Quantum-Chemical Simulation of Ni(ktf)$_2$ Adsorption on the Surface of Natural Silicon Oxide

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Abstract

The connection between the process of Ni(ktf)$_2$ molecule distortion as a result of chemisorption on SiO$_2$ surface and the magnetic state of the adsorbed molecules is analysed using model species by means of quantum-chemical techniques ZINDO/1(UHF) and DFT (B3LYP, basis LACVP**). It is demonstrated that the resulting distortion degree of the model molecule Ni(ktf)$_2$ is substantial. For example, the (γ)C—Ni—(γ)C angle changes from 180º in the flat square structure of the free state to about 120−150º. It is stated that the adsorption of the model molecule Ni(ktf)$_2$ on the SiO$_2$ surface with Ni atom above the surface O atom is accompanied by a substantial decrease in the difference between the energies of singlet and triplet states $\Delta\varepsilon_{t-s}$. The most substantial effect on the change of $\Delta\varepsilon_{t-s}$ is caused by the distortion of the first coordination sphere of Ni atom. The correlation is obtained between the splittings $\Delta\varepsilon_{t-s}$ calculated by means of semiempirical ZINDO/1 method and nonempirical DFT method. This allows to use a more simple calculative ZINDO/1 method in simulations of the adsorption of β-diketonates on the surface.

INTRODUCTION

Investigating the mechanism of the adsorption of Cu(II) and Ca(II) dipivaloylmethanates (dpm) on SiO$_2$ surface, the authors of [1] conclude on the basis of IR spectroscopic data and EXAFS of the adsorbed molecules that, independently of metal type, the adsorption of the complex is determined by the interaction of the ligand with OH groups present on the SiO$_2$ surface. The chelate centre MO$_4$ does not participate in the adsorption process and does not undergo spatial rearrangement.

The presented adsorption mechanism is in contradiction with the fact that the magnetic susceptibility of Ni(II) trifluoroketoiminate molecules changes as a result of their adsorption on the surface of hydrated natural silicon oxide [2]. Since the chelate centres of Ni(ktf)$_2$ molecule and CuO$_4$ groups of Ni(ktf)$_2$ and Cu(dpm)$_2$ molecules are similar and the structure of peripheral surroundings is of minor im-

portance for adsorption [1], the mechanisms of adsorption should be similar for the Ni(ktf)$_2$ and Cu(dpm)$_2$ molecules. The paramagnetism of the adsorbed Ni(ktf)$_2$ is connected with the electron rearrangement of its chelate ring caused either by spatial distortion of the molecule as a result of chemisorption or by the increase of the coordination number of the central atom due to donor-acceptor interaction with Si—O or Si—OH groups of the real silicon surface.

In the present work we analyse the connection between molecule distortions resulting from chemisorption and the magnetic state of molecules using model species. Other effects including possible decomposition of β-diketonate molecules on the surface are not considered. The behaviour of real Ni(ktf)$_2$ molecules during their adsorption on the surface of amorphous silicon oxide cannot be investigated directly because of the limitations of quantum-chemical methods.

CALCULATION MODELS
AND METHODS OF INVESTIGATION

Silicon surface under the experimental conditions (room temperature, no evacuation and no vacuum) [2] is covered with an amorphous film of the oxide and the adsorbed molecular groups OH, CO, *etc*. Modelling of this surface is inevitably connected with some limitations.

The position in the centre of the chelate unit of β-diketonate molecules is usually occupied by an atom of a transition metal. It is known that the correlation in the $3d$-shell of transition elements is very high, and the ratio of the correlation energy to the coulomb energy is tens times larger than that for the s- and p-shells [3]. So, calculations should be carried out using the methods that take account of electron correlation, for example perturbation theory − HF + MPn (Hartree − Fock + Moller − Plesset corrections of the order n), approximation by the electron density functionals DFT (Density Functional Theory), or multiconfiguration approach CI (Configuration Interaction). For these methods, it is impossible to optimize the geometry of β-diketonate molecules on SiO_2 surface because of immense difficulties connected with calculations.

Investigation methods used in the present study were: semiempirical ZINDO/1 [4] parameterized for the optimization of the geometry and for the calculation of energy states of the molecules with $3d$-elements; nonempirical DFT (B3LYP functional [5], LACVP** basis [6]) realized by the Jaguar 3.5 programme [7]. Semiempirical ZINDO/1 method was used to optimize the geometry of the molecule in the gas phase and on the surface because it is generally accepted that the accuracy of the obtained geometry corresponds to the experimental one even at the semiempirical level [8] while the nonempirical DFT method was used to calculate energy characteristics.

