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

SUPPLEMENTARY INFORMATION

Partitioning of interaction-induced nonlinear optical properties of molecular complexes. I. Hydrogen-bonded systems

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Table S1: Electronic and nuclear-relaxation (hyper)polarizabilities of studied molecular complexes computed using the aug-cc-pVTZ basis set. All values are given in au.

HCN...HCl

α^{el}	α^{nr}	β^{el}	β^{nr}	γ^{el}	$\gamma^{\mathrm{nr}} \times 10^3$	
46.92	10.92	-44.46	-760.49	7204	63.6	MP2
45.97	9.29	-37.71	-602.55	6601	43.9	CCSD
47.10	9.94	-39.54	-665.62	7559	49.8	CCSD(T)

HCN...HCCH

α^{el}	α^{nr}	β^{el}	β^{nr}	γ^{el}	$\gamma^{\mathrm{nr}} \times 10^3$	
58.01	3.61	-30.20	-184.48	8738	10.1	MP2
57.21	3.50	-24.78	-170.64	7577	9.2	CCSD
58.56	3.62	-23.61	-188.59	8519	9.9	CCSD(T)

HCN...HCCF

α^{el}	α^{nr}	β^{el}	β^{nr}	γ^{el}	$\gamma^{\mathrm{nr}} \times 10^3$	
59.89	6.58	91.77	-237.23	7631	11.6	MP2
58.78	6.38	84.17	-218.17	6762	10.0	CCSD
60.35	6.58	93.84	-242.95	7691	11.5	CCSD(T)

HCN...HNC

α^{el}	α^{nr}	β^{el}	β^{nr}	γ^{el}	$\gamma^{\mathrm{nr}} \times 10^3$	
52.01	8.38	-77.71	-345.17	8369	25.3	MP2
51.15	7.80	-75.50	-274.15	7914	19.3	CCSD
52.39	8.12	-74.39	-300.75	8974	22.2	CCSD(T)

HNC...HCN

α^{el}	α^{nr}	β^{el}	β^{nr}	γ^{el}	$\gamma^{\mathrm{nr}} \times 10^3$	
50.97	4.71	-63.51	-186.19	7840	11.8	MP2
50.29	4.55	-61.09	-157.64	7764	9.9	CCSD
51.52	4.71	-57.52	-175.21	8856	11.3	CCSD(T)

Table S1: *continued*

HNC...HNC

α^{el}	α^{nr}	β^{el}	β^{nr}	γ^{el}	$\gamma^{\mathrm{nr}} \times 10^3$	
54.04	8.54	-98.28	-356.58	9900	31.7	MP2
52.93	7.79	-103.07	-237.97	9847	21.5	CCSD
54.21	8.09	-100.14	-276.19	11406	26.4	CCSD(T)

FCN...HCN

α^{el}	α^{nr}	β^{el}	β^{nr}	γ^{el}	$\gamma^{\mathrm{nr}} \times 10^3$	
52.68	6.74	-104.28	-188.11	6126	12.6	MP2
51.71	6.44	-88.33	-180.51	5629	11.6	CCSD
53.24	6.73	-89.85	-190.24	6416	13.3	CCSD(T)

FCN...HF

α^{el}	α^{nr}	β^{el}	β^{nr}	γ^{el}	$\gamma^{\mathrm{nr}} \times 10^3$	
34.92	7.40	-62.49	-105.77	2663	8.5	MP2
34.05	6.96	-54.44	-90.38	2531	7.1	CCSD
35.12	7.22	-55.26	-92.45	2878	8.5	CCSD(T)

N2...HF

α^{el}	α^{nr}	β^{el}	β^{nr}	γ^{el}	$\gamma^{\mathrm{nr}} \times 10^3$	
23.06	3.46	-3.35	-64.23	1847	2.7	MP2
22.90	3.31	-2.90	-55.64	1760	1.9	CCSD
23.48	3.40	-3.41	-60.91	1932	2.3	CCSD(T)

OC...HF

α^{el}	α^{nr}	β^{el}	β^{nr}	γ^{el}	$\gamma^{\mathrm{nr}} \times 10^3$	
24.87	3.76	-33.63	-67.60	2164	3.6	MP2
24.15	3.59	-35.72	-45.93	2172	2.7	CCSD
24.73	3.66	-35.22	-53.97	2413	2.9	CCSD(T)

HCN...HF

α^{el}	α^{nr}	β^{el}	β^{nr}	γ^{el}	$\gamma^{\mathrm{nr}} \times 10^3$	
31.47	5.50	-1.91	-152.32	2852	7.9	MP2
31.04	5.14	0.43	-132.88	2711	6.8	CCSD
31.80	5.33	3.65	-141.65	3040	7.5	CCSD(T)

Table S2: Comparison of diagonal electronic first hyperpolarizability for HCN$\cdots$HCCH calculated using different geometries.

