IL NUOVO CIMENTO VOL. 19 D, N. 11 Novembre 1997

Adsorption of water on silica hydroxyls: DFT calculations (*)

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(ricevuto il 28 Febbraio 1997; approvato l'8 Maggio 1997)

Summary. — We re-examine two hypothetical mechanisms proposed in the literature for the coordination of H_2O on the isolated silica OH group by DFT calculations of related molecular models. The computed energies suggest that H_2O stabilizes on the isolated OH group by means of two hydrogen bonds, acting as a proton acceptor towards the silica OH group and as a proton donor towards a nearby SiOSi bridge. The alternative structure, with H_2O acting exclusively as a proton acceptor towards the isolated OH group, is found to be less stable by ∼ 8 kJ/mol. The calculations suggest no significant difference in mechanism between the adsorptions on the isolated and geminal OH groups of silica. On a geminal OH group H_2O can form an extra hydrogen bond not only with the nearby SiOSi bridge, but also with the complementary geminal OH group.

PACS 82.65.My – Chemisorption.
PACS 01.30.Cc – Conference proceedings.

1. – Introduction

Two mechanisms are proposed for the adsorption of water on the isolated silica OH group on the basis of *ab initio* energy calculations [1-9]. The first one, with H_2O acting towards 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 H_2O bonded to the OH group as a proton donor. The most sophisticated energy

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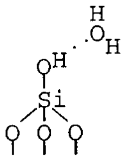
(*) Paper presented at the "First International Workshop on Reactivity of Oxide Materials. Theory and Experiment", Como, 8, 9 November 1996.

analysis of these two structures was performed by Ugliengo *et al.* [7, 8] at the MP2/TZ++(2*d*, 2*p*)//SCF/DZP level using H_3SiOH as a molecular model of the isolated OH group. The second mechanism was proposed in our investigation [9] at the SCF/6-31G(*d*) and MP2/6-31G(*d*, *p*)//SCF/6-31G(*d*) levels with the $Si(OH)_4$ model of the surface. In this mechanism the adsorbed H_2O acts simultaneously both as a proton acceptor towards the isolated OH group and as a proton donor towards a nearby O atom (structure 3). Moreover, we suggested structure 1 to be unstable: its optimization, allowing the O—H··O angle to vary, turned structure 1 into structure 3 without an energy barrier [9].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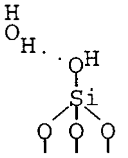
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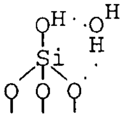
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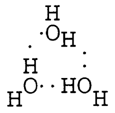
As an additional support of the two-fold hydrogen-bonded H_2O species on the OSiOH silica site, we note that they conform to the well-known bifunctionality of water and methanol [10-13], which leads these molecules to form similar cyclic hydrogen-bonded complexes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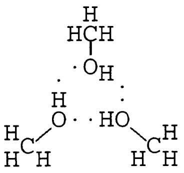
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in solution. In these complexes the energy gain due to the extra hydrogen bonding and the cooperative effect offset the energy loss for the strong deviation of the OH··O fragments from linearity [13].

Recently, Sauer *et al.* [8] reported BSSE corrected SCF/MINI-1 and MP2//SCF/DZP energy calculations of the closed and open H_2O species using $HOSiH_2OSiH_3$ as a molecular model of the OSiOH silica site, the nearby SiOSi bridge being mimicked by the $SiOSiH_3$ group. They found that there is no extra hydrogen bonding of H_2O on the isolated OH group: the H_2O experiences only a nonspecific interaction with the siloxane bridge, the smallest R_{OH} distance between the H_2O and SiOSi being larger than the sum of the H and O van der Waals radii (2.6 Å). The opposite result of our calculations [9] was suggested to be biased by the $Si(OH)_4$ model of the (Si)OSiOH site: in their opinion the SiOH moiety is not adequate for mimicking the SiOSi bridge in the discussed interaction. These calculations reinforced their previous theoretical inference about the one-fold hydrogen bonding of H_2O on the isolated OH group [1-4, 7, 8].

