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# Anomaly of the Charge Transfer Rate in the CsCl-$K_3CrF_6$ Melt: Quantum-Chemical Analysis

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Typically, the standard rate constants of charge transfer (RC) for the redox couples Nb(V)/Nb(IV), Cr(III)/Cr(II) increases in transition from fluoride-chloride molten salts containing fluoride complexes to pure chloride melts which contain chloride complexes of the same metal. However in Cs-melts containing chromium, an inverse relationship of RC was found: CsCl-$CrCl_3$ < CsCl-$K_3CrF_6$. In this work quantum-chemical analysis of molecular orbitals for the Cr-containing model systems has been done. It was found the probable cause is a different character of the lowest unoccupied molecular orbital, on which electron transfer occurs during recharging of Cr(III)→Cr(II), for the Cs-system, on the one hand, and for all other systems, on the other. Difference in the nature of these orbitals allows specifying the most probable mechanisms of charge transfer for both "anomalous" and "normal" electrochemical systems.

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**Keywords:** molten salts, chromium halide complexes, standard rate constants of charge transfer, frontier molecular orbitals

## 1. INTRODUCTION

Previously the standard rate constants of charge transfer (RC) $k_s$ were measured in some Nb- and Cr -containing molten salts [1-4]. In particular, such relation was observed for $k_s$ in the Nb-containing melts: NaCl-KCl-$K_2NbF_7$ < NaCl-KCl-$NbCl_5$, KCl-$K_2NbF_7$ < KCl-$NbCl_5$, CsCl-$K_2NbF_7$ < CsCl-$NbCl_5$, as well as in Cr-containing melts: NaCl-KCl-$K_3CrF_6$ < NaCl-KCl-$CrCl_3$, KCl-$K_3CrF_6$ < KCl-$CrCl_3$. At the same time in Cs-melts containing chromium, an inverse relationship of RC was found: CsCl-$CrCl_3$ < CsCl-$K_3CrF_6$ [4].

With regard to the melts of alkali metal halides in many cases qualitative interpretation of observed regularities can be given on the basis of correlations between the parameters of the charge transfer and such characteristics as the force constants of bonds in complex, the strength of outer-sphere (OS) bonds, the energy of the OS shell formation, and so on. However, in our case, such approach is not satisfactory, since these characteristics predict reverse ratio of RC. The ratio of activation energies of charge transfer also cannot serve as an explanation, since in a pure chloride system CsCl-$CrCl_3$ this value is smaller than in chloride-fluoride system CsCl-$K_3CrF_6$.

In addition, we should take into consideration the following. In chloride-fluoride systems of chromium the value of RC increases in the next row of OS cations: K < Na <Cs. Of all the Nb- and Cr-systems we studied, this system is the only one where the maximum value of RC is observed in cesium-containing melt. Clearly, in this system, charge transfer occurs by a different mechanism compared to other systems studied.

In this work we attempt to understand the reasons for this anomaly, based on the results of quantum-chemical analysis of the frontier molecular orbitals (MOs) for a number of model systems containing chromium complexes. Approaches based on the utilization of orbital energies are widely used in the analysis of chemical reactions [5,6]. Concerning to processes of electrochemical charge transfer such approach is also quite natural, however, in our case, the focus was on the analysis of *the nature* of these orbitals. Here we rely on the works [7,8], where the importance of the nature of frontier molecular orbitals was noted.

## 2. COMPUTATIONAL METHODS

The geometry optimization of structures was performed with the Firefly quantum-chemical package [9] partially based on the GAMESS(US) codes [10] by the density functional theory method (the spin-polarized version of the Kohn-Sham equations) with the use of the hybrid functional B3LYP. For model particles $4M^+\cdot[CrX_6]^{3-}$ and $4M^+\cdot[CrX_6]^{4-}$ (M - Na, K, Cs; X - F, Cl) the mixed all-electron basis set BSS-2 (6-311++G(2d, 2p) for fluorine, chlorine atoms and WTBS for other atoms [11,12]) have been used. For extended model systems $M_3CrX_6$ + 18MCl and $[Cs_3CrF_6]^{1-}$ + 18CsCl (M - Na, K, Cs; X - F, Cl) the quasi-relativistic ECP basis set of Stuttgart/Dresden groups was used for all atoms [13]. For comparison, with the same basis set calculations for the $4Cs^+\cdot[CrX_6]^{3-}$ and $4Cs^+\cdot[CrX_6]^{4-}$ particles were made.

The multiplicity of the Cr(III) and Cr(II) complexes was set at 4 and 5, respectively. All data reported correspond to true minima of the potential energy surface.

