−15.71	−16.16	−16.26	−16.29	−16.32	−16.32
$1a_22a_1$	−4.71	−6.62	−7.12	−7.28	−7.32	−7.35	−7.35
$1a_21e$	−31.46	−37.64	−38.89	−39.25	−39.35	−39.42	−39.42
Total	−58.35	−71.30	−74.09	−74.87	−75.09	−75.24	−75.24
$\bar{\Delta}_{abs}$	2.81	0.66	0.19	0.06	0.02	0.00	
Δ_{max}	3.98	0.89	0.26	0.08	0.03	0.00	

[a] The notation cc-pV(56)Z denotes extrapolated pair energies that were been obtained by inserting the cc-pV5Z and cc-pV6Z energies into eqs. (6) and (7).

HARTREE–FOCK RESULTS

Our R12/B results (Table I) include Hartree–Fock energies that are computed with a large basis set comprising 416 basis functions ([N/H] = [19*s*14*p*8*d*6*f*4*g*3*h*/9*s*6*p*4*d*3*f*]). In this basis, the Hartree–Fock contribution to the inversion barrier amounts to 1613 cm^{-1}. In the largest correlation-

TABLE III.

Basis-Set Dependence of the Valence-Shell CCSD(FC) Pair Energies (in mE_h) of the D_{3h} Structure of NH_3.

Pair	D	T	Q	5	6	(56)[a]	R12/B
			Singlet pairs				
$(2a'_1)^2$	−9.48	−11.26	−11.98	−12.22	−12.32	−12.45	−12.45
$1e'2a'_1$	−30.08	−38.81	−41.59	−42.51	−42.89	−43.40	−43.34
$(1e')^2$	−53.34	−60.53	−63.05	−63.87	−64.19	−64.64	−64.58
$1a''_22a'_1$	−10.66	−16.05	−17.72	−18.31	−18.55	−18.88	−18.84
$1a''_21e'$	−18.22	−23.54	−25.63	−26.37	−26.66	−27.06	−26.98
$(1a''_2)^2$	−19.93	−24.19	−25.56	−26.01	−26.20	−26.46	−26.44
Total	−141.70	−174.38	−185.53	−189.28	−190.80	−192.90	−192.63
$\bar{\Delta}_{abs}$	5.09	1.82	0.71	0.33	0.18	0.03	
Δ_{max}	8.18	2.79	1.12	0.53	0.29	0.05	
			Triplet pairs				
$1e'2a'_1$	−8.23	−10.47	−10.99	−11.14	−11.18	−11.21	−11.22
$(1e')^2$	−12.85	−14.90	−15.28	−15.38	−15.41	−15.43	−15.43
$1a''_22a'_1$	−4.74	−6.89	−7.46	−7.64	−7.69	−7.72	−7.72
$1a''_21e'$	−33.16	−39.54	−40.87	−41.24	−41.36	−41.43	−41.43
Total	−58.98	−71.79	−74.59	−75.40	−75.64	−75.80	−75.80
$\bar{\Delta}_{abs}$	2.80	0.67	0.20	0.07	0.03	0.00	
Δ_{max}	4.14	0.94	0.28	0.09	0.04	0.00	

[a] Cf. Table II.

TABLE IV.
Basis-Set Dependence of the Valence-Shell Energies (in E_h) of the C_{3v} and D_{3h} Reference Forms of NH_3.[a]