In the present study we re-examine the above-mentioned adsorption structures within the density functional theory (DFT) approximation. As the contradictory findings on the relative stabilities of the cyclic and open structures resulted from *ab initio* calculations on molecular models of different size [8, 9], we check the model size effect on the calculated adsorption energies. On the basis of the current view [14] of the prevailing electrostatic nature of the moderate strength H-bonding, we also perform an analysis of the Coulombic interactions between the H-bonded partners in the studied molecular models in order to interpret the results of the DFT energy calculations. We also touch upon the problem of the H_2O adsorption on the geminal silica OH groups [15].

2. – Details of calculations

DFT calculations were performed with the GAUSSIAN-94 package [16], using the exchange functional of Becke [17] with the correlation functional of Lee, Yang, and Parr [18] (BLYP). Corrections to the adsorption energies for the basis set superposition error (BSSE) were estimated by the counterpoise method [19]. 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 [20]. Corrections to SCF molecular electrostatic potentials due to the electron correlation are usually insignificant [14].

For all the examined models of the H_2O adsorption our calculation results show only one energy minimum corresponding to the two-fold H-bonding mechanism. The calculations of the constrained one-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 interpretations of 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. For the models involved in the electrostatic energy analysis the SCF H-bond lengths and OH··O bond angle of the (H)OH··O group are also reported.

3. – Results and discussion

3·1. *Energy analysis*

3·1.1. DFT calculations. In table I we report the BSSE corrected DFT binding energies of H_2O on the OSiOH site computed with

a) $H_2O \cdot HOSiH_2OSiH_3$ model (1a and 1b, fig. 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) $H_2O \cdot (HO)_3SiOSi(OH)_3$ model (2a and 2b, fig. 1) with the "natural" nearest surroundings of the Si atoms.

TABLE I. – BSSE *corrected* BLYP/CBS *binding energies of closed,* E^c, *and open,* E^o, H_2O *adsorption structures* ([a]) (kJ/mol).

Model	E^c	E^o
1a, 1b	24 (40)	21 (37)
2a, 2b	35 (51)	23 (39)
3a, 3b	36 (53)	24 (40)

([a]) $E^c(E^o) = E(\text{complex}) - [E(\text{substrate}) + E(\text{adsorbate})]$. Numbers in parentheses are BSSE uncorrected values.

A combined basis set (CBS) was used: the 6-311G(*d*, *p*) basis set for H_2O, 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. In the models the SiOSi angle was fixed to 140°, the averaged value for silica. The OSiO, OSiH and HSiH angles were kept equal to 109.5°. Models 1a and 2a of the closed H_2O structure were optimized under the C_s symmetry constraint. Models 1b and 2b of the open H_2O structure were optimized with the additional $\angle \text{O—H} \cdot\cdot \text{O} = 180°$ and $\angle \text{H} \cdot\cdot \text{O—X} = 123°$ geometry constraints allowing the formation of only one H-bond: these values correspond to the optimal ones for the one-fold H-bonding [6, 21].

The energy preference $E^c - E^o = 3$ kJ/mol of the closed to open structure computed with the $H_2O \cdot HOSiH_2OSiH_3$ model is too small for a definitive discrimination

