Benchmark ab initio thermochemistry of the isomers of diimide, \( \text{N}_2\text{H}_2 \), using accurate computed structures and anharmonic force fields

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Abstract

A benchmark ab initio study on the thermochemistry of the trans-HNNH, cis-HNNH, and \( \text{H}_2\text{NN} \) isomers of diazene has been carried out using the CCSD(T) coupled cluster method, basis sets as large as \([7s6p5d4f3g2h/5s4p3d2f1g]\), and extrapolations towards the 1-particle basis set limit. The effects on inner-shell correlation and of anharmonicity in the zero-point energy were taken into account: accurate geometries and anharmonic force fields were thus obtained as by-products. Our best computed \( \Delta H^\circ_{f,0} \) for trans-HNNH, 49.2±0.3 kcal/mol, is in very good agreement with a recent experimental lower limit of 48.8±0.5 kcal/mol. CCSD(T) basis set limit values for the isomerization energies at 0 K are 5.2±0.2 kcal/mol (cis-trans) and 24.1±0.2 kcal/mol (iso-trans). Our best computed geometry for trans-HNNH, \( r_e(NN)=1.2468 \ \text{Å} \),
$r_e(\text{NH}) = 1.0283$ Å, and $\theta_e = 106.17^\circ$, reproduces the precisely known ground-state rotational constants of trans-HNNH to within better than 0.1%. The rotation-vibration spectra of both cis-HNNH and H$_2$NN are dominated by very strong Coriolis and Fermi resonances. In addition, the NH stretches in H$_2$NN are so strongly anharmonic that vibrational perturbation theory breaks down, and the molecule appears to be an excellent test case for variational treatments of the vibrational Schrödinger equation.

I. INTRODUCTION

The existence of N$_2$H$_2$ (diazene, diimide) was suggested as early as 1892 [1] as an intermediate in the decomposition of azoformic acid. The trans isomer was finally discovered in 1958 by mass spectrometry as a gaseous discharge product of hydrazine [4], and around the same time in the infrared as a photolysis product of matrix isolated hydrazoic acid [3,4]. The compound is of importance in organic chemistry for the stereospecific reduction of olefins [5] and of course as the parent of a large number of azo compounds, and in inorganic chemistry as a ligand for transition metal complexes [3]. For comprehensive (if somewhat older) reviews on the preparation, properties, and reactions of diimide, the reader is referred to Back [7] and to a volume [8] in the Patai series on the chemistry of functional groups.

Early work on its rotation-vibration spectroscopy was reviewed by Craig and Levin [8] (CL). Its anharmonic force field was studied ab initio at the MP2/[4s3p2d1f] and CCSD/[3s2p1d] levels by Kobayashi, Blüdsky, Koch, and Jørgenson (KBKJ) [10] — who also considered the cis-diazene and isodiazene isomers — and very recently at the CCSD(T)/[4s3p2d1f] level by the present authors (MT) [11], who also reviewed more recent spectroscopic information. After publication of this latter paper, Demaison, Hegelund, and Bürger (DHB) [12] published new experimentally derived equilibrium geometry data, based in part on a re-analysis of recent high-resolution data for trans-HNNH [13], trans-DNND [14], and trans-HNND [15].
Experimental information on the cis isomer is quite limited, basically consisting of tentative assignments of bands at 3074 and 1279 cm$^{-1}$ by Rosengren and Pimentel (RP) \cite{4} and of bands at 1034, 1347, 3025, and 3116 cm$^{-1}$ by Wiberg, Fisher, and Bachhuber (WFB) \cite{16}. CL also derived estimated harmonic frequencies from an empirical force field based on the trans-HNNH frequencies. In light of the fact that some of these frequencies were misassigned \cite{11} and that various force constants had to be neglected for want of sufficient experimental data, these frequencies are of limited reliability.

The isodiazene isomer was predicted about a century ago to play a key role as an intermediate in the chemistry of azo compounds \cite{17}. Following earlier reporting of the synthesis of the substituted isodiazene (2,2,6,6-tetramethylpiperidyl)nitrene \cite{18}, isolation and characterization by low-temperature matrix infrared spectroscopy was reported by Sylwester and Derwan (SD) \cite{19}. Teles et al. (TMHS) \cite{20} obtained isodiazene by photolysis of aminoisocyanates in argon at 12 K, and recorded a complete infrared spectrum which they assigned with the help of fairly low-level ab initio harmonic frequency calculations. Finally, Goldberg et al. \cite{21} reported mass spectrometric detection of isodiazene and its cation in the gas phase. These authors also carried out G2 level calculations on the relative energies of various minima and transition states on the N$_2$H$_2$ potential surface, as did Smith \cite{22}.

Ab initio (e.g. \cite{23,25,21,26}) and density functional (e.g. \cite{27,28}) calculations on the relative stability of the trans-diazene, cis-diazene, and isodiazene isomers have consistently shown a stability ordering trans $>$ cis $>$ iso, as well as high (in excess of 40 kcal/mol) isomerization barriers between the isomers. (Very recently, the rigid cis-trans rotation of the molecule was proposed and studied \cite{29} as a test case for a new multireference coupled cluster method \cite{29}, the transition state being a ‘real-life’ alternative for H$_4$ as an essentially perfect two-configuration reference problem.)

The heat of formation of trans-HNNH is not very well established. The original paper by Foner and Hudson reports a mass spectrometric $\Delta H_{f,0}^{\circ} = 52.4 \pm 2.0$ kcal/mol. By photoionization mass spectrometry, Ruscić and Berkowitz \cite{30} established a lower limit, $\Delta H_{f,0}^{\circ} \geq 46.6 \pm 0.8$ kcal/mol, which is consistent with a calculated value using the G2 model
by Pople and Curtiss [25], 49.6 kcal/mol. The gap between theoretical value and experimental upper limit was narrowed by new vacuum UV photolysis experiments by Biehl and Stuhl (BS) [32] who obtained $\Delta H_{f,0}^\circ \geq 48.8 \pm 0.5$ kcal/mol. Clearly, the availability of a benchmark ab initio value would be highly desirable.

We have recently developed basis set extrapolation techniques [33,34] which permit the calculation of molecular total atomization energies (TAE$_e$ at the bottom of the well, TAE$_0$ at 0 K) with a mean absolute error as low as 0.12 kcal/mol. Using this technique, we were recently able [35] to resolve a long-standing controversy concerning the heat of formation of B(g). One objective of the present work is to obtain a benchmark heat of formation of trans-HNNH, as well as benchmark values for the isomerization energies in the \{trans,cis,iso\}diazene system.

As by-products of these calculations (which require inclusion of inner-shell correlation and of anharmonic contributions to the total atomization energy) we will also present accurate computed geometries and anharmonic force fields, although the latter are not the primary focus of the present work.

II. METHODS

All electronic structure calculations were carried out using the MOLPRO 96.4 [36] quantum chemistry package running on DEC Alpha 500/500 and SGI Origin 2000 computers at the Weizmann Institute, and on the Cray C90 at San Diego Supercomputer Center.

