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EFFECTS OF SILICA CLUSTER SIZE AND CHARGE STATE ON INTEGRAL CHARACTERISTICS

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The model sizes of solid particles as well as used quantum chemical methods can affect results of calculations with density functional theory (DFT) methods. The aim of this study was to analyze the effects of the silica cluster sizes, a number of bound water molecules, protonation and deprotonation of silanols, addition of Eigen cation alone or solvated, attachment of anions F^- *and* Cl^- *alone or solvated, and whole solvation effects (with SMD) with the DFT calculations using a functional ωB97X–D with the cc–pVDZ basis set. The calculations of the distribution functions of atom charges (CDF), chemical shifts of the proton resonance (SDF), and integral density of electron states (IDES) show that small clusters with 8 or 22 (*$SiO_{4/2}$*) units could give rather inappropriate results in contrast to larger clusters with 44 or 88 units. This is due to the fact that the small silica clusters do not have appropriate capability for delocalization of excess charges that leads to certain distortion of the electron states of the whole system. The IDES are more sensitive with respect to the cluster charging and less sensitive to the solvation effects than the CDF and SDF. As a whole, the use of several types of the distribution functions, such as integral characteristics with the CDF, SDF, and IDES, allows one to obtain a more detailed picture on the interfacial phenomena at silica surface for neutral and charged systems.*

Keywords: *silica clusters, neutral sorbates, charged sorbates, atom charge distribution function, DFT method, solvation method SMD*

INTRODUCTION

During sorption of various compounds onto a surface of nanooxides, *e.g.*, nanosilica, polar dispersion media play an important role [1–3]. In polar solvents, especially water, it is possible charging of both an adsorbent surface and adsorbed molecules that depends strongly on pH of the solution [3–9]. The charging differently affects various intermolecular interactions (electrostatic, van-der-Waals, hydrogen bonding, *etc.*) and the formation of secondary and supramolecular structures (clusters, aggregates, micelles, interfacial films, *etc.*), as well as surface reactions of the acid-base types [6–11]. Therefore, accurate modelling of these structures and appropriate description of the intermolecular interactions and formed bonds are of importance for correct analyses of the interfacial phenomena with water participation [10–14]. There are several aspects related to some restrictions of the models and various sources for minimization of possible errors in quantum chemical modelling of the interfacial phenomena: (i) selection of appropriate methods (*ab initio*, density functional theory, DFT, semiempirical, *etc.*); (ii) use of adequate basis sets (narrow or extended, optimal or inappropriate), correct account of electron correlation and exchange (perturbation theory in *ab initio*, various functionals in DFT, additional tools); (iii) use of corrections on basis set superposition errors (BSSE), temperature, zero point energy and vibrations; (iv) use of appropriate models (clusters, nanoparticles, primitive or expanded cells with periodic boundary conditions, *etc.*); (v) taking into account kinetic and dynamic aspects and some others [12–17]. Thus, the availability of a set of the factors of different “weights” makes difficult maximum appropriate and top-level modelling of the interfacial phenomena within the scope of the quantum chemistry methods (*ab initio* or DFT). In the present work, several aspects related mainly to the sizes of particle models, their charging and solvation are analyzed using DFT calculations (functional ωB97X–D and cc–pVDZ basis set [18, 19]) with the solvation modelled with SMD [20] and ^{1}H NMR spectra calculated using the gauge-including-atomic-orbital (GIAO) method [21].

CALCULATION METHODS

Free water clusters and interfacial water layer at a surface of silica nanoparticles are analyzed using the Gaussian 09 [21] and GAMESS 2020

R2 [22] program suits. The DFT calculations have been done using a hybrid functional ωB97X–D and the cc–pVDZ basis set. The GIAO method has been used to compute the chemical shifts of the proton resonance (δ_H) [21]. The solvation effects have been analyzed with the SMD method [20] implemented in the Gaussian and GAMESS program suits. The calculations have been carried out taking into account zero-point and thermal corrections to the Gibbs free energy in the gas phase and for solvated molecules and silica clusters using the geometry optimized with ωB97X–D/cc–pVDZ (with or without SMD). Note that ωB97X-D introduces empirical damped atom-pairwise dispersion terms into the functional containing range-separated Hartree-Fock exchange for better description of van-der-Waals interactions [18, 19]. Therefore, ωB97X–D has been selected to obtain more adequate results for the gas and liquid phases interacting with silica nanoparticles. The distribution functions (DF) of various parameters have been calculated with a simple equation [23-26]

$$f_n(X) = (2\pi\sigma_n^2)^{-0.5} \sum_j \frac{\exp[-(X_{n,j} - X)^2]}{2\sigma_n^2}, \quad (1)$$

