Hydroxylated crystalline edingtonite silica faces as models for the amorphous silica surface

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Abstract. Fully hydroxylated surfaces derived from crystalline edingtonite were adopted to model the variety of sites known to exist at the amorphous silica surface, namely isolated, geminal and interacting silanols. Structures, energetics and vibrational features of the surfaces either bare or in contact with water were modelled at DFT level using the B3LYP functional with a GTO basis set of double-zeta polarized quality using the periodic ab-initio CRYSTAL06 code. Simulated infrared spectra of both dry and water wet edingtonite surfaces were in excellent agreement with the experimental ones recorded on amorphous silica. Water interaction energies were compared with microcalorimetric differential heats of adsorption data showing good agreement, albeit computed ones being slightly underestimated due to the lack of dispersive forces in the B3LYP functional.

1. Introduction
Amorphous silica is a key material in metal-supported catalysts, surface functionalization and chromatography, just to mention few examples [1]. For these cases, the silica surface plays a leading role in: i) anchoring metals for catalysis; ii) grafting chemicals to impart specific functionality; iii) making selective H-bond interactions with adsorbates in chromatographic separations.

 Whereas the bulk of amorphous silica has been thoroughly studied using a variety of modeling techniques [2], much less resulted for the physico-chemical features of the amorphous silica surface. Two main reasons hampered the characterization of the amorphous silica surface by computer experiments: i) the non-crystalline nature of silica which forces the adoption of large unit cells to realistically model the material with exceedingly high computational demand; ii) the variety of surface sites which should be simultaneously present in the surface unit cell. It is indeed known from experiment [3] that the amorphous silica surface sports a variety of sites, namely: isolated silanol groups SiOH (so distant apart to avoid interaction), geminal (HO-Si-OH), vicinals (HO-Si-O-Si-OH), mutually H-bonded silanol groups (Si-OH···OH-Si) and the ubiquitously present siloxane Si-O-Si bonds (see Figure 1 for a schematic view). The distribution and typology of the various sites is a direct function of the temperature at which the silica sample was treated, whereas different conditions under which silica is synthesized are far less important in establishing the hydroxyls distribution [4].

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In the present work we propose a possible simple workaround to the difficulties described above. Instead of using a large and amorphous-like unit cell envisaging almost all silica surface sites, we have proposed in the past to adopt different hydroxylated surfaces derived from the crystalline edingtonite, a microporous material with very small and structurally rigid unit cell [5]. The physico-chemical properties computed for each separate crystalline face are then used to build a unified picture of the real surface, by combining the results for each separate surface. In this way, calculations are much faster and the only difficulty is left in properly designing the representative surfaces. In the past [5], the (100) hydroxylated surface of edingtonite was chosen to model the surface of amorphous silica pretreated at high T (about 600 °C), which only sports isolated silanols. The vibrational features due to the OH groups were shown to be in excellent agreement with the experimental ones, giving credit to this simple model. The same surface was then adopted [6] to model the interaction with NH$_3$, again showing excellent agreement with the experiment for the NH$_3$ adsorption energy and the perturbation of the OH stretching mode due to the H-bond interaction with NH$_3$.

Here, we extend upon our previous work by modeling two new hydroxylated surfaces, namely the (001) with either geminal or H-bonded silanols, the vicinal case being not addressed this time. These surfaces, together with the former (100) are then characterized as free and dry surfaces and as wet surfaces when water is considered as adsorbate.

