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Metastable Intermolecular Charge-Transfer Complexes with a Pentavalent Carbon Atom

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A novel type of metastable complexes of metal (such as Na) atoms with a super-fluorinated carbon molecule is investigated, with a carbon atom exhibiting a unique, pentavalent character. It is induced by the charge transfer from the alkali metal component, followed by a geometric compression of the ion pair system. Analysis of the electron-density distribution confirms the real chemical nature of the extra C−F bond. Structure and stability of the system are characterized ab initio, and a spectrum of electronic perturbations is considered. The ways of forming the systems are discussed, and the spectroscopic parameters are predicted, facilitating their detection in experiments.

1. Introduction

Carbon is a flexible atom offering a spectrum of bonds with other atoms via different possible sp^n hybridizations of its orbitals. This leads to a huge variety of properties of carbon-containing compounds, including those with important biological, medical, and materials applications (organic molecules, polymers, diamond, nanotubes, molecular electronics, and so forth). New bond patterns could thus mean new properties and new uses.

However, unlike heavier atoms with larger sizes allowing geometric accommodation of more neighbors, and with a larger number of readily accessible orbitals enabling actual bonding of these neighbors, carbon is rather stubborn in showing a hypervalent character. Rare examples include CLi_m ($m = 5$, 6)[1−3] and some complex organic compounds.[4,5] A reagent with a high chemical activity, commonly known to provoke such a character in heavier atoms, is fluorine. In particular, the nearest analogue of carbon, silicon, can form SiF_m and (more stable) SiF_m^- ($m = 5$, 6) compounds.[6−9] Similar carbon systems, CF_5 and CF_5^-, have been predicted to be weakly and somewhat more stable, respectively, to dissociation into $CF_4 + F$ (F^-).[6,10] In the present work, super-fluorination of the next larger saturated fluorocarbon, $C_2F_6 + F^{(-)} \rightarrow C_2F_7^{(-)}$, is considered.

2. Methods

Ab initio calculations have been carried out at the MP2 level by means of the *NWChem* package[11] and the produced results visualized using the Molekel package.[12] The basis sets employed have been cc-pVDZ for Na and aug-cc-pVDZ for C and F atoms, as incorporated into *NWChem*. Coordinates of all atoms have been optimized in the C_1 symmetry in order to minimize geometry constraints and thus avoid artificial stable geometries. A few subsequent calculations at the fixed optimized geometries have then been performed with larger basis sets, cc-pVTZ (Na) and aug-cc-pVTZ (C, F), to verify energy predictions.

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TABLE 1: Calculated vs Experimental Parameters: Ionization and Dissociation Energies, Electron Affinities (all in eV), and Equilibrium Distances (Å)

parameter	theory	experiment[13]	parameter	theory	experiment[13]
IE (Na)	4.96	5.14	D_e (NaF)	5.50	5.4[a]
EA (F)	3.55	3.40	r_e (NaF)	1.95	1.93
EA (CF_3)	1.71	1.82	r_e^{CF} (CF_3)	1.33	1.32

[a] $D_e \approx D_0 + h\omega_e/2$.

Test calculations at the MP2/(cc-pVDZ, aug-cc-pVDZ) level of theory for small constituents of the system are compared in Table 1 with experimental parameters available from the NIST online database.[13] The predicted values of relevant energies and distances are found to be correct within 5%.

3. Results and Discussion

First, the smaller neutral and ionic systems, $CF_5^{(-)}$ have been confirmed in this work to be weakly bound complexes CF_4:$F^{(-)}$, with a remote F or F^- (Figure 1a). The larger counterparts can be formally obtained by replacing the F atom of CF_4 (pointing away from $F^{(-)}$) by the CF_3 radical (Figure 1b). These are also weakly bound, van der Waals and charge-induced-dipole systems, respectively, with the C_2F_6:$F^{(-)}$ dissociation energies of ~0.01 and 0.3 eV, respectively. The one- and two-carbon cases are structurally similar as a closed-shell molecule (CF_4 and C_2F_6) plus an open-shell atom or closed-shell atomic ion at the hollow between three F atoms of the molecule. The presence of a second such site on the opposite side of the C_2F_6 molecule makes the two cases significantly different.

