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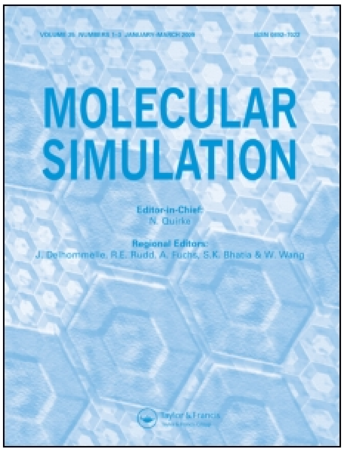

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Simulation of silicate structures in their aqueous solutions

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Simulated infrared spectra of ions derived from sodium monosilicate are compared with experimental spectra of aqueous sodium monosilicate solutions. It is demonstrated that models can only approximate the experimental IR spectra, if the calculations explicitly include a hydrate shell surrounding these ions. Applying the continuum solvent model alone does not change the qualitative behaviour of vibrational spectra.

Keywords: silicate; aqueous; infrared; modelling; BLYP

1. Introduction

Comparison of experimental and simulated IR spectra is a simple and quick method to confirm the reliability of models of small molecules and their presence in chemical systems. This principle can be applied for example to modelling the structures of alkaline silicate molecules dissolved in water. The average molweight of dissolved silicates varies from 1 to 13 [SiO_4] tetrahedra/mol depending on the concentration, the type of alkaline ion and the alkaline/silica ratio [1,2]. Although aqueous silicate solutions are important in biology, geology and a number of technical processes from zeolite synthesis to crude oil drilling [3], surprisingly little is known about their molecular constitution especially in the practically useful 0.1–3 mol/l concentration range at pH > 11.

Measuring the vibrational spectra of such solutions could be a convenient, widely accessible, non-invasive method for identifying some characteristic siloxane rings and Q^0, Q^1, Q^2 or Q^3 connectivities between their [SiO_4] building blocks in the sub-nanometer sized, dissolved silicate particles (Q^4 has not been identified in solutions; [1,2,4]). However, these structural assignments of vibrational spectra mostly rely on analogue studies on zeolites and glasses, the structures of which have been routinely analysed by IR and Raman spectroscopy for long. Since high resolution Si^{29} NMR studies indicate that the siloxane rings of the small soluble silicate ions might be quite different from those found in solids [5], confirmation of the vibrational spectra of such hypothetical structures by molecular models would be highly desirable.

It is well known that the electrostatic effect of highly polar solvents, like water, should be taken into account in order to make the models of polar molecules more reliable. We employed the well-established conductor-like screening model (COSMO) method [6] for modelling potential silicate molecules in their aqueous solution which has been also used by others [7]. It will be shown in this paper that this method is not adequate enough to generate even monosilicate models, which have reasonably similar IR spectra to the experimental spectra of corresponding dissolved silicates regardless of the approximation level used for the model calculations. It will be also shown that good spectral resemblance can be achieved when H_2O molecules surrounding the silicate ions are explicitly included into the calculations.

2. Experimental and computational methodology

Silicate solutions were made either from anhydrous Na_2SiO_3 from PQ Corporation (Metso Beads® 2048) or from $Na_2SiO_3 \times 9H_2O$ from Sigma (>98% purity) by dissolving appropriate amounts from these solids in deionised water. A Nicolet Magna 550 FTIR spectrometer equipped with a single bounce diamond ATR accessory was used for measuring the infrared spectra of the dissolved silicates. Further details of the solution preparation, properties and the spectroscopic methodology have been reported before [8].

The $DMol^3$ module [9] as implemented in Materials Studio® 4.0 program package by Accelrys was used to perform model calculations. Specifically, full geometry optimisations and vibrational frequency analysis were carried out using the BLYP gradient corrected density functional in conjunction with the DNP double-numeric basis set with polarisation functions in the all electron approximation using the fine quality throughout. Frequency and intensity benchmark calculations were carried out using Gaussian 03 [10].

