

The noticeable characteristics of conventional and nonconventional hydrogen bonds in the binary systems of chalcogenoaldehyde and chalcogenocarboxylic acid derivatives

Le Thi Tu Quyen,¹ Nguyen Tien Trung*^{1,2}

¹Laboratory of Computational Chemistry and Modelling (LCCM), Quy Nhon University, 170 An Duong Vuong Street, Quy Nhon City 590000, Vietnam

²Faculty of Natural Sciences, Quy Nhon University, 170 An Duong Vuong Street, Quy Nhon City 590000, Vietnam

SUPPORTING INFORMATION

Table S1a. The H \cdots Z interaction distance ($r_{H\cdots Z}$), Electron density [$\rho(r)$], Laplacian of electron density [$\nabla^2(\rho)$], individual energy of hydrogen bond (E_{HB}) and the ratio between the intermolecular distance and the sum of van der Waals radii of the H, Z atoms ($r_{H\cdots Z} / \sum r_{vdW}$) of HZ-RZ complexes (R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te)

Complex	Hydrogen bonds	$r_{H\cdots Z}$ (Å)	$\rho(r)$ (au)	$\nabla^2(\rho)$ (au)	E_{HB} (kJ.mol ⁻¹)	$r_{H\cdots Z} / \sum r_{vdW}$
HO-HO	C1-H4 \cdots O6	2.35	0.012	0.046	-10.0	0.86
	O7-H8 \cdots O2	1.76	0.040	0.094	-51.9	0.65
HO-FO	C1-H4 \cdots O6	2.39	0.011	0.043	-9.2	0.88
	O7-H8 \cdots O2	1.70	0.046	0.099	-62.2	0.62
HO-ClO	C1-H4 \cdots O6	2.39	0.011	0.043	-9.1	0.88
	O7-H8 \cdots O2	1.70	0.046	0.098	-61.9	0.63
HO-BrO	C1-H4 \cdots O6	2.38	0.011	0.043	-9.2	0.88
	O7-H8 \cdots O2	1.70	0.047	0.098	-62.8	0.62
HO-CH ₃ O	C1-H4 \cdots O6	2.33	0.013	0.049	-10.6	0.86
	O7-H8 \cdots O2	1.78	0.038	0.093	-48.7	0.65
HO-NH ₂ O	C1-H4 \cdots O6	2.29	0.014	0.054	-11.7	0.84
	O7-H8 \cdots O2	1.76	0.040	0.095	-51.1	0.65
HS-HS	C1-H4 \cdots S6	2.72	0.012	0.031	-8.1	0.91
	O7-H8 \cdots S2	2.25	0.028	0.043	-25.3	0.75
HS-FS	C1-H4 \cdots S6	2.74	0.011	0.030	-7.6	0.91
	O7-H8 \cdots S2	2.19	0.032	0.043	-30.0	0.73
HS-ClS	C1-H4 \cdots S6	2.74	0.011	0.030	-7.7	0.91
	O7-H8 \cdots S2	2.20	0.031	0.043	-29.2	0.73
HS-BrS	C1-H4 \cdots S6	2.73	0.011	0.030	-7.7	0.91
	O7-H8 \cdots S2	2.19	0.032	0.043	-29.7	0.73
HS-CH ₃ S	C1-H4 \cdots S6	2.72	0.012	0.031	-8.2	0.91
	O7-H8 \cdots S2	2.27	0.027	0.044	-24.2	0.76
HS-NH ₂ S	C1-H4 \cdots S6	2.67	0.013	0.034	-9.1	0.89
	O7-H8 \cdots S2	2.26	0.027	0.044	-25.0	0.75
HSe-HSe	C1-H4 \cdots Se6	2.75	0.013	0.030	-8.9	0.89
	O7-H8 \cdots Se2	2.34	0.027	0.037	-23.4	0.75
HSe-FSe	C1-H4 \cdots Se6	2.77	0.012	0.030	-8.5	0.89
	O7-H8 \cdots Se2	2.28	0.031	0.036	-27.2	0.74
HSe-ClSe	C1-H4 \cdots Se6	2.76	0.013	0.030	-8.6	0.89
	O7-H8 \cdots Se2	2.29	0.030	0.036	-26.4	0.74
HSe-BrSe	C1-H4 \cdots Se6	2.76	0.013	0.030	-8.6	0.89
	O7-H8 \cdots Se2	2.28	0.031	0.036	-26.9	0.74
HSe-CH ₃ Se	C1-H4 \cdots Se6	2.75	0.013	0.030	-8.9	0.89
	O7-H8 \cdots Se2	2.35	0.027	0.038	-22.7	0.76
HSe-NH ₂ Se	C1-H4 \cdots Se6	2.70	0.014	0.033	-9.7	0.87
	O7-H8 \cdots Se2	2.33	0.027	0.038	-23.4	0.75
HTe-HTe	C1-H4 \cdots Te6	2.91	0.012	0.025	-7.7	0.89
	O7-H8 \cdots Te2	2.50	0.026	0.030	-19.3	0.77
HTe-FTe	C1-H4 \cdots Te6	2.93	0.012	0.025	-7.5	0.90

	O7-H8...Te2	2.45	0.029	0.028	-22.2	0.75
HTe-ClTe	C1-H4...Te6	2.93	0.012	0.025	-7.5	0.90
	O7-H8...Te2	2.46	0.028	0.029	-21.6	0.75
HTe-BrTe	C1-H4...Te6	2.92	0.012	0.025	-7.6	0.90
	O7-H8...Te2	2.45	0.028	0.028	-21.8	0.75
HTe-CH₃Te	C1-H4...Te6	2.91	0.012	0.026	-7.8	0.89
	O7-H8...Te2	2.50	0.025	0.030	-19.2	0.77
HTe-NH₂Te	C1-H4...Te6	2.86	0.013	0.027	-8.5	0.88
	O7-H8...Te2	2.49	0.026	0.030	-20.0	0.76

Table S1b. The H...Z interaction distance ($r_{H...Z}$), Electron density [$\rho(r)$], Laplacian of electron density [$\nabla^2(\rho)$], individual energy of hydrogen bond (E_{HB}) and the ratio between the intermolecular distance and the sum of van der Waals radii of the H, Z atoms ($r_{H...Z}/$

$\sum r_{vdW}$) of **FZ-RZ** complexes (R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te)

