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Surface Science 602 (2008) 1207–1211
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Ammonia adsorption on Cl/Si(001): First-principles calculations

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Received 4 December 2007; accepted for publication 14 January 2008
Available online 31 January 2008

Abstract

Motivated by recent experiments [Finstad, Thorsness, Muscat, Surf. Sci. 600 (2006) 3363], the interaction between ammonia and the Cl-terminated Si(001) surface is studied using density functional theory (DFT). The reaction NH_3 (gas) + Si(001):Cl → Si(001):NH_2 + HCl (gas) is endothermic, even if temperature effects are included in the calculation. We find that the formation of ionic bonds between surface-bonded NH_3^+ and nearby Cl^- rather than the desorption of HCl corresponds to a local energy minimum.

Keywords: Ammonia; Chlorine; Silicon; Surface chemical reaction; DFT

The effective passivation of Si surfaces by foreign species is required for many technological steps in the semiconductor device production as well as crucial for the function of the Si devices themselves [1]. Recently, Finstad et al. investigated the reactivity of Cl-passivated Si(001) surfaces towards gas phase NH_3 [2]. While there exists a wide body of literature devoted to the interaction with ammonia with clean Si(001) surfaces [3–6], partially motivated by the technological importance of silicon nitride films, little is known about the reactivity of chemically modified Si surfaces towards NH_3. Surprisingly, Finstad and co-workers found that – in contrast to the hydrogen-terminated Si(001) surface which is essentially unreactive towards NH_3 – the Cl-terminated surface reacts with ammonia, resulting in surface-bonded Si–NH_2 species [2]. As discussed by Hamers [7], this finding is in fact intriguing: Both steric considerations (i.e., the reaction kinetics) as well as enthalpic considerations (i.e., the reaction thermodynamics) suggest the Cl-terminated surface to be even more efficiently passivated towards reactions with NH_3 than the H-terminated surface. The unexpected experimental result by Finstad et al. is the motivation for the present computational study.

The calculations are performed using the Vienna Ab-initio Simulation Package (VASP) implementation [8] of the gradient-corrected density functional theory (DFT-GGA) [9]. The electron-ion interaction is described by the projector augmented wave (PAW) method [10]. We expand the valence wave functions into plane waves up to an energy cutoff of 350 eV. The surface is modelled by periodically repeated slabs using supercells. They contain eight Si bulk layers oriented along the [001] direction and a vacuum region of similar thickness. Depending on the coverage, c(4 × 2) or (2 × 1) surface unit cells are studied. The Brillouin zone integrations are performed using sets corresponding to 144 **k** points in the full (1 × 1) surface brillouin zone (SBZ). All calculations are performed using the calculated Si equilibrium lattice constant of 5.456 Å. In good agreement with experiment [11] and earlier calculations [12,13], we determine a surface dimer bond length of 2.36 Å and a dimer tilt angle of 20° for the clean Si(001) surface. The structural data calculated here for the Cl-terminated surface are in close agreement with first-principles results by Lee and Kang [14]: We calculated a Si–Cl bond length of 2.07 Å and a dimer length of 2.41 Å.

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doi:10.1016/j.susc.2008.01.024

Moreover, the present methodology has been shown earlier to reliably describe molecules containing nitrogen and chlorine [15,16]. Therefore we expect it to be adequate for the present study.

We start the calculations by mapping the potential energy surface (PES) experienced by an ammonia molecule the nitrogen lone pair of which points to the surface. The lateral molecular position is kept fixed during the calculation, while all other degrees of freedom are allowed to relax. The result is shown in Fig. 1. As can be seen, the interaction between NH_3 and the Cl-terminated Si surface is purely repulsive, irrespective of the molecular position. For this reason, the plot shown in Fig. 1 actually does not correspond to a spatial map of the local energy minima assumed by the admolecule, but rather indicates energies that correspond to molecular (non-equilibrium) adconfigurations that fulfill the energy convergence criterion $\Delta E \leqslant 1 \times 10^{-5}$ eV for the change in total energy between two self-consistency steps. When discussing Fig. 1, one more word of caution is in order: Covalent and ionic chemical bonds are, in most cases, well described using GGA to account for the exchange and correlation energy of the electrons. This does not hold, however, for dispersion or van der Waals (vdW) forces [17,18]. The neglect of vdW forces in the present calculations may turn the weakly repulsive interaction predicted here in a physisorbed state [19]. Fig. 1 indicates that the lowest energy position of the molecule is between the Cl-terminated Si dimers.