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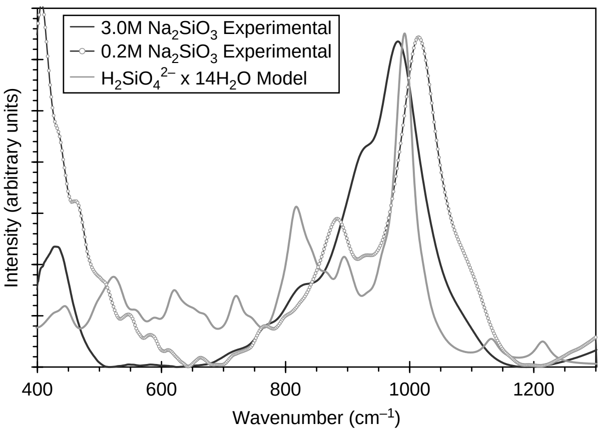

Figure 1. Experimental FTIR ATR spectra of 3 and 0.2 M aqueous Na_2SiO_3 solutions versus BLYP/DNP model spectrum of $H_2SiO_4^{2-}$ surrounded with 14 H_2O molecules.

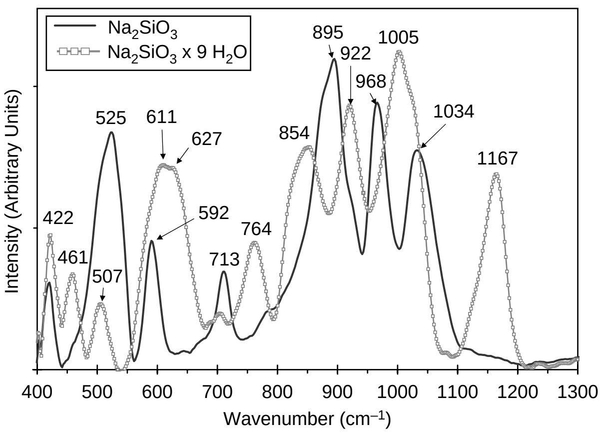

Figure 2. Experimental FTIR ATR spectra of the Q^2 type crystalline Na_2SiO_3 and that of the Q^0 type crystalline $Na_2SiO_3 \times 9H_2O$ (from [8]).

3. Results and discussion

The experimental FTIR spectra of a 3 and a 0.2 mol/l metasilicate solution are shown in Figure 1. It has been demonstrated before [8] that both solutions contain only $Na_2H_2SiO_4$ monomers from which about 32 and 82% of the Na^+ ions are dissociated at the higher (pH ~ 13.6) and the lower (pH ~ 13) concentrations, respectively.

For comparison, Figure 2 shows the spectra of the starting solids Na_2SiO_3 and $Na_2SiO_3 \times 9H_2O$. XRD studies proved that the crystals of the former, dehydrated silicate are built up from chains of $[\text{—O—}(SiO_2)^{2-}\text{—O—}]$ tetrahedra (overwhelmingly Q^2 structure) while the crystals of the hydrated metasilicate contain only isolated $[\text{H—O—}(SiO_2)^{2-}\text{—O—H}]$ tetrahedra (Q^0 structure; [11,12]). Further details about these structures and spectra have been reported before [8].

As theory predicts [13,14], the vibrational spectra of dissolved silicates contain fewer bands than those of the crystalline phases. Since substantial structural changes cannot take place in these monomer solutions [8], one must assume that the alteration of spectra with dilution as seen in Figure 1 is caused by the change of dissociation. This spectral difference manifests itself for example in the shift of the ν_{as} O—Si—O vibration from about 1020 to 980 cm^{-1} and the appearance of an intense band near 880 cm^{-1}, which has been associated with δ_{as} bending O—Si—O vibrations in the variously dissociated forms of the $Na_2H_2SiO_4$ molecule [8]. One characteristic of the FTIR spectra of these and many other silicates is the low intensity of their ν_{as} stretching and δ bending vibrations in the 500–750 cm^{-1} wavenumber range [2,4]. Since water has a rarely noted but extremely strong adsorption band between about 900 and 400 cm^{-1}, which might be due to H-bond hindered translational/rotational vibrations [15], one could suspect that despite its subtraction as background, this band might overlap and hide some weaker silica related IR bands from the solution spectrum. However, this clearly cannot happen with hydrophobic solid silicates which also show low absorption in this range [16,17].

To verify the conjectured effect of dissociation on the vibrational spectra of dissolved silicates, we calculated the virtual spectra of possible monosilicates at the BLYP/DNP level using simple chemical model systems. Figure 3 illustrates that, despite accurate full electron approximation and using COSMO for solvent effect, none of these model spectra resemble the experimental spectra shown in Figure 1. For comparison, Figure 3 also shows the calculated spectrum of the well-studied [18] H_4SiO_4 structure which cannot be present above about 2×10^{-3} M concentration near room temperature [19] at which the experimental spectra were obtained. It is unlikely that silicic acid or $HSiO_4^{3-}$ and SiO_4^{4-} ions form even at such low concentrations in our highly basic (pH > 13) solutions.

