Accurate Benchmark Calculations on the Gas-Phase Basicities of Small Molecules

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Accurate benchmark calculations of gas-phase basicities of small molecules are presented and compared with available experimental results. The optimized geometries and thermochemical analyses were obtained from MP2/aug-cc-pVTZ calculations. Two different ab initio electron-correlated methods MP2 and CCSD(T) were employed for subsequent gas-phase basicity calculations, and the single-point energies were extrapolated to the complete basis set (CBS) limit. The overall accuracy for different ab initio methods is compared, and the accuracy in descending order is CCSD(T)_CBS > CCSD(T)/aug-cc-pVDZ > (MP2/aug-cc-pVQZ ≈ MP2_CBS) > HF/aug-cc-pVQZ. The best root-mean-squared-error obtained was 1.0 kcal mol^{-1} at the CCSD(T)_CBS//MP2/aug-cc-pVTZ level for a test set of 41 molecules. Clearly, accurate calculations for the electron correlation energy are important for the theoretical prediction of molecular gas-phase basicities. However, conformational effects were also found to be relevant in several instances when more complicated molecules were examined.

Introduction

For continuum-based condensed-phase molecular dynamics simulations, an accurate continuum solvation model is important to accurately simulate the motions of atoms in the aqueous phase.[1] For many solvation models, a set of empirical parameters is finely tuned to reproduce experimental solvation free energies. To have a set of reliable experimental reference data, substantial effort has been devoted to compilations of solvation free energies.[2−7] For neutral species, Truhlar and co-workers have concluded that the uncertainty in experimental solvation free energies is typically as low as 0.2 kcal mol^{-1}.[8] On the other hand, for the aqueous solvation free energies of ionic species, a typical experimental error of 4−5 kcal mol^{-1} was estimated because of the uncertainties in associated experimental quantities.[8] Hence, the relatively large uncertainty of reference values for ionic solutes has hindered the critical assessment of current continuum solvation models.

The aqueous solvation free energies of an anion A^- ($\Delta G_{\mathrm{S}}^{*}(\mathrm{A}^-)$) can be determined using the thermodynamic cycle shown in Scheme 1, and $\Delta G_{\mathrm{S}}^{*}(\mathrm{A}^-)$ is defined as[9]

$$\Delta G_{\mathrm{S}}^{*}(\mathrm{A}^-) = \Delta G_{\mathrm{S}}^{*}(\mathrm{AH}) + \Delta G_{\mathrm{aq}}^{*}(\mathrm{AH}) - \Delta G_{\mathrm{S}}^{\mathrm{o}}(\mathrm{H}^+) - \Delta G_{\mathrm{bas}}^{\mathrm{o}}(\mathrm{A}^-) \quad (1)$$

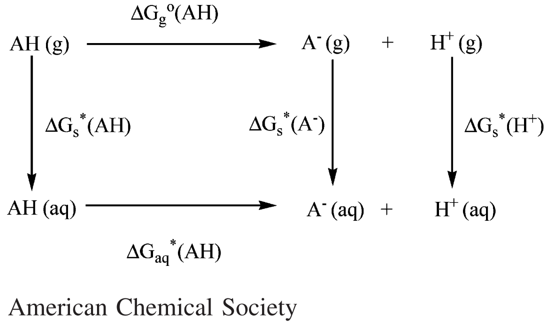
where $\Delta G_{\mathrm{S}}^{*}(\mathrm{AH})$ is the solvation free energy of the neutral species AH; and $\Delta G_{\mathrm{aq}}^{*}(\mathrm{AH})$ is equal to $2.303RT\mathrm{p}K_{\mathrm{a}}(\mathrm{AH})$ (where $\mathrm{p}K_{\mathrm{a}}(\mathrm{AH})$ is the negative common logarithm of the aqueous-phase acid dissociation constant of AH). $\Delta G_{\mathrm{S}}^{\mathrm{o}}(\mathrm{H}^+)$ is the standard aqueous solvation free energy of the proton, and $\Delta G_{\mathrm{bas}}^{\mathrm{o}}(\mathrm{A}^-)$ is the gas-phase basicity of the anion A^- defined as

$$\Delta G_{\mathrm{bas}}^{\mathrm{o}}(\mathrm{A}^-) = G_{\mathrm{gas}}^{\mathrm{o}}(\mathrm{A}^-) + G_{\mathrm{gas}}^{\mathrm{o}}(\mathrm{H}^+) - G_{\mathrm{gas}}^{\mathrm{o}}(\mathrm{AH}) \quad (2)$$

Kelly et al. have reported the estimated uncertainties for the solvation free energy of anions ($\Delta G_{\mathrm{S}}^{*}(\mathrm{A}^-)$) using the root-sum-of-squares combinations of the experimentally measured quantities on the right side of the eq 1.[3] The typical uncertainty of the solvation free energy of anions is 2−3 kcal mol^{-1}. An average uncertainty of 0.2 kcal mol^{-1} for the solvation energy of neutral solutes ($\Delta G_{\mathrm{S}}^{*}(\mathrm{AH})$) was previously estimated.[8] The experimental $\mathrm{p}K_{\mathrm{a}}(\mathrm{AH})$ within the range of 0−14 can be measured fairly precisely; therefore, the uncertainty of $\Delta G_{\mathrm{aq}}^{*}(\mathrm{AH})$ is negligible for the estimation of the overall uncertainty of $\Delta G_{\mathrm{S}}^{*}(\mathrm{A}^-)$. For the aqueous solvation free energy of the proton, Kelly et al. assigned an uncertainty of 2 kcal mol^{-1},[3] which has a large contribution to the overall uncertainty of $\Delta G_{\mathrm{S}}^{*}(\mathrm{A}^-)$. The gas-phase basicities of the anions $\Delta G_{\mathrm{bas}}^{\mathrm{o}}(\mathrm{A}^-)$ were originally taken from the NIST standard reference database.[10] In this study, we took the values and their uncertainties from the data sets collected by Kelly et al.[3] For several anions, there is more than one experimental measurement available, and a typical uncertainty of 2 kcal mol^{-1} is assigned for most of the anions.[11−14] For some cases, the uncertainties of the gas-phase basicities are as large as 2.8 kcal mol^{-1}, which significantly increases the overall uncertainties of the solvation free energies of anions.

