Profound Importance of Conventional O-H···O Hydrogen Bond versus Considerable Blue Shift of C_{sp2}-H bond in the Complexes of Substituted Carbonyls and Carboxyls

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Table S1. Selected typically computational parameters at MP2/6-311++G(2d,2p), the DPE values of O-H and C_{sp2}-H bonds and PA at the O site of the C=O group in the isolated monomers at CCSD(T)/aug-cc-pVTZ//MP2/6-311++G(2d,2p) and some experimental results (in parentheses) taken from NIST webpage

Monomer	**HCOOH**	**FCOOH**	**ClCOOH**	**BrCOOH**	**CH_3COOH**
r(O-H)/Å	0.9675	0.9645	0.9678	0.9689	0.9668
r(C=O)/Å	1.2050	1.1908	1.1939	1.1934	1.2099
σ*(O-H)/e	0.0309	0.0241	0.0296	0.0314	0.0295
ν(O-H) (cm^{-1})	3775.91	3828.55	3775.38	3757.87	3785.16
$PA(O)_{C=O}$	743.1 (742)	701.1	727.9	735.3	788.3 (783.7)
DPE(O-H)	1441.0 (1445.0)	1367.2	1293.3	1266.6	1456.5 (1457.0)
Monomer	**CH_3CH_2COOH**	**NH_2COOH**	**HCHO**	**CH_3CHO**	**NH_2CHO**
r(C/O-H)/Å	0.9668	0.963918	1.0988	1.1041	1.0986
r(C=O)/Å	1.2105	1.2125	1.2131	1.2155	1.2178
σ*(C/O-H)/e	0.0299	0.0255	0.0704	0.0814	0.08173
ν(C/O-H) (cm^{-1})	3784.9	3831.59	3009.51	2952.15	3021.26
$PA(O)_{C=O}$	797.8 (797.2)	816.0	712.0 (711.5)	771.3 (768.5)	832.6 (822.2)
DPE(O/C_{sp2}-H)	1454.0 (1454.0)	1453.9	1650.2 (1650.7)	1642.0 (1645.1)	1628.7 (1505.0)

PA: Proton Affinity, DPE: Deprotonation Enthalpy; energy given in $kJ.mol^{-1}$

Table S2. The intermolecular distances R(H···O), selected parameters at the BCPs of H···O contacts and individual hydrogen bond energies (E_{HB}) at MP2/6-311++G(2d,2p)

Complex	Contacts	R(H···O) (Å)	ρ(r) (au)	$\nabla^2\rho(r)$ (au)	H(r) (au)	E_{HB} (kJ.mol^{-1})
H-H	C1−H2···O6	2.37	0.0122	0.041	0.0011	-10.5
	O7−H8···O3	1.78	0.0362	0.106	-0.0022	-40.5
H-F	C1−H2···O6	2.41	0.0110	0.038	0.0011	-9.6
	O7−H8···O3	1.72	0.0415	0.118	-0.0037	-48.5
H-Cl	C1−H2···O6	2.41	0.0111	0.038	0.0011	-9.6
	O7−H8···O3	1.72	0.0415	0.116	-0.0038	-48.2
H-Br	C1−H2···O6	2.41	0.0111	0.038	0.0011	-9.6
	O7−H8···O3	1.72	0.0418	0.116	-0.0040	-48.6
H-CH_3	C1−H2···O6	2.34	0.0128	0.043	0.0012	-11.1
	O7−H8···O3	1.80	0.0347	0.100	-0.0018	-38.6
H-C_2H_5	C1−H2···O6	2.34	0.0128	0.044	0.0012	-11.2
	O7−H8···O3	1.80	0.0345	0.102	-0.0018	-38.4
H-NH_2	C1−H2···O6	2.31	0.0136	0.047	0.0014	-11.9
	O7−H8···O3	1.78	0.0357	0.106	-0.0021	-40.1

Table S2. Continued

Complex	Contacts	R(H···O) (Å)	ρ(r) (au)	$\nabla^2\rho(r)$ (au)	H(r) (au)	E_{HB} (kJ.mol^{-1})
CH_3-H	C1−H2···O6	2.37	0.0122	0.041	0.0011	-10.5
	O7−H8···O3	1.74	0.0395	0.112	-00032	-45.2
CH_3-F	C1−H2···O6	2.41	0.0110	0.038	0.0011	-9.6
	O7−H8···O3	1.68	0.0457	0.124	-0.0053	-54.6
CH_3-Cl	C1−H2···O6	2.40	0.0112	0.038	0.0011	-9.7
	O7−H8···O3	1.68	0.0458	0.122	-0.0055	-54.5
CH_3-Br	C1−H2···O6	2.40	0.0112	0.038	0.0011	-9.7
	O7−H8···O3	1.68	0.0463	0.122	-0.0057	-55.2
CH_3-CH_3	C1−H2···O6	2.35	0.0128	0.043	0.0012	-11.1
	O7−H8···O3	1.76	0.0378	0.109	-0.0027	-42.8
CH_3-C_2H_5	C1−H2···O6	2.34	0.0129	0.043	0.0012	-11.1
	O7−H8···O3	1.76	0.0376	0.108	-0.0027	-42.6
CH_3-NH_2	C1−H2···O6	2.31	0.0136	0.047	0.0013	-11.9
	O7−H8···O3	1.75	0.0387	0.111	-0.0030	-44.3
NH_2-H	C1−H2···O6	2.32	0.0132	0.046	0.0013	-11.5
	O7−H8···O3	1.69	0.0452	0.123	-0.0052	-53.8
NH_2-F	C1−H2···O6	2.36	0.0121	0.043	0.0014	-10.6
	O7−H8···O3	1.62	0.0528	0.135	-0.0082	-65.9
NH_2-Cl	C1−H2···O6	2.36	0.0121	0.043	0.0014	-10.6
	O7−H8···O3	1.62	0.0533	0.133	-0.0087	-66.5
NH_2-Br	C1−H2···O6	2.36	0.0121	0.043	0.0013	-10.5
	O7−H8···O3	1.61	0.0541	0.133	-0.0091	-67.5
NH_2-CH_3	C1−H2···O6	2.30	0.0138	0.048	0.0014	-12.1
	O7−H8···O3	1.71	0.0431	0.119	-0.0045	-50.8
NH_2-C_2H_5	C1−H2···O6	2.30	0.0139	0.048	0.0014	-12.2
	O7−H8···O3	1.71	0.0429	0.118	-0.0044	-50.5
NH_2-NH_2	C1−H2···O6	2.26	0.0147	0.052	0.0016	-13.03
	O7−H8···O3	1.70	0.0441	0.121	-0.0048	-52.4

