FULL CONFIGURATION INTERACTION ENERGIES, GEOMETRIES, AND QUARTIC FORCE FIELDS OF THE NITRENIUM ION

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Benchmark configuration interaction energies, geometries, dipole moments, and harmonic vibrational frequencies are obtained for four low-lying electronic states of NH_2^+ and for $\tilde{X}\ ^2B_1$ NH_2 by solving the electronic Schrödinger equation exactly within a double-ζ plus polarization (DZP) basis set and restricting the nitrogen 1s-like core orbital to remain doubly occupied. In addition, full quartic force fields have been determined, and sets of anharmonic spectroscopic constants and fundamental frequencies are reported for the $\tilde{a}\ ^1A_1$ state of NH_2^+. Vertical and adiabatic ionization potentials of NH_2 are also determined exactly within a DZP basis. The capability of less-complete electron correlation treatments to match these exact, full configuration interaction (full CI) results is assessed. The efficacy of obtaining anharmonic force fields at nonstationary geometries is also examined, and in agreement with previous work, it is found that the self-consistent field method can provide high quality cubic and quartic force constants when they are evaluated at the full CI equilibrium geometry. Both the CCSD(T) and CASSCF-SOCI methods provide geometric and spectroscopic data in excellent agreement with the Full CI results and are competitive in their reliability with more expensive procedures (*e.g.* CISDTQ). The second $^1A_1$ state in C_{2v} symmetry is predicted by the TZ2P(f,d) CASSCF-SOCI wavefunction to be linear (thus properly labeled as $\tilde{c}\ ^1\Sigma_g^+$), even though it is found to be quasilinear at the DZP full CI level.

Key words: Full configuration interaction; Nitrenium ion; Quartic force fields; Ionization potentials.

In the interstellar medium, it is generally understood that atoms and atomic ions may react to form molecules by (i) interaction on the surface of grains or (ii) two-body radiative associations[1]. While radiative associations between species are slow, fast ion-molecule reactions can occur as soon as there are suitable molecules present in the

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medium. The nitrenium ion, NH_2^+, may be an important intermediate in an ion-molecule pathway to create interstellar ammonia and the ammonium ion[1]. The dissociative ionization of N_2 with He^+ ions creates N^+, which can react successively with H_2 to eventually form NH_2^+. NH_2^+ can further react with H_2 to eventually create NH_4^+, which is able to dissociatively recombine with an electron to form ammonia,

$$NH_4^+ + e^- \rightarrow NH_3 + H \ . \qquad (1)$$

NH_2^+ may also be formed *via* the reaction of atomic nitrogen with H_3^+ (another common interstellar species[1b,1e]

$$N + H_3^+ \rightarrow NH_2^+ + H \ , \qquad (2)$$

and then enter the ammonia creating reaction pathway.

While NH_2^+ is an essential gas phase intermediate, it is also an important species for solvolytic reactions, as it is analogous in many respects to methylene. In 1970, Gassman proposed that in solution, electron-deficient divalent nitrogen species such as NH_2^+ (or in general, NR_2^+) may be involved in many reactions such as ring cleavages and rearrangements similar to those which involve carbenes and carbonium ions[2]. Gassman's work on the role of nitrenium ions as true interaction intermediates in some reactions has continued to stir scientific interest[3]. Moreover, nitrenium ions NR_2^+ continue to be of broad interest to organic chemists[4]. A detailed understanding of NH_2^+ chemistry requires the exploration of ground and excited state potential energy surfaces (PESs). *Ab initio* and experimental efforts have been fruitful in obtaining geometries, vertical and adiabatic excitation energies, and rovibronic spectra for several low-lying states of this ion.

The theoretical work to date has been comprehensive in its scope and achievements due to the relatively small size of NH_2^+ as well as its isovalency to the once controversial methylene molecule[5]. In light of the volume of this previous work, we shall concentrate on more recent contributions to this system. One is referred to the work of Stephens, Yamaguchi, Sherrill, and Schaefer[6] for a summary of the early theoretical studies.

The small size of NH_2^+ allowed for substantial multi-reference configuration interaction (MRCI) treatments as early as the late 1970s. Peyerimhoff and Buenker[7] utilized one such valuable technique – which they termed MRD-CI – in conjuction with a basis set of double-ζ plus polarization (DZP) quality to construct PESs with respect to the HNH bond angle and a fixed NH distance for fourteen electronic states of NH_2^+. The four lowest-lying electronic states were predicted to be $\tilde{X}\ ^3B_1$, $\tilde{a}\ ^1A_1$, $\tilde{b}\ ^1B_1$, and $\tilde{c}\ ^1\Sigma_g^+$

with corresponding equilibrium bond angles of [150°, 108°, 155°, 180°] and adiabatic excitation energies of [1.29 eV (29.9 kcal/mol), 2.03 eV (46.8 kcal/mol), 3.45 eV (79.6 kcal/mol)], respectively.

In 1987, Jensen, Bunker, and McLean applied large multiconfiguration self-consistent field second-order CI (MCSCF-SOCI) wavefunctions with a 4s3p2d1f on N and 3s2p on H (4s3p2d1f/3s2p) contracted Gaussian basis to construct extensive PESs for the $\tilde{X}\ ^3B_1$, $\tilde{a}\ ^1A_1$, and $\tilde{b}\ ^1B_1$ states of NH_2^+ (ref.[8]). Applying the Morse Oscillator–Rigid Bender Internal Dynamics (MORBID) Hamiltonian to the $\tilde{X}\ ^3B_1$ and $\tilde{a}\ ^1A_1$ *ab initio* surfaces, they obtained a singlet–triplet splitting of 1.30 eV (30.0 kcal/mol), anharmonic vibrational frequencies, and rovibrational energy levels for both of these states. In 1993, Jensen, along with Barclay and Hamilton, returned to the study of the $\tilde{X}\ ^3B_1$ and $\tilde{a}\ ^1A_1$ state PESs of NH_2^+ as well as those of CH_2 (ref.[9]). Their work was a comparison of the vibrational energy levels computed by fitting several different rovibrational Hamiltonians (such as MORBID) to *ab initio* and experimental PESs. A least-squares fit of the MORBID Hamiltonian to the rovibronic transitions around ν_3 measured by Okumura, Rehfuss, Dinelli, Bawendi, and Oka[10] (*vide infra*) produced a new potential surface for $\tilde{X}\ ^3B_1$ NH_2^+. This surface was generated assuming the rotational quantum number N to be zero. A further refinement of this surface was done in 1997, when Jensen[11] added $N > 0$ data fitted with the same potential function. This valuable study explored the quasilinearity of the $\tilde{X}\ ^3B_1$ state in some detail, and made the distinction between "linear" and "bent" descriptions of this state. Using the linear bending quantum number, ν_2^{linear}, the bending fundamental was determined to be 321 cm^{-1}.

Chambaud, Gabriel, Schmelz, Rosmus, Spielfiedel, and Feautrier[12] calculated three-dimensional PESs for the $\tilde{X}\ ^3B_1$, $\tilde{a}\ ^1A_1$, and $\tilde{b}\ ^1B_1$ states of NH_2^+ using the complete active space SCF MRCI (CASSCF-MRCI) method with Dunning's correlation consistent quadruple-ζ (cc-pVQZ) basis set. The $\tilde{X}\ ^3B_1$ state surface was fit to give considerable dynamical information including geometric parameters, fundamental vibrations, rovibronic energy levels (K_a = 0–3), electric dipole moment functions and transition intensities. They also fit the $\tilde{a}\ ^1A_1$ and $\tilde{b}\ ^1B_1$ states (which correlate to $^1\Delta_g$ at linearity) with a variational Renner–Teller model to account for vibrational-electronic coupling in this system. Osmann, Bunker, Jensen and Kraemer furthered the study of this bent/quasilinear $\tilde{a}\ ^1A_1$–$\tilde{b}\ ^1B_1$ system[13]. Their PESs were obtained using the CASSCF-MRCI method in conjunction with a large averaged ANO basis set (7s7p4d3f/6s4p3d). Fitting these with the rovibrational Hamiltonian incorporated in the RENNER program[14] and parametrizing the dipole moment functions along the surface, gave them detailed simulations of the absorption spectrum for this system. These results represent perhaps the most reliable theoretical description of the $\tilde{a}\ ^1A_1$ and $\tilde{b}\ ^1B_1$ states to date. As of yet, little work has been done on the elusive $\tilde{c}\ ^1\Sigma_g^+$ state. However, recent SOCI results obtained with a 7s5p3d2f/5s3p2d basis provided by Stephens, Yamaguchi, Sherrill, and Schaefer[6] yield the most reliable prediction for the location of this state [$T_e(T_0)$ = 3.36 (3.34) eV].

Relatively few spectroscopic experiments exist for NH_2^+. The first such study was done by Dunlavey, Dyke, Jonathan and Morris, who took the HeI photoelectron spectrum of the $\tilde{X}\ ^2B_1$ state of NH_2 produced from the reaction of F with NH_3 (ref.[15]). With the help of *ab initio* methods (DZP SCF and CISD) they were able to identify three bands corresponding to the $\tilde{X}\ ^3B_1$, $\tilde{a}\ ^1A_1$, and $\tilde{b}\ ^1B_1$ states of NH_2^+. Lying 11.46 eV (264 kcal/mol) – an adiabatic ionization potential (IP) – above the ground state of NH_2 was the $\tilde{X}\ ^3B_1$ state of NH_2^+. The $\tilde{a}\ ^1A_1$ state appeared at 12.45 eV (287 kcal/mol) yielding a singlet–triplet separation of 0.99 ± 0.02 eV (22.8 ± 0.5 kcal/mol), a value quite different from theoretical predictions. The $\tilde{b}\ ^1B_1$ state was assigned to the band appearing at 13.68 eV, giving a $\tilde{b}$–$\tilde{X}$ separation of 2.22 eV (51.2 kcal/mol). The authors also proposed a value of 840 ± 50 cm^{-1} for the bending vibrational frequency (ν_2) of the $\tilde{X}\ ^3B_1$ state. For the $\tilde{a}\ ^1A_1$ state, they acquired values of 2 900 ± 50 cm^{-1} and 1 350 ± 50 cm^{-1} for ν_1 and ν_2, respectively, while an estimate of 920 ± 150 cm^{-1} was given for ν_2 of the $\tilde{b}\ ^1B_1$ state. Gibson, Greene and Berkowitz utilized photoionization mass spectrometry to revise the adiabatic IPs of $\tilde{X}\ ^2B_1$ NH_2 determined by Dunlavey *et al.*[15] to 11.14 ± 0.01 eV ($\tilde{X}\ ^3B_1$) and 12.445 ± 0.002 eV (a $^1A_1$) above the $\tilde{X}\ ^2B_1$ state of NH_2 (ref.[16]). This significantly altered the experimental singlet–triplet splitting of NH_2^+ to 1.305 ± 0.01 eV (30.1 ± 0.2 kcal/mol), a value in much better agreement with theory[7,8]. Consequently, Jacox corrected the ΔE ($\tilde{b}\ ^1B_1 - \tilde{X}\ ^3B_1$) of Dunlavey *et al.* to 2.54 ± 0.02 eV (58.6 ± 0.5 kcal/mol)[17]. Most recently, Qi, Sheng, Zhang, Yu, and Li ascertained the first adiabatic IP of $\tilde{X}\ ^2B_1$ NH_2 to be 10.78 ± 0.05 eV by combining the techniques of molecular beam and vacuum ultraviolet synchrotron radiation photoionization mass spectroscopy[18]. Su, Hu, Li, Wang, and Wen later pointed out in a theoretical work that the 0.36 eV deviation of Qi *et al.*'s results from those of Gibson *et al.* may be due to an overestimation of the proton appearance potential in their experiment[19].

