Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

3c/4e σ̂-Type Long-Bonding Competes with ω-Bonding in Noble-Gas Hydrides HNgY (Ng= He, Ne, Ar, Kr, Xe, Rn; Y= F, Cl, Br, I): NBO/NRT Perspective

Table S1. The NRT weightings of three resonance structures（ω_I, ω_{II}, ω_{III} for RSI, RSII, RSIII , respectively, %） and the second-order perturbation stabilization energies ($\Delta E^{(2)}_{D\rightarrow A}$ kcal/mol) for HArF with different basis sets.

basis set	ω_I	ω_{II}	ω_{III}	$\Delta E^{(2)}_{nY\rightarrow\sigma^*HNg}$	$\Delta E^{(2)}_{nH\rightarrow\sigma^*NgY}$	$\Delta E^{(2)}_{nNg\rightarrow\ \delta^*HY}$
6-311++G**	65.06	5.64	29.29	41.46	676.97	362.83
aug-cc-pVDZ	66.37	4.87	28.76	35.11	564.24	354.09
aug-cc-pVTZ	67.10	5.18	27.72	39.76	679.97	362.97
aug-cc-pVQZ	67.48	6.45	26.07	37.71	695.79	370.84

Table S2. NPA charge (Q) of the HNgY species calculated at B3LYP/aug-cc-pVTZ(-pp) level of theory

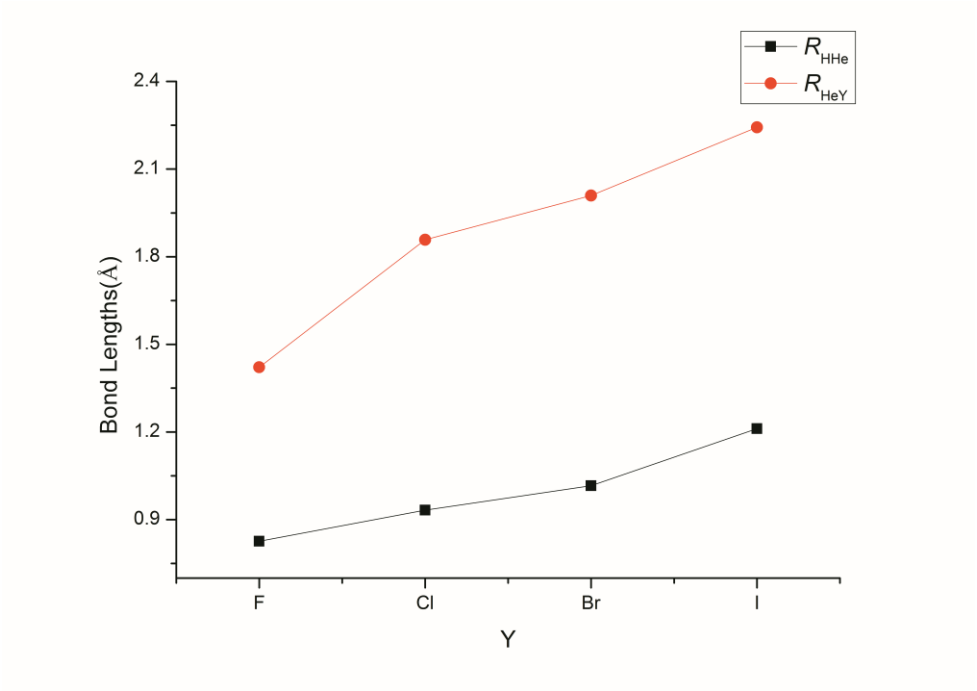
Species	Q(H)	Q(Ng)	Q(Y)
HHeF	0.322	0.328	-0.651
HHeCl	0.261	0.231	-0.492
HHeBr	0.207	0.190	-0.397
HHeI	0.109	0.127	-0.235
HNeF	0.403	0.178	-0.581
HNrCl	0.242	0.098	-0.340
HNeBr	0.171	0.072	-0.243
HNeI	0.080	0.047	-0.126
HArF	0.202	0.510	-0.712
HArCl	0.185	0.413	-0.598
HArBr	0.162	0.375	-0.537
HArI	0.112	0.317	-0.429
HKrF	0.090	0.632	-0.723
HKrCl	0.090	0.523	-0.613
HKrBr	0.076	0.484	-0.5603
HKrI	0.047	0.429	-0.4763
HXeF	-0.034	0.781	-0.746
HXeCl	-0.023	0.658	-0.635
HXeBr	-0.029	0.617	-0.587
HXeI	-0.045	0.563	-0.518
HRnF	-0.081	0.843	-0.762
HRnCl	-0.068	0.720	-0.652
HRnBr	-0.073	0.678	-0.605
HRnI	-0.088	0.624	-5.536

Table S3. Covalent, electrovalent (Ionic), and total contributions to the bond orders (b_{HNg}, b_{NgY}, b_{HY}) of the HNgY species at the B3LYP/aug-cc-pVTZ(-pp) level of theory.

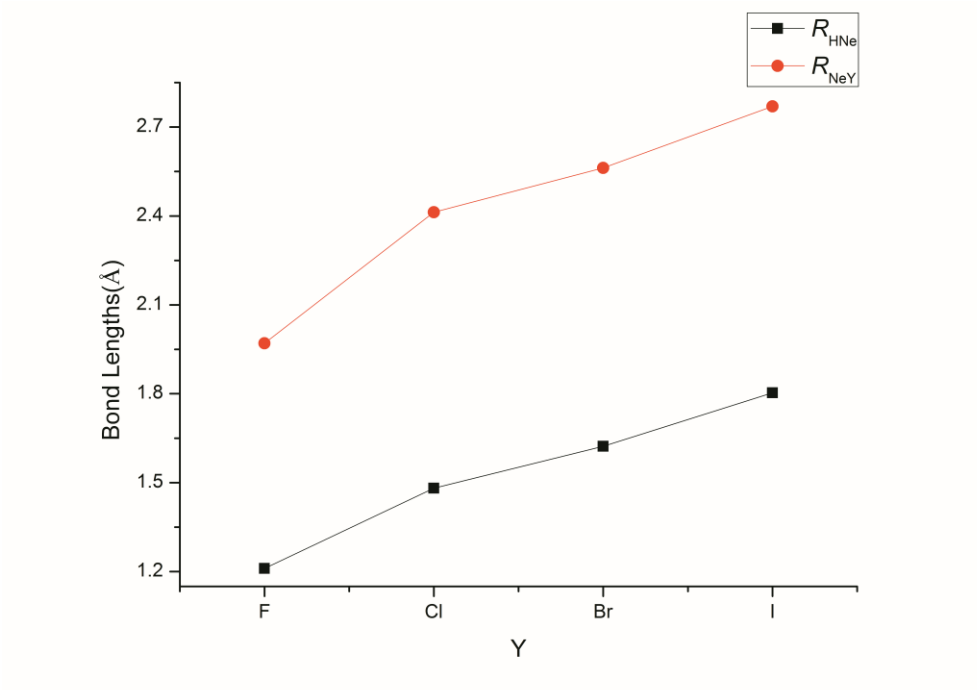
Species	b_{HNg}			b_{NgY}			b_{HY}			Sum
	Total	Covalent	Ionic	Total	Covalent	Ionic	Total	Covalent	Ionic	
HHeF	0.48	0.16	0.32	0.04	0.04	0.00	0.48	0.16	0.32	1.00
HHeCl	0.28	0.07	0.21	0.04	0.03	0.01	0.68	0.32	0.36	1.00
HHeBr	0.21	0.05	0.16	0.05	0.02	0.03	0.74	0.41	0.32	1.00
HHeI	0.12	0.02	0.10	0.06	0.01	0.05	0.82	0.59	0.23	1.00
HNeF	0.27	0.05	0.22	0.03	0.01	0.2	0.70	0.28	0.42	1.00
HNeCl	0.12	0.02	0.10	0.03	0.01	0.02	0.85	0.54	0.31	1.00
HNeBr	0.07	0.01	0.06	0.04	0.01	0.03	0.89	0.66	0.23	1.00
HNeI	0.04	0.00	0.04	0.03	0.0-	0.03	0.93	0.80	0.13	1.00
HArF	0.67	0.34	0.33	0.05	0.03	0.02	0.28	0.08	0.20	1.00
HArCl	0.56	0.23	0.33	0.06	0.05	0.01	0.38	0.15	0.23	1.00
HArBr	0.45	0.18	0.29	0.06	0.06	0.00	0.49	0.21	0.28	1.00
HArI	0.36	0.13	0.23	0.07	0.05	0.02	0.56	0.30	0.26	1.00
HKrF	0.71	0.44	0.27	0.08	0.04	0.04	0.21	0.06	0.15	1.00
HKrCl	0.60	0.31	0.29	0.08	0.06	0.02	0.32	0.13	0.19	1.00
HKrBr	0.51	0.26	0.25	0.08	0.07	0.01	0.41	0.17	0.24	1.00
HKrI	0.44	0.20	0.24	0.09	0.09	0.00	0.47	0.23	0.24	1.00
HXeF	0.74	0.56	0.18	0.11	0.04	0.07	0.15	0.04	0.11	1.00
HXeCl	0.65	0.41	0.24	0.09	0.06	0.03	0.26	0.10	0.16	1.00
HXeBr	0.58	0.36	0.22	0.16	0.08	0.08	0.26	0.12	0.14	1.00
HXeI	0.50	0.29	0.21	0.14	0.10	0.04	0.36	0.17	0.19	1.00
HRnF	0.75	0.60	0.15	0.12	0.04	0.08	0.13	0.04	0.09	1.00
HRnCl	0.65	0.44	0.21	0.14	0.07	0.07	0.21	0.08	0.13	1.00
HRnBr	0.57	0.38	0.19	0.15	0.08	0.07	0.28	0.11	0.17	1.00
HRnI	0.52	0.32	0.20	0.16	0.10	0.06	0.32	0.15	0.17	1.00

Figure S1. Trends in bond lengths (R_{HNg} and R_{NgY}, Å) in the HHeY (a), HNeY (b), HArY (c), HKrY (d), HRnY (e), Y= F, Cl, Br, I species.

