Definitive heat of formation of methylenimine, CH$_2$=NH, and of methylenimmonium ion, CH$_2$NH$^+$, by means of W2 theory*

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Abstract

A long-standing controversy concerning the heat of formation of methylenimine has been addressed by means of the W2 (Weizmann-2) thermochemical approach. Our best calculated values, $\Delta H_f^{o}(\text{CH}_2\text{NH})=21.1\pm0.5$ kcal/mol and $\Delta H_f^{o}(\text{CH}_2\text{NH}_2^+)=179.4\pm0.5$ kcal/mol, are in good agreement with the most recent measurements but carry a much smaller uncertainty. As a by-product, we obtain the first-ever accurate anharmonic force field for methylenimine: upon consideration of the appropriate resonances, the experimental gas-phase band origins are all reproduced to better than 10 cm$^{-1}$. Consideration of the difference between a fully anharmonic zero-point vibrational energy and B3LYP/cc-pVTZ harmonic frequencies scaled by 0.985 suggests

*Dedicated to Prof. Paul von Ragué Schleyer on the occasion of his 70th birthday

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that the calculation of anharmonic zero-point vibrational energies can gener-
ally be dispensed with, even in benchmark work, for rigid molecules.
Methylene imine (methanimine, formaldimine, CH\textsubscript{2}=NH) is a pyrolysis product of amines [1] as well as a photolysis product of methylazide [2] and diazomethane [3]. It has obvious chemical importance as the simplest imine [4], and with its carbon-nitrogen double bond, methylenimine is a bonding paradigm for numerous nitrogen-containing heterocycles. The molecule is also of astrophysical interest, having been detected in dark interstellar dust clouds [5].

The heat of formation of methylenimine (methanimine, formaldimine, CH\textsubscript{2}=NH), is the subject of a long-standing controversy in the literature. Experimental values for the heat of formation (\(\Delta H_f\)) of this molecule span a range of 10 kcal/mol, and have fairly large experimental uncertainties (about 2 to 3 kcal/mol). The first experiment, by DeFrees and Hehre in 1978, [6] used the bracketing method to evaluate the hydride affinity of HCNH\textsuperscript{+}, and hence derived \(\Delta H_f^{298}\)[CH\textsubscript{2}=NH]=26.4\pm3.2\text{ kcal/mol.}\) Ten years later, Grela and Colussi [7] obtained a value of 25\pm3\text{ kcal/mol from the deprotonation reaction of CH\textsubscript{3}NH.} A Moscow group had meanwhile obtained [8] 21\pm4\text{ kcal/mol by photoionization mass spectrometry of pyrolysis products of azetidine.} In 1990, Peerboom, Ingemann, Nibbering, and Liebman (PINL) [9] bracketed the proton affinity (PA) of CH\textsubscript{2}NH as 204\pm2\text{ kcal/mol by means of ion cyclotron resonance: in combination with an earlier determination of the heat of formation of CH\textsubscript{2}NH\textsubscript{2} (177–178 kcal/mol) by Lossing et al. [10] from appearance energy measurements, they obtained \(\Delta H_f^{298}[\text{CH}_2=\text{NH}]=16.5\pm2\text{ kcal/mol.}\) Then in 1992, Holmes et al. [11] determined the ionization potential of the CH\textsubscript{2}NH radical by means of energy-resolved electron impact, and derived an upper limit of 22\pm3\text{ kcal/mol for }\Delta H_f^{298}\text{[CH}_2=\text{NH]}: they propose an ‘evaluated’ }\Delta H_f^{298}\text{[CH}_2=\text{NH]}=21\pm4\text{ kcal/mol, which happens to be identical to the Moscow group value. Around the same time, Smith, Pople, Curtiss, and Radom (SPCR) [12] carried out a computational study in which reaction energies for ten reactions involving CH\textsubscript{2}NH were computed by means of G2 theory [13]: in combination with experimental data for the auxiliary species [14], they obtained }\Delta H_f^{298}=20.6\pm2.4\text{ kcal/mol averaged over the}
ten reactions. Although this is in good agreement with the Holmes et al. experiment, the error bars are still a far cry from ‘chemical accuracy’ (1 kcal/mol).

Very recently, two of us proposed [15] two new computational thermochemistry methods known as W1 and W2 (Weizmann-1 and Weizmann-2) theory which, for molecules dominated by dynamical correlation, yield heats of formation to within 0.25 kcal/mol (1 kJ/mol) accuracy, on average. A subsequent validation study [16] for a much larger data set came to similar conclusions. Since CH$_2$NH is still small enough for a W2 calculation to be carried out on fast workstation computers, this would appear to be the tool of choice for resolving the controversy on its heat of formation for once and for all. This is the primary purpose of the present paper.