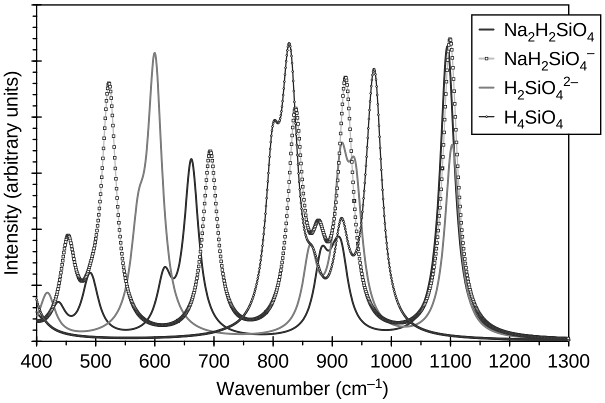

Figure 3. BLYP/DNP model spectra of various monosilicates without explicit consideration of hydration.

Table 1. Vibrational band intensities of $H_2SiO_4^{2-}$ calculated at various levels of approximation.

	Intensity (km/mol)				
Frequency (cm^{-1})	BLYP/DNP	BLYP/6-31-G*	BLYP/6-311 + G*	B3LYP/6-31G*	B3LYP-6-311 + G*
320 ± 8	12	–	7	–	5
335 ± 4	1	–	2	–	10
350 ± 1	5	–	–	–	1
371 ± 5	–	19	–	16	–
390	–	–	9	–	–
399	–	–	16	4	–
413 ± 4	7	20	–	–	13
426 ± 5	10	–	–	17	20
530	–	61	–	–	–
553 ± 8	–	21	41	27	–
579 ± 7	33	–	100	65	–
605 ± 5	100	79	–	–	40
636 ± 5	–	–	–	74	99
815	–	–	37	–	–
868 ± 5	29	64	–	–	36
888	–	–	38	–	–
910 ± 10	57	–	53	64	35
938 ± 4	50	100	–	–	52
966	–	–	–	93	–
1019	–	78	–	–	–
1 036 ± 8	–	–	97	75	–
1 099 ± 3	73	94	–	–	100
1149	–	–	–	100	–

In order to evaluate the accuracy of the BLYP/DNP level calculations against hybrid density functionals and larger basis sets, we used Gaussian 03 [10] to carry out benchmark calculations. Data in Table 1 indicate that neither the hybrid functionals nor the larger basis affect significantly the calculated IR spectrum. For example, each method generates a ν_{as} Si—O(H) related intense vibrational band near 600 cm^{-1} (where O(H) denotes a oxygen bonded to a hydrogen atom) and another ν_{as} Si—O related vibration around 1100 cm^{-1} (with oxygen atoms not bonded to hydrogens), which are absent from the experimental spectra in Figure 1. It is also worth pointing out that the Dmol^3 calculations require substantially less computational time (using the same hardware) than any of the other methods without significant loss in accuracy, as illustrated in Table 1.

We observed however remarkable changes in the model spectra when checked the explicit effect of hydrating water molecules. The solvent molecules were placed first to the proximity of a hydrogen or oxygen atom of the $H_2SiO_4^{2-}$ ion to generate the initial hydrogen bonds. After this, the system was relaxed. The resulting hydrate layer is very flexible and many local minima with similar total energies are expected to exist on the potential energy surface. Consequently, the calculated spectra can only represent one out of many possibilities, which are collectively present in the statistically averaged experimental spectrum. Figure 4 illustrates that an increasing number of H-bonded H_2O molecules around an $H_2SiO_4^{2-}$ ion shifts the positions and intensities of its IR bands substantially. The model spectrum with 14 H_2O molecules resembles quite well the experimental spectrum of the highly dissociated 0.2 M metasilicate solution (Figure 1) in which the $Na_2H_2SiO_4$ molecules were found to release more than 80% of their Na^+ content [8]. Considering the bond lengths and molecular distances in the energy minimised model of an $H_2SiO_4^{2-}$ ion hydrated by 14 H_2O molecules, one would estimate that approximately 18–20 H_2O is needed to form a full hydrate layer. This number coincides with the ~18 H_2O/[SiO_4] molar ratio in a 3 M silicate solution, which is considered to be the upper

