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Three Lowest-Lying Electronic States of NH_2

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The three lowest-lying electronic states, $\tilde{X}\ ^2B_1$, $\tilde{A}\ ^2A_1$, and $\tilde{B}\ ^2B_2$, as well as the lowest linear $^2\Pi$ stationary point of NH_2 have been investigated systematically using ab initio electronic structure theory. The SCF, CASSCF, CISD, CASSCF-SOCI, CCSD, and CCSD(T) levels of theory have been employed to determine total energies, equilibrium structures, and physical properties including dipole moments, harmonic vibrational frequencies, and infrared intensities of NH_2. According to the instability analysis of the reference SCF wave functions, physical properties of the three lowest-lying equilibrium states of NH_2 may be obtained correctly in the variational sense with all wave functions employed in this study. The lowest linear stationary point ($^2\Pi$) possesses two distinct imaginary vibrational frequencies along the bending coordinate, indicating a strong Renner−Teller interaction. The predicted geometries and physical properties of the two lowest states of NH_2 are in good agreement with available experimental results. At the CCSD(T) level of theory with the largest basis set, the triple-ζ (TZ) plus triple polarization with two sets of higher angular momentum and two sets of diffuse functions [TZ3P(2f,2d)+2diff], the $\tilde{A}\ ^2A_1$ state of NH_2, with a large bond angle of 144.9°, is predicted to lie 32.1 kcal/mol (1.39 eV, 11 200 cm^{-1}) above the ground state. This is in excellent agreement with the experimental T_0 value of 31.80 kcal/mol (1.379 eV, 11 122.6 cm^{-1}). The second excited state ($\tilde{B}\ ^2B_2$) possesses an acute bond angle of 49.3° and is determined to lie 100.1 kcal/mol (4.34 eV, 35 000 cm^{-1}) above the ground state. The classical (and effective) barriers to linearity for the $\tilde{X}\ ^2B_1$ and $\tilde{A}\ ^2A_1$ states were predicted to be 11 870 (12 310) cm^{-1} and 720 (790) cm^{-1}, which are again in good accord with the experimentally estimated values of 12 024 cm^{-1} ($\tilde{X}\ ^2B_1$) and 730 cm^{-1} ($\tilde{A}\ ^2A_1$).

1. Introduction

The so-called α-bands of ammonia which occur in emission in electric discharges through ammonia, in oxy-ammonia and other flames, and in the spectra of comets had long been suspected of being due to the free NH_2 radical. In 1952 the ultraviolet absorption spectrum of NH_2 in the photolysis of ammonia was reported by Herzberg and Ramsay.[1] In the following year, Ramsay also observed NH_2 in the flash photolysis of hydrazine.[2] In 1959 Dressier and Ramsay, in one of the truly classic papers in the history of spectroscopy, reported the first rotational analysis of the visible absorption spectrum of the $\tilde{A}\ ^2A_1-\tilde{X}\ ^2B_1$ transition of the NH_2 radical, recorded on photographic plates by flash-photolysis experiments.[3] From the detailed rotational and vibrational analyses, Dressler and Ramsay concluded that the carrier of the α-bands of ammonia is indeed the free NH_2 radical. The analysis was later extended into the near-infrared region by Johns, Ramsay, and Ross.[4] High vibrational levels of the ground state have been identified and the origin of the electronic transition was experimentally determined to be 11 122.6 cm^{-1}. For other experimental studies on NH_2 readers should refer to a superb compilation by Jacox.[5]

There are many theoretical studies on the ground and excited states of NH_2.[6−25] As early as in 1971 and 1977 one of us reported the three lowest-lying electronic states of NH_2 at the self-consistent field (SCF) and configuration interaction with single and double excitations (CISD) levels of theory.[8,9] With the DZP CISD method[9] the $\tilde{X}\ ^2B_1-\tilde{A}\ ^2A_1$ splitting was determined to be $T_e = 11\,830$ cm^{-1} (33.8 kcal/mol) and the $\tilde{X}\ ^2B_1-\tilde{B}\ ^2B_2$ splitting to be $T_e = 38\,640$ cm^{-1} (110.5 kcal/mol). The existence of this third valence-shell $\tilde{B}\ ^2B_2$ state was conclusively predicted using correlated wave functions in that paper. The classical barrier height to the linearity of the $\tilde{A}\ ^2A_1$ state was predicted to be 974 cm^{-1}. Recently, Brandi, Leonardi, and Petrongolo employed a multireference singles and doubles CI (MRD-CI) method (with full-CI estimates) with a 122 contracted Gaussian function basis set and determined the $\tilde{X}\ ^2B_1-\tilde{A}\ ^2A_1$ splitting to be $T_e = 11\,225$ cm^{-1} (32.1 kcal/mol), the $\tilde{X}\ ^2B_1-\tilde{B}\ ^2B_2$ splitting to be $T_e = 36\,304$ cm^{-1} (103.8 kcal/mol), and the classical barrier height to linearity of the $\tilde{A}\ ^2A_1$ state to be 803 cm^{-1}.[25] In the present work, the energetics and physical properties of the four (three bent equilibria and one linear stationary point) low-lying electronic states of NH_2 have been studied systematically using the highest levels of theory feasible in our laboratory with four large basis sets. All predicted physical properties are expected to be simultaneously consistent with experimental observations and the energetics to be within a chemical accuracy of ±1 kcal/mol.

2. Electronic Structure Considerations

The lowest electronic state of the linear NH_2 radical has the electronic configurations

$$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2(1\pi_i)^2(1\pi_o) \quad 1\ ^2\Pi \qquad (1)$$

$$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2(1\pi_o)^2(1\pi_i) \quad 1\ ^2\Pi \qquad (2)$$

where π_i and π_o stand for the in-plane and out-of-plane π molecular orbitals (MOs), respectively. This $^2\Pi$ state possesses two imaginary bending vibrational frequencies, 1646i cm^{-1} (in-plane) and 831i cm^{-1} (out-of-plane) with the TZ2P(f,d) CISD

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method, and the eigenvectors lead to the nonlinear bent $^2B_1$ and $^2A_1$ states. In other words, this 1 $^2\Pi$ state undergoes a Renner–Teller splitting to display two electronic states.[26–31] According to the analysis by Lee, Fox, Pitzer, and Schaefer,[32] the 1 $^2\Pi$ state of NH_2 is classified as a type D Renner–Teller molecule. The ground state of NH_2 is known to be bent with C_{2v} symmetry and its electronic configuration may be described as

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1) \quad \tilde{X}\ ^2B_1 \tag{3}$$

The first excited state may be expressed as

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1)^2 \quad \tilde{A}\ ^2A_1 \tag{4}$$

which corresponds to a single excitation $(3a_1) \rightarrow (1b_1)$ from the ground state. The second excited state may be written as

$$(1a_1)^2(2a_1)^2(1b_2)(3a_1)^2(1b_1)^2 \quad \tilde{B}\ ^2B_2 \tag{5}$$

which is again a single excitation $(1b_2) \rightarrow (1b_1)$ from the ground state.