Using a difference frequency laser spectrometer and a velocity modulated detector, Okumura *et al.*[10] were able to measure the ν_3 = 3 359.9 cm^{-1} absorption in the $\tilde{X}\ ^3B_1$ state of NH_2^+ generated in an $N_2/H_2/He$ glow discharge. This was in excellent agreement with the fundamental value of 3 363 cm^{-1} predicted by Jensen *et al.*[8]. Kabbadj, Huet, Uy, and Oka later examined four hot bands in the same region as ν_3 in the $\tilde{X}\ ^3B_1$ state vibrational spectrum using a similar technique[20]. In treating the "floppy" $\tilde{X}\ ^3B_1$ state of NH_2^+ with a Hamiltonian appropriate for linear molecules, they were able to extract an equilibrium rotational constant of 8.023 cm^{-1} which produces an NH bond length of 1.021 Å. An estimate of the bending frequency (ω_2 = 439 cm^{-1}) was made from the value of the *l*-type doubling constant.

Recently, we have undertaken several efforts to provide full configuration interaction (full CI) benchmarks for CH_2 (refs[21,22]), C_2 and CN^+ (ref.[23]). There are few polyatomic systems, other than CH_2, for which full CI optimized geometries[24,25] as well as dipole moments and harmonic vibrational frequencies[26,27] have been obtained. This is due to the computational difficulty imposed by the factorial dependence of the number of configuration state functions (CSFs) on the number of electrons and orbitals in a full CI procedure. Apart from experiment, though, the full CI method provides the only touchstone for theoretical methods. The full CI results represent the exact solution of the nonrelativistic electronic Hamiltonian within a truncated basis set under the Born–Oppenheimer and frozen-core approximations. Today, the wealth of advances in computer technology as well as improvements in full CI algorithms[28,29] allows for a greater variation in the production of these valuable benchmarks.

NH_2^+ is an excellent candidate for this type of study as its structural and chemical differences distinguish it from the isovalent CH_2 molecule. The ground state of methylene has a barrier to linearity *ca* 2 000 cm^{-1}, while the $\tilde{X}\ ^3B_1$ state of NH_2^+ is quasilinear to a greater degree with a 200 cm^{-1} barrier[9,12]. Thus, $^3B_1$ methylene can support several quanta of vibration in the bending potential, but the zero-point energy of the bending fundamental lies well above the barrier to linearity in $\tilde{X}\ ^3B_1$ NH_2^+. NH_2^+ is much more reactive than CH_2, and its chemistry more resembles that of the carbonium ion[2,3]. Of some interest is the $\tilde{c}$ state of this molecule, which is the second state of its spatial and spin symmetry (in the C_{2v} point group), and as such, is not well described by single-reference correlation procedures. Therefore, benchmark results for this state, in addition to those previously obtained for CH_2 (refs[21,22]) may be helpful for the calibration of various excited state methods such as equation-of-motion coupled-cluster (EOM-CC)[30].

Additionally, there have been numerous efforts directed towards configuration selection schemes for systematic approaches to the full CI limit. Methods such as CI+PT (ref.[31]) and CIPSI (ref.[32]) rely on the sparsity of the full CI Hamiltonian to generate a reference CI space while perturbation theory is used to estimate the contributions of neglected configurations. Wulfov proposed that the CI+PT method can reproduce full CI energies, equilibrium geometries, and harmonic vibrational frequencies for a number of diatomic molecules[31b]. While confirmation of these results with explicit full CI data was not possible at the time, the recent DZP full CI study of C_2 and CN^+ by Leininger *et al.*[23] indicates that the CI+PT method certainly outperforms CISDTQ and CCSDT while accurately reproducing the full CI energies, geometries, and harmonic vibrational frequencies to [(C_2,CN^+) – (0.26,0.38) mE_h, (0.0005,0.0008) Å, (3.4,3.6) cm^{-1}] at a dramatically reduced computational cost for these eight electron systems. Concern over whether PESs computed from these techniques may display discontinuites motivated them to elevate the correlation convergence of higher derivatives of the PES and anharmonic spectroscopic constants of C_2 and CN^+ at the DZP full CI level as goals toward which these CI selection schemes might aspire. With the goal of helping the development of new methods as well as providing additional insight into the effects of electron correlation on a range of molecular properties, reported herein are DZP full CI benchmark vertical and adiabatic excitation energies, and harmonic frequencies for four low-lying states of NH_2^+. The full quartic force field, fundamental vibrational frequencies, and anharmonic spectroscopic constants of the $\tilde{a}\ ^1A_1$ state of NH_2^+ are presented. Also, full CI vertical and adiabatic IPs are given for the $\tilde{X}\ ^2B_1$ state of NH_2.

THEORETICAL

Electronic Structure Considerations

At linearity the electronic configuration of NH_2^+ may be expressed as

$$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2(1\pi_u)^2\ . \tag{3}$$

In the ground state, the degenerate ππ configuration ($^3\Sigma_g^-$) deviates from $D_{\infty h}$ to C_{2v} symmetry, following Walsh's diagrams for AH_2 systems[33], and the $\tilde{X}\ ^3B_1$ electronic state arises from the configuration

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1)\ . \tag{4}$$

The $^1\Delta_g$ state which comes from Eq. (*3*) undergoes Renner–Teller splitting to form the next two electronic states, $\tilde{a}\ ^1A_1$ and $\tilde{b}\ ^1B_1$. While the lowest-lying electronic excited state, $\tilde{a}\ ^1A_1$, can be described as

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2\ , \tag{5}$$

it is probably best represented by a two-configuration wave function

$$C_1(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2 + C_2(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2 \tag{6}$$

to account for a second configuration which becomes equally important at linear geometries. It should be noted that the two CI coefficients C_1 and C_2 have opposite signs and $|C_1| \geq |C_2|$. The third electronic state, $\tilde{b}\ ^1B_1$, arises from the same configuration as the ground state; however the two open-shell electrons are singlet coupled rather than triplet coupled. The fourth electronic state of NH_2^+ considered in this study, $\tilde{c}\ ^1\Sigma_g^+$ must be represented at least by a two configuration reference due to the fact that it is the second state of its symmetry (when distorted from linearity) and is subject to the possibility of variational collapse of the wavefunction to the $\tilde{a}\ ^1A_1$ state[34]. This state may be represented with the same two configurations as the $\tilde{a}$ state, but having two CI coefficients with the same sign and with $|C_1| \leq |C_2|$. The $\tilde{X}\ {}^2B_1$ state of NH_2 differs from that of NH_2^+ only in that the $3a_1$ orbital is doubly rather than singly occupied.

Computational Details

Zeroth-order descriptions for the lowest three electronic states may be obtained using single-configuration restricted Hartree–Fock (RHF) or restricted open-shell Hartree–Fock (ROHF) self-consistent-field (SCF) wavefunctions, while the $\tilde{c}$ state requires a two-configuration SCF (TCSCF) and is appropriately described as the second eigenvector of the TCSCF secular equation. Using these reference wavefunctions, dynamical correlation effects were treated approximately using the configuration interaction singles and doubles (CISD) method and, where possible, the coupled-cluster singles and doubles (CCSD) approach[35,36]. The additional effects of connected triple excitations on the CCSD model were estimated perturbatively according to the CCSD(T) method[37]. For the $\tilde{X}\ {}^3B_1$ and $\tilde{a}\ {}^1A_1$ states, it was possible to include the full triples correction by employing the CCSDT method[38].

In order to more closely approximate the full configuration interaction (full CI) limit, the CI space is expanded to include through quadruple substitutions (CISDTQ). For the $\tilde{c}\ {}^1\Sigma_g^+$ state, it was useful to also include through pentuple substitutions (CISDTQP). Only a single-configuration reference was used for these wavefunctions, even for the $\tilde{c}\ {}^1\Sigma_g^+$ state, due to the decreasing importance of the zeroth-order wavefunction in these rather complete correlation procedures. For the $\tilde{a}\ {}^1A_1$ state, the SCF reference wavefunction is based on the configuration of Eq. (*3*), while the $(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2$ configuration is slightly more important in the bent conformation of the $\tilde{c}\ {}^1\Sigma_g^+$ state. Therefore, CISDTQ and CISDTQP wavefunctions based on each of these configurations are denoted CISDTQ I and CISDTQ II, and CISDTQP I and CISDTQP II, respectively. Another type of wavefunction which has been shown to closely parallel the full CI potential energy surface is the second-order configuration interaction wavefunction[39] (SOCI) constructed as all single and double excitations out of the reference space generated from a complete active space self-consistent-field[40] (CASSCF) procedure. In this study, the CASSCF wavefunctions were constructed with an active space comprising six (valence) electrons in six (valence) molecular orbitals, denoted as (6,6). The numbers of configuration state functions (CSFs) in C_{2v} symmetry for the four states were 51 ($\tilde{X}\ {}^3B_1$), 56 ($\tilde{a}\ {}^1A_1$), 39 ($\tilde{b}\ {}^1B_1$), and 56 ($2\ {}^1A_1$), respectively.

Using the full CI procedure (where the CI space includes all possible CSFs of the proper spatial and spin symmetry), it was possible to obtain exact solutions of the electronic Schrödinger equation within the DZP basis and subject to the frozen-core constraint. These full CI wavefunctions were evaluated using the determinant-based CI program, DETCI (ref.[41]), written by two of us (C. D. S. and M. L. L.) which has been shown to be dramatically faster than our loop-driven graphical unitary group CI program (LD-GUGA) for large-scale CI wavefunctions[42,43].

This study conjoins the standard Huzinaga–Dunning[44,45] double-ζ basis augmented with a set of Cartesian d-type polarization functions on each nitrogen [$\alpha_d(N) = 0.80$] and a set of p polarization functions on each hydrogen [$\alpha_p(H) = 0.75$], denoted DZP, with each method. The contraction scheme for this basis is N(9s5p1d/4s2p1d), H(4s1p/2s1p), and it consists of 26 contracted Gaussian functions. Six cartesian d-type and ten cartesian f-type functions were used throughout. A TZ2P(f,d) basis was employed which is comprised of standard Huzinaga[44] triple-ζ sp sets augmented with d- and f-type polarization manifolds on the nitrogen [$\alpha_d(N) = 1.60, 0.40$; $\alpha_f(N) = 1.00$] and p- and d-type polarization manifolds on the hydrogen [$\alpha_p(H) = 1.50, 0.375$; $\alpha_d(H) = 1.00$]. The basis set consisted of 66 contracted Gaussian functions, the contraction scheme being N(10s6p2d1f/5s3p2d1f) and H(5s2p1d/3s2p1d). The DZP basis is not large enough to provide accurate results even when the electronic Schrödinger equation is solved exactly within the space spanned by it, while the TZ2P(f,d) basis makes the full CI intractable. However, the TZ2P(f,d) CASSCF-SOCI results will lend creedence to our predictions, especially for the difficult $\tilde{c}$ state of NH_2^+.

In all correlated procedures, the core orbital (nitrogen 1s-like) was constrained to remain doubly occupied. For the configuration interaction wavefunctions[46], optimized geometries and harmonic vibrational frequencies were determined using either analytic Cartesian gradients[47–49] evaluated with the GUGA CI program or internal coordinate gradients and force constant matrices (FCMs) evaluated through central difference techniques from energy points produced by the DETCI program[41]. All coupled-cluster gradients and force constants were obtained numerically from energies. Finally, the SCF and TCSCF results were obtained using analytic first and second derivative methods[50]. The dipole moments computed in this study were determined with respect to the center of mass.

To investigate the effects of electron correlation on the anharmonic constants of the first three electronic states of NH_2^+, finite-difference procedures were used to determine complete quartic force fields from energies obtained at 34 displacements along the molecular potential energy surface. The size of these displacements (±0.01 and ±0.02 Å or ±0.02 and ±0.04 rad) are large enough to avoid numerical instabilities in the finite-difference formulas, but small enough to prevent higher-order deterioration of the procedure. All nonzero quadratic, cubic, and quartic force constants in internal coordinates were generated. The nonlinear transformation of the quartic force field from internal coordinates to the Cartesian space was performed with the INTDER95 program[51]. Force constants at nonstationary reference geometries were obtained in the same manner and the PES was shifted *via* a term which is linear in the set of internal coordinates used [$(r_{NH_1} \pm r_{NH_2})$, θ_{HNH}] eliminating residual nonzero gradients as well as rotational contamination. This procedure was systematically investigated in the work of Allen and Császár[52]. Application of second-order perturbation theory to the standard vibration–rotation Hamiltonian[53] containing a potential energy surface expansion through quartic terms allowed for the generation of vibration–rotation interaction (α_r^B) and vibrational anharmonic (χ_{rs}) constants. The α_r^B constants are completely determined by the cubic force field, while χ_{rs} requires quartic force constants as well. For an extensive discussion of second-order perturbation theory applied to asymmetric top molecules, one is referred to the study performed by Clabo, Allen, Remington, Yamaguchi and Schaefer[54]. The corresponding work on linear polyatomic molecules was carried out by Allen, Yamaguchi, Császár, Clabo, Remington, and Schaefer[55] in 1990.

