Adsorption of Water and Methanol on Silica Hydroxyls: Ab Initio Energy and Frequency Calculations

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Received: October 9, 1996

Two hypothetical mechanisms proposed in the literature for the coordination of H₂O and CH₃OH on the isolated silica OH group are reexamined by computations on the related molecular models at SCF, MP2, and DFT levels. The computed energies suggest that these molecules stabilize on the isolated OH group by means of two hydrogen bonds, acting as a proton acceptor toward the silica OH group and as a proton donor toward a nearby SiOSi bridge. The alternative surface structures, with H₂O and CH₃OH acting exclusively as a proton acceptor toward the isolated OH group, are found to be less stable by ~8 kJ/mol. The check of these mechanisms against experimental IR data using the computed frequency shifts of CH₃OH upon the adsorption supports these results. The ab initio calculations suggest no significant difference in mechanism between the adsorptions on the isolated and geminal OH groups of silica. When stabilizing on a geminal OH group, H₂O and CH₃OH can form the extra hydrogen bond not only with the nearby SiOSi bridge but also with the complementary geminal OH group.

Introduction

The mechanism of interaction between water and the isolated OH group of silica is a debated theoretical problem. Two alternatives are proposed for this mechanism on the basis of ab initio energy calculations on molecular models.¹⁻⁸ The first one, with H₂O acting toward the OH group as a proton acceptor (structure 1), was suggested in refs 1—8. In those studies structure 1 was shown to be significantly more stable than structure 2, the H₂O bonded to the OH group as a proton donor. The most sophisticated energy analysis of these two structures was performed by Ugliengo et al.⁷,⁸ at the MP2/TZ+ + (2d,2p)/SCF/DZP level using H₃SiOH as a molecular model of the isolated OH group. The second mechanism was suggested in our investigation⁹ at the SCF/6-31G(d) and MP2/6-31G(d)/SCF/6-31G(d) levels with the Si(OH)₄ model of the surface. In this mechanism H₂O acts both as a proton acceptor and as a proton donor simultaneously toward the OSiOH surface site including the isolated OH group and a nearby O atom (structure 3). Moreover, our calculations showed structure 1 to be unstable: its optimization, allowing the O–H···O angle to vary, turns structure 1 into structure 3 without an energy barrier.

Also, for the interaction of methanol with the isolated silica OH group, Ugliengo et al.⁷,⁸ proposed the adsorbed molecule to behave exclusively as a proton acceptor (structure 4). By analogy with their calculations of H₂O on the isolated OH group,⁷,⁸ they used the HOSiH₃ model of the surface which enabled only one alternative structure to be considered, namely structure 5. This structure was found to be substantially less stable than structure 4.¹⁰ The calculations were done at the SCF level with the 6-31G(d,p) and DZP (TZP on O atoms) basis sets. We studied this reaction at the SCF/6-31G(d) and SCF/3-21G levels using the CH₃OH-Si(OH)₄ model,¹¹,¹² which allowed us to examine not only structures 4 and 5 but also structure 6. Like for the H₂O adsorption, our results suggested the 2-fold H-bonded species (structure 6) to be the most energetically preferable.

In our studies¹¹,¹² we proposed to use also the computed Δν(CH₃) frequency shifts of CH₃OH upon the adsorption for discriminating between the alternative mechanisms. We showed that in H-bonding interactions the Δν(CH₃) shifts of the CH₃O-containing molecules depend on the electron charge shift on the CH₃ group: an electron charge shift which decreases/increases the C⁺⁻H⁻ polarity of the C–H bonds makes the ν(CH₃) frequencies shift to higher/lower wavenumbers due to the increase/decrease of the covalent contributions to the C–H bonds. This electron mechanism agrees with the second Gutmann’s rule¹³ and the Chung–Bennett empirical dependence.¹⁴ Therefore structure 4 proposed by Ugliengo et al.⁷,¹⁰ contradicts the experimental fact that the CH₃OH adsorption on the silica OH groups causes the ν(CH₃) to decrease.¹⁵⁻¹⁸ In this structure the withdrawal of the electron charge from the CH₃ group should increase the ν(CH₃) frequencies¹¹,¹² (the directions of electron charge transfer are indicated by arrows in the structures). For instance, in the similar interactions of CH₂OCH₃ with the silica and zeolitic OH groups (structures 7 and 8), the νₚ(CH₃), νₚ(CH₃), and νₚ(CH₃) frequencies increase by 9, 21, 11 and 23, 51, 24 cm⁻¹, respectively.¹⁷,¹⁸ As to structure 6, its computed Δν(CH₃) frequency shifts were found to be in good agreement with the IR data.¹¹,¹²

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As an additional support of the 2-fold hydrogen-bonded H$_2$O and CH$_3$OH species on the OSiOH silica site, we note that they conform to the well-known bifunctionality of water and methanol, which leads these molecules to form similar cyclic hydrogen-bonded complexes

Although results of energy and frequency calculations are complementary in our study, we believe that the frequency analysis provides the main proof for the proposed adsorption mechanism. As the frequency shifts of adsorbed molecules depend in unique fashion on the adsorption mechanism, experimental IR data can be very useful for discriminating among the alternative structures for which energy calculations lead to contradictory results. Another important point is that according to our results, the computed frequency shifts of simple probe molecules on oxides are significantly less sensitive to the model size and basis set effects than the computed binding energies. Moreover, in many cases, using well-established empirical dependencies of the frequency shifts of probe molecules on adsorption mechanism, a hypothetical structure can be supported or unambiguously ruled out on the basis of a simple qualitative analysis of experimental IR data.

Details of Calculations and Frequency Analysis

Ab initio calculations were performed with the GAUSSIAN-92 and GAUSSIAN-94 packages. Various approximations were used, depending on the desired accuracy. For convenience their specifications are given below when discussing particular problems. Corrections to the adsorption energies for the basis set superposition error (BSSE) were estimated by the counterpoise method. Electrostatic potential energy derived net charges (PED) were computed at SCF level by means of the GAUSSIAN-94 POP=CHELPG option which utilizes the Breneman–Wiberg approximation. Corrections to SCF molecular electrostatic potentials due to the electron correlation are usually insignificant.

