Supporting Information

Role of O–H···O/S conventional hydrogen bonds in considerable C_{sp2}–H blue-shift in the binary systems of acetaldehyde and thioacetaldehyde with the substituted carboxylic and thiocarboxylic acids

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Table S1. Intermolecular parameters (r: distances in *Å*, θ: angles in °, q: NBO charge in *e*) in the binary systems formed between CH_3CHZ and RCZOH (R = CH_3, H, F; Z = O, S) at MP2/6–311++G(3df,2pd)

Complex	r(H···Z) (*Å*)		θ (°)		q (*e*)			
	O–H···Z7	C_{sp2}–H···Z2	∠O-H-Z	∠C_{sp2}-H-Z	Z2	H[a)]	Z7	H[b)]
CH_3O–O	1.747	2.337	179.5	130.3	-0.621	0.502	-0.546	0.139
CH_3S–O	1.720	2.826	170.2	128.2	-0.119	0.507	-0.544	0.128
HO–O	1.727	2.359	179.7	130.4	-0.607	0.500	-0.547	0.138
HS–O	1.706	2.837	171.5	129.1	-0.115	0.502	-0.545	0.127
FO–O	1.666	2.389	179.0	127.9	-0.615	0.510	-0.550	0.138
FS–O	1.639	2.846	172.2	127.5	-0.148	0.516	-0.547	0.131
CH_3O–S	2.265	2.233	177.9	146.7	-0.613	0.482	0.067	0.207
CH_3S–S	2.246	2.718	167.7	145.1	-0.098	0.485	0.082	0.195
HO–S	2.242	2.252	178.8	146.8	-0.598	0.478	0.070	0.205
HS–S	2.228	2.722	169.2	150.0	-0.093	0.478	0.084	0.194
FO–S	2.180	2.282	179.8	143.6	-0.607	0.486	0.079	0.205
FS–S	2.164	2.741	170.1	143.7	-0.126	0.490	0.093	0.195

[a)]For H of –OH group of RCZOH in the complexes; [b)]For H of –CHZ group of CH_3CHZ in the complexes

Table S2. Selected parameters at the BCPs of intermolecular contacts at MP2/6-311++G(3df,2pd)

Complex	$\rho(r_C)$, in *au*		$\nabla^2\rho(r_C)$, in *au*		$H(r_C)$[a)], in *au*		E_{HB}[b)], in *kJ.mol^{-1}*		Comparison values
	O–H···Z7	C_{sp2}–H···Z2	(1)	(2)	(1)	(2)	(1)	(2)	
CH_3O–O	0.0405	0.0130	0.097	0.045	-0.0073	0.0012	-51.0	-11.4	**2.1**$^{(1)}$
CH_3S–O	0.0428	0.0102	0.100	0.027	-0.0084	0.0008	-55.0	-6.8	**2.2**$^{(1)}$
HO–O	0.0427	0.0125	0.098	0.042	-0.0084	0.0011	-54.5	-10.9	**2.1**$^{(1)}$
HS–O	0.0444	0.0099	0.101	0.027	-0.0094	0.0008	-57.7	-6.5	**2.2**$^{(1)}$
FO–O	0.0494	0.0115	0.103	0.040	-0.0124	0.0012	-66.6	-10.2	**2.2**$^{(1)}$
FS–O	0.0521	0.0096	0.105	0.027	-0.0142	0.0009	-71.8	-6.4	**2.3**$^{(1)}$
CH_3O–S	0.0264	0.0150	0.046	0.053	-0.0034	0.0015	-23.9	-13.5	**1.7**$^{(2)}$
CH_3S–S	0.0276	0.0118	0.046	0.031	-0.0039	0.0008	-25.2	-8.1	**1.7**$^{(2)}$
HO–S	0.0278	0.0145	0.046	0.051	-0.0040	0.0014	-25.6	-13.0	**1.6**$^{(2)}$
HS–S	0.0283	0.0121	0.046	0.030	-0.0040	0.0007	-25.7	-8.1	**1.7**$^{(2)}$
FO–S	0.0319	0.0133	0.045	0.048	-0.0060	0.0015	-30.5	-11.9	**1.6**$^{(2)}$
FS–S	0.0330	0.0110	0.044	0.030	-0.0065	0.0009	-31.7	-7.6	**1.6**$^{(2)}$

