

Supramolecular complexes with insertion-enhanced polarity and tuned IR spectra

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Abstract

Extensive computational studies of structure, stability and related properties of an uncommon intermolecular system and its conformers are reported. A small organic molecule is inserted and noncovalently trapped between alkali-halide counter-ions, with their recombination prevented by significant potential energy barriers. This produces an extremely polar complex near-degenerate in energy with its dissociation asymptote and metastable relative to the conformers with the components simply attached. Two possible ways of producing such systems are indicated. Analysis of contributing interactions and dipoles, and their respective additivities is performed. Properties of the ion-molecule sub-complexes are addressed. The IR intensity spectra are simulated and exhibit a peculiar evolution upon formation of the insertion complex, facilitating its experimental detection and differentiation from other conformers. An insight into the influence of the electric field of the counter-ions on a reaction inside the system is offered.

KEYWORDS

insertion complexes, ion pairs, IR spectroscopy, polarity

1 | INTRODUCTION

Interaction of a molecular system in a given electronic state with light is known to be determined by the dipole moment (e.g., for the microwave, or rotational transitions) or its variation (infrared, or vibrational transitions). This leads to numerous possible applications of polar systems in materials science and technology, including but not limited to solar cells [1], lasers [2], nonlinear optics [3]. Highly polar molecules also strongly interact with one another, promoting efficient complex formation and self-assembly, as well as chemical reactions.

The dipole moment value is defined by the separation between the positive and negative charges, so the increase of polarity could be achieved via stretching ion-pair systems, for instance alkali halides MX. The counter-ions could be held apart by inserting between them a molecule, preferably closed-shell one to prevent reactions with the ions, and with a suitably concave electron density to prevent the ion-pair recombination around the insert. However, the energy would increase with the distance between the opposite charges, thus potentially leading to a metastable state. This has indeed been found for a series of halocarbon and hydrocarbon inserts such as C_2F_6 [4], cyclic C_nH_{2n} ($n = 3, 4, 6$) [5–8], adamantane [7] and cubane [9]. Previous work on analogous systems involving benzene molecule and its derivatives was focused on the ion- π interactions, as reviewed recently [10,11].

Stabilization of such a system is possible via, for example, increasing the attraction of the framing ions to the inserted molecule, so a polar insert is preferred from this viewpoint. This was shown for complexes with all-cis isomers of cyclic $C_nH_nF_n$ ($n = 3, 4, 6$) [12–14,8] having large dipoles. In particular, such systems can be even more stable than their usual conformers with the molecule and diatom attached, as for all-cis $C_6H_6F_6$. Another way to stabilization is to increase the radial size of the insert, so that the ion-ion separation would increase if one ion moved around the molecule toward the other one. Examples include increase of the stabilizing barriers from C_2H_6 to C_2F_6 [4] and from cyclic C_3H_6 to cubane. Or, the system would reduce in energy (hence stabilize) if the inserted molecule was flatter, thus stretching the ion-pair less. In this case, however, the dipole would also decrease, as, for example, for the cubane versus cyclic- C_4H_8 complexes, so a suitable balance may be pursued.

Experiments have already explored the initial steps for producing such systems, via formation of constituent binary sub-complexes, for example, $\text{Na}^+\text{-C}_6\text{H}_6\text{F}_6$ and $\text{C}_6\text{H}_6\text{F}_6\text{-Cl}^-$ [15]. Due to a very high polarity of the molecule involved (with a dipole of about 6 D), these species are highly stable, with the dissociation energies of up to 2 eV, which makes them suitable long-living intermediates.

In this paper we expand the variety of the highly polar insertion systems to complexes of trioxane, small crown-type cyclic $\text{C}_3\text{O}_3\text{H}_6$, which is a polar and flatter structural analog of cyclic C_6H_{12} (with three CH_2 groups replaced by O atoms). Such a crown-like species is less polar (since being flatter, with the negatively charged O atoms incorporated in the cycle) than all-cis cyclic $\text{C}_6\text{H}_6\text{F}_6$, but also not so exotic or difficult to produce as the latter high-energy isomers [16]. Besides, previously the larger crown-type molecules helped to stabilize the elusive CF_3^- anion paired with an alkali cation [17], as well as to achieve a super-alkali behavior of their complexes with alkali metal atoms [18]. The latter feature is of interest to check for the smaller counterpart here.

Still larger structural counterparts of the above systems have also been studied, for instance hexacyclen and calix[4]pyrrole hosting pairs of alkali and halogen ions [19,20]. These are examples of a broad variety of macrocycles as receptors of inorganic ion-pairs [21], with the present systems representing smaller analogues.