For checking hypothetical CH$_3$OH surface species against experimental IR data, we used their computed $\Delta\nu_{\nu}$(CH$_3$), $\Delta\nu_{\nu}$(CH), $\Delta\nu_{\delta}$(OH), and $\Delta\delta$(OH) shifts. The calculated $\Delta\nu_{\nu}$(CH$_3$) shifts were not involved in our theoretical analysis, as the harmonic frequency approximation does not take into account the Fermi resonances of the $\nu_{\nu}$(CH$_3$) mode with the overtones and combinations of the $\delta$(CH$_3$) modes. Moreover, a conclusive experimental assignment of the $\nu_{\nu}$(CH$_3$) band of CH$_3$OH on the OH silica groups has been missing in the literature up to now.

When discussing the CH$_3$OH adsorption, we use the computed proton donor OH frequency shifts for a qualitative analysis only. Results of a recent theoretical analysis of the different contributions to the OH frequency shifts of water, methanol, and silanol dimers suggest that both the harmonic frequency approximation and the level of the ab initio treatment adopted in our study are not sufficient for a quantitative description of the proton donor OH frequency shifts (see also ref 34). Moreover, the quantitative prediction of these shifts for the case of the CH$_3$OH adsorption would be useless for identifying the discussed H-bonded species as their precise experimental values are unknown. As Borello et al. showed (see also below), the CH$_3$OH adsorption produces a very broad, complex OH stretching band in the 3600–3200 cm$^{-1}$ region, and it is impossible to distinguish all the subbands owing to their large width and strong overlap. The same sort of experimental difficulties have led to a significant discrepancy in the assignment of the H$_2$O and SiOH $\Delta\nu$(OH) shifts for the case of the H$_2$O adsorption on silica (see refs 7 and 8 and references therein). Therefore we also do not use the computed OH frequency shifts of the adsorbed H$_2$O for discriminating between the alternative mechanisms.

In analyzing experimental IR data, we consider the IR bands of methanol on silica hydroxyls to be produced mainly by CH$_3$-OH species on the isolated OH groups, the concentration of
the geminal OH groups being smaller than that of the isolated ones by a factor of at least 3 (ref 8 and references therein).

For all the examined models of the H2O and CH3OH adsorption, our calculation results show only one energy minimum corresponding to the 2-fold H-bonding mechanism. The calculations of the constrained 1-fold H-bonded structures are performed mainly for examining whether the energy preference of the closed to open structures is large enough for the extra H-bond to play a significant role in the adsorption. As mentioned in the Introduction this problem emerges from conflicting situation in interpreting the reaction mechanism by different authors, which is mainly caused by the choice of different models for silica hydroxyls. Therefore these results are also used to check the adequacy of these models, which is important for their further employment in studying the adsorption on silica.

In the figures, of all the optimized geometry parameters, only the H-bond lengths are reported, computed at MP2 level. The difference between the H-bond lengths predicted by the MP2 and DFT calculations is insignificant. For the models involved in the electrostatic energy analysis, the SCF H-bond lengths and OH⋯O bond angle including the H2O OH group are also reported.

### Results and Discussion

#### 1. Energy Analysis. 1.1 Ab Initio Calculations

In Table 1 we report the BSSE corrected MP2/6-31G(d) binding energies of H2O on the OSiOH site computed with

(a) the H2O-HOSiH2OSiH3 model (1a and 1b, Figure 1) used by Sauer et al.,8 some O atoms in the first coordination spheres of the Si atoms being mimicked by H atoms;

(b) the H2O-(HO)3SiOSi(OH)3 model (2a and 2b, Figure 1) with the “natural” nearest surrounding of the Si atoms. In these models the SiOSi angle was fixed to 140°, the averaged value for silica. The OSi, OSiH, and HSiH angles were kept equal to 109.5°. Models 1a and 2a of the closed H2O structure were optimized under the C symmetry constraint. Models 1b and 2b of the open H2O structure were optimized with the additional \( \angle O-H-H = 180° \) and \( \angle H-O-H = 123° \) geometry constraints allowing the formation of only one H-bond: these values correspond to the optimal ones for the 1-fold H-bonding.

The energy preference \( E' - E'' = 1 \) kJ/mol of the closed to open structure computed with the H2O-HOSiH2OSiH3 model is too small for a definitive discrimination between the two examined mechanisms. As we will show below, the zero-point and thermal corrections should cancel out this small difference in the binding energy. Thus, in agreement with the theoretical study by Sauer et al.,8 the H2O-HOSiH2OSiH3 model suggests that a nearby siloxane bridge does not play a significant role in stabilizing water complexes on the terminal OH groups. As to the extended H2O-(HO)3SiOSi(OH)3 model, the corresponding \( E' - E'' = 10 \) kJ/mol value implies the 2-fold H-bonding mechanism of the adsorption. We computed these models also by a DFT method using the GAUSSIAN-94 BLYP option, which combines the exchange functional of Becke36 with the correlation functional of Lee, Yang, and Parr.37 These calculations were performed with a larger, combined basis set (CBS1): the 6-311G(d,p) basis set for H2O, the adsorbing H atom, and the O atoms surrounding the Si atom bonded to the adsorbing OH group and the 6-31G(d) basis set for the rest of the models. The BLYP/CBS1 calculations reinforce the MP2/6-31G(d) results (Table 1). According to the generally accepted methodology of the molecular approach, among the two examined models H2O-(HO)3SiOSi(OH)3 has to be taken as the most reliable one, the H2O-HOSiH2OSiH3 model being obtained by its simplification. Therefore these results suggest that the H2O-HOSiH2OSiH3 model used by Sauer et al.8 is inadequate for studying the mechanism in question. The reason of this inadequacy is explained below by the analysis of the Coulombic interactions in these models.