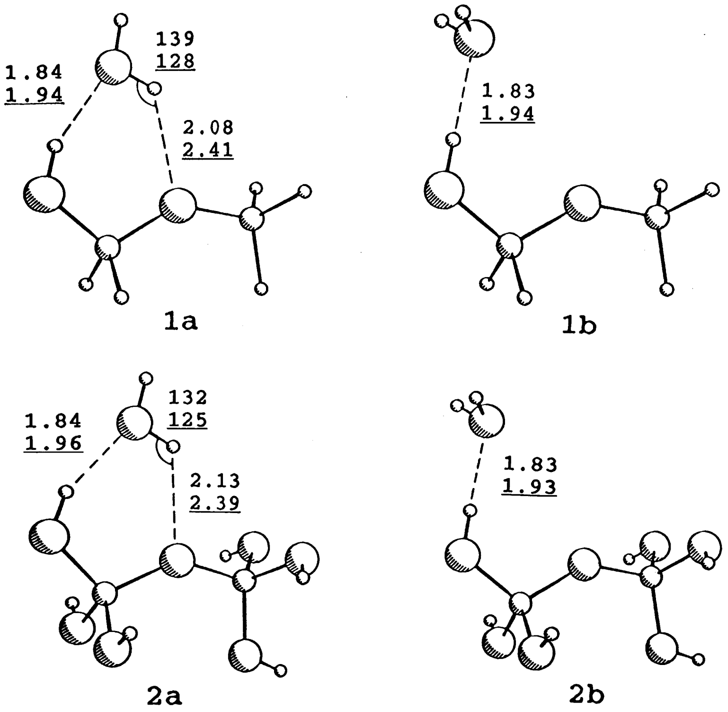
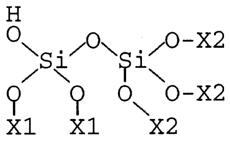


Fig. 1. – Molecular models of water on OSiOH site of silica. H-bond lengths in Å, bond angles in degrees at BLYP/CBS and SCF/6-31G(*d*) (underlined) levels.

between the two examined mechanisms. As we have shown recently [22], the zero-point and thermal corrections to the frozen nuclei binding energy should decrease the energy preference of the closed to open structure by ~ 2.5 kJ/mol. Thus, in agreement with the theoretical study by Sauer *et al.* [8], the $H_2O \cdot HOSiH_2OSiH_3$ 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 $H_2O{\cdot}(HO)_3SiOSi(OH)_3$ model, the corresponding $E^c - E^o = 12$ kJ/mol value implies the two-fold H-bonding mechanism of the adsorption. According to the generally accepted methodology of the molecular approach, among the two examined models $H_2O{\cdot}(HO)_3SiOSi(OH)_3$ has to be taken as a more reliable one. Therefore, these results suggest that the $H_2O{\cdot}HOSiH_2OSiH_3$ 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 BLYP/6-31G(*d*) level upon increasing the



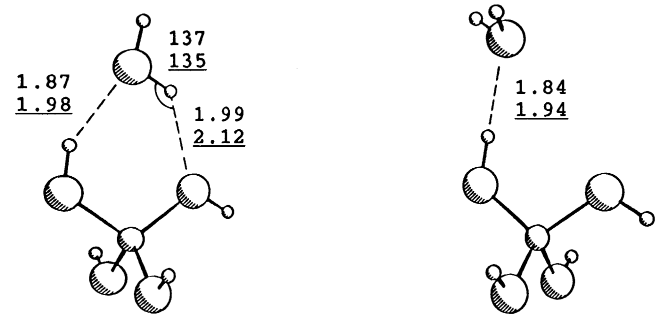
model size in the series $(X1 = X2 = H) < (X1 = Si(OH)_3,\ X2 = H) < (X1 = H,\ X2 = Si(OH)_3) < (X1 = X2 = Si(OH)_3)$. The models with X1 or/and $X2 = Si(OH)_3$ were computed without geometry optimization, the geometry of the $H_2O{\cdot}HOSiO_2SiO_3$ fragments of the closed and open structures being equal to those optimized for 2a and 2b (fig. 1). The BLYP/6-31G(*d*) calculations show that the increase of the model size does not affect the $E^c - E^o \simeq 10$ kJ/mol energy preference of the closed to open structure (table II). This result supports the adequacy of the $(HO)_3SiOSi(OH)_3$ model of the (Si)OSiOH site for studying the extra stabilization effect.

