ETS-NOCV description of σ-hole bonding

an insight based on
the natural orbitals for chemical valence (NOCV)
combined with
extended-transition-state method (ETS)

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Outline

introduction: definition of HB, experimental data, Politzer works, theoretical description of HB

theory: MEP, deformation density, ETS, NOCV, ETS-NOCV

methodology & model systems - fragments definition, plot constructions

results

conclusions

introduction

halogen bonding – does it exist?

weak, noncovalent interactions of halogen atoms

introduction

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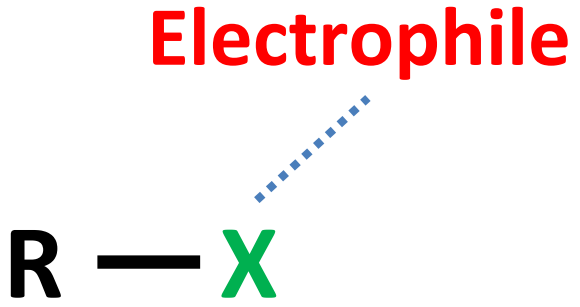
weak, noncovalent interactions of halogen atoms



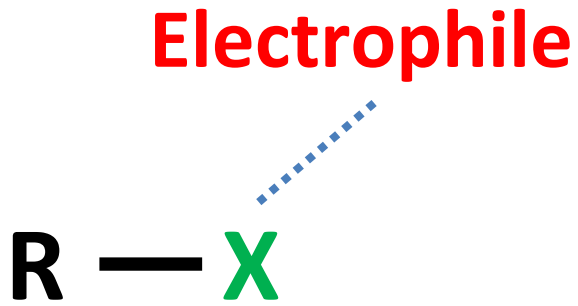
close contacts
with electrophiles
occurred at angles of 90°–120°
with the C–X bond

introduction

halogen bonding – does it exist?

weak, noncovalent interactions of halogen atoms

near-linear interactions
with nucleophiles
are known as
"**halogen bonding**".

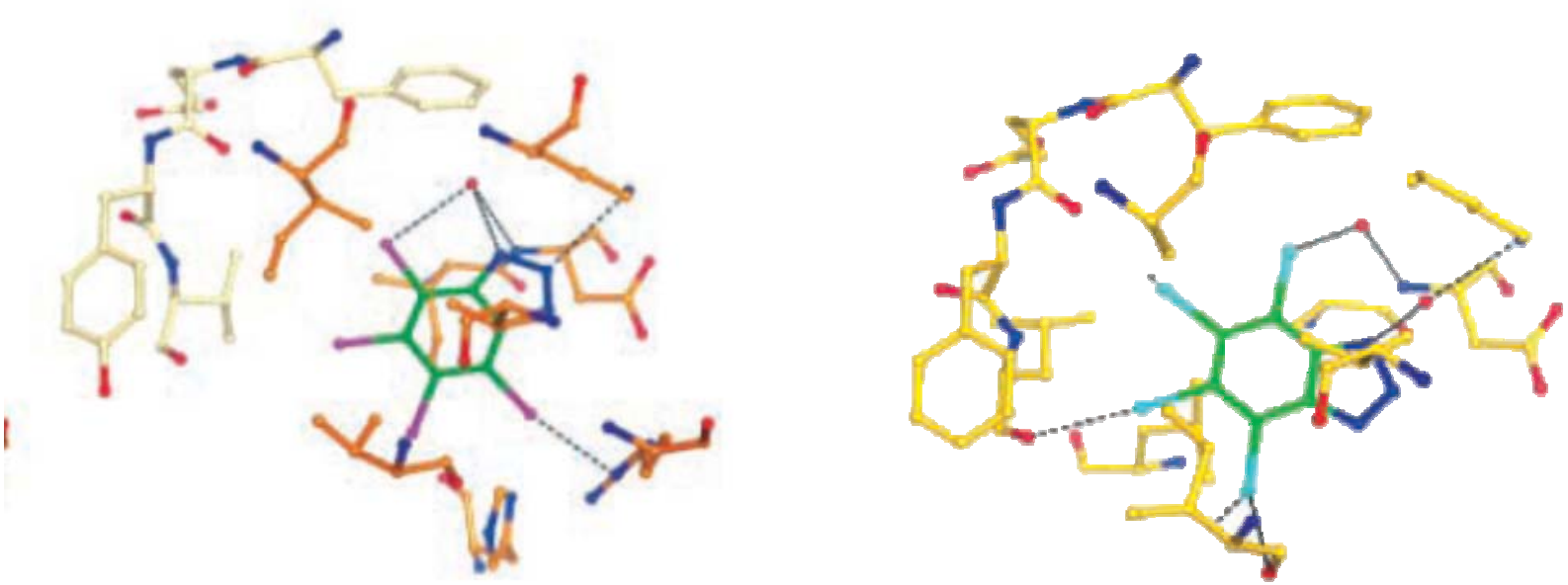


close contacts
with electrophiles
occurred at angles of 90°–120°
with the C–X bond

introduction

experimental data - biomolecular crystal structures

4,5,6,7-tetrabromobenzotriazole displaces charged ATP from its binding site on phospho-CDK2-cyclin A

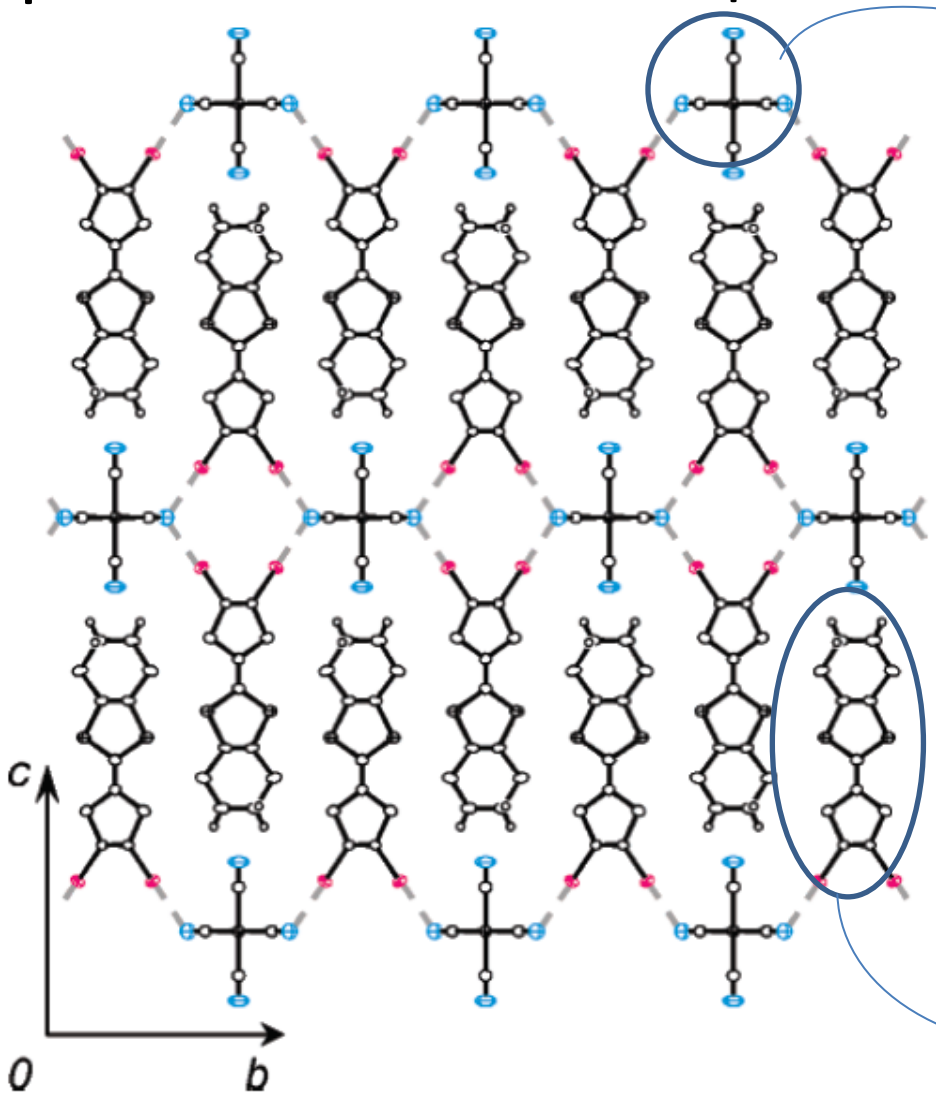


„some bromine recognition sites have sufficient features to **direct specificity**, other sites have weak specificity (...) that accounts for the differential binding of TBB to pCDK2 and CK2”

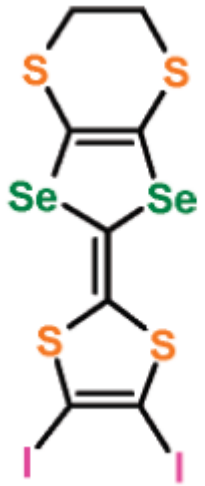
Ennifar, E., Bernacchi, S., Wolff, P. & Dumas, P. (2007) RNA, 13, 1445–1452.