In order to determine the energy barrier needed to chemically adsorb ammonia, we start from this lowest energy position. The vertical position of nitrogen is gradually decreased, while all other molecular and surface atomic degrees of freedom are allowed to relax. The resulting reaction pathway is shown in Fig. 2. After overcoming an energy barrier of approximately 0.6 eV, ammonia adsorbs underneath the Cl layer in the configuration labeled by the green circle in Fig. 2. Next, we lift one chlorine atom from the surface. This leads to a substantial increase of the total energy of our system. When the Si bonding position is available, the ammonia nitrogen bonds there and the energy is lowered again. Upon further increasing the distance between chlorine and the surface one ammonia hydrogen attaches to Cl, forming HCl. Interestingly, for reasons that will be discussed below, the energy of the H_2N–Si–Si–Cl surface + HCl gas (red circle in Fig. 2) is higher than the configuration where Cl remains close to the surface. The former configuration, where ammonia substitutes one chlorine as a primary amine, is characterized by a slight increase of the length of the remaining Si–Cl bond by 0.04 Å – 2.11 Å. The Si–N and N–H distances amount to 1.74 and 1.02 Å, respectively.

The deposition of a primary amine group (Si–NH_2) concluded from the experiments by Finstad et al. [2] is hard to reconcile with the energetics summarized in Fig. 2. In fact, if we compare the difference of the total energies of the completely Cl-terminated Si(001) surface with NH_3 in gas phase with the partially (one per Si dimer) NH_2 adsorbed surface with HCl in gas phase we obtain

$$\Delta E = E_{2\mathrm{Cl}\,@\,\mathrm{Si}(001)} + E_{\mathrm{NH_3}}(\mathrm{gas}) - E_{\mathrm{NH_2{+}Cl}\,@\,\mathrm{Si}(001)} - E_{\mathrm{HCl}}(\mathrm{gas}) = 0.45\ \mathrm{eV}, \quad (1)$$

i.e., the primary amine formation suggested in Ref. [2] is endothermic. Thereby we have compared the respective DFT total energies that refer to zero temperature. Experimentally, the primary amine formation was observed at 348 K. In order to assess the sign and magnitude of temperature effects, we calculate the free energy $F = U - TS$ using the DFT total energy to obtain U. The entropy S itself depends on the temperature and can be split into translational, rotational and vibrational contributions for the gas-phase molecules as well as a part related to the surface phonons. In detail, following [20], we calculate

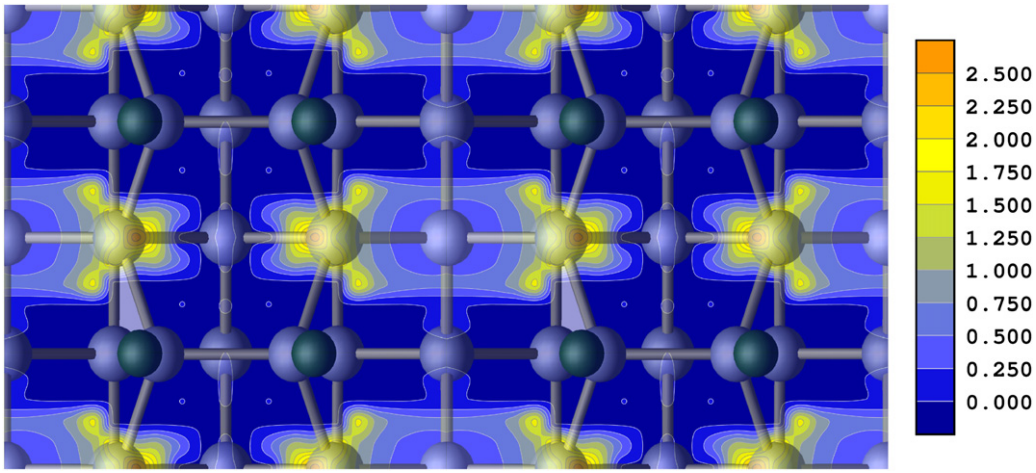

Fig. 1. Potential energy surface (PES) for NH_3 adsorbed on the chlorined Si(001) surface (see text). The energy scale gives the difference with respect to the surface + gas-phase ammonia in eV. The positions of the uppermost Si and Cl atoms are indicated.

