# Quantum-Chemical Estimation of Outersphere Cations Influence on Charge Transfer at the $NbF_7{}^{2-}$ Reduction. I. Electronic Structure of Complexes

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Z. Naturforsch. **65a,** 245 – 250 (2010); received January 13, 2009 / revised June 19, 2009

Quantum-chemical calculations of the parameters of the $n\mathrm{M}^+ \cdot \mathrm{NbF}_7{}^{q-}$ type particles, where M stands for Na, K, Cs; $q = 2,3$ and $n = 0-7$ have been performed. Within the framework of this approximation, compositions for the most stable particles in molten salts were obtained. It is shown that electron transfer onto the particle results in a different redistribution of the electron density with the Na and K-particles on one hand and Cs-containing particles on the other hand. Energies and some other characteristics of the electron structure and particle geometry were determined depending on the $n$ and M values.

*Key words: ab initio*; Outersphere Cations; Electron Transfer; Electrode Reaction; Niobium Fluoride Complex.

## 1. Introduction

The goal of this research is a quantum-chemical modelling of reactions of niobium (V) electroreduction from fluoride complexes contained in molten alkali metal chlorides or fluorides. The key point here is to determine the composition of electroactive particles participating in the elementary act of electron transfer from the electrode to a complex niobium particle. However, at the first stage one should attempt to reveal the most probable compositions of niobium complex particles in the melt bulk, i. e. ignoring the interaction with the electrode surface. As a first approximation for describing the volume characteristics of niobium fluoride complexes particles of the ($n\mathrm{M}^+ \cdot \mathrm{NbF}_7{}^{2-}$) composition were selected, where $n$ is the number of outersphere (OS) cations of an alkali metal and $\mathrm{M}^+$ means $\mathrm{Na}^+$, $\mathrm{K}^+$ or $\mathrm{Cs}^+$. So, the first coordination sphere of niobium (V) cations contains fluoride ligands, the second coordination sphere $\mathrm{M}^+$ cations.

This level of approximation has been extensively utilized to assess the effect of the second coordination sphere composition on the vibrational spectra, structure and mechanism of electroreduction of titanium, tungsten and also such anions as $CO_3{}^{2-}$, $NO_3{}^{-}$, etc. (see, for instance, [1 – 6]). With regard to the necessity of further sophistication of the model, we note, however, that many of the experimental facts can be adequately described within the framework of the proposed approximation, as shown in these publications.

The description of the principal results is given below and more detailed analysis will be given later.

## 2. Computational Method

Quantum-chemical calculations were performed at the HF level, using the PC GAMESS software [7, 8]. Huzinaga's 3 gaussian basis set (MINI) with one additional polarization function was used for all atoms. This basis set was successfully utilized earlier [4] for fluoride complexes and is quite sufficient for the given level of the model. It is necessary to note, that for chloride complexes more complex bases sets should be used.

The given data concern to particles with optimized geometric structures.

## 3. Results and Discussion

Examples of the optimized structures are shown in Figure 1 and some parameters of these structures are given in Table 1.

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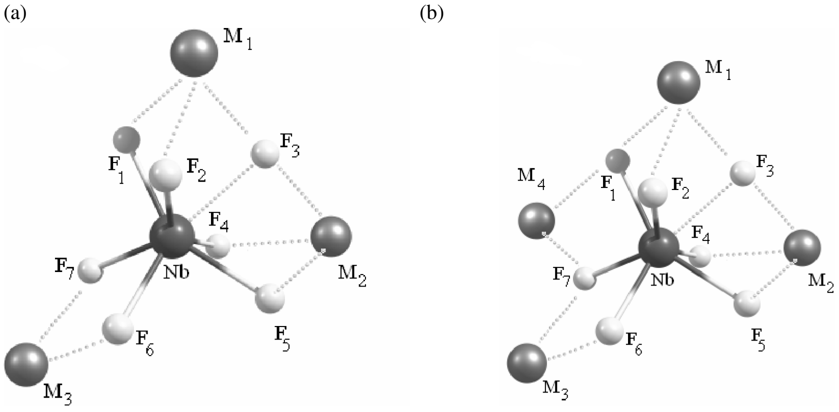

Fig. 1. Optimized geometric structure of the $3M^+ \cdot NbF_7{}^{2-}$ (a) and $4M^+ \cdot NbF_7{}^{2-}$ (b) particles.