introduction

experimental data – superconductor



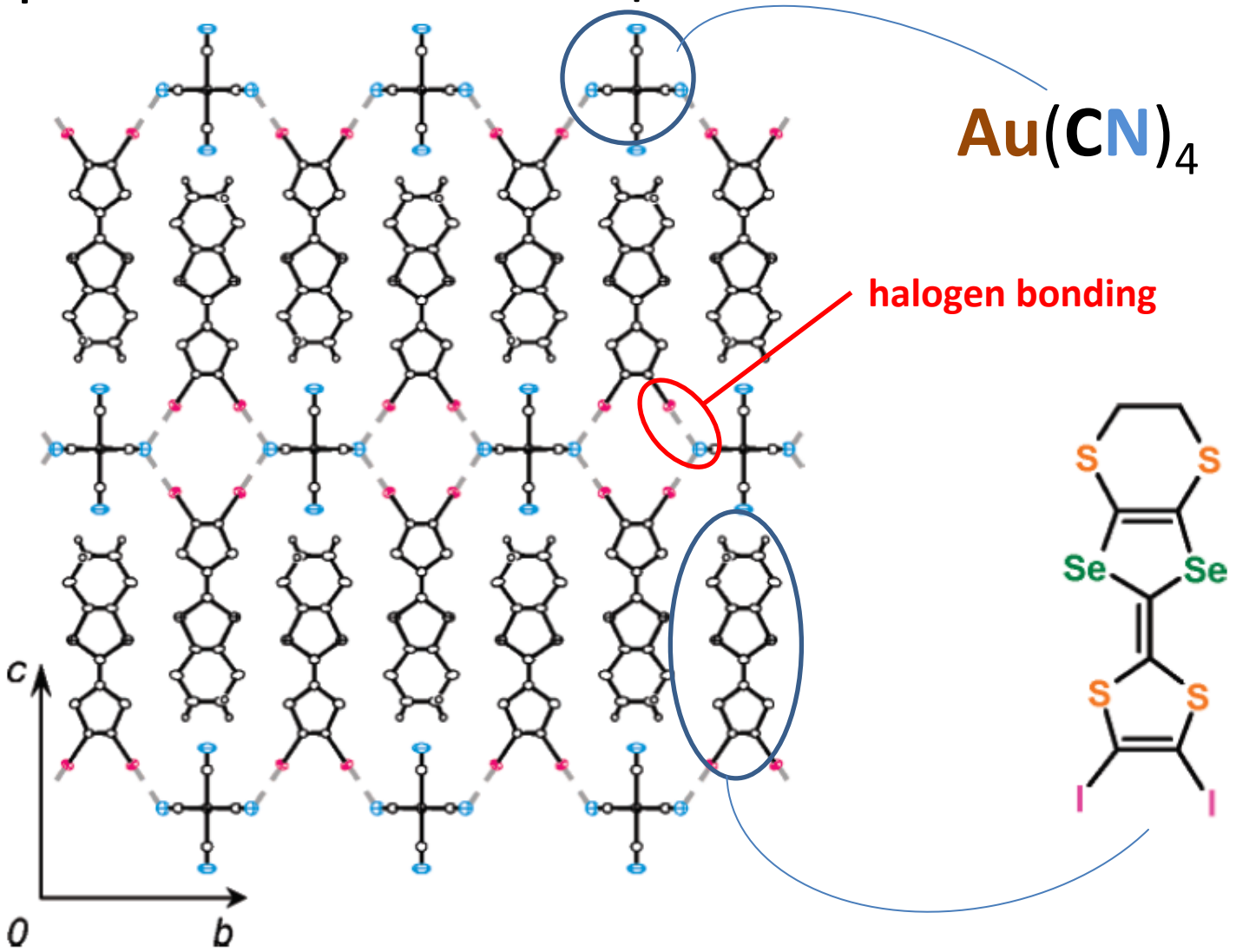
$Au(CN)_4$



Metrangolo P, Neukirch H, Pilati T, Resnati G (2005) Acc Chem Res 38:386–395

introduction

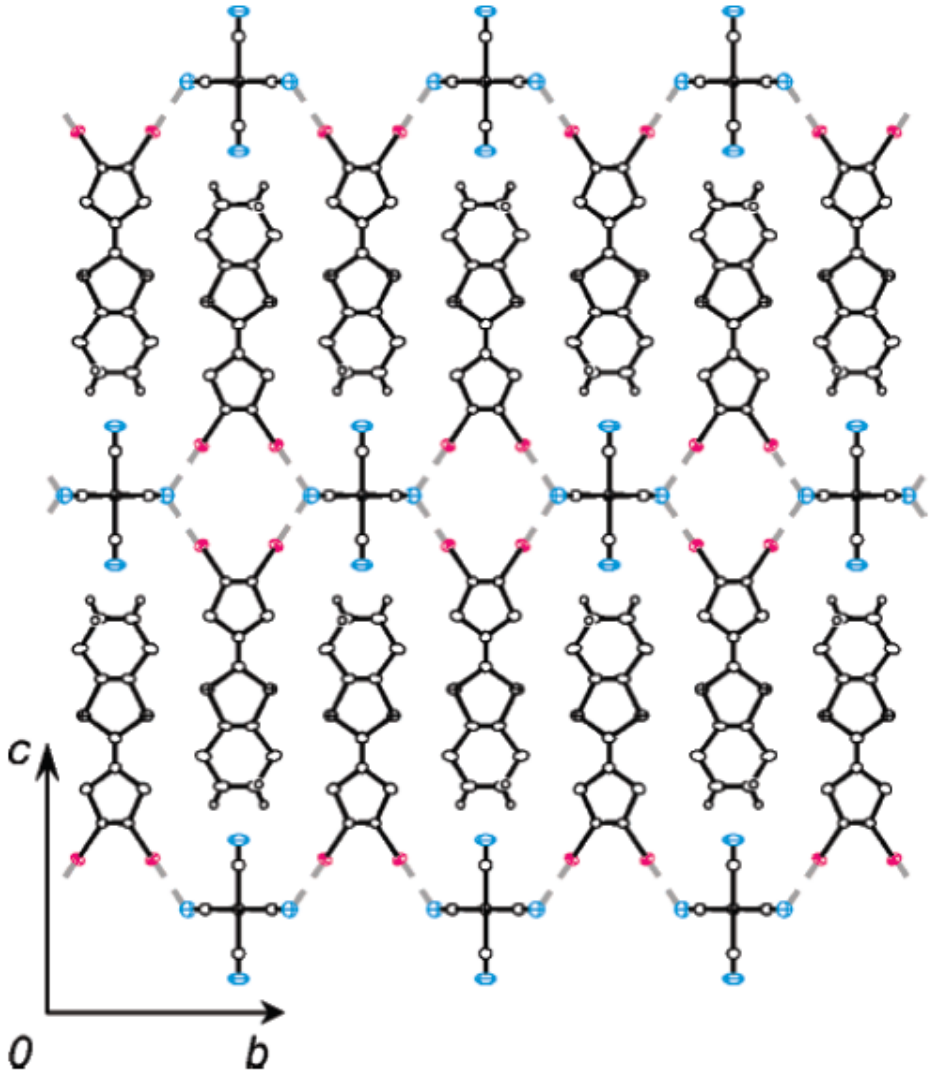
experimental data – superconductor



Metrangolo P, Neukirch H, Pilati T, Resnati G (2005) Acc Chem Res 38:386–395

introduction

experimental data - superconductor



organic conductor
Θ-$(DIETS)_2[Au(CN)_4]$

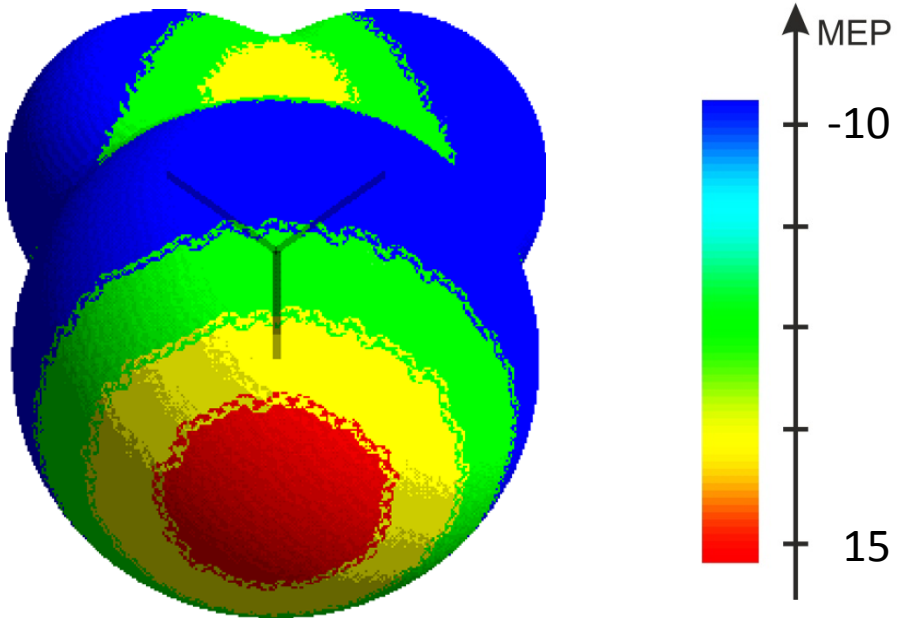
superconductor Tc= 8.6 K
the highest value among the known superconductors based on unsymmetrical organic ð-donors.

Metrangolo P, Neukirch H, Pilati T, Resnati G (2005) Acc Chem Res 38:386–395

Politzer works - origin of halogen bonding

Molecular **E**lectrostatic **P**otential (MEP) for CF_3Br

anisotrophy of the charge

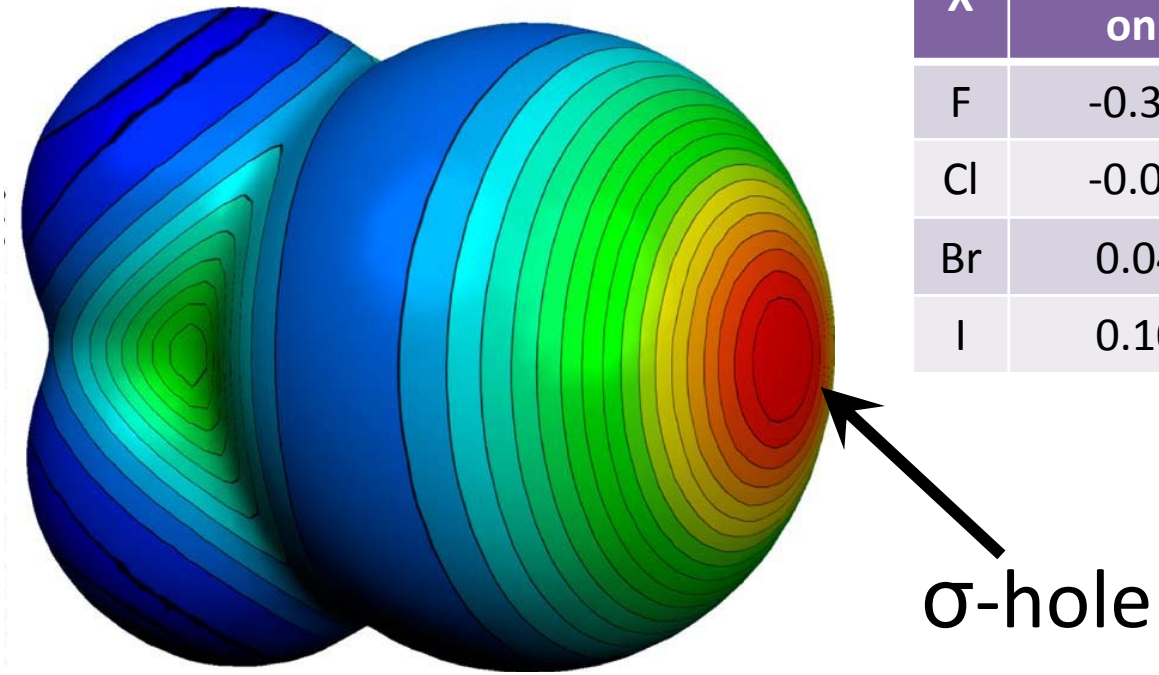


$$\phi(\boldsymbol{r},\boldsymbol{R}) = \sum_{\alpha=1}^{m} \frac{Z_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}|} - \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r}'$$

Politzer P, Lane P, Concha MC, Ma Y, Murray JS (2007) J Mol Model 13:305–311

introduction

Politzer and Clark - origin of halogen bonding



X	NBO charge on X	Halogen population in the σ_{CX}-NBO (%)
F	-0.332	71.4
Cl	-0.004	53.1
Br	0.041	49.4
I	0.107	45.7

Molecular Electrostatic Potential (MEP) for CF_3I

Clark T, Hennemann M, Murray JS ,Politzer P, (2007) J Mol Model 13:291–296

introduction

σ-hole concept

- How does the σ-hole size and depth vary for diffrent halogen atoms? How can it be described?

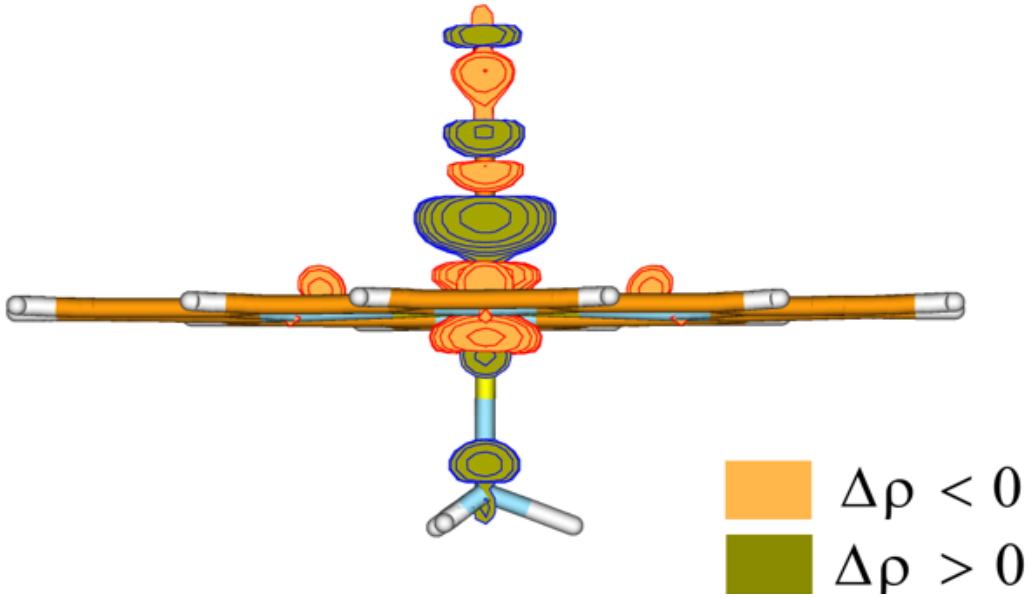
- Can halogen σ-hole be alternated by different alkyl substituents on halogen atom?

- Does σ-hole exist for other elements of periodic table?

theory

deformation density

$$\Delta\rho = \rho_{mol} - \rho_A^0 - \rho_B^0$$



Mitoraj, M., Michalak, A. (2007) Journal of Molecular Modeling 13 (2) , pp. 347-355

theory

NOCV Natural Orbitals for Chemichal Valence

NOCV $\psi_i = \sum_i C_{ij} * \lambda_i$ – vectors which diagonalize ΔP

$$\Delta P C_i = v_i C_i \quad ; \quad i = 1, M$$

where $\Delta P = P - P^0$

P matrix of charge and bond order in molecule

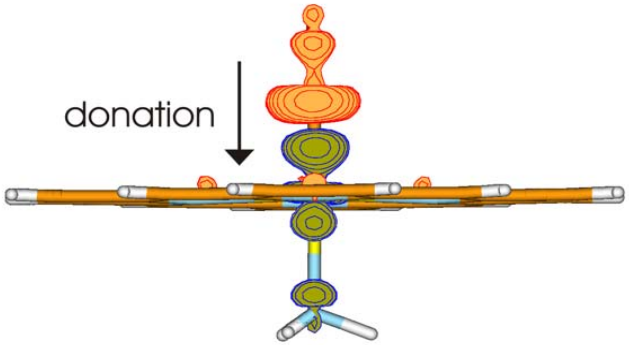
P^0 matrix of charge and bond order in promolecule

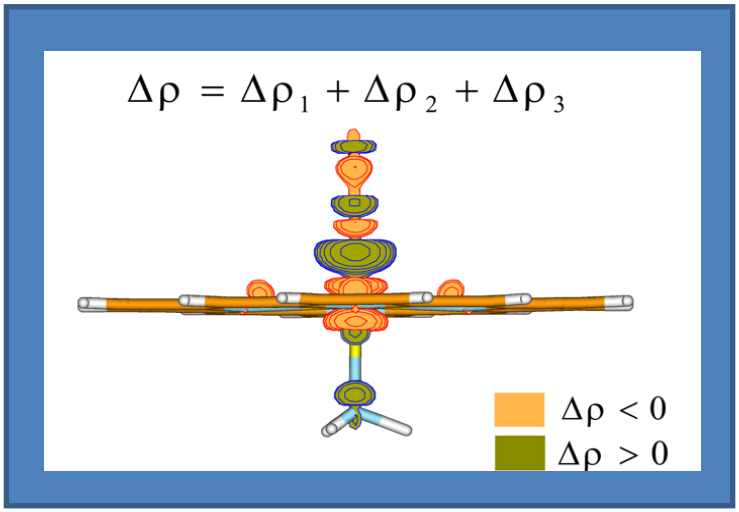
$$\Delta\rho(r) = \sum_{k=1}^{M/2} v_k[-\psi_{-k}^2(r) + \psi_k^2(r)] = \sum_{k=1}^{M/2} \Delta\rho_k(r)$$

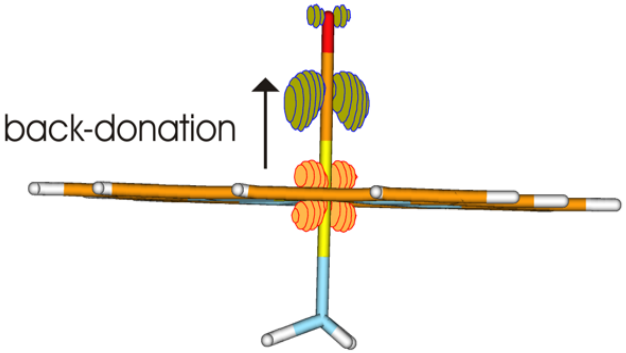
Mitoraj, M., Michalak, A. (2007) Journal of Molecular Modeling 13 (2) , pp. 347-355

NOCV applications

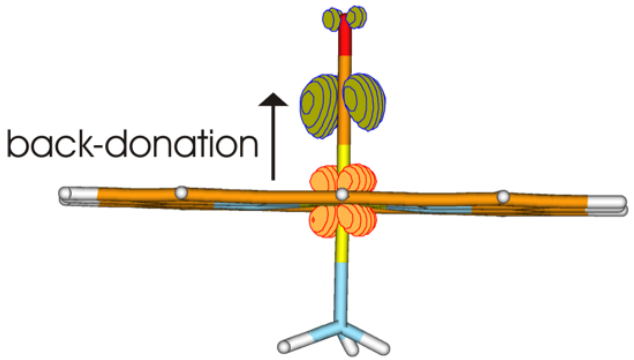
$$\Delta\rho_1 = -0.74 * \varphi_{-1}^2 + 0.74 * \varphi_1^2$$







$$\Delta\rho_2 = -0.52 * \varphi_{-2}^2 + 0.52 * \varphi_2^2$$



$$\Delta\rho_3 = -0.52 * \varphi_{-3}^2 + 0.52 * \varphi_3^2$$

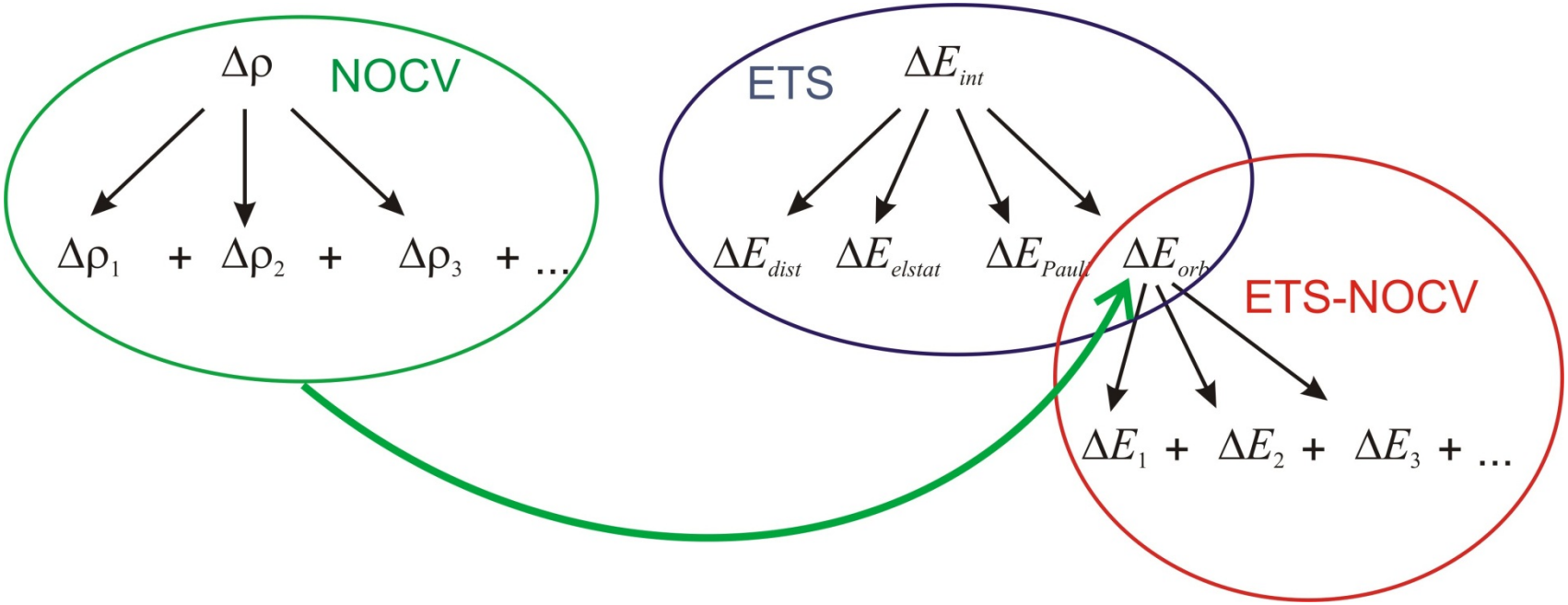
theory

ETS - NOCV

ETS - energy decomposition scheme

$$\Delta E = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$$

NOCV– representation of deformation density



Mitoraj, M.P., Michalak, A., Ziegler, T. (2009) J. Chem. Theory Comput. 5 (4) , pp. 962-975

methodology

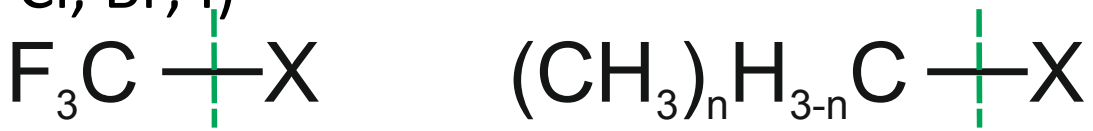
DFT calculations based on the Amsterdam Density Functional (ADF2009) program in which ETS-NOCV scheme was implemented .

