Intercalation of Halogen Molecules in Alkali Fluoride Lattices: A Theoretical Study

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Abstract: A theoretical study of the host ··· guest interactions in the intercalation compounds $MF \cdot XY$ and $2MF \cdot XY$ (M = Li, K, Cs; X, Y = Cl, Br, I) is presented. A qualitative description of the bonding is obtained in the form of a band interaction diagram by using a Crystal Orbital Difference (COD) analysis of extended Hückel tight-binding band calculations. Quantitative estimates of the host ··· guest interaction energies in these compounds are obtained from periodic Hartree–Fock (HF) calculations on the solids and molecular orbital calculations on a cluster model, including electron correlation through a second-order Moeller–Plesset (MP2) treatment. Periodic HF calculations correctly predict the trends in the structural and vibrational variations resulting from host ··· guest interactions, with formation energies of *ca.* 2 kcal/mol for the $CsF \cdot Br_2$ and $CsF \cdot I_2$ intercalates. General trends in the $MF \cdot XY$ family indicate that the intercalation compounds are not stable for M = K or Li and $XY = Br_2$, and that the host ··· guest interaction energy depends on the energy of the HOMO of the guest molecule XY and on its dipole moment.

Among the variety of intercalation compounds known,[1] those formed by inclusion of halogen molecules in a lattice of CsF[2] are unique in that the guest molecules are neither placed in the van der Waals gap of a two-dimensional lattice, as in graphite or in metal chalcogenide derivatives, nor occupying cages or channels in three-dimensional structures, as in zeolite intercalates. Instead, the halogen molecules transform the cubic lattice of CsF into a layered structure and intercalate between the ionically bound layers of CsF. The only compound previously reported in which Br_2 molecules are intercalated in a two-dimensional host is that of graphite.[3]

Several compounds with two different stoichiometries have been reported, $CsF \cdot X_2$ and $2CsF \cdot X_2$ (X = Br, I), but the only structurally characterized one so far is $CsF \cdot Br_2$. This yellow-orange product retains Br_2 molecules even when heated at 100 °C. The interesting structure of $CsF \cdot Br_2$ (Figure 1) can be described as formed by CsF layers parallel to the *ab* plane, with the Br_2 molecules acting as spacers between layers and alligned parallel to the *c* axis. Alternatively, the lattice can be described as formed by $(Br-Br \cdots F^-)_\infty$ chains and a tetragonal lattice of Cs^+ ions. The Br–Br bond is somewhat weaker (2.324 Å) than in the elemental structure (2.27 Å),[4] and the Br ··· F distance is clearly shorter than the van der Waals sum and longer than the bonding distance in the BrF molecule (1.759 Å).[4] Even if a large number of polyhalide chains have been structurally characterized,[5,6] the Br_2F^- chain is unique in its high symmetry. Previous theoretical studies on X_3^- and X_4^{2-} indicate that the former species is stable, whereas the latter is unstable toward dissociation.[5-7] It is therefore interesting to analyze the electronic structure and stability of the Br_2F^- chains in the matrix of alkaline cations and study how the host ··· guest interactions can compensate for the loss of the cubic CsF structure.

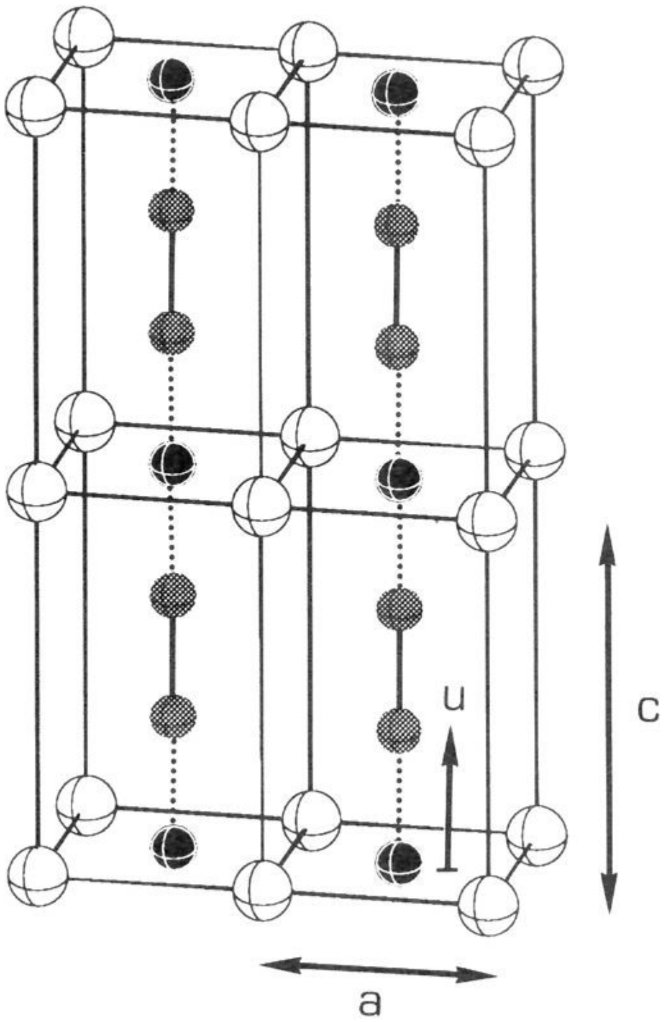

Figure 1. Structure and unit cell parameters of $CsF \cdot Br_2$ (space group *P4/mmm*). White, gray, and black circles represent Cs, Br, and F atoms, respectively.

Another interesting aspect of these intercalation compounds is their ability to add one F and one Br to double or triple bonds (C=C, C=N, or C≡N).[8-10] Previous to the structural characterization, it was suggested[10] that an anionic species Br_2F^- could

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[1] O'Hare, D. In *Inorganic Materials*; O'Hare, D., Bruce, D. W., Eds.; John Wiley and Sons: New York, 1992; pp 166–228.

[2] DesMarteau, D. D.; Grelbig, T.; Hwang, S.-H.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1448.

[3] Selig, H.; Ebert, L. B. *Adv. Inorg. Chem. Radiochem.* **1980**, *23*, 281.

[4] Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1984.

[5] Alvarez, S.; Novoa, J.; Mota, F. *Chem. Phys. Lett.* **1986**, *132*, 531.

[6] Alvarez, S.; Mota, F.; Novoa, J. *J Am. Chem. Soc.* **1987**, *109*, 6586.

[7] Novoa, J. J.; Mota, F.; Alvarez, S. *J Phys. Chem.* **1988**, *92*, 6561.