where j is the number of a certain type (n) of atoms or energetic level, σ^2 is the distribution dispersion, and X_j is the value of atomic charge (CDF) (Figs. 1–5), chemical shift δ_H (SDF) (Figs. 6 and 7), or electron energy of MO (integral density of electron states, IDES, Fig. 8), and X is the current value. For the electron-donor atoms (H, Si) (Figs. 1, 3, 4 *b*, 5 *a*, *b*, *e*, *f*), $\sigma = 0.01$ a.u., and $\sigma = 0.05$ a.u. for electron-acceptor (O, F, Cl) atoms (Figs. 2, 4 *a*, 5 *c*, *d*). This difference in the σ values is due to broadening of the CDF for atoms with excess electron density (*i.e.*, for electron-acceptor atoms) more strongly affected by the surroundings in comparison to the atoms with deficiency in the electron density (electron-donor atoms) with more compact electron clouds. For the SDF or IDES, $\sigma = 0.5$. To decrease small details in the distribution functions, the distribution dispersion should be increased up to the values corresponding to experimental peaks (*i.e.*, full width at the half-height, FWHH). As a whole, the distribution functions of certain characteristics may be calculated with Eq. (1) with any quantum chemical method. In the DFT calculations, several silica clusters have been studied with (i) 8 units ($SiO_{4/2}$) with 8OH, (ii) 22 units with 16OH, (iii) 43 units with 28OH, (iv) 44 units with 24OH, and (v) 88 units with 40OH with various neutral and charged sorbates differently hydrated with real water molecules or with a solvation model SMD. The cluster with 43 units models a lattice defect since a Si atom inside the cluster with 44 units was replaced by four H atoms.

RESULTS AND DISCUSSION

Obtained results show that a silica cluster with 8 units is rather inappropriate to study any aspect of the interfacial phenomena. First, its electronic structure is too sensitive to the formation of any charged functionality because of restricted capacity to delocalize excess positive (protonation of a SiOH group, $+H^+$) or negative (deprotonation of a ≡SiOH group, $-H^+$) charge (Figs. 1 *a*, 2 *a*, 3 *a*). Second, there is a certain excess of the hydroxyl groups in comparison to real silica since each Si atom has attached OH (Figs. 2 *a*, 4 *a*). Third, the electron state of the silanols neighboring to the charged functionality demonstrates stronger changes than that observed in larger clusters.

A silica cluster with 22 units and 16OH is less sensitive with respect to the states of the O and Si atoms in a reaction center than a cluster with 8 units (Figs. 2, 3). However, it is more strongly sensitive with respect to the states of the H atoms in the ≡SiOH groups than in a cluster with 44 units and 24OH (Fig. 1). However, this effect is smaller than that for a cluster with 8 units. The states of the H atoms in the ≡SiOH groups in the silica clusters with 22 or 44 units are relatively more sensitive to the solvation effects (SMD calculations with water as a solvent) than the O and Si atoms (Figs. 1–3). For the smallest cluster with 8 units, both the O and Si atoms are sensitive to the solvation effects similar to the H atoms in the ≡SiOH groups. Comparison of the CDF for the O and Si atoms in the silica clusters with 8 (8OH), 22 (16OH), 44 (24OH), and 88 (40OH) units (Fig. 4) show a significant difference for the smallest cluster, especially for the Si atoms because only in this cluster all Si atoms have the OH groups.

Thus, calculations of the CDF for silica clusters of different sizes and charging show that small clusters with 8 or 22 units (or smaller ones [10, 27]) are rather inappropriate for accurate studying the interfacial phenomena. Larger silica clusters with 44 (24OH) and 88 (40OH) units, demonstrating better results, could be used to study the interfacial phenomena.

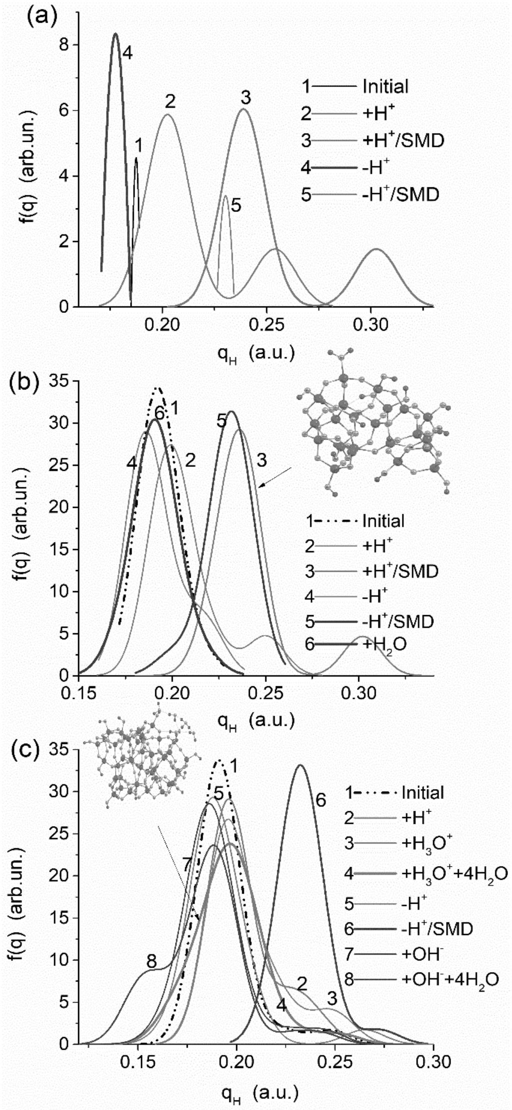

Fig. 1. Distribution functions of charges of the H atoms in neutral and charged silica clusters with (*a*) eight units, (*b*) 22 units and (*c*) 44 units: +H$^+$ and –H$^+$ corresponds to protonated and deproto-nated clusters, respectively; +OH$^-$ corresponds to the clusters with attached anion; +H$_3$O corresponds to attached Eigen cation; +4H$_2$O corresponds to structures with water molecules added close to charged particles; SMD corresponds to calculations taking into account the solvation effects in aqueous media (method ωB97X–D/cc–pVDZ)