We also computed the energy gain on going from the open to closed structure for the case of the H_2O adsorption on the geminal silica OH groups, the adsorbed molecule forming the extra H-bond towards the neighbouring OH group. The calculations were performed at the BLYP/CBS level with the $Si(OH)_4$ model of the geminal OH groups (fig. 2). Similar to the $(HO)_3SiOSi(OH)_3$ model of the (Si)OSiOH site, this model of the

TABLE II. – BLYP/6-31G(*d*) *binding energies of closed,* E^c, *and open,* E^o, H_2O *adsorption structures* ([a]) (kJ/mol).

$HOSi(OX1)_2OSi(OX2)_3$		E^c	E^o
$X1 = H$,	$X2 = H$	46	36
$X1 = Si(OH)_3$,	$X2 = H$	44	36
$X1 = H$,	$X2 = Si(OH)_3$	46	33
$X1 = Si(OH)_3$,	$X2 = Si(OH)_3$	44	33

(*a*) $E^c(E^o) = E(\text{complex}) - [E(\text{substrate}) + E(\text{adsorbate})]$.



3a

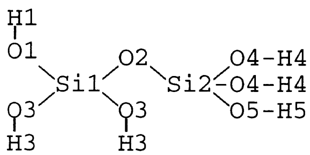
3b

Fig. 2. – Molecular models of water on geminal OH groups of silica. H-bond lengths in Å, bond angles in degrees at BLYP/CBS and SCF/6-31G(*d*) (underlined) levels.

(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 and 2b) and (H)OSiOH (3a and 3b) sites the difference in energy between the extra H-bond towards the complementary geminal OH group and towards the nearby siloxane bridge is insignificant (table I). This result also justifies the use of the $Si(OH)_4$ model for simulating the H_2O and CH_3OH adsorption on the (Si)OSiOH site in our previous studies [9, 23-25].

3·1.2. Electrostatic interaction analysis. Ugliengo *et al.* showed [14] 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 [8] implies that this bonding is mainly defined by the electrostatic interaction of the adsorbed molecule with "the site", *i.e.* a very few nearby surface atoms. Therefore, we investigated whether the difference in the extra stabilization energy between the $H_2O{\cdot}HOSiH_2OSiH_3$ model used by Sauer *et al.* [8] and the extended $H_2O{\cdot}(HO)_3SiOSi(OH)_3$ model can be interpreted in terms of the difference in the electrostatic properties between the OSiOH adsorbing sites of these models.

In table III we compare the electrostatic contributions to the H_2O extra stabilization energy from the atoms of the OSiOH site of the $HOSiH_2OSiH_3$ and $(HO)_3SiOSi(OH)_3$ models. The calculations were performed using the geometry and PED charges of the optimized 1a, 1b, 2a, and 2b SCF/6-31G(*d*) models. The numbering of the atoms of the $HOSiH_2OSiH_3$ and $(HO)_3SiOSi(OH)_3$ models is shown in the following schemes:



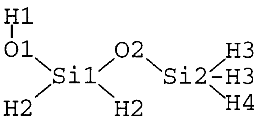


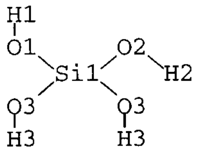
TABLE III. – *Electrostatic contributions to the extra stabilization effect on going from open to closed structure* ([a]) (kJ/mol).

	$H_2O{\cdot}HOSiH_2OSiH_3$	$H_2O{\cdot}(HO)_3SiOSi(OH)_3$	$H_2O{\cdot}Si(OH)_4$
O1H1	− 6	− 6	− 5
Si1	− 8	−27	1
O2	−21	−20	−50
Other atoms	16	17	17
Total	−19	−36	−37

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

The data of table III 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 H_2O 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 computed PED charges, this effect results from the significant underestimation (by 0.5 a.u.) of the corresponding q(Si) charge in the $HOSiH_2OSiH_3$ model (1.2 a.u.) compared to that in the extended $(HO)_3SiOSi(OH)_3$ model (1.7 a.u.). This underestimation is explained by the not realistic chemical surroundings of the Si atom in the $HOSiH_2OSiH_3$ model, with the two nearby O atoms being mimicked by H atoms. The data of table III 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 H_2O 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.