The CCSD(T) electron correlation method [37,38], as implemented by Hampel et al. [39], has been used throughout. (For the atomic calculations involved in the TAE determinations, the definition of the restricted open-shell CCSD(T) energy according to Ref. [38] is used.) The acronym stands for coupled cluster with all single and double substitutions [40] augmented by a quasiperturbative account for triple excitations [37]. From extensive studies (see [41] for a review) this method is known to yield correlation energies very close to the exact $n$-particle solution within the given basis set as long as the Hartree-Fock determinant
is a reasonably good zero-order reference wave function. The $T_1$ diagnostic, proposed \cite{12} as a measure of the importance of nondynamical correlation, was found to be 0.017 and 0.018, respectively, for trans-HNNH and cis-HNNH: these values suggest a wavefunction dominated by a single reference determinant. The computed $T_1$ for isodiazene, 0.030, suggests a mild degree of nondynamical correlation which experience suggests \cite{11} is still well within the range of applicability for CCSD(T).

Calculations including only valence correlation were carried out using the cc-pV$n$Z and aug'-cc-pV$n$Z ($n$=D, T, Q, 5) basis sets of Dunning and coworkers \cite{13,14}. The highest angular momenta present in these basis sets are \{d,f,g,h\} in the series \{D,T,Q,5\}. The augmented correlation consistent (aug-cc-pV$n$Z) basis sets differ from the parent cc-pV$n$Z basis set by the addition of one diffuse (anion) function for each angular momentum. It was previously established that such basis functions are essential for accurate computed bond angles \cite{45} and atomization energies \cite{33,46} of strongly polar molecules. The aug'-cc-pV$n$Z notation \cite{47} stands for the combination of a regular cc-pV$n$Z basis set on hydrogen with an aug-cc-pV$n$Z basis set on first-row atoms. We previously found \cite{33} that this affects computed atomization energies by less than 0.1 kcal/mol. In the interest of brevity, the standard acronyms cc-pV$n$Z and aug'-cc-pV$n$Z will be replaced by V$n$Z and A'V$n$Z, respectively.

The effect of inner-shell correlation was assessed by taking the difference between CCSD(T) calculations with and without constraining the inner-shell orbitals to be doubly occupied. Inner-shell correlation requires sufficient flexibility of the $s$ basis set in the high-exponent region as well as the presence of high-exponent $p$, $d$, and $f$ functions. In the present work, we have employed the Martin-Taylor core correlation basis set \cite{15}, which was previously found \cite{18} to recover essentially the entire differential effect of inner-shell correlation for first-row molecules.

Geometry optimizations were carried out by repeated multivariate parabolic interpolation with a step size of 0.001 $a_0$ or radian, and a convergence threshold of about $10^{-5}$ $a_0$ or radian. Quartic force fields were set up by finite differentiation in symmetry-adapted coordinates. In order to keep higher-order contamination in the quartic portion of the force field to
a minimum, fairly small step sizes 0.01 Å and radian were used and CCSD(T) energies converged to essentially machine precision. Generation of the displaced Cartesian geometries and transformation of the internal coordinate force field to Cartesian coordinates were carried out with the help of the INTDER program. The anharmonic spectroscopic analysis was carried out by standard second-order rovibrational perturbation theory using a modified version of SPECTRO. Cubic and quartic resonances were accounted for using the method previously described in MT, as implemented by one of us.

III. RESULTS AND DISCUSSION

A. Thermochemistry

All relevant data can be found in Table I. In this molecule, the SCF and valence correlation contributions to the total atomization energy (TAE) are clearly equally important. Using the cc-pVnZ basis sets, basis set convergence for the SCF contribution is atypically slow: enlarging the basis set from cc-pVTZ to cc-pVQZ affects all three TAE values by around 2 kcal/mol, while further basis set expansion to cc-pV5Z still contributes another 0.5 kcal/mol, on average. By contrast, convergence in the aug′-cc-pVnZ series is considerably faster: improving the basis set from aug′-cc-pVTZ to aug′-cc-pVQZ increases TAE by only about 1 kcal/mol, while further enlargement to aug′-cc-pV5Z affects all values by only 0.1–0.2 kcal/mol. It is also worth noting that the SCF/cc-pVDZ and SCF/aug′-cc-pVDZ TAE values differ by 5–5.5 kcal/mol. These observations clearly demonstrate that diffuse functions on N are essential for a balanced description of these species.

For the sake of elegance, an extrapolation to the one-particle basis set limit is required. We have considered two alternatives: an \( A + B/(l+1/2)^5 \) extrapolation following the suggestion of Petersson et al. and Ref. , and the geometric extrapolation formula originally proposed by Feller. The extrapolated limits from the VnZ and A′VnZ series differ appreciably with the former formula: the latter yields essentially identical results for both molecules. In order to clarify this matter further, we have considered extrapolated total
SCF energies for a number of systems for which numerical Hartree-Fock limits are available. These data are given in Table II. It is clearly seen that the geometric formula most closely reproduces the numerical SCF energies, although the value of an extrapolation with basis sets as large as those considered here is largely cosmetic.

Following the pioneering work by Schwartz [57], Hill [58] and Kutzelnigg and Morgan [59] showed that the basis set convergence of pair correlation energies can be expanded as an asymptotic series in \(1/(l + 1/2)\), with \(l\) the highest angular momentum appearing in the basis set. Based hereon, Martin [33] proposed the use of a 3-point extrapolation formula of the form \(A + B/(l + 1/2)^C\). In combination with appropriate SCF extrapolations and accounts for inner-shell correlation, the present authors [34] found that the very precisely known experimental TAEs of 15 small polyatomic molecules could be reproduced to within 0.12 kcal/mol.

In the present case, the A’VnZ basis sets systematically recover a slightly larger percentage of the correlation energy than their VnZ counterparts: however, the differences are much smaller than for the SCF portion of TAE. As we previously found [33, 40, 34] for molecules with polar bonds, the extrapolated values based on VnZ calculations are substantially higher (about 0.6 kcal/mol in this case) than those obtained from A’VnZ results. Relative to the CCSD(T)/A’V5Z result, the extrapolation accounts for 1.5–1.7 kcal/mol.

It is perhaps worth mentioning that the convergence of the sum of SCF and correlation energies for relatively small basis sets would be dominated to a substantial extent by the SCF convergence behavior, and leads to the erroneous conclusion that overall convergence behavior is best described by an exponential series.

Inner-shell correlation contributes 0.91, 0.87, and 1.04 kcal/mol, respectively, for the trans-, cis-, and isodiazene isomers. It thus leaves the cis-trans equilibrium fundamentally unchanged but does favor the isodiazene isomer somewhat compared to the other two isomers.

For the ‘bottom-of-the-well’ situation, our best calculations thus predict a cis-trans isomerization energy of 5.59 kcal/mol and an iso-trans difference of 24.95 kcal/mol. Inclusion of CCSD(T)/cc-pVQZ anharmonic zero-point energies considerably affects these values, fa-
voring cis over trans by 0.38 kcal/mol and isodiazene over trans-diazene by 0.83 kcal/mol. Our final best isomerization energies at 0 K are then 5.21 kcal/mol (cis-trans) and 24.12 kcal/mol (iso-trans), which we estimate to be accurate to about 0.1 kcal/mol. The G2 values of Goldberg et al., 5.0 and 24.1 kcal/mol, are in excellent agreement with our values.

