Trapped-molecule charge-transfer complexes with huge dipoles: M–C_2F_6–X (M = Na to Cs, X = Cl to I)†

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Novel intermolecular complexes, with a small molecule sterically trapped between a pair of ions, are designed and characterized. The molecule is found to undergo minor shape distortions and to remain almost neutral, and the complexes to have very large dipole moments (up to ~40 D). The systems' stability, ion-molecule interaction and stored energy are investigated, and the vertical excitation, ionization and electron-attachment are described. Variations of geometry and of the above properties with the alkali-metal and halogen components are analysed as well.

Introduction

Alkali-metal halides, MX, in their ground states are exemplary ion-pair systems with a strong charge separation. Upon stretching from its equilibrium, each such diatom is essentially a pair of ions, M^+ and X^-, up to a rather long distance (~10 Å) where the avoided crossing occurs, with the (singlet) excited state correlating diabatically to the neutral-atom asymptote. It appears interesting to try to insert a small molecule between these ions (there is sufficient room), and to see if it can be trapped, particularly when having a suitable concave geometry on both sides to prevent M^+ and X^- from slipping around the molecule and recombining.

If such complexes could be formed, they might find various applications, such as:

(1) molecular systems with very large dipole moments (due to the ion charges far separated by the inserted molecule) as potential highly sensitive sensors or intense emitters of radiation;

(2) storage of energy at molecular level, since the Coulomb attraction between the two separated ions could be recovered when they do recombine *via* breaking the complex; and

(3) molecular-scale devices for dealing with molecules in electric field (of ions) *via* a perturbation of their electronic structure as well as their geometry modification due to compression by the attracting ions.

Earlier studies[1] dealt, in particular, with a geometrically flat benzene molecule between alkali-metal and halogen ions, and the focus was on the ion–pi interactions. Another suitable type of molecules, with two concave (tripod-shaped) sides, is ethane and its halo-derivatives. In the present work, a series of corresponding M–C_2F_6–X complexes are studied in terms of their structure, stability, charge distributions, dipole moments and some other electronic properties such as spin excitation, ionization, and electron affinity.

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In the previous work,[2] for the case of dicarbon hexafluoride, C_2F_6, squeezed into (stretched) alkali fluorides, MF (M = Na to Cs), the resulting M–C_2F_7 complexes had the molecule significantly distorted and featuring a penta-valent carbon atom, with an additional C–F bond formed. The inserted molecule carried a considerable (negative) charge, thus leading to a strong ionic character of the overall binding, and in this regard the systems were qualitatively similar to analogous species with a (positively charged) single rare gas atom trapped between two atoms of different electronegativities, such as H and X.[3] The purpose of the present study is to investigate analogous M–C_2F_6–X systems with different axial halogens X = Cl to I and to check if the structure of the inserted molecule can be mainly preserved, the molecule remain essentially neutral, and the complex be stabilized mainly by non-covalent interactions with the molecule, such as polarization and steric entrapment.

Computational method

All *ab initio* calculations have been performed at the MP2 level with the basis sets aug-cc-pVDZ for C, F and Cl atoms, cc-pVDZ for Na, and Stuttgart's relativistic effective core potentials and associated basis sets RSC for K to Cs and RLC for Br and I.[4,5] The NWChem quantum-chemistry package,[6] incorporating these bases, has been employed. Full low-symmetry (C_1) optimizations have been carried out, followed by vibrational-frequency calculations to confirm the local minima of energy. The optimized structures have been plotted with the ViewMol3D software[7] and the electron-densities with the Molekel software.[8]

Test re-optimization of Na–C_2F_6–Cl with a larger, (aug-)cc-pVTZ basis set[4,5] has produced only minor variations in geometry, within 0.03 Å (or 1%) in atom–atom distances, the same relative deviation being observed for the dipole moment. The corresponding dissociation energy, as well as vertical perturbation (excitation, ionization, electron-attachment) energies have varied within 0.2 eV upon re-optimization, while being accurately reproduced (within 0.01 eV) by single-point calculation at the (aug-)cc-pVDZ geometry. The energy values for all other complexes, less sensitive to such a basis set alteration (affecting less atoms), have therefore been corrected by single-point calculations with the larger basis set.