## 3. RESULTS AND DISCUSSION

Examples of small systems $4M^+\cdot[CrX_6]^{3-}$ (type **I**) and extended systems $M_3CrX_6$ + 18MCl (type **II**) are shown in Figure 1.

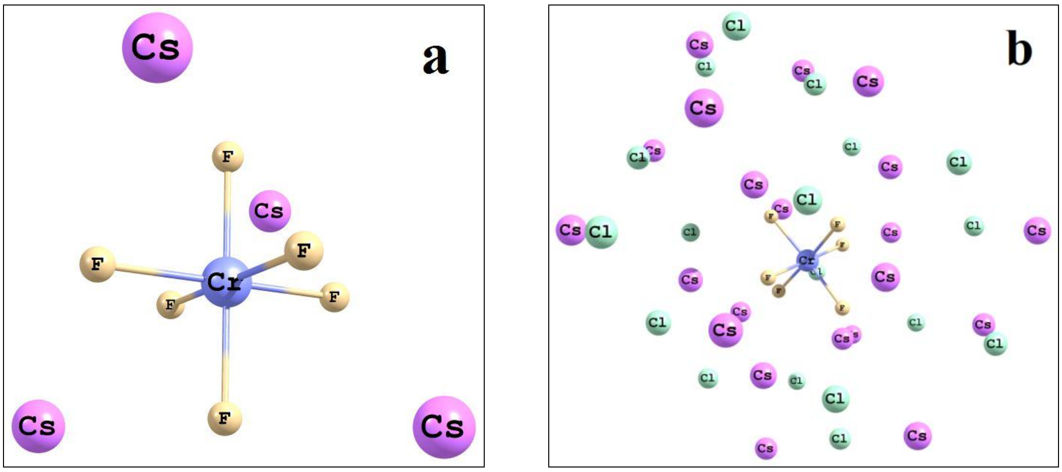

**Figure 1**. Optimized structures of (a) $4Cs^{+}\cdot[CrF_6]^{3-}$ and (b) $Cs_3CrF_6$+18CsCl.

The following Table shows in summary form the characters of frontier molecular orbitals for systems **I** and **II**. Here the LUMO Cr(III) and the HOMO Cr(II) are the lowest unoccupied molecular orbital (LUMO) in the Cr(III)-systems and the highest occupied molecular orbital (HOMO) in the Cr(II)-systems, respectively. Symbols Cl-S, F-S and Cl,F-S are defined to pure chloride (both **I** and **II** types), pure fluoride (type **I**, X=F) and chloride-fluoride systems (type **II**), respectively, and the first coordination number of chromium is labeled as CN1.

**Table 1.** The main contribution of atomic orbitals in the frontier MOs LUMO Cr(III)-systems and HOMO Cr(II)-systems

| Type of system | Parameter | | LUMO Cr(III) | | | HOMO Cr(II) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Na | K | Cs | Na | K | Cs | |
| **I** | Cl-S | CN1 | 6 | 6 | 6 | 5 | 5 | 5 | |
| | | AOs | d(Cr),<br>p(Cl) | d(Cr),<br>p(Cl) | d(Cr),<br>p(Cl)* | d(Cr),<br>p(Cl) | d(Cr),<br>p(Cl) | d(Cr),<br>p(Cl)* | |
| | F-S | CN1 | 6 | 6 | 6 | 6 | 5 | 6 | 5 |
| | | AOs | d(Cr),<br>p(F) | d(Cr),<br>p(F) | s(Cs),<br>p(F)* | d(Cr),<br>p(F) | d(Cr),<br>p(F) | s(Cs),<br>p(F)* | d(Cr),<br>p(F)* |
| **II*** | Cl-S | CN1 | 6 | 6 | 6 | 5 | 5 | 5 | |
| | | AOs | d(Cr),<br>p(Cl) | d(Cr),<br>p(Cl) | d(Cr),<br>p(Cl) | d(Cr),<br>p(Cl) | d(Cr),<br>p(Cl) | d(Cr),<br>p(Cl) | |
| | Cl,F-S | CN1 | 6 | 6 | 6 | 5 | 5 | 5 | 6 |
| | | AOs | d(Cr),<br>p(F) | d(Cr),<br>p(F) | s(Cs),<br>p(Cl) | d(Cr),<br>p(F) | d(Cr),<br>p(F) | d(Cr),<br>p(F) | s(Cs),<br>p(Cl)** |