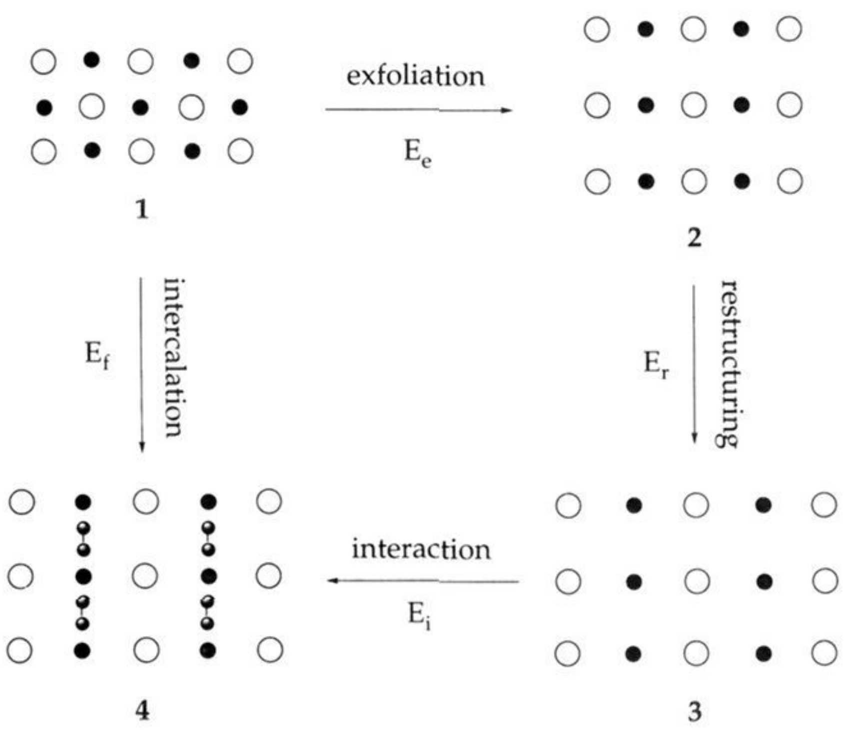
[8] Mir, Q.-C.; DesMarteau, D. D. *Inorg. Chem.* **1991**, *30*, 535.

[9] O'Brien, B. A.; DesMarteau, D. D. *J. Org. Chem.* **1984**, *49*, 1467.

[10] Zheng, Y. Y.; Mir, Q.-C.; O'Brien, B. A. *Inorg. Chem.* **1984**, *23*, 419.

form from the mixture of CsF and Br_2 and that this anion could be the active species in the heterohalogenation reaction. After full characterization of $CsF \cdot Br_2$, it is reasonable to assume that the process takes place at the surface of the solid, involving abstraction of a fluorine atom and de-intercalation of a bromine molecule. All these interesting aspects of the structure and chemistry of $CsF \cdot Br_2$ and its analogues prompted us to undertake a theoretical study of the electronic structure and bonding therein. In this paper we attempt to provide both a qualitative description of the bonding and a quantitative estimate of the host$\cdots$guest interaction energies in the known and yet to be prepared compounds of general formulae $MF \cdot XY$ and $2MF \cdot XY$ (M = Li, K, Cs; X, Y = Cl, Br, I).

For the subsequent discussion it will be useful to describe the formation of an intercalation compound, $CsF + X_2 \rightarrow CsF \cdot X_2$ (**1** → **4**), as a sequence of three hypothetical elementary steps: (i) the *ab* planes of the cubic CsF structure are exfoliated (**1** → **2**) by the simultaneous effect of a shear distortion and a separation of the CsF layers; (ii) the geometry of the CsF layers is restructured to adjust to that required for optimum interaction with the X_2 molecules (**2** → **3**), and (iii) the X_2 molecules interact with the layered CsF structure (**3** → **4**) to yield the intercalation compound at its most stable structure. According to this scheme, we first present a quantitative study of the energy involved in the exfoliation of the CsF planes from the rock-salt structure (E_e) and its effect on both the charge distribution and the Cs−F bonding within a layer by using periodic Hartree−Fock (HF) calculations for extended systems.[12] Next, we analyze qualitatively the interaction (**3** → **4**) energy (E_i) in $CsF \cdot Br_2$ and $CsF \cdot I_2$ from the orbital point of view, with the help of extended Hückel tight-binding (EHTB) band calculations and the corresponding Crystal Orbital Displacement (COD) curves.[11] The qualitative interpretation of the host$\cdots$guest interactions and of the induced structural and spectral changes is confirmed and put in a quantitative basis by more precise band calculations within the HF framework[12,13] and by molecular orbital calculations on a cluster model, including electron correlation through a second-order Moeller−Plesset (MP2) treatment.[14] With these quantitative estimates, we evaluate the overall formation energies (E_f) for the $CsF \cdot X_2$ compounds (X = Br, I) and finally present a prospective study of the energetics of intercalation for other compounds of the families $MF \cdot XY$ and $2MF \cdot XY$.



Exfoliation of the Cubic CsF Structure To Give a Two-Dimensional Lattice

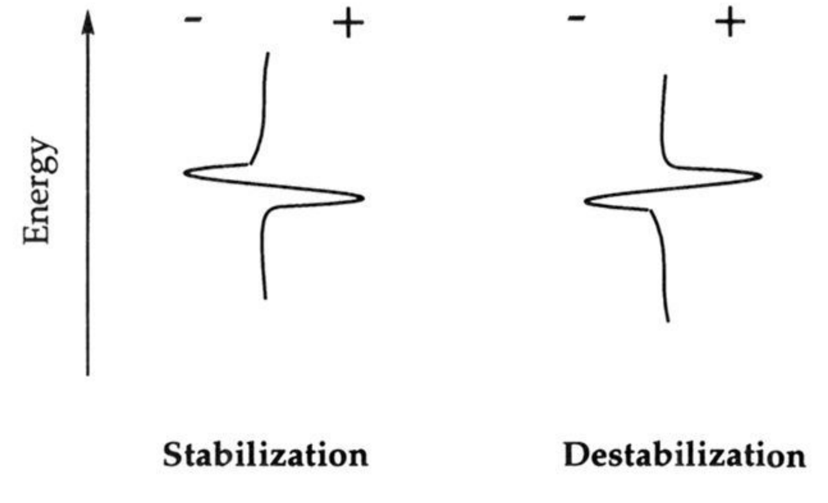
In order to obtain an estimate of the energy needed to transform the cubic lattice of CsF into the two-dimensional structure found in $CsF \cdot Br_2$ (**1** → **2**), we have performed two sets of periodic HF calculations. First, we have optimized the cubic CsF structure ($Fm\bar{3}m$ space group). The calculated unit cell parameter *a* (5.972 Å) and the Cs−F distance (2.986 Å) are in excellent agreement with the experimental values of 6.002 Å and 3.001 Å, respectively. A small amount of valence-electron density is found at the Cs atoms, and a small positive Cs−F overlap population (0.011) is calculated. Both results are consistent with a highly ionic interaction.

