SUPPLEMENTARY INFORMATION

Vibrational nonlinear optical properties of spatially confined weakly bound complexes

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Table S1: Interaction energy decomposition at the RHF/6-31G level of theory. The energy differences under confinement where evaluated at the CCSD(T)/aug-cc-pVTZ level of theory. All values (except ϕ, a.u.) are given in kcal/mol.

	HCN$\cdots$HCN	HCN$\cdots$HNC
	(4,4) carbon nanotube geometry of inner complex optimized with $\phi = 0.0$ a.u.	
$\epsilon_{\text{el}}^{(10)}$	-109	-112
$\Delta E_{\text{ex}}^{\text{HL}}$	269	272
$\Delta E_{\text{del}}^{\text{HF}}$	-27	-26
$\Delta E_{\text{int}}^{\text{HF}}$	133	134
	(4,4) carbon nanotube geometry of inner complex optimized with $\phi = 0.1$ a.u.	
$\epsilon_{\text{el}}^{(10)}$	-108	-111
$\Delta E_{\text{ex}}^{\text{HL}}$	267	271
$\Delta E_{\text{del}}^{\text{HF}}$	-27	-26
$\Delta E_{\text{int}}^{\text{HF}}$	132	134
$E(\phi = 0.1) - E(\phi = 0.0)$	108	110
$E(\phi = 0.2) - E(\phi = 0.0)$	415	419

Table S2: The effect of spatial confinement and geometry on longitudinal electronic (hyper)polarizabilities of the HCN$\cdots$HCN complex. The highlighted values are reported in Table 1 in the manuscript and correspond to geometries relaxed for the indicated potential amplitude. All properties are given in a.u. and were determined at the CCSD(T)/aug-cc-pVTZ level of theory.

	α^e			β^e			γ^e		
	geometry optimized with:			geometry optimized with:			geometry optimized with:		
	$\phi = 0.0$	$\phi = 0.1$	$\phi = 0.2$	$\phi = 0.0$	$\phi = 0.1$	$\phi = 0.2$	$\phi = 0.0$	$\phi = 0.1$	$\phi = 0.2$
$\phi = 0.0$	49.88	49.32	47.94	-28	-28	-29	6.5×10^3	6.3×10^3	5.9×10^3
$\phi = 0.1$	48.19	47.65	46.33	-25	-25	-26	5.3×10^3	5.2×10^3	4.9×10^3
$\phi = 0.2$	44.97	44.47	43.25	-22	-22	-23	4.0×10^3	3.9×10^3	3.6×10^3

Table S3: Electronic and vibrational contributions to (hyper)polarizabilities as a function of confinement strength (ϕ). The properties are given in atomic units and were computed at the CCSD(T)/aug-cc-pVTZ level of theory. The numbers in parentheses correspond to percentage relative errors between MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ data.

ϕ	α^e	α^{nr}	β^e	$[\mu\alpha]^{(0,0)}$	β^{nr}	γ^e	$[\alpha^2]^{(0,0)}$	$[\mu\beta]^{(0,0)}$	γ^{nr}
				HCN$\cdots$HCN					
0.0	49.88	4.75	-28	-167	-225	6.5×10^3	3.9×10^3	0.7×10^3	11.3×10^3
	(-1.46)	(-0.84)	(41.50)	(-6.10)	(-2.63)	(-3.51)	(-6.89)	(-4.97)	(-0.36)
0.1	47.65	4.59	-25	-157	-211	5.2×10^3	3.5×10^3	0.7×10^3	10.0×10^3
	(-1.51)	(-0.87)	(41.95)	(-6.00)	(-3.89)	(-4.29)	(-7.14)	(-5.95)	(-1.37)
0.2	43.25	4.19	-23	-137	-185	3.6×10^3	2.7×10^3	0.6×10^3	7.5×10^3
	(-1.60)	(-0.95)	(38.56)	(-5.96)	(-3.17)	(-5.30)	(-7.21)	(-4.28)	(0.90)
				HCN$\cdots$HNC					
0.0	52.39	8.12	-74	-182	-301	9.0×10^3	4.2×10^3	0.3×10^3	22.2×10^3
	(-0.73)	(3.20)	(4.46)	(5.82)	(14.77)	(-6.72)	(-0.38)	(-88.24)	(14.17)
0.1	50.01	7.79	-62	-169	-282	6.8×10^3	3.8×10^3	$<0.1\times10^3$	19.6×10^3
	(-0.80)	(3.21)	(5.28)	(5.75)	(14.45)	(-7.46)	(-0.77)	(>-100.00)	(15.67)
0.2	45.48	7.15	-53	-147	-250	4.5×10^3	3.0×10^3	-0.1×10^3	16.2×10^3
	(-0.86)	(3.22)	(5.50)	(5.36)	(13.72)	(-8.60)	(-1.24)	(238.03)	(10.54)