Molecular ions are stabilized in compounds with counterions. The above geometry of the C_2F_6:$F^{(-)}$ complex suggests trying to add a metal atom (ion) $M^{(+)}$ on the opposite side of the molecule, thereby attempting to stabilize the resulting M^+:C_2F_6:F^- system. The optimized structure of such a system for M = Na, of threefold symmetry, is shown in Figure 2. The calculated vibrational frequencies are all real, indicating a local minimum of energy. Such a structure is expected to be metastable and to have a higher energy relative to MF:C_2F_6. The latter isomer

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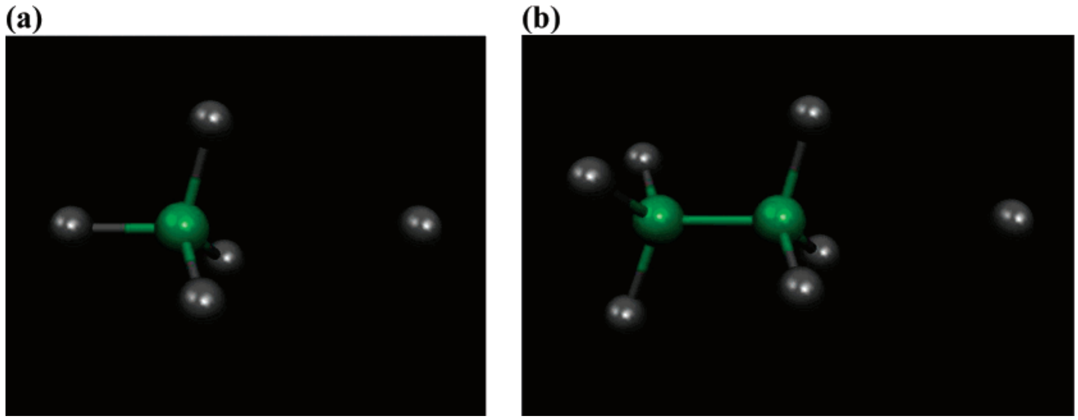

Figure 1. Optimized geometry of the (a) CF_4:F^- and (b) C_2F_6:F^- complexes (at the MP2/aug-cc-pvdz level of theory).

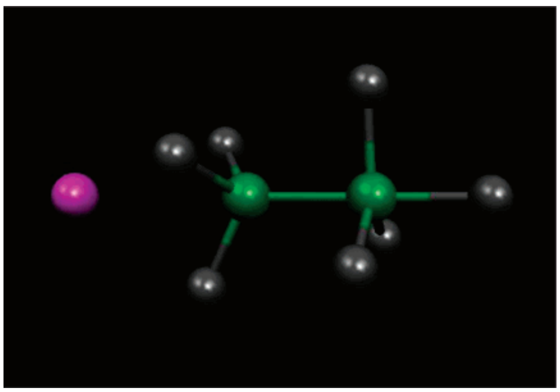

Figure 2. Optimized geometry of the metastable isomer of Na:C_2F_7 (at the MP2/aug-cc-pvdz level of theory).

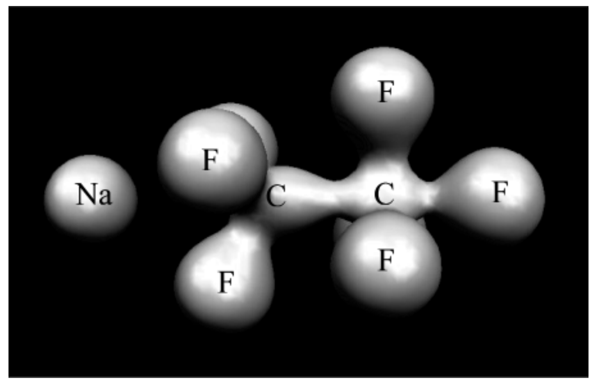

Figure 3. Electron-density isosurface (at 0.16 e/Å^3) for the metastable Na:C_2F_7 isomer (at the MP2/aug-cc-pvdz level of theory).