Table 1. Length of some bonds for the $3M^+ \cdot NbF_7{}^{2-}$ (a) and $4M^+ \cdot NbF_7{}^{2-}$ (b) particles [Å].

| | $Na^+$ | | $K^+$ | | $Cs^+$ | |
|---|---|---|---|---|---|---|
| Bond | a | b | a | b | a | b |
| $Nb$-$F_1$ | 1.908 | 1.875 | 1.910 | 1.953 | 1.912 | 1.927 |
| $Nb$-$F_7$ | 1.927 | 1.893 | 1.924 | 1.902 | 1.924 | 1.927 |
| $M_1$-$F_1$ | 2.134 | 2.225 | 2.512 | 2.592 | 2.892 | 2.827 |
| $M_3$-$F_7$ | 2.066 | 2.073 | 2.475 | 2.459 | 2.853 | 2.827 |

Table 2. Energy values ($-\Delta E_{OS} \cdot 10^{-3}$) of $nM^+ \cdot NbF_7{}^{2-}$ particles OS shell formation [$kJ \cdot mol^{-1}$].

| M | $n = 2$ | $n = 3$ | $n = 4$ | $n = 5$ | $n = 6$ | $n = 7$ |
|---|---|---|---|---|---|---|
| Na | 1.947 | **2.343** | **2.368** | 2.041 | 1.472 | 0.661 |
| K | 1.619 | **1.931** | **1.945** | 1.668 | 1.109 | – |
| Cs | 1.389 | **1.632** | **1.632** | 1.382 | 0.871 | 0.652 |

The relative stability of $nM^+ \cdot NbF_7{}^{2-}$ particles with different OS shell compositions was assessed by the $\Delta E_{OS}$ energy values of the OS shell formation. These energies were determined by the fragment method as a difference of the total energy of the $nM^+ \cdot NbF_7{}^{2-}$ particle and the energies of the $NbF_7{}^{2-}$ anion and $n$ OS cations:

$$\Delta E_{OS} = E(nM^+ \cdot NbF_7{}^{2-}) - E(NbF_7{}^{2-}) - nE(M^+). \quad (1)$$

It is found that within this model, the melt may produce particles with $n = 1-7$ (Table 2). As can be clearly seen from Table 2, most stable are particles with $n = 3$ and 4.

Interpretation of the results is not as easy as it may seem and requires further investigations and a comparison with the corresponding experimental data. Naturally, we do not claim the existence in the melt, let say, of $3Cs^+ \cdot NbF_7{}^{2-}$ particles whose second coordination sphere contains nothing but three cesium cations. Apparently, this coordination sphere is capable of accommodating more cesium cations, to say nothing of $Na^+$ and $K^+$ cations. The $NbF_7{}^{2-}$ complex is in dynamic equilibrium with OS cations and the Nb-M distances are not fixed. This results in a variation of the number of strong bonds between the OS cations and the niobium complex. But the life span of particles with different OS shell compositions should correlate with the $\Delta E_{OS}$ energies obtained. Of course, near the electrode surface the composition of the most stable particles may vary, but this level of approximation will be realized at the next stage of our work.

Adding the second coordination sphere cations to the $NbF_7{}^{2-}$ complex results in filling of the lowest unoccupied molecular orbital (LUMO) of the $NbF_7{}^{2-}$ complex caused by a strong interaction of F atoms with the $M^+$ cations. Thus, the LUMO of the $NbF_7{}^{2-}$ complex becomes the highest occupied molecular orbital (HOMO) in the $nM^+ \cdot NbF_7{}^{2-}$ particles. Populations on Lovdin [9] of these HOMOs are given in Table 3 (orbital population is number of electrons on orbital).

As is evident from Table 3, there is no obvious relation between the value of $n$ and the change in summary population at OS cations: whereas at $n = 2$ and 3 the population of $M^+$ cations decreases in the Na > K > Cs series, at $n = 4$ the order is reversed: K > Na > Cs.

The cation-anion interaction also results in decreasing of the bond orders ($B_{ij}$) (Table 4) in the Cs < K < Na series and distortion of the $NbF_7{}^{2-}$ anion original structure. Let's remind that the bond order is a measure of the covalent component of bonding [10].