As a by-product, we shall obtain an accurate ab initio anharmonic force field for CH$_2$NH. (For the highest possible accuracy, it is in principle advisable to obtain the molecular zero-point vibrational energy ZPVE from an anharmonic force field rather than from scaled harmonic frequencies.) Aside from matrix isolation work [2,17], a respectable amount of high-resolution IR data is available for this molecule. Following early high-resolution work by Johnson and Lovas [18], Allegrini et al. [19] obtained a high-resolution $\nu_4$ by CO laser Stark spectroscopy. Duxbury and Le Lerre [20] studied the $\nu_5$ and $\nu_6$ bands by Fourier transform IR (FTIR) spectroscopy, including an analysis of the Coriolis interaction (along the $c$ axis) between those modes. The $\nu_7$, $\nu_8$, and $\nu_9$ modes, as well as the strong Coriolis interactions between them, were studied by Halonen and Duxbury [21], while these same authors studied $\nu_2$ and the ($\nu_3, 2\nu_5$) Fermi resonant band pair in a companion paper [22] and reported $\nu_1$ elsewhere [23].

General harmonic force fields were derived by Jacox and Milligan [17], by Hamada et al. [24] and by Halonen, Deeley, and Mills [25]: the latter authors also remeasured and reanalyzed the ($\nu_7, \nu_8, \nu_9$) triad. (A microwave substitution structure was obtained by Pearson and Lovas [26].) To the authors’ knowledge, the only anharmonic force field available is a comparatively low-level (MP2/6-311G**) ab initio calculation by Pouchan and Zaki [27]. Extensive experience has shown (e.g. [28] and references therein) that the CCSD(T) (coupled
cluster with all single and double substitutions [29] and a quasiperturbative correction for connected triple excitations [30]) electron correlation method in conjunction with a basis set of \( spdf \) quality generally yields computed fundamentals within better than 10 cm\(^{-1} \) of the observed gas-phase values. Thus, obtaining a force field of such quality is the secondary purpose of the present note.

**II. COMPUTATIONAL METHODS**

Geometry optimizations and vibrational frequency calculations using the B3LYP (Becke 3-parameter-Lee-Yang-Parr [31,32]) density functional method have been carried out using Gaussian 98 revision A7 [33]. All other calculations were carried out using MOLPRO 98.1 [34], and a driver for the W1/W2 calculations [35] written in MOLPRO’s scripting language, running on Compaq XP1000 and Compaq ES40 computers in our research group.

W1 and W2 theory are described in detail elsewhere [15,16]. Briefly, both methods involve separate extrapolations to the infinite-basis limit, using a sequence of Dunning correlation consistent [36,37] (cc-pV\( n \)Z) and augmented correlation consistent [38] (aug-cc-pV\( n \)Z) basis sets, of the SCF, CCSD valence correlation, and (T) valence correlation energies. In addition, contributions of inner-shell correlation and (Darwin and mass-velocity [39,40]) scalar relativistic effects are obtained at the CCSD(T) and ACPF (averaged coupled pair functional [41]) levels with the MTsmall basis set [15]. While the more economical W1 theory uses a B3LYP/cc-pVTZ reference geometry and extrapolates from aug'-cc-pV\( n \)Z (\( n = D,T,Q \)) basis sets, the more expensive (and rigorous) W2 theory employs a CCSD(T)/cc-pVQZ reference geometry and aug'-cc-pV\( n \)Z (\( n = T,Q,5 \)) basis sets. (Regular cc-pV\( n \)Z basis sets are used throughout on hydrogen.) In addition, we considered W1h and W2h results, where the ‘h’ (for ‘hetero-atom’) indicates that augmented basis sets are only used on group V, VI, and VII elements and not on group III and IV elements.

The largest basis set CCSD calculations in W2 and W2h theory were carried out using the direct CCSD implementation [42] of Lindh, Schütz, and Werner as present in MOLPRO 98.1. All energies for the open-shell separated atoms were obtained using the restricted
open-shell CCSD(T) energy as defined in Ref. [43].

For comparison, we shall also present data for the isoelectronic C$_2$H$_4$ and N$_2$H$_2$ molecules.