To check whether the neglect of the surrounding lattice in the (HO)3SiOSi(OH)3 surface model can significantly influence the result, we examined the convergence of the extra stabilization energy at the SCF/6-31G(d) level upon increasing the model size in the series (X1 = X2 = H) \( \times (X1 = \text{Si(OH)}_3, X2 = \text{H}) < (X1 = \text{H}, X2 = \text{Si(OH)}_3) < (X1 = X2 = \text{Si(OH)}_3) \). Our calculations for the 1a, 1b, 2a, and 2b models (Table 1) suggest that in computing the binding energy the SCF/6-31G(d) and BSSE corrected MP2/6-31G(d) methods lead to nearly the same results: the MP2 and BSSE corrections to the \( E' \) and \( E'' \) energies on going from the SCF/6-31G(d) to BSSE corrected MP2/6-31G(d) approximation about compensate each other. Such mutual compensation of the MP2 and BSSE corrections takes place also for the binding energies of 2CH3OH, CH3OH-SiH3OH, and 2SiH3OH complexes computed with a DZP (TZP on oxygen) basis set.10 The models with X1 = Si(OH)3 and X2 = H or Si(OH)3 were computed without geometry optimization, the geometry of the H2O-HOSiH2OSiH3 fragments of the closed and open structures being equal to those optimized for

### Table 1: BSSE Corrected Binding Energies of Closed, \( E' \), and Open, \( E'' \), H2O and CH3OH Adsorption Structures

<table>
<thead>
<tr>
<th></th>
<th>6-31G(d)</th>
<th>MP2/6-31G(d)</th>
<th>BLYP/CBS1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E' )</td>
<td>( E'' )</td>
<td>( E' )</td>
</tr>
<tr>
<td>1a, 1b</td>
<td>29 (36)</td>
<td>28 (33)</td>
<td>36 (52)</td>
</tr>
<tr>
<td>2a, 2b</td>
<td>28 (35)</td>
<td>21 (26)</td>
<td>38 (54)</td>
</tr>
<tr>
<td>3a, 3b</td>
<td>38 (56)</td>
<td>26 (37)</td>
<td>34 (50)</td>
</tr>
<tr>
<td>4a, 4b</td>
<td>39 (54)</td>
<td>30 (40)</td>
<td>36 (55)</td>
</tr>
<tr>
<td>5a, 5b</td>
<td>39 (55)</td>
<td>32 (43)</td>
<td>36 (51)</td>
</tr>
</tbody>
</table>

\( E' - E'' = 10 \text{ kJ/mol} \) for the closed to open structure computed with the H2O-HOSiH2OSiH3 model.
The SCF/6-31G(d) calculations show that the increase of the model size does not effect the $E_c - E_o = 10$ kJ/mol energy preference of the closed to open structure (Table 2). This result supports the adequacy of the (HO)$_3$SiOSi(OH)$_3$ model of the (Si)OSiOH site for studying the extra stabilization effect.

Also for CH$_3$OH on the OSiOH site our MP2/6-31G(d) and BLYP/CBS1 calculations using the (HO)$_3$SiOSi(OH)$_3$ model (Figure 2) lead to a similar result: the closed CH$_3$OH structure (3a) is more stable than the open one (3b) by $\sim 10$ kJ/mol (Table 1). This reflects the closeness of the acid-base properties of H$_2$O and CH$_3$OH, which led us to suppose that these molecules interact with the isolated SiOH silica group by the same mechanism and involve both of them in the study of this mechanism.9,11,12,17

We also computed the energy gain on going from the open to closed structure for the case of the H$_2$O and CH$_3$OH adsorption on the geminal silica OH groups, the adsorbed molecule forming the extra H-bond toward the neighboring OH group. The calculations were performed at the MP2/6-31G(d) and BLYP/CBS1 levels with the Si(OH)$_4$ model of the geminal OH groups (Figure 3). Similar to the (HO)$_3$SiOSi(OH)$_3$ model of the (Si)OSiOH site, this model of the (H)OSiOH site includes only the first coordination sphere of silicon atoms with respect to the surface OH groups. Our calculations suggest that for the same configuration of the (Si)OSiOH (2a, 2b, 3a, and 3b) and (H)OSiOH (4a, 4b, 5a, and 5b) sites the difference in energy between the extra H-bonds toward the complementary geminal OH group and toward the nearby siloxane bridge is insignificant (Table 1). This result also justifies the use of the Si(OH)$_3$ model for simulating the H$_2$O and CH$_3$OH adsorption on the (Si)-OSiOH site in our previous studies.9,11,12,17

As the found difference of $\sim 10$ kJ/mol in binding energy between the open and closed structures is quite small, the zero-point and thermal corrections should be taken into account when discussing their relative stability. However, the geometry constraints imposed on the above-discussed models do not allow one to employ them for evaluating all the relevant vibrational frequencies. Therefore we used the fully optimized M-Si(OH)$_4$ and M-HOSiH$_3$ (M = H$_2$O, CH$_3$OH) MP2/6-31G(d) models (Figure 4) to examine the effect of these corrections for the 2-fold and 1-fold H-bonding mechanisms, respectively. According to the results of the extensive use of HOSiH$_3$ as a model of the isolated silica OH group,7,8,10,23,24 this model is adequate for the quantitative description of the 1-fold H-bonding interactions on silica hydroxyls. The M-HOSiH$_3$ normal mode which corresponds to the M torsion around the H-bond was treated as a free rotation, contributing $0.5RT$ to the enthalpy.38 The results of our calculations (Table 3) show that the zero-point ($\Delta ZPE$) and thermal ($\Delta H_{th}$) corrections to the frozen nuclei binding energies can decrease the difference in stability between the closed (6a and 7a) and open (6b and 7b) structures by $\sim 2.5$ kJ/mol. This effect is mainly accounted for by the inter-

### Table 2: SCF/6-31G(d) Binding Energies of Closed, $E_c$, and Open, $E_o$, Adsorption Structures of Water$^a$ (kJ/mol)

<table>
<thead>
<tr>
<th>HOSi(OX1)$_2$OSi(OX2)$_3$</th>
<th>$E_c$</th>
<th>$E_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>35</td>
</tr>
<tr>
<td>Si(OH)$_3$</td>
<td>H</td>
<td>31</td>
</tr>
<tr>
<td>H</td>
<td>Si(OH)$_3$</td>
<td>36</td>
</tr>
<tr>
<td>Si(OH)$_3$</td>
<td>Si(OH)$_3$</td>
<td>33</td>
</tr>
</tbody>
</table>

$^a E_c (E_o) = E_{(complex)} - [E_{(substrate)} + E_{(adsorbate)}].$

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**Figure 2.** Molecular models of methanol on the OSiOH site of silica. H-bond lengths in angstroms at the MP2/6-31G(d) level.