Another aspect is related to chemical reactions in electric fields found to be able to considerably affect the reaction probability [22,23]. In particular, the barrier for isomerization of the inserted molecule can be reduced significantly under the combined influence of the field and pressure of the (attracting) counter-ions, as demonstrated for cubane [9]. In the present case, due to the spatial proximity of the halogen atom to the hydrogen side of trioxane, hydrogen-atom transfer from the molecule to the halogen atom is possible, altering the system. In the insertion complexes $\text{M-C}_3\text{O}_3\text{H}_6\text{-X}$, this process would occur in the presence of the counter-ions. It is interesting to evaluate the effect of the intra-system field on the process probability.

2 | METHODS

Ab initio calculations at the MP2 level of theory appropriate for the relevant noncovalent interactions, in particular involving strong charge transfer, have been performed by means of the NWChem package [24]. The incorporated extensive aug-cc-pvtz basis sets for light atoms and Stuttgart's RLC effective core potentials and related basis sets for heavy atoms (Cs, I—with the core replacing 46 electrons) have been employed [25]. The adequacy and good performance of the approach are illustrated by favorable comparisons of the predicted and experimental equilibrium parameters of constituent diatomic interactions, as shown in Table 1. The deviations do not exceed 10% and are generally much smaller. These deviations are largest for the D_e values and expected to be smaller for the longer interatomic separations in the complexes due to potential energy curves converging to dissociation asymptotes.

Full symmetry-unconstrained optimizations have been carried out for all systems. The energy minima and transition states have been confirmed via vibrational frequencies. A sequence of shifts along appropriate coordinate while relaxing other coordinates have been used to evaluate the potential barriers. The atomic charges have been obtained within the natural bond orbital (NBO) formalism [28].

3 | RESULTS AND DISCUSSION

3.1 | Structures, stabilities and polarities

The trioxane molecule is shown in Figure 1 together with its electron density distribution. The equilateral triangles of (closer to axis) hydrogens on one side and oxygens of the other protrude in the opposite directions and can accommodate between them suitable ions in axial positions.

System	D_e (eV)	r_e (Å)	μ (D)
NaCl	4.24 (4.27 ± 0.09)	2.38 (2.36)	9.25 (9.00)
NaI	3.39 (3.15 ± 0.02)	2.73 (2.71)	9.46 (9.24)
NaO	2.80 (2.80 ± 0.04)	2.06 (2.05)	8.49
HCl	4.64 (4.47)	1.25 (1.28)	1.09 (1.11)
HI	3.41 (3.09)	1.59 (1.61)	0.42 (0.45)
CsCl	4.45 (4.62 ± 0.08)	2.93 (2.91)	10.7 (10.4)
CsI	3.59 (3.51 ± 0.02)	3.38 (3.32)	12.3 (11.7)
CsO	3.20 (3.04 ± 0.26)	2.34 (2.30)	8.00

TABLE 1 Equilibrium parameters of constituent atom-atom interactions

Note: Bracketed are experimental values [26,27].

Indeed, the alkali cation M^+ at the (negatively charged) oxygen side and halogen anion X^- at the (positive) hydrogen side can hold the molecule between them, forming an insertion complex (Figure 2), similar to the cases of other inserts such as cyclic C_6H_{12} (although capable of being trapped non-axially) and all-*cis* $C_6H_6F_6$ [7,14,8]. The length of the complex in terms of the M-X distance (5–7 Å) is determined, similar to the case of the free MX diatom, by the relative size of the framing ions, thus increasing from Na to Cs and, for a given M, from Cl to I in the studied series of systems (Table 2).

The dipole-dipole attraction also facilitates stability of other conformers with the MX diatom axially attached to the molecule by the M- or X-end at the oxygen or hydrogen side, respectively (Figure 2). Here the diatom-molecule separations (in terms of the M–O and H–X distances) again correlate to the relative sizes of M and X, so NaX and CsX approach trioxane more closely by their Na- and X-end, respectively. Accordingly, NaX approaches more closely than CsX by their M-ends, while MCl approach more closely than MI by their X ends (Table 2). The attached MX stretch very slightly (within 0.06 Å) and increasingly with the diatom size.

The insertion complexes M–mol–X vary in stability from metastable (for MX = CsCl) to near-degenerate (NaCl) to weakly bound (NaI, CsI)–with energy, respectively, slightly above, almost equal to, or slightly below that for separated mol + MX within about ± 0.1 eV (Table 2). The “attached” complexes are more stable (by up to about 1 eV), apparently due to the preserved strong Coulomb attraction in the unstretched diatoms, with the mol–MX species being more stable than MX–mol, especially for M = Na. The latter relation is readily expected for NaX due to the closer shorter separation for mol–NaX than for NaX–mol, while is less straightforward for CsX with the opposite situation.

