The Coulombic σ-hole model describes bonding in $CX_3I\ldots Y^-$ complexes completely

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Electronic Supplementary Information

Table of Contents

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1. Figure S1

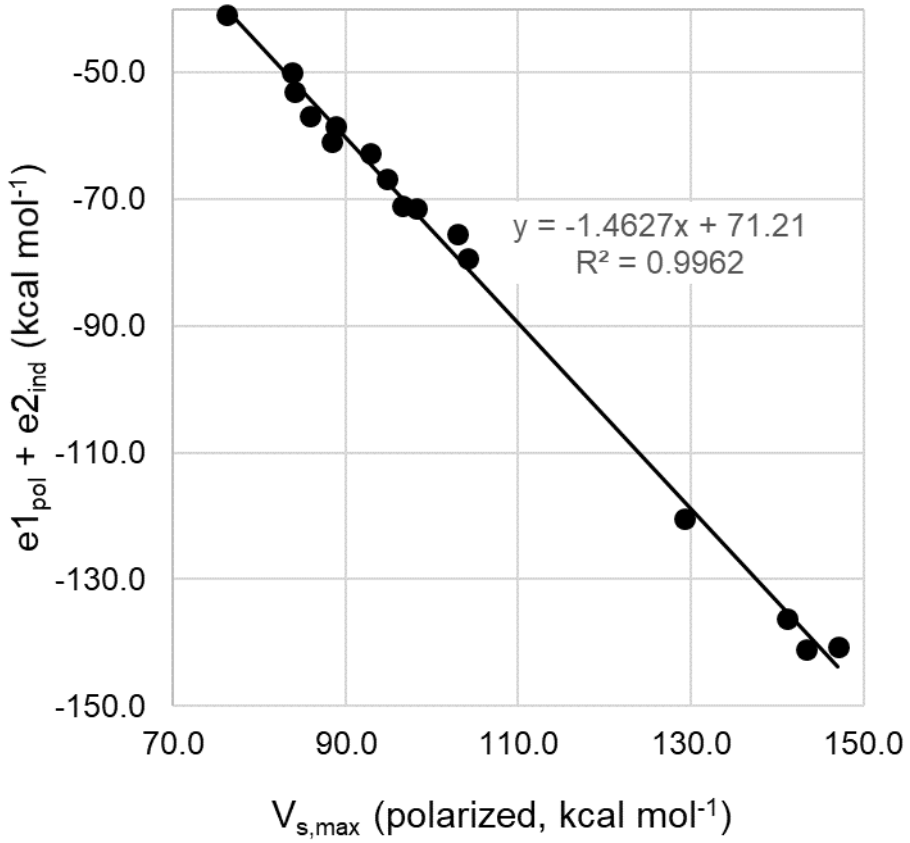

Figure S1: Correlation between the Coulombic interaction energy ($e1_{pol} + e2_{ind}$) from DFT-SAPT calculations and $V_{S,max}$ from the point-charge polarized CCSD/aug-cc-pVTZ calculations. The regression equation and R^2 are shown.

2. Geometries and energies

2.1 CF_3I complexes

$F_3CI…F^-$

Counterpoise corrected energy = -731.926169423256
BSSE energy = 0.002841711330
sum of fragments = -731.857060940152
complexation energy = -45.15 kcal/mole (raw)
complexation energy = -43.37 kcal/mole (corrected)

mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

F3CI…F-, C3V

-1,1
I,0,0.,0.,0.
C,0,0.,0.,2.185747
F,0,1.247729,0.,2.734158
F,0,-0.623865,1.080565,2.734158
F,0,-0.623865,-1.080565,2.734158
F,0,0.,0.,-2.216503

HF=-99.4508069
MP2=-99.7458784

$F_3CI…Cl^-$

Counterpoise corrected energy = -1091.935186271393
BSSE energy = 0.002144093741
sum of fragments = -1091.895175363120
complexation energy = -26.45 kcal/mole (raw)
complexation energy = -25.11 kcal/mole (corrected)

mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

F3CI…Cl-, C3V

-1,1
I,0,0.,0.,-0.078564
C,0,0.,0.,2.085402
F,0,1.246862,0.,2.614852
F,0,-0.623431,1.079814,2.614852
F,0,-0.623431,-1.079814,2.614852
Cl,0,0.,0.,-2.907429

HF=-459.5734815
MP2=-459.7807919

$F_3CI…Br^-$

Counterpoise corrected energy = -3204.924800106302
BSSE energy = 0.003357474259
sum of fragments = -3204.889640069748
complexation energy = -24.17 kcal/mole (raw)
complexation energy = -22.06 kcal/mole (corrected)

mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

F3CI Br-, C3V
-1,1
I,0,0.,0.,0.15951
C,0,0.,0.,2.323226
F,0,0.,1.247063,2.848255
F,0,-1.079988,-0.623531,2.848255
F,0,1.079988,-0.623531,2.848255
Br,0,0.,0.,-2.837037