**Figure 3.** Molecular models of water and methanol on geminal OH groups of silica. H-bond lengths in angstroms, bond angles in degrees at the MP2/6-31G(d) and SCF/6-31G(d) (underlined) levels.

**Figure 4.** M-Si(OH)$_4$ and M-HOSiH$_3$ (M = H$_2$O and CH$_3$OH) complexes fully optimized at the MP2/6-31G(d) level. H-bond lengths in angstroms.
TABLE 3: Adsorption Energy (−ΔE), Zero-Point (ΔZPE), and Thermal (∆H₉₀) Corrections and Standard Heat of Formation (∆H°) Corrections and Standard Heat of Formation (∆H°) (kJ/mol)

<table>
<thead>
<tr>
<th>model</th>
<th>−ΔE (kJ/mol)</th>
<th>ΔZPE (au)</th>
<th>∆H₉₀ (kJ/mol)</th>
<th>ΔH° (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>−35.7 (−55.9)</td>
<td>12.5</td>
<td>−3.3</td>
<td>−26.5</td>
</tr>
<tr>
<td>6b</td>
<td>−24.7 (−39.4)</td>
<td>8.2</td>
<td>−1.3</td>
<td>−17.8</td>
</tr>
<tr>
<td>7a</td>
<td>−35.5 (−57.8)</td>
<td>9.5</td>
<td>−0.8</td>
<td>−26.8</td>
</tr>
<tr>
<td>7b</td>
<td>−28.4 (−40.7)</td>
<td>6.4</td>
<td>−0.3</td>
<td>−22.3</td>
</tr>
</tbody>
</table>

* MP2/6-31G(d). Numbers in parentheses are not BSSE corrected values.

TABLE 4: Electrostatic Contributions to the Extra Stabilization Effect on going from Open to Closed Structure (kJ/mol)

<table>
<thead>
<tr>
<th></th>
<th>H₂O·H₂OSiH₃</th>
<th>H₂O·(HO)₂SiOSi(OH)₃</th>
<th>H₂O·Si(OH)₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₁</td>
<td>−2.1</td>
<td>−5.0</td>
<td>−2.1</td>
</tr>
<tr>
<td>Si₁</td>
<td>−1.7</td>
<td>−4.2</td>
<td>−1.7</td>
</tr>
<tr>
<td>O₂</td>
<td>−2.0</td>
<td>−4.0</td>
<td>−2.0</td>
</tr>
<tr>
<td>other atoms</td>
<td>−1.9</td>
<td>−4.2</td>
<td>−1.9</td>
</tr>
<tr>
<td>total</td>
<td>−19.9</td>
<td>−38.9</td>
<td>−19.9</td>
</tr>
</tbody>
</table>

* PED charges and geometries are derived from SCF/6-31G(d) 1a, 1b, 2a, 2b, 3a, and 4b models.

molecular vibrational frequencies of M-Si(OH)₃ being larger than those of M-HOSiH₃, which results from the extra H-bond in M-Si(OH)₃ and makes its ΔZPE be larger (Table 3). To summarize, these results suggest that the total effect of the zero-point and thermal corrections on the relative stability of the closed and open structures is not essential.

It is to be noted that the difference in the MP2/6-31G(d) adsorption energy between the fully optimized closed and open H₂O (6a and 6b) and CH₃OH (7a and 7b) structures closely corresponds to that between the related constrained models (4a, 4b, 5a, and 5b) (cf. Tables 1 and 3). This fact warrants our use of the constrained models for estimating the relative stability of the 2-fold and 1-fold H-bonded species.

1.2 Electrostatic Interaction Analysis. Ugliengo et al. showed²³ that the pure electrostatic interaction plays the predominant role in the moderate strength H-bonding. As a consequence, the successful use of small molecular models for describing the H-bonding on oxides implies that an H-bonding mechanism on an oxide should be mainly defined by the electrostatic interaction of the adsorbed molecule with "the site", i.e. a very few nearby surface atoms. Therefore, below we interpret the difference in the extra stabilization energy between the H₂O·H₂OSiH₃ model used by Sauer et al.⁸ and the extended H₂O·(HO)₂SiOSi(OH)₃ model in terms of the difference in the electrostatic properties between the OSiOH adsorbing sites of these models.

In Table 4 we compare the electrostatic contributions to the H₂O extra stabilization energy from the atoms of the OSiOH site of the HOSiH₂OSiH₃ and (HO)₂SiOSi(OH)₃ models. The calculations were performed using the geometry and PED charges (Table 5) of the optimized 1a, 1b, 2a, and 2b SCF/6-31G(d) models. The numbering of the atoms of the HOSiH₂OSiH₃ and (HO)₂SiOSi(OH)₃ models is shown in the following schemes

![Schematic diagram](image)

The data of Table 4 suggest that the difference in the extra stabilization energy between these models is mainly accounted for by the difference in the electrostatic interaction of the adsorbed H₂O molecule with the Si atom of the OSiOH site, the contributions to the extra stabilization from the adsorbing OH group, the bridging O atom, and the rest of the models being approximately equal. As follows from the data of Table 5, this effect results from the significant underestimation (by ~0.5 au) of the corresponding q(Si) charge in the HOSiH₂OSiH₃ model compared to that in the extended (HO)₂SiOSi(OH)₃ model. This underestimation is explained by the not realistic chemical surroundings of the Si atom in the HOSiH₂OSiH₃ model, with the two nearby O atoms being mimicked by H atoms. The data of Table 4 also suggest that the stabilization effect cannot be simply interpreted in terms of the additional H-bonding to the O atom of the SiOSi bridge: a significant contribution to the extra stabilization energy is due to the H₂O electrostatic interaction with the nearest Si atom. This result further stresses the importance of the correct description of the q(Si) charge of the OSiOH site in studying the discussed mechanism.

To check the cluster size effect on the electron distribution on the adsorption site, we examined the Mulliken atomic charges of the OSiOH site in the series of the SCF/6-31G(d) HOSi(OX)₁OSi(OX)₂ (X₁ = H, Si(OH)₃, and X₂ = H, Si(OH)₃) models. In agreement with the suggestion by Ugliengo et al.,¹⁹ we assumed that for a molecular fragment in a family of alike systems Mulliken populations should give a rough description of electronic flows. The averaged absolute charge of the OSiOH atomic charges is ~0.02 au only, which conforms to the insignificant change of the SCF/6-31G(d) binding energies of H₂O on the OSiOH site in this series (see above).