In the second set of calculations, the energies for the layered structure **2** (*P4/mmm* space group) were studied at different interlayer separations (c = 7.364, 8.00, and 20.00 Å), keeping the *ab* planes frozen at a = 4.048 Å. The energy required to exfoliate the CsF layers (i.e., to slip and separate the layers) to the distance found in the $CsF \cdot Br_2$ structure (c = 7.364 Å) is 10.5 kcal/mol. Further separation of the layers produces no significant change in the energy.

Orbital Model for the Host$\cdots$Guest Interactions in $CsF \cdot Br_2$

The density of states (DOS) of $CsF \cdot Br_2$, calculated at the EHTB level, can be straightforwardly described in terms of the orbitals of the constituent fragments, since the interactions between Cs^+, F^-, and Br_2 sublattices are weak. The energies and main contributions of the electronic bands are schematically represented in Figure 2 as a block diagram.

Since weak orbital interactions in the solid state are difficult to detect in a DOS diagram among the plethora of non-interacting orbitals, we have recently introduced the crystal orbital displacement (COD) functions as a tool for the analysis of weak interactions in the solid state.[11] In essence, the DOS of a sublattice (or one of its projections) is substracted from that of the complete crystal, and the difference is plotted as a function of the energy. In such a plot, all non-interacting levels vanish, and one is left with a map of the crystal orbitals displaced by interaction between the two sublattices. The two simplest types of peaks to be found in a COD diagram are schematically represented in **5** and correspond to the stabilization and destabilization of a band, respectively.



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The COD curves for the contributions of all the occupied molecular orbitals of Br_2 and of $\sigma^*(Br_2)$ to the DOS of $CsF \cdot Br_2$

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[11] Ruiz, E.; Alvarez, S.; Bernstein, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1994**, *116*, 8207.

[12] Pisani, C.; Dovesi, R.; Roetti, C. *Hartree−Fock Ab Initio Treatment of Crystalline Systems*; Springer-Verlag; Berlin, 1988.

[13] Dovesi, R.; Roetti, C.; Saunders, V. R. *CRYSTAL92*; Universitá di Torino, SERC Daresbury Laboratory, 1992.

[14] Moeller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

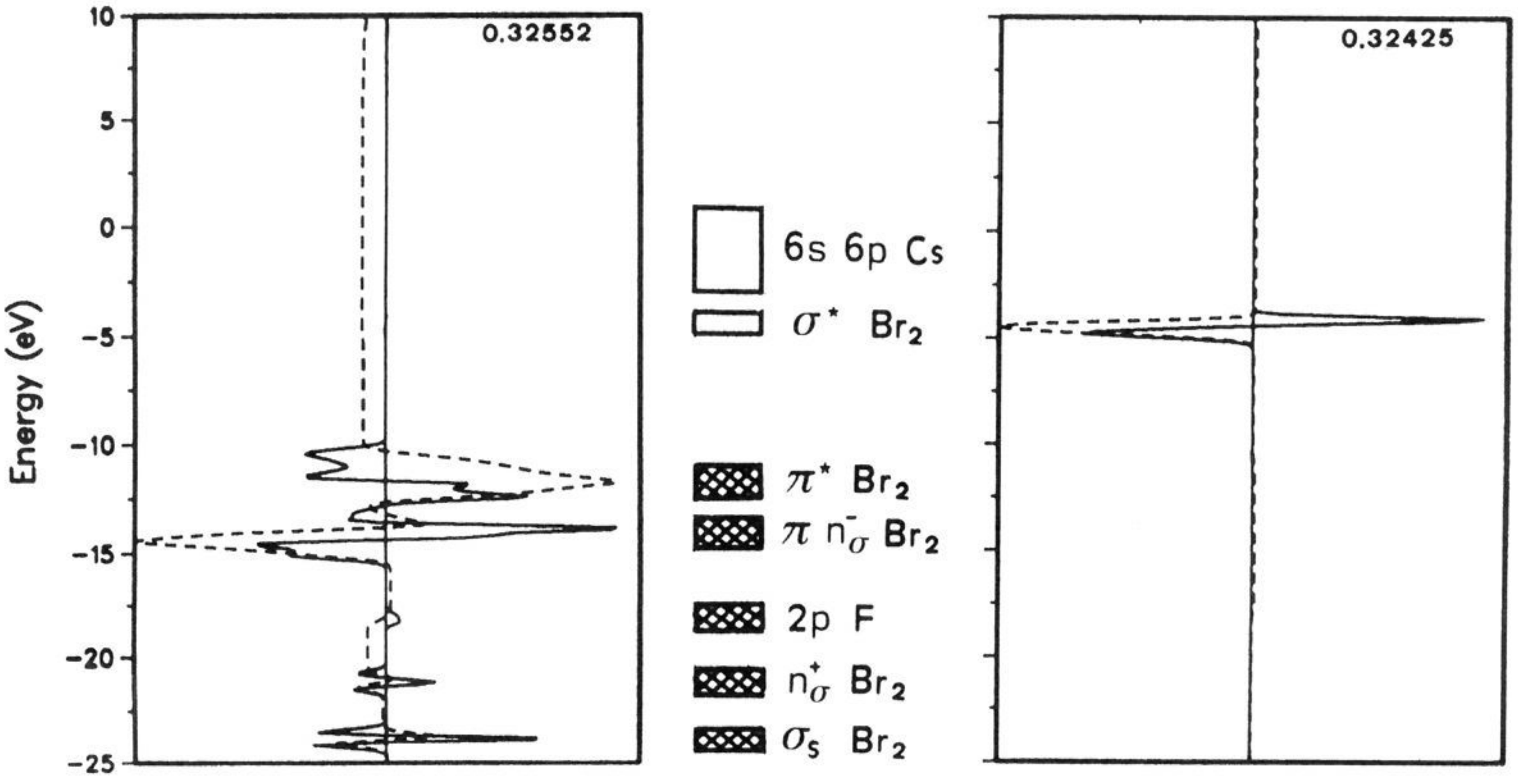

Figure 2. Crystal orbital displacement diagram (COD, solid line) and its integral (ICOD, dashed line) for all the occupied orbitals of Br_2 (left) and for the empty σ^* orbital of Br_2 in $CsF \cdot Br_2$ (right). The full scale corresponds to 0.3255 levels/unit. A block diagram representation of the DOS of $CsF \cdot Br_2$ is also shown.

