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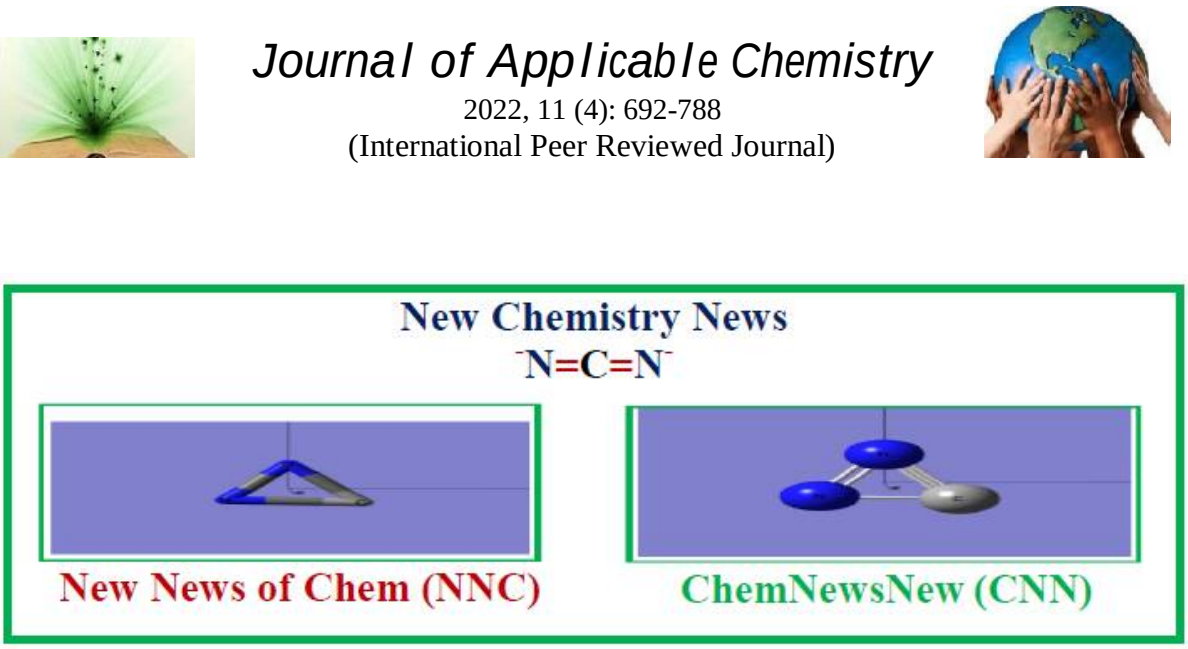
(International Peer Reviewed Journal)



CNN – 46 Sup Inf Fig (Sif)
Aerogenbonds

Information Source	ACS.org ; sciencedirect.com
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Coutesy from DOI: 10.1021/acs.accounts.9b00037

Term recommended by IUPAC

The term is used in the literature consistent with the proposed classification

Other cases

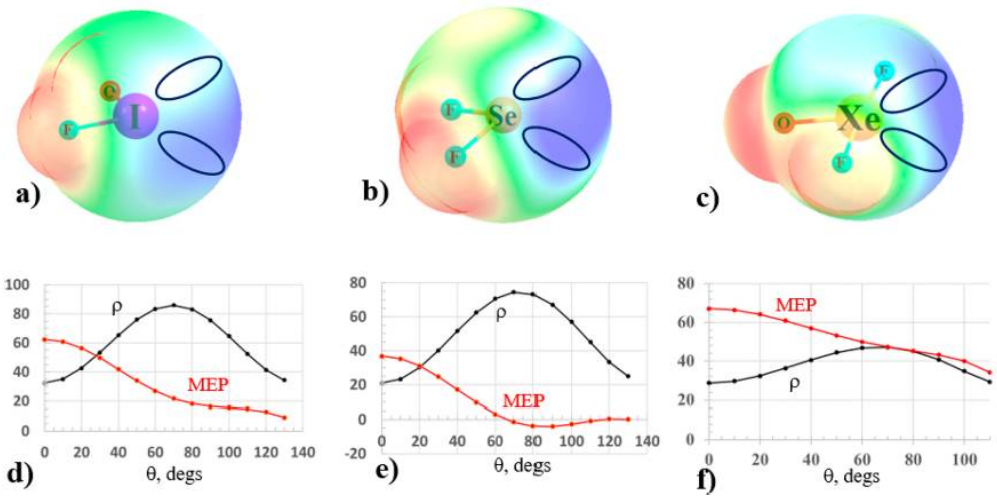
Experimental and theoretical evidences are reported for the formation of non-covalent adducts wherein the element is the electrophile

The electrophilic character of the element has been predicted by modelling or can be anticipated by analogy. The assigned color code for the elements is provisional; a comprehensive search of the literature may enable for a change from light green to green

Aerogen Bond (18 NgB)
[He Ne ArKr Xe Rn]

Aerogen Bond [Xe] [I] [Se]		NgB.	ACS.	02

MEP TED (ρ)

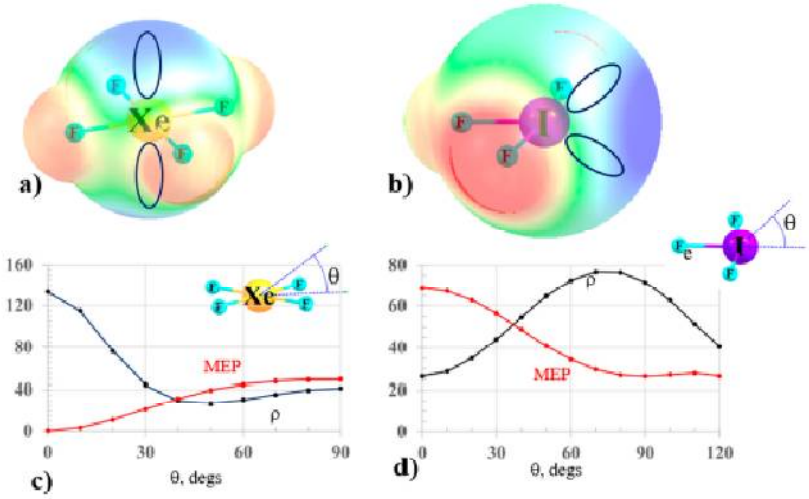


(a) IFO, (b) SeF2, and (c) XeF2O

θ = 0° corresponds to a point

- Directly opposite the F--O midpoint in IFO
- F--F midpoint in SeF2,
- The Oatom of XeF2O

MEP TED (ρ)



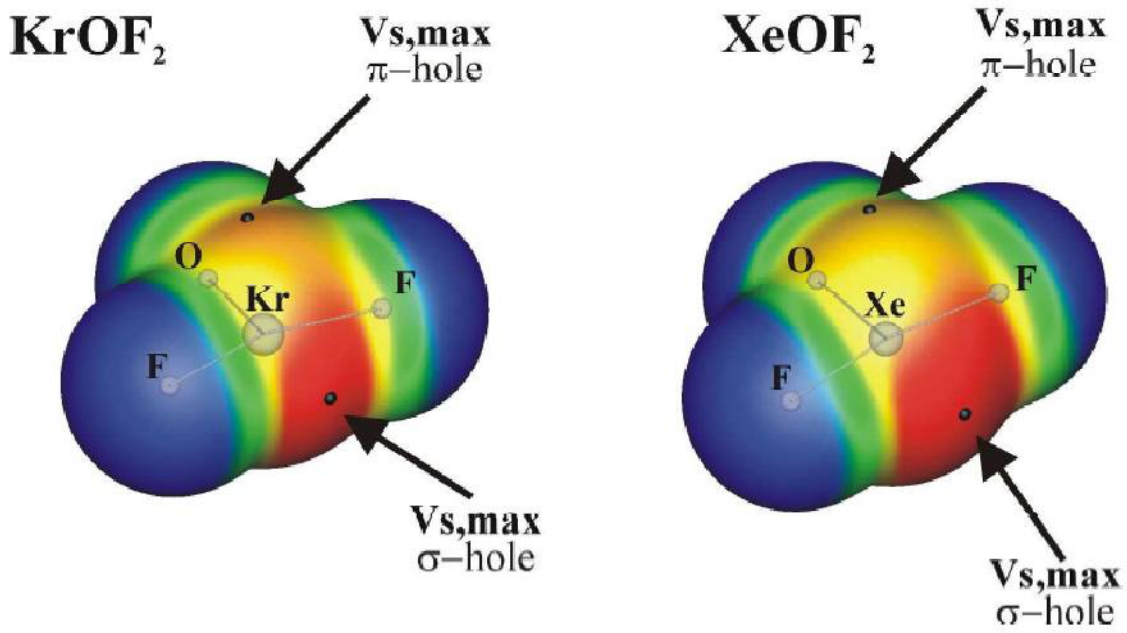
(a)XeF4 (b) IF3.

θ = 0° corresponds to a point

- Directly opposite F--F midpoint in XeF4
- Equatorial F atom of IF3

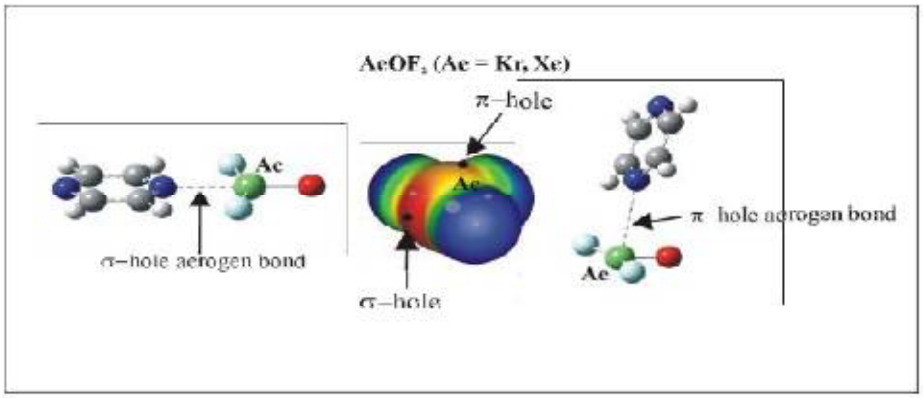
Aerogen Bond *[Kr Xe]*		NgB.	ACS.	**01**

MEP



- Isolated KrOF2 and XeOF2
- MP2/aug-cc-pVDZ level

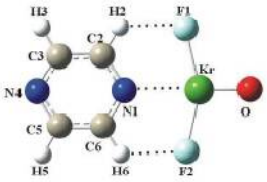
MP2-optimized structures



- AeOF2 (Ae=Kr, Xe) engages in noncovalent aerogen bonds with diazines, of both σ-hole and π-hole type.
- σ-hole species are several times stronger than typical H-bonds

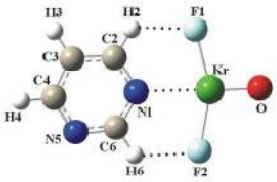
Aerogen Bond *[Kr Xe]* | NgB. | ACS. | 01

pyrazine···KrOF$_2$(σ)



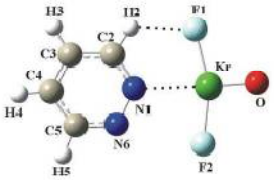
KrN1= 2.451
F1H2= 2.145
F2H6= 2.145

pyrimidine···KrOF$_2$(σ)



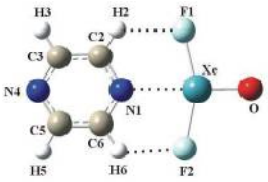
KrN1= 2.465
F1H2= 2.137
F2H6= 2.178

pyridazine···KrOF$_2$(σ)



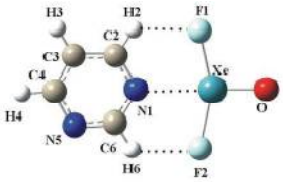
KrN1= 2.512
F1H2= 2.137

pyrazine···XeOF$_2$(σ)



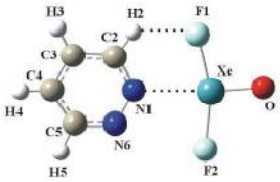
XeN1= 2.569
F1H2= 2.255
F2H6= 2.255

pyrimidine···XeOF$_2$(σ)



XeN1= 2.583
F1H2= 2.239
F2H6= 2.302

pyridazine···XeOF$_2$(σ)



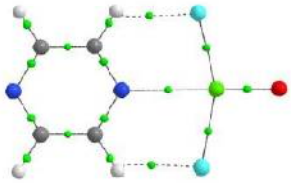
XeN1= 2.637
F1H2= 2.206

Aerogen Bond [Kr Xe]		NgB.	ACS.	01

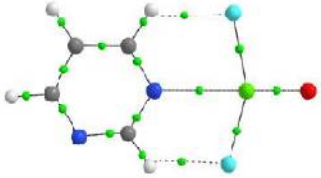
Molecular graphs

MP2/aug-cc-pVDZ

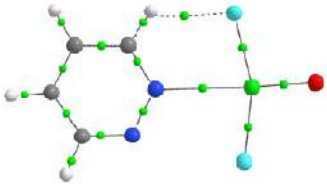
pyrazine··· $KrOF_2(\sigma)$



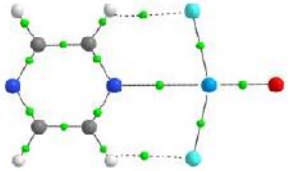
pyrimidine··· $KrOF_2(\sigma)$



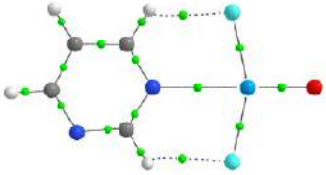
pyridazine··· $KrOF_2(\sigma)$



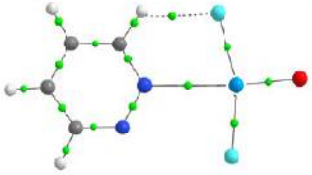
pyrazine··· $XeOF_2(\sigma)$



pyrimidine··· $XeOF_2(\sigma)$



pyridazine··· $XeOF_2(\sigma)$

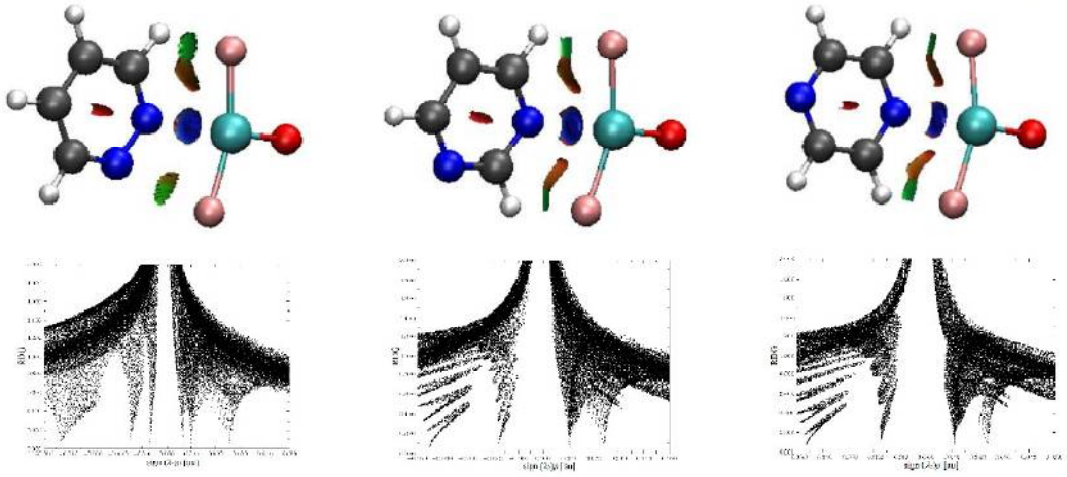


☞ Small green dots represent critical points

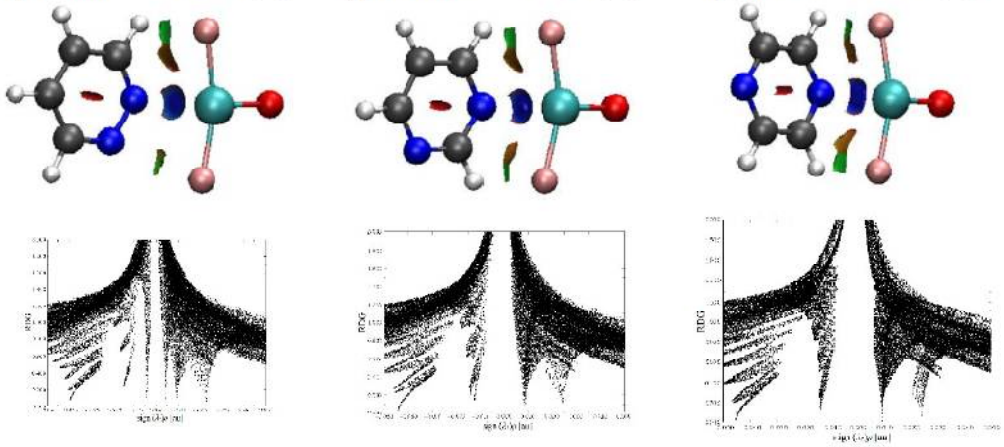
Plots of the RDG versus sign ($\lambda 2$)ρ

Noncovalent interaction regions

pyridazine···$KrOF_2(\sigma)$ pyrimidine···$KrOF_2(\sigma)$ pyrazine···$XeOF_2(\sigma)$

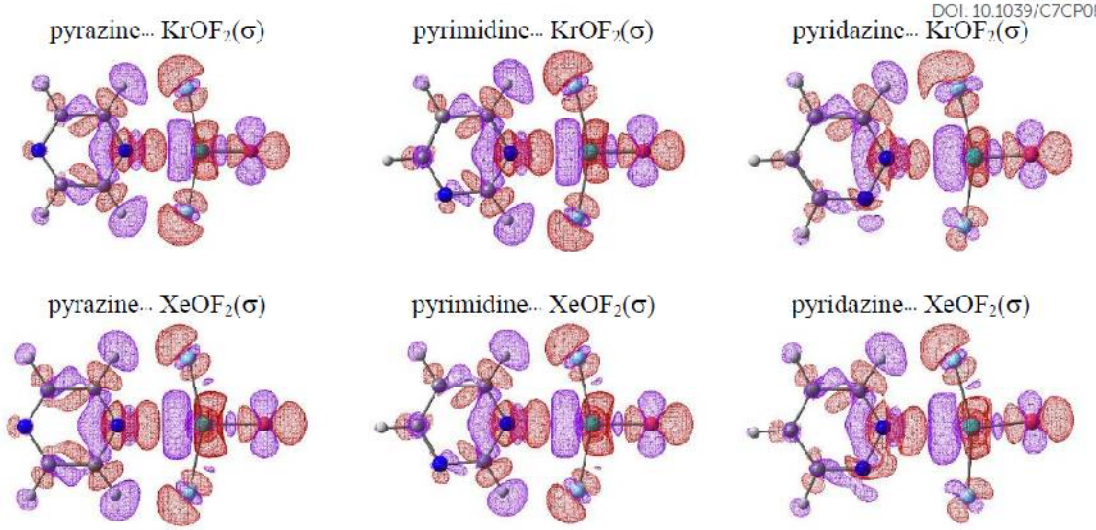


pyridazine···$XeOF_2(\sigma)$ pyrimidine···$XeOF_2(\sigma)$ pyrazine···$XeOF_2(\sigma)$

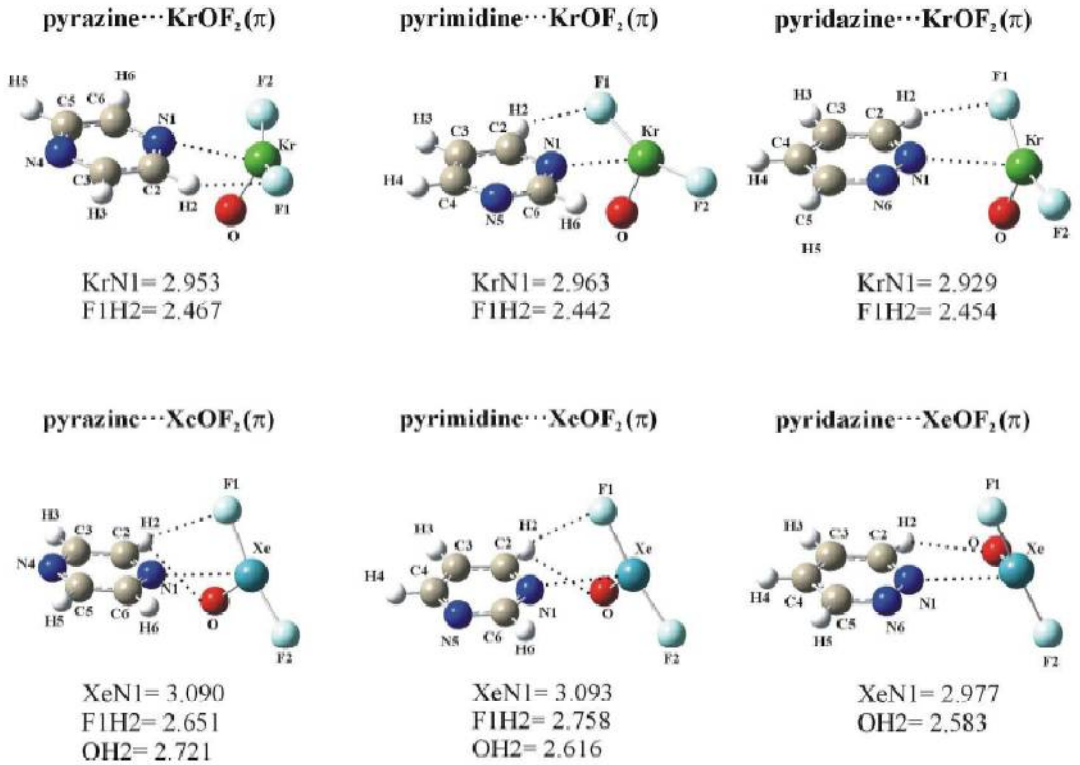


Electron density shift

MP2/aug-cc-pVDZ level



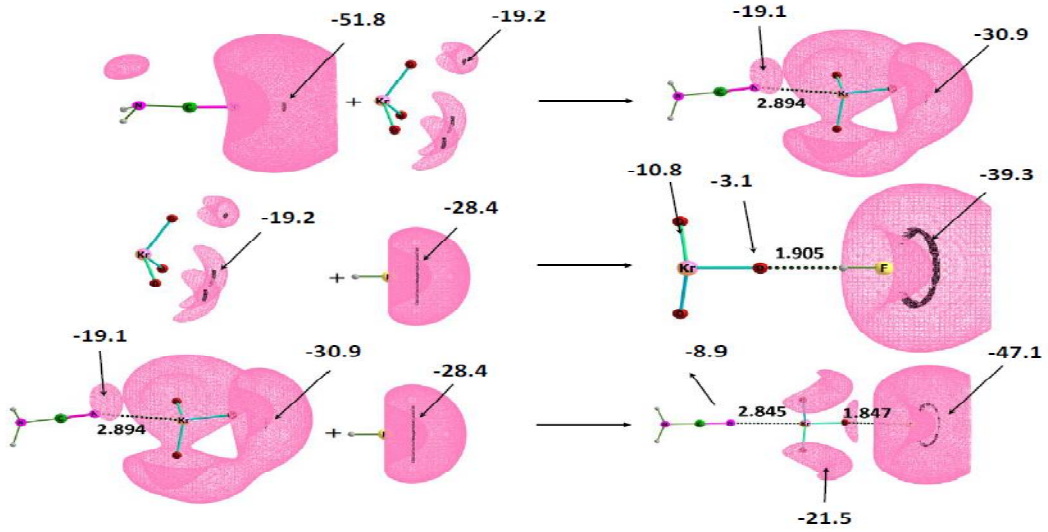
- Brown contours: Electron density accumulations
- Purple contours: Electron density loss



MP2 optimized structures of π-hole bonded AeOF2 (Ae = Kr, Xe) complexes with diazines

Aerogen Bond [Kr Xe]	Aerogen (Ng) bonded ternary complex NH2CN…KrO3…HF	NgB.	ACS.	01

MEP TED (ρ)



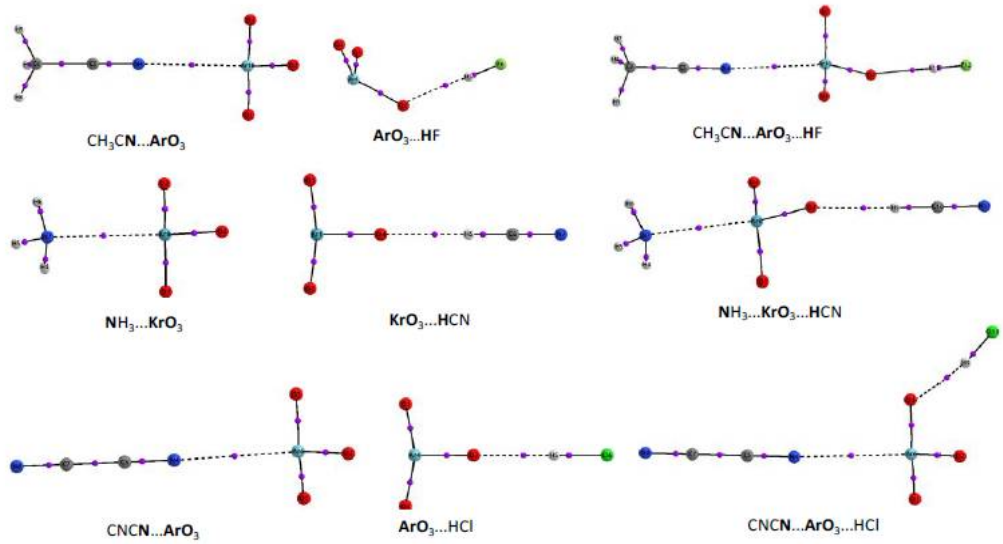
- NH2CN, KrO3, HF
- Aerogen bonded ternarycomplex, NH2CN…KrO3…HF along with their corresponding dimers

Aerogen Bond [Ar Kr]	Aerogen (Ng) bonded trimers and dimers	NgB.	ACS.	01

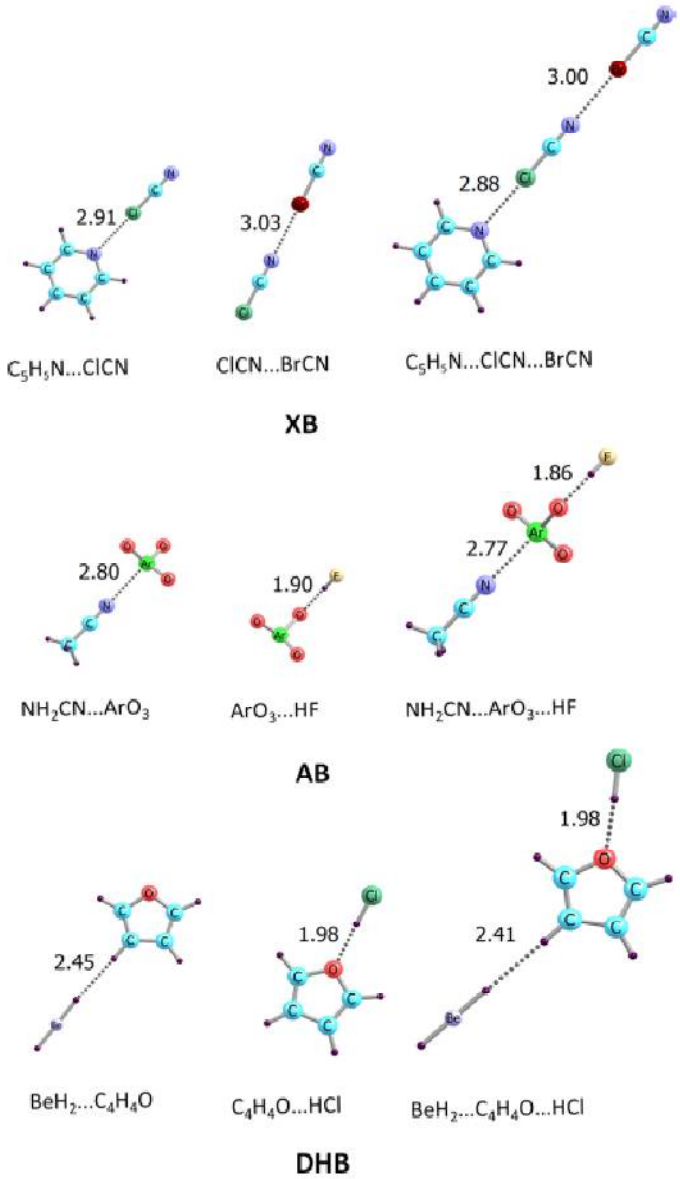
QTAIM bond critical points

MP2/6-311++G(d,p)

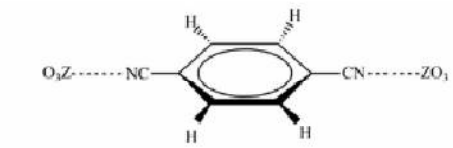
Aerogen bond



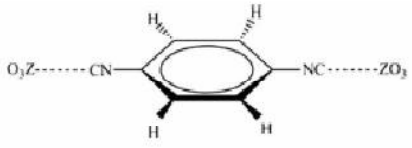
Optimized geometries



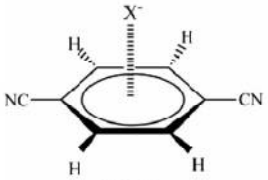
Structures of Ng compounds



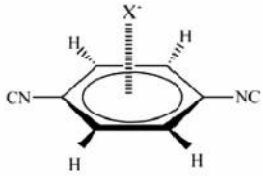
3. Z=Ar
4. Z=Kr



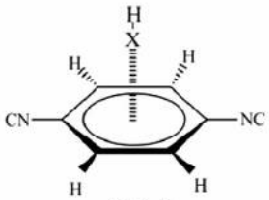
5. Z=Ar
6. Z=Kr



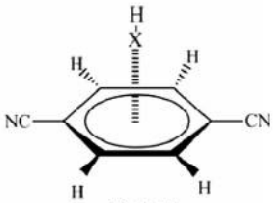
7. X=F
8. X=Cl
9. X=Br



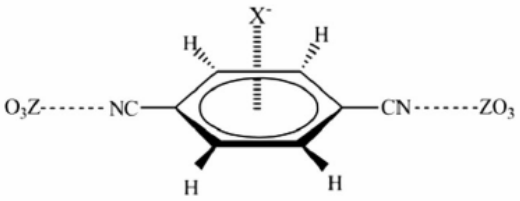
10. X=F
11. X=Cl
12. X=Br



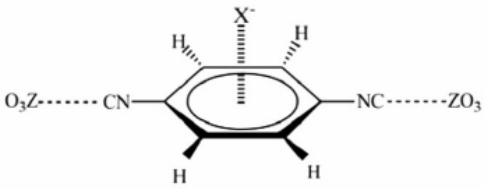
13. X=F
14. X=Cl
15. X=Br



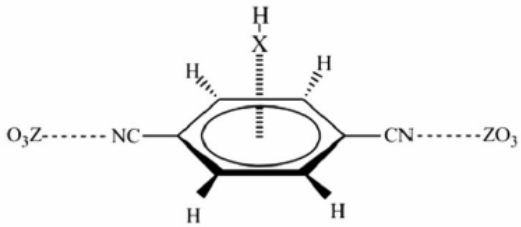
16. X=F
17. X=Cl
18. X=Br



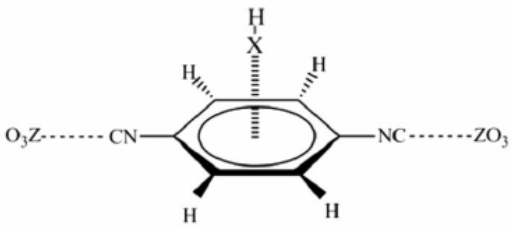
19. X=F, Z=Ar
20. X=F, Z=Kr
21. X=Cl, Z=Ar
22. X=Cl, Z=Kr
23. X=Br, Z=Ar
24. X=Br, Z=Kr



25. X=F, Z=Ar
26. X=F, Z=Kr
27. X=Cl, Z=Ar
28. X=Cl, Z=Kr
29. X=Br, Z=Ar
30. X=Br, Z=Kr



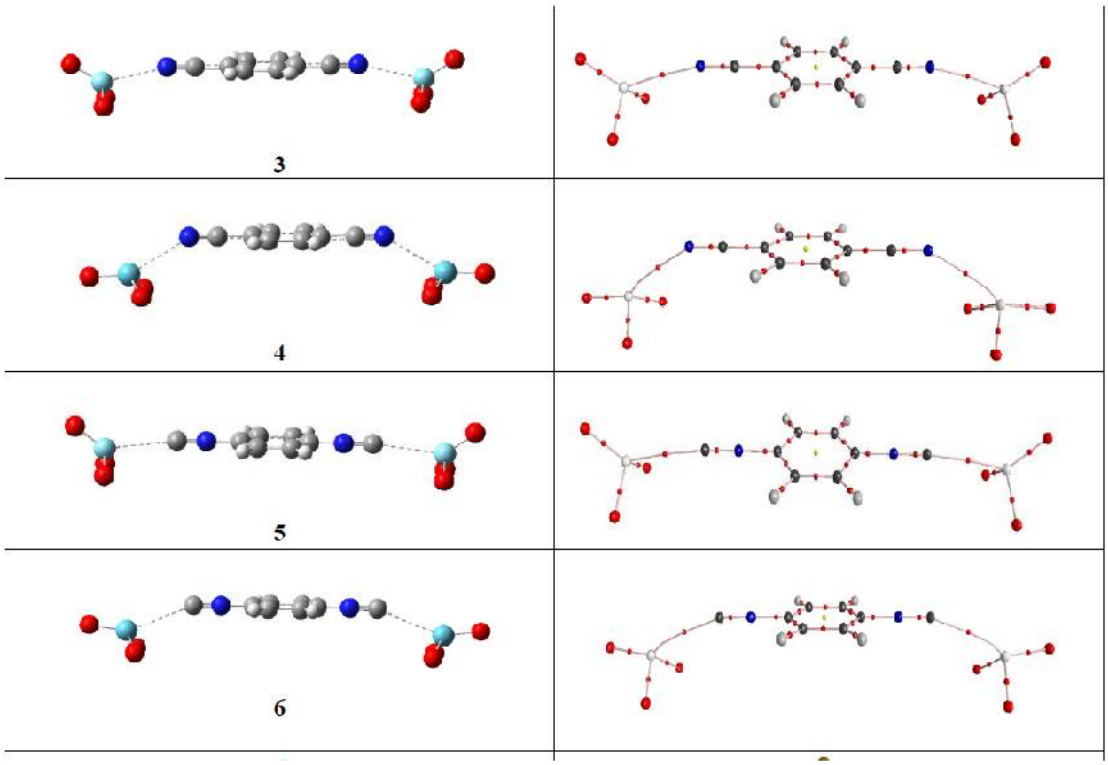
31. X=F, Z=Ar
32. X=F, Z=Kr
33. X=Cl, Z=Ar
34. X=Cl, Z=Kr
35. X=Br, Z=Ar
36. X=Br, Z=Kr