The PSI *ab initio* program package[56] was used for all SCF and CI procedures while all CC computations were carried out using the ACESII (ref.[57]) suite of programs.

RESULTS AND DISCUSSION

Geometries

The equilibrium geometries, dipole moments, and harmonic vibrational frequencies of NH_2^+ and $\tilde{X}\ ^2B_1$ NH_2 are reported in Tables I–V. It is reasonable to expect that the geometries presented here will not be in very good agreement with experiment, as the DZP full CI level of theory should overestimate equilibrium bond lengths[21]. Studies of small molecules have shown that it is important to balance the level of correlation achieved in any theoretical method with an appropriately sized basis set[58,59]. Double-ζ type basis sets are balanced by the SCF and CISD methods[58], while those methods such as CCSD and CCSD(T) are appropriately balanced by triple-ζ or larger basis sets[59]. However, it is important to contribute to an ever growing pool of benchmarks for molecular parameters other than total energies which allow for the quantitative examination of approximate correlation methods.

At the DZP level, the equilibrium geometry trends for NH_2^+ are similar to those found for methylene[21]. Experimental data exist only for the $\tilde{X}\ ^3B_1$ state. Note that DZP full CI overestimates this state's bond lengths by *ca* 0.01 Å and underestimates its bond angle by as much as 3.8°. DZP full CI was more successful for CH_2 bond angles (*ca* 1.8° difference from experiment) due to the difference in the well depths of the bending potentials between the two. Tables I–IV also contain equilibrium geometries determined using various approximate models of electron correlation. These results demonstrate how improved treatments of electron correlation affect the equilibrium geometries and converge upon the full CI values. The CISD [or (TC)CISD for the $\tilde{a}$ and $\tilde{c}$ states] method tends to increase the N–H bond length by about 0.015 Å and alters the bond angles by [+6.1°, –1.2°, –3.6°, and –2.0°] for the $\tilde{X}$, $\tilde{a}$, $\tilde{b}$, and $\tilde{c}$ states, respectively, from the SCF (or TCSCF) values. The disconnected higher-order excitations included in the CCSD model do not have as large an affect, increasing the bond length by an average of 0.0014 Å and changing the bond angle by no more than 0.7° over the CISD results. The perturbative triples correction provided by CCSD(T) lengthens the N–H bond another 0.0006 Å, while the full triples correction of CCSDT adds an addi-

TABLE I

Equilibrium geometries and harmonic vibrational frequencies of the $^3B_1$ electronic ground state of the nitrenium ion[a], NH_2^+

Method	Ref.	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	ZPVE
DZP SCF		1.0230	143.08	0.877	3 478	1 098	3 721	11.863
DZP CISD		1.0381	149.13	0.786	3 329	840	3 573	11.068
DZP CCSD		1.0397	149.85		3 309	812	3 555	10.973
DZP CCSD(T)		1.0405	149.97		3 298	807	3 544	10.936
DZP CCSDT		1.0407	150.01		3 296	805	3 542	10.926
DZP CASSCF-SOCI[b]		1.0408	150.07	0.767	3 293	803	3 540	10.918
DZP CISDTQ		1.0407	149.99	0.769	3 295	806	3 541	10.925
DZP full CI		1.0408	150.00	0.769	3 294	806	3 541	10.923
TZ2P(f,d) CASSCF-SOCI[b]		1.0328	152.28	0.683	3 253	744	3 506	10.726
TZ3P(2f,2d)+2diff CISD[c]	6	1.0281	150.40	0.715	3 295	814	3 549	10.95
6-311+G(3d,2p) MP2		1.025	149.4					
7s5p2d/2s1p MRD-CI+Q[c,d,e]	7	1.027	149.6					
4s3p2d1f/3s2p CASSCF-SOCI+Q[b,c,d,f]	8	1.0338	153.17		3 118	918	3 363	
cc-pVQZ CASSCF-MRCI[h]	12	1.029	152.07		3 128	914	3 369	
TZ2P CCSD(T)	63	1.032	150.5		3 264	831	3 504	
7s7p4d3f/6s4p3d CASSCF-MRCI[f]	13	1.0291	152.82	0.661	3 136	943	3 384	10.51
MORBID fit to experiment[g]	9	1.0302	153.78		3 052	848	3 360	
MORBID fit to experiment[g]	11				3 051	322[j]	3 360	
Experiment	20	1.021	180.00			439[j]		
Experiment	15					840 ± 50		
Experiment[i]	10	1.029	165				3 359.9	

[a] Bond lenghts in Å, bond angles in °, dipole moments (calculated with respect to the center of mass) in D, vibrational frequencies in cm^{-1} and ZPVE in kcal/mol. Unless otherwise noted, theoretical vibrational frequencies are determined in the harmonic approximation (ω), and theoretical results were obtained with the N 1s-like core frozen. [b] Second-order configuration interaction (SOCI) includes all configurations having no more than two electrons in external orbitals (see ref.[39]). [c] One frozen-core and one deleted virtual orbital. [d] +Q denotes the multireference Davidson correction for disconnected quadruple substitutions (see ref.[76]). [e] Polynomial fit to the estimated full CI data. [f] Predictions using the Morse oscillator-rigid bender internal dynamics (MORBID) Hamiltonian fit to *ab initio* data. Frequencies are fundamentals. [g] Predictions using the MORBID Hamiltonian fit to experimentally observed transitions. [h] Obtained with a variational potential energy function fit to *ab initio* data. Frequencies are fundamentals. [i] Bond length is r_0 value and bond angle is θ_0 value. [j] Assumes ν_2^{linear}.

TABLE II
Equilibrium geometries and harmonic vibrational frequencies of the $\tilde{a}\,^1A_1$ state of the nitrenium ion[a], NH_2^+

Method	Ref.	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	ZPVE
DZP SCF		1.0342	109.58	2.363	3 471	1 506	3 566	12.213
DZP TCSCF		1.0348	108.37	2.246	3 468	1 546	3 554	12.248
DZP CISD		1.0522	106.65	2.285	3 288	1 467	3 383	11.635
DZP (TC)CISD		1.0522	107.14	2.228	3 283	1 444	3 381	11.592
DZP CCSD		1.0545	106.71		3 256	1 449	3 357	11.526
DZP CCSD(T)		1.0551	107.00		3 246	1 428	3 350	11.471
DZP CCSDT		1.0550	107.31		3 246	1 413	3 352	11.452
DZP CASSCF-SOCI[b]		1.0554	107.25	2.220	3 239	1 413	3 346	11.434
DZP CISDTQ		1.0550	107.33	2.220	3 244	1 412	3 351	11.446
DZP full CI		1.0551	107.35	2.218	3 243	1 410	3 350	11.439
TZ2P(f,d) CASSCF-SOCI[b]		1.0499	107.96	2.124	3 180	1 389	3 272	11.209
TZ3P(2f,2d)+2diff (TC)CISD[c]	6	1.0445	107.99	2.110	3 239	1 429	3 324	11.42
6-311+G(3d,2p) MP2		1.043	107.1					
4s3p2d1f/3s2p CASSCF-SOCI+Q[b,c,d,e]	8	1.0510	108.37		3 027	1 289	3 111	
cc-pVQZ CASSCF-MRCI[f]	12	1.046	108.38		3 050	1 327	3 133	
7s7p4d3f/6s4p3d CASSCF-MRCI[g]	13	1.04	109	2.088	3 068	1 321	3 125	11.41
Experiment	15				2 900 ± 50	1 350 ± 50		

[a] Bond lenghts in Å, bond angles in °, dipole moments (calculated with respect to the center of mass) in D, vibrational frequencies in cm^{-1} and ZPVE in kcal/mol. Unless otherwise noted, theoretical vibrational frequencies are determined in the harmonic approximation (ω), and theoretical results were obtained with the N 1s-like core frozen. [b] Second-order configuration interaction (SOCI) includes all configurations having no more than two electrons in external orbitals (see ref.[39]). [c] One frozen-core and one deleted virtual orbital. [d] +Q denotes the multireference Davidson correction for disconnected quadruple substitutions (see ref.[76]). [e] Predictions using the Morse oscillator-rigid bender internal dynamics (MORBID) Hamiltonian fit to *ab initio* data. Frequencies are fundamentals. [f] Obtained from a variational Renner–Teller model fit to *ab initio* data. Frequencies are fundamentals. [g] Obtained with the RENNER program system (see ref.[14]). Rovibrational function fit to *ab initio* data. Frequencies are fundamentals.

tional 0.0002 Å. Extending the CI expansion to full triples and quadruples in CISDTQ lengthens the bonds by 0.0020–0.0030 Å above the CISD results. For the first three electronic states, the pentuples and sextuples included in the full CI serve to add ≤0.0001 Å to the bond lengths and change the bond angle by ≤0.02°.

For the $\tilde{c}$ state the error is more pronounced, and CISDTQ wavefunctions based on the first and second configurations of Eq. (*6*) (CISDTQ I and CISDTQ II) yield bond lengths 0.0007 Å and 0.0002 Å too short and bond angles differing from the full CI values by +4.9° and –2.1°, respectively. Full pentuples are needed to even approach the level of accuracy afforded by CISDTQ wavefunctions for the lower three states. Because of the near linearity of the $\tilde{c}$ state (within a DZP basis) the first and second configurations of Eq. (*6*) are approximately degenerate, necessitating a multi-reference treatment. When single and double excitations are included from a CASSCF (6,6) reference, the N–H bond lengths obtained are very close to the full CI results, differing by 0.04% or less at a much lower cost than CISDTQ. For the $\tilde{X}$ and $\tilde{a}$ states, the CCSD(T) and CCSDT methods do nearly as well as the CASSCF-SOCI technique or better; on the other hand, these methods are not applicable to the $\tilde{b}$ and $\tilde{c}$ states.

TABLE III
Equilibrium geometries and harmonic vibrational frequencies of the $\tilde{b}$ $^1B_1$ state of the nitrenium ion[a], NH_2^+

Method	Ref.	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	ZPVE
DZP SCF		1.0246	160.69	0.580	3 439	607	3 720	11.103
DZP CISD		1.0385	157.11	0.698	3 314	664	3 582	10.808
DZP CCSD		1.0399	156.49		3 299	679	3 568	10.787
DZP CASSCF-SOCI[b]		1.0410	156.09	0.727	3 283	694	3 552	10.762
DZP CISDTQ		1.0409	156.44	0.718	3 286	678	3 554	10.749
DZP full CI		1.0409	156.44	0.718	3 286	678	3 554	10.747
TZ2P(f,d) CASSCF-SOCI[b]		1.0325	160.54	0.557	3 246	543	3 530	10.462
TZ3P(2f,2d)+2diff CISD[c]	6	1.0280	160.92	0.539	3 281	564	3 562	10.59
4s3p2d1f/3s2p CASSCF-SOCI+Q[b,c,d,e]	8	1.0344	164.07					
cc-pVQZ CASSCF-MRCI[f]	12	1.029	160.92		3 083	702	3 304	
7s7p4d3f/6s4p3d CASSCF-MRCI[g]	13	1.03	159	0.586	3 091		3 291	
Experiment	15					920 ± 150		

[a–g] See footnotes to Table II.

