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Dependence of the structure of alkali metal–trifluoride ion pairs $F_3^-M^+$ on the counterion M^+ (M = Li, Na, K)

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The CCSD(T)/6-311+G(3df) calculations have shown that the geometry, bond nature and stability of alkali metal–trifluoride tight ion pairs $F_3^-M^+$ (M = Li, Na, K) are strongly dependent on the counterion M^+ and its position in these pairs.

The trifluoride anion F_3^- is the simplest hypervalent species with a three-center four-electron bond (3c-4e).[1,2] Both experimental[3–5] and theoretical[6–9] data point to the strong influence of the type and relative position of counterions M^+ on the configuration of the F_3^- anion inside the ion pair $F_3^-M^+$ (M = Li, Na, K). The exact geometries computed by *ab initio* and density functional theory methods significantly differ. However, the QCISD calculations[8] of the geometric and spectral characteristics of the F_3^- anion performed for $F_3^-M^+$ salts (M = Na, K, Rb, Cs) gave rise to the good agreement with the experimental data. These works[6–9] focused on the dissociation energy of the trifluoride anion through various reaction channels and the simulation of a vibrational spectrum paid no attention to the dependence of bond nature in the F_3^- anion on the position of counterions M^+. The

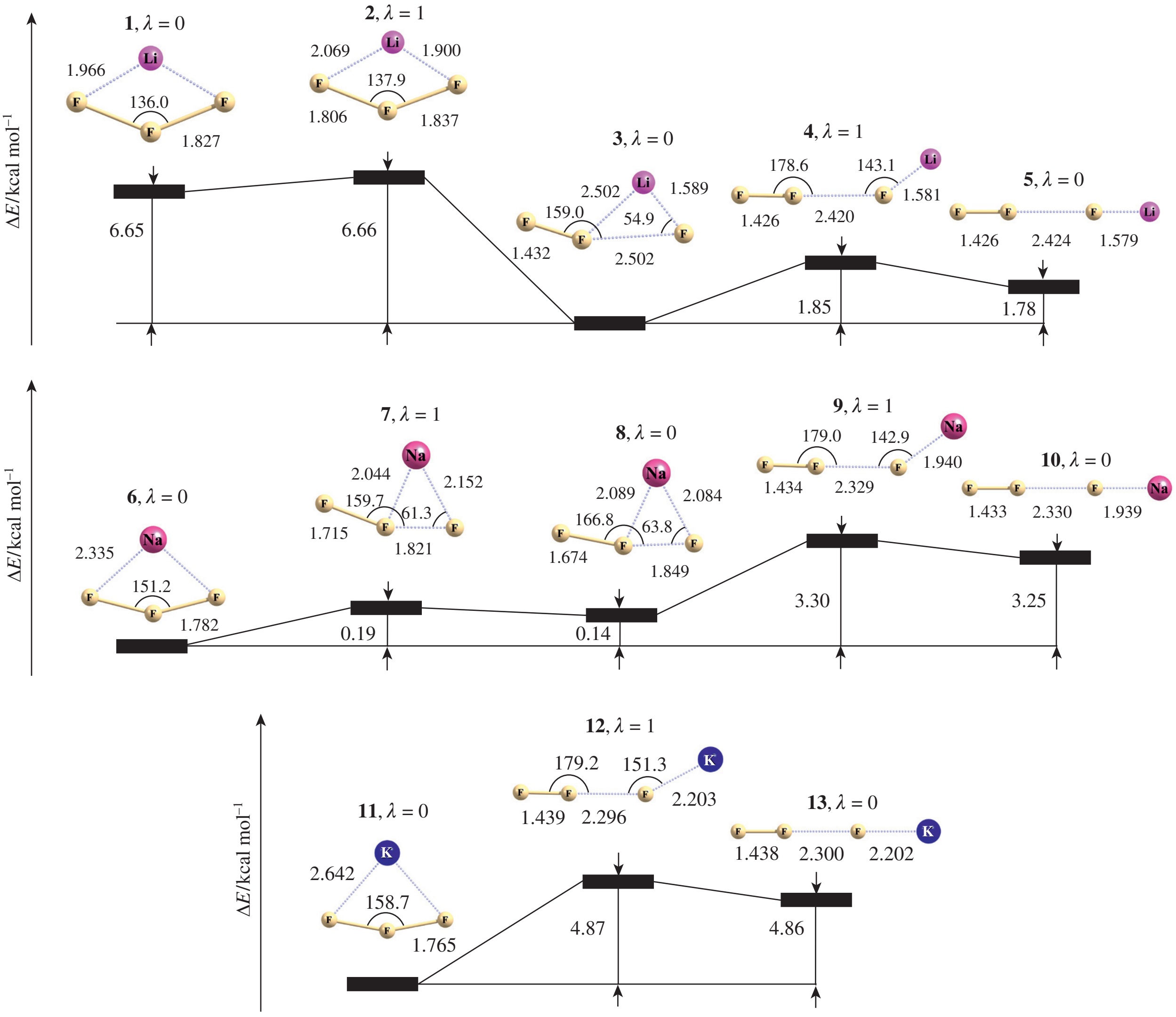

Figure 1 Geometry parameters of structures **1**–**13** calculated by the CCSD(T)/6-311+G(3df) method. The bond lengths and bond angles are given in angstrom units and degrees, respectively.

aim of this work was to perform a thorough computational study[†] of this effect and changes caused by a variation in the position of counterions M^+ on the nature of bonding in F_3^- moieties in the ion pairs $F_3^-M^+$ (M = Li, Na, K).

