REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE New Reprint	3. DATES COVERED (From - To) -

4. TITLE AND SUBTITLE
Calculation of the Gibbs free energy of solvation and dissociation of HCl in water via Monte Carlo simulations and continuum solvation models

5a. CONTRACT NUMBER
W911NF-09-1-0377

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHORS
I-F. Will Kuo, Brice F. Ngouana W., Matthew J. McGrath, Julius N. Ghogomu, Christopher J. Mundy, Aleksandr V. Marenich, Christopher J. Cramer, Donald G. Truhlar, J. Ilja Siepmann

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Minnesota - Minneapolis
450 McNamara Alumni Center
200 Oak Street SE
Minneapolis, MN 55455 -2070

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
56074-CH.13

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

The Gibbs free energy of solvation and dissociation of hydrogen chloride in water is calculated through a combined molecular simulation/quantum chemical approach at four temperatures between T = 300 and 450 K. The Gibbs free energy is first decomposed into the sum of two components: the Gibbs free energy of transfer of molecular HCl from the vapor to the aqueous liquid phase and the standard-state Gibbs free energy of acid dissociation of HCl in aqueous solution. The former quantity is calculated using Gibbs ensemble Monte Carlo simulations using either

15. SUBJECT TERMS
acid/base, ion dissociation, simulation

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Christopher Cramer
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU	UU		19b. TELEPHONE NUMBER 612-624-0859

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

Report Title

Calculation of the Gibbs free energy of solvation and dissociation of HCl in water via Monte Carlo simulations and continuum solvation models

ABSTRACT

The Gibbs free energy of solvation and dissociation of hydrogen chloride in water is calculated through a combined molecular simulation/quantum chemical approach at four temperatures between T = 300 and 450 K. The Gibbs free energy is first decomposed into the sum of two components: the Gibbs free energy of transfer of molecular HCl from the vapor to the aqueous liquid phase and the standard-state Gibbs free energy of acid dissociation of HCl in aqueous solution. The former quantity is calculated using Gibbs ensemble Monte Carlo simulations using either Kohn–Sham density functional theory or a molecular mechanics force field to determine the system's potential energy. The latter Gibbs free energy contribution is computed using a continuum solvation model utilizing either experimental reference data or micro-solvated clusters. The predicted combined solvation and dissociation Gibbs free energies agree very well with available experimental data.

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Continuation for Block 13

ARO Report Number 56074.13-CH
Calculation of the Gibbs free energy of solvation...

Block 13: Supplementary Note
© 2013 . Published in Physical Chemistry Chemical Physics, Vol. Ed. 0 15, (32) (2013), ((32). DoD Components reserve a royalty-free, nonexclusive and irrevocable right to reproduce, publish, or otherwise use the work for Federal purposes, and to authroize others to do so (DODGARS §32.36). The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

PCCP

RSCPublishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *Phys. Chem. Chem. Phys.*, 2013, **15**, 13578

Calculation of the Gibbs free energy of solvation and dissociation of HCl in water *via* Monte Carlo simulations and continuum solvation models

Matthew J. McGrath,*[ab] I-F. Will Kuo,[c] Brice F. Ngouana W.,[de] Julius N. Ghogomu,[d] Christopher J. Mundy,[f] Aleksandr V. Marenich,[b] Christopher J. Cramer,[b] Donald G. Truhlar[b] and J. Ilja Siepmann[bg]

Received 24th April 2013,
Accepted 21st June 2013

DOI: 10.1039/c3cp51762d

www.rsc.org/pccp

The Gibbs free energy of solvation and dissociation of hydrogen chloride in water is calculated through a combined molecular simulation/quantum chemical approach at four temperatures between $T = 300$ and 450 K. The Gibbs free energy is first decomposed into the sum of two components: the Gibbs free energy of transfer of molecular HCl from the vapor to the aqueous liquid phase and the standard-state Gibbs free energy of acid dissociation of HCl in aqueous solution. The former quantity is calculated using Gibbs ensemble Monte Carlo simulations using either Kohn–Sham density functional theory or a molecular mechanics force field to determine the system's potential energy. The latter Gibbs free energy contribution is computed using a continuum solvation model utilizing either experimental reference data or micro-solvated clusters. The predicted combined solvation and dissociation Gibbs free energies agree very well with available experimental data.

1 Introduction

The interaction between hydrogen chloride and water has been studied for many years due to the importance of HCl as a strong acid (including acid dissociation in very cold nanoclusters[1]) and of HCl–ice systems and chloride ions at the air/water interface in atmospheric chemistry.[2–5] Interest has also been shown in the supercritical water–HCl system, as supercritical water is becoming increasingly popular for applications such as waste disposal; the nature of supercritical water, however, drastically alters the behavior of strong acids.[6]

Studies of the thermophysical properties of HCl dissolution in water were performed early in the last century using electrochemical cells,[7,8] and the structures of both dilute and concentrated HCl solutions have been probed in neutron and X-ray diffraction experiments,[9,10] including studies on the chloride ion solvation structure.[11] Experimental measurements of the vapor pressures of HCl over water have been reported for various concentrations and temperatures,[12–19] including vapor- and liquid-phase mole fractions of HCl as functions of temperature.[20] Equations to predict the HCl vapor pressure,[21–25] as well as its Henry's law constants,[26] have also been developed based on previous experimental data.