The polarity of M–mol–X is clearly related to the M–X separation, with the dipole moments varying from about 16 for MX = NaCl to 22 D for MX = CsI. These values are almost double those for free MX even though being counter-contributed by the oppositely directed dipole of the

FIGURE 1 Optimized geometry (left) and calculated electron density of trioxane—on the hydrogen and oxygen (right) sides, for isosurface at 0.05 a.u

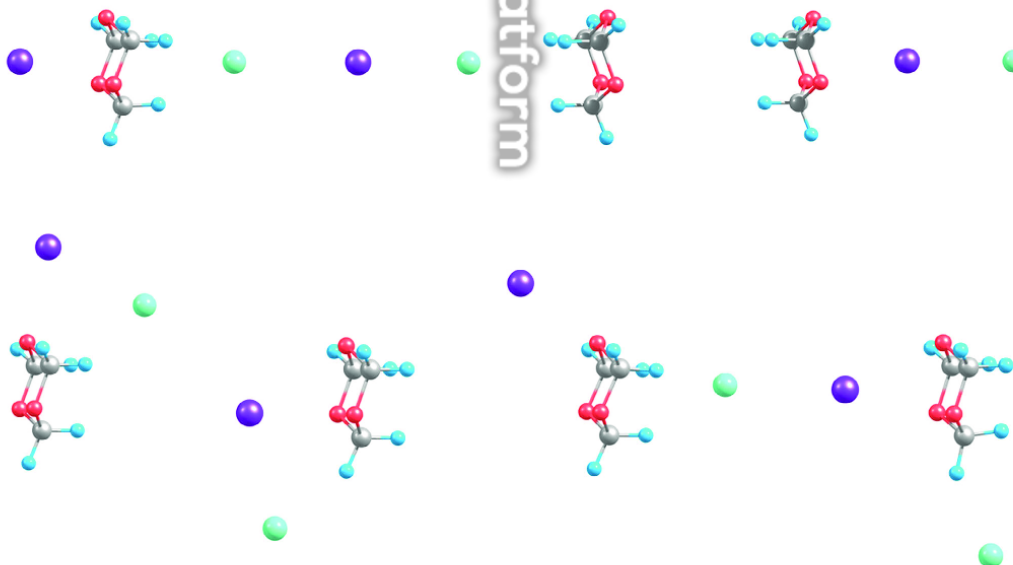
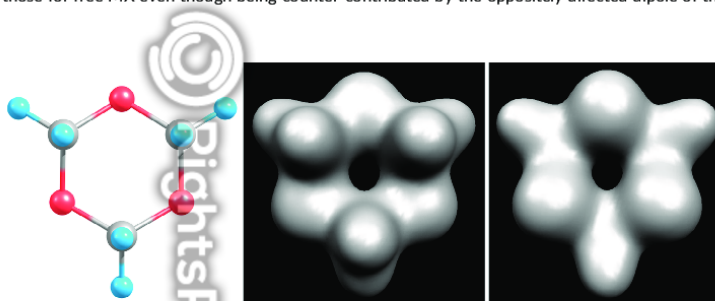


FIGURE 2 Optimized geometries of Cs–mol–I, CsI–mol, mol–CsI (top), CsI:mol, mol:Csl, and transitions states Cs:mol–I and Cs–mol:I (with mol = trioxane)

System	D_e (eV) ^a	r_e (M–O) (Å)	r_e (H–X)	r_e (M–X)	μ_e (D)
Na–mol–Cl	0.018	2.21	2.26	5.26	15.9
NaCl–mol	0.34		2.68	2.38	13.0
mol–NaCl	1.09	2.44		2.38	13.2
Na–mol–I	0.11	2.22	2.63	5.69	17.7
NaI–mol	0.28		3.10	2.74	12.9
mol–NaI	1.12	2.43		2.74	13.8
Cs–mol–Cl	–0.096	2.95	2.30	6.16	19.7
CsCl–mol	0.42		2.66	2.94	14.9
mol–CsCl	0.48	3.33		2.98	14.8
Cs–mol–I	0.055	2.98	2.68	6.62	21.8
CsI–mol	0.36		3.05	3.40	16.2
mol–CsI	0.54	3.30		3.44	16.7
CsI:mol	0.84	2.95	2.95	3.45	9.70
mol:CsI	0.74	3.11	2.71	3.46	11.8
Cs–mol–I [–]	0.52 ^b	3.13	2.77	6.89	
CsI [–] :mol	0.55 ^b		2.99	3.62	
mol–CsI [–]	0.12 ^b	3.20		3.53	
CsI [–] :mol	0.66 ^b	3.20	2.84	3.67	
mol:CsI [–]	0.54 ^b	3.22	2.64	3.66	
Cs–mol	0.31 ^c	3.27			5.88
mol–I	0.13 ^c		2.84		1.84
Cs ⁺ –mol	0.97 ^c	3.12			
mol–I [–]	0.68 ^c		2.94		

^aRelative to MX + mol; for D_e relative to M + mol + X add D_e (MX) from Table 1.

^bRelative to CsI[–] + mol; for D_e relative to Cs + mol + I[–] add D_e (CsI[–]) = 0.96 eV.

^cRelative to mol + atom/ion.