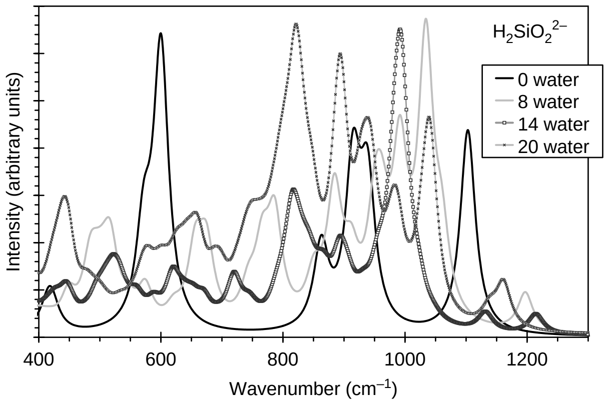

Figure 4. Effect of explicit consideration of H_2O molecules around a $H_2SiO_4^{2-}$ ion on its BLYP/DNP based IR spectrum.

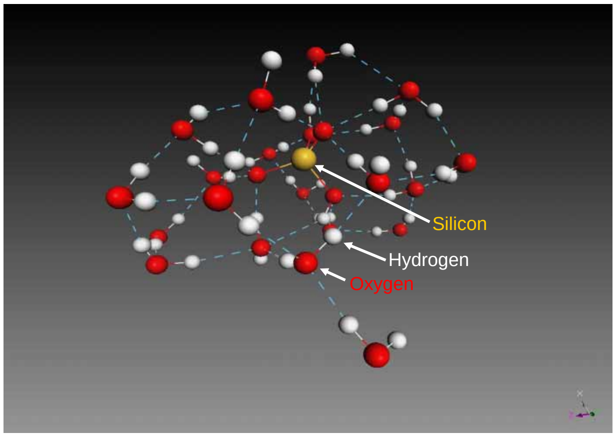

Figure 5. Arrangement of 20 H_2O molecules around a $H_2SiO_4^{2-}$ ion. The blue dashed lines represent hydrogen bonds.

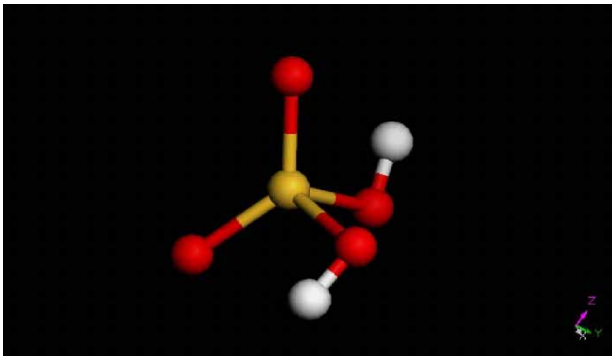

Figure 6. The $H_2SiO_4^{2-}$ ion after energy minimisation with BLYP/DNP COSMO model.

concentration limit of a ‘real’ solution, which has water-like viscosity and transparency and does not contain measurable amount of colloid sized (nm range) silica particles [19]. A typical arrangement of H_2O molecules around the $H_2SiO_4^{2-}$ ion after energy minimisation is shown in Figure 5, which also illustrates that the construction of a second hydrate shell began when the silicate ion was surrounded with 20 H_2O molecules in the model.[2] This seems to destroy the specific balance/symmetry of the system by overemphasising the typical 800 cm^{-1} band hence the calculated IR spectrum gets worse than the one modelled with 14 H_2O molecules (Figure 1). In contrast to prior assumptions [8,20], this band is associated with an asymmetric wagging motion of the H atoms, strongly coupled to changes in the arrangement of the water molecules so it is understandable that this mode is sensitive to the size and structure of the hydrating water cluster. Dilution, i.e. increasing water shell size around individual silicate molecules seems to intensify this band also experimentally in certain silicate solutions [2]. The exact arrangement of atoms in the energy-minimised model for the spectrum in Figure 1 and that of the models not containing explicit H_2O is given in the Supporting Information table. For comparison, Figure 6 shows the model of a $H_2SiO_4^{2-}$ ion without any explicit water hydration after minimised in the COSMO model. The relevant bond lengths and bond angles are indicated in Table 2 in comparison with the model considering also an explicit hydrate shell.

