Calculating the acidity of silanols and related oxyacids in aqueous solution

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Abstract—Ab initio molecular orbital theory was used to calculate deprotonation energies and enthalpies ($\Delta E_{d}$, $\Delta H_{d}$) of oxyacid monomers and oligomers. Results were interpreted with reference to current phenomenological models for estimating metal-oxide surface acidities. The ultimate goal is to predict surface acidities using the ab initio method.

We evaluated contributions to $\Delta E_{d}$ and $\Delta H_{d}$ from the electrostatic potential at the proton, electronic relaxation, geometric relaxation, solvation, and polymerization for the neutral-charge gas-phase molecules H$_2$O, CH$_3$OH, HCOOH, Si$_3$N$_4$, SiOH, Si$_2$O$_3$H, H$_3$PO$_4$, P$_2$O$_5$H$_4$, H$_2$SO$_4$, HSO$_3$, HOCl, HClO$_4$, Ge(OH)$_4$, As(OH)$_3$, and AsO$_2$(OH)$_3$. $\Delta E_{d}$, gas calculated at the modest 6-31G* HF theory level correlates well with experimental $pK_a$ in solution, because hydration enthalpies for the acid anions ($\Delta H_{hyd}$, A$^-$) are closely proportional to $\Delta E_{d}$, gas. That is, anion interaction energies with water in aqueous solution and with H$^+$ in the gas phase are closely correlated.

Correction for differential hydration between an acid and its conjugate base permits generalization of the $\Delta E_{d}$, gas – $pK_a$ correlation to deprotonation reactions involving charged acids. Thus, stable protonated, neutral, and deprotonated species Si(OH)$_3$(OH)$^+$, Si(OH)$_2^-$, Si(OH)$_3$O$^-$, and Si(OH)$_4$O$^{2-}$ have been characterized, and solution $pK_a$'s for Si(OH)$_3$(OH)$_3$ and Si(OH)$_2$O$^{2-}$ were estimated, assuming that the charged species (Si(OH)$_3$(OH)$_3$)$^+$, Si(OH)$_2$O$^{-}$) fit into the same $\Delta E_{d}$, gas – $pK_a$ correlation as do the neutral acids. The correlation yields a negative $pK_a$ ($\approx -5$) for Si(OH)$_3$(OH)$_3$. Calculated $\Delta E_{d}$, gas also correlates well with the degree of O under-bonding evaluated using Brown’s bond-length based approach. $\Delta E_{d}$, gas increases along the series HClO$_4$ – Si(OH)$_4$, mainly because of increasingly negative potential at the site of the proton, not because of differing electronic or geometric relaxation energies. Thus, $pK_a$ can be correlated with underbondings or local electrostatic energies for the monomers, partially explaining the success of phenomenological models in correlating surface $pK_a$ of oxides with bond-strengths.

Accurate evaluation of $\Delta H_{hyd}$, gas requires calculations with larger basis sets, inclusion of electron correlation effects, and corrections for vibrational, rotational, and translational contributions. Density functional and 2nd-order Møller-Plesset results for deprotonation enthalpies match well against higher-level G2(MP2) calculations.

Direct calculation of solution $pK_a$ without resorting to correlations is presently impossible by ab initio methods because of inaccurate methods to account for solvation. Inclusion of explicit water molecules around the monomer immersed in a self-consistent reaction field (SCRF) provides the most accurate absolute hydration enthalpy ($\Delta H_{hyd}$) values, but IPCM values for the bare acid (HA) and anion (A$^-$) give reasonable values of $\Delta H_{hyd}$, A$^-$ – $\Delta H_{hyd}$, HA values with much smaller computational expense.

Polymers of silicate are used as model systems that begin to approach solid silica, known to be much more acidic than its monomer, Si(OH)$_4$. Polymerization of silicate or phosphate reduces their gas-phase $\Delta E_{d}$, gas relative to the monomers; differences in the electrostatic potential at H$^+$, electronic relaxation and geometric relaxation energies all contribute to the effect. Internal H-bonding in the dimers results in unusually small $\Delta E_{d}$, gas which is partially counteracted by a reduced $\Delta H_{hyd}$. Accurate representation of hydration for oligomers persists as a fundamental problem in determining their solution $pK_a$, because of the prohibitive cost involved in directly modeling interactions between many water molecules and the species of interest. Fortunately, though, the local contribution to the difference in hydration energy between the neutral polymeric acid and its anion seems to stabilize for a small number of explicit water molecules. Copyright © 2000 Elsevier Science Ltd

1. INTRODUCTION

The surface charging properties and surface reactivities of minerals are often interpreted using a surface complexation model, in which reactive species on the mineral surfaces are hypothesized and their properties determined by fitting to experimental data (Parks, 1967; Schindler and Stumm, 1987). Several approaches have been developed to obtain the properties of these surface complexes using theory: (i) either a phenomenological model, whose parameters are ultimately fitted to experiment (Yoon et al., 1979; Bleam, 1993; Sverjensky, 1994; Sverjensky and Sahai, 1996; Hiemstra et al., 1989, Hiemstra et al., 1996); or (ii) nonempirical first-principles theory, employing approximate quantum methods (Goniakowski, et al., 1993) or pair potential approaches (Wasserman, et al., 1999). Other quantum mechanical approaches have evaluated deprotonation energies for gas phase systems, and have then determined aqueous $pK_a$’s using linear free-energy correlations (Rustad et al., 1996; Rustad et al., 1998; Rustad et al., 1999).

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In the phenomenological theories, much of the variation in acidity is correlated with changes in the ratio of the metal-oxygen bond strength to the metal-oxygen or metal-proton bond length. The bond strength is defined either using the original Pauling (1940) formulation as ion charge \( (Z) \) divided by coordination number \( (CN) \), or using the bond-strength vs. bond-length relationships developed by Brown and Altermatt (1985). Bleam (1993) has shown that for many species the correlation with experiment is just as good if the Brown bond-strength alone is used without invoking the metal-oxygen bond length. There are invariably some species which are anomalous, for which additional parameters must be introduced to obtain agreement with experiment. The most important of these are quartz and amorphous silica, whose surface acidities seem to be seriously underestimated by a one parameter approach. Based on their model for the change in solvation energy of the protonation reaction, Sverjensky (1994) and Sverjensky and Sahai (1996) introduced an additional dependence of surface \( pK_a \) on the dielectric constant of the solid, which is much smaller for quartz than for most all other minerals. Hiemstra et al. (1996) focused instead upon presumed differences in local solvation of the surface ionic groups between quartz and other minerals.

Rustad et al. (1998) have approached this problem at an atomistic level, but have employed molecular mechanics with pair potential force-fields and have relied upon linear free-energy relationships (LFER) to relate gas-phase deprotonation energies to solution \( pK_a \)'s. For example, they found that using their force-field approach, a protonated silicic acid molecule, \( \text{Si(OH)}_3\text{(OHH)}_2^{1+} \), surrounded by 8 water molecules was intrinsically unstable. However, we will show below that quantum mechanical calculations predict \( \text{Si(OH)}_3\text{(OHH)}_2^{1+} \) plus 4 or 8 water molecules to be a well-defined and locally stable species, i.e., it corresponds to a local minimum on the energy surface. They also found that using their calculated energies for a bare \( \text{Si(OH)}_3\text{(OHH)}_2^{1+} \) ion, they obtained much too positive a solution \( pK_a \) using the LFER. This was a result of their failure to recognize the difference in hydration energy effects for the deprotonation of \( \text{Si(OH)}_3 \) versus \( \text{Si(OH)}_2\text{(OHH)}_2^{1+} \), as we will show later in this paper. In their study on the acidity of trivalent, hexaquo ions (Rustad, et al., 1999), they obtained good results using a LFER approach because all the reactions studied had the same hydration energy effects.

Wasserman et al. (1999) have developed a periodic 2D approach to the surface acidity problem, again based upon a potential approach. Giordano et al. (1998) have recently addressed the problem of dissociation of water on a MgO surface using a first-principles density functional approach. They found that dissociation of water was favored, in agreement with experiment, if sufficient water molecules were available on the surface.

Nortier et al. (1997) have studied surface acidity using a cluster model and the Hartree-Fock method, although at a fairly low basis set level, without geometry optimization and using smaller clusters then considered here, e.g., only the monomer \( \text{Si(OH)}_4 \) as their model for the silica surface. Nevertheless, their work established that the calculated \( \Delta E_{d,gas} \) correlated strongly with the potential at the site of the proton, which in turn correlated strongly with the electrostatic potential from model charge-distributions. We will show results confirming these conclusions later in this paper.

Experimental values for acid dissociation constants in water of common oxyacids are available from a number of sources (Pitzer, 1937; Jolly, 1991; Corbridge, 1990). For silicic acids dissociation constants have been obtained by Seward (1974), Busey and Mesmer (1977), Sjoberg, et al. (1981) and Sjoberg, et al. (1985). \( pH \) values of zero surface charge and inferred surface acid dissociation constants have been tabulated by Parks (1967) and Schindler and Stumm (1987).