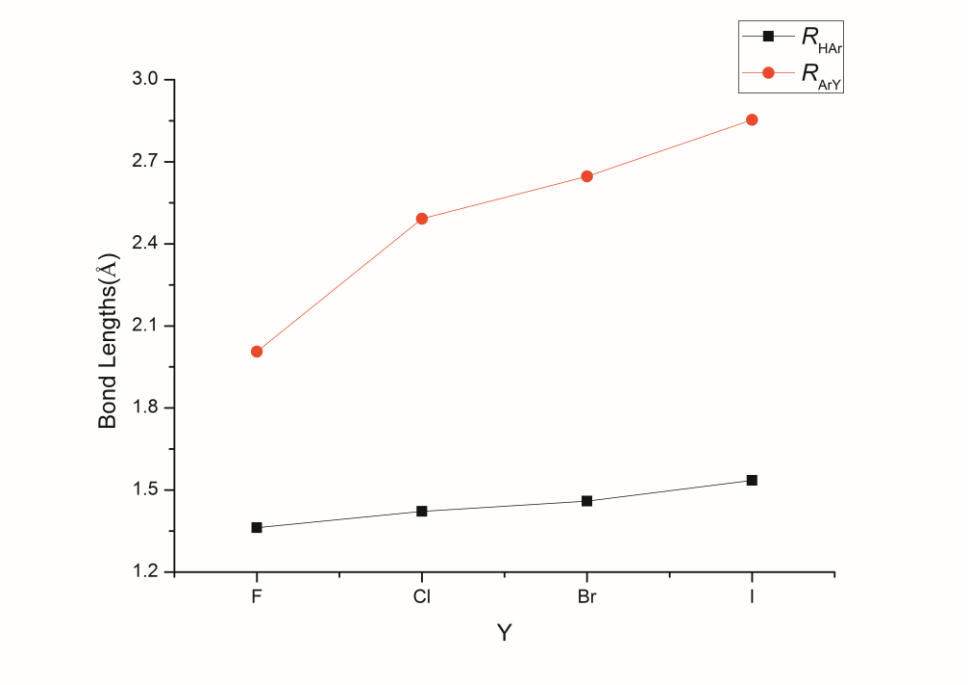
(a)HHeY



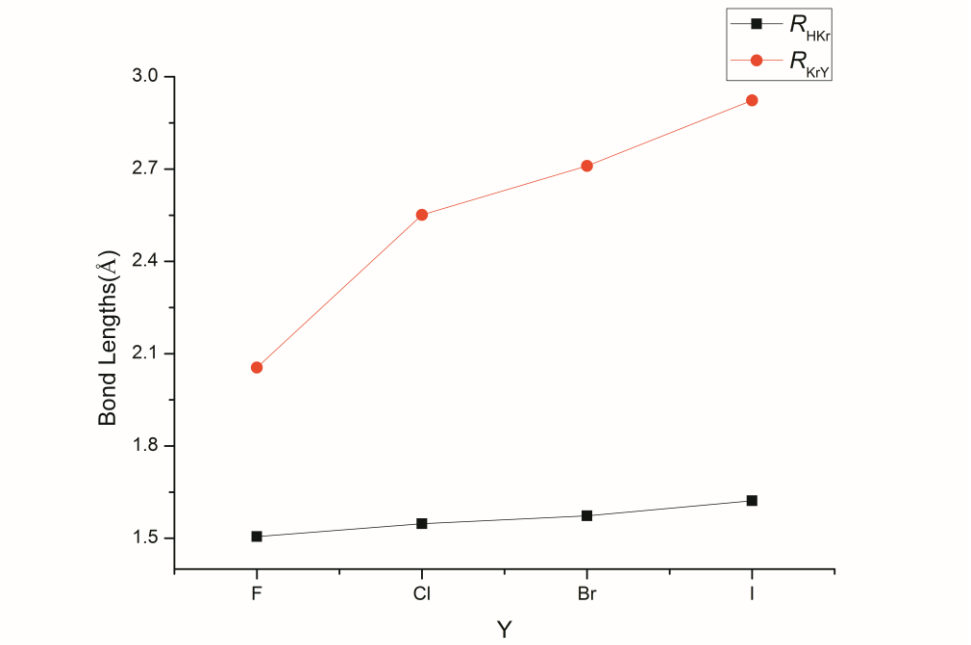
(b)HNeY



(c)HArY


R_{HAr}
R_{ArY}
3.0
2.7
2.4
2.1
1.8
1.5
1.2
Bond Lengths(Å)
F
Cl
Br
I
Y

(d)HKrY


R_{HKr}
R_{KrY}
3.0
2.7
2.4
2.1
1.8
1.5
Bond Lengths(Å)
F
Cl
Br
I
Y

(e)HRnY

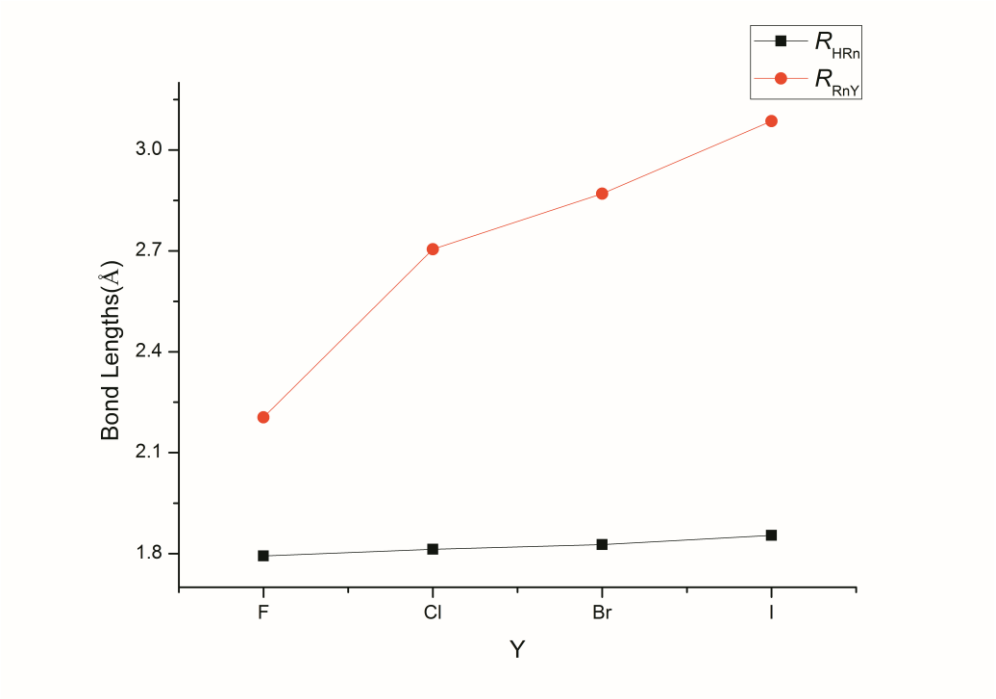


Figure S2. 3-D surface views of the $n_{He} \rightarrow \hat{\sigma}_{HI}$ donor-acceptor interaction in HHeI.

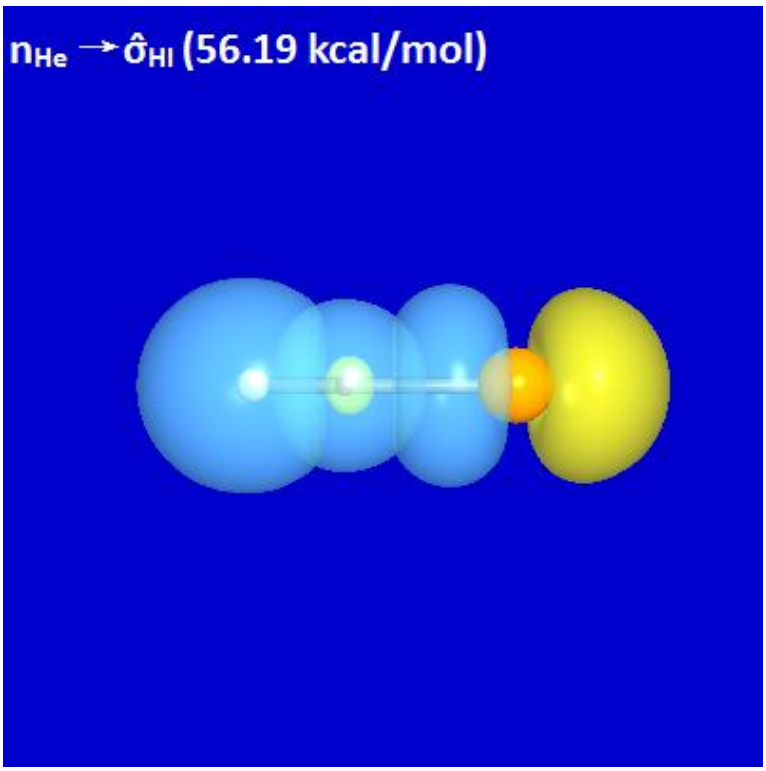
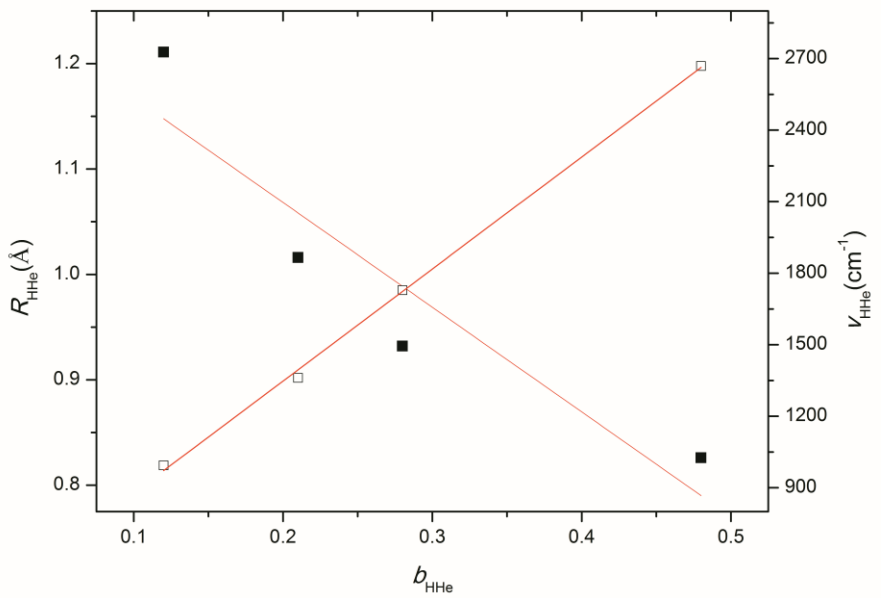


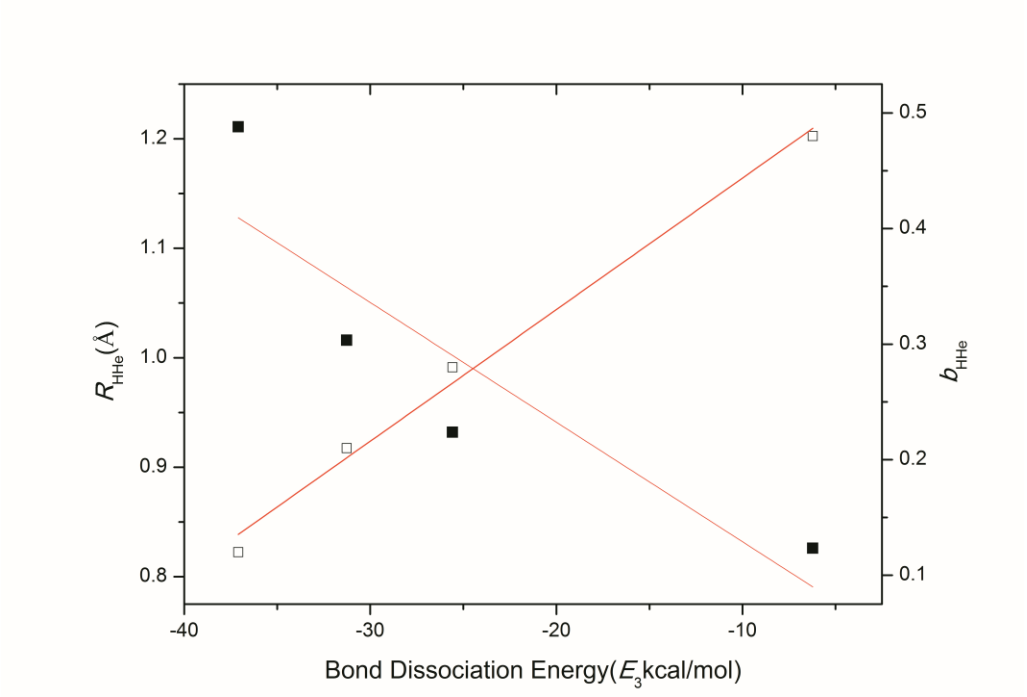
Figure S3. The results of linear correlation for HNgY (Ng= He, Ne, Kr, Xe, Rn; Y= F, Cl, Br I)

HHeY (Y= F, Cl, Br, I)

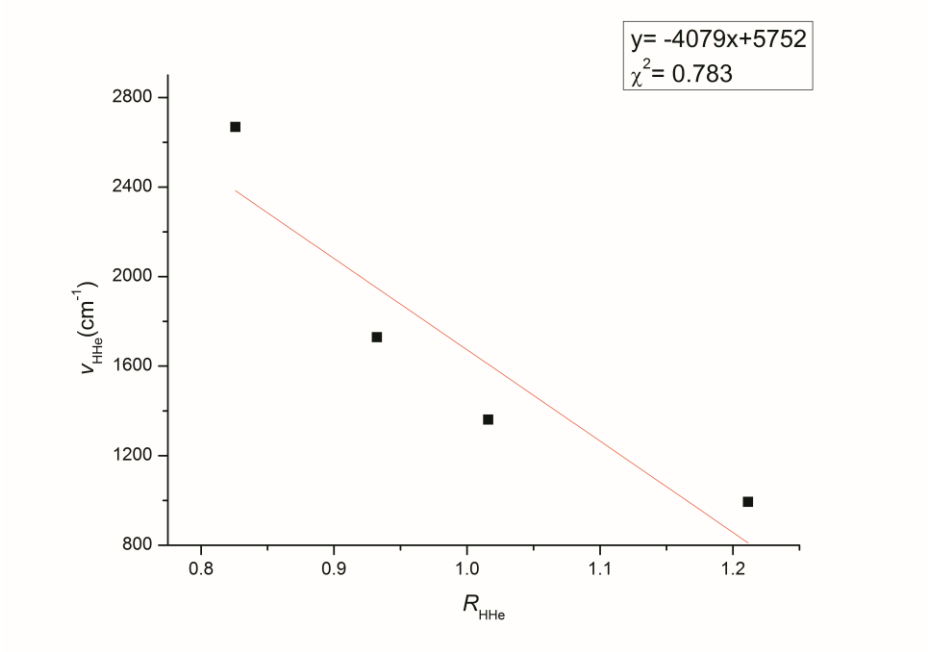
(a)Correlation plots for bond order-bond length (χ^2=0.806 for b_{HHe}-R_{HHe}) and bond order-bond frequency (χ^2=0.998 for b_{HHe}-ν_{HHe}) in HHeY.