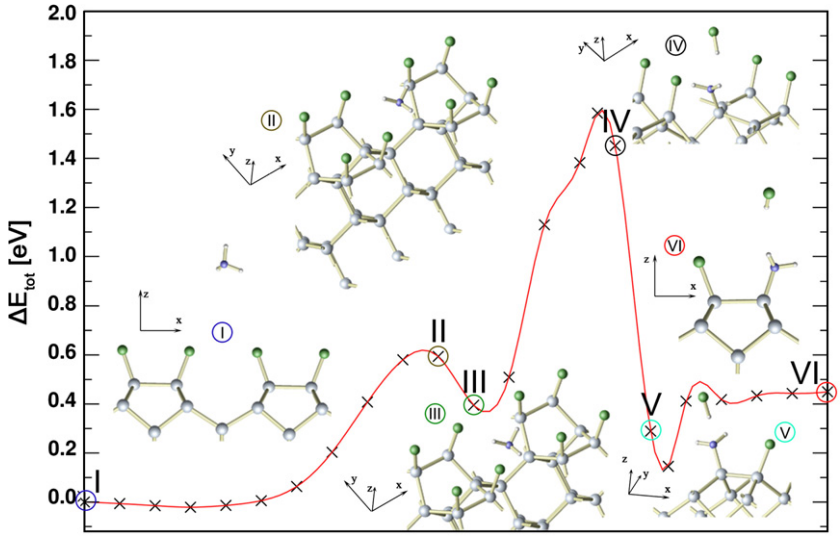

Fig. 2. Calculated reaction pathway of ammonia with the Cl/Si(001) surface (see text).

$$S_{\mathrm{trans}}(V,T) = \frac{3}{2}k_{\mathrm{B}} + k_{\mathrm{B}} \ln\left(V\sqrt{\frac{2\pi M k_{\mathrm{B}} T}{h^2}}^{3}\right), \tag{2}$$

$$S_{\mathrm{rot}}(T) = \begin{cases} k_{\mathrm{B}} + k_{\mathrm{B}} \ln\left(\frac{8\pi^2 k_{\mathrm{B}} T \Theta}{h^2 \sigma}\right) & \text{for linear molecules} \\ \frac{3}{2}k_{\mathrm{B}} + k_{\mathrm{B}} \ln\left(\frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{8\pi^2 k_{\mathrm{B}} T}{h^2}}^{3}\sqrt{\Theta_1\Theta_2\Theta_3}\right) & \text{for nonlinear molecules} \end{cases}, \tag{3}$$

$$S_{\mathrm{vib}}(T) = k_{\mathrm{B}} \sum_{i=1}^{3N-6(5)} \frac{h\nu_i}{k_{\mathrm{B}}T} \frac{1}{e^{\frac{h\nu_i}{k_{\mathrm{B}}T}} - 1} - \ln\left(1 - e^{-\frac{h\nu_i}{k_{\mathrm{B}}T}}\right), \tag{4}$$

where M represents the molecular mass and Θ_i the respective moment of inertia. The change of the free energy upon ammonia adsorption is calculated using the three partial entropy corrections for the free particles and the vibrational entropy correction for the surface. The latter is obtained from frozen-phonon calculations – similar to the ones described in Ref. [21] – that were restricted to the two uppermost silicon layers and the Γ point of the SBZ. For the experimental conditions of pressure and temperature, we find that indeed the adsorption energetics changes considerably compared to the zero-temperature results. However, the primary amine formation is now even less favorable (by 0.62 eV) than the Cl-terminated surface + NH_3 (gas phase). As shown in Fig. 3, the vibrational degrees of freedom are the most significant ones in modifying the adsorption energetics.