A full hydrate shell around a $NaH_2SiO_4^{-}$ ion or a non-dissociated $Na_2H_2SiO_4$ molecule must include many more water molecules than around the $H_2SiO_4^{2-}$ ion. To fully model a freely moving silicate ion in the liquid, one has to consider additional water layers externally bonded to the first hydrate shell. These clusters are prohibitively large for our current computing capacity and it is uncertain if it would further improve the quality of spectra compared to the optimum looking 14 $H_2O/H_2SiO_4^{2-}$ (Figure 1). Figure 7 illustrates that restricting ourselves only to 14

Table 2. Bond lengths and angles of $H_2SiO_4^{2-}$ calculated after minimisation with and without explicit hydrate shell.

	Vacuum	COSMO	14 explicit H_2O
Bonds		Bond length (Å)	
Si—O1	1.612	1.607	1.608
Si—O2	1.612	1.607	1.640
Si—O3	1.813	1.758	1.719
Si—O4	1.813	1.758	1.747
03—H1	0.977	0.974	0.991
O4—H2	0.977	0.974	0.982
Angles		Degree	
SJ-O3-O1	102.4	108.8	107.6
SJ-O3-O2	110.5	106.3	111.6
SJ-O3-O4	101.0	102.8	100.6
SJ-O1-O2	127.3	122.1	118.4

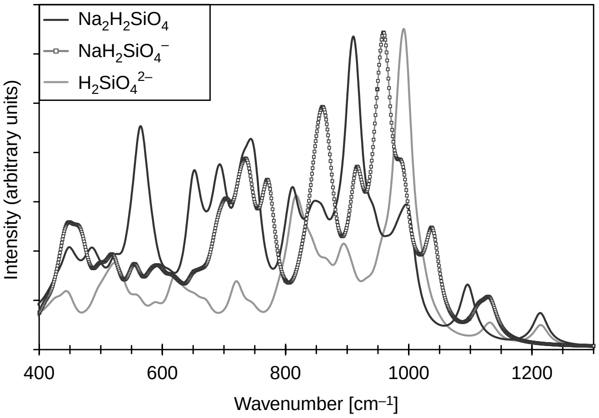

Figure 7. BLYP/DNP based IR spectra of variously dissociated $Na_2H_2SiO_4$ molecules surrounded with 14 H_2O molecules.

H_2O in the hydrate layer around the Na-containing monosilicates brought also much closer the appearance of the model IR spectra to the experimentally measured spectra (Figure 1 as discussed in [8]). Moreover, the shift of the most intense ν_{as} asymmetric stretching bands in the $900-1000\,cm^{-1}$ region is in excellent agreement with the predictions made from similar shifts in the experimental spectra [8] with increasing dissociation.

One can conclude therefore that in contrast to the common practice, it is imperial to include the hydrating water molecules to obtain a realistic model for the aqueous silicate molecules and presumably also other small molecules in their aqueous solutions. Some relevant results have been reported about other molecules and ions. For example, Suzuki and Sota [21] found that at least eight explicit water molecules had to be included into the model system of the glucose–water complex before the simulated IR spectrum (calculated with the implicit solvent model) agreed well with the experimental spectrum of the aqueous solution of glucose. Rodriguez-Ropear and co-authors [22] also found that the first solvation shell of a 2,2′-bithiophene molecule had to be completed by explicit water molecules before the bulk solvent effects were introduced to accurately simulate the relative energies of different conformers in aqueous solution. Kelly et al. [23] concluded that the pK_a value of some anions could only be calculated with acceptable accuracy when one or more explicit water molecules were included into the simulation, augmenting the implicit solvent model.

Summary

The IR spectra of some species relevant to the dissociation of $Na_2H_2SiO_4$ in aqueous solution were investigated using Dmol^3 as implemented in Materials Studio 4.0 by Accelrys. The BLYP functional with a double numeric polarised basis set was found to perform in vibrational frequency calculations about as good as the more accurate but much slower hybrid functionals and larger basis sets. Our results demonstrate that the chemical model system must contain explicit water molecules in order to reproduce the qualitative behaviour of experimental IR spectra.

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Notes

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2. Several attempts were made to place the additional H_2O molecules into positions which would complete the first hydration shell around the central ion, instead of starting the second hydration shell. In spite of all our efforts, the geometry optimisations generated structures similar to the one shown in Figure 5. One possible conclusion is that these arrangements are energetically strongly favored over the completion of the first hydrate shell and a complete second shell would be required (with a very large number of water molecules) to generate the expected arrangement of solvent molecules.

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