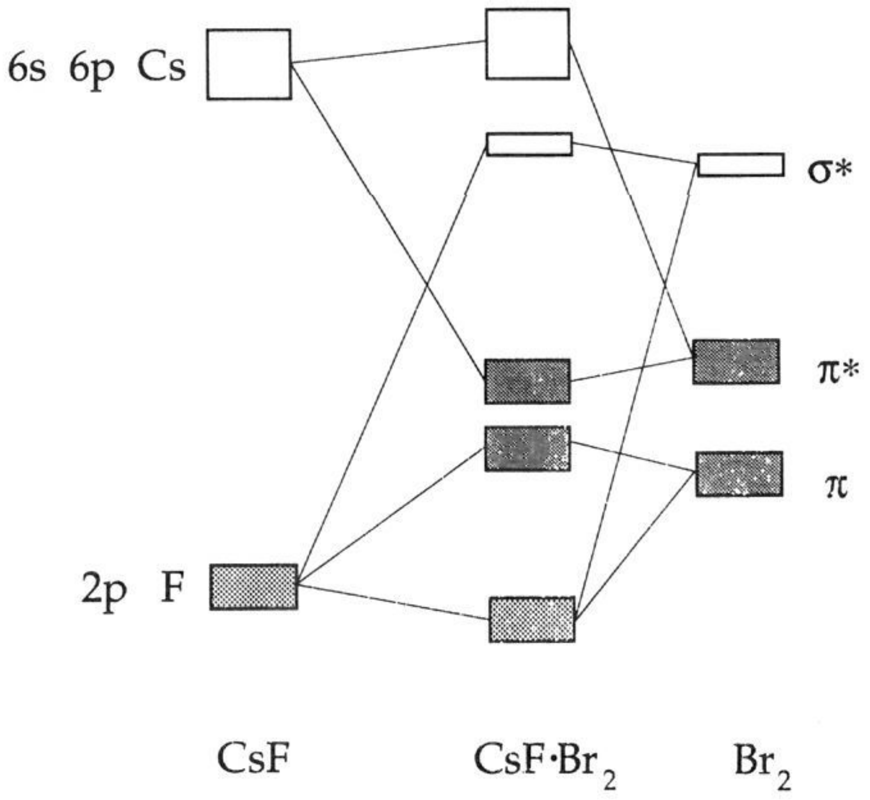

Figure 3. Block diagram for the interaction between the bands of the CsF layers and those of the Br_2 molecules in $CsF \cdot Br_2$, as deduced from the analysis of the COD curves.

are shown in Figure 2. The most intense peaks in the COD diagram for the occupied MO's of Br_2 (Figure 2, left) appear at the energies corresponding to the π and π^* orbitals. From the shapes of these peaks (see **5**) one can conclude that the π and π^* orbitals are respectively destabilized and stabilized upon interaction with the host CsF sublattice. The COD diagram for $\sigma^*(Br_2)$ (Figure 2, right) clearly indicates that this MO is destabilized upon interaction with the CsF sublattice. The analysis of the COD curves for the Cs and F atomic orbitals (not shown) allows us to conclude that the π and σ^* MO's of Br_2 interact with the fluoride ions, whereas the π^* MO's interact with the cesium cations. All this can be summarized in the band interaction diagram of Figure 3. A theoretical study of interactions between Cs^+ ions and independent Br_4^{2-} species, previously reported,[6] revealed a similar orbital interpretation.

The consequences of the host···guest interactions sketched in Figure 3 are the following: (a) The electron density at the Cs atoms is increased (by 0.03 electron in the EHTB calculations). (b) The Br−Br bond is slightly weakened relative to the free molecule. (c) A weak bonding interaction might exist between the Br and Cs atoms. (d) The overall Br···F interaction is predicted to be slightly repulsive from the small negative overlap population; this is a result of the combined effect of two center−four electron repulsions between the occupied π orbital of Br_2 and F^-, and the donor−acceptor interaction between F^- and $\sigma^*(Br_2)$. Such orbital interpretation is in good agreement with the well-known behavior of halogen molecules as acceptors in a variety of compounds.[3,15]

Ab Initio Study of the Host···Guest Interactions in $CsF \cdot Br_2$ and $CsF \cdot I_2$

In order to obtain nearly quantitative estimates of the host···guest interaction energy and of the structural and spectral changes induced by the formation of the inclusion compound, we have performed periodic Hartree−Fock calculations. In order to evaluate the effect of neglecting the electron correlation in the periodic HF calculations we have also carried out several calculations at the MP2 level, by adopting a cluster model (**6**). The computational details for these two types of calculations can be found in the Appendix.

First, we optimized the geometry of $CsF \cdot Br_2$ and $CsF \cdot I_2$. (Table 1) using periodic HF calculations. In general, all the predictions resulting from the qualitative orbital model presented above are confirmed by such calculations: (a) The electron population of Cs in $CsF \cdot Br_2$ increases by 0.02 electron, relative to that in CsF with the cubic NaCl structure. (b) The Br−Br bond is longer than in the elemental structure (by 0.03 Å, compared to an experimental variation of 0.04 Å), and the Br−Br stretching is shifted to smaller wavenumbers (calculated shift, -15 cm^{-1}; experimental shift, -25 cm^{-1}). (c) The I−I bond is slightly elongated, as happens in other I_2 intercalation compounds,[15] but its stretching is not significantly affected by intercalation. (d) A small, positive overlap population is found for the Cs···Br pairs, consistent with the experimentally observed contraction of the CsF layers upon intercalation. (e) The small negative calculated F···Br overlap population would suggest that the net F···Br interaction is destabilizing. However, an MP2 calculation (all-electron basis set) on a simple

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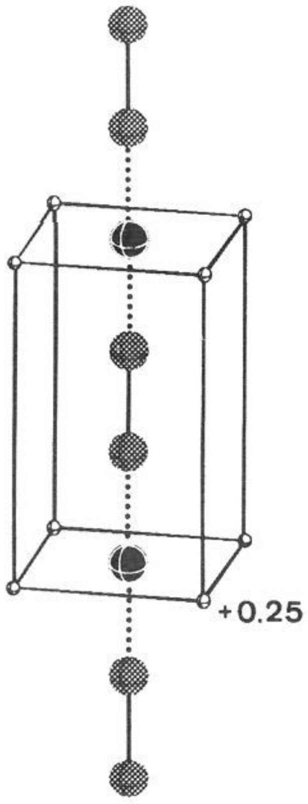
[15] Downs, A. J.; Adams, C. J. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Emeleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973; Vol. 2, pp 1201−1207.