There have also been several theoretical studies of the acidity of various T-O-H functional groups in the gas-phase, which have lead to an understanding of differences between deprotonation energies for C-O-H and Si-O-H groups (Sauer and Alhrichs, 1990; Curtiss et al., 1991) and for monomeric and oligomeric silicate Si-O-H groups (Sauer and Hill, 1994). Calculated energies were compared with experimental values obtained directly from gas-phase experiments or with values estimated from spectroscopic results such as \( \text{OH} \) stretching frequencies. Experimental values for \( \Delta H_{d,gas} \) are available for many weak acids, but only for a few that are relevant to this paper. For \( H_2O, CH_3OH, HOOCOH, \) and \( H_2SO_4 \) the experimental \( \Delta H_{d,gas} \) values are 390.8, 381.4, 345.2 and 309.6 kcal/mol (Saur and Alhrichs, 1990; Blades et al., 1995), with uncertainties of a few tenths of a kcal/mol. \( \Delta E_{d,gas} \) have also been calculated at very high levels for the hypohalous acids (Glukhovtsev et al., 1996) and for perchloric, sulfuric and related acids (Otto et al., 1997). A very useful scheme for decomposing deprotonation energies into components was developed earlier by Siggel and Thomas (1986) and has been used by several researchers.

Information on \( \Delta H_{\text{pK}_a,\text{gas}} \) for neutral acids and their anions is potentially available from gas-phase measurements, but the experiments are difficult and results have been obtained for only a few anions and with very few waters of hydration. For example, Blades et al. (1995), Blades et al. (1996) have obtained hydration free energies \( (\Delta G_{\text{h}_0}) \) for a number of phosphate anions and varying small numbers of waters. Calculations by Wu and Houk (1993) with 6-31+G* Hartree-Fock geometries and 4th order Moller-Plesset energies reproduce the experimental results of Blades et al. (1995), Blades et al. (1996) reasonably well. The fragmentary nature of the data prevents reliable extrapolation of these hydration free energies for small numbers of waters to bulk hydration free energies, although such a procedure has been carried out for the proton where \( \Delta G_{\text{h}_0} \) data is more complete (Tissandier, 1998). However, even with fragmentary data some interesting points emerge. Blades et al. (1995) have noted that their experimental hydration free energies for addition of the 1st molecule of water to various oxyanions correlate very well with the experimental proton affinities of these oxyanions (their Fig. 5). We will show a similar correlation in this paper.

There have recently been some calculations of solution acidities which combine high-level quantum mechanical calculation of \( \Delta E_{d,gas} \) with calculated hydration enthalpies of acid and conjugate base, obtained within a polarizable continuum approximation (Amekraz et al. 1996; Wiiberg et al., 1996). Such methods have already been applied to the As oxyacids (Tossell, 1997). However, obtaining energies accurate enough to determine reliable absolute \( pK_a^{aq} \) remains very difficult, as dis-
of simple organic and inorganic acids and to a number of
experiments to obtain acid dissociation enthalpies in solution (i.e., $\Delta H_{\text{hyd}} = \Delta H_{\text{d, aq}}$). We apply this approach both to a range of simple organic and inorganic acids and to a number of silicate oligomers. The oligomers provide a starting point for determining the pKa of the silica surface. We examine correlations between:

1. Experimental solution pK_a’s and $\Delta E_{\text{d, gas}}$ calculated at several different quantum mechanical levels;
2. $\Delta H_{\text{d, gas}}$ and differences in $\Delta H_{\text{hyd}}$ between neutral acid and anion;
3. Experimental solution pK_a and approximate calculated $\Delta E_{\text{d, aq}}$ and $\Delta H_{\text{d, aq}}$; and
4. $\Delta E_{\text{d, gas}}$ and M-O-H bond properties such as O underbondings and charge distributions.

We also examine the relationship between $\Delta H_{\text{d, gas}}$ and $\Delta H_{\text{d, aq}}$ for species of different charge. To do this, we have developed an approach for dealing with the different magnitude of stabilization that hydration produces for species of different charge, such as the reactants and products in an acid-dissociation reaction. By accounting for this “differential hydration” between an acid and its conjugate base, reactants and products with different charges can be shown to fall onto the same plot of gas-phase reaction energy vs. pKa.

Our goal in this paper is to combine high-level quantum mechanical calculations of deprotonation energies in the gas-phase with a medium-level description of hydration enthalpies to obtain acid dissociation enthalpies in solution (i.e., $\Delta H_{\text{hyd}} = \Delta H_{\text{d, aq}}$). We apply this approach both to a range of simple organic and inorganic acids and to a number of silicate oligomers. The oligomers provide a starting point for determining the pKa of the silica surface. We examine correlations between:

1. Experimental solution pK_a’s and $\Delta E_{\text{d, gas}}$ calculated at several different quantum mechanical levels;
2. $\Delta E_{\text{d, gas}}$ and differences in $\Delta H_{\text{hyd}}$ between neutral acid and anion;
3. Experimental solution pK_a and approximate calculated $\Delta E_{\text{d, aq}}$ and $\Delta H_{\text{d, aq}}$ respectively.

$\Delta E_{\text{d, gas}}$ reactions is calculated corresponding to the reaction:

$$\text{HA}(g) \rightarrow A^-(g) + H^+(g)$$

(2)

Reaction (1) can be written as a sum of reaction (2) and the two reactions:

$$\text{HA}(aq) \rightarrow A^-(aq) + H^+(aq)$$

(3)

$$\text{HA}(aq) \rightarrow A^-(g) + H^+(g)$$

(4)

For Eqn. 4,

$$\Delta H_4 = H(\text{HA}_g) + H(A^-_g) - H(\text{HA}_aq) - H(A^-_aq)$$

(5)

$$= \Delta H_{\text{A}^-, \text{hyd}} + \Delta H_{\text{HA}, \text{hyd}}$$

(6)

Therefore, the solution-phase deprotonation energy and enthalpy can be written as:

$$\Delta E_{\text{d, aq}} = \Delta E_1 = \Delta E_2 + \Delta E_3 + \Delta E_4$$

(7)

$$= \Delta E_{\text{d, gas}} + \Delta E_{\text{H}^+, \text{hyd}} + (\Delta E_{\text{A}^-, \text{hyd}} - \Delta E_{\text{HA}, \text{hyd}})$$

(8)

and

$$\Delta H_{\text{d, aq}} = \Delta H_4 = \Delta H_{\text{H}^+, \text{hyd}} + \Delta H_{\text{A}^-, \text{hyd}} - \Delta H_{\text{HA}, \text{hyd}}$$

(9)

That is, the enthalpy change for dissociation of HA in aqueous solution can be decomposed into a gas-phase enthalpy change ($\Delta H_{\text{d, gas}}$), a hydration enthalpy for the proton ($\Delta H_{\text{H}^+, \text{hyd}}$), and the difference between the hydration enthalpies of the anion and the neutral acid ($\Delta H_4 = \Delta H_{\text{A}^-, \text{hyd}} - \Delta H_{\text{HA}, \text{hyd}}$). $\Delta H_{\text{H}^+, \text{hyd}}$ is common to all the acid dissociations, so trends in the enthalpy of dissociation in solution depend on $\Delta H_{\text{d, gas}}$ and $\Delta H_4 = \Delta H_{\text{A}^-, \text{hyd}} - \Delta H_{\text{HA}, \text{hyd}}$.

To evaluate hydration enthalpies we use a multipart approach. For $H^+$ we use the newest “experimental” value of the hydration energy ($\sim 275.0$ kcal/mol), taken from Tissandier et al. (1998), although the best “theoretical” value is probably the
value of $-267.3$ kcal/mol obtained by Tawa et al. (1998). Nine years after Lim et al. (1991) discussed uncertainties in the quantities determining aqueous $pK_a$‘s, the energetics of proton hydration still remain uncertain.

For the conjugate acid anions and the neutral acids we determine the hydration enthalpies using a number of different procedures. For the bare acid and its anion we use: (i) the reformulated Born model (RH) approximating the effective Born radius by adding 1.495 Å to the average calculated distance from the central atom to the oxygen (Rashin and Honig, 1985); (ii) a self-consistent reaction field (SCRF) model, in which the radius is determined from an electron density criterion (a surface with electron density 0.001e/au$^3$); or (iii) an IPCM model with the radius determined by the same criterion (Wiberg et al., 1996; Foresman et al., 1996).

For some of the compounds we also generated supermolecules, with four water molecules coordinating the acid or its anion and then calculated hydration energies for this supermolecule using the R&H method, the SCRF method or the SCIPCM method. The supermolecule calculations were done at the 6 to 311+G(2d,p) MP2/6 to 311+G(2d,p) SCF level. Using such a supermolecule approach, we separate the hydration energy into a local term (the bond energy within the supermolecule) and a long-distance term (the hydration of the supermolecule).

For each type of calculation, we focus upon the hydration energy difference $\Delta H_{\text{hyd}} = \Delta H_{\text{HYD, gas}} - \Delta H_{\text{HYD, calc}}$ since this is the relevant quantity for determining the enthalpy of acid dissociation in solution. Also, due to anticipated cancellation of errors, the difference $\Delta H_{\text{hyd}} = \Delta H_{\text{HYD, gas}} - \Delta H_{\text{HYD, calc}}$ should be easier to calculate accurately than the hydration energy of either neutral acid or anion alone.