Method	Basis	$X = 2$	$X = 3$	$X = 4$	$X = 5$	$X = 6$	R12/B
C_{3v}, calculated							
RHF	cc-pVXZ	−56.19568	−56.21789	−56.22311	−56.22473	−56.22494	−56.22497
	aug-cc-pVXZ	−56.20541	−56.22033	−56.22398	−56.22487		
SD	cc-pVXZ	−0.20250	−0.24764	−0.26124	−0.26565	−0.26733	−0.26926
	aug-cc-pVXZ	−0.21431	−0.25187	−0.26279	−0.26625		
(T)	cc-pVXZ	−0.00379	−0.00763	−0.00870	−0.00907	−0.00920	−0.00916
	aug-cc-pVXZ	−0.00545	−0.00833	−0.00895	−0.00916		
C_{3v}, extrapolated[b]							
SD	cc-pVXZ		−0.26316	−0.27002	−0.26983	−0.26949	
	aug-cc-pVXZ		−0.26509	−0.26998	−0.26963		
D_{3h}, calculated							
RHF	cc-pVXZ	−56.18423	−56.20949	−56.21525	−56.21727	−56.21757	−56.21762
	aug-cc-pVXZ	−56.19737	−56.21289	−56.21662	−56.21751		
SD	cc-pVXZ	−0.20068	−0.24617	−0.26013	−0.26469	−0.26645	−0.26843
	aug-cc-pVXZ	−0.21328	−0.25067	−0.26183	−0.26537		
(T)	cc-pVXZ	−0.00340	−0.00733	−0.00844	−0.00886	−0.00900	−0.00898
	aug-cc-pVXZ	−0.00524	−0.00815	−0.00876	−0.00897		
D_{3h}, extrapolated[b]							
SD	cc-pVXZ		−0.26189	−0.26915	−0.26902	−0.26870	
	aug-cc-pVXZ		−0.26384	−0.26918	−0.26882		

[a] RHF is the restricted Hartree–Fock energy, SD is the CCSD(FC) correlation energy, and (T) denotes the perturbative correction for connected triple excitations at the CCSD(T)(FC) level.

[b] The two values in the column for a given X correspond to the extrapolated cc-pV($X-1, X$)Z and aug-cc-pV($X-1, X$)Z results.

consistent basis set of a given family, we obtain $B_e^{\mathrm{RHF}} = 1618/1614\ \mathrm{cm}^{-1}$ in the cc-pV6Z/aug-cc-pV5Z basis containing 413/367 functions.

We have also attempted to extrapolate—to the limit of a complete basis—the Hartree–Fock energies obtained in the correlation-consistent basis sets by fitting the energies from the three largest sets of a given family to the functional form[52–54]

$$E_X = E_\infty + a\exp(-bX). \tag{8}$$

TABLE V.
Calculated and Extrapolated Valence-Shell Electron-Correlation Contributions (in cm^{-1}) to the Equilibrium Inversion Barrier of NH_3.[a]

Method	Basis	$X = 2$	$X = 3$	$X = 4$	$X = 5$	$X = 6$	R12/B
Calculated							
RHF	cc-pVXZ	2513	1843	1726	1637	1618	1613
	aug-cc-pVXZ	1763	1634	1616	1614		
SD	cc-pVXZ	400	321	244	211	194	183
	aug-cc-pVXZ	225	262	210	193		
(T)	cc-pVXZ	87	67	55	46	43	40
	aug-cc-pVXZ	46	40	41	40		
Extrapolated[b]							
SD	cc-pVXZ		280	191	179	173	
	aug-cc-pVXZ		276	176	177		

[a,b] Cf. Table IV.

From a corresponding fit of RHF/cc-pVXZ energies for $X = 4, 5, 6$, we obtain total Hartree–Fock energies of $-56.224977/-56.217625$ E_h for the C_{3v}/D_{3h} geometries and a barrier of 1613 cm^{-1}. From the aug-cc-pVXZ family with $X = 3, 4, 5$, we obtain $-56.225148/-56.217793$ E_h, respectively, and a barrier of 1614 cm^{-1}.

Even though similar extrapolations taking into account energies from smaller basis sets (i.e., cc-pVTZ or aug-cc-pVDZ) appear to be not accurate enough, we can safely conclude from our best results that the Hartree–Fock limit for the energy difference between the fixed C_{3v} and D_{3h} geometries of the present study has been determined accurate to within 3 cm^{-1}. We, hence, adopt a value of $B_e^{\text{RHF}} = 1613 \pm 3$ cm^{-1} for the Hartree–Fock contribution to the inversion barrier.

In earlier work, Császár et al.[21] found $B_e^{\text{RHF}} = 1628$ cm^{-1} for slightly different geometries, but note that the Hartree–Fock contribution is quite sensitive to the geometries used. Our fixed geometries correspond to stationary points on the CCSD(T)(FU)/cc-pCVQZ potential energy surface (PES) but *not* to stationary points on the Hartree–Fock PES. The Hartree–Fock contribution thus depends to first order on small changes in the geometries while the total CCSD(T)(FU) barrier depends only to second order on such changes.