[a)] the total electron energy density; [b)] individual energy of each hydrogen bond; [(1)]for O–H···Z7 and [(2)]for C_{sp2}–H···Z2
E_{HB} in red for O–H···O7, E_{HB} in blue for O–H···S7, E_{HB} in yellow highlighted for C_{sp2}–H···O2 and E_{HB} in normal for C_{sp2}–H···S7

Table S3. Summary of stretching frequency changes of C–H bonds involving hydrogen bonds in the complexes

Complexes	Level of theory/Experiment	$\Delta\nu(C_{sp3}–H)$ (cm^{-1})	Ref
$CH_3CHO\cdots1H_2O/CH_3CHO\cdots2H_2O$	B3LYP/6-311++G(d,p)	6/-11	1
$CH_2FCHO\cdots1H_2O$		10;13	
$CH_2FCHO\cdots2H_2O$		-19;-21	
$CH_3CFO\cdots1H_2O/CH_3CFO\cdots2H_2O$		-2/-23	
$CH_3CHS\cdots1H_2O$	MP2/aug-cc-pVDZ	16.9	2
$CH_3CHS\cdots2H_2O$		26.7	
$CH_3CHS\cdots3H_2O$		15.6; -23.1	
$(CH_3CHO)_2$	M062X/6-311++G(3df,3pd)	-16, -14, -8	3
$CHX_3\cdots HNO$ (X = F, Cl, Br)	MP2/6-311++G(d,p)	7÷41	4
$F_3CH\cdots H_2O$	Exp.	20.3; 32.3	5
Complexes	**Level of theory/Experiment**	**$\Delta\nu(C_{sp2}–H)$ (cm^{-1})**	**Ref**
$RCHO\cdots1H_2O$ (R = H, F, CH_3, CH_2F, C_2H_5)	B3LYP/6-311++G(d,p)	28 ÷ 53	6
$CH_3CHO\cdots1H_2O/CH_3CHO\cdots2H_2O$	B3LYP/6-311++G(d,p)	52/93	1
$CH_2FCHO\cdots1H_2O/\ CH_2FCHO\cdots2H_2O$		44/61	
$CH_3CHS\cdots1H_2O$	MP2/aug-cc-pVDZ	24.0	2
$CH_3CHS\cdots2H_2O$		33.1	
$CH_3CHS\cdots3H_2O$		62.2	
$XCHO\cdots1H_2Z$	MP2/aug-cc-pVDZ	2.9 ÷ 52	7
$XCHO\cdots2H_2O$		4.0 ÷ 92.3	
(X= H, F, Cl, Br, CH_3; Z= O, S)			
$RCHZ\cdots HCOOH$ (R= H, F, Cl, Br, CH_3, NH_2; Z= O, S)	MP2/aug-cc-pVDZ	81÷96	8
$RCHO\cdots R'OH$ (R = NH_2, CF_3, CH_3O, CN, H; R' = H, CH_3, NH_2, C(O)H)	MP2/cc-pVTZ	23.01 ÷ 92.69	9
$(CH_3CHO)_2$	M062X/6-311++G(3df,3pd)	50	3
	MP2/6-311++G(d,p)	-	10
	MP2/6-31+G(d)	56.3; 56.6	11
$HCHO\text{-}NH_2OH$	Exp.	14.6	12
$CH_3COCHO\text{-}NH_2OH$		16.3	
$CHOCHO\cdots H_2O_2$	Exp.	28.9	13
$CHOCHO\cdots H_2O$	Exp.	2.5	14
$CHOCHO\cdots H_2O$	Exp.	14.7	14
4-fluorobenzaldehyde dimer	Exp.	8	15
2-methoxybenzaldehyde dimer	Exp.	21	16
Complexes	**Level of theory**	**$\Delta\nu(C_{sp}–H)$ (cm^{-1})**	**Ref**
$C_2HX\cdots C_6H_6$ (X = H, F, Cl, Br, CH_3, NH_2)	MP2/aug-cc-pVDZ	-15.7 ÷ -24.9	17
$C_2H_2\cdots C_2H_2$	MP2/aug-cc-pVTZ	-21	18
$C_2H_2\cdots HCN$		-61	
$C_6H_6\cdots C_2H_2$		-17	
$C_6H_6\cdots HCN$		-50	