In Table 4 we also report the electrostatic contributions to the extra stabilization energy for the case of the H₂O adsorption on the geminal OH groups. The calculations were performed with the geometry and PED charges (Table 5) of the 4a and 4b SCF/6-31G(d) models, the numbering of the atoms of the Si(OH)₄ model corresponding to the scheme

![Schematic diagram](image)

The comparison of the related contributions for the H₂O on the (Si)OSiOH and (H)OSiOH sites reveals a difference in the extra stabilization mechanism between these structures. As distinct from the H₂O adsorption on the (Si)OSiOH site, in the adsorption on the (H)OSiOH site the stabilization effect is mainly caused by the H₂O interaction with the O atom of the neighboring OH group, while the contribution from the Si atom is negligible. Also the difference in the geometry of the examined models conforms to this result (cf. the SCF/6-31G-
(d) geometry of 2a and 4a, Figures 1 and 3). In comparison with the (Si)OSiOH site, on the (H)OSiOH site the extra H-bond is shorter by ≈0.2 Å and the OHO angle of the OHNCd-O fragment including this bond is closer to the optimal ≈180° value by ≈10°. Both these differences in geometry strengthen the extra H-bond but nearly eliminate the extra stabilization effect from the Si atom for the H2O on the (H)OSiOH site. As a result, in spite of the difference in the electrostatic potential between the (Si)OSiOH and (H)OSiOH sites which causes the above-mentioned difference in geometry, the total extra stabilization effect on both the sites is approximately the same. Our analysis of the Coulombic interactions in the SCF/6-31G(d) 3a, 3b, 5a, and 5b models shows similar peculiarities for the mechanisms of the CH2OH stabilization on these sites. The found difference between the 2-fold H-bonded species on the isolated and on the geminal OH hydroxyls agrees with the suggestion by Ugliengo et al.,24 that the SiOSi oxygen should be less basic than that of the SiOH group.

According to our results, the main features of the studied mechanism are accounted for by the interaction of the adsorbed molecules with the very small group of nearby surface atoms, i.e., with the adsorbing site. This fact further supports the basic assumption of the molecular approach to the modeling of the adsorption on oxides. At the same time, considering the long-range character of the Coulombic interactions, the contribution to the bonding energy from the rest of the models is not negligible (Table 3). This means that in the real system, due to the heterogeneity of silica surface, the contribution from the rest of the surface should cause some variation of the bonding energy but should not change the general adsorption mechanism defined by the site. The small change of the HOSi(OX1)10OSi(OX2)2 binding energy in the series (X1 = Si(OH)3, X2 = H) < (X1 = Si(OH)3, X2 = H) < (X1 = H, X2 = Si(OH)3) supports this suggestion (Table 2).

PED models can provide only a rough description of the adsorption interactions.23 Even considering the fact that H-bonding is basically related to electrostatic interactions,10,23 the simulation of the electron density of molecules by simple monopoles centered on nuclei position is rather crude. However, according to the results for similar complexes,10 a reasonable explanation of the relative capacity of the models for the extra stabilization is mainly caused by the error in simulating the electron density on the O atoms. According to the results for similar complexes,10 a quantitative description of the Coulombic interactions involving OH groups requires a more sophisticated modeling of the electron density on oxygen by centering two more charges on the “lone pair” sites.10

To summarize, our ab initio calculations and electrostatic energy analysis suggest that H2O and CH3OH adsorb on silica hydroxyls by the 2-fold H-bonding mechanism, forming the extra H-bond to the O atom of the SiO$i$ or SiOH (in the case of the coordination on geminal OH groups) nearby site.

2. Frequency Analysis. 2.1 Frequency Shifts: Basis Set, Electron Correlation, and Model Size Effects. Although errors in the computed HF force fields are not insignificant, the HF harmonic frequency approximation correctly describes the intramolecular frequency shifts upon interaction,25,26,34,35 as for the same fragment in different chemical environments these errors are quantitatively systematic.39 To illustrate this fact for the involved frequencies, in Table 6 we compare the experimental ∆ν(CH3), ∆ν(OH), and ∆δ(OH) frequency shifts of CH3OH linear dimer in matrix isolation11,40,41 and of CH3OCH3 on the silica and zeolitic OH groups15 with the corresponding HF harmonic frequency shifts of the CH3OH dimer (8a) and of the CH3OCH3-Si(OH)4 (8b) and CH3OCH3-r(HO)3SiOHAl(OH)3 (8c) models (Figure 5). The calculations were performed with a combined basis set (CBS2): the 6-311++G(d,p) basis set for the methanol OH group, the dimethyl ether oxygen, and the interacting OH groups of the Si(OH)4 and HO3SiOHAl(OH)3 and the 6-31G(d) basis set for the rest of the complexes. The deviation between the computed and experimental ∆ν(CH3), ∆ν(OH), and ∆δ(OH) shifts is 3 (average), 2, and 5 cm$^{-1}$, respectively (Table 6). Considering the possible frequency shifts...
of a few cm$^{-1}$ due to the matrix isolation\textsuperscript{42} and the accuracy of the experimental measurements of a few cm$^{-1}$, we regard this agreement between the theoretical and experimental data as a very good one.

To check the basis set and electron correlation effects on the calculated shifts, the CH$_3$OH dimer was recomputed at the SCF/6-311G(d,p) and MP2/CBS2 levels; neither the extension of the basis set (cf. CBS2 and 6-311G(d,p)) nor the inclusion of the electron correlation (cf. CBS2 and MP2/CBS2) affect significantly the results (Table 6). Therefore, we suggest the CBS2 shifts to correspond to the theoretical limit of the harmonic approximation within a few cm$^{-1}$.

CH$_3$OCH$_3$:Si(OH)$_4$ (8b) was calculated also with a smaller combined basis set (CBS3): CBS2 basis set for the adsorbed molecule and the interacting SiOH fragment and the 3-21G basis set for the rest of the complex. This simplification of the description nearly does not change the computed shifts (Table 6). Therefore, to lower the computational cost, we calculated extended models of CH$_3$OCH$_3$ and CH$_3$OH on the OsSiOH site with the CBS3 basis set (see below).