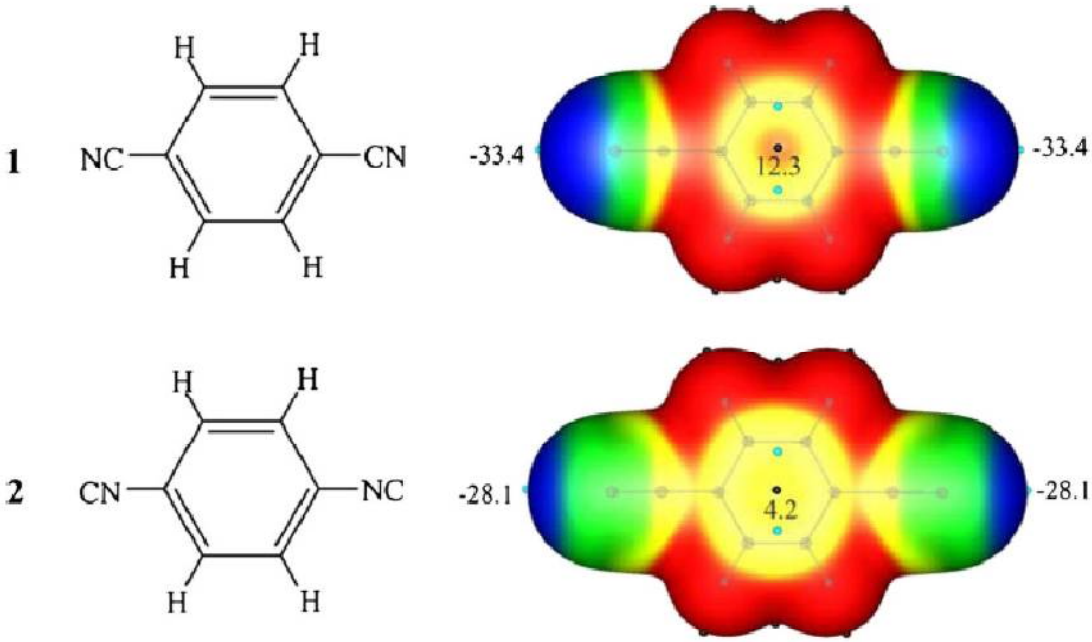
37. X=F, Z=Ar
38. X=F, Z=Kr
39. X=Cl, Z=Ar
40. X=Cl, Z=Kr
41. X=Br, Z=Ar
42. X=Br, Z=Kr

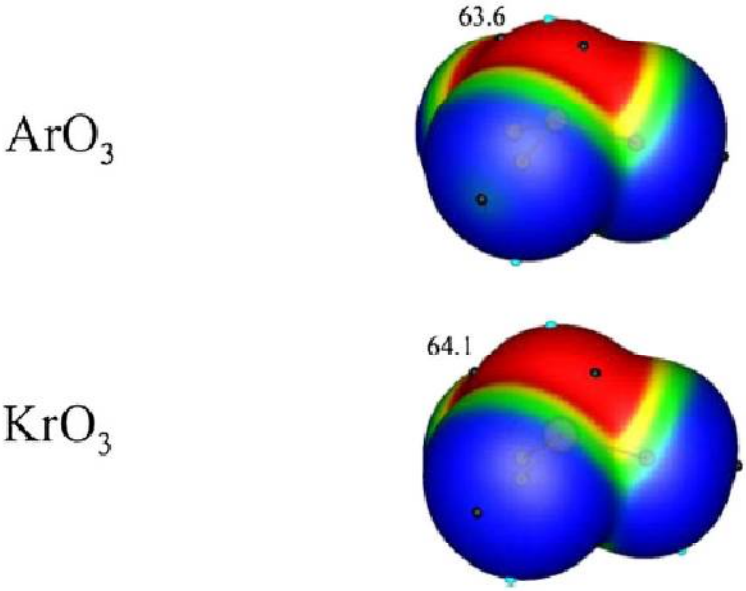
Aerogen-bonded 3–6, anion-π 7–12, lone pair-π 13–18, and multi-component complexes 19–30

Optimized structures Aerogen Bonded species



MESP-----π-acidic heteroaromatic rings





System		R	E_{int}	ρ_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}
3	$1 + 2ArO_3$	2.805	−11.06	15.11	63.39	3.47
4	$1 + 2KrO_3$	2.926	−11.36	15.90	77.30	2.46
5	$2 + 2ArO_3$	2.926	−10.84	14.22	51.49	2.73
6	$2 + 2KrO_3$	3.055	−11.13	14.84	62.66	1.94

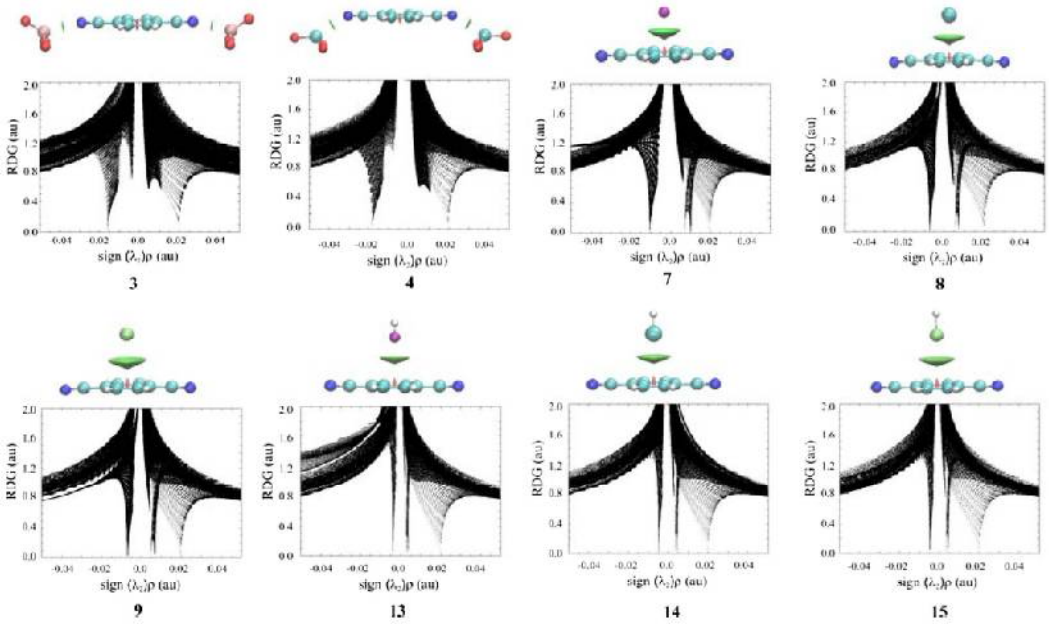
- Intermolecular distances (R; Å)
- Interaction energies (E_{int}; kcal/mol)
- Electron density (ρ_{bcp}; 10^{-3} au)
- Laplacian ($\nabla^2\rho_{bcp}$; 10^{-3} au) of Electron density

☞ Total electron energy density (H_{BCP}; 10^{-3} au) at BCPs

Aerogen bonded, anion-π, lone pair-π complexes

NCI isosurface

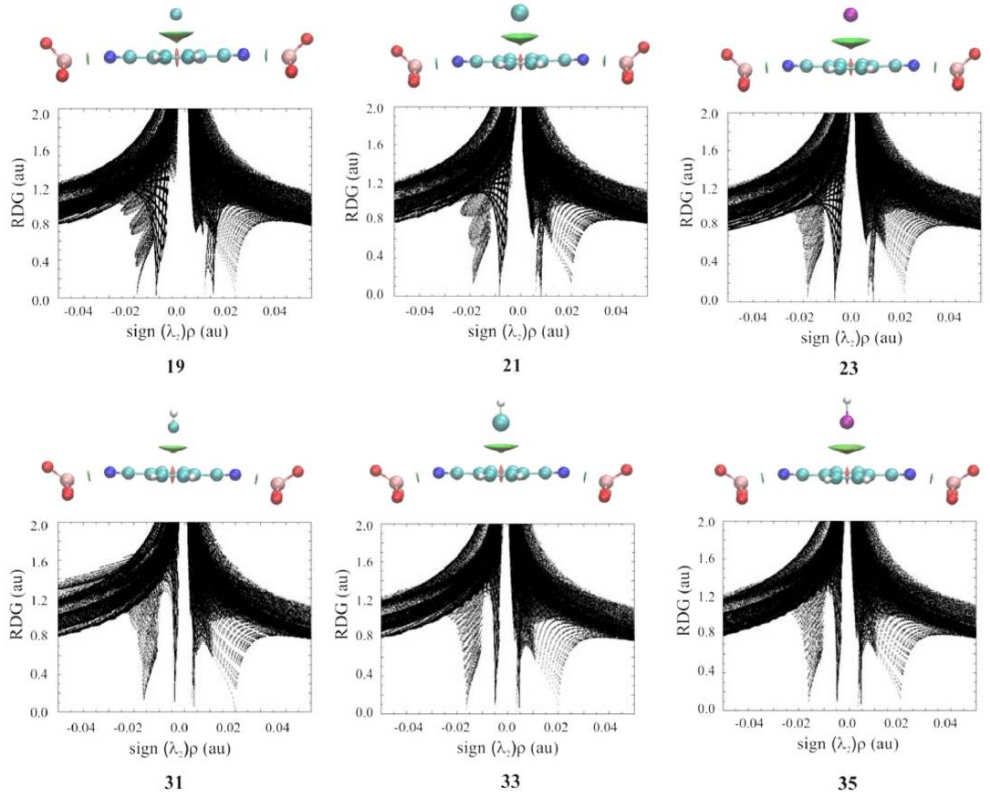
Reduced density gradient (RDG) versus sign (λ2)ρ



Multicomponent complexes

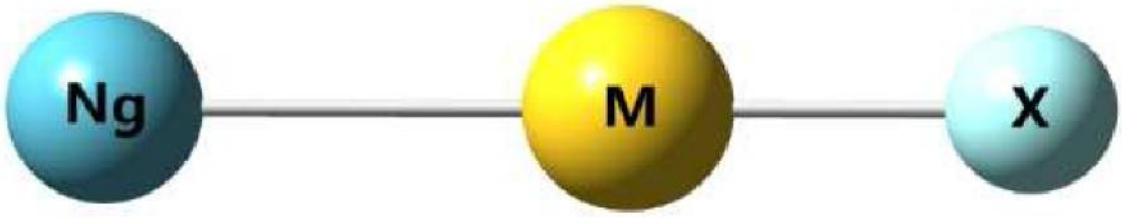
NCI isosurface

Reduced density gradient (RDG) versus sign (λ2)ρ



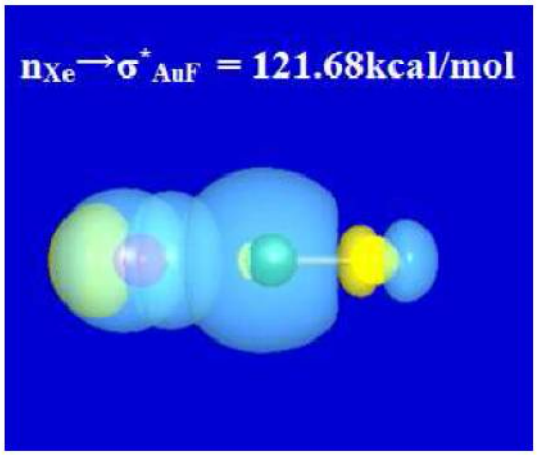
Aerogen Bond *[He, Ne, Ar, Kr, Xe, Rn]*	M = Cu, Ag, Au; X = [F, Cl, Br, I)	NgB.	ACS.	05

Optimized geometry



5

Hyperconjugative interaction



Resonance Bonding

Ng: M - X ⟷ Ng^+ - M :X^-

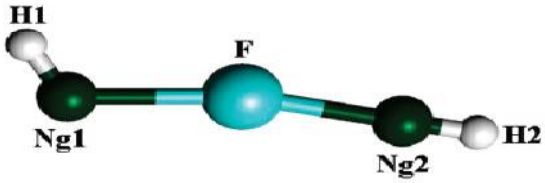
(M = Cu, Ag, Au)

Like H-bonding?

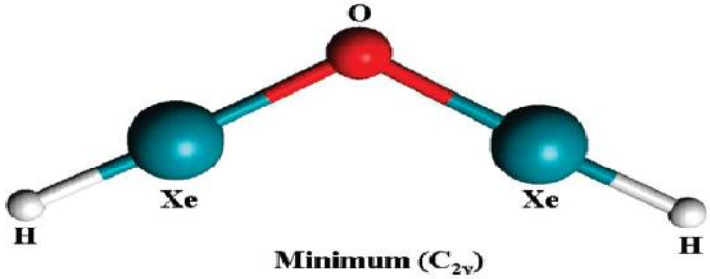
Aerogen Bond *[He Xe]*		NgB.	ACS.	09

Connectivities

Minima ($D_{\infty h}$)



TS1 (C_s)

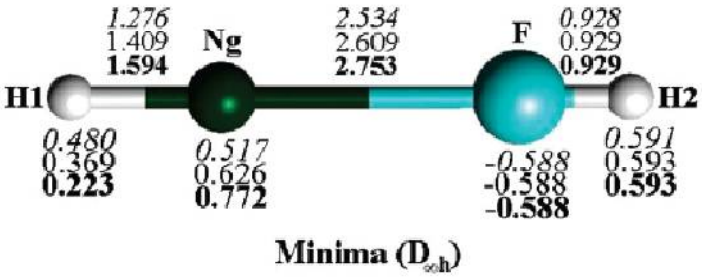


Minimum (C_{2v})

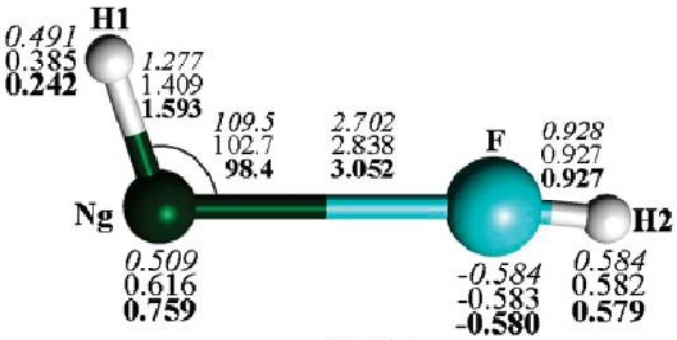
Aerogen Bond *[Ar, Kr,Xe]*	MP2/aug-cc-pVTZ/SDD :GeomOpt	NgB.	ACS.	09

NBO atomic charges

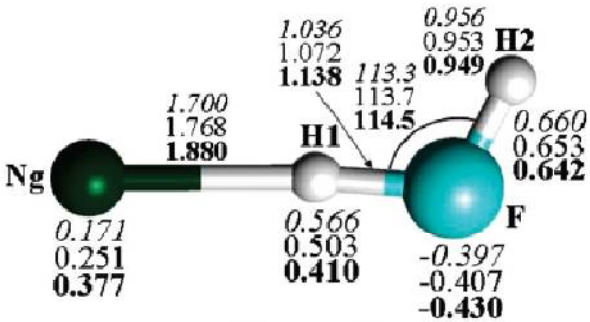
MP2/aug-cc-pVTZ/SDD



Minima ($D_{\infty h}$)



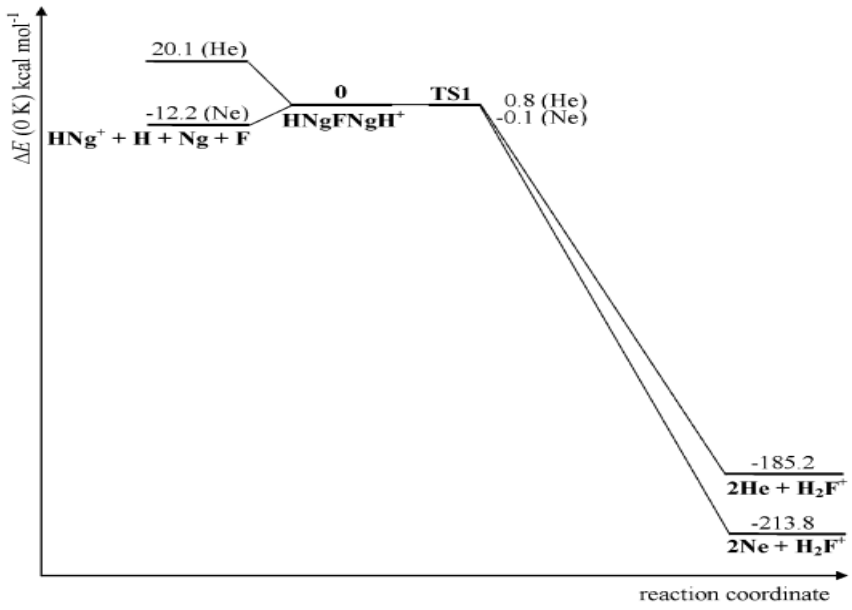
TS2 (C_s)



Minima (C_s)

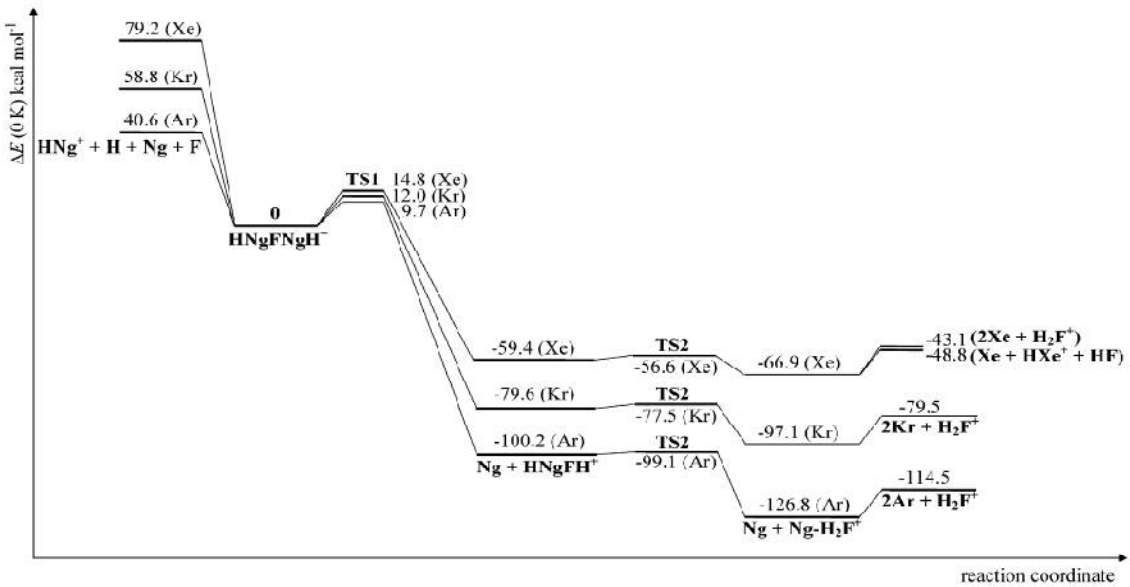
Decomposition paths of

$HHeFHeH^+$ and $HNeFNeH^+$



[GeomOpt//vib Freq] : CCSD(T)/aug-cc-pVTZ/SDD//MP2/aug-cc-pVTZ/SDD
Temp: 0 K

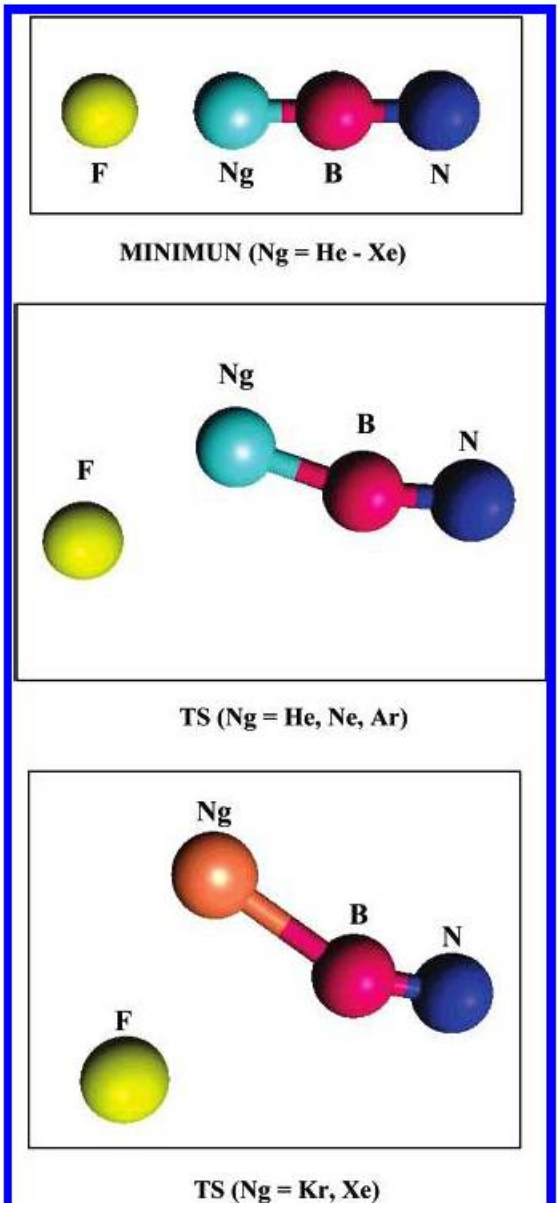
Decomposition paths of HNgFNgH+ (Ng)Ar, Kr, Xe)



[GeomOpt//vib Freq] :CCSD(T)/aug-cc-pVTZ/SDD//MP2/aug-cc-pVTZ/SDD
Temp: 0 K.

Connectivitystructures

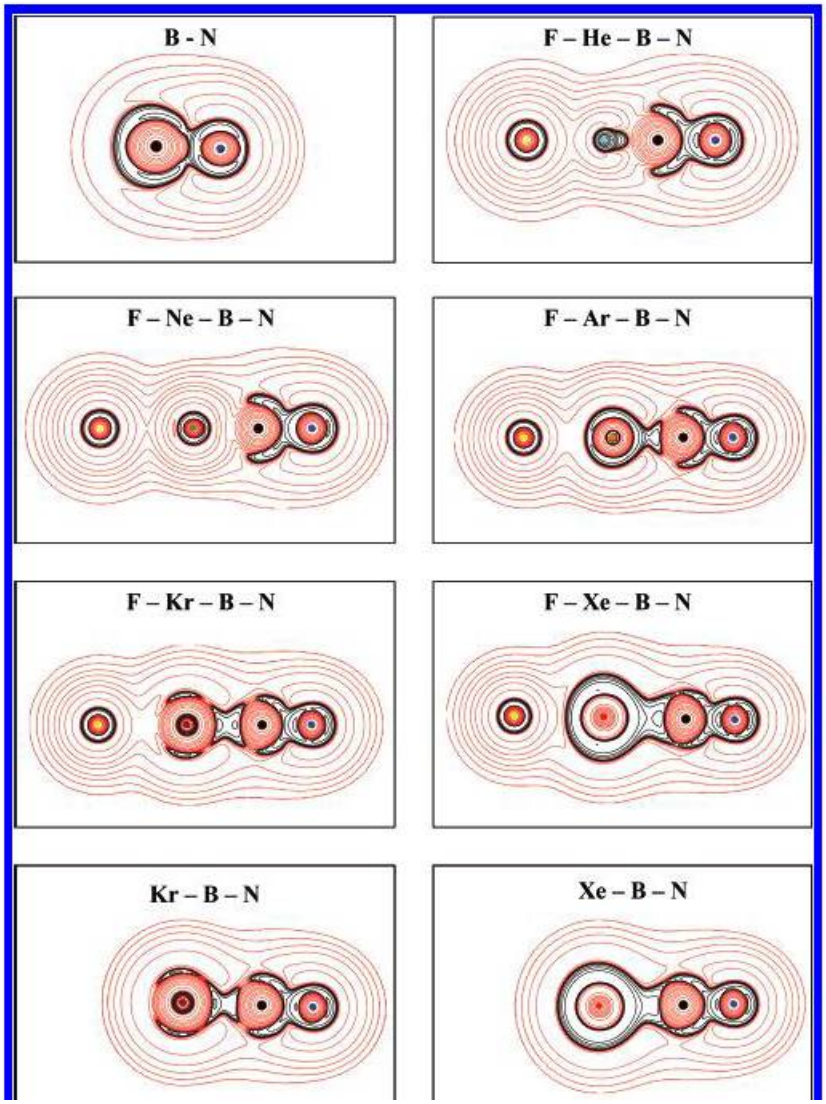
FNgBN



Contour lines diagrams

Laplacian of the electronic charge density

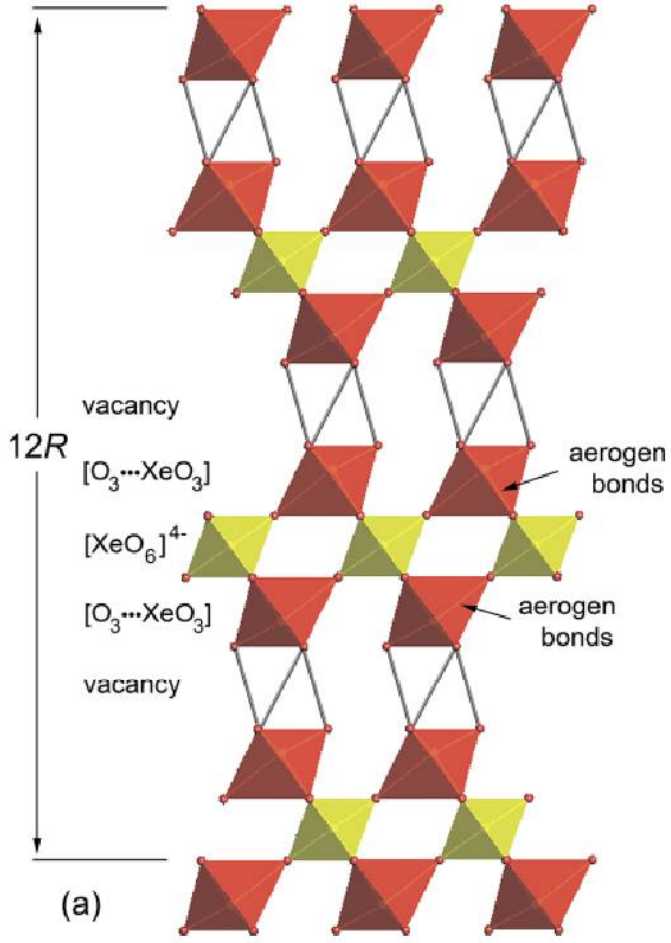
MP2/aug-cc-pVTZ/SDD

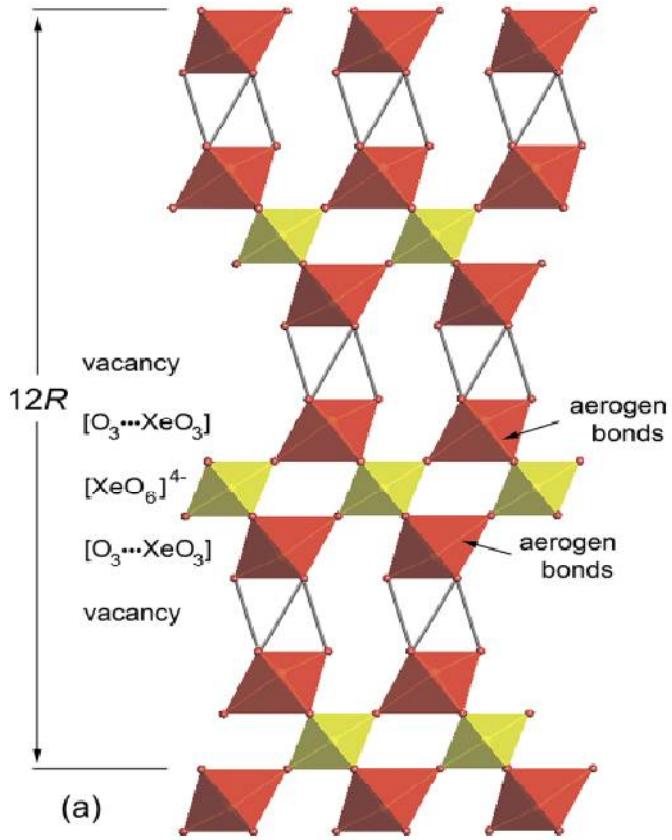


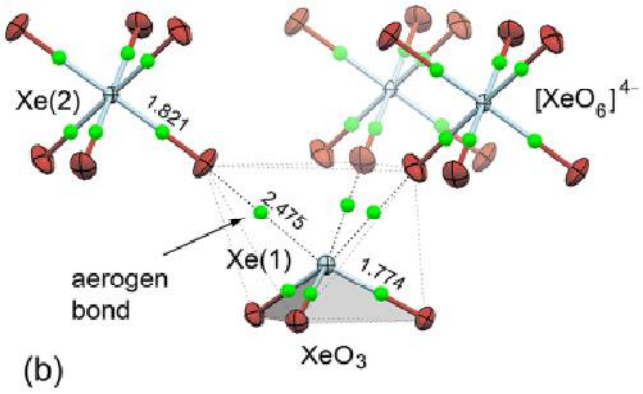
- Red lines: Regions of charge depletion (-32F(r) < 0)
- BlackLines : Charge concentration (-32F(r) > 0)

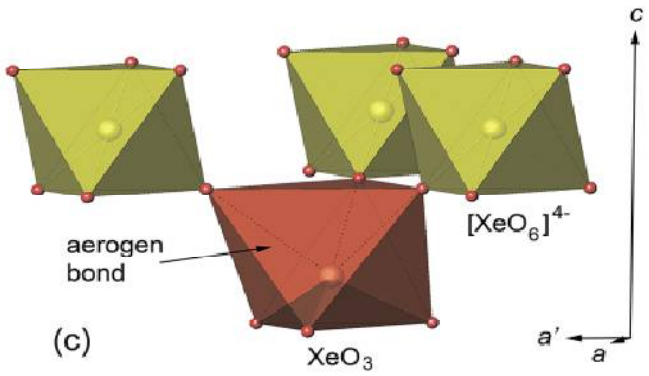
Aggregate of K4Xe3O12 platelets

XeO3









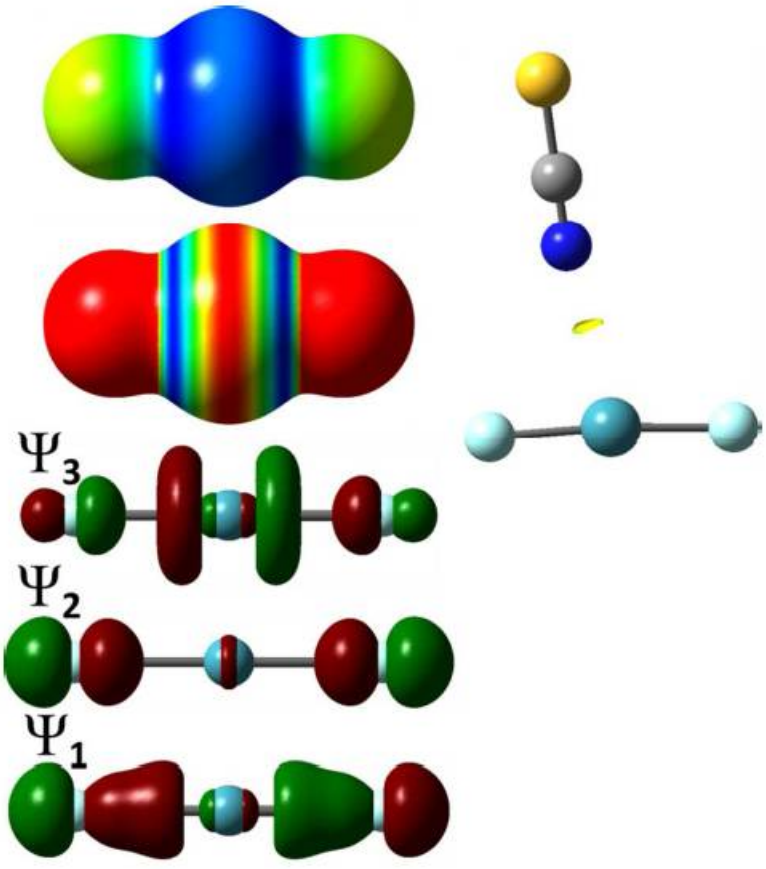
☞ Xe···O aerogen bonds

bond	distance (Å)	ρ_b (e Å^{-3})[a]	$\nabla^2(\rho)$ (e Å^{-5})[b]	H_b (a.u.)[c]	ε[d]	note
$K_4Xe_3O_{12}$						
Xe(1)···O(1)	2.475(9) × 3	0.3112	+3.4107	−0.0032	0.0331	aerogen bonds[e]
Xe(1)–O(2)	1.774(7) × 3	1.3814	+8.4690	−0.1439	0.0175	covalent bonds in $[XeO_3]^0$ molecule
Xe(2)–O(1)	1.821(9) × 6	1.2901	+6.3218	−0.1302	0.0006	covalent bonds in $[XeO_6]^{4-}$ octahedron[f]
XeO_3[g]						
Xe(1)–O(1)	1.74(3)	1.4655	+10.9628	−0.1584	0.0109	covalent bond at Xe(1)–O(1)···Xe(1) bridge
Xe(1)···O(1)	2.80(3)	0.1561	+2.0215	+0.0019	0.0607	aerogen bond at Xe(1)–O(1)···Xe(1) bridge
Xe(1)–O(2)	1.76(3)	1.4066	+8.9539	−0.1477	0.0130	covalent bond to nonbridging oxygen
Xe(1)–O(3)	1.77(3)	1.3987	+8.4175	−0.1479	0.0103	covalent bond at Xe(1)–O(3)···Xe(1) bridge
Xe(1)···O(3)	2.90(3) × 2	0.1260	+1.6600	+0.0021	0.0715	aerogen bonds at Xe(1)–O(3)···Xe(1) bridges