A complete CCSD(T)/cc-pVTZ quartic force field for CH$_2$NH was generated in internal coordinates (four stretches, three bends, two torsions). Internal coordinate geometries were generated by recursive application of the central difference formula to the coordinates being differentiated, with step sizes of 0.01 Å or radian around the minimum energy geometry being used. Cartesian coordinates for this ‘grande list’ of points were generated using INTDER [44]: this list of geometries was reduced to a ‘petite list’ of unique points by means of comparison of sorted distance matrices. Thus, 2241 points in $C_s$ symmetry and 460 additional points in $C_1$ symmetry are obtained. Since this type of application is a textbook example of an ‘embarrassingly parallel’ [45] computational problem, the energy calculations were carried out on a 26-node experimental PC-farm at the Department of Particle Physics, Weizmann Institute of Science. In order to minimize roundoff error in the finite differentiation, integral evaluation cutoffs as well as SCF and CCSD convergence criteria were tightened such that the energies are obtained to essentially machine precision. Quartic contamination was removed from the quadratic force constants. The final internal coordinate force field was transformed to Cartesian coordinates using INTDER, and transformed to normal coordinates as well as subjected to a standard second-order rovibrational perturbation theory (VIB-PT2) analysis [46] using SPECTRO [47] and POLYAD [48].

III. RESULTS AND DISCUSSION

A. Anharmonic force field

A plethora of resonances exists involving the three XH stretching modes $\nu_1, \nu_2, \nu_3$ on the one hand and two-quantum states within the $\nu_4, \nu_5, \nu_6$ block on the other hand (the modes involved are the CN stretch, the HNC bend, and the HCH scissoring mode, respectively). For this reason, we deperturbed the anharmonic constants for all resonances of the type $\nu_x \approx \nu_y + \nu_z$ (where $x = \{1, 2, 3\}$ and $y, z = \{4, 5, 6\}$, e.g. $\nu_2 \approx \nu_4 + \nu_6$ or $\nu_3 \approx 2\nu_5$), and set up
and diagonalized a $9 \times 9$ resonance matrix involving all these states. (Formulas for the various higher-order resonance matrix elements were taken from Ref. [49].) The resonance matrix and its eigensolution are given in Table I, while the computed harmonic frequencies and fundamentals (as well as any bands in resonance with them) are given in Table II, compared with experiment and with results from the previous lower-level (MP2/6-311G**) calculation by Pouchan and Zaki [27]. A complete force field and sets of spectroscopic constants are available as supplementary material to the present paper.

First of all, as readily seen from the solution of the $9 \times 9$ resonance matrix, the $\nu_3 \approx 2\nu_5$ resonance is so severe that the two perturbed states are basically 50:50 mixtures of the respective deperturbed states, and that an assignment of an observed band to either $\nu_3$ or $2\nu_5$ is somewhat academic. Similar remarks apply to the $\nu_2 \approx \nu_4 + \nu_6$ resonance: in both cases, the assignments in the table were made based on the ordering of the deperturbed states. The $\nu_1 \approx 2\nu_4$ resonance is also quite severe but an unambiguous assignment is still possible there. (For a system like this, a full nine-dimensional solution by variational methods [50] or high-order canonical Van Vleck perturbation theory [51] would certainly be helpful: this is however beyond the scope of the present study since we are primarily interested in the thermochemistry.)

This being said, agreement between computed and observed vibrational band origins is basically as good as we can reasonably expect at this level of theory, with all computed-observed discrepancies lying below 10 cm$^{-1}$. The very good agreement between the present band origins and the earlier lower-level results is somewhat fortuitous, given the discrepancies of up to 50 cm$^{-1}$ between the two sets of harmonic frequencies. It has been our experience that MP2 computed anharmonicities for XH stretching modes tend to be seriously overestimated, and the present system forms no exception.

The only experimental equilibrium geometry available from the literature is a microwave ($r_s$) substitution structure [26]. Agreement between our calculations and the $r_s$ geometry is as good as we can reasonably expect (Table III). The effect of correlating the (1s)-like inner-shell electrons on the geometry follows expected trends [52] (Table III). (The MTsmall
core correlation basis set [15] as used in W1 and W2 theory was employed for this purpose.)

No experimental \( r_e \) or \( r_z \) geometry is available, but an indirect measure of the quality of our computed CCSD(T)/MTsmall geometry can be obtained by substituting it in the VIB-PT2 analysis and comparing the ground-state rotational constants thus obtained with their precisely known [21] experimental counterparts. Our computed \( A_0=6.54242 \), \( B_0=1.15615 \), \( C_0=0.97936 \) cm\(^{-1}\) agree to better than 0.1\% with the observed values [21] 6.544896(1), 1.1555459(1), and 0.9790851(1) cm\(^{-1}\): given the quadratic dependence of the rotational constants on the geometry, this in fact suggests an even better agreement between the underlying computed \( r_e \) geometry and Nature. In order to assist future experimental work on the protonated species CH\(_2\)NH\(_2^+\), we have computed its geometry at the same level (Table III).

