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Supporting Information

Importance of Water and Intramolecular Interaction Governs Substantial Blue Shift of C_{sp2}–H Stretching Frequency in the Complexes between Chalcogenoaldehydes and Waters

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Table S1 Contact distances R1, R2, R3, R4 (Å) in the complexes at MP2/6-311++G(3df,2pd)

	HO-1	**FO-1**	**ClO-1**	**BrO-1**	**CH_3O-1**	**HS-1**	**FS-1**	**ClS-1**	**BrS-1**	**CH_3S-1**
R1	1.98	2.18	2.18	2.21	1.93	2.47	2.63	2.60	2.61	2.44
R2	2.62	2.45	2.43	2.42	2.66	2.45	2.33	2.32	2.33	2.47
	HSe-1	**FSe-1**	**ClSe-1**	**BrSe-1**	**CH_3Se-1**	**HTe-1**	**FTe-1**	**ClTe-1**	**BrTe-1**	**CH_3Te-1**
R1	2.61	2.73	2.72	2.72	2.58	2.82	2.93	2.91	2.91	2.79
R2	2.44	2.32	2.31	2.32	2.44	2.46	2.33	2.31	2.32	2.45
	HO-2	**FO-2**	**ClO-2**	**BrO-2**	**CH_3O-2**	**HS-2**	**FS-2**	**ClS-2**	**BrS-2**	**CH_3S-2**
R1	1.87	1.96	1.97	1.99	1.84	2.37	2.43	2.42	2.42	2.34
R2	2.28	2.15	2.14	2.13	2.31	2.22	2.12	2.10	2.10	2.24
R3	1.86	1.87	1.87	1.87	1.85	1.87	1.87	1.87	1.87	1.86
	HSe-2	**FSe-2**	**ClSe-2**	**BrSe-2**	**CH_3Se-2**	**HTe-2**	**FTe-2**	**ClTe-2**	**BrTe-2**	**CH_3Te-2**
R1	2.50	2.55	2.54	2.55	2.48	2.71	2.75	2.74	2.74	2.69
R2	2.22	2.12	2.11	2.11	2.23	2.24	2.14	2.12	2.12	2.25
R3	1.87	1.87	1.87	1.87	1.86	1.88	1.87	1.87	1.87	1.87
	HO-3	**FO-3**	**ClO-3**	**BrO-3**	**CH_3O-3**	**HS-3**	**FS-3**	**ClS-3**	**BrS-3**	**CH_3S-3**
R1	1.83	1.90	1.90	1.92	1.79	2.34	2.39	2.38	2.38	2.29
R2	2.19	2.04	2.03	2.01	2.24	2.16	2.05	2.03	2.02	2.44
R3	1.78	1.79	1.79	1.80	1.77	1.79	1.80	1.80	1.80	1.80
R4	1.81	1.79	1.80	1.80	1.81	1.81	1.80	1.80	1.80	1.82
	HSe-3	**FSe-3**	**ClSe-3**	**BrSe-3**	**CH_3Se-3**	**HTe-3**	**FTe-3**	**ClTe-3**	**BrTe-3**	**CH_3Te-3**
R1	2.48	2.51	2.51	2.51	2.43	2.69	2.71	2.71	2.71	2.64
R2	2.16	2.05	2.04	2.03	2.45	2.16	2.07	2.05	2.05	2.45
R3	1.80	1.80	1.80	1.80	1.80	1.80	1.81	1.81	1.81	1.81
R4	1.82	1.80	1.80	1.80	1.82	1.82	1.81	1.81	1.81	1.83

Table S2a Electron density (ρ(r)), Laplacian of electron density ($\nabla^2\rho(r)$), total electron energy density (H(r)) and individual energy of H-bond ($E_{H\text{-}bond}$) at BCPs of intermolecular contacts in **XZ-1**

Complex	H-bonds	ρ(r) (au)	$\nabla^2\rho(r)$ (au)	H(r) (au)	$E_{H\text{-}bond}$ (kJ.mol^{-1})
HO-1	C_{sp2}–H···O2	-	-	-	-
	O2–H1···O	0.0237	0.082	0.0003	-26.0
HS-1	C_{sp2}–H···O2	0.0089	0.038	0.0015	-8.7
	O2–H1···S	0.0165	0.043	0.0001	-14.1
HSe-1	C_{sp2}–H···O2	0.0088	0.038	0.0015	-8.5
	O2–H1···Se	0.0145	0.037	0.0004	-11.3
HTe-1	C_{sp2}–H···O2	0.0083	0.034	0.0013	-7.8
	O2–H1···Te	0.0122	0.028	0.0004	-8.1
FO-1	C_{sp2}–H···O2	0.0097	0.044	0.0018	-9.7
	O2–H1···O	0.0154	0.061	0.0015	-15.8
FS-1	C_{sp2}–H···O2	0.0111	0.047	0.0019	-10.6
	O2–H1···S	0.0120	0.036	0.0008	-9.7
FSe-1	C_{sp2}–H···O2	0.0112	0.047	0.0018	-10.6
	O2–H1···Se	0.0112	0.032	0.0008	-8.3
FTe-1	C_{sp2}–H···O2	0.0109	0.045	0.0017	-10.3
	O2–H1···Te	0.0103	0.025	0.0005	-7.0
ClO-1	C_{sp2}–H···O2	0.0099	0.044	0.0017	-9.8
	O2–H1···O	0.0155	0.061	0.0015	-16.0
ClS-1	C_{sp2}–H···O2	0.0099	0.044	0.0017	-9.8
	O2–H1···S	0.0127	0.037	0.0007	-10.4
ClSe-1	C_{sp2}–H···O2	0.0115	0.048	0.0018	-11.0
	O2–H1···Se	0.0117	0.033	0.0007	-8.8
ClTe-1	C_{sp2}–H···O2	0.0113	0.046	0.0017	-10.7
	O2–H1···Te	0.0105	0.026	0.0005	-7.2
BrO-1	C_{sp2}–H···O2	0.0102	0.044	0.0017	-10.0
	O2–H1···O	0.0145	0.057	0.0015	-14.9
BrS-1	C_{sp2}–H···O2	0.0113	0.047	0.0018	-10.8
	O2–H1···S	0.0126	0.037	0.0007	-10.3
BrSe-1	C_{sp2}–H···O2	0.0113	0.047	0.0018	-10.8
	O2–H1···Se	0.0117	0.033	0.0008	-8.8
BrTe-1	C_{sp2}–H···O2	0.0113	0.046	0.0017	-10.6
	O2–H1···Te	0.0106	0.026	0.0005	-7.2
CH_3O-1	C_{sp2}–H···O2	-	-	-	-
	O2–H1···O	0.0262	0.086	-0.0004	-29.4
CH_3S-1	C_{sp2}–H···O2	0.0089	0.037	0.0014	-8.7
	O2–H1···S	0.0176	0.045	-0.0002	-15.2
CH_3Se-1	C_{sp2}–H···O2	0.0085	0.035	0.0018	-6.7
	O2–H1···Se	0.0159	0.043	-0.0011	-17.3
CH_3Te-1	C_{sp2}–H···O2	0.0086	0.036	0.0013	-8.2
	O2–H1···Te	0.0130	0.029	0.0003	-9.0