To check the model size effect on the calculated shifts, we recomputed CH$_3$OCH$_3$ on the silica OH group (8b) with the CH$_3$OCH$_3$:HOSi(OX)$_3$ (X = Si(OH)$_3$) model (8b'). This inclusion of the second coordination sphere of silicon atoms with respect to the interacting OH group improves the results: the overestimation of the experimental $\Delta
u_{\text{CH}_3}$ (CH$_3$) and $\Delta
u_{\text{CH}_3}$ (CH$_3$) shifts by 2 and 5 cm$^{-1}$ decreases to 0 and 1 cm$^{-1}$, respectively (Table 6). Also in describing CO on the silica OH group such extension of the model causes a similar effect: the overestimation of the $\Delta\nu$ (CO) = 14 cm$^{-1}$ shift\textsuperscript{43} by 4 cm$^{-1}$ decreases to 0 cm$^{-1}$ on going from the CO:Si(OH)$_3$ (8d) to CO:HOSi(OX)$_3$ (X = Si(OH)$_3$) model (8d') (Table 6). According to the linear dependence of the frequency shifts of probe molecules on the adsorption interaction strength,\textsuperscript{44,46} these results suggest that the Si(OH)$_3$ model of the isolated OH group somewhat overestimates the interaction strength, while the extended HOSi(OX)$_3$ (X = Si(OH)$_3$) model provides a better description. Therefore, when calculating the frequency shifts of CH$_3$OH on the isolated OH group (see below), we used the extended CH$_3$O:HO:HOSi(OX)$_3$ (X = Si(OH)$_3$) model for the closed and open structures, respectively, containing the second coordination sphere of silicon atoms with respect to the OH and O interacting sites of the surface.

In Table 7 we report the $\nu$(CH$_3$), $\nu$(OH), and $\delta$(OH) frequencies of the 2-fold hydrogen-bonded CH$_3$OH:Si(OH)$_3$ complex computed with full geometry optimization (7a) and under the C$_s$ symmetry constraint (5a). The symmetry constraint insignificantly influences the $\nu$(CH$_3$) frequencies and does not change strongly the $\nu$(OH) and $\delta$(OH) frequencies. This result justifies the $C_s$ symmetry imposition for reducing the computational cost in our calculations.

2.2 Frequency Shifts: Dependence on the Adsorption Mechanism. The calculated and experimental data presented in Table 6 allow the derivation of some important qualitative dependencies of the frequency shifts on the hydrogen-bonding mechanism. First, as shown in refs 11 and 12, a hydrogen bond which causes a decrease of the electron charge on the CH$_3$ group (8a(2), 8b, and 8c) leads to an increase of the $\nu_{\text{CH}_3}$ (CH$_3$) and $\nu_{\text{CH}_3}$ (CH$_3$) frequencies and vice versa (8a(1)). Second, while the $\nu$(OH) and $\delta$(OH) frequencies of the proton donor CH$_3$OH (8a(1)) are known to shift noticeably to lower and higher frequencies, respectively,\textsuperscript{31,40,41,47} those of the proton acceptor CH$_3$OH (8a(2)) are nearly insensitive to the hydrogen bonding. (This was noticed also in a theoretical study by Ugliengo et al.\textsuperscript{10}) These data together with the experimental IR data on CH$_3$OH in NaZSM-5 and KZSM-5 zeolites\textsuperscript{48,49} and our results on the simplified CH$_3$OH+[NaOH-2H$_2$O] model (9, Figure 6) of CH$_3$OH in NaZSM-5 zeolite (Table 8) allow one to state that a coordination of CH$_3$OH through the oxygen should only slightly influence the $\delta$(OH) vibration in the general case, the $\delta$(OH) band being very sharp and falling in the narrow 1345–1360 cm$^{-1}$ spectral region (cf. IR spectra in refs 48 and 49, for example).

According to these dependencies, one should expect that if CH$_3$OH interacts with the isolated silica OH group as a proton acceptor, as proposed by Ugliengo et al.\textsuperscript{8,10}, then upon CH$_3$OH adsorption on hydroxylated silica (a) the $\nu_{\text{CH}_3}$ (CH$_3$) and $\nu_{\text{CH}_3}$ (CH$_3$) bands should shift to higher frequencies; (b) the very sharp band of the $\delta$(OH) mode should appear in the 1345–1360 cm$^{-1}$ region.

However, as follows from experimental IR data (see below), this is not the case.