The presence of electron-acceptor atoms with excess electron density (F$^-$, Cl$^-$) affects the CDF of other atoms (H, O, Si) in the silica clusters (Fig. 5). However, this effect on the q_H CDF is stronger in the range of minimal q_H values upon addition of water molecules around the charged center with ≡Si–F$^-$ or ≡Si–Cl$^-$ (Fig. 5 *a*, *b*). In this case, the water molecules take part in additional polarization of the ≡SiO–H bonds. An increase in the number of the water molecules from 4 to 9 H$_2$O attached to a neutral cluster leads to an increase in the q_H CDF in the range of maximal q_H values (Fig. 5 *a*, curve 4, 5 *b*, curve 3).

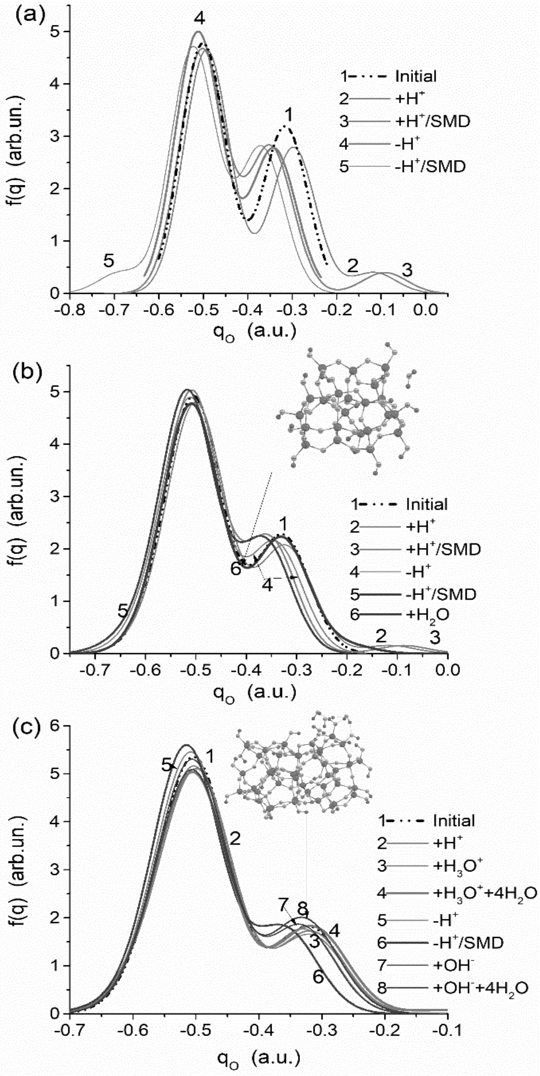

Fig. 2 Distribution functions of charges of the O atoms in neutral and charged silica clusters with (*a*) eight units, (*b*) 22 units and (*c*) 44 units: +H$^+$ and –H$^+$ corresponds to protonated and deprotonated clusters, respectively; +OH$^-$ corresponds to the clusters with attached anion; +H$_3$O$^+$ corresponds to attached Eigen cation; +4H$_2$O corresponds to structures with water molecules added close to charged particles; SMD corresponds to calculations taking into account the solvation effects in aqueous media (method ωB97X–D/cc–pVDZ)