Decrease of the bond orders is due to the charge transfer between the anions and cations. Analysis of the charge characteristics at the atoms of $nM^+ \cdot NbF_7{}^{2-}$ particles (Table 5) has revealed that the

Table 3. Population of $n$M$^+ \cdot NbF_7{}^{2-}$ particle HOMOs (selected data).

| | | — $n$ = 2 — | | | — $n$ = 3 — | | | — $n$ = 4 — | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Atom | $NbF_7{}^{2-}$ | M = Na | M = K | M = Cs | M = Na | M = K | M = Cs | M = Na | M = K | M = Cs |
| Nb | 0.000001 | 0.007728 | 0.007554 | 0.007775 | 0.007138 | 0.008151 | 0.00597 | 0.001189 | 0.00392 | 0.000092 |
| F | 0.000001 | 0.206901 | 0.192972 | 0.183804 | 0.087303 | 0.073361 | 0.160277 | 0.260962 | 0.255115 | 0.14167 |
| F | 0.000001 | 0.206788 | 0.193006 | 0.184266 | 0.776572 | 0.81523 | 0.698369 | 0.19698 | 0.200729 | 0.149484 |
| F | 0.401103 | 0.201157 | 0.187429 | 0.179343 | 0.086525 | 0.071768 | 0.157182 | 0.025274 | 0.037236 | 0.16914 |
| F | 0.404286 | 1.065256 | 1.124175 | 1.145354 | 0.251383 | 0.247805 | 0.238998 | 0.064158 | 0.301489 | 0.411852 |
| F | 0.396647 | 0.049839 | 0.050719 | 0.058361 | 0.2577 | 0.258224 | 0.245507 | 0.961588 | 0.480262 | 0.166903 |
| F | 0.401472 | 0.201118 | 0.187457 | 0.179245 | 0.257612 | 0.259478 | 0.24551 | 0.199175 | 0.336891 | 0.406869 |
| F | 0.396491 | 0.049884 | 0.050627 | 0.058187 | 0.251722 | 0.249034 | 0.239598 | 0.265819 | 0.327588 | 0.540434 |
| M(1) | | 0.005664 | 0.003029 | 0.001832 | 0.008901 | 0.006624 | 0.003176 | 0.003869 | 0.007912 | 0.006235 |
| M(2) | | 0.005664 | 0.003031 | 0.001833 | 0.006241 | 0.003699 | 0.002235 | 0.017656 | 0.021091 | 0.000589 |
| M(3) | | | | | 0.008902 | 0.006626 | 0.003178 | 0.003884 | 0.013047 | 0.000618 |
| M(4) | | | | | | | | 0.001823 | 0.014721 | 0.006297 |

Table 4. Values of calculated bond orders $B_{ij}$ for the $n$M$^+ \cdot NbF_7{}^{2-}$ particles (selected data).

| Species | $n$ | Nb-F$_{(1)}$ | M-F$_{(1)}$ |
|---|---|---|---|
| $n$Na$^+ \cdot NbF_7{}^{2-}$ | 0 | 0.792 | – |
| | 2 | 0.709 | 0.152 |
| | 3 | 0.725 | 0.136 |
| | 7 | 0.704 | 0.165 |
| $n$K$^+ \cdot NbF_7{}^{2-}$ | 2 | 0.746 | 0.084 |
| | 3 | 0.759 | 0.078 |
| | 7 | 0.670 | 0.087 |
| $n$Cs$^+ \cdot NbF_7{}^{2-}$ | 2 | 0.760 | 0 |
| | 3 | 0.772 | 0 |
| | 7 | 0.707 | 0.093 |

charge is transferred to the OS cations not only from fluorine atoms but also from the central niobium atom. This effect is more pronounced in the Cs < K < Na series, and also with the increase of $n$.