The Ni(NH—(CH)$_3$—O)$_2$ cluster composed of 19 atoms (model 1) is the fragment of Ni(ktf)$_2$ molecule incorporating chelate rings (Fig. 1, *a*). The end groups CH$_3$ and CF$_3$ of the Ni(ktf)$_2$ molecule in model 1 are replaced by hydrogen atoms in order to simplify the calculations.

The clusters [Si$_6$O$_{17}$H$_{12}$]$^{+2}$ (IIa) and Si$_6$O$_{19}$H$_{14}$ (IIb) (see Fig. 1, *b* and *c*) are not cluster fragments of the SiO_2 surface but cluster models built up according to the principles of cluster simulation [9]. In this case, we straightened the zigzag surface of the (100) face placing all the surface silicon and oxygen atoms in one plane in order to avoid geometric complications for adsorption. Other parameters of the models correspond to the crystal structure of SiO_2. Though the structure of the real oxidized silicon surface is amorphous, it should be noted that in local areas its geometry is close to crystal because the main elements of which it is built are SiO$_4$ tetrahedrons. Interatomic distances $R_{Si-O} = 1.6$ Å and $R_{Si-Si} = 2.64$ Å correspond to experimental ones [10], valence angles $\alpha_{Si-O-Si}$ are distorted by about 10°. Crystal fragment is cut so that oxygen atoms are the boundary atoms of clusters. In this case, the formal charge of the atoms that are torn off (Si) has the same sign as that of the atoms used for saturation (H).

In the IIa cluster, two central silicon atoms have only one unsaturated valence each because they are connected only with three oxygen atoms. In the IIb model, these valences are shut off by the OH groups. So, if it were possible to neglect geometric factors, the IIb cluster would simulate SiO_2 surface contaminated by the atomic OH groups.

The fragment cluster Si$_7$O$_{21}$H$_{14}$ (III) (see Fig. 1, *d*) and the model cluster O$_4$H$_8$ (IV) (see Fig. 1, *e*) are built up to simulate the adsorption of the model molecule Ni(ktf)$_2$ on the SiO_2 surface contaminated by molecular OH groups. The geometry of resulting fragment III, unlike model cluster II, corresponds completely to the experimental data ($R_{Si-O} = 1.6$ Å and $R_{Si-Si} = 2.64$ Å, valence angles $\alpha_{Si-O-Si} = 109.47°$) [10]. The broken bonds were saturated according to the same principles as those for model II.

OH groups adsorbed on the surface hinder the access of I molecule to the SiO_2 surface because the distance between them $R_{OH-OH} = 5.22$ Å (for the filling degree close to 1) which is less than the mean size of the model molecule Ni(ktf)$_2$. This allows us to simplify model III to model cluster IV composed of four OH groups. The broken bonds with SiO_2 surface are simulated by hydrogen atoms with the positions fixed spatially according to the geometry of SiO_2 substrate which is not taken into consideration.
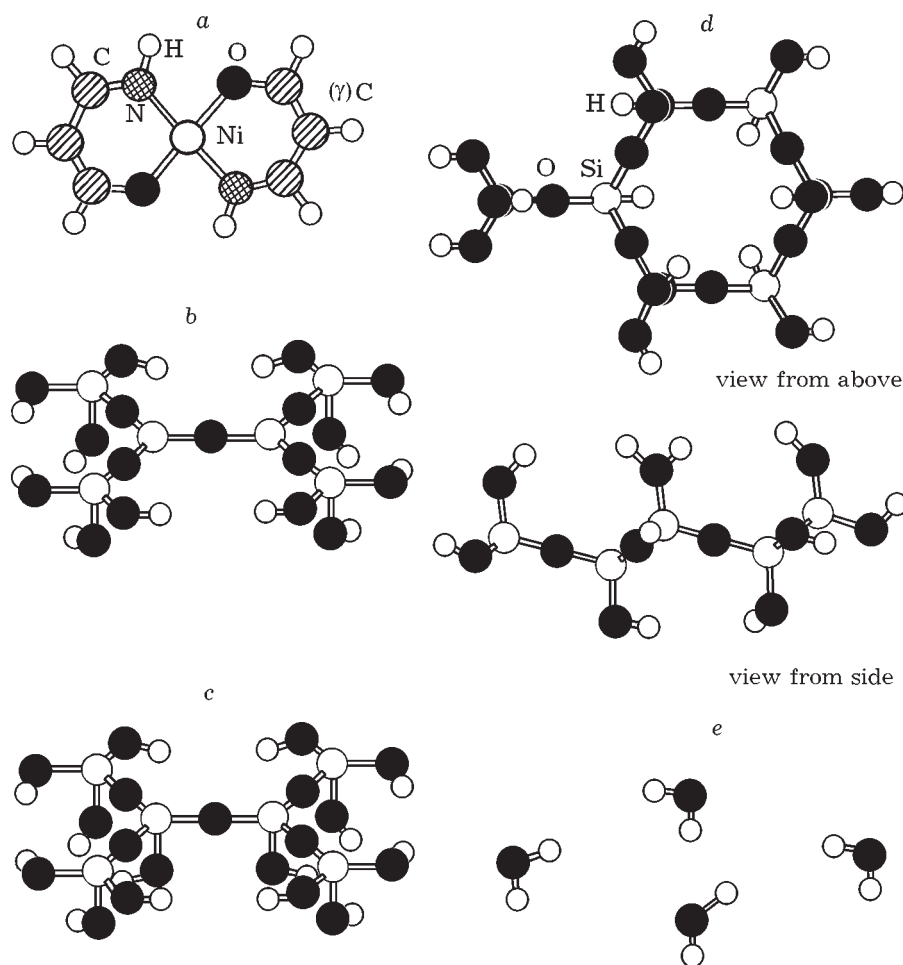
Fig. 1. The models of Ni(ktf)$_2$ molecule (*a*) and SiO$_2$ surface: IIa (*b*), IIb (*c*), III (*d*) and IV (*e*) used in calculations.