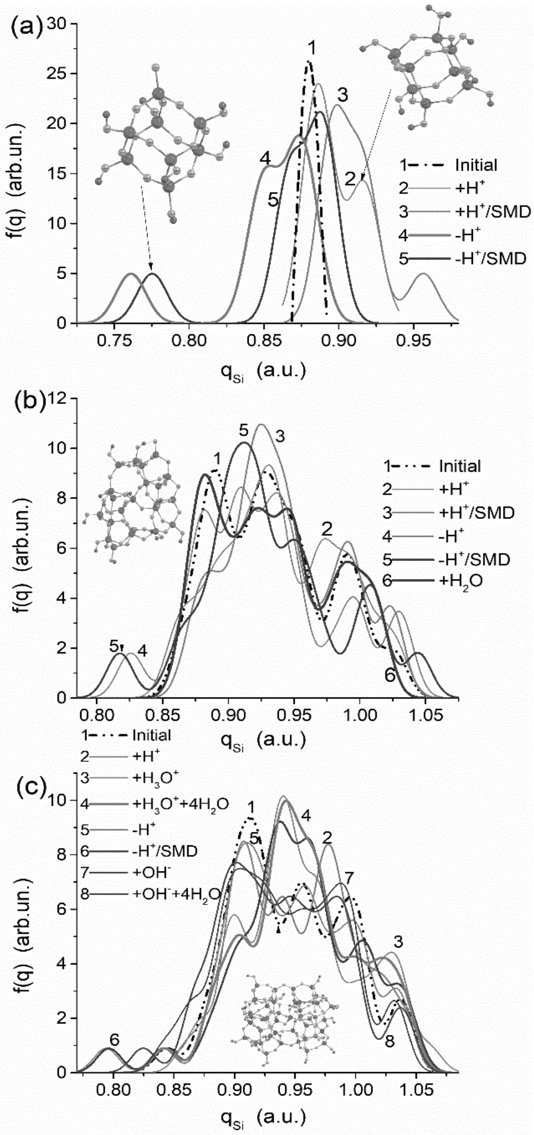

Fig. 3. Distribution functions of charges of the Si atoms in neutral and charged silica clusters with (*a*) eight units, (*b*) 22 units and (*c*) 44 units: $+H^+$ and $-H^+$ corresponds to protonated and deprotonated clusters, respectively; $+OH^-$ corresponds to the clusters with attached anion; $+H_3O^+$ corresponds to attached Eigen cation; $+4H_2O$ corresponds to structures with water molecules added close to charged particles; SMD corresponds to calculations taking into account the solvation effects in aqueous media (method ωB97X–D/cc–pVDZ)

As a whole, F^- and Cl^- or HF and HCl differently interact with a silica surface. For example, hydrofluoric acid can much easily dissolve silica than hydrochloric acid due to smaller size of the F^- ions than Cl^- that provides more effective interactions of F^- with silicon atoms in the silica lattice (with subsequent protolytic breakage of the siloxane bonds by solvated protons). This appears in the difference in the structures with two dissociated acids molecules solvated by $9H_2O$ and interacting with the silica cluster (Fig. 5 *e*, *f*, inserts). Both F^- ions attack the Si atom, but only one Cl^- interacts with the Si atom and another is solvated and does not interact with the Si atom. Therefore, the q_{Cl} CDF splits into two peaks (Fig. 5 *d*, curve 6) in contrast to the q_F CDF (Fig. 5 *c*, curve 8). The structural difference of the complexes with $[2H^+ + 2F^-] \times 9H_2O$ and $[2H^+ + 2Cl^-] \times 9H_2O$ at a silica surface more strongly affects the CDF of the H (Fig. 5 *a*, *b*) and Si (Fig. 5 *e*, *f*) atoms than the O CDF (Fig. 5 *c*, *d*) in the silica clusters.

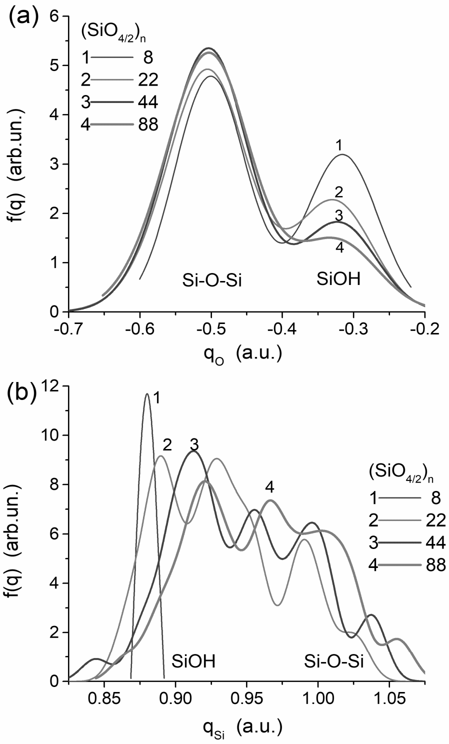

Fig. 4. Distribution functions of charges of (*a*) O atoms and (*b*) Si atoms in neutral silica clusters with 8, 22, 44, and 88 units (method ωB97X–D/cc–pVDZ)

Note that expansion of the basis set from cc–pVDZ to aug–cc–pVTZ (added diffuse functions and triple-zeta instead of double-zeta) weakly affects the ^{1}H NMR spectra (Fig. 6 *a*) of a water cluster with $44H_2O$ (initial geometry was taken from the hexagonal ice, Ih and its motives remain after the geometry optimization with DFT). Therefore, all other calculations (Fig. 6 *b*, *c*) were carried out using the GIAO/ωB97X–D/cc–pVDZ method.