Complex	Hydrogen bonds	$r_{H...Z}$ (Å)	$\rho(r)$ (au)	$\nabla^2(\rho)$ (au)	E_{HB} (kJ.mol ⁻¹)	$r_{H...Z}/\sum r_{vdW}$
FO-HO	C1-H4...O6	2.31	0.013	0.052	-11.1	0.85
	O7-H8...O2	1.85	0.031	0.089	-37.6	0.68
FO-FO	C1-H4...O6	2.34	0.012	0.049	-10.2	0.86
	O7-H8...O2	1.78	0.037	0.096	-47.0	0.65
FO-ClO	C1-H4...O6	2.35	0.012	0.048	-10.0	0.86
	O7-H8...O2	1.78	0.036	0.095	-45.9	0.66
FO-BrO	C1-H4...O6	2.35	0.012	0.048	-10.0	0.86
	O7-H8...O2	1.78	0.036	0.095	-46.3	0.66
FO-CH₃O	C1-H4...O6	2.28	0.014	0.056	-12.0	0.84
	O7-H8...O2	1.87	0.030	0.087	-35.2	0.69
FO-NH₂O	C1-H4...O6	2.22	0.016	0.062	-13.7	0.82
	O7-H8...O2	1.85	0.031	0.088	-37.1	0.68
FS-HS	C1-H4...S6	2.69	0.012	0.032	-8.5	0.90
	O7-H8...S2	2.31	0.024	0.043	-21.2	0.77
FS-FS	C1-H4...S6	2.71	0.012	0.032	-8.2	0.90
	O7-H8...S2	2.24	0.028	0.044	-25.6	0.75
FS-ClS	C1-H4...S6	2.71	0.012	0.031	-8.1	0.90
	O7-H8...S2	2.25	0.027	0.044	-24.6	0.75
FS-BrS	C1-H4...S6	2.71	0.012	0.031	-8.2	0.90
	O7-H8...S2	2.25	0.027	0.044	-25.0	0.75
FS-CH₃S	C1-H4...S6	2.69	0.013	0.032	-8.7	0.90
	O7-H8...S2	2.32	0.023	0.043	-20.3	0.77
FS-NH₂S	C1-H4...S6	2.63	0.014	0.036	-9.9	0.88
	O7-H8...S2	2.31	0.024	0.044	-21.2	0.77
FSe-HSe	C1-H4...Se6	2.72	0.014	0.031	-9.5	0.88
	O7-H8...Se2	2.38	0.025	0.038	-20.7	0.77
FSe-FSe	C1-H4...Se6	2.73	0.013	0.031	-9.3	0.88
	O7-H8...Se2	2.31	0.028	0.038	-24.1	0.75
FSe-ClSe	C1-H4...Se6	2.74	0.013	0.031	-9.2	0.88
	O7-H8...Se2	2.33	0.027	0.038	-23.3	0.75
FSe-BrSe	C1-H4...Se6	2.73	0.013	0.031	-9.2	0.88
	O7-H8...Se2	2.32	0.028	0.038	-23.7	0.75
FSe-CH₃Se	C1-H4...Se6	2.72	0.014	0.032	-9.6	0.88
	O7-H8...Se2	2.39	0.024	0.038	-20.0	0.77
FSe-NH₂Se	C1-H4...Se6	2.67	0.015	0.034	-10.7	0.86
	O7-H8...Se2	2.37	0.024	0.039	-20.7	0.77
FTe-HTe	C1-H4...Te6	2.88	0.013	0.026	-8.3	0.88
	O7-H8...Te2	2.53	0.024	0.031	-17.6	0.78
FTe-FTe	C1-H4...Te6	2.89	0.013	0.026	-8.2	0.88
	O7-H8...Te2	2.47	0.026	0.029	-20.4	0.76
FTe-ClTe	C1-H4...Te6	2.89	0.013	0.026	-8.1	0.89
	O7-H8...Te2	2.48	0.026	0.030	-19.7	0.76
FTe-BrTe	C1-H4...Te6	2.89	0.013	0.026	-8.1	0.89
	O7-H8...Te2	2.48	0.026	0.030	-19.9	0.76
FTe-CH₃Te	C1-H4...Te6	2.88	0.013	0.027	-8.5	0.88
	O7-H8...Te2	2.53	0.023	0.031	-17.5	0.78
FTe-NH₂Te	C1-H4...Te6	2.82	0.014	0.029	-9.4	0.87

Table S2. The maximum electrostatic potential ($V_{s,max}$) (kJ.mol⁻¹) and minimum electrostatic potential ($V_{s,min}$) (kJ.mol⁻¹) in XCHZ and RCZOH monomer with X= H, F; R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te

	HCOOH	FCOOH	CICOOH	BrCOOH	CH ₃ COOH	NH ₂ COOH
$V_{s,max}$ (kJ.mol ⁻¹)	246.1	306.4	287.5	284.4	224.1	227.9
$V_{s,min}$ (kJ.mol ⁻¹)	-144.6	-121.4	-120.8	-118.9	-157.1	-172.1
	HCSOH	FCSOH	CICSOH	BrCSOH	CH ₃ CSOH	NH ₂ CSOH
$V_{s,max}$ (kJ.mol ⁻¹)	242.5	299.3	274.1	269.9	224.2	226.1
$V_{s,min}$ (kJ.mol ⁻¹)	-86.5	-78.1	-76.6	-75.3	-93.7	-104.5
	HcSeOH	FcSeOH	CICSeOH	BrCSeOH	CH ₃ CSeOH	NH ₂ CSeOH
$V_{s,max}$ (kJ.mol ⁻¹)	243.8	299.8	271.6	267.3	225.8	227.7
$V_{s,min}$ (kJ.mol ⁻¹)	-83.9	-77.0	-75.9	-75.1	-91.1	-102.5
	HCTeOH	FTeOH	CICTeOH	BrCTeOH	CH ₃ CTeOH	NH ₂ CTeOH
$V_{s,max}$ (kJ.mol ⁻¹)	243.6	298.1	267.6	262.7	226.7	244.3
$V_{s,min}$ (kJ.mol ⁻¹)	-79.0	-73.6	-72.7	-71.9	-85.5	-96.8
	HCHO	HCHS	HCHSe	HCHTe		
$V_{s,max}$ (kJ.mol ⁻¹)	130.8	114.9	116.0	111.0		
$V_{s,min}$ (kJ.mol ⁻¹)	-146.6	-88.7	-84.8	-78.9		
	FCHO	FCHS	FCHSe	FCHTe		
$V_{s,max}$ (kJ.mol ⁻¹)	179.0	160.7	159.5	153.4		
$V_{s,min}$ (kJ.mol ⁻¹)	-117.0	-74.6	-73.1	-69.7		

Table S3. The NBO charge of H4, H8, Z2, and Z6 atoms in XZ-RZ complexes with X= H, F; R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te

	HO-HO	HO-FO	HO-CIO	HO-BrO	HO-CH ₃ O	HO-NH ₂ O
q(H8)	0.505	0.516	0.514	0.513	0.508	0.512
q(Z6)	-0.628	-0.627	-0.600	-0.600	-0.644	-0.692
q(H4)	0.158	0.157	0.155	0.155	0.159	0.163
q(Z2)	-0.546	-0.548	-0.546	-0.545	-0.546	-0.548
	HS-HS	HS-FS	HS-CIS	HS-BrS	HS-CH ₃ S	HS-NH ₂ S
q(H8)	0.486	0.498	0.493	0.491	0.492	0.500
q(Z6)	-0.153	-0.181	-0.092	-0.078	-0.167	-0.302
q(H4)	0.212	0.213	0.211	0.211	0.213	0.218
q(Z2)	0.052	0.060	0.063	0.065	0.049	0.044
	HSe-HSe	HSe-FSe	HSe-CISe	HSe-BrSe	HSe-CH ₃ Se	HSe-NH ₂ Se
q(H8)	0.479	0.491	0.487	0.484	0.487	0.495
q(Z6)	-0.093	-0.135	-0.032	-0.015	-0.110	-0.272
q(H4)	0.212	0.213	0.211	0.211	0.213	0.218
q(Z2)	0.150	0.161	0.165	0.167	0.147	0.141
	HTe-HTe	HTe-FTe	HTe-CITe	HTe-BrTe	HTe-CH ₃ Te	HTe-NH ₂ Te
q(H8)	0.472	0.482	0.478	0.475	0.480	0.488
q(Z6)	0.000	-0.064	0.059	0.083	-0.025	-0.229
q(H4)	0.207	0.209	0.206	0.206	0.209	0.213
q(Z2)	0.297	0.314	0.317	0.319	0.296	0.290
	FO-HO	FO-FO	FO-CIO	FO-BrO	FO-CH ₃ O	FO-NH ₂ O
q(H8)	0.508	0.519	0.517	0.516	0.509	0.514
q(Z6)	-0.628	-0.628	-0.602	-0.603	-0.646	-0.695
q(H4)	0.159	0.158	0.156	0.156	0.160	0.166
q(Z2)	-0.563	-0.568	-0.565	-0.564	-0.561	-0.564
	FS-HS	FS-FS	FS-CIS	FS-BrS	FS-CH ₃ S	FS-NH ₂ S
q(H8)	0.491	0.504	0.500	0.497	0.496	0.504
q(Z6)	-0.148	-0.177	-0.088	-0.075	-0.163	-0.298
q(H4)	0.194	0.196	0.194	0.193	0.196	0.201
q(Z2)	-0.007	-0.002	0.001	0.003	-0.009	-0.015
	FSe-HSe	FSe-FSe	FSe-CISe	FSe-BrSe	FSe-CH ₃ Se	FSe-NH ₂ Se
q(H8)	0.485	0.498	0.494	0.491	0.492	0.500
q(Z6)	-0.088	-0.130	-0.029	-0.011	-0.106	-0.268
q(H4)	0.193	0.195	0.192	0.192	0.195	0.200
q(Z2)	0.073	0.080	0.084	0.086	0.070	0.062
	FTe-HTe	FTe-FTe	FTe-CITe	FTe-BrTe	FTe-CH ₃ Te	FTe-NH ₂ Te
q(H8)	0.478	0.490	0.486	0.483	0.485	0.494

q(Z6)	0.006	-0.059	0.063	0.086	-0.020	-0.224
q(H4)	0.184	0.186	0.184	0.183	0.186	0.191
q(Z2)	0.193	0.205	0.209	0.210	0.190	0.182

