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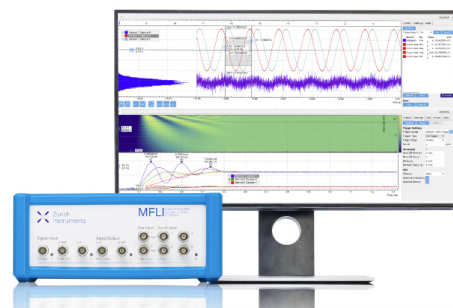
The aminoboranylidene–iminoborane isomerization

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We have determined the barrier and exothermicity of the aminoboranylidene (H_2NB) to iminoborane (HNBH) isomerization reaction using coupled cluster energies extrapolated to the complete basis set limit, including core-correlation corrections and zero-point vibrational energies based on computed fundamental frequencies. Our best estimates of the reaction energy and reaction barrier are -41.35 kcal/mol and 27.40 kcal/mol, respectively. In addition, coupled cluster structural properties and fundamental vibrational frequencies, including isotopic shifts, are compared against experimental data. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1620498]

I. INTRODUCTION

Boron–nitrogen (BN) compounds have attracted theoretical and experimental interest because they often bear considerable similarities to their hydrocarbon counterparts. The well-known isoelectronic pair borazine and benzene, for example, both lack bond alternation and their similarities give rise to fascinating questions regarding their comparable aromaticity.[1–5] However, the polarity of the BN bond gives rise to somewhat different reactivity, making borazine more susceptible to addition and substitution reactions.[6,7] Similarly, studies by McKee[8] and Sakai[9] of the formation of aminoborane from the ammonia–borane adduct, reveal that the reaction is comparable to the dehydrogenation of ethane to yield ethene. Westwood reported a photoelectron study of aminoborane[10] and found a correlation between its ionization potentials and those of ethene.

This work focuses on the B–N analogy of the vinylidene–acetylene rearrangement, which has received considerable attention in the past, in part because of controversy over the lifetime of vinylidene: early photodetachment spectra of the anion[11] and semiclassical dynamics of the isomerization[12] suggested vinylidene was metastable. But more recent Coulomb explosion experiments,[13] as well as theoretical simulations of the dynamics by Schork and Köppel,[14] by Carter and co-workers,[15] and by Zou, Bowman, and Adams[16,17] have revealed significantly longer lifetimes (by several orders of magnitude). High-level *ab initio* data[16,18,19] have provided the necessary potential energy surfaces for several of these dynamics studies, and have helped to unravel the complicated photoelectron spectrum of the vinylidene anion. The B–N analog of the acetylene–vinylidene reaction potentially involves a richer chemistry than its hydrocarbon mate due to its lower symmetry and the resulting pair of nonequivalent 1,2-hydrogen shift pathways: isomerization from the acetylene analog iminoborane (HBNH) can lead to either aminoboranylidene (BNH_2) or borylnitrene (NBH_2). On the other hand, the substantially larger barrier to isomerization (*vide infra*) implies that the aminoboranylidene lifetime will be much longer than its vinylidene counterpart, and its resulting vibronic spectrum will be much less complicated.

Meller[20] and Paetzold[21,22] reviewed the chemistry of iminoborane, and reports of its experimental detection as well as that of aminoboranylidene (BNH_2) and borylnitrene (H_2BN) are relatively scarce. Lory and Porter[23] detected iminoborane by trapping it in an argon matrix, and later Kawashima *et al.*[24] detected iminoborane in the gas phase using diode laser IR spectroscopy. Both studies reported values of the B–N stretching vibration at ≈ 1785 cm^{-1}. In the mid-1990s, Thompson *et al.*[25] published an extensive analysis of B–N products from laser ablation of boron in ammonia. They reported vibrational bands in an argon matrix consistent with aminoboranylidene, and supported their assignments with complete-active-space self-consistent field (CASSCF) calculations. Earlier, Pieper[26] reported trapping of triplet borylnitrene in the photolytic decomposition of azidoboranes.

Theoretical studies of the relevant B–N species are only slightly less rare. Early theoretical investigations of iminoborane include Hartree–Fock-level studies by Baird and Datta[27] and by Dill, Schleyer, and Pople,[28] coupled-electron pair-approximation calculations by Botschwina,[29] and configuration interaction calculations by DeFrees, Binkley, and McLean.[30] More recently, the aminoboranylidene–iminoborane isomerization was investigated by Guo[31] using second order perturbation theory (MP2), though no substantive comparison to the available experimental data was reported. The isomerization of boryl–nitrene to iminoborane was studied using fourth-order perturbation theory by Nguyen,[32] who identified the singlet state of borylnitrene as a saddle point and the triplet state as a minimum on the potential energy surface.