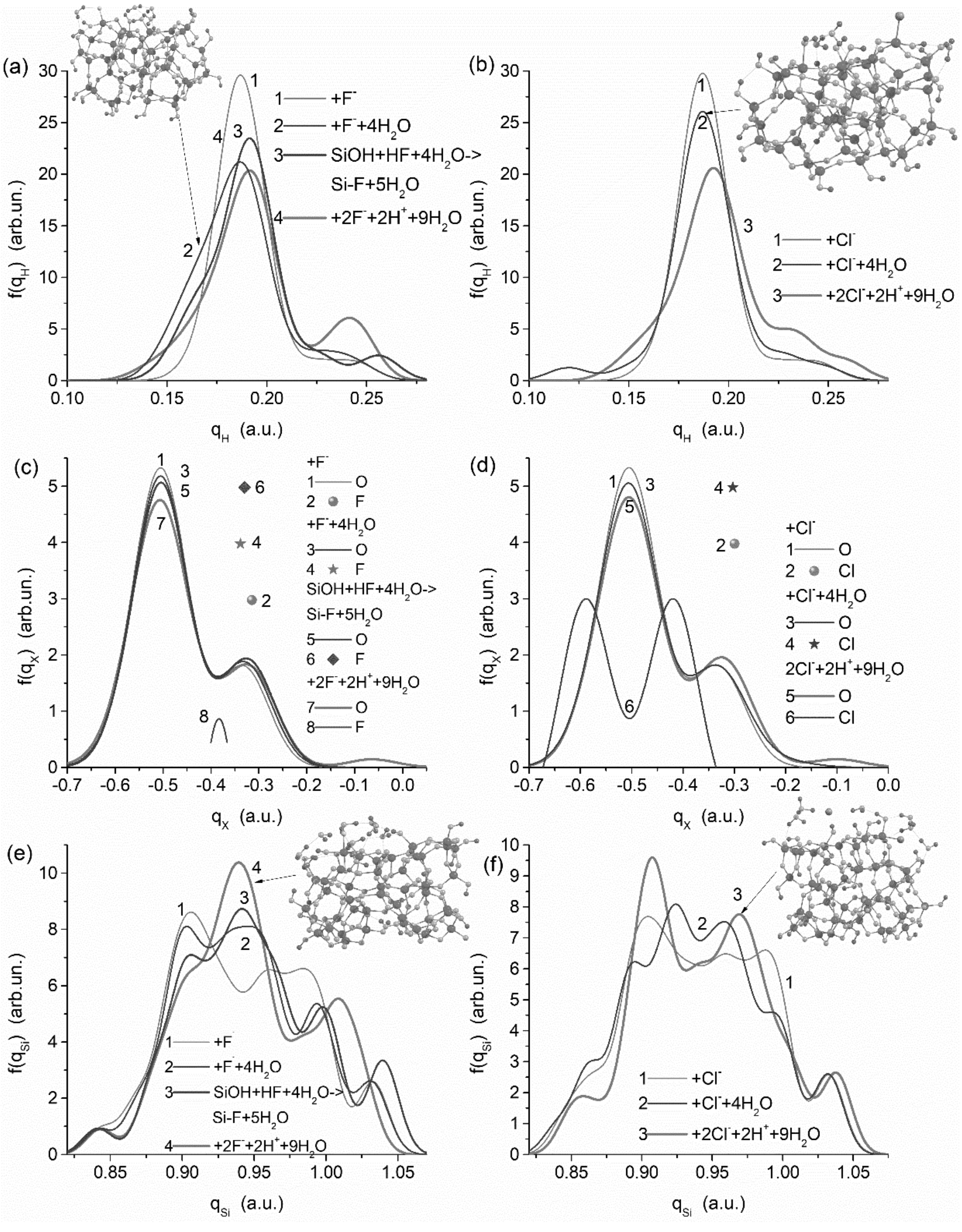

Fig. 5. Distribution functions of charges in neutral and charged silica clusters with 44 units (ωB97X–D/cc–pVDZ) containing attached F^-, HF, Cl^- or HCl alone or with addition of 4 or 9 water molecules for (*a*, *b*) H, (*c*, *d*) O, (*c*) F, (*d*) Cl, and (*e*, *f*) Si atoms (some details are shown in Figures)

An increase in the numbers of the water molecules in the solvate shell of a silica cluster results in ^{1}H NMR spectra broadening and downfield shift of the peaks due to (i) an increase in an average number of the hydrogen bonds per a molecule [10], and (ii) an increase in the polarization of both silanols and bound water molecules because of additional stabilization by the surroundings (similar stabilization of the electronic structure is observed upon an increase in the size of the silica clusters, Figs. 1–5). In the calculated spectra (Fig. 6 *b*, *c*), there are (i) unbound –OH in ≡SiOH and H_2O at δ_H = 1–2 ppm; (ii) typical hydrogen bonds in water or slightly distorted hydrogen bonds of the water molecules and silanols at δ_H = 4–6 ppm; (iii) strong hydrogen bonds at δ_H = 6–8 ppm; and (iv) the hydrogen bonds with significant transfer of the electron density at $\delta_H > 8$ ppm that correspond to acidic protons similar to that in the Eigen and Zundel cations (H_3O^+ and $H_5O_2^+$, respectively).

