On the physical origins of interaction-induced vibrational (hyper)polarizabilities
SUPPORTING INFORMATION

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Table 1 Electronic and nuclear relaxation polarizability and first hyperpolarizability of HCN monomer and dimer (given in a.u.) at equilibrium geometries corresponding to the indicated methods.

Method	α^e_{zz}	α^{nr}_{zz}	β^e_{zzz}	$[\mu\alpha]^{(0,0)}_{zzz}$	$[\mu^3]^{(1,0)}_{zzz}$	$[\mu^3]^{(0,1)}_{zzz}$	β^{nr}_{zzz}
				HCN			
MP2/aug-cc-pVDZ	22.80	0.17	3.40	-8.36	<0.01	-0.26	-8.62
MP2/aug-cc-pVTZ	22.20	0.18	0.43	-8.97	-0.02	-0.29	-9.28
MP2/aug-cc-pVQZ	22.09	0.18	-0.62	-9.14	-0.02	-0.29	-9.45
				HCN$\cdots$HCN			
MP2/aug-cc-pVDZ	50.60	4.84	-37.41	-163.75	-257.45	197.78	-223.42
MP2/aug-cc-pVTZ	49.15	4.71	-39.45	-157.04	-242.81	180.98	-218.87
CCSD/aug-cc-pVTZ	48.66	4.54	-29.91±0.1	$\cdots$	$\cdots$	$\cdots$	-210.50±0.2
CCSD(T)/aug-cc-pVTZ	49.92	4.71	-28.00	$\cdots$	$\cdots$	$\cdots$	-224.64±6
MP2/aug-cc-pVQZ	48.89	4.75	-39.84	-157.65	-246.61	189.39	-214.87

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Table 2 Results of decomposition of electronic and nuclear relaxation polarizability and first hyperpolarizability (given in a.u.) of HCN dimer, performed at the MP2 level of theory. Note that the estimated errors arising from numerical differentiation are given **independently** for each interaction energy component and theirs sums (ΔP^{HF}, ΔP^{MP2}).

	ΔP^{HF}				$\Delta P^{\mathrm{MP2}}_{\mathrm{corr}}$			
P	$\Delta P^{(10)}_{\mathrm{el}}$	$\Delta P^{\mathrm{HL}}_{\mathrm{ex}}$	$\Delta P^{\mathrm{HF}}_{\mathrm{del}}$	ΔP^{HF}	$\Delta P^{(12)}_{\mathrm{el,r}}$	$\Delta P^{(20)}_{\mathrm{disp}}$	$\Delta P^{(2)}_{\mathrm{ex}}$	ΔP^{MP2}
	aug-cc-pVTZ							
α^{e}_{zz}	5.04	-1.84	1.41	4.61	0.24	0.35	-0.55	4.65
α^{nr}_{zz}	10.02±0.03	-12.75±0.06	7.28±0.01	4.55	-0.30	2.05±0.02	-1.37±0.01	4.93
β^{e}_{zzz}	-14.9	13.9	-23.2	-24.2	-10.5	-0.2	-3.6	-38.5
β^{nr}_{zzz}	-448±6	672±10	-468±3	-245	3	-93±1	65±1	-264
	aug-cc-pVQZ							
α^{e}_{zz}	5.01	-1.83	1.40	4.58	0.21	0.35	-0.54	4.61
α^{nr}_{zz}	9.82	-12.44	7.22	4.59	-0.30	2.03	-1.26	5.06
β^{e}_{zzz}	-15.0	14.0	-23.2	-24.2	-10.4	-0.2	-3.6±0.1	-38.4
β^{nr}_{zzz}	-461±20	697±36	-489±11	-275±15	3	-108±5	75±2	-263±2

Table 3 Results of decomposition of electronic and nuclear relaxation polarizability and first hyperpolarizability (given in a.u.) of HCN dimer, performed at the DFT/aug-TZ2P level of theory.

	$P(\mathbf{AB})$	$P(\mathbf{A})$	$P(\mathbf{B})$	ΔP	ΔP_{Pauli}	ΔP_{el}	ΔP_{orb}	$\Delta P_{orb-\sigma}$	$\Delta P_{orb-\pi}$
					α^{e}_{zz}				
BLYP	52.98	23.85	23.69	5.43	-2.81±0.01	5.75±0.01	2.50±0.02	2.02±0.01	0.46
LC-BLYP	48.61	22.01	21.84	4.82	-2.70	5.49	2.02	1.67	0.35
LC-BLYP-dDsC	48.96±0.01	21.99	21.99±0.01	4.98	-2.99	5.74	2.18	1.80	0.38
					α^{nr}_{zz}				
BLYP	6.28±0.01	-0.87±0.01	0.18	7.03±0.02	-17.12±0.19	12.09±0.05	12.00±0.26	10.79±0.31	1.21±0.05
LC-BLYP	5.21	-0.78	0.23	5.84	-13.78±0.07	10.24±0.02	9.38±0.05	8.30±0.04	1.08±0.01
LC-BLYP-dDsC	5.02±0.2	-0.89±0.01	0.28±0.01	5.63±0.17	-11.62±0.58	8.81±0.31	8.67±0.22	7.69±0.19	0.98±0.02
					β^{e}_{zzz}				
BLYP	-38.5±0.5	9.0	8.2±0.1	-55.8±0.4	19.1±1.0	-21.9±0.1	-53.0±1.5	-54.9±1.0	0.5±1.9
LC-BLYP	-35.1	0.7	0.2	-36.2	22.2	-22.7	-35.4	-32.7	-2.7
LC-BLYP-dDsC	-35.7	0.4±0.1	1.2±0.3	-37.2±0.2	23.0	-22.4	-39.7	-34.0	-2.5
					β^{nr}_{zzz}				
BLYP	-293.9±0.9	107.6±1.0	-11.3	-390.5±3.8	1000.7±68.9	-584.7±37.2	-813.1±49.3	-675.2±42.7	-92.3±3.4
LC-BLYP	-224.6±23.3	55.2±16.6	-19.2±1.9	-269.5±7.0	1092.6±9.1	-683.6±31.0	-678.8±47.1	-585.1±49.6	-93.4±1.8