In this work, we have investigated the singlet isomerization surface of aminoboranylidene to iminoborane using high-level coupled-cluster methods[33–36] and large correlation-consistent basis sets. Using complete-basis-set extrapolations of the coupled cluster energies, including corrections for residual dynamic correlation effects, core-correlation, and vibrational anharmonicity, we have determined the isomerization barrier and exothermicity to a probable accuracy of ≈ 1 kcal/mol. In addition, based on

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explicitly computed anharmonicity constants, we have reconsidered the assignment of the experimental vibrational transitions for aminoboranylidene.[25] This study constitutes a first step towards the development of a potential energy surface for the aminoboranylidene–iminoborane system of accuracy comparable to that of acetylene–vinylidene.

II. COMPUTATIONAL METHODS

The properties of the three stationary points on the isomerization surface—iminoborane, aminoboranylidene, and the connecting transition state—were computed using the coupled cluster single- and double-excitation method, including a perturbative estimate of connected triple excitations [CCSD(T)] (Refs. 37–39) and the hierarchy of correlation-consistent (cc-pVXZ) basis sets developed by Dunning.[40] Structural optimizations were carried out at the cc-pVTZ/ and cc-pVQZ/CCSD(T) levels of theory using analytic energy gradients.[41–44] Harmonic vibrational frequencies were computed using analytic energy second derivatives.[45,46] In addition, the fundamental vibrational frequencies were determined using second-order vibrational perturbation theory with cubic and semidiagonal quartic force constants computed via finite-differences of analytic second derivatives using the method described by Stanton, Lopreore, and Gauss.[47] We further carried out full coupled cluster singles, doubles, and triples CCSDT (Refs. 48, 49) computations of harmonic vibrational frequencies for iminoborane and aminoboranylidene using finite differences of energies in order to determine the effects of higher-level dynamic correlation.

In order to estimate the barrier and exothermicity of the isomerization at the complete basis set (CBS) limit, we carried out separate extrapolations of the Hartree–Fock and (frozen-core) correlation components of the total energies using the equations,[40,50,51]

$$E_X^{HF} = E_\infty^{HE} + A e^{-BX} \qquad (1)$$

and

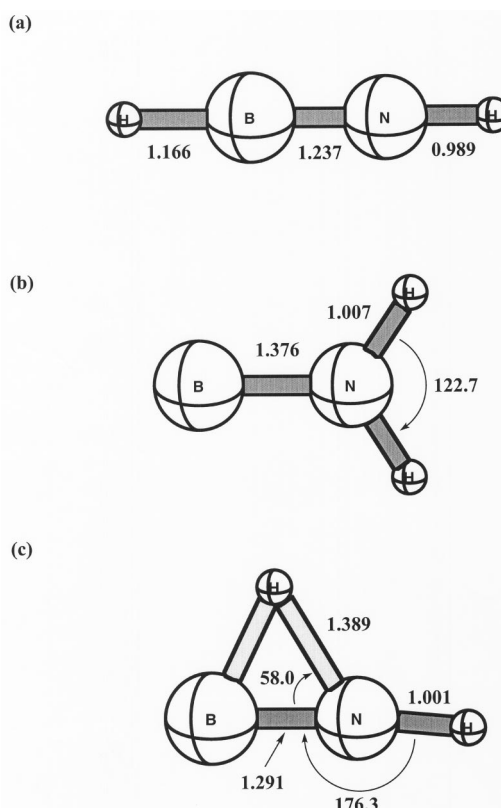$$E_X^{CC} = E_\infty^{CC} + A/X^3, \qquad (2)$$

FIG. 1. Optimized structures of (a) iminoborane at the cc-pVQZ/CCSD(T) level of theory, (b) aminoboranylidene at the cc-pVQZ/CCSD(T) level of theory, and (c) the isomerization transition structure at the cc-pVTZ/CCSD(T) level of theory. Bond lengths are given in Å and bond angles in deg.