As is known, the reduction of niobium fluoride complexes in molten salts occurs in two stages [11]:

$$\mathrm{Nb(V)} + \bar{e} \rightarrow \mathrm{Nb(IV)}, \tag{1a}$$

$$\mathrm{Nb(IV)} + 4\bar{e} \rightarrow \mathrm{Nb}. \tag{1b}$$

In this connection, valuable information can be obtained through the analysis of the $n$M$^+ \cdot NbF_7{}^{3-}$ particle characteristics (that is, after the electron has been transferred to the original $n$M$^+ \cdot NbF_7{}^{2-}$ particle), these particles being taken in the geometry of the initial $n$M$^+ \cdot NbF_7{}^{2-}$ complex (Table 6). In particular, for M = Na at all $n$ values, two centers of electron attack are observed: Na and, mainly, Nb. Figure 2 presents the dependence between the $\Delta Q$ charge value (in atomic units of charge) on niobium and sodium atoms and the niobium second coordination number $n$. Here $\Delta Q$ is equal to the difference between the charges of the final

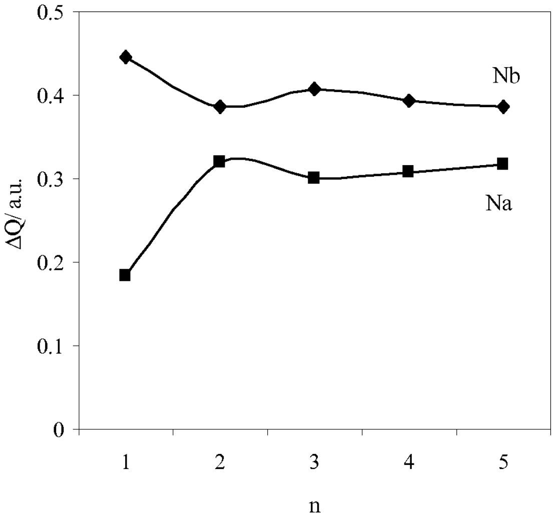

Fig. 2. Relationship between the values of charge redistribution (ΔQ) on the Nb and Na atoms due to the electron transfer and the coordination number (n) for the $n$M$^+ \cdot NbF_7{}^{2-}$ particles.

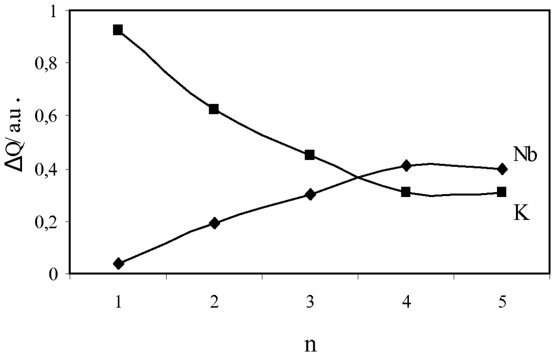

Fig. 3. Relationship between the values of charge redistribution (ΔQ) on the Nb and K atoms due to the electron transfer and the coordination number (n) for the $n$M$^+ \cdot NbF_7{}^{2-}$ particles.

Table 5. Charge values on the atoms of the $nM^+ \cdot NbF_7^{2-}$ particles (selected data).

| | | $n = 1$ | | | — $n = 2$ — | | | — $n = 3$ — | | | — $n = 4$ — | | | — $n = 5$ — | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Atom | $NbF_7^{2-}$ | M = Na | M = K | M = Cs | M = Na | M = K | M = Cs | M = Na | M = K | M = Cs | M = Na | M = K | M = Cs | M = Na | M = K | M = Cs |
| Nb | 1.114 | 1.273 | 1.209 | 1.168 | 1.378 | 1.260 | 1.171 | 1.431 | 1.300 | 1.207 | 1.478 | 1.339 | 1.215 | 1.501 | 1.340 | 1.226 |
| F(1) | −0.426 | −0.373 | −0.386 | −0.401 | −0.363 | −0.398 | −0.420 | −0.341 | −0.383 | −0.412 | −0.337 | −0.400 | −0.408 | −0.327 | −0.364 | −0.399 |
| F(7) | −0.450 | −0.369 | −0.387 | −0.397 | −0.368 | −0.403 | −0.422 | −0.332 | −0.376 | −0.406 | −0.337 | −0.403 | −0.443 | −0.329 | −0.387 | −0.423 |
| M(1) | | 0.448 | 0.663 | 0.816 | 0.581 | 0.760 | 0.879 | 0.623 | 0.785 | 0.893 | 0.678 | 0.819 | 0.917 | 0.743 | 0.851 | 0.920 |
| M(2) | | | | | 0.581 | 0.760 | 0.879 | 0.709 | 0.833 | 0.911 | 0.660 | 0.808 | 0.905 | 0.775 | 0.850 | 0.916 |
| M(3) | | | | | | | | 0.623 | 0.785 | 0.893 | 0.678 | 0.818 | 0.905 | 0.714 | 0.839 | 0.916 |
| M(4) | | | | | | | | | | | 0.756 | 0.864 | 0.916 | 0.775 | 0.877 | 0.920 |
| M(5) | | | | | | | | | | | | | | 0.711 | 0.839 | 0.936 |