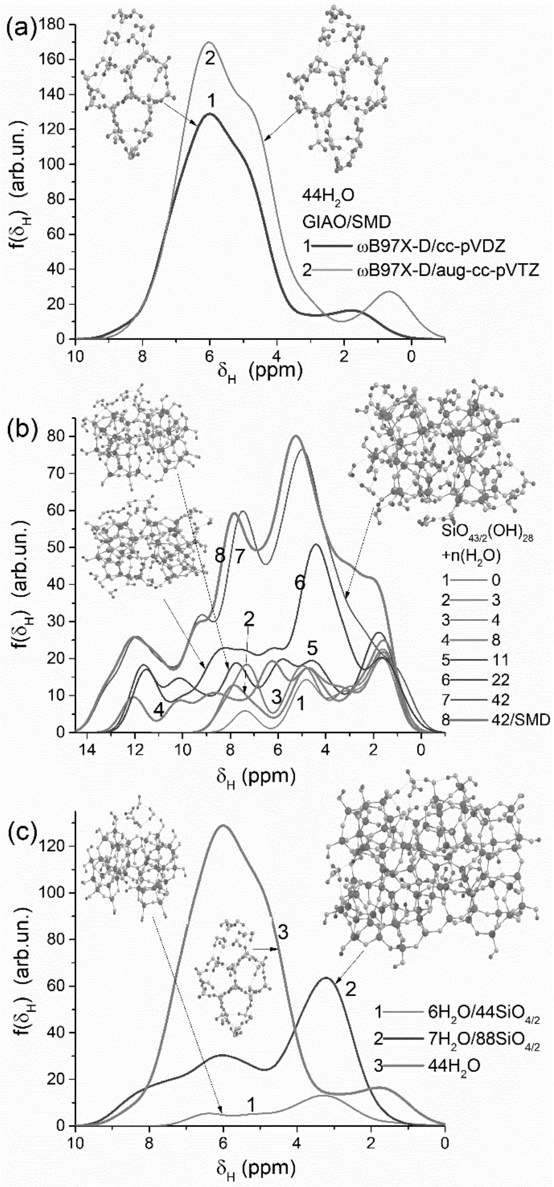

Fig. 6. ^{1}H NMR spectra calculated using the GIAO/ωB97X–D/cc–pVDZ (with or without SMD): (*a*) for water cluster with $44H_2O$ with initial structure corresponding to ice Ih comparing to calculation using GIAO/SMD/ωB97X–D/aug–cc–pVTZ; (*b*) cluster with 43 units (formed from the cluster with 44 units by replacing Si with 4H) with different numbers of bound water molecules (0, 3, 4, 8, 11, 22, and 42); and (*c*) weakly hydrated clusters with 44 ($+6H_2O$) and 88 ($+7H_2O$) units and pure water cluster with $44H_2O$

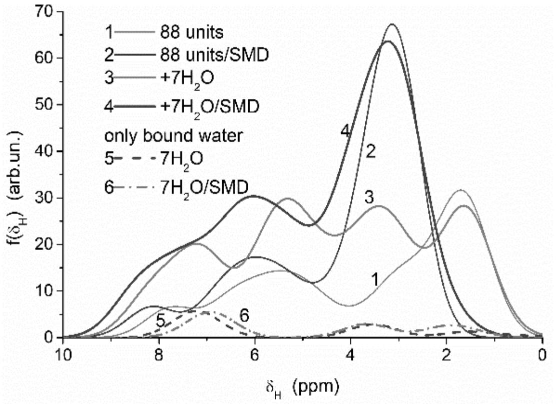

Fig. 7. ^{1}H NMR spectra calculated using the GIAO/ωB97X–D/cc–pVDZ (with (curves 2, 4, 6) or without (curves 1, 3, 5) SMD) for a silica cluster alone (curves 1 and 2) (88 units with 40OH) and with bound $7H_2O$ (curves 3 and 4), and only for bound water (curves 5 and 6)

Minimal magnetic shielding of the protons (*i.e.*, maximal δ_H values) are characteristic for the protons located in the middle of two O atoms of two water molecules or H_2O and ≡SiOH [10, 26]. The effects of the water cluster size, as well as the size of silica clusters, on the ^{1}H NMR spectra are well seen for weakly hydrated silica clusters with 44 units ($+6H_2O$) and 88 units ($+7H_2O$) (Fig. 6 *c*). The solvation effects modelled using the SMD method are stronger for the silanols (Fig. 7, curves 1–4) than for the bound water molecules (curves 5 and 6). This result may be explained by the fact that a significant fraction of silanols in the models does not have the hydrogen bonds, but all water molecules have the hydrogen bonds with silanols or neighboring molecules. Thus, the reactions or other interfacial processes at a silica surface in the aqueous media cannot be modelled without accurate consideration of the solvation effects.

Note that the SMD method (as well as other solvation methods) can underestimate the polarization of the OH groups without the hydrogen bonds with real molecules. Therefore, the peak of unbound silanols shifts toward downfield from 1.5 to 3 ppm for SMD-solvated clusters. However, the silanols with real hydrogen bonds are characterized by the δ_H values of 5–8 ppm (Fig. 7). Thus, a supermolecular approach (with a cluster of the solvent molecules around a reaction center) with alongside use of the SMD could be applied to study the interfacial phenomena.

Restricted amounts of units in a solid cluster (even 44 units) lead to significant changes in the energetic levels of molecular orbitals (MO) due protonation of a silanol or attachment of OH^-, F^-, Cl^- (Fig. 8 *b*–*d*). However, for neutral clusters, the effect of the cluster size on the IDES is small (Fig. 8 *a*). Addition of H_2O (upon the formation of Eigen cation), and $4H_2O$ or $9H_2O$ (upon bonding of OH^-, F^-, Cl^-) to the reaction center weakly affect the IDES of the system, in contrast to its charging.