respectively, where X represents the cardinal number of the basis set used (e.g., for the cc-pVQZ basis, $X=4$). Core-correlation effects were included by concomitant extrapolation of the all-electron correlation energies computed using the cc-pCVXZ basis sets by Woon and Dunning.[52] Zero-point corrections were included using both the harmonic and fundamental vibrational frequencies. Structural optimization and frequency calculations were performed using the ACESII

TABLE I. CCSD(T) structural and vibrational data for iminoborane using the cc-pVTZ and cc-pVQZ basis sets. Bond lengths are given in Å, bond angles in deg, the dipole moment in Debye, vibrational frequencies in cm^{-1}, and infrared intensities in parentheses in km/mol.

		cc-pVTZ		cc-pVQZ		Expt.[a]
r(B–N)		1.238		1.237		1.2381
r(B–H)		1.166		1.166		⋯
r(N–H)		0.988		0.989		⋯
μ^b		0.191		0.090		<0.1
		Harmonic	Fundamental	Harmonic	Fundamental	Expt.[c]
$\omega_1(\sigma_g^+)$	NH stretch	3915 (185)	3744	3887 (186)	3733	3700
$\omega_2(\sigma_g^+)$	BH stretch	2857 (10)	2771	2888 (11)	2831	⋯
$\omega_3(\sigma_g^+)$	BN stretch	1823 (27)	1792	1821 (33)	1796	1785
$\omega_4(\pi)$	NBH bending	720 (4)	685	732 (1)	621	⋯
$\omega_5(\pi)$	HNB bending	547 (111)	493	488 (113)	477	460

[a]Reference 24.
[b]The negative end of the dipole moment projects toward the nitrogen atom.
[c]Reference 23.

TABLE II. CCSD(T) structural and vibrational data for aminoboranylidene using the cc-pVTZ and cc-pVQZ basis sets. Bond lengths are given in Å, bond angles in deg, the dipole moment in Debye, vibrational frequencies in cm^{-1}, and infrared intensities in parentheses in km/mol.

		cc-pVTZ		cc-pVQZ		
r(B–N)		1.376		1.376		
r(N–H)		1.008		1.007		
θ(H–B–N)		122.8		122.7		
μ^a		3.70		3.66		
		Harmonic	Fundamental	Harmonic	Fundamental	Expt.[b]
$\omega_1(a_1)$	symmetric N–H stretch	3576 (58)	3411	3566 (58)	3402	···
$\omega_2(a_1)$	HNH bending	1591 (165)	1545	1579 (178)	1545	1533
$\omega_3(a_1)$	BN stretch	1281 (52)	1256	1271 (53)	1245	···
$\omega_4(b_1)$	asymmetric N–H stretch	3680 (75)	3502	3678 (78)	3498	···
$\omega_5(b_1)$	HNH wagging	604 (8)	552	613 (9)	594	···
$\omega_6(b_2)$	HNH oop bending	478 (174)	444	430 (172)	428	596

[a]The negative end of the dipole moment projects toward the nitrogen atom.
[b]Reference 25.

quantum chemical package,[53] and calculations with cc-pV5Z and cc-pCVXZ basis sets were carried out using the PSI3 package.[54]

III. OPTIMIZED STRUCTURES AND VIBRATIONAL ANALYSIS

Figure 1 reports on the optimized structures of iminoborane [cc-pVQZ/CCSD(T)], aminoboranylidene [cc-pVQZ/CCSD(T)], and the transition structure [cc-pVTZ/CCSD(T)]. Tables I, II, and III report the computed geometric parameters and vibrational frequency data for these species at the cc-pVTZ/ and cc-pVQZ/CCSD(T) levels of theory. These tables include computed fundamental frequencies and the available experimental values for comparison.

For linear iminoborane ($C_{\infty v}$), the cc-pVTZ/ and cc-pVQZ/CCSD(T) levels of theory yield a B–N distance of 1.2381 and 1.2369 Å, respectively, somewhat shorter than the 1.247 Å found at the MP2 level by Guo,[31] but in excellent agreement with the value of 1.2381 Å inferred by Kawashima *et al.*[24] from gas-phase rotational fine structure data. This result suggests that higher-level dynamic correlation effects—at least including connected triple excitations—should be included to obtain quantitatively accurate molecular properties for BN compounds. This conclusion may appear to be contrary to that of Fisher *et al.*,[55] who reported that the geometries of BN species are insensitive to inclusion of dynamic electron correlation in the model. However, their calculations focused on biological implications of B–N dative bond reactivity, and thus required only semiquantitative accuracy in computed properties. Comparison of the cc-pVQZ/CCSD(T) harmonic vibrational frequencies and the experimental (matrix-isolation) values[23] yield an average deviation of 84 cm^{-1} for iminoborane. Accounting for anharmonicity in the calculation reduces the average deviation to only 20 cm^{-1}. Inclusion of full triple excitations (cc-pVTZ/CCSDT) changes the corresponding CCSD(T) harmonic frequencies by at most 2 cm^{-1}.