*) For Stuttgart basis set

**) In the geometry structure of the Cr(III) Cl,F-S system

In these systems II, except Cs-containing chloride-fluoride system, characters of the LUMO Cr(III) and the HOMO Cr(II) are the same and determined by the antibonding interaction of chromium d-orbitals with p-orbitals of those ligands that belong to the first coordination sphere (CS) of chromium. The LUMO Cr(III) is separated from the HOMO by the energy gap ~300 kJ in Cl-S and ~500 kJ in Cl,F-S (K-containing Cl,F-S has two LUMOs close in energy). Above the LUMO Cr(III) there lie unoccupied MOs of another type which includes a main contribution from s-AOs $M^+$ cations and p-AOs Cl-ions of the second-third CS. The energy gap between these group of MOs and the LUMO Cr(III) is ~130 kJ in Cl-S and ~40-70 kJ in Cl,F-S.

In all systems II unpaired electrons are localized on 4-5 highest occupied MOs (including the HOMO Cr(II)) which are arranged in the energy range 70-100 kJ. As noted above, the main contribution to these orbitals bring d-AOs chromium and p-AOs ligands.

Some examples of frontier MOs in systems II are given in Figures 2-6 below.

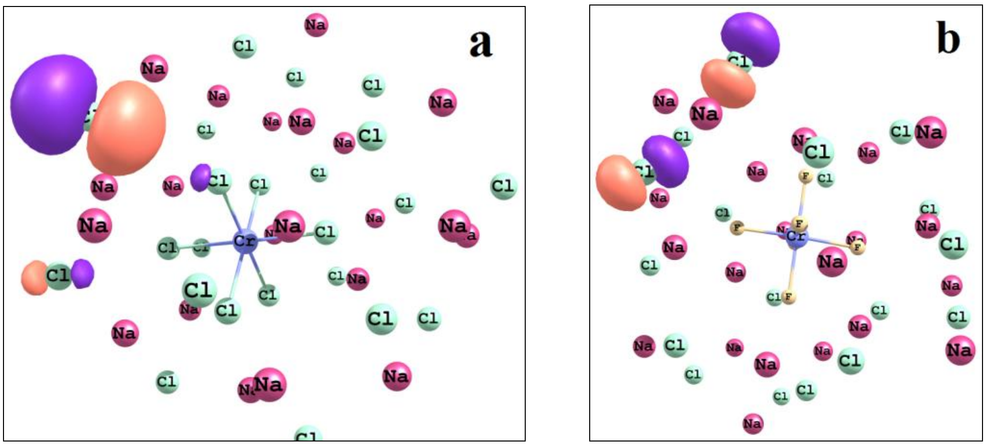

**Figure 2**. The HOMO Cr(III) in the Na-containing Cl-S **II** (a) and Cl,F-S **II** (b)**.** For other M (i.e. K and Cs), this orbital is the same character.

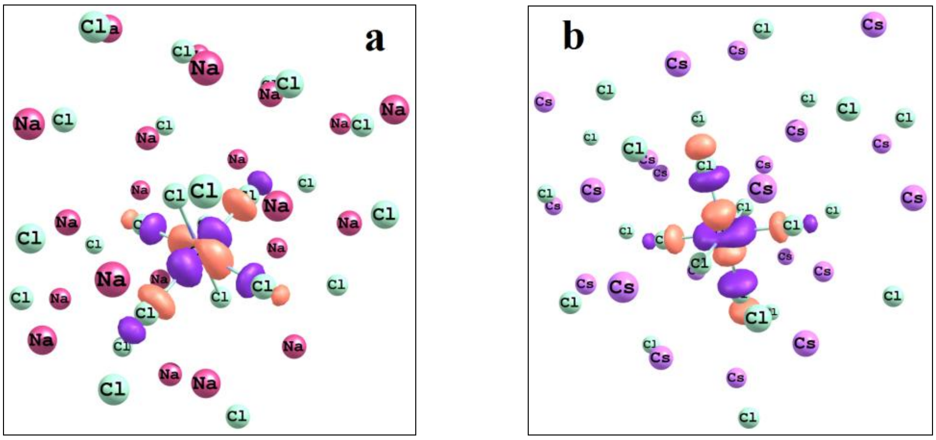

**Figure 3**. The LUMO Cr(III) in (a) the Na- and (b) the Cs-containing Cl-S **II.** For M=K this orbital has a similar form.