(b) Correlation plots for bond dissociation energy-bond length (χ^2=0.710 for E_3-R_{HHe}) and bond dissociation energy-bond order (χ^2=0.989 for E_3-b_{HHe}) in HHeY.

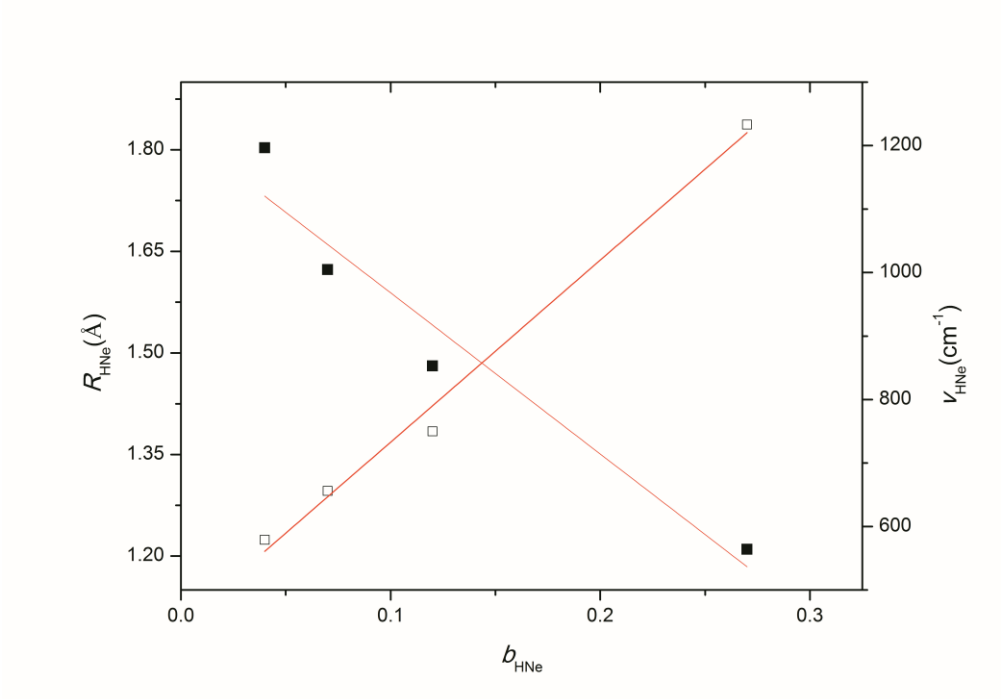


(c) Correlation plots for bond length-bond frequency (χ^2=0.783 for R_{HHe}-ν_{HHe}) in HHeY.

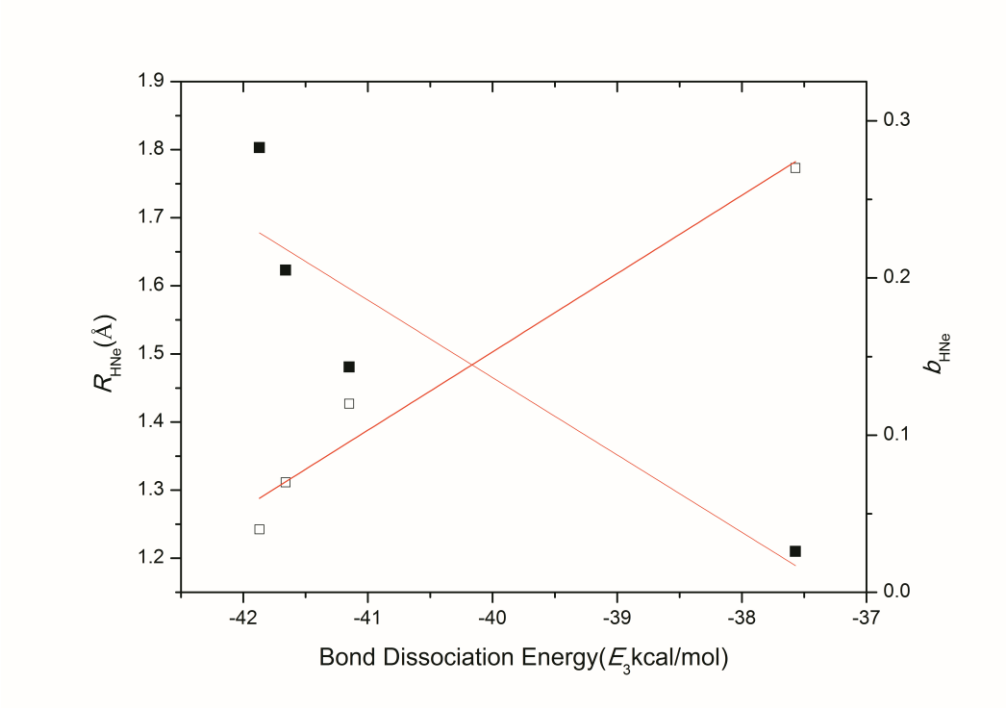


HNeY (Y= F, Cl, Br, I)

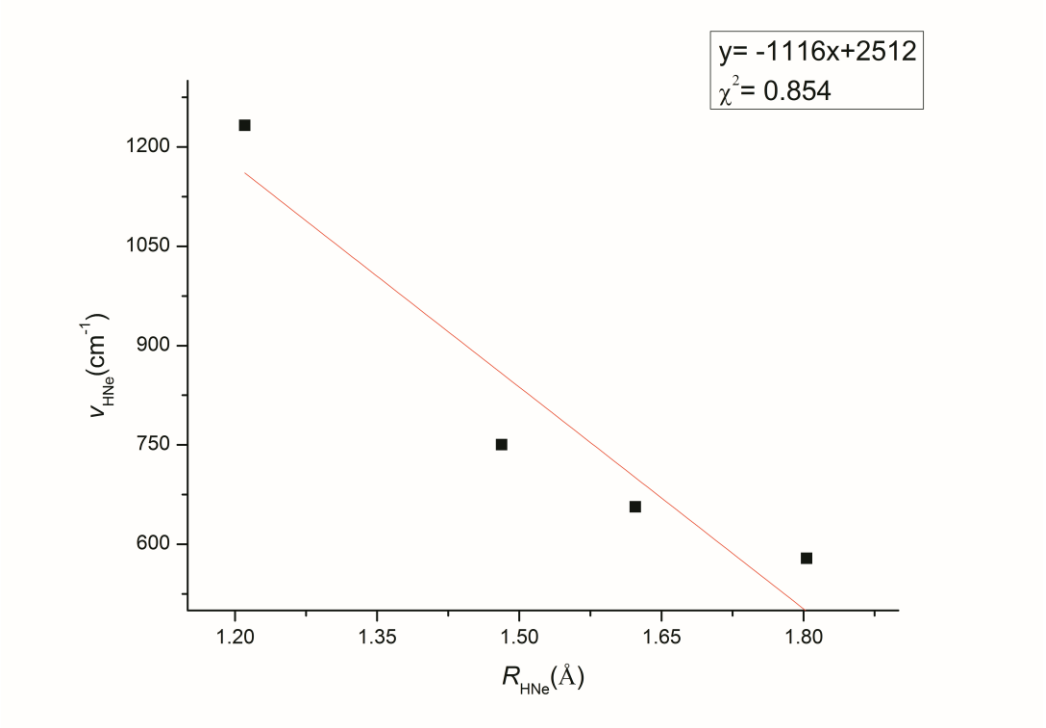
(a)Correlation plots for bond order-bond length (χ^2=0.914 for b_{HNe}-R_{HNe}) and bond order-bond frequency (χ^2=0.987 for b_{HNe}-ν_{HNe}) in HNeY.



(b) Correlation plots for bond dissociation energy-bond length (χ^2=0.758 for E_3-R_{HNe}) and bond dissociation energy-bond order (χ^2=0.952 for E_3-b_{HNe}) in HNeY.

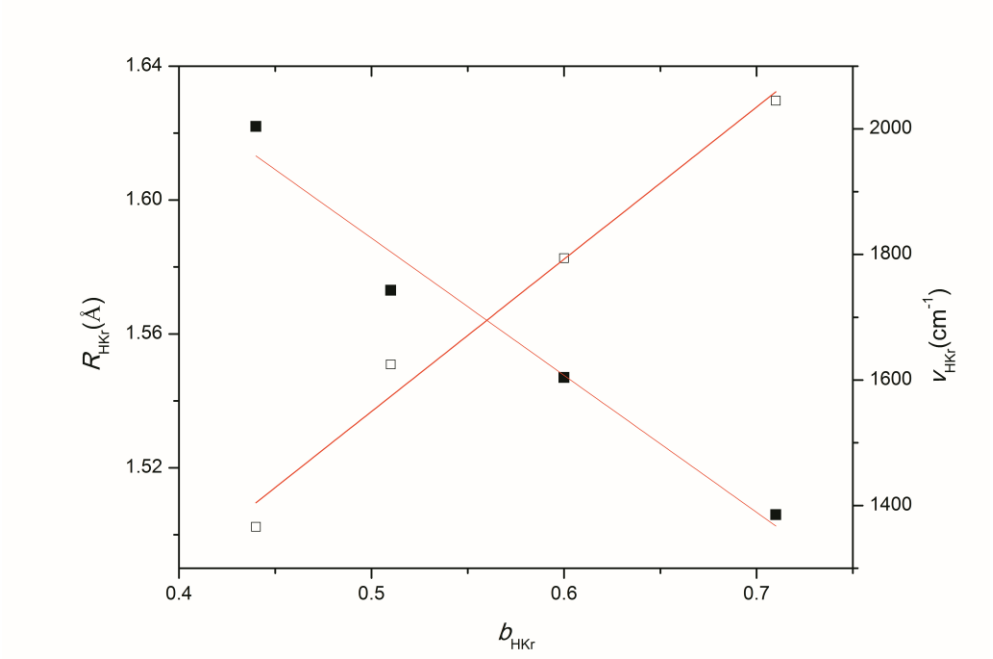


(c) Correlation plots for bond length-bond frequency (χ^2=0.854 for R_{HNe}-ν_{HNe}) in HNeY.

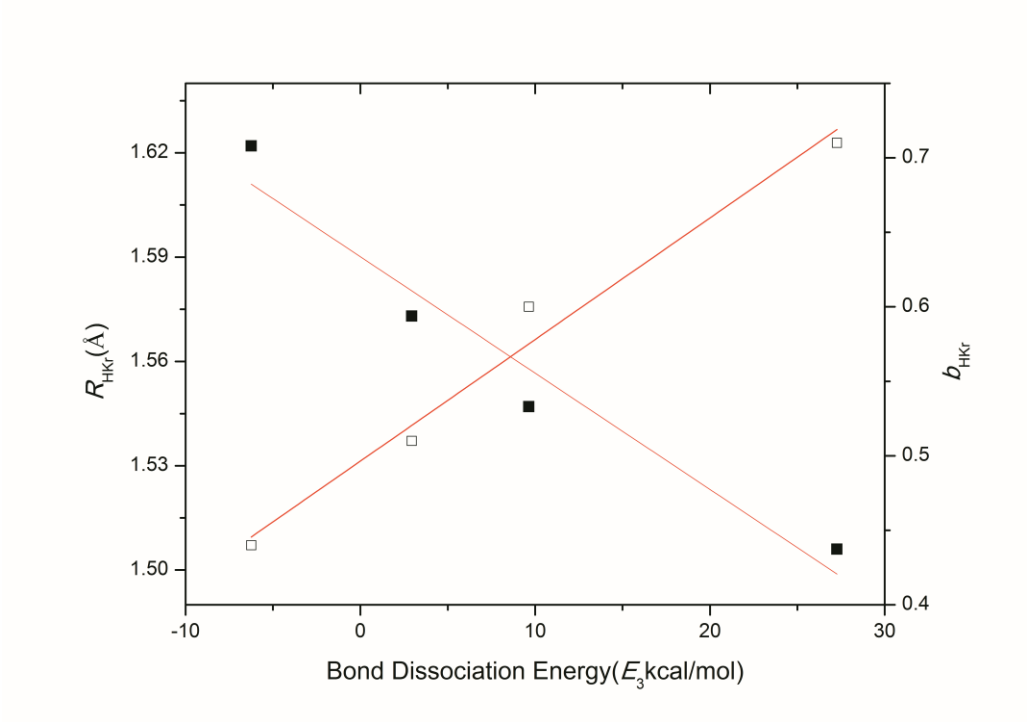


HKrY (Y= F, Cl, Br, I)