The most accurate experimental geometry of the ground state [r_e = 1.0302 Å, θ_e = 153.78°] is that given by the MORBID fit to experimental transitions around the ν_3 vibrational mode[9]. The bond length and angle reported by Okumura and coworkers assumes rigid rotor behavior, and these are vibrationally averaged r_0 and θ_0 values, thus not necessarily comparable to theory[10]. The most reliable theoretical geometries are those given by methods that are multi-reference in nature. Although the best equilibrium bond length was obtained by the variational treatment of the ground state PES generated with the cc-pVQZ CASSCF (6,6)-MRCI method[12], the bond angle given by Jensen *et al.*[8] who fit their *ab initio* surface with the MORBID Hamiltonian is in better agreement (perhaps fortuitously) with the experimental θ_e. The TZ2P(f,d) CASSCF (6,6)-SOCI geometry is also in very good agreement with the experimental equilibrium results. While the experimental bond length deduced by Kabbadj *et al.*[20] is 0.009 Å shorter than that given by Barclay *et al.*[9], it was obtained using a linear rovibrational Hamiltonian fit to the experimental absorptions around ν_3, and so it should not be strictly comparable to the other equilibrium geometries.

TABLE IV

Equilibrium geometries and harmonic vibrational frequencies of the $\tilde{c}\ ^1\Sigma_g^+$ ($^1A_1$) state of the nitrenium ion[a], NH_2^+

Method	Ref.	r_e	θ_e	μ_e	$\omega_1(\sigma_g,a_1)$	$\omega_2(\pi_u,a_1)$	$\omega_3(\sigma_u,b_2)$	ZPVE
DZP TCSCF		1.0253	180.00	0.000	3 435	555	3 728	11.828
DZP (TC)CISD		1.0396	178.01	0.065	3 305	127	3 587	10.033
DZP CASSCF-SOCI[c]		1.0428	175.07	0.180	3 267	315	3 551	10.197
DZP CISDTQ I[b]		1.0421	180.00	0.000	3 276	61	3 560	9.859
DZP CISDTQ II[b]		1.0426	172.98	0.255	3 271	450	3 552	10.396
DZP CISDTQP I[b]		1.0427	175.64	0.159	3 269	281	3 553	10.154
DZP CISDTQP II[b]		1.0428	174.35	0.206	3 268	363	3 551	10.267
DZP full CI		1.0428	175.12	0.178	3 267	314	3 551	10.197
TZ2P(f,d) CASSCF-SOCI[c]		1.0352	180.00	0.000	3 218	213	3 510	9.924
TZ3P(2f,2d)+2diff (TC)CISD[d]	6	1.0299	180.00	0.000	3 260	253	3 551	10.46

[a] Bond length in Å, bond angles in °, dipole moments (calculated with respect to the center of mass) in D, vibrational frequencies in cm^{-1} and ZPVE in kcal/mol. Vibrational frequencies (ω) are determined in the harmonic approximation and theoretical results were obtained with the N 1s-like core frozen. [b] Roman numeral I (II) signifies that the SCF reference for the $\tilde{c}$ state is the first (second) configuration in Eq. (*6*) (see text). [c] Second-order configuration interaction (SOCI) includes all configurations having no more than two electrons in external orbitals (see ref.[39]). [d] One frozen-core and one deleted virtual orbital.

The structures of the $\tilde{a}\ ^1A_1$ and $\tilde{b}\ ^1B_1$ states of NH_2^+ have not been determined experimentally. However, Gibson *et al.*'s[16] observation of a single prominent vibrational component in the Rydberg series convergent upon the $\tilde{a}$ state led them to believe that it should have a structure very similar to that of $\tilde{X}\ ^2B_1$ NH_2 [r_0 = 1.024 Å, θ_0 = 103.3°][60]. Indeed, the high-level MRCI calculations[8,12,13] show this to be true [$r_e \approx$ 1.05 Å, $\theta_e \approx$ 108°]. Owing to the strongly bent structure, we do not observe the large variation in bond angle with method and basis set that appears in the $\tilde{X}$, $\tilde{b}$, and $\tilde{c}$ states. With regards to the $\tilde{b}\ ^1B_1$ state, the Renner–Teller model fits to its PES by Chambaud *et al.*[12] and Osmann *et al.*[13] provide comparable r_e and θ_e values of 1.03 Å and *ca* 160°, respectively. The large basis CISD results of Stephens *et al.*[6] and our TZ2P(f,d) CASSCF (6,6)-SOCI results concur with these MRCI values.

While slightly bent at the DZP full CI level, the $\tilde{c}$ state is linear with a small bending frequency at other levels, including the large basis set CISD results of Stephens *et al.*[6] and the TZ2P(f,d) CASSCF (6,6)-SOCI results given here. This appears to be in agreement with recent extensive MRCI computations on the $\tilde{c}\ ^1A_1$ state of CH_2 performed by Bauschlicher[61], who found that improvements in the correlation treatment or the basis

TABLE V
Equilibrium geometries and harmonic vibrational frequencies of the $^2B_1$ electronic ground state of NH_2[a]

Method	Ref.	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	ZPVE
DZP SCF		1.0135	104.64	2.062	3 638	1 646	3 739	12.900
DZP CISD		1.0313	102.55	1.980	3 443	1 574	3 543	12.237
DZP CCSD		1.0343	102.34		3 400	1 564	3 505	12.107
DZP CCSD(T)		1.0356	102.17		3 380	1 557	3 487	12.043
DZP CCSDT		1.0358	102.16		3 377	1 556	3 484	12.033
DZP CASSCF-SOCI[b]		1.0375	101.96	1.957	3 365	1 559	3 459	11.983
DZP CASSCF′-SOCI[b,c]		1.0364	102.14	1.963	3 370	1 556	3 476	12.011
DZP CISDTQ		1.0359	102.15	1.959	3 376	1 556	3 482	12.029
DZP full CI		1.0361	102.14	1.959	3 374	1 555	3 480	12.021
TZ2P(f,d) CASSCF-SOCI[b]		1.0291	102.37	1.840	3 357	1 555	3 422	11.915
DZP′ full CI[d,e]	25	1.032	102.9					

[a] Bond length in Å, bond angles in °, dipole moments (calculated with respect to the center of mass) in D, vibrational frequencies in cm^{-1} and ZPVE in kcal/mol. Vibrational frequencies (ω) are determined in the harmonic approximation and theoretical results were obtained with the N 1s-like core frozen. [b] Second-order configuration interaction (SOCI) includes all configurations having no more than two electrons in external orbitals (see ref.[39]). [c] The prime emphasizes that a different active space (7 electrons in 8 molecular orbitals) was used. [d] One frozen-core and one deleted virtual orbital. [e] The prime emphasizes that the DZP′ basis differs from the one used in this work.

set tend to favor the linear geometry over the bent structure. In the case of $\tilde{c}\ ^1\Sigma_g^+$ NH_2^+, more complete correlation treatments with a DZP basis appear to favor the bent structure, while addition of higher angular momentum polarization functions to the basis set (f to N and d to H) yields a linear geometry regardless of correlation treatment. The geometry of this state has not been confirmed experimentally.

The same trends are observed for $\tilde{X}\ ^2B_1$ NH_2 (Table V) as the theoretical methods approach the correlation limit. The DZP full CI geometry is very similar to that obtained by Anglada and Bofill's previous DZP full CI study, the dissimilarity being attributed to slight differences in the polarization functions and frozen orbital approximations used[25]. Disappointingly, the DZP CASSCF (7,6)-SOCI method only slightly outperforms the CCSD approach in the reproduction of the full CI properties. This is attributed to an active space containing only the valence electrons in valence orbitals, which is not the optimum choice for NH_2. Analysis of the SCF orbital energies as well as the CISD natural orbital populations indicates that an extension of the space to include one a_1 and the one b_1 (Rydberg) orbital, (7 e^-/8 MO), should provide a more suitable active space for this radical. Optimizing the geometry under the new constraints reduces the error to 0.0003 Å and <0.01° at still only two-thirds of the cost of the CISDTQ method. For this open-shell system, the very efficient CCSD(T) method does exceedingly well, with an error of only 0.0005 Å and 0.03° in the bond length and angle, respectively.

Dipole Moments

The dipole moments, μ_e, of NH_2^+ and NH_2 are calculated with respect to the center of mass in Debye (1D ≈ 3.335 . 10^{-30} C m). Because their geometries and electronic configurations are similar, the $\tilde{X}\ ^3B_1$ and $\tilde{b}\ ^1B_1$ dipole moments differ by only 0.05 D at the DZP full CI level. There is a small variation in their values with correlation, and the dipole of the $\tilde{X}\ ^3B_1$ state appears to decrease with correlation. The dipole moment is largest (2.219 D at DZP full CI) for the $\tilde{a}\ ^1A_1$ state due to double occupancy of the in-plane $3a_1$ orbital. Again, the dipole appears to decrease with correlation. The slight bend from linearity in the $\tilde{c}$ state due to the small DZP basis allows for a dipole moment (0.178 D) at the DZP full CI level. The addition of higher angular momentum functions serves to remove this distortion. There is a wide variation in the predicted values, and full pentuples are required in a single reference treatment to even begin to approach the full CI value for the $\tilde{c}\ ^1\Sigma_g^+$ state. The CASSCF (6,6)-SOCI method, on the other hand, reproduces the full CI value within 0.002 D. The dipole of $\tilde{X}\ ^2B_1$ NH_2 also decreases with the inclusion of correlation, and the values smoothly converge to the full CI result of 1.959 D.

Harmonic Vibrational Frequencies

While various surface fitting and vibrational analysis techniques exist to generate fundamental frequencies which are directly comparable to experiment, theoretical vibrational frequencies are usually limited to the harmonic approximation. Harmonic frequencies are generally within a few percent of the fundamentals when anharmonic contributions are small, and they tend to follow Badger's rule, *i.e.* smaller bond lengths correlate to larger vibrational frequencies[62]. For example, SCF and CISD methods tend to provide good geometry predictions when paired with the DZP basis set, while they generally overestimate experimental frequencies by *ca* 10 and 5%, respectively[58]. From Table I, the DZP CISD method overestimates the antisymmetric stretching frequency by 6.3%. When the level of correlation is increased within the DZP basis, the bond lengths are overestimated, thus bringing the harmonic frequency into better agreement with the experimental fundamental. The remaining (considerable) error is attributed to the neglect of anharmonicity (*vide infra*) and basis set incompleteness.

At the full CI level, the frequency ordering among the four electronic states of NH_2^+ is very similar to that of CH_2 (ref.[21]). The only difference lies with the fact that the equilibrium bond lengths of the four states are nearly the same and Badger's rule[62] is not strictly followed for the antisymmetric stretching frequencies. For NH_2^+, it is found that although $r_e(\tilde{a}\ ^1A_1) > r_e(\tilde{c}\ ^1\Sigma_g^+) > r_e(\tilde{b}\ ^1B_1) > r_e(\tilde{X}\ ^3B_1)$, the antisymmetric frequencies are in the order $\omega_3(\tilde{b}\ ^1B_1) > \omega_3(\tilde{c}\ ^1\Sigma_g^+) > \omega_3(\tilde{a}\ ^1A_1) > \omega_3(\tilde{X}\ ^3B_1)$.

For the quasilinear ground state of NH_2^+, the SCF method predicts stretching harmonic frequencies in relatively good agreement with full CI, with an error of only 5.6 and 5.1% for ω_1 and ω_3, respectively. The bending frequency, however, is overestimated by 36.2%, which indicates the drastic need to account for electron correlation. The CISD method improves the bending frequency considerably, bringing the mean absolute percent error in ω to only 2.1%. Electron correlation beyond the CCSD method has little quantitative effect on the frequencies, which are within 0.4% of the full CI values. CCSD(T), CASSCF (6,6)-SOCI, CCSDT, and CISDTQ are at most a few wavenumbers from the full CI results. The situation for the $\tilde{a}\ ^1A_1$ state is similar; however, the bending frequency should not be too problematic as this state is strongly bent. In support of this theory, (TC)SCF predicts a bending frequency within 9.6% of the full CI value of 1 410 cm^{-1}. Again, (TC)CISD removes the majority of the error due to neglect of electron correlation. Apparently, the CCSD and CCSD(T) methods have some difficulty with the $\tilde{a}$ state bending potential, as the predicted frequency remains overestimated by 2.8 and 1.3%, respectively. The CASSCF (6,6)-SOCI, CCSDT, and CISDTQ methods all have comparable accuracy, and provide frequencies in error by less than 0.2%. The quasilinear $\tilde{b}\ ^1B_1$ state frequencies exhibit a sensitive dependence to the degree of electron correlation. The SCF and CISD methods both underestimate the bending frequency by 10.5 and 2.1%, respectively. The two-determinant CCSD method[36] actually outperforms the CASSCF (6,6)-SOCI method in this respect, as the latter method overestimates ω_2 by 16 cm^{-1}. Similar to the first two electronic states, the CISDTQ frequencies agree remarkably well with the full CI results, as pentuple and hextuple excitations do little to affect the geometries of these states.

