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Semi-experimental equilibrium (r_e^{SE}) and theoretical structures of hydrazoic acid (HN_3)

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Andrew N. Owen,[1] Nitai P. Sahoo,[2] Brian J. Esselman,[1] John F. Stanton,[2,a)] R. Claude Woods,[1,a)] and Robert J. McMahon[1,a)]

AFFILIATIONS

[1] Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA
[2] Quantum Theory Project, Departments of Physics and Chemistry, University of Florida, Gainesville, Florida 32611, USA

[a)] **Authors to whom correspondence should be addressed:** johnstanton@chem.ufl.edu; rcwoods@wisc.edu; and robert.mcmahon@wisc.edu

ABSTRACT

Hydrazoic acid (HN_3) is used as a case study for investigating the accuracy and precision by which a molecular structure—specifically, a semi-experimental equilibrium structure (r_e^{SE})—may be determined using current state-of-the-art methodology. The influence of the theoretical corrections for effects of vibration–rotation coupling and electron-mass distribution that are employed in the analysis is explored in detail. The small size of HN_3 allowed us to deploy considerable computational resources to probe the basis-set dependence of these corrections using a series of coupled-cluster single, double, perturbative triple [CCSD(T)] calculations with cc-pCV*X*Z (*X* = D, T, Q, 5) basis sets. We extrapolated the resulting corrections to the complete basis set (CBS) limit to obtain CCSD(T)/CBS corrections, which were used in a subsequent r_e^{SE} structure determination. The r_e^{SE} parameters obtained using the CCSD(T)/cc-pCV5Z corrections are nearly identical to those obtained using the CCSD(T)/CBS corrections, with uncertainties in the bond distances and angles of less than 0.0006 Å and 0.08°, respectively. The previously obtained r_e^{SE} structure using CCSD(T)/ANO2 agrees with that using CCSD(T)/cc-pCV5Z to within 0.000 08 Å and 0.016° for bond distances and angles, respectively, and with only 25% larger uncertainties, validating the idea that r_e^{SE} structure determinations can be carried out with significantly smaller basis sets than those needed for similarly accurate, strictly *ab initio* determinations. Although the purely computational r_e structural parameters [CCSD(T)/cc-pCV6Z] fall outside of the statistical uncertainties (2σ) of the corresponding r_e^{SE} structural parameters, the discrepancy is rectified by applying corrections to address the theoretical limitations of the CCSD(T)/cc-pCV6Z geometry with respect to basis set, electron correlation, relativity, and the Born–Oppenheimer approximation, thereby supporting the contention that the semi-experimental approach is both an accurate and vastly more efficient method for structure determinations than is brute-force computation.

INTRODUCTION

The recent theoretical and semi-experimental equilibrium structure determinations of pyrimidine,[1] thiophene,[2] thiazole,[3] and pyridazine[4] set an impressive standard for the agreement that is possible between semi-experimental (r_e^{SE}) and theoretical (r_e) equilibrium structures. Following the work on these larger aromatic systems,[1] we were interested in revisiting our previous work[5] on hydrazoic acid (HN_3) to determine how accurately the r_e^{SE} and r_e parameters could be determined for a small molecule by pushing the limits of computation. From both the experimental and theoretical points of view, HN_3 (Fig. 1) is nearly an ideal candidate for this type of investigation. On the experimental side, HN_3 is a small molecule that possesses a moderate dipole with both *a*- and *b*-axis components, producing intense rotational transitions across the microwave and millimeter-wave frequency range. It is easily synthesized from sodium azide and aqueous acidic solution, allowing for convenient isotopologue generation.[5] With only four atoms, rotational constants of 14 isotopologues (of 16 possible stable isotopologues) have been observed, providing 28 independent moments of inertia to determine its five independent structural parameters. One potential complication in the structure determination, however, is the presence of coupling between the ground vibrational state and low-lying, vibrationally excited states.[5,6] On the theoretical side, the

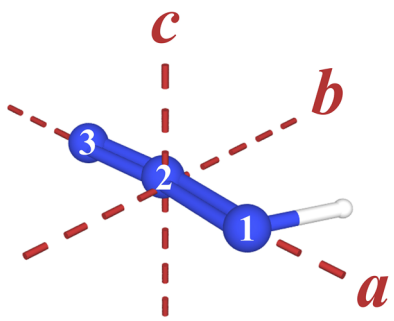


FIG. 1. Hydrazoic acid (HN_3, C_s, μ_a = 0.837 D, μ_b = 1.48 D, and κ = −0.999) with principal inertial axes and atom numbering.

electronic structure calculations involve only 22 electrons (including core electrons), allowing for fast computations of the geometry optimization and anharmonic vibrational frequencies, even when utilizing sophisticated treatments for electron correlation and larger basis sets. For these reasons, HN_3 can be used as a case study to probe the limits of structure determination for asymmetric top molecules.

The nearly linear arrangement of the nitrogen atoms in hydrazoic acid was established in the early 20th century, as well as the substantial deviation of the hydrogen atom from the axis of the nitrogen atoms.[7–9] Substitution structures refined the bond distances and the terminal N–N–H angle, but the position of the central nitrogen atom remained poorly determined,[10–14] and thus, the angle could only be estimated.[15] The crystal structure of hydrazoic acid, first reported by Evers *et al.*,[16] revealed the bent nitrogen chain (N–N–N angle 172.8°) in the solid state.[17] The first complete gas phase structure determination of hydrazoic acid was the recent semi-experimental substitution structure (r_e^{SE}) obtained using the rotational spectra of 14 isotopologues.[5] That work included isotopic substitutions of the central nitrogen atom for the first time and confirmed the N–N–N angle.