During the past two decades, great progress has been made toward achieving the goal of predicting thermodynamic proper-

SCHEME 1: Thermodynamic Cycle



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ties to "chemical" accuracy (1 kcal mol^{-1}).[15,16] High-level electron correlation theory, e.g., CCSD(T),[17] incorporating high angular momentum basis functions has become the "gold standard" approach for obtaining thermochemical properties to chemical accuracy. Higher accuracy can be further attained by extrapolation of the energies to the complete basis set limit (CBS).[18,19]

Previous studies[20−49] have been carried out to calculate the gas-phase basicities and acidities of molecules. Burk and co-workers[26,28] and Koppel et al.[21] have critically assessed the performance of density functional theory for prediction of gas-phase acidities and basicities. Burk et al. have concluded that the average absolute errors can fall below 2.5 kcal mol^{-1} for their test sets (49 acids and 32 bases) based on B3LYP/6-311+G(3df,3pd) calculations.[26] Many-body perturbation theory (MBPT)[50] and coupled-cluster theory (CC)[51−55] in conjunction with G2,[56] G3,[57] and "multi-level" approaches (e.g., CBS-QB3,[37,58] G3B3,[59] G3MP2B3,[59] MCCM/3,[60] and SAC/3[60]) have been proposed to obtain thermochemical data to chemical accuracy. In these procedures, a series of calculations are carried out at different levels of theory with different basis sets. Zero-point energy and high-level corrections were made based on the additivity approximation. For instance, the CBS-QB3 theory optimizes the geometries of molecules and calculates thermochemical data at the B3LYP/6-311G(2d,d,p) level, followed by a series of MP2, MP4, and CCSD(T) calculations using Pople-type basis sets to obtain the electron correlation energy. Ervin and Deturi have found that CCSD(T)/aug-cc-pVTZ calculations give more accurate gas-phase acidities than CBS-QB3 theory for the molecules they tested,[20] which indicates that large basis sets are required to obtain accurate electron correlation energies of molecules. However, CCSD(T) calculations using aug-cc-pVTZ are limited to small molecules due to the poor scaling properties (N^7 where N is the number of basis functions) for CCSD(T) calculations. In addition, they did not extrapolate the CCSD(T) energies to the complete basis set limit.

Martin and co-workers have developed the W1 and W2 methods,[32,34] where the CCSD and CCSD(T) energies are extrapolated to the infinite-basis limit. Moreover, contributions from inner-shell correlation, scalar relativity, atomic spin−orbit splitting, and anharmonic zero-point energies were also included. One of the most sophisticated computations which have been done so far is by Allen and co-workers.[27] They have performed all-electron coupled-cluster (AE-CC) calculations up to single, double, triple, quadruple, and pentuple excitations with Dunning's augmented correlation-consistent, atom-centered Gaussian basis sets. They have also included the core electron correlation, scalar relativistic effects, diagonal Born−Oppenheimer corrections (DBOC),[61−64] and anharmonic zero-point energies. However, such expensive calculations are currently limited to molecules with two heavy atoms and serve more as benchmark calculations rather than as an approach that can be applied generally.

It is well-known that accurate calculation of the electron correlation energy requires a large atom-centered Gaussian basis set. In this work, we use Dunning's augmented correlation-consistent basis sets (aug-cc-pVnZ)[65−67] (where n = D, T, Q) for benchmark MP2 and CCSD(T) calculations on gas-phase basicities and extrapolate the results to the complete basis set limit. Thereby, the errors arising from the incompleteness of the basis can be largely reduced.[68] The goals of this study are (1) to benchmark the accuracy of different ab initio theories (HF, MP2, and CCSD(T)) for the theoretical estimation of the gas-phase basicities of molecules and (2) to identify an efficient approach which is able to achieve chemical accuracy for gas-phase basicity calculations on systems containing up to 10 heavy atoms. We can use the resultant approach as a useful computational protocol to validate experimental gas-phase basicities, when more than one experimental measurement is available, and to even make accurate theoretical estimates for the cases where experimental values are not available. In this study, we include some unusual molecules, such as hydroperoxides, in the test set of 41 molecules; furthermore, we have also examined the conformational effects for accurately theoretical prediction of gas-phase basicities.

Computational Approaches. We used the Gaussain03 package[69] for all ab initio calculations. MP2/aug-cc-pVTZ calculations were carried out on all the molecules for geometry optimizations, vibrational frequencies, and thermochemical analyses. The zero-point vibrational energies (ZPVEs) only include harmonic contributions. Subsequently, frozen-core MP2 and CCSD(T) single-point energy calculations using augmented correlation-consistent basis sets (aug-cc-pVnZ) were employed on the optimized structures. The two point extrapolation scheme[18]

$$E_{\mathrm{MP2\_CBS}} = E_{\mathrm{MP2},x} + \mathrm{constant} \times x^{-3} \tag{3}$$

was used to obtain the complete basis set (CBS) extrapolated values of the MP2 correlation energies ($E_{\mathrm{MP2\_CBS}}$) from energy calculations using two different basis sets, aug-cc-pVTZ and aug-cc-pVQZ. The variable x in eq 3 represents their largest angular momentum of the basis set, i.e., $x = 3$ for aug-cc-pVTZ and $x = 4$ for aug-cc-pVQZ. The Hartree−Fock energies were not extrapolated and were simply taken from the results of the larger basis set (aug-cc-pVQZ) calculations. The CBS correlation energies for CCSD(T) were obtained using

$$E_{\mathrm{CCSD(T)\_CBS}} = E_{\mathrm{MP2\_CBS}} + (E_{\mathrm{CCSD(T),aug\text{-}cc\text{-}pVDZ}} - E_{\mathrm{MP2,aug\text{-}cc\text{-}pVDZ}}) \tag{4}$$

which is based on the observation that the difference between the MP2 and CCSD(T) correlation energies converges faster in basis set size than the correlation energies themselves.[70−72] The effectiveness of the computational approach shown in eq 4 is based on the propositions within the so-called focal-point analysis (FPA) scheme.[27,73−75] The internal thermal energy corrections (translational E_{trans}, rotational E_{rot}, and vibrational E_{vib}) were made to the electronic energy[76]

$$E_{\mathrm{tot}} = E_{\mathrm{elec}} + E_{\mathrm{trans}} + E_{\mathrm{rot}} + E_{\mathrm{vib}} \tag{5}$$