Table S2b Electron density (ρ(r)), Laplacian of electron density ($\nabla^2\rho(r)$), total electron energy density (H(r)) and individual energy of H-bond ($E_{H\text{-}bond}$) at BCPs of intermolecular contacts in **XZ-2**

Complex	H-bonds	ρ(r) (au)	$\nabla^2\rho(r)$ (au)	H(r) (au)	$E_{H\text{-}bond}$ (kJ.mol^{-1})
HO-2	C_{sp2}–H···O5	0.0128	0.047	0.0015	-11.6
	O2–H1···O	0.0296	0.090	-0.0017	-34.1
	O5–H4···O2	0.0299	0.095	-0.0015	-35.0
HS-2	C_{sp2}–H···O5	0.0145	0.052	0.0014	-13.5
	O2–H1···S	0.0211	0.045	-0.0013	-18.4
	O5–H4···O2	0.0296	0.093	-0.0014	-34.4
HSe-2	C_{sp2}–H···O5	0.0145	0.052	0.0013	-13.5
	O2–H1···Se	0.0188	0.039	-0.0008	-14.8
	O5–H4···O2	0.0294	0.093	-0.0014	-34.1
HTe-2	C_{sp2}–H···O5	0.0134	0.051	0.0017	-12.1
	O2–H1···Te	0.0160	0.030	-0.0004	-10.9
	O5–H4···O2	0.0271	0.091	-0.0012	-33.2
FO-2	C_{sp2}–H···O5	0.0166	0.064	0.0020	-15.8
	O2–H1···O	0.0228	0.081	0.0007	-24.7
	O5–H4···O2	0.0291	0.095	-0.0011	-34.0
FS-2	C_{sp2}–H···O5	0.0176	0.065	0.0015	-17.1
	O2–H1···S	0.0179	0.043	-0.0004	-15.0
	O5–H4···O2	0.0292	0.094	-0.0012	-33.9
FSe-2	C_{sp2}–H···O5	0.0178	0.064	0.0015	-17.2
	O2–H1···Se	0.0166	0.037	-0.0002	-12.7
	O5–H4···O2	0.0294	0.093	-0.0013	-34.1
FTe-2	C_{sp2}–H···O5	0.0172	0.062	0.0014	-16.5
	O2–H1···Te	0.0148	0.030	-0.0001	-9.9
	O5–H4···O2	0.0292	0.092	-0.0013	-33.8
ClO-2	C_{sp2}–H···O5	0.0173	0.065	0.0018	-16.5
	O2–H1···O	0.0226	0.079	0.0006	-24.4
	O5–H4···O2	0.0289	0.094	-0.0010	-33.6
ClS-2	C_{sp2}–H···O5	0.0187	0.067	0.0014	-18.3
	O2–H1···S	0.0185	0.043	-0.0005	-15.6
	O5–H4···O2	0.0293	0.094	-0.0012	-34.0
ClSe-2	C_{sp2}–H···O5	0.0186	0.066	0.0013	-18.1
	O2–H1···Se	0.0171	0.037	-0.0003	-13.1
	O5–H4···O2	0.0295	0.094	-0.0013	-34.2
ClTe-2	C_{sp2}–H···O5	0.0180	0.063	0.0013	-17.4
	O2–H1···Te	0.0150	0.030	-0.0001	-10.0
	O5–H4···O2	0.0291	0.092	-0.0013	-33.7
BrO-2	C_{sp2}–H···O5	0.0178	0.066	0.0018	-17.0
	O2–H1···O	0.0216	0.077	0.0009	-22.9
	O5–H4···O2	0.0288	0.094	-0.0010	-33.4
BrS-2	C_{sp2}–H···O5	0.0188	0.067	0.0013	-18.4
	O2–H1···S	0.0182	0.043	-0.0005	-15.3
	O5–H4···O2	0.0292	0.094	-0.0012	-33.8
BrSe-2	C_{sp2}–H···O5	0.0187	0.066	0.0013	-18.2
	O2–H1···Se	0.0169	0.037	-0.0003	-13.0
	O5–H4···O2	0.0294	0.093	-0.0013	-34.1
BrTe-2	C_{sp2}–H···O5	0.0182	0.064	0.0013	-17.5
	O2–H1···Te	0.0150	0.030	-0.0001	-10.0
	O5–H4···O2	0.0291	0.092	-0.0013	-33.6
CH_3O-2	C_{sp2}–H···O5	0.0122	0.044	0.0013	-10.9
	O2–H1···O	0.0324	0.093	-0.0029	-38.4
	O5–H4···O2	0.0304	0.095	-0.0017	-35.8
CH_3S-2	C_{sp2}–H···O5	0.0141	0.050	0.0013	-13.1
	O2–H1···S	0.0221	0.046	-0.0017	-19.5
	O5–H4···O2	0.0301	0.094	-0.0016	-35.1
CH_3Se-2	C_{sp2}–H···O5	0.0142	0.050	0.0013	-13.2
	O2–H1···Se	0.0196	0.039	-0.0010	-15.6
	O5–H4···O2	0.0299	0.093	-0.0016	-34.8
CH_3Te-2	C_{sp2}–H···O5	0.0139	0.049	0.0012	-12.8
	O2–H1···Te	0.0166	0.031	-0.0005	-11.4
	O5–H4···O2	0.0294	0.092	-0.0015	-33.9

Table S2c Electron density (ρ(r)), Laplacian of electron density ($\nabla^2\rho(r)$), total electron energy density (H(r)) and individual energy of H-bond ($E_{H\text{-}bond}$) at BCPs of intermolecular contacts in **XZ-3**