- The Becke-Perdew exchange-correlation functional (BP86) with an inclusion of the dispersion correction (BP86-D)
- triple-zeta STO basis containing two sets of polarization functions, based on the frozen core approximation, was adopted for all of the elements (TZ2P)
- Relativistic effects were included using the ZORA formalism

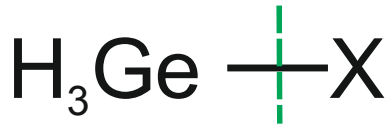
methodology

The ETS-NOCV analysis was applied to describe

- the σ-hole in a series of halogen compounds (X=F, Cl, Br, I)



- germanium-based systems $GeXH_3$, X=F, Cl, H.

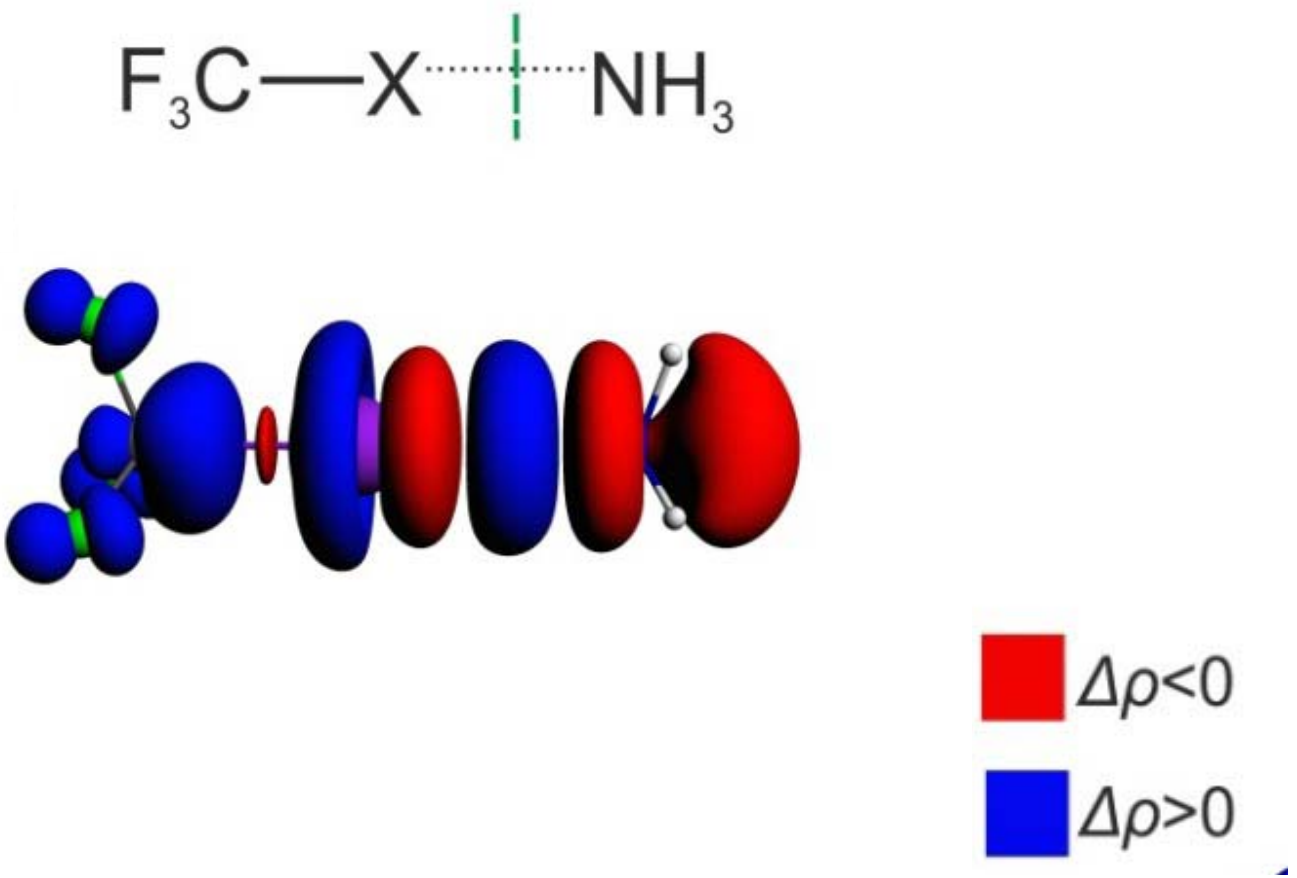


- Further to characterize bonding with ammonia for these systems

e.g. 

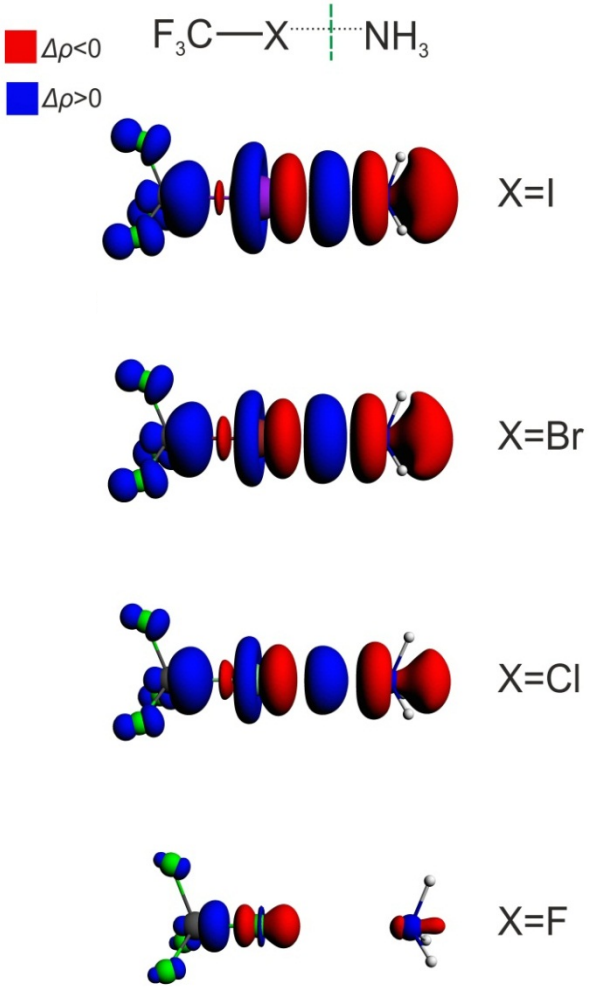
results

deformation density of dominating NOCV channel ($\Delta\rho_1$)



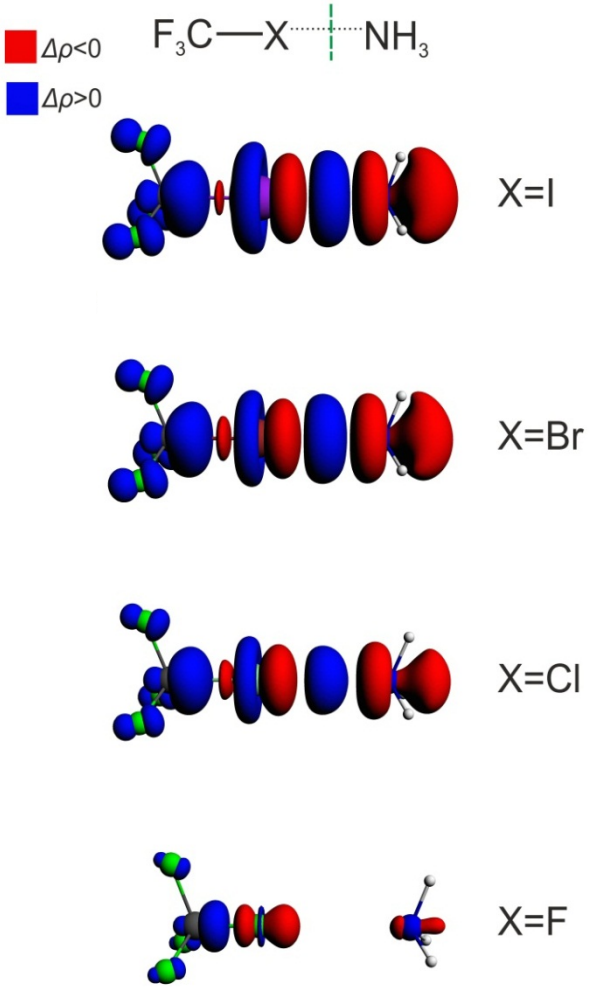
results

deformation density of dominating NOCV channel ($\Delta\rho_1$)



results

deformation density of dominating NOCV channel ($\Delta\rho_1$)

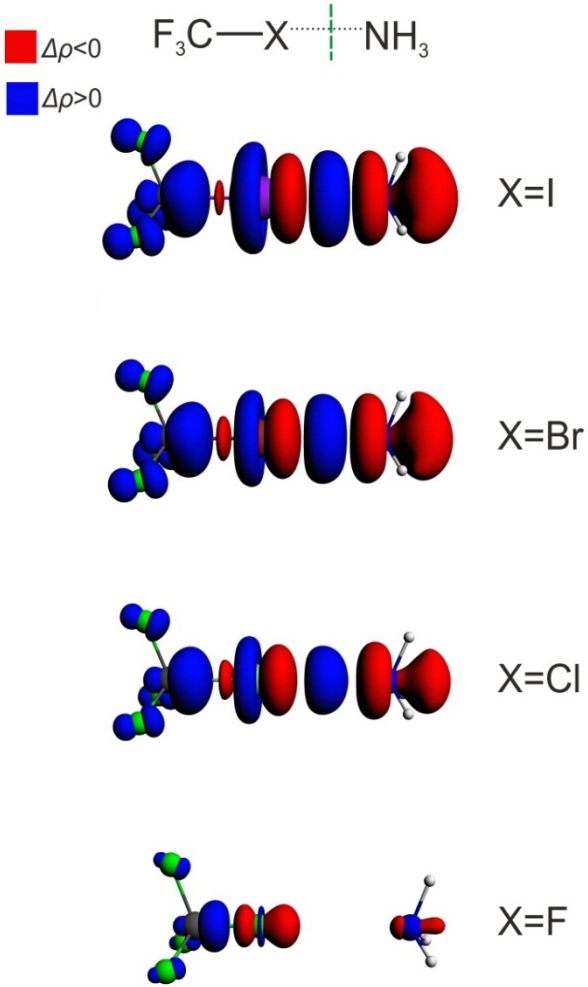


X	I	Br	Cl	F
ΔE_{tot}	-6.96	-4.34	-2.59	0.13

energy values in kcal/mol

results

deformation density of dominating NOCV channel ($\Delta\rho_1$)

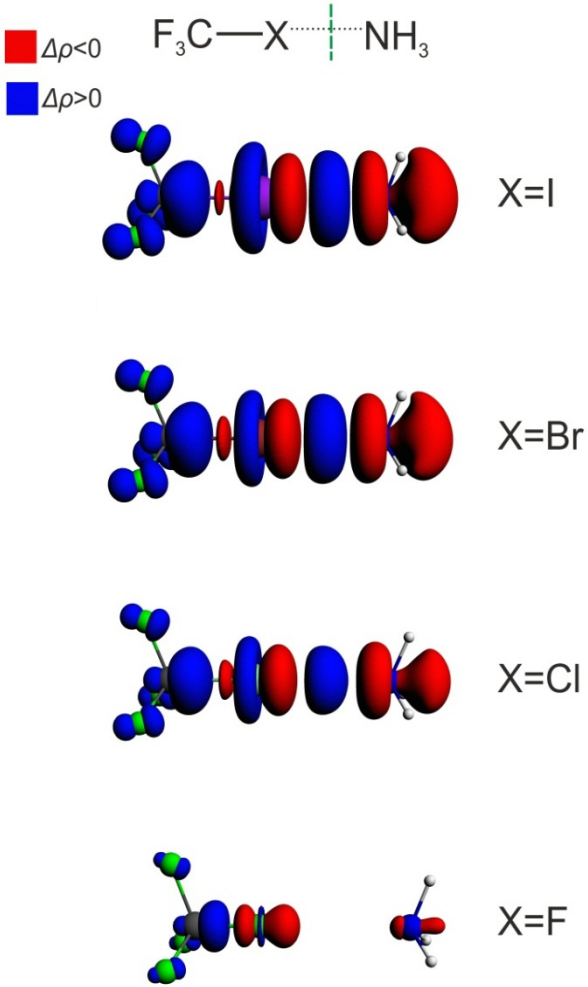


X	I	Br	Cl	F
ΔE_{tot}	-6.96	-4.34	-2.59	0.13
ΔE_{elstat}	-16.65	-10.44	-5.03	-0.50
ΔE_{orb}	-9.59	-5.78	-2.51	-0.28

energy values in kcal/mol

results

deformation density of dominating NOCV channel ($\Delta\rho_1$)



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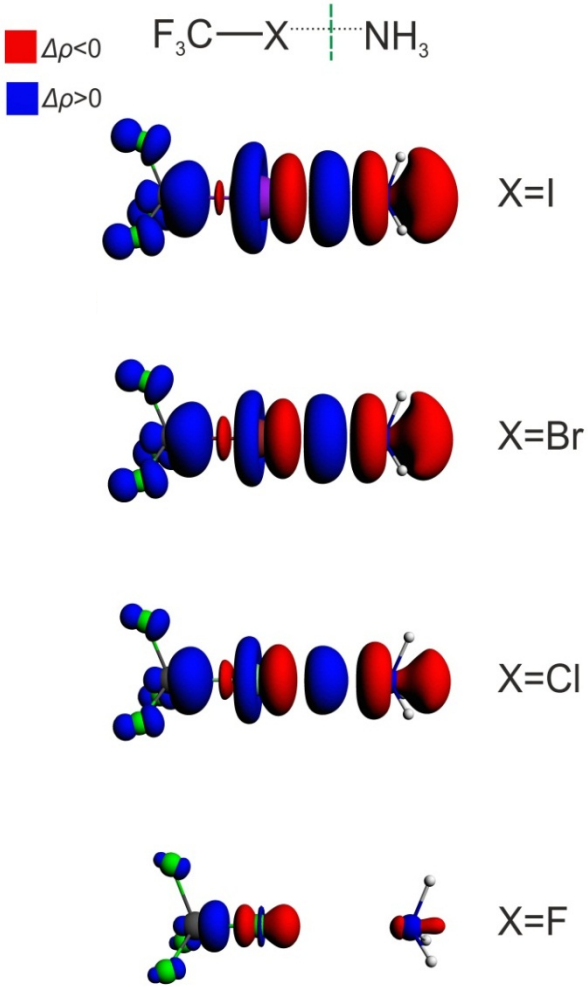
ΔE_{elstat}	-16.65	-10.44	-5.03	-0.50
ΔE_{orb}	-9.59	-5.78	-2.51	-0.28
ΔE_{orb1}	-8.9	-5.48	-2.43	-0.17

energy values in kcal/mol

results

deformation density of dominating NOCV channel ($\Delta\rho_1$)