VALENCE-ONLY CORRELATION

The valence-only CCSD(FC) pair energies of the pyramidal and planar structures of NH_3 are displayed in Tables II and III, respectively, as obtained in the cc-pVXZ basis sets with cardinal numbers ranging from $X = 2$ to 6. The columns under "(56)" show the pair energies that result from applying our extrapolation scheme—eqs. (6) and (7)—to the CCSD(FC)/cc-pV5Z and CCSD(FC)/cc-pV6Z pair energies. These extrapolated pair energies are compared with the calculated R12/B values.

The mean absolute deviations of the calculated singlet and triplet CCSD(FC)/cc-pVXZ pair energies from the corresponding R12/B reference values are depicted in Figure 1 for various cardinal numbers X. This log–log plot reveals the different convergence behaviors of the singlet and triplet pair energies in a very convincing manner—see also ref. 25.

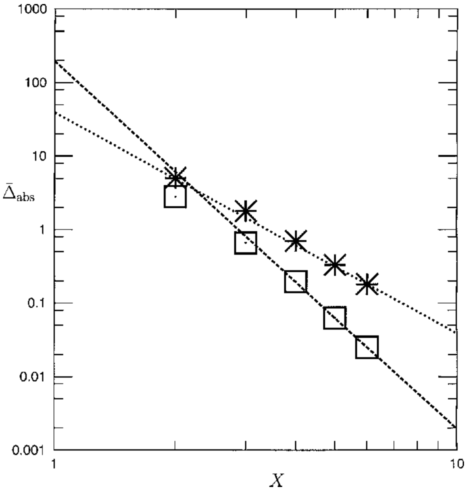

FIGURE 1. Mean absolute deviation ($\bar{\Delta}_{\text{abs}}$ in mE_h) of valence-shell singlet (∗) and triplet (□) CCSD/cc-pVXZ pair energies of the C_{3v} and D_{3h} structures of NH_3. Shown are the deviations from the CCSD-R12 reference values on a log–log scale as function of the cardinal number X. Also shown are lines with slopes of -3 (dotted) and -5 (dashed) through the CCSD/cc-pV6Z data.

The convergence to the basis-set limit (or R12/B reference values) is much accelerated by the extrapolation scheme. Whereas the calculated CCSD(FC)/cc-pV6Z singlet pair energies are in error by 0.18 mE_h (ca. 40 cm^{-1}) on average, this error is reduced to 0.02 mE_h (ca. 4 cm^{-1}) by the extrapolation procedure, which thus appears to be capable of reducing the error by one order of magnitude. The extrapolated triplet pair energies are in complete agreement with the R12/B calculation, confirming the X^{-5}-type convergence of these pairs.

Nevertheless, an error of ca. 4 cm^{-1} per singlet pair energy is still significant when considering the inversion barrier of NH_3. It has been demonstrated in earlier studies that X^{-k}-type extrapolations based on sequences of correlation-consistent basis sets yield total electronic energies of small closed-shell molecules accurate to within 1–3 mE_h[25] and their equilibrium atomization energies accurate to within 1–2 kJ/mol,[55–57] but it has not yet been investigated whether these extrapolation techniques can be applied successfully to small conformational energy differences such as the barrier in NH_3. We here investigate this aspect of the extrapolation techniques.

If the errors in the extrapolated energies would be strictly statistical, then the statistical error—compared with the R12/B reference value—in the extrapolated barrier would amount to ca. 20 cm^{-1}, as there are 10 valence pairs for both structures (degenerate pairs are counted separately). We observe, in fact, that the CCSD(FC)/cc-pV(56)Z and CCSD(FC)-R12/B correlation contributions to the barrier agree to within 10 cm^{-1} (173 vis-à-vis 183 cm^{-1}, cf. Table V).