Table 6. Charge values on the atoms of $nM^+ \cdot NbF_7^{2-}$ particles at one electron association (selected data).

| | | $n = 1$ | | | — $n = 2$ — | | | — $n = 3$ — | | | — $n = 4$ — | | | — $n = 5$ — | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Atom | $NbF_7^{2-}$ | M = Na | M = K | M = Cs | M = Na | M = K | M = Cs | M = Na | M = K | M = Cs | M = Na | M = K | M = Cs | M = Na | M = K | M = Cs |
| Nb | 0.663 | 0.828 | 1.173 | 1.149 | 0.992 | 1.071 | 1.155 | 1.023 | 0.996 | 1.199 | 1.087 | 0.931 | 0.940 | 1.116 | 0.939 | 0.896 |
| F(1) | −0.510 | −0.452 | −0.399 | −0.410 | −0.401 | −0.419 | −0.419 | −0.380 | −0.419 | −0.416 | −0.369 | −0.427 | −0.443 | −0.359 | −0.407 | −0.439 |
| F(7) | −0.540 | −0.448 | −0.395 | −0.405 | −0.408 | −0.431 | −0.422 | −0.380 | −0.416 | −0.405 | −0.369 | −0.427 | −0.476 | −0.367 | −0.430 | −0.458 |
| M(1) | | 0.264 | −0.262 | −0.148 | 0.422 | 0.450 | 0.389 | 0.518 | 0.639 | 0.496 | 0.597 | 0.736 | 0.764 | 0.674 | 0.780 | 0.803 |
| M(2) | | | | | 0.422 | 0.449 | 0.387 | 0.621 | 0.678 | 0.712 | 0.583 | 0.732 | 0.827 | 0.721 | 0.780 | 0.857 |
| M(3) | | | | | | | | 0.518 | 0.639 | 0.497 | 0.596 | 0.736 | 0.828 | 0.642 | 0.778 | 0.857 |
| M(4) | | | | | | | | | | | 0.688 | 0.794 | 0.765 | 0.723 | 0.833 | 0.802 |
| M(5) | | | | | | | | | | | | | | 0.641 | 0.778 | 0.889 |

Table 7. Values of vertical electron affinity $E_{aff} \cdot 10^{-3}$ for the $nM^+ \cdot NbF_7^{2-}$ · particles at one electron association [$kJ \cdot mol^{-1}$].

| M | $NbF_7^{2-}$ | $n = 1$ | $n = 2$ | $n = 3$ | $n = 4$ | $n = 5$ | $n = 6$ | $n = 7$ |
|---|---|---|---|---|---|---|---|---|
| Na | 1.292 | 0.724 | 0.109 | *−0.265* | −0.685 | −1.049 | −1.163 | −1.219 |
| K | 1.292 | 0.301 | 0.210 | *−0.051* | −0.410 | −0.781 | −0.839 | |
| Cs | 1.292 | 0.224 | 0.043 | *−0.158* | −0.238 | −0.523 | −0.766 | −0.744 |

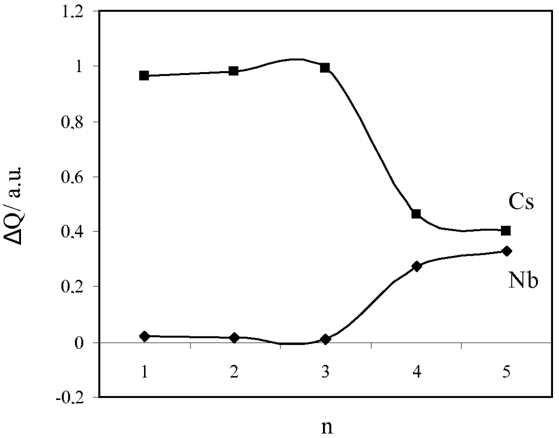

Fig. 4. Relationship between the values of charge redistribution (ΔQ) on the Nb and Cs atoms due to the electron transfer and the coordination number ($n$) for the $nM^+ \cdot NbF_7^{2-}$ particles.