The calculated total and relative energies and the geometries of structures **1–13** of ion pairs $F_3^-M^+$ with indications to the nature of the corresponding stationary points are given in Figure 1 (and Table S1, Online Supplementary Materials). It stems from the calculations that T-shaped structure **1** with a lithium counterion in the tight ion pair $F_3^-Li^+$ is by more than 6 kcal mol^{-1} thermodynamically less stable than isomeric complex **3**, which consists of individual weakly bound F_2 and LiF molecules. This finding explains the fact that the T-shaped structure was not experimentally observed in the F_3Li complex. At the same time, for $F_3^-Na^+$ and $F_3^-K^+$ ion pairs, T-shaped structures **6** and **11**, respectively, were experimentally detected by the observation of the NaF linear vibration (antisymmetric vibration band is not detected) with a frequency of 455 cm^{-1} (calculated 459 cm^{-1}) and the antisymmetric vibration band of F_3^- with a frequency of 550 cm^{-1} (calculated 585 cm^{-1}) in their IR spectra.[4] According to data in Table S1, accounting for zero-point vibration energy reverses positions of energy levels only in the cases of linear structures **5**, **10** and **13**, which became slightly energy disfavored compared to angular isomers **4**, **9** and **12**.

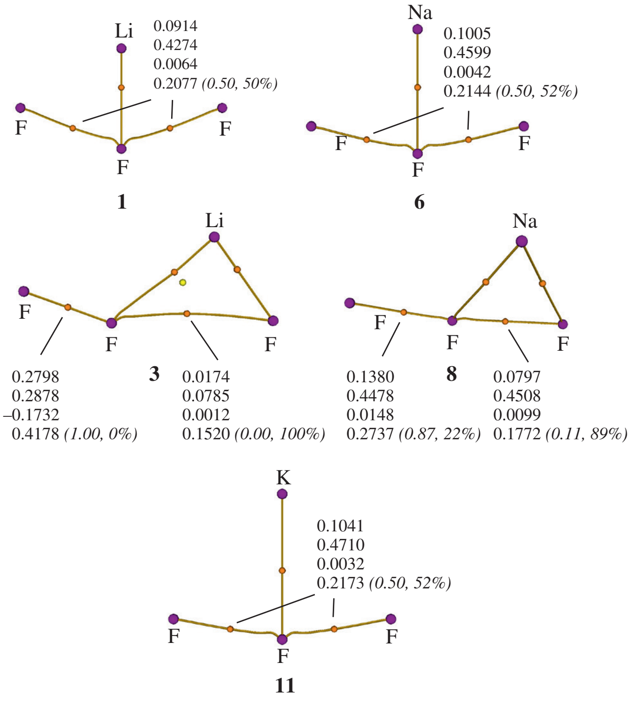

Figure 2 Critical points (3,–3), (3,–1), (3,+1) and bond paths for structures **1**, **3**, **6**, **8**, **11** obtained by the QTAIM method. For specified points, the values of $\rho(r)$, $\nabla^2\rho(r)$, $h_e(r)$, $\eta(r)$ are shown. The results of NRT analysis (bond order and ionicity) for corresponding bonds are shown in parentheses in italics.