Computational investigations of HN_3 have consistently supported the slight bend of the nitrogen-atom chain.[5,16,18–20] Amberger *et al.* reported a high-level computational study involving coupled-cluster theory with single, double, and perturbative triple excitations [CCSD(T)] and the cc-pCV5Z basis, which predicted bond distances and angles to within 0.0012 Å and 0.25°, respectively, of the r_e^{SE} structure determined therein.[5,31] While the agreement between the theoretical and r_e^{SE} structures published in that work was indeed quite good, improvements in our implementation of the r_e^{SE} structure analysis and those possible in the theoretical treatments of the equilibrium structure suggest even better agreement could be achieved.

METHODS

Rotational spectroscopy

The average "determinable rotational constants" (A_0'', B_0'', and C_0'')[21] for 14 isotopologues of HN_3 (determined from the spectroscopic constants in both A- and S-reduced Hamiltonians, I^r representation), were taken directly from the supplementary material of our previous work.[5] These determinable constants are free of the effects of centrifugal distortion and are independent of the choice of A or S reduction used in the least-squares fitting. Details of the synthesis of the isotopologues, the instrumentation, the spectra, and further analyses are reported in the earlier study. Due to complications arising from the coupling between the ground state and low-lying bending fundamentals ν_5 and ν_6, care must be taken to ensure that the rotational constants used in the structure determination are unperturbed. The rotational constants determined in our previous work[5] (which did not address the *c*-type Coriolis and *a*-type Coriolis couplings between the ground state and fundamentals ν_5 and ν_6, respectively) and determined in a more recent work[6] (which contains additional ground–state transitions and addresses the coupling of ν_5 and ν_6) are provided in Table I. Neither of these least-squares fits adequately addresses the coupling present in the system, as evidenced by the relatively poor agreement between the computed centrifugal distortion constants and their corresponding experimentally determined values. In particular, the *K*-dependent computed and experimental centrifugal distortion constants (Δ_K, δ_K, Φ_K, and ϕ_K) do not have the expected level of agreement, making it likely that both fits have allowed Coriolis coupling to be absorbed into those constants. A collaborative effort is under way to address the unresolved coupling issues of the ground and vibrationally excited states of HN_3 and DN_3. Fortunately, the close agreement of the rotational constants between the two previously published least-squares fits[5,6] provides confidence that the ground state rotational constants can be used in a structure determination without addressing the

TABLE I. Spectroscopic constants of HN_3 (A-reduced Hamiltonian, I^r representation).

	CCSD(T)/ cc-pCV5Z	Amberger *et al.*[5]	Vávra *et al.*[6,a]
A_0 (MHz)	611 182	611 034.132 (29)	611 036.218 (13)
B_0 (MHz)	12 053	12 034.983 (62)	12 035.035 74 (95)
C_0 (MHz)	11 801	11 780.6713 (66)	11 780.622 95 (77)
Δ_J (kHz)	4.75	4.9174 (10)	4.918 45 (24)
Δ_{JK} (kHz)	774	797.98 (15)	771.43 (61)
Δ_K (kHz)	226 000	267 559 (27)	146 050 (620)
δ_J (kHz)	0.0778	0.091 18 (22)	0.091 726 (28)
δ_K (kHz)	318	403.9 (31)	428.96 (41)
Φ_J (Hz)	−0.000 966	[0][b]	[0][b]
Φ_{JK} (Hz)	1.95	1.19 (10)	[0][b]
Φ_{KJ} (Hz)	−983	255 (14)	16.89 (42)
Φ_K (Hz)	282 000	[0][b]	661.1 (20)
ϕ_J (Hz)	0.000 078 4	[0][b]	[0][b]
ϕ_{JK} (Hz)	1.46	[0][b]	[0][b]
ϕ_K (Hz)	3960	[0][b]	[0][b]
L_{KKJ} (mHz)		−40 010 (400)	[0][b]
$\Delta_{i\,0}$ (uÅ^2)	0.0685	0.0794	0.0798
N_{lines}		78 mmw	273 mmw/859 ir
σ_{fit} (MHz)		0.032	0.042/72.5

[a] *a*-type and *c*-type Coriolis couplings addressed with the ground state, ν_5 and ν_6; see previous work for details.[6]

[b] Values fixed to zero. (Computed sextic centrifugal distortion constants were not available at the time of previous work.)

coupling. While addressing the Coriolis coupling in different ways, the two least-squares fits provided rotational constants that differ only in the sixth significant figure. Furthermore, the determinable constants from the A- or an S-reduction least-squares fit agree to within a few kHz. Confidence in the rotational constants derived from this agreement is critically important because the interactions between the ground state and vibrationally excited states for many isotopologues observed at natural abundance cannot be addressed in a practical manner due to the low intensity of the rotational transitions for these species.