It is useful to consider what accuracy we might expect to attain in evaluating the energetics for the reactions studied. Even an extremely accurate method such as G2(MP2), which incorporates electron correlation at a very high level, effectively extrapolates to the infinite basis set limit, and incorporates some minor empirical corrections, cannot obtain reaction energies to better average accuracy than $\pm 1.5$ kcal mol$^{-1}$ (Curtiss et al., 1993). This translates to errors in the equilibrium constant at room temperature of about a factor of 10. Most of the compounds in the set used to test the accuracy of G2(MP2) theory are much smaller than those considered here, and G2(MP2) is a considerably more accurate theory than the 6-311+G(2d,p) MP2/6-311+G(2d,p) HF approach which we have generally employed. Nonetheless, we have found that even at our lower level of theory, $\Delta H_{\text{d, gas}}$ for this series of compounds can be evaluated with an accuracy not greatly inferior to that of G2(MP2), partly because deprotonation is a fairly simple reaction. Invariably, many serious approximations need to be made for calculations on such systems to be feasible. We believe we have developed a computationally feasible model and method to describe the relative energetics of such reactions. It is important that the method be simple enough computationally that we can apply it to a wide range of acids.

We shall focus upon the calculation of the energies and enthalpies for various acid dissociation processes. The values of the acid dissociation constant, $K_a$, are of course determined by the free energies ($\Delta G$) for the processes, not the enthalpies. However, using a quantum mechanical approach for the free acids and anions or even for supermolecules with a small number of explicit waters we have no way to accurately calculate the entropy changes for the dissolution process in solution. Pitzer (1937) showed long ago that for a process like Eqn. 1 (dissociation of HA in aqueous solution), the entropy change was about $-22$ cal mol$^{-1}$ K$^{-1}$ for a wide range of weak acids. At 298K, this yields a free energy contribution of about +6.5 kcal mol$^{-1}$ corresponding to $-4.8$ in $pK_a$. That is, the actual $pK_a$‘s will be more positive than those obtained from the enthalpy difference alone by $-4.8$.

The alternative to including explicit water molecules is to use the IPCM and SCIPCM methods for estimating hydration energies. The IPCM and SCIPCM methods do yield free energy changes, but they do not properly account for the decrease in entropy since most of it arises from the local ordering of solvent molecules around the ions (Marcus, 1986). For the present, therefore, we shall ignore entropic effects completely, anticipating that they will be much the same for the different acids studied.

3. RESULTS AND DISCUSSION

3.1. Energy vs. Solution $pK_a$ Correlations

Calculated gas-phase energetics for the deprotonation of 15 different molecules, corresponding to $\Delta E_{\text{d, gas}}$ of Eqn. 2, are given in column 2 of Table 1. The molecules are arranged in order of decreasing $\Delta E_{\text{d, gas}}$ calculated at the 6-31G* HF level. The order of $\Delta E_{\text{d, gas}}$ is similar, but not identical, to the order of the experimental solution $pK_a$‘s (last column of Table 1). Also given are: $\Delta E_{\text{d, gas}}$ evaluated using the BLYP density functional and the 6-311+G(2d,p) basis; $\Delta H_{\text{d, gas}}$ evaluated either at the G2(MP2) level or at the 6-311+G(2d,p) MP2/6-311+G(2d,p) HF level, with vibrational corrections evaluated at a scaled 6-31G* SCF level; values of the O underbonding (2.0 minus the Brown-T-O bond strength, whose calculation is discussed below); the experimental values of $\Delta H_{\text{d, gas}}$; $\Delta H_{\text{d, gas}}$ from other high-level calculations are also included in parentheses in column 4. Our 6-311+G(2d,p) MP2/6-311+G(2d,p) HF calculations give $\Delta H_{\text{d, gas}}$ values which agree quite well with literature values, obtained mostly by G2 or G2(MP2) methods, and also agree well with the few experimental values available. Numerous studies have shown that deprotonation enthalpies obtained at the G2(MP2) level typically agree with experiment to within better than 2 kcal mol$^{-1}$ (e.g., Glukhovtsev et al., 1996), consistent with the results shown in Table 1. Our values typically lie $-2$ kcal/mol below the G2(MP2) or experimental values. Thus, we believe that our relative deprotonation enthalpies are at essentially the G2(MP2) level of accuracy. Correlation plots of several pairs of these quantities are shown in Fig. 1–7.

In Fig. (1), we plot the experimental solution $pK_a$‘s vs. the calculated 6-31G* Hartree-Fock gas-phase $\Delta E_{\text{d, gas}}$ for all 15 molecules. Clearly the correlation is quite good, with a correlation coefficient of 0.890. The experimental $pK_a$ values are generally known accurately, although those for highly acid molecules with negative $pK_a$‘s and for the silicate and phosphate dimers may be somewhat less accurate than those for weak monomeric acids like H$_3$PO$_4$. These results indicate
the overall trend of solution pKₐ is well reproduced by the gas-phase deprotonation energies. We will use this correlation line (expt. pKₐ = \(-55.95 + 0.172 \Delta E_{d, \text{gas}}\)) to predict pKₐ values for other molecules that are not included in Fig. (1) (see section “Acidities of silicate oligomers”). However, in many cases, the relative ordering of pKₐ’s for any two acid molecules are not correctly predicted by the correlation line, especially in the middle pKₐ range from \(-3\) to 10.

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Table 1. Calculated energetics for deprotonation and hydration, along with calculated underbonding and experimental pKₐ. Energies and enthalpies in kcalmol\(^{-1}\).

<table>
<thead>
<tr>
<th>molecule</th>
<th>(\Delta E_{d, \text{gas}})</th>
<th>(\Delta H_{d, \text{gas}})</th>
<th>(2 - s_i)</th>
<th>Exp. (\Delta H_k)</th>
<th>IPCM (\Delta H_k)</th>
<th>Exp. pKₐ</th>
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<tr>
<td>H₂O</td>
<td>429.3</td>
<td>392.2</td>
<td>1.19</td>
<td>-99.4</td>
<td>-75.0</td>
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<td>CH₃OH</td>
<td>408.4</td>
<td>384.2</td>
<td>1.01</td>
<td>-64.5</td>
<td>-65.1</td>
<td>15.2</td>
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<tr>
<td>SiH₂OH</td>
<td>376.8</td>
<td>359.2</td>
<td>0.78</td>
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</tr>
<tr>
<td>HClO</td>
<td>372.7</td>
<td>357.5</td>
<td>na(^d)</td>
<td>-75.7</td>
<td>-68.5</td>
<td>7.5</td>
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<tr>
<td>Ge(OH)₄</td>
<td>371.7</td>
<td>351.7</td>
<td>0.70</td>
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<td>-51.6</td>
<td>9.5</td>
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<tr>
<td>Si(OH)₄</td>
<td>368.0</td>
<td>351.7</td>
<td>0.75</td>
<td>≈ -63.0</td>
<td>-52.8</td>
<td>9.2</td>
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<tr>
<td>HCOOH</td>
<td>365.0</td>
<td>345.9</td>
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<td>-63.4</td>
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<td>Si₂O₅H₆</td>
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<td>331.3</td>
<td>0.76</td>
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<td>H₂SO₄</td>
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<td>H₃PO₄</td>
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<td>H₂SO₄</td>
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<td>P₂O₅H₄</td>
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<td>HClO₄</td>
<td>310.0</td>
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<td>0.36</td>
<td></td>
<td></td>
<td>-7.0</td>
</tr>
</tbody>
</table>

\(^a\) Experimental values from Blades et al. (1996) and Wiberg et al. (1996).

\(^b\) Glikhovtsev et al., 1996.

\(^c\) Otto et al., 1997.

\(^d\) na, no bond parameters available for Cl(I) in Brown and Altermatt (1985).

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Fig. 1. Correlation plot of experimental solution pKₐ’s vs. gas-phase 6-31G* deprotonation energies, \(\Delta E_{d, \text{gas}}\) (linear regression line is given on the figure).

Fig. 2. Correlation plot of experimental solution pKₐ’s vs. gas-phase \(\Delta H_{d, \text{gas}}\) obtained at the 6-311+G(2d,p) MP2/6-311+G(2d,p) HF level.
Figure (2) is a correlation plot of pKa vs. pHd, gas values, evaluated at the 6-311+G(2d,p) MP2/6-311+G(2d,p) HF level. The correlation coefficient is now slightly higher (0.924) than in Fig. (1). However, the number of data points is smaller than in Fig. (1), because the necessary calculations are much more demanding. There are two main contributions to the difference between the 6-31G* SCF energies (column 2 of Table 1) and the 6-311+G(2d,p) MP2/6-311+G(2d,p) HF enthalpies (column 4 of Table 1). First, the deprotonation energies are lower in the higher level calculation due to the larger basis set, particularly the inclusion of diffuse functions, and due to the inclusion of correlation effects. Second, and more importantly, the vibrational zero-point energy is reduced during the reaction because of the loss of an O-H bond in the dissociation process (roughly 6 to −7 kcal/mol). This second reason also explains why the BLYP energies in column 3 of Table 1 are consistently ~5 kcal/mol larger than the 6-311+G(2d,p) MP2 enthalpy values in column 4.

As stated previously, ΔHd, aq can be decomposed into ΔHd, gas, ΔHH+, hyd and ΔHd = ΔHL−, hyd − ΔHA, hyd. Assuming ΔHH+, hyd is −275.0 kcal mol−1 (Tissandier et al., 1998), knowing the experimental ΔHL−, aq for a few of the acids (Pitzer, 1937), and using our most accurate calculated values of ΔHd, gas at the 6-311+G(2d,p) MP2 or G2(MP2) levels, we can determine an “experimental” value for ΔHd. These “experimental” values of ΔHd are collected in column 6 of Table 1. Earlier results based on hydration enthalpies of salts and semiempirical estimates of lattice energies gave about −73 kcal mol−1 for the hydration enthalpy difference between H₃PO₄ and H₂PO₄⁻.
(George, 1970), which is considerably larger in magnitude than our result of about –52 kcal mol$^{-1}$. The number obtained by George (1970) has often been quoted as an accurate experimental value, when it is in fact only a rough estimate.