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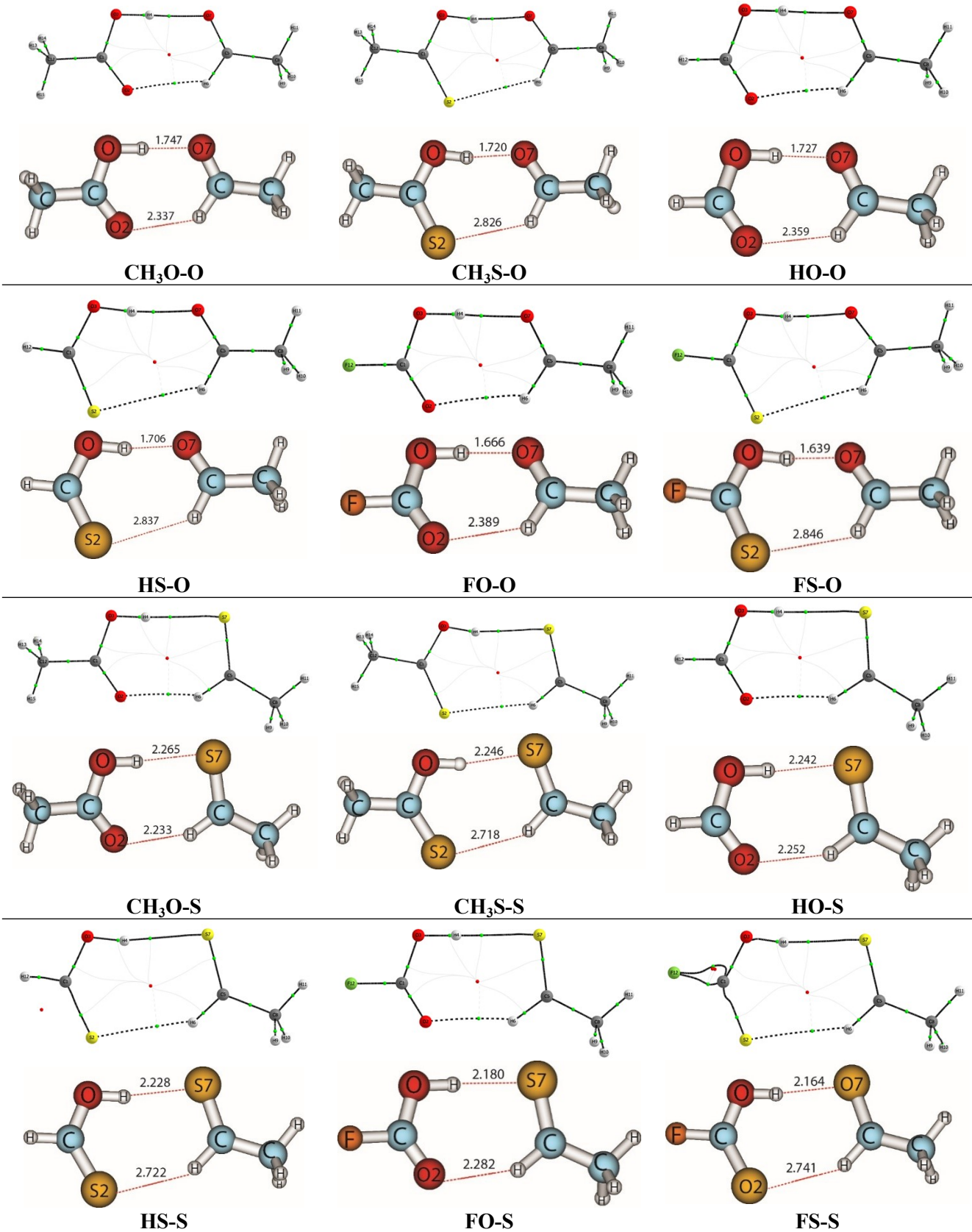