HF=-2572.5336777
MP2=-2572.7748313

F_3ClI^-

Counterpoise corrected energy = -927.111214668397
BSSE energy = 0.003509170372
sum of fragments = -927.080985685503
complexation energy = -21.17 kcal/mole (raw)
complexation energy = -18.97 kcal/mole (corrected)

mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

F3CI…I-, C3V

-1,1
I,0,0.,0.,0.
C,0,0.,0.,2.166122
F,0,1.246638,0.,2.686734
F,0,-0.623319,1.07962,2.686734
F,0,-0.623319,-1.07962,2.686734
I,0,0.,0.,-3.228595

HF=-294.7464575
MP2=-294.9658305

2.2 CCl_3I complexes

$Cl_3CI…F^-$

Counterpoise corrected energy	=	-1811.849479362937
BSSE energy	=	0.003289214624
sum of fragments	=	-1811.773570051289
complexation energy	=	-49.70 kcal/mole (raw)
complexation energy	=	-47.63 kcal/mole (corrected)

mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

Cl3CI---F-, C3V

-1,1
I,0,0.,0.,0.
C,0,0.,0.,2.232236
Cl,0,1.667659,0.,2.899362
Cl,0,-0.83383,1.444235,2.899362
Cl,0,-0.83383,-1.444235,2.899362
F,0,0.,0.,-2.158245

HF=-99.4508069
MP2=-99.7458784

$Cl_3CI…Cl^-$

Counterpoise corrected energy	=	-2171.856497132947
BSSE energy	=	0.002433451659
sum of fragments	=	-2171.810196421032
complexation energy	=	-30.58 kcal/mole (raw)
complexation energy	=	-29.05 kcal/mole (corrected)

#mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

Cl3CI…Cl-, C3V

-1,1
I,0,-0.000251,-0.000085,-0.150138
C,0,0.000205,-0.000005,2.068235
Cl,0,1.667669,-0.000464,2.717639
Cl,0,-0.832902,1.444269,2.71798
Cl,0,-0.8338,-1.443695,2.718093
Cl,0,-0.000921,-0.000019,-2.869609

HF=-459.5734815
MP2=-459.7807919

$Cl_3CI…Br^-$

Counterpoise corrected energy	=	-4284.845938239818
BSSE energy	=	0.003870694964
sum of fragments	=	-4284.804295032996
complexation energy	=	-28.56 kcal/mole (raw)
complexation energy	=	-26.13 kcal/mole (corrected)

mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

Cl3CI…Br-, C3V

-1,1
I,0,0.000289,-0.000055,-0.12472
C,0,-0.000053,-0.000008,2.098058
Cl,0,1.667301,-0.000157,2.743277
Cl,0,-0.833765,1.444173,2.742756
Cl,0,-0.834071,-1.443988,2.742815
Br,0,0.0003,0.000035,-2.999986

HF=-2572.5336777
MP2=-2572.7748313

$Cl_3CI…I^-$

Counterpoise corrected energy	=	-2007.032559072591
BSSE energy	=	0.004147912638
sum of fragments	=	-2006.995035188089
complexation energy	=	-26.15 kcal/mole (raw)
complexation energy	=	-23.55 kcal/mole (corrected)

#mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel
Cl3CI…I-, C3V
-1,1
I,0,0.,0.,0.
C,0,0.,0.,2.235684
Cl,0,1.667991,0.,2.87391
Cl,0,-0.833996,1.444523,2.87391
Cl,0,-0.833996,-1.444523,2.87391
I,0,0.,0.,-3.082181

HF=-294.7464575
MP2=-294.9658305

2.3 CBr_3I complexes

$Br_3CI\cdots F^-$

Counterpoise corrected energy = -8150.806199131169
BSSE energy = 0.003676257050
sum of fragments = -8150.728184459239
complexation energy = -51.26 kcal/mole (raw)
complexation energy = -48.95 kcal/mole (corrected)

mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

Br3CI…F-, C3V

-1,1
I,0,0.,0.,0.
C,0,0.,0.,2.237354
Br,0,1.81749,0.,2.956915
Br,0,-0.908745,1.573993,2.956915
Br,0,-0.908745,-1.573993,2.956915
F,0,0.,0.,-2.144422