TABLE 2 Calculated equilibrium parameters of the studied complexes (with M = alkali metal, X = halogen, mol = trioxane)

insert (2.2 D for the free molecule). The attached complexes are less polar by about 3–6 D, increasingly so for larger MX (Table 2), with a relatively small difference between mol–MX and MX–mol.

The Cs–mol–I insertion complex thus shows the highest polarity and the lowest reduction of stability relative to its “attached” counterparts, CsI–mol and mol–CsI. The further study is therefore focused on the CsI[–]-based system.

In particular, the weakly bound insertion complex has an intermediate stability between those for the Cs–C₆H₁₂–I and Cs–C₆H₆F₆–I counterparts (about 0.9 eV higher and lower in energy relative to CsI + mol, respectively). This is in accord with the relative polarities of the inserts (hence interactions with the counter-ions), which also correlate with the relative total dipoles of the systems, making the value for Cs–C₃O₃H₆–I intermediate. Similar relations are found among the analogous Cs–mol–Cl systems with these three inserts [8]. The CsI–mol and mol–CsI conformers are less different in energy than those involving C₆H₆F₆, and have opposite relative energies, with mol–CsI more stable by about 0.2 eV, likely due to a closer approach of CsI to trioxane at its flatter oxygen side.

The full axial length of Cs–C₃O₃H₆–I (in terms of r_e (Cs–I)) is about 0.8 Å smaller than for Cs–C₆H₆F₆–I, in accord with the relative axial sizes of the inserted molecules, but, counter-intuitively, almost same (within 0.03 Å) as for Cs–C₆H₁₂–I. Upon insertion in-between the counter-ions, the trioxane molecule is slightly distorted. In particular, the I-facing H-atoms converge by about 0.1 Å in the H–H distance, while the outer H atoms spread by about 0.03 Å. At the same time, the OCO and COC angles are reduced by about 2°, consistent with the Coulomb interactions of its (charged) atoms with the framing ions.

Two more conformers are found, CsI:mol and mol:CsI, with the diatom attached to trioxane not axially, but sideways, and with respectively I or Cs closer to axis (Figure 2). Both these conformers are more stable than those with the diatom attached axially (by 0.2–0.5 eV), with CsI:mol being the most stable of all (Table 2). The diatom is stretched a bit more (within 0.08 Å) when so attached.

These conformers are less polar due to no alignment of the component dipole moments. In CsI:mol, the dipoles of CsI and trioxane are more anti-directed, adding up to a smaller total value. By comparison, the component dipoles are fully aligned in CsI–mol and mol–CsI, leading to total dipoles about 2 D larger than the sum of those for free CsI and trioxane. This can give a measure of the induced-dipole contribution. Similarly for the insertion complex, approximating (within the point-charge model) the dipole moment of the Cs–I framing ion-pair as $e r_e$ (Cs–I) \approx 32 D and

subtracting the (anti-aligned) free-MX dipole, we can get a value about 9 D larger than the actual total dipole of Cs—mol—I. This value can be associated with the induced-dipole (negative) contributions—from the molecule polarized by the counter-ions plus from Cs⁺ and I⁻ polarized by the molecule and by each other.

The insertion complex is predicted to be stabilized by significant energy barriers of about 0.5 eV, separating it from the other conformers, as indicated in Figure 3. The barriers prevent recombination of Cs and I, and correspond to either Cs or I going around the inserted molecule (Figure 2) and thus increasing the Cs—I distance and therefore energy. Such barriers are intermediate in height between those for Cs—C₆H₁₂—I (0.2–0.3 eV) and Cs—C₆H₆F₆—I (0.7–1.0 eV) [8]. These barriers are still higher from the other side and thus hinder the insertion of the molecule in-between the counter-ions, hence formation of the insertion complex from the “attached” ones.

However, the sequential attachment of the ions or the corresponding neutral atoms on the opposite sides of the molecule provide an alternative, barrierless path toward Cs—mol—I (Figure 3). Here the first attachment corresponds to atom/ion–molecule binding in the range of 0.1–1 eV (Table 2), and the second attachment adds further 3.3–3.6 eV, dominating the stabilization of the system via strong ion–ion attraction, especially for the neutral channel involving charge-transfer. In particular, the Cs⁺—mol and mol—I⁻ binding energies for mol = trioxane fall between corresponding values for mol = C₆H₆F₆ and C₆H₁₂ [8], in accord with the relative polarities of the molecules. In the present case, however, the cationic binary complex is bound more strongly than an anionic one, opposite to the case of mol = C₆H₆F₆, consistent with the closer approach of Cs⁺ to trioxane at the flatter oxygen side, and different from the case of mol = C₆H₁₂ with near-identical binding of either ion. Apparently, the neutral-atom attachment channel to Cs—mol—I is less likely due to weaker binding of Cs—mol and, more so, mol—I as compared to Cs⁺—mol and mol—I⁻, respectively. This reduces the relative lifetimes of the neutral binary sub-complexes while they wait for the subsequent attachment of the other atom. It should be noted that for either channel, also likely is the second attachment on the same side, leading to recombination of CsI and possible formation of the “attached” conformers.