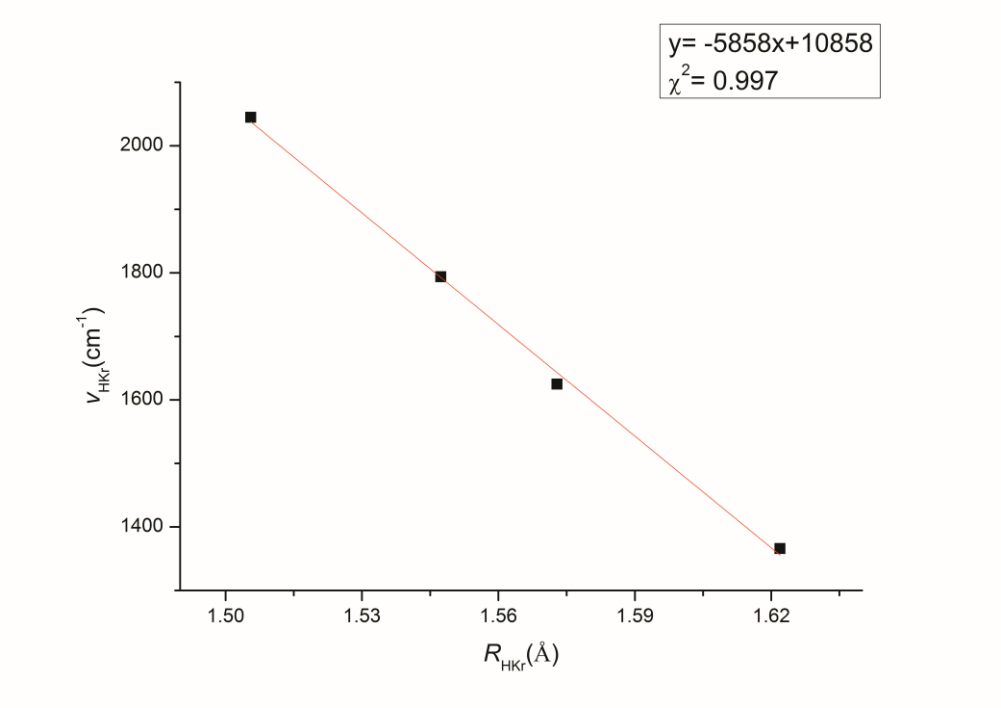
(a)Correlation plots for bond order-bond length (χ^2=0.953 for b_{HKr}-R_{HKr}) and bond order-bond frequency (χ^2=0.974 for b_{HKr}-ν_{HKr}) in HKrY.



(b) Correlation plots for bond dissociation energy-bond length (χ^2=0.927 for E_3-R_{HKr}) and bond dissociation energy-bond order (χ^2=0.969 for E_3-b_{HKr}) in HKrY.

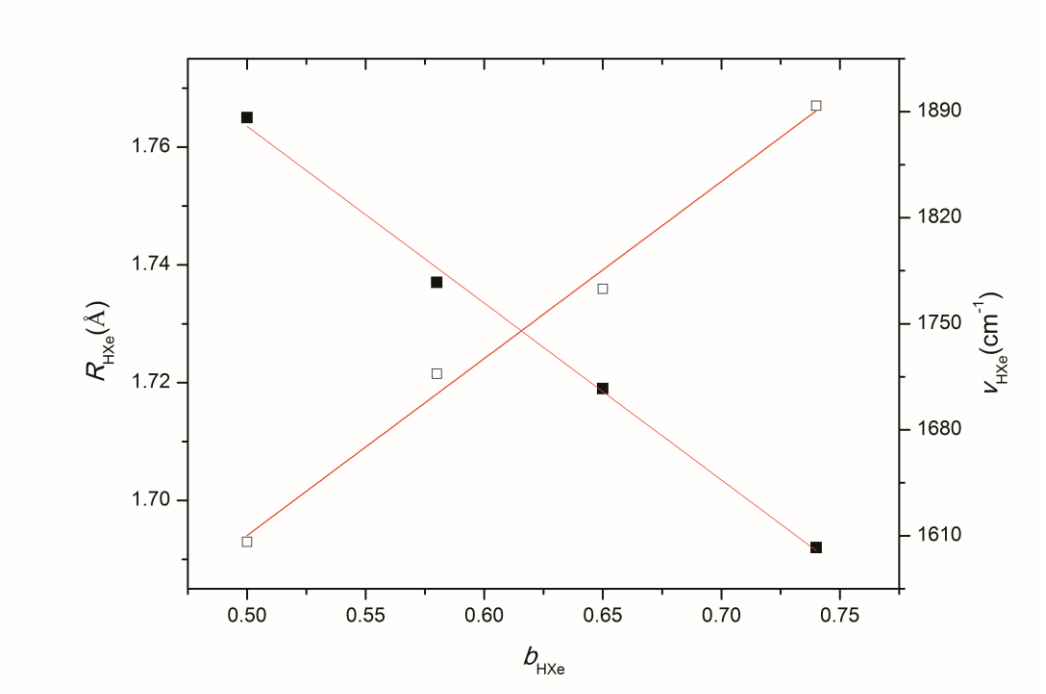


(c) Correlation plots for bond length-bond frequency (χ^2=0.997 for R_{HKr}-ν_{HKr}) in HKrY.

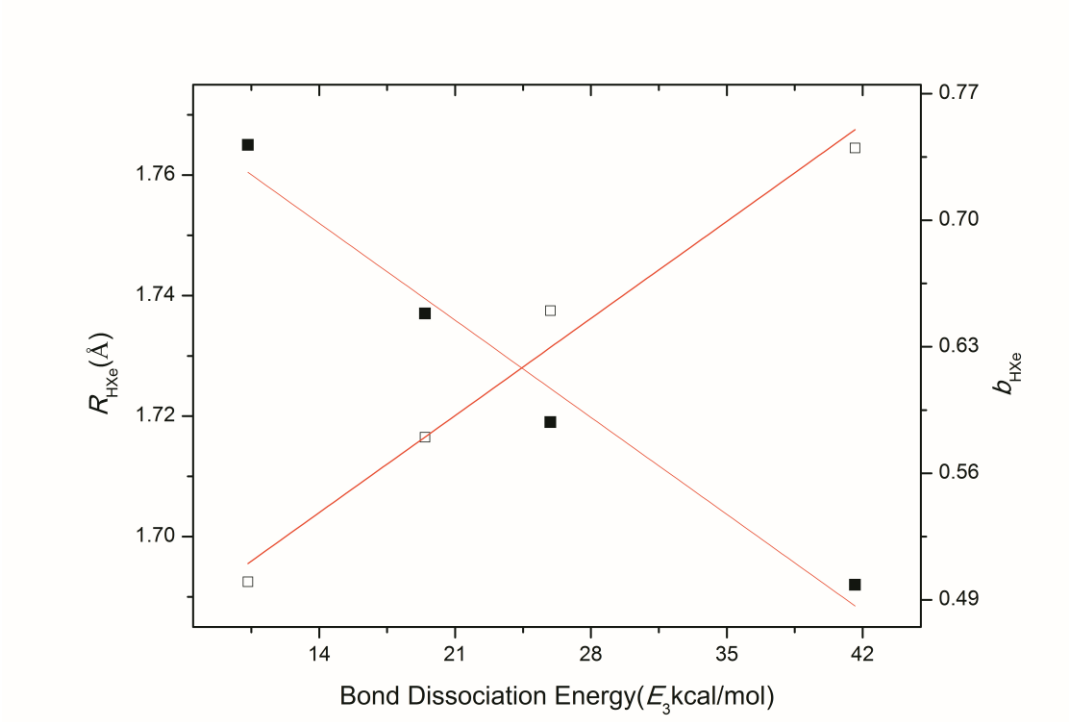


HXeY (Y= F, Cl, Br, I)

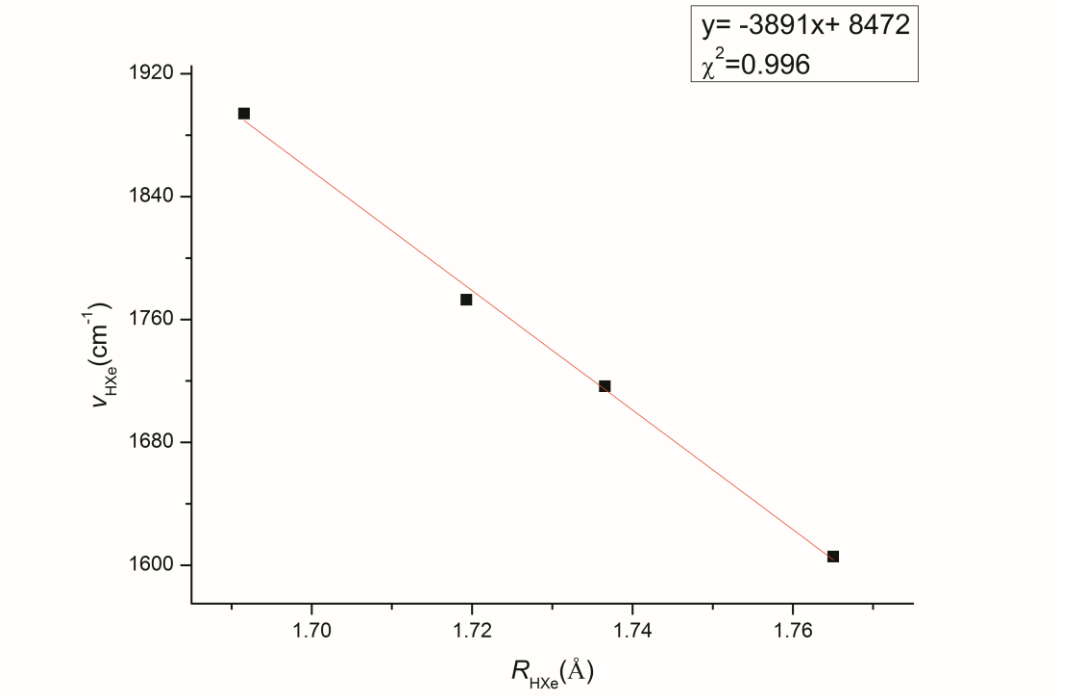
(a)Correlation plots for bond order-bond length (χ^2=0.995 for b_{HXe}-R_{HXe}) and bond order-bond frequency (χ^2=0.987 for b_{HXe}-ν_{HXe}) in HXeY.



(b) Correlation plots for bond dissociation energy-bond length (χ^2=0.962 for E_3-R_{HXe}) and bond dissociation energy-bond order (χ^2=0.970 for E_3-b_{HXe}) in HXeY.

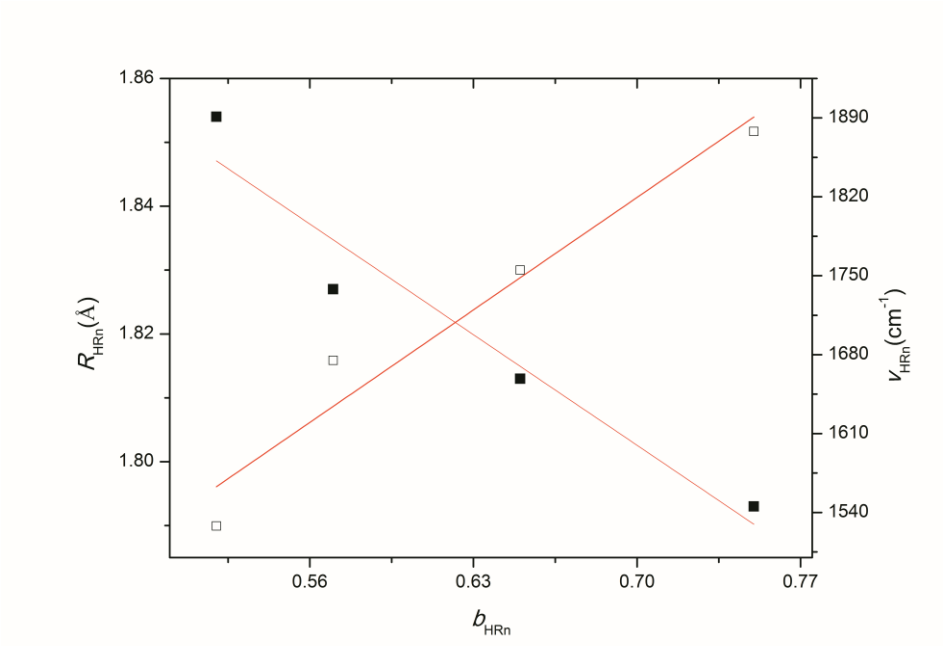


(c) Correlation plots for bond length-bond frequency (χ^2=0.996 for R_{HXe}-ν_{HXe}) in HXeY.