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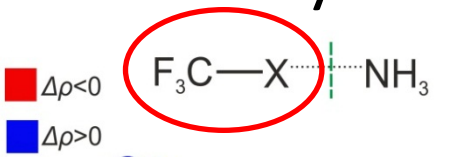
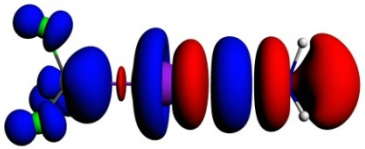
ΔE_{elstat}	-16.65	-10.44	-5.03	-0.50
ΔE_{orb}	-9.59	-5.78	-2.51	-0.28
ΔE_{Pauli}	20.6	12.9	5.75	0.88
ΔE_{disp}	-1.32	-1.02	-0.81	-0.47

energy values in kcal/mol

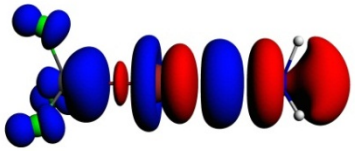
results

deformation density of dominating NOCV channel ($\Delta\rho_1$)

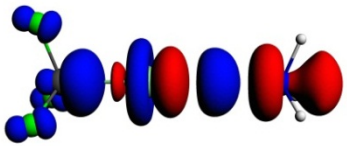




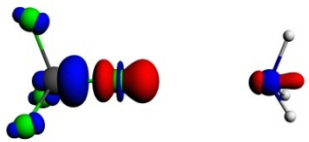
X=I



X=Br



X=Cl



X=F

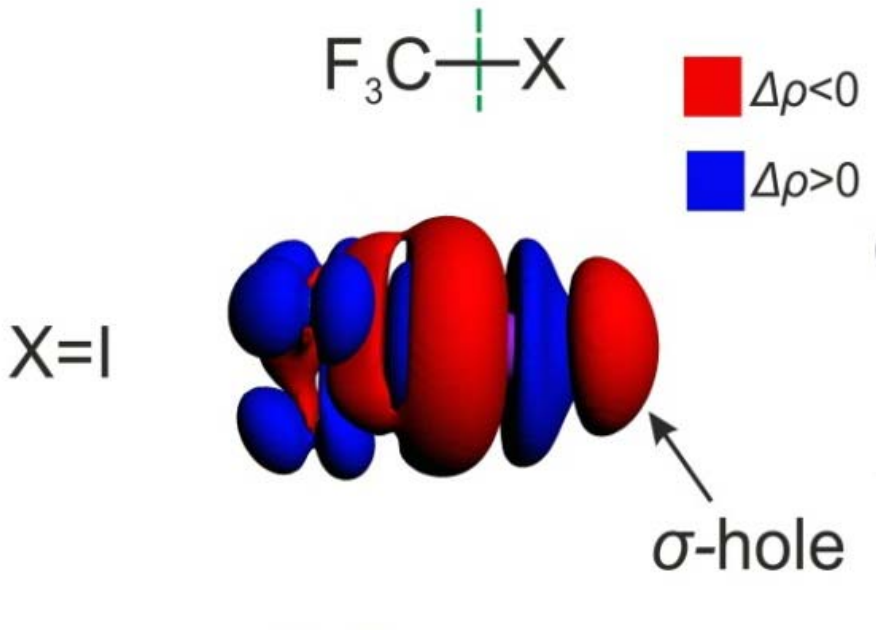
X	I	Br	Cl	F
ΔE_{tot}	-6.96	-4.34	-2.59	0.13
ΔE_{elstat}	-16.65	-10.44	-5.03	-0.50
ΔE_{orb}	-9.59	-5.78	-2.51	-0.28
ΔE_{Pauli}	20.6	12.9	5.75	0.88
ΔE_{disp}	-1.32	-1.02	-0.81	-0.47

energy values in kcal/mol

results

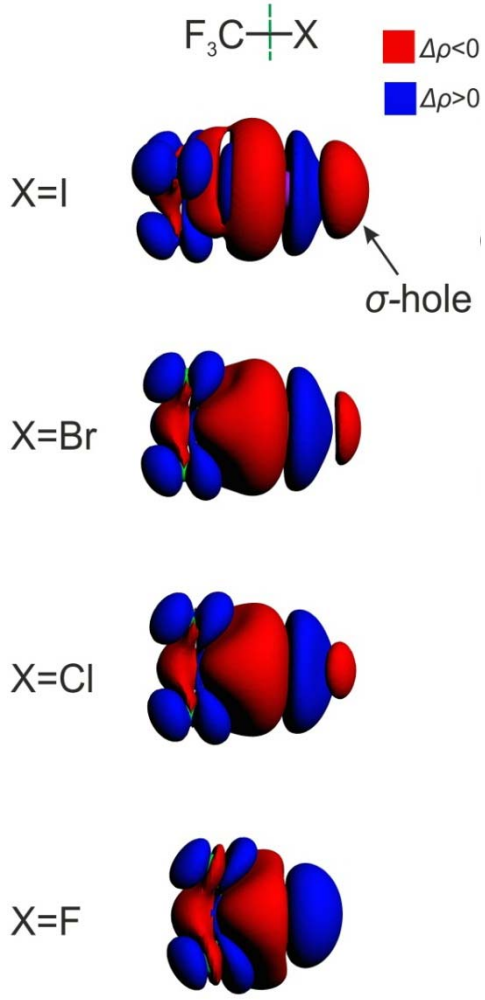
deformation density of dominating NOCV channel ($\Delta\rho_1$)

formation of carbon – halogen **σ bond**



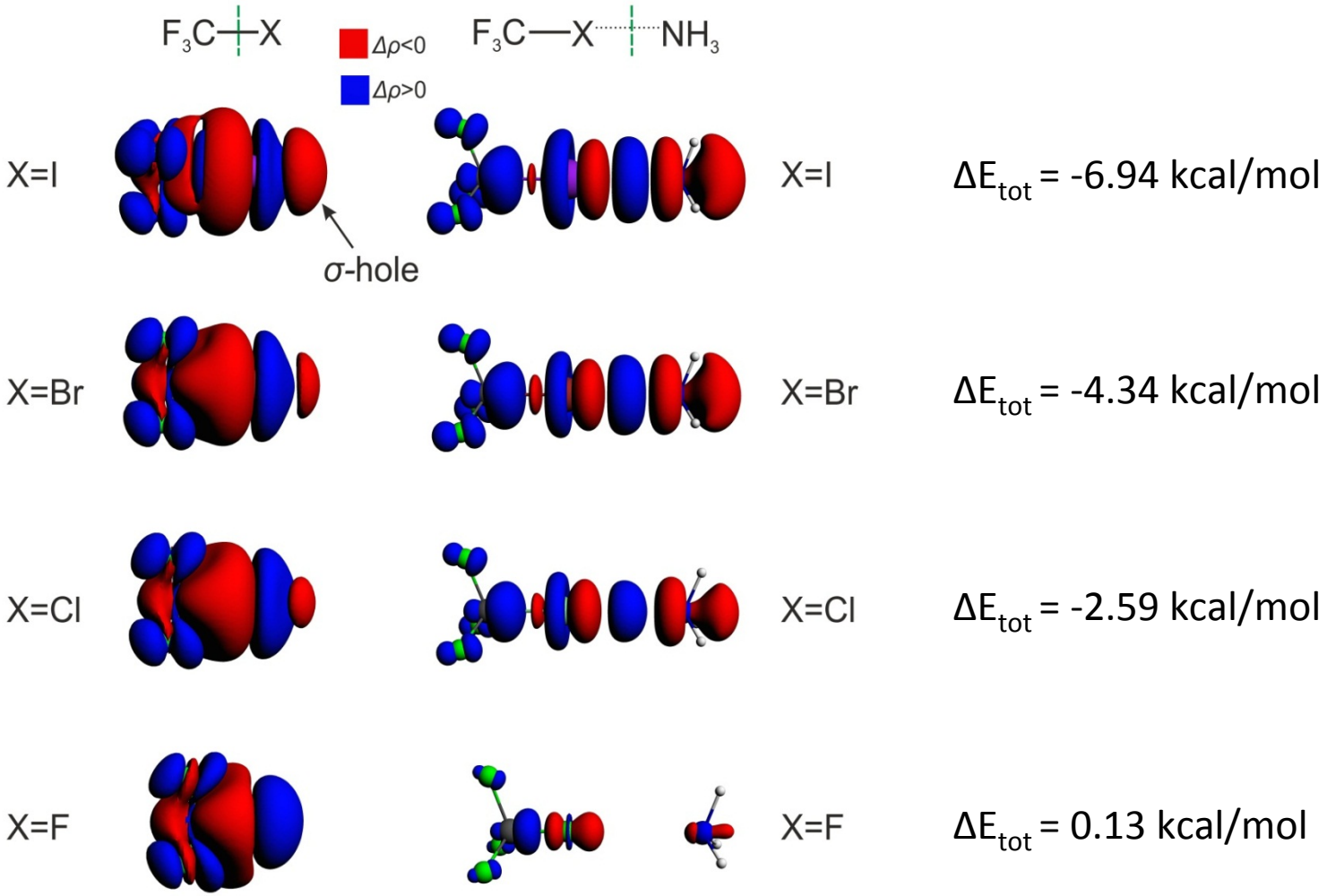
results

deformation density of dominating NOCV channel ($\Delta\rho_1$)

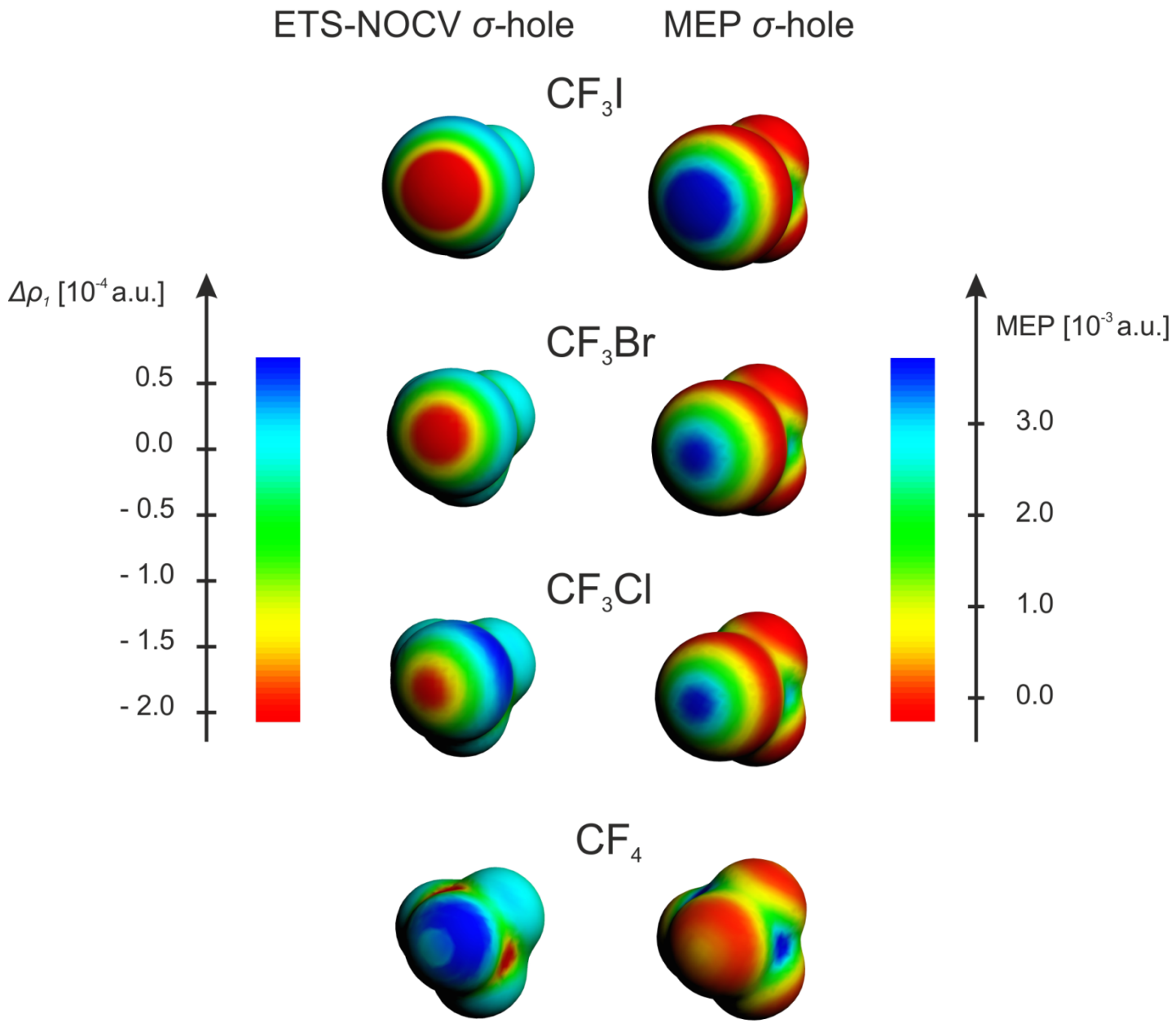


results

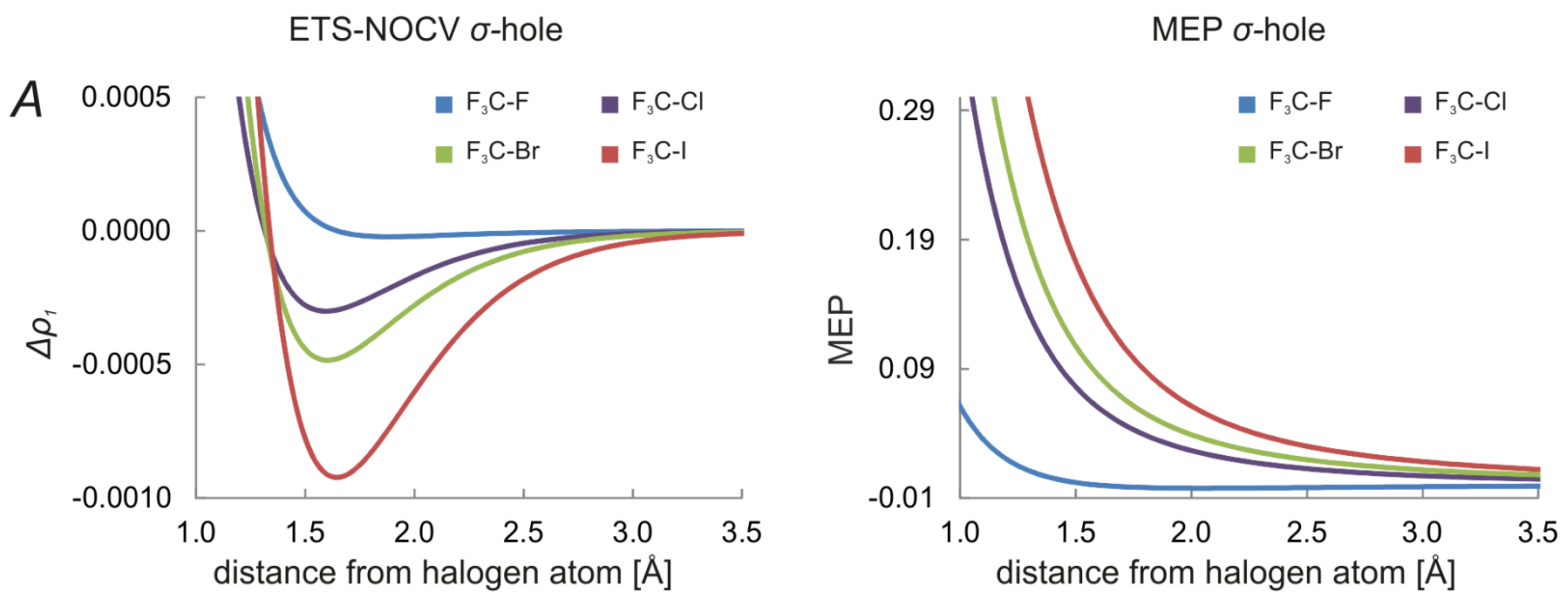
deformation density of dominating NOCV channel ($\Delta\rho_1$)