Property	//	Geometry	$\beta^{\mathrm{el}}_{zzz}$ [au]	Absolute relative error wrt. CCSD(T)//CCSD(T) [%]
CCSD(T)	//	CCSD(T)	-23.61	0
CCSD(T)	//	MP2	-23.13	2
MP2	//	MP2	-30.20	28

Table S3: Electron correlation effect on excess first hyperpolarizability of HCN$\cdots$HCCH.

Property	//	Geometry	$\Delta\beta^{\mathrm{el}}_{zzz}$ [au]	Absolute relative error wrt. CCSD(T)//MP2 [%]
CCSD(T)	//	MP2	-28.23	0
CCSD	//	MP2	-27.65	2
MP2	//	MP2	-29.55	5

Table S4: Absolute and relative VP-EDS contributions to excess nuclear relaxation polarizability calculated at the MP2/*aug*-cc-pVTZ level of theory.

System	$\Delta\alpha_{el}^{(10)}$	$\Delta\alpha_{ex}^{HL}$	$\Delta\alpha_{del}^{HF}$	$\Delta\alpha^{HF}$	$\Delta\alpha_{el,r}^{(12)}$	$\Delta\alpha_{disp}^{(20)}$	$\Delta\alpha_{ex}^{(2)}$	$\Delta\alpha^{MP2}$
HNC...HNC	15.51	-25.04	17.75	8.22	0.08	3.53	-0.99	10.85
HCN...HNC	14.43	-21.42	15.90	8.91	-0.29	3.00	-1.47	10.15
FCN...HF	8.50	-11.51	9.68	6.66	-0.12	1.44	-1.07	6.93
HCN...HCl	26.55	-46.39	28.57	8.73	-0.06	8.25	-3.60	13.32
HNC...HCN	9.82	-13.70	7.34	3.47	-0.01	2.07	-0.86	4.67
FCN...HCN	10.22	-13.01	7.28	4.50	-0.23	2.18	-1.31	5.12
OC...HF	5.85	-8.68	6.18	3.35	0.13	1.04	-0.38	4.13
HCN...HCCF	8.60	-9.75	4.95	3.80	-0.13	1.83	-1.24	4.26
HCN...HCCH	7.70	-8.91	4.45	3.23	-0.11	1.68	-1.21	3.59
N_2...HF	5.02	-5.74	4.24	3.52	-0.10	0.57	-0.35	3.64
Relative contributions								
HNC...HNC	143%	-231%	164%	76%	1%	33%	-9%	100%
HCN...HNC	142%	-211%	157%	88%	-3%	30%	-14%	100%
FCN...HF	123%	-166%	140%	96%	-2%	21%	-15%	100%
HCN...HCl	199%	-348%	214%	66%	0%	62%	-27%	100%
HNC...HCN	210%	-293%	157%	74%	0%	44%	-18%	100%
FCN...HCN	200%	-254%	142%	88%	-5%	42%	-26%	100%
OC...HF	142%	-210%	150%	81%	3%	25%	-9%	100%
HCN...HCCF	202%	-229%	116%	89%	-3%	43%	-29%	100%
HCN...HCCH	215%	-249%	124%	90%	-3%	47%	-34%	100%
N_2...HF	138%	-158%	116%	97%	-3%	16%	-10%	100%
Average	171%	-235%	148%	84%	-1%	36%	-19%	100%
Average deviation	34%	41%	20%	8%	2%	11%	8%	0%

Table S5: Absolute and relative VP-EDS contributions to excess nuclear relaxation first hyperpolarizability calculated at the MP2/*aug*-cc-pVTZ level of theory.