[a]Electron density at the BCP. [b]Laplacian of electron density at the BCP. [c]Total electronic energy density at the BCP. [d]Bond ellip

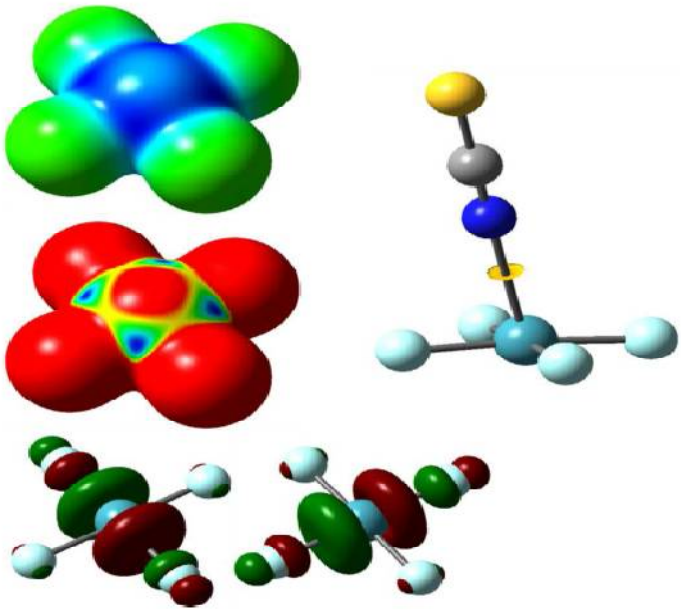
ESP---- XeF2

MOs, NCIPlots—of----NCS bond



ESP---- XeF4

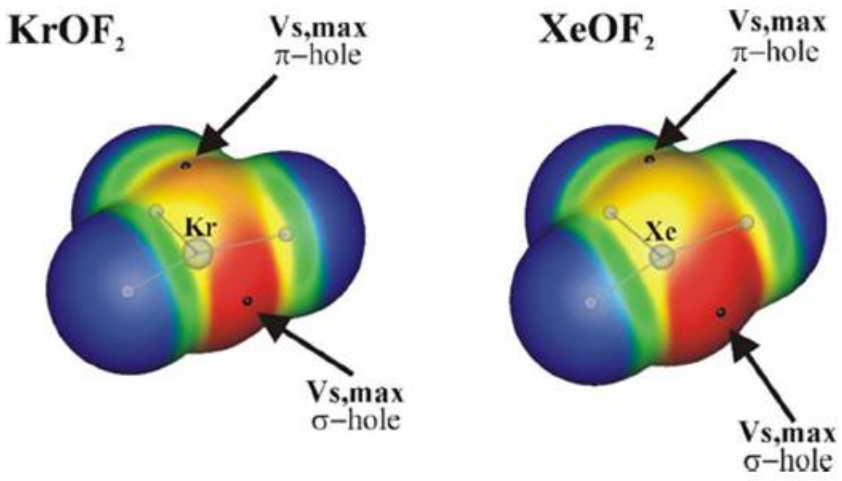
MOs, NCIPlots—of----NCS bond



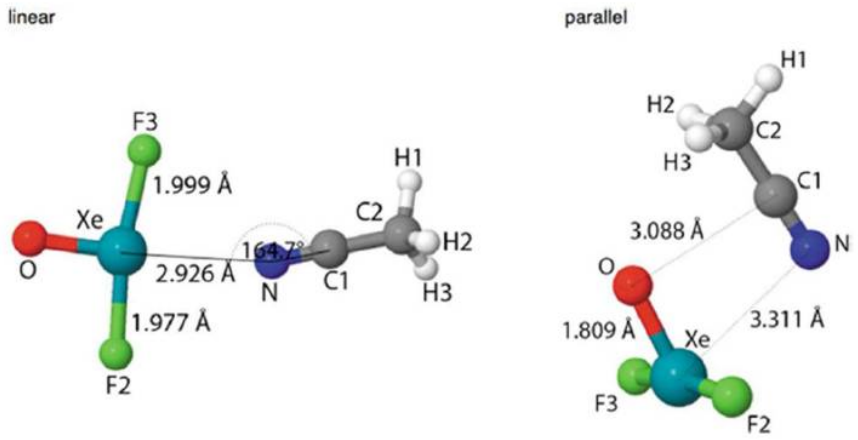
sigma-hole + pi-holes on same Ng atom

Aerogen Bond *[Kr Xe]*	sigma-hole + pi-holes on same atom	NgB.	ACS.	;

ESP----- KrOF2 ;XeOF2

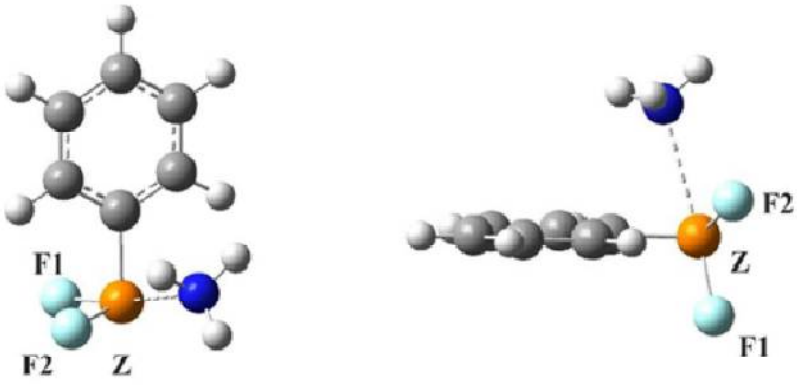


Two binding modes of XeOF2···NCCH3 complexes

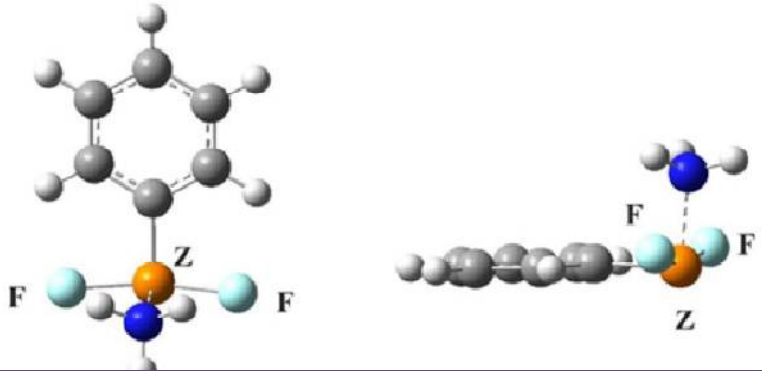


Bonding modes
MP2/aug-cc-pVDZ

σ-hole bonded complex



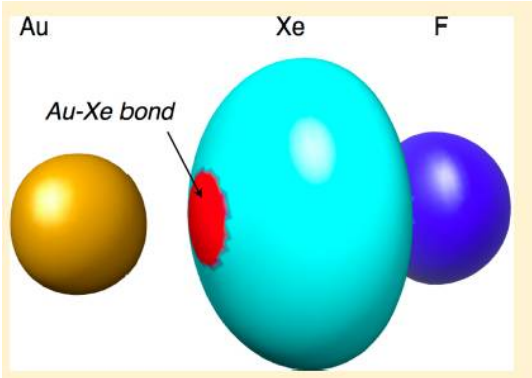
π-hole bonded complex



Nobel gas compounds
[He Ne ArKr Xe Rn]

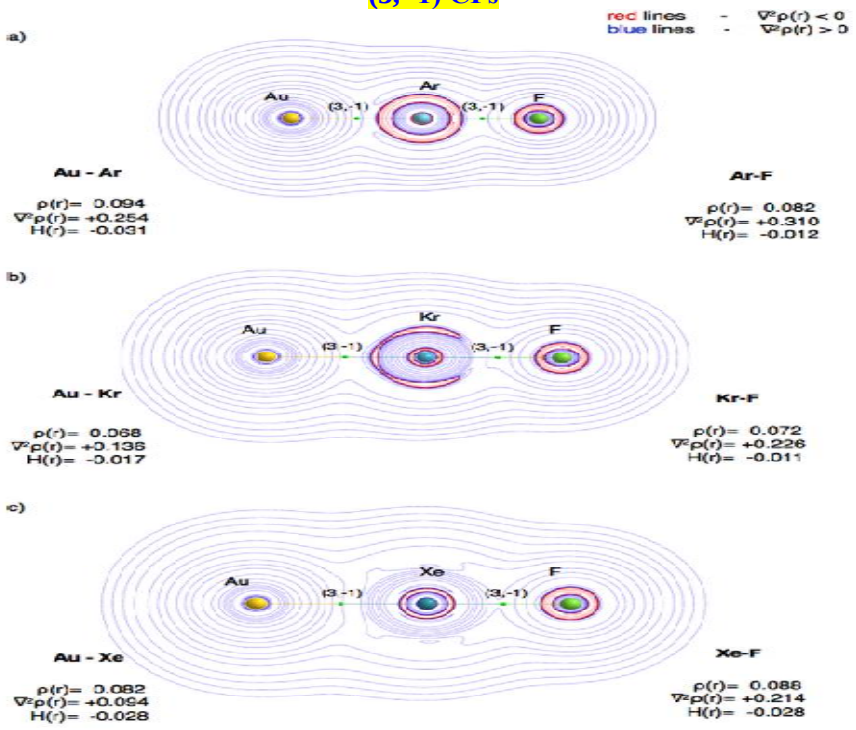
Ng Bond [Xe]		NgB.	ACS.	07

AuXeF bonds



Ng Bond [Ar Kr Xe]		NgB.	ACS.	07

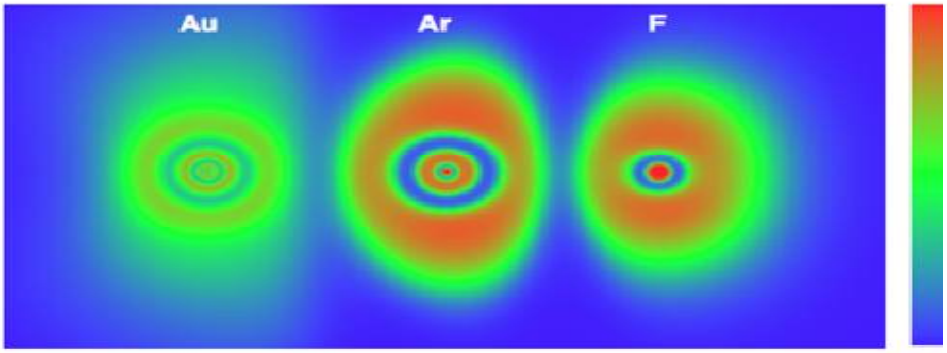
Laplacian of electron density
(3,–1) CPs



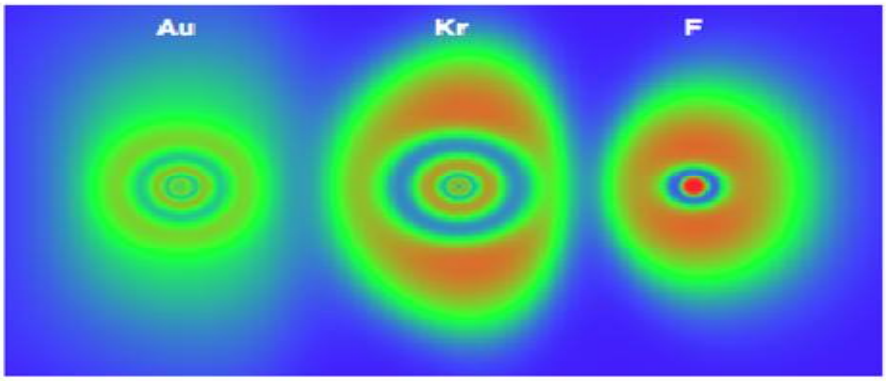
ELF(2D-)

AuNgF

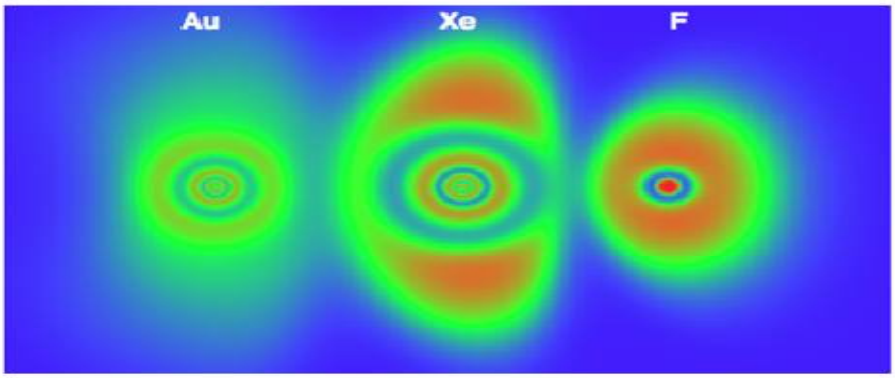
a) **AuArF**



b) **AKrF**



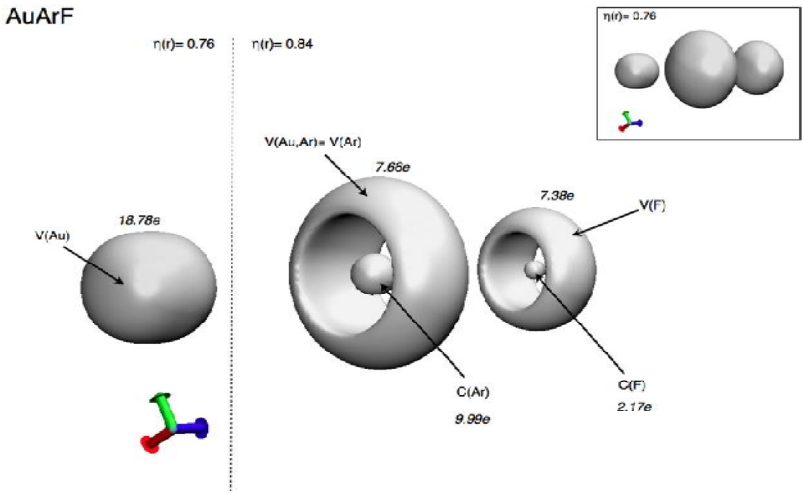
c) **AXeF**



- **DFT(B3LYP)/TZ2P**
- **ZORA included to take care of relativistic effects**

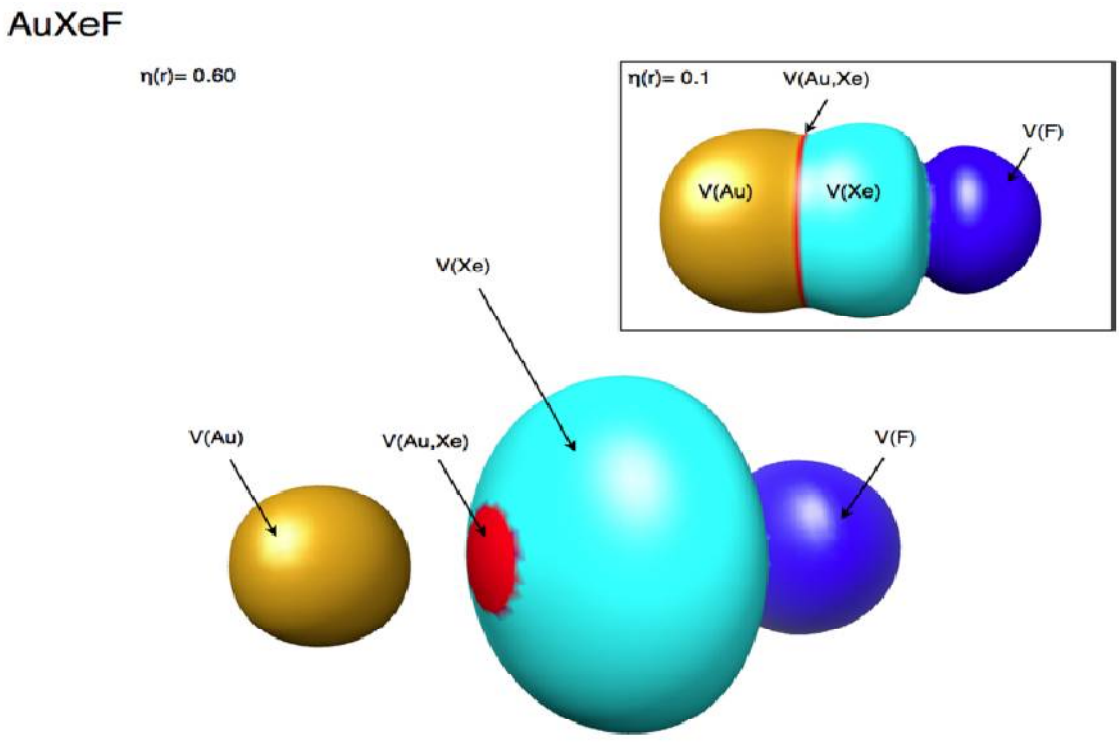
ELF(3D-)—AuArF

DFT(B3LYP)/Def2-TZVPPD



ELF(3D-)—AuXeF

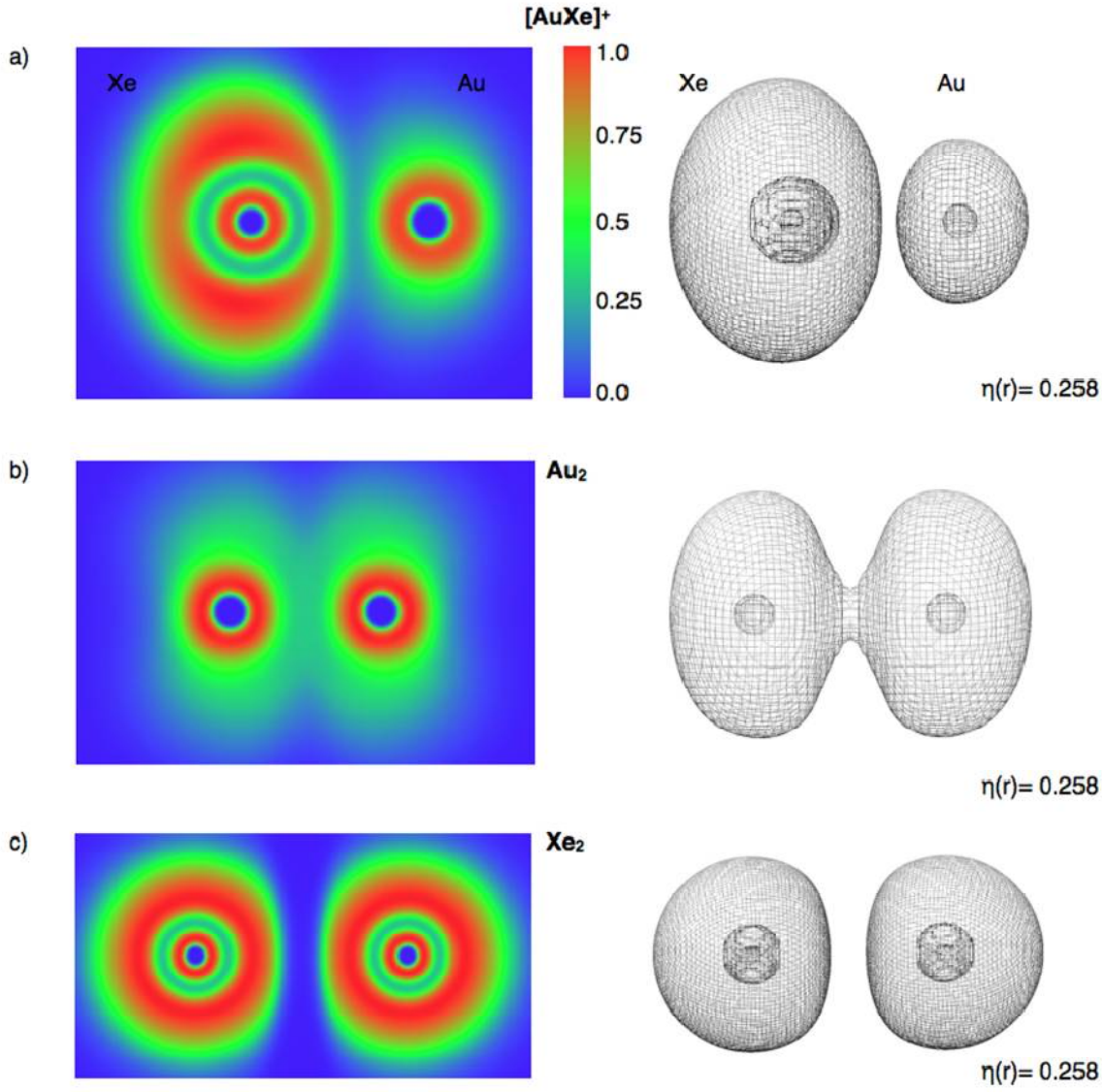
CCSD/Def2-TZVPPD



- Red patch :Bisynaptic bonding basin
- Corresponds to covalent-polarized Au−Xe bond with a very high delocalized electron density

ELF(3D-)—$AuXe^+$

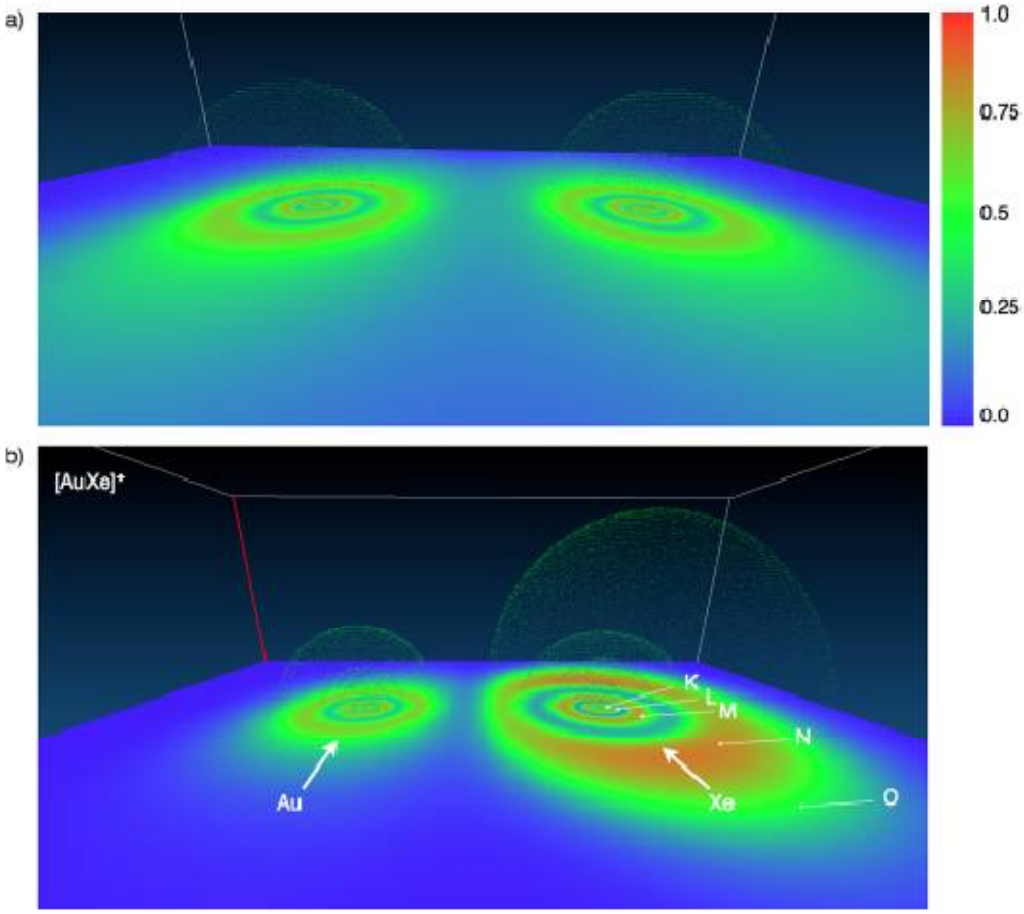
DFT(B3LYP)/Def2-TZVPPD



ELF(3D-)—Au_2--- $AuXe_2$

ELF(3D-)—Au2--- $[AuXe]^+$

DFT(B3LYP) + ZORA

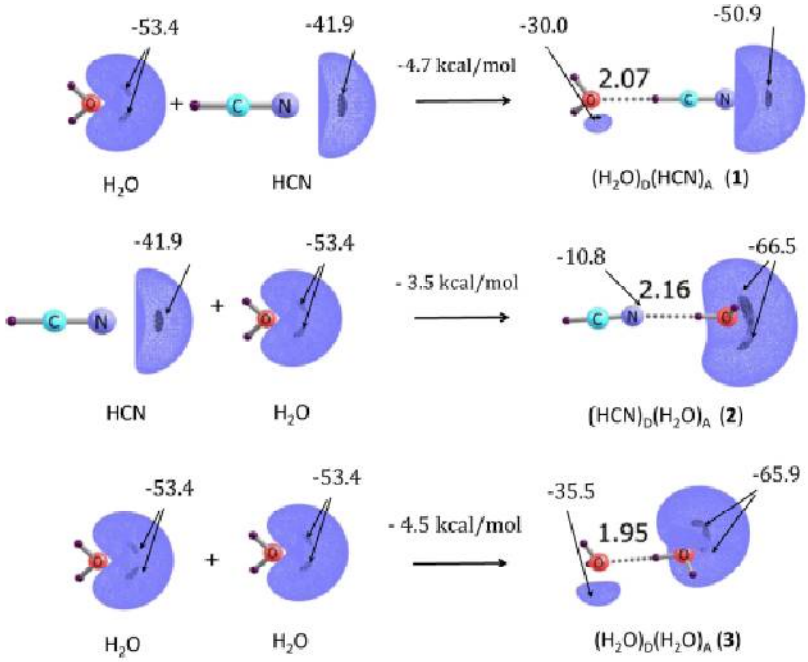


☞ **DFT(B3LYP) + ZORA: The electronic shells K, L, M, N, and O of 1s22s22p63s23p63d104s24p65s24d105p6 electron configuration of xenon are depicted**

Hydrogen Bond
1. HyB

Hyrogen Bond [H]	☞ (H2O)D(H2O)A ☞ (HCN)A(H2O)D ☞ (HCN)D(H2O)A	NgB.	ACS.	03

MESP



Hydrogen bond formation in dimers

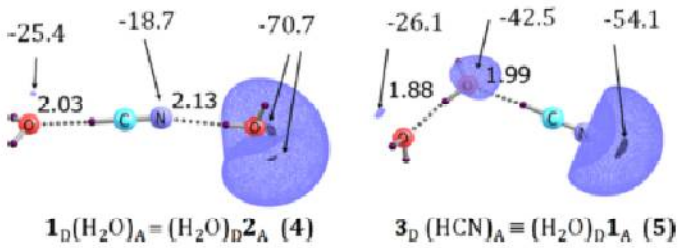
(H2O)D(H2O)A, (HCN)A(H2O)D, and (HCN)D(H2O)A

➔ **Consequent change in MESP**

Ternarycomplexes

1D(H2O)A ≡ (H2O)D2A and 3D(HCN)A ≡ (H2O)D1A

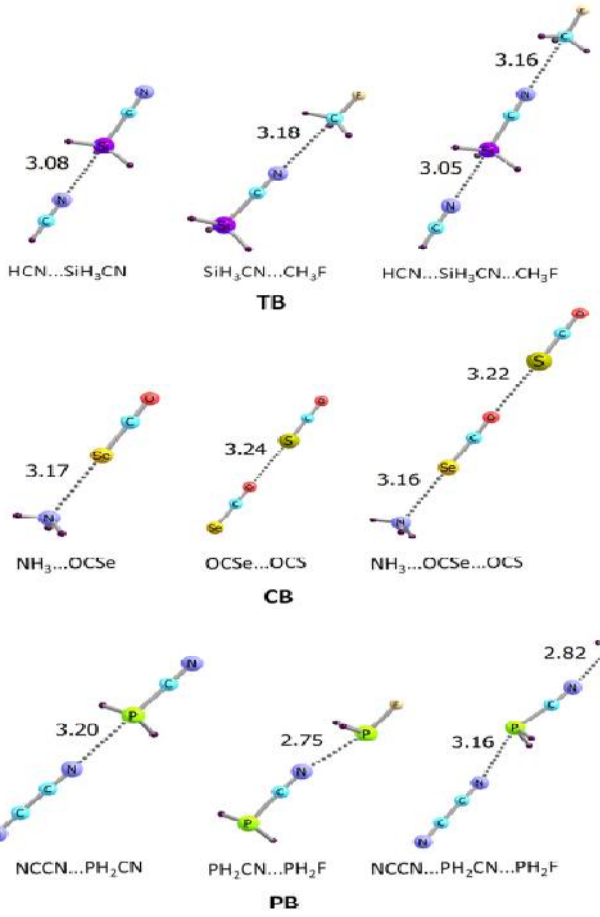
MESP



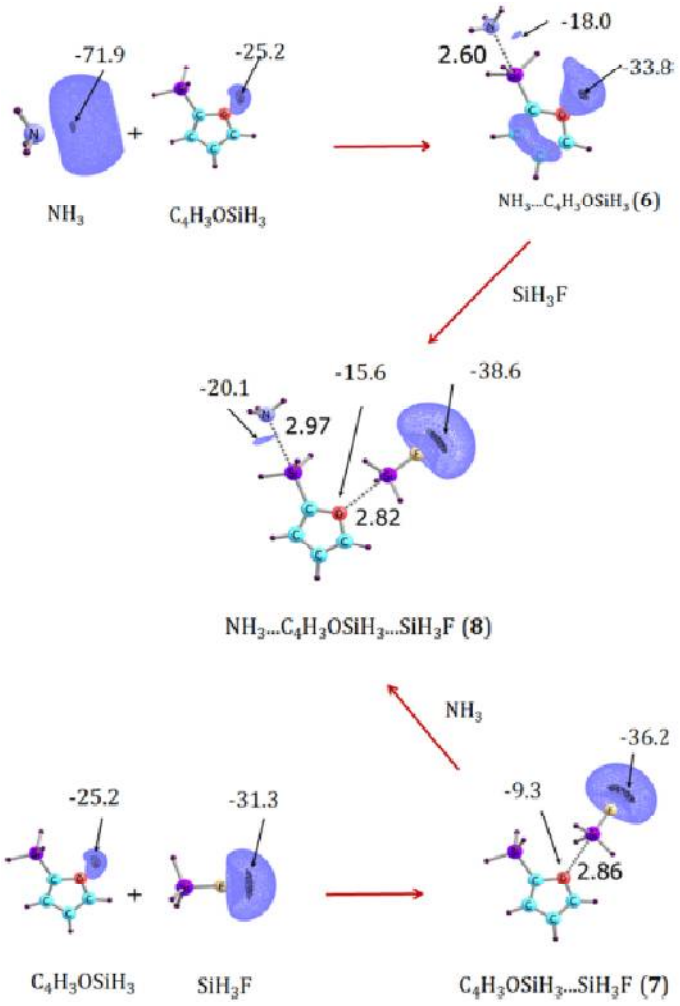
TtB ChBPtB

TtB ChB PtB ***[Si] [O] [P]***	☞ Dimers (XDYA, YDZA) ☞ Ternary complexes [XY]DZA or XD[YZ]A	NgB.	ACS.	**03**