TABLE 2: Internuclear Distances and Angles (in Å and deg) in the C_2F_6:F^- and $Na_{(3)}$:C_2F_7 Complexes[a] (at the MP2/aug-cc-pvdz level of theory)

system	Na−C/Na−F	C−F	C−C$^{(5)}$	C$^{(5)}$−F	F−C$^{(5)}$−F$^{(remote)}$
C_2F_6:F^-		1.35	1.55	1.34, 2.84[b]	
Na:C_2F_6:F	2.50/2.27	1.39	1.70	1.44, 1.52[b]	91.5
Na_3:C_2F_6:F	3.39/2.30	1.38	1.66	1.45, 1.53[b]	90.8

[a] C$^{(5)}$ represents 5-valent carbon in $Na_{(3)}$:C_2F_6:F. [b] For remote F.

corresponds to adding M on the same side as the additional F atom and forming with it a strongly bound diatom.

The charge transfer from Na to the fluorocarbon component and their subsequent attraction pulls the remote F atom toward Na and presses it into the C_2F_6 molecule, flattening the neighboring CF_3 group in the plane perpendicular to the C−C axis. The C atom of this group thus becomes formally pentavalent and acquires the typical trigonal−bipyramidal environment consisting in this case of four flourines and the other, still tetravalent carbon.

The system geometry parameters are collected in Table 2. The C−C distance stretches by 0.15 Å relative to C_2F_6:$F^{(-)}$, and the new C−F bond along the system axis is slightly longer than those almost perpendicular to it (in accord with the fivefold coordination), while being considerably shorter than in C_2F_6:$F^{(-)}$. The Na−C distance is 0.34 Å shorter than in the corresponding Na^+:C_2F_6 weakly bound (by ∼0.2 eV) complex with Na^+ along the C−C axis. The F−C$^{(pentavalent)}$−F$^{(remote)}$ angle is very close to 90°.

The charge distribution from the natural bond order (NBO) analysis is given in Table 3. The system exhibits a strong ionic character, with positive Na and most of the negative charge on the remote F atom, the C_2F_6 moiety being significantly charged as well. Note that in C_2F_6:F^- the negative charge is entirely on the remote F atom because of closed-shell C_2F_6. In Na^+:C_2F_6, however, the molecule is partially charged and hence attracts a part of the negative charge from F^- in Na:C_2F_6:F. All fluorines are comparably charged, identifying the C_2F_7 subsystem as an integral entity within the complex. The charges on the penta- and tetravalent carbons (hence on the two CF_3 moieties) are nearly equal as well (Table 3).

TABLE 3: Natural Charge Distribution (in e) in the Na:C_2F_7 and Na_3:C_2F_7 Complexes (at the MP2/aug-cc-pvdz level of theory)

system	Na/Na_3	C/F	C$^{(5)}$/F	F$^{(remote)}$
Na:C_2F_7	0.74	1.00/−0.37	1.05/−0.40	−0.47
Na_3:C_2F_7	0.98	1.04/−0.44	1.06/−0.42	−0.47

To verify the existence of a real new bond between C and F (along the system axis) and not only their proximity in space, the total electron density has been calculated (Figure 3). The density is quite significant in the region in question, with its minimal value (along the atom−atom axis) being close to that between the two C atoms and only slightly lower, by 10% and 15%, relative to C$^{(5)}$−F and C−F bonds, respectively. By comparison, Na shows no appreciable density in the ionic bond. The "atoms-in-molecules" formalism[14] predicts a critical point between C$^{(5)}$ and axial F at 0.62 Å from the carbon atom, with the electron density of 0.20, close to 0.19, 0.22, and 0.23 for the C−C$^{(5)}$ (with critical point 0.73 Å away from C$^{(5)}$), radial C$^{(5)}$−F, and C−F bonds, respectively.

The above Na:C_2F_7 complex is stable to dissociation into Na + C_2F_6 + F (hence to removal of Na or remote F) by ∼2.0 eV and is less stable (0.7 eV) to breaking the already stretched C−C bond and splitting into Na + CF_3 + CF_4. The system is, however, higher in energy (by 1.7 eV) relative to $NaCF_3$ +

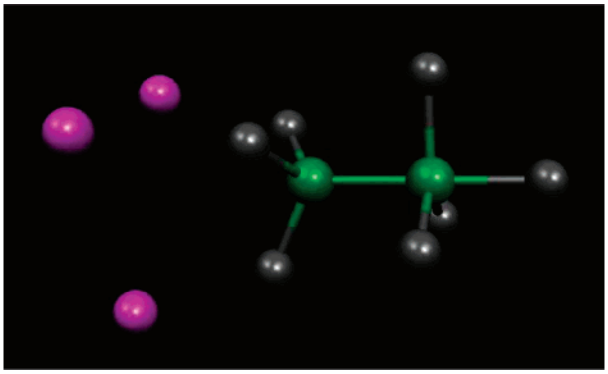

Figure 4. Optimized geometry of the metastable isomer of Na_3:C_2F_7 (at the MP2/aug-cc-pvdz level of theory).