Computations

A developmental version of CFOUR was used to conduct all *ab initio* calculations. These consisted of geometry optimizations, anharmonic VPT2, and magnetic properties calculations at CCSD(T) using frozen-core approximated (cc-pV*X*Z) or all-electron (cc-pCV*X*Z) Dunning-style basis sets (for X = D, T, Q, and 5). In addition, a geometry optimization using the cc-pCV6Z basis set was obtained. Isotopologue-dependent corrections to the rotational constants were calculated to account for vibration-rotation interactions using the results of the VPT2 calculations and for electron-mass distributions using the results of magnetic property calculations. These corrections were then combined with the average determinable A_0'', B_0'', and C_0'' constants to obtain semi-experimental equilibrium constants (B_e^x) for each isotopologue using Eq. (S1). The r_e^{SE} structure of HN_3 was then determined by a nonlinear least-squares fit of the corresponding moments of inertia, using the *xrefit* module included within CFOUR, with all values weighted equally.

Further analysis of the r_e^{SE} structure determination was conducted using the *xrefiteration* routine, which is described in detail elsewhere.[4] Concisely, an initial r_e^{SE} structure determination is obtained for the "minimal set" of isotopologues, which consists of the normal isotopologue and any isotopologue differing by a single isotopic substitution. The *xrefiteration* routine then obtains a set of r_e^{SE} structures where only one previously unincorporated isotopologue of those remaining is added into the dataset. The routine then estimates the overall "apparent precision" by calculating the total relative uncertainty (δr_e^{SE}) of the resulting structures using Eq. (1), where R_i, θ_i, and ϕ_i represent bond distances, angles, and dihedrals, respectively, and σ_{fit} is the statistical uncertainty from the least-squares fit of r_e^{SE},

$$\delta r_e^{SE} = \sqrt{\sum_i \left(\frac{2\sigma_{fit}(R_i)}{R_i}\right)^2 + \sum_i \left(\frac{2\sigma_{fit}(\theta_i)}{\theta_i}\right)^2 + \sum_i \left(\frac{2\sigma_{fit}(\phi_i)}{\phi_i}\right)^2}. \quad (1)$$

The r_e^{SE} structure with the smallest apparent precision is kept and the process is repeated until all isotopologues are included. As we demonstrated for thiophene,[2] thiazole,[3] and pyridazine,[4] the utility of this analysis lies in tracking the progression of the structural parameters in comparison to the theoretical values to assess the accuracy of the final structure.

Finally, we calculated a "best theoretical estimate" (BTE) equilibrium structure for HN_3 using the previously described methodology,[1–4] which takes into account the following contributions to the geometry beyond a normal coupled-cluster geometry optimization:

1. Residual basis set effects [Eq. (2)] by means of extrapolations to the complete basis set (CBS) limit using CCSD(T)/cc-pCV*X*Z (X = Q, 5, and 6),

$$\Delta R(\text{basis}) = R(\infty) - R(\text{CCSD(T)/cc-pCV6Z}). \quad (2)$$

2. Residual electron correlation effects [Eq. (3)] by use of CCSDT(Q),[22]

$$\Delta R(\text{corr}) = R(\text{CCSDT(Q)/cc-pCVTZ}) - R(\text{CCSD(T)/cc-pCVTZ}). \quad (3)$$

3. Scalar relativistic effects [Eq. (4)] by use of the X2C-1e variant of coupled-cluster theory,[23–25]

$$\Delta R(\text{rel}) = R(\text{CCSD(T)/cc-pCV5Z})_{\text{SFX2C-1e}} - R(\text{CCSD(T)/cc-pCV5Z}). \quad (4)$$

4. Effect of the Born–Oppenheimer approximation [Eq. (5)] by use of the diagonal Born–Oppenheimer correction (DBOC),[26,27]

$$\Delta R(\text{DBOC}) = R(\text{SCF/cc-pCVTZ})_{\text{DBOC}} - R(\text{SCF/cc-pCVTZ}). \quad (5)$$

The correction to the CCSD(T)/cc-pCV6Z optimization necessary to obtain the BTE is then given by the sum of the above corrections for each parameter, as given in the following equation:

$$\Delta R(\text{best}) = \Delta R(\text{basis}) + \Delta R(\text{corr}) + \Delta R(\text{rel}) + \Delta R(\text{DBOC}). \quad (6)$$

Output files for all calculations are provided in the supplementary material.

RESULTS AND DISCUSSION

Structure determinations

The planar structure of HN_3 allows an assessment of the quality of the computed corrections to the rotational corrections, specifically, by examining inertial defects associated with the experimental and semi-experimental rotational constants. The inertial defect is precisely zero for a rigid planar structure, but the uncorrected experimental rotational constants (B_0^x) will have a non-zero inertial defect ($\Delta_{i\,0}$) due to vibration-rotation interactions and the electron-mass distribution. These deviations are addressed by the computational corrections used to obtain the semi-experimental B_e^x rotational constants and should bring the approximate $\Delta_{i\,e}$ closer to zero. Previously, for HN_3,[5] the inertial defect was reduced to about 3% of its original value after the inclusion of the vibration–rotation corrections (Table II). Subsequent addition of an isotopologue-independent electron-mass correction to the rotational constants

TABLE II. Inertial defects (Δ_i) of hydrazoic acid isotopologues from various determinations of the moments of inertia.