Optimized geometries

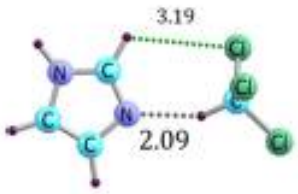


MESP
Tetrel-bonded
Dimer Trimer

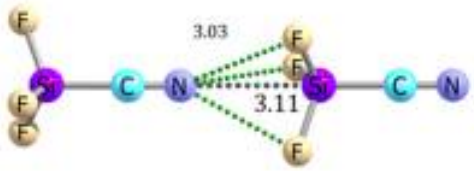


Tetrel Bond [C Si]	☞ Ternary complexes ☞ Dimer	NgB.	ACS.	01

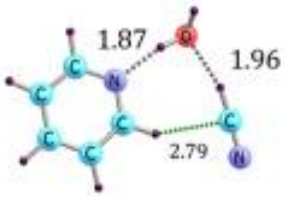
Secondary interactions weak



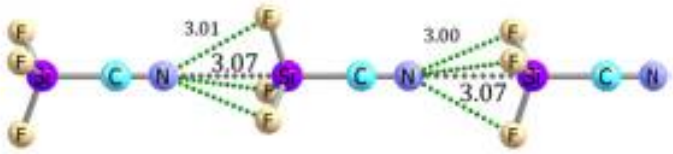
$C_3N_2H_4...CCl_3H$



$SiF_3CN...SiF_3CN$



$C_5H_5N...H_2O...HCN$



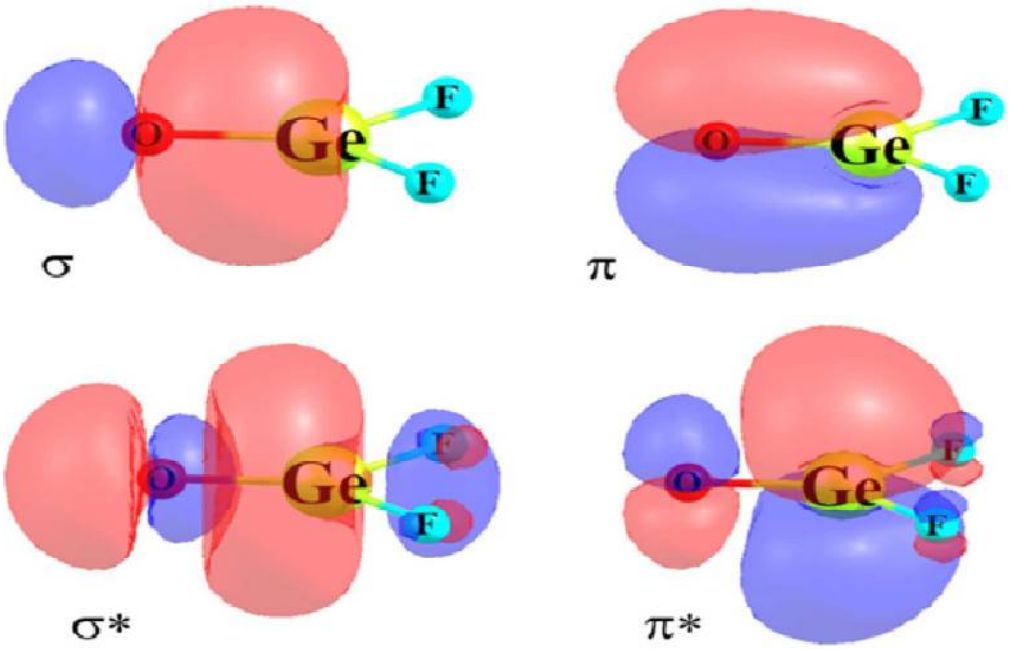
$SiF_3CN...SiF_3CN...SiF_3CN$

☞ Green fragmented lines represent secondary interactions

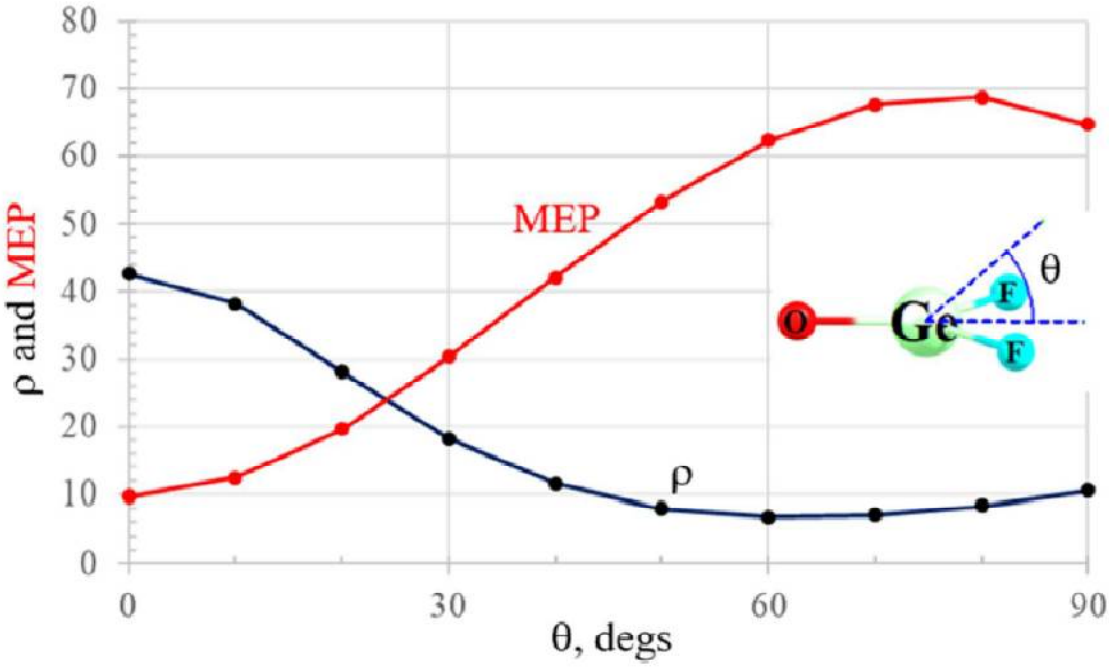
Tetrel Bond
14 TtB
sigma-hole + pi-holes on same molecule

Tt Bond [Ge]	sigma-hole + pi-holes on same molecule	NgB.	ACS.	16

Ge-O NBO bonding and antibonding orbitals of GeF2O



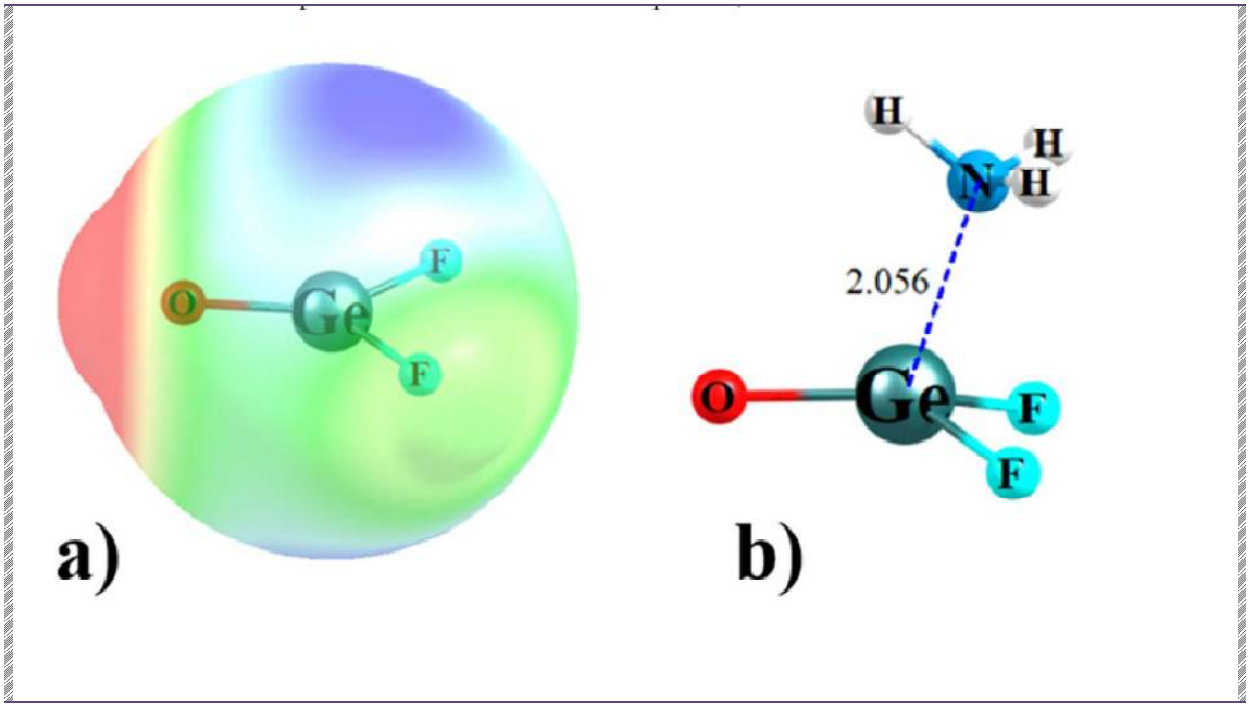
MESP TED (ρ)



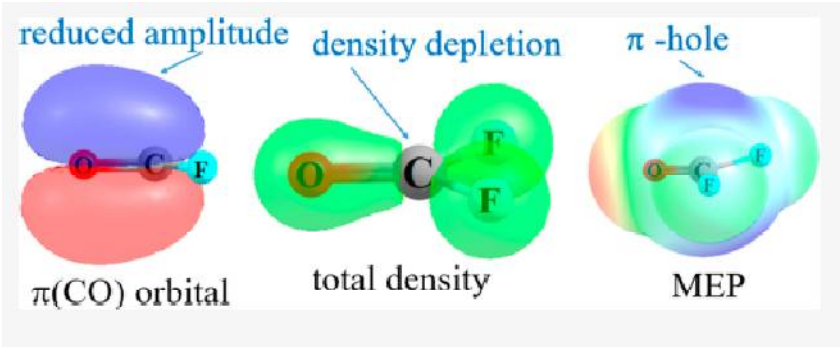
- Molecular plane is at a distance of 2.5 Å fromGe atom

Optimized Geomof GeF2O…NH3

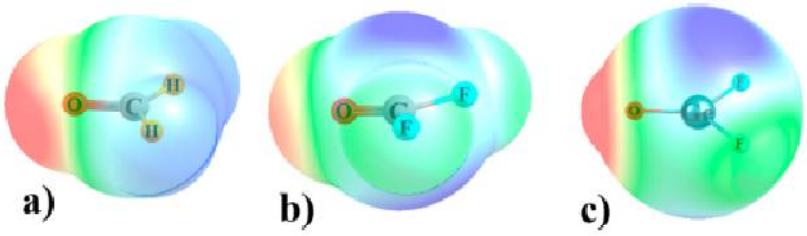
mp2/aug-ccpVDZ



Tetrel Bond [C Ge]		NgB.	ACS.	02

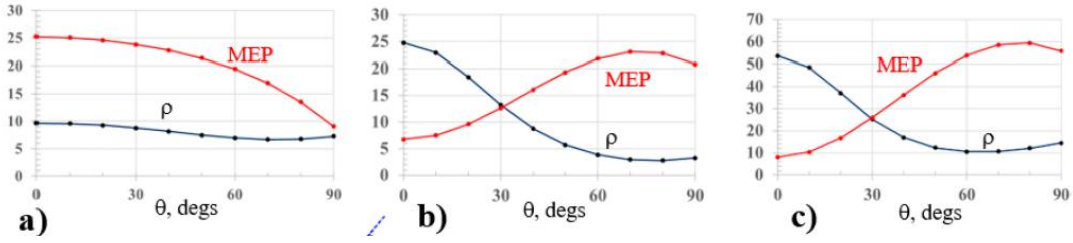


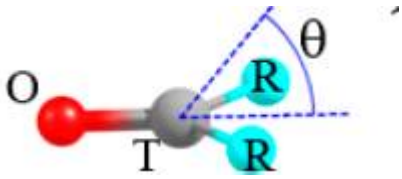
Tetrogen Bond [C Ge]		NgB.	ACS.	02
MEP				



(a)H2CO, (b) F2CO, and (c) F2GeO

MESP TED (ρ)



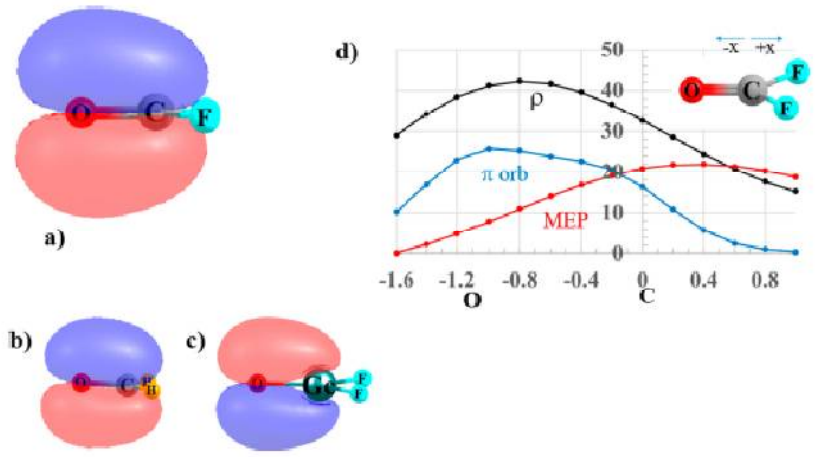


(a)H2CO, (b) F2CO, and (c) F2GeO

θ :Displacement of point of reference out of the molecular plane

Tetrel Bond ***[C Ge]***		NgB.	ACS.	**02**

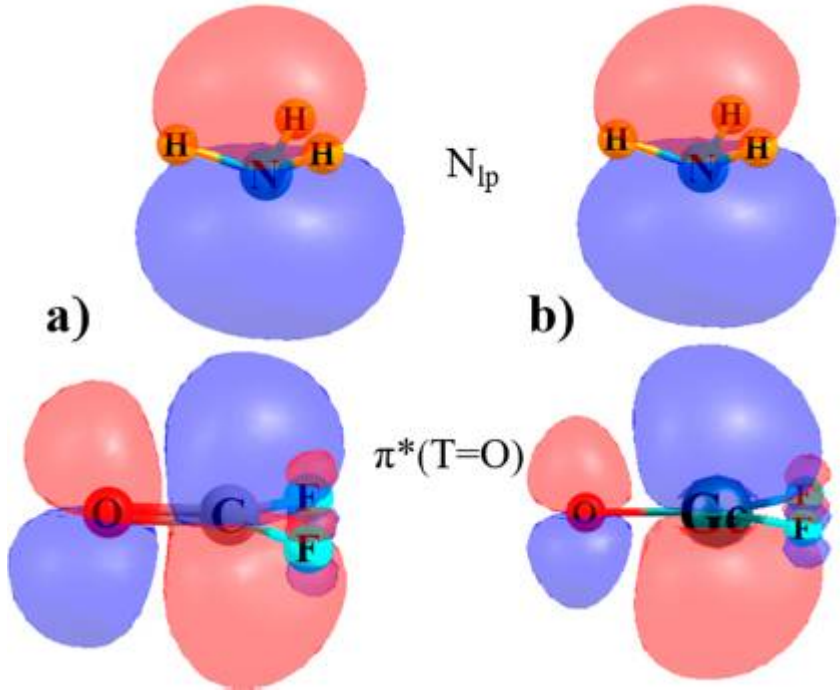
Localized orbitals



π(T⊕O) bonding orbital of (a) F2CO, (b) H2CO, (c)F2GeO

Tetrel Bond ***[F2CO...NH3]*** ***[F2GeO...NH3]***		NgB.	ACS.	**02**

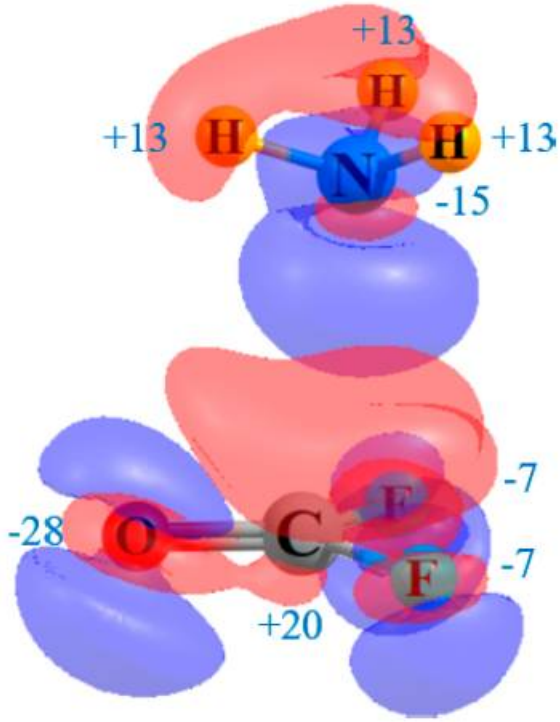
Localized orbitals



NBO localized orbitals of NH3 N lone pair and π*(T−O) for(a) F2CO and (b) F2GeO.

Tetrel Bond		NgB.	ACS.	02

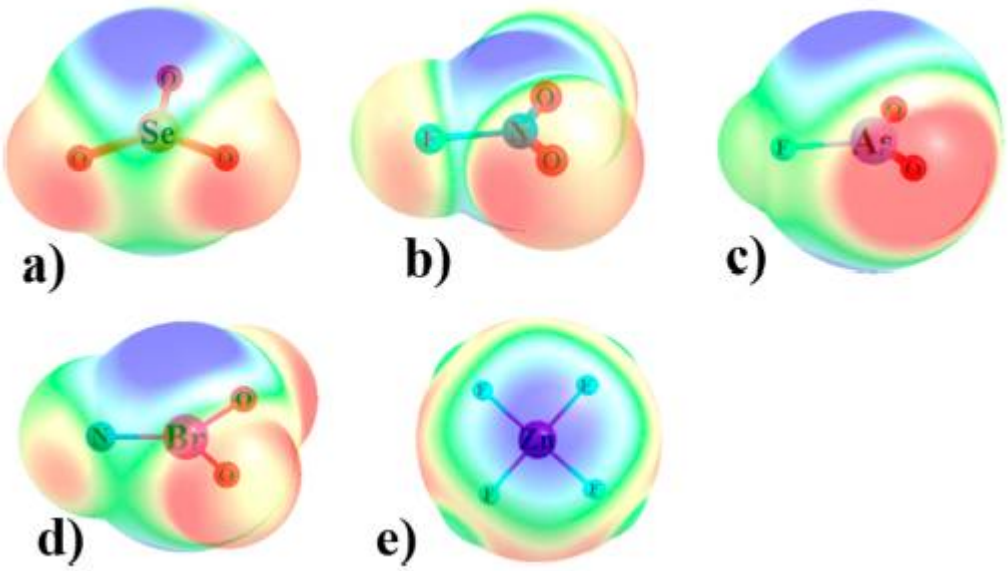
Density shiftsF2CO··NH3



- Numbers refer to NBO atomic charge changes
- Red and blue regions :loss and gain of density

Tetrel Bond [Se N As Br Zn]		NgB.	ACS.	02

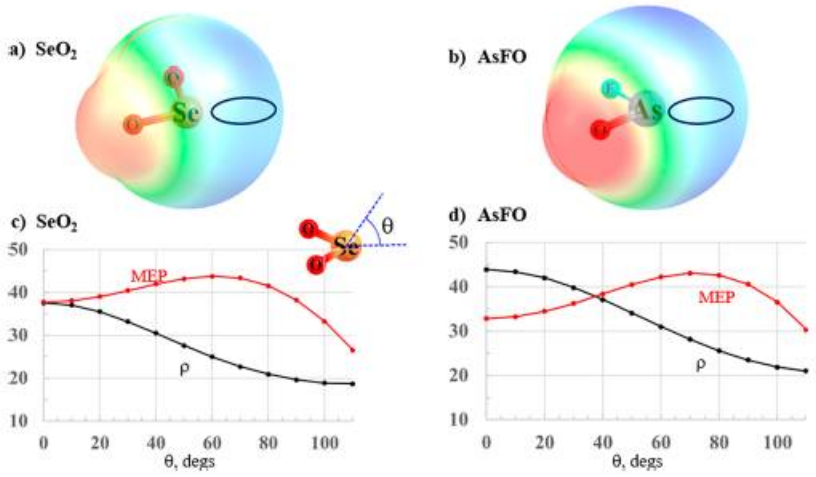
MEP TED (ρ)



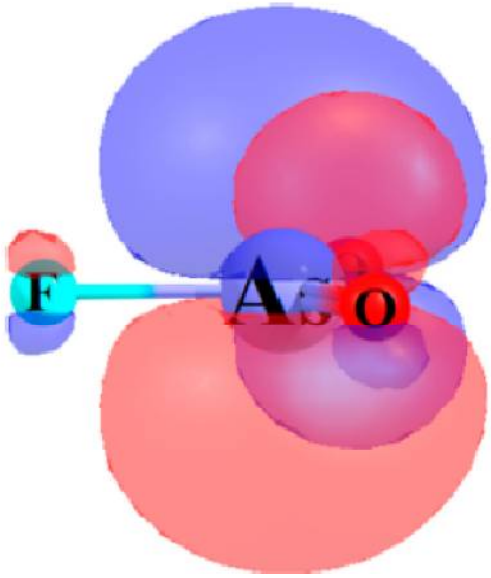
(a)SeO3, (b) NFO2, (c) AsFO2, (d) BrNO2, and (e) ZnF4

☞ Red and blue : negative and positive regions

Lone pair



NBO π*(As−O) orbital of AsFO2



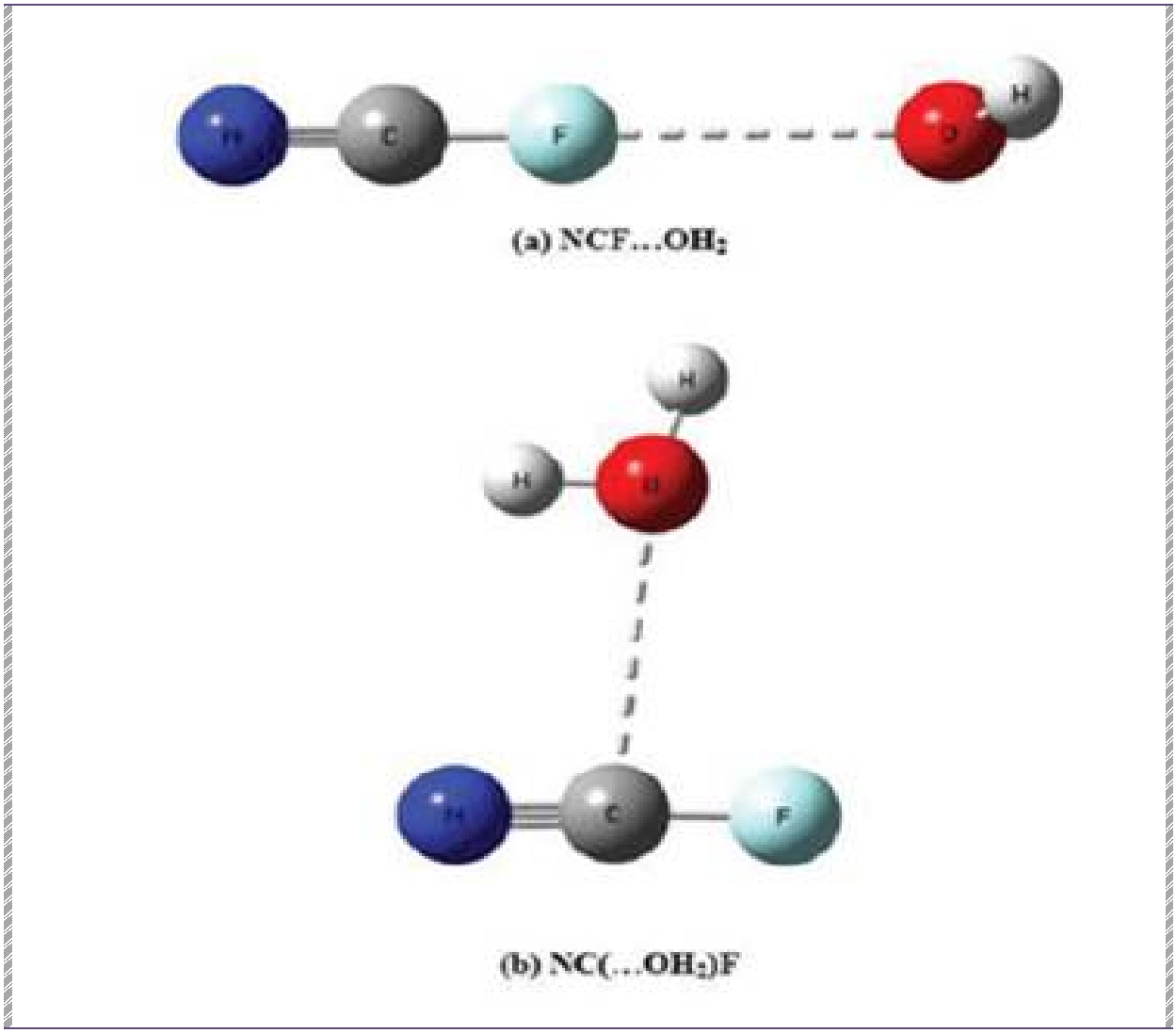
☞ Red and blue : opposite phase of wave function.

Pnictogen(orPnicogen) bonds
15PnB

pnictogen Bond *Carbon(Tt)bond*	🕮 NCF...OH2 🕮 NC(...OH2)F	NgB.	ACS.	16

σ-hole and pi-hole

Optimized structures

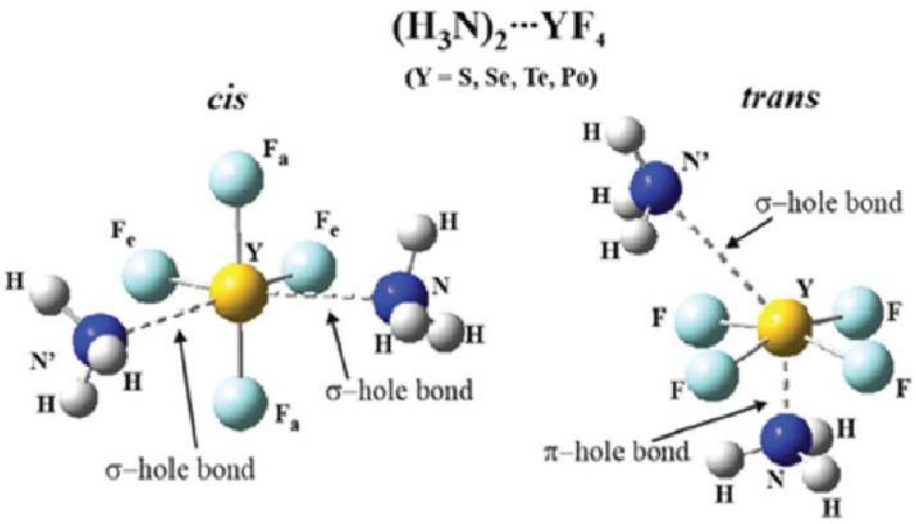


Chalcogen Bond
16 ChB

sigma-hole + pi-holes
on same molecule

Chalcogen Bond [S Se Te Po]	sigma-hole + pi-holes on same molecule	NgB.	ACS.	16

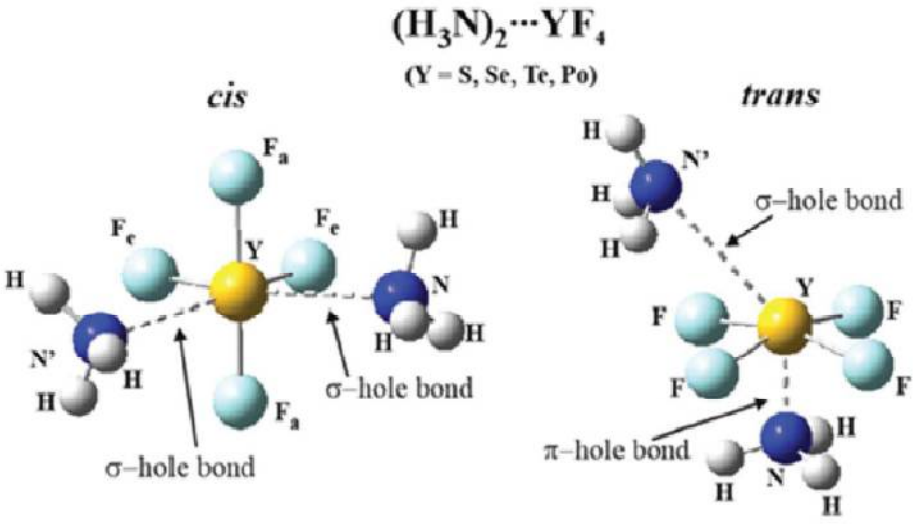
Cis and Trans arrangements



Chalcogen Bond ChA: [S Se Te Po]	sigma-hole + pi-holes on same molecule	NgB.	ACS.	16

Cis and Trans --- σ-hole and pi-hole

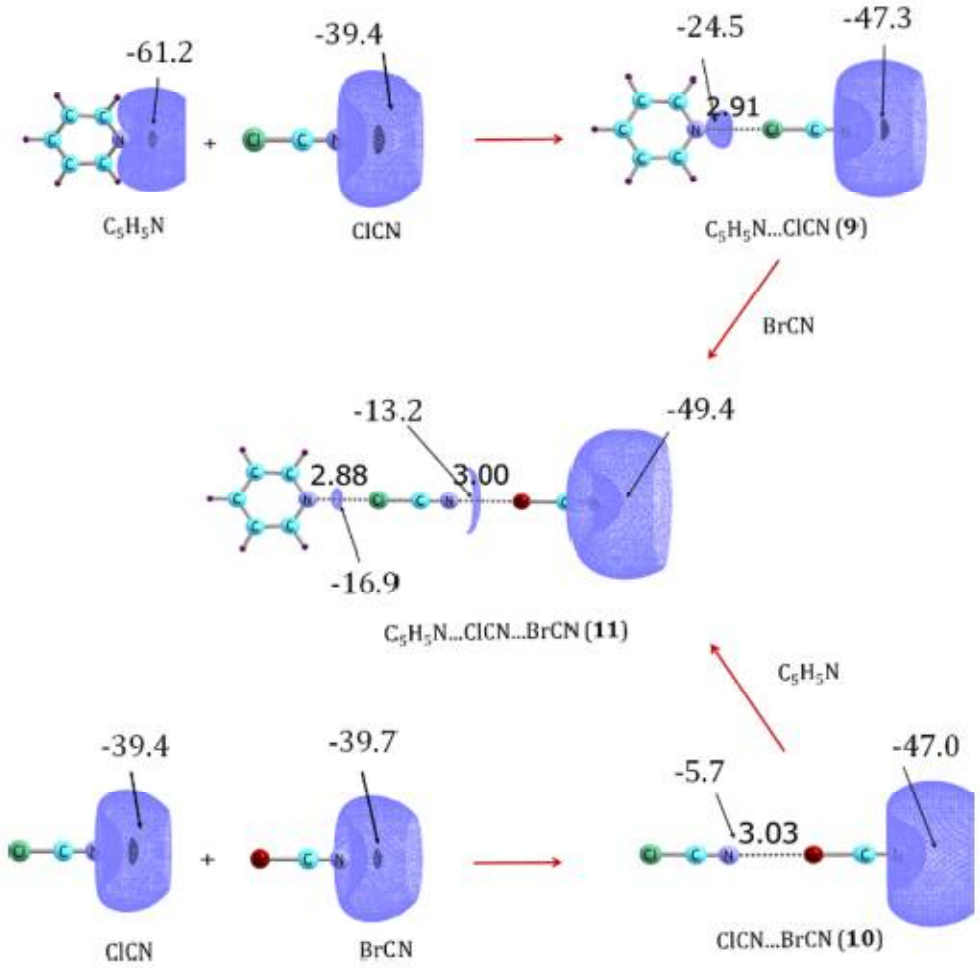
H3N…ChA…NH3



Halogen Bond
17 HaB

Halogen Bond [Cl]	☞ Ternary complexes ☞ Dimer	NgB.	ACS.	01

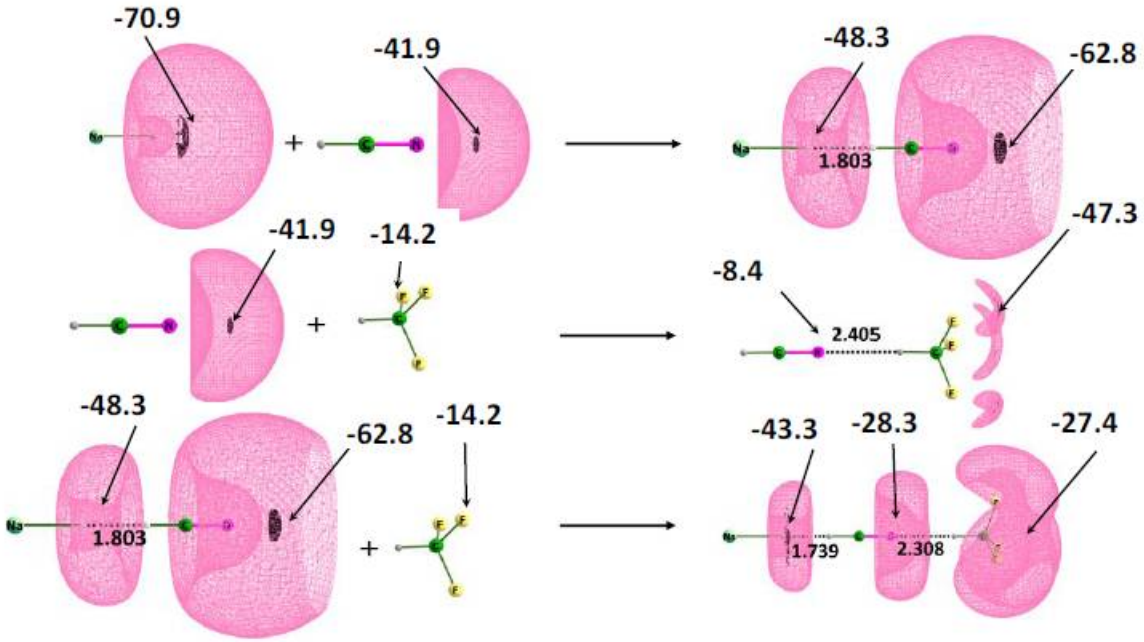
MESP



Halogen Bond *[I ; F]*	Ternarycomplex, NaH…HCN…CF3H	NgB.	ACS.	**01**

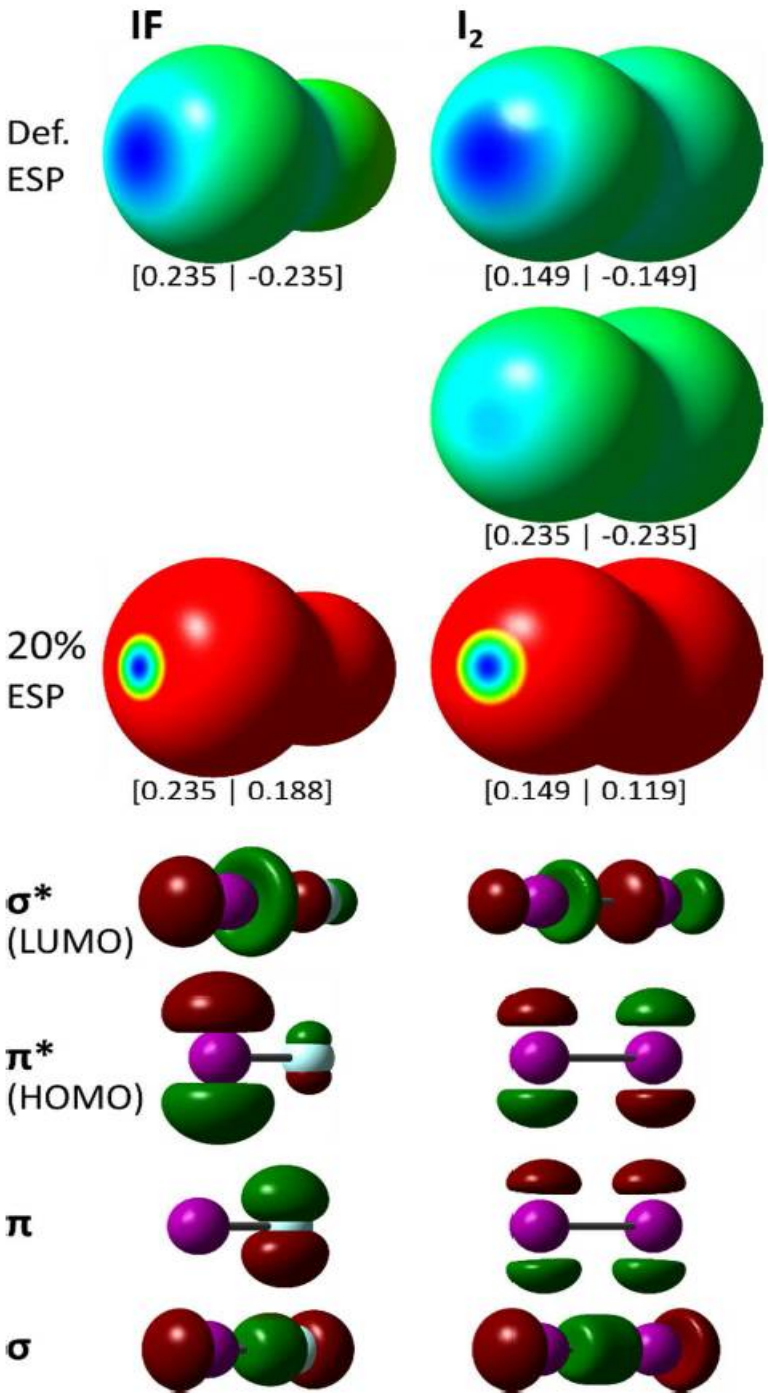
NCov Bond

[NaH, HCN, CF3H]