An interesting related feature is the near-degeneracy of the first steps of the ionic and neutral channels for the dissociation of Cs—mol—I (Figure 3). Indeed, the detachment of Cs⁺ needs only 0.05 eV less energy than the detachment of Cs. A similar situation, but even with inverted energy order is found for detachment of I⁻ versus I (Table 2). This is a consequence of the near-equality of the difference between the ion–molecule and atom–molecule binding energies to the energy gap (0.61 eV) between the ionic and neutral dissociation limits. As a result, the insertion complex could dissociate by either channel almost equally likely, different from the case of free CsI (with the lower-energy neutral channel prevailing).

The ionization energy of Cs—mol and electron affinity of mol—I can be evaluated as IE(Cs) + D_e(Cs—mol) – D_e(Cs⁺—mol) and EA(I) + D_e(mol—I) – D_e(mol—I), respectively. Using the calculated values (Table 2), we get IE(Cs—mol) = 3.1 eV and EA(mol—I) = 3.7 eV, that is, about 0.6 eV smaller and larger than the respective atomic values. In particular, this is a much weaker reduction of IE than found for an alkali-metal atom complexed with a larger crown molecule (up to about 2 eV) [17], likely due to its higher polarity and/or polarizability. Either factor reduces the energy gap between the cationic and neutral systems via stronger interactions with the ion. Indeed, a very crude estimate in terms of the

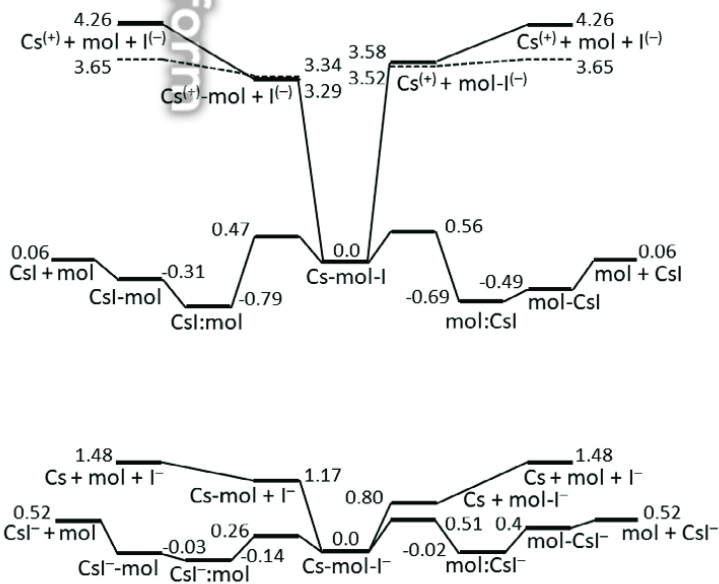


FIGURE 3 Energy diagrams for Cs—mol—I (top) and Cs—mol—I⁻, with mol = trioxane. The dashed lines in the top diagram correspond to the neutral-atom channel. Here the energy origin corresponds to the insertion complex, so that its stabilities relative to various asymptotes and the stabilizing barriers could be readily seen

reduction proportionate to the number of nonhydrogen atoms (hence isoelectronic units) in the crown, for example, 18 versus present 6, would reduce IE by about 1.8 eV, bringing it to about 2 eV.

Finally, addition of the binary interaction energies of Cs–I, Cs⁺–mol and mol–I[−] (relative to their respective dissociation asymptotes) calculated at their geometries inside Cs–mol–I gives a value about 0.54 eV smaller than $D_e(\text{Cs–mol–I})$ relative to its full-dissociation asymptote. This indicates cooperative interactions of the components in the total system, intermediate in value between those for the C₆H₆F₆ and C₆H₁₂ based counterparts (0.63 and 0.40 eV, respectively) [8]. The cooperativity can be attributed to the 3-body interactions dominated, according to the above considerations of polarity components, by the dipoles induced on the molecule by each ion and interacting with the other ion. The above $D(\text{Cs–I})$ value is only about 0.1 eV larger than $D(\text{Cs}^+ \text{–mol}) + D(\text{mol–I}^-)$, thus the ion-ion and ion-molecule interactions contribute almost equally here.

3.2 | Anionic system

All the predicted neutral complex conformers are found to have corresponding anionic analogues of essentially same shapes except CsI[−]:mol which has I notably closer to the axis. The Cs–I distance is increased in all cases (Table 2), in accord with its variation in the free diatom.