Figure. S1. Topological geometries and stable structures of complexes plotted at MP2/6-311++G(3df,2pd) (*values of distance in Å*)

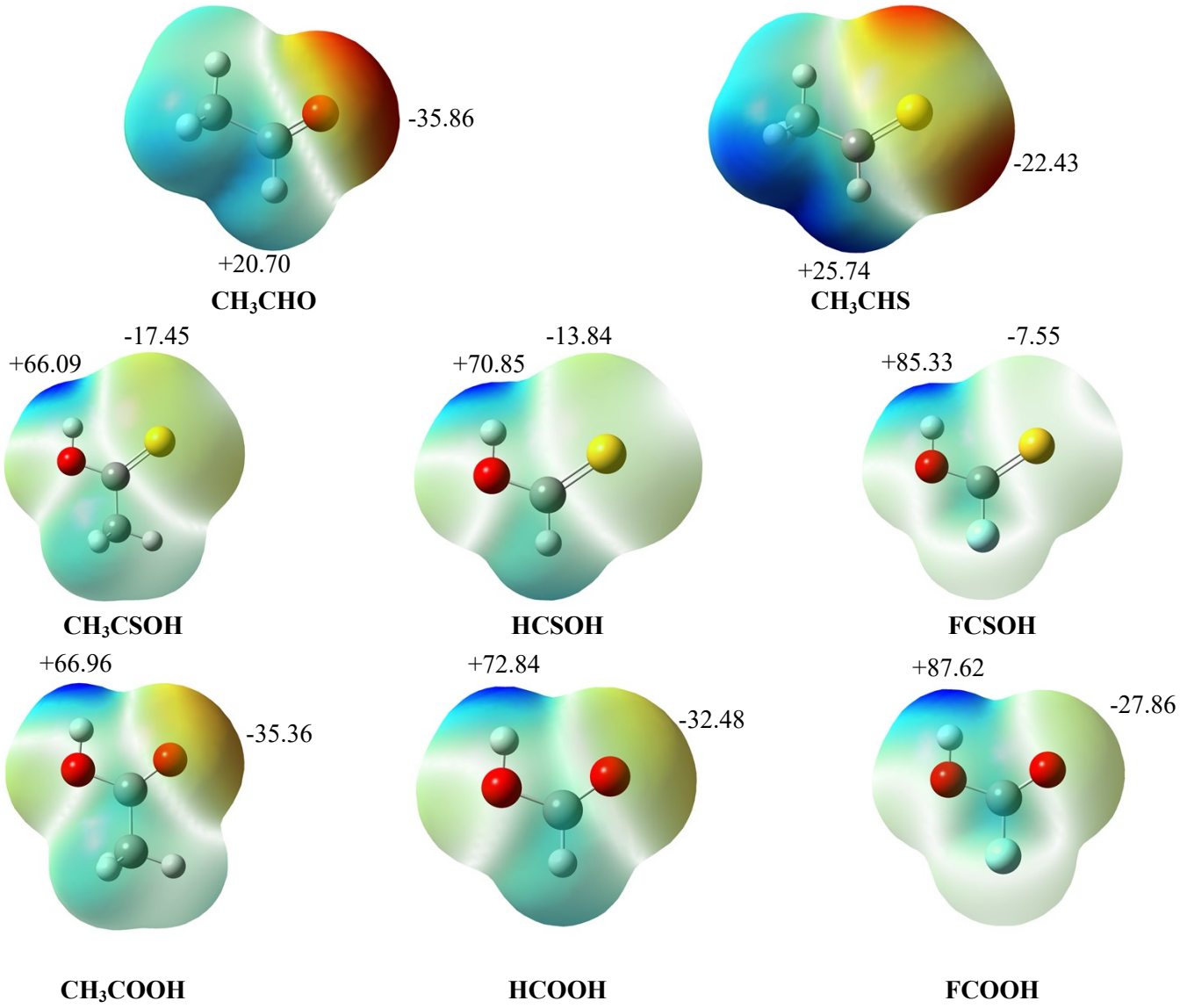

Figure. S2. Molecular electrostatic potential (in *kcal.mol*$^{-1}$) of the CH_3CHZ and RCZOH (R = CH_3, H, F; Z = O, S) at MP2/6–311++G(3df,2pd) level