Table 1. Results of Periodic HF Calculations for the Isolated X_2 Molecules and for Their Intercalation Compounds $CsF \cdot X_2$ (X = Br, I), with Experimental Values in Parentheses[a]

	Br_2	$CsF_2 \cdot Br_2$	I_2	$CsF \cdot I_2$
E_t, au	−26.02057	−50.15209	−22.43430	−46.56598
E_e, kcal/mol		10.98		10.98
E_r, kcal/mol		1.81		7.89
E_i, kcal/mol		−14.66 [−8.96]		−20.85 [−15.48]
E_f, kcal/mol		−1.87		−1.97
ν(X−X), cm^{-1}	340 (317)	325 (292)	218 (215)	222 (215)
crystal params				
a		4.340 (4.177)		4.650
c		7.554 (7.364)		8.005
u		0.3437 (0.3423)		0.3280
X−X	2.337 (2.27)	2.369 (2.324)	2.730 (2.662)	2.754
F···X		2.569 (2.521)		2.626
Cs···X		4.020 (3.873)		4.208
Cs···F		3.068 (2.940)		3.288
atomic charges				
Cs		+0.937		+0.966
F		−0.859		−0.808
X		−0.037		−0.079

[a] E_t is the total energy (pseudopotentials); E_e is the exfoliation energy (**1** → **2**); E_r is the energy of restructuring of the CsF layers (**2** → **3**), E_i is the host···guest interaction energy (value corrected for basis set superposition error given in brackets), and E_f is the formation energy of the intercalate from the cubic CsF and the elemental halogen X_2. Vibrational data for isolated molecules were taken from the following: Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.



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model cluster ($F^- \cdots Br_2 \cdots F^-$) estimates this interaction to be stabilizing (binding energy of −12.84 kcal/mol per each Br···F contact), indicating also that the $F^- \rightarrow \sigma^*(X_2)$ bonding interaction is stronger than the $F^-/\pi^*(Br_2)$ repulsion. (f) The relative importance of the two stabilizing interactions, $F^- \rightarrow \sigma^*(X_2)$ and $\pi^*(X_2) \rightarrow Cs^+$, can be gauged by the amount of charge transfer. For $CsF \cdot Br_2$ both terms have a similar weight (0.102 and 0.069 electron, respectively), whereas for $CsF \cdot I_2$ the former interaction is much stronger (0.192 and 0.034 electron, respectively).

The present periodic HF calculations seem to correctly predict the general trends in the structural and vibrational variations resulting from host···guest interactions, with a tendency to underestimate the experimental shifts. However, the calculated values for the unit cell parameters, bond distances, and stretching frequencies are in all cases slightly larger than the experimental ones. This result might be attributed to the non-inclusion of electron correlation in HF calculations, and it is therefore interesting to compare with the MP2 study of the cluster model **6** (Table 2). The Br−Br bond distances, both in Br_2 and in the cluster, reproduce the experimental values with an accuracy similar to that of the periodic HF calculations. The stretching frequencies, however, are closer to the experimental values in the cluster calculations (Tables 1 and 2). It is noteworthy that the *variations* produced by formation of the intercalate in both the Br−Br bond distance and stretching frequency are better reproduced by the periodic HF calculations than by the cluster calculation including electron correlation (MP2).

The energy of the host···guest interaction (E_i) is calculated to be stronger for I_2 than for Br_2 (see discussion below). However, the energy of restructuring of the CsF layer (E_r) needed to allow for intercalation of I_2 is greater (by about 6 kcal/mol) than that for Br_2. Since the exfoliation energies are identical in both cases, the formation energies (E_f) are roughly the same (*ca.* 2 kcal/mol) for the Br_2 and I_2 intercalates.

The interaction energy per Br···F *bond* (Table 2) calculated for model **6**, including electron correlation and using an all-electron basis set, compares well with the value obtained from a periodic HF calculation using pseudopotentials (−8.48 *vs* −8.96 kcal/mol). Inclusion of electron correlation increases the calculated interaction energy by 1−2 kcal/mol, whereas the use of the all-electron basis set results in smaller interaction energies (~3 kcal/mol). These results suggest that the error introduced in the HF band calculation by the use of pseudopotentials is roughly compensated by the neglect of electron correlation.

General Trends in the MF·XY Family

Influence of the Intercalated Halogen. In order to establish the relative stabilities of the intercalates of different halogen and interhalogenated molecules XY, we have optimized both the interlayer separation and the position of the XY molecule in the unit cell, keeping the X−Y distance frozen at the experimental values (periodic HF calculations). The results are shown in Table 3. For the derivatives of homonuclear halogens, $CsF \cdot X_2$, the host···guest interaction energies are increasingly negative along the series $Cl_2 < Br_2 < I_2$. According to the interaction diagram presented above (Figure 3), the host···guest binding energy in $CsF \cdot X_2$ is dominated by two stabilizing interactions: $F^- \rightarrow \sigma^*(X_2)$ and $\pi^*(X_2) \rightarrow Cs^+$. Consequently, the halogen having the most stable σ^* orbital (Table 3), is expected to produce a stronger $F^- \rightarrow \sigma^*(X_2)$ interaction. On the other hand, the higher the energy of the π^* orbital of the X_2 is, the stronger the π^*(XY)/Cs interaction should be. In

Table 2. MP2 Stretching Frequency and Bond Distance of Br_2 in the Cluster Model (**6**) of $CsF{\cdot}Br_2$ Calculated with Pseudopotentials and with an All-Electron Basis Set[a]

	ν(Br−Br), cm^{-1}			d(Br−Br), Å			E_i, kcal/mol	
	Br_2	cluster	shift	Br_2	cluster	shift	HF	MP2
pseudopotentials	324	258	−66	2.359	2.464	+0.105	−9.92	−11.95
all-electron	329	287	−42	2.321	2.394	+0.073	−7.02	−8.48
experimental	317	292	−25	2.27	2.324	+0.044		

[a] Experimental values included for comparison. Also given is the energy of interaction (E_i) between a Br_2 molecule and its environment in the cluster model, calculated with an all-electron basis set and pseudopotentials, at the Hartree−Fock (HF) and second-order Moeller−Plesset (MP2) levels.