2.3 Analysis of Experimental IR Data. The $\Delta\nu$(CH$_3$), $\Delta
u$(OH), and $\Delta\delta$(OH) shifts of methanol on the silica OH groups are of prime importance for our determination of the adsorption mechanism. Therefore our assignment of the related experimental frequencies deserves a separate comment. As suggested in ref 17, the first methanol doses admitted on silicalite and silica outgassed at $T \gtrsim 800$ K react with the edge-shared tetrahedral defects (structure 12) and with the strained siloxane bridges (structure 14)
producing isolated (structure 13) and hydrogen-bonded (structure 15) SiOCH₃ methoxy groups. The isolated SiOCH₃ group manifests itself by νₛ(CH₃) = 2997 cm⁻¹, νₛ''(CH₃) = 2959 cm⁻¹, and ν_(s)(CH₃) = 2857 cm⁻¹ bands; 15,17,18,32,48 (Figure 7). We first assigned the CH stretching frequencies to the hydrogen-bonded SiOCH₃ group; 17 from IR data and calculation results we inferred that the νₛ(CH₃), νₛ''(CH₃), and ν_(s)(CH₃) bands of this species should be shifted by ~20 cm⁻¹ to higher frequencies with respect to the corresponding 2997, 2959, and 2857 cm⁻¹ bands of the isolated SiOCH₃ groups; they should also be broadened due to the structural inhomogeneity of this species. The electron mechanism of these shifts is analogous to that of the upward Δνₛ(CH₃) and Δν_(s)(CH₃) shifts of the proton acceptor CH₃OH and CH₃OCH₃ molecules (see above). Only the broad νₛ''(CH₃) ~ 3020 cm⁻¹ band of this species is observable as a high-frequency shoulder of the 2997 cm⁻¹ band; 17 while the νₛ''(CH₃) and ν_(s)(CH₃) bands, expected at ~2980 and ~2880 cm⁻¹, cannot be distinguished among other sharp bands in the complex 3000–2860 cm⁻¹ spectral region. When the very active edge-shared defects and strained siloxane bridges are used upon successive increase of the coverage, the adsorption takes place on the OH groups. As Sneh and George showed; 20 at this stage CH₃OH initially forms 1:1 hydrogen-bonded complexes with the silica hydroxyls. This CH₃OH species gives rise to the ν_(s)(CH₃) band at 2984 cm⁻¹ and causes downward shifts of the νₛ''(CH₃) = 2997 cm⁻¹ and νₛ''(CH₃) = 2959 cm⁻¹ bands by 3 and 9 cm⁻¹, respectively (Figure 7). The appearance of the ν_(s)(CH₃) = 2845 cm⁻¹ band is accompanied by the appearance of a sharp band at 3632 cm⁻¹ and a broad band at 1390 cm⁻¹ (Figures 7 and 8). We assign them to the ν(OH) and δ(OH) modes of the hydrogen-bonded species, respectively. The 2845 and 3632 cm⁻¹ bands were also detected in very thorough IR investigations of the CH₃OH adsorption on silica by Borello et al. 15,16 and attributed to the ν_(s)(CH₃) and ν(OH) vibrations of methanol on the OH groups. The changes of the spectra upon the progressive desorption (Figures 7 and 8), which removes the hydrogen-bonded species, supports this assignment of IR bands to CH₃OH on silica OH groups.

Three important conclusions follow from these experimental data on the basis of the above-mentioned dependencies of the frequency shifts on the adsorption mechanism:

1. No sharp δ(OH) band appears in the 1345–1360 cm⁻¹ region upon the adsorption (Figure 8). This fact disagrees with the suggestion by Ugliengo et al. 8,10 that CH₃OH stabilizes on the isolated OH group through the oxygen only, i.e. that the hydrogen of the methanol OH group remains nonbonded and its in-plane COH bending vibration is unperturbed.

2. Also the Δνₛ''(CH₃) = -11 cm⁻¹, Δνₛ''(CH₃) = -3 cm⁻¹, and Δν(OH) = -35 cm⁻¹ shifts of the CH₃OH with respect to the free methanol νₛ''(CH₃) = 3005 cm⁻¹, ν_(s)(CH₃) = 2848 cm⁻¹, and ν(OH) = 3667 cm⁻¹ frequencies; 31,40 are at variance with the assumption of the CH₃OH 1-fold hydrogen bonding as a proton acceptor. The νₛ''(CH₃) and ν_(s)(CH₃) bands of a proton acceptor CH₃OH should undergo upward, not downward, shifts. As to the ν(OH) frequency, according to Ugliengo et al. 8,10 and our results (see above), in this mechanism it should change by a few cm⁻¹ only.

3. The following features of the Δν(OH) and Δδ(OH) frequency shifts suggest the 2-fold hydrogen bonding of CH₃OH on the OSiOH site:

(a) according to experimental IR data; 31,40,47 the upward Δδ(OH) = 42 cm⁻¹ shift is an indication of the interaction of CH₃OH as a proton donor. At the same time both IR data 15–17 and energy calculation results; 8,10–12,17 suggest the silica hydroxyls to be involved in the interaction as a proton donor too. To explain this fact one should assume that the CH₃OH acts simultaneously as a proton acceptor toward the SiOH group.

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**Figure 7.** IR spectra of methanol on silicalite (from ref 17). (a) Spectrum 1: silicalite outgassed at 773 K. Spectra 2–6: increasing number of doses up to CH₃OH pressure (2), 50, (3) 10², (4) 5 × 10², (5) 10³, and (6) 2 × 10³ Pa. (b) Extended view of the CH stretching region of (a) (after background and hydrogen-bond band tail subtraction). (c) Effect of outgassing. Spectrum 6 corresponds to spectrum 6 of (a). Spectra 7–11: effect of decreasing CH₃OH pressure to (7) 5 × 10², (8) 10², (9) 50, (10) 20, and (11) 5 Pa. (d) Extended view of the CH stretching region of (c) (after background and hydrogen-bond band tail subtraction).

**Figure 8.** IR spectra of the CH stretching region (from ref 17). (a) Increasing number of doses of CH₃OH. Spectra 2–6 correspond to spectra 2–6 of Figure 7. (b) Effect of outgassing. Spectra 6–10 correspond to spectra 6–10 of Figure 7.
TABLE 9: MP2/6-311++G** Δν(OH) Shift of DOH in Optimal and Strained DOH-OD2 Dimers* (cm⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>Δν'(CH3)</th>
<th>Δν''(CH3)</th>
<th>Δτ(OH)</th>
<th>Δδ(OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10a</td>
<td>183°</td>
<td>-117</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>10b</td>
<td>150°</td>
<td>-74</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>140°</td>
<td>-44</td>
<td>-45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>130°</td>
<td>-28</td>
<td>-39</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*With respect to free DOH ν(OH) = 3947 cm⁻¹ and δ(OH) = 1427 cm⁻¹ frequencies.

Figure 9. Optimized and strained DOH...OD2 dimers computed at the MP2/6-311++G(d,p) level. O--H...O angle of strained dimer is 140°. H-bond lengths are in angstroms.