We shall base our best estimate of the equilibrium inversion barrier on the average value of the extrapolated CCSD(FC)/cc-pV(56)Z, extrapolated CCSD(FC)/aug-cc-pV(Q5)Z, and CCSD(FC)-R12/B pair energies. Hence, we adopt a value of +178 cm^{-1} as our best estimate of the valence-only singles and doubles contribution, with an estimated error bar of 10 cm^{-1}. The corresponding focal-point value is +145 cm^{-1}.[21]

The valence-only (T)-triples corrections add 40 cm^{-1} to the barrier at the CCSD(T)-R12/B level (Table V). A two-point X^{-3}-type extrapolation of the triples contributions in the cc-pV5Z (46 cm^{-1}) and cc-pV6Z (43 cm^{-1}) basis sets suggests a limiting value of 39 cm^{-1}. The agreement between this extrapolated value and the R12/B value is remarkable, noting that the convergence behavior of the triples correction has not yet been investigated let alone established mathematically (numerical experiments seem to *indicate* that the leading term is of the order X^{-3}). In any case, we adopt a value of +40±2 cm^{-1} as our best estimate of the valence-only (T)-triples correction. This value is supported by the corresponding focal-point estimate of +39 cm^{-1}.[21]

CORE-VALENCE CORRECTION

The inclusion of the nitrogen 1*s*-core orbital into the CCSD(T)-R12/B correlation treatment decreases the inversion barrier by 64 cm^{-1} (cf. Table I). At the MP2-R12/B level (not reported), the barrier is reduced by 69 cm^{-1}, an amount quite similar to the CCSD(T)-R12/B value. It was observed in ref. 21 that the MP2 and CCSD(T) core-valence corrections were very similar, and accordingly, the correction obtained at the MP2/cc-pCVQZ level (64 cm^{-1}) was taken as the best estimate of the core-valence correlation effect in that work. This previous best estimate appears to coincide with our present CCSD(T)-R12/B value.

As core-valence correlation effects are usually very efficiently recovered by the R12/B approach, we attach a rather conservative error bar of 4 cm^{-1} to the CCSD(T)-R12/B value and conclude that core-valence correction effects lower the inversion barrier by 64 ± 4 cm^{-1}.

ZERO-POINT VIBRATIONAL ENERGIES

The available *ab initio* works[11, 12, 14, 58] on the vibrational band origins (especially the fundamentals) of one or both reference forms of NH_3 suggest a substantial zero-point vibrational energy (ZPVE) correction to the barrier height. For the pyramidal and the planar forms moderately accurate CISDTQ/DZP harmonic vibrational frequencies[11] are available to us. For the pyramidal form these calculations yield a complementary-mode ZPVE which is only 3.7% larger than the anharmonic result given by a highly accurate[59] CCSD(T)/cc-pVQZ complete quartic force field.[14] Using this same correction for the planar modes as for the pyramidal ones results in a ZPVE correction of 244 cm^{-1}, as reported in ref. 21. The recent variational results of Handy, Carter, and Colwell,[58] based on an accurate six-dimensional potential energy hypersurface, confirm this ZPVE correction estimate. The value of 244 cm^{-1} is adopted in the present work, with an estimated accuracy of ±15 cm^{-1}.

RELATIVISTIC CORRECTIONS

As has recently been demonstrated for the barrier to linearity of water,[21, 60, 61] relativistic effects, aris-

TABLE VI.
Relativistic First-Order Energies (in mE_h) Obtained at the RHF/cc-pCVXZ and CCSD(T)(FU)/cc-pCVXZ levels.[a]

	Pyramidal (C_{3v})				Planar (D_{3h})				
cc-pCV*X*Z	E^{MV}	E^{D1}	E^{D2}	$E^{\Delta DPT}$	E^{MV}	E^{D1}	E^{D2}	$E^{\Delta DPT}$	ΔB_e
				(RHF)					
$X = 2$	−143.341	+114.644	−2.197	+0.015	−142.939	+114.348	−2.191	+0.014	+0.111
$X = 3$	−143.915	+115.162	−2.198	+0.003	−143.538	+114.880	−2.193	+0.004	+0.101
$X = 4$	−146.175	+117.368	−2.199	−0.012	−145.808	+117.093	−2.194	−0.013	+0.096
				CCSD(T)(FU)					
$X = 2$	−143.542	+114.663	−2.064	+0.013	−143.122	+114.354	−2.059	+0.015	+0.118
$X = 3$	−144.255	+115.196	−2.009	+0.035	−143.869	+114.909	−2.004	+0.034	+0.103
$X = 4$	−146.483	+117.374	−1.970	−0.006	−146.116	+117.099	−1.965	−0.006	+0.097

[a] E^{MV} is the mass-velocity term, E^{D1} is the one-electron Darwin term, E^{D2} is the two-electron Darwin term, and $E^{\Delta DPT}$ is the difference between the first-order energy of DPT and the sum $E^{MV} + E^{D1} + E^{D2}$. ΔB_e is the first-order DPT energy contribution to the barrier height.