For the mode pairs in Coriolis resonance, the computed interaction constants \( \xi_{79}^a = 4.701 \), \( \xi_{79}^b = -0.315 \), \( \xi_{78}^a = 3.630 \), and \( \xi_{78}^b = 1.918 \) cm\(^{-1}\) are in fair agreement with the experimental values [21] 4.529(1), -0.3305(1), 4.212(1), and 1.8125(1) cm\(^{-1}\), respectively. The computed \( \xi_{56}^c = 0.552 \) cm\(^{-1}\) is likewise in reasonable agreement with the observed value [20] of 0.6911(1) cm\(^{-1}\).

Let us finally turn to the zero-point vibrational energy (ZPVE). Our computed value from the CCSD(T)/cc-pVTZ quartic force field, and including the \( E_0 \) correction, is 24.69 kcal/mol. As seen in Table IV, this differs by no more than 0.10 kcal/mol from the zero-point correction used in W1 theory, i.e. B3LYP/cc-pVTZ harmonic frequencies scaled by 0.985. The same remark holds true (Table IV) for the isoelectronic molecules C\(_2\)H\(_4\) (difference +0.04 kcal/mol) and trans-HNNH (difference +0.03 kcal/mol), for which large basis set CCSD(T) quartic force fields are available from previous work [53,54]. There are certainly situations (e.g. nonrigid molecules — i.e. those exhibiting low-barrier internal rotations and/or inversions, or very low frequency modes — or very anharmonic systems such as \( H_3^+ \)) where anything less than an anharmonic force field is fundamentally inappropriate for the zero-point energy. Yet it would appear to be that the immensely less expensive scaled harmonic B3LYP ZPVE is appropriate even for benchmark work: any situation where accuracy of ±0.1 kcal/mol on
the computed atomization energy is essential is presently beyond direct treatment even by W2 theory.

**B. Heat of formation**

Total atomization energies (TAE\(_c\) if zero-point exclusive, TAE\(_0\) at 0 K) at the W1, W1h, W2, and W2h levels for CH\(_2\)NH, CH\(_2\)NH\(^+\), trans-HNNH, and C\(_2\)H\(_4\) are given in Table IV, together with a breakdown by components of the results at the highest level of theory (W2).

In the light of our observation above, and in order to achieve consistency among the species considered (including CH\(_2\)NH\(^+\), for which no anharmonic force field is available), all heats of formation reported in Table IV use the scaled B3LYP ZPVEs rather than their anharmonic counterparts.

At the highest level of theory, we obtain \(\Delta H_{f,298}^\circ(\text{CH}_2\text{NH})=21.1\) kcal/mol. The W2h result is essentially identical; the W1 and W1h results are slightly different, but still by less than 0.2 kcal/mol. In the original W2 paper [15], the mean absolute error for a sample of some 30 very accurately known total atomization energies was 0.23 kcal/mol; we shall conservatively take our error bar to be twice that amount, or (after roundoff) ±0.5 kcal/mol.

Our calculation stays below the Holmes et al. upper limit and is in excellent agreement with both the Holmes et al. evaluated \(\Delta H_{f,298}^\circ\) and the G2-thermodynamic cycle derived value of SPCR: of course, our error bar is an order of magnitude smaller than the former and several times smaller than the latter.

What is the source of the 5 kcal/mol disagreement between these values and the earlier PINL measurement? In order to shed light upon this question, we calculated the heat of formation of protonated methylenimine, and hence also the PA of the latter compound. At the W1 and W2 levels, we find PA(CH\(_2\)NH)=207.8 and 207.5 kcal/mol, respectively: this is a minor exception to the rule [16] that W1 and W2 theory yield essentially identical proton affinities. Our W2 PA is 3.5 kcal/mol higher than the bracketed value of 204±2 kcal/mol, but lies within the error bar of the very recent Bouchoux and Salpin [55] value, 206.2±1.5 kcal/mol, obtained by the thermokinetic method. [56] We note that the accuracy
of the bracketing is, by its very nature, in turn dependent on the accuracy of the PAs of
the bases involved in the bracketing experiments. For the five bases used, namely pyrrole,
diisopropyl ether, ammonia, styrene, and diethyl ether, the PA values from the 1988 Lias et
al. compilation [57] employed by PINL differ by up to 2.5 kcal/mol from the more recent
1998 compilation of Hunter and Lias [58].