System	$\Delta\beta_{\mathrm{el}}^{(10)}$	$\Delta\beta_{\mathrm{ex}}^{\mathrm{HL}}$	$\Delta\beta_{\mathrm{del}}^{\mathrm{HF}}$	$\Delta\beta^{\mathrm{HF}}$	$\Delta\beta_{\mathrm{el,r}}^{(12)}$	$\Delta\beta_{\mathrm{d\ isp}}^{(20)}$	$\Delta\beta_{\mathrm{ex}}^{(2)}$	$\Delta\beta^{\mathrm{MP2}}$
HNC...HNC	-943.3	1777.6	-1463.0	-628.2	-15.7	-279.3	129.2	-794.0
HCN...HNC	-779.7	1383.9	-1180.8	-567.9	-3.2	-219.9	154.6	-635.8
FCN...HF	-248.0	457.4	-461.5	-254.7	1.2	-77.4	60.8	-268.0
HCN...HCl	-2073.7	4156.5	-2959.9	-877.2	28.7	-683.7	314.5	-1217.6
HNC...HCN	-458.0	746.0	-497.2	-209.2	-8.5	-102.0	56.6	-263.1
FCN...HCN	-448.5	679.9	-471.6	-243.7	-4.2	-93.5	66.2	-272.7
OC...HF	-119.9	251.9	-245.9	-113.9	-10.4	-37.6	27.7	-134.2
HCN...HCCF	-444.6	585.7	-352.1	-211.0	-0.2	-92.4	66.0	-236.3
N_2...HF	-83.1	166.6	-152.4	-68.8	-9.1	-31.4	24.8	-84.5
Relative contributions								
HNC...HNC	119%	-224%	184%	79%	2%	35%	-16%	100%
HCN...HNC	123%	-218%	186%	89%	1%	35%	-24%	100%
FCN...HF	93%	-171%	172%	95%	0%	29%	-23%	100%
HCN...HCl	170%	-341%	243%	72%	-2%	56%	-26%	100%
HNC...HCN	174%	-284%	189%	80%	3%	39%	-22%	100%
FCN...HCN	164%	-249%	173%	89%	2%	34%	-24%	100%
OC...HF	89%	-188%	183%	85%	8%	28%	-21%	100%
HCN...HCCF	188%	-248%	149%	89%	0%	39%	-28%	100%
N_2...HF	98%	-197%	180%	81%	11%	37%	-29%	100%
Average	135%	-235%	184%	84%	3%	37%	-24%	100%
Average deviation	31%	36%	13%	5%	3%	5%	3%	0%

Optimized geometries of molecular complexes (cartesian coordinates are given in Å).

HNC...HNC, CCSD(T)/aug-cc-pVTZ

C	0.00000	0.00000	2.79706
N	0.00000	0.00000	1.62208
H	0.00000	0.00000	0.60979
C	0.00000	0.00000	-1.47562
N	0.00000	0.00000	-2.64619
H	0.00000	0.00000	-3.64519

HCN...HNC, CCSD(T)/aug-cc-pVTZ

C	0.00000	0.00000	2.73474
N	0.00000	0.00000	1.56000
H	0.00000	0.00000	0.54971
N	0.00000	0.00000	-1.41776
C	0.00000	0.00000	-2.57492
H	0.00000	0.00000	-3.64356

FCN...HF, CCSD(T)/aug-cc-pVTZ

F	0.00000	0.00000	2.34725
C	0.00000	0.00000	1.08289
N	0.00000	0.00000	-0.07625
H	0.00000	0.00000	-1.94118
F	0.00000	0.00000	-2.87206

HCN...HCl, CCSD(T)/aug-cc-pVTZ

H	0.00000	0.00000	-3.78877
C	0.00000	0.00000	-2.72056
N	0.00000	0.00000	-1.56253
H	0.00000	0.00000	0.50942
Cl	0.00000	0.00000	1.79771

HNC...HCN, CCSD(T)/aug-cc-pVTZ

N	0.00000	0.00000	2.95043
C	0.00000	0.00000	1.78980
H	0.00000	0.00000	0.71597
C	0.00000	0.00000	-1.63315
N	0.00000	0.00000	-2.80556
H	0.00000	0.00000	-3.80435

FCN...HCN, CCSD(T)/aug-cc-pVTZ

F	0.00000	0.00000	3.03565
C	0.00000	0.00000	1.76942
N	0.00000	0.00000	0.60800
H	0.00000	0.00000	-1.60266
C	0.00000	0.00000	-2.67483
N	0.00000	0.00000	-3.83534