Due to much weaker binding in CsI[−] (about 1 eV) as compared to the neutral diatom, and due to Cs interacting with the molecule more weakly compared to Cs⁺, the energy diagram for the corresponding anionic systems spans a much narrower energy range (Figure 3). Unlike for the neutral system, the anionic insertion complex is near-degenerate (within about 0.1 eV) with the attached conformers except mol–CsI[−] which is even significantly less stable. In addition, the energy barrier stabilizing Cs–mol–I[−] toward side-attached CsI[−]:mol is almost halved relative to the neutral case (0.26 vs. 0.47 eV), while that toward mol:CsI[−] is essentially preserved (0.51 vs. 0.56 eV). In addition, the respective reverse barriers from the side-attached toward the insertion conformer reduce more drastically, by about two thirds and more than half, now dropping below the CsI[−] + mol asymptote. So the formation of Cs–mol–I[−] is more likely than for the neutral case, especially via approach of CsI[−] to the molecule by the I-end.

The anionic insertion complex is significantly stabilized relative to the CsI[−] + mol asymptote (by about 0.5 eV), different from the neutral case, again due to much less stable CsI[−] compared to CsI. If for the neutral system, the overall energy barrier between that asymptote and the insertion complex are 0.4–0.5 eV, then for the anionic system the CsI[−] + mol → Cs–mol–I[−] path is overall-barrierless. All anionic attached conformers are less stable relative to the above asymptote as compared to the neutral case (by about 0.2–0.4 eV), with exception of the opposite situation for CsI[−]:mol which is more stable by about 0.2 eV (Table 2).

Alternatively, the (most stable) readily forming CsI:mol complex could perhaps be anionized via electron attachment. The resulting CsI[−]:mol is essentially degenerate with Cs–mol–I[−] and separated from it by a relatively low barrier, thus making the formation of the anionic insertion complex possible via such a channel as well.

Similar to neutral Cs–mol–I, the anionic insertion complex could also be formed via sequential attachment of Cs and I[−] in either order, with no energy barriers (Figure 3). Once the anionic insertion complex is formed in one way or another, photodetachment of the extra electron could lead to the neutral counterpart.

The electron affinity of a CsI-based complex can be evaluated as $EA(\text{CsI}) + D_e(\text{anionic complex}) - D_e(\text{complex})$. In particular, for the calculated values (Table 2) we obtain $EA(\text{Cs–mol–I}) = 1$ eV only, in spite of the very large dipole. Accordingly, the less polar "attached" conformers have still lower EA values in the range of 0.1–0.7 eV. Notably, the limiting values of this range are associated with mol–CsI and CsI–mol, respectively, both having comparable (large) dipoles. The lowest EA value for mol–CsI seems therefore to reflect another factor related to the accessibility of the main electron-density acceptor, cesium cation (see the section below) which is "hidden" between the molecule and iodine in this case, while protrudes outwards in CsI–mol.

3.3 | Charge distributions

Charge transfer is found to mainly involve electron density shift from Cs to I, and show a near-complete transfer of a single electron in all conformers of the neutral system (Table 3). This is consistent with almost no interference of the molecule in the "attached" conformers. In the insertion complex, however, the molecule separates the counter-ions and thus stands in the way of the charge, therefore keeping its small, but appreciable portion of −0.15 e. This value coincides with that for mol = C₆H₁₂ and is slightly smaller than −0.20 e for mol = C₆H₆F₆ [8].

In the corresponding anionic complexes the extra electron predominantly neutralizes the cesium cation, diminishing its charge, with only minor portion going to iodine or molecule (Table 3). An exception occurs for mol–CsI[−], with Cs remaining significantly positive and more than a third of the extra charge going to the molecule. This is possibly due to the molecule being in the remotest position from I, thus allowing the longest distribution of the extra-charge density.

TABLE 3 Atomic natural charges in the studied complexes (with mol = trioxane)

System	$q(\text{Cs})$ (e)	$q(\text{I})$	$q(\text{mol})$
Cs–mol–I	0.995	−0.849	−0.146
CsI–mol	0.979	−0.942	−0.037
mol–CsI	0.965	−0.966	0.001
CsI:mol	0.975	−0.922	0.053
mol:CsI	0.928	−0.925	−0.003
Cs–mol–I [−]	0.055	−0.886	−0.169
CsI [−] –mol	−0.011	−0.935	−0.054
mol–CsI [−]	0.339	−0.979	−0.360
CsI [−] :mol	0.020	−0.911	−0.109
mol:CsI [−]	0.020	−0.927	−0.093