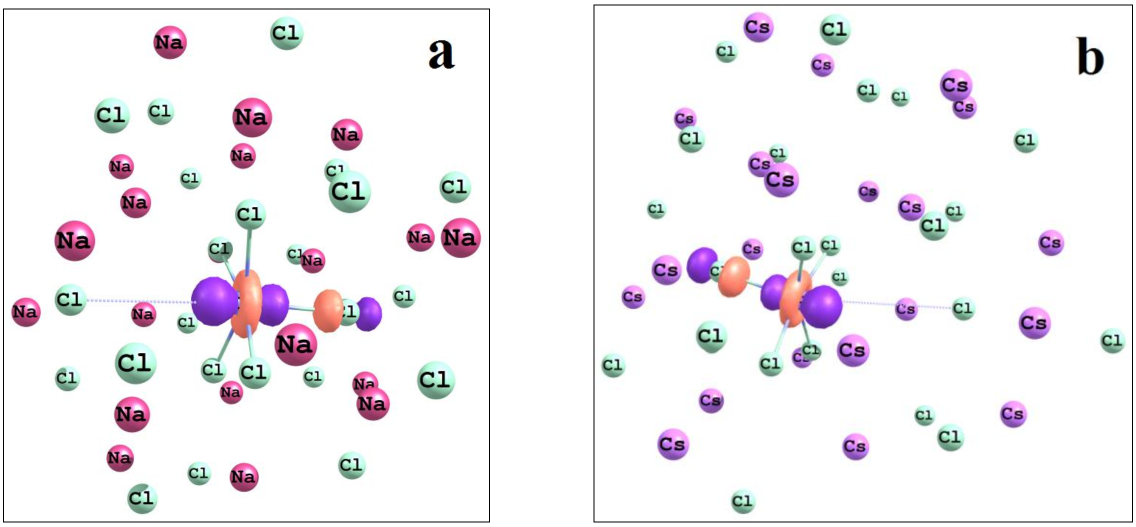

**Figure 4**. The HOMO Cr(II) in (a) the Na- and (b) the Cs-containing Cl-S **II.** For M=K this orbital is the same character.

The character of the HOMO Cr(III) (it is not specified in the Table) is the same in all systems **II**: 50-60 the highest occupied MOs located in the energy range 100-150 kJ have the same character as the HOMO of the system and p-orbitals of Cl-ions in both Cl-S **II** and in Cl,F-S **II** systems make the main contribution to these orbitals.

Examples of frontier MOs in chloride-fluoride systems Cl,F-S **II** are given in Figures 5-6.

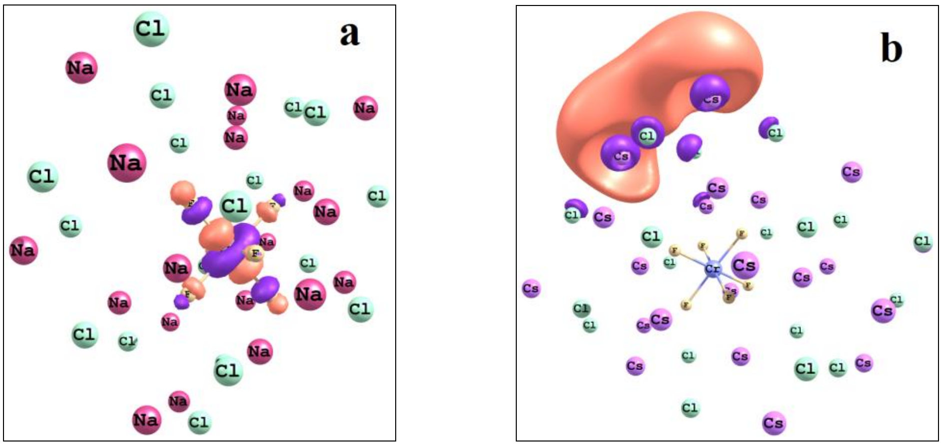

**Figure 5**. The LUMO Cr(III) in (a) the Na- and (b) the Cs-containing Cl,F-S **II.** For M=K this orbital has a similar form as for the Na- containing Cl,F-S **II**.

In Cs-containing system Cl,F-S the nature of the LUMO differs from the others (Fig. 5). Table shows the s-AOs of cesium and p-AOs of chlorine make the main contribution to this LUMO. The unoccupied MOs located above the LUMO in the range of energy ~100 kJ have the same character.

It would seem, we can state that after the charge transfer from an electrode, unpaired electron should be localized on one of such orbitals. However, as it follows from Table, the additional electron is localized at the HOMO, which has the same character as in the Na - and K-containing systems of this type. The reason is the change in the first coordination number of chromium (II) from six to five after electron transfer (ET). The result is a strong change in the electronic structure of the system.