There is some disagreement in the literature concerning the value of the acid dissociation constant of HCl in aqueous solution ($K_{a,aq}$). Ruaya and Seward[27] report values for a wide range of temperatures, including a value of 0.71 at $T = 298$ K, showing good agreement with some previous studies. However, a value of $K_{a,aq}$ less than unity would imply a significant amount of undissociated HCl at room temperature, which is unexpected at low temperatures for a strong acid, and Ruaya and Seward[27] mention other values that are about an order of magnitude larger. Much larger values make more intuitive sense and have been reported by various research groups.[23,24,28,29] It is also of interest to note that Clegg and Brimblecombe[24] recommended using a form of Henry's law constant that avoids

---

[a] *Laboratoire des Sciences du Climat et de l'Environnement, CEA-Orme des Merisiers, F-91191 Gif-sur-Yvette CEDEX, France. E-mail: matthew.mcgrath@lsce.ipsl.fr*

[b] *Department of Chemistry, Chemical Theory Center, and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455, USA*

[c] *Physical and Life Sciences Directorate, Lawrence Livermore National Livermore, California 94550, USA*

[d] *Department of Chemistry, University of Dschang, B.P. 67, Dschang, Cameroon*

[e] *Laboratoire Subatech, 4 rue Alfred Kastler, La Chantrerie BP 20722, 44307 Nantes CEDEX 3, France*

[f] *Physical Sciences Division, Pacific Northwest National Livermore, P.O. Box 999, Richland, Washington 99352, USA*

[g] *Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, USA*

the need to know "inaccessible parameters" including the acid dissociation constant, and commented on the difficulty in determining its true value. Balbuena *et al.*[30] report the Gibbs free energy of HCl dissociation in water along the water saturation curve below the critical temperature, ranging from about -11 kcal mol^{-1} at $T = 300$ K to around -5 kcal mol^{-1} near $T = 500$ K (based on experimentally measured acid dissociation constants[31]). Ho *et al.*[32] give a formula to estimate $K_{a,aq}$ at elevated temperatures as a function of the solvent density and temperature. At $T = 473$ K (the lowest temperature at which their formula is valid), this formula predicts $\log(K_{a,aq}) = 0.55$, which gives a Gibbs free energy of acid dissociation, $\Delta G_{a,aq}$, of 1.2 kcal mol^{-1}. Robinson,[28] Marsh and McElroy,[23] and Pokrovskii[33] all give values of $\Delta G_{a,aq} = -8.4$ kcal mol^{-1} at $T = 298$ K. Pokrovskii[33] points out a discrepancy between their values and those of Ruaya and Seward,[27] and argues that the data used by the latter group can be interpreted in multiple ways.

In contrast, the Henry's law constant of HCl in water appears to be less ambiguous. Clegg and Brimblecombe[34] report a value of $K_H = 1.84 \times 10^6$ mol^2 kg^{-2} atm^{-1} under ambient conditions. The following year, Clegg and Brimblecombe[24] reported values around 2.0×10^6 mol^2 kg^{-2} atm^{-1} for concentrations of HCl in solution between 0 and 200 mol kg^{-1} by using data from a variety of sources, while Brimblecombe and Clegg[26] recommend a value of 2.04×10^6 mol^2 kg^{-2} atm^{-1} at $T = 298$ K. Marsh and McElroy[23] calculated equilibrium constants for both the transfer of molecular HCl from the vapor to aqueous phase (dimensionless) and the dissociation of HCl in water (in units of mole dm^{-3}). Combining these values (*via* eqn (11) in their paper) and converting units results in $K_H = 1.85 \times 10^6$ mol^2 kg^{-2} atm^{-1}, which is very close to previous values, although Clegg and Brimblecombe[24] note that the disagreement grows at lower temperatures.

The simulation literature surrounding the HCl–water system is just as extensive; in the interest of brevity, the following summary will only be concerned with calculations involving the bulk aqueous system and bulk solvation (*i.e.*, studies dealing only with clusters or ice will be ignored). Molecular simulations of hydrogen chloride in water have mostly been performed with the molecular dynamics technique, including simulations from first-principles[35–41] and using empirical force fields,[30,42–45] including a study of HCl at the air–water interface using QM/MM techniques.[46] Some of these studies compute the p$K_{a,aq}$ of HCl in water,[30,42,43] others compute the potential of mean force,[44] while the rest examine the structure of the solvating water molecules around the ions. A few of the simulations were performed at elevated temperatures,[30,37,44] mostly near the critical temperature of water.

Less frequently, Monte Carlo approaches have also been used to examine the aqueous HCl system, although until this point all calculations employing this method have used empirical force fields to represent the solvated HCl molecule; this includes some work on the Gibbs free energy curves along the reaction coordinate to determine the most probable dissociation mechanism,[47] and other work using Monte Carlo simulations to reinterpret previous experimental data to determine the structure.[48,49]

In addition to molecular simulation, the Gibbs free energy of solvation of hydrogen chloride in water has been computed with various other techniques. Among these are QM/MM methods[50,51] and calculation from experimental data,[52] such as gas-phase proton affinities and aqueous p$K_{a,aq}$ values.[53] The structure of concentrated HCl solutions has also been determined by empirically fitting X-ray scattering data.[54]

In the above molecular simulation studies, no effort was made to compute the Gibbs free energy of aqueous solvation for HCl or its Henry's law constant. The goal of the current study is to compute these thermodynamic properties across a temperature range of 150 K ($T = 300$–450 K), through the use of first principles Monte Carlo simulations and quantum mechanical continuum solvation approaches. The chemical equilibria for the solvation and dissociation of gaseous HCl are given by:

$$\mathrm{HCl_{(g)}} \leftrightarrow \mathrm{H_{(aq)}}^{+} + \mathrm{Cl_{(aq)}}^{-} \tag{1}$$

$$\mathrm{HCl_{(g)}} \leftrightarrow \mathrm{HCl_{(aq)}} \tag{2}$$

$$\mathrm{HCl_{(aq)}} \leftrightarrow \mathrm{H_{(aq)}}^{+} + \mathrm{Cl_{(aq)}}^{-} \tag{3}$$

with the Henry's law constant of

$$K_H = \frac{c_{H^+} c_{Cl^-}}{p_{HCl}} \gamma_{HCl}{}^2 \tag{4}$$

where c_X is the concentration of species X in the aqueous phase, γ_{HCl} is the geometric mean activity coefficient of H$^+$and Cl$^-$ in solution, and p_{HCl} is the partial pressure of HCl over the solution.[26] It should be noted that other definitions of K_H can be found in the literature. Eqn (4) can be rewritten in terms of the Gibbs free energy changes associated with eqn (2) and (3):

$$K_H = \exp\left(-\frac{\Delta G_{comb}}{RT}\right)\frac{(c^{\ominus})^2}{p^{\ominus}} \tag{5}$$

$$\Delta G_{comb} = \Delta G_{trans} + \Delta G^o_{a,aq} \tag{6}$$

where ΔG_{trans}, $\Delta G^o_{a,aq}$, and ΔG_{comb} are the Gibbs free energy of transfer of molecular HCl (obtained from the ratio of number densities), the standard-state Gibbs free energy of acid dissociation in aqueous solution, and the Gibbs free energy of the combined solvation–acid dissociation process, respectively. $p^{\ominus}$ and $c^{\ominus}$ are the standard pressure and the standard concentration, respectively.