	Expt.[5]	ANO2[5]		cc-pCV5Z		CBS	
Isotopologue	Δ_{i0} (uÅ^2)	Δ_{ie} (uÅ^2)[a]	Δ_{ie} (uÅ^2)[b]	Δ_{ie} (uÅ^2)[a]	Δ_{ie} (uÅ^2)[b]	Δ_{ie} (uÅ^2)[a]	Δ_{ie} (uÅ^2)[b]
Normal	0.0735	0.003 53	0.003 60	0.002 73	0.002 80	0.002 74	0.002 89
[^{2}H]	0.0963	0.003 42	0.003 43	0.002 36	0.002 43	0.002 76	0.002 91
[1-^{15}N]	0.0738	0.003 55	0.003 63	0.002 74	0.002 81	0.002 71	0.002 86
[2-^{15}N]	0.0736	0.003 50	0.003 57	0.002 70	0.002 77	0.002 75	0.002 90
[3-^{15}N]	0.0736	0.003 53	0.003 62	0.002 73	0.002 80	0.002 38	0.002 53
[^{2}H, 1-^{15}N]	0.0967	0.003 45	0.003 45	0.002 37	0.002 45	0.002 40	0.002 55
[^{2}H, 2-^{15}N]	0.0962	0.003 45	0.003 46	0.002 39	0.002 46	0.002 41	0.002 56
[^{2}H, 3-^{15}N]	0.0964	0.003 43	0.003 44	0.002 36	0.002 44	0.002 39	0.002 54
[1,2-^{15}N]	0.0739	0.003 54	0.003 62	0.002 73	0.002 80	0.002 75	0.002 90
[1,3-^{15}N]	0.0739	0.003 54	0.003 63	0.002 73	0.002 80	0.002 75	0.002 90
[2,3-^{15}N]	0.0737	0.003 48	0.003 56	0.002 67	0.002 74	0.002 69	0.002 84
[^{2}H, 1,2-^{15}N]	0.0966	0.003 46	0.003 47	0.002 39	0.002 46	0.002 41	0.002 56
[^{2}H, 1,3-^{15}N]	0.0969	0.003 46	0.003 47	0.002 38	0.002 46	0.002 41	0.002 56
[^{2}H, 2,3-^{15}N]	0.0963	0.003 43	0.003 45	0.002 37	0.002 44	0.002 39	0.002 54
Average ($\bar{x}$)	0.0851	0.003 48	0.003 53	0.002 55	0.002 62	0.002 57	0.002 72
Std. Dev. (s)	0.0118	0.000 05	0.000 08	0.000 18	0.000 18	0.000 18	0.000 18

[a]Vibration–rotation interaction corrections only.
[b]Vibration–rotation interaction and electron-mass corrections.

did not further reduce the magnitude of the inertial defect but slightly increased its value. In cases where the electron-mass distribution in the molecule is not well-described by subsuming the electron masses into the nearby nuclei,[1–4,28] the use of isotopologue-dependent electron-mass corrections has been shown to reduce the Δ_{ie} by about one order of magnitude. In this study, CCSD(T)/cc-pCV5Z corrections have been applied to the rotational constants, resulting in inertial defects roughly two-thirds the magnitude of the ANO2-corrected inertial defects. The inertial defects with both vibration-rotation and electron-mass corrections, however, are still slightly larger than those using just the vibration–rotation corrections at the cc-pCV5Z level, similar to the relationship previously observed at the ANO2 level. The extensive computational analysis in the current study allows us to extrapolate the vibration-rotation and electron-mass corrections to the rotational constants to the CBS limit (Table S1). Application of these CBS corrections to the B_0^x constants to obtain the semi-experimental B_e^x constants results in inertial defects that are nearly identical to those obtained at the cc-pCV5Z level, with identical standard deviations (Table II). The close agreement of the inertial defects obtained using either cc-pCV5Z or CBS corrections suggests that the cc-pCV5Z basis is sufficient for obtaining accurate corrections to the rotational constants. The lack of improvement to the inertial defect with the inclusion of the electron-mass correction is consistent with the earlier study[5] and this lack of improvement is broadly consistent with the near-cylindrical nature of HN_3 where electron mass is radially distributed around the H–N–N–N backbone in the in-plane and out-of-plane π orbitals.[20]

The r_e^{SE} structure determinations in Table III (and visualized in Fig. S1) using previously obtained data and increasingly larger correlation-consistent basis sets clearly demonstrate the improvement in the fitting of the structural parameters as the basis set grows larger. The structure obtained using corrections with the largest basis set (cc-pCV5Z, Fig. 2) has the smallest statistical uncertainties

TABLE III. Summary of r_e^{SE} structural parameters of hydrazoic acid.[a]

Parameter	ANO2[5]	cc-pCVDZ	cc-pCVTZ	cc-pCVQZ	cc-pCV5Z	CBS
R_{H-N1} (Å)	1.015 77(32)	1.015 72(59)	1.015 71(33)	1.015 83(26)	1.015 84(24)	1.015 84(25)
R_{N1-N2} (Å)	1.241 74(74)	1.241 66(133)	1.241 66(74)	1.241 76(58)	1.241 78(55)	1.241 78(57)
R_{N2-N3} (Å)	1.130 66(76)	1.130 80(136)	1.130 66(75)	1.130 68(59)	1.130 68(56)	1.130 68(58)
$\theta_{H-N1-N2}$ (deg)	109.133(34)	109.192(62)	109.148(35)	109.116(27)	109.118(26)	109.117(27)
$\theta_{N1-N2-N3}$ (deg)	171.50(10)	171.47(18)	171.53(10)	171.499(80)	171.497(76)	171.495(79)

[a]Evaluated from the average determinable rotational constants of 14 isotopologues with corrections for vibration–rotation coupling and electron-mass distribution computed at CCSD(T) using the specified basis set.