Results and discussion

First, complexes with the ethane molecule have been studied and found to be unstable for any alkali-metal : halogen (M : X) combination attempted, with the "linear" (regarding the M–C–C–X arrangement) M–C_2H_6–X geometry corresponding to the saddle point. Upon energy minimization, the M and X atoms (ions) move around the inserted molecule and recombine into the MX diatom. The CH_3 "tripod" thus appears to be too shallow to stop the mutually attracting ions, apparently because of rather short ($\approx$1 Å) CH bonds. The calculated electron density distribution of C_2H_6 is shown in Fig. 1 and exhibits no visible barriers for a spherical ion (M^+ or X^-) to slip between the CH bonds. One could also expect that the electron density being pulled from H to C reduces the axial concavity as well.

A higher concavity along the C–C axis, due to longer carbon–halogen bonds, can be provided by ethane hexahalides, for instance C_2F_6. In addition, the electron density is expected to concentrate on the highly electronegative fluorines. Calculations confirm this and predict appreciable axial density-depressions (hollows) at the ends of C_2F_6 (Fig. 1). Inserting such a molecule between the (stretched) alkali-halide ion-pairs MX leads, upon optimization, to stable "linear" isomers with the molecule trapped between the ions. In the present work, a series of such complexes have been generated for M = Na to Cs with X = Cl, and for M = Cs with X = Cl to I. A typical optimized geometry, similar for all complexes, is illustrated in Fig. 2. Each system is of C_3 symmetry and has ^{1}A ground electronic state.

The inserted molecule generally preserves its structure and forms no new bonds, unlike in the case of analogous M–C_2F_7[2] (with one flattened CF_3 group and an additional axial C–F bond and hence penta-valence of one carbon). For M–C_2F_6–X (X = Cl to I) this can be interpreted in terms of lower chemical activity of heavier X compared to F, difficulty for larger X to approach C closely enough, and weaker M–X attraction at longer distance (due to the larger size of X).

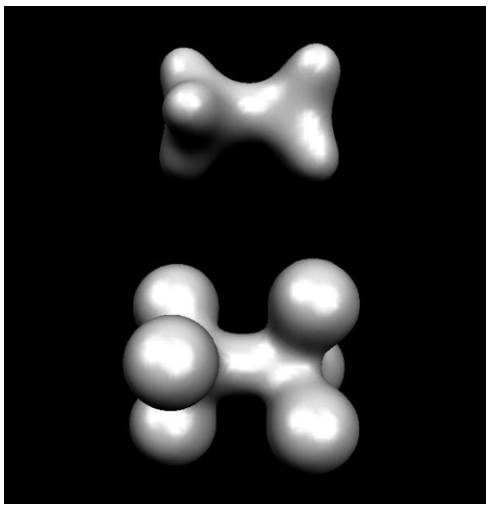

Fig. 1 Electron density distributions in C_2H_6 (top) and C_2F_6 (bottom), for the cut-off value of 0.1 a.u.

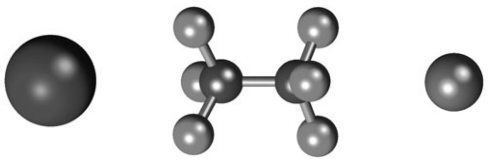

Fig. 2 Equilibrium geometry of Cs–C_2F_6–Cl.

Within the complexes, the C_2F_6 molecule has an almost unchanged (within 0.01 Å) C–C bond length and slightly modified C–F distances and CCF angles (Table 1). By comparison, in M–C_2F_7 the C–C and C–F bonds stretch by up to $\approx$0.1 Å.[2] The CF_3 group slightly opens on the X side and slightly closes on the M side of M–C_2F_6–X (by within 3° in CCF), likely due to the electrostatic interactions between the negative charges on X and F and a positive one on M. The CF_3 distortion is accompanied by minor shortening and lengthening (within 0.03 Å), respectively, of the C–F bonds. All M–X separations are between 7 and 9 Å and thus within the ion-covalent crossing distance, ensuring the ion-pair character of the two terminal atoms.