2. Computational details

All calculations have been carried out at B3LYP level using the CRystAL06 periodic code [7]. The GTO basis set consisted of a 6-21G(d) ($\alpha_{p}=0.13$, $\alpha_{d}=0.5$), 6-31G(d) ($\alpha_{p}=0.2742$, $\alpha_{d}=0.6$) and a 31G(p) ($\alpha_{s}=0.1613$, $\alpha_{p}=1.1$) for Si, O and H, respectively (outer shell exponents in Bohr$^{-2}$). The Hamiltonian matrix is diagonalized in 4$k$ points, corresponding to a shrinking factor=2. Values (6,6,6,6,12) of the tolerances controlling Coulomb and exchange series have been adopted for all calculations. The exchange and correlation functional is integrated numerically on a pruned grid consisting of 75 radial points and 5 sub-intervals with (86, 194, 350, 974, 350) angular points, respectively. Standard internal defaults for geometry optimization were adopted for all calculations. Harmonic frequencies at $\Gamma$ point [8] have been computed for the SiOH/H$_2$O fragments only. Because
of the sizeable anharmonicity of the OH stretching modes, the harmonic values were all scaled by the same numerical factor derived by comparing the harmonic and the fully anharmonic B3LYP OH stretching value computed for the (100) hydroxylated surface [5], which only contains isolated SiOH groups. In this way the original $\omega _{h}(\text{OH})$ 3891 cm$^{-1}$ harmonic value corresponds to a fundamental $\omega _{01}(\text{OH})$ value of 3737 cm$^{-1}$, in excellent agreement with the 3740 cm$^{-1}$ value measured on amorphous silica [3]. The ratio $\omega _{01}(\text{OH})/\omega _{h}(\text{OH})$ defines the scale factor 0.960 which has been used to scale the B3LYP OH harmonic stretching frequencies for all considered models, including the OH stretching belonging to the H$_2$O molecule. Water interaction energies were all corrected for both basis set superposition error and lateral interactions (water/water interactions).

3. Structural models of the free edingtonite surfaces

Figure 2 shows the edingtonite bulk structure and the cuts (dotted lines) along chosen planes in order to define the various hydroxylated surfaces. Edingtonite is computationally convenient as a model for silica surfaces, due to its small unit cell (SiO$_2$)$_5$, high symmetry (P-4m2 space group) and rigidity. Also, for the corresponding surfaces, some symmetry is left: P2mm for ISO, P112 for GEM and Pm11 for INT, respectively. The scaled B3LYP OH stretching frequencies for the ISO and GEM surfaces are 3737, 3733 and 3735 cm$^{-1}$, respectively, showing an almost negligible change in frequency for the geminal silanols compared with the isolated ones, in agreement with experimental evidence.[3] The case of the INT surface is more tricky. The fully optimized structure resulted in a H·OH H-bond distance of 1.912 Å. The OH frequency of the H-bond SiOH donor of 3533 cm$^{-1}$ was shifted towards lower wavenumbers than the H-bond SiOH acceptor value of 3727 cm$^{-1}$ which is very close to the frequency of the ISO surface. However, in the real silica surface it is expected that different degrees of H-bond interactions are present, with consequently different bathochromic shifts suffered by the SiOH donor. To mimic this situation, the H···OH bond was fixed at five different distances ranging from its optimum value to 2.605 Å. For each H···OH configuration, a constrained optimization was carried out and OH frequencies computed accordingly.

Figure 2. Definition of edingtonite surfaces by cutting the bulk and healing the dangling bonds with H atoms. Dotted lines indicate the height at which the bulk is cut to give rise to: a) ISO, surface with isolated SiOH, b) INT, interacting Si-OH···OH-Si, c) GEM, geminal OH-Si-OH. Vectors are normal to the (100), (010) and (001) crystal planes, respectively.

