Induced hyper-valence of carbon in metal:fluorocarbon complexes

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Received 20th June 2006, Accepted 23rd August 2006
First published as an Advance Article on the web 1st September 2006
DOI: 10.1039/b608712d

Charge-transfer in combination with geometric features induces a pentavalent state of the carbon atom in metastable super-fluorinated alkali-metal compounds, M:C_2F_7 (M = K to Cs).

The valence of atoms is known to determine the relative stabilities of their compounds. Saturated valence corresponds to the most stable systems, while under-saturation leads to an increased chemical activity of radicals and over-saturation (hyper-valence) generally implies an instability or metastability. Stable hyper-valent compounds are usually attributed to heavier atoms, starting from the 3rd row of the Periodic Table. Standard examples are, in particular, PF_5 and SF_6, with the highly active fluorine causing hyper-valence in other atoms. Such systems are stable in their negative ionic states as well. Moreover, anions can also be stabilized for the super-fluorinated compounds whose neutral counterparts may be unstable, including the SiF_5^- case.[1] The extra electron in such systems closes the electronic shell and formally compensates for the lack of valence electrons, so that Si^- can become pentavalent in its high-spin state. The 2nd row analogue, CF_5^-, has also been studied and found to be weakly stable.[2] More stable, rather unique hyper-valent carbon compounds are represented by CLi_n (n = 5, 6).[3]

Different valence states are associated with different bond patterns, and the latter determine physico-chemical properties of compounds. Hyper-valent carbon-based systems may possess unique characteristics and may offer interesting applications. The metastable states are important as well, for instance as transition states in reactions. The present work investigates a family of larger dicarbon super-fluorinated compounds with a hyper-valent C atom. The ionic systems are normally stabilized when combined with counterions, and here this is attempted using alkali-metals.

Calculations have been performed with the NWChem *ab initio* package,[4] and all images generated by means of the Molekel package.[5] The MP2 level of theory has been employed using the basis set aug-cc-pvdz for the C and F atoms, and Stuttgart's relativistic effective core potentials plus matching basis sets for K to Cs (all being incorporated into the NWChem library). At this level, the Ionization Energies (IE) of K, Rb, Cs are calculated as 4.0, 3.8, 3.5 eV, reproducing the respective experimental values[6] of 4.3, 4.2, 3.9 eV within 10%. The calculated Electron Affinity (EA) of F, 3.55 eV, is 5% above the experimental value, 3.40 eV. The predicted MF dissociation energies 4.93, 4.84, 4.92 eV and equilibrium distances 2.32, 2.45, 2.56 Å (for M = K, Rb, Cs, respectively) deviate from the experimental values of 5.2, 5.1, 5.2 eV and 2.17, 2.27, 2.35 Å[6] within 10%. The C–F bond length in CF_3 (≈half-C_2F_6) is 1.33 Å calculated and 1.32 Å measured, and its predicted atomization energy is 14.7 as compared to experimental 14.6 eV. Finally, all-atom optimizations of the studied system geometries have been done in the C_1 symmetry, and local energy-minima verified by the frequency analysis.

Both the CF_5^- and $C_2F_7^-$ species are found to be weakly bound complexes of saturated neutral molecules and an atomic ion, CF_4:F^- and C_2F_6:F^-, respectively, with remote F^- at the hollow site between three F atoms of the molecule (along the C–C axis for the larger species, Fig. 1). The symmetric (trigonal bypiramidal) CF_5^-, with a pentavalent carbon, is a transition state of the system 0.50 eV above the CF_4 + F^- asymptote, unlike for the silicon-based counterpart.[1] The CF_4–F^- binding energy is calculated to be 0.28 eV, with the remote F^- (carrying the entire negative charge) 2.85 Å away from the C atom. The respective values for C_2F_6:F^- are very similar, 0.30 eV and 2.84 Å. The standard counterpoise correction of the basis-set superposition error weakly affects the binding energies (0.31 eV for CF_4:F^- and 0.33 eV for C_2F_6:F^-). Similar results are obtained for the corresponding neutral systems, the binding of remote neutral F being much weaker (around ≈0.01 eV). Only the larger, C_2F_6-based species are discussed hereafter.