The Gibbs free energy G was calculated from

$$H = E_{\mathrm{tot}} + RT \tag{6}$$

$$G = H - TS_{\mathrm{tot}} \tag{7}$$

where R is the gas constant; T is the temperature; H is the enthalpy; and $S_{\mathrm{tot}} = S_{\mathrm{trans}} + S_{\mathrm{rot}} + S_{\mathrm{vib}} + S_{\mathrm{elec}}$ (contributions from translational, rotational, vibrational, and electronic motions, respectively). The gas-phase basicity of a species A$^-$ is defined in eq 2. The standard state was 298.15 K and 1 atm pressure.

TABLE 1: Calculated and Experimental Gas-Phase Basicities of Five Representative Small Molecules (in kcal mol^{-1})[a]

	HF/aug-cc-pVQZ	MP2/aug-cc-pVQZ	CCSD(T)/aug-cc-pVDZ	MP2_CBS	CCSD(T)_CBS	CCSD(T)/aug-cc-pVTZ	CCSD(T)/aug-cc-pVQZ	exptl[10]
H_2O	393.7 (+10.0)	380.0 (−3.7)	381.9 (−1.8)	379.8 (−3.9)	383.7 (0.0)	384.1 (+0.4)	384.3 (+0.6)	383.7 ± 0.2
H_2S	346.8 (+1.9)	342.9 (−2.0)	343.8 (−1.1)	342.4 (−2.5)	345.5 (+0.6)	345.5 (+0.6)	345.2 (+0.3)	344.9 ± 1.2
HCN	342.5 (−1.2)	342.4 (−1.3)	340.8 (−2.9)	342.3 (−1.4)	343.1 (−0.6)	343.4 (−0.3)	343.3 (−0.4)	343.7 ± 0.3
H_2O_2	375.4 (+6.8)	368.0 (−0.6)	367.6 (−1.0)	367.8 (−0.8)	369.2 (+0.6)	368.9 (+0.3)	369.1 (+0.5)	368.6 ± 0.6
C_2H_2	372.7 (+2.7)	368.9 (−1.1)	365.5 (−4.5)	369.0 (−1.0)	369.5 (−0.5)	369.4 (−0.6)	−	370.0 ± 1.8
MAXE	10.0	−3.7	−4.5	−3.9	0.6	0.6	0.6	
MSE	4.0	−1.7	−2.3	−1.9	0.0	0.1	0.3	
MUE	4.5	1.7	2.3	1.9	0.5	0.4	0.5	
RMSE	5.6	2.0	2.6	2.2	0.5	0.5	0.5	

[a] For the five columns (HF/aug-cc-pVQZ, MP2/aug-cc-pVQZ, CCSD(T)/aug-cc-pVDZ, MP2_CBS, and CCSD(T)_CBS), geometry optimizations and thermochemical analyses were all performed at the MP2/aug-cc-pVTZ level. The ZPVEs only include the harmonic contributions. The electronic energies on the optimized geometries were calculated at HF/aug-cc-pVQZ, MP2/aug-cc-pVQZ, and CCSD(T)/aug-cc-pVDZ and extrapolated to the complete basis set limit for the MP2 and CCSD(T) level using eqs 3 and 4, respectively. For the other two columns (CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ), the geometry optimizations and Gibbs free energy calculations were performed at the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ level, respectively. The numbers shown in parentheses are the deviations of calculated gas-phase basicities compared to the experimental values. (MAXE: maximum error; MSE: mean signed error; MUE: mean unsigned error; RMSE: root-mean-square error).

Results and Discussion

Gas-Phase Basicity Calculations. First, to assess the accuracy of the complete basis set limit for MP2 and CCSD(T) calculations, we carried out full ab initio CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ calculations on five small molecules (H_2O, H_2S, HCN, C_2H_2, H_2O_2) for comparison. One can see from Table 1, for the same optimized geometries obtained from MP2/aug-cc-pVTZ calculations, HF/aug-cc-pVQZ has the largest RMSE of 5.6 kcal mol^{-1} compared to experimental values. MP2/aug-cc-pVQZ, MP2_CBS (MP2 with complete basis set estimate), and CCSD(T)/aug-cc-pVDZ results have smaller RMSEs between 2.0 kcal mol^{-1} and 2.6 kcal mol^{-1}. CCSD(T)_CBS (CCSD(T) with complete basis set estimate) performs just as well as the significantly more expensive CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ levels. Note that the CCSD(T)_CBS results are extrapolated from MP2_CBS and CCSD(T)/aug-cc-pVDZ calculations with no additional computational cost. Due to the poor scaling of CCSD(T), it is not economical to calculate the Gibbs free energy for relatively larger molecules using large basis sets such as aug-cc-pVTZ and aug-cc-pVQZ; however, the extrapolation using eq 4 strikes a compromise between the computational expense incurred and the attained accuracy for our test on five representative small molecules.

Next, we applied the extrapolation approach using eq 4 for the remaining 36 molecules, and the results are shown in Table 2. HF/aug-cc-pVQZ has the largest overall RMSE for this test set. MP2/aug-cc-pVQZ and MP2_CBS have similar performance with very close RMSEs of 3.1 and 3.2 kcal mol^{-1}, respectively. CCSD(T)/aug-cc-pVDZ outperforms the MP2 results, with a RMSE of 2.2 kcal mol^{-1}. Among all the approaches we tested, CCSD(T)_CBS has the lowest RMSE of 1.0 kcal mol^{-1}. Only six gas-phase basicities (hydrogen cyanide, methanol, cyanamide, methyl hydroperoxide, acetic acid, and 1,2-ethanediol) out of 41 obtained by CCSD(T)_CBS calculations fell outside the experimentally measured range. As the ab initio electron-correlation level increases from MP2 to CCSD(T), the accuracy gets better. From this comparison, we conclude, not unexpectedly, that accurate estimation of the electron correlation energy is important for theoretical gas-phase basicity predictions. Moreover, CCSD(T)_CBS calculations provide reliable gas-phase basicities of molecules at chemical accuracy at an affordable computational cost.