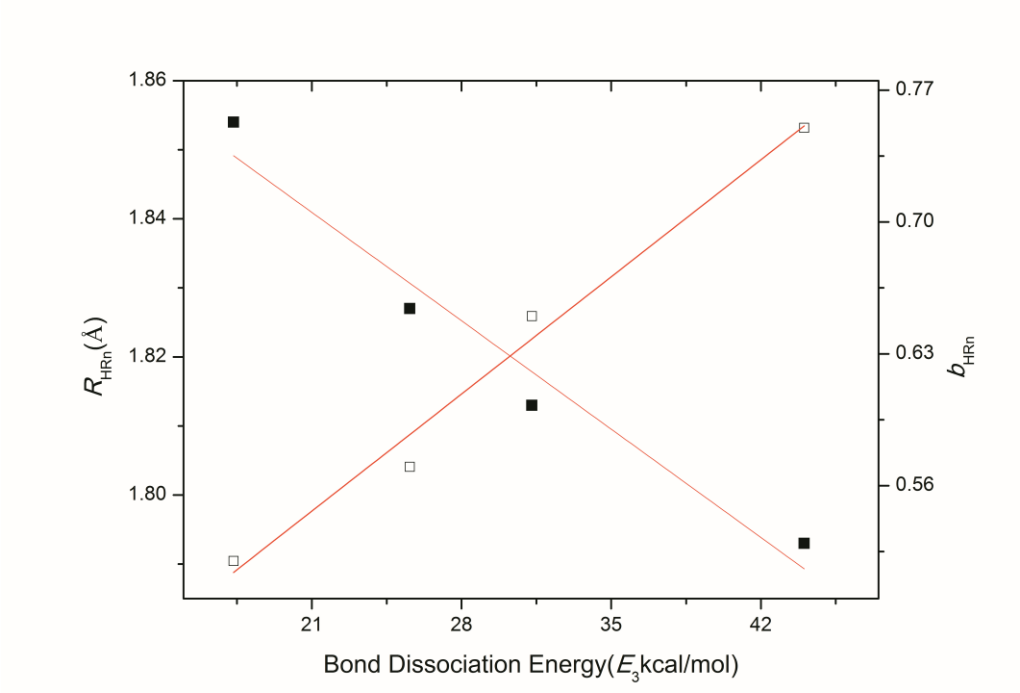


HRnY (Y= F, Cl, Br, I)

(a)Correlation plots for bond order-bond length (χ^2=0.909 for b_{HRn}-R_{HRn}) and bond order-bond frequency (χ^2=0.928 for b_{HRn}-ν_{HRn}) in HRnY.



(b) Correlation plots for bond dissociation energy-bond length (χ^2=0.944 for E_3-R_{HRn}) and bond dissociation energy-bond order (χ^2=0.976 for E_3-b_{HRn}) in HRnY.



(c) Correlation plots for bond length-bond frequency (χ^2=0.998 for R_{HRn}-ν_{HRn}) in HRnY.

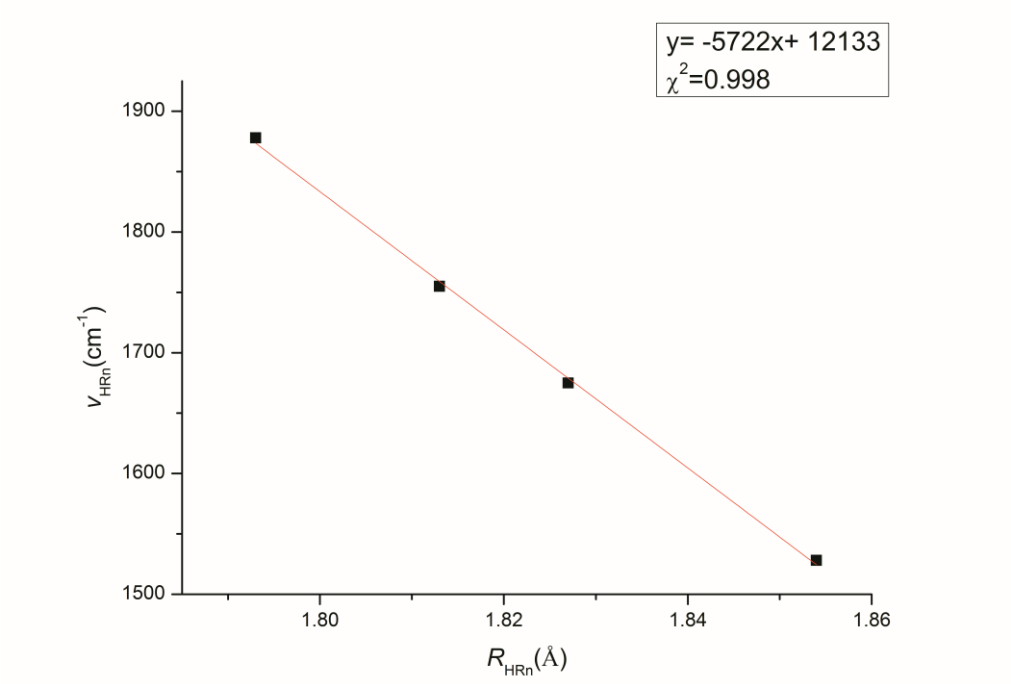
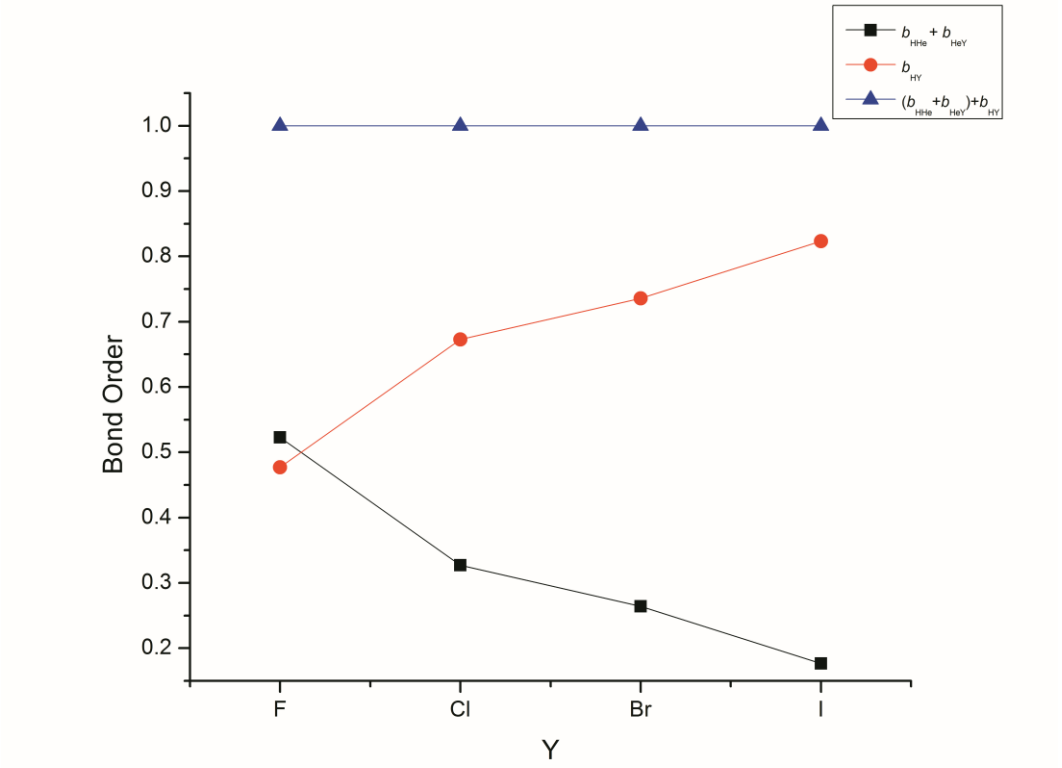
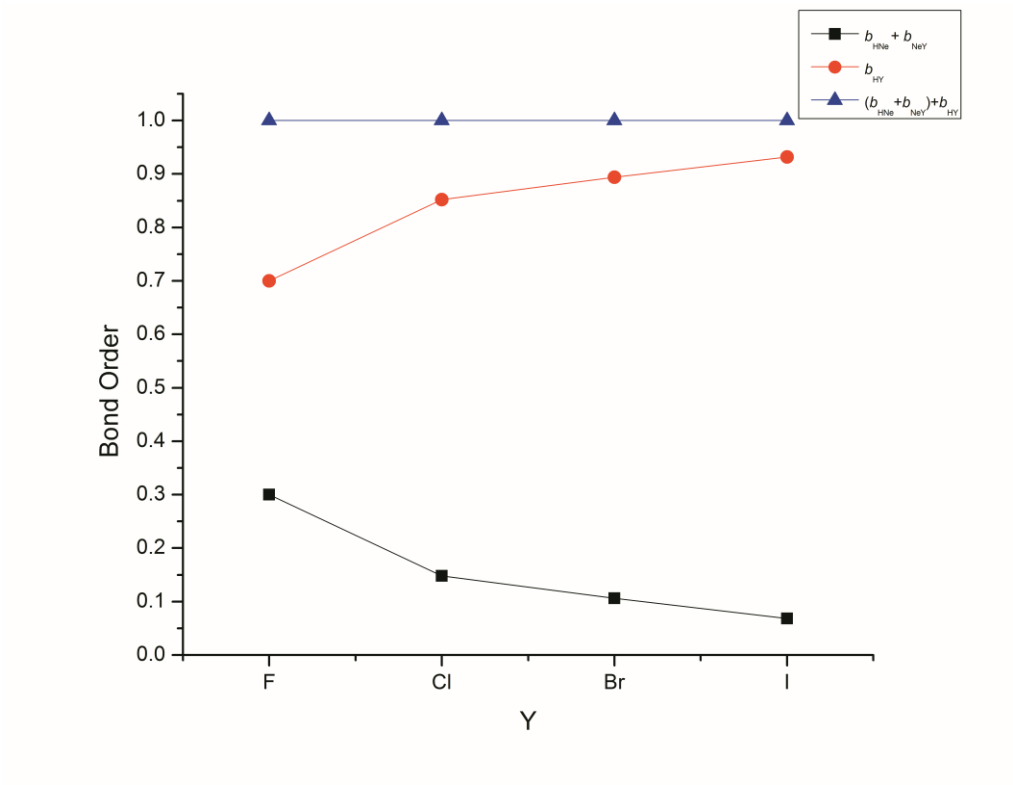


Figure S4. Schematic diagram of competition of 3c/4e ω-bonding and ô-type long-bonding in HHeY (a), HNeY (b), HKrY (c), HXeY (d), HRnY (e), Y=F, Cl, Br, I.