OC...HF, CCSD(T)/aug-cc-pVTZ

O	0.00000	0.00000	-1.96982
C	0.00000	0.00000	-0.83740
H	0.00000	0.00000	1.24395
F	0.00000	0.00000	2.17083

FCCH...NCH, CCSD(T)/aug-cc-pVTZ

F	0.00000	0.00000	3.15020
C	0.00000	0.00000	1.86365
C	0.00000	0.00000	0.65972
H	0.00000	0.00000	-0.40643
N	0.00000	0.00000	-2.72362
C	0.00000	0.00000	-3.88261
H	0.00000	0.00000	-4.95070

HCCH...NCH, CCSD(T)/aug-cc-pVTZ

H	0.00000	0.00000	4.01981
C	0.00000	0.00000	2.95541
C	0.00000	0.00000	1.74413
H	0.00000	0.00000	0.67636
N	0.00000	0.00000	-1.66503
C	0.00000	0.00000	-2.82410
H	0.00000	0.00000	-3.89214

N2...HF, CCSD(T)/aug-cc-pVTZ

N	0.00000	0.00000	-1.98892
N	0.00000	0.00000	-0.88599
H	0.00000	0.00000	1.18084
F	0.00000	0.00000	2.10471

HNC...HNC, MP2/aug-cc-pVTZ

C	0.00000	0.00000	2.77993
N	0.00000	0.00000	1.60356
H	0.00000	0.00000	0.58887
C	0.00000	0.00000	-1.45710
N	0.00000	0.00000	-2.62862
H	0.00000	0.00000	-3.62759

HCN...HNC, MP2/aug-cc-pVTZ

C	0.00000	0.00000	2.72042
N	0.00000	0.00000	1.54408
H	0.00000	0.00000	0.53221
N	0.00000	0.00000	-1.39929
C	0.00000	0.00000	-2.56330
H	0.00000	0.00000	-3.62943

FCN...HF, MP2/aug-cc-pVTZ

F	0.00000	0.00000	2.34529
C	0.00000	0.00000	1.08369
N	0.00000	0.00000	-0.08315
H	0.00000	0.00000	-1.93274
F	0.00000	0.00000	-2.86597

HCN...HCl, MP2/aug-cc-pVTZ

H	0.00000	0.00000	-3.75854
C	0.00000	0.00000	-2.69287
N	0.00000	0.00000	-1.52789
H	0.00000	0.00000	0.48672
Cl	0.00000	0.00000	1.77412

HNC...HCN, MP2/aug-cc-pVTZ

N	0.00000	0.00000	2.94546
C	0.00000	0.00000	1.77786
H	0.00000	0.00000	0.70576
C	0.00000	0.00000	-1.62416
N	0.00000	0.00000	-2.79790
H	0.00000	0.00000	-3.79650

FCN...HCN, MP2/aug-cc-pVTZ

F	0.00000	0.00000	3.03169
C	0.00000	0.00000	1.76822
N	0.00000	0.00000	0.59879
H	0.00000	0.00000	-1.59287
C	0.00000	0.00000	-2.66310
N	0.00000	0.00000	-3.83047

OC...HF, MP2/aug-cc-pVTZ

O	0.00000	0.00000	-1.96277
C	0.00000	0.00000	-0.82700
H	0.00000	0.00000	1.22995
F	0.00000	0.00000	2.15908

FCCH...NCH, MP2/aug-cc-pVTZ

F	0.00000	0.00000	3.14315
C	0.00000	0.00000	1.85936
C	0.00000	0.00000	0.65301
H	0.00000	0.00000	-0.41115
N	0.00000	0.00000	-2.71029
C	0.00000	0.00000	-3.87633
H	0.00000	0.00000	-4.94181

HCCH...NCH, MP2/aug-cc-pVTZ

H	0.00000	0.00000	4.00947
C	0.00000	0.00000	2.94737
C	0.00000	0.00000	1.73400
H	0.00000	0.00000	0.66807
N	0.00000	0.00000	-1.65297
C	0.00000	0.00000	-2.81909
H	0.00000	0.00000	-3.88453

N2...HF, MP2/aug-cc-pVTZ

N	0.00000	0.00000	-1.99169
N	0.00000	0.00000	-0.87848
H	0.00000	0.00000	1.17613
F	0.00000	0.00000	2.10146