According to the reaction path shown schematically in Fig. 2, the primary amine formation + desorption of HCl does not even correspond to a clear local minimum of the reaction energy. Rather, Cl prefers to stay close to the sur-

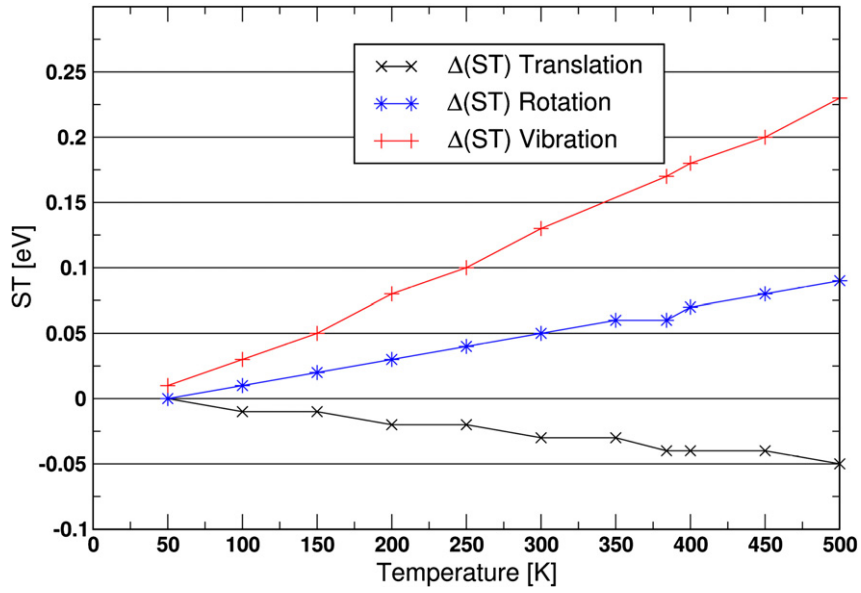

Fig. 3. Calculated temperature dependent contributions of the translational, rotational and vibrational degrees of freedom to the adsorption energetics where $\Delta(ST) = (S_{\mathrm{Si(001):Cl+NH_3(gas)}} - S_{\mathrm{Si(001):ClNH_2+HCl(gas)}})T$ (see text).

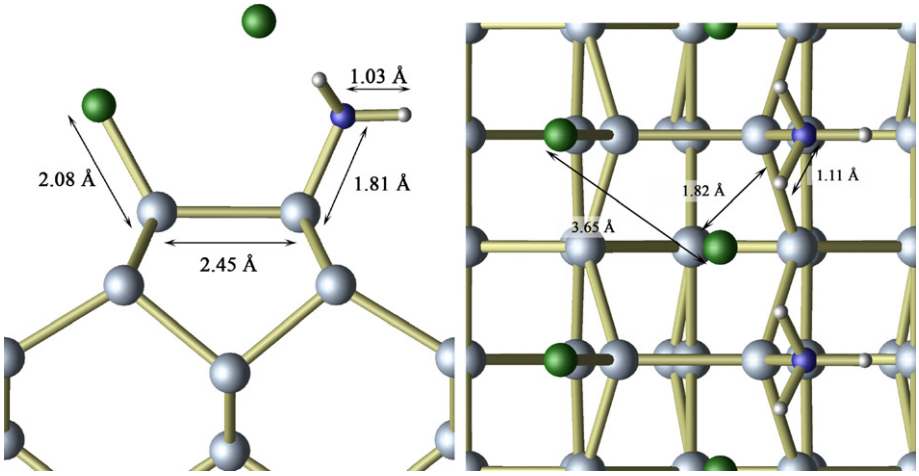

Fig. 4. Schematic structure and geometrical data for the ionic complex (see text).

face. The actual minimum energy configuration (corresponding to the data point right from configuration *V* in Fig. 2) with relevant geometry parameters is shown in Fig. 4. Here one surface chlorine atom is replaced by ammonia but stays close to one NH_3 hydrogen. This structure is energetically more stable (by 0.28 eV) than HCl desorption. This seems at first counter-intuitive, because electron-counting arguments show that this structure cannot be covalently bonded.