Complex	H-bonds	ρ(r) (au)	$\nabla^2\rho(r)$ (au)	H(r) (au)	$E_{H\text{-}bond}$ (kJ.mol^{-1})
HO-3	C_{sp2}–H···O8	0.0155	0.056	0.0015	-14.5
	O2–H1···O	0.0323	0.093	-0.0030	-38.5
	O5–H4···O2	0.0360	0.103	-0.0043	-45.0
	O8–H7···O5	0.0339	0.098	-0.0034	-41.1
HS-3	C_{sp2}–H···O8	0.0164	0.059	0.0015	-15.6
	O2–H1···S	0.0224	0.046	-0.0018	-19.7
	O5–H4···O2	0.0348	0.101	-0.0038	-42.9
	O8–H7···O5	0.0336	0.098	-0.0032	-40.7
HSe-3	C_{sp2}–H···O8	0.0164	0.059	0.0015	-15.6
	O2–H1···Se	0.0199	0.039	-0.0012	-15.9
	O5–H4···O2	0.0345	0.100	-0.0036	-42.4
	O8–H7···O5	0.0334	0.098	-0.0031	-40.4
HTe-3	C_{sp2}–H···O8	0.0162	0.059	0.0015	-15.4
	O2–H1···Te	0.0171	0.031	-0.0006	-11.7
	O5–H4···O2	0.0340	0.100	-0.0034	-41.7
	O8–H7···O5	0.0329	0.095	-0.0021	-36.5
FO-3	C_{sp2}–H···O8	0.0208	0.076	0.0015	-21.1
	O2–H1···O	0.0258	0.088	-0.0002	-29.3
	O5–H4···O2	0.0349	0.102	-0.0037	-43.2
	O8–H7···O5	0.0351	0.100	-0.0039	-43.0
FS-3	C_{sp2}–H···O8	0.0206	0.075	0.0014	-20.8
	O2–H1···S	0.0194	0.044	-0.0008	-16.6
	O5–H4···O2	0.0341	0.100	-0.0034	-41.8
	O8–H7···O5	0.0345	0.099	-0.0036	-42.1
FSe-3	C_{sp2}–H···O8	0.0204	0.074	0.0014	-20.6
	O2–H1···Se	0.0179	0.038	-0.0006	-14.0
	O5–H4···O2	0.0341	0.100	-0.0034	-41.8
	O8–H7···O5	0.0344	0.099	-0.0036	-42.0
FTe-3	C_{sp2}–H···O8	0.0198	0.072	0.0014	-19.8
	O2–H1···Te	0.0159	0.030	-0.0003	-10.8
	O5–H4···O2	0.0339	0.099	-0.0034	-41.3
	O8–H7···O5	0.0340	0.099	-0.0034	-41.4
ClO-3	C_{sp2}–H···O8	0.0218	0.078	0.0013	-22.3
	O2–H1···O	0.0256	0.086	-0.0002	-28.9
	O5–H4···O2	0.0345	0.101	-0.0036	-42.7
	O8–H7···O5	0.0350	0.099	-0.0039	-42.9
ClS-3	C_{sp2}–H···O8	0.0216	0.077	0.0012	-22.1
	O2–H1···S	0.0200	0.044	-0.0010	-17.2
	O5–H4···O2	0.0342	0.100	-0.0035	-42.0
	O8–H7···O5	0.0345	0.099	-0.0036	-42.2
ClSe-3	C_{sp2}–H···O8	0.0213	0.076	0.0012	-21.6
	O2–H1···Se	0.0184	0.038	-0.0007	-14.4
	O5–H4···O2	0.0342	0.100	-0.0035	-41.9
	O8–H7···O5	0.0344	0.099	-0.0036	-42.0
ClTe-3	C_{sp2}–H···O8	0.0206	0.073	0.0013	-20.7
	O2–H1···Te	0.0162	0.030	-0.0004	-10.9
	O5–H4···O2	0.0339	0.099	-0.0034	-41.3
	O8–H7···O5	0.0340	0.099	-0.0034	-41.3
BrO-3	C_{sp2}–H···O8	0.0227	0.080	0.0011	-23.3
	O2–H1···O	0.0246	0.084	0.0001	-27.3
	O5–H4···O2	0.0342	0.101	-0.0034	-42.1
	O8–H7···O5	0.0350	0.100	-0.0039	-42.9
BrS-3	C_{sp2}–H···O8	0.0219	0.077	0.0011	-22.4
	O2–H1···S	0.0199	0.044	-0.0010	-17.0
	O5–H4···O2	0.0341	0.100	-0.0034	-41.8
	O8–H7···O5	0.0345	0.099	-0.0036	-42.1
BrSe-3	C_{sp2}–H···O8	0.0214	0.076	0.0012	-21.8
	O2–H1···Se	0.0183	0.038	-0.0007	-14.3
	O5–H4···O2	0.0341	0.100	-0.0034	-41.7
	O8–H7···O5	0.0343	0.099	-0.0035	-41.9

Table S2c Continued

Complex	H-bonds	ρ(r) (au)	$\nabla^2\rho(r)$ (au)	H(r) (au)	$E_{H\text{-}bond}$ (kJ.mol^{-1})
BrTe-3	C_{sp2}–H···O8	0.0209	0.074	0.0013	-21.0
	O2–H1···Te	0.0161	0.030	-0.0004	-10.9
	O5–H4···O2	0.0338	0.099	-0.0033	-41.2
	O8–H7···O5	0.0339	0.099	-0.0043	-41.2
CH_3O-3	C_{sp2}–H···O8	0.0142	0.051	0.0014	-13.1
	O2–H1···O	0.0361	0.097	-0.0047	-44.2
	O5–H4···O2	0.0366	0.103	-0.0046	-45.9
	O8–H7···O5	0.0336	0.098	-0.0032	-40.7
CH_3S-3	C_{sp2}–H···O8	0.0102	0.037	0.0012	-9.0
	O2–H1···S	0.0247	0.048	-0.0026	-22.6
	O5–H4···O2	0.0343	0.101	-0.0035	-42.4
	O8–H7···O5	0.0325	0.098	-0.0027	-39.2
CH_3Se-3	C_{sp2}–H···O8	0.0100	0.036	0.0011	-8.8
	O2–H1···Se	0.0218	0.041	-0.0018	-18.1
	O5–H4···O2	0.0341	0.100	-0.0034	-41.9
	O8–H7···O5	0.0324	0.098	-0.0026	-39.0
CH_3Te-3	C_{sp2}–H···O8	0.0099	0.035	0.0011	-8.7
	O2–H1···Te	0.0183	0.032	-0.0009	-12.9
	O5–H4···O2	0.0335	0.099	-0.0032	-40.9
	O8–H7···O5	0.0320	0.097	-0.0025	-38.5

Table S3 Concise summary of interaction energies of **$(H_2O)_n$** systems, with n=2, 3, 4 (kJ.mol^{-1})

Complexes	Level of theory	Interaction energy (kJ.mol^{-1})	Source
$(H_2O)_2$	MP2/aug-cc-pVDZ	-18.5[a]	[1]
	MP2/aug-cc-pVDZ	-19.4[a]	[1]
	CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ	-11.3[b], -20.0[a]	This work
	CCSDT/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd)	-10.4[b], -19.3[a]	This work
	Experiment	-22.6 ± 2.9	[2]
$(H_2O)_3$	MP4SDQ/6-31+G(2d,2p)	-45.1[b]	[3]
	CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ	-41.6[b], -64.2[a]	This work
	CCSDT/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd)	-39.2[b], -61.6[a]	This work
$(H_2O)_4$	MP2/6-31+G(d,p)	-117.9[a]	[4]
	MP2/6-311+G(2d,2p)	-102.5[a]	[4]
	CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ	-79.2[b], -113.7[a]	This work
	CCSDT/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd)	-74.1[b], -108.7[a]	This work

[a] Corrected by only BSSE
[b] Corrected by both ZPE and BSSE

[1] S. S. Xantheas and T. H. Dunning Jr, *J. Chem. Phys.*, 1993, **99**, 8774-8792.
[2] L. A. Curtiss, D. J. Frurip, and M. Blander, *J. Chem. Phys.*,1979, **71**, 2703.
[3] O. Mo, M. Yanez, and J. Elguero, *J. Chem. Phys.*, 1992, **97**, 6628.
[4] M. Masella, N. Gresh and J. P. Flament, *J. Chem. Soc. Faraday Trans*, 1998, **94**, 2745-2753.