The geometry of aminoboranylidene (C_{2v}) corresponds to an sp^2-hybridized nitrogen atom. The cc-pVTZ/ and cc-pVQZ/CCSD(T) levels of theory predict a B–N bond length of 1.3770 and 1.3756 Å, respectively, in this case somewhat

longer than the 1.348 Å found by Guo at the MP2 level.[31] The H–N–H bending fundamental frequency is predicted to be 1545 cm^{-1} with both the cc-pVTZ and cc-pVQZ basis sets, in excellent agreement with the experimental value of 1533 cm^{-1} when including anharmonicity.[25] Inclusion of full triples (cc-pVTZ/CCSDT) changes the CCSD(T) harmonic frequencies by <1 cm^{-1}, suggesting that the remaining discrepancy of 12 cm^{-1} with experiment may result primarily from Ar-matrix effects.

Thompson *et al.* assigned a measured vibrational band at 596 cm^{-1} to the out-of-plane bending mode of aminoboranylidene based in part on comparison with cc-pVDZ/CASSCF calculations, which predict a harmonic frequency of 404.4 cm^{-1} and gave strong agreement with the experimentally measured isotopic shifts.[25] They attributed the remaining 192 cm^{-1} discrepancy to anharmonic effects. However, the CCSD(T) fundamental frequency calculations reported here indicate that the anharmonicity correction for this mode is small: only 34 and 2 cm^{-1} with the cc-pVTZ and cc-pVQZ basis sets, respectively. Furthermore, inclusion of full triples (cc-pVTZ/CCSDT) again changes the harmonic frequencies only by 1 cm^{-1} or less. These results suggest that the assignment of the 596 cm^{-1} experimental fre-

TABLE III. CCSD(T)/cc-pVTZ structural and vibrational data for the iminoborane–aminoboranylidene transition state. Bond lengths are given in Å, bond angles in deg, the dipole moment in Debye, harmonic vibrational frequencies in cm^{-1}, and infrared intensities in parentheses in km/mol.

r(B–N)		1.291
r(N–H$_a$)		1.389
r(N–H$_b$)		1.001
θ(B–N–H$_b$)		176.3
θ(H$_a$–N–B)		58.0
μ^a		3.00
$\omega_1(a')$	reaction coord.	1592i (594)
$\omega_2(a')$	NH$_b$ stretch	3733 (113)
$\omega_3(a')$	BH$_a$N bending	2242 (57)
$\omega_4(a')$	BN stretch	1608 (64)
$\omega_5(a')$	BNH$_b$ bending	839 (104)
$\omega_6(a'')$	BNH$_6$ oop bending	372 (157)

[a]The negative end of the dipole moment projects towards the nitrogen atom.

TABLE IV. cc-pVTZ/CCSD(T) predictions of isotopic shifts (in cm^{-1}) in harmonic vibrational frequencies for the H–N–H symmetric bend, H–N–H wagging, and H–N–H out-of-plane bending vibrations for aminoboranylidene. Experimental frequencies taken from Ref. 25.

Substitution	H–N–H bend	H–N–H wag	H–N–H oop bend
11-14-1-1			
obs.	1533.2		596.0
calc.	1591.2	604.5	478.4
ratio	0.9635	0.9859	1.2458
11-15-1-1			
obs.	1521.9		592.0
calc.	1579.6	601.4	475.0
ratio	0.9635	0.9844	1.2463
10-14-1-1			
obs.	1538.8		596.5
calc.	1596.8	606.8	478.9
ratio	0.9637	0.9830	1.2456
10-15-1-1			
obs.	1527.1		592.5
calc.	1584.4	603.7	475.5
ratio	0.9638	0.9814	1.2461
11-14-2-2	1387.1	471.3	376.2
11-15-2-2	1367.5	468.0	371.9
10-14-2-2	1415.7	474.2	376.9
10-15-2-2	1396.6	470.9	372.6

