Theor Chem Acc (2006) 115: 379–384
DOI 10.1007/s00214-006-0075-7

REGULAR ARTICLE

G. Berthier · R. Savinelli · C. Adamo · I. Ciofini

Theoretical study of sticking processes on molecular models of silica surfaces

Received: 22 July 2005 / Accepted: 7 December 2005 / Published online: 4 February 2006

Abstract The adsorption of small charged and neutral molecules on silica supports was modelled using perturbative post-Hartree–Fock quantum chemical methods (MP2 and MP4). The simplest spherosiloxane compound ($H_4Si_4O_6$) was used to mimic the surface while several molecules (namely CH_4, NH_4^+, NH_3, OH_3^+ and H_3^+) were considered as adsorbed species. Direct sticking of the molecules on one of the $(Si–O)_3$ ring leads to very different binding energies for cations (more than 11 kcal/mol) and neutral molecules (a few kcal/mol). These results indicate a dominant strong ion–multipole interaction for the first ones and a weak dispersion-type interaction for the latter. If the spherosiloxane cluster is screened by a mantle of accreted dust as it is the case in interstellar environment, the value of the binding energies, computed using the continuum dielectric theory, are predicted to be significantly reduced.

Keywords Adsorption · Silica surfaces · Spherosiloxane · Modelling · MP2

1 Introduction

Surface adsorption of molecular species is a prerequisite for various chemical processes, either directly in catalytic reactions or indirectly to convey molecules (reactants). In this work, theoretical calculations concerning the sticking of simple compounds on a silica support are presented. The background for this study was the understanding of some molecular processes occurring in astrophysics. It has been repeatedly stated that building up complex chemical species from smaller units cannot be explained not only by gas-phase reactions at very low pressure and temperature, but also involves chemical reactions assisted by interstellar dust grains (for recent surveys and references see reference [1]). The surface adsorption of precursors is currently invoked, using crude models of grains composed of refractory materials, such as silicates, surrounded by a porous mantle of dust of various chemical nature (ice, charcoals, etc.)[2,3]. Once a suitable model of the dust grain has been proposed on the basis of the experimental indications, the surface adsorption of molecular species can be then studied.

Adsorption on grain surfaces is interpreted in terms of weak physical phenomenon if the London component of van der Waals forces dominates the energy balance, or in terms of stronger chemical effect if Keesom–Debye attractive forces play a major role.

In order to consider adsorption, there are several possibilities for quantum-mechanical treatments: the super-molecule technique, simulating total adsorption complex by an appropriate finite cluster, the embedded-molecule technique, using an infinite periodic lattice and various composite methodologies using different theoretical level of description for different parts of the total system [4]. In any case, electron correlation has to be included, which causes computational difficulties for an (in principle) infinite number of electrons [5–7]. As already done in previous investigations concerning the adsorption on pregraphitic surfaces [8] we have preferred the super-molecule approach, considering one of the $(Si–O)_3$ rings of spherosiloxanes as a model of the surface.

Molecules belonging to the siloxane family, $(XSiO_{3/2})_{2n}$ ($n = 2, 3, 4, \ldots X =$ H, OR, halogens…), have been already suggested as models of silica surfaces [9,10]. The mechanism of formation of these compounds has been theoretically studied at the semi-empirical level [11], and the properties of their hydroxyl derivatives (silicic acids) have been computed by density functional theory (DFT) [12]. Here the simplest spherosiloxsane, namely the tetrahydrido-silsesquioxane ($n = 2$, $X =$ H), whose very symmetrical cage-like structure –T_d– includes the minimal number of border

G. Berthier (✉) · R. Savinelli
Laboratoire de Chimie Théorique Université Pierre et Marie Curie, CNRS-UMR 7616, Case 137, 4 place Jussieu, 75252
Paris Cedex 05, France
E-mail: berthier@lct.jussieu.fr

C. Adamo · I. Ciofini
Laboratoire d'Electrochimie et Chimie Analytique, UMR 7575, Ecole Nationale Supérieure de Chimie de Paris,
11 rue Pierre et Marie Curie, 75231
Paris Cedex 05, France