The positions of all the atoms except the atoms of the Ni(ktf)$_2$ molecule to be adsorbed are fixed during optimization. The necessity to fix the geometry arises due to the presence of substantial internal strains in the models of the surface. Cluster simulation and the conservation of only one layer of the surface with the breakage of all the excess bonds introduce an uncontrolled error into the calculation of the electron properties of the surface. However, we assume that the models allow to find some laws that govern the changes of the geometry and the magnetic state of β-diketonate molecules during their adsorption on SiO$_2$ surface.

RESULTS OF CALCULATIONS

The geometry of cluster I (see Fig. 1, *a*) is optimized by ZINDO/1. The results of optimiza-tion show that the chelate centre of model I in the gas phase is a plain square. For the possible propeller-type configuration with a 45° angle between the planes of chelate rings, the total energy of the molecule is higher by 9.1 kcal/mol. For the plain square structure, at the semiempirical (ZINDO/1) and nonempirical (*ab initio* HF [7], 6-31G ** basis) levels of the theory in UHF approximation (Unrestricted Hartree − Fock), the energy of the triplet state is lower with respect to the singlet state (by 4.1 and 23.6 kcal/mol, respectively) which is in con-tradiction with experiment [2]. The account of the correlation corrections leads to the inver-sion of the triplet and singlet states. The calcu-lation HF + MP2 [7] gives the main singlet state with a difference of 7.1 kcal/mol with respect to the triplet state. A similar result was also ob-tained using the Jaguar programmes (DFT, B3LYP functional, LACVP** basis) and
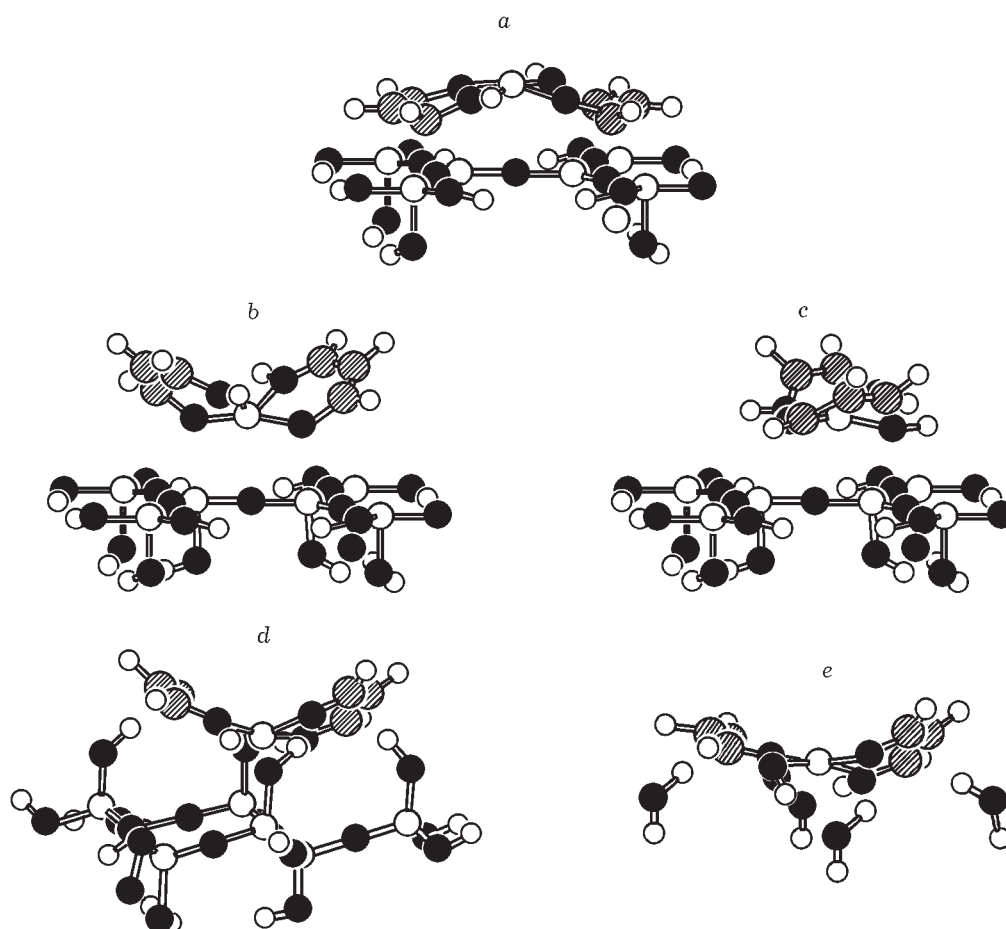
Fig. 2. Optimized geometry of the model molecule $Ni(ktf)_2$ (I) on model SiO_2 surface (II−IV): a − IIa + I, b − IIb + I (1), c − IIb + I (2), d − III + I, e − IV + I.