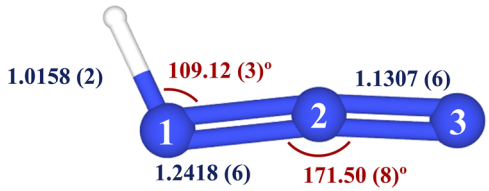
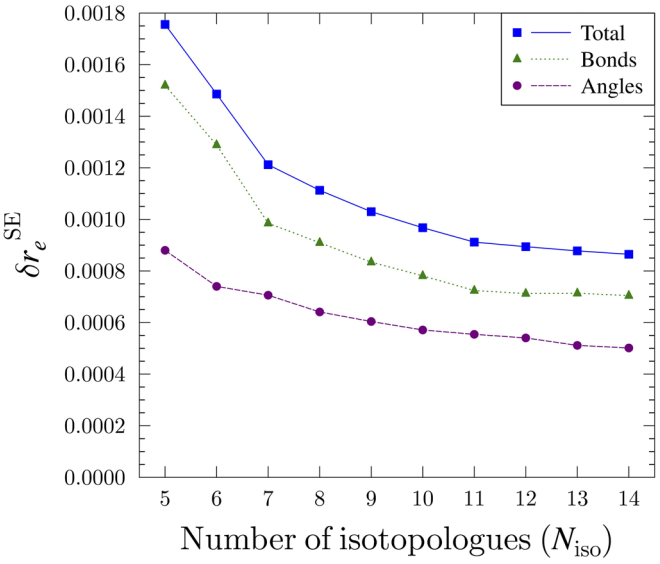


FIG. 2. Semi-experimental equilibrium structure (r_e^{SE}) of hydrazoic acid with 2σ statistical uncertainties from least-squares fitting the isotopologue moments of inertia, after applying computed corrections [CCSD(T)/cc-pCV5Z] for the effects vibration–rotation coupling and electron-mass distribution.

and agrees well with the r_e^{SE} structure obtained using the CBS corrections described above. Unsurprisingly, the parameters of the r_e^{SE} cc-pCVDZ structure are the most poorly determined of all the r_e^{SE} structures, with uncertainties in the parameters nearly twice as large as those obtained using the triple-zeta basis. Notably, the r_e^{SE} structure previously obtained using the ANO2 corrections is similar to that using the cc-pCVTZ corrections with nearly identical 2σ uncertainties in the parameters and with values of the parameters in better agreement with the r_e^{SE} cc-pCV5Z values.

To examine the effects of the different isotopologues on the r_e^{SE} structure, we conducted an *xrefiteration* analysis[4] on the r_e^{SE} CCSD(T)/cc-pCV5Z structure. For hydrazoic acid, the minimal set necessary to obtain a substitution structure is comprised of the normal isotopologue and the singly substituted isotopologues ([^{2}H]$^-$, [1-^{15}N]$^-$, [2-^{15}N]$^-$, and [3-^{15}N]-hydrazoic acid). Using the *xrefiteration* routine, we obtained the r_e^{SE} structure using this minimal set as the initial set and then iteratively expanded the set of isotopologues until all were included. The isotopologue added to expand the set was that with the lowest "apparent precision," calculated using Eq. (1), in which δr_e^{SE} is the total relative (i.e., dimensionless) uncertainty of the structural parameters explicitly determined in the fit. As shown in Fig. 3 (and enumerated in Table S2), the effect of adding isotopologues beyond the minimal set required for a substitution structure is immediately noticeable, with the inclusion of the first additional isotopologue ([^{2}H, 3-^{15}N]) reducing δr_e^{SE} by 15%. The addition of the next isotopologue ([^{2}H, 1,2-^{15}N]) reduces δr_e^{SE} by 30% relative to the minimal set. With each iteration of the algorithm, δr_e^{SE} of the resulting r_e^{SE} structure continues to decrease, eventually to 50% smaller than the initial value. Notably, a rise in the δr_e^{SE} at the end of the *xrefiteration* analysis, observed in previous studies,[2–4] did not occur here. In those previous studies, we observed that the last few isotopologues tend to increase the δr_e^{SE} due to the nature of the algorithm: the isotopologues that raise the δr_e^{SE} are only added at the end of the analysis, after all isotopologues that lower the δr_e^{SE} have been added. The absence of such behavior for the HN_3 r_e^{SE} structure suggests that even the "worst" of the isotopologues in the dataset still lower the δr_e^{SE},[32] giving us confidence that the underlying spectroscopic data and theoretical corrections for the r_e^{SE} structure determination are consistent. Therefore, given that the dataset contains 14 of the 16 possible stable isotopologues of HN_3, we suspect that such consistency corresponds to accuracy.

To assess the quality of the r_e^{SE} structure of HN_3, we examined how the parameters of the structure change throughout the *xrefiteration* analysis. As demonstrated in Fig. 4 and Table IV, there is remarkably little change in the parameter values throughout the *xrefiteration* analysis. The variation in the values of the bond distances and angles is <0.000 05 Å and <0.001°, respectively, which is well within the 2σ uncertainties of the respective parameters. Such variation in the parameters throughout the *xrefiteration* analysis contrasts with that observed in our previous studies: ~0.0004 Å and ~0.05° for the bond distances and angles of pyridazine and thiophene and ~0.0014 Å and ~0.4° for the bond distances and angles of thiazole, respectively. It appears that the HN_3 structure converges very rapidly, and, after nine isotopologues, the only change in the structural parameter values is 0.000 01 Å for R_{N1-N2}. The convergence of the structural parameters and their close agreement with



N_{iso}	Isotopologue Added
5	Minimal Set
6	[^{2}H, 3-^{15}N]
7	[^{2}H, 1,2-^{15}N]
8	[1,2-^{15}N]
9	[2,3-^{15}N]
10	[^{2}H, 2,3-^{15}N]
11	[^{2}H, 1-^{15}N]
12	[^{2}H, 2-^{15}N]
13	[1,3-^{15}N]
14	[^{2}H, 1,3-^{15}N]

FIG. 3. Plot of the δr_e^{SE} value as a function of the number of isotopologues (N_{iso}) incorporated into the r_e^{SE} CCSD(T)/cc-pCV5Z structure determination dataset. The total relative statistical uncertainty (δr_e^{SE}, blue squares), the relative statistical uncertainty in the bond distances (green triangles), and the relative statistical uncertainty in the bond angles (purple circles) are presented.