quency to the H–N–H out-of-plane bend is incorrect. Furthermore, the weaker-intensity H–N–H wagging mode, which is predicted at the cc-pVQZ/CCSD(T) level to lie at 594 cm^{-1}, may be a better candidate for this assignment. This conclusion is further supported by the isotopic shift data given in Table IV: substitution at B and N leads to comparable agreement with the data reported by Thompson *et al.*[25] However, it should be noted that, because both H–N–H wagging and out-of-plane bending are dominated by the hydrogen-atom motions, isotopic labeling of B and N is unlikely to distinguish conclusively between the two modes. For this reason, we have also included deuterium-substitution shifts in Table IV for future comparison to experimental data.

In the transition structure, the B–N bond length is almost halfway in between the bond lengths for the reactants and seems less strongly affected by the inclusion of connected triple excitations in the model: our B–N bond length of 1.291 Å differs little from the 1.295 Å obtained by Guo at the MP2 level.[31] The transition structure is planar (C_s sym-

TABLE V. CCSD(T) energies (in E_h) for BNH$_2$→HBNH reaction.

	cc-pVTZ	cc-pVQZ	cc-pV5Z
HF energies			
HBNH	−80.325 945	−80.332 321	−80.333 661
BNH$_2$	−80.274 682	−80.280 556	−80.281 895
TS	−80.197 860	−80.204 059	−80.205 410
Correlation corrections			
HBNH	−0.359 050	−0.406 060	−0.424 921
BNH$_2$	−0.347 901	−0.394 528	−0.412 475
TS	−0.374 998	−0.420 962	−0.439 509

TABLE VI. Core-valence correlation energies (in E_h) for BNH$_2$→HBNH isomerization. Energies are the difference of single points CCSD(T)/cc-pCVXZ minus CCSD(T)/cc-pVXZ.

	TZ	QZ	5Z
HBNH	−0.102 627	−0.110 056	−0.112 176
BNH$_2$	−0.101 526	−0.108 700	−0.110 727
TS	−0.102 022	−0.109 299	−0.111 332

metry) with an imaginary harmonic frequency of 1592i cm^{-1}, with the hydrogen migration from B to N occuring without breaking the molecular plane of aminoboranylidene, just as predicted for the comparable acetylene–vinylidene isomerization.

IV. COMPLETE BASIS SET EXTRAPOLATION AND ZERO-POINT VIBRATIONAL ENERGY CORRECTIONS

Table V reports the Hartree–Fock energies and the CCSD(T) correlation corrections for a hierarchy of correlation consistent basis sets. As expected, the HF energies converge quickly to the CBS limit while the correlated corrections converge much more slowly (see Table VI). Table VII shows the CBS limits after fitting to Eqs. (1) and (2). We estimate the CBS limits for the classical barrier and the reaction energy to be 31.26 kcal/mol and −40.30 kcal/mol, respectively. Taking the nonextrapolated results at the cc-pVTZ/CCSD(T) level, the values of the barrier and the reaction energy are 31.20 and −39.16 kcal/mol, respectively, indicating that the barrier is only slightly affected by the extrapolation (0.06 kcal/mol), while the reaction energy varies more significantly (1.14 kcal/mol).

Using the harmonic vibrational frequencies only, the ZPVE's for iminoborane, the transition structure, and BNH$_2$ are 15.91, 12.57, and 16.03 kcal/mol, respectively. These values are similar to those reported by Chang[18] for acetylene (16.08), the HCCH transition structure (12.99) and vinylidene (14.86). Correcting the CBS limits for these ZPVE's, the barrier and the reaction energy become 27.81 and −40.42 kcal/mol, respectively. This means a value of 0.86 kcal/mol lower than the barrier at the MP2 level, and a value of reaction energy 2.47 kcal/mol smaller than the MP2 prediction. Adding the core-valence correlation contributions (cf. Table VI) further reduces the classical barrier to 27.40 kcal/mol and increases the magnitude of the reaction energy to −41.39 kcal/mol.

Using the fundamental frequencies for HBNH and BNH$_2$, the ZPVE's are 15.67 and 15.75 kcal/mol. Correcting the CBS limits (without core-correlation corrections) with these ZPVE's reduces the reaction energy to −40.38 kcal/

TABLE VII. CBS limit extrapolated energies (in E_h) for the BNH$_2$→HBNH isomerization.