deMon4.0 [11] (DFT, BW91 functional [12], cc-pVTZ basis [13]) with the difference in singlet and triplet energies 16.1 and 37.5 kcal/mol, respectively.

An optimized geometry of model I at surfaces II−IV is shown in Fig. 2. The optimization was carried out under the condition of C_2 symmetry conserved for the united systems II + I or IV + I (for the system III+I, the symmetry is C_1). So, we considered only the cases when model I reached the surface so that Ni (model I) and O (model II) atoms occupied the positions at the symmetry axis of the system. It seems reasonable to place Ni atom above the atom of O since these atoms differ in the sign of the formal charge. The difference between cases IIb(1) and IIb(2) is only that model I is turned over 90° around the symmetry axis C_2. In the simulation of adsorption of SiO_2 surface contaminated with OH groups, Ni atom was placed above the empty interatomic space of clusters III and IV.

The shape of the adsorbed model molecule $Ni(ktf)_2$ changes from the plain one to concave. When placed onto the surface with unsaturated valences of Si atoms (model IIa+I), the flexure of model I is directed aside from the surface cluster (IIa) and the adsorption is carried out by means of ligand atoms. In all the other cases (clusters with unsaturated valences of Si atoms (IIb, III) and without Si atoms (IV)) the flexure of model I is directed towards the opposite side and the adsorption is carried out by the chelate centre $Ni(—O—NH)_2$. The distortion of the adsorbed molecule is very large. For example, the angle $(\gamma)C—Ni—(\gamma)C$ decreases from 180° in the plain square structure of the free state of $Ni(ktf)_2$ to 128 (IIb(1)), 146 (IIb(2)), 132.8 (III), and 153° (IV).

Table 1 shows the triplet-singlet splitting energies $\Delta\varepsilon_{t-s} = \varepsilon_t - \varepsilon_s$ calculated by ZINDO/1 (UHF) and DFT. The first two columns present the data on singlet-triplet splittings for the

TABLE 1

Energies of singlet-triplet splitting ($\Delta\varepsilon_{t-s} = \varepsilon_t - \varepsilon_s$) obtained in the simulation of the adsorption of a model molecule Ni(ktf)$_2$ (I) on model SiO$_2$ surface (II−IV) by means of ZINDO/1 (UHF) [4] and DFT[7], kcal/mol

Cluster	$\Delta\varepsilon_{t-s}$ for the Ni(ktf)$_2$ molecule on the surface		$\Delta\varepsilon_{t-s}$ due to the geometry of the Ni(ktf)$_2$ molecule	
	ZINDO/1, UHF	DFT	ZINDO/1, UHF	DFT
I	−4.1	16.1	−4.1	16.1
IIa + I	−3.1	NC	−16.8	37.8
IIb + I (1)	−27.0	1.8	−28.0	0.8
IIb + I (2)	−22.5	NC	−14.3	15.7
III + I	−26.1	NC	−10.7	22.0
IV + I	−20.4	22.7	−13.1	19.7