The SiOH stretching frequency of the H-bond acceptor remains the same for all five cases, whereas the SiOH stretching frequency for the H-bond SiOH donor increases up to 3673 cm$^{-1}$ for the largest
H-OH considered distance. Comparison with experiment is not straightforward because rather broad bands are observed in the spectrum of amorphous silica outgassed at 423K, as a consequence of the H-bond interactions between surface silanols. A feature of H-bond is that not only the OH stretching band of the H-donor suffers bathochromic shift and intensification compared to the free OH mode, but also band broadening is usually observed [3]. This effect cannot be predicted ab-initio by the adopted methodology, therefore we resort to an empirical correlation \( \Delta_i = \frac{(\Delta \omega_i - a)}{b} \) between the band width at half-height, \( \Delta_i \), and the bathochromic shift, \( \Delta \omega_i \), of the the \( \text{i-OH} \) frequency, with \( a \) and \( b \) being empirical parameters [9]. A Lorentzian function \( Y_i(v) = S_i \Delta_i / (\pi(v - \omega_i)^2 + (\Delta_i/2)^2) \) is then adopted to represent an IR band centered at frequency \( v \) by means of the \( \Delta_i \) values, the B3LYP infrared intensities \( S_i \) and \( \omega_i \) frequency of the \( \text{i-OH} \) mode. Obviously, \( S_i = \int Y_i(v) \, dv \) so that the complete IR spectrum \( H(v) \) in the OH stretching region resulted as: \( H(v) = \sum \gamma_i Y_i(v) \), in which each band \( Y_i(v) \) is weighted by the factor \( \gamma_i \) derived from the experimental population of the ISO, GEM and INT sites, as derived from Zhuralev [4] for various silica samples. The resulting spectrum is shown in Figure 3, together with the experimental one [10] measured for an amorphous silica sample (Aerosil 300) outgassed at 423 K. The agreement is striking, considering the rather crude approximations adopted to arrive at the final simulated spectrum.

![Figure 3](image_url). B3LYP infrared simulated spectrum (blue continous line) compared to the experimental one (red dashed line) measured for amorphous silica (Aerosil 300) outgassed at 423 K.

As already stated, the OH frequencies for ISO and GEM sites are almost indistinguishable and both contribute to the sharp peak around 3740 cm\(^{-1}\), whereas the INT sites with a variable degree of H-bond strength are responsible of the broad band spanning a range of more than 300 cm\(^{-1}\) to lower wavenumbers.

4. Structural models of the edingtonite surfaces in interaction with water

In the previous section we showed that simulation of the IR spectrum of amorphous silica is possible by merging physico-chemical spectral features computed for the independent hydroxylated surfaces.
derived from the edingtonite crystalline material. A much more severe test of the present model is to simulate the adsorption of water on the considered surfaces. Water is an ubiquitous molecule in adsorption phenomena and its interaction with oxide surfaces is difficult to model because a variety of H-bond interactions of different strengths usually occurs. Figure 4 shows the different cases considered in the present ab-initio simulation. In general, water interacts more strongly as a H-bond acceptor (S bonds in Figure 4) than as a H-bond donor (L bonds in Figure 4), due to the rather low basicity of surface OH and Si-O-Si groups. ISO-W1 and ISO-W2 give rise to isolated H-bonded water molecules. The ISO-W3 case, represents the formation of the first water monolayer adsorbed on the ISO surface and mimic the condition of high water loading adsorbed on amorphous silica. For GEM-W1 H$_2$O bridges two geminal groups giving rise to H-bond rings, whereas GEM-W2 brings the rings in contact via rather weak hydrogen bonds (F bonds in Figure 4) through an extra water molecule. For INT-W surface, water bridges two interacting sites giving rise to infinite mono-dimensional chains with the highest degree of H-bond cooperativity.

**Figure 4.** Different views of the ISO, GEM and INT surfaces interacting with water molecules (in light colour). Different configurations and water loadings have been considered giving rise to short (S), long (L) and far (F) hydrogen bonds between water and the surface hydroxyls. For the INT-W case, the S and L hydrogen bonds are connected via the intra-surface H-bond (I) resulting in infinite chains. ISO-W3 case represents the highest water loading considered (ten H$_2$O per unit cell).

The rather diverse interactions envisaged by the considered models should be hopefully representative of the complex scenario occurring at the real silica surface. We adopted two different ways to prove that: on the one hand, the interaction energies between water and the surfaces were computed and compared with the differential heat of adsorption of water on Aerosil 300 obtained from microcalorimetric measurements [11], and on the other hand, the B3LYP infrared spectrum in the OH stretching region was computed following the same method described in the previous section.
and compared with the experimental spectrum recorded on the Aerosil 300 exposed at low water vapour pressure [10].