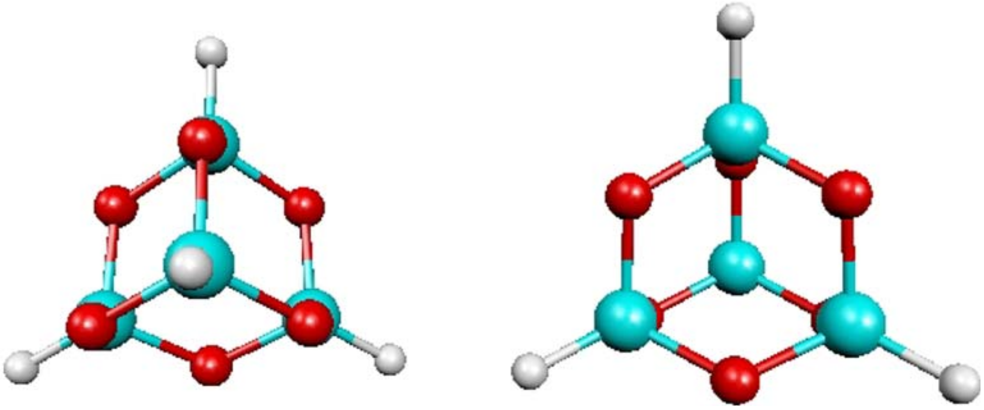

Fig. 1 Schematic drawn of the $H_4Si_4O_6$ spherosiloxane: *top* (*left*) and *side* (*right*) view. Oxygen atoms in *red*, silicon atoms in *cyan*

atoms instead of dangling bonds (Fig. 1), was used. This small model already provides meaningful information on the absorption phenomena [9] and its size allows for the use of correlated electronic methods, quite expensive in terms of computer resources. Indeed, such methods are mandatory for accurate study of weak (e.g. van der Waals) interactions [8].

Adsorption of molecules on spherosiloxane was studied for the following species: OH_3^+, NH_3, NH_4^+, CH_4, H_3^+. In addition to their intrinsic interest as building-blocks for larger compounds [13], these molecules possess a threefold axial symmetry that allows for an easy symmetry-based docking of three hydrogens of the molecules with the spherosiloxane. As a consequence, the interaction energy should be maximized for this conformation with respect to other kind of approaches (i.e. through a $-O \cdots H-N$ hydrogen bond)

2 Computational details

In most of the cases, the calculations were performed at the MP2 level including both core and valence electrons (i.e. full-MP2) using the Gaussian 98 and 03 [14] programs packages. Only the evaluation of zero-point vibrational energies corrections was done at the HF level.

A modified (enlarged) 6-311G basis set was used for all atoms. In particular, polarization and special semi-diffuse functions were added. The latter were selected variationally by maximizing the electric polarizability tensors of corresponding hydrides [15], a procedure recognized very effective for van der Waals energy calculations as early as the 1960s [16]. The values of polarization and semi-diffuse function's exponents for the various atoms are given in Appendix.

The structure of all isolated species was fully optimized at the MP2 level and kept provisionally frozen. Then the distance between the two moieties was varied and the binding energy obtained in this way was corrected from basis set superposition errors (BSSE) using the usual counterpoise procedure [17].

Additional calculations were performed in order to discuss the validity of our predictions concerning the magnitude of the adsorption energies computed for the siloxanes. These calculations include complete geometry optimizations at the MP2 level, MP4 calculations at frozen molecular MP2 structure and an estimation of dielectric screening effects from interstellar dust accreted on silica structures (see discussion below). Molekel [18] and GaussView [19] packages were used for the visualization of the results.

3 Results and discussion

The geometrical parameters of our basic model ($A = H_4Si_4O_6$) optimized at the MP2 level are consistent with the bond lengths derived from inelastic neutron scattering of various spherosiloxanes: d(Si–H)=1.454 Å and d(Si-O)=1.674 Å as compared to d(Si-H)=1.48 Å and d(Si-O)=1.62 Å experimentally [20]. Those of the hydrides used as adsorbed species are very close to the standard values reported in literature (for instance $d(O^+–H)$=0.981 Å and d(N–H)=1.014 Å).