As for the heat of formation of CH$_2$NH$_2^+$, our computed W1 and W2 values are 1.0
and 1.4 kcal/mol higher, respectively, than the value of Lossing et al. [10] used by PINL.
Hammerum and Sølling (HS) [59] recently re-evaluated the experimental data of Lossing et
al., using the 298 K enthalpy contributions of Traeger and McLoughlin [60] to convert
the reported threshold energy measurements into heats of formation at 298 K. In this manner,
the value found for methylenimine is 179.7 kcal/mol, in excellent agreement with our W2
calculated result of 179.4±0.5 kcal/mol. HS also calculated the heat of formation of CH$_2$NH$_2^+$
at the G2(MP2) and CBS-Q levels, and found 179.0 and 180.2 kcal/mol, respectively. For
CH$_2$NH, the corresponding values are 20.8 and 22.0 kcal/mol; agreement with our W1 and
W2 values is as good as can reasonably be expected for the G2(MP2) and CBS-Q methods.

W2 is most reliable for molecules that are dominated by dynamical correlation energy.
One index which we found to be very reliable for this purpose is the percentage of the binding
energy that is recovered at the SCF level. For CH$_2$NH this is found to be 70%, which is
closer to C$_2$H$_4$ (77%) and to molecules essentially devoid of nondynamical correlation at
their equilibrium geometry (e.g. water, H$_2$) than to trans-HNNH (52%, comparable to N$_2$)
which is in a regime of moderate nondynamical correlation. For CH$_2$NH$_2^+$, SCF accounts for
about 63% of the binding energy.

Interestingly, the reaction

$$\frac{1}{2} H_2 C = CH_2 + \frac{1}{2} trans - H N = NH \rightarrow H_2 C = NH$$  \hspace{1cm} (1)$$
is computed to be exergonic by about 9 kcal/mol. At the SCF level, this is even slightly
larger: electron correlation reduces the difference by about 1.1 kcal/mol. For comparison,
the reaction
\[
\frac{1}{2} \text{H}_3\text{C} - \text{CH}_3 + \frac{1}{2} \text{H}_2\text{N} = \text{NH}_2 \rightarrow \text{H}_2\text{C} = \text{NH}
\]

is exergonic by 6.7 kcal/mol [61], while

\[
\frac{1}{2} \text{HC} \equiv \text{CH} + \frac{1}{2} \text{N} \equiv \text{N} \rightarrow \text{HC} \equiv \text{N}
\]

is endergonic by 6.9 kcal/mol [62].

IV. CONCLUSIONS

We have calculated benchmark heats of formation of methylenimine and protonated methylenimine by means of W2 theory. Our best calculated values, \(\Delta H_{f,298}^0(\text{CH}_2\text{NH}) = 21.1 \pm 0.5\) kcal/mol and \(\Delta H_{f,298}^0(\text{CH}_2\text{NH}_2^+) = 179.4 \pm 0.5\) kcal/mol, are in good agreement with the most recent measurements but carry a much smaller uncertainty. As such, they resolve a long-standing experimental controversy.

As for many other systems, the difference between a fully anharmonic ZPVE (zero-point vibrational energy) and a simple B3LYP/cc-pVTZ calculation scaled by 0.985 is negligible for our purposes.

A first-ever high-quality quartic force field for CH\(_2\)NH has been made available. Agreement with experimental high-resolution IR data is better than 10 cm\(^{-1}\). Reliable band origins for the stretching modes require diagonalization of a 9 \(\times\) 9 resonance polyad involving \(\nu_x + \nu_y\) (\(x, y=4,5,6\)).

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Supplementary material

The CCSD(T)/cc-pVTZ quartic force field of methylenimine in internal and in normal coordinates is available on the World Wide Web at the Uniform Resource Locator (URL) http://theochem.weizmann.ac.il/web/papers/ch2nh.html
REFERENCES


[14] Holmes and his coworkers derived the current value using estimated values for the enthalpy of formation of azetidine and propargylamine; the Moscow group was likewise


This driver is available on request from the authors.


[44] W. D. Allen, intder, a program for general internal coordinate transformations (Stanford University, 1992).

[45] To the authors’ knowledge, the term ‘embarrassingly parallel’ was introduced in G. C. Fox, P. Messina, and R. Williams, ”Parallel Computing Works!” (Morgan Kauffman, San Francisco, 1994), Chapter 7; see also http://www.npac.syr.edu/copywrite/pcw/.


[48] J. M. L. Martin, POLYAD, a program for vibrational anharmonic spectroscopy of asymmetric and symmetric top molecules (Weizmann Institute of Science, 1997).