Table S3. WBI of the examined complexes calculated at ωB97X-D/6-311++G(2d,2p)

Complex	**H-H**	**H-F**	**H-Cl**	**H-Br**	**H-CH_3**	**H-C_2H_5**	**H-NH_2**
WBI(O···H) /O-H···O	0.0573	0.0706	0.0709	0.0715	0.0535	0.053	0.0558
WBI(H···O) /C_{sp2}-H···O	0.0054	0.0039	0.0041	0.0041	0.0057	0.0057	0.0063
Complex	**CH_3-H**	**CH_3-F**	**CH_3-Cl**	**CH_3-Br**	**CH_3-CH_3**	**CH_3-C_2H_5**	**CH_3-NH_2**
WBI(O···H) /O-H···O	0.0659	0.082	0.0832	0.0842	0.0614	0.0609	0.0639
WBI(H···O) /C_{sp2}-H···O	0.0056	0.0041	0.0043	0.0043	0.0059	0.0059	0.0064
Complex	**NH_2-H**	**NH_2-F**	**NH_2-Cl**	**NH_2-Br**	**NH_2-CH_3**	**NH_2-C_2H_5**	**NH_2-NH_2**
WBI(O···H) /O-H···O	0.0806	0.1005	0.1028	0.1046	0.0751	0.0745	0.0779
WBI(H···O) /C_{sp2}-H···O	0.0067	0.0049	0.005	0.005	0.0069	0.0069	0.0076

Table S4: Comparision of the interaction energies (in kJ.mol^{-1}) corrected by both ZPE and BSSE using different levels of theory, including two double hybrid functionals, CCSD(T) and CBS extrapolation.

Basis set	*6-311++G(2d,2p)*				*aug-cc-pVTZ*		*CBS*
Functional	***DSD-PBEP86***		***B2GP-PLYP+D2*** *Grimme's dispersion*		***CCSD(T)***		
Complex	*ΔE^**	*BSSE*	*ΔE^**	*BSSE*	*ΔE^**	*BSSE*	*ΔE**
H-H	*-32.5*	*3.9*	*-34.7*	*3.4*	*-31.3*	*3.5*	*-36.9*
CH_3-H	*-38.2*	*4.4*	*-40.4*	*3.8*	*-36.2*	*3.8*	*-41.8*
NH_2-H	*-47.1*	*4.7*	*-49.5*	*4.1*	*-44.2*	*4.3*	*-49.9*

Table S5a. The parameters of the CBS exponential extrapolation in the form of $E^{HF}(X) = E_{CBS}^{HF} + B.\exp(-\alpha X)$, for the Hartree-Fock total energies of the structures involved in the **H-H**, **CH_3-H** and **NH_2-H** compelexes, where $E^{HF}(X)$ is the total energy at HF/aug-cc-pVXZ (X=2 for DZ, X=3 for TZ and X=4 for QZ) corrected by the both ZPE and BSSE computed at the corresponding level and E_{CBS}^{HF} is the HF total energy at the CBS limit.

Complex	***Parameter***	***Structures involved in the complex***		
		Aldehyde	***HCOOH***	***Complex***
H-H	α	1.35		1.30
	B	1547.4		3747.2
CH_3-H	α	1.37	1.32	1.32
	B	2126.8	2418.2	4303.5
NH_2-H	α	1.33		1.30
	B	2157.9		4340.9

Table S5b. The extrapolated HF total energies E_{CBS}^{HF}, CCSD(T) correlation enegies E_{CBS}^{corr} and the CCSD(T) total energies extrapolated at the CBS limit $E_{CBS}^{CCSD(T)}$ for the structures involved in the **H-H**, **CH_3-H** and **NH_2-H** compelexes, where $E_{CBS}^{CCSD(T)} = E_{CBS}^{HF} + E_{CBS}^{corr}$. All energetical values are in kJ.mol^{-1}.

Complex	***Structures involved in the complex***								
	Aldehyde			***HCOOH***			***Complex***		
	E_{CBS}^{HF}	E_{CBS}^{corr}	$E_{CBS}^{CCSD(T)}$	E_{CBS}^{HF}	E_{CBS}^{corr}	$E_{CBS}^{CCSD(T)}$	E_{CBS}^{HF}	E_{CBS}^{corr}	$E_{CBS}^{CCSD(T)}$
H-H	-299036.3	-1209.3	**-300245.6**	-495766.3	-1902.7	**-497669.0**	-794826.2	-3125.3	**-797951.5**
CH_3-H	-401524.1	-1746.4	**-403270.5**				-897317.9	-3663.5	**-900981.4**
NH_2-H	-443638.8	-1835.7	**-445474.5**				-939439.6	-3753.8	**-943193.4**