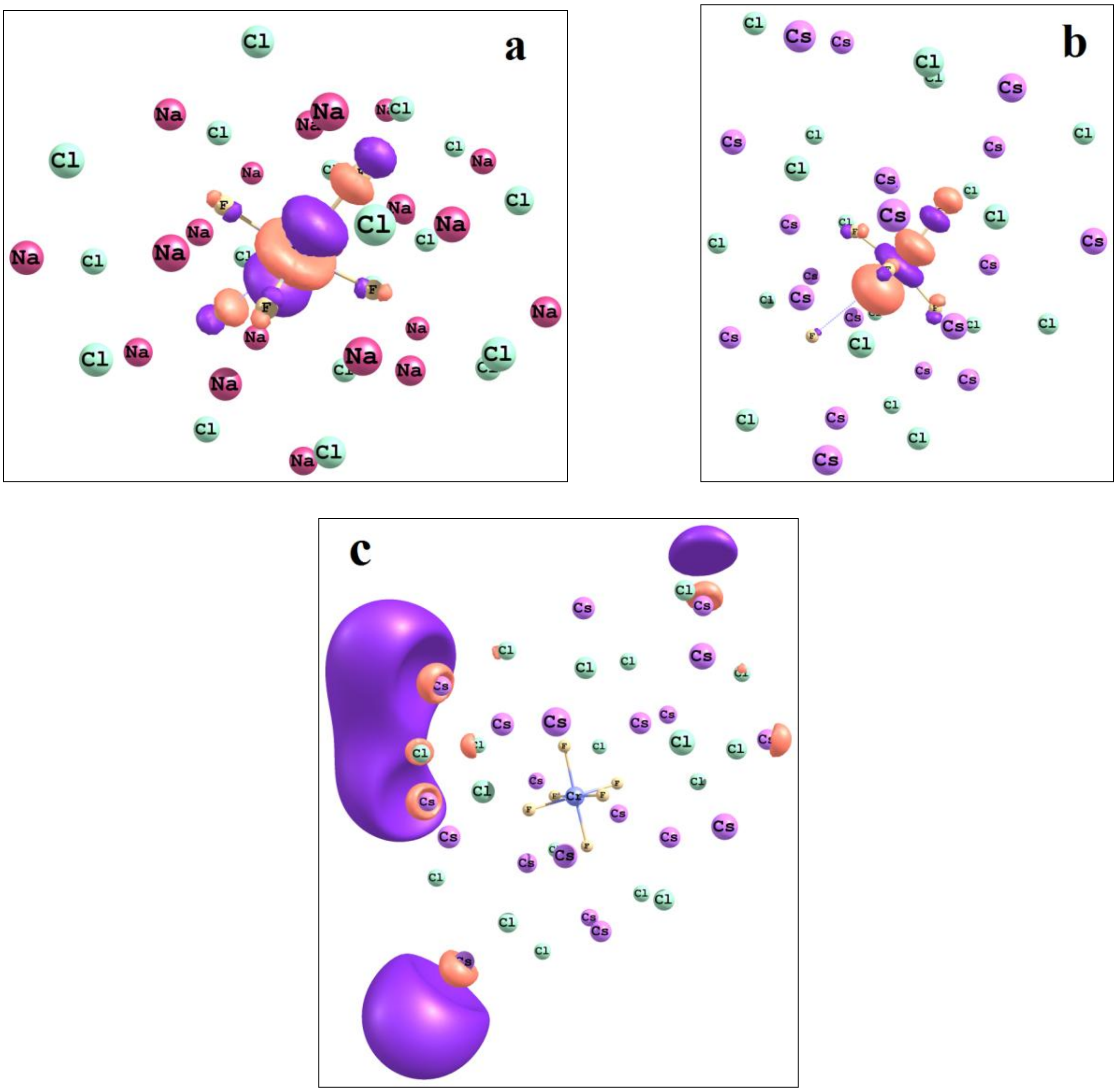

**Figure 6**. HOMO Cr(II) in the Na- and Cs-containing Cl,F-S **II**: Na – (**a**), Cs – (**b**) for CN1=5 and (**c**) for CN1=6. For M=K this orbital has the same character as for the Na- containing Cl,F-S **II**.