4.1. Water interaction energy

In a periodic treatment of surface adsorption phenomena, the interaction energy per unit cell per adsorbate molecule \( M \) is a negative quantity (for a bounded adsorbate) defined as:

\[
\Delta E = E(\text{SM//SM}) - E(S//S) - E_M(M//M)
\]

where \( E(\text{SM//SM}) \) is the energy of a fully relaxed unitary cell containing the surface slab \( S \) in interaction with the adsorbate molecules \( M \) (in the present case \( M = H \)), \( E(S//S) \) is the energy of a fully relaxed unitary cell containing the slab alone and \( E_M(M//M) \) is the molecular energy of the free, fully optimized adsorbate molecule (the symbol following the double slash identifies the geometry at which the energy has been computed). The above expression can also be equivalently recast to take into account the energy of deformation due to the change in geometry of both the adsorbed molecule and the surface upon interaction, by means of the following expressions:

\[
\Delta E = \Delta E^* + \delta E_S + \delta E_M
\]

\[
\delta E_S = E(S//S) - E(S//S) \quad \delta E_M = E(M//SM) - E_M(M//M) = \Delta E_M + \Delta E_L
\]

\[
\Delta E^* = E(\text{SM//SM}) - E(S//S) - E_M(M//M)
\]

in which \( \delta E_S \) is the deformation energy of the surface (\( \delta E_S > 0 \)) whereas \( \delta E_M \) accounts for both the deformation energy of the molecule (\( \Delta E_M \), *vide infra*) and the lateral intermolecular interactions (\( \Delta E_L \), *vide infra*) between the infinite molecule images in the same spatial configuration occurring in the SM periodic system. The purely molecule's deformation energy can be computed as:

\[
\Delta E_M = E_M(M//SM) - E_M(M//M)
\]

in which \( E_M(M//SM) \) is the molecular energies of the molecule frozen at the geometry occurring on the surface and \( E_M(M//M) \) is the molecular energy of a fully optimized free molecule, so that \( \Delta E_M > 0 \). The lateral intermolecular interactions, \( \Delta E_L \), are defined as:

\[
\Delta E_L = E(M//SM) - E_M(M//SM)
\]

and can be either positive (repulsion) or negative (attraction). With those positions, the \( \Delta E^* \) interaction energy is then deformation and lateral interactions free, being the result of energy differences between periodic calculations all carried out at the geometry of the SM system. For instance, \( E(\text{SM//SM}) \) is the energy of the unit cell of a crystal containing only a molecule in the same geometry assumed in the periodic calculations all carried out at the geometry of the SM system. The purely molecule's deformation energy can be computed as:

\[
\Delta E_M = E_M(M//SM) - E_M(M//M)
\]

in which \( E_M(M//SM) \) is the molecular energies of the molecule frozen at the geometry occurring on the surface and \( E_M(M//M) \) is the molecular energy of a fully optimized free molecule, so that \( \Delta E_M > 0 \). The lateral intermolecular interactions, \( \Delta E_L \), are defined as:

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\[
\Delta E_L = E(M//SM) - E_M(M//SM)
\]
Table 1. B3LYP energetic data for the water/edingtonite surface models. See the text for the meaning of the various terms. All data in kJ/mol.

| Model  | δE_S | δE_M | ΔE_M | ΔE_* | ΔE* | ΔE* | ΔE* | ΔE* |
|--------|------|------|------|------|------|------|------|------|
| ISO-W1 | 6    | -2   | 0    | -2   | -67  | -50  | -63  | -46  |
| ISO-W2 | 5    | 0    | 0    | 0    | -68  | -43  | -64  | -38  |
| ISO-W3 | 2    | -31  | 2    | -33  | -26  | -14  | -55  | -43  |
| GEM-W1 | 4    | -3   | 2    | -4   | -77  | -56  | -76  | -55  |
| GEM-W2 | 3    | -5   | 1    | -6   | -57  | -42  | -59  | -44  |
| INT-W  | 5    | 1    | 2    | -1   | -85  | -66  | -78  | -60  |