Note. NC − no congruence.

states of model I placed on the surface; the first line corresponds to the free state of the molecule (infinitely remote surface). A part of the data related to the DFT calculation could not be obtained due to poor convergence of self-consistency procedure in the corresponding calculations. The trouble with self-consistency is characteristic of the transition metals of the first row [8]. The 3rd and 4th columns show singlet-triplet splittings due to the geometry (distortion) of the molecule itself. In order to obtain these data, we took the united systems optimized by the geometry II + I, III + I and IV + I, and excluded subsystems II, III and IV imitating the surface and OH groups; for the residual distorted model molecule Ni(ktf)$_2$, the energies of the singlet and triplet states were additionally calculated. In order to demonstrate the cor-

Fig. 3. Correlation diagram of the energy of singlet-triplet splitting $\Delta\varepsilon_{t-s}$ obtained in different series of simulations: *1* − model I + models (II−IV) of the surface, ZINDO/1 (UHF); *2* − the same, DFT(B3LYP, LACVP** basis); *3* − model I, ZINDO/1; *4* − the same, DFT.

relation between the data, the figures are represented graphically (Fig. 3). The curves are shifted along the vertical axis so that their initial points coincide. Since we lack the data to build up curve *2* (no congruence for a half of the figures in column 2), the corresponding plot is drawn hypothetically using only three points that were obtained.

The correlation between ZINDO/1 (UHF) and DFT calculations allows us to simulate adsorption using relative $\Delta\varepsilon_{t-s}$ values calculated with the ZINDO/1 (UHF). The attribution to absolute values should be performed by means of additional DFT calculation. A noticeable difference in the IIa point is connected with the change in the bonding character in the system (the presence of unsaturated valence of Si atoms). Practical coincidence of the three points in curve *2* (see Fig. 3) with the corresponding points of curve *4* shows that nearly the whole effect of $\Delta\varepsilon_{t-s}$ change in the system is due to the distortion of the model molecule Ni(ktf)$_2$ when it is placed onto the surface. The most substantial effect on $\Delta\varepsilon_{t-s}$ change is caused by the first coordination sphere of the transition atom. For example, the angle (γ)C—Ni—(γ)C characterizing the total flexure of the molecule for case III is close to that for case IIb(1) (132 and 128º, respectively); however, $\Delta\varepsilon_{t-s}$ are substantially different which is due to the additional propeller-type spinning of the molecule (the difference between the N—Ni—N and O—Ni—O angles is 36.3 and 18.3º, respectively). Calculations show that the adsorption in position IIb(1) causes a sharp decrease in the energy of singlet-triplet splitting. These data, together with
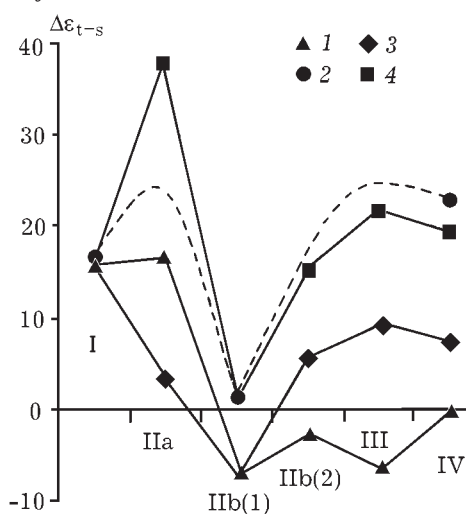
the error of DFT calculations which is about 10 kcal/mol per each broken or formed bond [14] (for the constant chemical bonds, one can expect the compensation of errors), do not allow us to arrive at an unambiguous conclusion concerning the change of the magnetic state of Ni(ktf)$_2$ molecules during the adsorption on real silicon oxide surface.

CONCLUSION

A correlation is obtained between the energy of singlet-triplet splitting $\Delta\varepsilon_{t-s}$ calculated by the semiempirical ZINDO/1 (UHF) and nonempirical DFT (B3LYP, LACVP** basis) methods. This allows us to use the former method, which is more simple from the calculation viewpoint, to simulate the adsorption of β-diketonates on the surface. It is stated that $\Delta\varepsilon_{t-s}$ substantially decreases during the adsorption of the model molecule Ni(ktf)$_2$ on the SiO$_2$ surface when Ni atom is placed above the surface O atom. It is demonstrated that the most part of the effect of $\Delta\varepsilon_{t-s}$ change in the system is connected with the change in the geometry of the first coordination sphere of the Ni atom.

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