We can check these data using small systems I. As a rule, the effect of OS cations is even more pronounced in such systems. Previously [14-17], in quantum-chemical calculations for model systems **I**, containing a complex anion $[AX_p]$ with a cation OS shell $(M^+)_n$ (A – Nb, Cr; X – F, Cl; p = 6, 7; M = Na, K, Cs; $n = 1 \div n_{lim}$), it was found that compositions with an intermediate number of OS cations $m < n_{lim}$ are thermodynamically most stable ($n_{lim}$ is the limiting number of OS cations bound to a complex). To verify these findings computations of the interaction energy of fragments with various compositions have been carried out in extended model systems **II**. It has been found that in systems **II** the composition of the second coordination sphere of the most stable fragments either coincides with the OS composition of the most stable particles in systems **I** or contains one more cation. That is, significant differences between the systems **I** and **II** in this respect are not observed. Based on these results, in this work we made analysis of the frontier MOs for the Cr-containing particles, such as $4M^{+}\cdot[Cr(III)X_6]^{3-}$ and $4M^{+}\cdot[Cr(II)X_6]^{4-}$ (M - Na, K, Cs; X - F, Cl). Particles of this composition are the most thermodynamically stable in systems of the $nM^{+}\cdot[CrX_6]^{3-}$ type (n = 1 ÷ 6).

The corresponding results for these systems are shown in the same Table. However, note that the boundary orbitals have the same character also in particles with one OS cation less. That is, in this case, the choice of the OS environment is not critical.

Examples of frontier MOs in chloride systems Cl-S **I** and fluoride systems F-S **I** are presented in Figures 7-8 and 9-10 respectively.

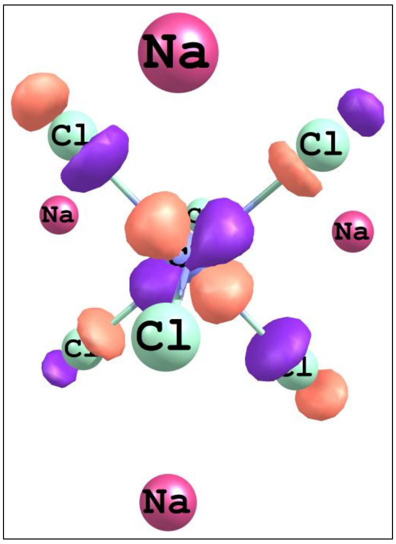

**Figure 7**. The LUMO Cr(III) in Cl-S **I** $4Na^{+}\cdot[CrCl_6]^{3-}$. For M=K and Cs this orbital is the same character.

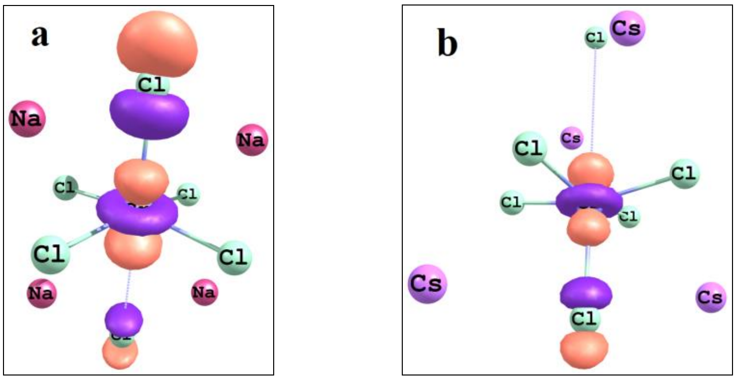

**Figure 8**. The HOMO Cr(II) in Cl-S **I** $4Na^{+}\cdot[CrCl_6]^{3-}$ (**a**) and $4Cs^{+}\cdot[CrCl_6]^{3-}$ (**b**). For M=K this orbital has a similar form.

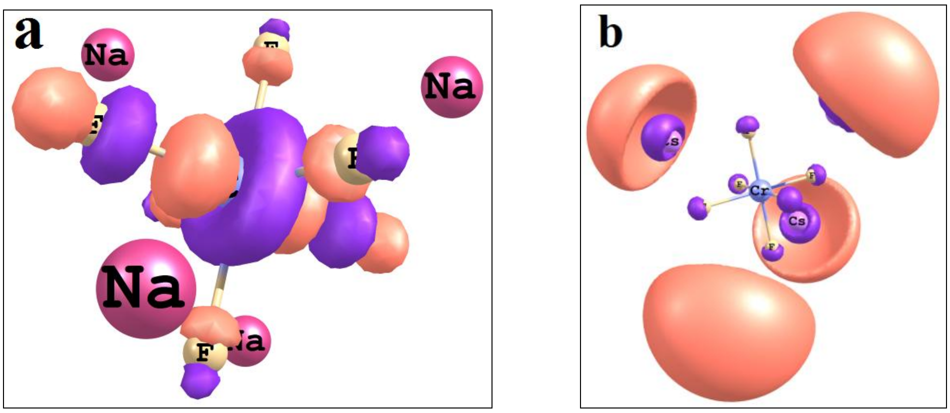

**Figure 9**. The LUMO Cr(III) in F-S **I** $4Na^+ \cdot [CrF_6]^{3-}$ (**a**) and $4Cs^+ \cdot [CrF_6]^{3-}$ (**b**). For M=K this orbital has the same character as for the Na-system.