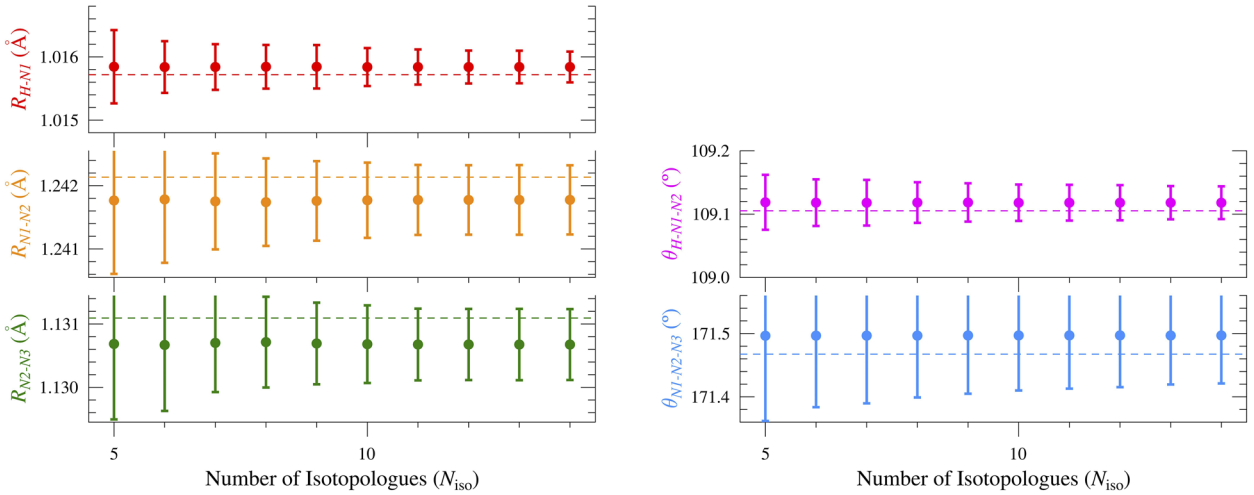


FIG. 4. Plots of the r_e^{SE} CCSD(T)/cc-pCV5Z structural parameters of hydrazoic acid as a function of the number of isotopologues (N_{iso}) and their 2σ uncertainties with consistent scales for each distance (0.002 Å) and each angle (0.2°). The dashed line in each plot is the BTE value calculated for that parameter. The isotopologue ordering along the *x* axis is the same as that in Fig. 3.

their BTE values (dotted lines in Fig. 4) provides confidence that the resulting r_e^{SE} structure is both accurate and precise, despite the unaddressed coupling in the least-squares fits used to determine the experimental rotational constants.

Theoretical predictions

As with the aromatic heterocycles that we have recently studied,[1–4] we obtained CCSD(T) geometry optimizations using up to and including the all-electron quintuple-zeta basis set. The small size of HN_3 allowed us to expand the basis set even further to the all-electron sextuple-zeta basis set. Interestingly, we see that the purely theoretical r_e structural parameters computed using CCSD(T)/cc-pCV6Z do not fall within the statistical uncertainties of the r_e^{SE} parameters. As we noted in related works,[1–4] molecular structures predicted using CCSD(T) computations with a large basis set—while an adequate approach in a wide variety of computational contexts[29,30]—are insufficiently accurate for comparison to the high precision of r_e^{SE} structure determinations. Furthermore, extrapolating the parameters to the CBS limit [Table S4, "$r_e + \Delta R$(basis)"] is not sufficient to bring the theoretical parameters into an agreement with the r_e^{SE} parameters.

Similar to that observed with the r_e^{SE} structures when the basis set increases in size, the r_e parameters also converge at an

TABLE IV. Values of the structural parameters of hydrazoic acid during the iterative analysis of the r_e^{SE} CCSD(T)/cc-pCV5Z (*xrefiteration*).