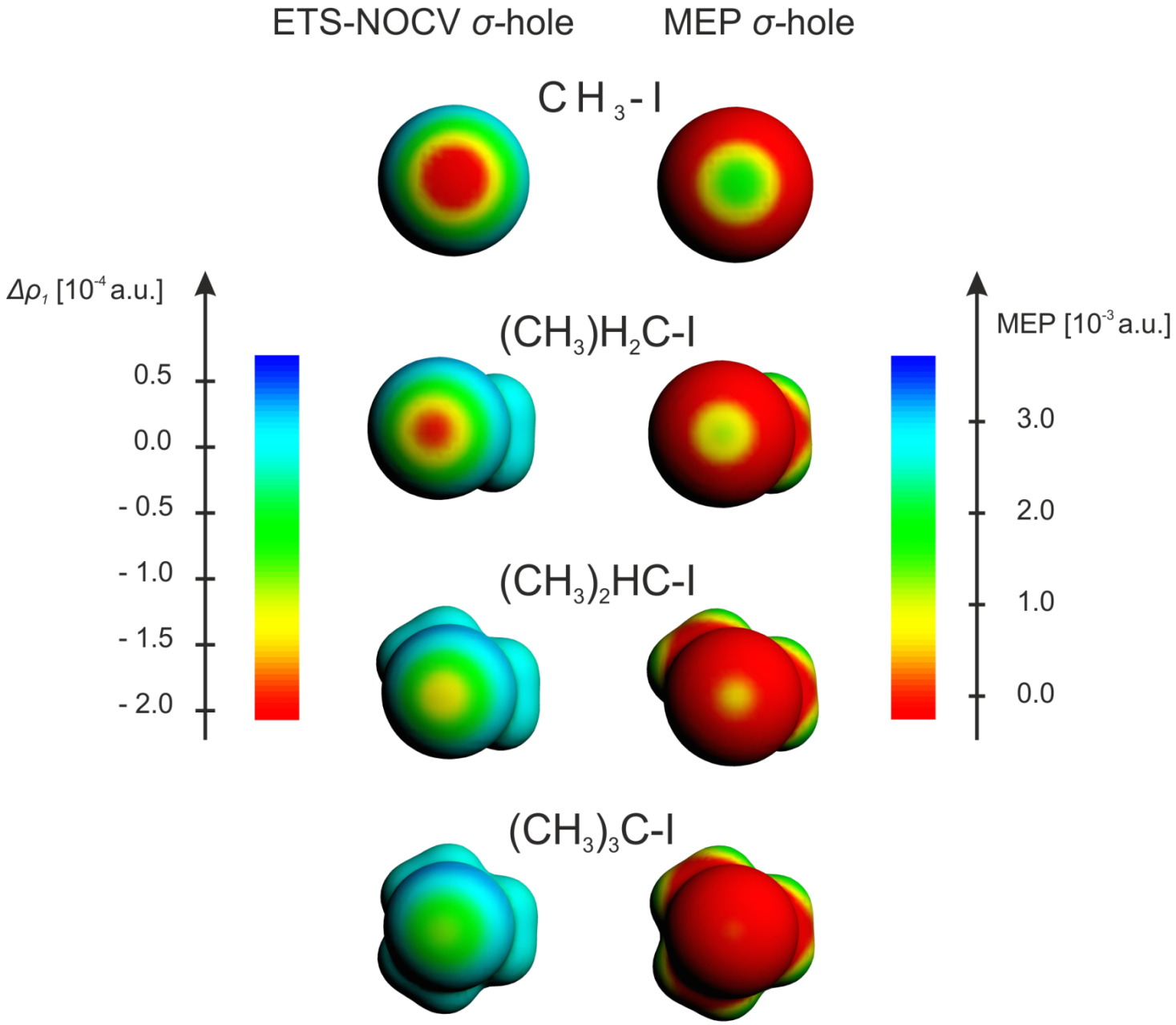
results


ETS-NOCV σ-hole
MEP σ-hole
CF3I
CF3Br
CF3Cl
CF4
Δρ1 [10-4 a.u.]
0.5
0.0
- 0.5
- 1.0
- 1.5
- 2.0
MEP [10-3 a.u.]
3.0
2.0
1.0
0.0

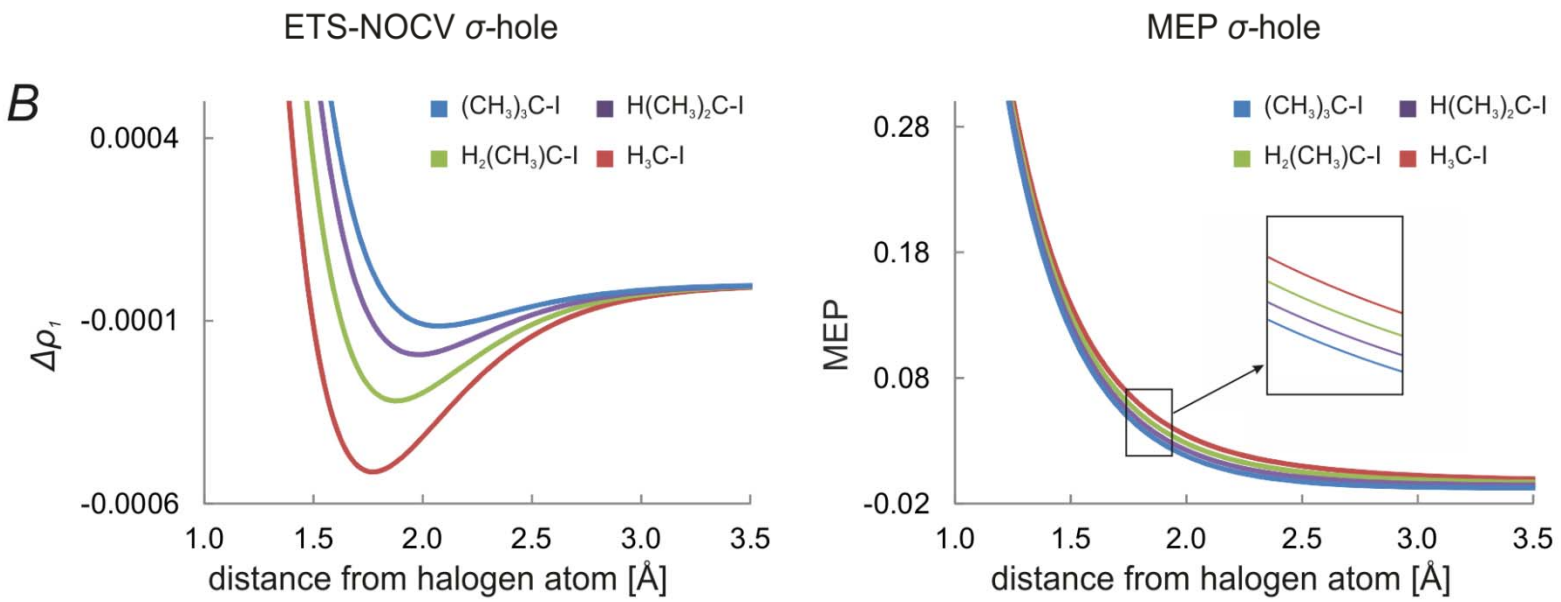
results


ETS-NOCV σ-hole
A
0.0005
0.0000
-0.0005
-0.0010
Δρ1
F3C-F
F3C-Cl
F3C-Br
F3C-I
1.0
1.5
2.0
2.5
3.0
3.5
distance from halogen atom [Å]
MEP σ-hole
0.29
0.19
0.09
-0.01
MEP
F3C-F
F3C-Cl
F3C-Br
F3C-I
1.0
1.5
2.0
2.5
3.0
3.5
distance from halogen atom [Å]

results

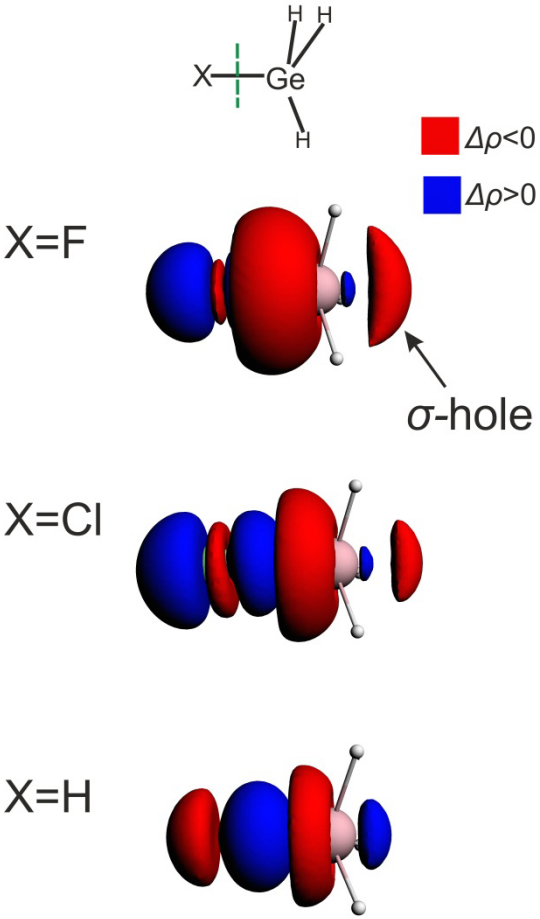

ETS-NOCV σ-hole
MEP σ-hole
CH3-I
(CH3)H2C-I
(CH3)2HC-I
(CH3)3C-I
Δρi [10-4 a.u.]
0.5
0.0
- 0.5
- 1.0
- 1.5
- 2.0
MEP [10-3 a.u.]
3.0
2.0
1.0
0.0

results


B
ETS-NOCV σ-hole
(CH3)3C-I
H(CH3)2C-I
H2(CH3)C-I
H3C-I
0.0004
-0.0001
-0.0006
Δρ1
1.0
1.5
2.0
2.5
3.0
3.5
distance from halogen atom [Å]
MEP σ-hole
(CH3)3C-I
H(CH3)2C-I
H2(CH3)C-I
H3C-I
0.28
0.18
0.08
-0.02
MEP
1.0
1.5
2.0
2.5
3.0
3.5
distance from halogen atom [Å]

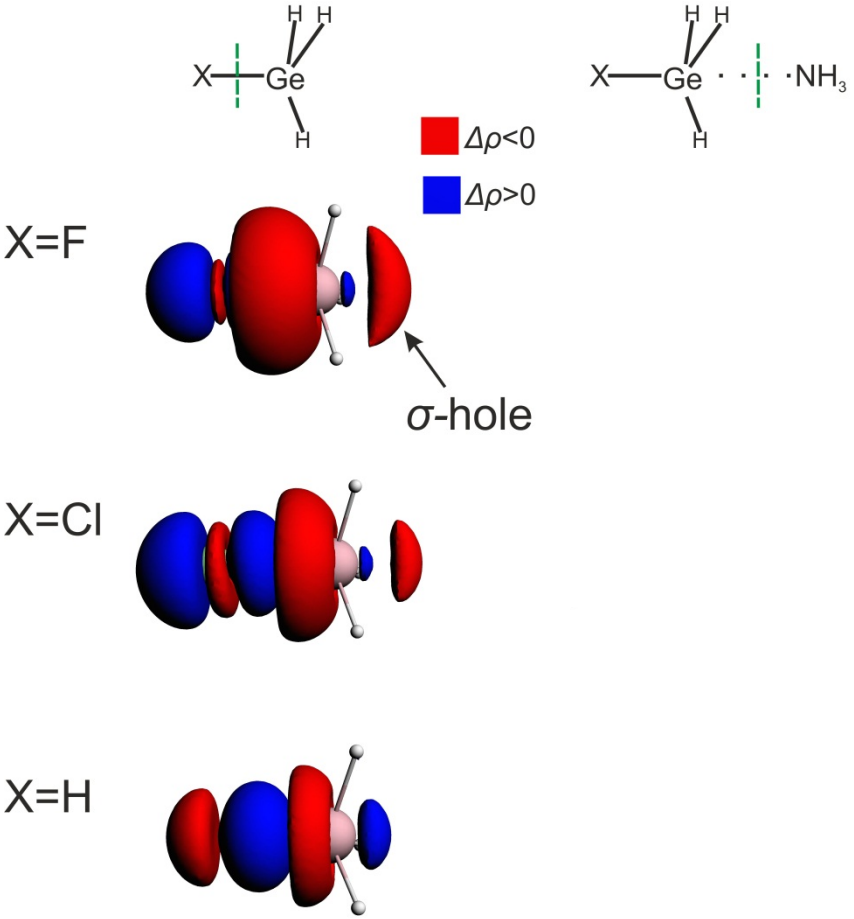
results

deformation density of dominating NOCV channel ($\Delta\rho_1$)