To further check the convergence of the extrapolation approach, we chose six molecules (hydrogen cyanide, methanol, cyanamide, methyl hydroperoxide, acetic acid, and 1,2-ethanediol) whose calculated gas-phase basicities deviated from the experimental values for further analysis. As shown in eq 8, we computed the complete basis set limit for CCSD(T) by extrapolating the energies from CCSD(T)/aug-cc-pVTZ calculations instead of from the CCSD(T)/aug-cc-pVDZ level

$$E_{\mathrm{CCSD(T)\_CBS}} = E_{\mathrm{MP2\_CBS}} + (E_{\mathrm{CCSD(T),aug\text{-}cc\text{-}pVTZ}} - E_{\mathrm{MP2,aug\text{-}cc\text{-}pVTZ}}) \quad (8)$$

As shown in Table 3, the CCSD(T)_CBS extrapolated from CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ levels yields almost identical gas-phase basicities. In addition, we also obtained the CBS extrapolated values of the MP2 correlation energies ($E_{\mathrm{MP2\_CBS}}$) from energy calculations using two larger basis sets, aug-cc-pVQZ and aug-cc-pV5Z, using eq 3 (where $x = 4$ for aug-cc-pVQZ and $x = 5$ for aug-cc-pV5Z), and the Hartree−Fock energies were taken from the results of HF/aug-cc-pV5Z calculations. As shown in Table 3, using the MP2 CBS energies extrapolated from larger basis sets, the gas-phase basicities obtained from CCSD(T) CBS energies have very subtle changes. Therefore, the results are likely converged, or nearly converged, for these six molecules. It indicates that the CBS limit of CCSD(T) extrapolated from the CCSD(T)/aug-cc-pVDZ level is, indeed, reliable for gas-phase basicity calculations.

Following the spirit of the FPA approach,[27,75] we further check the convergence of the HF, MP2, and CCSD(T) CBS limits using an extrapolation based on aug-cc-pV5Z and aug-cc-pV6Z for five representative molecules. For extrapolation of the Hartree−Fock energies, the two-parameter exponential functions were used.[77,78]

$$E_X^{\mathrm{HF}} = E_{\mathrm{CBS}}^{\mathrm{HF}} + a(X + 1)\mathrm{e}^{-9\sqrt{X}} \quad (9)$$

The MP2 and CCSD(T) CBS energies were extrapolated using eq 3. As shown in Table 4, the gas-phase basicities calculated using MP2 energies extrapolated from smaller basis sets aug-cc-pVTZ and aug-cc-pVQZ are very close to those extrapolated gas-phase basicities using the much larger basis sets aug-cc-pV5Z and aug-cc-pV6Z. Among the five small molecules, the largest deviation of the MP2 extrapolated values is 0.39 kcal mol^{-1} for H_2O. Meanwhile, the CCSD(T) computed gas-phase

TABLE 2: Calculated and Experimental Gas-Phase Basicities of 41 Small Molecules (kcal mol^{-1})[a]