In the M–C_2F_6–Cl series, the M-nearest C and Cl-nearest C axial distances monotonically increase (the latter much more slowly) from M = Na to Cs (Table 1). This is apparently due to, respectively, increasing size of M (similar to the case of M–C_2F_7[2]) and, as a result, reducing M–Cl Coulomb attraction (at relatively slowly increasing M–Cl distance). Here the charge on C_2F_6 is ignored, as justified later in this paper. Similar interpretation applies to the mirror variations in the Cs–C_2F_6–X series, with the X–C distances increasing faster (with the size of X), than the Cs–C ones (with reducing electrostatic interaction with X). The total M–X length of the complex steadily increases from M = Na to Cs and then from X = Cl to I.

The energy D_e for the system dissociation into components, *i.e.* M + C_2F_6 + X, is on the $\approx$1–2 eV scale and increases from M = Na to Cs (Table 1) in M–C_2F_6–Cl, seemingly contradicting the above stated reduction of the M–Cl attraction. Note, however, that the longer M–Cl separation does imply a lower energy for dissociation into the M^+ and Cl^- *ions* (relevant for the above interpretation) while the D_e values are relative to *neutral* M and Cl. The atomic ionization energy decreases from M = Na to Cs, thus raising the energy of the M + C_2F_6 + Cl neutral asymptote, −IE(M) + EA(X) relative to the ionic one, hence leading to the increase in D_e. By comparison, in M–C_2F_7 the D_e values increase as well from M = Na to Cs and are larger (up to $\approx$2.5 eV)[2] due to opposite charges being closer to one another. In Cs–C_2F_6–X, the relative energy of the neutral asymptote also increases from X = Cl to I *via* decreasing EA(X), but more slowly. As a result, the D_e value drops in this series of complexes (Table 1).

The calculated natural charges (Table 2) indicate an almost complete transfer of a single electron from M to X, while the inserted molecule remains almost neutral, with a charge $q(C_2F_6) = -q(M) - q(X)$ between −0.07 and +0.01 e. This is much less (in absolute value) compared to up to −0.5 e on C_2F_6 in M–C_2F_7.[2] The far-separated M^+–X^- ion-pair produces a very large dipole moment (above 30 Debye) in the complex, the value varying in accord with the M–X

Table 1 Equilibrium parameters (in eV, Å, degree) of the M–C_2F_6–X complexes

System	D_e[a]	R_e (M–C)	R_e (C–C)	R_e (C–F)	R_e (C–X)	∠F–C–C
C_2F_6			1.54	1.34		110
Na–C_2F_6–Cl	1.46	2.57	1.54	1.35, 1.31[b]	3.11	113, 106[b]
K–C_2F_6–Cl	1.96	3.13	1.55	1.36, 1.33[b]	3.19	113, 106[b]
Rb–C_2F_6–Cl	2.10	3.30	1.55	1.36, 1.33[b]	3.20	112, 106[b]
Cs–C_2F_6–Cl	2.37	3.50	1.55	1.36, 1.33[b]	3.22	112, 106[b]
Cs–C_2F_6–Br	1.60	3.51	1.54	1.36, 1.33[b]	3.38	112, 107[b]
Cs–C_2F_6–I	1.37	3.52	1.54	1.36, 1.33[b]	3.62	112, 107[b]

[a] M–C_2F_6–X → M + C_2F_6 + X. [b] On the X side.