Table 3. Periodic HF Calculated Parameters for Several Compounds of the General Formula CsF·XY, Calculated with Pseudopotentials[a]

XY	*d*(XY), Å	*c*, Å	δ, Å	*d*(X···F), Å	*d*(Y···F), Å	E_i, kcal/mol	$E(\sigma^*)$, au	$E(\pi^*)$, au	μ, D
Cl_2	1.988	7.362	0.	2.687	2.687	−10.25	0.0336	−0.4493	0
BrCl	2.138	7.512	0.15	2.537	2.837	−13.26	0.0193	−0.4229	0.658 (0.57)
Br_2	2.290	7.664	0.	2.687	2.837	−13.97	0.0076	−0.4043	0
I_2	2.662	7.964	0.	2.651	2.501	−15.71	−0.0199	−0.3571	0
IBr	2.470	8.024	0.30	2.477	3.077	−17.37	−0.0087	−0.3758	0.931 (0.65)
ICl	2.303	7.627	0.24	2.422	2.902	−18.99	−0.0028	−0.3875	1.606 (1.21)

[a] The experimental XY distances were kept fixed in these calculations. δ represents the shift of the XY molecule from the center of the unit cell, and μ is the calculated dipole moment (experimental values given in parentheses, taken from: Kucharski, S. A.; Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1988**, *88*, 1035).

Table 4. Energies and Unit Cell Parameters for Three Alkali Fluorides, Their Hypothetical Two-Dimensional Structures, and Their Interaction Energies with Bromine in the $4MF{\cdot}Br_2$ Intercalates[a]

	CsF	KF	LiF
cubic structure (1)			
E_t, au	−24.12853	−24.16649	−24.27053
a, Å	5.972 (6.002)	5.424 (5.344)	3.981 (4.026)
M−F, Å	2.986 (3.001)	2.712 (2.672)	1.990 (2.013)
layered structure (**2**)			
E_t, au	−24.11178	−24.14825	−24.25758
a, Å	4.048	3.678	2.650
M−F, Å	2.862	2.601	1.874
E_e, kcal/mol	10.98	12.53	10.78
E_x, kcal/mol	−0.48	−1.09	−2.65
E_{hg}, kcal/mol	−16.80	−9.93	+2.54

[a] E_e is the energy of exfoliation of the MF rigid layers, E_x is the energy of relaxation of the exfoliated lattice, and E_{hg} is the host ··· guest part of the interaction energy (see eq 3). Experimental values are given in parentheses.

fact, the energies of the σ^* and π^* orbitals of the X_2 molecules happen to be linearly related: the lower the energy of π^* is, the higher the energy of σ^* is. It is therefore not surprising that the calculated interaction energies correlate well with the energy of both the LUMO (σ^*) and the HOMO (π^*) of the intercalated X_2 molecule, resulting in the proposed ordering of interaction energies.

For the heteronuclear derivatives studied (BrCl, IBr, and ICl), the results indicate that the XY molecules are shifted from the center of the unit cell along the *c* direction, in such a way that the less electronegative atom (X) is closer to a CsF plane than the more electronegative one (Y). This result can be accounted for by the orbital interaction diagram presented above (Figure 3). In a heteroatomic XY molecule, the π^* orbital is mostly localized on the less electronegative atom (X), and the $\pi^* \rightarrow Cs^+$ interactions are improved upon approaching the X end of XY to the neighboring CsF plane. An unexpected corollary is that the intermolecular distance to the bulkiest atom of XY (X ··· F) is predicted to be shorter than that for the smaller atom (Y ··· F).

For the six molecules of type XY (XY = Cl_2, Br_2, I_2, BrCl, ICl, and IBr) studied, an excellent linear correlation is found between the energy of the LUMO (σ^*) and that of the HOMO (π^*), as illustrated by the least-squares fitting of eq 1 (HF energies in atomic units, regression coefficient 0.999; standard error of the estimate 0.0006 au). The relationship found above between host ··· guest interaction energies and the energies of the HOMO or LUMO for the X_2 molecules gives a poor correlation when the XY molecules are also considered. However, if their calculated dipole moments are taken into account, a fair correlation results. Given the linear dependence found between the energy of the HOMO and that of the LUMO for a particular XY molecule, the interaction energy can be expressed as a function of the calculated dipole moment and the energy of one of the frontier orbitals. A least-squares fitting is presented in eq 2 (regression coefficient 0.99; standard error

$$E_{\rm LUMO} = -0.2286 - 0.5843E_{\rm HOMO} \qquad (1)$$

$$E_{\rm i} = -38.347 - 62.322E_{\rm HOMO} - 2.80\mu \qquad (2)$$

of the estimate 0.6 kcal/mol), where μ is the dipole moment of XY (in debyes), the orbital energies are in hartrees, and the interaction energy (E_i) is in kilocalories per mole. It is worth stressing the qualitative description of the factors affecting the interaction energy summarized by eq 2, rather than its quantitative significance: In addition to the effect of the energies of HOMO or LUMO, eq 2 tells us that, other things being equal, the XY molecules with larger dipole moments are expected to yield more stable intercalates.

Substitution of the Alkaline Cation. The experimental studies[10] indicate that the tendency of MF to intercalate a halogen decreases with the size of the alkaline cation. We have performed periodic HF calculations on the Br_2 intercalates of CsF, KF, and LiF, in search of a rationalization of the experimental trend.

The optimization of the unit cell parameter, *a*, for the three salts with the NaCl structure gave the results shown in Table 4, in excellent agreement with the experimental data.[16] Optimization of the *a* parameter in the exfoliated 2D structures (**2**) with the fixed interlayer distance compatible with bromine intercalation (*c* = 7.364 Å) indicates a slight contraction of the layers, associated with a small relaxation energy (E_x). A recently reported calculation on a LiF layer with a better basis set (all-electron with triple-ζ quality) gives practically the same result (Li−F = 1.889 Å).[17] From Table 4, it is clear that the exfoliation and relaxation energies for the three alkali fluorides studied differ only slightly from each other. Hence, differences

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(16) Landolt-Börnstein *Neue Serie* **1973**, *III/7a*, 1.

(17) Nada, R.; Saunders, V. R.; Pisani, C. *Chem. Phys.* **1993**, *169*, 297.

in the intercalation energies must be related to differences in guest$\cdots$guest and/or host$\cdots$guest interaction energies.