A^-	AH	HF/aug-cc-pVQZ	MP2/aug-cc-pVQZ	CCSD(T)/aug-cc-pVDZ	MP2_CBS	CCSD(T)_CBS	exptl[10]
HO^-	water	393.7	380.0	381.9	379.8 (−3.9)	383.7 (0.0)	383.7 ± 0.2
HS^-	hydrogen sulfide	346.8	342.9	343.8	342.4 (−2.5)	345.5 (+0.6)	344.9 ± 1.2
CN^-	hydrogen cyanide	342.5	342.4	340.8	342.3 (−1.4)	343.1 **(−0.6)**	343.7 ± **0.3**
HC_2^-	acetylene	372.7	368.9	365.5	369.0 (−1.0)	369.5 (−0.5)	370.0 ± 1.8
HO_2^-	hydrogen peroxide	375.4	368.0	367.6	367.8 (−0.8)	369.2 (+0.6)	368.6 ± 0.6
HCO_2^-	formic acid	343.4	333.9	335.5	333.7 (−4.6)	336.8 (−1.5)	338.3 ± 1.5
CH_3O^-	methanol	384.6	373.1	373.9	373.0 (−2.0)	375.8 **(+0.8)**	375.0 ± **0.6**
$C_2H_5O^-$	ethanol	382.0	369.3	369.9	369.2 (−2.1)	371.7 (+0.4)	371.3 ± 1.1
CCl_3^-	chloroform	357.9	351.6	347.9	350.8 (+1.1)	350.5 (+0.8)	349.7 ± 2.0
$NCNH^-$	cyanamide	347.5	338.7	340.7	338.5 (−5.5)	341.7 **(−2.3)**	344.0 ± **2.0**
CH_3S^-	methanethiol	354.0	348.6	349.1	348.2 (−2.4)	351.1 (+0.5)	350.6 ± 2.0
$C_2H_5S^-$	ethanethiol	352.0	345.5	346.0	345.1 (−3.8)	348.1 (−0.8)	348.9 ± 2.0
$CH_3CH_2CH_2O^-$	1-propanol	380.8	367.6	368.2	367.5 (−1.9)	370.0 (+0.6)	369.4 ± 1.4
$(CH_3)_2CHO^-$	2-propanol	380.4	367.1	367.7	367.0 (−1.8)	369.5 (+0.7)	368.8 ± 1.1
$CH_2(O)CH^-$	acetaldehyde	368.8	356.6	359.4	356.2 (−3.2)	359.7 (+0.3)	359.4 ± 2.0
CH_2CN^-	acetonitrile	372.2	364.1	366.2	363.8 (−2.2)	366.3 (+0.3)	366.0 ± 2.0
$CH_2NO_2^-$	nitromethane	355.5	349.5	351.3	349.0 (−1.4)	350.8 (+0.4)	350.4 ± 2.0
$CH_2ClCO_2^-$	chloroacetic acid	334.5	325.3	326.4	325.0 (−3.9)	327.7 (−1.2)	328.9 ± 2.0
CH_3OO^-	methyl hydroperoxide	372.1	364.6	364.2	364.4 (−3.2)	365.5 **(−2.1)**	367.6 ± **0.7**
$CH_3CH_2OO^-$	ethyl hydroperoxide	371.5	363.7	363.1	363.5 (−0.4)	364.4 (+0.5)	363.9 ± 2.0
CH_3CONH^-	acetamide	365.8	354.0	354.0	353.9 (−1.1)	356.0 (+1.0)	355.0 ± 2.0
$CH_3S(O)CH_2^-$	dimethyl sulfoxide	379.1	365.7	367.8	365.4 (−1.4)	368.3 (+1.5)	366.8 ± 2.0
$C_6H_5S^-$	thiophenol	338.0	330.1	330.9	329.7 (−4.1)	333.3 (−0.5)	333.8 ± 2.0
$CH_3C(O)CH_2^-$	acetone	373.3	360.4	363.1	360.1 (−2.1)	363.5 (+1.3)	362.2 ± 2.0
$C(CH_3)_3O^-$	*t*-butanol	379.3	365.8	366.8	365.7 (−2.2)	368.3 (+0.4)	367.9 ± 1.1
$CH_3COCO_2^-$	pyruvic acid	332.2	325.0	325.7	324.8 (−1.7)	327.3 (+0.8)	326.5 ± 2.8
$CF_3CO_2^-$	trifluoroacetic acid	322.9	313.8	314.8	313.6 (−3.1)	316.4 (−0.3)	316.7 ± 2.0
$H_2C{=}CHCH_2O^-$	allyl alcohol	376.5	363.8	364.8	363.6 (−3.0)	366.3 (−0.3)	366.6 ± 2.8
$H_2C{=}CHCO_2^-$	acrylic acid	344.0	333.9	335.2	333.7 (−3.5)	336.5 (−0.7)	337.2 ± 2.8
$CH_3CH_2CO_2^-$	propanoic acid	346.7	336.6	337.7	336.4 (−4.0)	339.0 (−1.4)	340.4 ± 2.0
$CH_3CO_2^-$	acetic acid	346.1	336.3	337.6	336.2 (−5.2)	338.9 (−2.5)	341.4 ± 2.0
$CH_2OHCH_2O^-$	1,2-ethanediol	372.5	355.5	357.3	355.3 (−5.6)	358.4 (−2.5)	360.9 ± 2.0
$CF_3CH_2O^-$	2,2,2-trifluoroethanol	362.9	352.2	352.5	352.0 (−2.1)	354.5 (+0.4)	354.1 ± 2.0
$C_6H_5O^-$	phenol	350.4	339.4	340.2	339.3 (−3.6)	342.2 (−0.7)	342.9 ± 1.3
$C_3H_7S^-$	1-propanethiol	351.6	345.0	345.5	344.6 (−3.3)	347.5 (−0.4)	347.9 ± 2.0
$CHCl_2CO_2^-$	dichloroacetic acid	326.7	317.4	318.8	317.1 (−4.4)	320.0 (−1.5)	321.5 ± 2.0
O_2^-	Hydroperoxyl radical	361.8	339.9	345.2	339.7 (−7.0)	347.0 (+0.3)	346.7 ± 0.8
$CH(CF_3)_2O^-$	1,1,1,3,3,3 -hexafluoropropan-2-ol	344.8	334.8	334.9	334.6 (−3.8)	336.9 (−1.5)	338.4 ± 2.0
$C_6H_5CO_2^-$	benzoic acid	340.3	329.7	331.2	329.4 (−3.6)	332.4 (−0.6)	333.0 ± 2.0
$CH_3CH_2CHOCH_3^-$	2-butanol	379.2	365.3	366.0	365.2 (−2.3)	367.6 (+0.1)	367.5 ± 2.0
$ClC_6H_4O^-$	2-chlorophenol	344.3	334.2	334.7	334.1 (−3.0)	336.9 (−0.2)	337.1 ± 2.0
	MAXE	15.1	−6.8	−4.5	−7.0	−2.5	
	MSE	7.3	−2.6	−1.8	−2.9	−0.2	
	MUE	7.4	2.7	1.9	2.9	0.8	
	RMSE	8.0	3.1	2.2	3.2	1.0	

[a] Similar to Table 1, geometry optimizations and thermochemical analyses were all performed at the MP2/aug-cc-pVTZ level. The ZPVEs only include the harmonic contributions. The electronic energies on the optimized geometries were calculated at HF/aug-cc-pVQZ, MP2/aug-cc-pVQZ and CCSD(T)/aug-cc-pVDZ and extrapolated to the complete basis set limit for MP2 and CCSD(T) using eqs 3 and 4, respectively. The numbers shown in parentheses are the deviations of the calculated values compared to the experimental values. The deviations larger than the experimental error bars are highlighted in bold.