Table S4a. The extrapolated HF total energies E_{CBS}^{HF} (a.u.), CCSD(T) correlation energies E_{CBS}^{corr} (au), the CCSD(T) total energies extrapolated at the CBS limit $E_{CBS}^{CCSD(T)}$ (au), interaction energies extrapolated at the CBS limit ΔE_{CBS}^* (kJ.mol⁻¹), and parameters of CBS extrapolation (α , B) for the structures involved in the **XO-HO**, **XO-FO**, and **XO-NH₂O** (with X= H, F)

	E_{CBS}^{HF} (a.u)	E_{CBS}^{corr} (a.u)	$E_{CBS}^{CCSD(T)}$ (a.u)	ΔE_{CBS}^* (kJ.mol ⁻¹)	$\alpha^{(i)}$	$B^{(i)}$
HO-HO	-794825.0	-3117.0	-797942.0	-36.4	1.33	3948.88
HO-FO	-1054567.0	-3823.8	-1058390.7	-43.5	1.35	5544.40
HO-NH₂O	-939415.3	-3735.8	-640355.8	-37.5	1.32	4535.75
FO-HO	-1054585.9	-3829.6	-1058415.4	-32.1	1.35	5539.86
FO-FO	-1314323.9	-4538.9	-1318862.8	-37.8	1.36	7265.11
FO-NH₂O	-1199179.1	-4448.7	-1203627.7	-36.4	1.33	6075.88

⁽ⁱ⁾ Parameters of CBS exponential extrapolation in the form of $E^{HF}(X) = E_{CBS}^{HF} + B \cdot \exp(-\alpha X)$, for the Hartree-Fock total energies calculated at HF/aug-cc-pVnZ (n = 2 for DZ, n = 3 for TZ, and n = 4 for QZ) level of theory.

Table S4b. The extrapolated HF total energies E_{CBS}^{HF} (au), CCSD(T) correlation energies E_{CBS}^{corr} (au), the CCSD(T) total energies extrapolated at the CBS limit $E_{CBS}^{CCSD(T)}$ (au), and parameters of CBS extrapolation (α , B) for the **XCHO**, and **RCOOH** monomers (with X= H, F; R= H, F, NH₂)

	E_{CBS}^{HF} (a.u)	E_{CBS}^{corr} (a.u)	$E_{CBS}^{CCSD(T)}$ (a.u)	$\alpha^{(i)}$	$B^{(i)}$
HCHO	-299036.3	-1205.4	-300241.7	1.35	1549.98
FCHO	-558797.2	-1922.2	-560719.4	1.36	3122.33
HCOOH	-495766.3	-1897.6	-497663.9	1.32	2418.50
FCOOH	-755501.3	-2604.2	-758105.5	1.34	4013.27
NH₂COOH	-640355.8	-2516.1	-642871.9	1.32	3017.81

⁽ⁱ⁾ Parameters of CBS exponential extrapolation in the form of $E^{HF}(X) = E_{CBS}^{HF} + B \cdot \exp(-\alpha X)$, for the Hartree-Fock total energies calculated at HF/aug-cc-pVnZ (n = 2 for DZ, n = 3 for TZ, and n = 4 for QZ) level of theory.

The HF total energy [$E^{HF}(X)$] from CBS exponential extrapolation at HF/aug-cc-pVnZ (n = 2, 3, 4) in the form:

$$E^{HF}(X) = E_{CBS}^{HF} + B \cdot \exp(-\alpha X),$$

in which, the E_{CBS}^{HF} is the HF total energy at the CBS limit.

The CCSD(T) total energies extrapolated at the CBS limit $E_{CBS}^{CCSD(T)}$ in the form:

$$E_{CBS}^{CCSD(T)} = E_{CBS}^{HF} + E_{CBS}^{corr},$$

in which, the correlation energy at CCSD(T)/aug-cc-pVnZ is fitted with the expression of the power form:

$$E^{corr}(X) = E_{CBS}^{corr} + A \cdot X^{-3}$$

The two-point fitting scheme for n = 2 and n = 3 and eliminating the fitting parameter A, the CCSD(T) correlation energy at the CBS limit can be obtained by the expression:

$$E_{CBS}^{corr} = \frac{E^{corr}(DZ) \cdot 2^3 - E^{corr}(TZ) \cdot 3^3}{2^3 - 3^3}$$

in which, the CCSD(T) correlation energies are obtained using the two basis sets aug-cc-pVDZ and aug-cc-pVTZ on the MP2/aug-cc-pVTZ geometries:

$$E^{corr}(DZ) = E^{CCSD(T)}(DZ) - E^{HF}(DZ); E^{corr}(TZ) = E^{CCSD(T)}(TZ) - E^{HF}(TZ)$$

Table S5. The percentage contribution of energy components to the stability of **XZ-RZ** complexes with X= H, F; R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te at def2-TZVPD basis set

Complex	%eles	%disp	%ind	Complex	%eles	%disp	%ind
HO-HO	51.2	17.0	31.9	FO-HO	52.0	17.9	30.0
HO-FO	51.2	15.9	32.9	FO-FO	51.5	17.3	31.2
HO-ClO	50.4	16.3	33.2	FO-ClO	50.6	17.8	31.6
HO-BrO	50.0	16.4	33.6	FO-BrO	50.2	17.9	32.0
HO-CH₃O	51.2	17.6	31.2	FO-CH₃O	52.3	18.4	29.3

HO-NH ₂ O	51.5	17.4	31.1	FO-NH ₂ O	53.0	18.0	29.1
HS-HS	40.2	19.8	40.0	FS-HS	39.7	20.8	39.4
HS-FS	40.0	18.8	41.2	FS-FS	39.0	20.1	40.9
HS-ClS	39.4	19.4	41.2	FS-ClS	38.5	20.7	40.8
HS-BrS	39.1	19.4	41.5	FS-BrS	38.1	20.8	41.1
HS-CH ₃ S	40.2	20.3	39.5	FS-CH ₃ S	40.0	21.2	38.8
HS-NH ₂ S	40.6	19.9	39.4	FS-NH ₂ S	40.8	20.6	38.6
HSe-HSe	35.4	18.8	45.8	FSe-HSe	34.9	19.6	45.6
HSe-FSe	35.6	18.3	46.1	FSe-FSe	34.7	19.3	46.1
HSe-ClSe	34.7	18.7	46.6	FSe-ClSe	33.9	19.7	46.4
HSe-BrSe	34.8	18.5	46.7	FSe-BrSe	33.9	19.5	46.6
HSe-CH ₃ Se	35.0	19.2	45.8	FSe-CH ₃ Se	34.7	19.9	45.3
HSe-NH ₂ Se	35.5	18.9	45.6	FSe-NH ₂ Se	35.6	19.4	45.0
HTe-HTe	46.0	0.2	53.8	FTe-HTe	46.0	0.3	53.8
HTe-FTe	46.0	0.5	53.4	FTe-FTe	45.7	0.6	53.6
HTe-ClTe	46.1	0.4	53.5	FTe-ClTe	45.7	0.4	53.9
HTe-BrTe	46.2	0.3	53.5	FTe-BrTe	46.1	0.4	53.5
HTe-CH ₃ Te	46.2	0.4	53.4	FTe-CH ₃ Te	46.0	0.5	53.5
HTe-NH ₂ Te	45.7	0.5	53.8	FTe-NH ₂ Te	45.7	0.7	53.6