Combining our computed TAE$_0$ of 278.76 kcal/mol for the trans form with the JANAF heats of formation of N($g$) and H($g$), we obtain a computed CCSD(T) basis set limit $\Delta H_{f,0}^0$(trans-HNNH)=49.57 kcal/mol, to which we assign a conservative error bar of ±0.2 kcal/mol. The G2 value of 49.6 kcal/mol [25] is in perfect agreement with our calibration calculation. The most recent experimental value is a lower limit of 48.8 ± 0.5 kcal/mol by Biehl and Stuhl [32], which is quite consistent with our calculations.

A litmus test for basis set convergence of our computed value would be if a 3-point extrapolation from AVQZ, AV5Z, and AV6Z were to yield the same result as above (AVTZ,AVQZ,AV5Z). While a CCSD(T)/AV6Z calculation on trans-HNNH is beyond our computational resources, we can certainly carry out such calculations for the prototype systems N$_2$ and NH. For these systems, we find differences of -0.13 and -0.045 kcal/mol, respectively, adding up for HNNH to an estimated difference of only -0.04 kcal/mol. We can therefore assume that our result is converged with respect to the 1-particle basis set.

The remaining discrepancy with experiment for N$_2$, then, appears to be to some extent due to imperfections in the CCSD(T) treatment. Because their magnitude in trans-HNNH is somewhat hard to quantify, we affix an overall error bar of about 0.5 kcal/mol to our computed TAE$_e$.

In Ref. [34], it was proposed to add a correction term of 0.126 kcal/mol per bond order involving at least one N atom, which greatly improved agreement with experiment for such compounds as N$_2$, NH$_3$, NNO, and HNO. If the same were done here, this would lead to an increase of 0.504 kcal/mol in the computed TAE$_0$ to 279.26 kcal/mol, and a decrease in the computed $\Delta H_{f,0}^0$ to 49.07 kcal/mol, which is within the error bar of the Biehl and Stuhl lower limit.

Alternatively, we may use the 3-parameter empirical correction due to Martin [61,62]
\[
\Delta E_{\text{correction}} = a_{\sigma}n_{\sigma} + b_{\pi}n_{\pi} + (n_{\sigma} + n_{\pi} + n_{\text{lone pair}})c_{\text{pair}}
\]

in which \(n_{\sigma}, n_{\pi}, n_{\text{lone pair}}\) represent the numbers of \(\sigma\) bonds, \(\pi\) bonds, and lone pairs, respectively, and the coefficients \(a_{\sigma}, b_{\pi}, c_{\text{pair}}\) are specific for the basis set, electron correlation treatment, and (level of theory used for the) reference geometry. (They are determined by least-squares fitting to a fairly small sample of very accurately known TAEs.) Ref. [46] lists two sets of parameters, one which only attempts to correct for basis set incompleteness in the valence correlation treatment (the inner-shell correlation contribution being computed explicitly), and another which attempts to absorb the inner-shell correlation contribution in the parametrization. In the present case, as seen in Table I, the ‘implicit core correlation’ set of parameters yields essentially identical results to the set of parameters with explicit inclusion of core correlation. The 3-parameter corrected values converge surprisingly rapidly as a function of basis set (Table I): from VTZ to AV5Z, the variation is no larger than about 0.15 kcal/mol. The highest-level value, AV5Z with explicit core correlation, is TAE\(_e\)=296.5 kcal/mol, or TAE\(_0\)=279.0 kcal/mol, that is \(\Delta H_{f,0}^\circ=49.37\) kcal/mol. (The mean absolute error for the “training set” in Ref. [46] is 0.20 kcal/mol at this level.) Taking the average between the extrapolated and empirically corrected values and using twice the difference between the values as an estimated error bar, we finally suggest \(\Delta H_{f,0}^\circ=49.2 \pm 0.3\) kcal/mol as our best estimate for the heat of formation of trans-diazene.

As expected, basis set convergence for the cis-trans and iso-trans isomerization energies is quite fast, and there is no reason why our computed basis set limits should not be accurate to as little as 0.1 kcal/mol: we will conservatively double these error bars, leading to final best computed isomerization energies at 0 K of 5.2\(\pm\)0.2 (cis-trans) and 24.1\(\pm\)0.2 (iso-trans) kcal/mol.

Finally, in order to assess the performance of the ”Complete Basis Set” (CBS) hybrid extrapolation/empirical correction schemes of Petersson and coworkers [61] for this problem, we have calculated the TAE of \(N_2N_2\) and the isomerization energies using the CBS-Q and CBS-QCI/APNO models [55,61] as implemented in GAUSSIAN 94 [62]. The computed \(\Delta H_{f,0}^\circ\) values of 50.9 (CBS-Q) and 50.8 (CBS-QCI/APNO) kcal/mol agree fairly poorly
with the present best estimate: about one-third of the discrepancy (0.61 kcal/mol) is due to error in the approximate zero-point energy. The fact that G2 theory apparently agrees better with the benchmark heat of formation for N$_2$H$_2$ than the CBS-Q and particularly the CBS-QCI/APNO models goes against the general trend: e.g. for 14 experimentally very precisely (0.1 kcal/mol or better) known total atomization energies, one of us [63] found mean absolute errors of 1.32 kcal/mol for G2 theory, 0.82 kcal/mol for CBS-Q, and 0.45 kcal/mol for CBS-QCI/APNO. (We recall for comparison that the corresponding error statistics for the best extrapolation and 3-parameter correction used in the present work are 0.12 and 0.20 kcal/mol, respectively.) The cis-trans isomerization energy is computed as 5.2 kcal/mol using both models, in perfect agreement with our best computed value; like for G2 theory, the iso-trans isomerization energy is underestimated, at 23.6 kcal/mol by CBS-Q and 23.7 kcal/mol by the CBS-QCI/APNO model.

B. Geometries

All relevant data can be found in Table IV. Only for trans-HNNH are experimental geometric data available. Until recently, these essentially consisted of the older $r_s$ (substitution) structure of Carlotti et al. [64]. Very recently, Demaison, Hegelund, and Bürger (DHB) [12] published a newly refined $r_z$ geometry: $r_z$(NH)=1.041(1) Å, $r_z$(NN)=1.252(1) Å, and $\theta$=106.3(1)$^\circ$. (For an overview of the definitions of various experimentally derived bond distances, see the review by Kuchitsu [53].) Using the average of $r_z$ – $r_e$ corrections obtained in three different ways (extrapolation from different isotopic values of $r_z$, CCSD(T)/cc-pVTZ calculated rotation-vibration coupling constants from Ref. [11], and their own MP2/6-311+G(2d,p) harmonic force field), they obtained the $r_e$ geometry $r_e$(NH)=1.030(1) Å, $r_e$(NN)=1.247(1) Å, and $\theta_e$=106.3$^\circ$.