In this work, particle-based Monte Carlo simulations are carried out to compute ΔG_{trans}, and continuum solvation models are used to compute $\Delta G^o_{a,aq}$. Notice that ΔG_{trans} is not equivalent to the standard-state Gibbs free energy of transfer as the simulations are carried out at the equilibrium vapor pressure of HCl above the aqueous solution (in the case of the first-principles simulations) or at the equilibrium vapor pressure of the binary mixture (for the simulations with an empirical force field). Further details are given below, but in both cases the pressure is a function of the temperature. The standard-state Gibbs free energy of acid dissociation of HCl in aqueous solution is given by:

$$\Delta G^o_{a,aq} = G^o_{aq,H^+} + G^o_{aq,Cl^-} - G^o_{aq,HCl} \tag{7}$$

and $G^o_{aq,X}$ is defined as

$$G^o_{aq,X} = G^o_{g,X} + \Delta G^o_{S,X} \tag{8}$$

The first term in eqn (8) is the standard-state Gibbs free energy of the species in an ideal gas at 1 bar pressure, and the second term is the standard-state Gibbs free energy of solvation, *i.e.*, the Gibbs free energy of transfer of a species from the gas phase at a solute partial pressure of 1 bar to a 1 M ideal solution. The standard-state Gibbs free energy of solvation is expressed as

$$\Delta G^{\text{o}}_{\text{S,X}} = \Delta G^{*}_{\text{S,X}} + RT\ln\frac{RT}{pV^{*}} \qquad (9)$$

where the first term is the fixed-concentration Gibbs free energy of solvation, in other words, the Gibbs free energy of transfer of the solute from the gas phase with a solute concentration of 1 mol L^{-1} to 1 M solution. Here, we take $V^* = 1$ L mol^{-1} and $p = 1$ bar.

It is important to emphasize some notational conventions. $\Delta G^{\text{o}}_{\text{S,X}}$, the standard-state Gibbs free energy of solvation, and ΔG_{trans}, the Gibbs free energy of transfer, describe the transfer process of a molecule–ion from the gas phase to the liquid phase. However, they are labeled distinctly due to the fact that $\Delta G^{\text{o}}_{\text{S,X}}$ is always computed for the case of infinitely dilute gases and solutions and converted to standard-state conditions with the convention of an ideal gas at $P = 1$ bar and an ideal solution at $c = 1$ M, while ΔG_{trans} directly relates to an equilibrium constant and involves no ideality convention. In this manuscript, the quantities are also computed with different methods, making such a distinction even more useful. One similar quantity, ΔG_{comb}, indicates the combined process of the Gibbs free energy of transfer of HCl and its dissociation in the solvent (see eqn (6)).

The layout of the remainder of this paper is as follows. Section 2 describes the details of the particle-based Monte Carlo simulations and of the different methods for computing the standard-state Gibbs free energy of acid dissociation with an implicit solvation model. Section 3 presents the resulting Gibbs free energies of transfer from the vapor to the liquid phase at several temperatures, combines these with the standard-state Gibbs free energy of acid dissociation calculations to estimate the Gibbs free energy of the combined solvation–acid dissociation of HCl in water, and compares the results to experimental results in the literature. Section 4 summarizes the findings reported here.

2 Computational details

2.1 Gibbs free energy of transfer

2.1.1 First principles Monte Carlo simulations. In order to calculate the Gibbs free energy of transfer of molecular HCl from the gas to the aqueous phase, first principles Monte Carlo (FPMC) simulations[55,56] were run in the NVT-Gibbs ensemble[57,58] using the CP2K software.[59,60] The simulated system consisted of one HCl and 63 H_2O molecules in two boxes. Due to the expense of these simulations, water molecules were confined to the liquid-phase simulation box, *i.e.*, the gas phase is assumed to be ideal since the single HCl molecule does not interact with any other molecules. NVT-Gibbs ensemble simulations require particle transfer moves between the phases to equilibrate the chemical potential of a given species, volume moves to reach mechanical equilibrium, and translational, rotational, and conformational moves to reach thermal equilibrium. In the present FPMC simulations, the probabilities of performing a given move type were as follows: 50% to swap HCl between the boxes, 5% to change the volume of the boxes, and the remaining 45% was divided equally between molecular translations, rotations, and conformational changes of water molecules (with the bond length of HCl being held rigid). Because of the larger fraction of water molecules, 95% of the rotations and translations were attempted on water. Maximum displacements for molecular translations, rotations around the center of mass, conformational changes, and volume moves were adjusted during the equilibration period to give acceptance rates of $\approx 50\%$. Four independent simulations were carried out at each of four temperatures ($T = 300$, 350, 400, and 450 K), and the production periods consisted of 1000 Monte Carlo cycles, where each cycle consists of 64 FPMC moves.