In table III we report the electrostatic contributions to the extra stabilization energy also for the case of the H_2O adsorption on the geminal OH groups. The calculations were performed with the geometry and PED charges of the 3a and 3b SCF/6-31G(d) models, the numbering of the atoms of the $Si(OH)_4$ model corresponding to the scheme



The comparison of the related contributions for the H_2O on the (Si)OSiOH and (H)OSiOH sites reveals a difference in the extra stabilization mechanism between these structures. As distinct from the H_2O adsorption on the (Si)OSiOH site, in the adsorption on the (H)OSiOH site the stabilization effect is mainly caused by the H_2O interaction with the O atom of the neighbouring 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 3a, figs. 1 and 2). 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 OH··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 H_2O 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 sites is approximately the same. The found difference between the two-fold H-bonded species on the isolated and on the geminal OH hydroxyls agrees with the suggestion by Ugliengo *et al.* [15] 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 is 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 binding energy from the rest of the models is not negligible (table III). 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 binding energy, but should not change the general adsorption mechanism defined by the site. The small change of the $HOSi(OX1)_2OSi(OX2)_3$ binding energy in the series $(X1 = X2 = H) < (X1 = Si(OH)_3,\ X2 = H) < (X1 = H,\ X2 = Si(OH)_3) < (X1 = X2 = Si(OH)_3)$ supports this suggestion (table II).

PED models can provide only a rough description of the adsorption interactions [14]. Even considering the fact that H-bonding is basically related to electrostatic interactions [14, 26], the simulation of the electron density of molecules by simple monopoles centered on nuclei positions is rather crude. However, in agreement with a conclusion by Ugliengo *et al.* [14], our results suggest that for closely related complexes the errors are very systematic. Therefore, although the PED models overestimate the extra stabilization energy by ~ −20 kJ/mol compared with the DFT models (cf. tables I and III), they reproduce and reasonably explain the relative capacity of the models for the extra stabilization. We suggest that the overestimation is mainly caused by the error in simulating the electron density on the O atoms. According to the results for similar complexes [26], 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 [26].

To summarize, our DFT calculations and electrostatic energy analysis suggest that H_2O adsorbs on silica hydroxyls by the two-fold H-bonding mechanism, forming the extra H-bond to the O atom of the SiOSi or SiOH (in the case of the coordination on geminal OH groups) nearby site.

4. – Conclusion

Two conflicting theoretical interpretations of the adsorption of water on silica hydroxyls have been proposed by us [9] and by other authors [1-8]. The contradiction emerged due to the choice of different molecular models and *ab initio* approximations. In order to resolve the problem, we have revised our previous conclusions [9] and those of refs. [1, 8] using the density functional theory.

The calculations of molecular models suggest that H_2O stabilizes on the isolated silica OH group by means of two hydrogen bonds, acting as a proton acceptor towards the silica OH group and as a proton donor towards a nearby SiOSi bridge of the surface. The calculations predict this adsorption species to be more stable by ∼ 8 kJ/mol than the one-fold hydrogen-bonded H_2O structure proposed in refs. [1-8], with the adsorbed molecules acting towards the OH group exclusively as a proton acceptor. When stabilizing on the geminal silica OH groups H_2O can form the extra hydrogen bond not only with the nearby SiOSi bridge, but also with the nearby OH group.

The check of model size effect on the computed adsorption energies supports the reliability of our results. The analysis of the electrostatic interactions in the $H_2O \cdot HOSiH_2OSiH_3$ 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 non-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.

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We are grateful to both the Italian CNR and MURST for financial support of this research. AGP gratefully acknowledges the Italian CNR for a NATO Guest fellowship.

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