Table 2 Natural atomic charges and dipole moments (in e and D) of M–C_2F_6–X

System	q(M)	q(C)	q(F)	q(X)	μ
C_2F_6		1.06	−0.35		
Na–C_2F_6–Cl	0.97	1.05, 1.10[a]	−0.39, −0.33[a]	−0.98	29.8
K–C_2F_6–Cl	0.99	1.03, 1.06[a]	−0.38, −0.34[a]	−0.92	33.6
Rb–C_2F_6–Cl	0.99	1.03, 1.06[a]	−0.38, −0.34[a]	−0.92	34.7
Cs–C_2F_6–Cl	1.00	1.03, 1.06[a]	−0.38, −0.34[a]	−0.93	35.8
Cs–C_2F_6–Br	1.00	1.04, 1.09[a]	−0.38, −0.33[a]	−0.98	36.7
Cs–C_2F_6–I	1.00	1.04, 1.08[a]	−0.38, −0.33[a]	−0.98	38.0

[a] On the X side.

distance from the smallest one for Na–C_2F_6–Cl to the largest one for Cs–C_2F_6–I. These values significantly exceed those for M–C_2F_7 (up to 21 D) as a result of incomplete charge transfer to the remote (axial) F in those systems.

Fluorines in C_2F_6 are negative and carbons are essentially positive ions, the charges being very similar in any M–C_2F_6–X (Table 2). By comparison, in M–C_2F_7 the F atoms are somewhat more negative due to the extra charge on the molecule.[2] Comparison with the (natural) charge distribution in the isolated C_2F_6 (calculated at the same level of theory) shows polarization of the molecule in the dipole field of the ions (Table 2). The positive charge is a little higher on the carbon farther from M^+ and the negative charges on F atoms are a little lower near X^-. As a result, the CF_3 groups on the M and X sides are, respectively, slightly negative and positive (within ≈0.1 e), leading to an induced dipole moment directed oppositely to the overall dipole of the system. In particular in Na–C_2F_6–Cl, for the essentially neutral (since q(Na) ≈ − q(Cl)) inserted molecule, $\mu_{ind}(C_2F_6)$ ≈ μ(complex) − q(Na) R_e(Na–Cl) = −3.7 D. This value reduces to ≈−3.2 D in Cs–C_2F_6–I, for the weaker field of the more distant ions.

Such a significant dipole moment would suggest an appreciable contribution from polarization. On the other hand, the mutually attracting M^+ and X^- ions squeeze the inserted molecule, so electrostatic repulsion can contribute as well. The corresponding energy component can be estimated by approximately separating the Coulomb interaction of the terminal ions: $V \approx q(M)q(X)/R(M–X) + V_{int}$. Then $V_{int}(R_e) \approx -[q(M)q(X)/R_e(M–X) + IE(M) - EA(X) + D_e]$, with $R_e(M–X) = R_e(M–C) + R_e(C–C) + R_e(C–X)$, represents all the ion–molecule interaction components at the equilibrium geometry. These V_{int} values are negative, with largest for Na–C_2F_6–Cl (−0.91 eV) and almost invariant (−0.66 ± 0.02 eV) for the heavier systems, indicating the repulsion between the ions and the inserted molecule to be weaker (in energy) than its polarization by the ions. Comparison with $-D_e$ values shows the significance of this interaction in the total binding (up to ≈60% for Na–C_2F_6–Cl).

Vertical ionization of an M^+–C_2F_6–X^- system is dominated by removal of the extra electron from X^-, in accord with the calculated natural charges in $(M–C_2F_6–X)^+$ at the neutral-system geometry. This requires less energy for a less electronegative X and if the nearby alkali cation is farther away. Accordingly, the energies for the process decrease from X = Cl to I in Cs–C_2F_6–X and from M = Na to Cs in M–C_2F_6–Cl (Table 3), being significantly higher than EA(X) due to attraction of the electron to M^+. These VIE values are about half those for M–C_2F_7 (about 11 eV)[2] apparently due to C_2F_7 having a high energy in its resulting neutral state not stabilized by M^+ like its anion.