CF_4. These values remain unchanged (within 0.04 eV) when recalculated with the larger, triple-ζ basis set at the fixed geometries (optimized with the double-ζ basis set). The other isomers, with intact NaF along the C−C axis, NaF:C_2F_6 (C−F distance 2.97 Å) and FNa:C_2F_6 (Na−C distance 3.20 Å), are weakly bound (by ~0.2 and ~0.1 eV) and are significantly lower in energy (by 3.3 and 3.2 eV, respectively). The complex featuring a pentavalent C atom is thus indeed metastable. Single-point calculations with the larger basis set confirm these values.

By comparison, the analogous Li:C_2F_7 complex is unstable to dissociation into $LiCF_3 + CF_4$, while heavier M:C_2F_7 (M = K, Rb, Cs) are again metastable. The stability appears to be inversely related to the ionization energy, which decreases from 5.4 eV for Li to 3.9 eV for Cs[13] and determines the charge transfer governing the system formation. This is consistent with the predicted instability of the Al-, Cu-, and Au-based counterparts and will be addressed in detail in a separate publication.

The energy barrier for the M:$C_2F_7 \rightarrow MCF_3 + CF_4$ dissociation is found to be only ~0.01 eV for M = Na and to steadily increase with the M size to 0.15 eV for M = Cs (to be detailed in a separate paper). On the other hand, the ionization energy is known to be significantly lower, at 4.0 eV, for the Na_3 cluster,[13] suggesting another way of stabilization. The optimized structure of the corresponding Na_3:C_2F_6:F complex is shown in Figure 4, with the equilateral-triangular Na_3 unit (Na−Na distance of 3.44 Å) perpendicular to the C−C axis and in front of the three fluorines of the CF_3 group. All real vibrational frequencies confirm this to be a local energy minimum.The geometry parameters are collected in Table 2 and show only minor variations from the case of a single Na atom (except for the increased Na−C separation). The minimal electron density and critical point location between the $C^{(5)}$ and axial F atoms are essentially unaffected as well. Breaking of the C−C bond in this system is associated with the energy barrier of ~0.08 eV, expectedly higher than for Na:C_2F_6:F. The (NBO) electron transfer from the metal component increases, mainly to the C_2F_6 molecule (Table 3). The cluster-based counterpart is more stable toward $Na_3 + C_2F_6 + F$ products (D_e = 2.54 eV) but is still metastable toward $Na_3CF_3 + CF_4$ (1.47 eV lower in energy) due to a higher Na_3−CF_3 binding energy of 2.74 eV. A more detailed study of this and similar heavier-alkali systems is to be reported separately.

The Na:C_2F_7 system considered so far is in its closed-shell, singlet electronic state. Vertical excitation to triplet (with an energy of 6.3 eV) is found to dissociate the system into Na + $CF_3 + CF_4$. This can be associated with no charge transfer between Na and F in the triplet state of NaF. A similar process (except that Na^+ is produced) is to occur upon ionization (with a vertical energy VIE = 10.7 eV, intermediate between IE(Na) = 5.1 eV and IE(C_2F_6) ≈ 14 eV[13]). This could be interpreted in terms of Na^+ not forming a similar complex due to a hindered electron transfer from the positive ion and in terms of the weaker Na^+−F interaction compared to Na−F. The electron attachment, however (with a vertical energy VEA = 1.2 eV falling between the EA values for F and Na), appears to recover the molecule via dissociation into Na + $C_2F_6 + F^-$. This can be due to the higher EA value of F compared to Na and CF_3 (which also preserves C_2F_6) and due to a weaker attraction between Na and F^- compared to that in NaF. The above predictions are based on optimization of the product states starting from the geometry of the original complex.