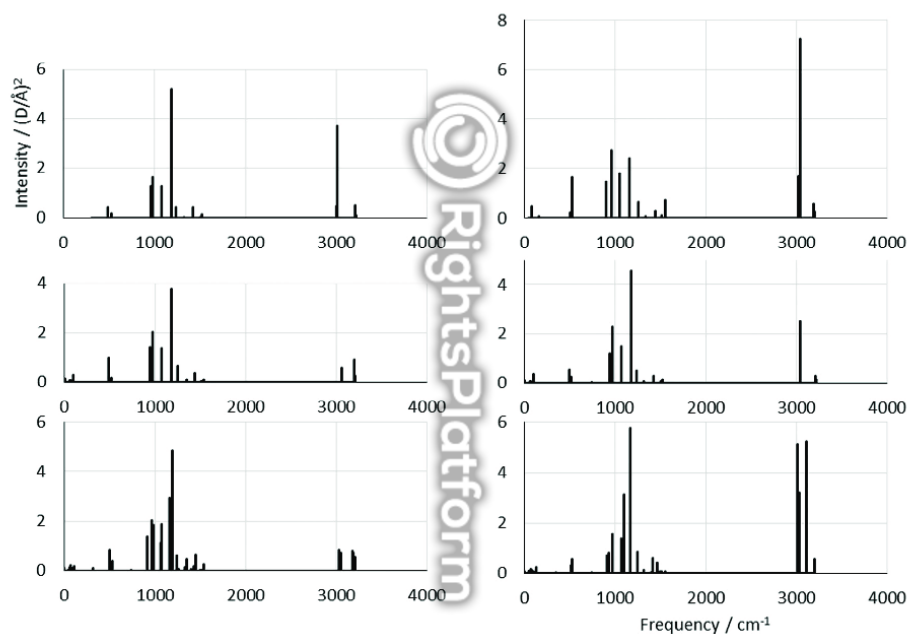


FIGURE 4 Simulated IR intensity spectra of mol (=trioxane) and Cs–mol–I (top), CsI–mol and mol–CsI (middle), CsI:mol and mol:CsI (bottom)

3.4 | IR spectra

The calculated IR intensity spectrum of trioxane exhibits two major lines, near 1200 and 3000 cm^{-1} . The former is brighter (Figure 4) and involves vibrations of the C_3O_3 ring accompanied by rocking motions of the CH_2 groups, while the latter line corresponds to the axial C–H stretch involving the inner H-atoms. In comparison, the spectra of C_6H_{12} and $\text{C}_6\text{H}_6\text{F}_6$ are dominated by only the corresponding higher- or lower-frequency lines, respectively, both being less intense [8]. In the insertion complex Cs–mol–I, the lower-frequency line halves in intensity, likely due to the molecule held tightly between the counterions hindering its vibrations, and the higher-frequency one doubles in intensity, apparently due to the axial C–H stretch occurring along the counter-ions' electric field. By comparison, for mol = C_6H_{12} and $\text{C}_6\text{H}_6\text{F}_6$, the latter increase of intensity is much stronger (about an order of magnitude and more), making the high-frequency lines brighter than for mol = trioxane. Oppositely to the present case, for Cs– $\text{C}_6\text{H}_6\text{F}_6$ –I the lower-frequency line brightens (about threefold) as well, becoming more intense than for the trioxane-based case.

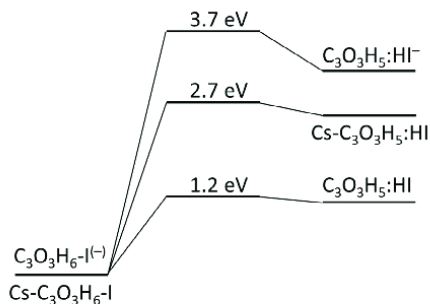


FIGURE 5 Calculated H-transfer reaction barriers for different trioxane complexes

The axial attachment of CsI weakens both these lines, more so for CsI—mol, and more strongly near 3000 cm^{-1} . In particular, the sharp drop of the higher-frequency line intensity for CsI—mol is consistent with the C—H stretch being hindered by CsI attached on the H side, which is apparently not compensated by the added (weaker) dipole field of the diatom. On the contrary, for CsI— $\text{C}_6\text{H}_6\text{F}_6$, both corresponding lines about doubled in intensity. For the side attachment, however, the variations are dissimilar: the lower-frequency line slightly weakens or strengthens for CsI:mol and mol:CsI, respectively, while the higher-frequency one diminishes for the former but increases in intensity and even acquires a “twin” near 3100 cm^{-1} for the latter complex. The suppression of the near- 3000 cm^{-1} line for CsI:mol, even with CsI off-axis and less interfering with the axial C—H stretch, can be associated with the CsI dipole (hence field) here oriented unfavorably (largely against the molecule’s dipole). The high-frequency doublet corresponds to different combination of the motions of the H atoms, predominantly those in CH_2 nearest to CsI. In addition, with reducing the system symmetry upon the side-attachment, there appear less, but significantly bright satellites of the major lines, with very close frequencies.

The insertion complex thus shows distinct spectral features, enabling its experimental detection. The smallest variations of the IR intensity spectra can be noted between the free molecule and mol—CsI, as well as between CsI—mol and CsI:mol, which may complicate their differentiation.