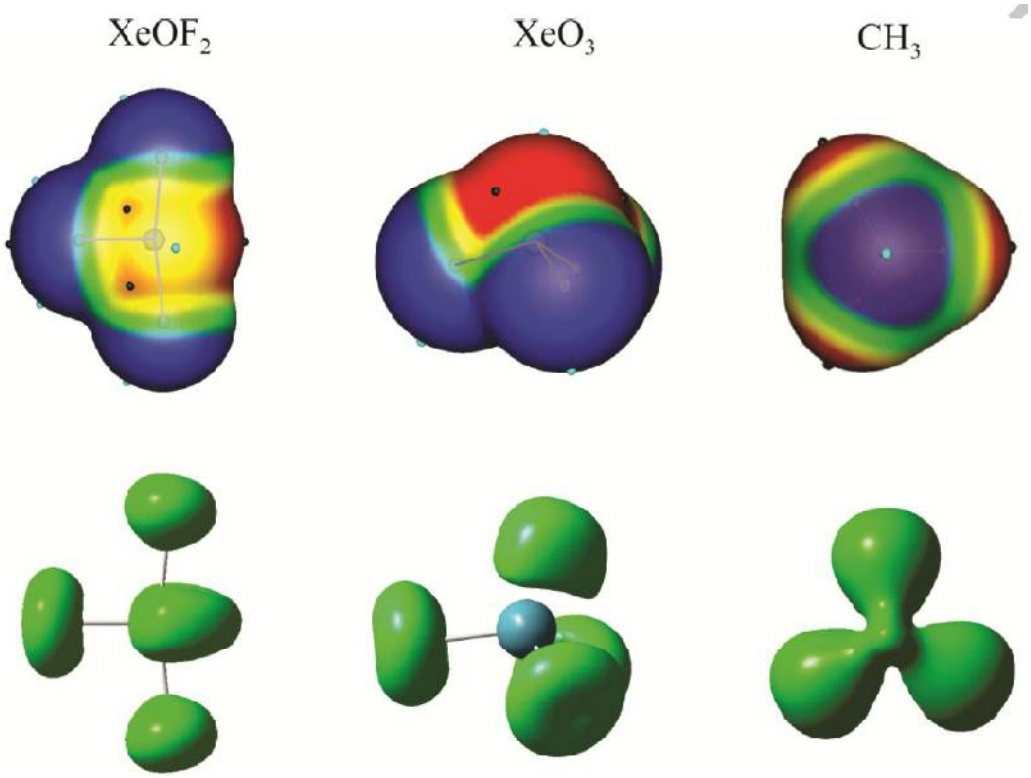
- NaH, HCN, CF3H
- Dihydrogen bonded ternary complex, NaH…HCN…CF3H along with their corresponding dimers

ESP---frontier orbitals



Aerogen Bond		NgB.	SD.	26
[Xe]				

ESP (above; isovalue=0.001 au)
red > 40.9; blue < 0
Black and blue :circles surface maxima and minima



ELF (belowisovalue=0.75 au)

complex	$V_{S,max}$	$V_{S,min}$	R_{int}	$\theta_{O\text{-}Z\cdots C}$	E_{int}
$OF_2Kr\cdots CH_3$	61.1	-8.3	2.800	179	-4.30
$OF_2Kr\cdots C_2H_5$	61.1	-10.9	2.623	178	-7.05
$OF_2Xe\cdots CH_3$	61.8	-8.3	2.993	180	-4.95
$OF_2Xe\cdots C_2H_5$	61.8	-10.9	2.869	178	-6.48
$O_3Kr\cdots CH_3$	62.8	-8.3	3.159	154	-2.72
$O_3Kr\cdots C_2H_5$	62.8	-10.9	3.019	158	-3.86
$O_3Xe\cdots CH_3$	70.8	-8.3	3.141	165	-3.56
$O_3Xe\cdots C_2H_5$	70.8	-10.9	2.966	164	-5.35

Isolated monomers	SEAB complexes
MEP maxima ($V_{S,max}$, kcal/mol)	Binding distance (R_{int}, Å)
MEP minima ($V_{S,min}$, kcal/mol)	Binding angles ($\theta_{O\text{-}Z\cdots C}$, °)
	Interaction energy (E_{int}, kcal/mol)

complex	ρ_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}	Δq	$E^{(2)}$	q_{CT}	WBI
$OF_2Kr\cdots CH_3$	0.022	0.058	-0.001	0.017	6.28	0.024	0.031
$OF_2Kr\cdots C_2H_5$	0.034	0.072	-0.005	0.022	10.42	0.031	0.055
$OF_2Xe\cdots CH_3$	0.025	0.067	-0.002	0.030	8.74	0.028	0.038
$OF_2Xe\cdots C_2H_5$	0.038	0.082	-0.006	0.039	14.60	0.035	0.063
$O_3Kr\cdots CH_3$	0.011	0.034	0.001	0.013	2.14	0.001	0.012
$O_3Kr\cdots C_2H_5$	0.015	0.044	0.000	0.016	4.33	0.011	0.013
$O_3Xe\cdots CH_3$	0.015	0.037	0.001	0.023	3.75	0.003	0.025
$O_3Xe\cdots C_2H_5$	0.028	0.046	-0.002	0.028	6.59	0.014	0.036

[a] All ρ_{BCP}, $\nabla^2\rho_{BCP}$ and H_{BCP} values in au, $E^{(2)}$ in kcal/mol, Δq and q_{CT} in e.

SEAB complexes

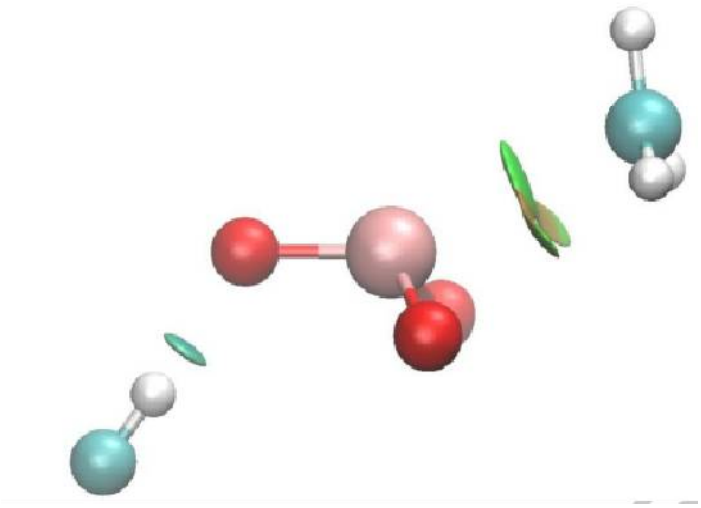
Topological parameters	Charge
☞ Electron density (at BCP, ρBCP),	☞ NBO atomic charge change (Δq)of Z atom
☞ Laplacian, ∇2ρBCP	☞ Charge-transfer energy (E(2))
☞ Total electron energy density, HBCP	☞ Net charge-transfer (qCT)
	☞ Wiberg bond index (WBI)

complex	$R_{Z\cdots C}$	$\Delta R_{Z\cdots C}$	$E_{int,total}$	$E_{int,\,Z\cdots C}$	E_{coop}
$FH\cdots OF_2Kr\cdots CH_3$	2.743	-0.057	-9.20	-4.99	-0.92

FH···OF_2Xe ···CH_3	2.924	-0.069	-11.35	-5.86	-1.28
FH···O_3Kr···CH_3	3.112	-0.047	-6.71	-3.10	-0.71
FH···O_3Xe ···CH_3	3.078	-0.063	-8.73	-4.14	-0.89

Ternary complexes			
SEAB distances	(RZ···C, Å)	Total interaction energies	(Eint,total, kcal/mol)
Relative changes to binary complexes	(ΔRZ···C, Å)	Interaction energies of SEAB	(Eint, Z···C, kcal/mol)
		Cooperative energies	(Ecoop, kcal/mol)

Aerogen Bond *[Xe]*		NgB.	SD.	26



Interaction energies of SEAB in the trimers			
Eint,AB(T) = EABC − (EA + EBC) – Eint,AC(T)			
Total energy of triad	EABC	Energy of fully relaxed	EBC
Energy of the isolated optimized A monomer	EA	Energy of dyad	BC
Interaction energy of AC pair in the geometry of triad	Eint,AC(T)		

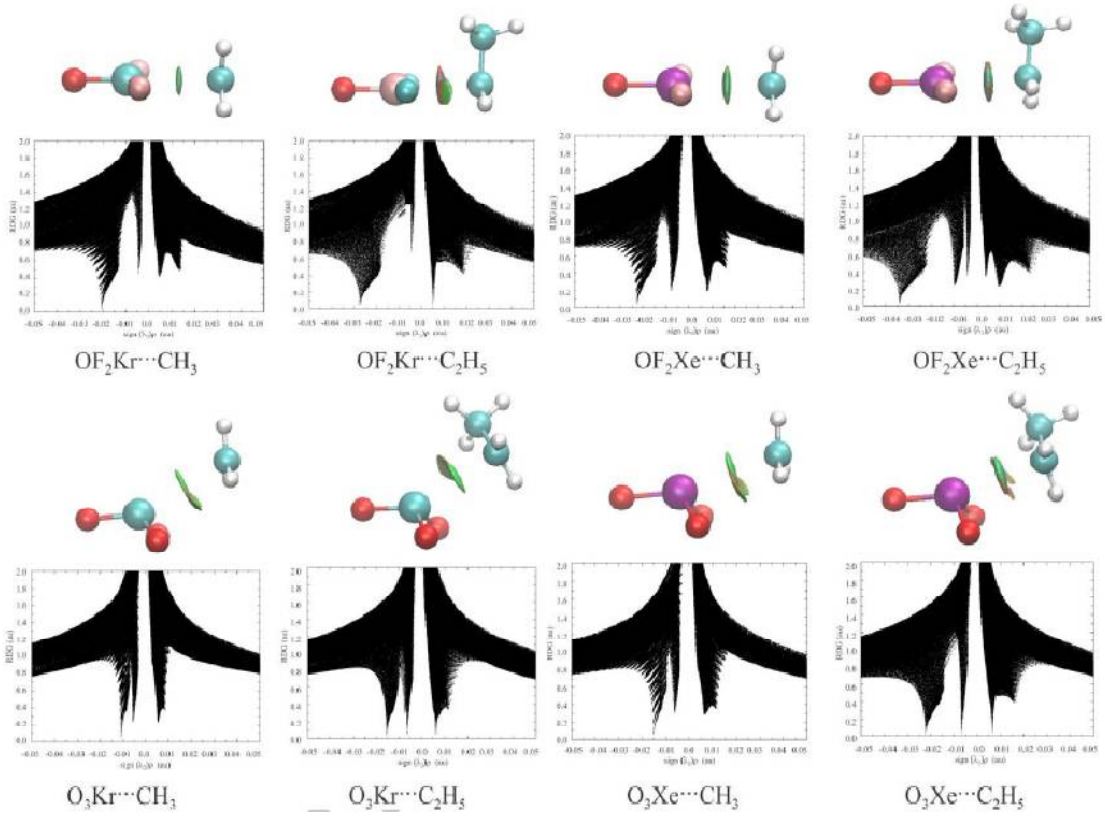
Cooperative energies

Ecoop=Eint,ABC − Eint,AB − Eint,BC – Eint,AC (T)

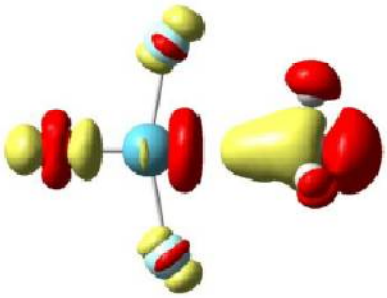
Interaction energy Of ternary complex	Eint, ABC		Eint,AB	Interaction energy isolated binary complexes
			Eint,BC	

Non-covalent interaction (NCI) isosurface

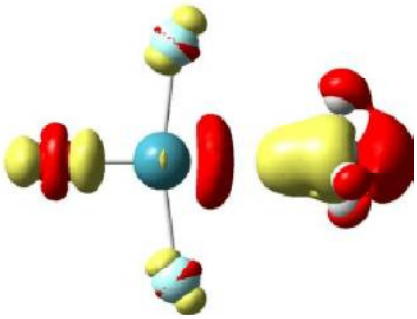
Reduced density gradient (RDG) versus sign (λ2)ρ



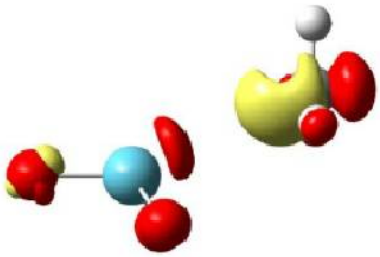
Electron density shift



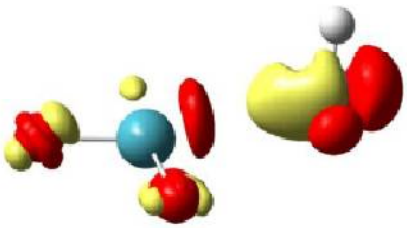
$OF_2Kr\cdots CH_3$



$OF_2Kr\cdots CH_3$



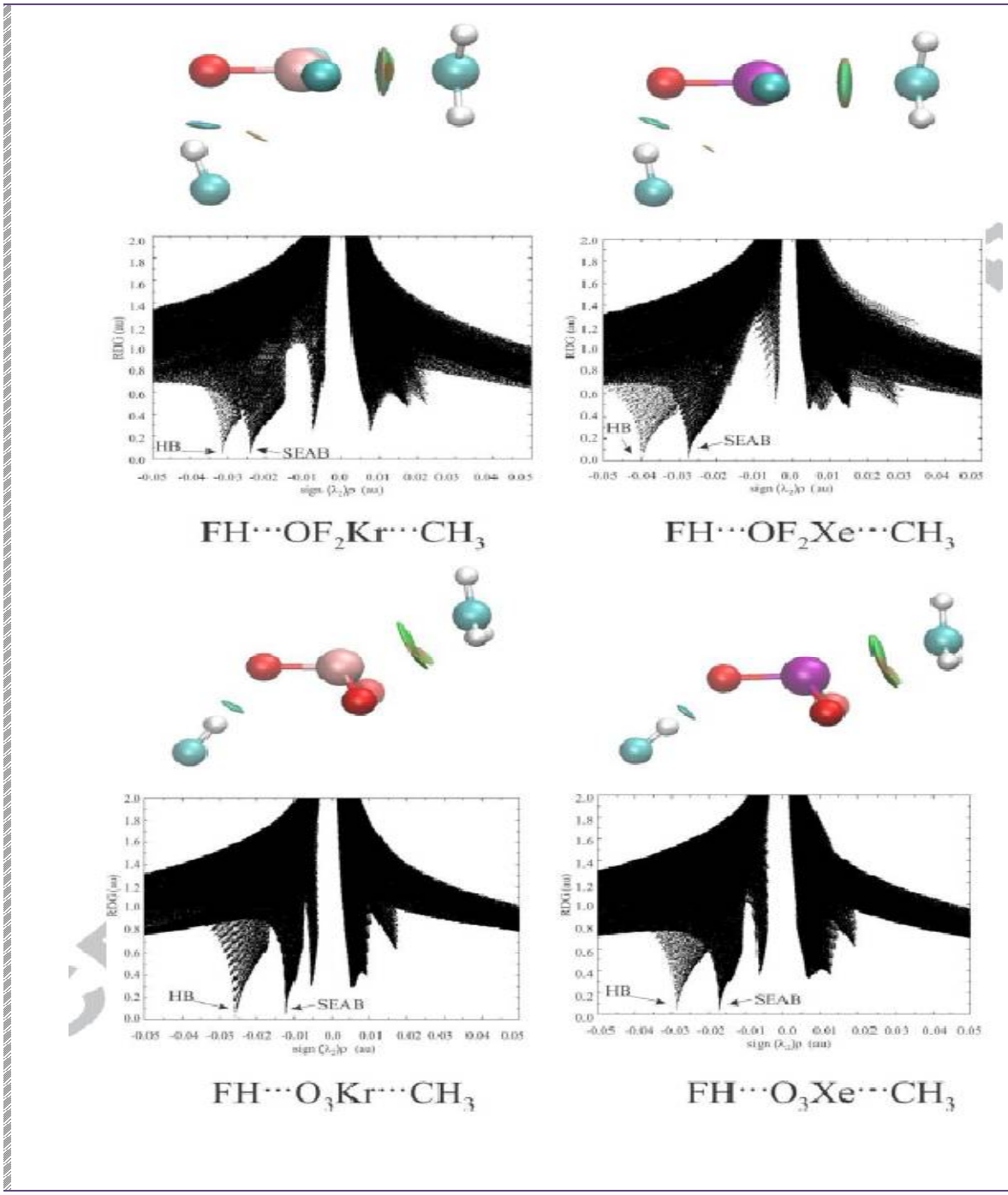
$O_3Kr\cdots CH_3$



$O_3Xe\cdots CH_3$

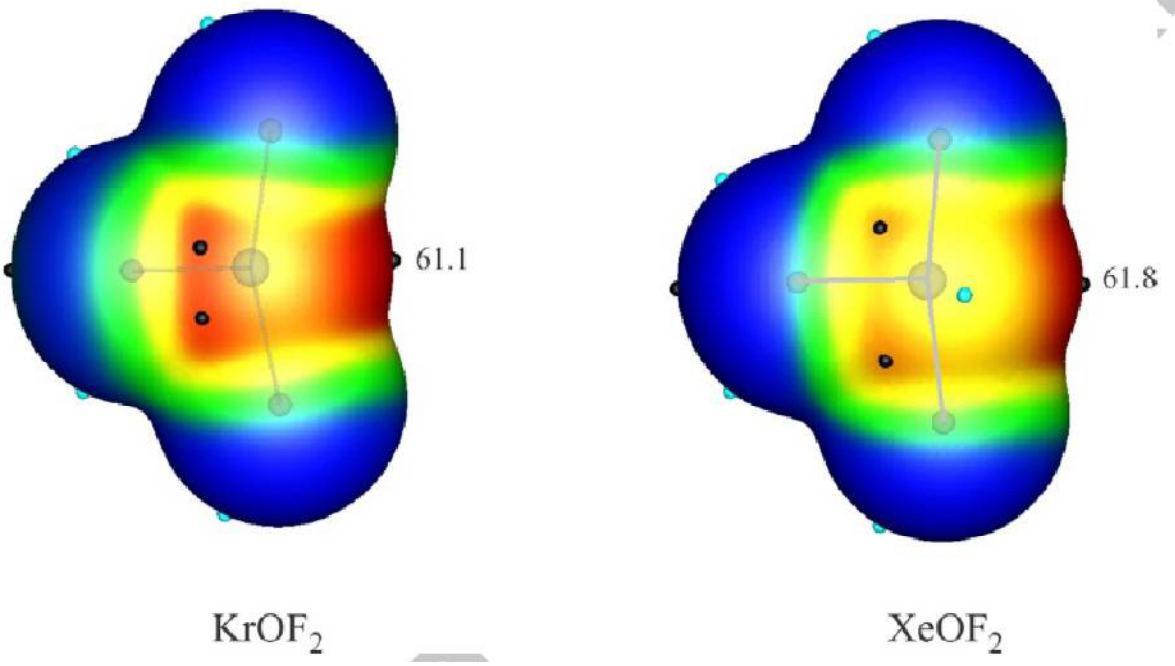
Non-covalent interaction (NCI) isosurface

Reduced density gradient (RDG) versus sign ($\lambda 2)\rho$


HB
SEAB
RDG (au)
sign (λ2)ρ (au)
FH···OF2Kr···CH3
FH···OF2Xe···CH3
FH···O3Kr···CH3
FH···O3Xe···CH3

Aerogen Bond [Kr Xe]	Aerogen-hydride interaction	NgB.	SD.	27

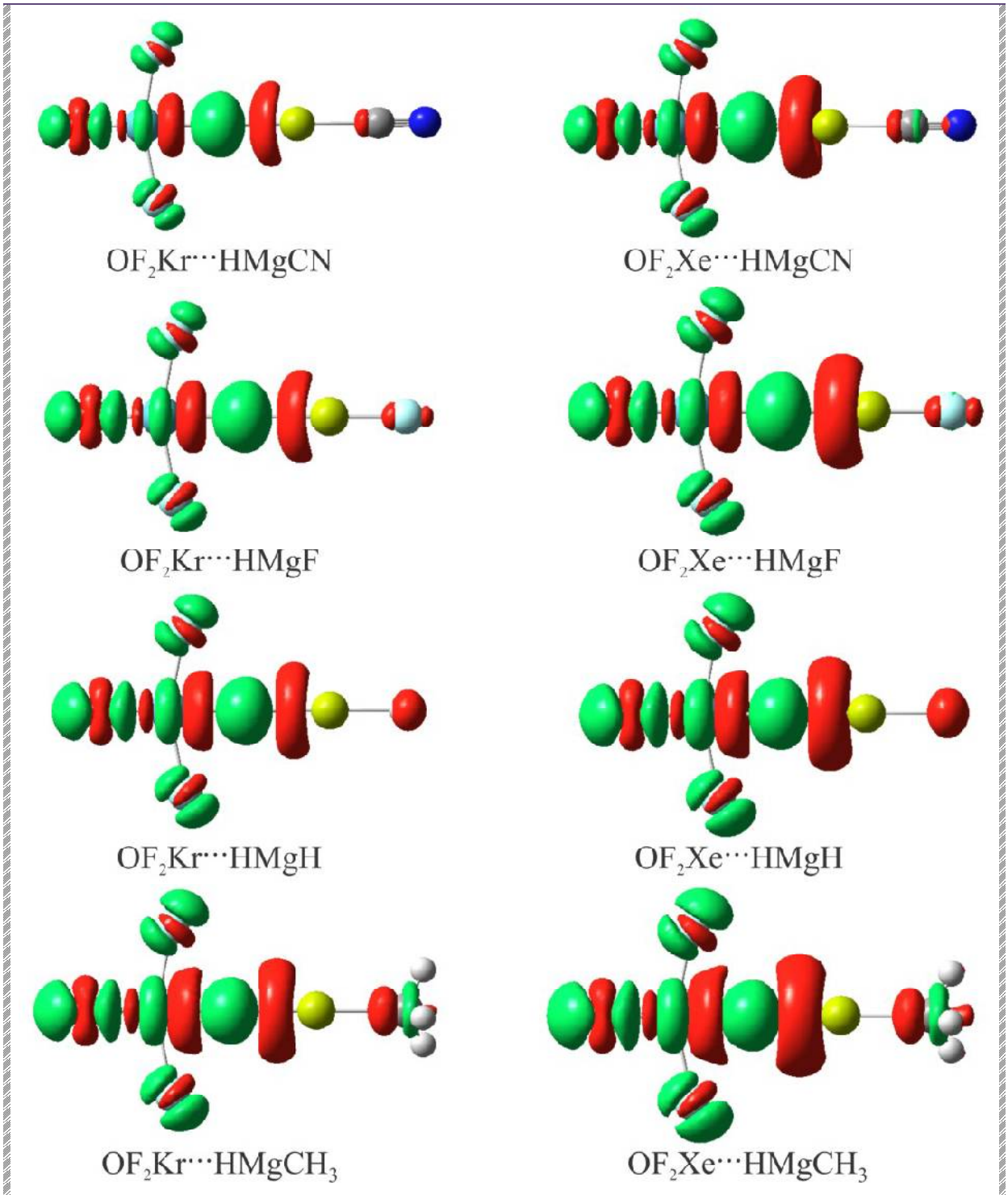
ESP: red > 40.9;; blue < 0



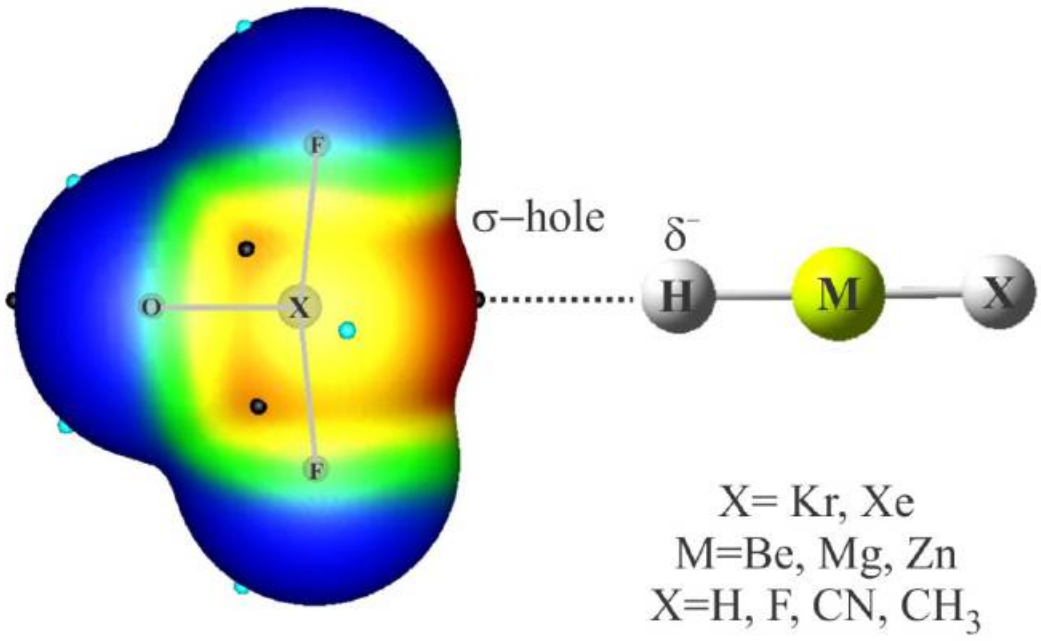
- σ-hole associated with Kr-O or Xe-O bond
- Red > 40.9; 20.0 < yellow < 40.9; 0 < green < 20.0; blue < 0