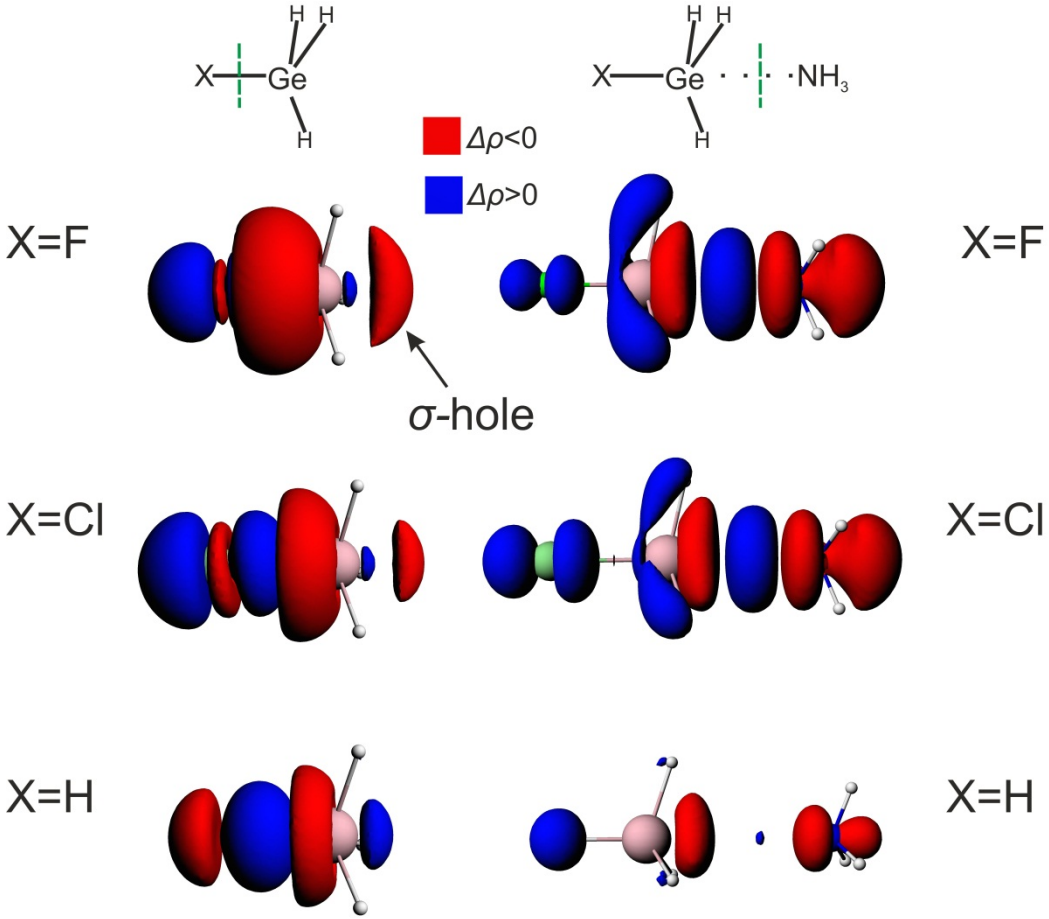
results

deformation density of dominating NOCV channel ($\Delta\rho_1$)



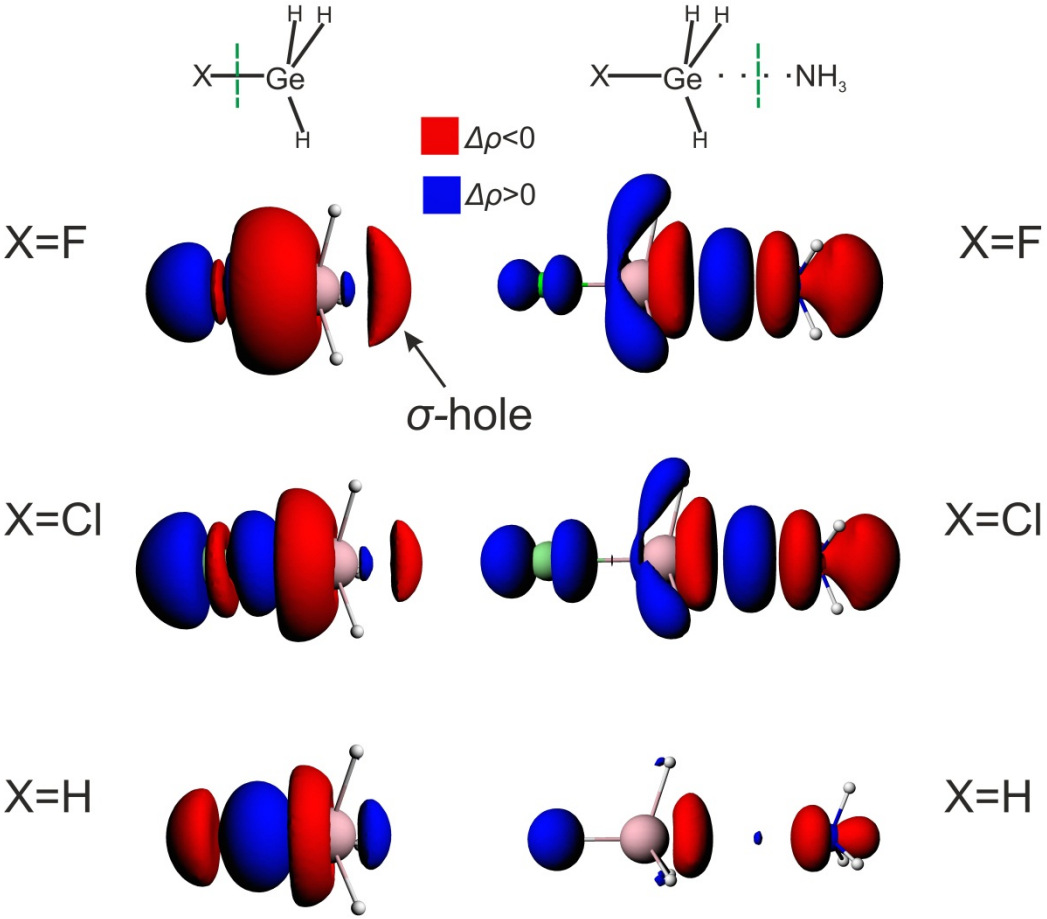
results

deformation density of dominating NOCV channel ($\Delta\rho_1$)



results

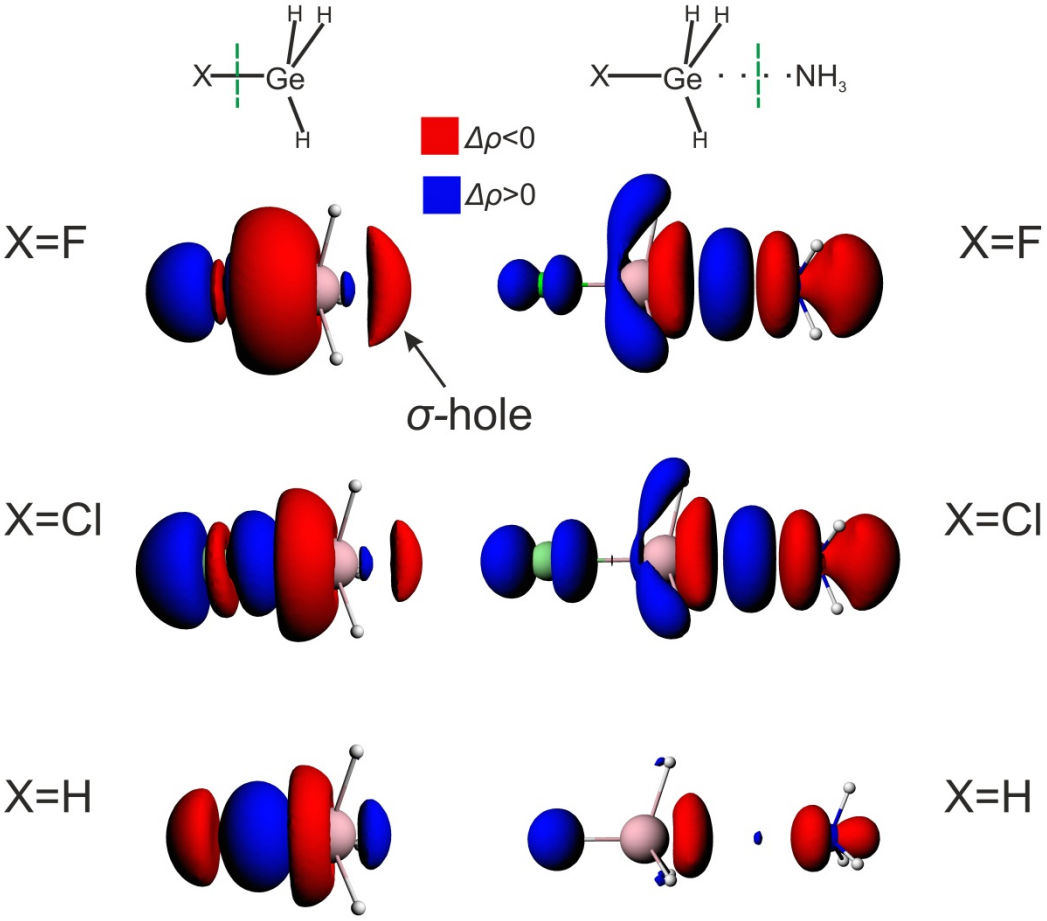
deformation density of dominating NOCV channel ($\Delta\rho_1$)



X	**F**	**Cl**	**H**
ΔE_{tot}	-5.74	-5.32	-1.13

results

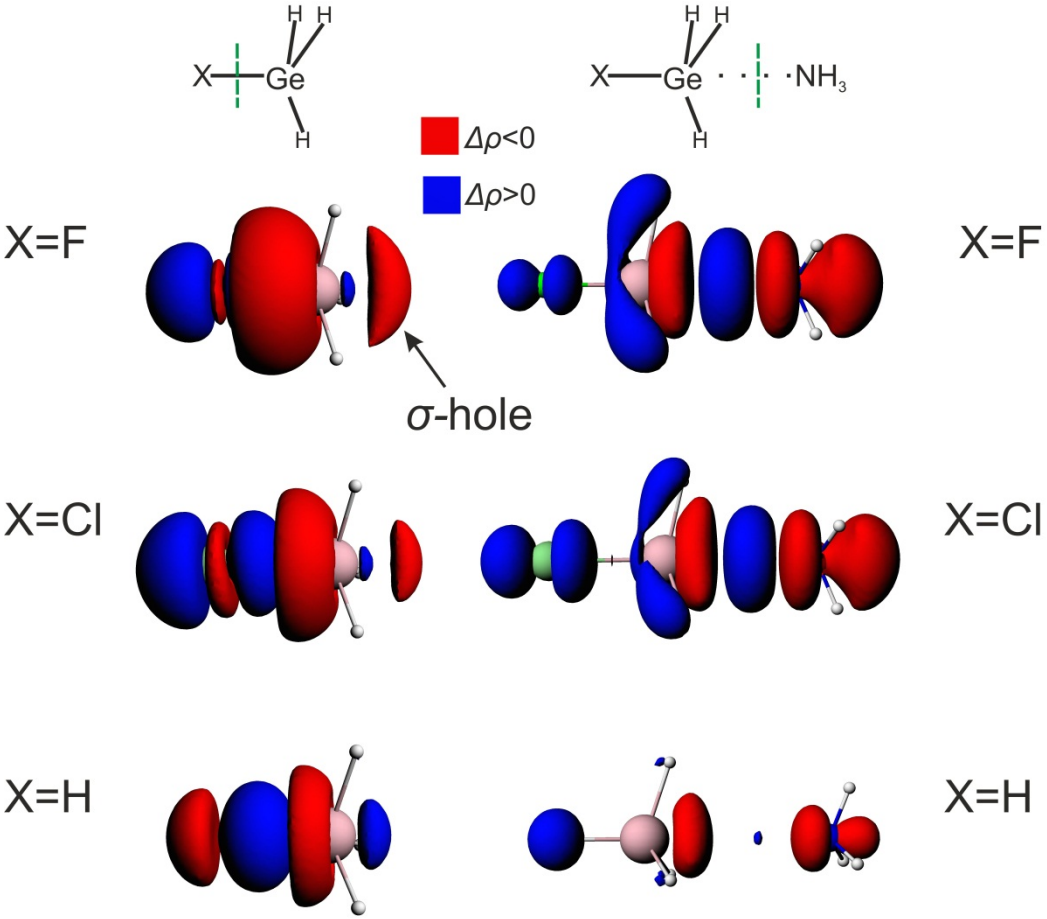
deformation density of dominating NOCV channel ($\Delta\rho_1$)



X	F	Cl	H
ΔE_{tot}	-5.74	-5.32	-1.13
ΔE_{elstat}	-20.3	-16.3	-3.81
ΔE_{orb}	-9.34	-7.66	-1.57

results

deformation density of dominating NOCV channel ($\Delta\rho_1$)



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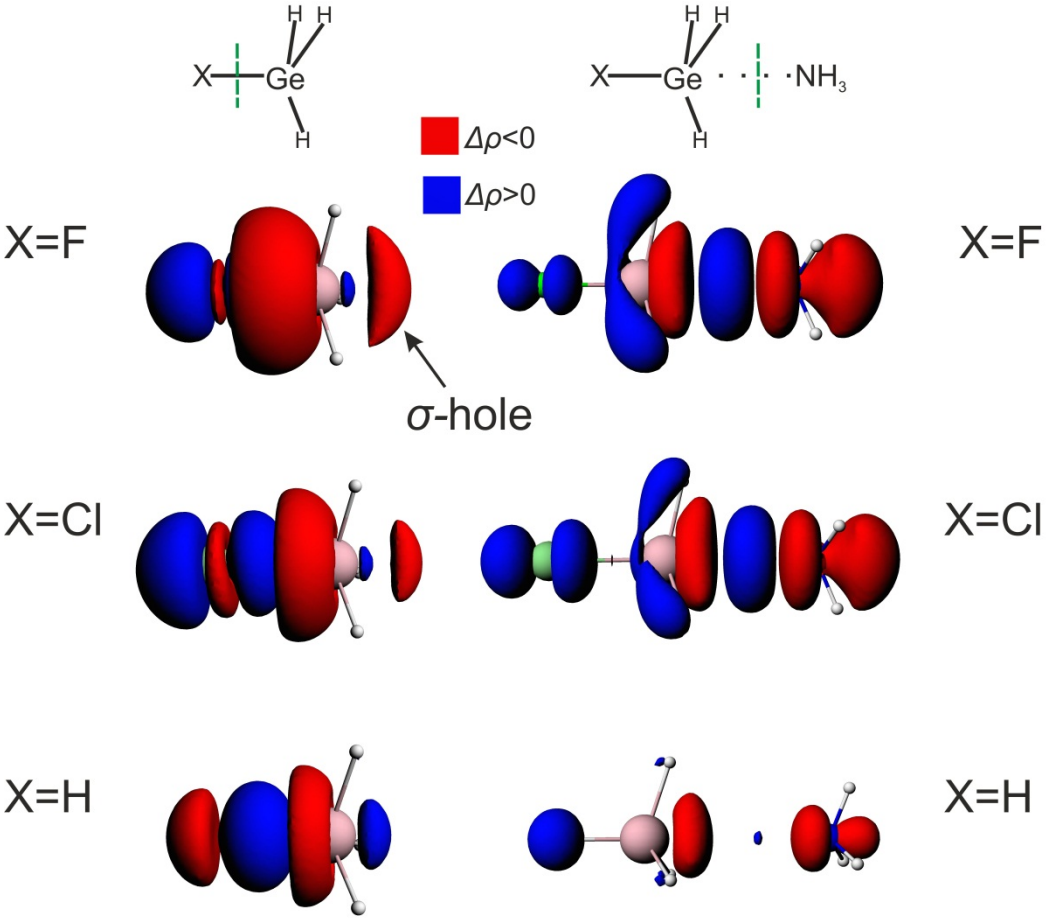
ΔE_{orb}	-9.34	-7.66	-1.57
ΔE_{orb}^{1}	-8.02	-6.58	-1.27