$nM^+ \cdot NbF_7^{3-}$ particle and the initial $nM^+ \cdot NbF_7^{2-}$ particle.

For M = K at $n = 1-3$, the main center subjected to electron attack is the potassium cation, whereas starting from $n = 3$, it is the niobium atom (Fig. 3).

At the same time, at all $n$ values, the centres mostly attacked in Cs-complexes are cesium cations (Fig. 4). At $n = 1-3$, the Cs cations accept all the additional charge. This fact is of electrochemical interest since the appearance of cesium cations in the melt not infrequently complicates the kinetics of Nb and Ta fluoride complexes electroreduction.

These findings suggest the following results of analysis of atom orbital populations before and after the electron transfer to the $nM^+ \cdot NbF_7^{2-}$ particle. For M = Na, the electron density increases substantially on certain 4d-orbitals of niobium and, simultaneously, on the sodium 3s-orbitals. This confirms the above conclusion about the presence of two electron attack centres on the $nM^+ \cdot NbF_7^{2-}$ particles.

For M = K at $n = 1-3$, the electron density predominantly increases on 4s- and $4p_x$-orbitals of the OS cations, whereas at $n > 3$ it mostly increases on 4d-orbitals of niobium.

And, finally, for M = Cs at $n = 1-3$, the greatest density increase is observed on 6s- and $6p_x$-orbitals of $Cs^+$, and at $n > 3$ on 4d-orbitals of niobium, which corresponds to the character of curves variations seen in Figure 4. These findings allow to suggest that the above mentioned problems in the recharge process kinetics in Cs-containing melts are caused by the localization of an extra electron on cesium cations.

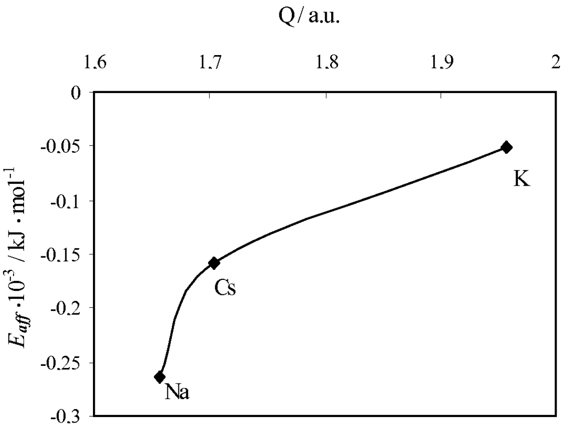

Fig. 5. Relationship between vertical electron affinity ($E_\text{aff} \cdot 10^{-3}$) and the Q charge value on $Na^+$, $K^+$, and $Cs^+$ cations for the $nM^+ \cdot NbF_7^{3-}$ particles at $n = 3$.

Calculated values of vertical electron affinity, $E_\text{aff}$, [12] are also interesting. The $E_\text{aff}$ values were determined as the difference between total energies of the $nM^+ \cdot NbF_7^{3-}$ particle and initial $nM^+ \cdot NbF_7^{2-}$ particle (Table 7). Here the $nM^+ \cdot NbF_7^{3-}$ particle had the geometry of the initial particle.

Note also, the $E_\text{aff}$ values correlate with the charge values of OS cations after one electron transfer (Fig. 5).

Supplemented by the data on total energies of the initial and final particles, the $E_\text{aff}$ values allow to determine the mutual position of multidimensional surfaces of the initial ($U_\text{i}$) and final ($U_\text{f}$) states of the model system. In absence of OS cations the $U_\text{f}$ value of final $NbF_7^{3-}$ complex is less negative than the $U_\text{i}$ value of initial $NbF_7^{2-}$ complex whereas the energy values of final $nM^+ \cdot NbF_7^{3-}$ particles grow more negative in comparison with the energies of the initial $nM^+ \cdot NbF_7^{2-}$ particles for all M at $n \geq 3$. The same pattern is observed for $E_\text{aff}$ values (Table 7). Thus, at $n \geq 3$ the minimum of the $U_\text{f}$ surface is below that of the $U_\text{i}$ surface for all types of OS cations.