Aerogen Bond [Kr Xe]	Aerogen-hydride interaction	NgB.	SD.	27

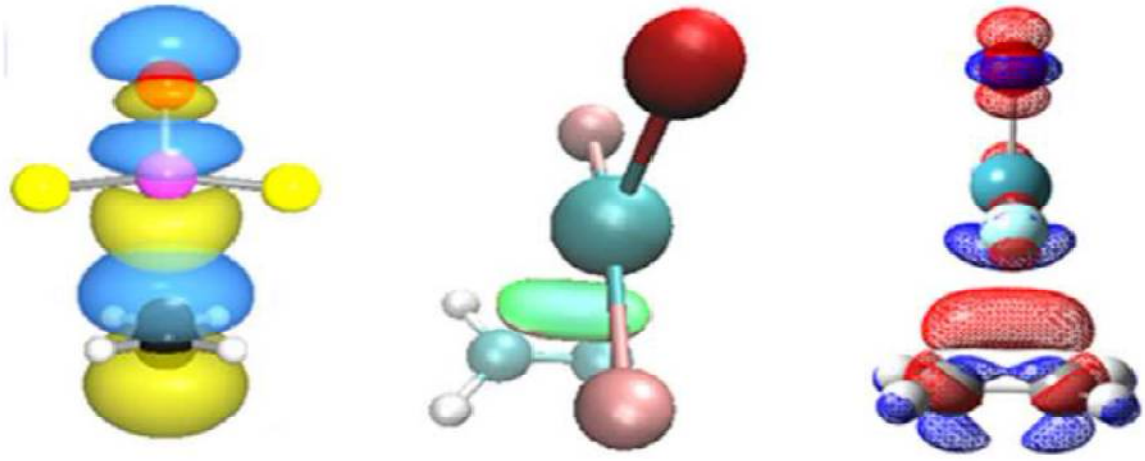
Electron density difference



☞ Red and green regions : decreased and increased electron densities

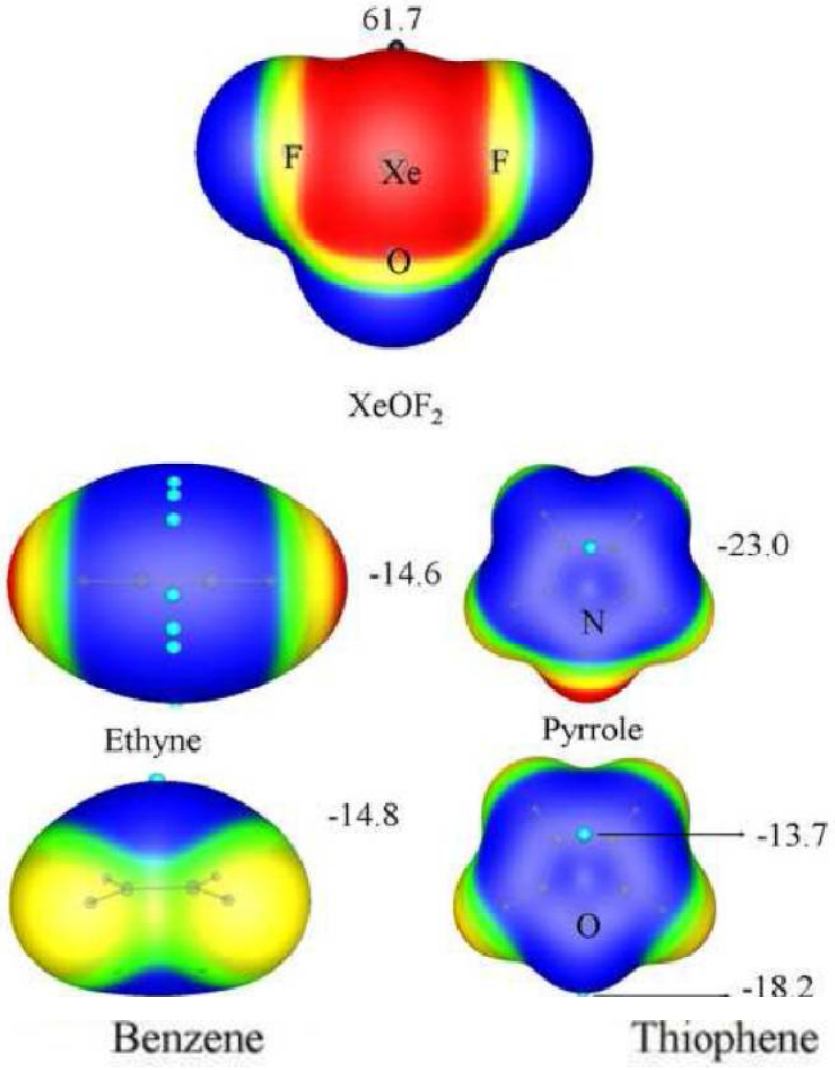


Interactions

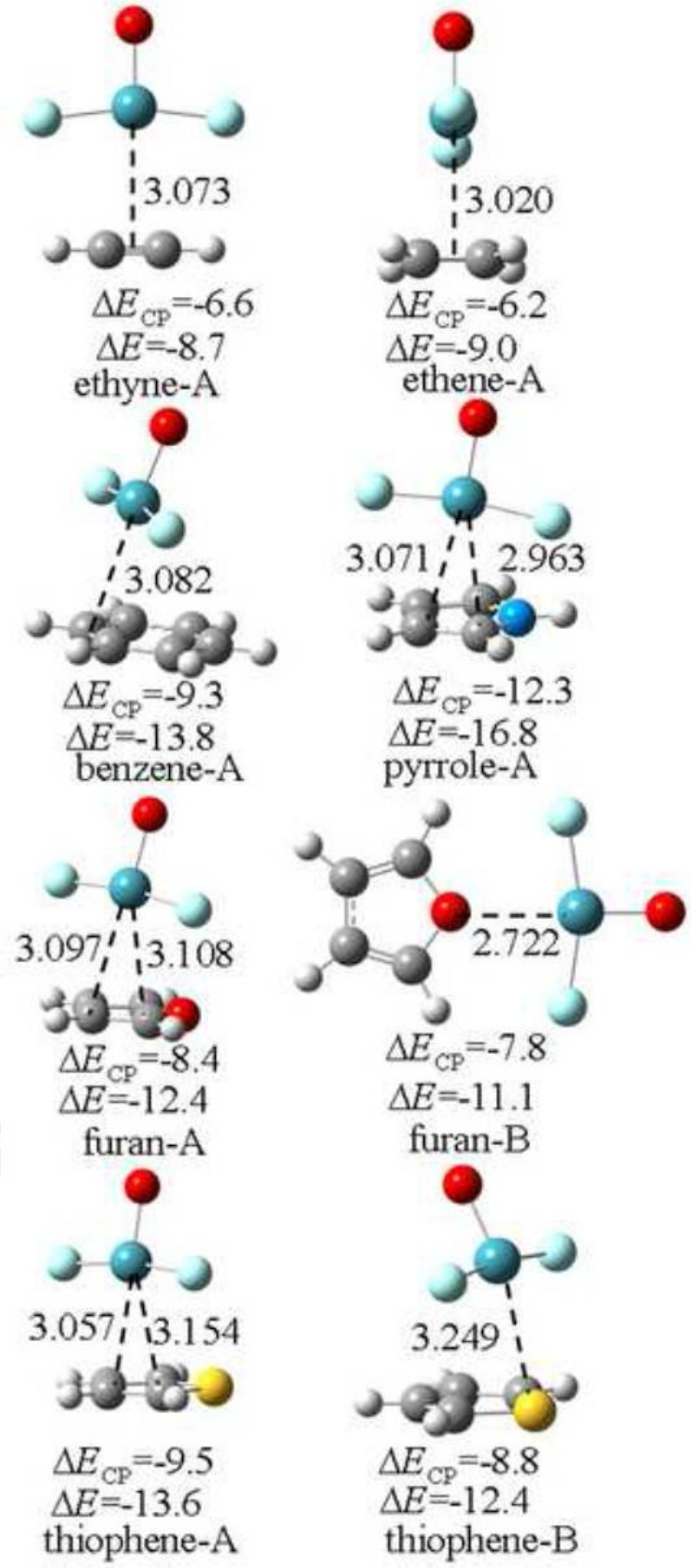


ESP: red >18; blue < 0

Figure



Opt Geometries

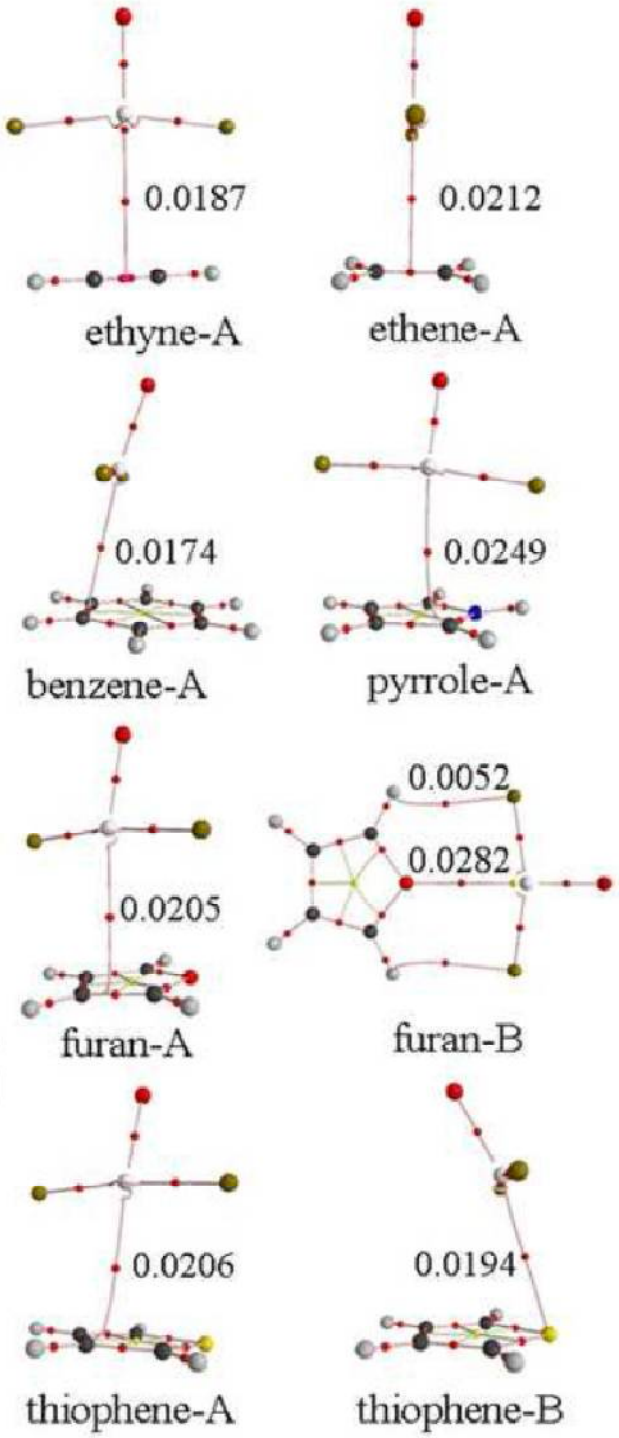


☞ ΔECP : Interaction energies corrected for BSSE

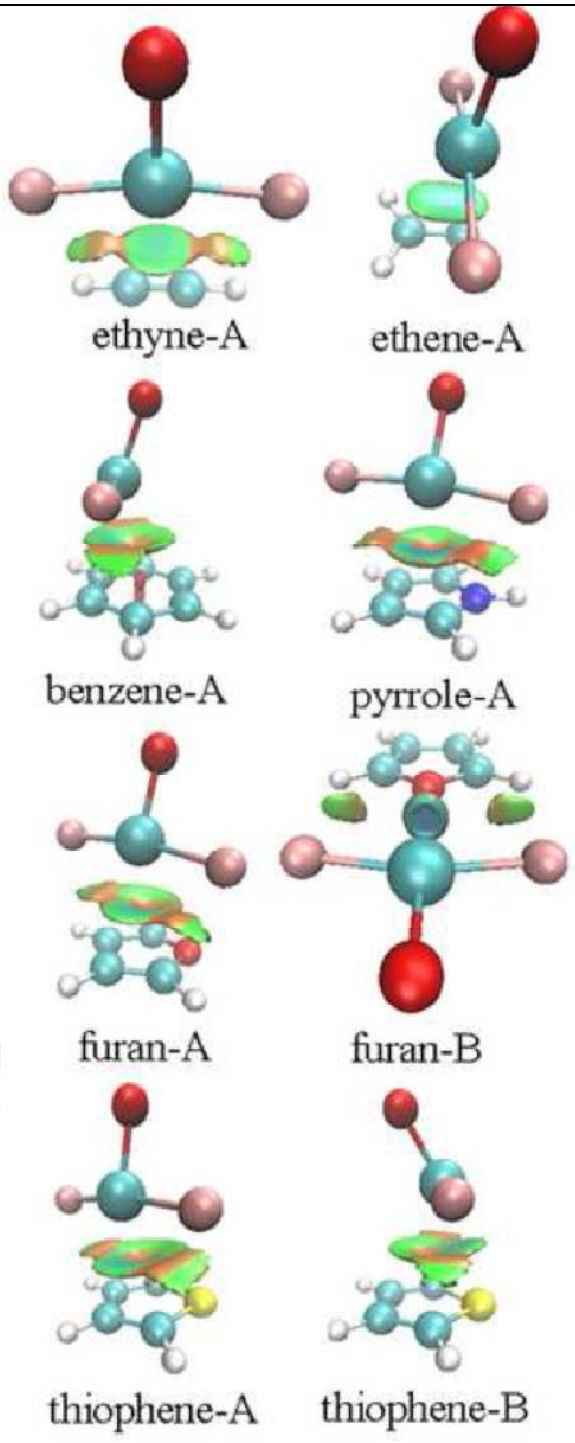
☞ ΔE :Uncorrected for BSSE

Molecular maps

Aerogen–bonded stable complexes

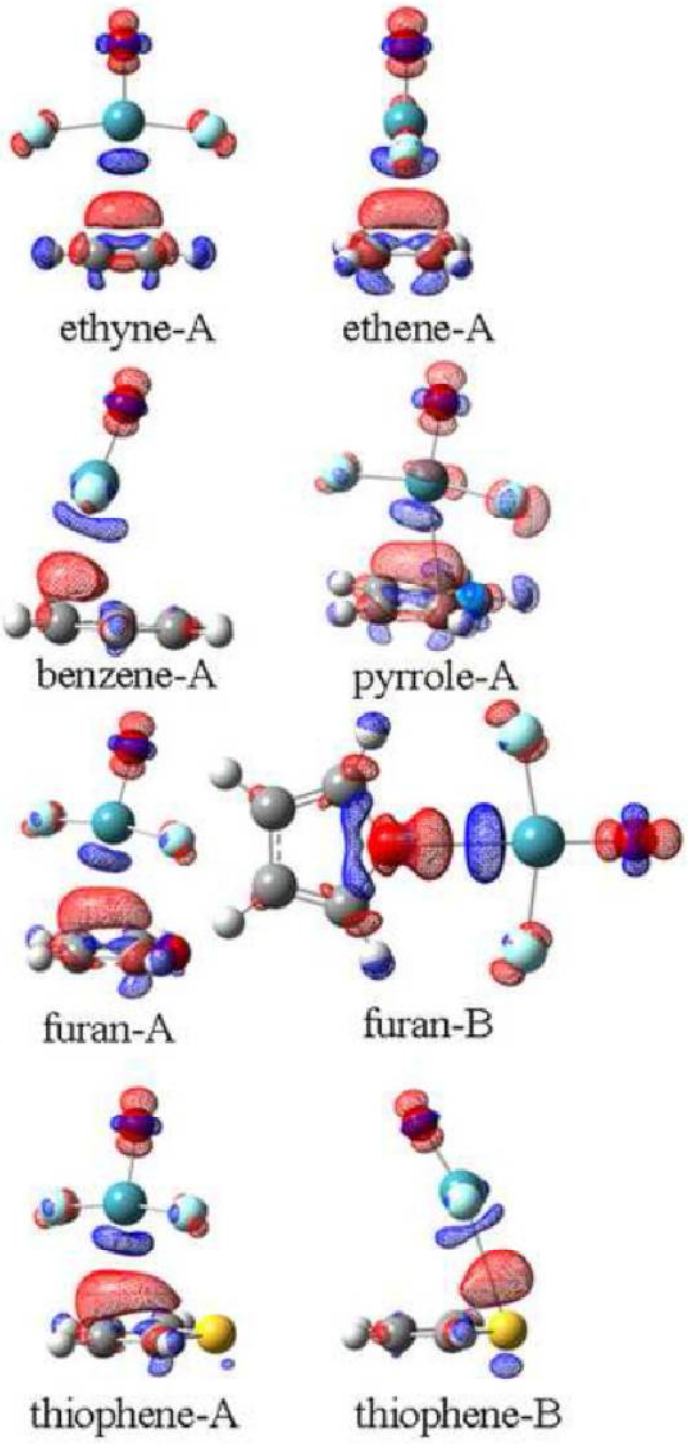


Gradient isosurfaces



	Interactions
Blue	Strong attractive
Green	Weak attractive
Orange	Weak repulsion

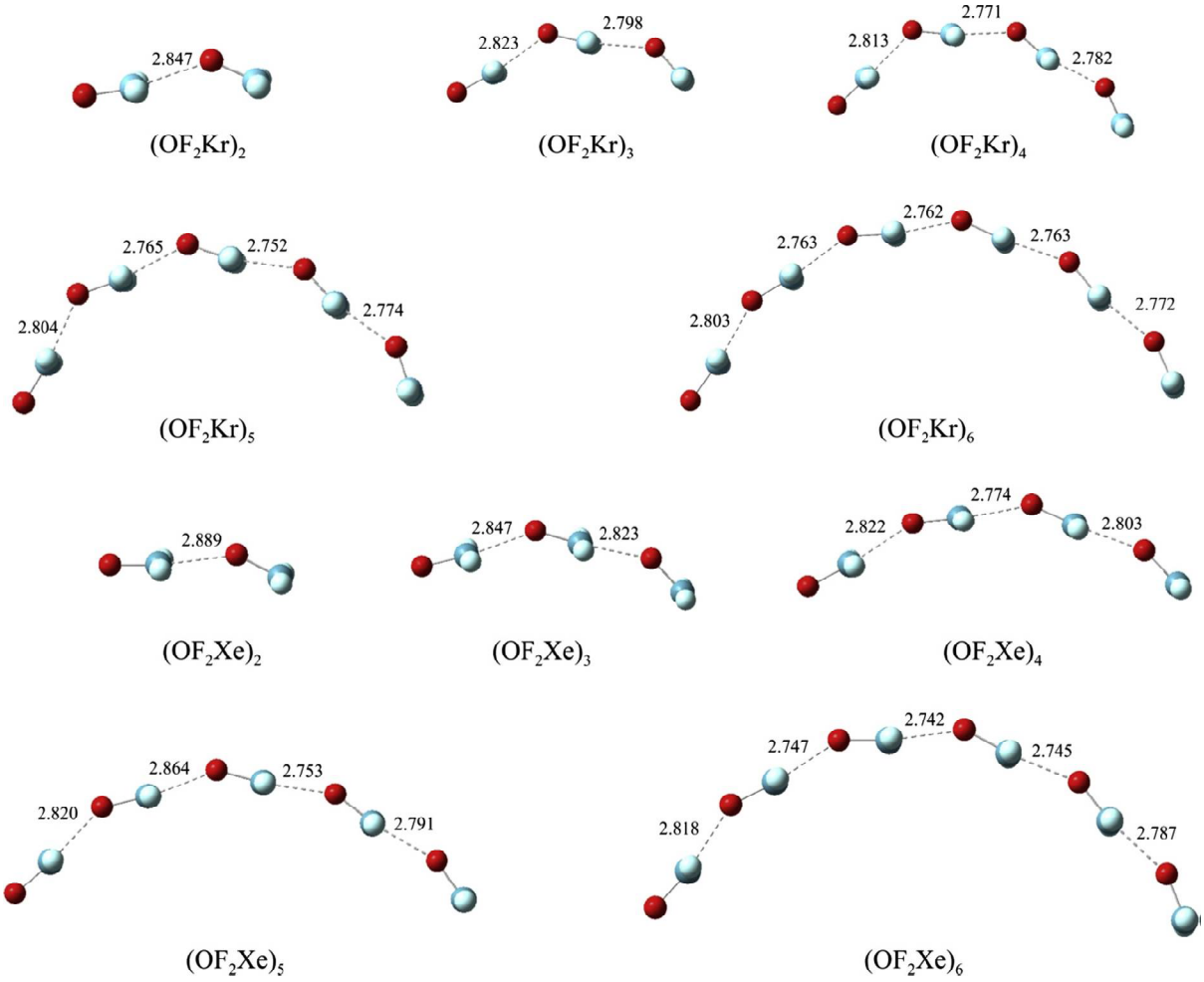
Electron density shifts



Blue	Decreased electrondensity
Red	Increased electron density

Optimized structures

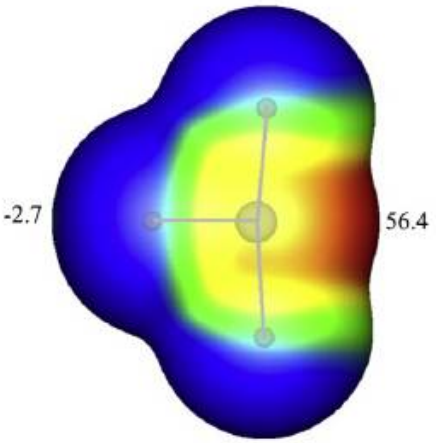
M06-2X/def2-TZVPPD



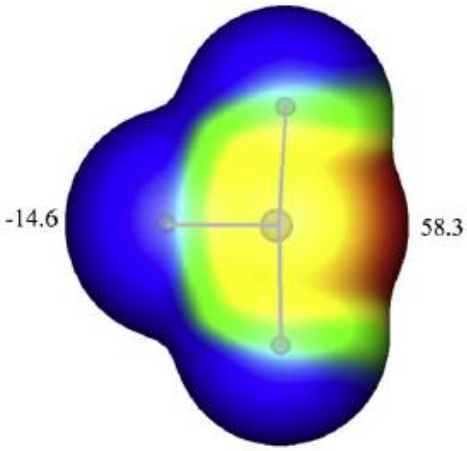
ESP on contour of the electronic density

M06-2X/def2-TZVPPD

red >30; blue < 0



KrF_2O

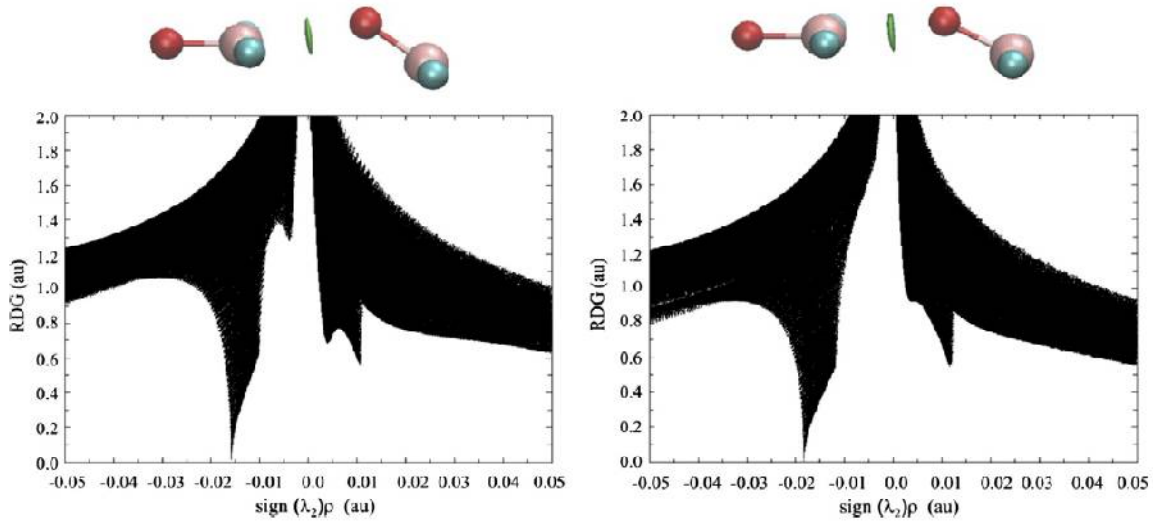


XeF_2O

cluster	$V_{S,max}$	$V_{S,min}$
$(KrF_2O)_2$	65.6	-8.0
$(KrF_2O)_3$	70.3	-10.1
$(KrF_2O)_4$	71.1	-10.9
$(KrF_2O)_5$	71.8	-11.5
$(KrF_2O)_6$	72.2	-11.7
$(XeF_2O)_2$	70.6	-22.0
$(XeF_2O)_3$	76.9	-25.8
$(XeF_2O)_4$	78.9	-27.7
$(XeF_2O)_5$	80.4	-29.1
$(XeF_2O)_6$	81.1	-30.0

Non-covalent interaction (NCI) isosurface

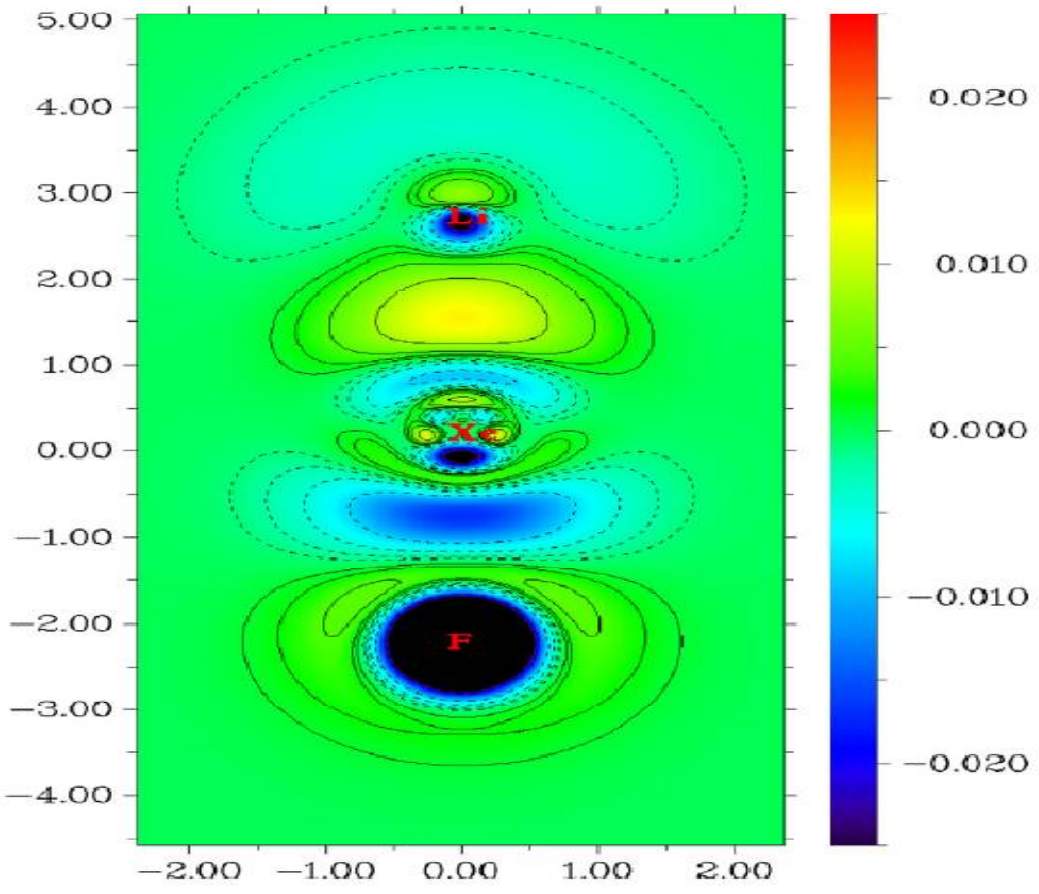
Reduced density gradient (RDG) versus sign (λ2)ρ



$(KrF_2O)_2$ and $(XeF_2O)_2$ complexes

Ng Bond *[Xe]*		NgB.	SD.	20

Charge difference densityLiXeF



OptGeom

B3LYP, MP2 and CCSD(T)

(a)

	B3LYP	MP2	CCSD(T)	R_{cov}[a]	R_{vdW}[b]
R_{Li-Kr}	2.312	2.293	2.296	2.462	2.67
R_{Li-Xe}	2.521	2.509	2.512	2.602	2.88
R_{Li-Rn}	2.626	2.603	2.606	2.712	3.00
	B3LYP	MP2	CCSD(T)	R_{cov}[a]	R_{vdW}[b]
R_{Kr-F}	2.411	2.413	2.411	1.876	3.43
R_{Xe-F}	2.426	2.423	2.426	2.016	3.64
R_{Rn-F}	2.453	2.447	2.449	2.126	3.76

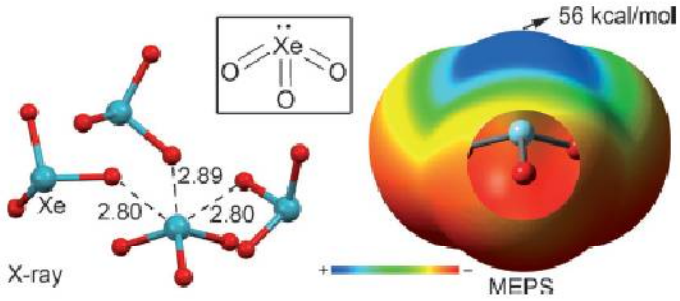
Ground State

(b)

	B3LYP	MP2	CCSD(T)
R_{Li-Xe}	2.455	2.469	2.469
R_{Li-Rn}	2.539	2.545	2.545
	B3LYP	MP2	CCSD(T)
$\theta_{Li-Xe-F}$	125.4	153.1	131.3
$\theta_{Li-Rn-F}$	117.1	122.3	121.7
	B3LYP	MP2	CCSD(T)
R_{Xe-F}	2.485	2.472	2.476
R_{Rn-F}	2.533	2.515	2.519

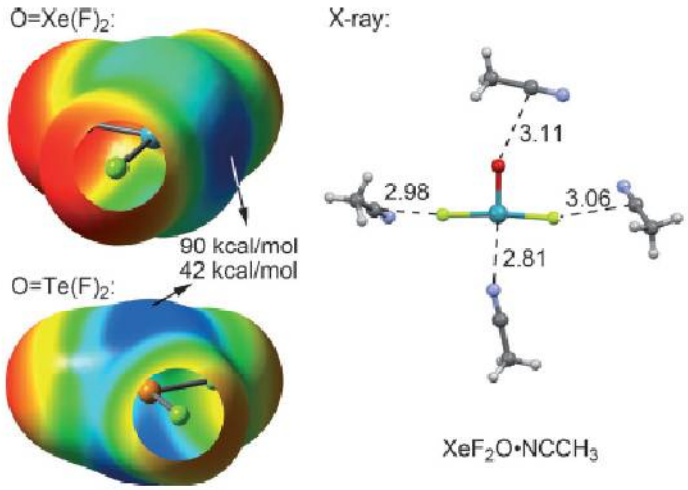
Transition State

ESP



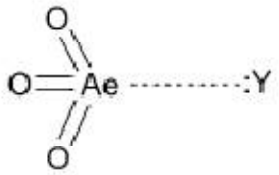
X-ray structure MESP of XeO3

ESP



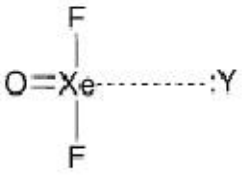
Aerogen Bond *[Ar Kr Xe]*		NgB.	SD.	40

Species Binary

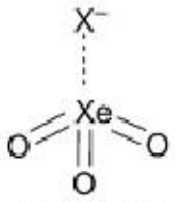


1, Ae = Ar, Y = CH_3CN
2, Ae = Ar, Y = NH_3
3, Ae = Kr, Y = CH_3CN
4, Ae = Kr, Y = NH_3
5, Ae = Xe, Y = CH_3CN
6, Ae = Xe, Y = NH_3

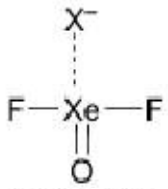
CH_3CN: ····· IF **7**
CH_3CN: ····· TeF_2 **8**
CH_3CN: ····· SbF_3 **9**
CH_3CN: ····· SnF_4 **10**



11, Y = CH_3CN
12, Y = NH_3



13, X = Cl
14, X = Br

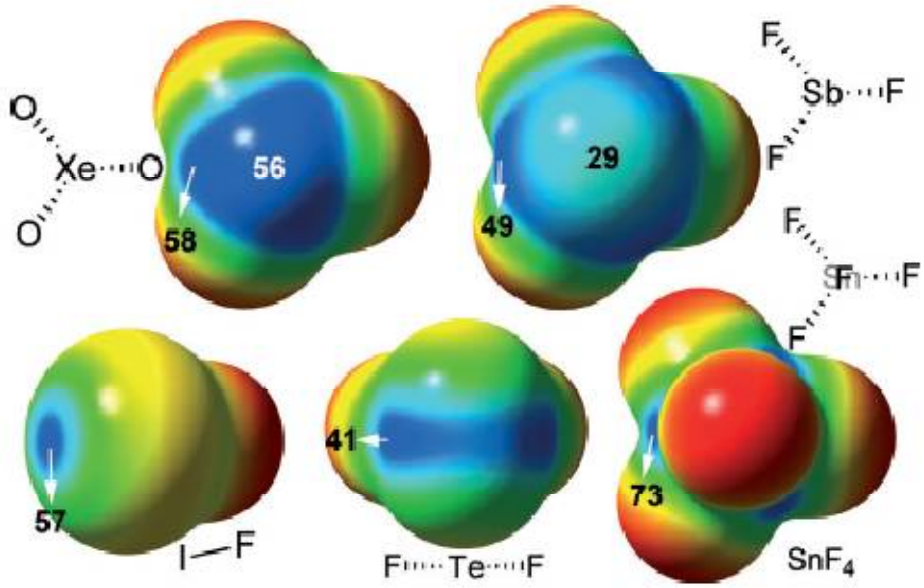


15, X = Cl
16, X = Br

Aerogen Bond *[Xe]*		NgB.	SD.	40

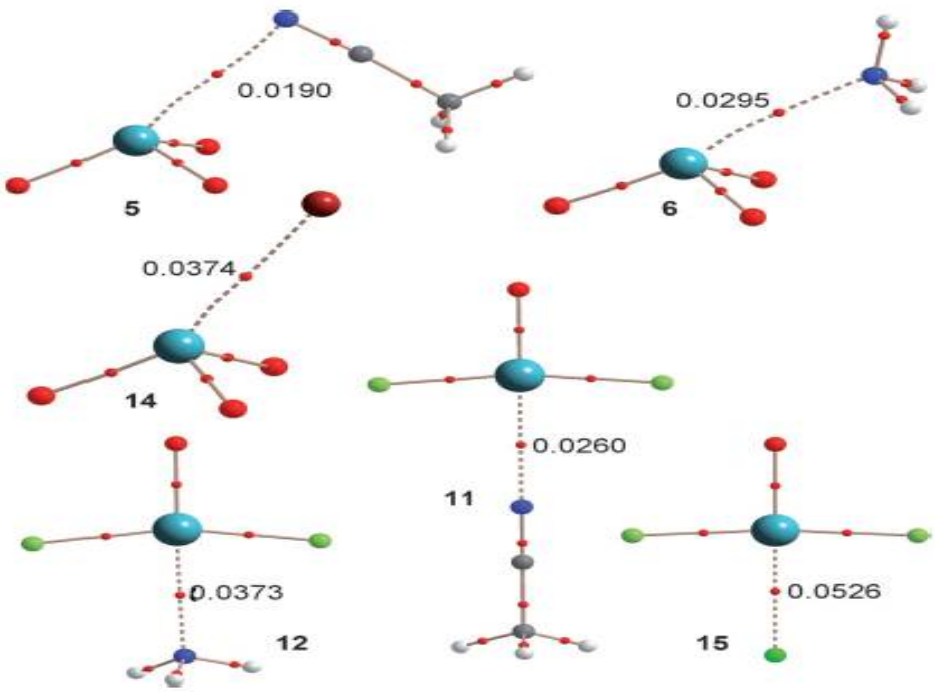
ESP

MP2/aug-cc-pVTZ

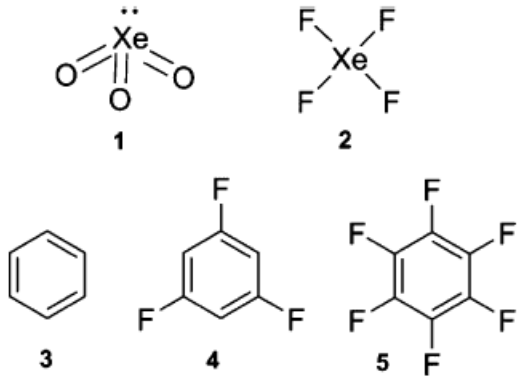


AIM distribution of critical points

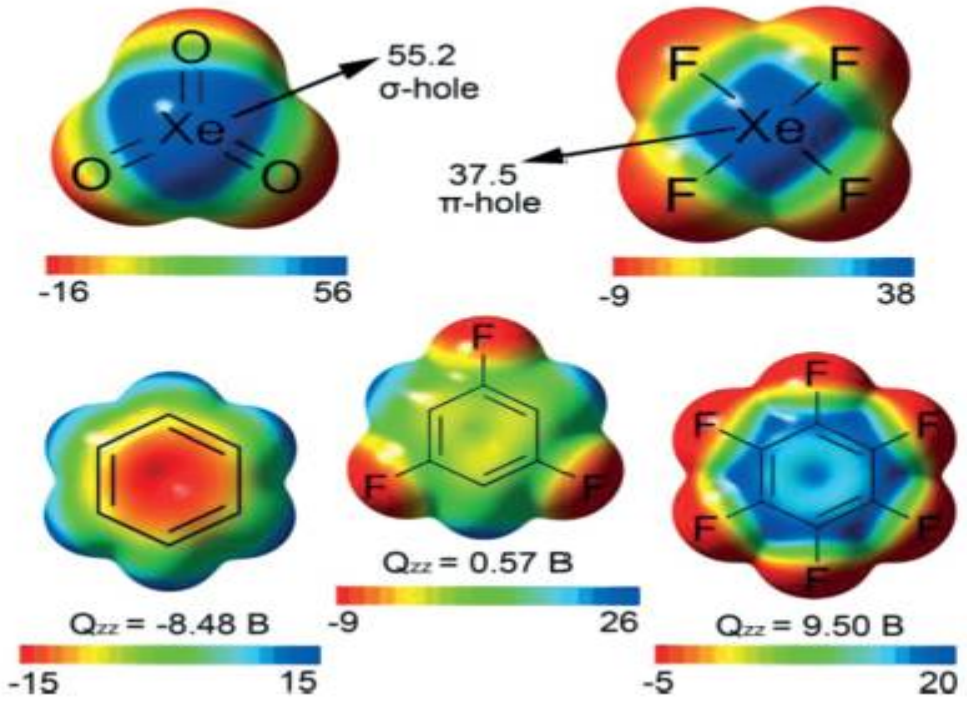
MP2/aug-cc-pVTZ



☞ 1(r) values at the bond critical points are in atomic units (a.u.).



ESP



Xe-Complexes

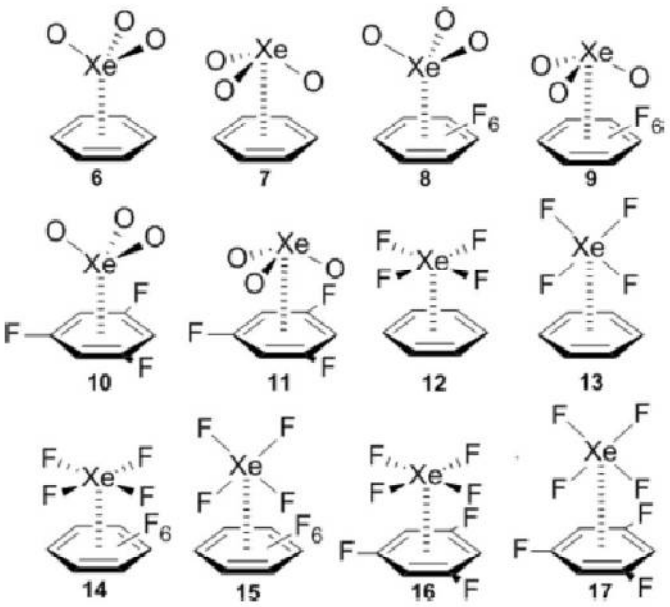


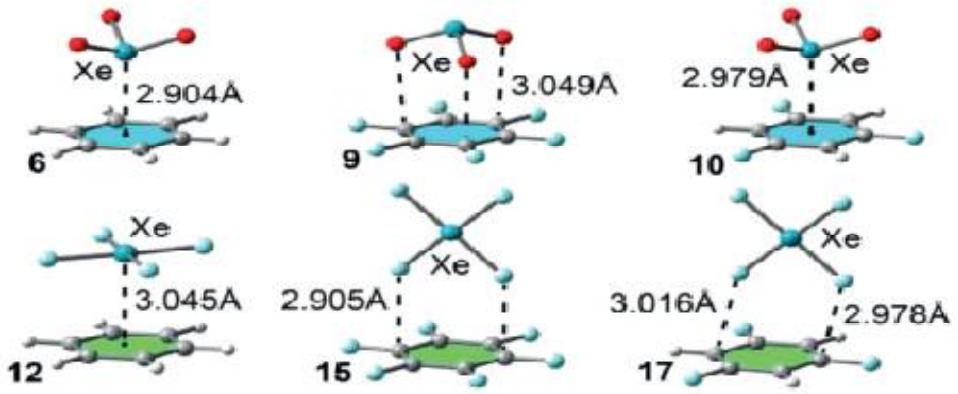
Table 1. Interaction energies of complexes 6–17 at the RI-MP2/aug-cc-pVTZ level of theory without and with the BSSE correction (E and E_{BSSE} in kcal mol^{-1}, respectively), equilibrium distances (R_e in Å) and value of the density at the cage critical point (ρ, a.u.).