According to our instability analysis for SCF wave functions,[33] the linear 1 $^2\Pi$ state MO Hessian (the second derivatives of the electronic energy with respect to the MO rotations) has one zero eigenvalue. The eigenvector of this eigenvalue mainly corresponds to a MO rotation between the $1\pi_i$ and $1\pi_o$ orbitals, indicating that the exchange of 1 π_i and 1 π_o MO does not change the SCF energy. The first excited state ($\tilde{A}\ ^2A_1$) presents an instability index (the number of negative eigenvalues of the MO Hessian) of 1, suggesting the instability of the SCF wave function. The eigenvector of the SCF MO Hessian associated with the negative eigenvalue involves a $(3a_1) \rightarrow (1b_1)$ MO rotation. This means that there is one lower-lying state ($\tilde{X}\ ^2B_1$) at the equilibrium geometry of the first excited state. The second eigenvalue is positive with the eigenvector involving a $(3a_1) \rightarrow (1b_2)$ MO rotation. Therefore, the $\tilde{B}\ ^2B_2$ state lies *above* the $\tilde{A}\ ^2A_1$ state at this geometry. This instability analysis for the $\tilde{A}\ ^2A_1$ state is consistent with the CI potential energy curves of the ground and various excited states of NH_2 by Peyerimhoff and Buenker (Figure 1 in ref 10). Although the $\tilde{A}\ ^2A_1$ state of SCF wave function is unstable, the asymmetric stretching frequency may be determined appropriately due to the orthogonality of the first two states in C_s symmetry ($\tilde{X}$ 1 $^2A''$ and $\tilde{A}$ 1 $^2A'$).

The instability index of the second excited state ($\tilde{B}\ ^2B_2$) of NH_2 is also found to be 1. The eigenvector associated with the negative eigenvalue involves a $(1b_2) \rightarrow (1b_1)$ MO rotation. This indicates that the SCF wave function is unstable and there is one lower-lying state ($\tilde{X}\ ^2B_1$) at the equilibrium geometry of the second excited state. The second MO Hessian eigenvalue is positive with the eigenvector involving a $(1b_2) \rightarrow (3a_1)$ MO rotation. Thus, the $\tilde{A}\ ^2A_1$ state lies *above* the $\tilde{B}\ ^2B_2$ state and the $\tilde{X}$ 1 $^2A''$ and $\tilde{B}$ 2 $^2A'$ states are orthogonal at this geometry. This analysis based on the MO Hessian is again in accord with the CI potential energy curves by Peyerimhoff and Buenker.[10] Even if the $\tilde{B}\ ^2B_2$ state of SCF wave function is unstable, the asymmetric stretching frequency may be obtained without variational collapse at the equilibrium geometry. Therefore, the physical properties of the three electronic states of NH_2 treated in this research may be determined correctly in the variational sense at their equilibrium geometries.

3. Theoretical Procedures

In this research four basis sets were employed. The basis sets of triple-ζ (TZ) quality are derived from Dunning's triple-ζ contraction[34] of Huzinaga's primitive Gaussian functions[35] and they are designated (10s6p/5s3p) for N and (5s/3s) for H. The orbital exponents of the polarization functions are: $\alpha_d(N) = 1.60$ and 0.40 and $\alpha_d(H) = 1.50$ and 0.375 for double polarization (TZ2P); $\alpha_d(N) = 3.20$, 0.80, and 0.20 and $\alpha_p(H) = 3.00$, 0.75, and 0.1875 for triple polarization (TZ3P). The orbital exponents of the higher angular momentum functions are $\alpha_f(N) = 1.00$ and $\alpha_d(H) = 1.00$ for a single set of higher angular momentum functions [TZ2P(f,d)]; and $\alpha_f(N) = 2.00$ and 0.50 and $\alpha_d(H) = 2.00$ and 0.50 for two sets of higher angular momentum functions [TZ3P(2f,2d)]. The orbital exponents of the diffuse functions are $\alpha_p(N) = 0.049\,59$ and $\alpha_s(N) = 0.067\,42$, $\alpha_s(H) = 0.030\,16$ for a single set of diffuse functions [TZ2P(f,d)+diff]; $\alpha_p(N) = 0.049\,59$, 0.018 09 and $\alpha_s(N) = 0.067\,42$ and 0.023 00, $\alpha_s(H) = 0.030\,16$ and 0.009 247 for two sets of diffuse functions [TZ3P(2f,2d)+2diff]. Six Cartesian d-like and 10 Cartesian f-like functions were used throughout. The largest basis set, TZ3P(2f,2d)+2diff, comprises 112 contracted Gaussian functions with a contraction scheme of N (12s8p3d2f/7s5p3d2f) and H (7s3p2d/5s3p2d).

The zeroth-order description of the four electronic (three bent equilibria and one linear stationary point) states of NH_2 may be obtained using single-configuration SCF wave functions. Correlation effects were included using SCF-CISD, CASSCF,[36–38] CASSCF-SOCI,[39] coupled cluster with single and double excitations (CCSD),[40] and CCSD with perturbative triple excitations [CCSD(T)][41] levels of theory. In all the CISD and SOCI procedures, one core (N 1s-like) orbital was frozen and the corresponding virtual (N 1s*-like) orbital was deleted. The CASSCF and CASSCF-SOCI energies were determined for the three equilibrium states at their CISD optimized geometries with the same basis set. For the CASSCF wave functions two different active spaces were employed. The first active space was selected as seven (valence) electrons in six (valence) molecular orbitals (7e/6MO = $2a_1,3a_1,4a_1,1b_1,1b_2,2b_2$). The numbers of the configuration state functions (CSFs) for the three states are 49 ($\tilde{X}\ ^2B_1$), 59 ($\tilde{A}\ ^2A_1$), and 56 ($\tilde{B}\ ^2B_2$), respectively. A second active space was chosen as seven (valence) electrons in eight molecular orbitals (7e/8MO = $2a_1,3a_1,4a_1,5a_1,1b_1,2b_1,1b_2,2b_2$). The numbers of CSFs for the three states are 588 ($\tilde{X}\ ^2B_1$), 616 ($\tilde{A}\ ^2A_1$), and 588 ($\tilde{B}\ ^2B_2$), respectively. The SOCI wave functions were constructed including single and double excitations out of the CASSCF (full CI in the active space) references mentioned above. With the TZ3P(2f,2d)+2diff basis set, the numbers of CSFs of the three equilibrium states in C_{2v} symmetry for CASSCF(7e/6MO)-SOCI and CASSCF(7e/8MO)-SOCI wave functions are 685 091 and 3 337 758 ($\tilde{X}\ ^2B_1$), 695 437 and 3 344 144 ($\tilde{A}\ ^2A_1$), and 694 574 and 3 342 174 ($\tilde{B}\ ^2B_2$), respectively.

The geometries of the four states of NH_2 were optimized via standard analytic derivative methods.[42–44] The harmonic vibrational frequencies and associated IR intensities were determined analytically at the SCF levels of theory and by finite differences of analytic gradients and/or energies for the CISD, CCSD and CCSD(T) levels of theory. All computations were performed using the PSI 2.0 suite of ab initio quantum mechanical programs[45] and the ACES II package.[46]

4. Results and Discussion

Some of the total energies (without physical properties) for the ground state of NH_2 have already been reported elsewhere[47] for theoretical determination of the ionization potentials. All total energies reported here were determined in the present research.