As for the guest$\cdots$guest interactions, at the optimized structures of the exfoliated and relaxed MF lattices the $Br_2\cdots Br_2$ distance within the *ab* planes (coincident with *a*) is shorter (hence the $Br_2\cdots Br_2$ repulsions stronger) for the lighter alkaline cations. Notice that the Br$\cdots$Br distance in solid bromine is 3.99 Å,[4] hence the shorter distances needed for the $MF\cdot Br_2$ lattices (M = K and Li) in the layered structures **2** are strongly destabilizing. Alternatively, if the geometry of the layers is adjusted to provide space for the Br_2 molecules, a destabilization of the ionic MF layers would result. In order to analyze the trends in host$\cdots$guest interactions excluding the $Br_2\cdots Br_2$ repulsions, we have carried out calculations on hypothetical compounds with a lower ratio of intercalated bromine, $4MF\cdot Br_2$, and the resulting interaction energies, E_{hg}, are presented in Table 3. The $Br_2\cdots Br_2$ interaction energy in $MF\cdot Br_2$, E_{gg}, can then be evaluated from eq 3 as +2.83 kcal/mol at the experimental geometry of $CsF\cdot Br_2$. From Table 3 one can deduce that Br_2 can be absorbed by KF at low intercalation ratios, as is experimentally found.[10]

$$E_{gg} = E_i - E_{hg} \tag{3}$$

As seen in the band interaction diagram (Figure 3), the most important host$\cdots$guest interactions are those between $\sigma^*(Br_2)$ and the fluoride ions, and between $\pi^*(Br_2)$ and the empty orbitals of the alkali cation. How are these interactions affected by substitution of the alkali metal? According to the orbital interaction rules,[18] the $\pi^* \rightarrow M$ interaction must be weaker for the more electropositive metal, as is actually found in the calculated host$\cdots$guest interaction energies E_{hg} (Table 3). Notice that the interlayer separation has been kept constant for the different alkaline cations, because such spacing is determined by the Br−Br and Br$\cdots$F distances. Therefore, the M$\cdots$Br distance is the same for the different metals, and interaction of the smaller metal ions is poorer.

On the other hand, the alkali metal has an indirect effect on the $F^- \rightarrow \sigma^*(Br_2)$ interaction: in the more ionic metal fluoride, the charge on the fluoride ions is higher and the donor−acceptor interaction $F^- \rightarrow \sigma^*(Br_2)$ is stronger. This argument can be tested by a simple theoretical experiment: contracting the smallest valence orbital of Li (i.e., increasing its exponent by 0.10 unit) results in a decrease of the valence electron population of Li from 0.123 to 0.078 and the host$\cdots$guest interaction energy is made more bonding by 2 kcal/mol. The improved bonding cannot be ascribed to changes in the $\pi^* \rightarrow M^+$ interaction, which is expected to be weaker due to the decrease in the Br/M overlap when M is smaller. Similar results are obtained when modifying the size of the Cs atomic orbitals.

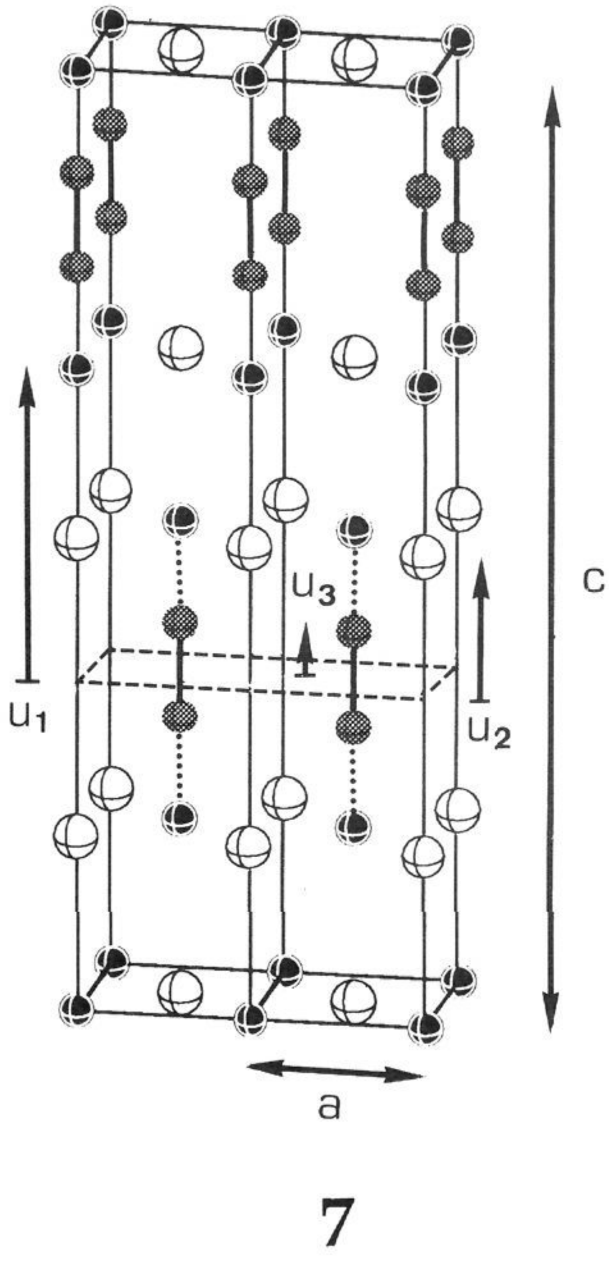
In summary, the energy needed to separate the layers of the MF lattice to the distance required to allow incorporation of Br_2 molecules (c = 7.364 Å) is not significantly different for the alkali cations studied. The Cs^+ ion is the one having the optimum size and ionicity to provide a sufficiently stabilizing host$\cdots$guest interaction. At the same time, a large separation between neighboring Br_2 molecules, resulting in reduced guest$\cdots$guest repulsions, is obtained only for $M = Cs^+$. Only with lower intercalation ratios can KF accommodate the Br_2 molecules without strong guest$\cdots$guest repulsions.

Table 5. Optimized Crystallographic Parameters, Atomic Charges, and Interatomic Overlap Populations for the 2:1 Phase $2CsF\cdot Br_2$ with the Structure Proposed in **7**

a, Å	4.332	*q*(Cs)	+0.931
c, Å	27.057	*q*(F)	−0.898
u_1	0.3599	*q*(Br)	−0.040
u_2	0.1421	Cs−F	0.011
u_3	0.0436	F$\cdots$Br	−0.007
Br−Br, Å	2.360	Cs$\cdots$Br	0.002
ν(Br−Br), cm^{-1}	328	Br−Br	0.130

Low Intercalation Ratios

When the amount of halogen present in the reaction mixture is smaller than the stoichiometric ratio, the obtained intercalation compound presents a $CsF:Br_2$ ratio of 2:1. In general, intercalation compounds with low concentrations of the guest species have structures in which two or more layers of the host lattice are preserved.[1] Hence, we have investigated the energetics of the intercalation compound with the stoichiometry $2CsF:Br_2$ and the hypothetical structure shown in **7**. The data for the optimized structure are presented in Table 5. Notice that the interatomic distance and the stretching frequency of the Br−Br bond are practically identical to those in the 1:1 phase. The thickness of the Cs_2F_2 layers (5.89 Å) is similar to, if somewhat smaller than, the interlayer distance calculated for cubic CsF (5.97 Å). On the other hand, the thickness of the layers containing the guest molecules (7.69 Å) is only slightly larger than in the 1:1 phase (7.55 Å). Energywise, however, the 2:1 phase with structure **7** is predicted to be unstable in our calculations, the starting products being ~20 kcal/mol more stable than the intercalation compound.