In these FPMC simulations, the potential energy of the interacting system was computed using Kohn–Sham density functional theory (KS-DFT)[61] with the Becke–Lee–Yang–Parr (BLYP) exchange and correlation functionals,[62,63] a triple-ζ basis set with two polarization functions, and the norm-conserving Goedecker–Teter–Hutter pseudopotentials.[64] Use of a reference cell for the plane-wave grids allowed the use of a relatively low plane-wave cutoff of 280 Ry for the electronic density that has the benefit of giving fairly accurate liquid densities and Gibbs free energies of transfer for neat water.[56,65,66] Previous simulation studies have also shown qualitative agreement between plane-wave BLYP simulations and higher-level methods on small H_2O–HCl clusters at very low temperatures.[67,68]

As in previous FPMC simulations,[55,56] empirical biasing potentials are used for pre-sampling sequences[69,70] including molecular translations, rotations, and conformational changes within a single FPMC move and for configurational-bias swap moves.[71–73] The empirical biasing potentials were parameterized to reproduce the energy differences between configurations obtained with KS-DFT. These biasing potentials used Lennard-Jones (only on O and Cl) and Coulombic interactions of atomic sites for the intermolecular interactions ($\varepsilon/k_B = 120$ K for Cl and 89.3 K for O, $\sigma = 3.38$ Å for Cl and 3.19 Å for O, $q = -0.15$ $|e|$ for Cl and -0.784 $|e|$ for O). The Lorentz–Berthelot combining rules[74] were used for unlike interactions, and all interactions were truncated and shifted to zero at $r_{\text{cut}} = 6.0$ Å. Intramolecular parameters for harmonic bond stretching and bending were also fit for water ($r_{\text{OH}} = 0.983$ Å, $k_r/k_B = 1.181 \times 10^6$ K Å^{-2}, $\theta_{\text{HOH}} = 101.2^\circ$, and $k_\theta/k_B = 15.07$ K deg^{-2}), while HCl was kept rigid ($r_{\text{HCl}} = 1.35$ Å) throughout the simulations. To improve the statistics for the computation of ΔG_{trans}, a balancing factor[75,76] was added that changes the potential energy of HCl in the vapor phase and allows one to find HCl with appreciable probabilities in both phases throughout a simulation. This balancing factor was determined during a short pre-simulation ($\Delta\eta/k_B = 3600$ K at $T = 300$ K and 2700 K for the other three temperatures), and it is removed in the calculation of ΔG_{trans} from the ratio of number densities.[77]

2.1.2 Monte Carlo simulations with empirical force field. Gibbs ensemble Monte Carlo simulations were also run with an empirical force field (EFF) at the same four temperatures to assess the system-size dependence and to provide an additional data set. A two-site HCl model with Lennard-Jones and Coulomb potentials was fit to reproduce the experimental critical temperature and liquid density near the triple point (ε_{Cl}/k_B = 175 K, σ_{Cl} = 3.5 Å, $q_{Cl} = -0.17$ |e|, ε_H/k_B = 40 K, and σ_H = 2.1 Å). The TIP4P model[78] was used for water. The systems consisted of one HCl molecule and either 64, 128, or 500 water molecules. Approximately 5×10^4 cycles were used for equilibration, with another 2×10^5 cycles for production (where a cycle is N steps, with N being the total number of molecules in the system). In these simulations, the water molecules were also allowed to transfer between the two phases.

2.2 Standard-state Gibbs free energy of acid dissociation

In order to compute $\Delta G^o_{a,aq}$ *via* eqn (7), two different methods were employed here. Method SM-ref calculates $\Delta G^o_{a,aq}$ at different temperatures using experimental reference values for the gas-phase standard-state Gibbs free energy of acid dissociation and for the solvation Gibbs free energies of H^+ and Cl^- at 298 K. Method SM-cluster does not require any reference data but employs micro-solvated clusters in the continuum solvation model calculations.

2.2.1 Method SM-ref. One can rewrite eqn (7) as

$$\Delta G^o_{a,aq} = \Delta G^o_{a,g} + \Delta G^o_{S,H^+} + \Delta G^o_{S,Cl^-} - \Delta G^o_{S,HCl} \tag{10}$$

where the first term on the right side is the standard-state Gibbs free energy of acid dissociation of HCl in the gas phase at 1 bar. The temperature dependence of this term is calculated by:

$$\Delta G^o_{a,g}(T) = \Delta G^o_{a,g,ref}(298) + \Delta G^o_{a,g,calc}(T) - \Delta G^o_{a,g,calc}(298) \tag{11}$$

where the first term is the experimental standard-state gas-phase Gibbs free energy of acid dissociation at 298 K.[79] The second and third terms are obtained from the $G^o_{a,g}$ of individual compounds calculated by Gaussian09[80] at the gas/M06-2X/MG3S level of theory.[81–83]

The standard-state Gibbs free energy of solvation of HCl at different temperatures is obtained by eqn (9) from the fixed-concentration Gibbs free energy of solvation, $\Delta G^*_{S,HCl}(T)$, calculated by the SM8T solvation model[84,85] at the SM8T/M06-2X/6-31G(d)//gas/M06-2X/MG3S level of theory using a locally modified version of Gaussian 09. Note that SM8T at 298 K is identical to SM8.[86] The standard-state Gibbs free energies of solvation of the proton and chloride anion are obtained from the corresponding fixed-concentration Gibbs free energies of solvation calculated by the following equation

$$\Delta G^*_{S,X}(T) = \Delta G^*_{S,X,ref}(298) + \Delta G^*_{S,X,calc}(T) - \Delta G^*_{S,X,calc}(298) \tag{12}$$

where X = H^+ and Cl^-. The first term in eqn (12) is the reference fixed-concentration solvation Gibbs free energies of the proton (-265.9 kcal mol^{-1}) and the chloride anion (-74.6 kcal mol^{-1}) at T = 298 K obtained using data from Tissandier *et al.*[87] The last two terms in eqn (12) are calculated by SM8T/M06-2X/6-31G(d).

2.2.2 Method SM-cluster. The standard state Gibbs free energy of solute X in aqueous solution, $G^o_{aq,X}$, can be computed as follows

$$G^o_{aq,X} = G^o_{aq,Xn_X} - n_X G^o_{aq,H_2O} - n_X RT\ln(c_{wat}) \tag{13}$$

where the notation Xn_X denotes a supersolute with n_X water molecules added explicitly to the molecule X. The last term of eqn (13) is the concentration term, equal to $\approx$2.38 kcal mol^{-1} for n_X = 1 at 298 K. The quantity $c_{wat} = \rho_{wat}/M_{wat}$ is the concentration of liquid water in mol L^{-1} ($c_{wat} \approx$ 55.3 M at 298 K).