The correlation energy at CCSD(T)/aug-cc-pVXZ is fitted with the expression of the power form:

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

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

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

in which, the CCSD(T) correlation energies are obtained using the two basis sets aug-cc-pVDZ and aug-cc-pVTZ on the MP2/6-311++G(2d,2p) geometries:

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

Table S6. Contributions of different components in the overall interaction energy calculated by using SAPT2+ approach, (ΔE_{SAPT2+}, kJ.mol^{-1}) with the aug-cc-pVDZ basis set

Complex	**E_{elst}**	**E_{ind}**	**E_{disp}**	**$\delta E_{int,r}^{HF}$**	**E_{exch}**	**ΔE_{SAPT2+}**
H-H	-65.3(47.7)	-39.0(28.5)	-21.8(15.9)	-10.9(7.9)	86.5	-50.5
H-F	-71.2(47.4)	-44.2(29.4)	-22.2(14.8)	-12.7(8.4)	93.3	-57.0
H-Cl	-70.8(46.6)	-44.9(29.6)	-23.0(15.1)	-13.2(8.7)	95.9	-55.9
H-Br	-71.1(46.2)	-45.8(29.8)	-23.4(15.2)	-13.5(8.8)	97.9	-55.9
H-CH_3	-63.6(47.8)	-37.2(27.9)	-22.1(16.6)	-10.2(7.7)	84.1	-49.0
H-C_2H_5	-63.3(47.6)	-37.1(27.9)	-22.3(16.8)	-10.2(7.7)	84.1	-48.7
H-NH_2	-66.5(48.0)	-38.6(27.9)	-22.6(16.4)	-10.6(7.7)	87.1	-51.3
CH_3-H	-71.8(47.1)	-44.1(28.9)	-23.9(15.7)	-12.6(8.3)	96.6	-55.7
CH_3-F	-79.7(46.9)	-50.9(29.9)	-24.4(14.4)	-14.9(8.8)	105.8	-64.1
CH_3-Cl	-79.5(46.1)	-51.9(30.1)	-25.4(14.8)	-15.6(9.0)	109.3	-63.2
CH_3-Br	-80.1(45.7)	-53.1(30.3)	-25.9(14.8)	-16.1(9.2)	111.9	-63.4
CH_3-CH_3	-69.3(47.2)	-41.8(28.4)	-24.1(16.4)	-11.7(8.0)	93.5	-53.6

CH_3-C_2H_5	-69.0(47.0)	-41.7(28.4)	-24.3(16.6)	-11.7(8.0)	93.4	-53.3
CH_3-NH_2	-72.0(47.4)	-43.2(28.4)	-24.6(16.2)	-12.1(8.0)	96.2	-55.7
NH_2-H	-87.8(47.2)	-55.0(29.6)	-27.1(14.5)	-16.2(8.7)	118.8	-67.3
NH_2-F	-98.3(46.9)	-63.8(30.5)	-27.9(13.3)	-19.4(9.3)	131.1	-78.3
NH_2-Cl	-98.5(46.0)	-65.8(30.8)	-29.2(13.6)	-20.5(9.6)	136.4	-77.6
NH_2-Br	-99.4(45.5)	-67.6(31.0)	-29.8(13.6)	-21.3(9.9)	140.1	-78.0
NH_2-CH_3	-84.4(47.3)	-52.0(29.1)	-27.2(15.2)	-15.0(8.4)	114.3	-64.3
NH_2-C_2H_5	-83.9(47.1)	-51.9(29.1)	-27.4(15.4)	-15.0(8.4)	114.3	-64.0
NH_2-NH_2	-87.3(47.5)	-53.4(29.1)	-27.7(15.0)	-15.4(8.4)	117.2	-66.7

Values in parentheses are the percentages (%) of the corresponding energy components contributing to interaction energy of the complexes