E	E_{BSSE}	R_e	Complex type	$10^2\times\rho$
−16.6	−12.4	2.904[a]	σ–hole	1.08
−4.5	−2.5	3.259[b]	lone pair–π	0.18
−6.2	−2.2	3.061[a]	σ–hole	0.94
−8.1	−5.1	3.049[a]	lone pair–π	0.26
−10.7	−6.7	2.979[b]	σ–hole	1.02
−6.3	−3.7	3.119[a]	lone pair–π	0.23
−12.9	−8.8	3.045[b]	π–hole	0.91
−3.4	−1.9	3.026[a]	lone pair–π	0.16
−8.1	−3.5	3.096[b]	π–hole	0.89
−5.3	−3.1	2.905[a]	lone pair–π	0.21
−10.0	−5.7	3.097[a]	π–hole	0.88
−4.3	−2.4	2.978[b]	lone pair–π	0.27

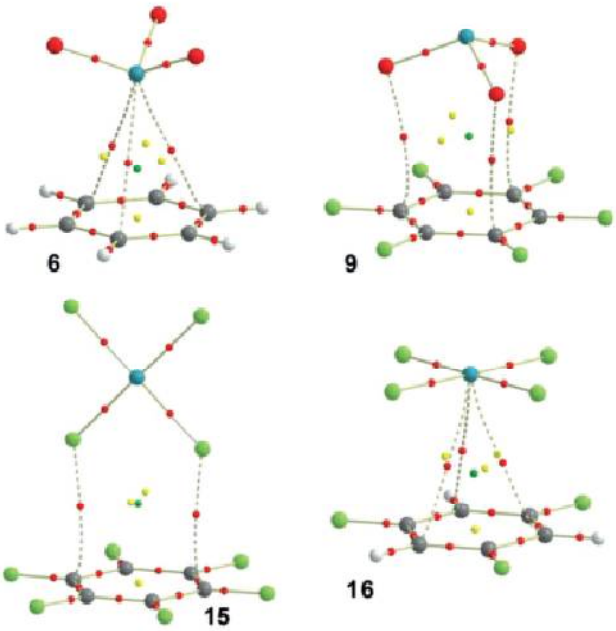
[a] Distances measured from the Xe atom to the ring centroid. [b] Shortest distance measured from the O/F atom to the closest C atom of the ring.

Optimized geometries

RIMP2/aug-cc-pVTZ

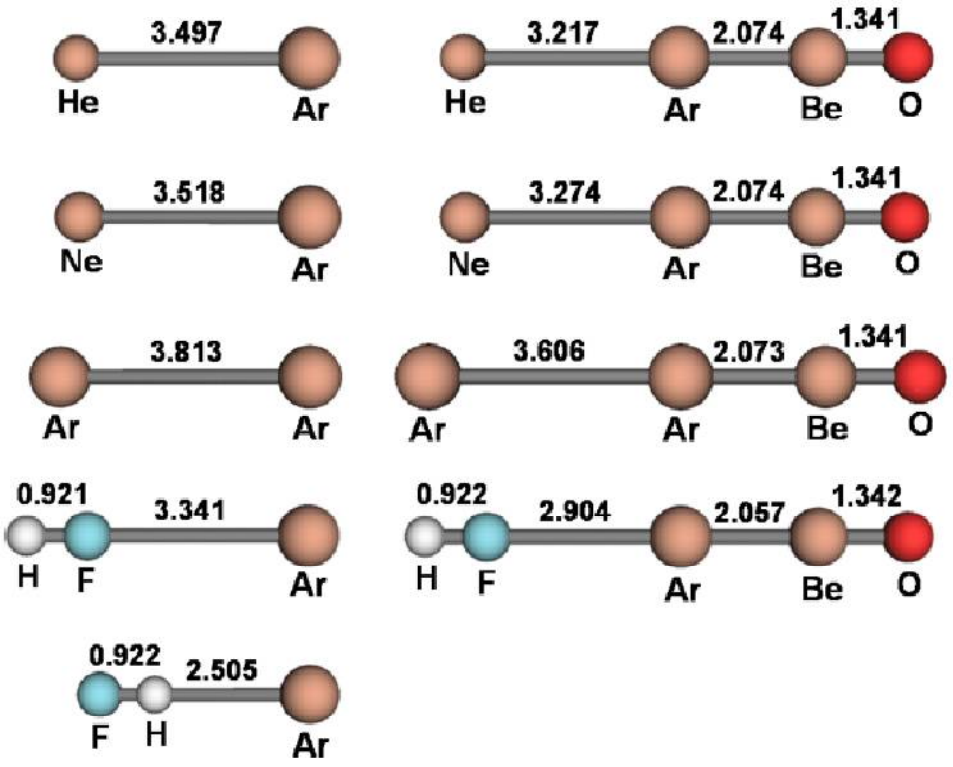


CPs and bond paths

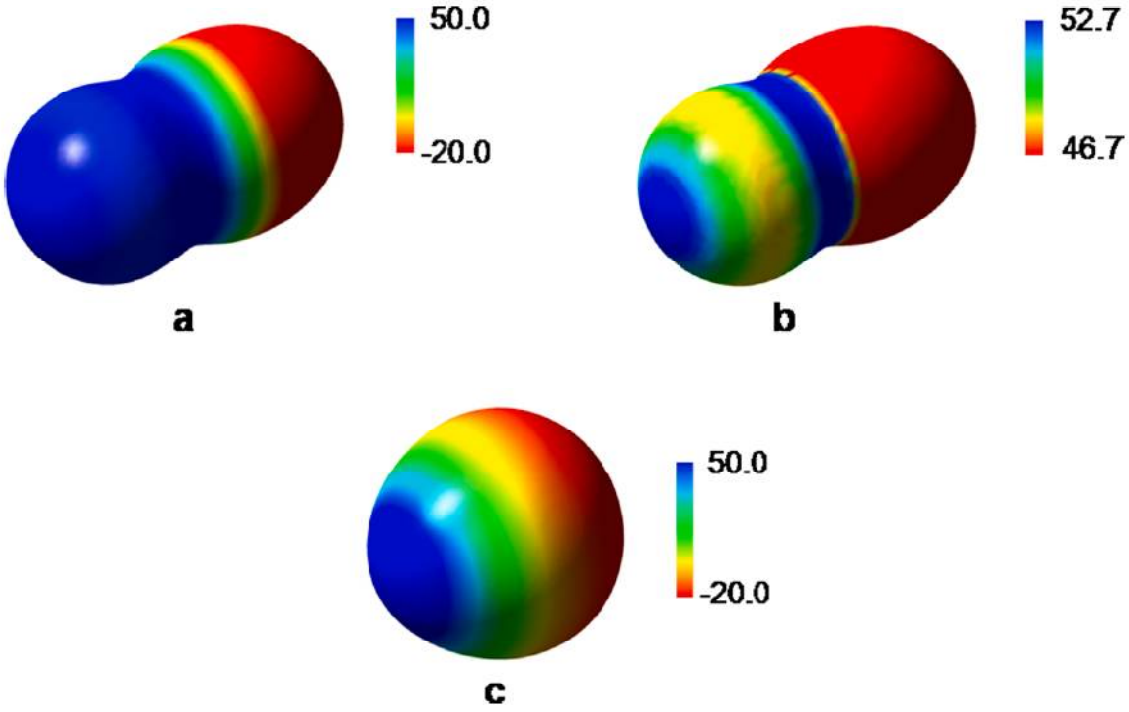


CCSD(T)/aVTZ bond distances

He, Ne, Ar,

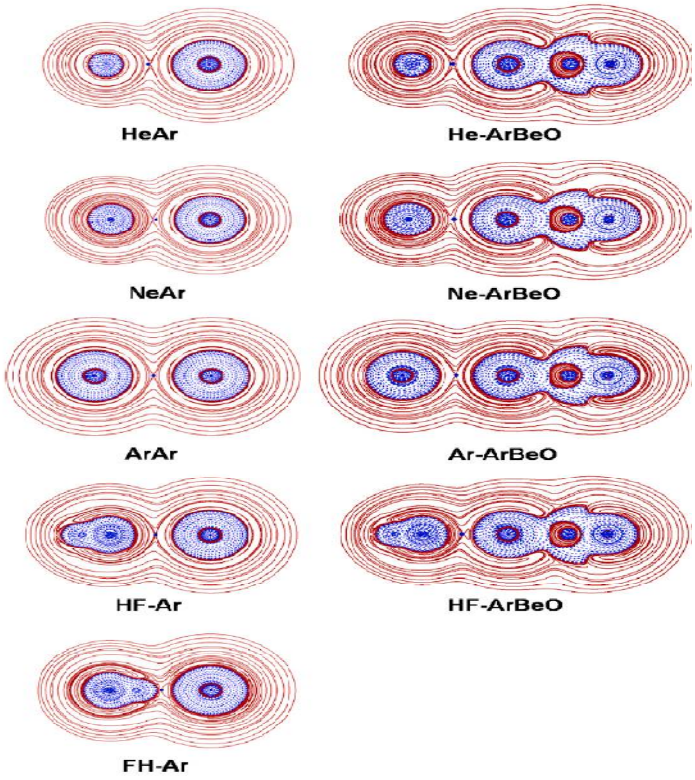


Isodensity surface-- CCSD/aVTZ MEP



☞ ArBeO (a, b) ; HF (c)

2D-plots of H(r)

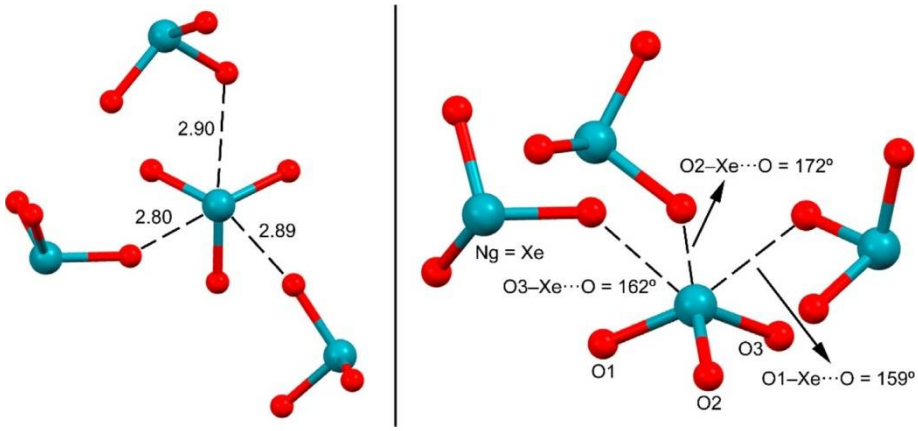


☞ Solid/brown and dashed/blue lines : positive and negative values)

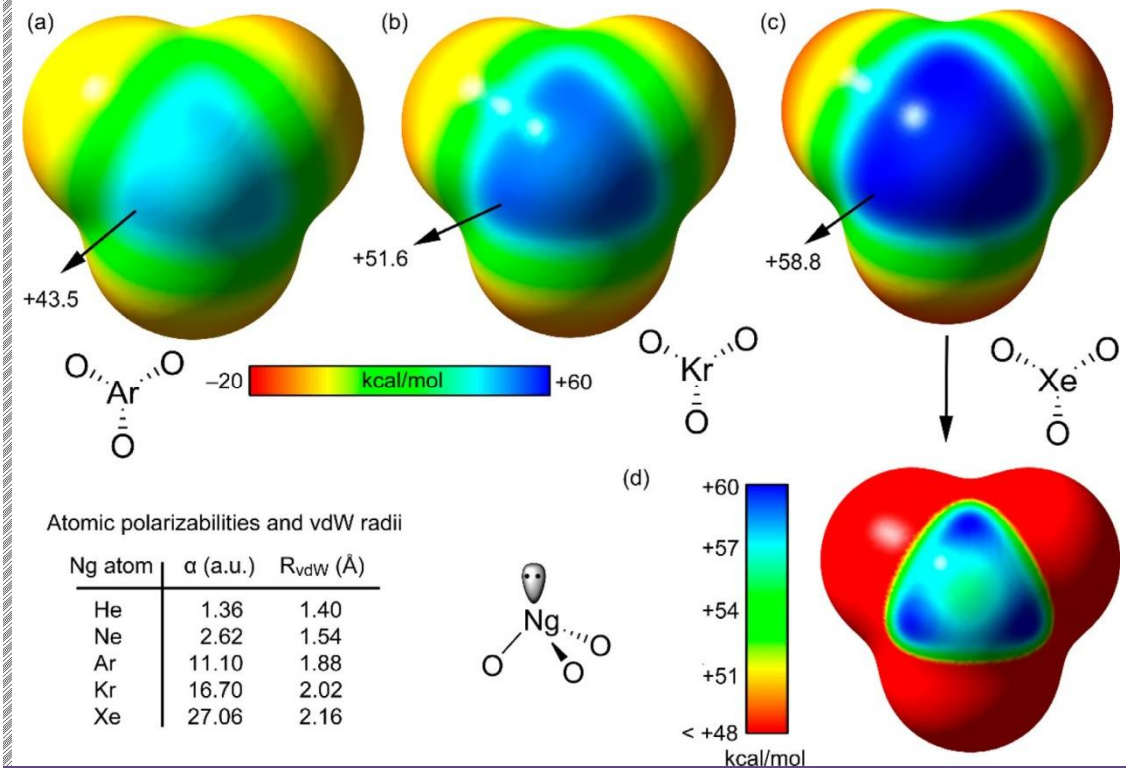
☞ Blue dot : BCP

https://doi.org/10.1016/j.ccr.2019.213112

X-ray structure of XeO3



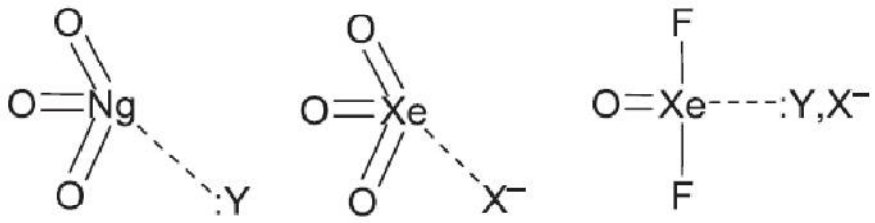
MEP surfaces --- MP2/aug-cc-pVQZ



Atomic polarizabilities and vdW radii

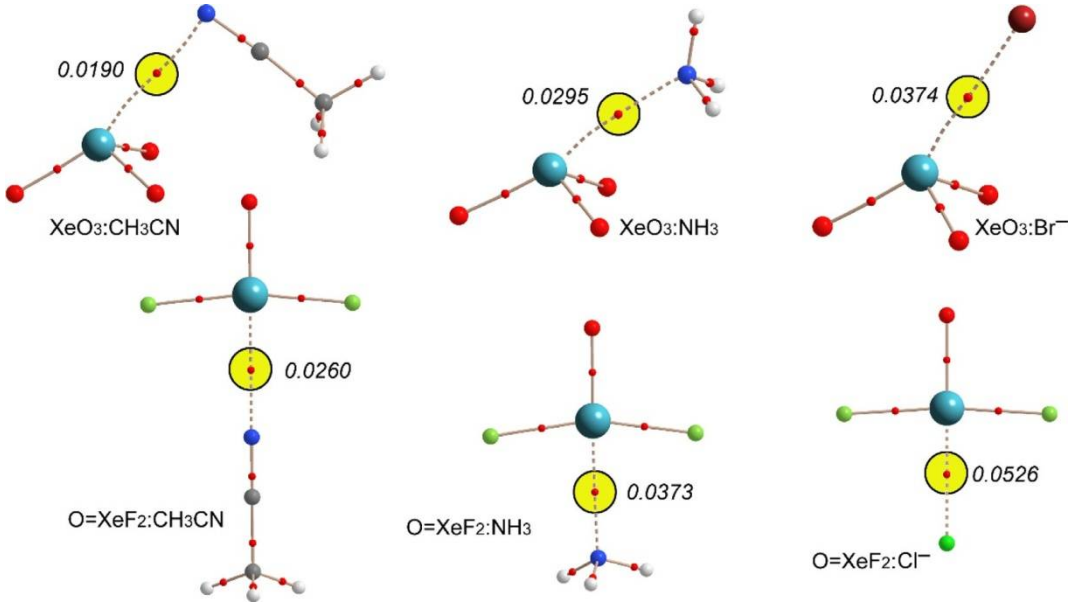
Ng atom	α (a.u.)	R_{vdW} (Å)
He	1.36	1.40
Ne	2.62	1.54
Ar	11.10	1.88
Kr	16.70	2.02
Xe	27.06	2.16

Xx

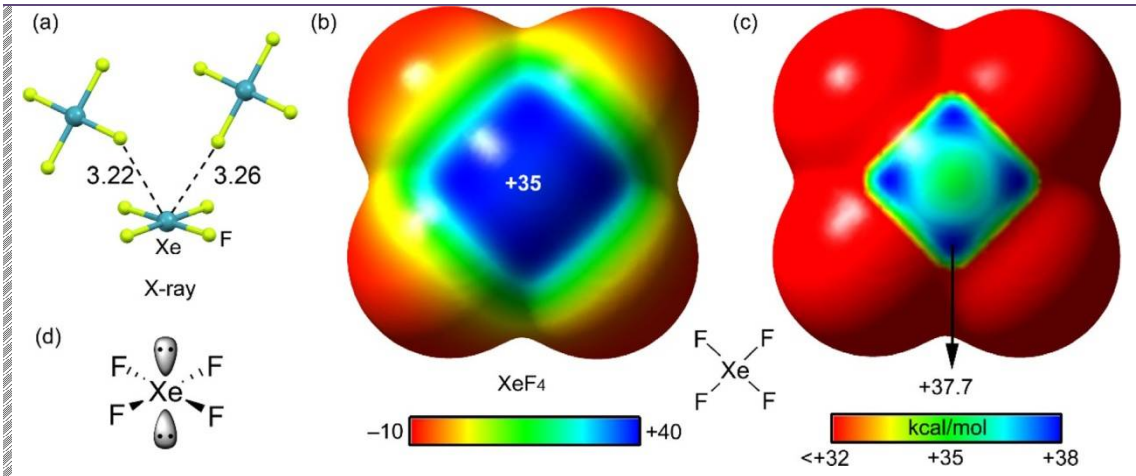


X =

Distribution of bond CPs (in red)

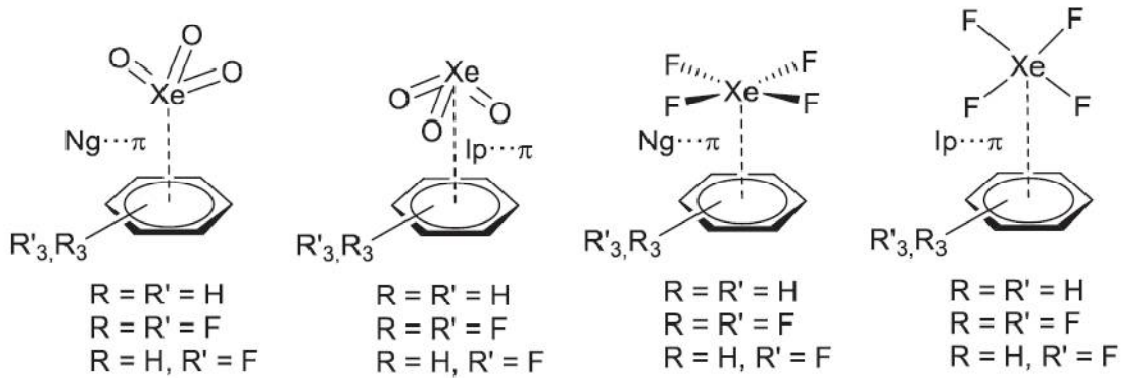


X-ray structure of XeF4 (from ICSD)

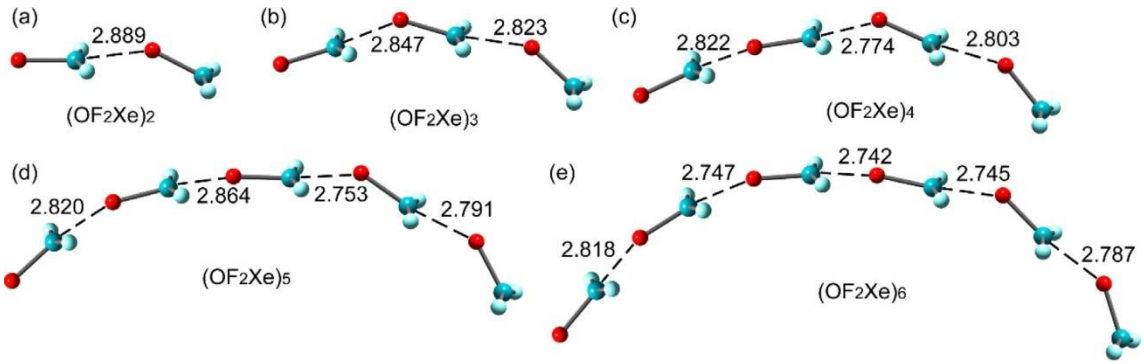


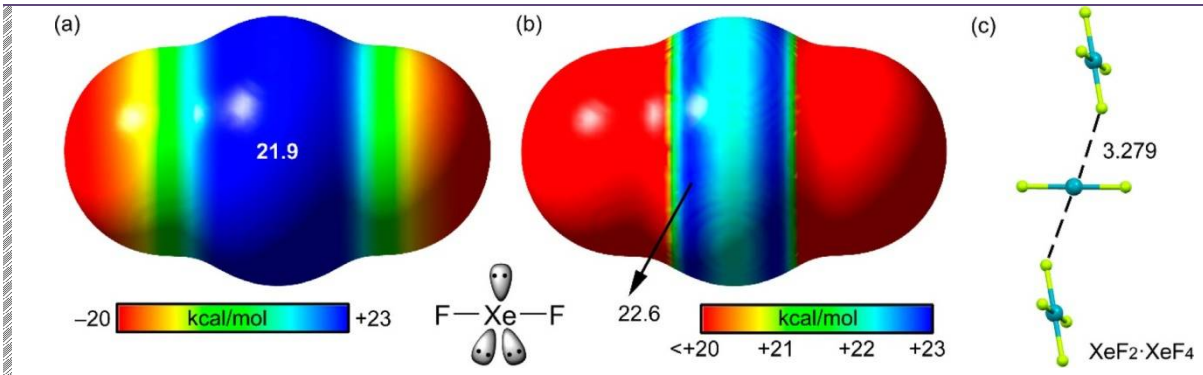
(b,c) MEP surfaces (MP2/aug-cc-pVQZ)
(d) XeF4 with lone pair

Ng·· ·p and LP–p complexes



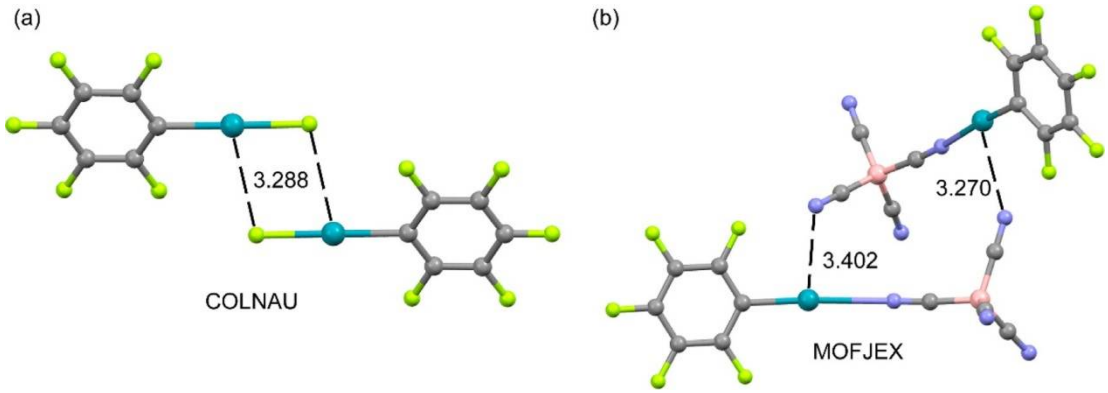
Clusters of (XeOF2)n=2–6



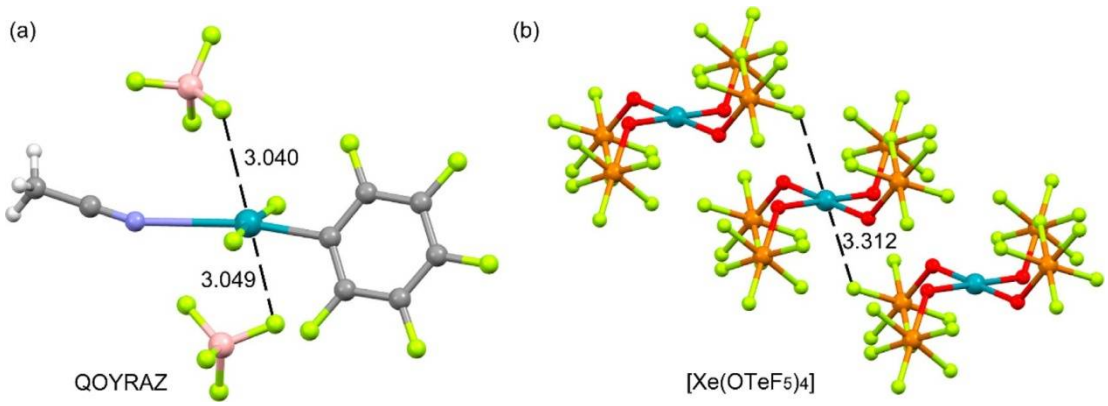


☞ (a,b) MEP surfaces XeF2 (MP2/aug-cc-pVQZ).
☞ (c) X-ray structure of XeF2·XeF4 co-crystal

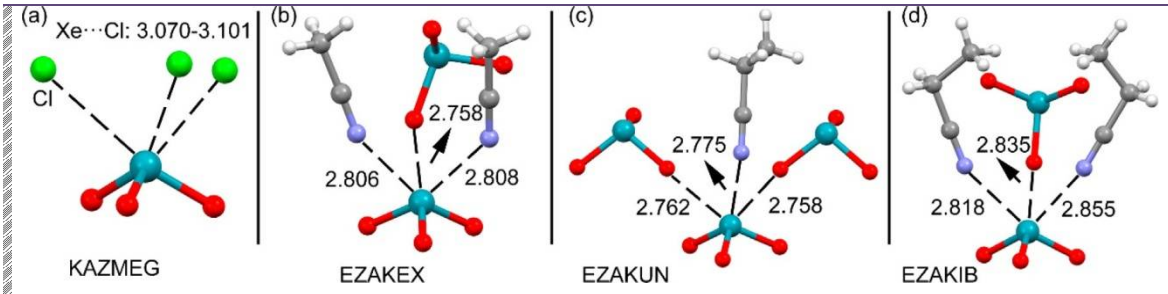
Distances in Å



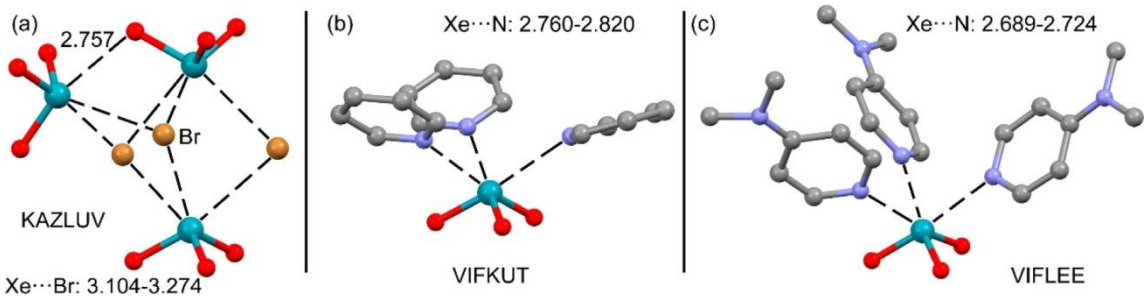
Distances in Å



Distances in Å

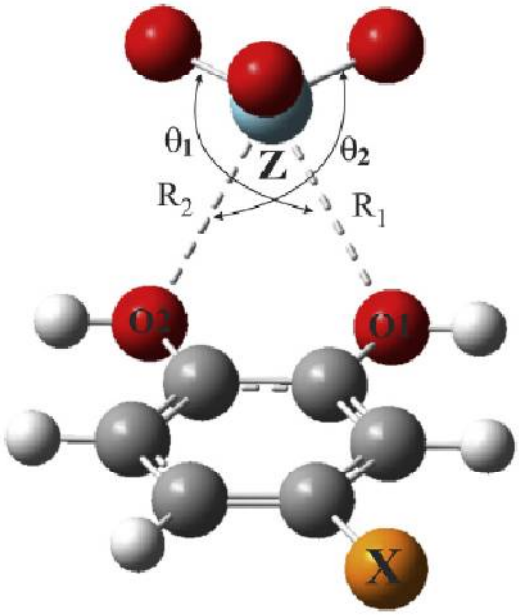


Distances in Å



Aerogen Bond *[Ar Kr Xe]*		NgB.	SD.	16

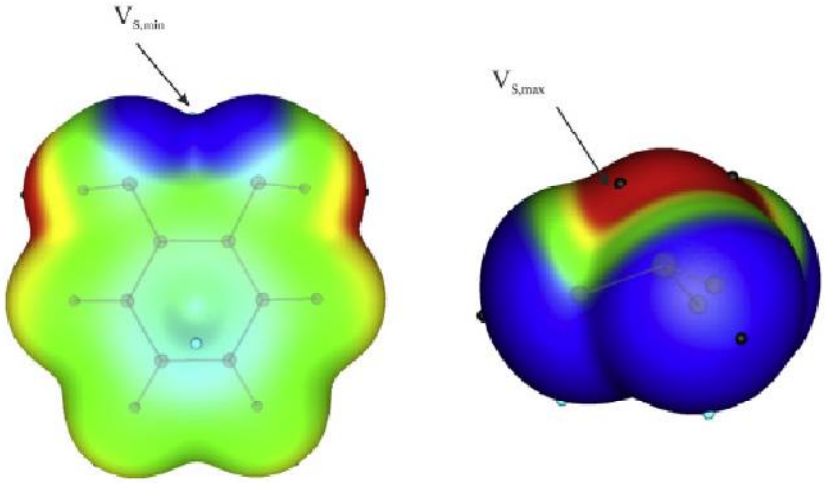
BAB bonded complexes



1. Z=Ar, X=H
2. Z=Ar, X=NH_2
3. Z=Ar, X=OH
4. Z=Ar, X=F
5. Z=Ar, X=CN
6. Z=Kr, X=H
7. Z=Kr, X=NH_2
8. Z=Kr, X=OH
9. Z=Kr, X=F
10. Z=Kr, X=CN
11. Z=Xe, X=H
12. Z=Xe, X=NH_2
13. Z=Xe, X=OH
14. Z=Xe, X=F
15. Z=Xe, X=CN

MEP onto the van der Waals surface

DHB-H ArO3

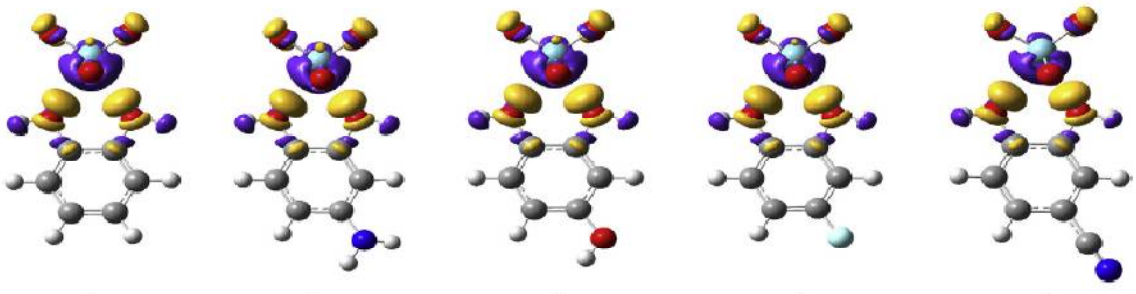


☞ red >28 ; blue < 4 ;

molecule	$V_{S,min}$	$V_{S,max}$
ArO_3	-	47.1
KrO_3	-	54.7
XeO_3	-	61.8
DHB-H	-39.7	-
DHB-CN	-29.4	-
DHB-F	-36.5	-
DHB-OH	-40.2	-
DHB-NH_2	-42.4	-