From the point of view of electrochemistry, it is interesting to look at the anomalous $E_\text{aff}$ ratio of values at $n = 3$: $E_\text{aff}(\text{Na}) < E_\text{aff}(\text{Cs}) < E_\text{aff}(\text{K})$. Of course, we cannot state with confidence whether this anomaly also exists for the $E_\text{act}$ activation energies of electron transfer. Nevertheless, we note that this anomalous ratio of $E_\text{aff}$ values has to be further compared with calculated activation energies. The considerable attention paid to this ratio of the $E_\text{act}$ values is explained by the fact that it corresponds to the experimentally observed ratio of the standard rate constants of charge transfer for $NbF_7^{2-}$ complexes in NaCl, KCl, and CsCl melts [13].

## 4. Conclusions

In conclusion, it should be noted that the results presented here are by no means final. They will be verified using a more sophisticated model. However, even this fairly simple model allows to obtain a set of valuable results and to formulate some suppositions concerning the strategy of quest for saddle points through relatively minor expenditures of computer time.

Later it is intended to evaluate the effect of the third coordination sphere on the basic characteristics of these particles and then proceed to consideration of the "electroactive species – electrode surface" system and evaluate the influence of a double layer and an external electric field. Let's notice, that *ab initio* investigations of such level already are available for molten salts [14, 15].

*Acknowledgement*

The authors are grateful to the Russian Foundation for Basic Research (grant 08-03-00397-a) for the financial support of this study.

[1] V.I. Shapoval, V.V. Solovyov, E.D. Lavrinenko-Ometsinskaya, and K.B. Kushkhov, Ukr. Khim. Zh. (Russ. Ed.) **50**, 917 (1984).

[2] V.I. Shapoval, K.B. Kushkhov, and V.V. Solovyov, Ukr. Khim. Zh. (Russ. Ed.) **51**, 1263 (1985).

[3] V.I. Shapoval, K.B. Kushkhov, V.V. Solovyov, and V.G. Shevchuk, Ukr. Khim. Zh. (Russ. Ed.) **50**, 1184 (1984).

[4] V.V. Solovyov and L.A. Chernenko, Ukr. Khim. Zh. (Russ. Ed.) **71**, 91 (2005).

[5] A.V. Voit, E.I. Voit, and V.I. Sergienko, J. Struct. Chem. **40**, 1037 (1999).

[6] V.I. Shapoval, V.V. Solovyov, and V.V. Malyshev, Russ. Chem. Rev. **70**, 181 (2001).

[7] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, and J.A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).

[8] A.V. Nemukhin, B.L. Grigorenko, and A.A. Granovsky, Vestn. Mosk. Univ. Ser. 2: Khim. **45**, 75 (2004).

[9] W.D. Cornell, in: P. von Rague Schleyer (ed.), The Encyclopedia of computational chem-

istry, John Wiley & Sons Ltd, New York 1998, p. 259.

[10] J. Cioslowski, in: P. von Rague Schleyer (ed.), The Encyclopedia of computational chemistry, John Wiley & Sons Ltd, New York 1998, p. 896.

[11] S. A. Kuznetsov, A. L. Glagolevskaya, P. T. Grinevich, and P. T. Stangrit, Russ. J. Electrochem. **28**, 1344 (1992).

[12] Thermodynamic aspects of inorganic chemistry, Mir, Moscow 1985. (Russ. Ed.)

[13] A. V. Popova, V. G. Kremenetsky, L. A. Chernenko, V. V. Solovyov, and S. A. Kuznetsov, in: EUCHEM 2008. Conference on Molten Salts and Ionic Liquids, Copenhagen, Denmark. Book of Abstracts, ISC, Department of Chemistry, Technical University of Denmark 2008, p. 211.

[14] S. K. Reed, P. A. Madden, and A. Papadopoulos, J. Chem. Phys. **128**, 124701 (2008).

[15] P. Madden and M. Pounds, in: EUCHEM 2008. Conference on Molten Salts and Ionic Liquids, Copenhagen, Denmark. Book of Abstracts, ISC, Department of Chemistry, Technical University of Denmark 2008, p. 3.