7

Addition to Double and Triple Bonds

The $MF\cdot Br_2$ compounds can be used as reagents for the asymmetric halogenation of double and triple bonds. For instance, reaction of $MF\cdot Br_2$ with $CF_2{=}NCl$ yields

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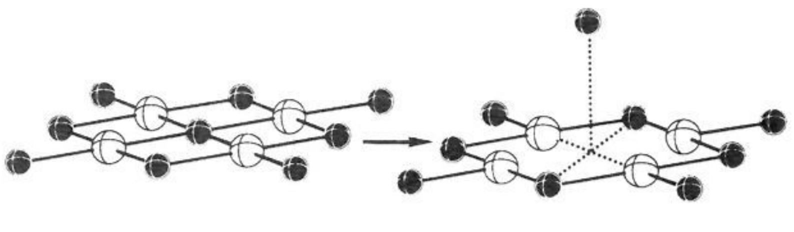
[18] Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; John Wiley: New York, 1985.

$CF_3{-}NBrCl$.[8-10] The proposed mechanism involves the formation of $CF_3{-}NCl^-$, possibly by abstraction of a fluoride ion from the surface of the intercalation compound, followed by the attack of a deintercalated halogen molecule. In a simplified approach, one can assume that adsorption of the $CF_2{=}NCl$ molecule on the surface is not strongly dependent on the nature of M. Within this approximation, the activation energy for the process would come from the fluoride abstraction or from halogen de-intercalation, or both. To obtain an estimate of the energy needed for the fluoride abstraction in different $MF \cdot Br_2$ compounds, we have performed periodic HF calculations on a one-layer slab of CsF (**8**). A 3 × 3 supercell was used, corresponding to a coverage of 1/9. The energy needed to take a fluoride ion 5 Å apart from the surface is 124.3, 151.0, and 234.0 kcal/mol for CsF, KF, and LiF, respectively.



8

Of course, a one-layer slab represents a crude model for the surface of the inclusion compounds $MF \cdot Br_2$. Hence, we made a check calculation on a thicker slab of $CsF \cdot Br_2$, having two layers of CsF and a sandwiched layer of Br_2. The energy needed to pull the fluoride ion 5 Å apart from its lattice position was calculated now to be 122.3 kcal/mol, only 2 kcal/mol smaller than calculated with the simpler model. This makes us feel confident that the energy needed for the fluoride abstraction follows the order calculated above: Cs < K < Li. This trend is in agreement with the fact that CsF is much more active in this kind of reaction than other alkali halides. Also, the fact that the abstraction energy is much higher than that needed to de-intercalate a halogen molecule, according to the calculated host$\cdots$guest interaction energies (Table 1), supports the idea that the rate-determining step is the fluoride abstraction.

Appendix

Computational Details. Extended Hückel tight-binding band calculations[19-21] were carried out using the modified Wolfsberg−Helmholz formula[22] and atomic parameters deposited as supplementary material (Table S1). The Slater exponents for Cs were obtained as the coefficient-weighted average of the exponents for Ba^+ (isoelectronic with Cs) in the multi-ζ basis set of McLean.[23] Other atomic parameters were taken from the literature. Property calculations (DOS and COD diagrams) were obtained by averaging throughout the Brillouin zone using a mesh of 126 k-points for $CsF \cdot Br_2$ and the two-dimensional layers of CsF, and of 84 k-points for CsF with the rock-salt structure.

The periodic Hartree−Fock calculations were carried out by using the CRYSTAL92 computer programs.[13] For the calculation of Coulomb and exchange integrals, tolerance factors[12] 6, 6, 6, 6, and 12 were used. The pseudopotentials of Durand and Barthelat[24] were used for all atoms (Li, K, Cs, F, Cl, Br, and I), and the valence basis sets used are deposited as supplementary material (Table S2). For the alkaline metals, the coefficients of the most diffuse Gaussian valence functions were optimized by minimizing the total energy for the experimental geometry of LiF, KF, and CsF.[16] Also the coefficient for the most diffuse function of F and a polarization function have been optimized by minimizing the energy of the experimental geometry of CsF. The valence basis sets for Cl, Br, and I were taken from the literature.[25]

In the cluster MP2 calculations, the Cs^+ ions were substituted by point charges of +0.25. The inclusion of Cs atoms in the cluster model would have concentrated their Coulombic effect on one Br_2 molecule, at difference with the situation in the real crystal, in which the positive charge of each cation is attenuated by the negative charge of neighboring anions. In addition, two neighboring fluoride ions and two more Br_2 molecules were included, resulting in the model cluster **6**. For such calculations, the programs GAUSSIAN90 and GAUSSIAN92[26] were used. In all-electron calculations, a 6-31+G* basis set was used for the fluorine atoms and that proposed by Binning[27] for Br, including one diffuse function and one polarization function. The pseudopotential basis set was the same employed for the periodic HF calculations. The basis set superposition error in the calculation of interaction energies was corrected by applying the counterpoise method.[28] The stretching frequency and bond distance of the intercalated Br_2 molecule were calculated by optimizing the Br−Br distance while keeping the structure of the rest of the cluster fixed as in the experimental structure of $CsF \cdot Br_2$.

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Supplementary Material Available: Atomic parameters used for EH calculations and Gaussian basis set for the valence shell of the Li, K, Cs, F, Cl, Br, and I atoms in the pseudopotentials periodic HF calculations (Tables S1 and S2) (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(19) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093.

(20) Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London, Ser. A* **1979**, *366*, 23.

(21) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(22) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(23) McLean, A. D. *At. Data Nucl. Data Tables* **1981**, *26*, 209.

(24) Durand, P.; Barthelat, J.-C. *Theor. Chim. Acta* **1975**, *38*, 283.

(25) Bouteiller, Y.; Mijoule, C.; Nizam, M.; Barthelat, J. C.; Daudey, J. P.; Pelissier, M.; Silvi, B. *Mol. Phys.* **1988**, *65*, 295.

(26) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian, Inc., 1992.

(27) Binning, R. C., Jr.; Curtiss, L. A. *J. Comp. Chem.* **1990**, *11*, 1206.

(28) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.