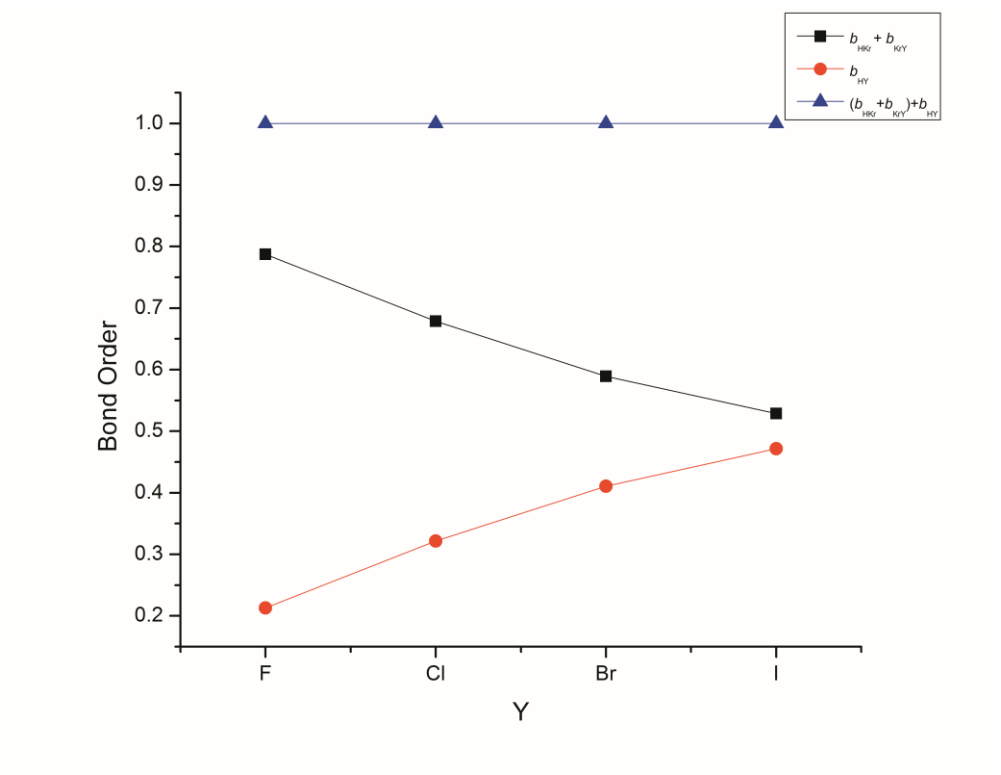
(a)HHeY



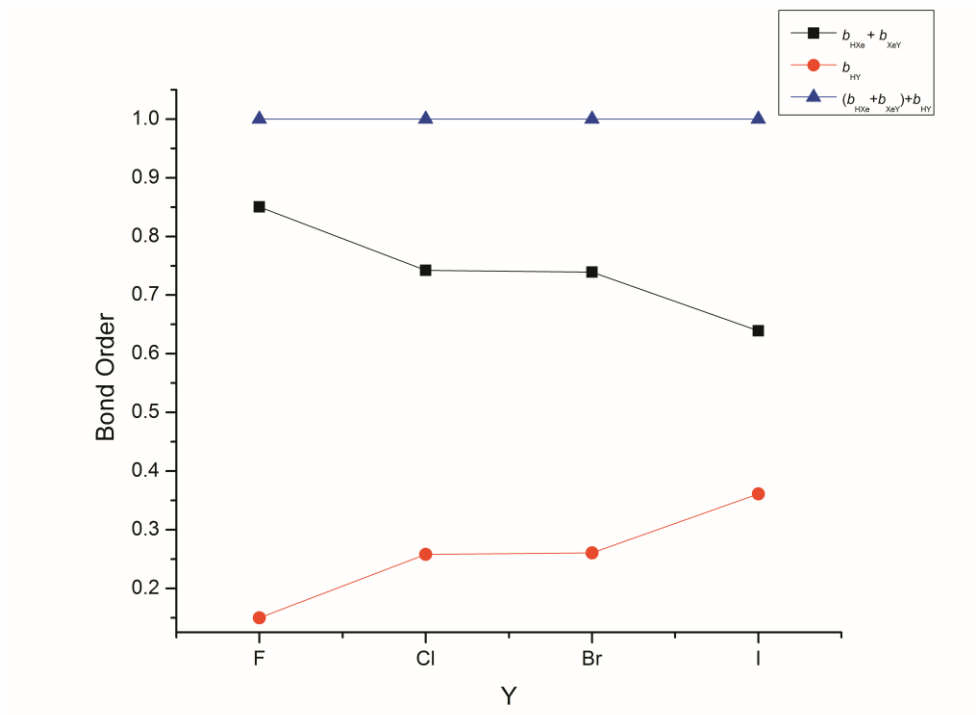
(b)HNeY


$b_{HNe} + b_{NeY}$
b_{HY}
$(b_{HNe}+b_{NeY})+b_{HY}$
Bond Order
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
F
Cl
Br
I
Y

(c)HKrY


$b_{HKr} + b_{KrY}$
b_{HY}
$(b_{HKr}+b_{KrY})+b_{HY}$
Bond Order
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
F
Cl
Br
I
Y

(d)HXeY


$b_{HXe} + b_{XeY}$
b_{HY}
$(b_{HXe} + b_{XeY}) + b_{HY}$
Bond Order
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
F
Cl
Br
I
Y

(e)HRnY

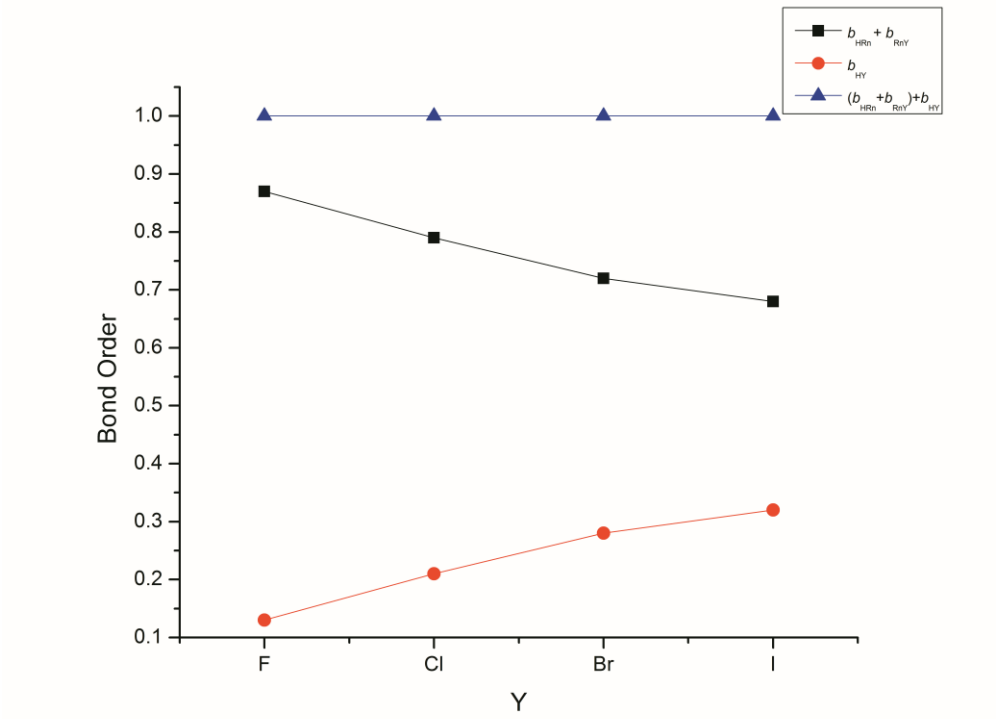
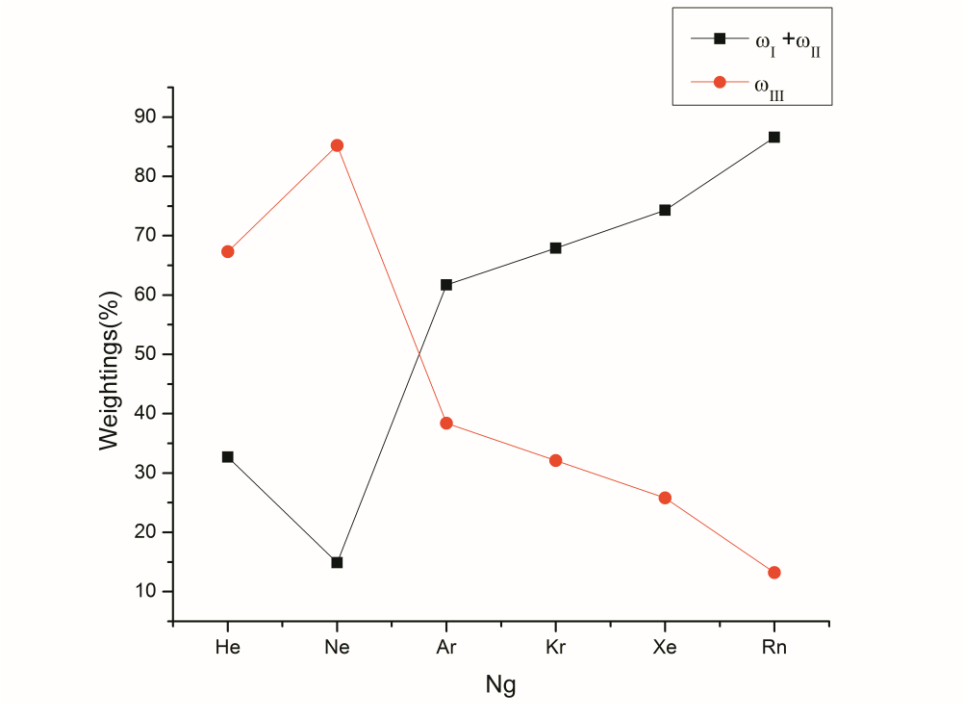
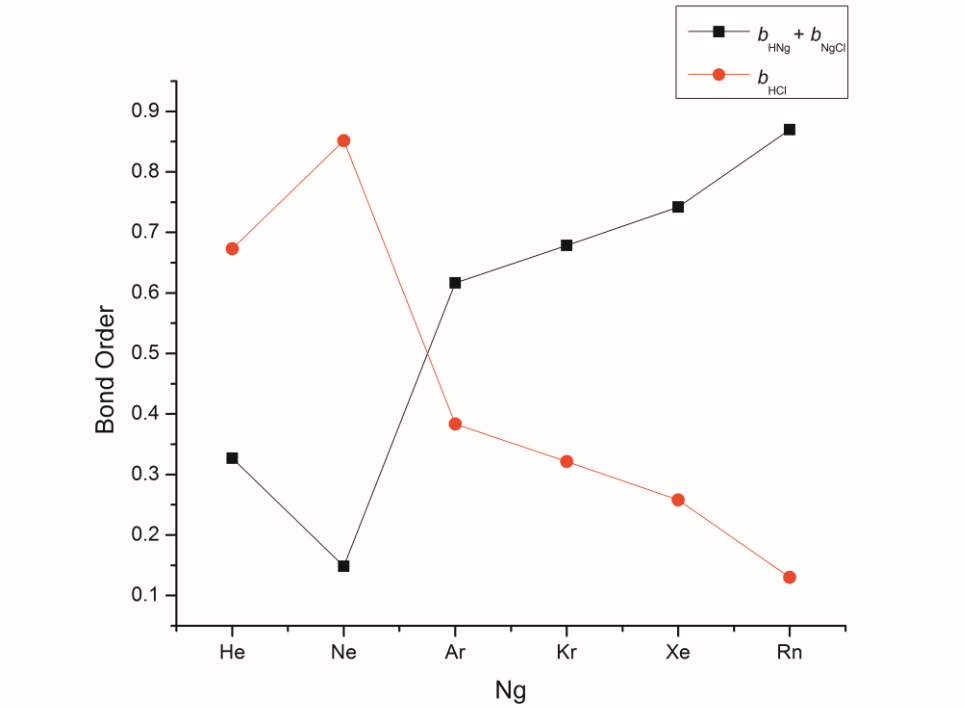

$b_{HRn} + b_{RnY}$
b_{HY}
$(b_{HRn} + b_{RnY}) + b_{HY}$
Bond Order
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
F
Cl
Br
I
Y

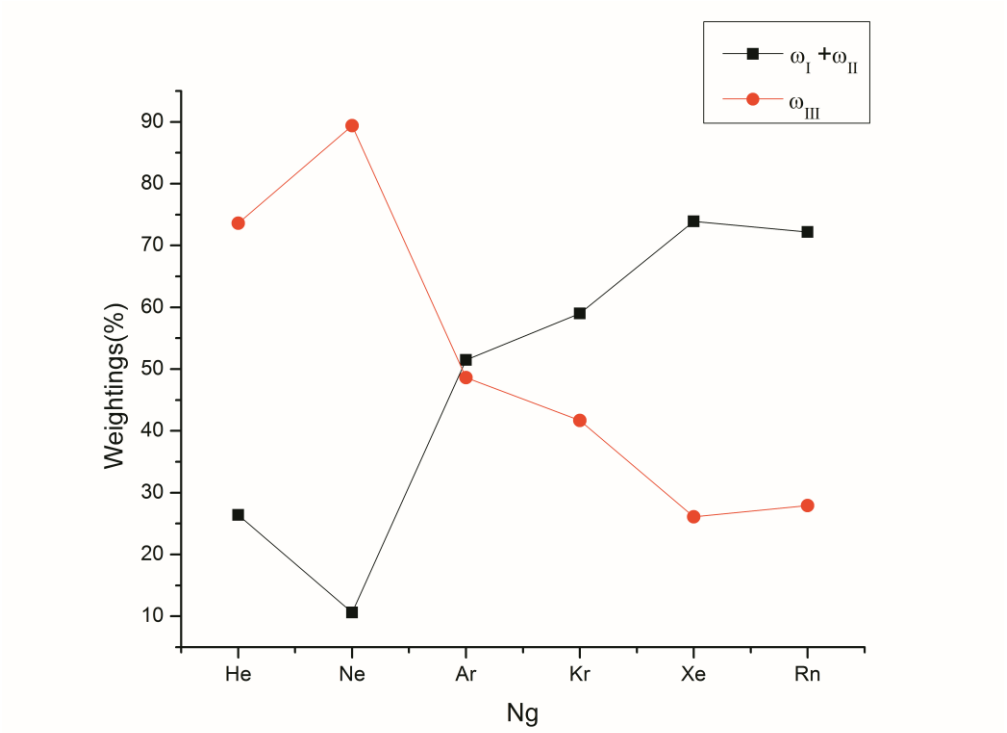
Figure S5. The influence of the central noble-gas atom on the NRT weightings and NRT bond orders of 3c/4e ω-bonded structures and ô-type long-bonded structure in HNgCl (a), HNgBr (b), HNgI (c), Ng= He, Ne, Ar, Kr, Xe, Rn.