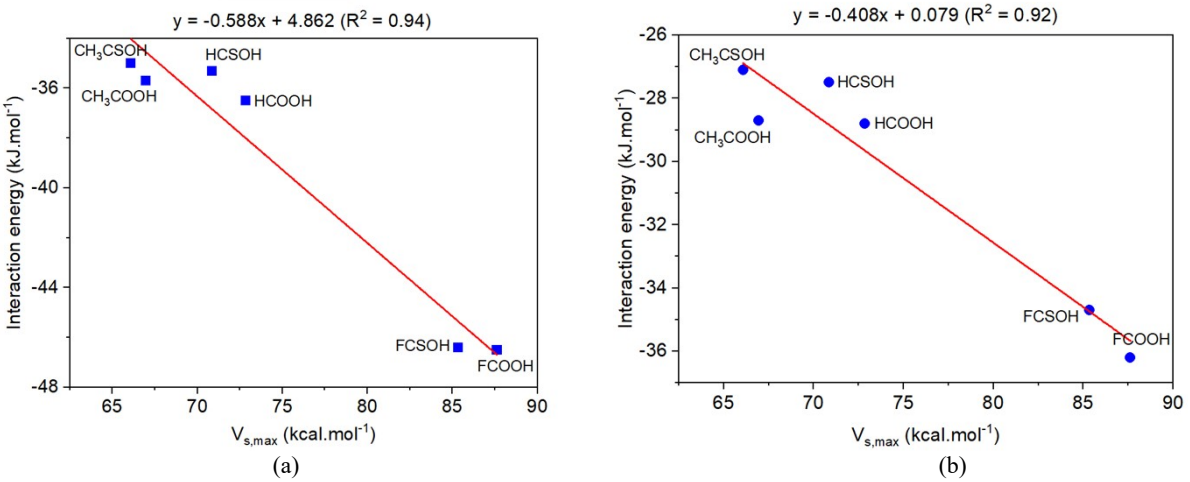

Figure. S3. Relationship of the interaction energies of the investigated complexes for CH_3CHO-complexes (a) and for CH_3CHS-complexes (b) with electrostatic potential of H atom in monomers acting as proton donor at MP2/6-311++G(3df,2pd) level.

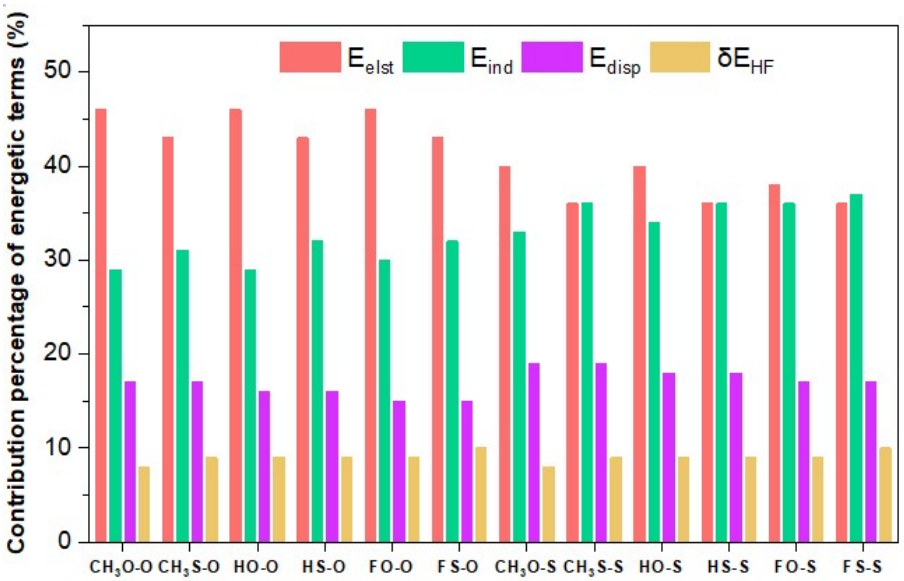

Figure. S4. Diagram for contribution percentage of different energy components into total stabilization energy of the complexes for RCZOH···CH_3CHZ, with R = CH_3, H, F; Z = O, S