We found that the $r_z$ – $r_e$ difference is only weakly affected by basis set expansion beyond CCSD(T)/cc-pVTZ: at the CCSD(T)/cc-pVQZ level, we obtain the correction $r_z$ – $r_e$(NH)=0.01357 Å, $r_z$ – $r_e$(NN)=0.00550 Å, and $\theta_z$ – $\theta_e$=0.061$^\circ$. Applying these to
the DHB $r_z$ values, we obtain an $r_e$ geometry that principally differs by $r$(NH) being about 0.002–0.003 Å shorter.

Another approach, such as we have followed in previous studies on e.g. ethylene [66] and acetylene [67], consists of obtaining a best calculated geometry and computing ground state rotational constants from it and the anharmonic force field, then comparing the rotational constants with experiment. For good agreement with experiment in directly calculated bond distances, inclusion of inner-shell correlation is absolutely essential [48]. In this work, we find that inner-shell correlation shortens $r$(NN) by 0.0026 Å and $r$(NH) by 0.0013 Å, and opens up the NNH bond angle by 0.12°. Adding these contributions in to the CCSD(T)/cc-pVQZ equilibrium geometry, we obtain $r_e$(NN)=1.2468 Å, $r_e$(NH)=1.0283 Å, and $\theta_e$=106.17°. From these parameters and the CCSD(T)/cc-pVQZ force field, we obtain $A_0$, $B_0$, and $C_0$ values which deviate from experiment by -0.04%, -0.06 %, and -0.07 %, respectively. These small discrepancies suggest that our calculated geometry is considerably closer to experiment than 0.001 Å and 0.1°.

However, it could be argued that since trans-HNNH has quite polar bonds, the use of diffuse function basis sets is in order. And indeed, as can be seen from Table [IV], adding diffuse functions considerably speeds up basis set convergence in the bond angle, with CCSD(T)/A′VTZ and CCSD(T)/A′VQZ bond angles now only differing by 0.13° (compared to 0.32° between CCSD(T)/VTZ and CCSD(T)/VQZ). Applying core-correlation corrections now to the CCSD(T)/A′VQZ geometry, we obtain $r_e$(NN)=1.2464 Å, $r_e$(NH)=1.0288 Å, and $\theta_e$=106.37°. Together with the CCSD(T)/cc-pVQZ force field, our deviations for the ground-state rotational constants are then +0.19%, -0.11%, and -0.09%, respectively. Presumably due to an error compensation, the VQZ+core geometry appears to be the closer to experiment.

Both extrapolated geometries are in agreement about the fact that the DHB value for $r_e$(NH) is about 0.002 Å too long. Other discrepancies with DHB fall within the latter’s error bars.

Our predicted geometries and ground-state rotational constants (Table [IV]) for the cis-
diazene and isodiazene isomers may facilitate future experimental work on these species.

C. Vibrational frequencies

Computed harmonic frequencies can be found in Table V. Computed and observed fundamentals are given in Table VI, while computed anharmonicities and rotation-vibration coupling constants are presented in Tables VII and VIII, respectively, together with the relevant resonance constants.

The CCSD(T)/cc-pVQZ anharmonic force fields obtained in the present study were principally calculated in order to obtain reliable zero-point vibrational energies for the thermochemical calculations. The vibrational spectroscopy of trans-HNNH was discussed in detail in MT, while too little experimental information is available for cis-HNNH to make a meaningful comparison possible.

Based on our anharmonic force field calculations, however, we can draw some qualitative conclusions on the rotation-vibration spectrum of cis-HNNH. In particular, both $\nu_1$ and $\nu_5$ are involved in resonance triads, the former with $2\nu_3$ and $2\nu_6$, the latter with $\nu_2 + \nu_6 \approx \nu_5$ and $\nu_2 + \nu_6 \approx \nu_5$. The eigenvectors of the former triad include essentially perfect 50:50 mixtures of $\nu_1$ and $2\nu_6$ states:

\[
\begin{pmatrix}
|100000\rangle \\
|100000\rangle \\
|002000\rangle \\
|000002\rangle
\end{pmatrix}
\begin{pmatrix}
1000000 \\
3010.07 \\
-91.580 \\
-65.556
\end{pmatrix}
\begin{pmatrix}
|002000\rangle \\
|002000\rangle \\
|000002\rangle \\
|000002\rangle
\end{pmatrix}
\begin{pmatrix}
002000 \\
2680.61 \\
0.910 \\
3039.32
\end{pmatrix} (2)
\]

with the eigensolution

\[
\begin{pmatrix}
2652.5 & 2986.5 & 3091.1 \\
|100000\rangle & -0.273 & 0.680 & -0.680 \\
|002000\rangle & -0.961 & -0.219 & 0.166 \\
|000002\rangle & -0.036 & 0.700 & 0.714
\end{pmatrix}
\]
Because of the relative positions of the deperturbed $\nu_1^*(3010.7 \text{ cm}^{-1})$ and $2\nu_6^*(3039.3 \text{ cm}^{-1})$ band origins, one could assign the 2986.5 cm\(^{-1}\) band to $\nu_1$ and the 3091.1 cm\(^{-1}\) band to $2\nu_6$; however, this labeling is somewhat academic.

The resonance matrix involving $\nu_5$ has the structure:

$$
\begin{pmatrix}
|000010\rangle & |010001\rangle & |001001\rangle \\
|000010\rangle & 2920.83 & 21.149 & -114.943 \\
|010001\rangle & 21.149 & 3061.78 & 1.963 \\
|001001\rangle & -114.943 & 1.963 & 2852.64
\end{pmatrix}
$$

with the eigensolution

$$
\begin{pmatrix}
2766.2 & 3002.5 & 3066.6 \\
|000010\rangle & 0.600 & 0.766 & -0.231 \\
|010001\rangle & -0.048 & -0.254 & -0.966 \\
|001001\rangle & 0.798 & -0.591 & 0.115
\end{pmatrix}
$$

where we can again label the 2766.2 and 3002.5 cm\(^{-1}\) states as $\nu_3 + \nu_6$ and $\nu_5$, respectively, based on the deperturbed band origins, but the states mix so strongly that the labeling is again largely meaningless.

A very strong Coriolis resonance ($Z_{a46}^b=7.79 \text{ cm}^{-1}$) between $\nu_4$ and $\nu_6$ is predicted around the $a$ axis, as is a strong Coriolis resonance around the $b$ axis between $\nu_3$ and $\nu_4$ ($Z_{34}^b=-2.40 \text{ cm}^{-1}$) and a weaker one between $\nu_2$ and $\nu_6$ around the $c$ axis ($Z_{26}^c=0.84 \text{ cm}^{-1}$). The quality of the computed Coriolis interaction parameters can be gauged by comparing CCSD(T)/cc-pVQZ computed with experimentally derived values for trans-HNNH. While agreement between the computed very large $Z_{a46}^b=8.708 \text{ cm}^{-1}$ and the experimental value of Hegelund et al. \cite{13}, 9.18234(58) cm$^{-1}$, is not as good as one would hope, the more recent value of DHB \cite{12}, 8.5895 cm$^{-1}$, is actually midway between our CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ values. Agreement between computed and observed $Z_{a46}^b$ is likewise quite satisfactory.