[61] This is based on $\Delta H^\circ_{f,298}[\text{C}_2\text{H}_6]=-20.08\pm0.09$ kcal/mol [64], $\Delta H^\circ_{f,298}[\text{N}_2\text{H}_4]=22.75\pm0.12$ kcal/mol [64], and $\Delta H^\circ_{f,298}[\text{H}_3\text{CNH}_2]=-5.38$ kcal/mol from M. Frenkel, K. N. Marsh, R. C. Wilhoit, G. J. Kabo, and G. N. Roganov, *Thermodynamics of Organic Compounds in the Gas State*, Thermodynamics Research Center, Texas A&M University, College Station, TX, 1994.


TABLE I. Computed harmonic frequencies $\omega_i$ of CH$_2$NH; computed and observed fundamental frequencies and selected overtones and combination bands of CH$_2$NH. All quantities in cm$^{-1}$.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$\omega_i$ CCSD(T)/cc-pVTZ</th>
<th>$\omega_i$ MP2/6-311G**</th>
<th>$\nu_i$ Expt gas phase</th>
<th>$\nu_i$ Expt Ar matrix$^a$</th>
<th>$\nu_i$ CCSD(T)/cc-pVTZ</th>
<th>$\nu_i$ MP2/6-311G**</th>
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<tr>
<td>1</td>
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<td>3491.5</td>
<td>3262.622$^b$</td>
<td>3268.5</td>
<td>3260.7</td>
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<td>3024.452$^c$</td>
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<td>3024.7</td>
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<tr>
<td>$\nu_4 + \nu_5$</td>
<td></td>
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<td>3064.2</td>
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<td>2944.2</td>
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<td>2796.1</td>
<td>2781.4</td>
<td></td>
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</tbody>
</table>

(a) Refs. [2,17] (b) Ref. [23] (c) Ref. [22] (d) Ref. [63] (e) Ref. [20] (f) Ref. [21]
except for the eigenvectors, which are dimensionless.

<table>
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<th>Eigenvectors:</th>
<th>2ν₆</th>
<th>ν₅ + ν₆</th>
<th>2ν₅</th>
<th>ν₃</th>
<th>ν₄ + ν₅</th>
<th>ν₂</th>
<th>ν₃ + ν₄</th>
<th>2ν₄</th>
<th>ν₁</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>2685.5</td>
<td>2796.1</td>
<td>2878.4</td>
<td>2914.4</td>
<td>2958.3</td>
<td>3024.7</td>
<td>3080.9</td>
<td>3257.2</td>
<td>3268.5</td>
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<tr>
<td>[100000000]</td>
<td>-0.132</td>
<td>-0.014</td>
<td>0.010</td>
<td>0.019</td>
<td>-0.040</td>
<td>0.034</td>
<td>-0.017</td>
<td>0.434</td>
<td>0.889</td>
</tr>
<tr>
<td>[010000000]</td>
<td>-0.018</td>
<td>0.167</td>
<td>-0.056</td>
<td>0.217</td>
<td>-0.579</td>
<td>-0.746</td>
<td>-0.172</td>
<td>-0.027</td>
<td>0.008</td>
</tr>
<tr>
<td>[001000000]</td>
<td>-0.052</td>
<td>-0.112</td>
<td>-0.719</td>
<td>-0.612</td>
<td>-0.261</td>
<td>0.082</td>
<td>-0.108</td>
<td>-0.076</td>
<td>0.031</td>
</tr>
<tr>
<td>[000110000]</td>
<td>0.001</td>
<td>-0.008</td>
<td>0.090</td>
<td>0.055</td>
<td>0.088</td>
<td>0.165</td>
<td>-0.976</td>
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<td>-0.010</td>
</tr>
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<td>[000101000]</td>
<td>-0.022</td>
<td>0.056</td>
<td>0.089</td>
<td>0.268</td>
<td>-0.718</td>
<td>0.627</td>
<td>0.065</td>
<td>-0.039</td>
<td>-0.044</td>
</tr>
<tr>
<td>[000011000]</td>
<td>-0.009</td>
<td>-0.978</td>
<td>0.088</td>
<td>0.112</td>
<td>-0.113</td>
<td>-0.104</td>
<td>-0.005</td>
<td>-0.009</td>
<td>-0.017</td>
</tr>
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<td>[000010100]</td>
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<td>-0.004</td>
<td>-0.058</td>
<td>-0.037</td>
<td>-0.047</td>
<td>-0.001</td>
<td>-0.032</td>
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<td>-0.438</td>
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<td>-0.014</td>
<td>-0.671</td>
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<td>0.236</td>
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<td>0.011</td>
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</tr>
<tr>
<td>[000002000]</td>
<td>-0.989</td>
<td>0.012</td>
<td>0.041</td>
<td>0.013</td>
<td>0.045</td>
<td>-0.008</td>
<td>0.009</td>
<td>-0.059</td>
<td>-0.116</td>
</tr>
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</table>