In order to understand the mechanism that stabilizes this complex, we calculate the charge transfer. In detail, the charge density difference of the reacted and the isolated systems is calculated according to

$$\Delta n = n_{\text{total}} - n_{\text{total-Cl}} - n_{\text{total-NH}_3} + n_{\text{substrat}}. \tag{5}$$

Here, $n_{\text{total}}, n_{\text{total-Cl}}, n_{\text{total-NH}_3}$, and n_{substrat} refer to the charge density of the complete adsystem, of the adsystem reduced by the charge densities of gas-phase Cl and NH_3, respectively, and the charge density of the Si substrate with adsorbates removed. The regions of electron accumulation and depletion are indicated in blue and red, respectively, in Fig. 5. The figure indicates a charge accumulation at chlorine, while there is a charge lowering at the adsorbed ammonia. The reduction in charge between Si and NH_3 is accompanied by an increased (with respect to the Cl–NH_3 substituted structure) bond length of 1.81 Å (see Fig. 4. The distance between the not Si-bonded Cl and the nearest hydrogen is 1.82 Å, i.e., 0.5 Å larger than the HCl bond length. This, in conjunction with the charge transfer, indicates that the Cl atom is not covalently but ionic bonded to the surface, forming an adsorbed NH_3^+ Cl^- complex. This is corroborated by Møller–Plesset (MP2) cluster calculations performed using the ORCA package [22] that result in Mulliken charges of −0.765 e at Cl and 0.758 e at NH_3. The cluster calculations were performed

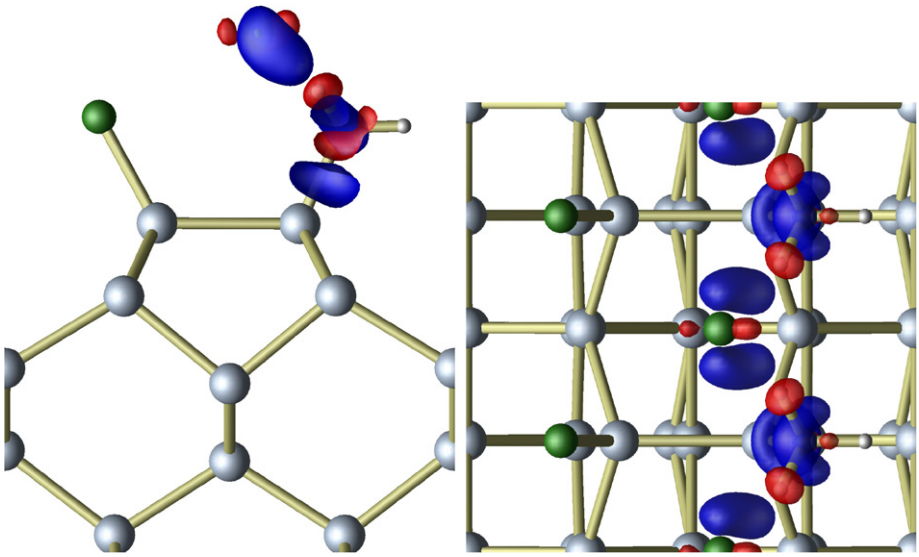

Fig. 5. Electron accumulation (blue) and depletion (red) with respect to the isolated species due to the formation of the structure shown in Fig. 4. Shown are isosurfaces at $\Delta n = \pm 0.06$ e/Å. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

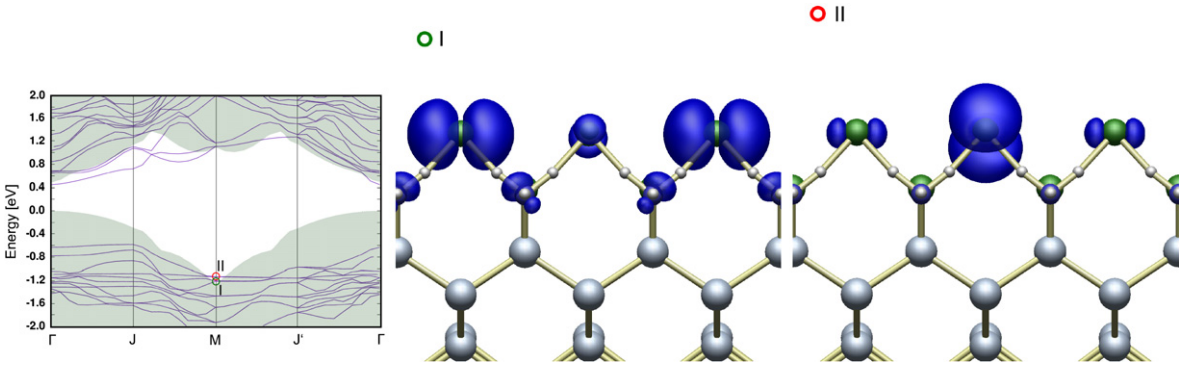

Fig. 6. (Left) Band structure of the adsorption configuration shown in Fig. 4. The projected Si bulk band structure is indicates in gray. (Middle and right) Orbital character of bound surface states indicated in the band structure.

for a Cl–SiH_2–SiH_2–NH_3 complex with one additional Cl atom.