TABLE 1: Theoretical Predictions of the Total Energy (in hartree), Bond Length (in Å), and Harmonic Vibrational Frequencies (in cm^{-1}) for the Linear 1 $^2\Pi$ Stationary Point of the NH_2 Molecule[a]

level of theory	energy	r_e	$\omega_1(\sigma_g)$	$\omega_2(\pi_i)$	$\omega_2(\pi_o)$	$\omega_3(\sigma_u)$
TZ2P(f,d) SCF	−55.528 772	0.9787	3859	1692i	1010i	4259
TZ2P(f,d)+diff SCF	−55.529 601	0.9790	3854	1687i	1007i	4254
TZ3P(2f,2d) SCF	−55.529 280	0.9783	3853	1696i	1013i	4254
TZ3P(2f,2d)+2diff SCF	−55.530 065	0.9786	3850	1690i	1008i	4251
TZ2P(f,d) CISD (1cor/1vir)	−55.728 493	0.9875	3740	1646i	831i	4113
TZ2P(f,d)+diff CISD (1cor/1vir)	−55.729 612	0.9881	3732	1643i	829i	4106
TZ3P(2f,2d) CISD (1cor/1vir)	−55.735 050	0.9863	3733	1655i	847i	4107
TZ3P(2f,2d)+2diff CISD (1cor/1vir)	−55.736 104	0.9868	3727	1646i	842i	4102
TZ2P(f,d) CCSD (1cor/1vir)	−55.736 020	0.9898	3707	1640i	809i	4078
TZ2P(f,d)+diff CCSD (1cor/1vir)	−55.737 240	0.9904	3698	1638i	807i	4070
TZ3P(2f,2d) CCSD (1cor/1vir)	−55.742 816	0.9887	3699	1649i	826i	4071
TZ3P(2f,2d)+2diff CCSD (1cor/1vir)	−55.743 971	0.9892	3692	1640i	821i	4065
TZ2P(f,d) CCSD	−55.755 722	0.9889	3706	1638i	807i	4077
TZ2P(f,d)+diff CCSD	−55.756 952	0.9894	3697	1635i	804i	4069
TZ3P(2f,2d) CCSD	−55.770 793	0.9879	3706	1644i	820i	4079
TZ3P(2f,2d)+2diff CCSD	−55.771 939	0.9884	3700	1634i	814i	4072
TZ2P(f,d) CCSD(T) (1cor/1vir)	−55.741 841	0.9915	3684	1632i	790i	4054
TZ2P(f,d)+diff CCSD(T) (1cor/1vir)	−55.743 154	0.9921	3674	1625i	778i	4046
TZ3P(2f,2d) CCSD(T) (1cor/1vir)	−55.749 298	0.9905	3672	1619i	768i	4045
TZ3P(2f,2d)+2diff CCSD(T) (1cor/1vir)	−55.750 547	0.9911	3665	1617i	787i	4038
TZ2P(f,d) CCSD(T)	−55.761 672	0.9905	3683	1630i	788i	4053
TZ2P(f,d)+diff CCSD(T)	−55.762 994	0.9911	3672	1622i	772i	4044
TZ3P(2f,2d) CCSD(T)	−55.777 519	0.9898	3680	1615i	765i	4052
TZ3P(2f,2d)+2diff CCSD(T)	−55.778 762	0.9904	3672	1613i	782i	4045

[a] Note that the two distinct imaginary bending vibrational frequencies correspond to the two Renner−Teller components.

TABLE 2: Theoretical Predictions of the Total Energy (in hartree), Bond Length (in Å), Bond Angle (in deg), Dipole Moment (in debye), Harmonic Vibrational Frequencies (in cm^{-1}), Infrared Intensities (in Parentheses in km mol^{-1}), and Zero-Point Vibrational Energy (ZPVE in kcal mol^{-1}) for the Bent $\tilde{X}$ $^2B_1$ Ground State of the NH_2 Molecule[a]

level of theory	energy	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	ZPVE
TZ2P(f,d) SCF	a	1.0082	104.77	1.930	3618(3.8)	1643(38.9)	3707(0.0)	12.82
TZ2P(f,d)+diff SCF	a	1.0082	104.79	1.942	3619(3.7)	1640(34.6)	3708(0.0)	12.82
TZ3P(2f,2d) SCF	a	1.0081	104.71	1.865	3615(4.2)	1643(39.3)	3703(0.1)	12.81
TZ3P(2f,2d)+2diff SCF	a	1.0081	104.78	1.874	3616(4.2)	1640(38.2)	3704(0.2)	12.81
TZ2P(f,d) CISD (1cor/1vir)	a	1.0211	103.21	1.870	3440(7.9)	1569(27.3)	3531(0.9)	12.21
TZ2P(f,d)+diff CISD (1cor/1vir)	a	1.0212	103.22	1.884	3441(7.8)	1565(23.2)	3531(0.4)	12.20
TZ3P(2f,2d) CISD (1cor/1vir)	a	1.0198	103.24	1.794	3447(8.6)	1574(28.9)	3536(0.2)	12.23
TZ3P(2f,2d)+2diff CISD (1cor/1vir)	a	1.0198	103.34	1.804	3448(8.6)	1571(27.9)	3538(0.1)	12.23
TZ2P(f,d) CCSD (1cor/1vir)	a	1.0242	103.00		3395(−)	1557(−)	3488(−)	12.07
TZ2P(f,d)+diff CCSD (1cor/1vir)	a	1.0244	103.02		3395(−)	1553(−)	3488(−)	12.06
TZ3P(2f,2d) CCSD (1cor/1vir)	a	1.0230	103.04		3402(−)	1563(−)	3493(−)	12.09
TZ3P(2f,2d)+2diff CCSD (1cor/1vir)	a	a	a		3402(−)	1560(−)	3494(−)	12.09
TZ2P(f,d) CCSD	−55.809 988	1.0231	103.08	1.865	3394(9.1)	1558(26.1)	3487(1.3)	12.06
TZ2P(f,d)+diff CCSD	−55.810 788	1.0232	103.10	1.880	3393(9.1)	1554(22.0)	3487(0.7)	12.06
TZ3P(2f,2d) CCSD	−55.825 107	1.0218	103.16	1.789	3412(9.8)	1563(27.9)	3504(0.3)	12.12
'TZ3P(2f,2d)+2diff CCSD	−55.825 672	1.0218	103.27		3412(−)	1560(−)	3505(−)	12.12
TZ2P(f,d) CCSD(T) (1cor/1vir)	a	1.0266	102.74		3363(−)	1546(−)	3462(−)	11.97
TZ2P(f,d)+diff CCSD(T) (1cor/1vir)	a	1.0268	102.76		3363(−)	1542(−)	3459(−)	11.96
TZ3P(2f,2d) CCSD(T) (1cor/1vir)	a	1.0255	102.79		3368(−)	1552(−)	3463(−)	11.98
TZ3P(2f,2d)+2diff CCSD(T) (1cor/1vir)	a	a	a		3369(−)	1548(−)	3467(−)	11.99
TZ2P(f,d) CCSD(T)	−55.815 983	1.0255	102.82	1.852	3361(11.0)	1547(24.3)	3461(2.0)	11.96
TZ2P(f,d)+diff CCSD(T)	−55.816 839	1.0257	102.84	1.867	3361(10.9)	1543(20.3)	3457(1.2)	11.95
TZ3P(2f,2d) CCSD(T)	−55.831 798	1.0244	102.92	1.772	3377(11.8)	1552(26.2)	3477(0.7)	12.02
TZ3P(2f,2d)+2diff CCSD(T)	−55.832 403	1.0244	103.03		3378(−)	1548(−)	3473(−)	12.01
expt r_0 structure, ref 3		1.024	103.3					
expt r_0 structure, ref 49		1.0246	103.33					
expt μ_0 value, ref 51				1.82				
expt ν values, ref 56					3220	1499		
expt ν values, refs 57−59					3219	1497	3301	

[a] The missing total energies and geometries (indicated as a) may be found in ref 47.