In order to overall-neutralize the above singly-charged system while keeping it negative for stronger bonding, the easily ionizable alkali-metal atoms M are employed here. Addition of M to C_2F_6:F from the remote-F side creates a linear MF:C_2F_6 complex (with MF along the C–C axis, Fig. 2). It has a low binding energy of ≈0.2 eV, intermediate between those of C_2F_6:F^- and C_2F_6:F, as expected (interaction of a closed-shell molecule with a dipole *versus* ion and neutral atom). The axial F–C distance between MF and C_2F_6 is almost constant, 2.97 to 2.93 Å, for M = K to Cs. The other linear (FM:C_2F_6, with M pointing to the molecule) and nonlinear (side-to-side) isomers are bound still more weakly (within ≈0.1 eV).

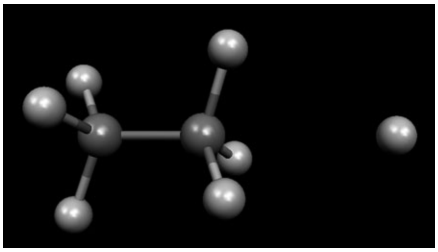

Fig. 1 Optimized geometry of the C_2F_6:F^- complex.

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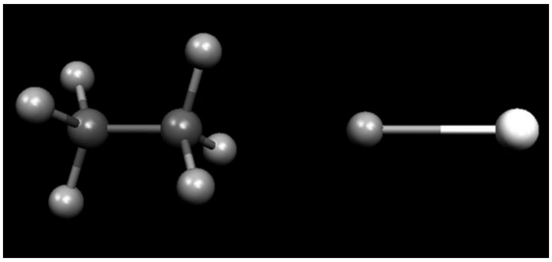

Fig. 2 Optimized geometry of the KF:C_2F_6 isomer.

Adding M (=K to Cs) to C_2F_6:F on the opposite side from the remote F, at the identical hollow site near the second CF_3 group, produces a higher-energy (due to dissociated MF) linear M:C_2F_6:F isomer shown in Fig. 3. The local energy-minimum is confirmed by all vibrational frequencies being real. For M = Li, however, the system is found to dissociate (upon optimization) into $LiCF_3$ + CF_4. This can be viewed as due to a higher ionization energy (IE = 5.4 eV) of Li relative to other alkalis, and thus due to a shorter-range charge-transfer from Li, effectively localized on the nearest CF_3 group of the molecule. A more detailed investigation of the Li-based system is beyond the scope of the present Communication. The interpretation for the Li case is supported by additional calculations for still-higher IE M = Mg, Al, Cu, and Au, which exhibit a similar instability. The M = Na ultimate case (IE = 5.1 eV) exhibits a weak stability and is to be detailed in a separate publication. For the lower-IE heavier alkali metals, the charge-transfer reaches remote F on the opposite side and then contracts the system (with geometric parameters collected in Table 1). As a result, the CF_3 group near remote F is flattened perpendicular to the C–C axis, apparently under pressure from that atom. This leads to a trigonal bipyramidal structure of atoms surrounding the C atom of the group, characteristic of pentavalent bonding.

Inspection of Table 1 reveals a slow evolution of the complex parameters from M = K to Cs, the M–C distance increasing due to the metal atom size, the C–C bond slightly shortening, and the distance between pentavalent C (denoted C^5) and remote F (denoted F*) slightly stretching. The F–C^5–C angle weakly increases with the M size, reaching almost exactly 90° at M = Cs. These variations are consistent with increasing resistance of the system to dissociation into MCF_3 + CF_4 (corresponding to short M–C and C–F and long C–C distances, as well as a sharper F–C^5–C angle). The C^5–F* distance is appreciably longer than for C^5–F (consistent with the five-fold coordination), both exceeding the C–F distance for the other, tetravalent, carbon. This and all other distances are stretched relative to those in the isolated C_2F_6 (C–C = 1.54 Å and C–F = 1.34 Å).

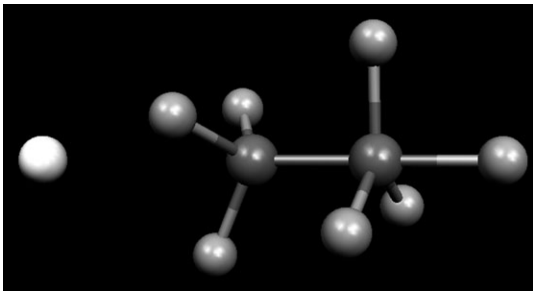

Fig. 3 Optimized geometry of the Rb:C_2F_7 isomer.