Our calculations are rather difficult to reconcile with the assignments of WFB, as well as with the 1279 cm\(^{-1}\) assignment of RP; their 3074 cm\(^{-1}\) assignment could correspond to our
computed $\nu_2 + \nu_6$ band. Further experimental work on the cis molecule is clearly required: we hope that our calculations may assist the latter.

In isodiazene, our calculations likewise find four Fermi resonances: $\nu_1 \approx 2\nu_3$, $\nu_1 \approx 2\nu_6$, $\nu_2 \approx 2\nu_4$, and $\nu_5 \approx \nu_2 + \nu_6$. Aside from these strong resonances, however, the computed vibrational anharmonicities on the deperturbed $\nu_1$ and $\nu_5$ bands are exceedingly high: 274.5 and 314.8 cm$^{-1}$ at the CCSD(T)/cc-pVQZ level. The only case known to the present authors of a similarly large stretching anharmonicity in a tightly bound molecule is for the H–N stretch in HNO, for which Lee et al. \cite{68} calculated an anharmonic correction of 287.1 cm$^{-1}$ at the same level of theory as used here. These authors, in comparisons between variational calculations and vibrational perturbation theory found that the latter essentially breaks down completely for HNO. It would then stand to reason that the same would occur for isodiazene, and preliminary variational calculations with the POLYMODE program \cite{69} do indeed suggest such strong mixing that second-order perturbation theory is fundamentally inappropriate as a treatment. In the light thereof, it is perhaps not surprising that the agreement between the computed fundamentals and the matrix IR data of Teles et al. is atypically poor for this level of theory. Moreover, we find that the computed harmonic frequencies and vibrational anharmonicities are unusually sensitive to the basis set. That is, the deperturbed anharmonic corrections for $\nu_1$ and $\nu_5$ at the CCSD(T)/VTZ level are 278.4 and 335.8 cm$^{-1}$ (the latter a difference of no less than 20 cm$^{-1}$ with the CCSD(T)/VQZ value!), while the corresponding harmonic frequencies change by 16 and 25 cm$^{-1}$, respectively.

In addition we find a very strong Coriolis resonance $Z_{16}^{a6} = -11.96$ cm$^{-1}$, aside from a weaker one, $Z_{65}^{a6} = 1.02$ cm$^{-1}$. Under these circumstances, it seems almost certain that a variational treatment based on an approximate kinetic energy operator in the Watson Hamiltonian \cite{70} (such as implemented in the POLYMODE \cite{69,71} program) will be likewise inadequate. No tetratomic variational code with an exact kinetic energy operator (e.g. \cite{72,73}) is available to the present authors, and since this study principally concerns thermochemistry, we will not pursue this point further in the present paper.
IV. CONCLUSIONS

A benchmark ab initio study on the thermochemistry of the trans-HNNH, cis-HNNH, and H₂NN isomers of diazene has been carried out. Our best computed \( \Delta H_{f,0} \) for trans-HNNH, 49.2±0.3 kcal/mol, is in very good agreement with a recent experimental lower limit of 48.8±0.5 kcal/mol. CCSD(T) basis set limit values for the isomerization energies, including contributions of inner-shell correlation and anharmonicity in the zero-point energy, are 5.2±0.2 kcal/mol (cis-trans) and 24.1±0.2 kcal/mol (iso-trans). Performance of more approximate methods such as G2 theory and the CBS-Q and CBS-QCI schemes was assessed in detail for this system. For extrapolation of the SCF contribution to atomization energies, the Feller-type exponential extrapolation \( A + B.C^{-l} \), rather than the two-point \( A + B/(l + 1/2)^5 \) extrapolation, appears to be the formula of choice.

Our best computed geometry for trans-HNNH, \( r_e(\text{NN})=1.2468 \ \text{Å}, r_e(\text{NH})=1.0283 \ \text{Å}, \) and \( \theta_e=106.17^\circ \), reproduces the precisely known ground-state rotational constants of trans-HNNH to within better than 0.1 %. We conclude that the NH bond distance in the recent experimental \( r_e \) geometry of Demaison et al. \[12\] is about 0.002 Å too long.

The rotation-vibration spectra of both cis-HNNH and H₂NN are predicted to have very strong Coriolis and Fermi resonances. In addition, the NH stretches in H₂NN are so strongly anharmonic that vibrational perturbation theory breaks down, and the molecule appears to be an excellent test case for variational treatments of the vibrational Schrödinger equation.

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### TABLE I. Convergence of different components (kcal/mol) of the total atomization energy of trans-HNNH and the cis-trans and iso-trans isomerization energies

|                  | TAE(trans-HNNH) | ∆E(cis-trans) | ∆E(iso-trans) |
|------------------|----------------|--------------|--------------|
| **SCF contribution** |                |              |              |
| SCF/VDZ          | 143.18         | 5.78         | 18.07        |
| SCF/VTZ          | 152.61         | 5.88         | 17.83        |
| SCF/VQZ          | 154.63         | 5.98         | 17.96        |
| SCF/V5Z          | 155.15         | 6.07         | 17.96        |
| SCF/V∞Z (a)      | 155.29         | 6.10         | 17.94        |
| SCF/V∞Z (b)      | 155.46         | 6.12         | 17.95        |
| SCF/A′VDZ        | 148.63         | 6.18         | 18.20        |
| SCF/A′VTZ        | 154.05         | 6.16         | 17.91        |
| SCF/A′VQZ        | 155.26         | 6.18         | 18.04        |
| SCF/A′V5Z        | 155.30         | 6.09         | 17.99        |
| SCF/A′V∞Z (a)    | 155.30         | 6.08         | 17.98        |
| SCF/A′V∞Z (b)    | 155.33         | 6.04         | 17.96        |
| **Valence correlation contribution** |          |              |              |
| CCSD(T)-SCF/VDZ  | 115.64         | -0.70        | 9.05         |
| CCSD(T)-SCF/VTZ  | 129.40         | -0.74        | 7.89         |
| CCSD(T)-SCF/VQZ  | 135.57         | -0.77        | 7.15         |
| CCSD(T)-SCF/V5Z  | 137.94         | -0.74        | 6.98         |
| CCSD(T)-SCF/V∞Z (c) | 140.56         | -0.63        | 6.99         |
| CCSD(T)-SCF/A′VDZ| 116.40         | -0.86        | 7.92         |
| CCSD(T)-SCF/A′VTZ| 130.96         | -0.79        | 7.24         |
| CCSD(T)-SCF/A′VQZ| 136.44         | -0.79        | 6.86         |
| CCSD(T)-SCF/A′V5Z| 138.33         | -0.72        | 6.88         |
| CCSD(T)-SCF/A′V∞Z (c) | 140.05         | -0.53        | 7.10         |
| **Other contributions** |          |              |              |
| CCSD(T)/MTcore-MTnocore | 0.908          | 0.039        | -0.127       |
| best at bottom of well | 296.26        | 5.59         | 24.95        |
| ∆ZPE             | -17.527        | -0.38        | -0.83        |
| best at 0 K      | 278.73         | 5.21         | 24.12        |