3.5 | Intracomplex reactions

Another potential channel of the destabilization of the insertion complex is the hydrogen/proton transfer to the adjacent halogen atom/anion. Such reactions were found to sometimes readily proceed for the case of alkali-fluoride diatom [9], while the process with a rather modest barrier of about 1 eV for the present mol—I species (see below) might be favored in the field of the framing ions. To analyze such a reaction for Cs—mol—I, one C—H bond pointing to I is stretched stepwise, with other atoms fully relaxed along the way. The energy barrier is predicted to be considerable at about 3 eV. Relaxation of the system after the barrier is passed leads to a metastable system of Cs— $\text{C}_3\text{O}_3\text{H}_5$ and HI attached sideways, separated by about only 0.1 eV barrier from the original complex which could thus readily recover.

To check how the electric field of the counter-ions affects this process, the binary complexes mol—I and mol—I[−] have been similarly investigated. The H-transfer to neutral I corresponds to less than a half of the barrier for the insertion complex (Figure 5), resulting in the $\text{C}_3\text{O}_3\text{H}_5:\text{HI}$ species almost unstable with respect to reversal. For the anionic counterpart, however, the barrier rises to 1 eV higher than for the insertion complex case, and the $\text{C}_3\text{O}_3\text{H}_5:\text{HI}^-$ product is stabilized by about 0.6 eV with respect to the reverse reaction. The triplication of the barrier height from mol—I to mol—I[−] is consistent with the relative reactivity of the halogen atom and its (closed shell) anion. The same argument can apply to more-than-duplication of that barrier for Cs—mol—I, where iodine is essentially anion. Here, however, the presence of Cs⁺ assists, via the electric field, the detachment of the positively charged H atom, thereby moderating the barrier. Overall, the H-transfer is considerably less likely in the Cs—mol—I complex as compared to mol—I.

4 | CONCLUSIONS

A common trioxane molecule is employed as an insert in the uncommon complexes of molecules inserted between alkali-halide counter-ions, with a focus on the Cs—I pair selected due to offering a higher overall stabilization. The so produced Cs—mol—I systems are near-equal (slightly lower) in energy to the CsI + mol dissociation asymptote, thus showing an intermediate case between non- and highly polar (but exotic) inserts corresponding to metastable and stable complexes.

The insertion complex is separated by appreciable (half-eV) energy barriers from the more stable, usual "attached" conformers. One such barrier is, however, significantly reduced and the insertion complex is stabilized relative to the "attached" conformers as well as to the dissociation asymptote, in the corresponding anionic system. The anion-precursor channel could thus be one way of forming the neutral insertion complex, while another one is via subsequent (barrierless) attachment of counter-ions or even neutral atoms.

Curiously, insertion of trioxane into CsI appears to make the system dissociation via neutral-atom or ion detachment equally likely. Another feature is that the electric field of the counter-ions significantly affects the transfer of hydrogen from the molecule to the adjacent halogen atom, making the related energy barrier (hence reaction probability) intermediate between those in mol-I and mol-I⁻. This reflects the interplay of the ions' field favoring the (charged) H transfer and of the anion's reduced reactivity inhibiting the process.

The interplay of the ion-pair and insert polarities results in a high polarity of the Cs—mol—I complex, significantly contributed by the induced polarization of components, which also dominates the cooperative nonadditive interactions. In particular, the dipole moment of the system exceeds 20 D, falling between those for the complexes based on the non- and more polar inserts. This suggests possible applications of such systems, based on light-matter interactions, for example, in microwave and IR spectral ranges, including light detection/sensing and absorption/utilization. It should be noted here that the insertion complex structure is more stabilized by the energy barriers than the axially-attached ones which are vulnerable to relaxation into the much less polar side-attached conformers. The increased polarity could also facilitate stronger inter-complex interactions up to assembly into oligomers.

In spite of the high polarity, the electron affinities of the insertion complex and other conformers are rather low, under 1 eV, although the binary complex mol—I shows an increase of EA from the value for I. This, in particular, would suggest low reactivity of such systems as electron acceptors. The obtained decrease of ionization energy in Cs—mol from that of Cs appears to match the predicted superalkali features in the complexes of alkali metal atoms with larger crown molecules, proportionately to the number of atoms in the molecule.

Formation of the insertion complex is found to notably intensify the characteristic high-frequency IR spectral line of the molecule at the expense of the other, low-frequency line. Such tuning of the IR intensity spectrum is a unique feature as compared to spectral variations for attachment of CsI to the molecule when forming other conformers, which should allow a reliable identification of the insertion complex in experiments. The above evolution of the IR spectrum also differentiates the present system from the C₆H₁₂ or C₆H₆F₆ based counterparts, and suggests potential applications needing similar spectra alterations.

It is hoped that the reported results will stimulate experimental efforts for producing such ternary systems, for example, starting from already accessible binary sub-species. Apparently, the systems studied here represent a huge variety of similar species with different inserted molecules and counter-ions which may have attractive properties.

AUTHOR CONTRIBUTIONS

Mason Sullivan: Data curation; formal analysis; investigation; visualization. **Fedor Naumkin:** Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources; software; supervision; validation; writing-original draft.

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