Table S4. Changes of H-bond lengths (Δr, in mÅ) and their corresponding stretching frequencies (Δν, in cm^{-1}) in complexes at MP2/6-311++G(3df,2dp)

	HO-1	**FO-1**	**ClO-1**	**BrO-1**	**CH_3O-1**	**HS-1**	**FS-1**	**ClS-1**	**BrS-1**	**CH_3S-1**
Δr(C_{sp2}–H)	-2.9	-1.3	-1.3	-1.2	-3.5	-0.3	-0.3	0.2	0.4	-0.7
Δr(O2–H1)	7.4	3.7	3.8	3.4	9.0	6.8	4.1	4.6	4.5	7.8
Δν(C_{sp2}–H)	45.8	24.4	27.3	28.1	49.4	15.6	13.9	11.5	9.7	19.9
Δν(O2–H1)	-147.5	-66.2	-68.3	-60.0	-181.7	-141.5	-81.2	-91.8	-89.6	-163.3
	HSe-1	**FSe-1**	**ClSe-1**	**BrSe-1**	**CH_3Se-1**	**HTe-1**	**FTe-1**	**ClTe-1**	**BrTe-1**	**CH_3Te-1**
Δr(C_{sp2}–H)	0	0	0.4	0.5	-0.4	0.4	0.1	0.4	0.6	-0.1
Δr(O2–H1)	6.4	4.4	4.8	4.7	7.3	5.7	4.4	4.7	4.7	6.6
Δν(C_{sp2}–H)	10.1	10.8	7.5	6.5	15.4	4.6	9.3	6.4	4.6	11.5
Δν(O2–H1)	-134.7	-87.6	-96.9	-95.6	-153.8	-121.2	-90.3	-95.5	-96.0	-139.0
	HO-2	**FO-2**	**ClO-2**	**BrO-2**	**CH_3O-2**	**HS-2**	**FS-2**	**ClS-2**	**BrS-2**	**CH_3S-2**
Δr(C_{sp2}–H)	-4.6	0.1	-0.1	0.3	-5.9	0.6	2.1	2.7	3.1	-0.9
Δr(O2–H1)	13.1	8.8	8.7	8.2	15.4	12.2	9.5	10.1	10.0	13.4
Δr(O5–H4)	12.6	12.3	12.1	12.0	13.2	12.2	11.9	12.0	11.9	12.7
Δν(C_{sp2}–H)	72.8	11.3	17.7	14.5	86.4	7.9	-15.4	-20.8	-25.3	27.7
Δν(O2–H1)	-255.7	-159.9	-161.4	-150.6	-303.0	-247.8	-188.9	-203.3	-200.6	-273.0
Δν(O5–H4)	-249.7	-240.6	-237.2	-234.0	-260.4	-240.8	-234.3	-237.1	-235.1	-250.8
	HSe-2	**FSe-2**	**ClSe-2**	**BrSe-2**	**CH_3Se-2**	**HTe-2**	**FTe-2**	**ClTe-2**	**BrTe-2**	**CH_3Te-2**
Δr(C_{sp2}–H)	1.3	2.5	3.1	3.4	-0.1	5.4	2.4	3.0	3.3	0.5
Δr(O2–H1)	11.6	9.7	10.3	10.2	12.7	9.7	9.7	10.0	10.0	11.8
Δr(O5–H4)	12.0	12.0	12.1	12.0	12.5	12.0	12.0	11.9	11.9	12.2
Δν(C_{sp2}–H)	-4.2	-20.9	-27.1	-30.9	16.4	-13.7	-20.5	-27.6	-32.0	7.5
Δν(O2–H1)	-237.2	-195.4	-207.6	-205.9	-259.2	-221.5	-195.5	-202.9	-201.8	-239.4
Δν(O5–H4)	-238.0	-237.4	-239.0	-237.6	-248.1	-230.8	-236.5	-235.9	-235.0	-241.1
	HO-3	**FO-3**	**ClO-3**	**BrO-3**	**CH_3O-3**	**HS-3**	**FS-3**	**ClS-3**	**BrS-3**	**CH_3S-3**
Δr(C_{sp2}–H)	-5.0	1.9	1.6	2.3	-7.4	0.6	2.9	3.5	3.9	-3.1
Δr(O2–H1)	14.9	10.1	10.1	9.5	17.9	13.4	10.6	11.3	11.2	15.3
Δr(O5–H4)	17.4	16.5	16.3	16.0	18.0	16.3	15.7	15.8	15.7	15.9
Δr(O8–H7)	15.9	16.9	16.8	16.8	15.8	15.3	16.0	16.0	16.0	14.7
Δν(C_{sp2}–H)	80.1	-14.3	-7.1	-15.9	109.0	8.7	-27.3	-32.1	-38.5	51.6
Δν(O2–H1)	-294.6	-190.2	-191.7	-180.5	-358.2	-274.9	-213.0	-228.7	-227.6	-317.0
Δν(O5–H4)	-341.6	-322.7	-317.8	-312.1	-354.2	-319.6	-307.2	-309.8	-307.8	-313.1
Δν(O8–H7)	-315.2	-346.5	-344.9	-334.6	-311.3	-304.4	-329.6	-330.7	-318.7	-289.5
	HSe-3	**FSe-3**	**ClSe-3**	**BrSe-3**	**CH_3Se-3**	**HTe-3**	**FTe-3**	**ClTe-3**	**BrTe-3**	**CH_3Te-3**
Δr(C_{sp2}–H)	1.5	3.2	3.7	4.1	-2.5	2.3	3.0	3.6	4.0	-2.1
Δr(O2–H1)	12.8	10.8	11.4	11.3	14.3	12.1	10.8	11.2	11.1	13.1
Δr(O5–H4)	16.0	15.7	15.8	15.7	15.7	15.6	15.5	15.5	15.5	15.3
Δr(O8–H7)	15.1	15.9	15.9	15.8	14.5	14.8	15.5	15.5	15.5	14.1
Δν(C_{sp2}–H)	-5.6	-31.5	-37.0	-42.0	43.3	-16.6	-28.1	-35.7	-41.3	37.8
Δν(O2–H1)	-262.9	-219.1	-231.8	-230.7	-298.0	-248.2	-219.2	-227.5	-227.1	-280.7
Δν(O5–H4)	-314.9	-307.8	-309.9	-307.7	-298.7	-307.6	-305.3	-306.0	-304.7	-300.0
Δν(O8–H7)	-300.3	-327.9	-328.0	-315.4	-284.7	-292.9	-309.8	-309.8	-309.1	-276.7