(a) Using geometric extrapolation \[54\], \(A + B.C^{-l}\), from SCF components of TAE\(_e\) with three largest basis sets in series

(b) Using extrapolation \[55\] \(A + B/(l+1/2)^5\) from SCF components of TAE\(_e\) with two largest basis sets in series
(c) Using variable-exponent $t$-extrapolation $[33], \ A + B/(l + 1/2)C$, from correlation components of TAE$_e$ for three largest basis sets in series

|                | numerical HF$^a$ | Feller(Q56)$^b$ | Schwartz5(56)$^c$ |
|----------------|------------------|-----------------|-------------------|
| Ne             | -128.54709809    | -128.547089     | -128.547284       |
| $\text{N}_2(R=2.068 \ a_0)$ | -108.9938257     | -108.993818     | -108.993988       |
| BH($R=2.336 \ a_0$) | -25.1315987      | -25.131601      | -25.131629        |
| $\text{H}_2(R=1.4 \ a_0)$ | -1.13362957      | -1.133625       | -1.133634         |
| H              | -0.5 exactly     | -0.500000       | -0.500003         |
| BF($R=2.386 \ a_0$)$^d$ | -124.1687792     | -124.16875956   | -124.168904       |

(a) D. Moncrieff and S. Wilson, *Mol. Phys.* 85, 103 (1995); J. Kobus, D. Moncrieff, and S. Wilson, *Mol. Phys.* 86, 1315 (1995). Bond distances $R$ taken from these references

(b) geometric extrapolation $A + B.C^{-t}$ from SCF/cc-pVQZ, SCF/cc-pV5Z, and SCF/cc-pV6Z energies

(c) 2-point extrapolation $A + B/(l + 1/2)^5$ from SCF/cc-pV5Z and SCF/cc-pV6Z energies

(d) aug-cc-pV$n$Z basis sets used $[35]$
|                     | implicit core corr. | explicit core corr. |
|---------------------|---------------------|---------------------|
| CCSD(T)/VDZ         | 297.96              | 297.97              |
| CCSD(T)/VTZ         | 296.53              | 296.55              |
| CCSD(T)/VQZ         | 296.44              | 296.45              |
| CCSD(T)/V5Z         | 296.50              | 296.51              |
| CCSD(T)/A'VDZ       | 297.87              | 297.88              |
| CCSD(T)/A'VTZ       | 296.59              | 296.60              |
| CCSD(T)/A'VQZ       | 296.50              | 296.51              |
| CCSD(T)/A'V5Z       | 296.49              | 296.50              |
| l-extrapolated†     | 296.26              | 296.26              |

(a) core correlation absorbed in the parametrization of the correction
(b) core correlation contribution computed explicitly as difference between CCSD(T)/MTcore and CCSD(T)/MTnocore
(c) See Table I
TABLE IV. Convergence of CCSD(T) computed $r_e$ geometries (Å, degrees), best computed $r_z$ and $r_g$ geometries (Å, degrees) and best computed and observed ground-state rotational constants (cm$^{-1}$)

|       | trans       | cis          | iso          |
|-------|-------------|--------------|--------------|
|       | $r_e$(NN)   | $r_e$(NH)    | $r_e$(NN)    | $r_e$(NH)    | $r_e$(NN)    | $r_e$(NH)    | $r_e$(NN)    | $r_e$(NH)    |
| VDZ   | 1.2643      | 1.0447       | 104.97       | 1.2592       | 1.0501       | 111.48       | 1.2280       | 1.0528       | 124.46       |
| VTZ   | 1.2536      | 1.0310       | 105.73       | 1.2512       | 1.0360       | 111.64       | 1.2214       | 1.0370       | 123.70       |
| VQZ   | 1.2494      | 1.0294       | 106.05       | 1.2481       | 1.0343       | 111.79       | 1.2194       | 1.0351       | 123.49       |
| A'VDZ | 1.2660      | 1.0423       | 105.74       | 1.2652       | 1.0463       | 111.53       | 1.2373       | 1.0443       | 123.50       |
| A'VTZ | 1.2529      | 1.0320       | 106.12       | 1.2525       | 1.0367       | 111.77       | 1.2242       | 1.0361       | 123.39       |
| A'VQZ | 1.2489      | 1.0300       | 106.25       | 1.2486       | 1.0347       | 111.85       | 1.2206       | 1.0350       | 123.36       |
| MTcore| 1.2471      | 1.0285       | 105.97       | 1.2450       | 1.0334       | 111.83       | 1.2153       | 1.0351       | 123.70       |
| MTnocore| 1.2497      | 1.0297       | 105.85       | 1.2475       | 1.0346       | 111.75       | 1.2175       | 1.0360       | 123.71       |
| best calc.$^a$ | 1.2468      | 1.0281       | 106.17       | 1.2456       | 1.0331       | 111.88       | 1.2172       | 1.0342       | 123.49       |
| Expt. $^{[12]}$ | 1.247(1)   | 1.030(1)     | 106.3(1)     | —            | —            | —            | —            | —            | —            |

|       | $A_e$       | $B_e$       | $C_e$       | $A_e$       | $B_e$       | $C_e$       | $A_e$       | $B_e$       | $C_e$       |
|-------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| best calc.$^a$ | 10.12689    | 1.31151     | 1.31151     | 9.75433     | 1.30580     | 1.15163     | 11.24253    | 1.29790     | 1.16357     |
| $A_0$ | $B_0$       | $C_0$       | $A_0$       | $B_0$       | $C_0$       | $A_0$       | $B_0$       | $C_0$       |
| best calc.$^a$ | 10.00064    | 1.30354     | 1.14917     | 9.65724     | 1.29706     | 1.13945     | 11.06453    | 1.29487     | 1.15518     |
| expt. $^{[13]}$ | 10.001203(5)| 1.3043373(6)| 1.1499757(6)| —           | —           | —           | —           | —           | —           |

|       | $r_z$(NN)   | $r_z$(NH)   | $\theta_z$(NH) | $r_z$(NN)   | $r_z$(NH)   | $\theta_z$(NH) | $r_z$(NN)   | $r_z$(NH)   | $\theta_z$(NH) |
|-------|-------------|-------------|----------------|-------------|-------------|----------------|-------------|-------------|----------------|
| best calc.$^a$ | 1.2523      | 1.0418      | 106.23         | 1.2503      | 1.0471      | 112.33        | 1.2194      | 1.0498      | 123.59        |
| Expt. $^{[12]}$ | 1.252(1)    | 1.041(1)    | 106.3(1)       | —           | —           | —             | —           | —           | —             |

|       | $r_g$(NN)   | $r_g$(NH)   | $\theta_g$(NH) | $r_g$(NN)   | $r_g$(NH)   | $\theta_g$(NH) | $r_g$(NN)   | $r_g$(NH)   | $\theta_g$(NH) |
|-------|-------------|-------------|----------------|-------------|-------------|----------------|-------------|-------------|----------------|
| best calc.$^a$ | 1.2524      | 1.0507      | 106.18         | 1.2506      | 1.0561      | 112.18        | 1.2198      | 1.0596      | 123.28        |