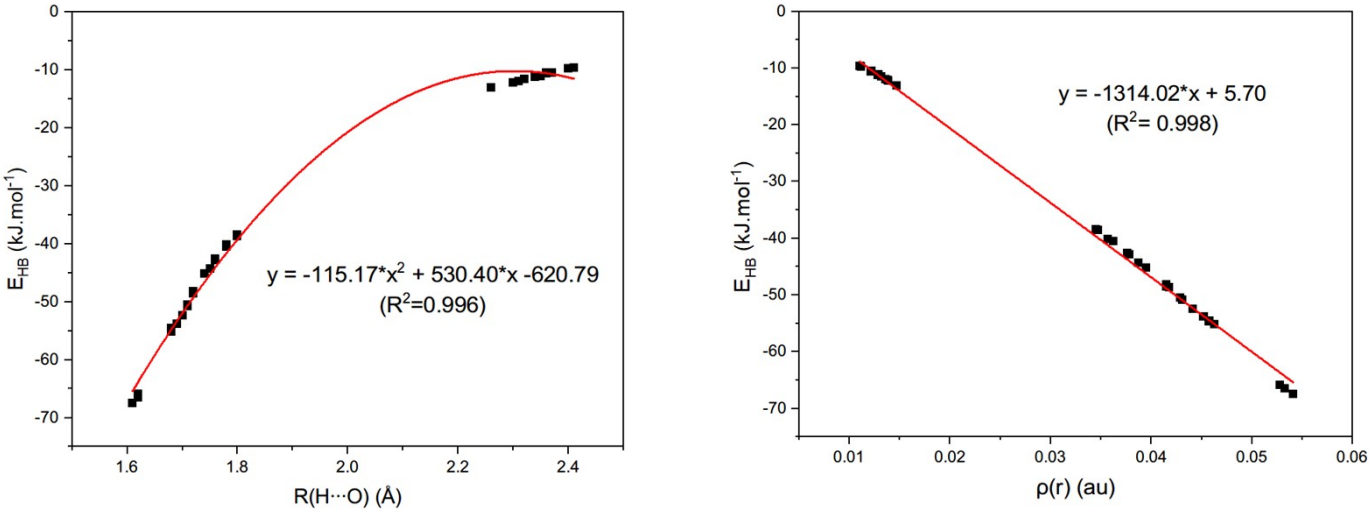
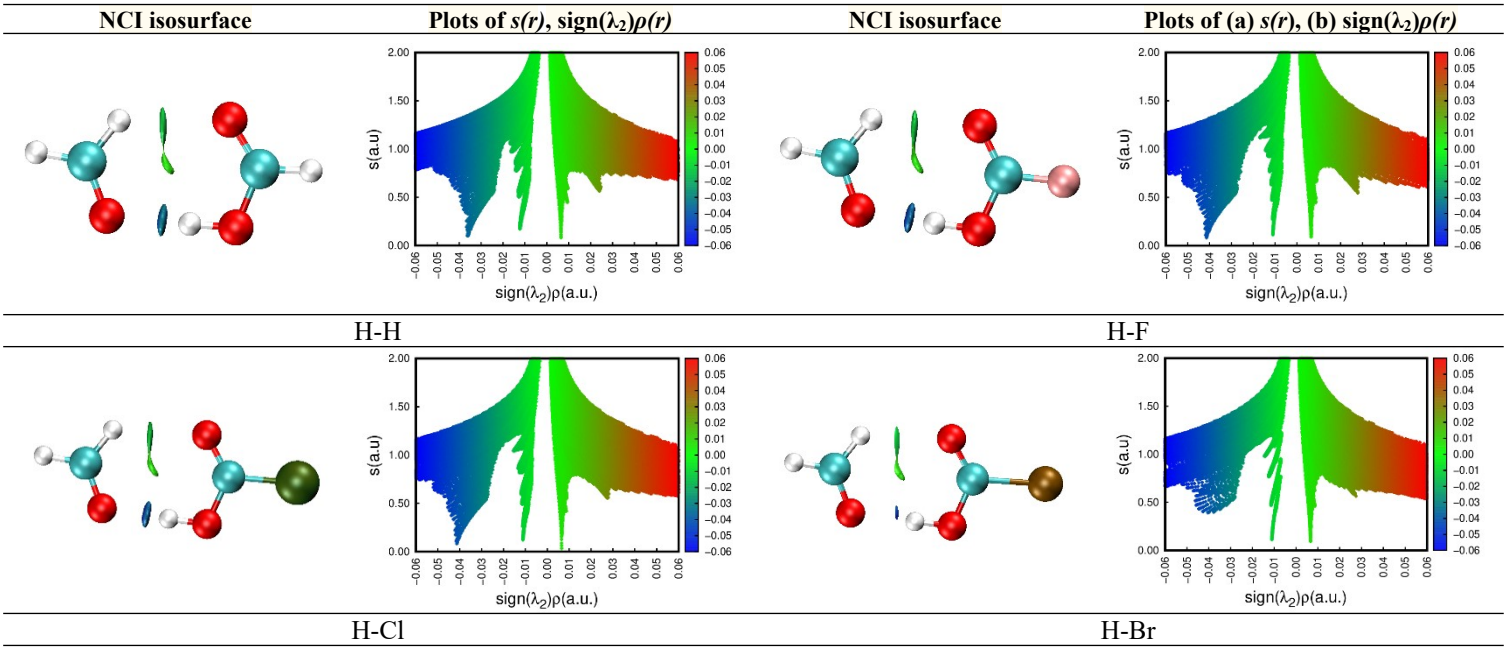


Figure S1. The high correlations between individual hydrogen-bonded energies (E_{HB}, kJ.mol^{-1}) and the intermolecular distances (R(H···Z), Å) and electron density (ρ(r), au)