In Table 1 the predicted total energies, bond lengths, and harmonic vibrational frequencies for the lowest linear (1 $^2\Pi$) state of NH_2 are presented at 24 levels of theory. The total energies, bond lengths, bond angles, dipole moments, harmonic vibrational frequencies, and associated infrared intensities for the three lowest-lying states are shown in Tables 2−4. The relative energies at the SCF, CASSCF(7e/6MO), CASSCF(7e/8MO), CISD, CASSCF(7e/6MO)-SOCI, and CASSCF(7e/8MO)-SOCI levels of theory are presented in Table 5. The energetics at the CCSD and CCSD(T) levels of theory with the frozen core-deleted virtual approximations, denoted as (1cor/1vir), and without such approximations, denoted as (0cor/0vir), are shown in Table 6.

A. Geometries. The bond distance of the lowest linear (1 $^2\Pi$) stationary point of NH_2 in Table 1 is elongated with inclusion of correlation effects, as is usually the case. At the

TABLE 3: Theoretical Predictions of the Total Energy (in hartree), Bond Length (in Å), Bond Angle (in deg), Dipole Moment (in debye), Harmonic Vibrational Frequencies (in cm^{-1}), Infrared Intensities (in Parentheses in km mol^{-1}), and Zero-Point Vibrational Energy (ZPVE in kcal mol^{-1}) for the Bent $\tilde{A}\ ^2A_1$ State of the NH_2 Molecule

level of theory	energy	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	ZPVE
TZ2P(f,d) SCF	−55.534 160	0.9851	142.61	0.746	3807(18.0)	1170(86.3)	4122(177.7)	13.01
TZ2P(f,d)+diff SCF	−55.534 939	0.9853	142.69	0.751	3804(18.1)	1167(86.2)	4120(184.6)	13.00
TZ3P(2f,2d) SCF	−55.534 713	0.9849	142.54	0.717	3800(15.8)	1172(78.9)	4116(170.8)	12.99
TZ3P(2f,2d)+2diff SCF	−55.535 426	0.9850	142.64	0.718	3799(16.2)	1168(79.1)	4115(178.5)	12.98
TZ2P(f,d) CISD (1cor/1vir)	−55.731 951	0.9931	144.73	0.706	3692(15.5)	1019(87.5)	3999(170.8)	12.45
TZ2P(f,d)+diff CISD (1cor/1vir)	−55.733 028	0.9935	144.84	0.712	3686(15.7)	1015(88.2)	3995(178.0)	12.43
TZ3P(2f,2d) CISD (1cor/1vir)	−55.738 671	0.9922	144.41	0.672	3685(13.3)	1029(77.3)	3997(159.0)	12.45
TZ3P(2f,2d)+2diff CISD (1cor/1vir)	−55.739 658	0.9925	144.56	0.672	3682(13.7)	1024(77.7)	3994(167.6)	12.44
TZ2P(f,d) CCSD (1cor/1vir)	−55.739 270	0.9952	145.02		3662(−)	997(−)	3969(−)	12.33
TZ2P(f,d)+diff CCSD (1cor/1vir)	−55.740 448	0.9957	145.13		3655(−)	993(−)	3964(−)	12.31
TZ3P(2f,2d) CCSD (1cor/1vir)	−55.746 240	0.9943	144.66		3654(−)	1008(−)	3965(−)	12.33
TZ3P(2f,2d)+2diff CCSD (1cor/1vir)	−55.747 326	0.9947	144.82		3650(−)	1003(−)	3962(−)	12.31
TZ2P(f,d) CCSD	−55.758 938	0.9941	145.11	0.699	3660(15.1)	996(87.9)	3969(168.8)	12.33
TZ2P(f,d)+diff CCSD	−55.760 119	0.9946	145.23	0.705	3653(15.2)	992(88.8)	3963(175.9)	12.31
TZ3P(2f,2d) CCSD	−55.774 135	0.9935	144.83	0.663	3663(12.8)	1003(77.4)	3974(156.5)	12.35
TZ3P(2f,2d)+2diff CCSD	−55.775 213	0.9939	144.99		3658(−)	998(−)	3971(−)	12.33
TZ2P(f,d) CCSD(T) (1cor/1vir)	−55.745 018	0.9968	145.07		3638(−)	987(−)	3949(−)	12.26
TZ2P(f,d)+diff CCSD(T) (1cor/1vir)	−55.746 288	0.9974	145.20		3630(−)	983(−)	3941(−)	12.23
TZ3P(2f,2d) CCSD(T) (1cor/1vir)	−55.752 637	0.9961	144.72		3628(−)	997(−)	3942(−)	12.25
TZ3P(2f,2d)+2diff CCSD(T) (1cor/1vir)	−55.753 814	0.9966	144.90		3623(−)	992(−)	3937(−)	12.22
TZ2P(f,d) CCSD(T)	−55.764 812	0.9958	145.17	0.696	3636(14.6)	986(87.3)	3948(164.0)	12.25
TZ2P(f,d)+diff CCSD(T)	−55.766 085	0.9963	145.30	0.702	3628(14.7)	981(88.3)	3940(171.3)	12.22
TZ3P(2f,2d) CCSD(T)	−55.780 775	0.9953	144.90	0.658	3637(12.3)	992(76.5)	3951(151.0)	12.26
TZ3P(2f,2d)+2diff CCSD(T)	−55.781 945	0.9957	145.08		3631(−)	986(−)	3945(−)	12.24
expt r_0 structure, refs 29 and 30		1.004	144					
expt r_0 structure, ref 31		1.007	144.2					
expt ν values, refs 3 and 30					3325	633		

TABLE 4: Theoretical Predictions of the Total Energy (in hartree), Bond Length (in Å), Bond Angle (in deg), Dipole Moment (in debye), Harmonic Vibrational Frequencies (in cm^{-1}), Infrared Intensities (in Parentheses in km mol^{-1}), and Zero-Point Vibrational Energy (ZPVE in kcal mol^{-1}) for the Bent $\tilde{B}\ ^2B_2$ State of the NH_2 Molecule