We used n_X = 0, 1, and 3 for HCl, Cl^-, and H^+, respectively, which is equivalent to studying the reaction

$$HCl + 4H_2O \Leftrightarrow H_7O_3{}^+ + H_2O{\cdot}Cl^- \tag{14}$$

The quantities G^o_{aq} on the right hand side of eqn (13) were calculated *via* eqn (8), using the $G^o_{g,X}$ energies of individual compounds computed with Gaussian09 by the gas/M06-2X/MG3S method and the fixed-concentration Gibbs free energies of solvation $\left(\Delta G^*_{S,X}\right)$ obtained from SM8T/M06-2X/6-31G(d)//gas/M06-2X/MG3S.

It is difficult to estimate the reliability of eqn (8) with the SM8 solvation model for clusters, but we note that previous tests[88,89] of similar models for Gibbs free energies of aqueous solvation of clustered ions gave mean unsigned errors in the range 3.3–5.3 kcal mol^{-1}. Note though that eqn (10) involves both a proton and a chloride. In such a case the proton and chloride hydration Gibbs free energies could be combined together to give the hydration Gibbs free energy of a fully dissociated HCl molecule (at infinite dilution). This would not have any material effect on the resulting total numbers, but it would avoid references to estimated single-ion quantities and avoid the portion of the error associated with separating Gibbs free energy values pertaining to the neutral species into contributions from oppositely charged ions and with the unknown surface potential of water and its temperature dependence (the surface contributions to cations and anions will cancel out for neutral species, whether or not they are dissociated). Therefore the errors might actually be less than those estimated based on single-ion values.

3 Results and discussion

The Gibbs free energies of transfer for molecular HCl determined from the Gibbs ensemble simulations with the BLYP functionals or the EFF are summarized in Table 1. The uncertainties for the Monte Carlo EFF and BLYP simulations are about 0.1 and 1 kcal mol^{-1}, respectively. These estimates are the standard errors of the mean taken from four independent simulations for each model–temperature combination. Values for EFF/64 and BLYP/63 (where the number after the solidus is the number of water molecules in the simulation) at T = 300 K are not provided because for the former the simulation box for the liquid phase became smaller than allowed by the potential truncation and for the latter the number of successful swap moves was deemed too small. Even at the three higher temperatures, long periods without successful swap moves were

Table 1 Gibbs free energies of transfer (in kcal mol^{-1}) for molecular HCl from the vapor phase to aqueous solution computed using the BLYP functionals and the EFF for different system sizes

Model/N_{H_2O} T [K]	BLYP/63	EFF/64	EFF/128	EFF/500
300	N/A	N/A	0.6	0.8
350	1.9	1.1	1.0	1.0
400	2.9	1.2	1.2	1.1
450	3.6	1.0	1.2	1.2

observed, but these were interspersed by periods with relatively high frequencies of particle transfers. Analysis of the trajectories showed that the HCl molecule can become "trapped" (*i.e.*, the acceptance rate for particle transfer moves becomes very low) when it acts as the donor of a strong hydrogen bond (as indicated by a shortening of the $H\cdots O$ distance by ≈ 0.2 Å, from around 1.8 to about 1.6 Å) to a neighboring water molecule. It should be noted that this trapping was only observed in some BLYP simulations and not those performed with an empirical force field. Such a strongly-bound configuration may be the precursor for a proton transfer event but acid dissociation is not allowed in the present MC simulations. In addition, different types of local solvation environments have also been observed for undissociated HNO_3 in aqueous solution by EXAFS and first principles molecular dynamics.[90] The EFF simulations indicate that the system size effects in ΔG_{trans} are negligible. The FPMC simulations exhibit a larger temperature dependence with a slope of about 20 cal mol^{-1} K^{-1}, whereas the slope is about one order of magnitude smaller for the EFF simulations.

Table 2 provides the standard-state Gibbs free energy of acid dissociation of HCl in aqueous solution calculated with methods SM-ref and SM-cluster, as well as some of the experimental data.[33] At $T = 300$ K and $p = 1$ bar, both computational methods predict $\Delta G_{a,aq}$ that is slightly more favorable than deduced from experiment. The SM-ref and SM-cluster methods yield temperature derivatives ($\Delta G_{a,aq}/\Delta T$) of 10 and 20 cal mol^{-1} K^{-1}, respectively, whereas the experimental estimate is about 30 cal mol^{-1} K^{-1}.[33] However, as discussed in the Introduction, there is considerable spread in experimental values caused by the difficulty of measuring the association constant of a strong acid as noted by Clegg and Brimblecombe.[24]

Table 2 The standard-state Gibbs free energy of acid dissociation (in kcal mol^{-1}) for molecular HCl and $pK_{a,aq}$. The experimental values are estimated from Fig. 1 in Pokrovskii[33]

	SM-ref		SM-cluster		Exp.
T [K]	$\Delta G^{o}_{a,aq}$	$pK_{a,aq}$	$\Delta G^{o}_{a,aq}$	$pK_{a,aq}$	$\Delta G^{o}_{a,aq}$
300	−9.7	−7.08	−10.2	−7.45	−8.4
350	−9.3	−5.83	−9.2	−5.75	−7.2
400	−8.8	−4.83	−8.2	−4.47	−5.5
450	−8.3	−4.04	−7.1	−3.46	−3.8

Table 3 The Gibbs free energies of the combined solvation–acid dissociation process for HCl in water, in kcal mol^{-1}, calculated using eqn (6) and the corresponding Henry's law constants. The Henry's law constants are in units of mol^2 kg^{-2} atm^{-1}