Table S5. NBO charges of Z atoms (Z = O, S, Se, Te) in monomers at ωB97XD/6-311++G(3df,2pd)

	HCHO	**FCHO**	**ClCHO**	**BrCHO**	**CH_3CHO**
q(O)/e	-0.514	-0.493	-0.455	-0.445	-0.506
	HCHS	**FCHS**	**ClCHS**	**BrCHS**	**CH_3CHS**
q(S)/e	0.114	0.075	0.156	0.177	0.089
	HCHSe	**FCHSe**	**ClCHSe**	**BrCHSe**	**CH_3CHSe**
q(Se)/e	0.202	0.148	0.238	0.261	0.175
	HCHTe	**FCHTe**	**ClCHTe**	**BrCHTe**	**CH_3CHTe**
q(Te)/e	0.290	0.211	0.309	0.337	0.234

Table S6. Concise summary of stretching frequency changes of C_{sp}–H, C_{sp2}–H and C_{sp3}–H bonds involving hydrogen bond

Complexes	Level of theory/ Experiment	$\Delta\nu(C_{sp3}–H)$ (cm^{-1})	Source
$C_2HX\cdots C_6H_6$ (X = H, F, Cl, Br, CH_3, NH_2)	MP2/aug-cc-pVDZ	15.7 ÷ 24.9	[5]
$CH_3CN/CH_3NC\cdots H_2O$	B3LYP/ aug-cc-pVTZ	5-14	[6]
$CHX_3\cdots NH_2Y$ (X=F, Cl; Y=H, F, Cl, Br)	MP2/6-311++G(d,p)	9.4 ÷ 36.3	[7]
DMSO ··· CO_2 DMSO···$1H_2O$ DMSO···$2H_2O$ (has water bridge O–H···O) DMSO···$2H_2O$ (no water bridge O–H···O)	MP2/6–311++G(2d,2p)	35 29.7 33.2 25.7	[8]
$Cl_3CH\cdots NCCH_3$	Exp.	8.7	[9]
F_3CH···ammonia F_3CH···pyridine	Exp.	7.6 3	[10]
$F_3CH\cdots OH_2$	Exp. MP2/6- 311++G(d,p)	20.3 39.4	[11]
Complexes	**Level of theory/ Experiment**	**$\Delta\nu(C_{sp2}–H)$ (cm^{-1})**	**Source**
RCHZ···HCOOH (R= H, F, Cl, Br, CH_3, NH_2; Z= O, S)	MP2/aug-cc-pVDZ	81÷96	[12]
$CH_3CHO\cdots 1H_2O$ $CH_3CHO\cdots 2H_2O$	B3LYP/6-311++G(d,p)	52 93	[13]
$HCHO\cdots 1H_2O$ $HCHO\cdots 2H_2O$	B3LYP/6-311++G(d,p)	45 66	[14]
$CH_3CHZ\cdots 1H_2O$ (Z=O, S, Se, Te) $CH_3CHZ\cdots 2H_2O$ $CH_3CHZ\cdots 3H_2O$	MP2/6-311++G(3df,2dp)	11.5 ÷ 49.4 7.5 ÷ 86.4 37.8 ÷ 109.0	This work
BIM(benzimidazole)···$2H_2O$ MBIM(N-methylbenzimidazole)···$4H_2O$	Exp. Exp.	14 14	[15]
Complexes	**Level of theory/ Experiment**	**$\Delta\nu(C_{sp}–H)$ (cm^{-1})**	**Source**
RCHO···HCN	MP2/aug-cc-pVDZ	-56.7 ÷ -107.8	[16]
RCCH···NH_3 (R= H, F, Cl, CH_3, CH_2F, CHF_2, CF_3, CH_2Cl, $CHCl_2$, CCl_3, CN, HCC, FCC, ClCC)	B3LYP/6-31(d,p)	-193 ÷ -324	[17]
(o-Chlorobenzoacetylen)$_3$	Exp.	-69	[18]
(2-ethynyladamantan-2-ol)	Exp.	-130	[19]

[5] P. N. Khanh, V. T. Ngan, N. T. H. Man, N. T. A. Nhung, A. K. Chandra and N.T. Trung, *RSC Adv.*, 2016, **6**, 106662-106670.
[6] D. L. Cao, X. Q. Feng, J. L. Wang, Y. X. Li, Z. Y. Hu and S. S. Chen, *J. Mol. Struct.: THEOCHEM*, 2008, **849**, 76-83.
[7] N.T.H. Man, P. L. Nhan, V. Vien, D.T. Quang and N. T. Trung, *Int. J. Quantum Chem*, 2017, **117**, e25338.
[8] P. N. Khanh, P. D. Cam-Tu, H. Q. Dai, V. Q. Van, V. T. Ngan, M. T. Nguyen and N. T. Trung, *J. Comput. Chem.*, 2019, **140**, 464-474.
[9] B.Behera and P. K. Das, *J. Phys. Chem. A*, 2019, **123**, 1830-1839.
[10] W. A. Herrebout, S. M. Melikova, S. N. Delanoye, K. S. Rutkowski, D. N. Shchepkin and B. J. van der Veken, *J. Phys. Chem. A*, 2005, **109**, 3038-3044.
[11] R. Gopi, N. Ramanathan and K. Sundararajan, *Chem. Phys.*, 2016, **476**, 36-45.
[12] N. T. Trung, P. N. Khanh, A. J. P. Carvalho and M. T. Nguyen, *J. Comput. Chem.*, 2019, **40**, 1387-1400.
[13] A. K. Chandra and T. Zeegers-Huyskens, *J. At. Mol. Phys.*, 2012, **2012**.
[14] A. K. Chandra, T. Zeegers-Huyskens, *J. Comput. Chem.*, 2012, **33**, 1131-1141.
[15] A. Bhattacherjee and S. Wategaonkar, *Phys. Chem. Chem. Phys.*, 2016, **18**, 27745-27749.
[16] N. N. Tri, N. T. H. Man, N. L. Tuan, N. T. T. Trang, D. T. Quang and N. T. Trung, *Theor. Chem. Acc.*, 2017, **136**, 1-12.
[17] V. Dimitrova, S. Ilieva and B. Galabov, *J. Phys. Chem. A*, 2002, **106**, 11801-11805.
[18] G. Ferguson and K.M.S. Islam, *J. Chem. Sot B*, **1966**, 593.
[19] E. Steinwender, E. T. G. Lutz, J. H. Van der Maas and J. A. Kanters, 1993, ***4***, 217-229.