The experimental $\Delta H_d$ is shown in Figure 3 versus the highest level calculated $\Delta H_d$, gas values. The number of data points is only five, since we have been able to find experimental $\Delta H_d$, gas for only five of the acids. Nonetheless, the correlation is very strong, with a correlation coefficient of 0.933. The strong correlation obtained in Figure 3 tells us that the $\Delta H_d$, gas is strongly correlated with the hydration enthalpy difference, $\Delta H_d$. Since $\Delta H_d$ is dominated by the hydration enthalpy of the anion ($\Delta H_{Hyd}$, $\lambda$), this also indicates a strong correlation between $\Delta H_{Hyd}$, $\lambda$ and $\Delta E_d$, gas. That is, the more strongly basic an anion is, the more strongly it interacts both with protons in the gas-phase and with groups of water molecules in solution. This is consistent with the correlation of hydration free energy and proton affinity noted earlier by Blades et al., 1995 (their Fig. 5). This basically means that if an anion interacts very strongly with $H^+$ it will also interact very strongly with an environment of water molecules. Since $\Delta E_d$, gas is strongly correlated with $\Delta H_d$, gas, it correlates well with the solution $pK_a$, whose variation depends upon both $\Delta H_d$, gas and $\Delta H^\ddagger$.

Note, however, that all the molecules considered in Figure 3 are small, compact monomers, so the hydration of the molecule will not be hindered by size or shape effects. Conceivably, such a correlation might be poorer if size effects hindered the hydration.

The experimental solution $pK_a$ is compared to the approximate calculated solution $\Delta H_d$,aq in Fig. 4. The calculated solution $\Delta H_d$,aq was obtained as the value of $\Delta H_d$, gas at 6-311+G(2d,p) MP2 level, plus an estimate of $\Delta H_d$ from IPCM calculations on bare $\Lambda^-$ and HA (column 7 of Table 1), plus $\Delta H_{4P}$, hyd from Tissandier et al. (1998). The number of points in the correlation is fairly small (six) but we now obtain a correlation coefficient of 0.988. We also obtain the correct order of $\Delta H_d$,aq relative to experimental $pK_a$ for almost all molecules, except CH$_3$OH and H$_2$O, which are still in inverted order.

Sometware surprisingly, this improvement in the correlation occurs even though the IPCM values of $\Delta H_d$ are not really highly accurate, as will be discussed later in the section “Other methods for computing hydration enthalpies.” The IPCM result for the bare acids and anions is not our most accurate or most computationally intensive estimate of the $\Lambda^-$ and HA hydration energies. In fact, the IPCM calculation is a trivial computation compared to the high-level gas-phase energy optimizations. This observation suggests that if we are able to carry out the gas-phase enthalpy calculation at the G2(MP2) level or close to it, and obtain even a reasonably accurate estimate of the hydration enthalpy difference ($\Delta H_d$) we can accurately predict solution $pK_a$’s.

As shown in Figure 5, there is also a good correlation between the 6-311+G(2d,p) BLYP $\Delta E_d$, gas or the 6-311+G(2d,p) MP2 $\Delta H_d$, gas and the 6-31G* HF $\Delta E_d$, gas values. Therefore, in principle for even larger molecules we could use the less computationally demanding BLYP energies to accurately predict MP2 level enthalpies. We could then add to these gas-phase enthalpies the experimental value of $\Delta H_{H^+}$, hyd and IPCM values of $\Delta H_d$, and correlate that sum with solution $pK_a$’s.

### 3.2. Deprotonation Energies and Bonding Character

It is also useful and desirable to interpret the deprotonation energies and solution $pK_a$’s in structural terms. A number of different quantities, such as $T$ electronegativity, $T$-O bond strength (where $T$ is the central atom), etc. might be correlated with the deprotonation energies. We first focus on the Pauling bond strength ($Z$/CN) of the $T$ atom (Pauling, 1961), where $Z$ is the formal charge and CN is the coordination number. The underbonding of the $O$ in a $T$-$O$-$H$ linkage is defined as its valence of 2.0 minus the sum of the bond strengths it receives, or 2.0 – $Z$/CN using the Pauling definition. We can plot the $\Delta E_d$, gas calculated at 6-31G* HF level for 20 neutral molecules vs. 2.0 – $Z$/CN. This results in a linear correlation with a correlation coefficient of ~0.699 (Fig. 6). The Brown bond-strength is defined as (Brown and Altermatt, 1985):

$$s_i = \exp\left[ (r_0 - r) / b \right]$$

where the $r_0$ and $b$ parameters are 1.624 Å for Si-O and 0.37 Å$^{-1}$ from their Table 1, and $r$ is obtained from the geometry of the acid anion at the 6-31G* HF level. For example, for $Si(OH)_3O^-$, with a calculated Si-O distance of 1.542 Å, the Si-O bond strength ($s_1$) is 1.248, and the underbonding $2 - s_1$ is 0.752. Using the Brown approach the correlation of $\Delta E_d$, gas with underbonding is now substantially improved as shown in Figure 7, with a correlation coefficient of 0.805. Since our calculated underbondings are simply related to calculated bond distances in the anions, this correlation establishes a close relationship between the structure of the monomeric anion and its protonation energy in the gas-phase. Of course, as noted by Bleam (1993), the underbonding $2 - s_1$ also correlates directly with the experimental solution $pK_a$’s.
Table 2. Calculated 6-31G* HF deprotonation energies, underbondings at O, calculated pK_a and experimental values of pK_a, for positive and negative ions. ∆E_\text{deg} values have been corrected by calculated IPCM hydration energies as described in text. Energies in kcal mol^{-1}.

<table>
<thead>
<tr>
<th>molecule</th>
<th>∆E_{\text{deg}}</th>
<th>2.0 - s_n</th>
<th>calc. pK_a =</th>
<th>exp. pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutral silicates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(OH)_4</td>
<td>368.0</td>
<td>0.75</td>
<td>7.3</td>
<td>9.5(^a)</td>
</tr>
<tr>
<td>Si_2O_4H_6</td>
<td>347.4</td>
<td>0.76</td>
<td>7.3</td>
<td>7.75(^a)</td>
</tr>
<tr>
<td>Si_3O_7H_7</td>
<td>360.0</td>
<td>0.71</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>Si_4O_12H_8</td>
<td>361.9</td>
<td>0.70</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>Si_3O_9H_6</td>
<td>347.5</td>
<td>0.72</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Si_5O_12H_8</td>
<td>353.2</td>
<td>0.65</td>
<td>4.8</td>
<td>amorphous silica 6.71(^b)</td>
</tr>
</tbody>
</table>

| charged silicates         |                 |           |              |           |
| Si(OH)\text{ONa}          | 392.2           | 11.5      |              |           |
| Si(OH)\text{OCl}          | 324.0           |           | -0.2         |           |

| other neutral silicates   |                 |           |              |           |
| Si(OH)\_\text{O}         | 395.0           | 12.0      | 12.7         |           |
| NaAl(OH)_4                | 401.0           | 13.0      | ~14.5        |           |

| other anions              |                 |           |              |           |
| H_2SO_4                  | 346.1           | 3.6       | 1.8\(^a\)    |           |
| H_2PO_4                  | 343.2           | 3.1       | 2.2\(^a\)    |           |

| a compounds from Table (1) that were used to obtain the correlation calc. pK_a = -55.95 + 0.1720\(\Delta E_{\text{deg}}\).
| b Schindler and Stumm (1987).

### 3.3. Acidities of Silicate Oligomers

We now consider in more detail the relative acidities of different oligomeric silicate species. We have calculated gas-phase deprotonation energies at the 6-31G* HF level for the silicate monomer, dimer, 3-ring trimer, 4-ring tetramer, double 4-ring octamer and for Si_2O_7H_5, a fully hydroxylated version of an incompletely condensed silsesquioxane (Si_2O_6H_10) which has been proposed as a model for the cristobalite surface (Feher et al., 1989). The calculated ∆E_{\text{deg}} are collected in Table 2. The double 4-ring, Si_2O_7H_6, had been studied previously by Sauer and Hill (1994). They found that Si_2O_7H_6 had a smaller deprotonation energy than Si(OH)_4, which was consistent with the experimental value estimated from vibrational spectroscopy and also with the increased acidity of silica surfaces compared to the silicate monomer.

We find that the deprotonation energies are indeed smaller for the oligomeric species than for the monomer, consistent with a lower pK_a for solid silica than for Si(OH)_4. However, both Si_2O_6H_4 and Si_2O_5H_10 have unusually small deprotonation energies compared to the other oligomers. This is a result both of the greater geometrical flexibility of the anions in these two cases and of the presence of internal H-bonding in Si_2O_6H_4. If we temporarily ignore these two molecules, we find a fairly systematic decrease in deprotonation energy as the degree of polymerization of the oligomer increases, with a value of 368 kcal mol^{-1} for the Q^3 Si(OH)_4 species, around 360 kcal for the rigid Q^2 3-ring and 4-ring species and around 353 kcal mol^{-1} for the Q^2 double 4-ring species. This decrease in deprotonation energy is associated with a decrease in the Si-O' bond distance in the anion, from ~1.54 to 1.53 to 1.51 Å for the Q^3, Q^2 and Q^1 species, giving larger values of s_n and consequently smaller magnitudes of underbonding 2-s_n. The decrease in Si-O' distance is also associated with the presence of more Si-O'bridging bonds, which are typically longer than Si-OH bonds. It is worthwhile noting the difference in behavior of the monomeric acids, such as the HClO_2-Si(OH)_4 series, compared to the behavior of the silicate oligomers in Figure 7. The oligomers fall below the correlation line defined by the monomers. There is a suggestion that they may define a separate line with lower deprotonation energies, although, admittedly, there are few points and considerable scatter.