			SM-ref		SM-cluster	
T [K]		Exp.[23]	EFF	BLYP	EFF	BLYP
300	ΔG_{comb}	−8.6	−8.9	N/A	−9.4	N/A
	$K_H/10^6$	1.86	3.0	N/A	7.3	N/A
350	ΔG_{comb}	−7.6	−8.3	−7.4	−8.2	−7.3
	$K_H/10^4$	5.97	16	4.4	13	3.7
400	ΔG_{comb}	N/A	−7.7	−6.0	−7.0	−5.3
	$K_H/10^2$	N/A	170	18	71	7.9
450	ΔG_{comb}	N/A	−7.1	−4.7	−6.0	−3.5
	$K_H/10$	N/A	300	20	80	5.2

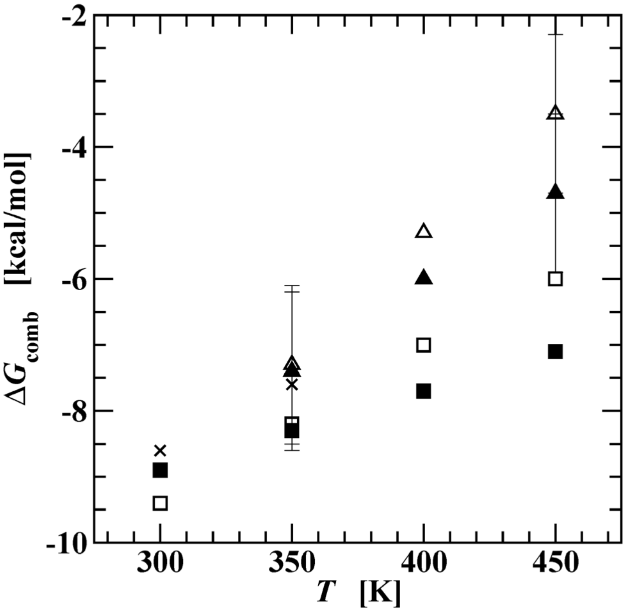

Fig. 1 The Gibbs free energy of the combined solvation–acid dissociation of HCl in water computed by eqn (6), taken from Table 3. The experimental,[23] BLYP/SM-ref, BLYP/SM-cluster, EFF/SM-ref, and EFF/SM-cluster results are depicted with X's, filled triangles, open triangles, filled squares, and open squares, respectively.

The primary results of this paper, namely $\Delta G_{comb}(T)$ for a wide range of temperatures, are shown numerically in Table 3 and graphically in Fig. 1. For comparison, the experimental data taken from Marsh and McElroy[23] are also provided. We feel justified in using this data set for comparison because it is the most complete data set available, and questions were raised primarily for the data below temperatures in which we are interested in here. Unfortunately, no data could be found for temperatures exceeding the normal boiling point of water. The agreement between experimental and computational predictions is very satisfactory with the predicted values at the two lowest temperatures falling within 1 kcal mol^{-1} of the best experimental estimate. The predictions using the BLYP functional for ΔG_{trans} and either method for $\Delta G^{o}_{a,aq}$ are even closer to the experimental value at $T = 350$ K. This gives us confidence in our predictions at higher temperatures for which experimental data are not available. Assuming that the temperature dependence of the experimental data at the lower temperatures is a good guide, the BLYP/SM-ref combination appears to give the most accurate predictions. The EFF/SM-cluster combination also yields a good temperature dependence, but the ΔG_{comb} values are too favorable by about 0.7 kcal mol^{-1}. The BLYP/SM-cluster and EFF/SM-ref combinations either over- or underestimated the temperature dependence but agree quite well with the experimental data at ambient conditions (using a linear extrapolation for the BLYP/SM-cluster method).

It can be seen in Tables 2 and 3 that the agreement between the simulated and experimental results increases for the combined Gibbs free energy compared to that seen in the standard-state Gibbs free energy of acid dissociation. This implies a fortuitous cancelation of errors, although the improvement is still within the estimated uncertainty for each method. In addition, the spread in the calculated results increases with increasing temperatures (by about 3 kcal mol^{-1} over 100 K).

For completeness, the K_{H} values are also listed in Table 3 because these allow for easier comparison with previous experimental data. As noted in the Introduction, Marsh and McElroy[23] and Clegg and Brimblecombe[24,26,34] report K_{H} values around 2×10^6 mol^2 kg^{-2} atm^{-1} at ambient conditions. The predictions based on EFF values for $\Delta G_{\mathrm{trans}}$ yield a slight over estimation of K_{H} at T = 300 K, and the four computational methods bracket the experimental value at 350 K.

4 Summary and conclusions

We report the Gibbs free energy of the combined solvation–acid dissociation of hydrogen chloride in aqueous solution; the values were obtained by using a combined molecular simulation and implicit solvation model approach. This was done by dividing the total Gibbs free energy change into two distinct steps. The Gibbs free energy change in the first step, transfer of molecular HCl from the vapor phase into liquid water, was calculated *via* Monte Carlo simulation in the Gibbs ensemble using either Kohn–Sham density functional theory or an empirical force field to describe the interactions. The second step, dissociation of molecular HCl in liquid water, was examined *via* a continuum solvation model utilizing either experimental reference data or microsolvated clusters. The calculations were performed at four different temperatures ranging from 300 to 450 K. All four combined methods yield predictions with satisfactory accuracy, but the combination using the BLYP functional for the molecular simulations and the reference data for the solvation model stands out in accuracy with a value of ΔG_{solv} = −7.4 kcal mol^{-1} at T = 350 K (only 0.2 kcal mol^{-1} deviation from the best estimate based on various experimental data) and a temperature dependence of about 30 cal mol^{-1} K^{-1}. With this validation in hand, the combined molecular simulation/implicit solvation approach is used to predict experimentally inaccessible quantities relating to the solvation of strong acids in water and to provide microscopic-level information on local solvation structure. Such solvation processes have wide applicability in chemical synthesis, environmental chemistry, and atmospheric science.

Acknowledgements

MJM gratefully acknowledges support from a National Science Foundation International Research grant (OISE-0853294). Part of this work was performed during a Peace Corps assignment of MJM at the University of Dschang. Additional financial support from the National Science Foundation (CBET-0756641 and CBET-1159837) and the U.S. Army Research Laboratory under Grant No. W911NF09-100377. Part of this work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory (LLNL) under contract No. W-7405-Eng-48. CJM was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy. This work was also supported in part by the NSF under CDI Grant No. CHE-1051396. Computer resources were provided by Livermore Computing and the Minnesota Supercomputing Institute.