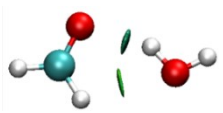
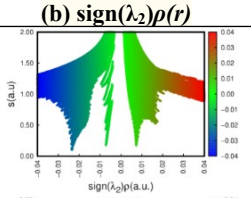
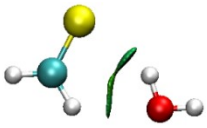
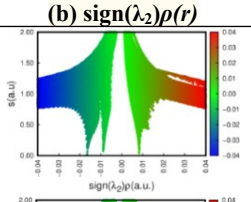
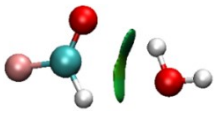
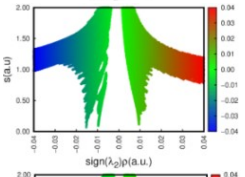
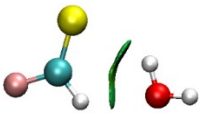
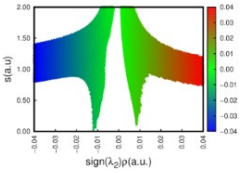
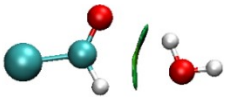
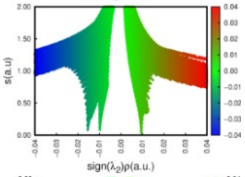
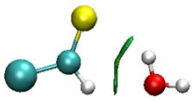
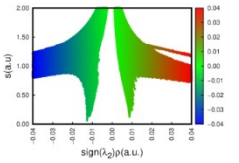
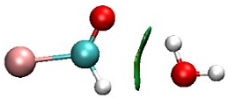
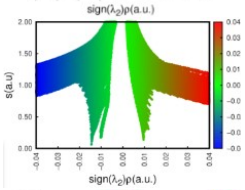
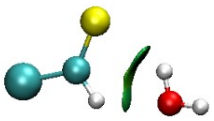
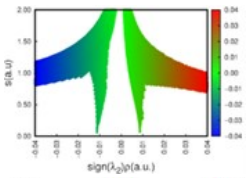
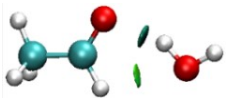
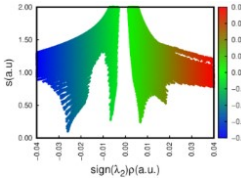
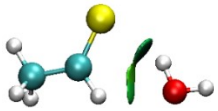
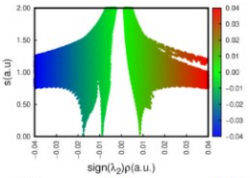
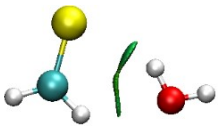
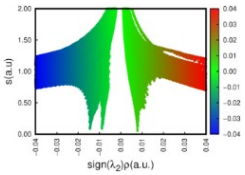
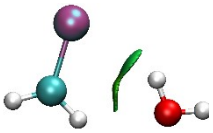
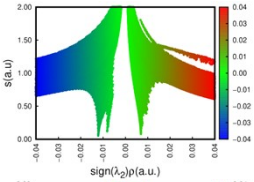
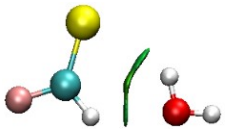
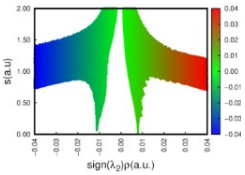
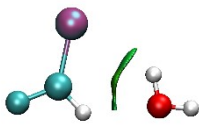
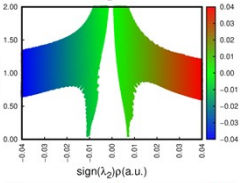
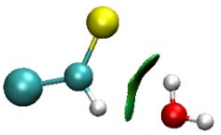
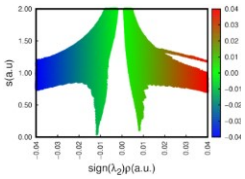
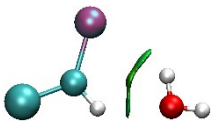
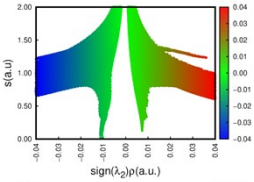
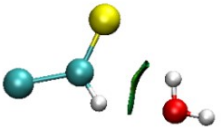
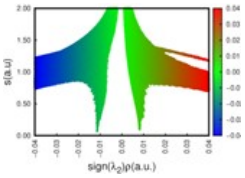
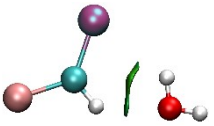
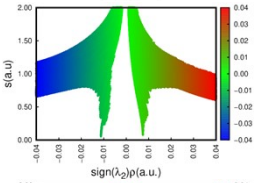
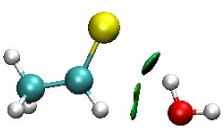
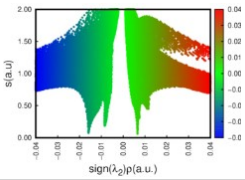
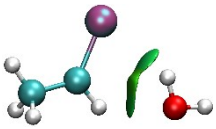
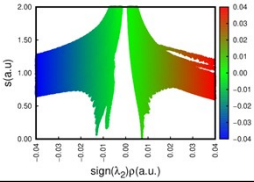
Complex	NCI isosurface	Plots of (a) *s(r)*, (b) sign(λ_2)ρ*(r)*	Complex	NCI isosurface	Plots of (a) *s(r)*, (b) sign(λ_2)ρ*(r)*
HO-1			**HS-1**		
FO-1			**FS-1**		
ClO-1			**ClS-1**		
BrO-1			**BrS-1**		
CH_3O-1			**CH_3S-1**		
HSe-1			**HTe-1**		
FSe-1			**FTe-1**		
ClSe-1			**ClTe-1**		
BrSe-1			**BrTe-1**		
CH_3Se-1			**CH_3Te-1**		

Figure S1a. NCI isosurface and plots of s(r) as a function of sign(λ_2)ρ(r) for **XZ-1** 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 a.u*)