☞ VS,max and VS,min values in table are in kcal/mol

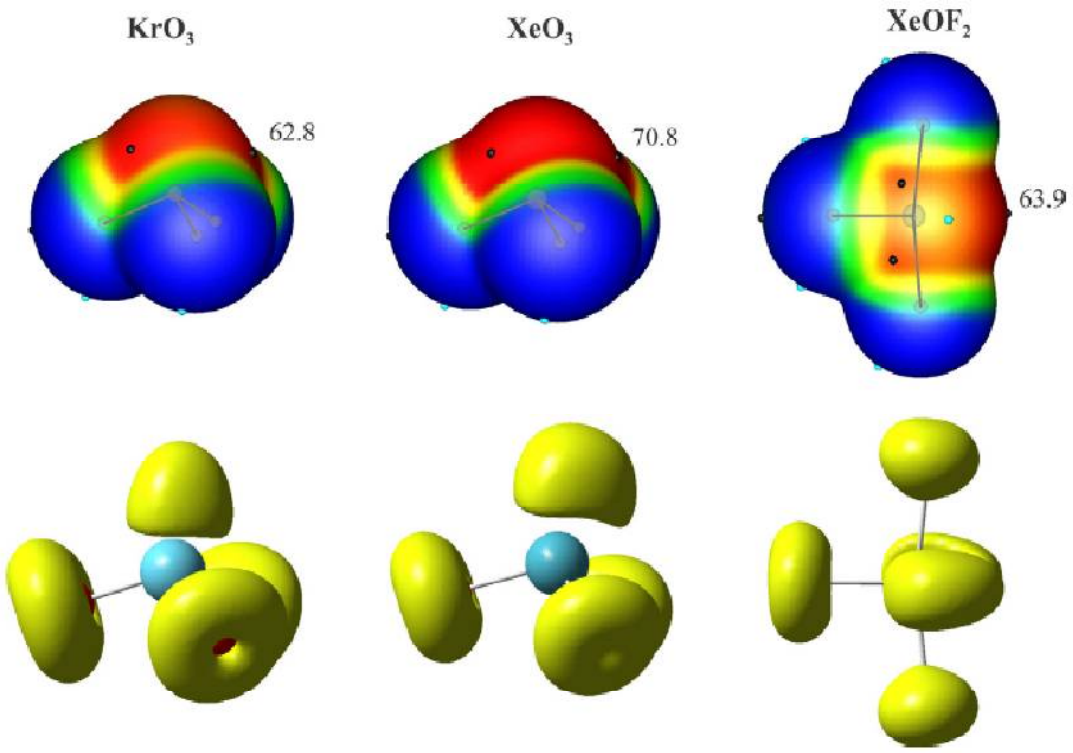
Electron density shift isosurfaces



☞ Violet and yellow colors: regions of decreased and increased electron densities

ESP : red > 40;; blue < 0

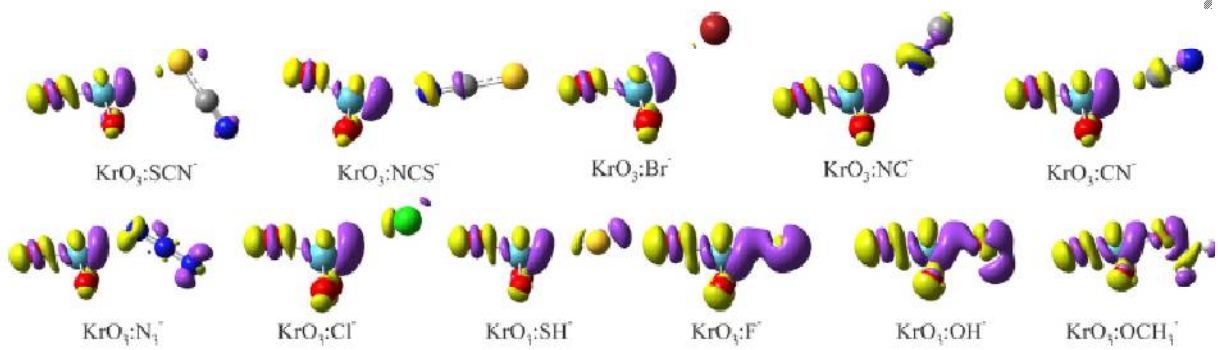
ELF (0.75 au) isosurfaces



- aug-cc-pVTZ-PP basis set for Xe
- All-electron aug-ccpVTZ for all other atoms
- Theory level: MP2
- Black circles: σ-holes at Z (Kr, Xe) associated with the Z-O bond

Electron density difference plots (±0.004 au)

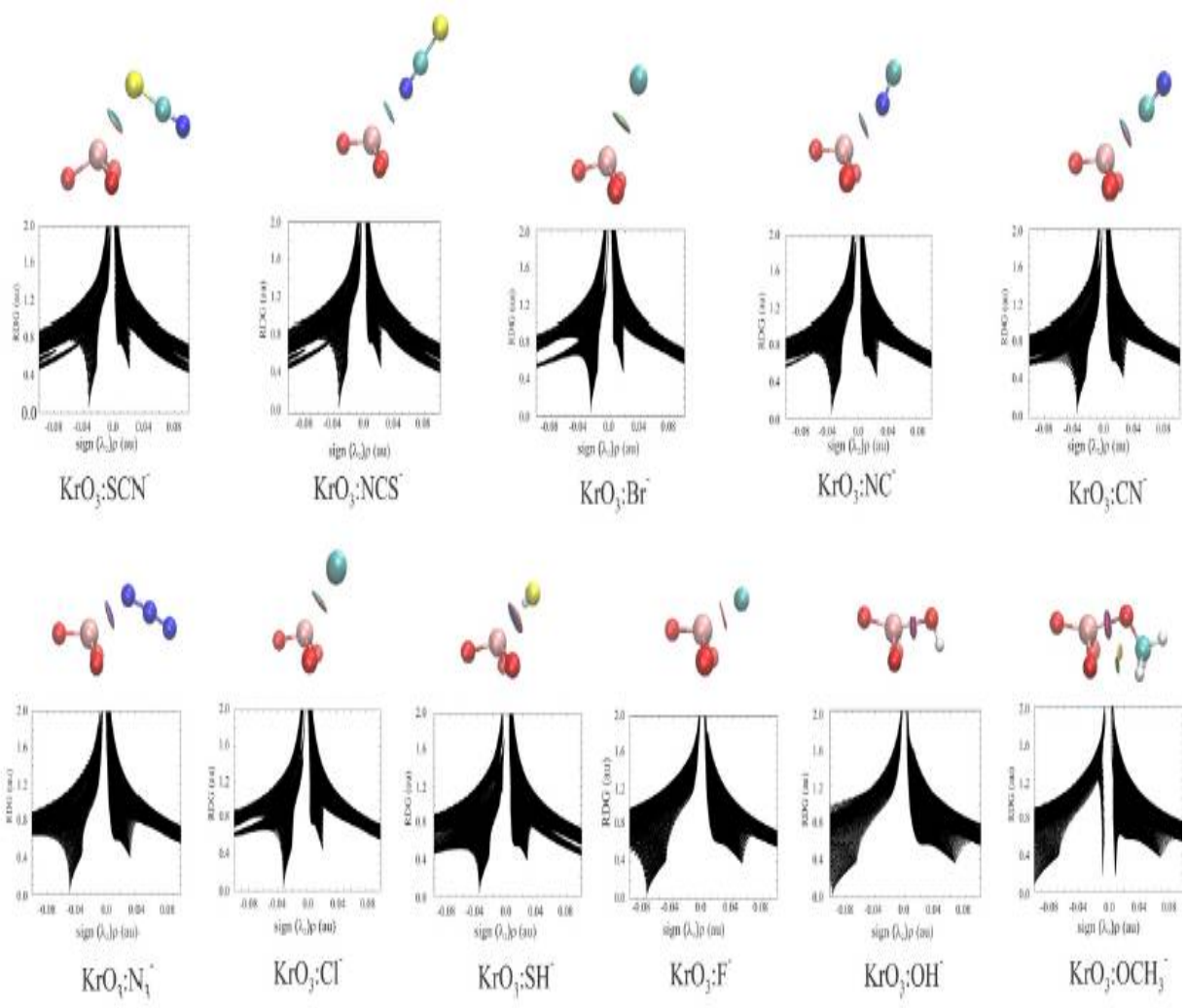
KrO3:X⁻ complexes



- **Electron densities -- Violet: decreased; yellow: increased**

Non-covalent interaction (NCI) isosurface

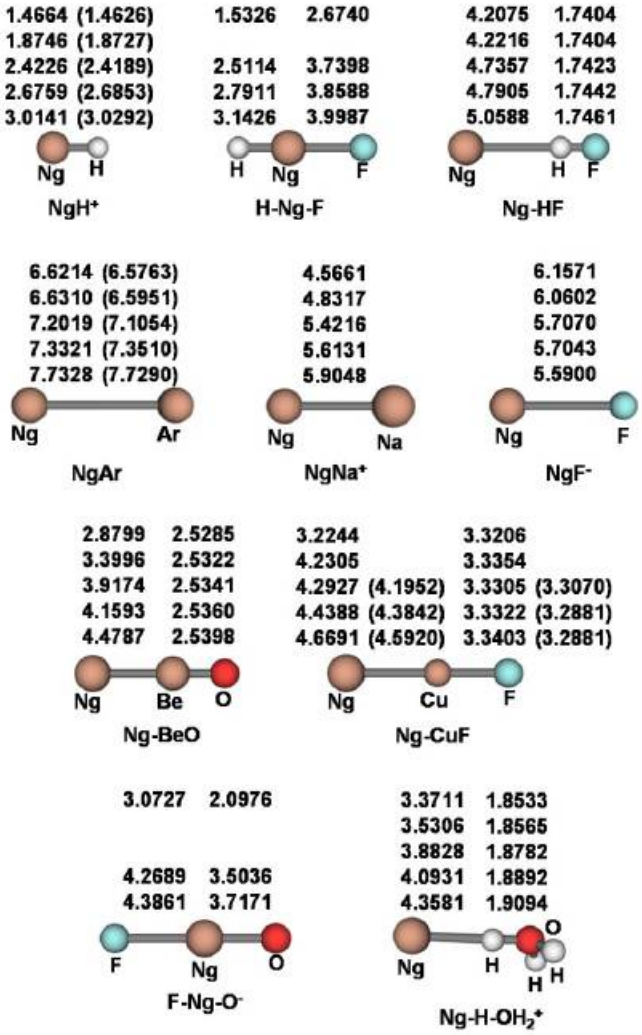
Reduced density gradient (RDG) versus sign (λ2)ρ



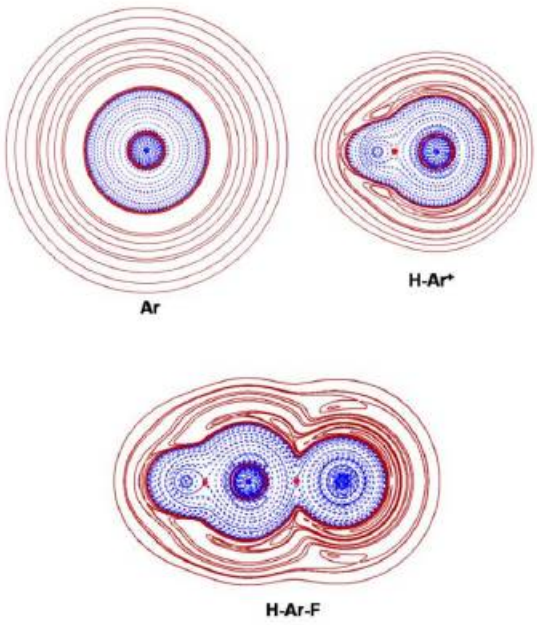
Aerogen Bond [He, Ne, Ar, Kr, Xe]	NgBC47reference set	NgB.	SD.	41

Bond distances

Ng = He, Ne, Ar, Kr, Xe

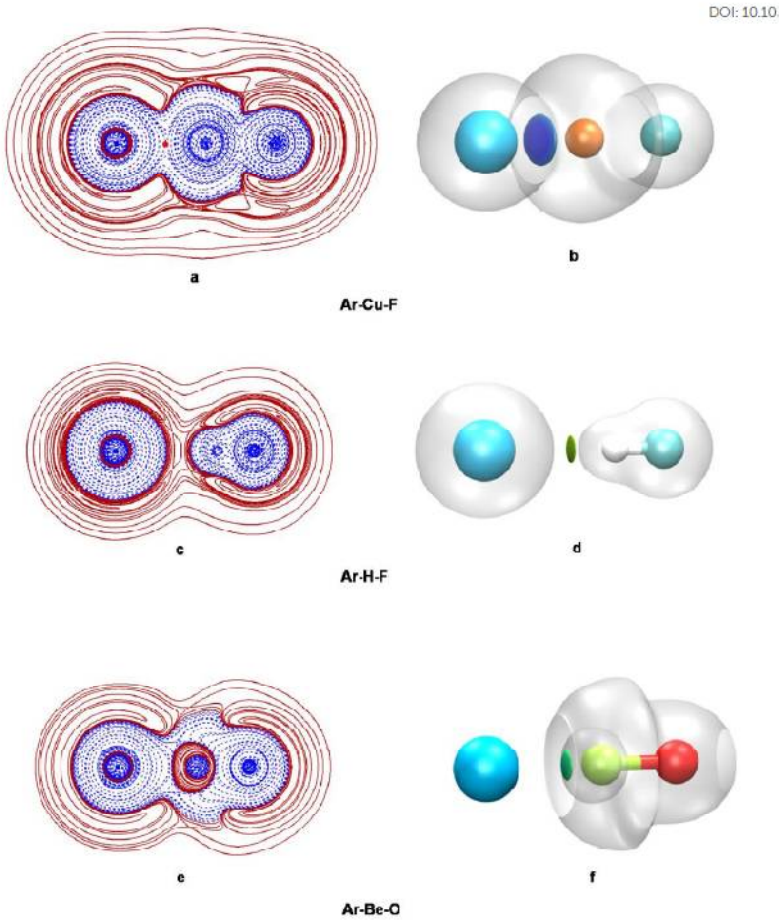

1.4664 (1.4626)
1.8746 (1.8727)
2.4226 (2.4189)
2.6759 (2.6853)
3.0141 (3.0292)
Ng H
NgH+
1.5326 2.6740
2.5114 3.7398
2.7911 3.8588
3.1426 3.9987
H Ng F
H-Ng-F
4.2075 1.7404
4.2216 1.7404
4.7357 1.7423
4.7905 1.7442
5.0588 1.7461
Ng H F
Ng-HF
6.6214 (6.5763)
6.6310 (6.5951)
7.2019 (7.1054)
7.3321 (7.3510)
7.7328 (7.7290)
Ng Ar
NgAr
4.5661
4.8317
5.4216
5.6131
5.9048
Ng Na
NgNa+
6.1571
6.0602
5.7070
5.7043
5.5900
Ng F
NgF-
2.8799 2.5285
3.3996 2.5322
3.9174 2.5341
4.1593 2.5360
4.4787 2.5398
Ng Be O
Ng-BeO
3.2244 3.3206
4.2305 3.3354
4.2927 (4.1952) 3.3305 (3.3070)
4.4388 (4.3842) 3.3322 (3.2881)
4.6691 (4.5920) 3.3403 (3.2881)
Ng Cu F
Ng-CuF
3.0727 2.0976
4.2689 3.5036
4.3861 3.7171
F Ng O
F-Ng-O-
3.3711 1.8533
3.5306 1.8565
3.8828 1.8782
4.0931 1.8892
4.3581 1.9094
Ng H O H H
Ng-H-OH2+

H(r) plot

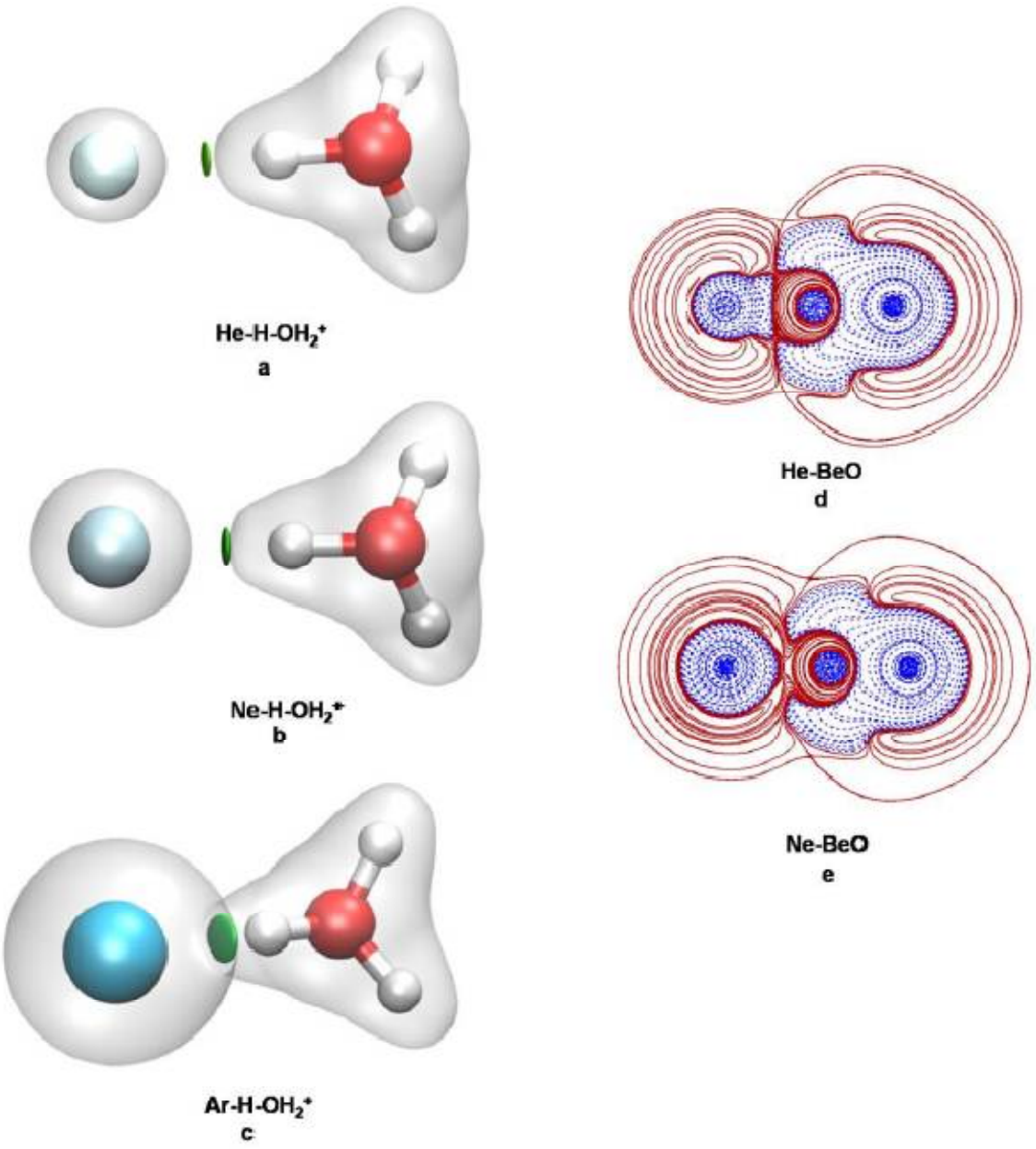

Ar
H-Ar+
H-Ar-F

- Red dots: HCPs
- Solid/brown and dashed/blue lines : Positive and negative values

Plots of H(r) and s(r)

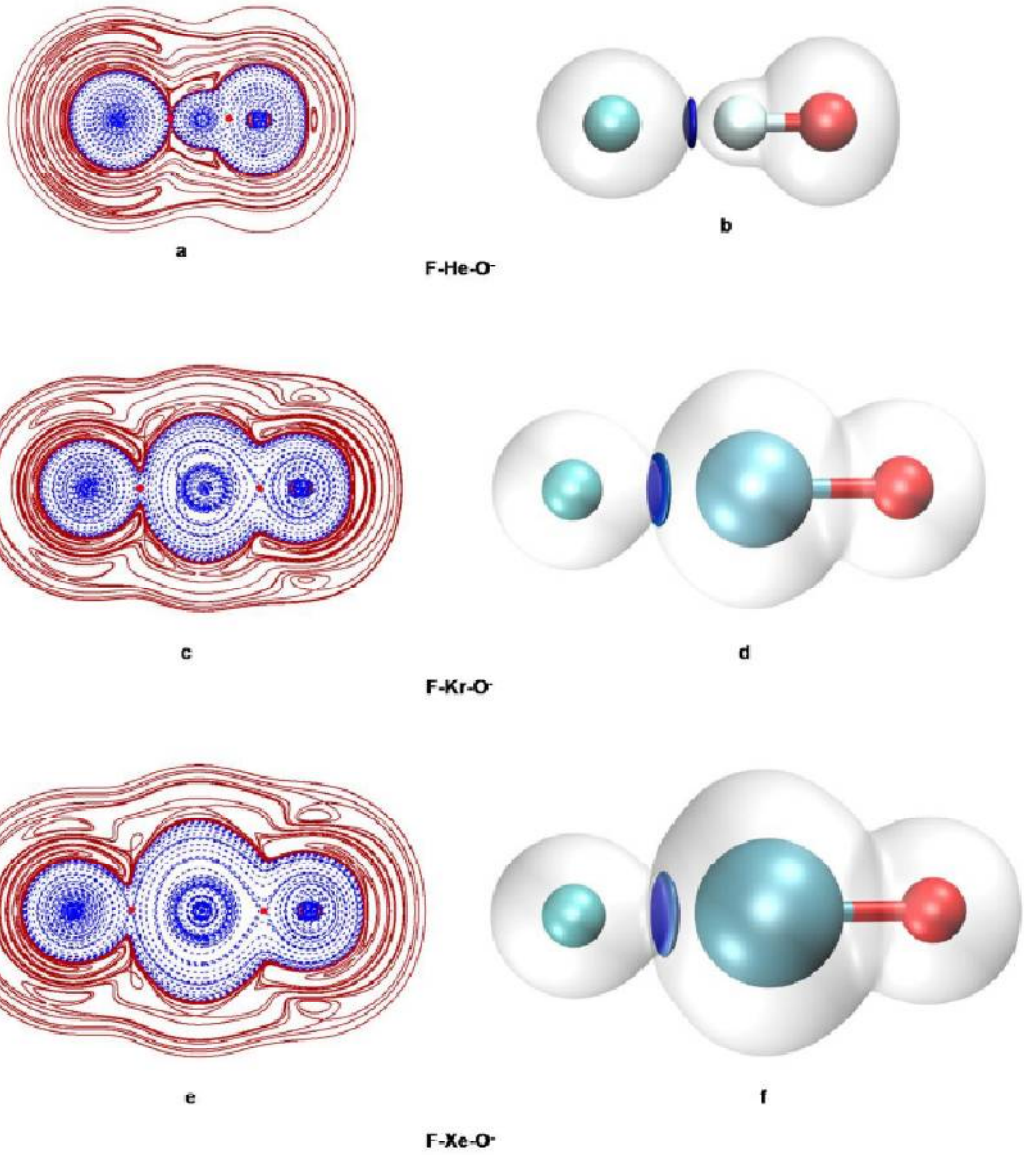


Plots of 3D- H(r) and Iso-surface of s(r)



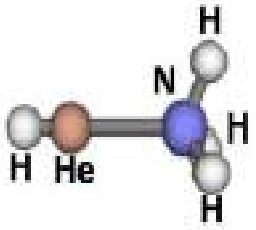
☞ (a, b, c): 3D-plots of the H(r) =0 ; s(r) = 0.4 isosurfaces for Ng-H-OH2+ (Ng = He, Ne, Ar).
☞ (d, e) : 2D plots H(r) of He-BeO and Ne-BeO

Plots of 2D-and 2D- H(r) and Iso-surface of s(r)



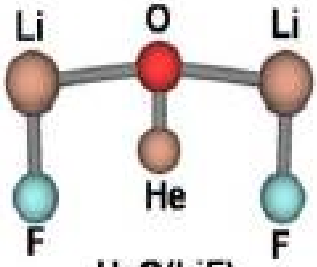
- (a, c, e): 2D-plots of H(r) in planes containing nuclei
  - solid/brown and dashed/blue lines : positive and negative values
  - Red dots : HCP
- (b, d, f): 3Dplots of the H(r) = 0

Connectivities

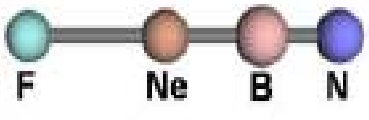


$HHeNH_3^+$

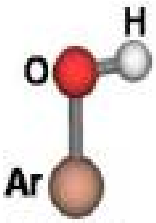
$HeBO^+$



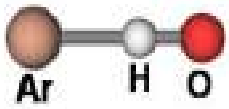
$HeO(LiF)_2$



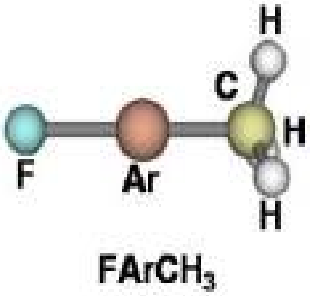
$FNeBN^-$



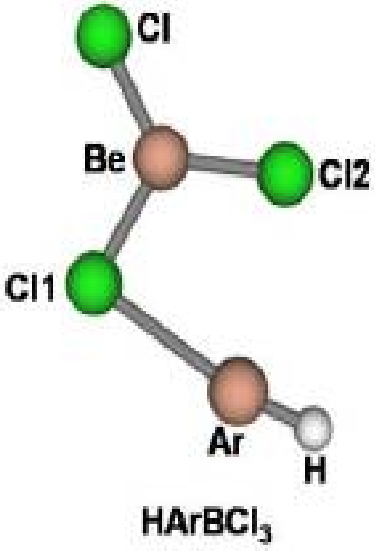
$ArOH^+$
$(^1A')$



$ArHO^+$
$(^3\Sigma^-)$

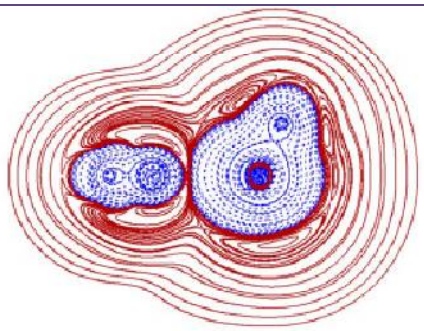


$FArCH_3$



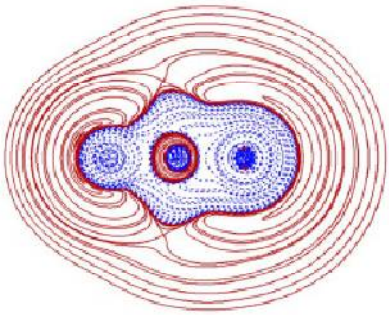
$HArBCl_3$

Plots of 2D- and 2D- H(r) and Iso-surface of s(r)



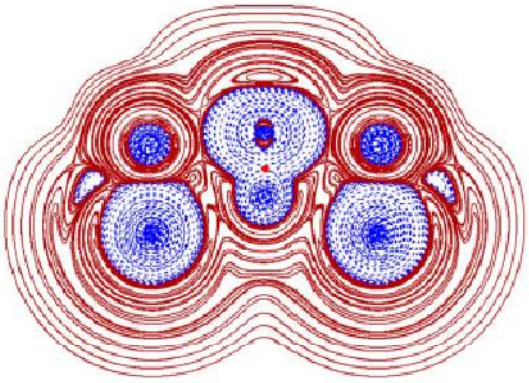
H-He-NH_3^+

a

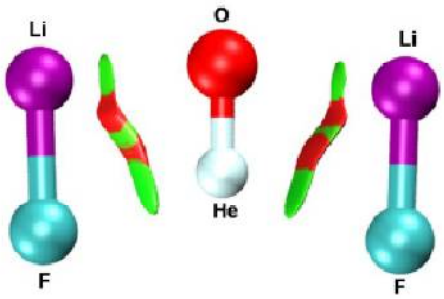


He-B-O$^+$

b

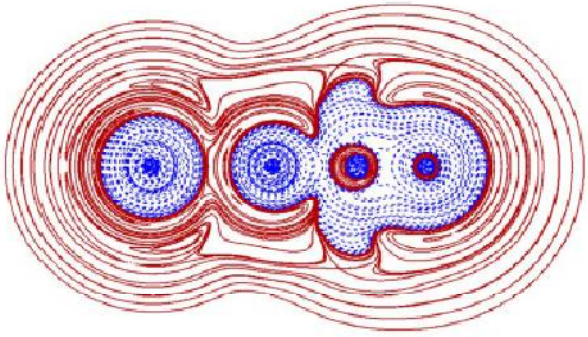


c



d

$HeO(LiF)_2$

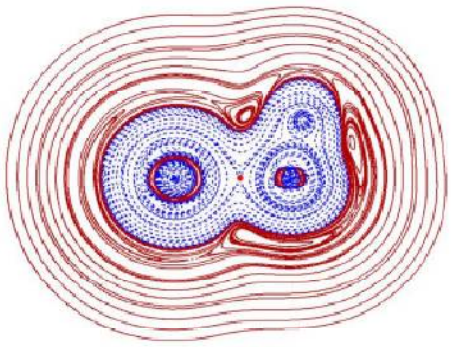


F-Ne-B-N$^-$

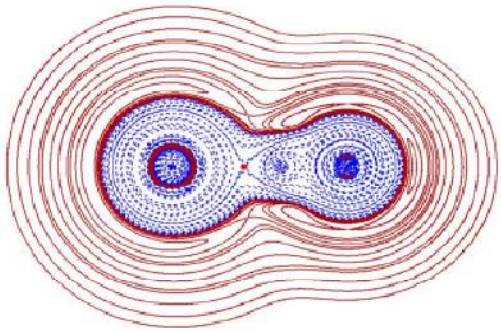
e

☞ 2D-plots of H(r) ☞ Symmetry planes of HHeNH3 +, HeBO+; HeO(LiF)2, and FNeBN-	a, b, c, e
☞ Red dot : HCP	c
☞ 3D-plot of the s(r)= 0.4 isosurface of HeO(LiF)2	d .

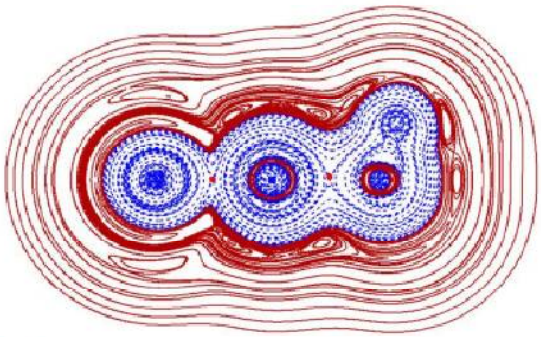
Plots of 2D- H(r)



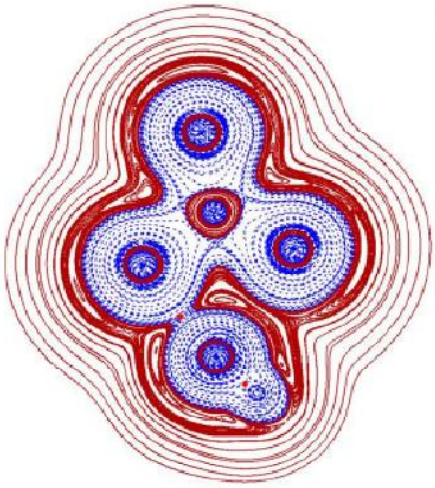
Ar-O-H⁺ (¹A')
a



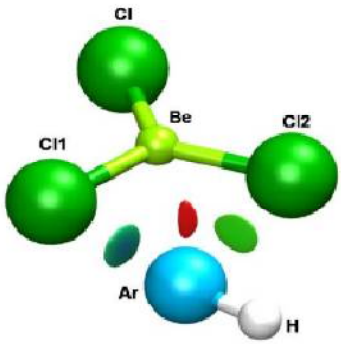
Ar-H-O⁺ (³Σ⁻)
b



F-Ar-CH_3
c



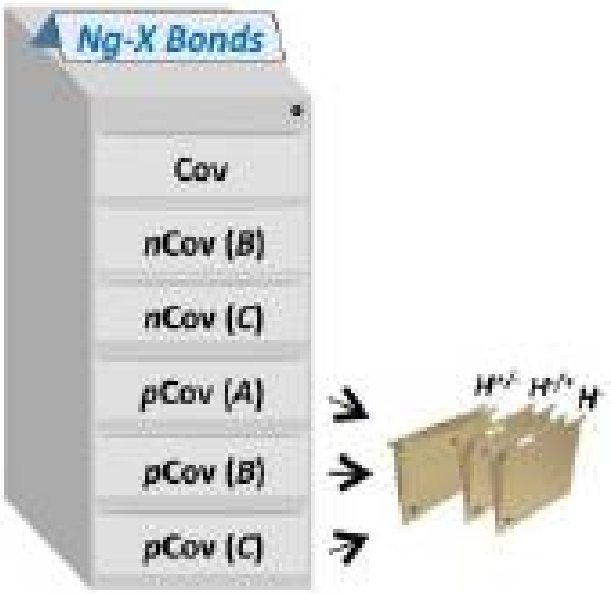
d



e

H-Ar-$BeCl_3$

☞ 2D-plots of H(r) ☞ Symmetry planes of ArOH+ (1A' and 3Σ-), FArCH3, HArBeCl3	a-d
☞ Red dot : HCP ☞ solid/brown lines : positive ☞ dashed/blue : negative values	
☞ 3D-plot of the s(r) = 0.3 isosurfaces of HArBeCl3.	e



If	Hs negative (H-), or range from negative to positive, being on the average positive (H+/-) or negative (H-/+).
Then	pCov

Ng-X bonds classification	Probe
☞ Covalent (Cov) ☞ Partially-covalent (pcov) ☞ Non-covalent (nCov)	▪ H(r) plot ▪ Values Hs that the H(r) takes over the volume enclosed by the s(r) = 0.4 isosurface at around the AIM BCP

	Plotted $H(r)$	H_s	Examples[a]
Cov	*A*, with ρ(BCP) > 0.08		Ng-H^+, H-Ng-F, H-HeNH_3^+, He-O(LiF)$_2$, Ar-OH^+, F-Ar-CH_3
*p*Cov	*A*, with ρ(BCP) ≤ 0.08	$H^{+/-}$, $H^{-/+}$, or *H*	F-NgO$^-$ ($H^{+/-}$) (Ng = He, Kr, Xe), Ng-HOH_2^+ (Ng = Ar-Xe) (*H*), Ng-CuF (*H*) (Ng = He, Ar-X
	B	$H^{+/-}$, $H^{-/+}$, or *H*	Ar-BeO ($H^{+/-}$), Kr-BeO ($H^{-/+}$), Xe-BeO ($H^{-/+}$)
	C	$H^{+/-}$, $H^{-/+}$, or *H*	Ne-HOH_2^+ ($H^{+/-}$), F-ArO$^-$ ($H^{+/-}$)
*n*Cov	*C*	positive	Ng-*L* (*L* = Ar, HF, F$^-$, Na$^+$), He-HOH_2^+, He-BeO, Ne-BeO, Ne-CuF
	B	positive	less common

[a] The assigned bonds are dotted.