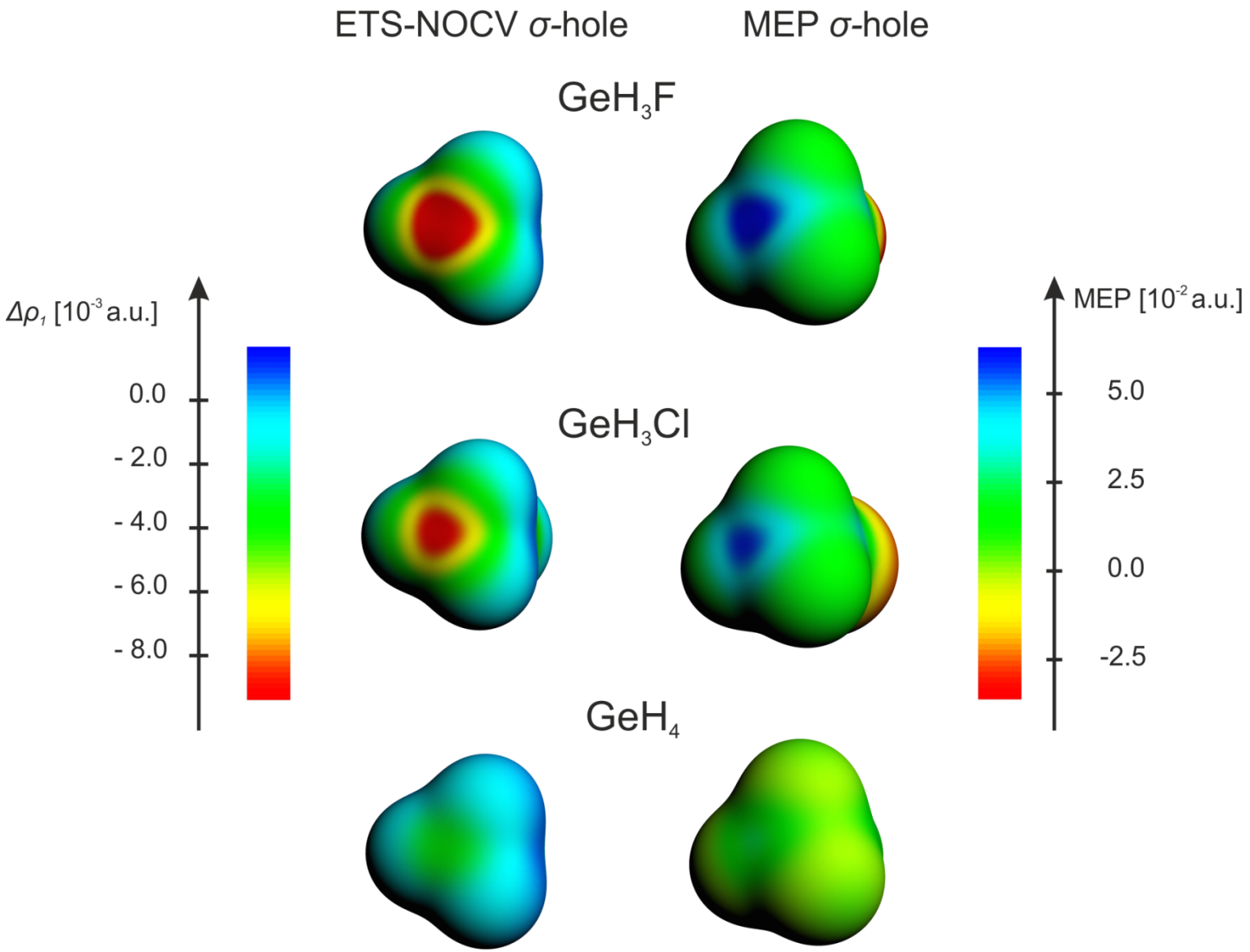
results

deformation density of dominating NOCV channel ($\Delta\rho_1$)

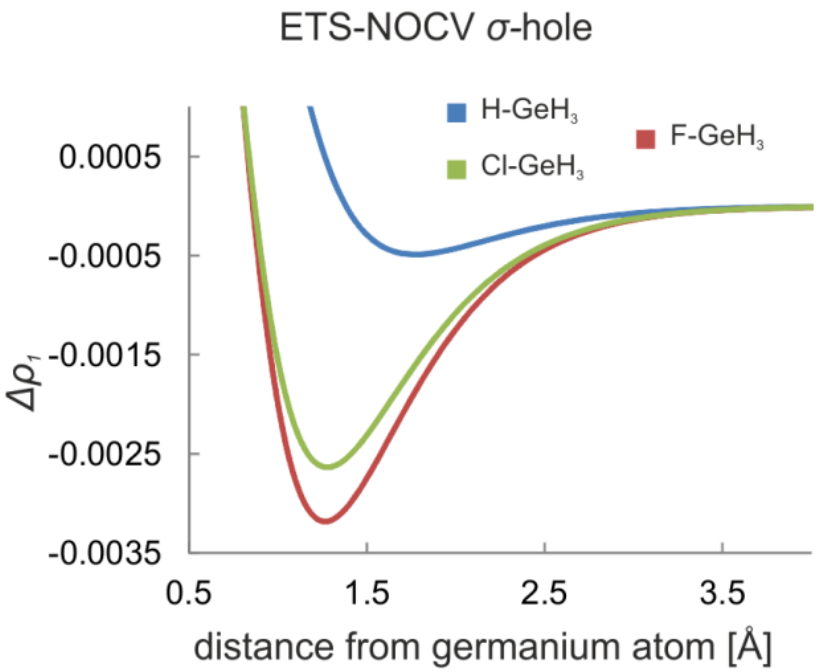


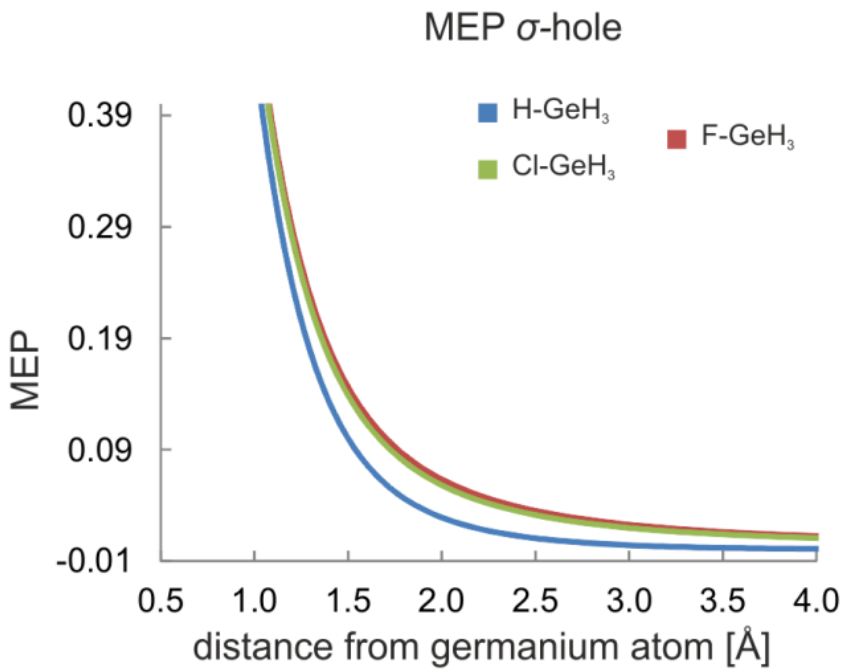
X	F	Cl	H
ΔE_{tot}	-5.74	-5.32	-1.13
ΔE_{elstat}	-20.3	-16.3	-3.81
ΔE_{orb}	-9.34	-7.66	-1.57
ΔE_{Pauli}	26.22	20.8	5.85
ΔE_{disp}	-2.30	-2.14	-1.60

results

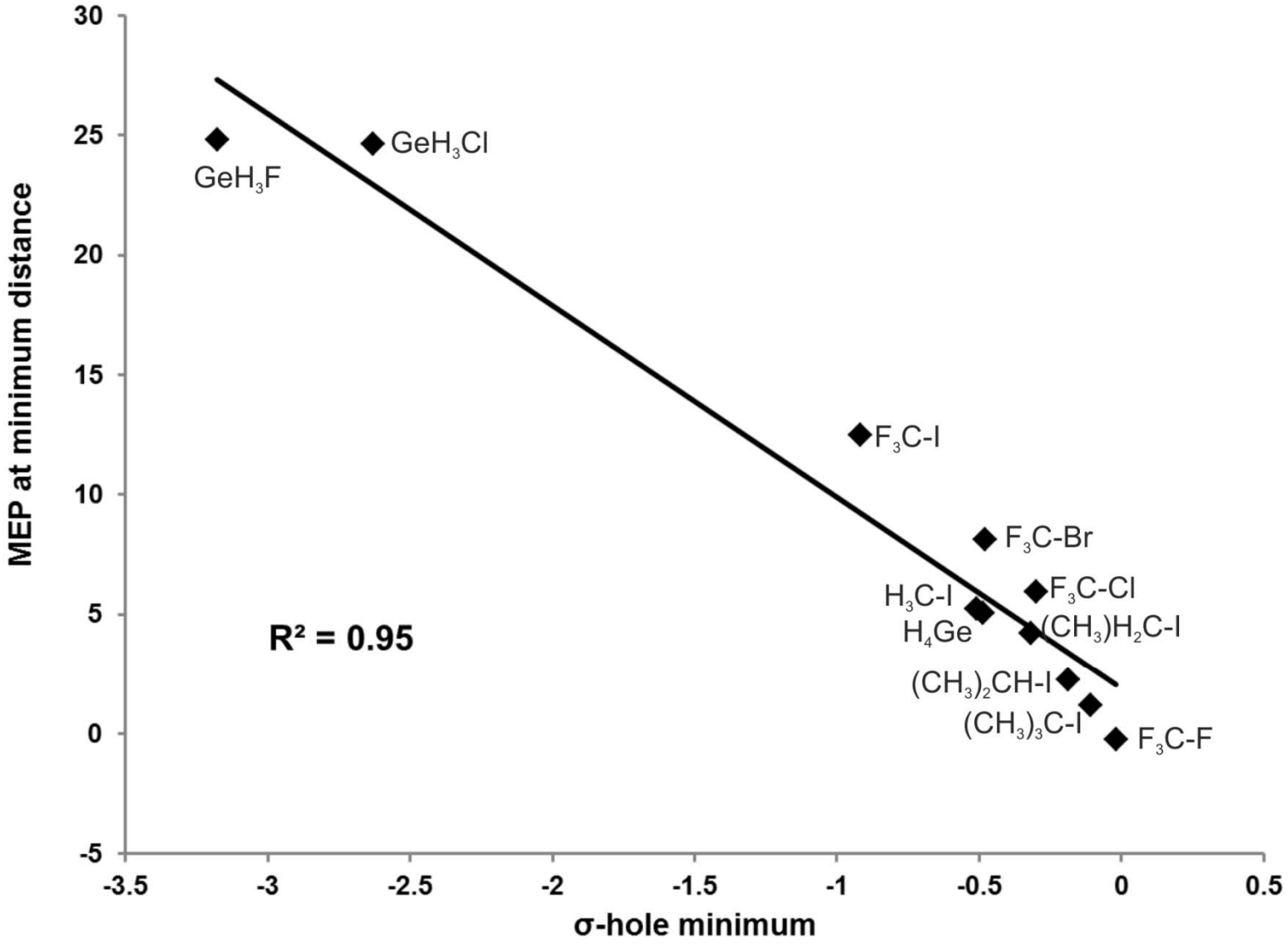

ETS-NOCV σ-hole
MEP σ-hole
GeH3F
GeH3Cl
GeH4
Δρ1 [10-3 a.u.]
0.0
- 2.0
- 4.0
- 6.0
- 8.0
MEP [10-2 a.u.]
5.0
2.5
0.0
-2.5

results


ETS-NOCV σ-hole
H-GeH3
F-GeH3
Cl-GeH3
0.0005
-0.0005
-0.0015
-0.0025
-0.0035
Δρ1
0.5
1.5
2.5
3.5
distance from germanium atom [Å]


MEP σ-hole
H-GeH3
F-GeH3
Cl-GeH3
0.39
0.29
0.19
0.09
-0.01
MEP
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
distance from germanium atom [Å]

conclusions



conclusions

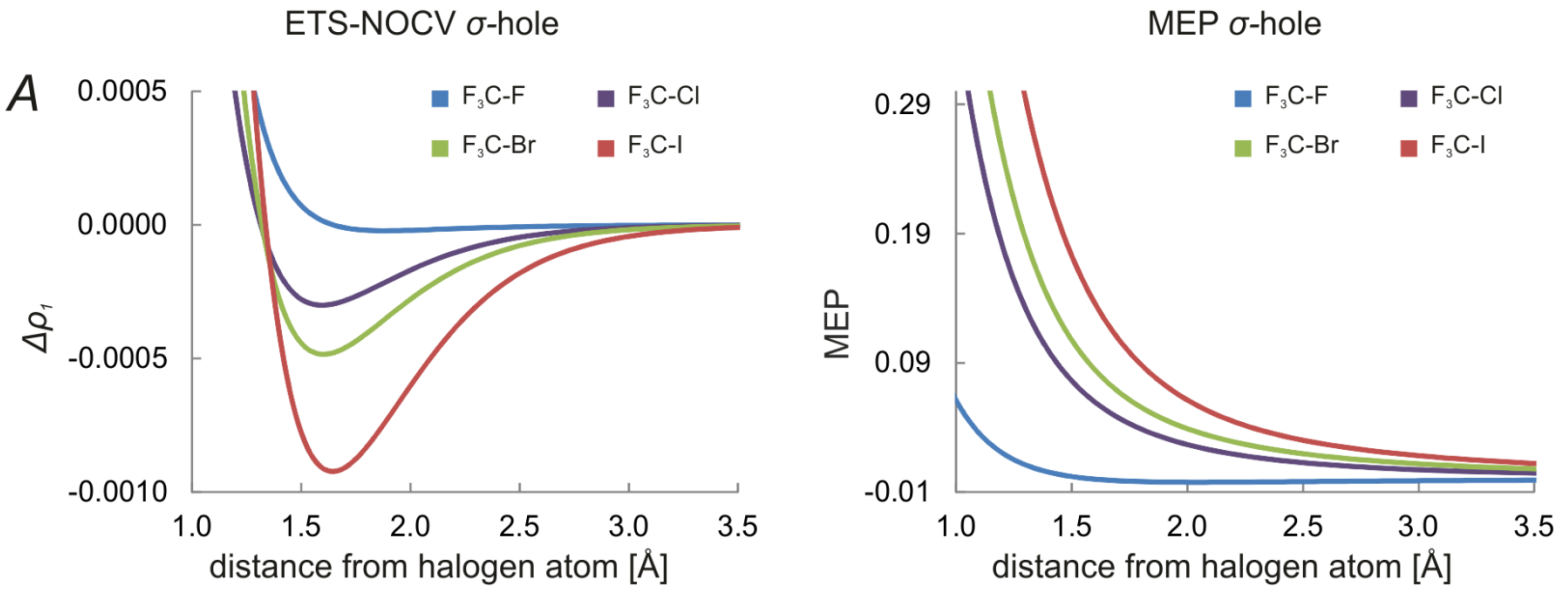
dominating contribution to the deformation density, $\Delta\rho_1$ exhibits the negative-value area (σ-hole area) with a minimum.