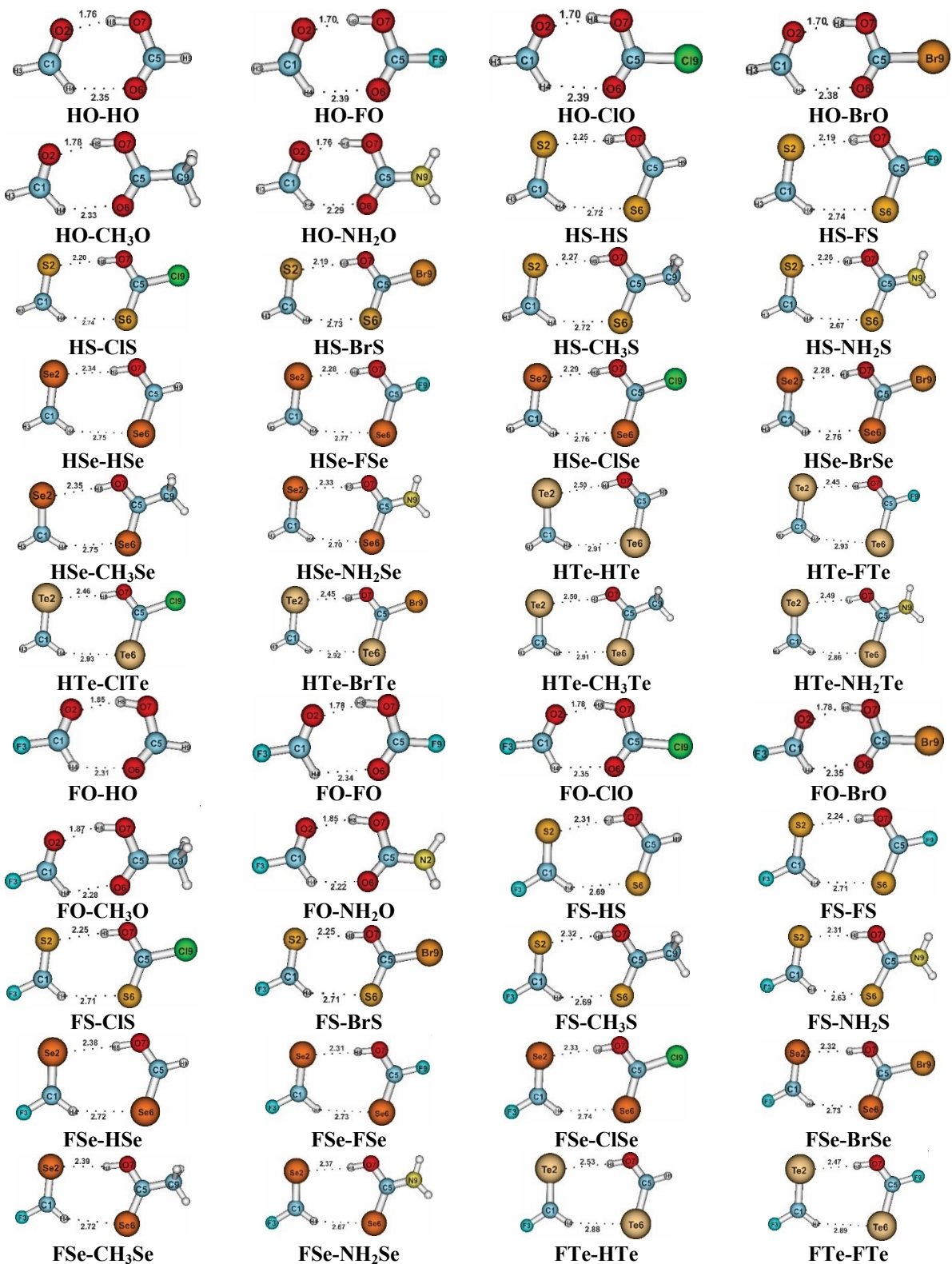
Table S6a. Change in bond lengths and stretching frequencies of O-H and C_{sp2}-H bonds in HZ-RZ complexes, with R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te

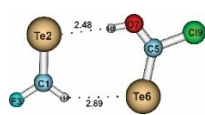
Complex	HO-HO	HO-FO	HO-ClO	HO-BrO	HO-CH ₃ O	HO-NH ₂ O
$\Delta r(C_{sp2}-H)$	-0.0051	-0.0058	-0.0056	-0.0055	-0.0052	-0.0059
$\Delta r(O-H)$	0.0186	0.0240	0.0237	0.0240	0.0169	0.0182
$\Delta \nu(C_{sp2}-H)$	78.5	86.9	83.5	82.5	79.5	81.0
$\Delta \nu(O-H)$	-375.4	-481.4	-473.3	-477.9	-342.8	-373.0
Complex	HS-HS	HS-FS	HS-ClS	HS-BrS	HS-CH ₃ S	HS-NH ₂ S
$\Delta r(C_{sp2}-H)$	0.0002	-0.0011	-0.0007	-0.0006	0.0001	0.0001
$\Delta r(O-H)$	0.0166	0.0224	0.0214	0.0218	0.0153	0.0161
$\Delta \nu(C_{sp2}-H)$	1.4	19.5	13.8	12.0	2.6	2.8
$\Delta \nu(O-H)$	-346.5	-472.7	-444.7	-451.7	-318.8	-342.2
Complex	HSe-HSe	HSe-FSe	HSe-ClSe	HSe-BrSe	HSe-CH ₃ Se	HSe-NH ₂ Se
$\Delta r(C_{sp2}-H)$	0.0013	-0.0001	0.0003	0.0004	0.0011	0.0013
$\Delta r(O-H)$	0.0181	0.0242	0.0228	0.0233	0.0169	0.0178
$\Delta \nu(C_{sp2}-H)$	-15.9	3.2	-2.4	-4.8	-14.0	-15.6
$\Delta \nu(O-H)$	-373.8	-509.0	-473.2	-479.9	-349.9	-375.3
Complex	HTe-HTe	HTe-FTe	HTe-ClTe	HTe-BrTe	HTe-CH ₃ Te	HTe-NH ₂ Te
$\Delta r(C_{sp2}-H)$	0.0029	0.0017	0.0020	0.0021	0.0027	0.0031
$\Delta r(O-H)$	0.0187	0.0256	0.0238	0.0241	0.0185	0.0197
$\Delta \nu(C_{sp2}-H)$	-40.3	-24.4	-29.0	-34.6	-38.3	-42.7
$\Delta \nu(O-H)$	-386.9	-535.4	-490.8	-491.4	-382.3	-414.6

Table S6b. Change in bond lengths and stretching frequencies of O-H and C_{sp2}-H bonds in FZ-RZ complexes, with R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te

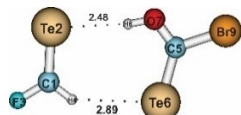
Complex	FO-HO	FO-FO	FO-ClO	FO-BrO	FO-CH ₃ O	FO-NH ₂ O
$\Delta r(C_{sp2}-H)$	-0.0017	-0.0020	-0.0019	-0.0019	-0.0018	-0.0018
$\Delta r(O-H)$	0.0114	0.0157	0.0149	0.0149	0.0102	0.0112
$\Delta \nu(C_{sp2}-H)$	32.9	37.8	35.7	35.0	34.2	34.8
$\Delta \nu(O-H)$	-228.1	-313.4	-296.9	-296.2	-206.5	-230.5
Complex	FS-HS	FS-FS	FS-ClS	FS-BrS	FS-CH ₃ S	FS-NH ₂ S
$\Delta r(C_{sp2}-H)$	0.0010	0.0000	0.0002	0.0003	0.0009	0.0012
$\Delta r(O-H)$	0.0120	0.0170	0.0158	0.0160	0.0110	0.0117
$\Delta \nu(C_{sp2}-H)$	-10.4	4.0	0.6	-0.9	-9.6	-12.3
$\Delta \nu(O-H)$	-252.6	-362.2	-331.4	-334.8	-231.0	-251.5
Complex	FSe-HSe	FSe-FSe	FSe-ClSe	FSe-BrSe	FSe-CH ₃ Se	FSe-NH ₂ Se
$\Delta r(C_{sp2}-H)$	0.0021	0.0010	0.0012	0.0013	0.0020	0.0023
$\Delta r(O-H)$	0.0141	0.0195	0.0180	0.0183	0.0131	0.0139
$\Delta \nu(C_{sp2}-H)$	-27.2	-11.3	-14.2	-15.8	-25.7	-30.5
$\Delta \nu(O-H)$	-293.5	-413.6	-376.5	-380.9	-273.0	-294.8
Complex	FTe-HTe	FTe-FTe	FTe-ClTe	FTe-BrTe	FTe-CH ₃ Te	FTe-NH ₂ Te
$\Delta r(C_{sp2}-H)$	0.0029	0.0020	0.0021	0.0021	0.0028	0.0033

$\Delta r(\text{O-H})$	0.0157	0.0218	0.0202	0.0204	0.0153	0.0163
$\Delta v(\text{C}_{\text{sp}^2}\text{-H})$	-42.6	-29.1	-30.2	-31.7	-41.0	-48.2
$\Delta v(\text{O-H})$	-325.8	-459.2	-419.0	-421.0	-318.0	-345.8