TABLE 3: Gas-Phase Basicity Complete Basis Set Estimations Using Two Different Extrapolation Schemes[a,b]

A^-	AH	(a) CCSD(T)_CBS (from aug-cc-pVDZ)	(b) CCSD(T)_CBS (from aug-cc-pVTZ)	(c) CCSD(T)_CBS (from aug-cc-pVTZ)	exptl[10]
CN^-	hydrogen cyanide	343.1 (−0.6)	343.2 (−0.5)	342.9 (−0.8)	343.7 ± 0.3
CH_3O^-	methanol	375.8 (+0.8)	375.9 (+0.9)	375.7 (+0.7)	375.0 ± 0.6
NCNH-	cyanamide	341.7 (−2.3)	341.5 (−2.5)	341.3 (−2.7)	344.0 ± 2.0
$CH3OO^-$	methyl hydroperoxide	365.5 (−2.1)	365.6 (−2.0)	365.4 (−2.2)	367.6 ± 0.7
$CH3CO_2^-$	acetic acid	338.9 (−2.5)	338.9 (−2.5)	338.8 (−2.6)	341.4 ± 2.0
$CH_2OHCH_2O^-$	1,2-ethanediol	358.4 (−2.5)	358.7 (−2.2)	358.7 (−2.2)	360.9 ± 2.0

[a] (a) Calculated using eq 4. (b) Calculated using eq 8. (c) MP2_CBS is extrapolated from aug-cc-pVQZ and aug-cc-pV5Z energies, and HF energy is using HF/aug-cc-pV5Z. Then CCSD(T)_CBS is calculated using eq 8. [b] The numbers shown in parentheses are the deviations of calculated gas-phase basicities compared to the experimental values. The ZPVEs only include the harmonic contributions.

basicities using the extrapolation scheme of eq 4 are also very close to the CCSD(T) CBS limits. The largest deviation is also as low as 0.39 kcal mol^{-1} for C_2H_2 comparing the computed gas-phase basicities using eq 4 with the CCSD(T) CBS extrapolated values based on aug-cc-pV5Z and aug-cc-pV6Z basis sets. The observed deviations from the CBS limit

TABLE 4: Calculated and Experimental Gas-Phase Basicities (ΔG in kcal mol^{-1}) of Five Representative Small Molecules[a]

(a)	ΔG (RHF)	ΔG (MP2)	ΔG [CCSD(T)]	MP2_CBS[b]	CCSD(T)_CBS[c]	exptl[10]
aug-cc-pVDZ	391.56	378.08	381.91	379.84 (−3.86) [+0.39]	383.67 (−0.03) [+0.06]	383.7 ± 0.2
aug-cc-pVTZ	393.37	379.85	383.74			
aug-cc-pVQZ	393.74	380.00	383.95			
aug-cc-pV5Z	393.82	379.85	383.88			
aug-cc-pV6Z	393.82	379.68	383.76			
CBS	393.82	379.45	383.61			
Δ(CBS-Exp.)	+10.12	−4.25	−0.09			
(b)	ΔG (RHF)	ΔG (MP2)	ΔG [CCSD(T)]	MP2_CBS[b]	CCSD(T)_CBS[c]	exptl[10]
aug-cc-pVDZ	343.51	340.72	343.81	342.37 (−2.53) [−0.18]	345.46 (+0.56) [+0.33]	344.9 ± 1.2
aug-cc-pVTZ	346.15	343.00	345.39			
aug-cc-pVQZ	346.76	342.89	345.13			
aug-cc-pV5Z	347.18	342.97	345.32			
aug-cc-pV6Z	347.26	342.83	345.27			
CBS	347.28	342.55	345.13			
Δ(CBS-Exp.)	+2.38	−2.35	+0.23			
(c)	ΔG (RHF)	ΔG (MP2)	ΔG [CCSD(T)]	MP2_CBS[b]	CCSD(T)_CBS[c]	exptl[10]
aug-cc-pVDZ	340.17	340.04	340.80	342.30 (−1.40)[+0.24]	343.06 (−0.64)[−0.04]	343.7 ± 0.3
aug-cc-pVTZ	342.43	342.45	343.30			
aug-cc-pVQZ	342.54	342.41	343.28			
aug-cc-pV5Z	342.60	342.28	343.21			
aug-cc-pV6Z	342.61	342.19	343.17			
CBS	342.61	342.06	343.10			
Δ(CBS-Exp.)	−1.09	−1.64	−0.60			
(d)	ΔG (RHF)	ΔG (MP2)	ΔG [CCSD(T)]	MP2_CBS[b]	CCSD(T)_CBS[c]	exptl[10]
aug-cc-pVDZ	369.53	364.94	365.47	368.99 (−1.01)[+0.09]	369.51 (−0.49)[−0.39]	370.0 ± 1.8
aug-cc-pVTZ	372.52	368.66	369.43			
aug-cc-pVQZ	372.71	368.93	369.78			
aug-cc-pV5Z	372.79	368.97	369.88			
aug-cc-pV6Z	372.80	368.95	369.89			
CBS	372.80	368.90	369.90			
Δ(CBS-Exp.)	+2.80	−1.10	−0.10			
(e)	ΔG (RHF)	ΔG (MP2)	ΔG [CCSD(T)]	MP2_CBS[b]	CCSD(T)_CBS[c]	exptl[10]
aug-cc-pVDZ	373.03	366.27	367.60	367.82 (−0.78) [+0.35]	369.15 (+0.55) [+0.03]	368.6 ± 0.6
aug-cc-pVTZ	374.95	367.89	369.27			
aug-cc-pVQZ	375.40	368.04	369.42			
aug-cc-pV5Z	375.49	367.86	369.31			
aug-cc-pV6Z	375.50	367.70	−			
CBS	375.50	367.47	369.12[d]			
Δ(CBS-Exp.)	+6.90	−1.13	+0.52			

[a] Geometry optimizations and thermochemical analyses were all performed at the MP2/aug-cc-pVTZ level. The ZPVEs only include the harmonic contributions. The electronic energies on the optimized geometries were extrapolated to complete basis set limit for HF, MP2, and CCSD(T) level using electronic energies calculated with aug-cc-pV5Z and aug-cc-pV6Z basis sets. The numbers shown in parentheses are the deviations of calculated gas-phase basicities compared to the experimental values. The numbers shown in bracket are the deviations of extrapolated gas-phase basicities using smaller basis sets (see text for more details) compared to the CBS estimated values using aug-cc-pV5Z and aug-cc-pV6Z basis sets (the values listed in the seventh line of each part of the table). (a) H_2O, (b) H_2S, (c) HCN, (d) C_2H_2, (e) H_2O_2. [b] The MP2_CBS energies were extrapolated based on eq 3 using aug-cc-pVTZ and aug-cc-pVQZ electronic energies. [c] The CCSD(T)_CBS energies were extrapolated using eq 4. [d] The CBS limit is extrapolated from aug-cc-pVQZ and aug-cc-pV5Z.

calculations are well below our target accuracy (1 kcal mol^{-1}). Overall, it is not currently routinely feasible to carry out MP2 and CCSD(T) calculations using aug-cc-pV5Z and aug-cc-pV6Z basis sets for molecules with more than two heavy atoms. Therefore, we conclude that the scheme proposed in this study provides an affordable approach for theoretical predictions of the gas-phase basicities of larger molecules within the accuracy of 1 kcal mol^{-1}.