level of theory	energy	r_e	θ_e	$r_{N\cdots H_2}$	r_{HH}	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	ZPVE
TZ2P(f,d) SCF	−55.408 486	1.1396	47.98	1.0412	0.9268	2.867	2964(6.6)	1446(31.8)	2482(32.8)	9.85
TZ2P(f,d)+diff SCF	−55.409 797	1.1394	48.06	1.0406	0.9279	2.859	2964(6.2)	1452(29.9)	2486(38.1)	9.87
TZ3P(2f,2d) SCF	−55.410 047	1.1389	48.07	1.0402	0.9277	2.764	2967(5.5)	1461(26.5)	2488(36.3)	9.89
TZ3P(2f,2d)+2diff SCF	−55.410 828	1.1387	48.11	1.0398	0.9283	2.771	2966(4.9)	1464(25.6)	2490(38.9)	9.89
TZ2P(f,d) CISD (1cor/1vir)	−55.614 481	1.1460	49.17	1.0421	0.9535	2.736	2841(9.7)	1597(13.8)	2310(22.3)	9.65
TZ2P(f,d)+diff CISD (1cor/1vir)	−55.616 173	1.1459	49.26	1.0417	0.9551	2.730	2839(8.8)	1599(12.0)	2314(26.6)	9.65
TZ3P(2f,2d) CISD (1cor/1vir)	−55.622 320	1.1440	49.25	1.0400	0.9533	2.612	2846(8.3)	1613(10.8)	2321(25.0)	9.69
TZ3P(2f,2d)+2diff CISD (1cor/1vir)	−55.623 386	1.1441	49.28	1.0399	0.9540	2.619	2844(7.3)	1612(10.0)	2322(27.3)	9.69
TZ2P(f,d) CCSD (1cor/1vir)	−55.623 088	1.1501	49.16	1.0459	0.9569		2808(−)	1584(−)	2255(−)	9.50
TZ2P(f,d)+diff CCSD (1cor/1vir)	−55.624 904	1.1502	49.25	1.0456	0.9585		2805(−)	1586(−)	2260(−)	9.51
TZ3P(2f,2d) CCSD (1cor/1vir)	−55.631 281	1.1484	49.23	1.0440	0.9566		2811(−)	1599(−)	2264(−)	9.54
TZ3P(2f,2d)+2diff CCSD (1cor/1vir)	−55.632 443	1.1485	49.26	1.0440	0.9573		2809(−)	1598(−)	2265(−)	9.54
TZ2P(f,d) CCSD	−55.642 181	1.1489	49.26	1.0444	0.9577	2.722	2807(10.8)	1588(13.0)	2258(20.2)	9.51
TZ2P(f,d)+diff CCSD	−55.644 002	1.1489	49.35	1.0440	0.9593	2.716	2804(9.7)	1590(11.2)	2262(24.4)	9.52
TZ3P(2f,2d) CCSD	−55.658 312	1.1463	49.37	1.0416	0.9576	2.598	2813(9.4)	1605(10.1)	2273(23.0)	9.56
TZ3P(2f,2d)+2diff CCSD	−55.659 470	1.1465	49.41	1.0416	0.9583		2811(−)	1604(−)	2273(−)	9.56
TZ2P(f,d) CCSD(T) (1cor/1vir)	−55.630 801	1.1544	49.18	1.0497	0.9607		2774(−)	1589(−)	2213(−)	9.40
TZ2P(f,d)+diff CCSD(T) (1cor/1vir)	−55.632 735	1.1544	49.28	1.0493	0.9625		2771(−)	1590(−)	2212(−)	9.40
TZ3P(2f,2d) CCSD(T) (1cor/1vir)	−55.639 723	1.1528	49.26	1.0479	0.9608		2775(−)	1603(−)	2223(−)	9.44
TZ3P(2f,2d)+2diff CCSD(T) (1cor/1vir)	−55.640 981	1.1530	49.30	1.0479	0.9617		2772(−)	1602(−)	2219(−)	9.43
TZ2P(f,d) CCSD(T)	−55.650 036	1.1532	49.27	1.0482	0.9614	2.685	2773(12.4)	1592(12.7)	2214(17.9)	9.41
TZ2P(f,d)+diff CCSD(T)	−55.651 977	1.1533	49.37	1.0479	0.9633	2.680	2770(11.1)	1593(10.7)	2214(21.8)	9.40
TZ3P(2f,2d) CCSD(T)	−55.667 026	1.1508	49.40	1.0456	0.9618	2.556	2776(11.0)	1608(9.7)	2229(20.2)	9.45
TZ3P(2f,2d)+2diff CCSD(T)	−55.668 280	1.1511	49.44	1.0456	0.9626		2774(−)	1607(−)	2225(−)	9.44

CCSD and CCSD(T) levels of theory, the frozen core and deleted virtual approximations are found to elongate bond distances by as much as 0.001 Å compared to predictions without these approximations. Dressler and Ramsay obtained a bond length of 0.975 Å from the electronic absorption spectra assuming a linear configuration,[3] while Jungen et al. used a bond length of 1.000 Å at linearity for their experimental fit.[31] A theoretical bond length of 0.991 Å at the TZ3P(2f,2d)+2diff CCSD(T) (1cor/1vir) level of theory is reasonably close to these experimental estimates. The decrease in the NH bond length observed upon the addition of core correlation effects is not surprising given the inclusion of the "tighter" core molecular orbitals into the wave function. However, it should be noted that the basis sets employed in this study were not designed to adequately described the core region, and thus, the results obtained with the frozen core and deleted virtual approximations may be more reliable.

The ground state ($\tilde{X}\ ^2B_1$) of NH_2 has a significantly bent structure as predicted from the Walsh diagram.[48] The experimental r_0 structure is $r_0 = 1.024 \pm 0.005$ Å and 103.3° ± 0.5° from the rotational constants of the (0 0 0) level (derived from observed combination differences of the absorption spectra) by Dressler and Ramsay[3] and $r_0 = 1.0246$ Å and $\theta_0 = 103.33° \pm 0.07°$ from the analysis of the laser magnetic resonance spectra

TABLE 5: Relative Energies T_e (in kcal mol^{-1}) (T_0 Values in Parentheses) for the Three Lowest-Lying Electronic States of NH_2 Using the SCF, CASSCF, CISD, and CASSCF-SOCI Methods

level of theory	$\tilde{X}\ ^2B_1$	$\tilde{A}\ ^2A_1$	$\tilde{B}\ ^2B_2$
TZ2P(f,d) SCF	0.0	31.22(31.41)	110.08(107.11)
TZ2P(f,d)+diff SCF	0.0	31.07(31.25)	109.59(106.64)
TZ3P(2f,2d) SCF	0.0	31.33(31.51)	109.56(106.64)
TZ3P(2f,2d)+2diff SCF	0.0	31.12(31.29)	109.30(106.38)
TZ2P(f,d) CASSCF(7e/6MO)	0.0	37.63(37.87)	111.12(108.56)
TZ2P(f,d)+diff CASSCF(7e/6MO)	0.0	37.47(37.70)	110.67(108.12)
TZ3P(2f,2d) CASSCF(7e/6MO)	0.0	37.72(37.94)	110.66(108.12)
TZ3P(2f,2d)+2diff CASSCF(7e/6MO)	0.0	37.49(37.70)	110.40(107.86)
TZ2P(f,d) CASSCF(7e/8MO)	0.0	32.46(32.70)	105.64(103.08)
TZ2P(f,d)+diff CASSCF(7e/8MO)	0.0	32.17(32.40)	104.93(102.38)
TZ3P(2f,2d) CASSCF(7e/8MO)	0.0	32.66(32.88)	104.86(102.32)
TZ3P(2f,2d)+2diff CASSCF(7e/8MO)	0.0	32.27(32.48)	104.46(101.92)
TZ2P(f,d) CISD	0.0	32.06(32.30)	105.77(103.21)
TZ2P(f,d)+diff CISD	0.0	31.84(32.07)	105.17(102.62)
TZ3P(2f,2d) CISD	0.0	32.10(32.32)	105.11(102.57)
TZ3P(2f,2d)+2diff CISD	0.0	31.81(32.02)	104.77(102.23)
TZ2P(f,d) CASSCF(7e/6MO) SOCI	0.0	32.42(32.66)	104.11(101.55)
TZ2P(f,d)+diff CASSCF(7e/6MO) SOCI	0.0	32.17(32.40)	103.47(100.92)
TZ3P(2f,2d) CASSCF(7e/6MO) SOCI	0.0	32.41(32.63)	103.36(100.82)
TZ3P(2f,2d)+2diff CASSCF(7e/6MO) SOCI	0.0	32.08(32.29)	102.99(100.45)
TZ2P(f,d) CASSCF(7e/8MO) SOCI	0.0	32.43(32.67)	103.70(101.14)
TZ2P(f,d)+diff CASSCF(7e/8MO) SOCI	0.0	32.16(32.39)	103.02(100.47)
TZ3P(2f,2d) CASSCF(7e/8MO) SOCI	0.0	32.45(32.67)	102.89(100.35)
TZ3P(2f,2d)+2diff CASSCF(7e/8MO) SOCI	0.0	32.08(32.29)	102.49(99.95)
theor ref 9	0.0	33.82	110.48
theor ref 10	0.0		106.08
theor ref 14	0.0	32.45	
theor ref 25	0.0	32.09	103.80
expt refs 4 and 31	0.0	(31.80)	