While the stretching frequencies smoothly converge upon the full CI results with increases in the excitation level, the bending frequency of the $\tilde{c}$ state displays a strong dependence on the reference wavefunction. These effects are similar to those seen previously in our benchmark studies on CH_2 (refs[21,22]). The two CISDTQ predictions differ by 389 cm^{-1} corresponding to the 7.0° difference in bond angle and are at least 135 cm^{-1} from the full CI value. Adding full pentuples improves the situation, but the frequencies are still at least 30 cm^{-1} different from full CI. This demonstrates the necessity for a multireference treatment such as the CASSCF (6,6)-SOCI method, which narrows the error in the bending vibration to 1 cm^{-1}.

For the ground state, the most accurate experimental data exists for the antisymmetric stretching frequency[10]. The value for ω_3 given by the TZ3P(2f,2d)+2diff CISD method is within 5.6% of experiment[6]. However, when MRCI methods are employed with large basis sets and anharmonicity is accounted for with various rovibrational Hamiltonians[8,12,13] exemplary accord with experiment (<0.8% error) is achieved for this frequency. Few experimental data exist for the other frequencies. The bending frequency is perhaps the most interesting, as the molecule exists in a dynamical conformation; and neither a linear nor a bent characterization is particularly appropriate. In general, previous work has concentrated on describing the molecule as bent, while the recent work of Jensen[11] and Osmann *et al.*[13] contend that one should consider both bent and linear aspects of this molecule. The real problem with quasilinear species lies in the choice of a basis. The quantum numbers defining a bent or a linear species' energy levels are slightly different, especially with regards to the bending fundamental. In the harmonic approximation, ω_2^{linear} is exactly half of ω_2^{bent}, therefore, as Jensen points out[11], the "bending fundamental energy" will depend on one's choice of quantum numbers to label the molecular energies. Kabbadj *et al.*[20], who fit their absorption spectra under the assumption of a linear molecule, arrived at an ω_2^{linear} of 439 cm^{-1}, while Dunlavey *et al.*[15] determine a value of 840 ± 50 cm^{-1} for ν_2^{bent}. Jensen[11] assigns a value of 322 cm^{-1} to ν_2^{linear} and when quanta are also assigned to ν_2^{bent} he arrives at 847 cm^{-1}. Osmann *et al.*[13] report $\nu_2^{\text{linear}} = 335$ cm^{-1} and $\nu_2^{\text{bent}} = 943$ cm^{-1}. While the MORBID potential used in both of these studies can treat the bent and linear forms of the $\tilde{X}$ state without prejudice, clearly, a better description of quasilinear molecules is warranted to avoid this dilemma. At present, the recommendation for experimentalists is to search for the bending absorption in the 300–400 cm^{-1} range of the spectrum.

The $\tilde{a}\ {}^1A_1$ state, on the other hand, does not provide as large a challenge to theory, as it is strongly bent. The fundamental vibrations determined by Jensen *et al.*[8], Chambaud *et al.*[12], and Osmann *et al.*[13] are all in reasonable agreement with each other and with experiment. This occurs in spite of the neglect of Renner–Teller coupling to the $\tilde{b}$ state in the 1987 work. Note that the harmonic frequencies predicted by the TZ2P(f,d) CASSCF (6,6)-SOCI method are usually within 5% of these results.

Dunlavey *et al.*[15] estimated a value of 920 ± 150 cm^{-1} for the bending vibration of the $\tilde{b}\ ^1B_1$ state. However, this value appears to be too high, even if we consider this very floppy molecule to be bent. The bond angle of this state is larger than that of the ground state, and so we would expect that the bending frequency should decrease rather than increase. Theory supports this assumption, and the value of 702 cm^{-1} is a more reliable target for this fundamental[12]. Notice that for quasilinear molecules, account for nondynamical correlation effects and larger basis sets are needed in general to achieve consistency in the results with respect to experiment. Primarily, multireference methods provide the most balanced treatment of these species, as the $3a_1$ and $1b_1$ orbitals approach degeneracy as the molecule approaches linearity. Also, larger basis sets will provide better opportunity for these orbitals to mix properly in the quasilinear configuration.

For the ground state of NH_2, the trend in vibrational frequencies is similar to that seen in the first three states of NH_2^+. In general, the frequencies decrease with correlation, and the CISDTQ values are very close to the DZP full CI results. An increase in the CASSCF active space from six to eight molecular orbitals dramatically improves agreement between the SOCI and full CI results. If one cannot afford a SOCI wavefunction, the CCSD(T) wavefunction produces harmonic frequencies a mere 0.2% in error from full CI for this strongly bent, radical species.

Anharmonicity

Due to the large volume of data generated in any study of anharmonicity of polyatomic systems, we choose to present the results of only the $\tilde{a}\ ^1A_1$ state of NH_2^+ in Tables VI–IX and we relegate the data for the $\tilde{X}\ ^3B_1$ and $\tilde{b}\ ^1B_1$ states to supplementary material[64]. Also, the particular vibrational perturbation theory treatment which is used herein becomes suspect for these two quasilinear species, as will be discussed below, therefore the anharmonic constants determined for the $\tilde{a}\ ^1A_1$ state should be the most reliable and are sufficient to establish correlation trends. Also, the constants quoted herein are used merely to provide insight into the effects of electron correlation on anharmonicity and are of limited use in the interpretation of experimental observations owing to the small DZP basis set used.

When the correlation limit is attained, errors due to basis set deficiencies and anharmonicity can remain in the theoretically predicted vibrational frequencies. While extension of the basis set size should provide a better balance to the full CI wavefunction, in general this makes the calculations unmanageable. It is possible, though, to examine the effects of anharmonicity at the DZP full CI level *via* an evaluation of the full quartic force field using second-order spectroscopic perturbation theory. The foundation of this theory lies in the fact that vibrational and rotational terms are largely separable in the

TABLE VI
Theoretical force constants of $\tilde{a}\,^1A_1$ NH_2^+ obtained with the DZP basis set[a]

Force constant	(TC)SCF	(TC)CISD	CCSD	CCSD(T)	CCSDT	CAS-SOCI	CISDTQ	Full CI
f_{11}	6.8276	6.1160	6.0125	5.9748	5.9777	5.9538	5.9735	5.9664
f_{12}	0.18535	0.22269	0.22412	0.22349	0.22137	0.22241	0.22153	0.22112
f_{22}	0.69986	0.63487	0.64291	0.62554	0.61166	0.61218	0.61052	0.60897
f_{33}	6.8509	6.2112	6.1248	6.0959	6.1011	6.0807	6.0980	6.0930
f_{111}	–30.64	–28.22	–27.91	–27.83	–27.85	–27.78	–27.84	–27.83
f_{112}	–0.5204	–0.4810	–0.4680	–0.4612	–0.4555	–0.4571	–0.4556	–0.4545
f_{122}	–0.4480	–0.4159	–0.4391	–0.4342	–0.4271	–0.4269	–0.4272	–0.4279
f_{133}	–30.67	–28.16	–27.81	–27.72	–27.74	–27.658	–27.73	–27.71
f_{222}	–0.7140	–0.7068	–0.6787	–0.7019	–0.7421	–0.7418	–0.7437	–0.7471
f_{233}	0.1501	0.1501	0.1600	0.1520	0.1464	0.1461	0.1446	0.1439
f_{1111}	123	112	111	110	110	110	110	110
f_{1112}	0.588	0.607	0.602	0.608	0.619	0.666	0.616	0.624
f_{1122}	0.344	0.490	0.557	0.558	0.565	0.519	0.564	0.562
f_{1133}	123	112	110	110	110	110	110	110
f_{1222}	0.904	1.16	1.08	1.12	1.13	1.14	1.13	1.12
f_{1233}	–0.379	–0.341	–0.357	–0.337	–0.314	–0.285	–0.317	–0.322
f_{2222}	–1.07	–1.05	–0.965	–1.09	–1.26	–1.28	–1.26	–1.27
f_{2233}	–1.05	–1.03	–1.00	–0.988	–0.982	–1.03	–0.983	–0.976
f_{3333}	124	113	112	111	111	111	111	111
Mean absolute % error from Full CI								
Quadratic	14.5	2.4	2.1	1.0	0.2	0.4	0.2	0.0
Cubic	8.1	3.6	4.4	2.4	0.5	0.6	0.2	0.0
Quartic	15.6	5.9	5.2	2.6	0.7	3.8	0.6	0.0

[a] Quadratic, cubic, and quartic force constants are reported in symmetrized internal coordinates. The units for the force constants are consistent with energy measured in aJ, stretching coordinates in Å, and bending coordinates in radians.

energy expressions of well-behaved systems like the $\tilde{a}$ state of NH_2^+ or the ground state of the amino radical[53b,65]. Quasilinear molecules though, are not amenable to this type of analysis, as the large amplitude bending vibration, ν_2, is strongly coupled with rotation about one of the molecular axes.

The quadratic, cubic, and quartic force constants of the $\tilde{a}$ $^1A_1$ state of NH_2^+ are presented in Table VI in symmetrized internal coordinates. In general, it is assumed that highly correlated methods combined with large basis sets are necessary for the reproduction of experimental force constants. Indeed, correlation appears to have quite a drastic effect on those derivatives presented here. The mean absolute percent error from full CI in the (TC)SCF quadratic, cubic, and quartic force constants is 14.5, 8.1, and 15.6%, respectively. This error is reasonable and is in the range expected for force constants obtained *via* RHF theory. It is well known that semidiagonal cubics and quartics require a more sophisticated theoretical treatment to acquire accurate values than diagonal force constants. This is certainly the case here; for example, the f_{1111} stretch-

TABLE VII
Theoretical vibration–rotation interaction constants ($\alpha_r^{(A,B,C)}$) and rotational constants (A, B, C) in cm^{-1} of $\tilde{a}$ $^1A_1$ NH_2^+. All theoretical results were obtained with the DZP basis set[a]

	(TC)SCF	(TC)CISD	CCSD	CCSD(T)	CCSDT	CAS-SOCI	CISDTQ	Full CI
α_1^A	0.3913	0.4962	0.5070	0.5190	0.5233	0.5264	0.5248	0.5260
α_2^A	–2.5606	–2.4849	–2.3463	–2.4652	–2.6129	–2.5986	–2.6213	–2.6334
α_3^A	0.8317	0.9204	0.9128	0.9349	0.9507	0.9517	0.9524	0.9541
α_1^B	0.2097	0.2081	0.2102	0.2100	0.2092	0.2097	0.2093	0.2095
α_2^B	–0.0936	–0.0864	–0.0962	–0.0848	–0.0685	–0.0687	–0.0676	–0.0660
α_3^B	0.1319	0.1233	0.1252	0.1244	0.1232	0.1235	0.1233	0.1234
α_1^C	0.1374	0.1472	0.1501	0.1511	0.1511	0.1516	0.1512	0.1514
α_2^C	0.1299	0.1251	0.1276	0.1259	0.1244	0.1246	0.1243	0.1242
α_3^C	0.1088	0.1194	0.1194	0.1215	0.1224	0.1228	0.1226	0.1228
A_e	26.0893	24.5051	24.1568	24.2883	24.4764	24.4195	24.4833	24.4895
B_e	11.8765	11.6678	11.6834	11.6263	11.5823	11.5834	11.5788	11.5729
C_e	8.1613	7.9043	7.8748	7.8626	7.8620	7.8566	7.8611	7.8590
A_0	26.7581	25.0393	24.6200	24.7939	25.0459	24.9798	25.0554	25.0661
B_0	11.7525	11.5453	11.5638	11.5015	11.4504	11.4511	11.4463	11.4395
C_0	7.9732	7.7084	7.6762	7.6634	7.6631	7.6571	7.6620	7.6598

[a] Rotaional constants reported are at equilibrium (B_e), and correscted for zero-point vibrational energy (B_0).

ing constant is 11.8% from the full CI value of 110 aJ/Å^4 at the (TC)SCF level, while f_{1122} stretch-bend constant is underestimated by 39%. Dynamical correlation recovered by the (TC)CISD method greatly improves the agreement with full CI, eliminating 80% of the error in the quadratic force field and *ca* 60% of the error in the cubic and quartic force fields. Little additional improvement is seen in the CCSD force fields; however, the CCSD(T) method removes another 50% of the remaining error from the (TC)CISD values. At this level, full CI force constants which include only stretching modes are reproduced to within 1% – within the numerical significance of the method – while those constants involving the bending coordinate still show significant variation (*e.g.* 14.2% for f_{2222}). While the quadratic and cubic force constants obtained with the CASSCF (6,6)-SOCI method are of essentially the same quality as those predicted with the CISDTQ and CCSDT methods (error <1%), the semi-diagonal fourth derivatives are actually slightly worse (on average) than those of the CCSD(T) method. As is expected, the CCSDT and CISDTQ methods perform remarkably well in comparison to full CI. From these results, it would be reasonable to assume that a rather complete treatment of electron correlation is needed to provide accurate results for anharmonic force fields.