HF=-99.4508069
MP2=-99.7458784

$Br_3CI\cdots Cl^-$

Counterpoise corrected energy = -8510.812837961297
BSSE energy = 0.002817390696
sum of fragments = -8510.764459627151
complexation energy = -32.13 kcal/mole (raw)
complexation energy = -30.36 kcal/mole (corrected)

mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

Br3CI…Cl-, C3V

-1,1
I,0,-0.000039,0.000044,-0.160999
C,0,0.000055,0.000006,2.064796
Br,0,1.81771,0.000301,2.767755
Br,0,-0.909012,1.573953,2.767869
Br,0,-0.908462,-1.574274,2.767807
Cl,0,-0.000252,-0.00003,-2.854718

HF=-459.5734815
MP2=-459.7807919

$Br_3CI\cdots Br^-$

Counterpoise corrected energy = -10623.802288398010

BSSE energy	=	0.004359606079
sum of fragments	=	-10623.758456775530
complexation energy	=	-30.24 kcal/mole (raw)
complexation energy	=	-27.50 kcal/mole (corrected)

#mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

Br3CI…Br-, C3V
-1,1
I,0,-0.000056,-0.000028,-0.13662
C,0,-0.000014,-0.000006,2.09442
Br,0,1.817954,-0.000392,2.792798
Br,0,-0.908663,1.57463,2.792754
Br,0,-0.909357,-1.574231,2.792767
Br,0,0.000134,0.000026,-2.98361

HF=-2572.5336777
MP2=-2572.7748313

$Br_3CI…I^-$

Counterpoise corrected energy	=	-8345.989068957093
BSSE energy	=	0.004688856734
sum of fragments	=	-8345.948958216213
complexation energy	=	-28.11 kcal/mole (raw)
complexation energy	=	-25.17 kcal/mole (corrected)

#mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

Br3CI…I-, C3V

-1,1
I,0,0.,0.,0.
C,0,0.,0.,2.246664
Br,0,1.818967,0.,2.938601
Br,0,-0.909484,1.575272,2.938601
Br,0,-0.909484,-1.575272,2.938601
I,0,0.,0.,-3.048346

HF=-294.7464575
MP2=-294.9658305

2.1 Cl_4 complexes

I_3ClF^-

Counterpoise corrected energy = -1317.356488383735
BSSE energy = 0.003731617322
sum of fragments = -1317.277117952241
complexation energy = -52.15 kcal/mole (raw)
complexation energy = -49.81 kcal/mole (corrected)

mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

I3Cl…F-, C3V
-1,1
I,0,0.,0.,0.
C,0,0.,0.,2.251589
I,0,2.023733,0.,3.033946
I,0,-1.011866,1.752604,3.033946
I,0,-1.011866,-1.752604,3.033946
F,0,0.,0.,-2.129774

HF=-99.4508069
MP2=-99.7458784

I_3ClCl^-

Counterpoise corrected energy = -1677.363047706493
BSSE energy = 0.002841002609
sum of fragments = -1677.312959857242
complexation energy = -33.21 kcal/mole (raw)
complexation energy = -31.43 kcal/mole (corrected)

#mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

I3Cl…Cl-, C3V
-1,1
I,0,0.001355,0.000171,-0.172746
C,0,-0.000365,0.000002,2.070345
I,0,2.025178,0.002179,2.837975
I,0,-1.012069,-1.755895,2.835401
I,0,-1.016033,1.753502,2.835677
Cl,0,0.001935,0.000042,-2.83938

HF=-459.5734815
MP2=-459.7807919

I_3ClBr^-

Counterpoise corrected energy = -3790.352650538836

BSSE energy = 0.004462479319
sum of fragments = -3790.306830654295
complexation energy = -31.55 kcal/mole (raw)
complexation energy = -28.75 kcal/mole (corrected)

#mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

I3Cl…Br-, C3V

-1,1
I,0,0.,0.000037,-0.150042
C,0,-0.000102,0.000003,2.099621
I,0,2.02652,0.000391,2.861414
I,0,-1.013151,-1.75541,2.861125
I,0,-1.013887,1.754983,2.861117
Br,0,0.000619,-0.000003,-2.965963

HF=-2572.5336777
MP2=-2572.7748313

$I_3Cl…Br^-$

Counterpoise corrected energy = -1512.539870026951
BSSE energy = 0.004835289040
sum of fragments = -1512.497037760089
complexation energy = -29.91 kcal/mole (raw)
complexation energy = -26.88 kcal/mole (corrected)

mp2/aug-cc-pvtz counterpoise=2 extrabasis pseudo=read guess=huckel

I3Cl…I-, C3V

-1,1
I,0,0.,0.,0.
C,0,0.,0.,2.269196
I,0,2.029159,0.,3.02386
I,0,-1.01458,1.757304,3.02386
I,0,-1.01458,-1.757304,3.02386
I,0,0.,0.,-3.01048

HF=-294.7464575
MP2=-294.9658305