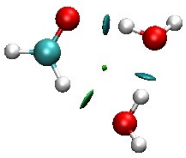
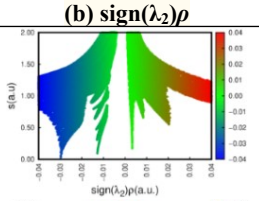
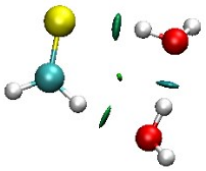
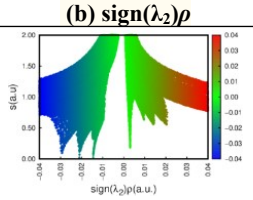
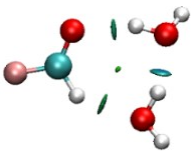
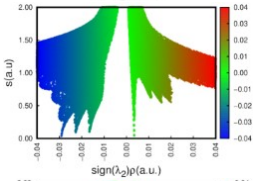
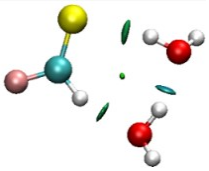
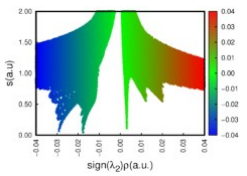
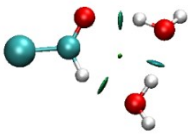
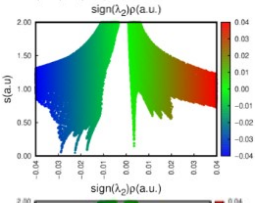
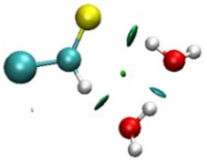
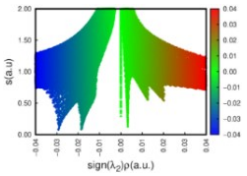
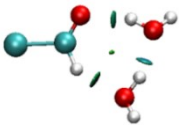
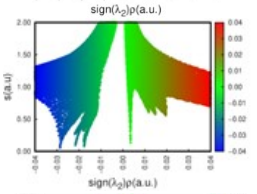
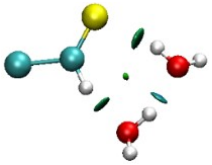
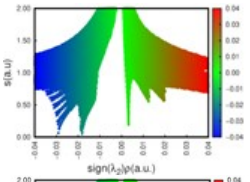
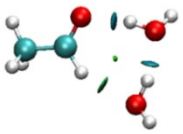
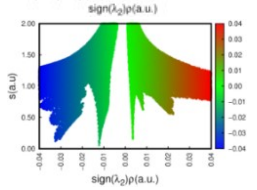
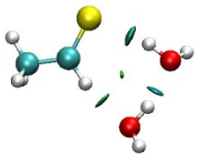
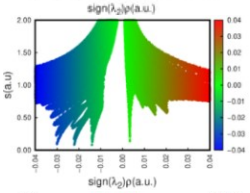
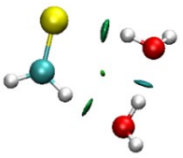
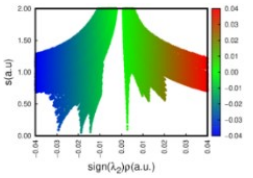
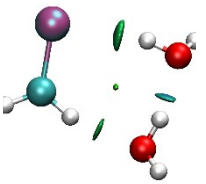
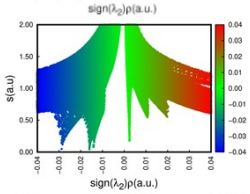
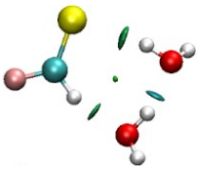
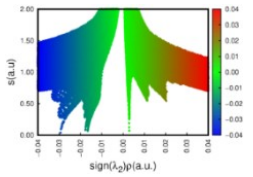
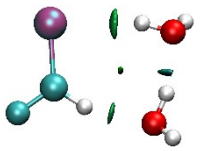
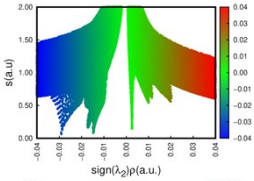
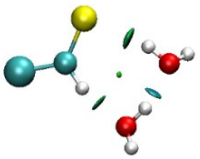
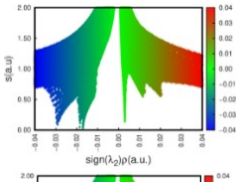
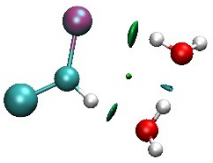
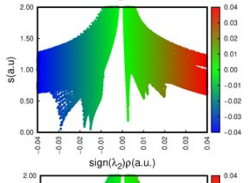
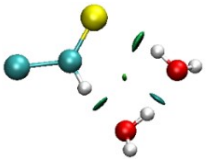
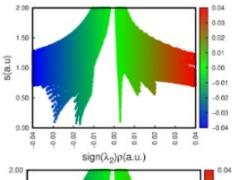
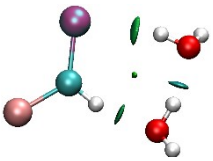
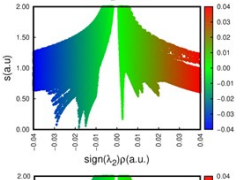
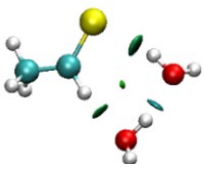
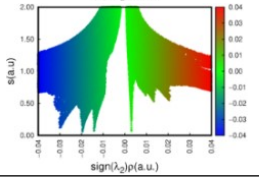
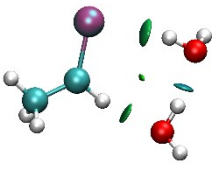
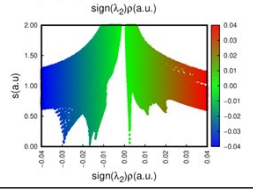
Complex	NCI isosurface	Plots of (a) $s(r)$, (b) $\text{sign}(\lambda_2)\rho$	Complex	NCI isosurface	Plots of (a) $s(r)$, (b) $\text{sign}(\lambda_2)\rho$
HO-2			HS-2		
FO-2			FS-2		
ClO-2			ClS-2		
BrO-2			BrS-2		
CH_3O-2			CH_3S-2		
HSe-2			HTe-2		
FSe-2			FTe-2		
ClSe-2			ClTe-2		
BrSe-2			BrTe-2		
CH_3Se-2			CH_3Te-2		

Figure S1b. NCI isosurface and plots of s(r) as a function of $\text{sign}(\lambda_2)\rho(r)$ for **XZ-2** complexes
(*The surfaces are colored on a blue-green-red scale according to the values of $\text{sign}(\lambda_2)\rho(r)$ ranging from −0.04 to 0.04 a.u*)