The fact that the computed results indicate that they are likely converged suggests that the experimental values may have larger associated errors than what have been estimated. This notion is bolstered by the fact that for 35 of the cases examined we obtained results well within experimental error, while for only six cases we found more significant differences between theory and experiment. For methyl hydroperoxide, whose predicted gas-phase basicity has the largest deviation from the experimental value, we have also examined the possible rearranged species $CH_2^-{-}O{-}O{-}H$ and $H{-}O{-}CH_2{-}O^-$ for the anion of methyl hydroperoxide, but the calculated gas-phase basicities for these two species are even poorer indicating that rearranged species are unlikely. Hence, at least for the case of methyl hydroperoxide, we suggest that it would be worthwhile reexamining the experimental value to validate that theory is failing. This is true in this case given that only one experimental measurement[79] is cited in the NIST standard reference database[10] for this compound. Further corrections examined previously, like relativistic, anharmonic effects or diagonal Born−Oppenheimer corrections are much smaller (~0.2 kcal mol^{-1})[27] than the

TABLE 5: Harmonic and Anharmonic ZPVEs for Six Molecules (H_2O_2, CH_3OH, $NCNH_2$, CH_3OOH, CH_3COOH, and CH_2OHCH_2OH) and Their Anions Computed at the MP2/aug-cc-pVTZ Level[a]

molecule		harmonic ZPVE (a)	anharmonic ZPVE (b)	b-a	ΔG [CCSD(T)] with harmonic ZPVE (c)	ΔG [CCSD(T)] with anharmonic ZPVE (d)	d-c	exptl[10]
A^-	HO_2^-	8.35	8.21	−0.14	369.15 (+0.55)	369.29 (+0.69)	+0.14	368.6 ± 0.6
AH	hydrogen peroxide	16.63	16.35	−0.28				
A^-	CH_3O^-	22.67	22.17	−0.50	375.78 (+0.78)	375.77 (+0.77)	−0.01	375.0 ± 0.6
AH	methanol	32.55	32.06	−0.49				
A^-	NCNH-	12.81	12.69	−0.12	341.65 (−2.35)	341.80 (−2.20)	+0.15	344.0 ± 2.0
AH	cyanamide	21.33	21.05	−0.28				
A^-	$CH3OO^-$	26.41	26.05	−0.36	365.46 (−2.14)	365.60 (−2.00)	+0.14	367.6 ± 0.7
AH	methyl hydroperoxide	34.61	34.11	−0.50				
A^-	$CH3CO_2^-$	30.37	29.89	−0.48	338.86 (−2.54)	338.90 (−2.50)	+0.04	341.4 ± 2.0
AH	acetic acid	39.00	38.48	−0.52				
A^-	$CH_2OHCH_2O^-$	44.67	43.72	−0.95	358.39 (−2.51)	358.29 (−2.61)	−0.10	360.9 ± 2.0
AH (1,2-ethanediol)	tGg’	54.12	53.31	−0.81				
	g’Gg’	53.93	52.98	−0.95				
	gGg’	54.17	53.36	−0.81				

[a] The calculated CCSD(T) CBS (using eq 4) and experimental gas-phase basicities of these six molecules (in kcal mol^{-1}) are also listed. The numbers shown in parentheses are the deviations of calculated gas-phase basicities compared to the experimental values.

present computed error, but given the unusual nature of this molecule, we cannot rule out theoretical shortcomings entirely.

Anharmonicity Correction. We further check the role anharmonic effects play on the gas-phase basicities for the molecules which were found to have relatively larger deviations from experiment. One can see from Table 5 the anharmonic effect lowers the ZPVE by 0.1−1.0 kcal mol^{-1}. Especially for the relatively floppy molecule 1,2-ethanediol, the anharmonic correction has the largest value of −0.95 kcal mol^{-1} among the six molecules we have examined in Table 5. However, the anharmonic correction is largely canceled out when we calculate the gas-phase basicities by deducting the anharmonic correction of the molecule from its anion. As shown in Table 5, the anharmonic effects on the gas-phase basicities are less than or equal to 0.15 kcal mol^{-1} for all six molecules, which is much smaller than our target accuracy 1 kcal mol^{-1}. Therefore, we conclude that the harmonic ZPVE is adequate for our theoretical prediction on the gas-phase basicities.

Conformational Effects. For a few flexible molecules in this test set, we performed geometry optimizations from different starting geometries. Different initial conformations are usually trapped at different local minima at the end of the geometry optimization. We took the structure with the lowest free energy for the gas-phase basicity calculation when the energy difference between the two conformers was larger than 2.0 kcal mol^{-1}. Otherwise, we took the ensemble average of all low energy conformations (<2.0 kcal mol^{-1} energy difference) based on the Maxwell−Boltzmann statistics

$$E = \sum_i p_i \varepsilon_i \tag{10}$$

$$p_i = \frac{g_i e^{-\varepsilon_i/k_B T}}{\sum_i g_i e^{-\varepsilon_i/k_B T}} \tag{11}$$

where ε_i is the free energy of the *i*th conformer and g_i is the degeneracy of the energy level ε_i.