Table 1 Equilibrium bond lengths (Å) and angles (degrees) of the M:C_2F_7 complexes

System	M–C	C–F	F–C–C^5	C–C^5	C^5–F, –F*	F–C^5–C
K:C_2F_7	3.04	1.39	114.9	1.66	1.44, 1.55	89.5
Rb:C_2F_7	3.19	1.38	114.6	1.66	1.44, 1.56	89.8
Cs:C_2F_7	3.34	1.38	114.4	1.65	1.44, 1.57	90.0

[a] C^5 = pentavalent carbon; F* = remote (axial) fluorine.

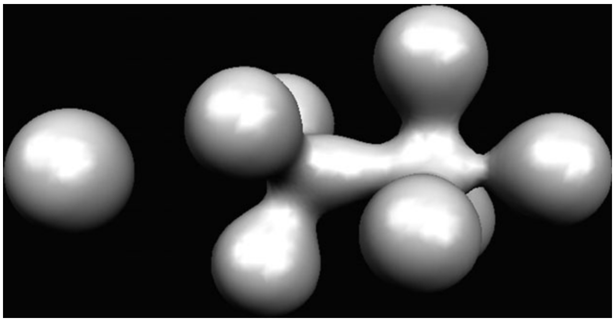

Fig. 4 Electron density iso-surface at 0.15 e Å^{-3} for the Cs:C_2F_7 complex.

The calculated electron density distribution, similar for all M, is illustrated in Fig. 4. The new C–F bond (along the C–C axis) is found to be true (not just a geometric proximity of the two atoms), although somewhat weaker than other bonds. According to the atoms-in-molecules analysis,[7] the minimum electron densities at the atom–atom axes relate as ≈0.18:0.22:0.21:0.24 (M = K, Rb) and ≈0.18:0.22:0.22:0.24 (M = Cs) for the C^5–F*, C^5–F, C^5–C, and C–F bonds, respectively. The axial C^5–F* bond is thus comparable to the others and has a somewhat lower electron density than the radial C^5–F bond, both being inferior to the normal C–F bond, as expected. The M atom, in turn, is ionically bound *via* an ion-pair interaction with much lower electron density. The critical point between the C^5 and F* atoms is 0.65–0.66 Å away from carbon for all systems.

The linear M:C_2F_6:F complex is 2 to 2.5 eV stable relative to dissociation into M + C_2F_6 + F (Table 2), hence, to removal of either M or remote F (as either van der Waals remainder, C_2F_6:F or M:C_2F_6, is very weakly bound). The system is higher in energy than the MF + C_2F_6 dissociation products by 2.5 ± 0.1 eV. The geometry of the system, however, implies a potential barrier to such a dissociation. Another, geometrically more accessible, channel is breaking the C–C bond. Splitting into M + CF_3 + CF_4 requires around 1 eV of energy, the

Table 2 Dissociation energies (eV) of the M:C_2F_7 complexes

System	M + C_2F_6 + F	M + CF_3 + CF_4	MF + C_2F_6	MCF_3 + CF_4
K:C_2F_7	2.19	0.92	–2.62	–1.38
Rb:C_2F_7	2.27	1.00	–2.47	–1.29
Cs:C_2F_7	2.48	1.21	–2.44	–1.19

Table 3 Natural atomic charges (e) in the M:C_2F_7 complexes[a]

System	M	C/F	C^5/F	F*
K:C_2F_7	0.99	1.03/−0.41	0.98/−0.42	−0.50
Rb:C_2F_7	0.99	1.02/−0.41	0.98/−0.42	−0.50
Cs:C_2F_7	1.00	1.02/−0.41	0.98/−0.42	−0.51

[a] C^5 = pentavalent carbon; F* = remote (axial) fluorine.

M + $2CF_3$ + F channel is apparently still more energetic (as needing additional C–F bond breaking in CF_4), while the MCF_3 + CF_4 product is lower by 1.3 ± 0.1 eV due to a considerable M–CF_3 bonding energy (2.3–2.4 eV).

The potential barrier to dissociation into MCF_3 + CF_4 has been found to increase from ≈0.08 eV for M = K to 0.15 eV for M = Cs, with the C–C bond stretched by ≈0.3 Å. For comparison, the barrier is only ≈0.01 eV high (the bond stretch ≈0.1 Å) for M = Na. The M:C_2F_6:F systems can thus be metastable at sufficiently low temperatures, more likely for species with heavier M.