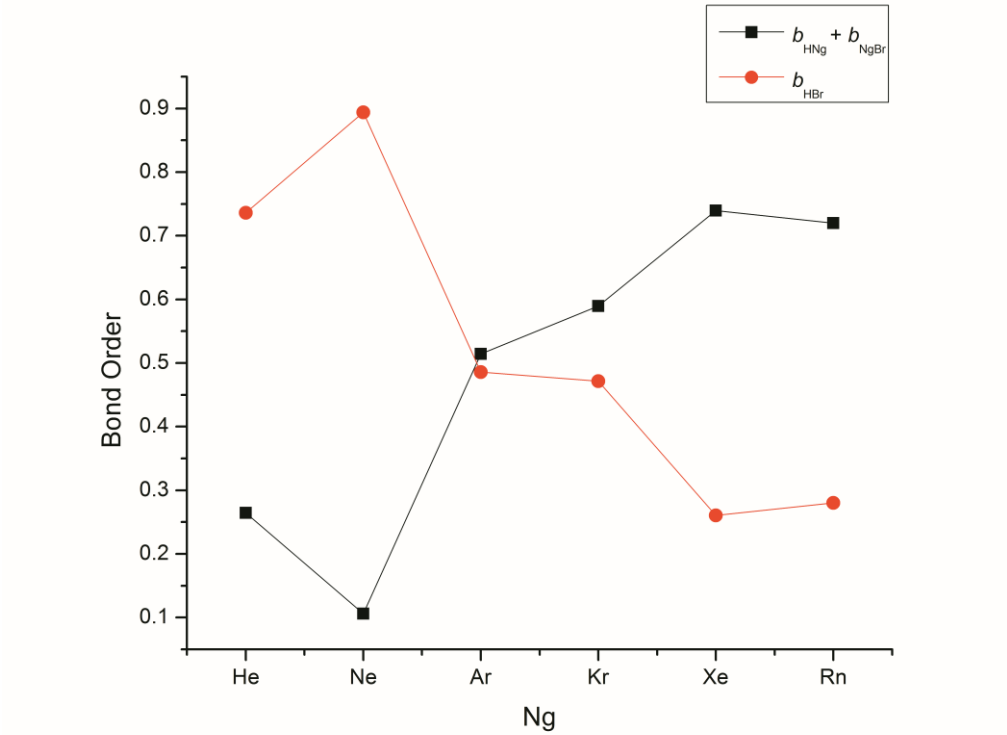
(a)HNgCl



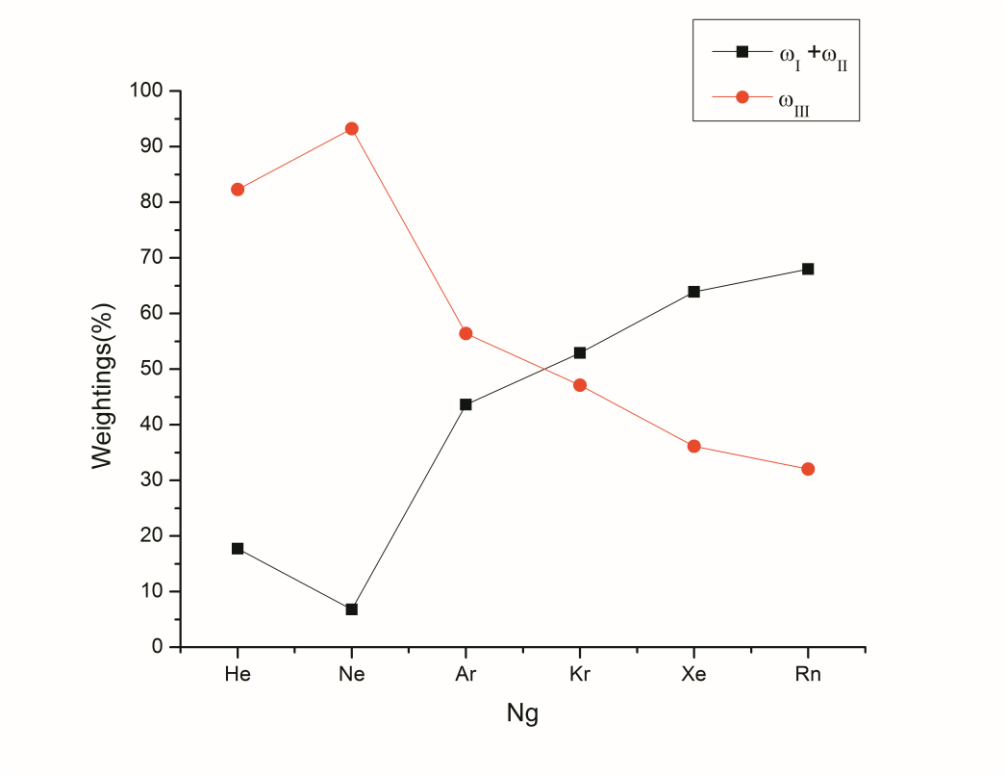


(b)HNgBr


ω_I +ω_II
ω_III
Weightings(%)
90
80
70
60
50
40
30
20
10
He
Ne
Ar
Kr
Xe
Rn
Ng


b_HNg + b_NgBr
b_HBr
Bond Order
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
He
Ne
Ar
Kr
Xe
Rn
Ng

(c)HNgI


ω_I +ω_II
ω_III
Weightings(%)
100
90
80
70
60
50
40
30
20
10
0
He
Ne
Ar
Kr
Xe
Rn
Ng

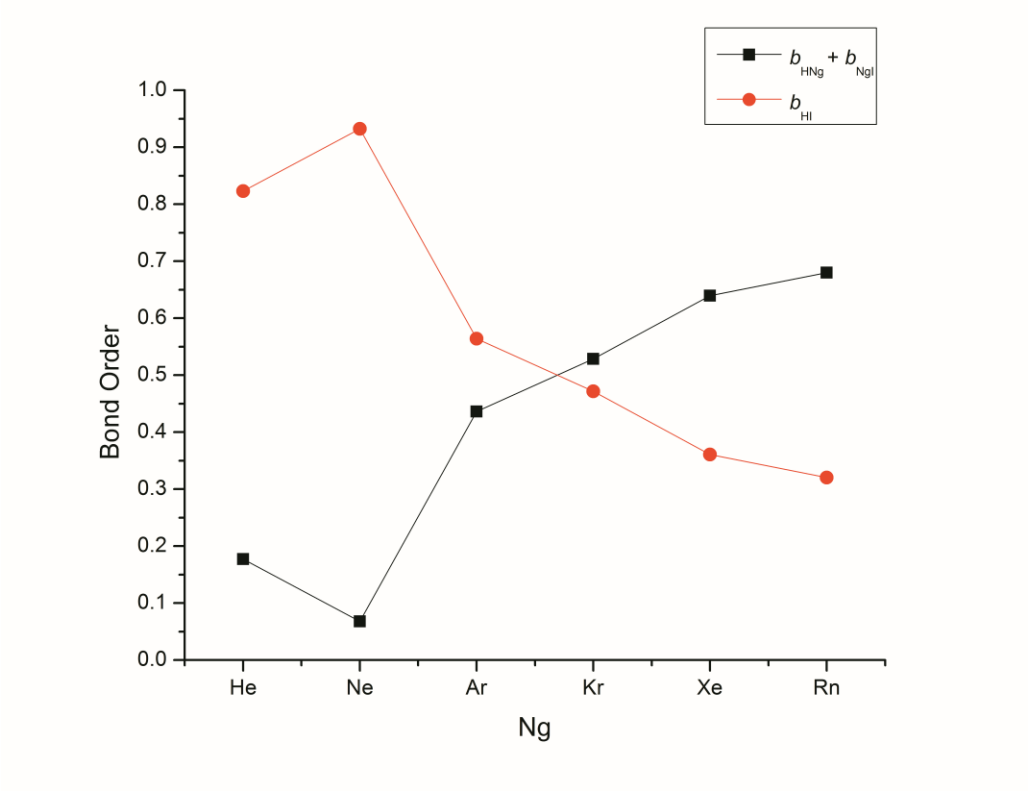
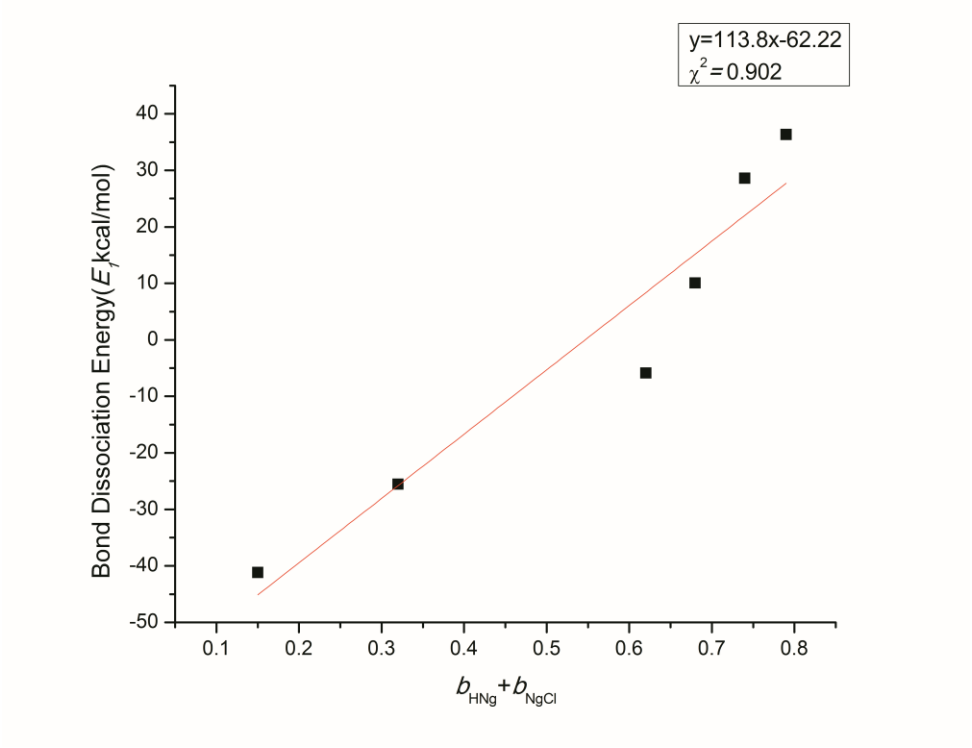
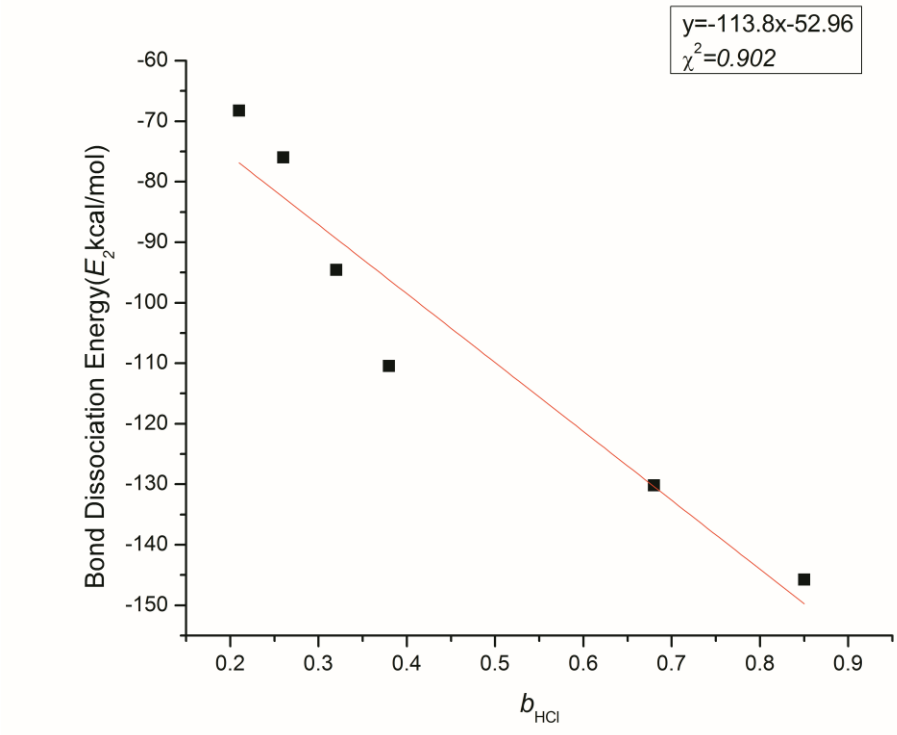

b_HNg + b_NgI
b_HI
Bond Order
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
He
Ne
Ar
Kr
Xe
Rn
Ng