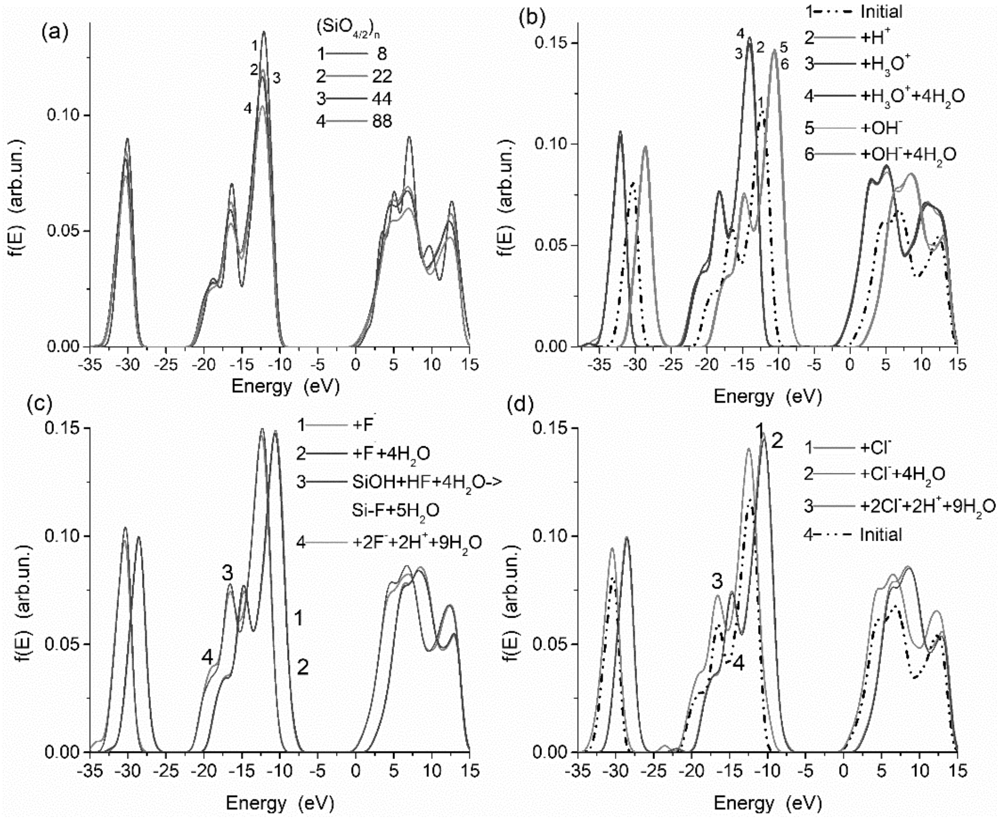

Fig. 8. Distribution functions of integral electron states of (*a*) neutral silica clusters with 8, 22, 44 and 88 units, (*b*) neutral and charged silica clusters (protonation of SiOH, addition of H_3O^+ alone or with $4H_2O$, binding of OH^- alone or with $4H_2O$), (*c*) F^- and HF, (*d*) $Cl^-$and HCl alone or with addition of 4 or 9 water molecules (*b*–*d*) clusters with 44 units (method ωB97X–D/cc–pVDZ)

CONCLUSION

The analysis of the effects of silica cluster sizes, numbers of bound water molecules, protonation and deprotonation of silanols, addition of Eigen cation alone or solvated, attachment of anions F^- and Cl^- alone or solvated or dissociated HF and HCl molecules, and whole solvation effects (with SMD), using the DFT with ωB97X–D/cc–pVDZ to compute the distribution functions of atom charges, chemical shift of the proton resonance, and integral density of electron states, shows that small silica clusters with 8 (8OH) or 22 (16OH) units could give inappropriate results in contrast to larger clusters with 44 (24OH) or 88 (40OH) units. Note that the SiOH/SiOSi ratio decreases with increasing size of the clusters used. The small clusters do not have appropriate capability for delocalization of excess charges that leads to strong distortion of the electron states in the whole systems.

The IDES are more sensitive with respect to cluster charging and less sensitive to the solvation effects than the CDF and SDF. As a whole, the use of several types of the distribution functions, such as CDF, SDF, and IDES, allows one to obtain more detailed picture on the interfacial phenomena at a silica surface.

Вплив розмірів та зарядового стану кластерів кремнезему на інтегральні характеристики

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Розміри модельних твердих частинок та використані методи квантової хімії можуть впливати на результати розрахунків методами теорії функціоналу густини (ТФГ). Для того, щоб проаналізувати ефекти розмірів кластерів кремнезему, кількості сорбованих молекул води, протонування та депротонування силанольних груп, сорбції катіона Ейджена, окремо чи сольватованого, сорбції аніонів F^- та Cl^-, окремо та сольватованих, загальних сольватаційних ефектів (з SMD), було виконано ТФГ розрахунки з використанням функціоналу ωB97X–D з базисним набором cc–pVDZ. Розрахунки функцій розподілу зарядів (CDF), хімічного зсуву протонів (SDF) та інтегральної густини електронних станів (IDES) показали, що малі кластери з 8 чи 22 одиниць ($SiO_{4/2}$) можуть давати менш коректні результати у порівнянні з більшими кластерами з 44 чи 88 одиниць. Це можна пояснити тим, що малі кластери кремнезему не мають достатньої можливості для делокалізації надлишкових зарядів, що призводить до додаткового викривлення електронних станів всієї системи. IDES є більш чутливими до надлишкового заряду кластерів та менш чутливими до ефектів сольватації, ніж CDF та SDF. У цілому використання кількох типів функцій розподілу, таких як CDF, SDF та IDES, дозволяє отримати більш детальну картину для явищ на межах поділу біля поверхні кремнезему для нейтральних та заряджених систем.