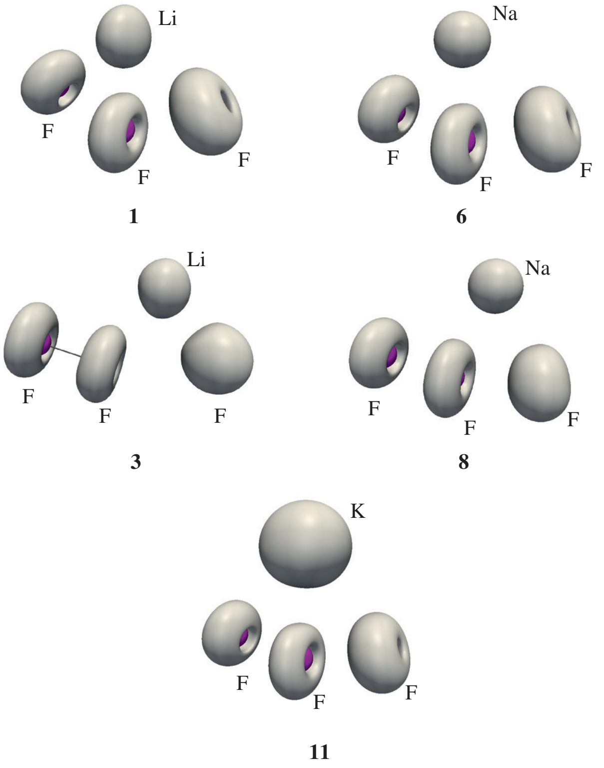

Figure 3 ELF function for F–F bonds in structures **1**, **3**, **6**, **8**, **11**. Isosurfaces of the ELF are depicted at a value of 0.8.

Note that structures **1**, **6** and **11** are extremely stereochemically nonrigid, as manifested by very low energy barriers of the displacement of alkali metal ions in the plane of the trifluoride anion. Shifting the alkali atom along the anion leads to changes in the nature of chemical bond in trifluoride from hypervalent (3c-4e) to usual two-center two-electron (2c-2e) bond. These changes are testified by the electronic charge density $\rho(r)$, its Laplacian $\nabla^2\rho(r)$, the electronic energy $h_e(r)$, additional index $\eta(r)$ [$\eta(r) = |\lambda_3(r)|/\lambda_1(r)$, where λ_3 and λ_1 are the lowest and the highest eigenvalues of Hessian matrix of $\rho(r)$, respectively][13,19,20] and ELF and NRT analysis as shown in Figures 2, 3.

Hypervalent nature of the valence bonds of F_3^- was studied by the QTAIM analysis of T-shaped structures **1**, **6** and **11** (Figure 2). The central divalent fluorine atom is connected by valence bonds (3c-4e) with two lateral fluorine atoms. This is also evidenced by the isosurface images of the ELF function, showing the localization of electron pairs in $F_3^-M^+$. When the alkali metal is moving from the central position toward its position in structure **3** or **8** and further to a linear form (**5**, **10** and **13**), the electron density is shifted from the nearest FF bond to form a two-electron FM bond. A FF bond from which the electron density is removing converts to a weak electrostatic-type F···M bond (see Figures 1, 2).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.11.005.

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[†] The calculations related to a gas phase were carried out on a computing cluster of the Southern Federal University using the coupled cluster method CCSD(T)/6-311+G(3df)[10] and the Gaussian 03[11] software. The relation of test structures to various stationary points on the potential energy surface (PES) (minimum, $\lambda = 0$, and transition state, $\lambda = 1$) has been verified by the calculations of the vibration spectrum (force constant matrix) of the systems. The location of structures corresponding to the found stationary points relative to each other was tested by determining gradient lines (lines of the steepest descent) connecting the saddle points (transition states) with neighboring local minima. The QTAIM method[12] was applied to the topological analysis of the electron density distribution function with the use of the Multiwfn program.[13] The electron localization functions (ELF)[14] and the visualization of corresponding isosurfaces were obtained through the Dgrid[15] and ParaView[16] programs. Natural resonance theory (NRT) analysis, which allows one to obtain the bond order and bond ionicity, was performed by the Firefly program.[17,18]

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