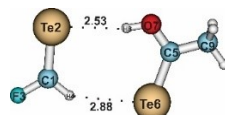




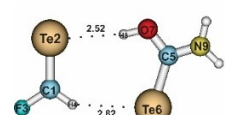
FTe-CITe



FTe-BrTe

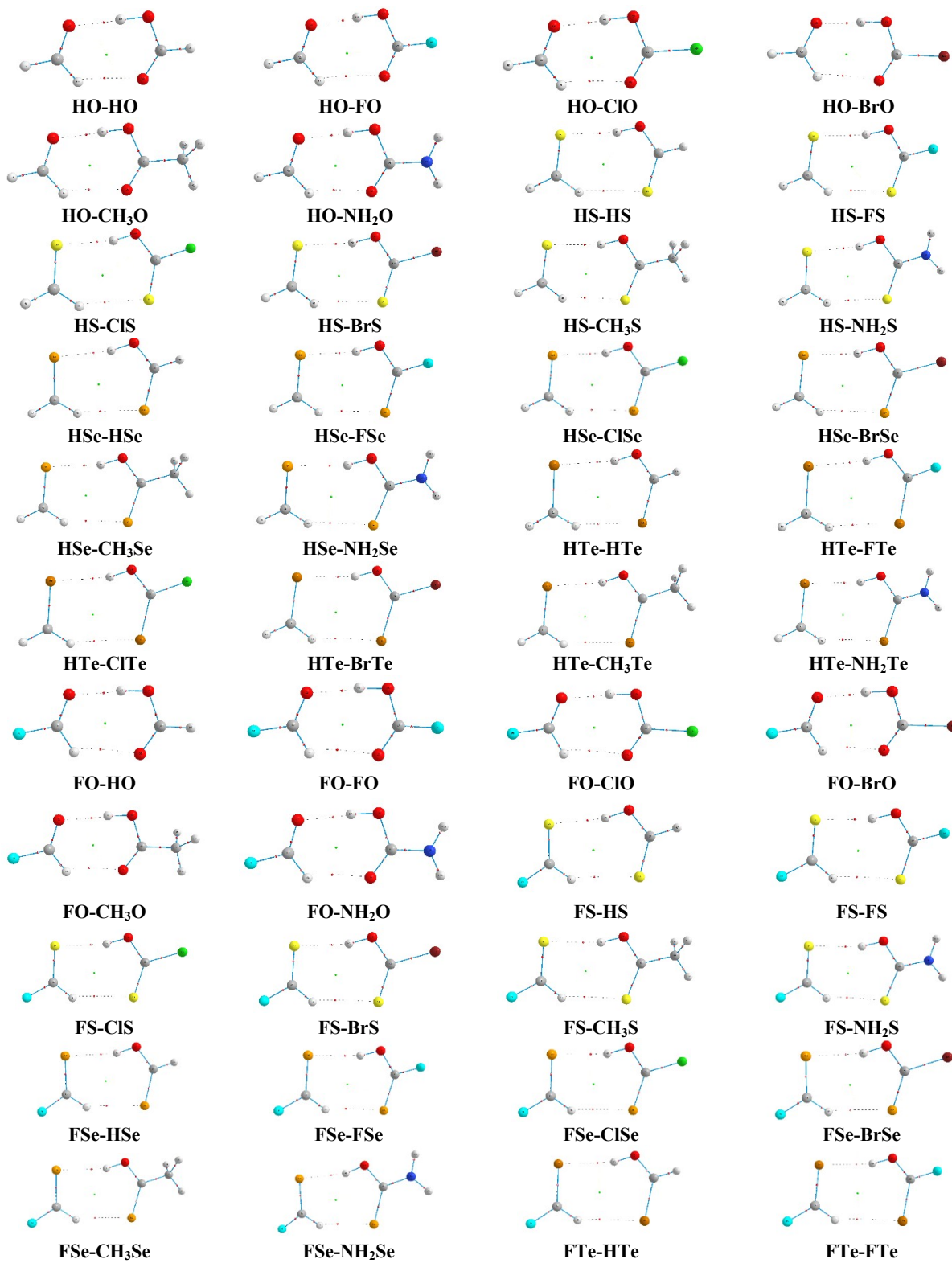


FTe-CH₃Te



FTe-NH₂Te

Figure S1. The stable geometrical structures of $XZ-RZ$ complexes, with $X = H, F$; $R = H, F, Cl, Br, CH_3, NH_2$; $Z = O, S, Se, Te$



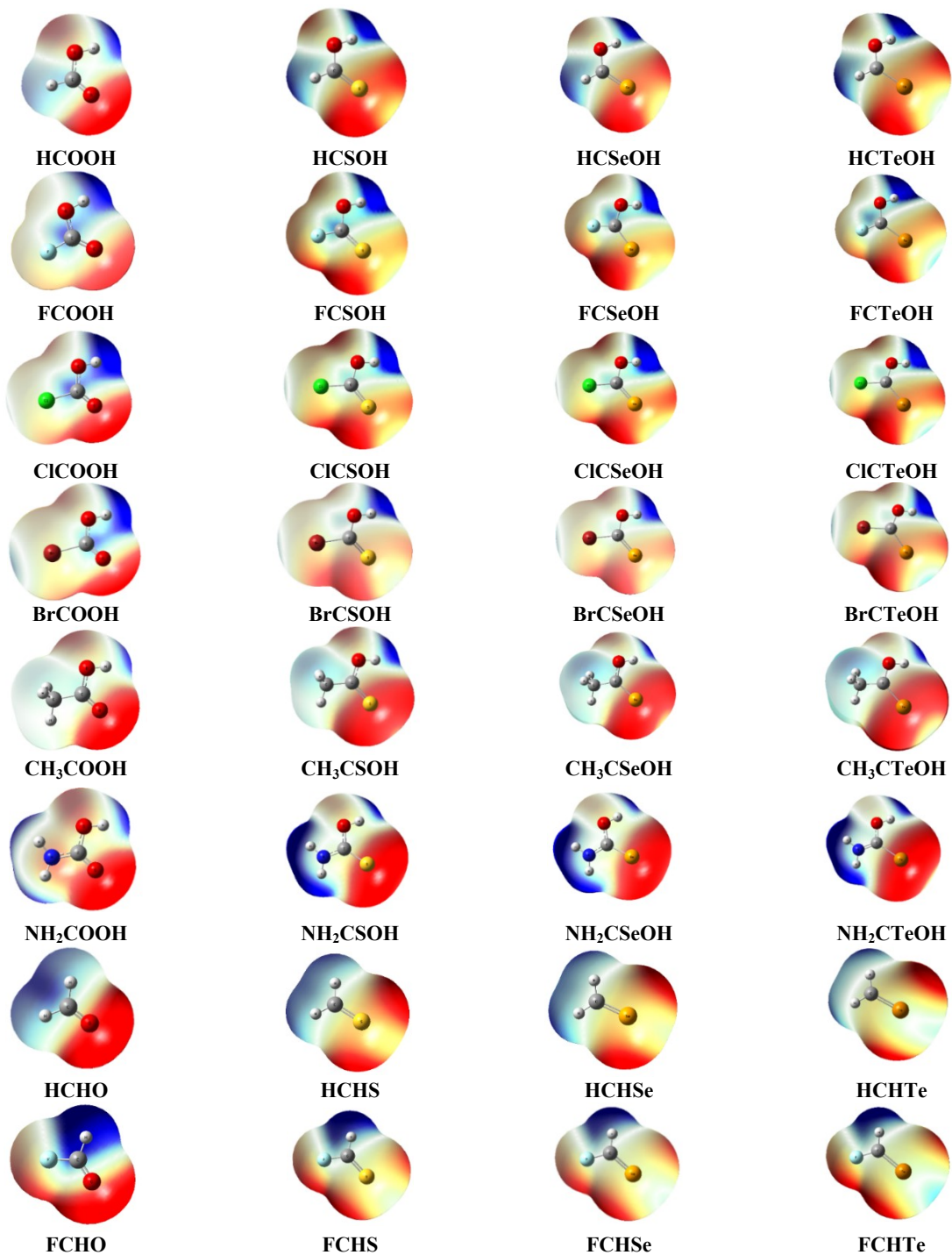
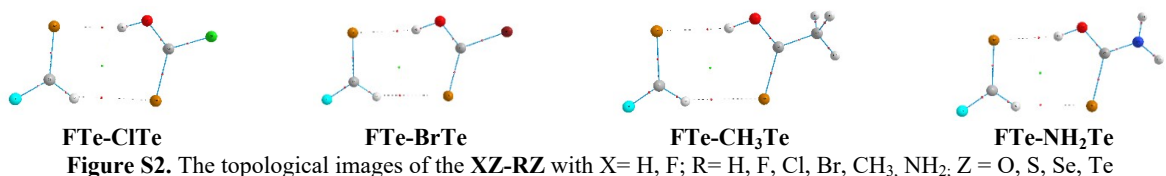