TABLE VIII
Theoretical anharmonic constants (χ_{rs}) and fundamental frequencies of $\tilde{a}\ {}^1A_1\ NH_2^+$. All quantities are reported in cm^{-1}. All theoretical results were obtained with the DZP basis set

	(TC)SCF	(TC)CISD	CCSD	CCSD(T)	CCSDT	CAS-SOCI	CISDTQ	Full CI	Exp.
χ_{11}	–34.02	–37.56	–38.41	–38.83	–38.82	–39.08	–38.89	–38.98	
χ_{12}	–15.46	–15.48	–15.92	–16.35	–16.34	–16.64	–16.38	–16.49	
χ_{13}	–137.11	–148.35	–150.31	–151.54	–151.48	–152.11	–151.65	–151.78	
χ_{22}	–18.49	–19.58	–18.17	–19.91	–22.38	–22.57	–22.48	–22.73	
χ_{23}	–24.22	–22.90	–24.19	–23.50	–22.41	–22.76	–22.39	–22.32	
χ_{33}	–37.99	–42.07	–42.45	–42.90	–42.95	–43.18	–43.01	–43.08	
ν_1	3 324	3 126	3 096	3 084	3 084	3 077	3 083	3 080	2 900±50[a]
ν_2	1 489	1 385	1 393	1 369	1 349	1 348	1 347	1 345	1 350±50[a]
ν_3	3 397	3 212	3 185	3 176	3 179	3 172	3 178	3 176	
Δ_1	–144.3	–157.0	–159.9	–161.6	–161.6	–162.5	–161.8	–162.1	
Δ_2	–56.8	–58.4	–56.4	–59.7	–64.1	–64.8	–64.4	–64.9	
Δ_3	–156.6	–169.8	–172.2	–173.3	–172.9	–173.8	–173.0	–173.2	

[a] See ref.[15].

TABLE IX
DZP (TC)SCF force constants, vibration–rotation interaction constants, harmonic frequencies, anharmonic constants and fundamental vibrations of the $\tilde{a}\,^1A_1$ state of NH_2^+ determined at the DZP Full CI equilibrium geometry. The values in parentheses were evaluated using the Full CI quadratic force constants along with the (TC)SCF cubic and quartic force fields[a,b]

Force constants													
f_{11}	6.0060	f_{33}	6.0168	f_{122}	–0.4538	f_{233}	0.1574	f_{1122}	0.382	f_{1233}	–0.419	f_{3333}	111
f_{12}	0.17860	f_{111}	–27.32	f_{133}	–27.33	f_{1111}	110	f_{1133}	109	f_{2222}	–1.07		
f_{22}	0.69921	f_{112}	–0.5084	f_{222}	–0.6687	f_{1112}	0.693	f_{1222}	0.923	f_{2233}	–1.05		

Vibration–rotation interaction constants								
α_1^A	α_2^A	α_3^A	α_1^B	α_2^B	α_3^B	α_1^C	α_2^C	α_3^C
0.4151	–2.2250	0.8188	0.2194	–0.0988	0.1431	0.1440	0.1363	0.1117
(0.4886)	(–2.5223)	(0.9427)	(0.2074)	(–0.0896)	(0.1181)	(0.1466)	(0.1248)	(0.1192)

Harmonics			Anharmonic constants						Fundamentals		
ω_1	ω_2	ω_3	χ_{11}	χ_{12}	χ_{13}	χ_{22}	χ_{23}	χ_{33}	ν_1	ν_2	ν_3
3 254	1 515	3 329	–35.44	–13.27	–143.38	–18.23	–26.54	–39.54	3 105	1 458	3 165
(3 243)	(1 410)	(3 350)	(–36.21)	(–18.47)	(–142.70)	(–19.25)	(–24.25)	(–40.98)	(3 090)	(1 350)	(3 184)

[a] Quadratic, cubic, and quartic force constants are reported in symmetrized internal coordinates. The units for the force constants are consistent with energy measured in aJ, stretching coordinates in Å, and bending coordinates in radians. [b] The α, ω, χ_{rs}, and ν values are reported in cm^{-1}.

An issue which remains in this benchmark study is the difference between error due to an incomplete treatment of electron correlation *versus* error due to an improper choice of reference geometry. A longstanding controversy exists which pits a phenomenological view of quantum chemistry *versus* an empirical one. The problem of whether to evaluate force constants at optimized equilibrium geometries or at experimental equilibrium structures is (albeit poorly appreciated), according to Pulay *et al.*[66], "…the most difficult problem confronting the systematic *ab initio* calculation of force constants". Recently, several studies have examined this dilemma in detail, and the following arguments are expanded in the 1993 work of Allen and Császár[52]. The total energy [$U(r)$] of a molecule consists of two parts which are of opposite sign, the electronic energy (E_e) and the nuclear–nuclear repulsion energy (V_n). While we can solve for the V_n term exactly, the E_e term is approximated by various methods. This situation results in an unbalanced procedure for calculating force constants based on a cancellation of errors. The E_e and V_n contributions to $U''(r)$ nearly cancel each other, but, in higher order the contributions of V_n become dominant. This cancellation at second order results in very poor quadratic force constants at the SCF level. Be that as it may, due to the dominance of V_n at third and fourth order, improvements in correlation generally offer little improvement in the cubic and quartic force constants when evaluated at the same equilibrium geometries. This underappreciated notion should present a powerful alternative for anharmonic force field evaluations. Although it is certainly possible to calculate cubic and quartic force constants for NH_2^+ with correlation treatments as complete as full CI within the DZP basis set, the lack of analytic second and higher derivatives for most correlated methods means that obtaining these quantities with a reasonably sized basis set (including f functions, for example) at even the CCSD level for larger molecules such as butane remains a computational challenge. A problem with this method is that the molecule is no longer at a stationary point on the PES, *i.e.*, residual gradients remain which must be dealt with in some fashion. Herein, we eliminate these forces as well as rotational contamination by modifying the PES so as to have a minimum at the new reference geometry. This shifting is linearly dependent on our internal coordinate set; however, as there is no ambiguity in the choice of coordinates for NH_2^+, we expect the results to be reasonable. The Cartesian projection scheme, which is invariant to one's choice of internal coordinates and is described in detail in Allen and Császár's work[52] provides an alternative treatment of this "non-zero force dilemma" for strongly bonded molecular systems, such as the $\tilde{a}$ state of NH_2^+, and we will consider its performance for the prediction of fundamental frequencies below.

Table IX contains the (TC)SCF force constants evaluated at the full CI equilibrium geometry. Overall, the geometry shift reduces the mean per cent error by *ca* 23% compared to the (TC)SCF force constants in Table VI. Note that the main improvement lies in the diagonal force constants and those semi-diagonal cubics and quartics that deal only with stretching terms. For example, the f_{1111} value when calculated at the full CI geometry is exactly that obtained at the full CI level, within the numerical significance of the method. Those force constants involving the bending coordinate are not improved when evaluated at the full CI geometry, in fact, the agreement decreases somewhat for f_{12}, f_{122}, f_{222}, and f_{1233}. This result is in accord with previous studies on the anharmonic force fields of F_2O (ref.[52]) and N_2O (refs[52,67]), in which the dominant diagonal stretching constants are most affected by changes in the geometric structure, while the coupling constants require a more sophisticated correlation treatment. And so, even though the barrier to linearity of the $\tilde{a}$ state is approximately 5 000 cm^{-1} (ref.[9]) it appears that the bending potential is still difficult to accurately represent without significantly accounting for electron correlation effects. In fact, even the CCSD(T) method still underestimates f_{2222} by 12.6% at the full CI geometry. By freezing the structure to that of the full CI, it is possible to see exactly which force constants depend on correlation and which are affected primarily by geometry. Császár and Allen[68] found the same to hold true in a study of core correlation effects in N_2, except their method of choice was CCSD(T) rather than full CI.

The theoretical vibration–rotation interaction constants (α_r^B) and rotational constants for $\tilde{a}\ {}^1A_1$ NH_2^+ are presented in Table VII. According to spectroscopic perturbation theory, vibrational and rotational terms are properly separable if the α_r^B constants have a magnitude on the order of 10^{-2} of the corresponding rotational constants[69]. All of the vibration–rotation constants appear to be well-behaved in this case. Although there is a rather strong coupling of the bending vibration with the molecular *a* axis, α_2^A is approximately 10% of the rotational constant A_e, and while slightly suspect, is still within a reasonable range for perturbation theory. Similar behavior is seen when perturbation theory is applied to the quartic force field of the $\tilde{a}\ {}^1A_1$ state of CH_2 (ref.[54]). Correlation has a marked effect on these constants, and the α's describing coupling between bending and rotation appear to be very difficult to pinpoint. CCSD(T) appears to model the coupling between stretching vibrations and rotation to within 2% of full CI; however, the α_2 values are still overestimated by 28.5%. The higher level CASSCF (6,6)-SOCI, CCSDT, and CISDTQ methods eliminate this error and all deviate from full CI to virtually the same degree.

The marked change in rotational constants that denotes a severe change in geometry when correlation is accounted for would seem to suggest that a proper choice of reference geometry should improve results for these vibration–rotation interaction constants. This turns out not to be the case. The (TC)SCF results for the α constants evaluated at the equilibrium full CI geometry are actually slightly worse, on average, than those calculated at the stationary (TC)SCF geometry. Nevertheless, it has been noted[70] that these interaction constants are strongly dependent on one's choice of quadratic force constants as well. Without an excellent quadratic force field, it is nearly impossible to extract accurate anharmonic constants from the SCF approach. To test this contention, the (TC)SCF cubic and quartic force constant were spliced to the full CI quadratics, and indeed, the vibration–rotation interaction constants obtained with this approach are superb, with the mean absolute error decreasing to 4.2, 13.8, and 2.2% for α_r^A, α_r^B, and α_r^C, respectively. This competes fairly well with CCSD as well as CCSD(T).

The anharmonicity constants (χ_{rs}) and fundamental frequencies of $\tilde{a}$ $^1A_1$ NH_2^+ are reported in Table VIII. The Δ values are the total anharmonicities. The correlation trend for these values is similar to that of the α constants. In general, the approximate methods underestimate anharmonicity effects. The constant χ_{23} is the only exception which is overestimated by 8.5% at the (TC)SCF level, and does not come within 2% of the full CI value until treatments as complete as CCSDT are utilized. Also note that the anharmonicity constants involving the bending term are the most troublesome, with CCSD(T) still underestimating χ_{22} by 12%. Fortunately, those mixing terms involving the bend, χ_{13} and χ_{23}, are small, and do not adversely affect the total anharmonicities, Δ_1 and Δ_3, to any large extent. Even the diagonal bending constant is rather small, and so overall a reasonable value for Δ_2 is attained. (TC)SCF appears to uniformly underestimate anharmonicity by 11.2% and overestimate the fundamental frequencies by 8.5%. Again, dynamical correlation recovered by (TC)CISD substantially improves agreement with full CI – by 54% for χ_{rs} and 78% for the fundamentals. The improvement in the fundamental frequencies is similar to that seen in the harmonic frequencies when correlation is accounted for. For CCSD(T) the fundamentals are in error from full CI by a mere 0.6%, even though the total anharmonicity values are in error by 2.8%, which is almost totally due to the troublesome bending constants. The fundamentals predicted by this method (as well as those obtained with the CASSCF (6,6)-SOCI, CCSDT, CISDTQ, and full CI approaches) are in excellent agreement with those reported by Chambaud *et al.*[12] and Jensen *et al.*[8]. This result is suspect, though, as the use of a rather complete correlated method like CCSD(T) in conjunction with the DZP basis will substantially overestimate equilibrium bond lengths, thus artificially lowering the values for predicted fundamentals.