(a) CCSD(T)/cc-pVQZ+CCSD(T)/MTcore-CCSD(T)/MTnocore
| Trans-diazene | VDZ  | VTZ  | VQZ  | A'VDZ | A'VTZ | A'VQZ | MTcore | MTnocore |
|--------------|------|------|------|-------|-------|-------|--------|----------|
| \(\omega_1 (a_g)\) | 3281.7 | 3269.8 | 3278.3 | 3242.4 | 3264.2 | 3276.9 | 3276.7 | 3268.9 |
| \(\omega_2 (a_g)\) | 1614.8 | 1621.8 | 1619.9 | 1608.4 | 1612.3 | 1616.3 | 1625.3 | 1623.7 |
| \(\omega_3 (a_g)\) | 1569.4 | 1558.4 | 1567.3 | 1550.0 | 1552.5 | 1564.8 | 1566.7 | 1559.4 |
| \(\omega_4 (a_u)\) | 1317.5 | 1328.4 | 1327.7 | 1304.6 | 1319.2 | 1323.2 | 1334.2 | 1331.8 |
| \(\omega_5 (b_u)\) | 3248.9 | 3301.6 | 3310.1 | 3271.4 | 3296.8 | 3309.1 | 3309.2 | 3301.7 |
| \(\omega_6 (b_u)\) | 1343.0 | 1350.3 | 1349.8 | 1341.8 | 1345.1 | 1348.2 | 1355.5 | 1353.2 |

| Cis-diazene | VDZ  | VTZ  | VQZ  | A'VDZ | A'VTZ | A'VQZ | MTcore | MTnocore |
|-------------|------|------|------|-------|-------|-------|--------|----------|
| \(\omega_1 (a_1)\) | 3185.2 | 3235.9 | 3245.4 | 3205.9 | 3231.9 | 3243.8 |        |          |
| \(\omega_2 (a_1)\) | 1588.3 | 1575.7 | 1582.7 | 1556.9 | 1564.9 | 1578.2 |        |          |
| \(\omega_3 (a_1)\) | 1347.1 | 1371.6 | 1370.1 | 1356.7 | 1364.6 | 1367.7 |        |          |
| \(\omega_4 (a_2)\) | 1247.8 | 1258.7 | 1261.8 | 1237.4 | 1251.7 | 1258.7 |        |          |
| \(\omega_5 (b_2)\) | 3085.1 | 3146.5 | 3160.7 | 3118.6 | 3147.3 | 3160.9 |        |          |
| \(\omega_6 (b_2)\) | 1560.7 | 1565.3 | 1562.9 | 1548.1 | 1556.1 | 1559.8 |        |          |

| Isodiazene | VDZ  | VTZ  | VQZ  | A'VDZ | A'VTZ | A'VQZ | MTcore | MTnocore |
|------------|------|------|------|-------|-------|-------|--------|----------|
| \(\omega_1 (a_1)\) | 3028.1 | 3107.4 | 3123.3 | 3103.6 | 3124.7 | 3129.1 |        |          |
| \(\omega_2 (a_1)\) | 1726.0 | 1728.4 | 1728.9 | 1721.7 | 1725.2 | 1727.4 |        |          |
| \(\omega_3 (a_1)\) | 1602.4 | 1584.6 | 1588.9 | 1571.0 | 1574.1 | 1585.0 |        |          |
| \(\omega_4 (b_1)\) | 972.2 | 995.6 | 999.1 | 969.6 | 991.2 | 997.0 |        |          |
| \(\omega_5 (b_2)\) | 2990.8 | 3103.5 | 3128.9 | 3120.0 | 3135.8 | 3141.0 |        |          |
| \(\omega_6 (b_2)\) | 1316.0 | 1323.0 | 1326.9 | 1302.3 | 1317.2 | 1324.6 |        |          |
TABLE VI. Computed and observed fundamentals (cm$^{-1}$) for isomers of HNNH

|                  | trans-HNNH | cis-HNNH   | H$_2$NN     |
|------------------|------------|------------|-------------|
|                  | CCSD(T)/cc-pVQZ (this work) | CCSD/cc-pVDZ (Ref. [10]) | Experiment |
| $\nu_1$          | 3051.0$^a$ | 2986.5     | 2866.5      |
| $\nu_2$          | 1578.5     | 1548.4     | 1665.3      |
| $\nu_3$          | 1528.2     | 1334.7     | 1560.4      |
| $\nu_4$          | 1294.2     | 1231.9     | 991.0       |
| $\nu_5$          | 3133.3     | 3002.5     | 2769.7      |
| $\nu_6$          | 1317.4     | 1520.7     | 1292.7      |

|                  | CCSD/cc-pVDZ (Ref. [10]) | Experiment |
| $\nu_1$          | 3005        | 2962       | 2838        |
| $\nu_2$          | 1609        | 1622       | 1679        |
| $\nu_3$          | 1584        | 1340       | 1613        |
| $\nu_4$          | 1329        | 1244       | 2724        |
| $\nu_5$          | 3096        | 2947       | 1305        |
| $\nu_6$          | 1310        | 1536       | 977         |

(a) $\nu_2 + \nu_3 = 3127.9$ cm$^{-1}$

(b) clearly $\nu_2 + \nu_3$ misassigned to fundamental

(c) Craig and Levin [9]

(d) Ref. [13]

(e) Estimates of Craig and Levin [9], based on approximate force field derived from trans-HNNH

(f) A. P. Sylwester and P. B. Dervan, J. Am. Chem. Soc. 106, 4648 (1984)
TABLE VII. CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ zero-point energies, anharmonic corrections, and anharmonicity constants for HNNH isomers. Quantities deperturbed for resonances are marked by an asterisk. All units are cm$^{-1}$ unless indicated otherwise.