Figure S3. Molecular Electrostatic Potential (MEP) surface of XCHZ and RCZOH monomers with X= H, F; R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te

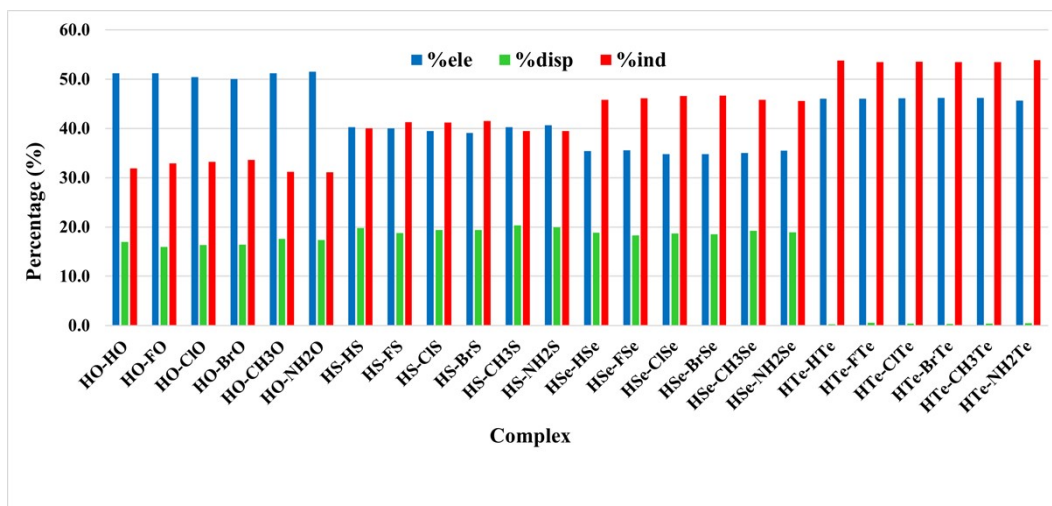


Figure S4a. The percentage contribution (%) of energy components to the stability of **HZ-RZ** at def2-TZVPD level, with R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te

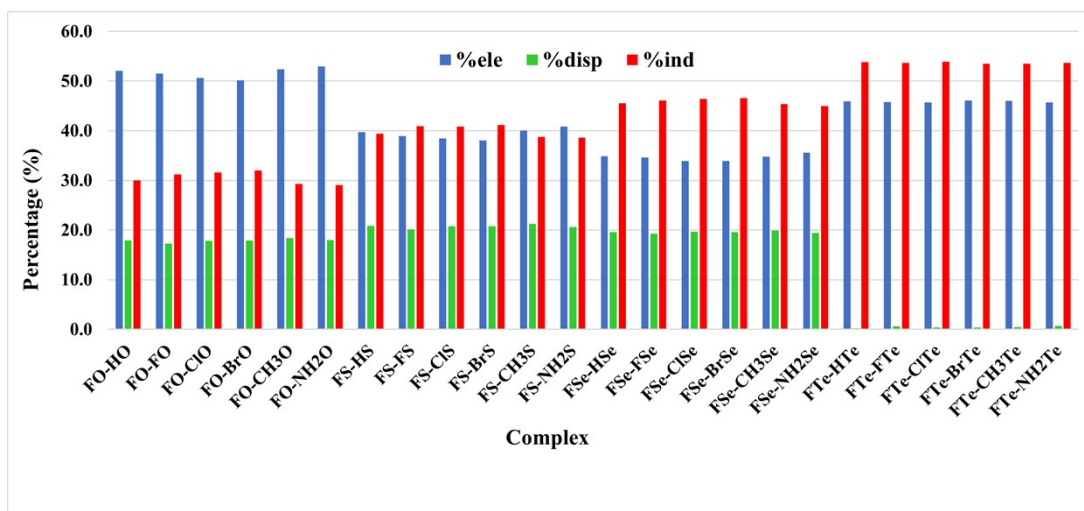
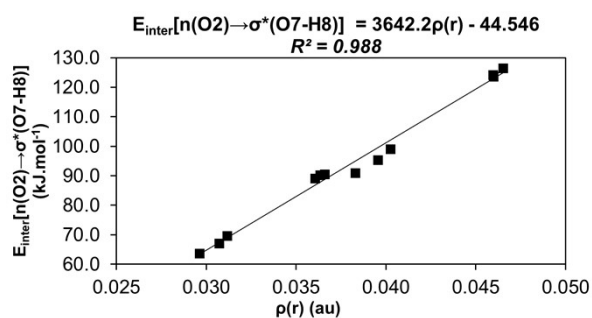
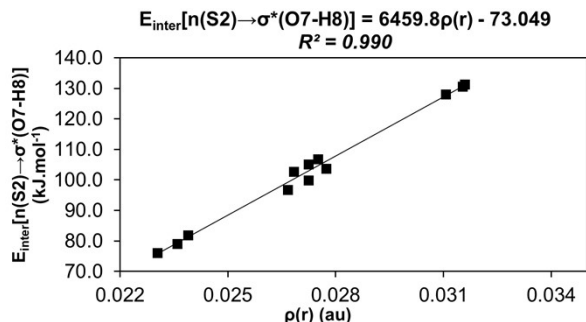


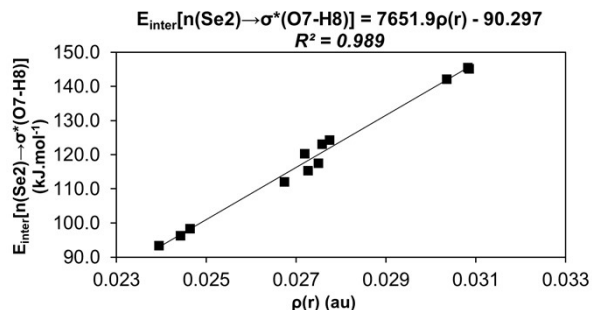
Figure S4b. The percentage contribution (%) of energy components to the stability of **FZ-RZ** at def2-TZVPD level, with R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te



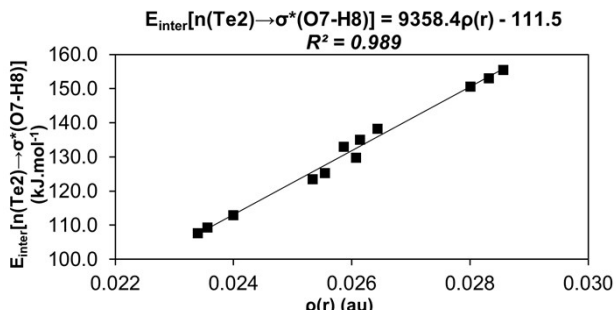
XO-RO



XS-RS

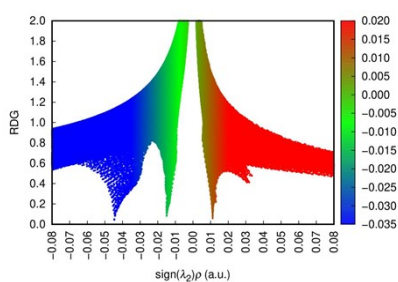


XSe-RSe

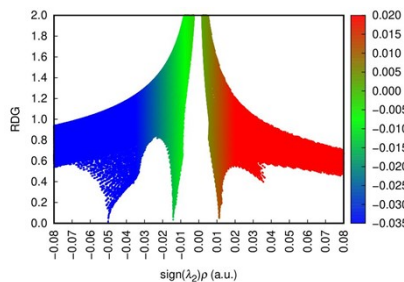
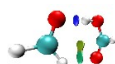


XTe-RTe

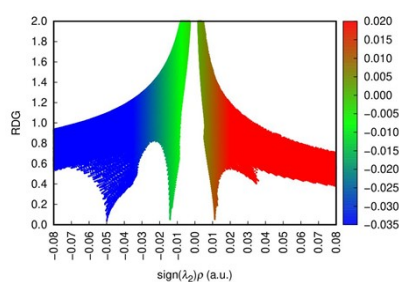
Figure S5. The linear correlation between the intermolecular electron transfer ($E_{\text{inter}}[\text{n}(Z2) \rightarrow \sigma^*(\text{O}7\text{-H}8)]$, kJ.mol⁻¹) and electron density ($\rho(r)$, au) at BCPs of O-H...Z hydrogen bonds in **XZ-RZ** (X= H, F; R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te)