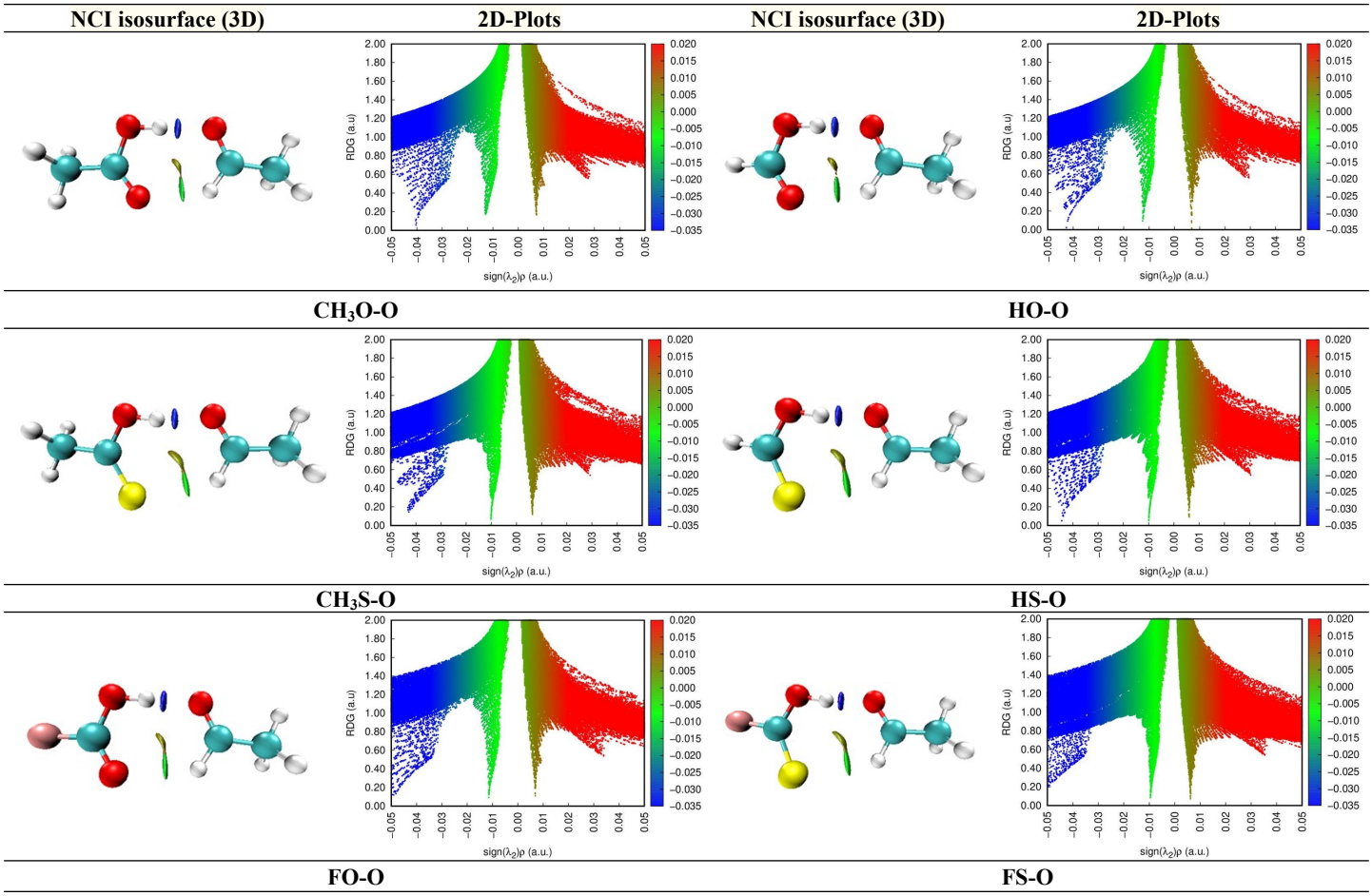

Figure. S5a**.** NCI isosurface and 2D-plots of reduced density gradient (RDG) versus the electron density multiplied by the sign of the second Hessian eigenvalue (sign(λ_2)ρ(r_C)) for **RZ-O** complexes, with R= CH_3, H, F; and Z = O, S.
(*The surfaces are colored on a blue-green-red scale according to the values of sign(λ_2)ρ(r_C) ranging from −0.05 to 0.05 au*)