The optimized 6-31G* HF geometries of Si_2O_7H_6, Si_3O_7H_7, and Si_4O_12H_8 are shown in Figure 8. Movement of the Si-O' group in the anion to facilitate the internal H-bonding is evident in the figure. The O-H..O distance of 2.66 Å is within the range of H-bonded distances for oxyacids (Wells, 1975). The decomposition of the deprotonation energy shown in Table 3 and discussed below also establishes that geometric relaxation is considerably larger for Si_2O_7H_6 than for the other silicates (and slightly larger for Si_4O_12H_10).

Using the linear regression equation relating the experimental pK_a and the gas-phase 6-31G* ∆E_{\text{deg}} shown in Fig. 1, our pK_a estimate for Si(OH)_4 is 7.3, reasonably close to the experimental value of 9.5 (Sjoberg et al., 1981). If we assume that differences in hydration enthalpies between neutral acids and their anions (i.e., the value of ∆H_4) are about the same for the oligomers as for Si(OH)_4 (although they are probably not exactly the same, as we discuss later), we would expect the deprotonation energies and pK_a's of the oligomers to follow the same trend as that shown in Figure 1 for the monomers. Thus, using the same linear regression we can estimate pK_a's for the oligmeric species.

Estimated pK_a values for oligomers are shown in Table 2. All the oligomers show somewhat smaller pK_a values than the monomer. The flexible dimer and Si_3O_7H_7 species show more dramatic lowerings of pK_a. Of course, we can anticipate that for the Si_4O_12H_8^4- ion, which shows internal H-bonding, the enthalpy of hydration might be reduced, because the internal H-bond must be partially broken to form the H-bond to the water molecule. This will result in a reduced stability in aqueous solution. We will return to this point later in “Trends in local hydration enthalpies…”

### 3.4. Acidities of Polyprotic Acids

We can also use our 6-31G* values of ∆E_{\text{deg}} corrected by approximate hydration enthalpies (such as IPCM values of ∆H_4), to estimate solution pK_a's for species with different charges, or equivalently different order pK_a's, such as pK_{A2} for the polyprotic acids. For example, we have characterized the species Si(OH)_3(OH)_2^+ and Si(OH)_4^2- as bare molecules at the 6-311+G(2d,p) MP2/6-31+G(2d,p) HF level, and as supermolecules with four waters at the 6-31G* HF level. We find them both to be stable molecules, corresponding to local...
minima on the energy surface. The optimized geometry for Si(OH)$_3$(OH$_2$)$_1$...H$_2$O is shown in Figure 9. We have also established that the Si(OH)$_3$(OH$_2$)$_1$ is at least a local energy minimum, even in the presence of eight water molecules, contrary to the Molecular Dynamics result of Rustad et al. (1998).

![Fig. 8.](image)

Table 3. Calculated components of 6-31G* gas-phase deprotonation energy, along with potential determined charges, and sums of electrostatic H$^+$ – O and H$^+$ – T interactions. Energies in kcalmol$^{-1}$.

<table>
<thead>
<tr>
<th>molecule</th>
<th>potential at proton</th>
<th>electronic relaxation energy</th>
<th>geometric relaxation energy</th>
<th>R(O–H)</th>
<th>R(T–H)</th>
<th>potential derived charges (PDC)</th>
<th>electrostatic energy from PDC</th>
<th>NBO charges</th>
<th>electrostatic energy from NBO charges</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO</td>
<td>589.9</td>
<td>−217.1</td>
<td>−0.1</td>
<td>0.951</td>
<td>2.126</td>
<td>−0.49</td>
<td>0.03</td>
<td>0.49</td>
<td>−7.0</td>
</tr>
<tr>
<td>HClO$_3$</td>
<td>535.6</td>
<td>−216.6</td>
<td>−18.0</td>
<td>0.960</td>
<td>2.102</td>
<td>−0.48</td>
<td>1.05</td>
<td>0.49</td>
<td>−7.8</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>554.1</td>
<td>−214.4</td>
<td>−20.6</td>
<td>0.954</td>
<td>2.103</td>
<td>−0.56</td>
<td>1.20</td>
<td>0.48</td>
<td>−2.9</td>
</tr>
<tr>
<td>H$_3$PO$_4$</td>
<td>576.3</td>
<td>−214.8</td>
<td>−18.5</td>
<td>0.955</td>
<td>2.126</td>
<td>−0.62</td>
<td>1.22</td>
<td>0.47</td>
<td>−1.0</td>
</tr>
<tr>
<td>Si(OH)$_3$</td>
<td>604.7</td>
<td>−218.1</td>
<td>−18.6</td>
<td>0.947</td>
<td>2.225</td>
<td>−0.79</td>
<td>1.33</td>
<td>0.45</td>
<td>−1.6</td>
</tr>
<tr>
<td>Si$_2$O$_7$H$_6$</td>
<td>603.5</td>
<td>−219.7</td>
<td>−36.4</td>
<td>0.948</td>
<td>2.217</td>
<td>−0.78</td>
<td>1.24</td>
<td>0.46</td>
<td>−1.6</td>
</tr>
<tr>
<td>P$_2$O$_7$H$_5$</td>
<td>571.6</td>
<td>−216.5</td>
<td>−37.0</td>
<td>0.951</td>
<td>2.125</td>
<td>−0.64</td>
<td>1.10</td>
<td>0.48</td>
<td>−1.0</td>
</tr>
<tr>
<td>Si$_3$O$_9$H$_6$</td>
<td>600.8</td>
<td>−221.6</td>
<td>−19.2</td>
<td>0.944</td>
<td>2.273</td>
<td>−0.80</td>
<td>1.51</td>
<td>0.44</td>
<td>−1.6</td>
</tr>
<tr>
<td>Si$<em>4$O$</em>{12}$H$_8$</td>
<td>605.4</td>
<td>−222.2</td>
<td>−21.3</td>
<td>0.944</td>
<td>2.270</td>
<td>−0.81</td>
<td>0.62</td>
<td>0.50</td>
<td>−1.1</td>
</tr>
<tr>
<td>Si$<em>7$O$</em>{19}$H$_{10}$</td>
<td>595.3</td>
<td>−222.7</td>
<td>−25.1</td>
<td>0.943</td>
<td>2.288</td>
<td>−0.86</td>
<td>0.93</td>
<td>0.51</td>
<td>−8.6</td>
</tr>
<tr>
<td>Si$<em>8$O$</em>{20}$H$_8$</td>
<td>597.6</td>
<td>−223.3</td>
<td>−22.1</td>
<td>0.947</td>
<td>2.232</td>
<td>−0.80</td>
<td>1.11</td>
<td>0.50</td>
<td>−5.8</td>
</tr>
</tbody>
</table>
The pKa values for these species can be estimated based on the 6-31G* HF energies for the bare molecules. Consider the reactions:

\[
\begin{align*}
\text{H}_3\text{A}^+(\text{aq}) & \rightarrow \text{HA}(\text{aq}) + \text{H}^+(\text{aq}) \quad (11) \\
\text{HA}(\text{aq}) & \rightarrow \text{A}^-(\text{aq}) + \text{H}^+(\text{aq}) \quad (12)
\end{align*}
\]

The energetics of these two equations differ from that of Eqn. 1 partly because of different hydration enthalpy contributions from the acid and conjugate base, due to their different charges. For Eqn. 1 the relevant hydration energy is given by Eqn. 4, which is dominated by the \(\Delta H_{\text{hyd}}\) of the monopositive reactant. This results in a substantial stabilization of the product side of reaction (12), the reactant side is stabilized by the hydration energy of the mononegative anion. This stabilization is only partially compensated by the hydration energy of the dinegative anion. Thus, for Eqn. 13 we can re-write Eqns. 13–15 as

\[
\begin{align*}
\Delta H_{\text{d, aq}, 11} & = \Delta H_{\text{d, gas}, 11} + \Delta H_{\text{H}^+, \text{hyd}} + \Delta H_{\text{A}^-, \text{hyd}} - \Delta H_{\text{HA}, \text{hyd}} \quad (16) \\
\Delta H_{\text{d, aq}, 12} & = \Delta H_{\text{d, gas}, 12} + \Delta H_{\text{H}^+, \text{hyd}} + 3 \Delta H_{\text{A}^-, \text{hyd}} - \Delta H_{\text{HA}, \text{hyd}} \quad (17)
\end{align*}
\]