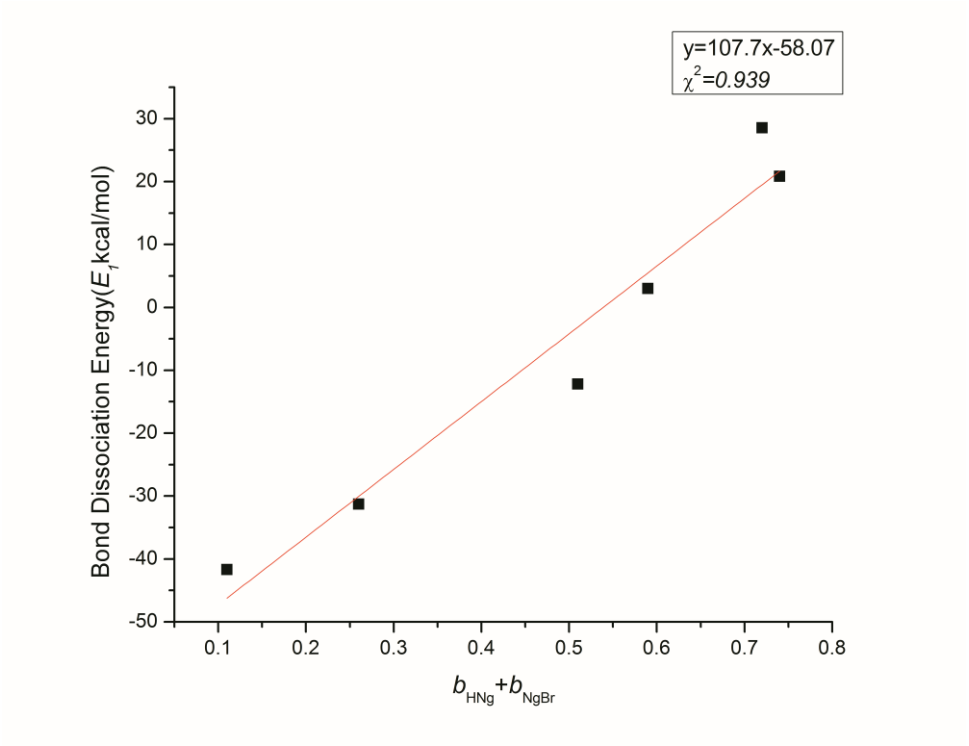
Figure S6. Correlation plots for bond order-bond dissociation energy (b_{HNg}+b_{NgY} *vs.* E_1 and b_{HY} *vs.* E_2) for HNgCl (a), HNgBr (b), HNgI (c), Ng= He, Ne, Ar, Kr, Xe, Rn.

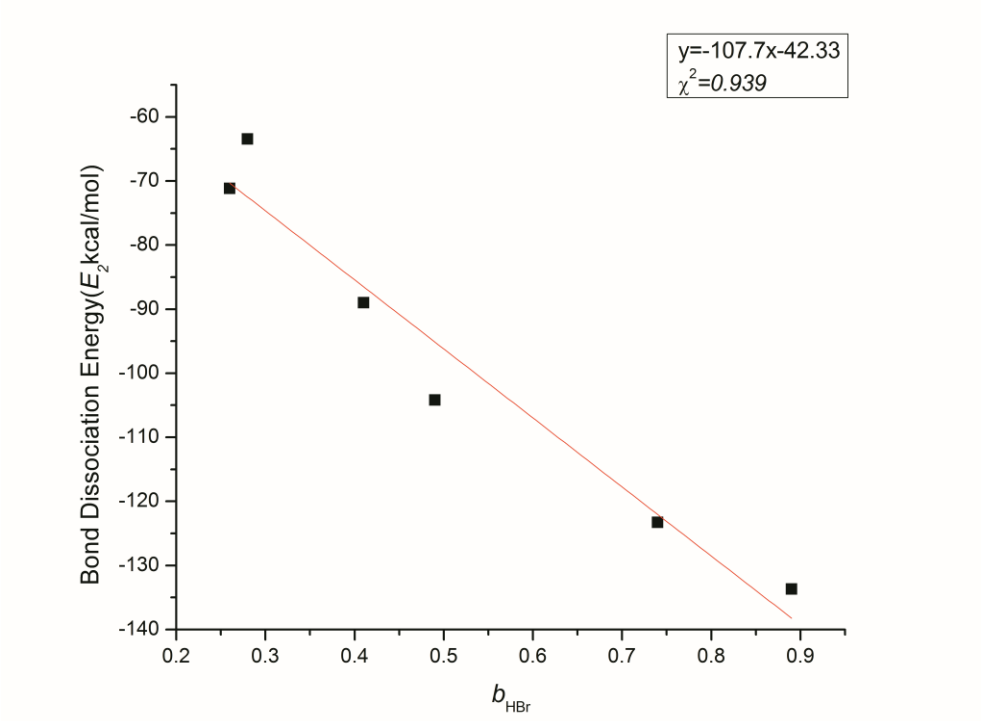
(a)HNgCl



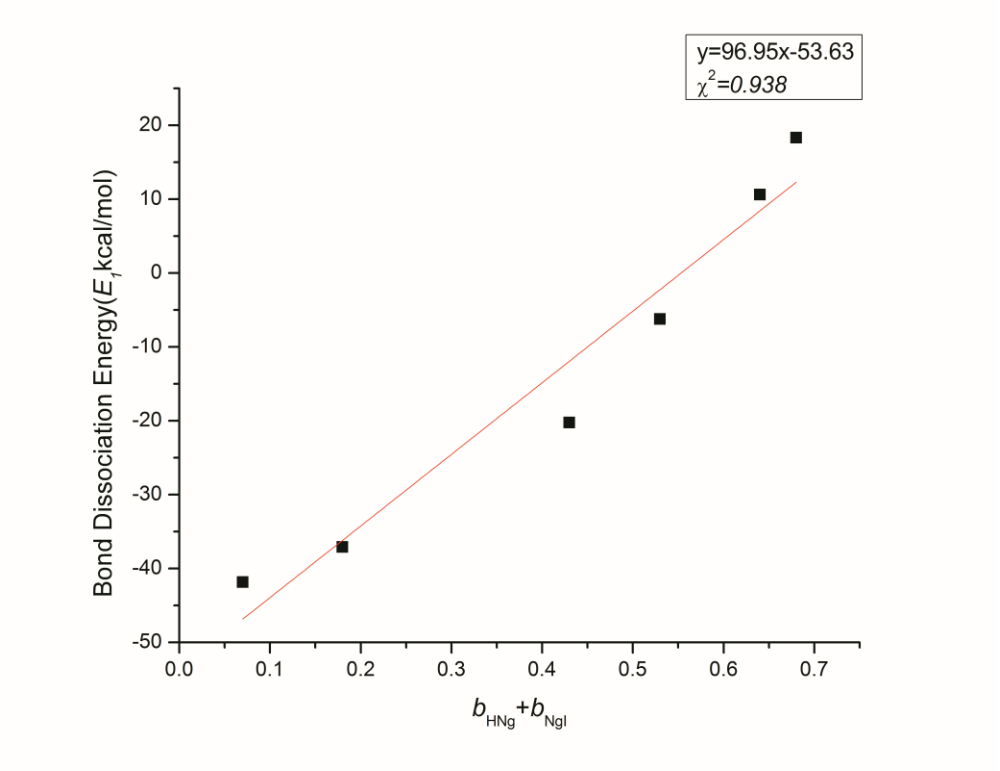


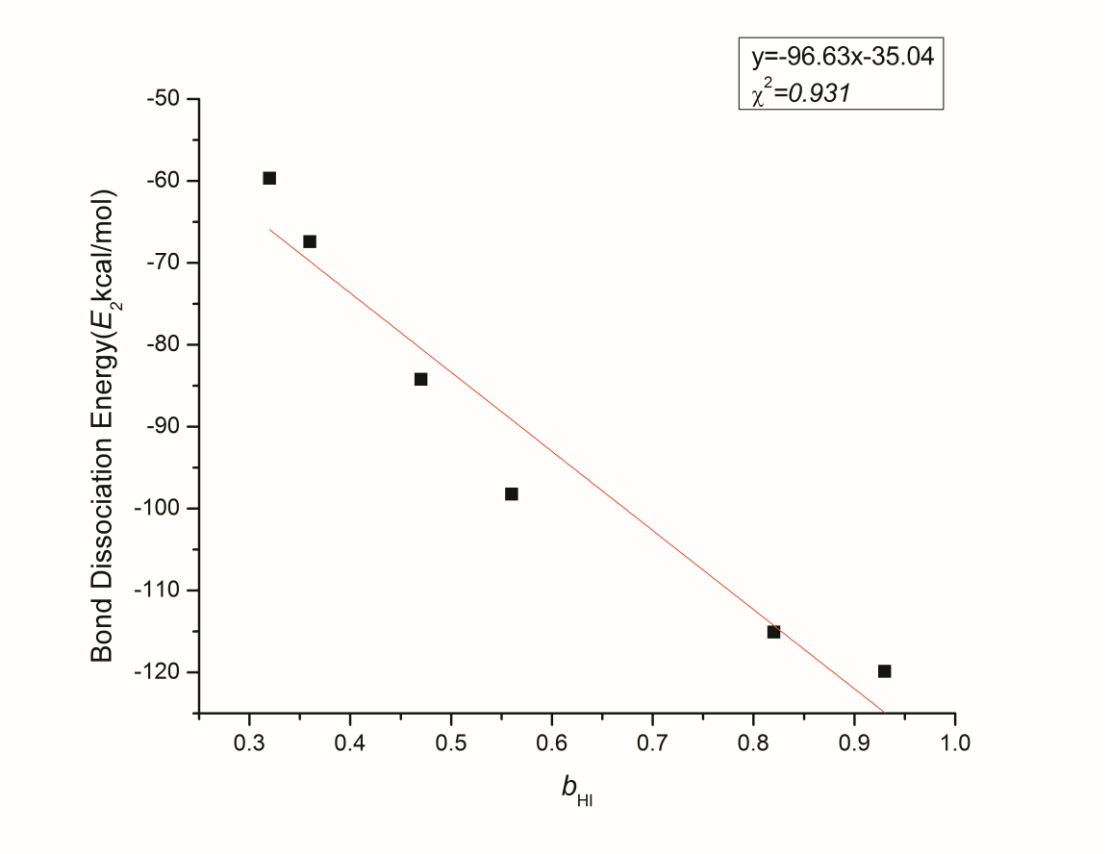
(b)HNgBr


y=107.7x-58.07
χ^2=0.939
Bond Dissociation Energy(E_1 kcal/mol)
30
20
10
0
-10
-20
-30
-40
-50
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
$b_{HNg}+b_{NgBr}$


y=-107.7x-42.33
χ^2=0.939
Bond Dissociation Energy(E_2 kcal/mol)
-60
-70
-80
-90
-100
-110
-120
-130
-140
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
b_{HBr}

(c)HNgI


y=96.95x-53.63
χ^2=0.938
Bond Dissociation Energy(E_1 kcal/mol)
$b_{HNg}+b_{NgI}$


y=-96.63x-35.04
χ^2=0.931
Bond Dissociation Energy(E_2 kcal/mol)
b_{HI}