Fig. 6 shows the band structure of the ionic $NH_3^+Cl^-$ complex formed at the Si(001) surface together with the orbital character of state for the two highest occupied surface states. As can be seen, the surface is semiconducting. The fundamental band gap of bulk Si is nearly free of states. At the *M* point, two occupied bound surface states appear. Both are mainly derived from Cl p orbitals with some contributions from NH_3 sp^3 hybrid orbitals (green and red circles in Fig. 6).

To summarize, motivated by recent experiments, we performed first-principles calculations on the adsorption of NH_3 on Cl/Si(001). The total-energy results show that the primary amine formation as suggested by Finstad et al. [2] is endothermic, even if entropy contributions to the adsorption energetics are taken into account. Our findings suggest that factors not yet investigated, such as the microscopic roughness of the Si(001), possibly enhanced by Cl etching [7], might be responsible for the surprising reactivity of Cl-terminated Si(001) towards ammonia. Interestingly, we find that the formation of an ionic NH_3^+ Cl^- complex at the surface is more stable than the desorption of HCl.

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft as well as supercomputer time provided by the Höchstleistungs–Rechenzentrum Stuttgart and the Paderborn Center for Parallel Computing PC^2.

References

[1] J. Dabrowski, H.-J. Müssig, Silicon Surfaces and Formation of Interfaces, World Scientific, Singapore, 2000.
[2] C.C. Finstad, A.G. Thorsness, A.J. Muscat, Surf. Sci. 600 (2006) 3363.
[3] P.A. Taylor, R.M. Wallace, W.J. Choyke, M.J. Dresser, J.T. Yates, Surf. Sci. 215 (1989) L286.
[4] O.N. Chung, H. Kim, S. Chung, J.Y. Koo, Phys. Rev. B 73 (2006) 033303.
[5] O.N. Chung, H. Kim, J.Y. Koo, S. Chung, Phys. Rev. B 74 (2006) 193312.
[6] J.C.F. Rodriguez-Reyes, A.V. Teplyakov, Phys. Rev. B 76 (2007) 075348.
[7] R.J. Hamers, Surf. Sci. 600 (2006) 3361.
[8] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15.
[9] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
[10] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
[11] W. Mönch, Semiconductor Surfaces and Interfaces, Springer-Verlag, Berlin, 1995.
[12] P. Krüger, J. Pollmann, Phys. Rev. Lett. 74 (1995) 1155.
[13] W.G. Schmidt, F. Bechstedt, J. Bernholc, Phys. Rev. B 63 (2001) 045322.
[14] J.Y. Lee, M.-H. Kang, Phys. Rev. B 69 (2004) 113307.
[15] M. Preuss, W.G. Schmidt, F. Bechstedt, J. Phys. Chem. B 108 (2004) 7809.
[16] M. Preuss, W.G. Schmidt, K. Seino, F. Bechstedt, Appl. Surf. Sci. 234 (2004) 155.
[17] H. Rydberg, M. Dion, N. Jacobson, E. Schröder, P. Hyldgaard, S. Simak, D. Langreth, B. Lundqvist, Phys. Rev. Lett. 91 (2003) 126402.
[18] O.A. von Lilienfeld, I. Tavernelli, U. Rothlisberger, D. Sebastiani, Phys. Rev. Lett. 93 (2004) 153004.
[19] F. Ortmann, W.G. Schmidt, F. Bechstedt, Phys. Rev. Lett. 95 (2005) 186101.
[20] F. Jensen, Introduction to Computational Chemistry, Wiley, Chichester, 2002.
[21] W.G. Schmidt, F. Bechstedt, G.P. Srivastava, Phys. Rev. B 52 (1995) 2001.
[22] F. Neese, J. Inorg. Biochem. 100 (2006) 716.