Starting from optimized geometries at the MP2 level for the isolated fragments, different rigid approaches of the species B (B = OH_3^+, NH_3, NH_4^+, CH_4, H_3^+) to the siloxane (A) could be envisaged. Here we limited ourselves to the study of a "parallel" approach between the plane containing three symmetry equivalent H atoms of B and one of the faces of siloxane (A). This approach is more adapted than a one-site approach to describe the sticking process on siloxane since the concerted interaction with the three hydrogens is, from an energetic point of view, more convenient that a hypothetical single hydrogen bond to a Si–O–Si group. However, there are several possibilities of "parallel" binding: towards the silicon or the oxygens of A (Fig. 2a, b, respectively), or on a Si–O bond (Fig. 2c). In addition, for species like OH_3^+ and NH_3 we could imagine also an "inverted-parallel" approach simply by inverting the three bonds formed by the central atom of B in a pyramidal fashion.

All these type's conformations have been investigated in the rigid-approach picture; that is varying the intermolecular distance d(A–B) without relaxing the internal geometrical parameters of A and B. This approximation should be correct if the interaction energy in the complex is not too large,

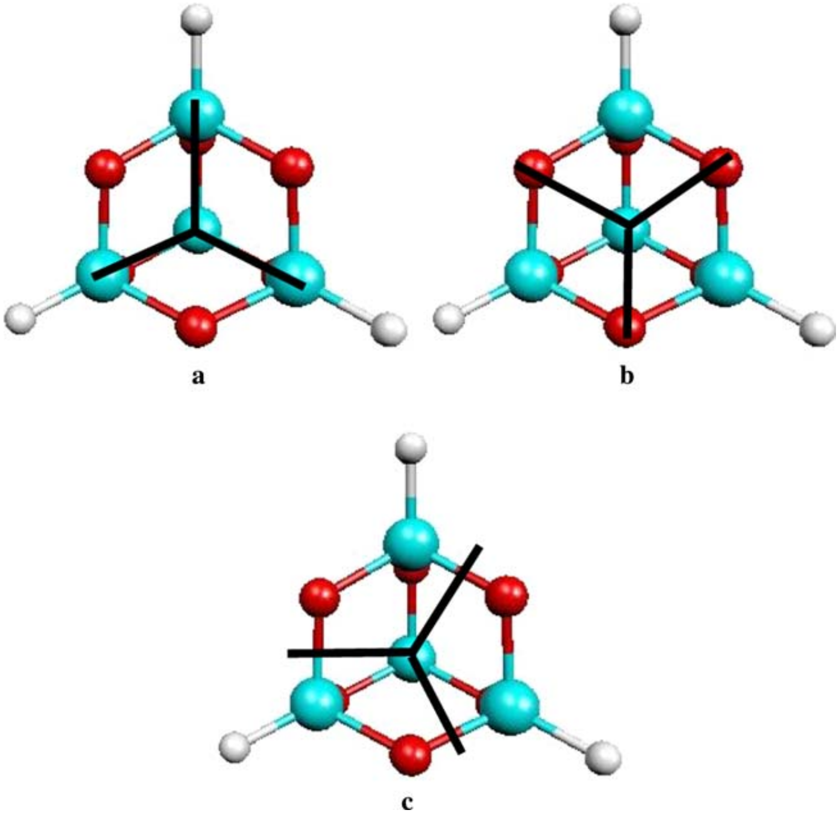

Fig. 2 Different absorption modes of C_3 symmetric species (depicted as *black line*) on the spherosiloxane cage: (**a**) on silicon atoms ($SphSi_{3par}$) (**b**) on oxygen atoms ($SphO_{3par}$) (**c**) on the Si–O bonds ($SphSiO_{bond}$)

which is the case of neutral species, but not necessarily for ions, as discussed below.

In this scan procedure where only intermolecular distances d(A–B) are varied, we assume that the relaxation of the geometrical parameters of A and B moieties is negligible, as already found on similar weak complexes [21]

The "parallel" type of approach described above may be considered as preferential on the basis of simple electrostatic arguments. In fact, the computed electrostatic potential, reported in Fig. 3, shows that the oxygen atoms are the most probable sites for an electrophilic approach (most negative electrostatic potential) while the silicon atoms should be the preferential sites for a nucleophilic attack.

The adsorption energies reported in Table 1 indicate that the bonding of molecule B to the oxygens of the siloxane A through its hydrogen in a parallel way gives always the most stable structure. With respect to this arrangement, the values obtained in the case of an "inverted-parallel" approach are significantly reduced, from 0.78 to 0.11 kcal/mol for NH_3 and from 16.3 to 6.44 kcal/mol for OH_3^+.