It is reasonable to expect that the success afforded by evaluating the (TC)SCF anharmonic force field at the full CI equilibrium geometry should again provide an improvement in the anharmonicities and fundamental frequencies predicted by this method. In fact, the harmonic frequencies are substantially enhanced as well, as shown in Table IX. (TC)SCF is able to produce harmonic vibrational frequencies within 2.8% of the full CI when the (TC)SCF quadratic force field is obtained at the full CI geometry. This is a substantial improvement, and is in excellent competition with even the CCSD(T) method for the stretching vibrations. The frequency ω_2 is still overestimated by 7.4%, indicating the need for electron correlation. As with the α constants, the anharmonicity constants are not improved when the geometry is naively shifted. The values of the fundamental vibrations, following the enhancement of the harmonics, are now within 3.2% of the full CI fundamentals. By re-evaluating the anharmonicities and fundamentals with the full CI quadratic and (TC)SCF cubic and quartic force constants, the results are very encouraging. The χ's are now within 9.0% of full CI, and the fundamentals are in error by a scant 0.3%, of course following the fact that the harmonic vibrations are exactly those of the full CI. Alternatively, one could determine the bending fundamentals after shifting the PES using the Cartesian projection scheme outlined in 1993 by Allen and Császár. When applied to this system, one arrives at a better description of the stretching potentials, and ν_1 and ν_3 are reproduced to within 0.5 and 0.1% of full CI, respectively. However, due to the extensive curvilinearity of the bending motion, subsequent projections of the molecule into Cartesian space to remove internal coordinate dependencies and rotational variances do not perform as well. The bending fundamental predicted with such a treatment (1 533 cm^{-1}) is in error by 14% from full CI, which is substantially worse than that obtained even at the (TC)SCF equilibrium geometry. Again, though, use of the full CI quadratic constants substantially improves this situation, and the bending fundamental drops to 1 431 cm^{-1}. From these results, it is easy to see why obtaining SCF anharmonic force fields at nonstationary reference geometries is an important issue which should be explored further.

When the quartic force field of the $\tilde{X}\ ^3B_1$ state of NH_2^+ is evaluated, SCF provides reasonable results for the diagonal stretching terms. In spite of that, the bending and stretch–bending force constants are substantially in error (many are of the wrong sign), with f_{2222} being underestimated by nearly 800%! By shifting the geometry to that of the full CI, the dominant diagonal stretching and stretch–stretch coupling force constants are improved and are essentially equal to those predicted by full CI; though the overall SCF force field is of dubious quality. Here again, the correlation dependence of individual force constants can be determined by evaluating the SCF force field at the exact geometry. The correlation trends of the quasilinear $\tilde{X}\ ^3B_1$ and $\tilde{b}\ ^1B_1$ force fields are similar to those for the $\tilde{a}\ ^1A_1$ state; however much more electron correlation is needed to nail down the difficult stretch–bend semi-diagonal cubic and quartic force constants. For these difficult states, one really needs a treatment at least as complete as CCSD(T) to yield accurate descriptions of their PESs. Due to the strong vibration–rotation coupling in these molecules, the second order spectroscopic perturbation theory is not reliable, and can really only give reasonable results for stretching anharmonicities. The vibrational analyses of Jensen *et al.*[8,11] and Chambaud *et al.*[12], respectively, should be much more reliable as they are not biased toward either the bent or linear extremes[11]. The interested reader is referred to the supplementary material for more information[64].

Energetics

Total energies are presented in Table X. All energies in the present study were determined at equilibrium geometries, while some previous studies have used non-equilibrium geometries. For these latter studies, we denote a single-point energy computed with method A at a geometry optimized using method B as A//B.

TABLE X

Total energies in hartrees (subtract 55) for $\tilde{X}\ ^2B_1$ NH_2 and the four lowest-lying electronic states of NH_2^+

Method	Ref.	NH_2	NH_2^+			
		$\tilde{X}\ ^2B_1$	$\tilde{X}\ ^3B_1$	$\tilde{a}\ ^1A_1$	$\tilde{b}\ ^1B_1$	$\tilde{c}\ ^1\Sigma_g^+$
DZP SCF		–0.573 493	–0.219 778	–0.146 979	–0.143 116	
DZP (TC)SCF[a]		–0.573 493	–0.219 778	–0.170 652	–0.143 116	–0.072 920
DZP (TC)CISD[a]		–0.735 054	–0.344 661	–0.294 829	–0.268 152	–0.213 071
DZP CCSD		–0.740 959	–0.347 655	–0.295 923	–0.270 223	
DZP CCSD(T)		–0.743 792	–0.349 376	–0.298 841		
DZP CCSDT		–0.744 131	–0.349 688	–0.299 549		
DZP CASSCF-SOCI[b]		–0.741 172	–0.348 786	–0.298 801	–0.271 550	–0.218 342
DZP CISDTQ I[c]		–0.744 169	–0.349 689	–0.299 647	–0.272 843	–0.218 742
DZP CISDTQ II[c]		–0.744 169	–0.349 689	–0.299 647	–0.272 843	–0.218 767
DZP full CI		–0.744 381	–0.349 742	–0.299 816	–0.272 889	–0.219 473
DZP′ full CI[d,e]	25	–0.743 324				
TZ2P(f,d) CASSCF-SOCI[b]		–0.791 126	–0.388 416	–0.341 338	–0.317 308	–0.264 213
TZ3P(2f,2d)+2diff (TC)CISD[a,d]	6		–0.387 464	–0.341 668	–0.318 233	–0.262 871
TZ3P(2f,2d)+2diff SOCI// TZ3P(2f,2d)+2diff (TC)CISD[a,d]	6		–0.393 270	–0.347 097	–0.323 089	–0.269 860
6-311+G(3d2f,2p) MP4(SDTQ)// 6-311+G(3d,2p) MP2			–0.383 30	–0.332 60		
4s3p2d1f/3s2p CASSCF-SOCI+Q[b,d,f,g]	8		–0.386 746	–0.339 017	–0.316 590	
TZ2P CCSD(T)	63		–0.395 510			
12s9p8d1f/5s2p MC-CEPA	75		–0.387 406	–0.338 591	–0.316 767	

[a–g] See footnotes to Table XI.

More chemically relevant are the adiabatic excitation energies, T_e and T_0, given in Table XI. Unlike methylene, the theoretical studies of NH_2^+ appear to have concentrated equally on the singlet–triplet gap, ΔE ($\tilde{a}\ ^1A_1 - \tilde{X}\ ^3B_1$), and the second singlet–triplet gap, ΔE ($\tilde{b}\ ^1B_1 - \tilde{X}\ ^3B_1$). T_0 ($\tilde{a}\ ^1A_1$) has been experimentally established with photoionization mass spectroscopy as 30.1 ± 0.2 kcal/mol (1.305 ± 0.01 eV)[16]. In general, the DZP basis yields excitation energies which are 2 kcal/mol too high, a result which is slightly better than the 3 kcal/mol error for similar calculations on methylene[21]. Following our theme of comparison to the full CI, the single configuration SCF method overestimates T_e ($\tilde{a}\ ^1A_1$) by 14 kcal/mol, an error which is considerably reduced by the (TC)SCF method. On the other hand, the single reference Hartree–Fock treatment of the $\tilde{b}$ state does remarkably well, yielding only an error of 0.12 kcal/mol for T_e ($\tilde{b}\ ^1B_1$). Yet even a two-configuration SCF treatment of the $\tilde{c}$ state deviates by 10.4 kcal/mol from full CI, necessitating the addition of dynamical correlation to the wavefunction. While improving T_e ($\tilde{c}\ ^1\Sigma_g^+$) dramatically, the (TC)CISD method reduces the error in T_e ($\tilde{a}\ ^1A_1$) and T_e ($\tilde{b}\ ^1B_1$) by only 0.5 and 0.1 kcal/mol, respectively. Nearly the same trends were seen for CH_2 (ref.[21]). Note that, as another resemblance to CH_2, T_e ($\tilde{a}\ ^1A_1$) actually lies below the full CI value owing to the overcompensation of non-dynamical correlation in the (TC)CISD approach for the $\tilde{a}\ ^1A_1$ state.

Single reference DZP CCSD overestimates T_e ($\tilde{a}\ ^1A_1$) by 1.1 kcal/mol, as it can not account for the importance of the second configuration of the $\tilde{a}$ state. While not as good as CISD for T_e ($\tilde{b}\ ^1B_1$), two-determinant CCSD (ref.[36]) does do reasonably well and overestimates by only 0.36 kcal/mol. Connected triples added *via* CCSD(T) and the full triples of CCSDT decrease the error in T_e ($\tilde{a}\ ^1A_1$) to 0.38 and 0.13 kcal/mol, respectively. While the CISDTQ method provides excitation energies in excellent agreement with full CI for all but the difficult $\tilde{c}$ state (for which the error is *ca* 0.4 kcal/mol), the CASSCF (6,6)-SOCI method outperforms CISDTQ for all but the $\tilde{b}$ state, where it is in error by 0.24 kcal/mol.

The most reliable experimental value for T_0 ($\tilde{a}\ ^1A_1$) is 30.1 ± 0.2 kcal/mol. However, this is not the "best" value for comparison to theory. Theory, in general, can give T_e values but its T_0 values are calculated from an estimate of the ZPVE obtained within the harmonic approximation. Other deficiencies include the neglect of relativistic effects as well as corrections for the Born–Oppenheimer approximation. With this in mind, the TZ2P(f,d) CASSCF (6,6)-SOCI method gives $T_0 = 30.025$ kcal/mol (1.302 eV), a value within experimental error. Jensen *et al.*[8] and Osmann *et al.*[13], with their anharmonic fits to the ground and excited state PESs, zero-point correct their energies using fundamental values for the vibrations, and achieve T_0 values in excellent agreement with experiment 30.53 and 30.06 kcal/mol, respectively. Without ZPVE corrections, it is difficult to quantify the accuracy of many of the assesments of ΔE ($\tilde{a}\ ^1A_1 - \tilde{X}\ ^3B_1$). But an estimate of +0.5 kcal/mol for the ΔZPVE is reasonable, and in general, the MRCI method combined with a sizeable basis provides high accuracy, while the Møller–

TABLE XI
Relative energies T_e in kcal/mol for the three lowest-lying electronic excited states of nitrenium. Zero-point corrected values T_0 are in parentheses