The increasing stability of M:C_2F_6:F with the size of M is apparently related to decreasing IE (5.1 eV to 4.3 to 3.9 eV for Na to K to Cs) and hence stronger charge-transfer. This is supported by the calculated natural charges on atoms (Table 3), very similar for M = K to Cs and showing a +1 charge on the heavier alkalis, with the negative counter-charge equally shared by C_2F_6 and remote F. By comparison, the charge is +0.74 on M = Na and the charge on C_2F_6 is reduced accordingly. Since in C_2F_6:F^- the (closed-shell) molecule is found to be neutral, in M:C_2F_6:F it is M^+, which pulls a half-charge to the molecule. This can be further rationalized by considering that the molecule is significantly positive in M^+:C_2F_6 complexes, therefore attracting a part of the electron density from F^- in M:C_2F_6:F. Both C atoms are equally charged (with the weaker C^5–F bonds compensated by their larger number), the same being true for all F atoms except the slightly more negative axial (remote) one.

Such an extended charge-transfer, with the M-F* distance of up to 6.6 Å in the Cs-based system (Table 1), produces a very large dipole moment of up to 21 D (Table 4). This should facilitate experimental detection of the complexes, even as transient species. It appears plausible that the systems in question could form upon photodissociation of MF in cluster or solid matrices (for instance, of He or other rare gases) also containing C_2F_6 molecules. In order to assist future microwave spectroscopy experiments, *e.g.* in He nanodroplets, the calculated rotational constants of the M:C_2F_6:F complexes are listed in Table 4. The table also contains their calculated vibrational frequencies corresponding to the highest IR intensities (also tabulated), for possible identification of the species.

Table 4 Spectroscopic parameters of the M:C_2F_7 complexes: dipoles, rotational constants, vibrational frequencies and IR intensities

System	μ/D	A, B = C/cm^{-1}	ν/cm^{-1} , I/(D/Å)^2
K:C_2F_7	19.4	0.0807, 0.0195	797, 16.6; 2 × 1076, 11.3; 430, 5.7
Rb:C_2F_7	20.2	0.0807, 0.0129	800, 16.5; 2 × 1082, 11.0; 422, 5.7
Cs:C_2F_7	21.0	0.0806, 0.0100	805, 16.2; 2 × 1088, 10.9; 416, 5.6

Electronic excitation of the above closed-shell systems to the triplet states and subsequent optimization leads to dissociation into M + CF_3 + CF_4 due to no stabilizing charge-transfer in that state (similar to the MF case). The corresponding vertical excitation energies slightly increase from 6.72 to 6.92 to 7.27 eV for M = K to Rb to Cs. Ionization of the neutral complexes is predicted to induce dissociation in a similar way, producing M^+ + CF_3 + CF_4, as a consequence of the hindered electron-donation from M^+. The vertical ionization energies are essentially invariant at 10.7–10.8 eV for different M, as it is the almost identical (Table 1) fluorocarbon remainder from which the (extra) electron is detached. Electron attachment is found to result in a different dissociation, into M + C_2F_6 + F^-, with the original molecule recovered. The associated vertical energies slightly decrease from 1.11 to 1.06 to 0.91 eV for M = K to Rb to Cs, following the decrease of the IE of the metals. This is in accord with the electron attaching to M^+ within M:C_2F_6:F, thus destabilizing the ion-pair system.

To conclude, *ab initio* studies of the complexes of alkali-metal atoms (M = K, Rb, Cs) with a superfluorinated dicarbon species have been performed and revealed the existence of a metastable linear M:C_2F_6:F isomer among others. It exhibits one C atom as pentavalent, with an additional bond to the axial F atom, and with a low barrier to dissociation into MCF_3 + CF_4. A strong charge transfer, as well as geometric features, induce the hypervalence in carbon and stabilize the M:C_2F_7 complexes. They have very large dipole moments and are characterized by rotational and vibrational spectroscopic parameters, which facilitate experimental observation at low temperatures. The complexes could perhaps be formed by photodissociating MF in clusters or solid matrices doped also with C_2F_6, *via* sandwiching the molecule between recombining M and F. The complexes may represent transient species of the reactions M + C_2F_6 + F → MCF_3 + CF_4 as well. The reaction precursors MF:C_2F_6 are the lowest-energy, weakly bound isomers of the systems.

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