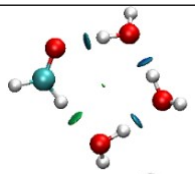
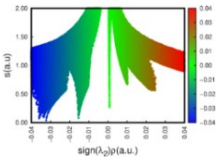
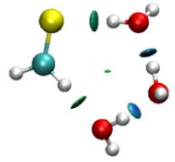
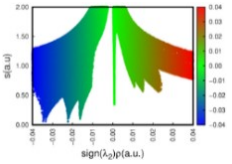
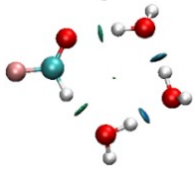
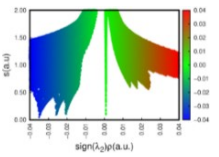
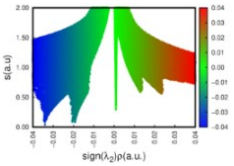
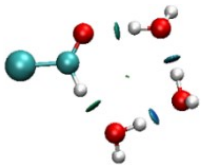
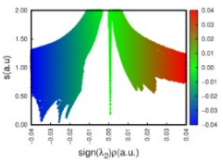
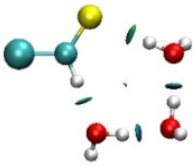
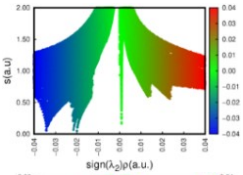
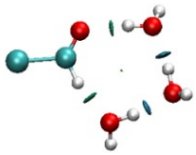
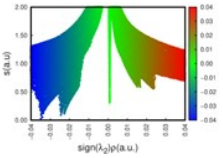
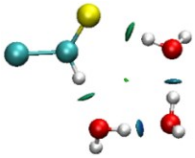
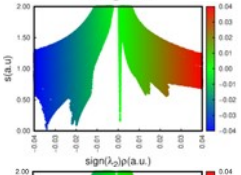
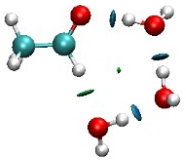
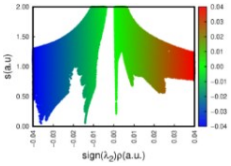
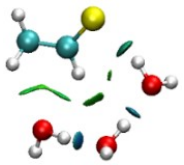
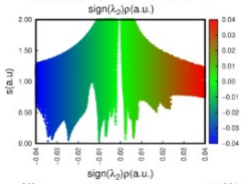
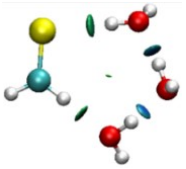
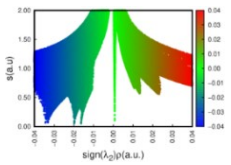
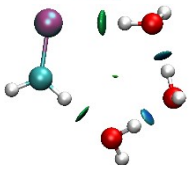
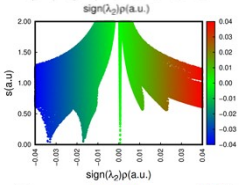
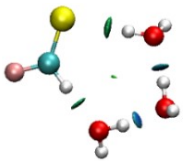
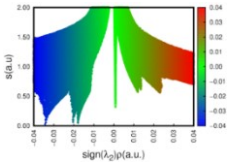
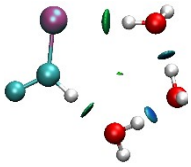
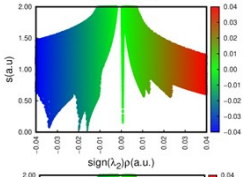
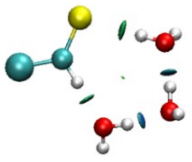
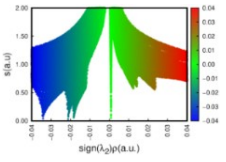
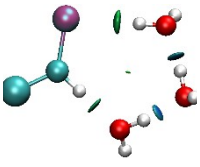
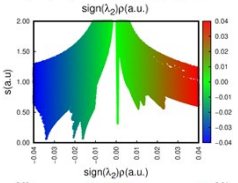
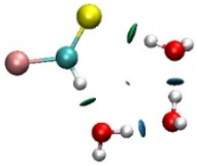
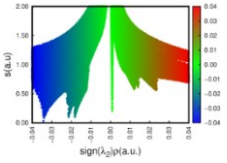
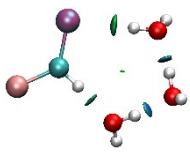
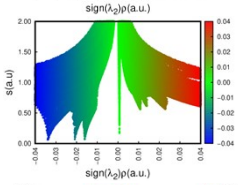
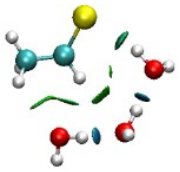
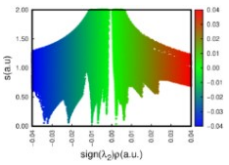
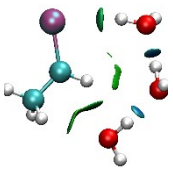
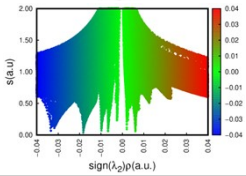
Complex	NCI isosurface	Plots of (a) $s(r)$, (b) sign(λ_2)$\rho(r)$	Complex	NCI isosurface	Plots of (a) $s(r)$, (b) sign(λ_2)$\rho(r)$
HO-3			HS-3		
FO-3			FS-3		
ClO-3			ClS-3		
BrO-3			BrS-3		
CH_3O-3			CH_3S-3		
HSe-3			HTe-3		
FSe-3			FTe-3		
ClSe-3			ClTe-3		
BrSe-3			BrTe-3		
CH_3Se-3			CH_3Te-3		

Figure S1c. NCI isosurface and plots of s(r) as a function of sign(λ_2)ρ(r) for **XZ-3** complexes
(*The surfaces are colored on a blue-green-red scale according to the values of sign(λ_2)$\rho(r)$ ranging from −0.04 to 0.04 a.u*)

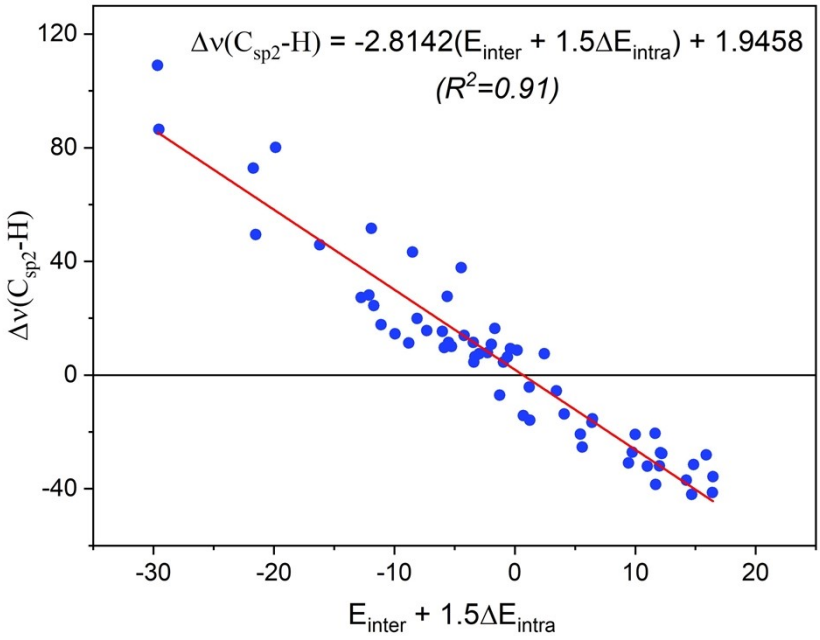


Figure S2. The linear correlation of change in stretching frequency $\Delta\nu(C_{sp2}\text{-H})$ with respective to intermolecular hyperconjugative interaction energies and changes of intramolecular hyperconjugative interaction energies (E_{inter} + $1.5\Delta E_{intra}$) for the obtained complexes at ωB97X-D/6-311++G(3df,2pd), with X = H, F, Cl, Br, CH_3; Z = O, S, Se, Te, n = 1-3.