Our results can be summarized as follows: clearly, surface adsorption of cations (binding energy in the range 6.44–21.04 kcal/mol) is a stronger interaction than that of neutral molecules (binding energy in the range 0.11–0.91 kcal/mol). The former is ruled by charge–multipole type interactions, while the latter by a weak interaction of dispersion type. A similar behaviour is computed for the PAHs and benzene itself (19.5 and 1.1 kcal/mol, including BSSE corrections for a coplanar approach of three hydrogens of OH_3^+ and NH_3, respectively, towards carbons). Furthermore, the magnitude of the binding energies of cations, especially H_3^+, with spherosiloxane suggests that silicates are adsorption supports almost as efficient as carboneous compounds. In contrast, the almost zero values obtained for the binding energy of neutral systems after ZPVE corrections (of the order of 0.4 kcal/mol for the methane–siloxane complex) suggest that the formation of such species is possible only at very low-temperature conditions, as in the case of non-ionized PAHs [8].

The numerical similitude of the values reported above for non-corrected and BSSE-corrected interaction energies of OH_3^+ and NH_3 with those mentioned above for adsorption on benzene suggests that the energy lowering especially strong obtained for ions should have a – so to speak – common origin, namely a charge–multipole attraction, well known in the case of aromatics by the name of cation–π interaction [22]. Here, the role of the aromatic sextet is played by three oxygen doublets located on the adsorption face of spherosiloxane. In fact, the highest occupied molecular orbitals (HOMOs) of the spherosiloxane, shown in Fig. 3, are a set of three degenerate molecular orbitals (T_2 symmetry) resulting from an in-phase linear combination of p orbitals centred on oxygen atoms. Most probably, the small decrease in binding

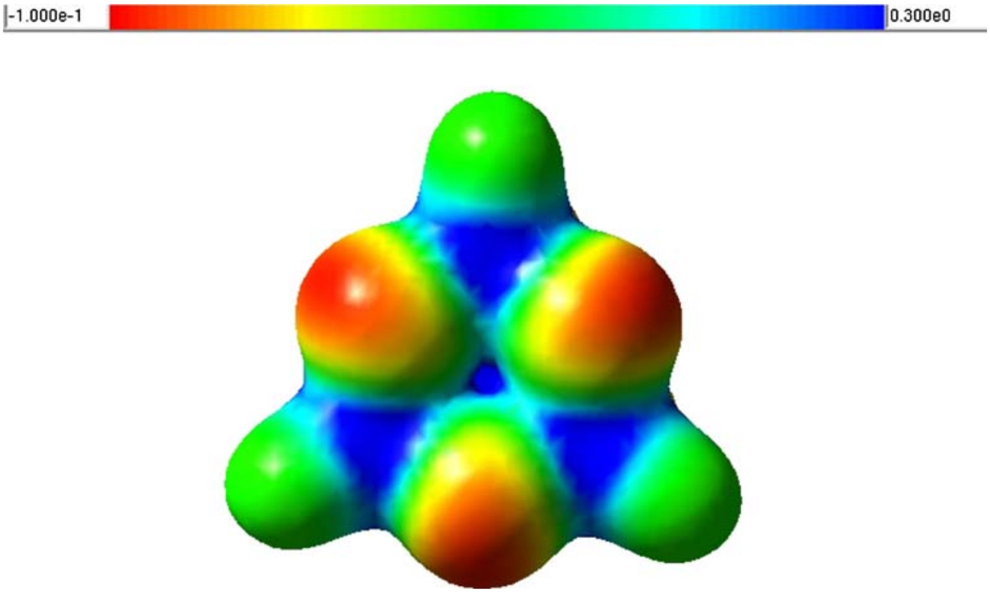

Fig. 3 Computed electrostatic potential mapped on an isodensity surface (isovalue 0.02 Å) of the siloxane

energy with respect to benzene (19.5 kcal/mol with respect to 16.3 kcal/mol in case of the absorption of OH_3^+) arises from the fact that the three axes of the localized orbitals describing electron pairs on oxygens are not exactly directed along the normal of the adsorption plane. Assuming a rule in $\cos^2\theta$1 for the ratio benzene/siloxane interaction energies computed for OH_3^+, we find 24°4′, not too far from 19°5′ in the case of tetrahedral lone-pairs.