In a similar way, vertical electron attachment is associated with adding an extra electron to the M^+ component. This will release less energy for lower IE(M) but more energy if the nearby anion is farther away. The former factor appears to win in the M–C_2F_6–Cl series, and the VEA energies decrease (Table 3), being much less than IE(M) due to the extra-electron repulsion from the anion (*i.e.* the electron is attached to a dipole rather than ion). The increase of VEA from X = Cl to I in the Cs–C_2F_6–X series can be due to the other factor, *via* the increasing size of X. For M–C_2F_7 the VEA values are

Table 3 Vertical energies (in eV) of ionization, electron-attachment, and singlet–triplet excitation, and stored energies of M–C_2F_6–X

System	VIE	VEA	VE* (S = 0 → 1)	E_{stored}[a]
Na–C_2F_6–Cl	6.26	2.25	2.08	2.92
K–C_2F_6–Cl	6.09	1.82	2.50	2.38
Rb–C_2F_6–Cl	5.94	1.78	2.45	2.21
Cs–C_2F_6–Cl	5.82	1.61	2.61	2.06
Cs–C_2F_6–Br	4.99	1.64	1.75	1.70
Cs–C_2F_6–I	4.69	1.69	1.45	1.33

[a] $D_e(MX) - D_e$.

significantly lower (about 1 eV),[2] consistent with the negative charge being closer to M^+ (hence smaller dipole).

The vertical excitation from the ground to the triplet state in M–C_2F_6–X is essentially the transition from ionic to neutral M and X, similar to the case of isolated MX diatom. Like for MX at long M–X distances, the M–X interaction in the triplet-state M–C_2F_6–X can be expected to be rather weak. The same applies to the interactions of M and X with closed-shell C_2F_6. The variation of the singlet-to-triplet excitation energy VE* for different complexes, therefore, follows the dissociation energy of the complex (Table 1), increasing from M = Na to Cs and then decreasing from X = Cl to I (Table 3). The considerably higher VE* values (about 7 eV) for M–C_2F_7[2] can again be associated with a high energy of C_2F_7 in the final state of the system.

The VE* values of M–C_2F_6–X are actually somewhat higher than D_e, indicating the triplet-state interaction to be repulsive at the ground-state R_e. The singlet–triplet excitation can therefore be expected to lead to the system dissociation, similar to the M–C_2F_7 case.[2] This is confirmed by test re-optimization of the system in its triplet state, with M and X withdrawing from C_2F_6. The VE* − D_e difference gives the kinetic energy of the fragments, reducing from $\approx$0.7 eV in Na–C_2F_6–Cl to $\approx$0.1 eV in Cs–C_2F_6–I.

Assuming that the M and X atoms produced *via* the dissociation of M–C_2F_6–X can then recombine into the ground state MX diatom, the net energy released in the total process is D_e(MX) − D_e(complex). These values steadily reduce from $\approx$3 eV for the Na : Cl to $\approx$1 eV for the Cs : I based system (Table 3), due to the increase of D_e(M–C_2F_6–Cl) from M = Na to Cs and due to decrease of D_e(CsX) from X = Cl to I. They also evaluate the meta-stability of the complexes which are higher in energy than the MX + C_2F_6 products by the above differences (plus some MX–C_2F_6 polarization).

An efficient channel for releasing the energy stored in the complex could be its photo-excitation to the excited *singlet* state. In isolated MX, the atom–atom interaction in such a state is rather weak as well (similar to the excited triplet state case), and the same can be reasonably expected for M–C_2F_6–X. The overall process and its energy balance would then be similar to the triplet excitation, except with the VE* value for the excited singlet state.

Calculated vibrational frequencies with the highest IR intensities are listed in Table 4 (a full list can be found in the ESI†). They are pretty similar for all complexes, reflecting similar vibrational modes associated mainly with the identical C_2F_6 component, and mainly red-shifted from the values for the isolated molecule. A notable difference is the low-frequency M–X axial stretch, with a significant intensity for relatively light (mobile) M = Na and K but reducing for the heavier metal atoms. The latter mode incorporates in-phase M–C_2F_6 and C_2F_6–X stretches, with the molecule parallel-shifting as a total.