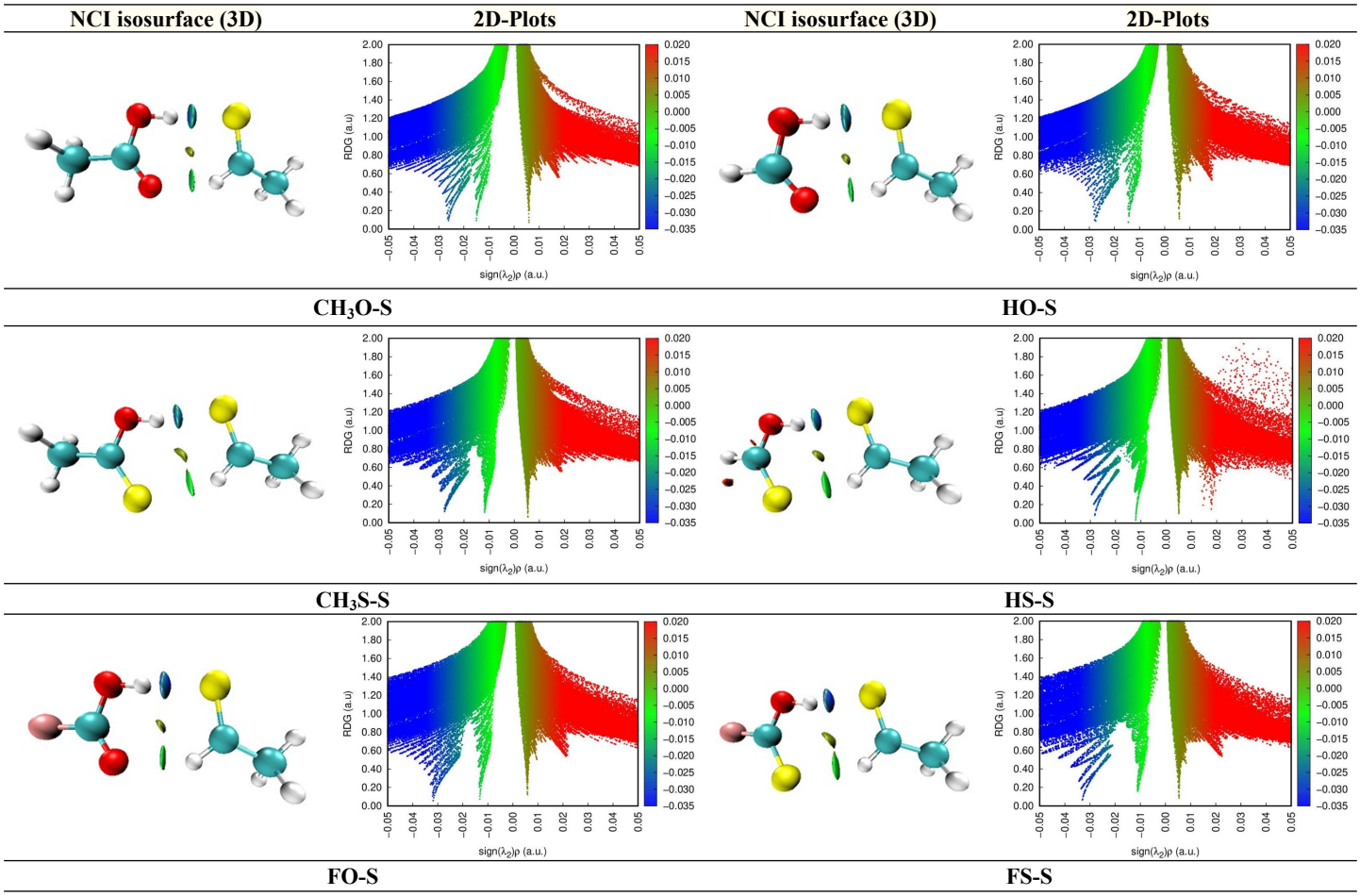

Figure. S5b**.** NCI isosurface and 2D-plots of reduced density gradient (RDG) versus the electron density multiplied by the sign of the second Hessian eigenvalue ($sign(\lambda_2)\rho(r_C)$) for **RZ-S** complexes, with R= CH_3, H, F; and Z = O, S
(*The surfaces are colored on a blue-green-red scale according to the values of* $sign(\lambda_2)\rho(r_C)$ *ranging from −0.05 to 0.05 au*)

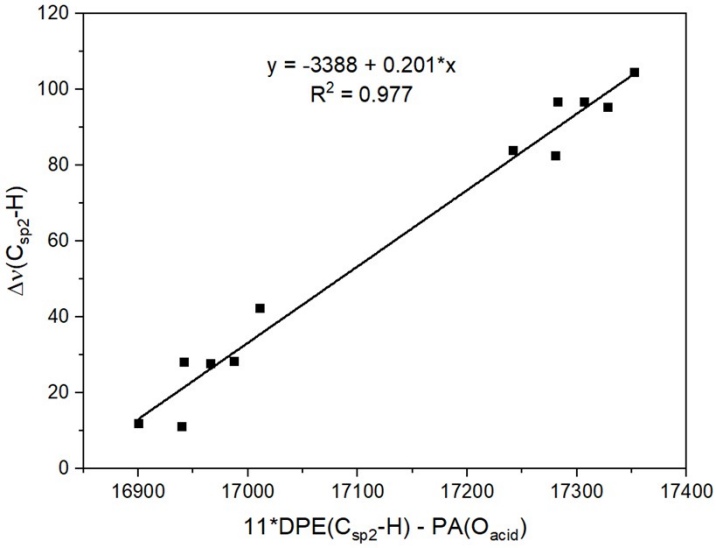