		Parameters				
N_{iso}[a]	Isotopologue added	R_{H-N1} (Å)	R_{N1-N2} (Å)	R_{N2-N3} (Å)	$\theta_{H-N1-N2}$ (deg)	$\theta_{N1-N2-N3}$ (deg)
5	Minimal set[b]	1.015 84 (58)	1.241 77 (116)	1.130 69 (119)	109.119 (43)	171.496 (135)
6	[^{2}H, 3-^{15}N]	1.015 84 (41)	1.241 78 (100)	1.130 67 (104)	109.118 (37)	171.497 (113)
7	[^{2}H, 1,2-^{15}N]	1.015 84 (36)	1.241 75 (76)	1.130 70 (78)	109.118 (36)	171.497 (107)
8	[1,2-^{15}N]	1.015 84 (35)	1.241 74 (69)	1.130 71 (72)	109.118 (32)	171.497 (98)
9	[2,3-^{15}N]	1.015 84 (34)	1.241 76 (63)	1.130 69 (64)	109.118 (30)	171.497 (92)
10	[^{2}H, 2,3-^{15}N]	1.015 84 (30)	1.241 77 (59)	1.130 68 (61)	109.118 (29)	171.497 (87)
11	[^{2}H, 1-^{15}N]	1.015 84 (28)	1.241 77 (55)	1.130 68 (57)	109.118 (28)	171.497 (84)
12	[^{2}H, 2-^{15}N]	1.015 84 (26)	1.241 77 (55)	1.130 68 (56)	109.118 (28)	171.497 (82)
13	[1,3-^{15}N]	1.015 84 (26)	1.241 78 (55)	1.130 68 (56)	109.118 (26)	171.497 (77)
14	[^{2}H, 1,3-^{15}N]	1.015 84 (24)	1.241 78 (55)	1.130 68 (56)	109.118 (26)	171.497 (76)

[a]Number of isotopologues in the iteration.
[b]The initial iteration consists of the normal isotopologue and [^{2}H]$^-$, [1-^{15}N]$^-$, [2-^{15}N]$^-$, and [3-^{15}N]-hydrazoic acid.

TABLE V. Corrections used in determining the best theoretical estimate (BTE) of the equilibrium structural parameters of hydrazoic acid, with comparison to the r_e^{SE} determined values.

Parameter	ΔR(basis) Eq. (2)	ΔR(corr) Eq. (3)	ΔR(rel) Eq. (4)	ΔR(DBOC) Eq. (5)	ΔR(best) Eq. (6)	CCSD(T)/ cc-pCV6Z	BTE[a]	r_e^{SE} CCSD(T)/ cc-pCV5Z
R_{H-N1} (Å)	−0.000 010	0.000 14	0.000 027	0.000 078	0.000 24	1.015 48	1.015 72	1.015 84 (24)
R_{N1-N2} (Å)	−0.000 11	0.001 33	0.000 19	−0.000 065	0.001 35	1.240 78	1.242 13	1.241 78 (55)
R_{N2-N3} (Å)	−0.000 078	0.002 13	−0.000 19	−0.000 015	0.001 85	1.129 25	1.131 09	1.130 68 (56)
$\theta_{H-N1-N2}$ (deg)	0.015	0.062	−0.087	0.012	0.001 8	109.103	109.105	109.118 (26)
$\theta_{N1-N2-N3}$ (deg)	0[b]	−0.208	−0.026	0.004 1	−0.166	171.697	171.467	171.497 (76)

[a]Obtained by adding the ΔR(best) correction to the CCSD(T)/cc-pCV6Z optimized values.
[b]This angle does not converge at an exponential rate with respect to the size of the basis set, leading to a spurious $R(\infty)$ value upon extrapolation. As such, the $R(\infty)$ value for this angle has been set to that of the CCSD(T)/cc-pCV6Z structure, which results in a ΔR(basis) of this angle of zero per Eq. (2).

exponential rate (Table S3 and Fig. S2) with the exception of $\theta_{N1-N2-N3}$. The non-exponential behavior of this angle leads to a spurious $R(\infty)$ value that is closer to the triple-zeta value than it is to the sextuple-zeta value. As such, we set the $R(\infty)$ value for $\theta_{N1-N2-N3}$ to the sextuple-zeta value, which is equivalent to setting the ΔR(basis) correction for $\theta_{N1-N2-N3}$ to zero, as given in Table V. Ultimately, this change has practically no effect on the outcome of the BTE structure and the following discussion: the angle is now slightly smaller but still well within the statistical uncertainty of the r_e^{SE} CCSD(T)/cc-pCV5Z value.

The precision of the r_e^{SE} structure is such that correcting for the size of the basis set is insufficient to bring the r_e structure into an agreement. To do so, the r_e structure must also be treated for electron correlation and for effects due to relativity and the (diagonal) Born-Oppenheimer correction. As demonstrated in Table V and Fig. 5, the inclusion of such effects results in a best theoretical estimate (BTE) structure that is in complete agreement with the r_e^{SE} structure. All parameters from the BTE structure fall within the statistical uncertainties of the r_e^{SE} structure. As is typically the case, the CBS correction [Eq. (2)] contracts the bond lengths while the correlation correction [Eq. (3)] lengthens the bonds (Table V). Unlike pyrimidine, where the DBOC correction lengthened the bonds and the relativistic correction contracted the bonds, we observe mixed effects of the DBOC and relativistic