Three (including one doubly degenerate) tabulated highly IR-active modes of isolated C_2F_6 are represented by different combinations of antisymmetric C–F stretches coupled with FCF bends. Two lower-frequency modes correspond, in effect, to the dicarbon oscillating perpendicular to the system axis, and the higher-frequency degenerate mode involves the parallel-shifts of C_2 along the axis as well. In the complex, the M and X atoms hold the molecule relatively tightly, hindering the motions of the F atoms. The two lower-frequency modes of (isolated) C_2F_6 transform into those with the dicarbon oscillating *along* the complex axis (with the higher frequency for the motion with the CF_3 groups opening–closing in anti-phase), apparently due to the effectively increased mass of the fluorine periphery (in contact with M and X). The degenerate mode of (isolated) C_2F_6 splits into two doubly degenerate modes in the complex, each represented mainly by *one* of carbon atoms oscillating perpendicular to the system axis, the frequency being higher (and slightly blue-shifted from the original isolated-C_2F_6 value) for the C atom on the X side.

Conclusions

Parameters of a series of intermolecular complexes consisting of a molecule (C_2F_6) trapped between two atomic ions (stretched alkali-halide diatom, MX) are analysed computationally. The systems are found to be stabilized by a long-range harpooning (electron transfer from the alkali metal to the halogen) through the inserted molecule. The molecule preserves its geometry, is strongly polarized by the ions and held in place by steric interactions due to its concave electron density distribution. With the molecule remaining almost neutral and with $\approx \pm 1$ charges on M and X, such complexes could be formally considered as ultimate molecular-scale devices involving electron transfer through the molecule.

The M–C_2F_6–X systems are metastable, being higher in energy than the recombined MX plus the released molecule. This might allow application of such systems for energy storage at molecular level, at 2 ± 1 eV per system.

The complexes are predicted to have very large dipole moments, in excess of 30 D and increasing with the system size. This is associated with the unit charges localised on atoms of the alkali-halide pair which is considerably stretched by the inserted molecule. Such dipoles could be expected to make these systems very sensitive to light, and to manifest presence and facilitate detection of the complexes, upon their formation, *via* intense photo-spectra.

Table 4 Vibrational frequencies and IR intensities (in cm^{-1} and $D^2/Å^2$) of M–C_2F_6–X

System	ν	I
C_2F_6	693, 1102, 2 × 1237	0.79, 6.40, 2 × 12.76
Na–C_2F_6–Cl	120, 685, 1072, 2 × 1135, 2 × 1282	1.49, 1.82, 8.77, 2 × 4.61, 2 × 6.16
K–C_2F_6–Cl	101, 682, 1076, 2 × 1150, 2 × 1276	1.62, 1.63, 8.76, 2 × 4.54, 2 × 6.35
Rb–C_2F_6–Cl	78, 681, 1077, 2 × 1154, 2 × 1275	0.93, 1.64, 8.86, 2 × 4.43, 2 × 6.41
Cs–C_2F_6–Cl	65, 681, 1078, 2 × 1157, 2 × 1273	0.68, 1.66, 9.03, 2 × 4.30, 2 × 6.46
Cs–C_2F_6–Br	53, 681, 1079, 2 × 1159, 2 × 1273	0.58, 1.83, 9.43, 2 × 4.26, 2 × 6.38
Cs–C_2F_6–I	48, 682, 1082, 2 × 1163, 2 × 1270	0.46, 1.91, 9.94, 2 × 4.23, 2 × 5.95

The $M–C_2F_6–X$ systems could possibly be produced by photodissociation of MX diatoms in a cluster of C_2F_6 molecules or in another cluster (say of rare gas atoms) containing both these and alkali-halide molecules. The parting M and X atoms may recoil from the cluster surroundings and move back towards each other, either reforming the diatom or, with some probability, trapping C_2F_6 if it happens to be in their way. This scenario is quite similar to that for formation of MRgX systems in rare gas solids.[3]

An inverse of the above sequence, *i.e.* photodissociation of $M–C_2F_6–X$ and subsequent formation of alkali-halide diatoms could be a way for retrieving the energy stored in the complexes. Again, in a cluster such a process could be more efficient. The complexes could thus be formed and broken by irradiation at different wavelengths.

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