References

1 A. Gutberlet, G. Schwaab, Ö. Birer, M. Masia, A. Kaczmarek, H. Forbert, M. Havenith and D. Marx, *Science*, 2009, **324**, 1545–1548.
2 M. J. Molina, T.-L. Tso, L. T. Molina and F. C.-Y. Wang, *Science*, 1987, **238**, 1253–1257.
3 B. J. Gertner and J. T. Hynes, *Science*, 1996, **271**, 1563–1566.
4 J. P. Devlin, N. Uras, J. Sadlej and V. Buch, *Nature*, 2002, **417**, 269–271.
5 E. M. Knipping, M. J. Lakin, K. L. Foster, P. Jungwirth, D. J. Tobias, R. B. Gerber, D. A. Dabdub and B. J. Finlayson-Pitts, *Science*, 2000, **288**, 301–306.
6 P. Kritzer, *J. Supercrit. Fluids*, 2004, **29**, 1–29.
7 S. J. Bates and H. D. Kirschman, *J. Am. Chem. Soc.*, 1919, **41**, 1991–2001.
8 H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, 1933, **55**, 2179–2193.
9 R. Triolo and A. H. Narten, *J. Chem. Phys.*, 1975, **63**, 3624–3631.
10 A. Botti, F. Bruni, S. Imberti, M. A. Ricci and A. K. Soper, *J. Chem. Phys.*, 2004, **121**, 7840–7848.
11 D. H. Powell, G. W. Neilson and J. E. Enderby, *J. Phys.: Condens. Matter*, 1993, **5**, 5723–5730.
12 J. S. Dunn and E. K. Rideal, *J. Chem. Soc., Trans.*, 1924, **125**, 676–984.
13 F. C. Zeisberg, *Chem. Metall. Eng.*, 1925, **32**, 326–327.
14 W. F. K. Wynne-Jones, *J. Chem. Soc.*, 1930, 1064–1071.
15 G. Åkerlöf and J. W. Teare, *J. Am. Chem. Soc.*, 1937, **59**, 1855–1868.
16 J. J. Fritz and C. R. Fuget, *Ind. Eng. Chem.*, 1956, **1**, 10–12.
17 R. H. Perry and D. W. Green, *Perry's Chemical Engineers' Handbook*, McGraw-Hill, New York, 6th edn, 1984.
18 T. Sako, T. Hakuta and H. Yoshitome, *J. Chem. Eng. Data*, 1985, **30**, 224–228.
19 N. Elm, J. Zipprian and K. Schaber, *Fluid Phase Equilib.*, 2001, **189**, 163–178.
20 T. Sako, T. Hakuta and H. Yoshitome, *J. Chem. Eng. Jpn.*, 1984, **17**, 381–388.
21 T.-J. Chou and A. Tanioka, *Fluid Phase Equilib.*, 1997, **137**, 17–32.