TABLE II. Resonance matrix involving the stretching modes and eigensolution. Units are cm⁻¹
### TABLE III. Computed and observed equilibrium geometries for CH$_2$NH and CH$_2$NH$_2^+$

<table>
<thead>
<tr>
<th></th>
<th>CCSD(T)/cc-pVTZ</th>
<th>CCSD(T)/cc-pVTZ</th>
<th>CCSD(T)/cc-pVTZ</th>
<th>CCSD(T)/cc-pVQZ</th>
<th>CCSD(T)/MTsmall</th>
<th>CCSD(T)/MTsmall</th>
<th>Ref. [26]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r_e$</td>
<td>$r_{g} - r_e$</td>
<td>$r_z - r_e$</td>
<td>$r_{e}$</td>
<td>$r_{e}$</td>
<td>$r_{e}$</td>
<td>$r_{s}$</td>
</tr>
<tr>
<td>$r$(CN)</td>
<td>1.27746</td>
<td>0.00626</td>
<td>0.00576</td>
<td>1.27416</td>
<td>1.27331</td>
<td>1.27077</td>
<td>1.273</td>
</tr>
<tr>
<td>$r$(NH)</td>
<td>1.02168</td>
<td>0.02040</td>
<td>0.00863</td>
<td>1.02000</td>
<td>1.02033</td>
<td>1.01912</td>
<td>1.021</td>
</tr>
<tr>
<td>$r$(CH) cis</td>
<td>1.09236</td>
<td>0.02164</td>
<td>0.01088</td>
<td>1.09148</td>
<td>1.09168</td>
<td>1.09033</td>
<td>1.09</td>
</tr>
<tr>
<td>$r$(CH) trans</td>
<td>1.08815</td>
<td>0.02141</td>
<td>0.01060</td>
<td>1.08728</td>
<td>1.08733</td>
<td>1.08602</td>
<td>1.09</td>
</tr>
<tr>
<td>$\theta$(HNC)</td>
<td>109.510</td>
<td>0.131</td>
<td>0.271</td>
<td>109.934</td>
<td>109.640</td>
<td>109.784</td>
<td>110.4</td>
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<tr>
<td>$\theta$(NCHcis)</td>
<td>124.624</td>
<td>-0.133</td>
<td>0.194</td>
<td>124.418</td>
<td>124.614</td>
<td>124.591</td>
<td>125.1</td>
</tr>
<tr>
<td>$\theta$(NCHtrans)</td>
<td>118.637</td>
<td>-0.320</td>
<td>-0.091</td>
<td>118.672</td>
<td>118.679</td>
<td>118.715</td>
<td>117.9</td>
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</tbody>
</table>

**CH$_2$NH$_2^+$**

<table>
<thead>
<tr>
<th></th>
<th>CCSD(T)/cc-pVTZ</th>
<th>CCSD(T)/cc-pVTZ</th>
<th>CCSD(T)/cc-pVTZ</th>
<th>CCSD(T)/cc-pVQZ</th>
<th>CCSD(T)/MTsmall</th>
<th>CCSD(T)/MTsmall</th>
<th>Ref. [26]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r_e$</td>
<td>$r_{g} - r_e$</td>
<td>$r_z - r_e$</td>
<td>$r_{e}$</td>
<td>$r_{e}$</td>
<td>$r_{e}$</td>
<td>$r_{s}$</td>
</tr>
<tr>
<td>$r$(CN)</td>
<td>1.27995</td>
<td>1.27693</td>
<td>1.27631</td>
<td>1.27393</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r$(NH)</td>
<td>1.01657</td>
<td>1.01549</td>
<td>1.01550</td>
<td>1.01465</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r$(CH)</td>
<td>1.08350</td>
<td>1.08271</td>
<td>1.08264</td>
<td>1.08136</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$\theta$(HNC)</td>
<td>121.510</td>
<td>121.501</td>
<td>121.525</td>
<td>121.534</td>
<td></td>
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<td></td>
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<tr>
<td>$\theta$(HCN)</td>
<td>119.404</td>
<td>119.394</td>
<td>119.425</td>
<td>119.457</td>
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</tbody>
</table>

For an overview of the different types of molecular geometries and the mathematical relationships between them, see the review by Kuchitsu [65]. $r_e$ is the bottom-of-the-well equilibrium geometry, $r_z$ the position-averaged geometry in the vibrational ground state, while $r_g$ is the geometry obtained in a gas-phase electron diffraction experiment.
TABLE IV. Computed and observed heats of formation of CH\(_2\)NH and CH\(_2\)NH\(_2^+\), and breakdown by components of the W2 computed heat of formation. All values in kcal/mol.