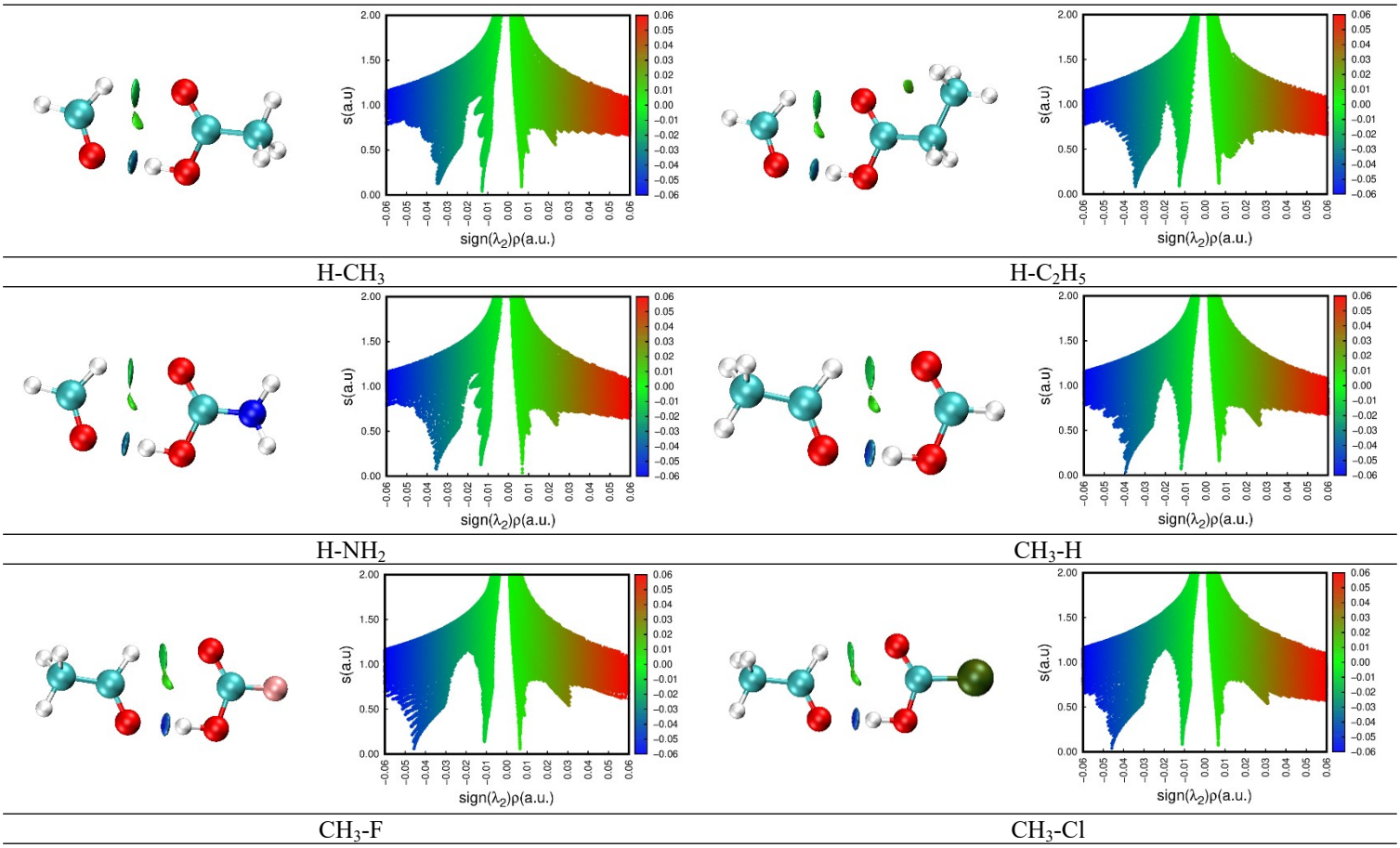
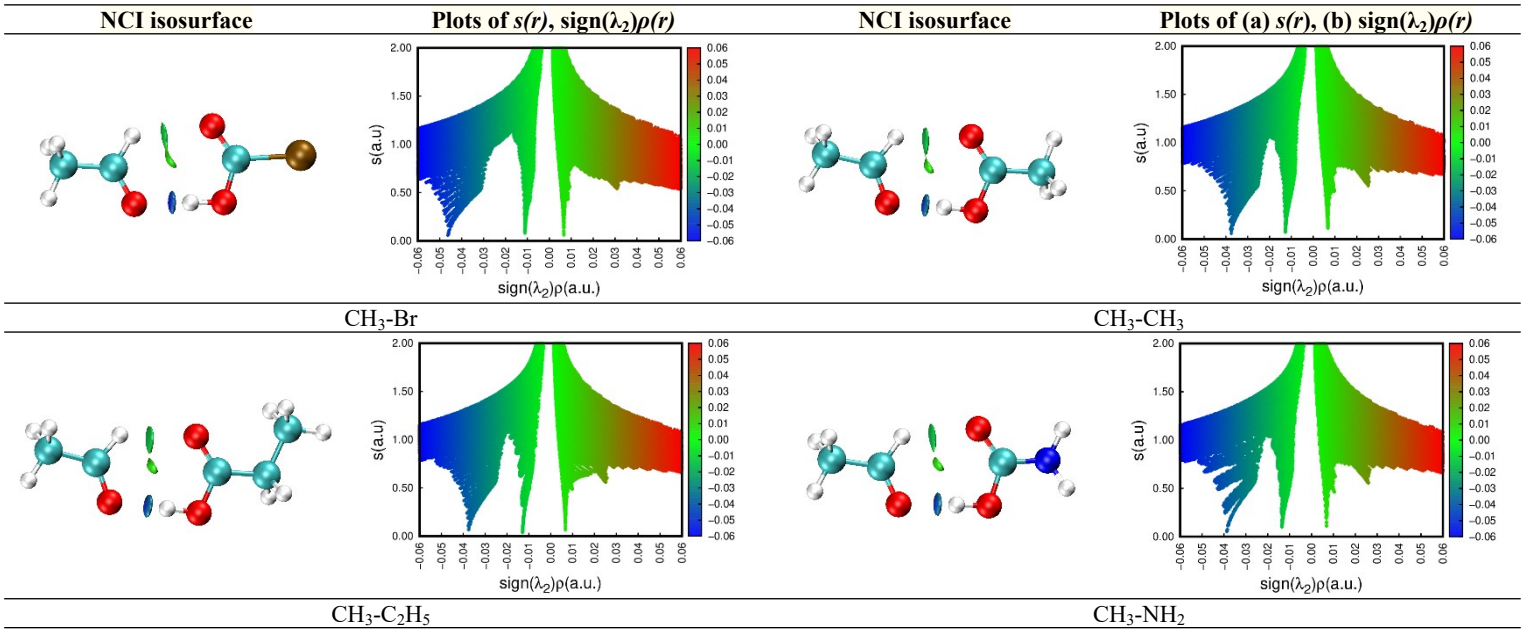


Figure S2a. NCI isosurface and plots of s(r) as a function of sign(λ_2).ρ(r) *for all complexes*
(The surfaces are colored on a blue-green-red scale
according to the values of sign(λ_2).ρ(r) ranging from −0.04 to 0.04 au)