These equations reflect the magnitude of the overall stabilization due to hydration in Eqn. 20 is 1 unit, while in Eqn. 21 the stabilization is \(-1\) unit, and in Eqn. 22 it is \(-3\) units where each unit is \(\Delta H_{\text{A}^-, \text{hyd}}\). Using Eqn. 20 as a “reference” level, we can determine the magnitude of stabilization due to all other effects except hydration, by adding \(2\Delta H_{\text{hyd}, \text{HA}}\) to Eqn. 21 and adding \(-2\Delta H_{\text{hyd}, \text{HA}}\) to Eqn. 22. This brings all the three equations to the same “level” of stabilization due to hydration. Any differences in energy are now purely due to non-solvation effects. Thus, Eqns. 20–22 now become:

\[
\begin{align*}
\Delta H'_{\text{d, aq}, 1} & = \Delta H_{\text{d, gas}, 1} + 2 \Delta H_{\text{H}^+, \text{hyd}} + \Delta H_{\text{A}^-, \text{hyd}} \quad (19) \\
\Delta H'_{\text{d, aq}, 11} & = \Delta H_{\text{d, gas}, 11} + \Delta H_{\text{H}^+, \text{hyd}} + \Delta H_{\text{A}^-, \text{hyd}} \quad (20) \\
\Delta H'_{\text{d, aq}, 12} & = \Delta H_{\text{d, gas}, 12} + \Delta H_{\text{H}^+, \text{hyd}} + \Delta H_{\text{A}^-, \text{hyd}} \quad (21)
\end{align*}
\]

For example, the hydration energy of the silicate monomer of charge magnitude 1 is \(-56.1\) kcal/mol according to the Rashin and Honig (1985) model. The correction for the monopositive ions \(\text{Si(OH)}_3^+\), \(\text{Si}_2\text{O}_7\text{H}^+\) and \(\text{Si}_3\text{O}_9\text{H}^+\), will then be \(2 \times \Delta H_{\text{hyd}, \text{HA}}\) for each of them.

Using other estimates of the hydration enthalpy gives fairly similar results. Using the least squares equation shown in Figure 1, this gives estimated solution pK\(_a\) values of \(-4.7\), \(-2.9\) and \(-3.0\) for these three cationic species. If we had used for \(\text{Si(OH)}_3\text{(OH)}_2^+\) the Molecular Dynamics deprotonation energy of 175 kcal/mol from Rustad et al. (1998) with our hydration correction, we would have obtained a corrected energy of \(-278\) kcal/mol and an estimated pK\(_a\) of about \(-8.1\). Thus, the hydration correction brings even the MD value to at least a rough approximation of our ab initio value of \(-4.7\).

For the dimer and cyclic trimer cations, note that the most stable cation has the proton bonded to a bridging O, not a terminal OH group. This is the main reason for the difference in deprotonation energy and pK\(_a\) between these oligomeric cationic species and the monomer.

In the same way, we can obtain a corrected deprotonation energy for \(\text{Si(OH)}_3\text{O}^+\) by adding twice the monopositive hydration energy of \(-51.6\) kcal/mol to the gas-phase deprotonation energy of 498.2 kcal/mol to get \(\Delta E'_{\text{aq}} = 395.0\) kcal/mol. This value projects a pK\(_a\) of 12.0 for this species, or equivalently, a value of 12.0 for pK\(_{\text{A2}}\) of \text{Si(OH)}_3\text{O}. Using IPM values for the hydration enthalpy of the monoanion, we can apply the same procedure to determine the pK\(_{\text{A2}}\) of \(\text{H}_2\text{SO}_4\) and \(\text{H}_3\text{PO}_4\). We obtain values of 11.1 and 8.1 compared with experimental values of 8.3 and 7.1 (Table 2). Although our projected values differ significantly from experiment, our approach does give...
Calculating acidity of silanols

\[ \text{pK}_{42} - \text{pK}_{41} \] differences of 7.5 and 5.0 for the two acids, which match well against the experimental differences of 6.5 and 4.9, supporting the validity of our scheme for referencing the deprotonation energies to a common level.

We should note that there is a simpler way to approach the problem of calculating higher or lower order \( \text{pK}_n \)'s. We could simply add ions to the charged silicate species to give a neutral compound, e.g., \( \text{Si(OH)}_4 \) ONa to model \( \text{pK}_{24} \) for the monomer \( \text{Si}_3\text{O}_9\text{H}_7^- \) and \( \text{Si(OH)}_3\text{(OH)}_2\text{Cl}^- \) to model deprotonation of the cation. Gas-phase deprotonation energies evaluated at the 6-31G* HF level for these species and the correlation line from Figure 1 give \( \text{pK}_2 \) values of 11.5 and \(-0.2\), reasonably close to the values of 12.0 and \(-4.7\) evaluated from our referencing scheme. However, this approach suffers from the presence of specific interactions which might not be present for silica. For example, the species with formula \( \text{Si(OH)}_4\text{(OH)}_2\text{Cl}^- \) is actually \( \text{Si(OH)}_4 \) complexed with \( \text{HCl} \), which probably gives it too high a deprotonation energy, and too positive a \( \text{pK}_2 \).

We can now estimate pH values which would give zero charge \( (\text{pH}_{24}) \) for the silicate monomer and the silicate oligomers. For the monomer we would average 7.3 for \( \text{Si(OH)}_4 \) and \(-4.7\) for \( \text{Si(OH)}_3\text{(OH)}_2\text{Cl}^- \) to give 1.3, while for the cyclic trimer we would average 6.0 for \( \text{Si}_3\text{O}_9\text{H}_6^- \) and \(-3.0\) for \( \text{Si}_3\text{O}_9\text{H}_8^- \) to give 1.5.

As an exercise, we can even stretch our analysis to include tetrahedral aluminate groups, Al-O-H. If we choose a simple \( \text{NaAl(OH)}_4 \) model for the aluminate group and simply calculate its gas-phase deprotonation energy at the 6-31G* HF level we get 401.0 kcal/mol, which projects a \( \text{pK}_2 \) of 13.0. Early studies (e.g., Parks, 1967, as discussed in Blum and Lasaga, 1991) strongly supported the idea that tetrahedral Al-O-H linkages were less strongly acidic than tetrahedral Si-O-H linkages, by \(-5\) \( \text{pK}_2 \) units, which is close to the difference we obtain comparing \( \text{Si(OH)}_4 \) and \( \text{NaAl(OH)}_4 \). Such a comparison is certainly a crude one, but it seems to capture a good deal of the basic physics of the problem.

### 3.5. Decomposition of the Deprotonation Energy

To obtain a better understanding of the deprotonation energy we can decompose it into a sum of terms as done by Siggel and Thomas (1986). We can write:

\[ \Delta E = \Delta V - \Delta R_e - \Delta R_N \]  (22)

using a symbolism like that in Eqn. 9 of Siggel and Thomas (1986), in which the terms on the right are:

- \( \Delta V \): the potential at the site of the proton in the neutral molecule;
- \( -\Delta R_e \): the energy lowering due to relaxation of the electron density in going from the neutral to the anion; and
- \( -\Delta R_N \): the energy lowering due to relaxation of the nuclear positions between the neutral and the anion. The effect of nuclear or geometric relaxation was actually ignored in Siggel and Thomas (1986) so they did not have the \( -\Delta R_N \) term.

Sauer and Ahlrichs (1990) used the same approach to show that the difference in deprotonation energy between \( \text{CH}_3\text{OH} \) and \( \text{SiH}_3\text{OH} \) was determined mainly by the difference in \( \Delta V \), with only minor contributions from electronic and geometric relaxation. Calculated energy components for HClO, the HClO4 – Si(OH)4 series and for some silicate and phosphate oligomers are given in Table 3.

The first point to note is that \( \Delta V \), or equivalently, the energy for removal of a proton from the frozen nuclear and electronic charge distribution of the neutral, correlates well with the overall \( \Delta E_{\text{D,Gas}} \) (given in Table 1). For the set of compounds shown in Table 3, the correlation coefficient is 0.80. This strong correlation occurs because the electronic relaxation and nuclear relaxation energies are considerably smaller in magnitude than the potential at the proton and are fairly constant from one compound to another (with the exception of the nuclear relaxation energy in some of the oligomers).

Although the oxyanions \( \text{ClO}_4^- \) – \( \text{Si(OH)}_3\text{O}^- \) differ by \(-20\%\) in calculated total electric dipole polarizabilities (JAT, unpublished results), their electronic relaxation energies (which are related to the polarization energies for the anion) differ by only a few percent. Likewise, there is very little contribution of differential nuclear relaxation energies to the deprotonation energy differences, except for the silicate and phosphate dimers.

The cyclic silicate trimer shows almost the same nuclear relaxation energy as the silicate monomer. Examining the silicates in more detail, we see that the oligomers generally have smaller potentials at the proton, more negative electronic relaxation energies, and slightly more negative geometric relaxation energies. The difference in electronic relaxation energy indicates that the oligomeric silicates are somewhat more polarizable by the proton than is the monomeric silicate anion.

We can also try to analyze the differences in potential at the proton using a model based on the charge density. Although the charge on an atom within a molecule cannot be uniquely defined, there are several approaches that seem to give meaningful relative effective charges. One popular approach is to calculate the potential at an array of points outside the molecule (i.e., near the surface defined by the atomic van der Waals radii), and to perform a least squares fit of effective atomic charges to best reproduce these potentials. We have chosen the version of this approach developed by Spackman (1996) and implemented in the program GAMESS. The potential derived charges (PDC) obtained using this method, are given in Table 3. Alternatively, we can define charges using a natural bond orbital (NBO) analysis, pioneered by Weinhold (Reed et al., 1988) and implemented in GAUSSIAN. The NBO charges are defined for all levels of quantum mechanical treatment (e.g., for correlated methods) and are stable toward basis set expansion, in contrast to Mulliken charges which tend to change erratically with basis set (Jensen, 1999, pp. 217–234). NBO charges for are also given in Table 3. Note that the PDC and NBO charges are quite different, in both magnitude and trend, and that the PDC charges seem to change rather erratically with polymerization.