Table S4: The convergence of square bracket terms with respect to normal mode contributions for HCN$\cdots$HCN and $\phi = 0.1$ a.u. All values are given in a.u.

mode	$[\mu^2]_{zz}^{(0,0)}$		$[\mu\alpha]_{zzz}^{(0,0)}$		$[\alpha^2]_{zzzz}^{(0,0)}$		$[\mu\beta]_{zzzz}^{(0,0)}$		$\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}$	$\left[\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}\right]^2$	$\left[\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}\right]^3$	$\left[\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}\right]^4$
	sum	i	sum	i	sum	i	sum	i				
1	3.562	3.562	-86.546	-86.546	701.012	701.012	453.030	453.030	-0.33×10^4	0.11×10^8	-0.37×10^{11}	0.12×10^{15}
2	3.562	0.000	-86.546	0.000	701.012	0.000	453.030	0.000	0.87×10^{-3}	0.76×10^{-6}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
3	3.562	0.000	-86.546	0.000	701.013	0.001	453.038	0.007	0.10×10^1	0.11×10^1	0.11×10^1	0.11×10^1
4	3.562	0.000	-86.546	0.000	701.013	0.000	453.038	0.000	0.37×10^{-4}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
5	3.562	0.000	-86.546	0.000	701.015	0.001	453.037	0.000	-0.60×10^0	0.36×10^0	-0.22×10^0	0.13×10^0
6	3.562	0.000	-86.546	0.000	701.015	0.000	453.037	0.000	0.17×10^{-3}	0.30×10^{-7}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
7	3.562	0.000	-86.546	0.000	701.015	0.001	453.038	0.001	0.12×10^0	0.15×10^{-1}	0.18×10^{-2}	0.21×10^{-3}
8	3.562	0.000	-86.546	0.000	701.015	0.000	453.038	0.000	0.23×10^{-4}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
9	3.562	0.000	-86.546	0.000	701.017	0.001	453.039	0.000	0.14×10^0	0.20×10^{-1}	0.29×10^{-2}	0.41×10^{-3}
10	3.653	0.092	-100.852	-14.306	1446.236	745.219	490.323	37.284	0.31×10^2	0.96×10^3	0.30×10^5	0.93×10^6
11	3.683	0.030	-111.521	-10.669	2700.691	1254.455	464.897	-25.426	0.18×10^2	0.31×10^3	0.55×10^4	0.98×10^5
12	4.464	0.780	-149.473	-37.952	3315.989	615.298	731.003	266.106	0.57×10^2	0.32×10^4	0.18×10^6	0.10×10^8
13	4.587	0.123	-157.428	-7.956	3487.735	171.746	655.780	-75.223	0.22×10^2	0.49×10^3	0.11×10^5	0.24×10^6

Table S5: The convergence of square bracket terms with respect to normal mode contributions for HCN$\cdots$HCN and $\phi = 0.2$ a.u. All values are given in a.u.