To check the accuracy of the MP2 binding energies reported above, additional calculations were performed for the NH_3 and OH_3^+ adducts with siloxane, using a somewhat reduced basis set (6–31 G(*d,p*)). First the stability of our MP2 values has been verified by comparing them to those obtained for the preceding intermolecular distances (2.39 Å. for OH_3^+ and 3.27 Åfor NH_3), using MP4 treatments reduced to valence molecular orbitals.

The adsorption energies remain remarkably stable when going from MP2 to MP4. In the case of the OH_3^+ species we compute a BSSE-corrected binding energy equal to 13.23, 13.22 and 13.21 kcal/mol for full-MP2, valence-MP2 and valence-MP4, respectively. At the same level of theory the NH_3 species is found to have practically zero binding energy.

Next, the C_{3v} symmetric structures of both adduct were fully optimized at MP2 level. The behaviour of the strong complex formed by the OH_3^+ ion is different from that of the weak adduct formed by NH_3. In fact, no appreciable change in interaction energy is found for the neutral species while the charged complex with OH_3^+ is stabilized (up to 22 kcal/mol when using the reduced 6–31 G(*d,p*) basis). So we can expect that structural relaxation will induce a significant energy increase only in the case of cations.

Charge distributions computed from NBO analyses [23] lead us to an interesting comparison between the two types of complexes. In the case of the ionized compound formed by OH_3^+, the formal charge +1 of the ligand is somewhat reduced, both at the SCF level including electrostatic, polarization and exchange effect [24], and at the MP2 level involving additional dispersion contributions, namely, a decrease of 0.036 $|e^-|$ and 0.059 $|e^-|$ for HF and MP2 calculations, respectively. On the other hand, in the weakly bonded complex formed by neutral ammonia, there is only a very small transfer of electron giving a very slightly positive fragment NH_3 (i.e. a charge of 0.002 or 0.005, respectively).

Last, the role of the dust mantle accreted on grains in interstellar conditions was tentatively taken into account according to the primitive picture of a dielectric continuum as often used in astrophysics to model light extinction irrespective

Table 1 Computed intermolecular distances (d_{A-B} in Å), MP2 binding energies (in kcal/mol) and basis set superposition errors (BSSE)-corrected MP2 binding energies (in kcal/mol) of spherosiloxane complexes in vacuum

	d_{A-B}	ΔE	$ΔE_{BSSE}$
Cations			
B: OH_3^+			
$SphO_{3par}$	2.39	19.19	16.13
$SphSi_{3par}$	3.23	12.02	9.70
$SphO_{3perp}$	2.56	8.76	6.44
B: NH_4^+			
$SphO_{3par}$	2.58	14.45	11.74
$SphSi_{3par}$	3.34	10.08	8.12
B: H_3^+			
$SphO_{3par}$	2.72	23.40	21.04
$SphSi_{3par}$	3.50	17.27	15.46
Neutral			
B: NH_3			
$SphO_{3par}$	3.27	2.34	0.78
$SphSi_{3par}$	4.05	1.66	0.35
$SphO_{3perp}$	3.19	1.49	0.11
B: CH_4			
$SphO_{3par}$	3.30	2.57	0.91
$SphSi_{3par}$	3.83	2.19	0.52

Table 2 Computed intermolecular distances (d_{A-B} in Å), MP2 binding energies (in kcal/mol) and BSSE-corrected MP2 binding energies (in kcal/mol) of spherosiloxane complexes in vacuum and in PCM.