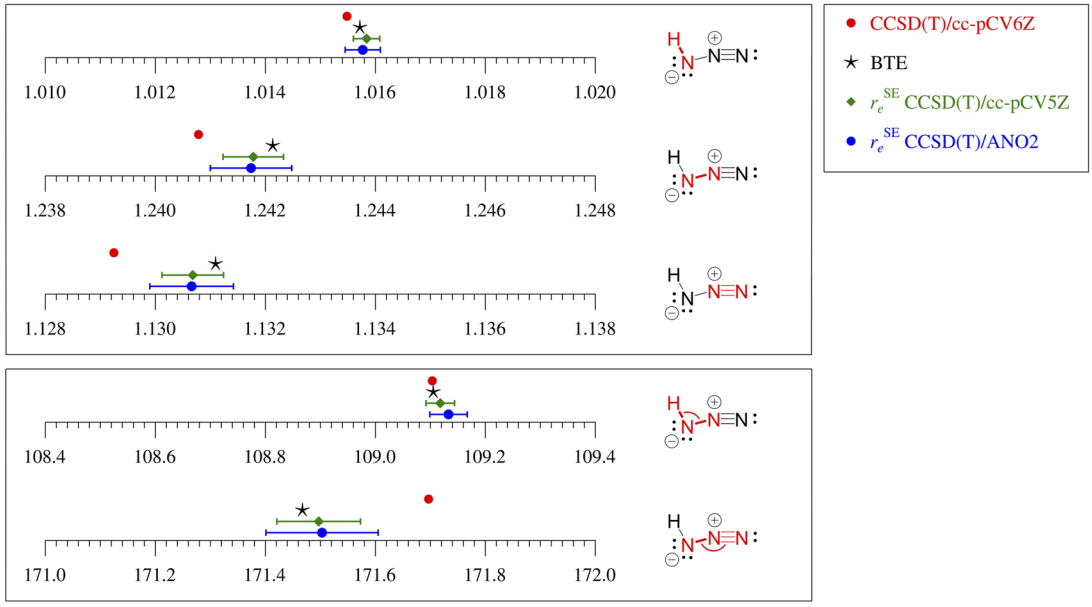


FIG. 5. Graphical comparison of the hydrazoic acid structural parameters with bond distances in angstroms (Å) and angles in degrees (°). Uncertainties shown are 2σ. Data for r_e^{SE} CCSD(T)/ANO2 are taken from Ref. 5.

corrections on the HN_3 bond lengths (Table V); such was also the case for pyridazine.[4] The largest magnitude correction is the correlation correction for all parameters except $\theta_{H\text{–}N1\text{–}N2}$.

CONCLUSIONS

The r_e^{SE} structure determination of HN_3 using CCSD(T)/cc-pCV5Z corrections for the effects of vibration–rotation coupling and electron-mass distribution resulted in a modest reduction of the statistical uncertainties (2σ) of the structural parameters over those previously obtained with CCSD(T)/ANO2 corrections. Given that these two r_e^{SE} structures determined the bond distances and bond angles to within 0.0001 Å and 0.02° of each other, the smaller ANO2 basis is recommended for r_e^{SE} structure determinations of larger molecules, where a quintuple-zeta basis set is impractical. In our previous work on pyridazine, the application of isotopologue-dependent electron-mass corrections resulted in a dramatic improvement in the semi-experimental inertial defects (Δ_{ie}), but a similar treatment for HN_3 in this work did not. The lack of a reduction in Δ_{ie} for HN_3 upon inclusion of the isotopologue-dependent electron-mass corrections is puzzling. While HN_3 is highly prolate and pyridazine is highly oblate, why (or even if) the near-cylindrical shape and radial distribution of the electrons of HN_3 would affect the electron-mass corrections is not clear. The more likely explanation is that the VPT2 corrections for treating the vibration–rotation interactions—while reducing the inertial defect—are not accurately adjusting the rotational constants and the subsequent electron-mass corrections (being smaller in magnitude) are unable to affect a change, in which case higher order perturbation theory may be required.

Given the high level of theory used to obtain the corrections and the inclusion of rotational constants from 14 of the 16 possible isotopologues, further improvement to the r_e^{SE} structure determination will be difficult to achieve. Analysis of the present r_e^{SE} structure determination using the *xrefiteration* routine revealed continuous improvement in the r_e^{SE} structure as additional isotopologues were included in the dataset, with very little variation in the values of the structural parameters, suggesting the underlying data are remarkably self-consistent. While the purely theoretical r_e structural parameters computed using CCSD(T)/cc-pCV6Z do not fall within the statistical uncertainties (2σ) of the r_e^{SE} structure, structural parameters obtained as the "best theoretical estimate" are in excellent agreement with the semi-experimental values. The molecular structure of hydrazoic acid, already known to high precision through previous work, has been further refined by improvements in computational methods and theoretical analyses, illustrating the state-of-the-art for contemporary gas-phase structure determination.

SUPPLEMENTARY MATERIAL

Output files of the geometry optimizations, the vibrational corrections, the electron mass corrections, the *xrefit* analyses, and the *xrefiteration* analysis, along with an accompanying *.pdf file including summaries of the outputs and the supplementary tables and figures referenced throughout the article are provided in the supplementary material.

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AUTHOR DECLARATIONS

Conflict of Interest

There are no conflicts to declare.

Author Contributions

Andrew N. Owen: Formal analysis (equal); Writing-original-draft (equal). **Nitai P. Sahoo:** Formal analysis (equal). **Brian J. Esselman:** Conceptualization (equal); Formal analysis (equal); Writing-review-editing (equal). **John F. Stanton:** Conceptualization (equal); Funding acquisition (equal); Writing-review-editing (equal). **R. Claude Woods:** Conceptualization (equal); Formal analysis (equal); Writing-review-editing (equal). **Robert J. McMahon:** Funding acquisition (equal); Project administration (equal); Writing-review-editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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[32] The use of the word "worst" here refers to the degree to which information provided by the isotopologue in question is consistent with the information provided by the other isotopologues in the dataset and does not necessarily reflect the quality of the spectroscopic data or computed corrections for that isotopologue. As seen in pyridazine,[4] the inclusion of the final isotopologue resulted in a dramatic increase in the δr_e^{SE} but was required for accurate determination of several parameters.