Several phenomenological schemes focus on an electrostatic attraction of the proton and its nearest neighbour oxygen, coupled with the electrostatic repulsion of the proton and its second nearest neighbor metal cation (Parks, 1967; Hiemstra et al., 1989; Sverjensky and Sahai, 1996). Sverjensky and Sahai (1996) calculated this term using the formal charges of +1 and –2 for the proton and its nearest neighbor O, and approximated the residual charge on T as the strength of the T-O bond, given by Z/CN. That is, in our terminology, they use the formula:

\[ \text{pK}_{42} - \text{pK}_{41} \]
dent charges (PDC) and the natural bond orbital (NBO) charges give a poor correlation while the NBO charges yield a somewhat exaggerated. However, the difference between silicate monomer and oligomers (as indicated also by the results of Sauer and Hill, 1994) suggests that the anomalously high acidity of silica compared to the Si(OH)₄ monomer may be an intrinsic property of the silicate species that the anomolously high acidity of silica compared to the Si(OH)₄ monomer may be an intrinsic property of the silicate species.

3.6. Implications for Phenomenological Models

The results in the preceding paragraphs may be summarized as:

1. Deprotonation energies are well correlated with the underbondings of the oxygens in the anions, and with the electrostatic potentials at the sites of the protons.
2. Silicate and phosphate oligomers are more acidic (smaller deprotonation energies) than the corresponding monomers, with the acidity generally increasing with degree of polymerization.
3. For the dimer and cyclic silica trimer, the most stable form of the cationic species has the proton bonded to a bridging oxygen, not to a terminal OH group, which is mainly responsible for the large increase in their acidities relative to the monomer.
4. The anomalously low acidity of the flexible silica dimer may be related to the fact that the terminal oxygen atom in the deprotonated form of the acid tends to bend back in towards the molecule forming internal H-bonds. The calculated O...H...O distance is 2.66 Å, which is in the range of H-bonding distances observed in acid salts or hydrates (Wells, 1975). It is not clear to what extent this effect would persist if the flexible dimer were explicitly solvated by a sufficient number of water molecules. Accurate calculation of energies for explicitly solvated large oligomers is computationally very expensive.

5. Contributions of the geometric relaxation energies and electronic relaxation energies to the trends in deprotonation energy are relatively small - most of the change in deprotonation energy arises from changes in the potential at the proton.

It should be remembered that our calculations were done on gas-phase molecules and have been extended to obtain approximate solution pKₐ's. The implications of our results for phenomenological models that predict surface pKₐ's must, therefore, be taken as conditional. Equally important, it should be realized that our calculations were restricted to anionic oxyacids such as (Si(OH)₃O)⁺ and did not include any cationic metal acids such as [Al(OH)₂(H₂O)₄]⁺. So the interpretation of phenomenological surface complexation models, which were developed mainly for metal-oxides, in terms of our results is, perhaps, an overextension of our results. With this caveat in mind, we may then continue as follows.

Point (1) provides validation for several of the models that have been used in the past to relate the deprotonation energy to underbondings or electrostatic potentials. Point (2) suggests that the anomalously high acidity of silica compared to the Si(OH)₄ monomer may be an intrinsic property of the silicate oligomers (as indicated also by the results of Sauer and Hill, 1994). If this polymerization effect is properly accounted for, there may be no need to invoke any other parameters related to ion stabilization or hydration such as the dielectric constant (Sverjkensky, 1994; Sverjensky and Sahai, 1996) or the local hydration of the ions (Hiemstra et al., 1996). Point (3) appears to support one feature of the revised MUSIC model of Hiemstra.
et al. (1996), because that model assumes that the acidic proton on the positively-charged surface site is bonded to a bridging rather than a terminal oxygen.

However, to obtain a critical test of Hiemstra et al.’s (1996) model of surface hydration we would need to include sufficient waters of hydration around the larger oligomers in our calculations, to determine if the local hydration effects assumed by Hiemstra et al. are actually present. Also, to critically test the Sverjensky and Sahai (1996) model, we would need to calculate the pH’s for monomers and oligomers of metal-oxides other than silica, such as Al2O3 or TiO2.

3.7. Other Methods for Computing Hydration Enthalpies

The relative hydration enthalpies for A− and HA in Table 1 were obtained using the very simple IPCM method. Other much more complicated and demanding approaches are certainly possible and even desirable. An excellent example is the calculation of the proton hydration enthalpy and free energy by Tawa et al. (1998). In their approach the proton was hydrated with a number of explicit water molecules and this “supermolecule” was then immersed in a polarizable continuum. Results converged well with respect to the size of the supermolecule when it contained only four water molecules and was treated at the BLYP or MP2 level with a 6-311+G(d,p) basis. Such calculations are possible but are computationally very demanding for species such as Si(OH)4. Part of the problem is the flexibility of the supermolecule due to the relatively weak interaction of water with the solute (particularly for the neutral acids), coupled with several different possible H-bonding schemes involving the waters, leading to slow, tedious convergence of the geometry optimizations.

We have calculated optimized energies at the 6-311+G(2d,p) MP2/6 to 311+G(2d,p) HF level for supermolecules consisting of either H2O, HClO, H3PO4, Si(OH)4 or one of their corresponding conjugate acids coordinated to four water molecules. However, we have not been able to carry out a force constant analysis for the neutral solute supermolecules. The calculated supermolecule interaction energy values are given in Table 4 as the local terms, along with the long-range contributions to the hydration enthalpy difference calculated using either the Rashin and Honig prescription, the SCRF method or the SCIPCM method (we encountered severe convergence problems using the IPCM method).

The first point to note in Table 4 is that the local contributions and the long-range contributions to the hydration enthalpy difference are roughly equal in magnitude, so that both must be considered to get reasonable hydration enthalpies. The second point is that while the R&H and SCRF values are quite similar, the SCIPCM values are often much smaller in magnitude. This difference arises from a much larger stabilization of the neutral molecule in the SCIPCM calculations. It appears that the SCIPCM results are less reliable since they regularly lead to underestimates of the difference of acid and anion hydration enthalpy differences, although one could possibly avoid this problem by adjusting the electron density criterion for defining the isodensity surface. A third point is that even though the two more reliable methods (the semiempirical R&H and the SCRF) show some differences, the calculated total differential hydration enthalpies match quite well against the experimental values. Still, we should remember that some potentially important trends have been ignored, e.g., the change in zero point energy during the formation of the supermolecule due to our failure to obtain the vibrational spectra. Also, the hydration enthalpy for the proton is uncertain by ~8 kcal mol−1. Thus, it appears that it is not yet possible to calculate absolute deprotonation enthalpies in solution with chemical accuracy. The situation is not much better for the relative values, since the calculated hydration enthalpy difference seems to be larger in magnitude for H3PO4 than for Si(OH)4, which is opposite to the experimental values of ΔHf.

3.8. Trends in Local Hydration Enthalpies from Supermolecule Calculations

Although the absolute hydration enthalpies from our supermolecule calculations leave much to be desired, it may be useful to consider some trends seen in these calculated energies, for different numbers of water molecules, and silicate anions of different size. All the calculations described in this section were done at the HF level using the 6-31G* basis. Results are given in Table 5.

We first studied the stabilization of the monomer anion Si(OH)3O−, relative to the neutral monomer Si(OH)4, produced by adding various numbers of water molecules to each species. The calculated geometry for Si(OH)3O− with four waters is shown in Figure 11a. The differential hydration energies are 16.5, 14.2 and 21.0 kcal mol−1 for 1, 2 and 4 water molecules respectively. This indicates that although the total interaction energy of water with the solute (particularly for the neutral acids), coupled with several different possible H-bonding schemes involving the waters, leading to slow, tedious convergence of the geometry optimizations.

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to $\text{Si}_2\text{O}_7\text{H}_5^{1-}..7\text{H}_2\text{O}$, produced by adding a single water molecule to each is only 3.4 kcalmol$^{-1}$, compared to 16.5 kcalmol$^{-1}$ for the monomer. This reflects the fact that the Si-O$^-$ group in $\text{Si}_2\text{O}_7\text{H}_5^{1-}$ is already internally H-bonded. However, when water is present this internal H-bond is partially broken. The addition of other water molecules produces a larger differential stabilization for the $\text{Si}_2\text{O}_7\text{H}_5^{1-}$ anion, so that by the time 7 water molecules have been added (Fig. 11b), the energy difference has been reduced by 14 kcalmol$^{-1}$ from the gas-phase value.

For $\text{Si}_3\text{O}_9\text{H}_6$, the stabilization of anion compared to neutral produced by a single water molecule is actually larger than that produced by three waters. It is clear that the local contribution to the hydration energy difference between neutral acid and anion converges for a relatively small number of waters. However, there seems to be considerable scatter in the results, which may be due to our simple approach to geometry optimization, where the global minimum has not necessarily been reached.