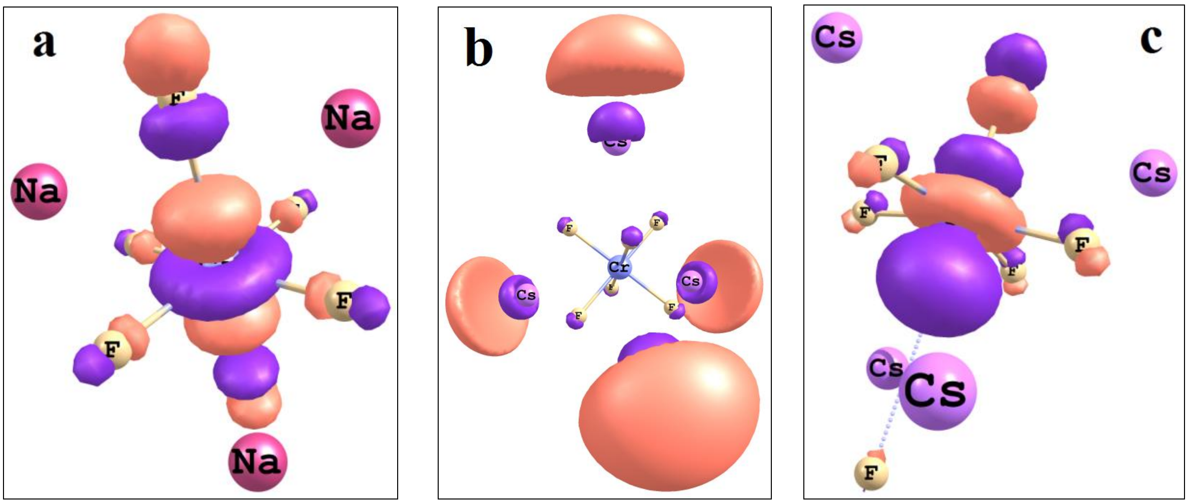

**Figure 10**. The HOMO Cr(II) in the Na- and Cs-containing F-S **I**: $4Na^+ \cdot [CrF_6]^{3-}$ (**a**); $4Cs^+ \cdot [CrF_6]^{3-}$ for CN1=6 (**b**) and for CN1=5 (**c**). For M=K this orbital has a similar form as for the Na-system.

The LUMO and HOMO characters in Cs-containing F-S systems **I**, i.e. $4Cs^+ \cdot [CrF_6]^{3-}$ and $4Cs^+ \cdot [CrF_6]^{4-}$, differ from other systems (see Table and Figs. 9-10). When CN1=6, main contribution to LUMO and HOMO make s-AOs of cesium and p-AOs of fluorine ligands. However, for Cr(II) there is one more structure with CN1=5 and close energy which is more only on 14 kJ/mol. According to Table and Fig. 10, difference between these structures is that in the first of them (CN1=6), an additional electron is localized predominantly on 4s-AOs of cesium cations, while in the second (CN=5) it is localized on 3d-AOs of chromium. That is, only after CN1 changes from six to five an extra electron is localized on chromium. In the Na-, K-containing systems after ET, the relative stability of structures with CN1=5 substantially higher than structures with CN1=6 (for Cs-containing system **I** vice versa). Anomalous effect of cesium cations on the distribution of the electron density in complex was noted earlier for $NbF_7$-systems I [18].

In the Cs-containing system Cl,F-S **II** after ET the structure with CN1=5 becomes more stable, than those with CN1=6. However, if the CN1 value *is kept equal to six*, then the HOMO character *after*

ET coincides with the LUMO character *before* the charge transfer (see Table, data for HOMO Cr(II) in the Cs-containing system Cl,F-S with CN1=6, and Figs. 5b. 6c). This computation refers to the geometric structure of the *initial* state of the system, but *after* ET. Geometric structures with intermediate lengths of the Cr-F bonds (between lengths of these bonds in initial and final systems) have a different LUMO character, namely, the same as HOMO of the final structure, and could not provide the "anomalous" ET mechanism. In similar Na - K-systems it is not observed: even when CN1 is kept equal to six, the HOMO character remain the same, as when CN1=5.