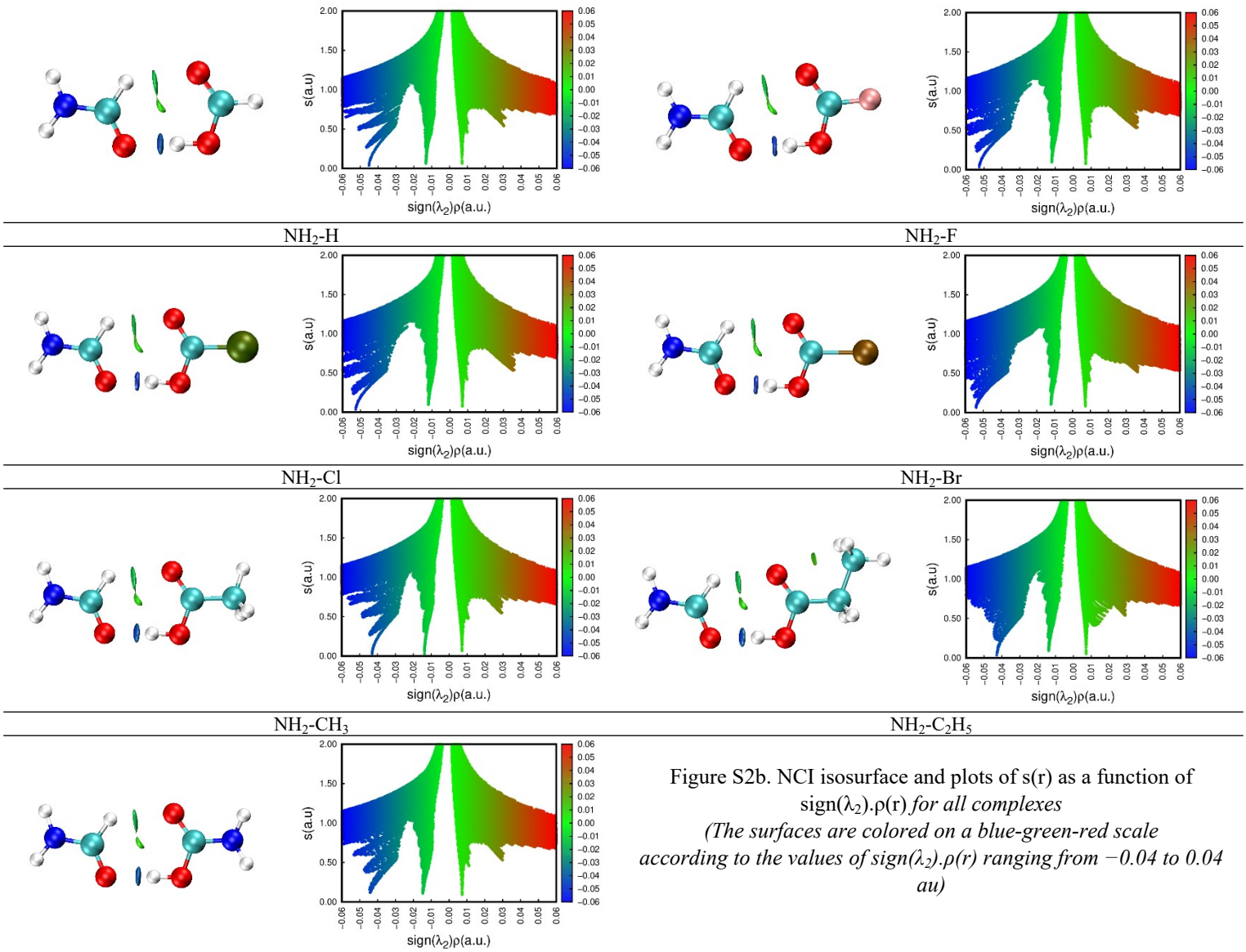


Figure S2b. NCI isosurface and plots of s(r) as a function of sign(λ_2).ρ(r) *for all complexes*
(The surfaces are colored on a blue-green-red scale according to the values of sign(λ_2).ρ(r) ranging from −0.04 to 0.04 au)

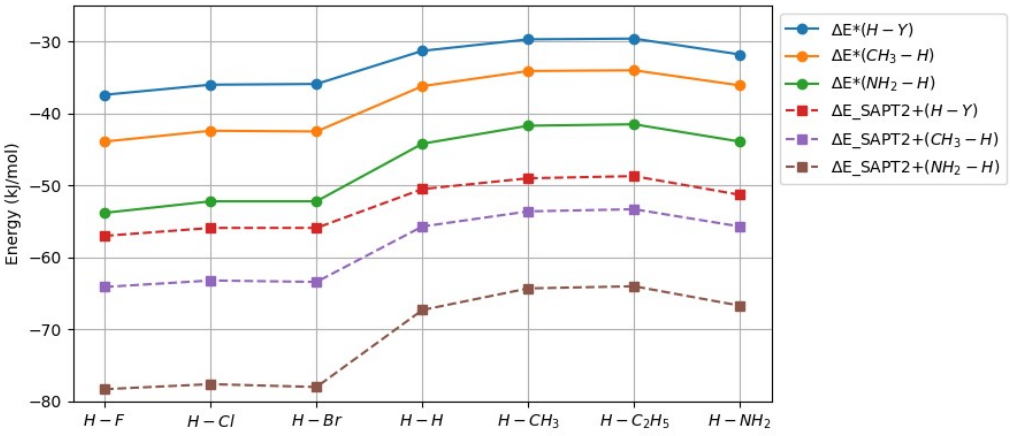


Figure S3. Relationships of the interaction energies (ΔE^* and ΔE_{SAPT2+}) and the substituent Y for the investigated complexes