The deformation energy contributions (δE_S and ΔE_M) are in general small. These results are in fair agreement with the available differential heat of water adsorption on Aerosil 300, recently measured by means of microcalorimetry technique [11], spanning a range between 80/50 kJ/mol, with the smallest values corresponding to the highest water loading. We suggest that the general underestimation that occurs with the computed values may be due to the dispersion energy contribution to the interaction energy, not accounted for by the B3LYP functional and obviously present in the experimental heat of adsorption.

4.2. Infrared spectra of the edingtonite/water model systems

The IR spectra in the OH stretching region have been simulated following the same procedure already described for the free silica surface. Here, also the OH stretching modes from the water molecules were included in the spectra convolution. The comparison between the experimental spectrum, taken for an Aerosil 300 amorphous silica (previously outgassed at 423 K) after contacting with small water vapour pressure [10] and the B3LYP one is very good: the very broad feature extending to very low wavenumbers (about 1000 cm⁻¹ of bathochromic shift compared to the free SiOH frequency) due to the H-bonding contribution is well reproduced.

Figure 5. B3LYP infrared simulated spectrum (blue continuous line) and experimental one (red dashed line) measured for amorphous silica (Aerosil 300) outgassed at 423 K and exposed to low pressure of water vapour.
As expected, the smallest OH shifts compared to the unperturbed SiOH of the free ISO surface are due to water interacting with either ISO or GEM surface. Larger OH shifts occur either when the water loading is at its maximum (ISO-W3) or for the INT surface, in which H-bonding cooperativity plays a central role. Interestingly, the larger the interaction energy the higher are the OH frequency shifts.

5. Conclusions
The present results show that the ab-initio simulation of hydroxylated amorphous silica surfaces (both free and interacting with H$_2$O) is feasible without resorting to extremely demanding computer resources. The clue is to adopt a variety of hydroxylated surfaces cut out from the crystalline edingtonite structure: energetic and vibrational features for each separate crystalline face can be properly merged to arrive at a unified and satisfactory prediction of both water adsorption energy and infrared spectra of the bare and wet silica surfaces in the 2800-3800 cm$^{-1}$ frequency range.

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References

[1] Iler R K 1979 *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica* New York. John Wiley & Sons, Inc.
[2] Herzbach D, Mueser M and Binder K 2005 *J. Chem. Phys.* **123** 124711
[3] Knozinger H 1976. *The Hydrogen Bond*. Schuster P, Zundel G and Sandorfy C. Amsterdam, North Holland. III: 1263
[4] Zhuravlev L T 1997 *Langmuir* **3** 316
[5] Civalleri B, Casassa S, Garrone E, Pisani C and Ugliengo P 1999 *J. Phys. Chem. B* **103** 2165
[6] Civalleri B and Ugliengo P 2000 *J. Phys. Chem. B* **104** 9491
[7] Dovesi R, Saunders V R, Roetti C, Orlando R, Zicovich-Wilson C M, Pascale F, Civalleri B, Doll K, Harrison N M, Bush I J, D’Arco P and Llunell M 2006 *CRYSTAL06 User’s Manual* Torino (Italy). University of Turin. [http://www.crystal.unito.it](http://www.crystal.unito.it)
[8] Zicovich-Wilson C, Pascale F, Roetti C, Saunders V, Orlando R and Dovesi R 2004 *J. Comp. Chem.* **25** 1873
[9] Thiel M V, Becker E D and Pimentel G 1957 *J. Chem. Phys.* **27** 95
[10] Magnacca G *personal communication*
[11] Bolis V, Busco C and Ugliengo P 2006 *J. Phys. Chem. B* **110** 14849
[12] Boys S and Bernardi F 1970 *Mol. Phys.* **19** 553