|               | trans-HNNH | cis-HNNH | H$_2$NN |
|---------------|------------|----------|---------|
|               | cc-pVTZ    | cc-pVQZ  | cc-pVTZ | cc-pVQZ  | cc-pVTZ | cc-pVQZ |
| ZPE(kcal/mol) | 17.492     | 17.527   | 17.101  | 17.148   | 16.607  | 16.699  |
| $E_0$         | 20.359     | 20.594   | 34.341  | 32.295   | 35.785  | 35.263  |
| $\omega_1 - \nu_1^*$ | 210.6     | 209.7    | 236.5   | 235.3    | 278.4   | 274.5   |
| $\omega_2 - \nu_2$ | 42.4      | 41.4     | 35.0    | 34.2     | 56.9    | 55.7    |
| $\omega_3 - \nu_3$ | 39.1      | 39.1     | 38.4    | 35.5     | 28.8    | 28.5    |
| $\omega_4 - \nu_4$ | 34.2      | 33.5     | 31.1    | 30.0     | 11.2    | 8.1     |
| $\omega_5 - \nu_5^*$ | 227.4     | 226.4    | 240.4   | 239.9    | 335.8   | 314.8   |
| $\omega_6 - \nu_6$ | 32.8      | 32.5     | 42.7    | 42.2     | 31.2    | 34.3    |
| $X_{11}$      | -47.016    | -46.808  | -45.549 | -45.693  | -57.506 | -56.621 |
| $X_{22}$      | -1.865     | -2.133   | -12.350 | -12.138  | -3.209  | -3.279  |
| $X_{33}$      | -11.126    | -10.019  | 4.992   | 5.638    | -11.290 | -11.061 |
| $X_{44}$      | -6.347     | -6.174   | -3.769  | -3.899   | 2.158   | 1.908   |
| $X_{55}$      | -45.556    | -45.332  | -46.301 | -46.397  | -79.637 | -76.380 |
| $X_{66}$      | -4.813     | -4.704   | -1.047  | -1.008   | 1.437   | -0.233  |
| $X_{21}$      | -27.577    | -25.420  | 2.181   | 2.222    | -32.983 | -33.673 |
| $X_{31}$      | -3.877     | -5.914   | -40.740 | -40.264  | 8.589   | 7.786   |
| $X_{32}$      | -8.636     | -9.773   | -7.165  | -6.854   | -6.152  | -6.059  |
| $X_{41}$      | -13.653    | -13.854  | -16.641 | -15.054  | -5.591  | -5.666  |
| $X_{42}$      | -4.380     | -4.565   | -10.042 | -9.841   | -7.964  | -7.089  |
| $X_{43}$      | -9.650     | -9.169   | -4.170  | -3.713   | -13.963 | -13.415 |
| $X_{51}$      | -180.771   | -179.861 | -201.169| -200.502 | -267.335| -260.605|
| $X_{52}$      | -32.750    | -29.999  | 1.948   | 1.854    | -52.212 | -49.283 |
| $X_{53}$      | -6.506     | -9.206   | -41.131 | -39.299  | 12.772  | 12.432  |
| $X_{54}$      | -19.012    | -18.833  | -17.851 | -17.555  | -13.165 | -1.266  |
| $X_{61}$      | -7.235     | -7.347   | -34.364 | -34.197  | -29.518 | -30.291 |
| $X_{62}$      | -4.048     | -4.644   | -7.666  | -7.322   | -1.706  | -2.095  |
| $X_{63}$      | -5.045     | -4.127   | -3.501  | -2.700   | -13.692 | -13.412 |
| $X_{64}$      | 3.602      | 3.786    | 1.638   | 1.826    | 9.735   | 3.549   |
| $X_{65}$      | -33.615    | -33.765  | -37.468 | -38.006  | -33.028 | -25.402 |

For trans-HNNH, the following resonance constants appear in resonance polyads involving fundamentals (CCSD(T)/cc-pVQZ): $k_{122}=48.367$, $k_{123}=127.771$, $k_{256}=-243.953$, $k_{133}=47.116$, $k_{356}=-210.321$ cm$^{-1}$; $K_{22:23}=7.451$, $K_{23:33}=21.293$, $K_{21:31}=-24.145$, $K_{25:35}=-31.927$, $K_{24:34}=2.687$, $K_{26:36}=8.428$, $K_{22:33}=-5.680$ cm$^{-1}$.
For cis-HNNH, \( k_{133} = -198.795 \), \( k_{166} = -108.090 \), \( K_{33;66} = 1.820 \); \( k_{256} = -59.817 \) cm\(^{-1} \); \( K_{22;23} = -12.588 \); \( K_{33;32} = -9.784 \); \( K_{21;31} = 5.516 \); \( K_{24;34} = -0.645 \); \( K_{25;35} = 2.384 \); \( K_{26;36} = 2.422 \).

For H\(_2\)NN, CCSD(T)/cc-pVQZ \( k_{133} = 37.952 \), \( k_{166} = -147.470 \), \( K_{33;66} = -5.086 \); \( k_{244} = -100.842 \), \( k_{256} = -262.610 \) cm\(^{-1} \).
TABLE VIII. CCSD(T) computed rotational, rotation-vibration coupling, and Coriolis coupling constants (cm⁻¹)

|                | trans-HNNH | cis-HNNH | H₂NN |
|----------------|------------|----------|------|
|                | cc-pVTZ    | cc-pVQZ  | cc-pVTZ | cc-pVQZ | cc-pVTZ | cc-pVQZ |
| A_e            | 10.00200   | 10.08275 | 9.66754 | 9.71969 | 11.23667 | 11.22354 |
| B_e            | 1.30099    | 1.30712  | 1.29594 | 1.30132 | 1.28780  | 1.29338  |
| C_e            | 1.15124    | 1.15712  | 1.14275 | 1.14766 | 1.15538  | 1.15973  |
| α₁a            | 0.21332    | 0.21358  | 0.17466 | 0.17547 | 0.21871  | 0.21673  |
| α₂a            | -0.15339   | -0.14991 | 0.02869 | 0.02918 | -0.05290 | -0.05192 |
| α₃a            | 0.00250    | -0.01664 | -0.19817 | -0.20356 | 0.01040  | 0.00947  |
| α₄a            | 0.14715*   | 0.14717* | 0.14862* | 0.14814* | 0.19226* | 0.18978* |
| α₅a            | 0.16364    | 0.16447  | 0.16068 | 0.16110 | 0.14159  | 0.14166  |
| α₆a            | -0.11293*  | -0.11623* | -0.11352* | -0.11683* | -0.14907* | -0.15040* |
| α₁b            | -0.00111   | +0.00068 | 0.01187 | 0.01171 | -0.00636 | -0.00645 |
| α₂b            | 0.01133    | 0.01044  | 0.00557* | 0.00550* | 0.01183  | 0.01173  |
| α₃b            | 0.00291*   | 0.00287* | 0.00275* | 0.00282* | 0.00931  | 0.00938  |
| α₄b            | -0.00088   | -0.00082 | -0.00147 | -0.00142 | -0.00438 | -0.00415 |
| α₅b            | 0.00375*   | 0.00373* | -0.00131 | -0.00133 | -0.00123 | -0.00128 |
| α₁c            | 0.00106    | 0.00111  | 0.00167 | 0.00168 | -0.00094 | -0.00075 |
| α₂c            | 0.00437*   | 0.00456* | 0.01065* | 0.01060* | 0.00554  | 0.00550  |
| α₃c            | 0.01136*   | 0.01105* | 0.00607 | 0.00599 | 0.01080* | 0.01068* |
| α₄c            | 0.00069    | 0.00063  | 0.00023 | 0.00020 | -0.00048 | -0.00050 |
| α₅c            | 0.00145    | 0.00150  | 0.00092 | 0.00097 | -0.00319 | -0.00308 |
| α₆c            | 0.00498    | 0.00496  | 0.00480* | 0.00479* | 0.00486* | 0.00483* |

Rotation-vibration coupling constants marked with an asterisk have had terms deleted that were near-singular due to Coriolis resonance.

(a) Experimental values [13]: $Z^{a}_{46}=9.18234(58)$, $Z^{b}_{46}=-2.3663(34)$ cm⁻¹. Re-analysis by DHB [12]: $Z^{a}_{46}=8.5895$, $Z^{b}_{46}=-2.41605(7)$ cm⁻¹.