According to these data, an abnormally high rate of ET in the Cs-containing Cl,F-S is a consequence of the abnormal LUMO character in the transition state of the system. In other words, the LUMO characters in the initial and transition states are the same. Now we cannot correctly find a transition state, as it requires high computational costs, but on the basis of our data, we can say: when the geometric structure of the transition state is close to that of the initial state, then the nature of the LUMO in the transition state is the same as in the initial one. This is a consequence of the fact that in structures, which are close to the initial state, the nature of LUMO before ET coincides with the character of HOMO after ET (see Table). Therefore, in the intermediate (transition) state the LUMO character is the same.

Based on these data, we can state that for the Cs-containing system Cl,F-S the LUMO character in the initial and transition states coincides and geometrical structure of the transition state is close to the initial structure, while for the Na- and K-containing systems type of LUMO in the transition state is close to the HOMO type of the final state. As a result, mechanisms of charge transfer in these systems are different.

In the Cs-system ET occurs on the Cs cation, and only after one of the Cr-F bonds ruptures, this electron is localized on chromium. This type of complex recharging does not require substantial reorganization of the second coordination sphere of electroactive species.

In the Na - and K-systems additional electron comes to the orbital delocalized on ligands and chromium. This requires pre-reorganization of an OS environment in the transient state. OS cations must be displaced to provide access of F or Cl ligands of the first coordination sphere of chromium to the electrode surface in Cl,F-S or Cl-S respectively. Obviously, in this case the ET rate should be less than at the direct transfer over the OS cation. This is consistent with the above experimental facts.

For the Cs-containing Cl,F-system we can note one more feature. Fig. 5b shows that the LUMO in the initial system of this type is delocalized over the boundary Cs and Cl ions. This can lead to preliminary transfer of electron on such orbital and then on the electroactive species. That is, our calculations indicate the possibility of electron delocalization over the electrolyte ions, which are located near the surface of the electrode (on the edge of melt). If this phenomenon is really observed in this system, then ET to the electroactive species can occur in two ways: either from the electrode surface directly on electroactive particle or by transfer from the delocalized ("solvated") state of electron. After ET the CN1 value reduced from 6 to 5 and electron is localized in the HOMO orbital, mainly belonging to chromium (Fig. 6b). This assumption requires careful verification in more complex model systems; however, we express it, as one follows from our calculations. At this stage of research, we cannot specify which path of the electron transfer is more preferable in this system.

Note, in the Cs-containing pure chloride system II (Cl-S) kind of the LUMO is different (see Table and Fig. 3b). Consequently, the marked feature of the LUMO in the Cs-containing Cl,F-system **II** is result of the effect of fluoride complex ions $[CrF_6]^{3-}$ on the state of the chromium third coordination sphere. If so, transfer of electrons in the above "solvated" state may occur only at complex approach to the electrode surface when the ions of the third coordination sphere are at an edge of the melt.

## 4. CONCLUSIONS

1) The analysis of the nature of the frontier MOs in model Cr-types systems I and II is carried out. It is found that character of the LUMO Cr(III) in the "abnormal" Cs- containing system Cl,F-S differs from that in the other systems. The LUMO Cr(III) in the transition state has the same character, if the geometric structure in this state is close to that of the initial system. In this case, originally electron is transferred to the surrounding ions and delocalized between them. In the second stage CN1 of the complex is reduced from 6 to 5, and electron is localized on the complex. This mechanism does not require pre-deformation of the OS shell and accelerates ET.

2) The different nature of the frontier MOs leads to differences in the mechanisms of electron transfer in the compared systems and explains the higher rate of charge transfer in the "anomalous" Cs-system. Perhaps the electron transfer can occur in the "abnormal" Cs-system in two ways: directly on the complex (via OS cations of Cs) and through the stage of "solvated" electron.

3) In other systems, the ET step is preceded by deformation of the OS shell, which provides direct contact of the ligands of the first coordination sphere with the electrode surface. Probably, this stage is limiting.

4) Previously, we have investigated in detail the area of geometric parameters which are intermediate between the initial and final structures of the several model systems. The aim of that work was a searching of the structures corresponding to the transition state. However, the result was negative. The findings of this study allow us to understand the reasons of this failure. As noted above, with the exception of the "anomalous" Cs-containing Cl,F-S system in other systems the transition state is significantly different from both the initial and final states. However, it is precisely such systems we have investigated earlier.

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