TABLE 6: Relative Energies T_e (in kcal mol^{-1}) (T_0 Values in Parentheses) for the Three Lowest-Lying Electronic States of NH_2 Using the CCSD and CCSD(T) Methods

level of theory	$\tilde{X}\ ^2B_1$	$\tilde{A}\ ^2A_1$	$\tilde{B}\ ^2B_2$
TZ2P(f,d) CCSD (1cor/1vir)	0.0	32.19(32.45)	105.09(102.52)
TZ2P(f,d)+diff CCSD (1cor/1vir)	0.0	31.95(32.20)	104.45(101.90)
TZ3P(2f,2d) CCSD (1cor/1vir)	0.0	32.23(32.47)	104.37(101.82)
TZ3P(2f,2d)+2diff CCSD (1cor/1vir)	0.0	31.90(32.12)	103.99(101.44)
TZ2P(f,d) CCSD	0.0	32.03(32.30)	105.30(102.75)
TZ2P(f,d) +diff CCSD	0.0	31.80(32.05)	104.66(102.12)
TZ3P(2f,2d) CCSD	0.0	31.99(32.22)	104.67(102.11)
TZ3P(2f,2d)+2diff CCSD	0.0	31.66(31.87)	104.29(101.73)
TZ2P(f,d) CCSD(T) (1cor/1vir)	0.0	32.26(32.55)	103.93(101.36)
TZ2P(f,d)+diff CCSD(T) (1cor/1vir)	0.0	32.00(32.27)	103.25(100.69)
TZ3P(2f,2d) CCSD(T) (1cor/1vir)	0.0	32.26(32.53)	103.11(100.57)
TZ3P(2f,2d)+2diff CCSD(T) (1cor/1vir)	0.0	31.90(32.13)	102.70(100.14)
TZ2P(f,d) CCSD(T)	0.0	32.11(32.40)	104.13(101.58)
TZ2P(f,d)+diff CCSD(T)	0.0	31.85(32.12)	103.45(100.90)
TZ3P(2f,2d) CCSD(T)	0.0	32.02(32.26)	103.40(100.83)
TZ3P(2f,2d)+2diff CCSD(T)	0.0	31.66(31.89)	102.99(100.42)
theor ref 9	0.0	33.82	110.48
theor ref 10	0.0		106.08
theor ref 14	0.0	32.45	
theor ref 25	0.0	32.09	103.80
expt refs 4 and 31	0.0	(31.80)	

by Davies et al.[49] The theoretical NH bond distance (r_e value) again lengthens with an improved treatment of correlation effects, while the bond angle decreases. The predicted r_e structures from the correlated wave functions are consistent with each other. With the two best methods employed in this research, using the TZ3P(2f,2d)+2diff basis set, the r_e structure is predicted to be $r_e = 1.0230$ Å and $\theta_e = 103.14°$ [CCSD (1cor/1vir)] and $r_e = 1.0255$ Å and $\theta_e = 102.91°$ [CCSD(T) (1cor/ivir), respectively.[47] These theoretical structures are consistent with the experimental r_0 structure.

The first excited state ($\tilde{A}\ ^2A_1$) of NH_2 has the shortest bond length and the largest bond angle among the three equilibrium states. The experimental r_0 structure of the $\tilde{A}\ ^2A_1$ state is $r_0 = 1.004$ Å and $\theta_e = 144°$ (from Dixon's analysis[29]) from the compilation by Herzberg[30] and $r_0 = 1.007$ Å and $\theta_0 = 144.2°$ from the experimental fitting by Jungen et al.[31] Given a basis set, the theoretical NH bond length and bond angle increase with improved treatments of correlation effects. At the TZ3P(2f,2d)+2diff CCSD(T) (1cor/1vir) level of theory, the equilibrium geometry is determined to be $r_e = 0.9966$ Å and $\theta_e = 144.90°$, which is in accord with the experimental r_0 structure.

The second excited state ($\tilde{B}\ ^2B_2$) of NH_2 is characterized by its acute bond angle of about 49°. The NH bond length for this state is found to be 12.4% longer than that of the ground state. This state is also considered to be a T-shaped structure and/or a complex of the type $N\cdots H_2$. The distance between the N atom and the center of the two H atoms ($r_{N\cdots H_2}$ in Table 3) is 1.048 Å and the distance between the two H atoms (r_{HH} in Table 3) is 0.962 Å. The equilibrium bond lengths of H_2 and H_2^+ are experimentally determined to be 0.7414 and 1.052 Å, respectively.[50] Thus, the HH distance of $\tilde{B}\ ^2B_2$ state is 29.7% longer than that for the H_2 molecule but 8.6% shorter than that for the H_2^+ molecule. The NH bond length, $r_{N\cdots H_2}$, and r_{HH} increase with improved treatments of correlation effects. With the frozen core-deleted virtual approximations the CCSD and CCSD(T) wave functions yield slightly longer bond distances, as was found for the 1 $^2\Pi$ state, and smaller bond angles for the three equilibrium electronic states of NH_2 than those predicted without these approximations.

B. Dipole Moments. The theoretical dipole moment of the ground state of NH_2 decreases with improved treatments of correlation effects. The addition of higher angular momentum functions to the basis set decreases the dipole moment, whereas the augmentation of the basis set with diffuse functions increases it. With the TZ3P(2f,2d) CCSD(T) (0cor/0vir) level of theory, the dipole moment of the $\tilde{X}\ ^2B_1$ state is predicted to be 1.77 debye, which is in good agreement with the experimental μ_0 value of 1.82 ± 0.05 debye, determined via optical Stark spectroscopy with a tunable, single-frequency dye laser by Brown, Chalkley, and Wayne.[51] The magnitude of the dipole moment should be large enough to allow microwave spectroscopic investigations.[49,51−55]

Due to a large bond angle, the dipole moment of the $\tilde{A}\ ^2A_1$ state of NH_2 is substantially smaller than that of the ground state. At the TZ3P(2f,2d) CCSD(T) (0cor/0vir) level of theory it is determined to be 0.66 debye. With the same method the dipole moment of the $\tilde{B}\ ^2B_2$ state of NH_2 is predicted to be 2.56 debye. The magnitude of the dipole moment of this small-angle state is the largest among the three equilibrium states studied in this research. The electrons in the $3a_1$ orbital appear to enhance the polarity of the molecule as seen by the dipole moments for the $\tilde{X}\ ^2B_1$ state ($\mu_e = 1.77$ debye) and the $\tilde{B}\ ^2B_2$ state ($\mu_e = 2.56$ debye).