"size" (spatial extension of negative value) and "depth" (minium value) of the σ-hole varies for different elements and is strongly affected by substituens

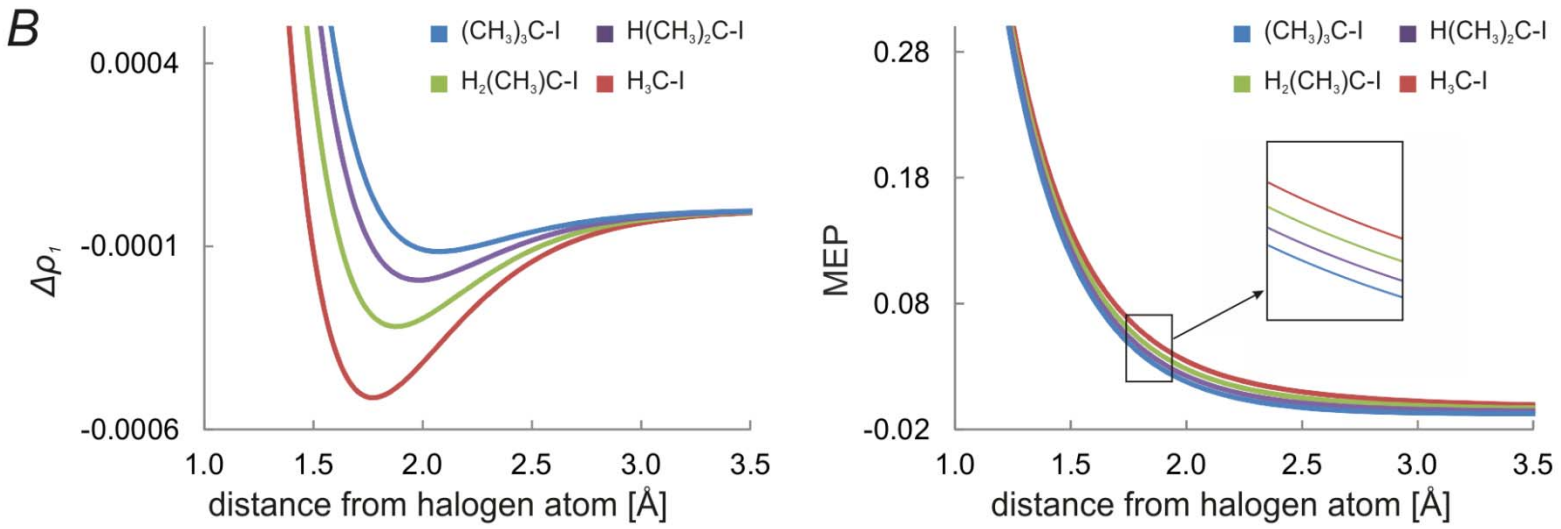
"size" and "depth" of the ETS-NOCV representation of σ-hole by Δρ1 corresponds qualitatively to the positive MEP area at the extension of σ-hole generating bond.

σ-hole bonding with ammonia is dominated by electrostatic component. However, both $\Delta E_{orb}{}^{1}$ and $\Delta\rho_1$, indicate a non-negligible covalent contribution.

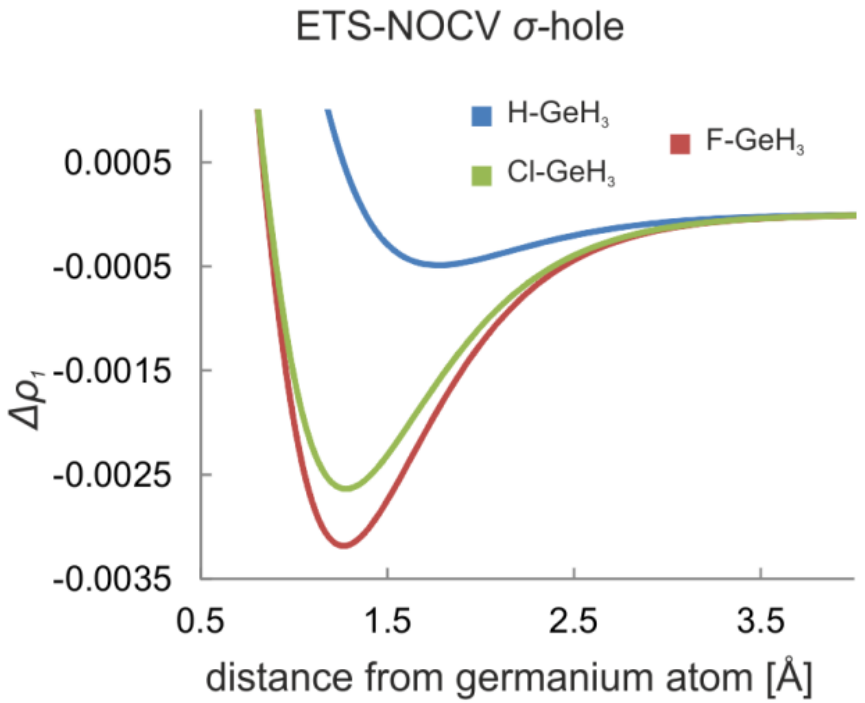
Dziękuję za uwagę

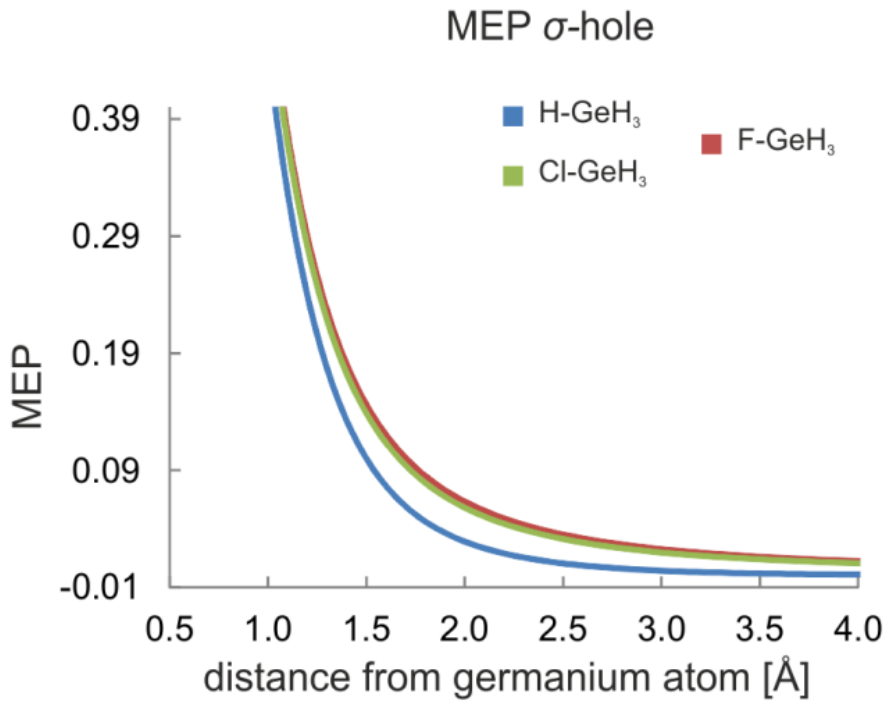


molecule	σ-hole minimum (10^{-3})	minimum distance	MEP at minimum distance (10^{-2})
CF_3I	-0.92	-1.64	12.50
CF_3Br	-0.48	-1.62	8.15
CF_3Cl	-0.30	-1.60	5.96
CF_4	-0.02	-1.88	-0.22



molecule	σ-hole minimum (10^{-3})	minimum distance	MEP at minimum distance (10^{-2})
C H_3I	-0.51	-1.79	5.27
C(CH_3)H_2I	-0.32	-1.86	4.25
C(CH_3)$_2$HI	-0.19	-1.99	2.26
C(CH_3)$_3$I	-0.11	-2.09	1.18

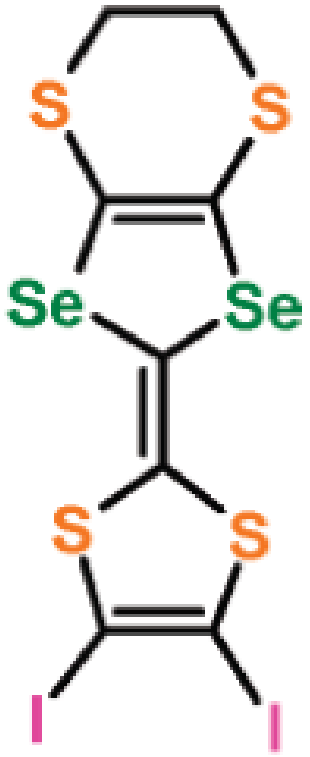




molecule	σ-hole min (10^{-3})	minimum distance	MEP at minimum distance (10^{-2})
GeH_3F	-3.18	1.28	24.85
GeH_3Cl	-2.63	1.25	24.65
GeH_4	-0.49	1.76	5.07

molecule	ΔE_{tot}	ΔE_{disp}	ΔE_{elstat}	ΔE_{Pauli}	ΔE_{orb}	ΔE_{orb}^{1}
F_3C-I···NH_3	-6.96	-1.32	-16.65	20.60	-9.59	-8.90
F_3C-Br···NH_3	-4.34	-1.02	-10.44	12.90	-5.78	-5.48
F_3C-Cl···NH_3	-2.59	-0.81	-5.03	5.75	-2.51	-2.43
F_3C-F···NH_3	(Repulsive interaction energy; no halogen-bond minimum found)					
H_3C-I···NH_3	-3.01	-1.19	-8.05	10.72	-4.49	-3.95
$H_2(CH_3)C$-I···NH_3	-2.46	-1.21	-5.93	8.18	-3.50	-3.14
$H(CH_3)_2C$-I···NH_3	-2.07	-1.24	-5.90	8.65	-3.57	-3.12
$(CH_3)_3C$-I···NH_3	-1.87	-1.25	-5.60	8.49	-3.51	-3.09

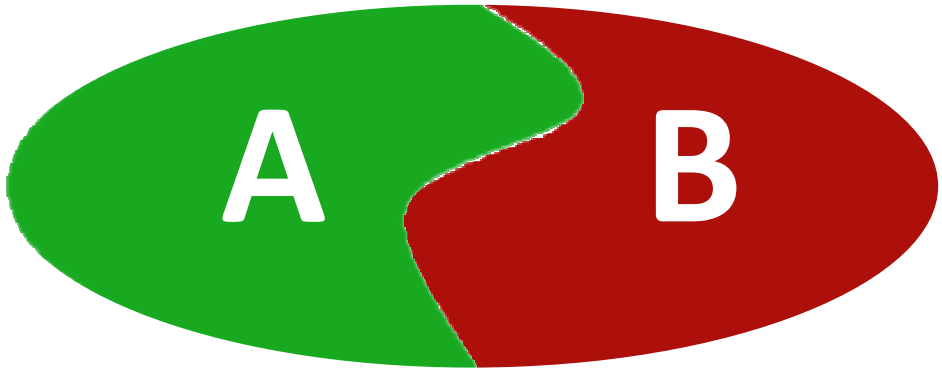
(DIETS) diiodo(ethylenedithio)-diselenadithiafulvalene)



ETS - energy decomposition scheme

Total interaction synergy

$$\Delta E_{int} = \Delta E_{dist} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$$



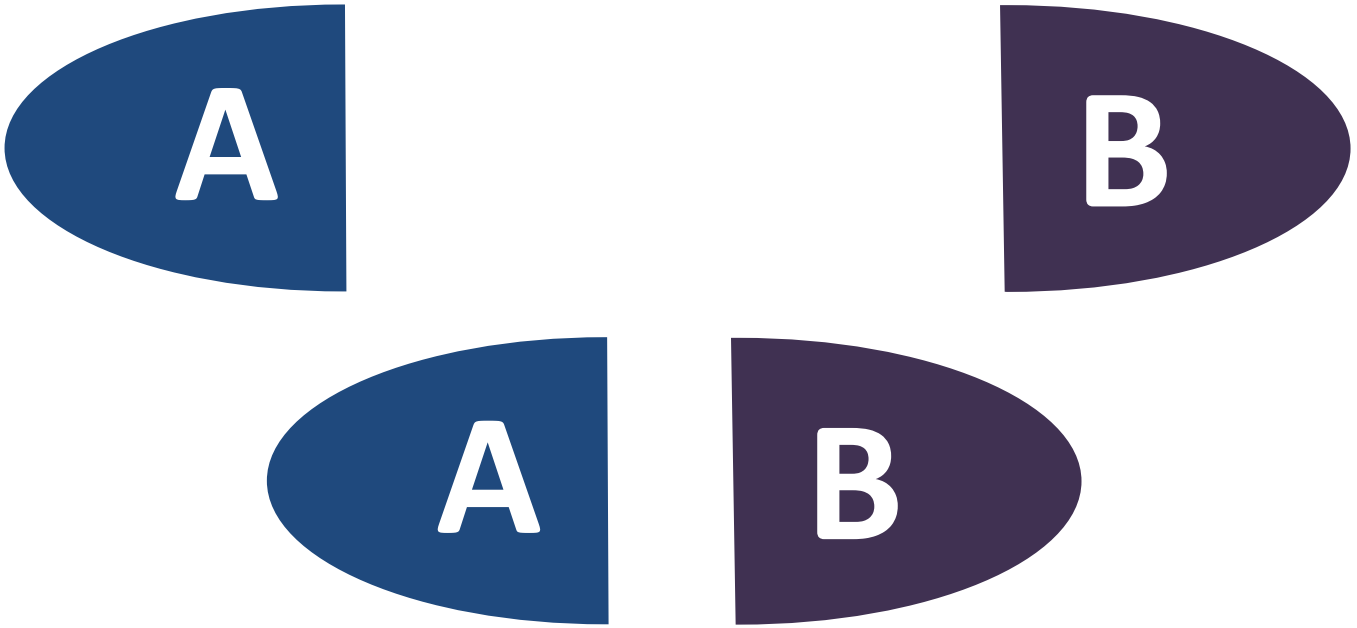
ETS - energy decomposition scheme

$$\Delta E_{dist} = \left(E_A - E_A^{opt}\right) + \left(E_B - E_B^{opt}\right)$$

ETS - energy decomposition scheme

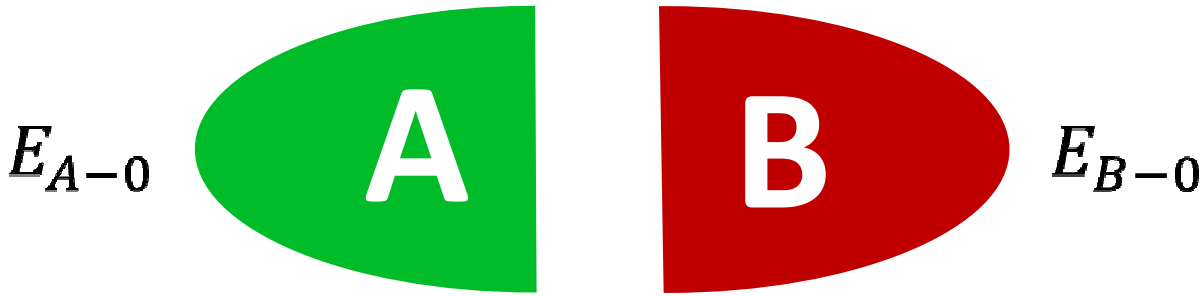
$$\Delta E_{elstat} = \sum_{\alpha \in A, \beta \in B} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} + \int \frac{\rho_A(r_1)\rho_B(r_2)}{r_{12}} dr_1 dr_2 +$$

$$+ \sum_{\beta \in A} \int \frac{\rho_\beta(r) Z_\beta}{|R_\beta - r|} dr + \sum_{\alpha \in B} \int \frac{\rho_\alpha(r) Z_\alpha}{|R_\alpha - r|} dr$$



ETS - energy decomposition scheme

$$\Delta E_{Pauli} = (E_{A-0} - E_A) + (E_{B-0} - E_B)$$



ETS - energy decomposition scheme

$$\Delta E_{orb} = \sum_{\alpha}^{N} \sum_{\beta}^{N} \Delta P_{\alpha\beta}^{orb} F_{\alpha\beta}^{TS} = Tr\left(\Delta P^{orb} F^{TS}\right)$$