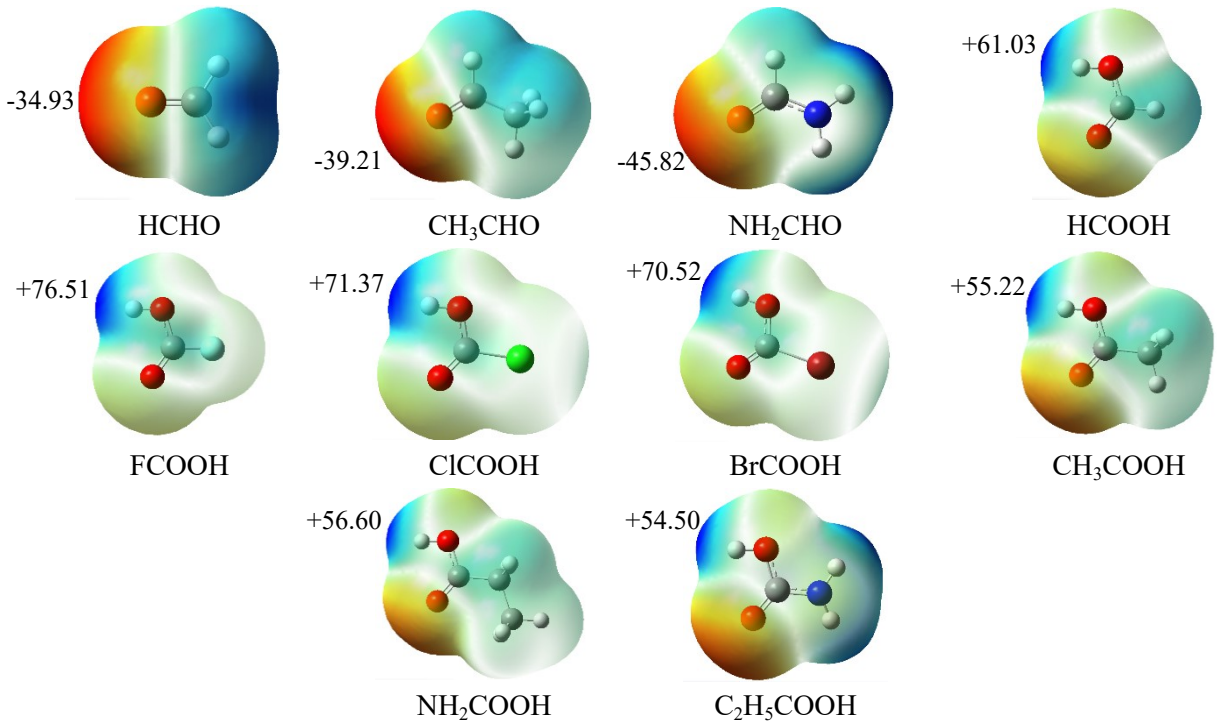


Figure S4. MEP on the surface of monomers plotted at MP2/6-311++G(2d,2p) (isovalue = 0.0004 au) with the values of the maximum surface electrostatic potential ($V_{s,max}$) at H atom of OH group in YCOOH and the minimum surrface electrostatic potential ($V_{s,min}$) at O atom of C=O group in XCHO

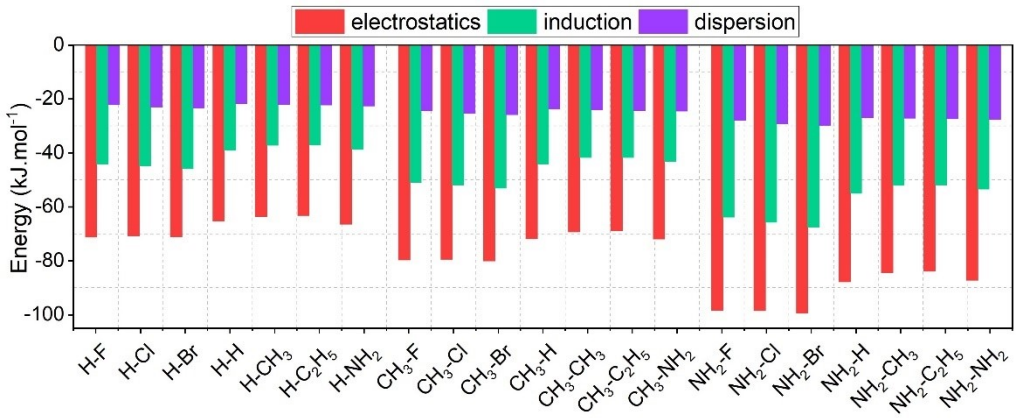
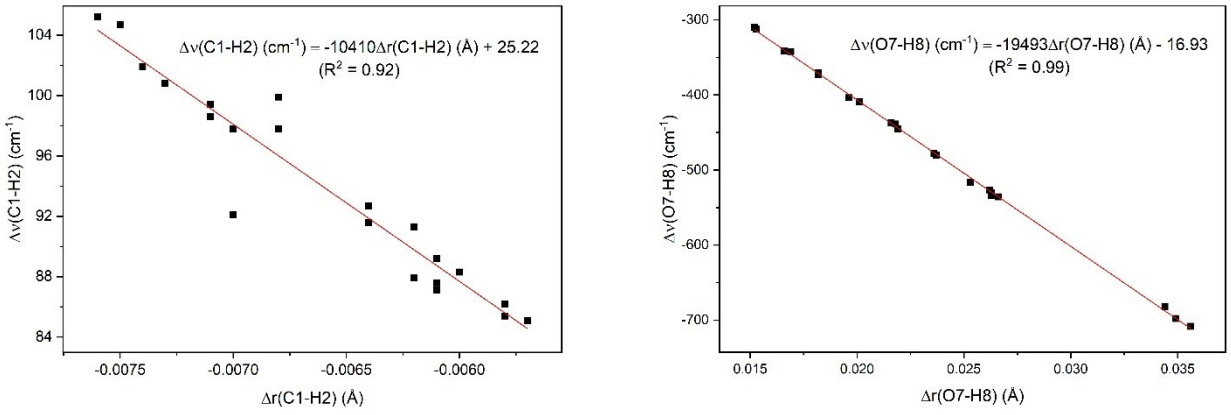