C. Harmonic Vibrational Frequencies. The magnitudes of the two stretching harmonic vibrational frequencies of the linear stationary point (1 $^2\Pi$) diminish with improved treatments of correlation effects, probably due to the increase of the bond lengths. The magnitudes of the in-plane and out-of-plane bending (imaginary) frequencies also decrease with correlation effects. This feature implies that the barriers to linearity for the $\tilde{X}\ ^2B_1$ and $\tilde{A}\ ^2A_1$ states would be predicted to be lower with improved treatments of correlation effects. With the TZ3P(2f,2d)+2diff CCSD(T) (1cor/1vir) method, the in-plane and out-of-plane bending frequencies are 1617i and 787i cm^{-1}, respectively.

For the ground state ($\tilde{X}\ ^2B_1$) of NH_2, the fundamental vibrational frequencies were experimentally measured to be 3220 (ν_1) and 1499 cm^{-1} (ν_2) from the matrix-isolated IR spectrum,[56] and 3219 (ν_1) and 3301 cm^{-1} (ν_3) from the tunable difference frequency laser IR spectrum,[57] 1497 cm^{-1} (ν_2) from the laser magnetic resonance IR spectrum[58] and from the Fourier transform IR spectrum.[59] Harmonic vibrational frequencies with the TZ3P(2f,2d)+2diff CCSD(T) (1cor/1vir) method are 3369 (ω_1), 1548 (ω_2), and 3467 cm^{-1} (ω_3). The theoretical harmonic vibrational frequencies for small molecules at the CCSD(T) level with a TZ2P(f,d) quality basis set provide values about 5% above the experimental fundamental frequencies.[60] Considering this general tendency, the theoretical (harmonic) and experimental (fundamental) vibrational frequencies are reasonably consistent.

The stretching vibrational frequencies (ω_1 and ω_3) for the first excited state ($\tilde{A}\ ^2A_1$) are significantly larger relative to those of the ground state due to a shorter (about 2.8%) NH bond length. However, they are marginally smaller relative to those for the linear stationary point due to a slightly longer (about 0.6%) NH bond length. On the other hand, the bending frequency (ω_2) is smaller than that of the ground state owing to the larger bond angle of this state. The symmetric stretching and bending frequencies were measured to be 3325 and 633 cm^{-1} from the detailed analysis of the electronic absorption spectrum.[3,30] Corresponding theoretical frequencies of 3623 and 992 cm^{-1} are higher by 9.0% (ω_1) and 56.7% (ω_2). It is seen that the $\tilde{A}\ ^2A_1$ state with its large bond angle appears to display very substantial anharmonicity effects.

As mentioned in subsection A, the $\tilde{B}\ ^2B_2$ state of NH_2 may be regarded as a T-shaped structure and/or a $N\cdots H_2$ complex. Thus the harmonic vibrational frequencies for this state may be assigned as $\omega_1 = 2772$ (a_1, HH stretch), $\omega_2 = 1602$ (a_1, NH_2 symmetric stretch), and $\omega_3 = 2219$ cm^{-1} (b_2, NH_2 asymmetric stretch), respectively. The experimental harmonic vibrational frequencies of the H_2 and H_2^+ are determined to be 4401 and 2322 cm^{-1},[50] respectively. The frequency of the ω_1 mode for the $\tilde{B}\ ^2B_2$ state NH_2 is, therefore, smaller than that for H_2 but larger than that for H_2^+.

D. Infrared (IR) Intensities. For the $\tilde{X}\ ^2B_1$ state of NH_2 the symmetric stretching mode (ω_1) shows a significantly larger IR intensity than the asymmetric stretching mode (ω_3), which is consistent with the experimental observation of the tunable difference frequency laser IR spectrum by Amano.[57] The bending mode (ω_2) has the largest IR intensity among the three vibrational motions. This feature also agrees with the matrix-isolated IR spectrum of the $\tilde{X}\ ^2B_1$ state of NH_2 by Milligan and Jacox.[56]

For the $\tilde{A}\ ^2A_1$ state the IR intensities of the three vibrational modes are larger than those for the ground state. Specifically the IR intensity of the asymmetric stretching mode (ω_3) is comparatively large. Although the permanent dipole moment of the $\tilde{A}\ ^2A_1$ state is smaller than that of the $\tilde{X}\ ^2B_1$ state, the changes in the dipole moment caused by the molecular vibrations seem larger for the $\tilde{A}\ ^2A_1$ state than the $\tilde{X}\ ^2B_1$ state. The IR intensities of the three vibrational modes for the $\tilde{B}\ ^2B_2$ state have comparable magnitudes to those of the ground state, but are smaller than those of the first excited state.

E. Energetics *1. $\tilde{X}\ ^2B_1-\tilde{A}\ ^2A_1$ Splitting.* The energy separation (T_0 value) between the ground and first excited states is experimentally determined to be 31.80 kcal/mol (1.379 eV, 11 122.6 cm^{-1}).[4,31] This energy gap is well reproduced at all levels of theory (less than 1 kcal/mol deviation) except the CASSCF(7e/6MO) wave function. Addition of the $5a_1$ and $2b_1$ orbitals into the active space of the CASSCF wave function is seen to significantly improve the energetic prediction. Although there is a large difference in energetics between the CASSCF (7e/6MO) and CASSCF (7e/8MO) wave functions, there is only a small difference between the analogous two types of CASSCF SOCI wave functions. With the largest basis set, the predicted $\tilde{X}-\tilde{A}$ splittings (T_0 values) are 32.0 (CISD), 32.3 [CASSCF-(7e/6MO)-SOCI], 32.3 [CASSCF(7e/8MO)-SOCI], 32.1 (CCSD), and 32.1 kcal/mol [CCSD(T)], respectively. Our previous T_e value was 11 830 cm^{-1} (33.8 kcal/mol) using the DZP-CISD method,[9] while Buenker et al. obtained a T_e value of 11 350 cm^{-1} (32.5 kcal/mol) employing the MRD-CI method with 72 contracted Gaussian functions.[14] The T_e energy separation of 11 225 cm^{-1} (32.1 kcal/mol) based on the MRD-CI method with a 122 contracted Gaussian basis set by Brandi et al.[25] presents a very similar result to our CASSCF-SOCI wave function with the largest basis set. Our best T_0 value is 32.1 kcal/mol (1.39

eV, 11 200 cm^{-1}), which is in excellent agreement with the experimental value of 11 122.6 cm^{-1}.[4,31] It is clearly seen that improved treatments of correlation effects and expansion of basis set enhance the agreement between the theoretical predictions and experimental observation.