To illustrate this, we carried out a conformational study on 1,2-ethanediol. As shown in Figure 1a−d, four different local minima (tTt, tGg’, gGg’, and g’Gg’) were found for 1,2-ethanediol at the MP2/aug-cc-pVTZ level, which is consistent with previous studies.[80−82] The conformer tGg’ with a weak intramolecular hydrogen bond is 2.0 kcal mol^{-1} lower in total free energy than the conformer tTt without the intramolecular hydrogen bond. The other two conformers gGg’ and g’Gg’ are 0.5 and 0.3 kcal mol^{-1} higher than the conformer tGg’, respectively. A previous study has shown that the conformer gGg’ has a lower free energy than g’Gg’ based on MP2/6-31G* calculations using the geometries optimized at the HF/6-31G* level,[80] while in this study, we find g’Gg’ is more stable than

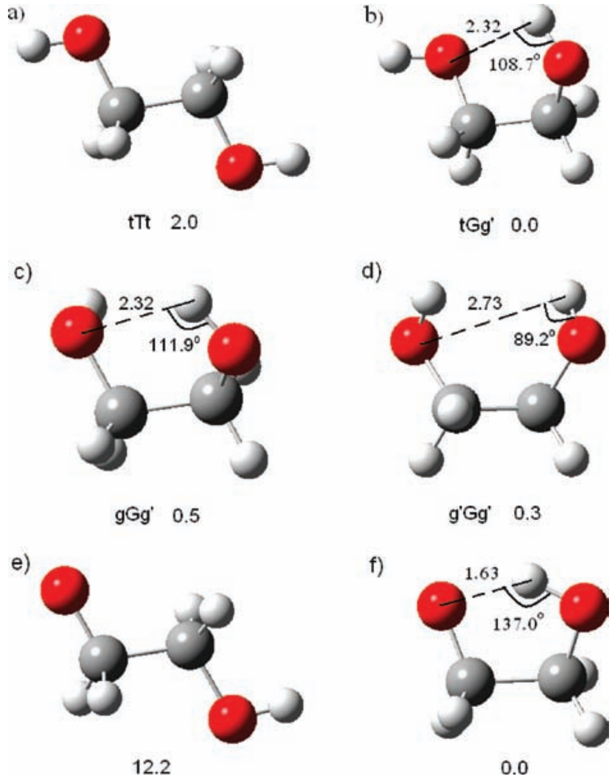

Figure 1. Different local minima for 1,2-ethanediol CH_2OHCH_2OH (a, b, c, and d) and for the anion of 1,2-ethanediol $CH_2OHCH_2O^-$ (e and f) optimized at the MP2/aug-cc-pVTZ level. The number below each conformer is the relative free energy in kcal mol^{-1}. (Carbon, oxygen, and hydrogen atoms are represented in gray, red, and white color, respectively. The distance between the oxygen atom and hydrogen atom is in Å). The ZPVEs only include the harmonic contributions.

TABLE 6: Gas-Phase Basicity of the Anion of 1,2-Ethanediol Calculated Using Different Local Minima

A^-	AH	MP2_CBS	CCSD(T)_CBS	exptl
(e)	(a)	366.0 (+5.1)	368.6 (+7.7)	360.9 ± 2.0
(f)	(b), (c), (d)[a]	355.3 (−5.6)	358.4 (−2.5)	

[a] Ensemble average over conformers (b), (c), and (d).

gGg' at the MP2/aug-cc-pVTZ level. Moreover, for the anion of 1,2-ethanediol ($CH_2OHCH_2O^-$), the conformer shown in Figure 1f has a stronger intramolecular hydrogen bonding interaction in terms of the donor−acceptor distance. Compared to the neutral 1,2-ethanediol at the tGg' configuration, the distance between the hydrogen donor and the oxygen acceptor is decreased from 2.32 to 1.63 Å, and the O−H−O angle is increased from 108.7° to 137.0°; thus, the total free energy of the conformer shown in Figure 1f is 12.2 kcal mol^{-1} lower than the conformer without the intramolecular hydrogen bond shown in Figure 1e. The gas-phase basicity calculations on 1,2-ethanediol further confirm that the structures with the intramolecular hydrogen bonds should be used for computing chemical properties. One can also see from Table 6 the calculated CCSD(T)_CBS gas-phase basicity of 1,2-ethanediol has a 2.5 kcal mol^{-1} deviation from experiment using the geometries with the lower energies (conformer f and ensemble average over b, c, and d). On the other hand, the CCSD(T)_CBS predicted value derived from conformer (e) and (a) (see Figure 1) has a larger deviation of 7.7 kcal mol^{-1}. This shows that conformational effects are relevant for theoretical predictions of the gas-phase basicities of molecules. Thus, sampling represents yet another challenge associated with computing gas-phase basicities using extraordinarily sophisticated computational techniques.[27] Further conformational studies for allyl alcohol, acrylic acid, propanoic acid, 2,2,2-trifluoroethanol, pyruvic acid, and 2-butanol are presented in the Supporting Information.

Conclusions

Through the theoretical study of the gas-phase basicities of 41 small molecules, chemical accuracy was achieved via CCSD(T) calculations with CBS extrapolation. For 35 of the cases studied, theory and experiment were in excellent accord, while for six cases (hydrogen cyanide, methanol, cyanamide, methyl hydroperoxide, acetic acid, and 1,2-ethanediol) theory predicted values outside of the experimental error bars. We suggested that a re-examination of the experimental value for methyl hydroperoxide will help us determine whether some aspect of the theoretical approach is less than optimal or if the experimental uncertainties are larger than currently believed. The electron correlation energy was found to be an important component in the theoretical estimation of gas-phase basicities. The least inexpensive ab initio electron correlation method MP2, which scales with the fifth power of molecular size, was not adequate for gas-phase basicity prediction. For cases where experimental gas-phase basicities are not available, or large uncertainties (∼3.0 kcal mol^{-1}) are associated with the available values, the computational procedure proposed in this study provides a validated approach to accurately predict the gas-phase basicities of molecules with near chemical accuracy. Even though the computational expense scales with the seventh power of the molecular size for CCSD(T) calculations, modern parallel implementation of CCSD(T) calculations[83−87] and low-order scaling local electron correlation methods[88−91] have extended the power of coupled-cluster theory to systems beyond 10 heavy atoms.

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Supporting Information Available: Conformational studies on several medium-sized floppy molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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