### 3.9. Calculation of NMR Shieldings of $^{29}\text{Si}$ and $^1\text{H}$ and Electric Field Gradients at O for Silicates of Various Charges and Degrees of Hydration

To better understand the nature of the hydration of the silica oligomers and the surface of silica, it would be desirable to have a spectral probe for the local geometry of the water about the silanol group. $^1\text{H}$- and $^{29}\text{Si}$-NMR are potentially useful probes. Fleischer et al. (1993) established that the $^1\text{H}$-NMR shielding was correlated with the deprotonation energy for a restricted set of molecules, relevant as models for surface hydroxides. Civalleri et al. (1999) found that $^1\text{H}$-NMR shieldings obtained for model silicates interacting with water could reproduce some of the experimental data for water on silica surfaces. Moravetski et al. (1996) observed that interaction of $\text{Si(OH)}_4$ or $\text{Si(OH)}_2\text{O}_2^{1-}$ with water increased the Si-NMR shielding.

We have calculated $^{29}\text{Si}$ and $^1\text{H}$-NMR shieldings for a range of species as shown in Table 6. We find that protonation of bare $\text{Si(OH)}_4$ increases the $^{29}\text{Si}$ shielding: the first deprotonation decreases $^{29}\text{Si}$ shielding substantially, and the second deprotonation causes little change. When the silicate species is part of a supermolecule with four waters this trend in $^{29}\text{Si}$ shielding is tempered and even reversed slightly, with the deprotonated species actually being slightly more shielded. Both bare silicate and supermolecule results, thus, indicate that a $\text{Si(OH)}_2\text{OH}_2^{1-}$ species might be distinguishable by $^{29}\text{Si}$-NMR but that the other species would have very similar shifts. For the cyclic trimer, $\text{Si}_3\text{O}_9\text{H}_6$, the $^{29}\text{Si}$ shielding is larger, as expected for a more polymerized species, but the change upon deprotonation is about the same.

The $^1\text{H}$-NMR shows considerable change from the $\text{OH}_2$ proton of $\text{Si(OH)}_2\text{OH}_2^{1+}$ to the $\text{OH}$ protons of $\text{Si(OH)}_2\text{O}_2^{1-}$, and this difference persists in the supermolecules. This indicates that $^1\text{H}$-NMR might be useful for determining the charge of the silicate group if the spectrum were well resolved. The calculations indicate that hydration deshields the protons of $\text{Si(OH)}_4$ by 1 to 2 ppm, in the same direction as observed experimentally (Caillerie et al., 1997) but of smaller magnitude. Note that the neutral monomer and cyclic trimer give essentially the same $^1\text{H}$-NMR although they differ in deprotonation energy by $\approx 8$ kcalmol$^{-1}$, so that small changes in deprotonation energy associated with oligomerization are

### Table 5. Energy difference at 6-31G* HF level of $n_3$ acid and anion, hydrated by differing numbers of water molecules, for various silicates. Energies in kcalmol$^{-1}$.

<table>
<thead>
<tr>
<th>molecule/n</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Si(OH)}_4$</td>
<td>368.0</td>
<td>353.8</td>
<td>348.1</td>
<td>-</td>
<td>349.0</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Si}_2\text{O}_7\text{H}_6$</td>
<td>347.4</td>
<td>344.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>334.8</td>
</tr>
<tr>
<td>$\text{Si}_3\text{O}_9\text{H}_6$</td>
<td>360.0</td>
<td>343.5</td>
<td>-</td>
<td>351.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 6. Calculated $^{29}$Si and $^1$H NMR shieldings and electric field gradients at O for bare and hydrated silicate monomers and for bare trimers (6-31G* SCF, $\omega^I = 32.2$ ppm in H$_2$O(g)).

<table>
<thead>
<tr>
<th>molecule</th>
<th>$\sigma^{\text{Si}}$ (ppm)</th>
<th>$\sigma^{\text{H}}$ (ppm) for ionizable proton</th>
<th>$q^I$ (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(OH)$_3$(OH$<em>2$)$</em>{1.1}$</td>
<td>527.4</td>
<td>27.5</td>
<td>1.40–1.44 (OH), 1.32 (OH$_2^-$)</td>
</tr>
<tr>
<td>Si(OH)$_3$</td>
<td>510.2</td>
<td>31.4</td>
<td>1.44 (OH)</td>
</tr>
<tr>
<td>Si(OH)$_3$O$^{-1}$</td>
<td>506.7</td>
<td>32.9</td>
<td>0.35 O$^-$, 1.50 (OH)</td>
</tr>
<tr>
<td>Si(OH)$_2$O$_2^{-2}$</td>
<td>506.9</td>
<td>34.2</td>
<td>0.43–0.44 (O$^-$), 1.50–1.56 (OH)</td>
</tr>
<tr>
<td>Si$_3$O$_9$H$_6$</td>
<td>525.5</td>
<td>31.40</td>
<td>1.51 (OH)</td>
</tr>
<tr>
<td>Si$_3$O$_9$H$_5$</td>
<td>522.3, 2 × 523.8</td>
<td>32.4–32.6</td>
<td>1.46–1.55 (OH), 0.37 (O$^-$)</td>
</tr>
<tr>
<td>Si$_3$O$_9$H$_5$O$^{-1}$</td>
<td>517.1</td>
<td>22.4, 28.1</td>
<td>1.16–1.21 (OH), 1.20 (OH$_2^-$)</td>
</tr>
<tr>
<td>Si$_3$O$_9$H$_5$O$^{-2}$</td>
<td>511.1</td>
<td>29.0–30.6</td>
<td>1.28–1.35 (OH)</td>
</tr>
<tr>
<td>Si(OH)$_3$(OH)$_2$O$_2$</td>
<td>512.8</td>
<td>32.2</td>
<td>0.40 (O$^-$), 1.41–1.48 (OH)</td>
</tr>
<tr>
<td>Si(OH)$_3$(OH)$_2$O$_2^{-1}$</td>
<td>513.9</td>
<td>33.3</td>
<td>0.50–0.51 (O$^-$), 1.47 (OH)</td>
</tr>
</tbody>
</table>

probably not discernable from the $^1$H-NMR. On the other hand, if we consider the series Si(OH)$_3$(OH)$_2$O$^{-1}$ – Si(OH)$_3$O$^{-1}$ we see a substantial change in $^1$H shielding, where the species with the larger deprotonation energy, Si(OH)$_3$O$^{-1}$, is more shielded. A similar trend was found by Fleischer et al. (1993) (their Fig. 5).

We find that $-\text{OH}_2$ oxygens and $-\text{OH}$ oxygens have rather similar electric field gradients (EFG), 1.3 to 1.5 atomic units, corresponding roughly to quadruple coupling constants of 6.8 to 7.8 MHz. These values are distinct from $-\text{O}^-$ oxygens which have much smaller electric field gradients. Hydration reduces the EFG of the $-\text{OH}$ oxygens and increases that for the $-\text{O}^-$ oxygens, but by only a modest amount. Thus, $^{17}$O NMR is potentially a means for assessing the interactions of neutral and ionized silanols with water.

In closing, we should caution that some basic questions concerning oxianion speciation may still be unresolved. We have assumed that the species formed by acid dissociation of Si(OH)$_4$ is the 4-coordinate Si(OH)$_3$O$^-$. An alternative is that OH$^-$ adds to Si(OH)$_4$ to form 5-coordinate Si(OH)$_5$O$^-$. Weldon, et al. (personal communication) have recently presented IR spectroscopic and computational evidence for 5-coordinate anionic centers on the surface of silica. Our own computational studies on Si(OH)$_3$O$^-...$H$_2$O and Si(OH)$_5$O$^-...$H$_2$O indicate that their relative energies are very close and fairly sensitive to the level of treatment. At the 6-31G* HF level assuming the 5-coordinate anionic species would change the deprotonation energy by $-5$ kcal/mol, projecting a change in pKa of only $-0.8$ units. Therefore, at this level of accuracy we can not really distinguish between 4-coordinate and 5-coordinate conjugate base species.

4. CONCLUSIONS

Our results indicate that it is presently impossible to calculate accurate absolute solution pK$_a$’s completely from first principles due to (i) inaccuracies in the available methods for evaluating hydration enthalpies of ions; and (ii) uncertainty in the proton hydration enthalpy. On the other hand, deprotonation energies in the gas phase can be calculated with an accuracy of a few kcal/mol, at least for monomeric oxyacids. However, it is possible to estimate solution pK$_a$’s reliably by using a correlation between experimental pK$_a$ values and calculated gas-phase or solution enthalpies. This correlation becomes better as the level of the calculation is improved, but it is already quite good at the 6-31G* HF level. Approximate correction for differential hydration enthalpies makes it possible to generalize this correlation so that several different types of acid dissociation reactions can be treated.

We find that gas-phase deprotonation energies are strongly correlated with the underbonding at the O, and that calculated potentials at the proton are correlated with electrostatic energies obtained using a simple charge model, based on formal or NBO charges. Thus, it is possible to establish a good correlation of pK$_a$’s with underbondings or with electrostatic energies for the monomeric oxyacids.

Polymerization invariably decreases the deprotonation energy, with changes in the potential at the proton, the electronic relaxation energy and the geometric relaxation energy all contributing. At least part of this variation is correlated with changes in the underbonding of the O, but none of the electrostatic models are able to reproduce the trend. The phosphate and silicate dimers have particularly small deprotonation energies due to internal H-bonding, which is compensated to some extent by reduced hydration enthalpies.

Hydration energies for the larger silicate species are difficult to calculate accurately but it appears generally that the difference in the local contributions to hydration enthalpies between the neutral acid and anion reaches a constant value for a relatively small number of explicit molecules of water. This suggests that determining the relative energetics of hydration of acid and anion entirely from quantum mechanics will soon be feasible.

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