<table>
<thead>
<tr>
<th></th>
<th>CH(_2)NH</th>
<th>C(_2)H(_4)</th>
<th>trans-HNNH</th>
<th>(a) CH(_2)NH(_2^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF/AV5Z</td>
<td>305.38</td>
<td>434.93</td>
<td>155.30</td>
<td>-10.27</td>
</tr>
<tr>
<td>SCF/AV(_\infty)Z</td>
<td>305.44</td>
<td>434.98</td>
<td>155.31</td>
<td>-10.30</td>
</tr>
<tr>
<td>CCSD–SCF/AV5Z</td>
<td>122.30</td>
<td>117.90</td>
<td>128.52</td>
<td>0.91</td>
</tr>
<tr>
<td>CCSD–SCF/AV(_\infty)Z</td>
<td>123.96</td>
<td>119.40</td>
<td>130.30</td>
<td>0.89</td>
</tr>
<tr>
<td>(T)/AVQZ</td>
<td>8.23</td>
<td>7.18</td>
<td>9.66</td>
<td>0.19</td>
</tr>
<tr>
<td>(T)/AV(_\infty)Z</td>
<td>8.51</td>
<td>7.45</td>
<td>9.97</td>
<td>0.20</td>
</tr>
<tr>
<td>inner-shell corr.</td>
<td>1.53</td>
<td>2.27</td>
<td>0.74</td>
<td>-0.03</td>
</tr>
<tr>
<td>scalar relativistic</td>
<td>-0.34</td>
<td>-0.33</td>
<td>-0.31</td>
<td>0.02</td>
</tr>
<tr>
<td>spin-orbit coupling</td>
<td>-0.08</td>
<td>-0.17</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>TAE(_e)</td>
<td>439.02</td>
<td>563.64</td>
<td>296.04</td>
<td>-9.18</td>
</tr>
<tr>
<td>ZPVE(scaled B3LYP(^b))</td>
<td>24.59</td>
<td>31.48</td>
<td>17.50</td>
<td>-0.10</td>
</tr>
<tr>
<td>anharmonic ZPVE</td>
<td>24.69(^c)</td>
<td>31.52(^d)</td>
<td>17.53(^e)</td>
<td>-0.17</td>
</tr>
<tr>
<td>TAE(_0)</td>
<td>414.43</td>
<td>532.16</td>
<td>278.54</td>
<td>-9.08</td>
</tr>
</tbody>
</table>

Previous benchmark

<p>| | | | | |</p>
<table>
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<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>W2 (\Delta H_f^{\circ})(_{f,0})</td>
<td>22.98</td>
<td>14.33</td>
<td>49.78</td>
<td>-9.08</td>
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<td>W2 (\Delta H_f^{\circ})(_{f,298})</td>
<td>21.08</td>
<td>12.28</td>
<td>48.07</td>
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<td>W2h</td>
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<td>-9.07</td>
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<tr>
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<td>47.80</td>
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<td>W1h</td>
<td>20.86</td>
<td>12.12</td>
<td>47.80</td>
<td>-9.10</td>
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Expt.  

<p>| | | | | |</p>
<table>
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<tbody>
<tr>
<td>26.4±3.2 ([6], 25±3 ([7]), 12.52±0.12 ([64])</td>
<td>≥47.1±0.5(^g)</td>
<td>178±1 ([10]), 179.7 ([59])</td>
<td>20.6±2.4(^f)</td>
<td></td>
</tr>
</tbody>
</table>

(a) reaction energy of \((1/2)\) C\(_2\)H\(_4\) + (1/2) trans-N\(_2\)H\(_2\) → CH\(_2\)=NH with zero-point or temperature corrections following descriptions in the first column

(b) B3LYP/cc-pVTZ harmonic frequencies scaled by 0.985, as prescribed in Ref. [15].

(c) CCSD(T)/cc-pVTZ quartic force field, this work.

(d) CCSD(T)/cc-pVQZ harmonics with CCSD(T)/cc-pVTZ anharmonicities, Ref. [53]. At CCSD(T)/cc-pVTZ level 31.50 kcal/mol. Best estimate in that reference is 31.59 kcal/mol.

(e) CCSD(T)/cc-pVQZ, Ref. [54]. At CCSD(T)/cc-pVTZ level 17.49 kcal/mol.

(f) from G2 reaction energies for 10 reactions, and expt. thermochemical data for auxiliary species [12]

(g) From thermal correction in this work and \(\Delta H_f^{\circ}\)\(_{f,0}\) ≥48.8±0.5 kcal/mol in H. Biehl and F.Stuhl, J. Chem. Phys. 100, 141 (1994)