Figure. S6. The linear correlation of $\Delta\nu(C_{sp2}\text{-H})$ (in cm^{-1}) versus $DPE(C_{sp2}\text{-H})$ (in $kJ.mol^{-1}$) of CH_3CHZ and PA(O) (in $kJ.mol^{-1}$) of RCZOH

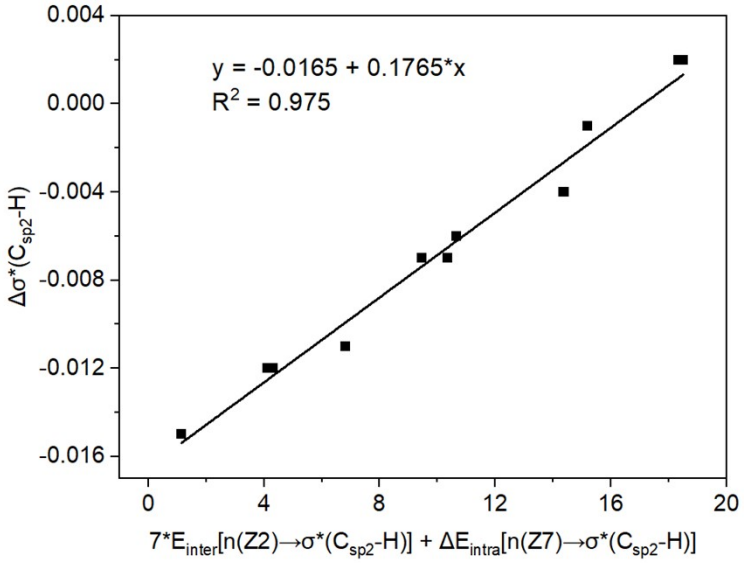

Figure. S7. The linear correlation of $\Delta\sigma^*(C_{sp2}\text{-H})$ (in electron) versus intermolecular hyperconjugative interaction energies (in kJ.mol^{-1}) and changes of intramolecular hyperconjugative interaction energies ($7^*E_{inter} + \Delta E_{intra}$) (in kJ.mol^{-1}) for the complexes