TABLE VII.
Relativistic Energy Corrections (in mE_h) Beyond the Dirac–Coulomb Hamiltonian.[a]

	Pyramidal (C_{3v})			Planar (D_{3h})			
Basis	E^{Gaunt}	$E^{\text{Ret.}}$	E^{Lamb}	E^{Gaunt}	$E^{\text{Ret.}}$	E^{Lamb}	ΔB_e
u-cc-pCVDZ	+4.941	−0.156	+2.562	+4.952	−0.160	+2.555	+0.000
u-cc-pCVTZ	[+4.792]		2.575	[+4.799]		+2.568	+0.000

[a] All values are obtained at the Hartree–Fock level. Values in brackets are the full Breit energies, $E^{\text{Breit}} = E^{\text{Gaunt}} + E^{\text{Ret.}}$. The Lamb-shlft values are obtained according to eq. (3) of ref. 62.

ing from consideration of special relativity, make a surprisingly large contribution to the barrier. Although the relativistic contribution to the barrier of NH_3 is only about one-half of that in water (there is only one lone pair of electrons allowed to rehybridize during the large-amplitude motion vs. the two lone pairs of electrons of water), the correction is still substantial. In fact, in a relative sense it is more substantial than in water, because the barrier in NH_3 is only about 1/6 of the barrier in water.

Relativistic results obtained as part of this study are collected into Tables VI and VII. The DPT correction to the barrier decreases with extension of the basis both at the RHF and CCSD(T)(FU) levels. Our final estimate for this first-order relativistic correction is +19 cm^{-1}. Relativistic corrections beyond DPT also influence the barrier. We summarize the results as follows: (a) as expected, the Gaunt energies approximate the total Breit energies to within 5%; (b) while the directly computed Breit energies (Gaunt + Ret., cf. Table VII) change slightly upon extension of the basis from u-cc-pCVDZ to u-cc-pCVTZ, the Breit correction to the barrier has a negligible basis set dependency; (c) the Lamb-shift energy correction[62] is comparable to that of the Breit energy correction. The Lamb-shift effect on the barrier is not dependent on the basis and small for both the u-cc-pCVDZ and u-cc-pCVTZ sets. Overall, relativistic effects not considered in the Dirac–Coulomb Hamiltonian seem to have a marginal (+1 cm^{-1}) correction to the equilibrium inversion barrier of ammonia. Therefore, the total relativistic correction to the barrier of NH_3 is +20 cm^{-1} with an estimated error of a few cm^{-1}.

Summary

At the valence-shell CCSD(T)(FC) level, our best estimate of the barrier amounts to $1613 + 178 + 40 = 1831 \pm 11$ cm^{-1}. Relativistic effects increase the barrier by 20 ± 2 cm^{-1} while core-valence correlation effects reduce the barrier by 64 ± 4 cm^{-1}. Thus, the total electronic barrier is estimated as 1788 ± 12 cm^{-1} at the Born–Oppenheimer relativistic all-electron CCSD(T)(FU) level. Correlation effects beyond the CCSD(T)(FU) level are presumably very small (a few cm^{-1})[21] while taking into account the diagonal Born–Oppenheimer correction[21]—of the order of -10 cm^{-1} for the isotope $^{14}NH_3$—yields a final adiabatic equilibrium value of $B_e = 1777 \pm 13$ cm^{-1} for $^{14}NH_3$.

To obtain an *effective* barrier for the one-dimensional treatment of the tunneling motion in NH_3, the zero-point vibrational energy of the complementary vibrational modes must be taken into account. This ZPVE amounts to 244 ± 15 cm^{-1} and yields an effective one-dimensional barrier of 2021 ± 20 cm^{-1}.

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