	HF	Correlated	Core-valence
HBNH	−80.334 018	−0.442 227	−0.115 015
BNH$_2$	−80.282 291	−0.429 733	−0.113 471
TS	−80.205 787	−0.456 417	−0.114 119

J. Chem. Phys., Vol. 119, No. 20, 22 November 2003
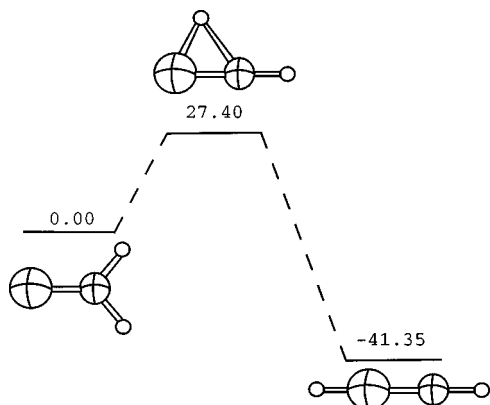
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FIG. 2. HBNH→BNH$_2$ reaction at the cc-pVTZ/CCSD(T) level of theory plus CBS limit extrapolations, ZPVE corrections, and core-valence correlation corrections.

mol. (Note that, because we have chosen not to compute fundamental vibrational frequencies for the transition state, we retain the harmonic ZPVE's for determining the reaction barrier.) Core-valence corrections shift the reaction energy back to −41.35 kcal/mol. [For comparison, using the nonextrapolated cc-pVTZ/ and cc-pVQZ/CCSD(T) results, the reaction energy is −39.97 kcal/mol.] Thus, the reaction energy is essentially unaffected (0.04 kcal/mol) by the anharmonic corrections to the ZPVE's.

In summary, our best estimate for the isomerization barrier is 27.40 kcal/mol. This contrasts with the much lower 1.5 kcal/mol value found by Chang et al.[18] for the vinylidene rearrangement. On the other hand, our best-estimate of the reaction exothermicity (−41.35 kcal/mol) resembles more closely the vinylidene value of −42.95 kcal/mol. Figure 2 summarizes the energy profile for the aminoboranylidene to iminoborane rearrangement, and Fig. 3 shows the total energy fit for the CBS extrapolations.

V. CONCLUSIONS

We estimate the value of the classical barrier for the isomerization of aminoboranylidene to iminoborane to be 27.40 kcal/mol, adjusted for harmonic-frequency-based
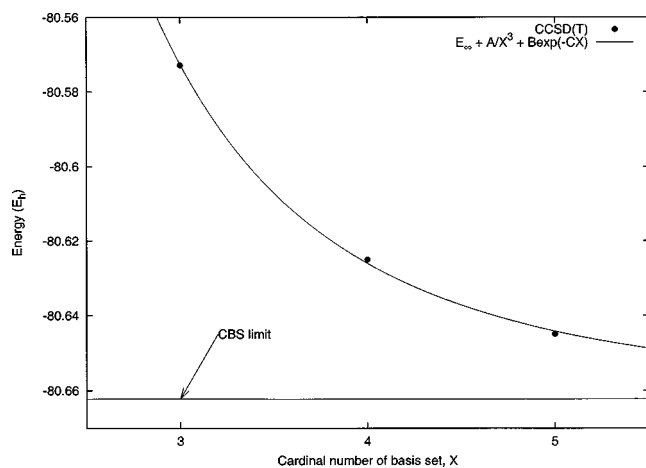
ZPVE's and core-valence correlation contributions. Our best estimate of the theoretical reaction energy is −41.35 kcal/mol including fundamental-frequency ZPVE's and core correlation corrections. The probable accuracy of these data is within 1 kcal/mol, based on previous experience with CBS extrapolations and the convergence behavior described above. The largest remaining errors in this theoretical treatment are expected to be small and will obviously arise from (1) higher levels of dynamic electron correlation, (2) residual basis set effects, (3) relativistic effects. To obtain accurate geometries of BN compounds, it appears advisable to include at least perturbative connected triple excitations in the coupled-cluster density. In addition, based on cc-pVQZ/CCSD(T) fundamental frequency calculations, we suggest reassignment of the Ar-matrix band at 596 cm^{-1} from the H–N–H out-of-plane bend to the weaker H–N–H wagging mode.

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FIG. 3. Convergence of transition structure energies vs cardinal number, X, of the cc-pVXZ basis set using the CCSD(T) level of theory.

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