2. $\tilde{X}\,^2B_1-\tilde{B}\,^2B_2$ Splitting. The theoretical energy difference between the $\tilde{X}\,^2B_1$ and $\tilde{B}\,^2B_2$ states is more sensitive to the level of sophistication than the $\tilde{X}-\tilde{A}$ case. The SCF and CASSCF (7e/6MO) wave functions overestimate this energy difference by 6−7.5 kcal/mol. The CASSCF SOCI wave functions predict similar energy splittings as those from the CCSD(T) methods. Our previous T_e value was 38 640 cm^{-1} (110.5 kcal/mol) using the DZP-CISD method,[9] whereas Peyerimhoff and Buenker determined a T_e value of 37 101 cm^{-1} (106.1 kcal/mol) using the MRD-CI method (with full-CI estimates) with 56 contracted Gaussian functions.[10] The T_e energy separation of 36 304 cm^{-1} (103.8 kcal/mol) with the MRD-CI method by Brandi et al.[25] is about 0.8 kcal/mol larger than the result from our CASSCF-SOCI wave functions. With the TZ3P(2f,2d)+2diff CCSD(T) (1cor/1vir) method, the excitation energy of the second excited state of NH_2 is predicted to be $T_e = 102.7$ kcal/mol (4.45 eV, 35 900 cm^{-1}), and the T_0 value is 100.1 kcal/mol (4.34 eV, 35 000 cm^{-1}). This energy separation is the smallest among all the theoretical energy splittings reported to date. In Tables 5 and 6 a convergent pattern for the energy separations in term of correlation level and basis set size is observed.

The electronic transition $\tilde{B}\,^2B_2 \leftarrow \tilde{X}\,^2B_1$ is dipole forbidden.[3] However, according to the MRD-CI study by Brandi et al., the $\tilde{B}\,^2B_2$ state is bound by 19 413 cm^{-1} (55.2 kcal/mol) with respect to the NH($\tilde{b}\,^1\Sigma^+$) + H($\tilde{X}\,^2S_g$) dissociation and by 7556 cm^{-1} (21.6 kcal/mol) with respect to the N($\tilde{a}\,^2D_u$) + H_2($\tilde{X}\,^1\Sigma_g^+$) dissociation. Thus, the $\tilde{B}\,^2B_2$ state may be able to support several rovibrational bound states.[25]

3. Barriers to Linearity for the $\tilde{X}\,^2B_1$ and $\tilde{A}\,^2A_1$ States. The barriers to linearity for the two lowest-lying electronic states of NH_2 are shown in Table 7. The experimentally adjusted barriers to linearity by Jungen et al.[31] are 12 024 cm^{-1} for the $\tilde{X}\,^2B_1$ state and 730 cm^{-1} for the $\tilde{A}\,^2A_1$ state, respectively. As mentioned earlier in section 4C, the barriers to linearity decrease with improved treatments of correlation effects. At the TZ3P(2f,2d)+2diff CCSD(T) level of theory, the classical barriers to linearity are determined to be 11 870 cm^{-1} for the $\tilde{X}\,^2B_1$ state and 720 cm^{-1} for the $\tilde{A}\,^2A_1$ state. The effective barrier heights to linearity were evaluated by adding the zero-point vibrational energy (ZPVE) correction for only the stretching modes to the classical barrier heights. The highly correlated wave functions with large basis sets provide significantly improved agreement with experimental barrier estimates than the earlier studies.[9,14] Our best effective barriers are 12 310 cm^{-1} for the ground state and 790 cm^{-1} for the first excited state, which are in excellent agreement with Jungen's values of 12 024 cm^{-1} ($\tilde{X}\,^2B_1$) and 730 cm^{-1} ($\tilde{A}\,^2A_1$).[31]

5. Concluding Remarks

The three lowest-lying electronic states, $\tilde{X}\,^2B_1$, $\tilde{A}\,^2A_1$, and $\tilde{B}\,^2B_2$, as well as the lowest linear 1 $^2\Pi$ state of NH_2 have been systematically studied using ab initio electronic structure theory. The stability of the reference SCF wave functions has been discussed using the MO Hessian. It was found that the energetics and physical properties of the three equilibrium states investigated in the present study may be correctly obtained in the variational sense. The theoretically predicted geometries and physical properties agree quite well with the available experimental values. The newly predicted geometry for the $\tilde{B}\,^2B_2$ state of NH_2 is $r_e = 1.1530$ Å and $\theta_e = 49.30°$.

TABLE 7: Classical and Effective (in Parentheses) Barrier Heights to Linearity (in cm^{-1}) for the Two Lowest-Lying Electronic States of NH_2

level of theory	$\tilde{X}\,^2B_1$	$\tilde{A}\,^2A_1$
TZ2P(f,d) SCF	12100(12500)	1183(1278)
TZ2P(f,d)+diff SCF	12040(12430)	1172(1264)
TZ3P(2f,2d) SCF	12150(12540)	1192(1288)
TZ3P(2f,2d)+2diff SCF	12060(12450)	1177(1271)
TZ2P(f,d) CISD (1cor/1vir)	11970(12410)	759(840)
TZ2P(f,d)+diff CISD (1cor/1vir)	11890(12320)	750(829)
TZ3P(2f,2d) CISD (1cor/1vir)	12020(12450)	795(874)
TZ3P(2f,2d)+2diff CISD (1cor/1vir)	11900(12330)	780(857)
TZ2P(f,d) CCSD (1cor/1vir)	11970(12420)	713(790)
TZ2P(f,d)+diff CCSD (1cor/1vir)	11880(12320)	704(779)
TZ3P(2f,2d) CCSD (1cor/1vir)	12030(12460)	751(827)
TZ3P(2f,2d)+2diff CCSD (1cor/1vir)	11900(12330)	736(809)
TZ2P(f,d) CCSD	11910(12360)	706(783)
TZ2P(f,d)+diff CCSD	11820(12260)	695(770)
TZ3P(2f,2d) CCSD	11920(12360)	733(807)
TZ3P(2f,2d)+2diff CCSD	11790(12220)	719(791)
TZ2P(f,d) CCSD(T) (1cor/1vir)	11980(12440)	697(773)
TZ2P(f,d)+diff CCSD(T) (1cor/1vir)	11880(12330)	688(763)
TZ3P(2f,2d) CCSD(T) (1cor/1vir)	12020(12460)	733(807)
TZ3P(2f,2d)+2diff CCSD(T) (1cor/1vir)	11870(12310)	717(789)
TZ2P(f,d) CCSD(T)	11920(12380)	689(765)
TZ2P(f,d)+diff CCSD(T)	11820(12270)	678(752)
TZ3P(2f,2d) CCSD(T)	11910(12350)	715(787)
TZ3P(2f,2d)+2diff CCSD(T)	11770(12210)	699(770)
theor ref 9	12804(−)	974(−)
theor ref 14	12330(−)	980(−)
theor ref 25	12028(−)	803(−)
theor ref 22	11914	863
expt ref 29		777
expt ref 31	12024	730

The $\tilde{X}\,^2B_1-\tilde{A}\,^2A_1$ energy separation is predicted to be 32.1 kcal/mol (1.39 eV, 11 200 cm^{-1}), which is in excellent agreement with the experimental value of 31.80 kcal/mol (1.379 eV, 11 122.6 cm^{-1}). The second excited state is determined to lie 100.1 kcal/mol (4.34 eV, 35 000 cm^{-1}) above the ground state. It is hoped that the present study would help to detect the $\tilde{B}\,^2B_2$ state with its acute bond angle. The classical (and effective) barriers to linearity for the $\tilde{X}\,^2B_1$ and $\tilde{A}\,^2A_1$ states were determined to be 11 870 (12 310) cm^{-1} and 720 (790) cm^{-1}, which are in good agreement with the experimentally estimated values of 12 024 cm^{-1} ($\tilde{X}\,^2B_1$) and 730 cm^{-1} ($\tilde{A}\,^2A_1$). It is demonstrated that by employing highly correlated wave functions and large basis sets the energetic predictions reach a chemical accuracy of ±1 kcal/mol.

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