***Ключові слова**: кластери кремнезему, нейтральні сорбати, заряджені сорбати, функції розподілу атомних зарядів, DFT метод, сольватаційний метод SMD*

REFERENCES

1. Iler R.K. *The Chemistry of Silica*. (Chichester: Wiley, 1979).
2. Legrand A.P. *The Surface Properties of Silicas*. (New York: Wiley, 1998).
3. Bergna H.E., Roberts W.O. *Colloidal Silica: Fundamentals and Applications*. (Boca Raton: CRC Press, 2006).
4. Adamson A.W., Gast A.P. *Physical Chemistry of Surface*. 6th edition. (New York: Wiley, 1997).
5. Tapia O., Bertrán J. (Eds.) *Solvent Effects and Chemical Reactivity*. (New York: Kluwer Academic Publishers, 2000).
6. Somasundaran P. (Ed.) *Encyclopedia of Surface and Colloid Science*. Third Edition. (Boca Raton: CRC Press, 2015).
7. Henderson M.A. Interaction of water with solid surfaces: fundamental aspects revisited. *Surf. Sci. Report*. 2002. **46**(1–8): 1.
8. Birdi K.S. (Ed.) *Handbook of Surface and Colloid Chemistry*. Third edition. (Boca Raton: CRC Press, 2009).
9. Al-Abadleh H.A., Grassian V.H. Oxide surfaces as environmental interfaces. *Surf. Sci. Report*. 2003. **52**(3–4): 63.
10. Gun'ko V.M., Turov V.V. *Nuclear Magnetic Resonance Studies of Interfacial Phenomena*. (Boca Raton: CRC Press, 2013).
11. Canuto S. (Ed.) *Solvation Effects on Molecules and Biomolecules. Computational Methods and Applications*. (Springer, Dordrecht, 2008).
12. Schleyer P.v.R. (Ed.) *Encyclopedia of Computational Chemistry*. (New York: John Wiley & Sons, 1998).
13. Dykstra C.E., Frenking G., Kim K.S., Scuseria G.E. (Eds.) *Theory and Applications of Computational Chemistry, the First Forty Years*. (Amsterdam: Elsevier, 2005).
14. Cramer C.J. *Essentials of computational chemistry: theories and models*. Second edition. (Chichester, UK: John Wiley & Sons, Ltd, 2008).
15. Helgaker T., Jorgensen P., Olsen J. *Molecular Electronic Structure Theory*. (New York: John Wiley & Sons, 2014).
16. Martin R.M., Reining L., Ceperley D.M. *Interacting Electrons: Theory and Computational Approaches*. (UK: Cambridge University Press, 2016).
17. Engel E., Dreizler R.M. *Density Functional Theory: An Advanced Course*. (Springer, 2013).

18. Yang K., Zheng J., Zhao Y., Truhlar D.G. Tests of the RPBE, revPBE, τ-HCTHhyb, ωB97X-D, and MOHLYP density functional approximations and 29 others against representative databases for diverse bond energies and barrier heights in catalysis. *J. Chem. Phys*. 2010. **132**(16): 164117.
19. Becke A.D. Perspective: Fifty years of density-functional theory in chemical physics. *J. Chem. Phys.* 2014. **140**(18): 18A301.
20. Marenich A.V., Cramer C.J., Truhlar D.G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B.* 2009. **113**(18): 6378.
21. Frisch M.J., Trucks G.W., Schlegel H.B. et al. *Gaussian 09, Revision D.01.* (Gaussian, Inc. Wallingford CT, 2013).
22. Barca G., Bertoni C., Carrington L., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G.A., Nakatsuji H., Caricato M., Li X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J.A., Peralta J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Rega N., Millam J.M., Klene M., Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi J.E., Pomelli C., Ochterski J.W., Martin R.L., Morokuma K., Zakrzewski V.G., Voth G.A., Salvador P., Dannenberg J.J., Dapprich S., Daniels A.D., Farkas Ö., Foresman J.B., Ortiz J.V., Cioslowski J., Fox D.J. Recent developments in the general atomic and molecular electronic structure system. *J. Chem. Phys.* 2020. **152**: 154102.
23. Gun'ko V.M. Modeling of interfacial behavior of water and organics. *J. Theor. Comput. Chem.* 2013. **12**(07): 1350059.
24. Gun'ko V.M. Interfacial phenomena: effects of confined space and structure of adsorbents on the behavior of polar and nonpolar adsorbates at low temperatures. *Current Physical Chemistry.* 2015. **5**(2): 137.
25. Gun'ko V.M. Effects of methods and basis sets on calculation results using various solvation models. *Him. Fiz. Tehnol. Poverhni.* 2018. **9**(1): 3.
26. Gun'ko V.M. Charge distribution functions for characterization of complex systems. *Him. Fiz. Tehnol. Poverhni.* 2021. **12**(1): 3.
27. Gun'ko V.M., Turov V.V. Structure of hydrogen bonds and ^{1}H NMR spectra of water at the interface of oxides. *Langmuir*. 1999. **15**(19): 6405.

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