22 E. C. Chen and G. McGuire, *AIChE J.*, 1970, **16**, 686–687.
23 A. R. W. Marsh and W. J. McElroy, *Atmos. Environ.*, 1985, **19**, 1075–1080.
24 S. L. Clegg and P. Brimblecombe, *Atmos. Environ.*, 1986, **20**, 2483–2485.
25 J. I. Partanen, P. M. Juusola, K. P. Vahteristo and A. J. G. de Mendonca, *J. Solution Chem.*, 2007, **36**, 39–59.
26 P. Brimblecombe and S. L. Clegg, *J. Atmos. Chem.*, 1988, **7**, 1–18.
27 J. Ruaya and T. Seward, *Geochim. Cosmochim. Acta*, 1987, **51**, 121–130.
28 R. A. Robinson, *Trans. Faraday Soc.*, 1936, **32**, 743–744.
29 H. C. Helgeson, *Am. J. Sci.*, 1969, **267**, 729–804.
30 P. B. Balbuena, K. P. Johnston and P. J. Rossky, *J. Phys. Chem.*, 1996, **100**, 2716–2722.
31 R. E. Mesmer, W. L. Marshall, D. A. Palmer, J. M. Simonson and H. F. Holmes, *J. Solution Chem.*, 1988, **17**, 699–718.
32 P. C. Ho, D. A. Palmer and M. S. Gruszkiewicz, *J. Phys. Chem. B*, 2001, **105**, 1260–1266.
33 V. A. Pokrovskii, *Geochim. Cosmochim. Acta*, 1999, **63**, 1107–1115.
34 S. L. Clegg and P. Brimblecombe, *Atmos. Environ.*, 1985, **19**, 465–470.
35 K. E. Laasonen and M. L. Klein, *J. Phys. Chem. A*, 1997, **101**, 98–102.
36 D. Marx, M. E. Tuckerman, J. Hutter and M. Parrinello, *Nature*, 1999, **397**, 601–604.
37 A. J. Sillanpää and K. Laasonen, *Phys. Chem. Chem. Phys.*, 2004, **6**, 555–565.
38 D. Asthagiri, L. R. Pratt and J. D. Kress, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 6704–6708.
39 J. M. Headrick, E. G. Diken, R. S. Walters, N. I. Hammer, R. A. Christie, J. Cui, E. M. Myshakin, M. A. Duncan, M. A. Johnson and K. D. Jordan, *Science*, 2005, **308**, 1765–1769.
40 T. Marakhtina, J. Heuft, E. J. Meijer and D. Sebastiani, *ChemPhysChem*, 2006, **7**, 2578–2584.
41 H.-S. Lee and M. E. Tuckerman, *J. Phys. Chem. A*, 2009, **113**, 2144–2151.
42 M. Čuma, U. W. Schmitt and G. A. Voth, *Chem. Phys.*, 2000, **258**, 187–199.
43 K. P. Johnston, G. E. Bennett, P. B. Balbuena and P. J. Rossky, *J. Am. Chem. Soc.*, 1996, **118**, 6746–6752.
44 A. A. Chialvo, P. T. Cummings and J. M. Simonson, *J. Chem. Phys.*, 2000, **113**, 8093–8100.
45 T. Ishiyama and A. Morita, *J. Phys. Chem. A*, 2007, **111**, 9277–9285.
46 D. Ardura and D. J. Donaldson, *Phys. Chem. Chem. Phys.*, 2009, **11**, 857–863.
47 K. Ando and J. T. Hynes, *J. Phys. Chem. B*, 1997, **101**, 10464–10478.
48 I. Harsányi and L. Pusztai, *J. Phys.: Condens. Matter*, 2005, **17**, S59–S65.
49 A. Botti, F. Bruni, M. A. Ricci and A. K. Soper, *J. Chem. Phys.*, 2006, **125**, 014508.
50 H. Sato and F. Hirata, *J. Am. Chem. Soc.*, 1999, **121**, 3460–3467.
51 T. Shoeib, G. D. Ruggiero, K. W. M. Siu, A. C. Hopkinson and I. H. Williams, *J. Chem. Phys.*, 2002, **117**, 2762–2770.
52 A. Ben-Naim, *J. Phys. Chem.*, 1985, **89**, 3791–3798.
53 R. G. Pearson, *J. Am. Chem. Soc.*, 1986, **108**, 6109–6114.
54 N. Agmon, *J. Phys. Chem. A*, 1998, **102**, 192–199.
55 I.-F. W. Kuo, C. J. Mundy, M. J. McGrath, J. I. Siepmann, J. VandeVondele, M. Sprik, J. Hutter, B. Chen, M. L. Klein, F. Mohamed, M. Krack and M. Parrinello, *J. Phys. Chem. B*, 2004, **108**, 12990–12998.
56 M. J. McGrath, J. I. Siepmann, I.-F. W. Kuo, C. J. Mundy, J. VandeVondele, J. Hutter, F. Mohamed and M. Krack, *J. Phys. Chem. A*, 2006, **110**, 640–646.
57 A. Z. Panagiotopoulos, *Mol. Phys.*, 1987, **61**, 813–826.
58 A. Z. Panagiotopoulos, N. Quirke, M. Stapleton and D. J. Tildesley, *Mol. Phys.*, 1988, **63**, 527–545.
59 CP2K Developers, *Open Source Molecular Dynamics*, Development Version, http://www.cp2k.org.
60 J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, *Comput. Phys. Commun.*, 2005, **167**, 103–128.
61 W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133–A1138.
62 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.
63 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785–789.
64 S. Goedecker, M. Teter and J. Hutter, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 1703–1710.
65 M. J. McGrath, J. I. Siepmann, I.-F. W. Kuo, C. J. Mundy, J. VandeVondele, J. Hutter, F. Mohamed and M. Krack, *ChemPhysChem*, 2005, **6**, 1894–1901.
66 M. J. McGrath, J. I. Siepmann, I.-F. W. Kuo and C. J. Mundy, *Mol. Phys.*, 2006, **104**, 3619–3626.
67 M. Masia, H. Forbert and D. Marx, *J. Phys. Chem. A*, 2007, **111**, 12181–12191.
68 U. F. T. Ndongmouo, M.-S. Lee, R. Rousseau, F. Baletto and S. Scandolo, *J. Phys. Chem. A*, 2007, **111**, 12810–12815.
69 R. Iftimie, D. Salahub, D. Wei and J. Schofield, *J. Chem. Phys.*, 2000, **113**, 4852–4862.
70 L. D. Gelb, *J. Chem. Phys.*, 2003, **118**, 7747–7750.
71 J. I. Siepmann and D. Frenkel, *Mol. Phys.*, 1992, **75**, 59–70.
72 G. C. A. M. Mooij, D. Frenkel and B. Smit, *J. Phys.: Condens. Matter*, 1992, **4**, L255–L259.
73 B. Smit, S. Karaborni and J. I. Siepmann, *J. Chem. Phys.*, 1995, **102**, 2126–2140.
74 M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids*, Oxford University Press, Oxford, 1987.
75 A. P. Lyubartsev, A. A. Martsinovski, S. V. Shevkunov and P. N. Vorontsov-Velyaminov, *J. Chem. Phys.*, 1992, **96**, 1776–1783.
76 B. Chen and J. I. Siepmann, *J. Phys. Chem. B*, 2006, **110**, 3555–3563.
77 M. G. Martin and J. I. Siepmann, *Theor. Chem. Acc.*, 1998, **99**, 347–350.
78 W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey and M. L. Klein, *J. Chem. Phys.*, 1983, **79**, 926–935.

79 *National Institute of Standards and Technology Chemistry Webbook*, http://webbook.nist.gov/chemistry/.

80 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 Revision A.1*, Gaussian Inc., Wallingford, CT, 2009.

81 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

82 Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.*, 2008, **41**, 157–167.

83 B. J. Lynch, Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2003, **107**, 1384–1388.

84 A. C. Chamberlin, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2006, **110**, 5665–5675.

85 A. C. Chamberlin, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2008, **112**, 8651–8655.

86 A. V. Marenich, R. M. Olson, C. P. Kelly, C. J. Cramer and D. G. Truhlar, *J. Chem. Theory Comput.*, 2007, **3**, 2011–2033.

87 M. D. Tissandier, K. A. Cowen, W. Y. Feng, E. Gundlach, M. H. Cohen, A. D. Earhart and J. V. Coe, *J. Phys. Chem. A*, 1998, **102**, 7787–7794.

88 C. P. Kelly, C. J. Cramer and D. G. Truhlar, *J. Chem. Theory Comput.*, 2005, **1**, 1133–1152.

89 C. P. Kelly, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2006, **110**, 16066–16081.

90 T. Lewis, B. Winter, A. C. Stern, M. D. Baer, C. J. Mundy, D. J. Tobias and J. C. Hemminger, *J. Phys. Chem. B*, 2011, **115**, 9445–9451.