mode	$[\mu^2]^{(0,0)}_{zz}$		$[\mu\alpha]^{(0,0)}_{zzz}$		$[\alpha^2]^{(0,0)}_{zzzz}$		$[\mu\beta]^{(0,0)}_{zzzz}$		$\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}$	$\left[\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}\right]^2$	$\left[\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}\right]^3$	$\left[\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}\right]^4$
	sum	i	sum	i	sum	i	sum	i				
1	3.302	3.302	-76.575	-76.575	591.945	591.945	403.341	403.341	-0.31×10^4	0.95×10^7	-0.29×10^{11}	0.91×10^{14}
2	3.302	0.000	-76.575	0.000	591.945	0.000	403.341	0.000	0.35×10^{-3}	0.12×10^{-6}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
3	3.302	0.000	-76.575	0.000	591.945	0.000	403.342	0.000	0.67×10^{-1}	0.45×10^{-2}	0.30×10^{-3}	0.21×10^{-4}
4	3.302	0.000	-76.575	0.000	591.945	0.000	403.342	0.000	-0.34×10^{-3}	0.12×10^{-6}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
5	3.302	0.000	-76.575	0.000	591.946	0.001	403.342	0.000	0.55×10^{-1}	0.30×10^{-2}	0.17×10^{-3}	0.93×10^{-5}
6	3.302	0.000	-76.575	0.000	591.946	0.000	403.342	0.000	0.15×10^{-3}	0.23×10^{-7}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
7	3.302	0.000	-76.575	0.000	591.946	0.001	403.341	0.000	0.68×10^{-1}	0.47×10^{-2}	0.32×10^{-3}	0.22×10^{-4}
8	3.302	0.000	-76.575	0.000	591.946	0.000	403.341	0.000	0.86×10^{-3}	0.74×10^{-6}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
9	3.302	0.000	-76.575	0.000	591.947	0.001	403.341	0.000	0.10×10^{0}	0.11×10^{-1}	0.11×10^{-2}	0.12×10^{-3}
10	3.392	0.091	-89.049	-12.474	1164.916	572.969	437.024	33.682	0.30×10^{2}	0.88×10^{3}	0.26×10^{5}	0.78×10^{6}
11	3.424	0.032	-98.437	-9.388	2090.149	925.233	417.132	-19.891	0.17×10^{2}	0.30×10^{3}	0.53×10^{4}	0.92×10^{5}
12	4.093	0.668	-130.151	-31.714	2591.830	501.681	639.872	222.740	0.50×10^{2}	0.25×10^{4}	0.13×10^{6}	0.65×10^{7}
13	4.189	0.096	-136.501	-6.349	2731.348	139.518	583.934	-55.937	0.19×10^{2}	0.35×10^{3}	0.67×10^{4}	0.13×10^{6}

Table S6: The convergence of square bracket terms with respect to normal mode contributions for HCN$\cdots$HNC and $\phi = 0.1$ a.u. All values are given in a.u.

mode	$[\mu^2]^{(0,0)}_{zz}$		$[\mu\alpha]^{(0,0)}_{zzz}$		$[\alpha^2]^{(0,0)}_{zzzz}$		$[\mu\beta]^{(0,0)}_{zzzz}$		$\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}$	$\left[\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}\right]^2$	$\left[\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}\right]^3$	$\left[\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}\right]^4$
	sum	i	sum	i	sum	i	sum	i				
1	5.196	5.196	-86.757	-86.757	482.845	482.845	-351.228	-351.228	0.31×10^4	0.96×10^7	0.30×10^{11}	0.91×10^{14}
2	5.196	0.000	-86.757	0.000	482.845	0.000	-351.228	0.000	0.22×10^{-3}	0.50×10^{-7}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
3	5.196	0.000	-86.757	0.000	482.847	0.001	-351.235	-0.008	0.18×10^1	0.34×10^1	0.62×10^1	0.11×10^2
4	5.196	0.000	-86.757	0.000	482.847	0.000	-351.235	0.000	-0.67×10^{-3}	0.44×10^{-6}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
5	5.196	0.000	-86.757	0.000	482.848	0.001	-351.231	0.005	-0.96×10^0	0.91×10^0	-0.87×10^0	0.84×10^0
6	5.196	0.000	-86.757	0.000	482.848	0.000	-351.231	0.000	-0.93×10^{-4}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
7	5.196	0.000	-86.757	0.000	482.850	0.002	-351.230	0.000	0.12×10^0	0.14×10^{-1}	0.16×10^{-2}	0.19×10^{-3}
8	5.196	0.000	-86.757	0.000	482.850	0.000	-351.230	0.000	0.52×10^{-3}	0.27×10^{-6}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
9	5.196	0.000	-86.757	0.000	482.852	0.002	-351.232	-0.002	0.20×10^0	0.39×10^{-1}	0.77×10^{-2}	0.15×10^{-2}
10	5.266	0.070	-71.380	15.377	1611.670	1128.818	-330.190	21.042	-0.28×10^2	0.78×10^3	-0.22×10^5	0.60×10^6
11	5.290	0.024	-80.131	-8.750	2681.826	1070.156	-361.785	-31.595	0.16×10^2	0.24×10^3	0.38×10^4	0.60×10^5
12	5.520	0.230	-93.363	-13.232	2935.406	253.580	-447.464	-85.679	0.30×10^2	0.92×10^3	0.28×10^5	0.84×10^6
13	7.789	2.269	-169.344	-75.981	3783.393	847.988	2.755	450.218	0.91×10^2	0.82×10^4	0.75×10^6	0.68×10^8