	OH_3^+				NH_3		
	d_{A-B}	ΔE	ΔE_{BSSE}		d_{A-B}	ΔE	ΔE_{BSSE}
Vacuum/vacuum[a]	2.39	19.19	16.13	Vacuum/vacuum[a]	3.27	2.34	0.78
D = 1.43				D = 1.43			
Vacuum/PCM[b]	2.39	10.87	7.81	Vacuum/PCM[b]	3.27	1.91	0.36
PCM/PCM[c]	2.41	10.90	7.91	PCM/PCM[c]		No binding	
D = 2.25				D = 2.25			
Vacuum/PCM[b]	2.39	3.47	0.41	Vacuum/PCM[b]	3.27	1.40	<0
PCM/PCM[c]	2.69	4.10	1.81	PCM/PCM[c]		No binding	
D = 24.55				D = 24.55			
Vacuum/PCM[b]	2.39	−5.62	<0	Vacuum/PCM[b]	3.27	<0	<0

[a] Intermolecular distance optimized in vacuum, binding energy computed in vacuum
[b] Intermolecular distance optimized in vacuum, binding energy computed in PCM
[c] Intermolecular distance optimized in PCM, binding energy computed in PCM

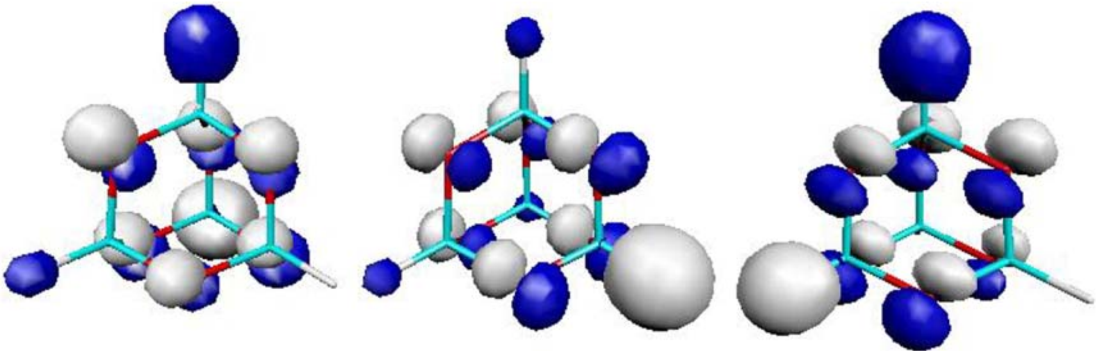

Fig. 4 Isovalue representation (contour value 0.05 Å) of the three degenerate highest occupied molecular orbital (HOMO) of the siloxane

of the physical and chemical characteristic of the medium [25]. Our calculations were performed in the framework of cavity model borrowed to the solvation theory used in quantum chemistry, assuming it may be applied in other condition (such for instance to study liquid crystals) [26,27]. The main ingredients introduced in this model (the so called CPCM [28–31]) for numerical purpose are the dielectric constant D of the medium and the shape of the cavity, here defined using the united atom topological model (UATM) [32]. The dielectric medium simulating the mantle was added using different values of the constant D, namely in the ascending order of its effect on electronic energies (i.e.): 1.43 (argon), 2.247 (benzene), 24.55 (ethanol).

The values reported in Table 2 for the binding energies of OH_3^+ and NH_3 are those obtained in the presence of a dielectric, using the BSSE corrections computed in the gas phases for the spherosiloxane complexes at the geometry optimized in the presence of a dielectric. The salient feature of these results is a progressive cancellation of all the interaction energies when the screening effect, introduced by the PCM model, increases. For high dielectric constants, no direct adsorption on the core is possible, even in the case of ions, but a possibility remains for sufficient low values of D.

Looking at the results obtained when computing the binding energy of the OH_3^+ complex at the frozen vacuum geometry, we can notice that the interaction energy of this charged species is reduced from 16.3 to 0.41 kcal/mol as soon as the dielectric constant becomes equal to 2.25 and then goes to zero for higher values of D (for instance 24.55). Relaxing the distance d_{A-B} between the two moieties of the complex in presence of a medium favouring charge separation produces elongated structures. Even if, for small values of D, this yields a small positive increment in binding energy, it should be noted that there is simultaneously an increase in the intermolecular distance and in the electrostatic interaction with the medium, which is destabilizing with respect to its dissociation products. Indeed no binding is computed for large D values.

Using the language of the theory of dielectrics, we can speak of screening for the vanishing interaction of a dressed spherosiloxane, as a result of its electrostatic interaction with a polarizable continuum. Numerically, this comes from a balance between the values of the molecular energies, the most affected ones being those of the smallest species. As it concerns the neutral species, there is no significant binding even for the lowest dielectric constant we considered.