Method	Ref.	$\tilde{a}\,^1A_1$	$\tilde{b}\,^1B_1$	$\tilde{c}\,^1\Sigma_g^+$
DZP SCF		45.68 (46.03)	48.11 (47.35)	
DZP (TC)SCF[a]		30.83 (31.21)	48.11 (47.35)	92.15 (92.12)
DZP (TC)CISD[a]		31.27 (31.79)	48.01 (47.75)	82.57 (81.54)
DZP CCSD		32.46 (33.02)	48.59 (48.40)	
DZP CCSD(T)		31.71 (32.25)		
DZP CCSDT		31.46 (31.99)		
DZP CASSCF-SOCI[b]		31.37 (31.88)	48.47 (48.31)	81.85 (81.13)
DZP CISDTQ I[c]		31.40 (31.92)	48.22 (48.05)	82.17 (81.10)
DZP CISDTQ II[c]		31.40 (31.92)	48.22 (48.05)	82.15 (81.63)
DZP Full CI		31.33 (31.85)	48.23 (48.05)	81.75 (81.02)
TZ2P(f,d) CASSCF-SOCI[b]		29.54 (30.02)	44.62 (44.36)	77.94 (77.14)
TZ3P(2f,2d)+2diff (TC)CISD[a,d]	6	28.74 (29.21)	43.44 (43.08)	78.18 (77.19)
TZ3P(2f,2d)+2diff SOCI// TZ3P(2f,2d)+2diff (TC)CISD[a,d]	6	28.97 (29.44)	44.04 (43.68)	77.44 (76.95)
6-311+G(3d,2f,2p) MP4(SDTQ)// 6-311+G(3d,2p) MP2		31.8		
12s9p8d1f/5s2p MC-CEPA	75	30.63	44.33	
7s5p2d/2s1p MRD-CI+Q[d,e,f]	7	29.9	46.8	79.6
4s3p2d1f/3s2p CASSCF-SOCI+Q[b,d,e,g]	8	29.95 (30.53)	44.024	
cc-pVQZ CASSCF-MRCI[b,h]	12	29.14	43.64	
7s7p4d3f/6s4p3d CASSCF-MRCI[i]	13	29.16 (30.06)	43.55 (46.14)	
Experiment	15	(22.8 ± 0.5)	(51.2)	
Experiment	16	(30.1 ± 0.2)		

[a] (TC) designates a two-configuration reference for the $\tilde{a}$ and $\tilde{c}$ states; otherwise a one-configuration reference. [b] Second-order configuration interaction (SOCI) includes all configurations having no more than two electrons in external orbitals (see ref.[39]). [c] Roman numeral I (II) signifies that the SCF reference for the $\tilde{c}$ state is the first (second) configuration in Eq. (*6*) (see text). [d] One frozen-core and one deleted virtual orbital. [e] The prime emphasizes that the DZP′ basis differs from the one used in this work. [f] +Q denotes the multireference Davidson correction for disconnected quadruple substitutions (see ref.[76]). [g] Predictions using the Morse oscillator-rigid bender internal dynamics (MORBID) Hamiltonian fit to *ab initio* data. [h] Obtained from a variational Renner–Teller model fit to ab initio data. [i] Obtained with the RENNER program system (see ref.[14]). Rovibrational function fit to *ab initio* data.

Plesset and MC-CEPA methods, even when used in conjunction with very extensive basis sets, yield values which are slightly less satisfactory.

Dunlavey *et al.*[15] claimed to have observed the appearance of the $\tilde{b}\ ^1B_1$ state at 13.68 eV in their spectrum. This gives a T_0 for the $\tilde{b}\ ^1B_1 - \tilde{X}\ ^3B_1$ splitting of 2.22 eV (51.2 kcal/mol). Gibson *et al.*[16] did not see evidence for this state, and based on their correction of Dunlavey and coworkers' first adiabatic IP of $\tilde{X}\ ^2B_1$ NH_2, T_0 ($\tilde{b}\ ^1B_1$) is listed as 2.54 eV (58.6 kcal/mol) in Jacox's compilation[17]. While the $\tilde{b}\ ^1B_1$ state is highly quasilinear and is affected by both Renner–Teller interactions with the $\tilde{a}\ ^1A_1$ state and spin-orbit interactions with the $\tilde{X}\ ^3B_1$ state, the agreement achieved for T_0 ($\tilde{a}\ ^1A_1$) by rovibrational Hamiltonian fits to MRCI surfaces generated for the $\tilde{X}$ and $\tilde{a}$ states implies that this experimental value is too large. The two Renner–Teller treatments[12,13] of the $\tilde{b}$ state PES produce very similar T_e ($\tilde{b}\ ^1B_1$) values, and 46.14 kcal/mol is a more reliable estimate for T_0 ($\tilde{b}\ ^1B_1$).

The TZ3P(2f,2d)+2diff SOCI excitation energies of Stephens *et al.*[6] are within a few tenths of a kcal/mol for the $\tilde{a}$ state. In a similar study on isovalent CH_2, Yamaguchi *et al.*[71], using the same method and basis set, achieved comparable accuracy for the $\tilde{a}$ and $\tilde{b}$ states. This suggests that their T_e (T_0) results for the state of NH_2^+ [77.44 (76.95) kcal/mol] and CH_2 [59.51 (59.08) kcal/mol] may have analogous accuracy. The TZ2P(f,d) SOCI excitation energy for the $\tilde{c}$ state is in good agreement with Stephens and coworkers[6], while that of Peyerimhoff *et al.*[7] appears slightly overestimated, probably due to the small basis set and constrained geometries used.

Vertical and Adiabatic Ionization Potentials

Generally, an accurate prediction of a molecule's ionization potential (IP) using conventional *ab initio* theory is difficult as it involves determining the small energy difference between a species with *n* electrons and its cation with *n*–1 electrons[72]. Thus, it is necessary to recover large amounts of the correlation energy using rather computationally expensive methods and sizeable basis sets. New inexpensive techniques for calculating IPs, including density functional theory, G2 methods, and Green's function approaches like MCSTEP (ref.[73]), have been applied in recent years with some success. To assist in the calibration of these methods, full CI benchmarks for the vertical ionization potentials of CH_2 were provided by Bauschlicher and Taylor[74] in 1987. In the same vein, we provide adiabatic and vertical ionization potentials at the DZP full CI level for $\tilde{X}\ ^2B_1$ NH_2 in Table XII.

The full CI agreement with the experimental IPs is fairly poor, therefore when using convergent *ab initio* methods, larger basis sets should be used for reliable determination of these quantities. Single- or multi-reference Hartree–Fock treatments clearly can not predict reliable IPs, as the values are usually in error from full CI by 1.0 eV. Dynamical correlation added above the CISD level is adequate to come within 0.1 eV of the full CI results. The coupled-cluster methods are nearly as successful as CISDTQ at repro-

TABLE XII

Vertical ionization potentials (zero-point corrected adiabatic ionization potentials in parentheses) in kcal/mol from the ground state of NH_2 to the four lowest-lying states of NH_2^+

Method	Ref.	$\tilde{X}\,^2B_1$	$\tilde{X}\,^3B_1$	$\tilde{a}\,^1A_1$	$\tilde{b}\,^1B_1$	$\tilde{c}\,^1\Sigma_g^+$
DZP (TC)SCF		0.0	239.05 (220.92)	253.53 (252.13)	296.45 (268.27)	379.66 (313.04)
DZP (TC)CISD		0.0	265.03 (243.81)	277.04 (275.60)	318.46 (291.56)	393.50 (325.35)
DZP CCSD		0.0	267.11 (245.67)	279.99 (278.68)	320.75 (294.07)	
DZP CCSD(T)		0.0	267.93 (246.39)	279.96 (278.64)		
DZP CCSDT		0.0	267.96 (246.41)	279.76 (278.40)		
DZP CAS-SOCI[a]		0.0	266.84 (245.16)	278.35 (277.04)	320.06 (293.47)	394.19 (326.30)
DZP CISDTQ I[b]		0.0	267.98 (246.44)	279.62 (278.36)	321.07 (294.48)	396.06 (327.54)
DZP CISDTQ II[b]		0.0	267.98 (246.44)	279.62 (278.36)	321.07 (294.48)	395.13 (328.06)
DZP full CI		0.0	268.08 (246.54)	279.76 (278.39)	321.18 (294.59)	395.29 (327.56)
TZ2P(f,d) CAS-SOCI[a]		0.0	273.37 (251.52)	283.15 (281.54)	323.05 (295.87)	395.78 (328.65)
12s9p8d1f/7s2p MC-CEPA	75	0.0	273.3 (253.0)	284.1 (283.6)	323.1 (297.2)	
TZ2P(f,d) CCSD(T)	63	0.0	(251.6)			
aug-cc-pVTZ CCSD(T)//6-31G** MP2	19	0.0	(255.5)	(286.1)		
G2	63	0.0	(253.9)			
cc-pVQZ MCSTEP	73	0.0	270.7	284.6	324.5	
Experiment[c]	15	0.0	276.7 (264.3)	287.1 (287.1)	329.1 (315.5)	
Experiment[d]	16	0.0	(256.9 ± 0.2)	(287.0 ± 0.05)		
Experiment[e]	18	0.0	(248.6 ± 1)			

[a] Second-order configuration interaction (SOCI) includes all configurations having no more than two electrons in external orbitals (see ref.[39]). [b] Roman numeral I (II) signifies that the SCF reference for the $\tilde{c}$ state is the first (second) configuration in Eq. (*6*) (see text). [c] HeI photoelectron spectroscopy. [d] Photoionization mass spectrometry. [e] Combined molecular beam and vacuum ultraviolet synchrotron radiation photoionization mass spectroscopy.

ducing the full CI values with the largest error within 0.045 eV (1.0 kcal/mol). The CASSCF-SOCI results are slightly less satisfying than CISDTQ. However, the error for all predicted IPs from this method are at worst 0.06 eV (1.4 kcal/mol).

The TZ2P(f,d) CASSCF-SOCI results should provide reasonable predictions for the vertical and adiabatic IPs of $\tilde{X}\ {}^2B_1\ NH_2$. Comparison to the experimental values of Gibson *et al.*[16] reveals that our adiabatic IPs are in error by 5.4 kcal/mol (0.23 eV) for both ΔE ($\tilde{X}\ {}^3B_1\ NH_2^+ - \tilde{X}\ {}^2B_1\ NH_2$) and ΔE ($\tilde{a}\ {}^1A_1\ NH_2^+ - \tilde{X}\ {}^2B_1\ NH_2$). We can reasonably expect that the error in the TZ2P(f,d) CASSCF-SOCI results for the $\tilde{b}\ {}^1B_1$ and $\tilde{c}\ {}^1\Sigma_g^+$ states will be similar. Also notice that the less conventional approaches to the ionization potential problem, such as G2 theory[63] and MCSTEP (ref.[73]), provide comparable accuracy to our SOCI results. Hopefully, more definitive experimental IPs can be obtained for the $\tilde{b}$ state.

CONCLUSIONS

We have reported optimized geometries, harmonic vibrational frequencies, dipole moments, and energies for the $\tilde{X}\ {}^3B_1$, $\tilde{a}\ {}^1A_1$, $\tilde{b}\ {}^1B_1$, and $\tilde{c}\ {}^1\Sigma_g^+$ states of NH_2^+ and for $\tilde{X}\ {}^2B_1$ NH_2 with the full CI method using a DZP basis set. Ionization potentials of the ground state of NH_2 and full quartic force fields for the $\tilde{a}\ {}^1A_1$ state of NH_2^+ were also reported. These full CI benchmarks allow one to examine the effects on molecular property predictions caused by various approximations in the treatment of electron correlation. For "floppy" molecules such as ${}^3B_1$ or ${}^1B_1$ NH_2^+, an analysis of current and previous data leads to the conclusion that nondynamical correlation is necessary to pinpoint their structures, frequencies, and spectroscopic constants. While the CASSCF (6,6)-SOCI method appears to parallel the full CI surface well and is competitive with CISDTQ and CCSDT, one must carefully choose an appropriate active space when determining quantities like ionization potentials, for which the electronic environment differs from one species to the next. While not as accurate as the extensive CI calculations, the CCSD(T) method is a viable, comparatively inexpensive alternative where it can be applied, and it yields predictions in good agreement with full CI. For spectroscopic data, the CCSD(T) method performs very well, reproducing full CI results within 1% for harmonic and fundamental frequencies and within 3% for most vibration–rotation interaction (α_r^B) and anharmonicity (χ_{rs}) constants of the $\tilde{a}\ {}^1A_1$ state. It is recommended that the best available equilibrium geometry be used be used for force field evaluations. By a careful choice of reference geometry, very accurate cubic and quartic force constants can be obtained even at the Hartree–Fock level. Also, to obtain highly accurate anharmonic constants *via* RHF, the use of higher-level quadratic force constants is strongly recommended, if possible. The results herein should be seen as encouraging for the production of highly accurate spectroscopic constants and fundamental frequencies at a less-than-expected computational cost for larger systems. In addition, the explicit full CI benchmark data for higher-order force constants should aid the development of selected CI methods and their correlation extrapolations.

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