Table S7: The convergence of square bracket terms with respect to normal mode contributions for HCN$\cdots$HNC and $\phi = 0.2$ a.u. All values are given in a.u.

mode	$[\mu^2]^{(0,0)}_{zz}$		$[\mu\alpha]^{(0,0)}_{zzz}$		$[\alpha^2]^{(0,0)}_{zzzz}$		$[\mu\beta]^{(0,0)}_{zzzz}$		$\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}$	$\left[\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}\right]^2$	$\left[\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}\right]^3$	$\left[\frac{1}{\omega_i^2}\frac{\partial\mu_z}{\partial Q_i}\right]^4$
	sum	i	sum	i	sum	i	sum	i				
1	4.779	4.779	-74.231	-74.231	384.357	384.357	-365.401	-365.401	0.28×10^4	0.78×10^7	0.22×10^{11}	0.61×10^{14}
2	4.779	0.000	-74.231	0.000	384.357	0.000	-365.401	0.000	0.20×10^{-3}	0.40×10^{-7}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
3	4.779	0.000	-74.231	0.000	384.357	0.000	-365.401	0.000	0.85×10^{-1}	0.72×10^{-2}	0.61×10^{-3}	0.52×10^{-4}
4	4.779	0.000	-74.231	0.000	384.357	0.000	-365.401	0.000	0.10×10^{-3}	0.11×10^{-7}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
5	4.779	0.000	-74.231	0.000	384.357	0.001	-365.400	0.000	0.41×10^{-1}	0.17×10^{-2}	0.71×10^{-4}	0.29×10^{-5}
6	4.779	0.000	-74.231	0.000	384.357	0.000	-365.400	0.000	-0.11×10^{-3}	0.12×10^{-7}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
7	4.779	0.000	-74.231	0.000	384.359	0.002	-365.396	0.004	0.12×10^{0}	0.15×10^{-1}	0.19×10^{-2}	0.23×10^{-3}
8	4.779	0.000	-74.231	0.000	384.359	0.000	-365.396	0.000	0.93×10^{-4}	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$	$<1.00\times10^{-8}$
9	4.779	0.000	-74.231	0.000	384.360	0.001	-365.394	0.002	0.11×10^{0}	0.12×10^{-1}	0.12×10^{-2}	0.13×10^{-3}
10	4.836	0.057	-62.002	12.228	1259.821	875.461	-356.903	8.491	-0.24×10^{2}	0.58×10^{3}	-0.14×10^{5}	0.34×10^{6}
11	4.862	0.027	-70.052	-8.049	2068.551	808.729	-382.513	-25.610	0.16×10^{2}	0.25×10^{3}	0.40×10^{4}	0.64×10^{5}
12	5.048	0.185	-80.706	-10.654	2272.870	204.319	-447.148	-64.635	0.26×10^{2}	0.68×10^{3}	0.18×10^{5}	0.46×10^{6}
13	7.147	2.099	-147.098	-66.393	2972.785	699.915	-70.774	376.374	0.84×10^{2}	0.71×10^{4}	0.60×10^{6}	0.51×10^{8}

HCN-HCN@(4,4)

HCN-HNC@(4,4)

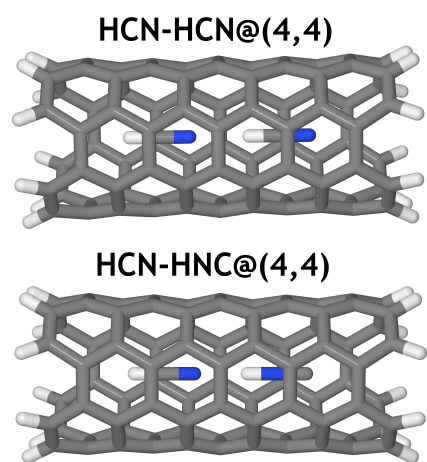Figure S1: Geometries of studied complexes encapsulated inside (4,4) SWCNT.

Figure S2: Lowest-frequency mode ($n = 1$) for spatially confined HCN$\cdots$HCN complex.