The vibrational frequencies of the ground-state metastable Na:C_2F_7 complex are calculated to range from 80 to 1185 cm^{-1}, with those at 776, 1050, 466, and 285 cm^{-1} corresponding to the highest infrared intensities (16, 13, 5.4, and 2.4 $(D/Å)^2$, respectively). The rotational constants are predicted to be A = 0.0812 and $B = C$ = 0.0274 cm^{-1}. The experimental tests of the calculations, in particular, by means of microwave or IR spectroscopy, should be facilitated by a very large dipole moment of this extended charge-transfer system, predicted to reach ~16 D, about twice the value for NaF.

The Na:C_2F_7 system could perhaps be formed in experiments by photodissociating NaF in the clusters of the C_2F_6 molecules or in other host (for instance, He or other rare gas) clusters doped with both components, via insertion of C_2F_6 between the recombining Na and F. Even the metastable state may survive for long enough, at sufficiently low temperatures, to be detected with modern techniques capable of tracking transition states. The formation of the Na_3:C_2F_7 counterpart may be more demanding, perhaps with NaF in a sufficiently high initial concentration or with a third dopand, Na_2, present as well.

4. Conclusion

Novel charge-transfer intermolecular complexes, $Na_nC_2F_7$ (n = 1, 3) are designed and confirmed ab initio to be metastable. They have a low barrier to breaking the C−C bond, increasing with descreasing ionization energy of the metal component. Their special feature is a pentavalent carbon atom in the super-fluorinated component, with the additional bond confirmed in terms of the electron density distribution. A set of parameters (structural and spectroscopic) and processes (electronic excitation, ionization, electron attachment) is predicted in order to facilitate experimental (e.g., microwave, IR) observations. The detection of the systems should be assisted by their large dipole moments but may be complicated by their weak stability.

A family of similar systems with unusual bond patterns and unique properties may exist and be produced in experiments. Their investigation is currently in progress. New bond patterns in carbon-based systems may result in new chemical and physical properties of interest.

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References and Notes

(1) Kudo, H. *Nature (London)* **1992**, *355*, 432.
(2) Harcourt, R. D. *J. Organomet. Chem.* **1994**, *478*, 131.
(3) Wang, Z. Z.; Zheng, X. G.; Tang, A. C. *THEOCHEM* **1998**, *453*, 225.
(4) Akiba, K. Y.; Moriyama, Y.; Mizozoe, M.; Inohara, H.; Nishii, T.; Yamamoto, Y.; Minoura, M.; Hashizume, D.; Iwasaki, F.; Takagi, N.; Ishimura, K.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 5893.
(5) Yamashita, M.; Yamamoto, Y.; Akiba, K. Y.; Hashizume, D.; Iwasaki, F.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 4354.

(6) Gutsev, G. L. *Chem. Phys.* **1992**, *166*, 57.
(7) Gutsev, G. L. *J. Chem. Phys.* **1993**, *99*, 3906.
(8) Cooper, D. L.; Cunningham, T. P.; Gerratt, J.; Karadakov, P. B.; Raimondi, M. *J. Am. Chem. Soc.* **1994**, *116*, 4414.
(9) King, R. A.; Mastryukov, V. S.; Schaefer, H. F. *J. Chem. Phys.* **1996**, *105*, 6880.
(10) Gutsev, G. L. *Chem. Phys.* **1992**, *163*, 59.
(11) Aprà, E.; Windus, T. L.; Straatsma, T. P.; Bylaska, E. J.; de Jong, W. et al. *NWChem, A Computational Chemistry Package for Parallel Computers*, version 4.7; Pacific Northwest National Laboratory, Richland, WA 99352-0999, 2005; http://www.emsl.pnl.gov/docs/nwchem/.
(12) Flükiger, P.; Lüthi, H. L.; Portmann, S.; Weber, J. MOLEKEL 4.3; Swiss Center for Scientific Computing, Manno, Switzerland, 2002; http://www.cscs.ch/molekel/.
(13) *NIST Chemistry WebBook*; NIST Standard Reference Database Number 69, June 2005 release; http://webbook.nist.gov/chemistry/.
(14) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, 1990.