4 Conclusions

To sum up, direct adsorption of ions on the surface model provided by spherosiloxane $H_4Si_4O_6$ is quite efficient for ions in vacuum, because it is monitored by the usual cation–multipole attraction process, but there is still a weak adsorption possibility for neutrals, due to standard dispersion forces. Actually, the silica materials are not much less performing than PAHs regarding direct surface adsorption of molecules in dry conditions (for instance, some planetary atmospheres). When screening effects from accreted interstellar dust are considered all adsorption energies are strongly reduced so that direct adsorption of neutrals becomes rather improbable.

Acknowledgements The authors thank Prof. C. Pisani and P. Ugliengo (University of Turin) for helpful information on their calculations on silicates. One of us (G.B.) is indebted of many discussions on this problem to Prof. M. Nait Achour (University of Alger) in the frame of a C.M.E.P. contract. The "Institut de Developpement et Ressources en Informatique Scientifique" (CNRS, Orsay) is acknowledged for an important allocation of computer time.

Appendix

Orbital exponents of the polarization and semi-diffuse functions added to the standard using 6-311G Gaussian basis set.

	Si	C, N, O	H
d	0.45	0.75, 0.80, 0.85	–
p	–	–	1.10
$s = p$	0.04	0.05	0.065
d	0.10	0.30	–

References

1. Witt AN, Clayton DD, Braine B (2004) Astrophysics of dust. ASP confer ser 309:665
2. d'Hendecourt LB, Allamendola JL, Greenberg LM (1985) Astron Astrophys 152:180
3. Duley WW, Jones AP, Williams DA (1989) Mon Nat R Astron Soc 236:709
4. Maseras F, Morokuma K (1995) J Comput Chem 6:1170
5. Kudin KN, Scuseria GE (2000) Phys Rev B 61:16440
6. Albrecht M, Fulde P (2002) Phys Stat Sol 234:313
7. Pisani C, Busso M, Capecchi G, Casassa S, Dovesi R, Maschio L, Zicovich C, Schutz M (2005) J Chem Phys 122:094113
8. Tran F, Weber J, Wesolowski T, Cheikh F, Ellinger Y, Pauzat F (2002) J Phys Chem A106:8696
9. Feher FJ, Newman DA, Walzer JF (1989) J Am Chem Soc 111:1741
10. Burgi H, Calzaferri G, Herren D, Zhdanov A (1991) Chimia 45:3
11. Wichmann D, Jug K (1999) J Phys Chem B 103:10087
12. Civalleri B, Garrone E, Ugliengo P (1999) Langmuir 15:5859
13. Lequecux J, Roueff E (1991) Phys Rep 200:241
14. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery, Jr JA, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill, PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, Revision B.04. Gaussian, Inc., Wallingford
15. Berthier G, Savinelli R, Pullman A (1997) Int J Quan Chem 63:567
16. Salem L (1960) Mol Phys 3:441
17. Boys SF, Bernardi F (1970) Mol Phys 9:553
18. Portmann S, Lüthi HP (2000) MOLEKEL: an interactive molecular graphics tool. Chimia 54:766
19. Gauss View 3.0 (2004) Gaussian Inc
20. Marcolli, C, Lainé P, Bühler R, Calzaferri G, Tomkinson J (1997) Phys Chem B 101:117
21. Adamo C, Berthier G, Savinelli R (2004) Theor Chem Acc 111:176
22. Dougherty DA, Stauffer DA (1990) Science 250:1558
23. Reed AE, Weinhold F (1983) J Chem Phys 78:4066
24. Kitaura K, Morokuma K (1976) Int J Quan Chem 16:325
25. Whittet DCB (1981) QJR Astr Soc 22:3
26. Pavanello M, Mennucci B, Ferrarini A (2005) J Chem Phys 122:64906
27. Benzi C, Cossi M, Barone V, Tarroni R, Zannoni C (2005) J Phys Chem B 109:2584
28. Miertus S, Scrocco E, Tomasi J (1981) J Chem Phys 55:117
29. Barone V, Cossi M (1998) J Phys Chem A 102:1995
30. Cossi M, Rega N, Scalmani G, Barone V (2003) J Comp Chem 24:669
31. Tomasi J, Mennucci B, Cammi R (2005) Chem Rev 105:2999
32. Barone V, Cossi M, Tomasi J (1997) J Chem Phys 107:3210