Figure S5. Contributions of different energetic components into interaction energy of the complexes



(a) (b)

Figure S6. The linear correlations of the changes of the C_{sp2}-H and O-H stretching vibrational frequencies versus the changes of their corresponding bond lengths

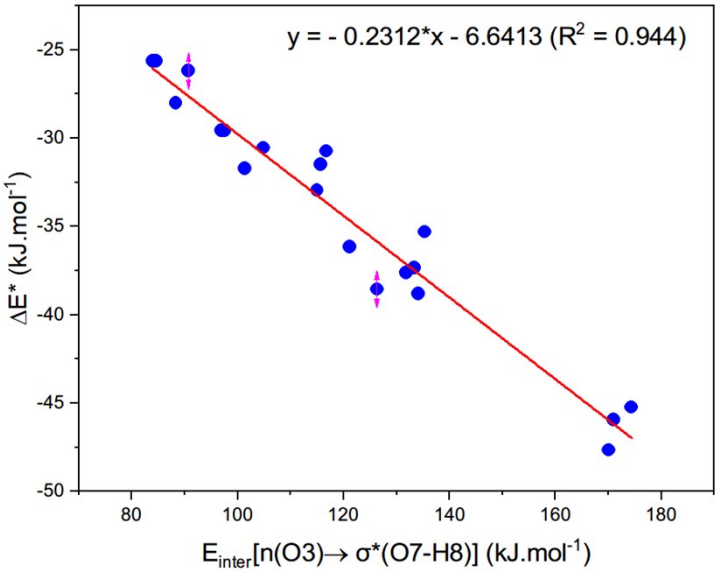


Figure S7. The linear correlation between the interaction energy of complexes and intermolecular hyperconjugation energy of the charge-transfer interaction derived from n(O3) lone pair to σ*(O7–H8) orbital

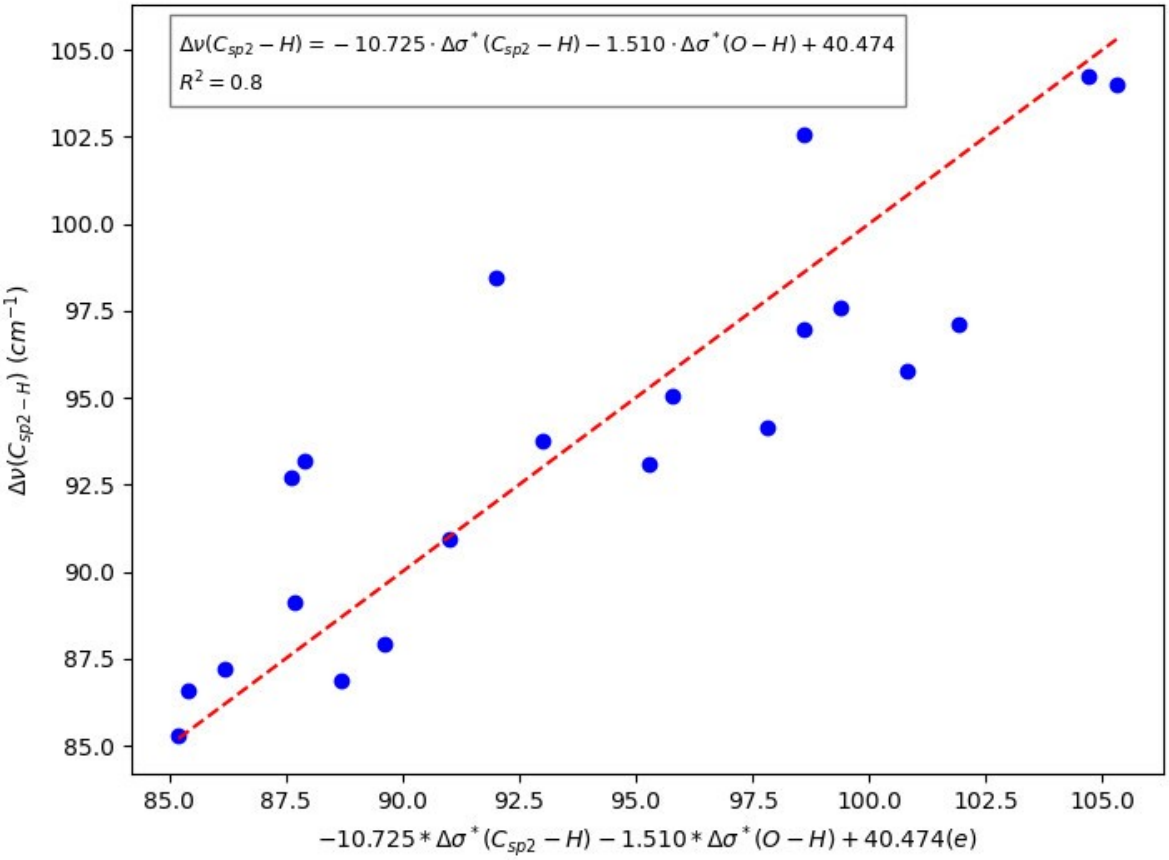


Figure S8. The linear correlation between changes of C_{sp2}–H stretching frequency $\Delta\nu(C_{sp2}\text{-H})$ versus $\Delta\sigma^*(C_{sp2}\text{-H})$ and $\Delta\sigma^*(\text{O-H})$ values