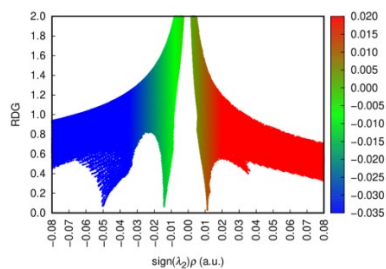
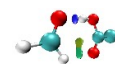
HO-HO



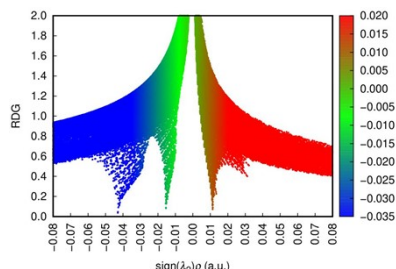
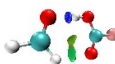
HO-FO



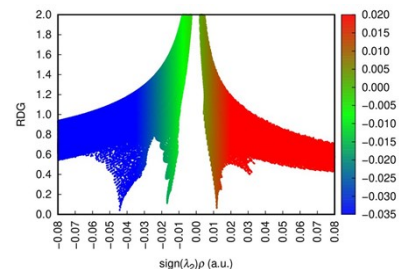
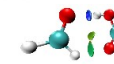
HO-ClO