TABLE 10: Frequency Shifts of CH3OH on the OSiOH Site (cm⁻¹)

<table>
<thead>
<tr>
<th>Model</th>
<th>Δν'(CH3)</th>
<th>Δν''(CH3)</th>
<th>Δτ(OH)</th>
<th>Δδ(OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a'</td>
<td>5</td>
<td>12</td>
<td>3</td>
<td>-3</td>
</tr>
<tr>
<td>3b'</td>
<td>-11</td>
<td>-3</td>
<td>-35</td>
<td>32</td>
</tr>
<tr>
<td>expd</td>
<td>-16</td>
<td>1</td>
<td>-75</td>
<td>53</td>
</tr>
</tbody>
</table>

CBS basis set (6-311+G(d,p) basis set for oxygen participating in extra H-bond in 3a'). With respect to free CH3OH ν''(CH3) = 3311 cm⁻¹, ν'(CH3) = 3192 cm⁻¹, τ(OH) = 4190 cm⁻¹, and δ(OH) = 1490 cm⁻¹ frequencies. With respect to free CH3OH ν''(CH3) = 3005 cm⁻¹, ν'(CH3) = 2848 cm⁻¹, τ(OH) = 3667 cm⁻¹, and δ(OH) = 1348 cm⁻¹ frequencies. Reference 17. Used for qualitative analysis only (see text).

and as a proton donor toward a nearby oxygen of the surface, i.e. by the 2-fold hydrogen-bonding mechanism;\(^{11,12,17}\)

(b) although the Δδ(OH) = 42 cm⁻¹ is comparable with the Δδ(OH) shifts of methanol upon hydrogen bonding of moderate strength,\(^{31,40,47}\) the Δτ(OH) = -35 cm⁻¹ is too small to be accounted for by the formation of an ordinary moderate hydrogen bond. The fact that |Δτ(OH)|/|Δδ(OH)| < 1, while usually |Δτ(OH)|/|Δδ(OH)| ≥ 2,\(^{47}\) can be accounted for by the 2-fold hydrogen bonding, i.e. by the formation of a strained cyclic structure. As an example, in Table 9 we report the calculated MP2/6-311++G(d,p) Δτ(OH) and Δδ(OH) shifts of the proton donor DOH molecule in optimal and strained DOH-OD2 water dimers (10a and 10b): the O--H...O angles of the three calculated strained dimers were fixed at 150°, 140°, and 130° during the optimization. (The deuterated molecules were used to exclude the coupling effect between the O--H oscillators.) The deviation of the O--H...O angle from the optimum value by more than ~40° (the corresponding deviation for the MP2/6-31G(d) 3a model is 47°) leads to the unusual |Δτ(OH)|/|Δδ(OH)| < 1 ratio. We suggest that in comparison with the optimal structure in the strained one the OH stretching/bending vibration of the proton donor OH group is accompanied by the smaller/larger change of the hydrogen bond length (Figure 9), which weakens/strengthens the hydrogen-bonding effect on the corresponding frequency.

The computed frequency shifts of the 3a' and 3b' extended models of the closed and open CH3OH structures (Table 10) reinforce this qualitative analysis. The predicted frequency shifts of the open structure conflict with the experimental IR data: the calculations suggest very small Δτ(OH) and Δδ(OH) shifts to higher and lower frequencies, while significant, opposite shifts to lower and higher frequencies are observed.\(^{15-18}\) Moreover, the predicted Δν''(CH3) = 5 cm⁻¹ and Δν'(CH3) = 12 cm⁻¹ shifts contradict the experimental shifts of the ν''(CH3) and ν'(CH3) bands to lower frequencies.\(^{15-18}\) Unlike the 3b' model, the 3a' model of the closed CH3OH structure shows very good quantitative agreement with the experimental Δν''(CH3) and Δν'(CH3) shifts and qualitative agreement with the experimental Δτ(OH) and Δδ(OH) shifts.

Conclusion

Two conflicting theoretical interpretations of the adsorption of water and methanol on silica hydroxyls have been proposed by us\(^{9,11,12,17}\) and by other authors.\(^{1-8,10}\) The contradiction emerged due to the choice of different molecular models and ab initio approximations, and also due to the fact that in our studies we sought an adsorption mechanism which can satisfy results of both energy calculations and frequency analysis, while in refs 1–8 and 10 the most informative experimental IR data on the involved interaction were ignored. In order to resolve the problem, we have revised our previous conclusions\(^{9,11,12,17}\) and those of refs 1–8 and 10 using more sophisticated theoretical approaches.

The energy calculations of molecular models suggest that both H2O and CH3OH stabilize on the isolated silica OH group by means of two hydrogen bonds: the adsorbing molecules act as a proton acceptor toward the silica OH group and as a proton donor toward a nearby SiOSi bridge of the surface. The calculations predict these adsorption species to be more stable by ~8 kJ/mol than the 1-fold hydrogen-bonded H2O and CH3OH structures proposed in refs 1–8 and 10, with the adsorbed molecules acting toward the OH group exclusively as a proton acceptor. When stabilizing on the gennal silica OH groups, H2O and CH3OH can form the extra hydrogen bond not only with the nearby SiOSi bridge but also with the nearby OH group.

The analysis of the experimental frequency shifts of CH3OH upon the adsorption reinforces the energy calculation results: the 1-fold hydrogen-bonded CH3OH species disagree with the observed Δτ(CH3), Δτ(OH), and Δδ(OH) shifts of methanol on silica hydroxyls, while the 2-fold hydrogen-bonded species is in good agreement with the experimental IR data.

The checks of basis set, electron correlation, and model size effects on the computed adsorption energies and frequencies support the reliability of our results. The analysis of the electrostatic interactions in the H2O-HOSiH3OSiH2 model used in ref 8 suggests that this model is not adequate for studying the mechanism in question. The inadequacy mainly results from a significant underestimation of the q(Si) charge of the Si atom bonded to the adsorbing OH group, due to the not realistic chemical coordination of this Si atom in the model compared with its pure oxygen surroundings in silica. Considering the prevailing role of the Coulombic interactions in the moderate strength H-bonding, the use of such models for examining small differences in binding energy between hypothetical adsorption mechanisms is doubtful.

Acknowledgment. We are grateful to both the Italian CNR and MURST for financial support of this research. A.G.P. gratefully acknowledges the Italian CNR for a NATO Guest fellowship. We also thank Prof. Adriano Zecchina and Dr. Silvia Bordiga for very useful discussion of our calculation results.

References and Notes

Adsorption of H₂O and CH₃OH on Silica Hydroxyls

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(38) We follow the recommendation proposed in ref 33 to consider the normal modes characterized by frequencies less then 500 cm⁻¹ and corresponding to the torsion around a single bond as pure rotations. The computed MP2/6-31G(d) frequencies of the H₂O and CH₃OH torsion around the H-bond in models 6b and 7b are 115 and 60 cm⁻¹, respectively.