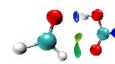
HO-BrO

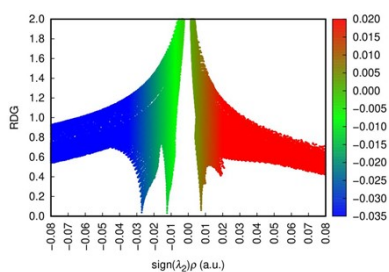


HO-CH₃O

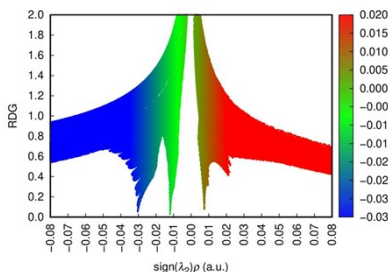


HO-NH₂O

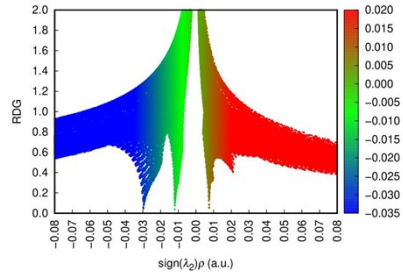




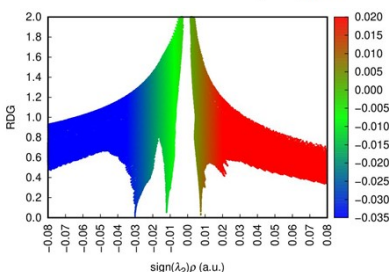
HS-HS



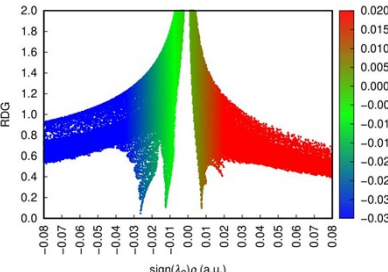
HS-FS



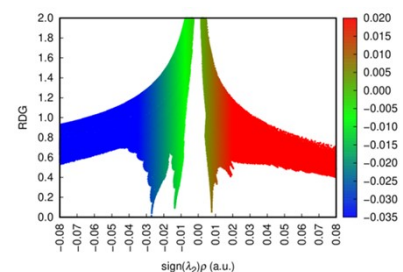
HS-CIS



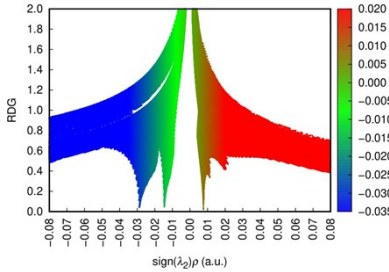
HS-BrS



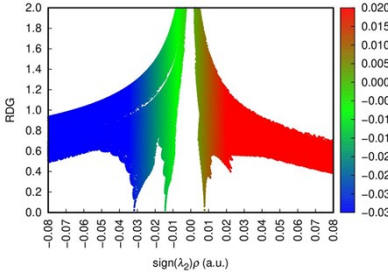
HS-CH₃S



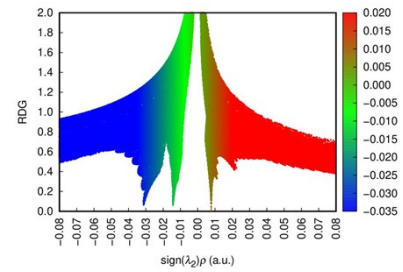
HS-NH₂S



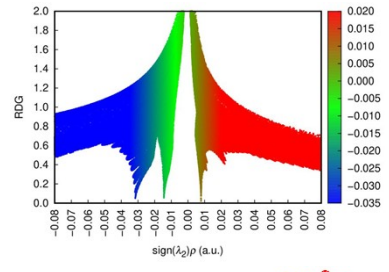
HSe-HSe



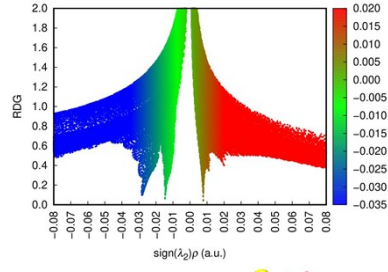
HSe-FSe



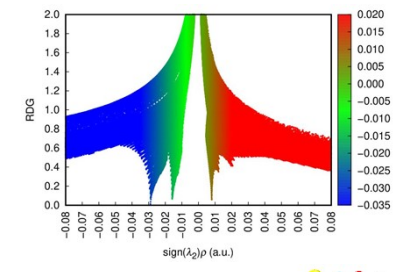
HSe-CISe



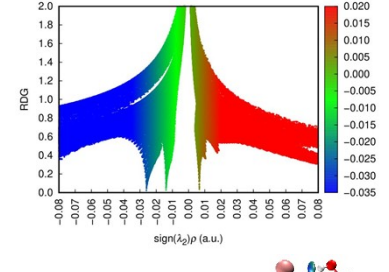
HSe-BrSe



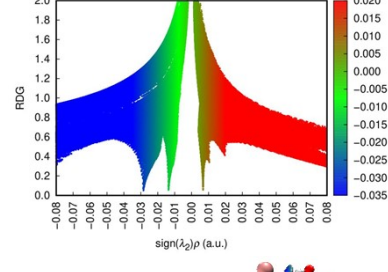
HSe-CH₃Se



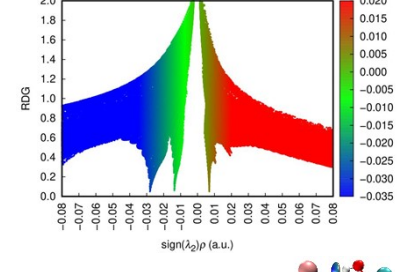
HSe-NH₂Se



HTe-HTe



HTe-FTe



HTe-CITe

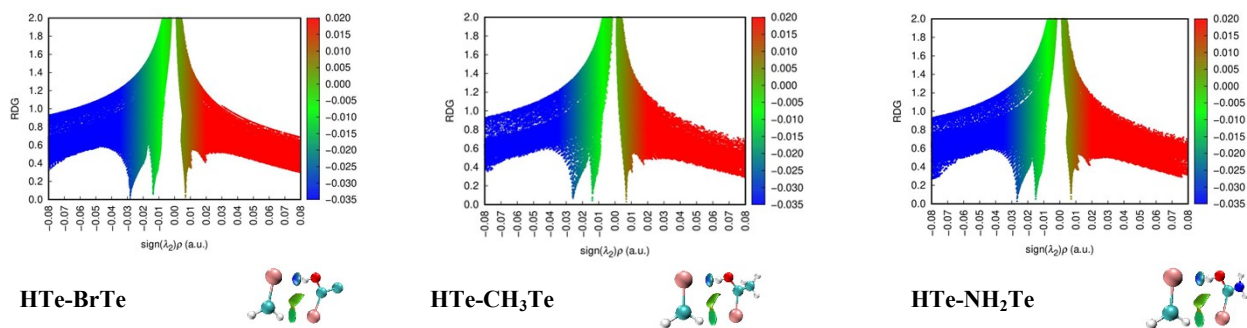
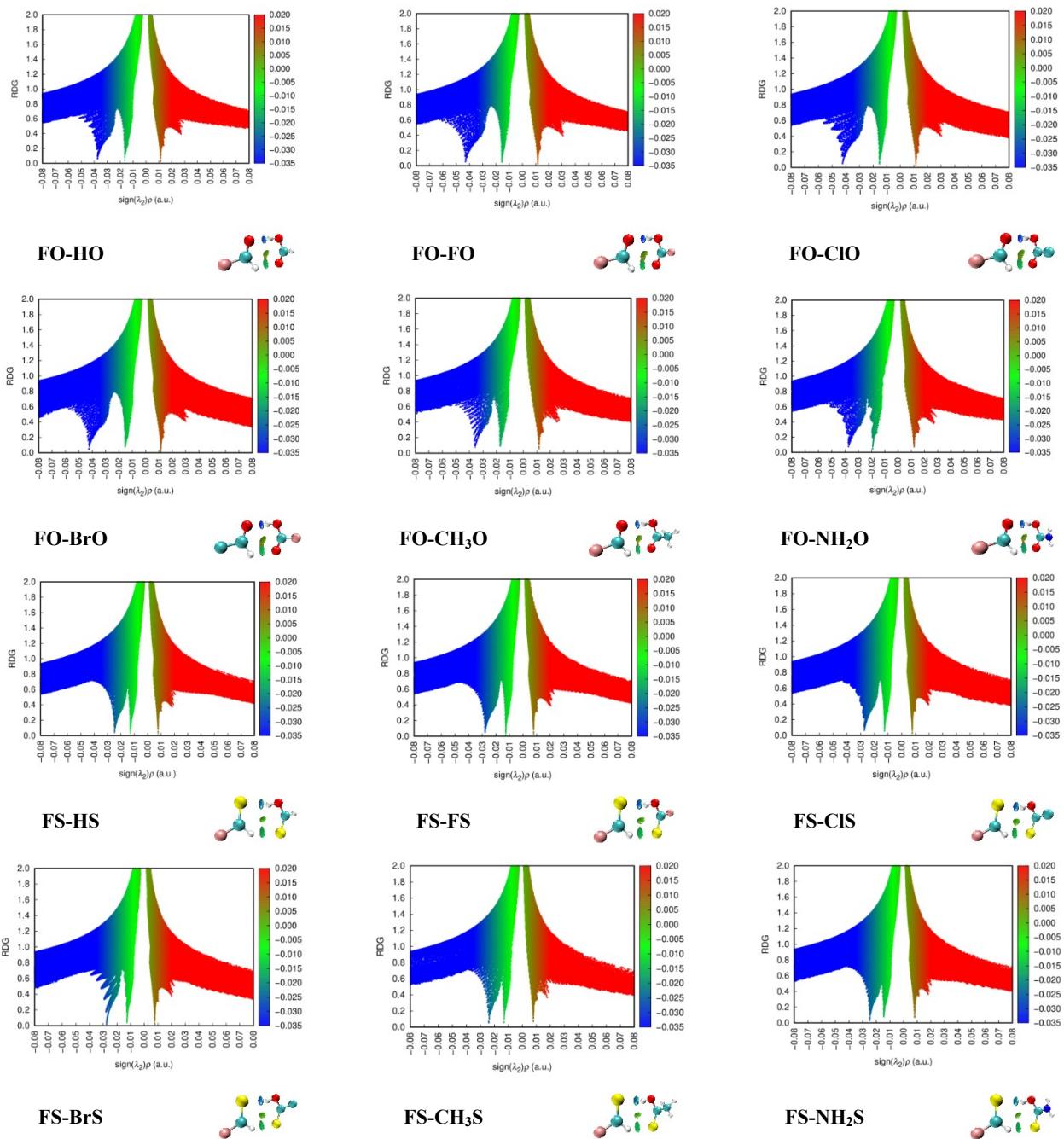


Figure S6a. Plots of the reduced density gradient (s, au) versus the electron density multiplied by the sign of the second Hessian eigenvalue ($\text{sign}(\lambda_2)\rho$, au) for the **HZ-RZ** complexes (R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te)



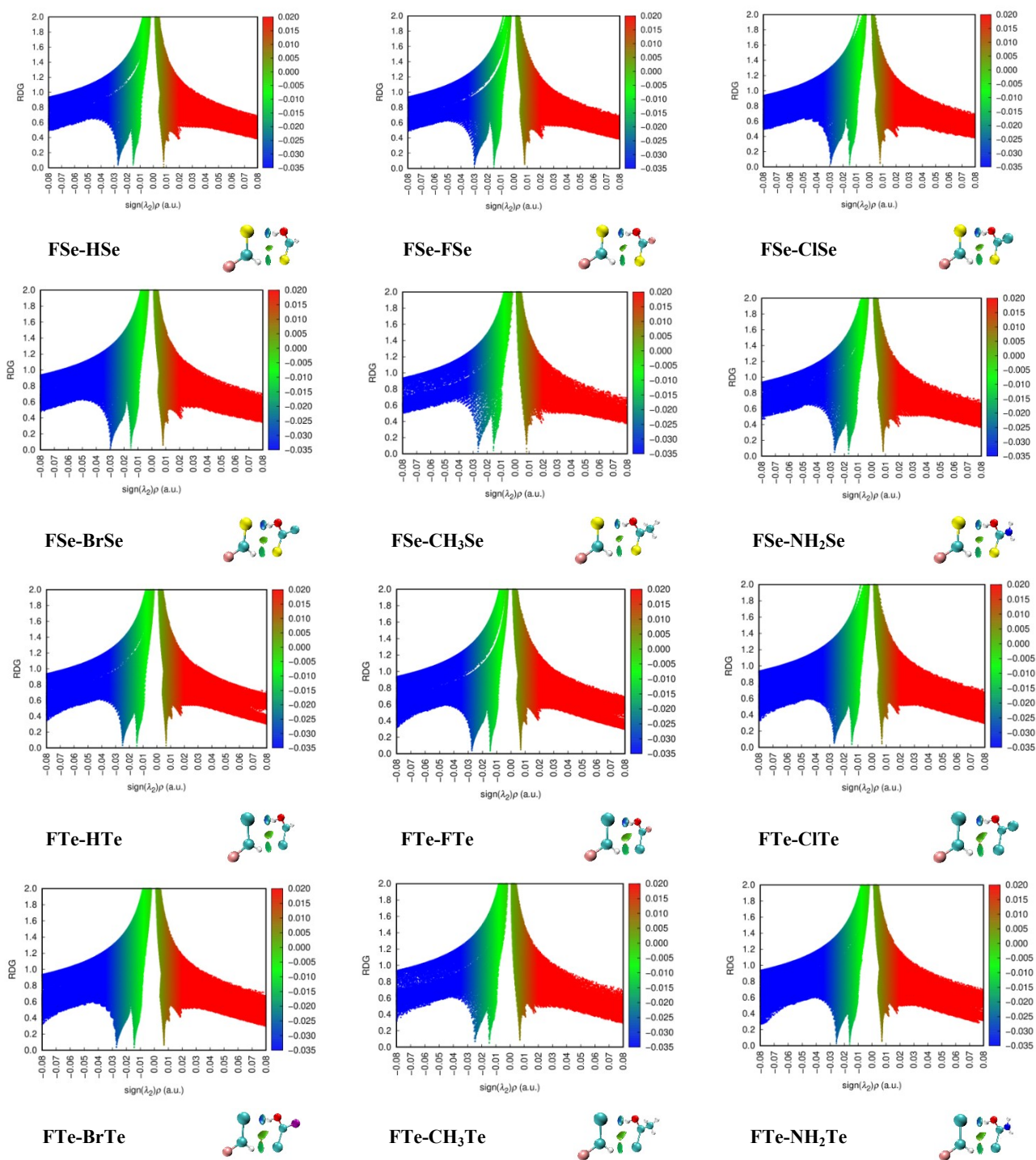


Figure S6b. Plots of the reduced density gradient (s, au) versus the electron density multiplied by the sign of the second Hessian eigenvalue ($\text{sign}(\lambda_2)\rho$, au) for the FZ-RZ complexes (R= H, F, Cl, Br, CH₃, NH₂; Z= O, S, Se, Te)