Hydrogen bonding inside and outside carbon nanotubes: HF dimer as a case study

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Electronic Supplementary Information

Table 1 The interaction energy values [kcal/mol] calculated for the isolated hydrogen fluoride dimer at different levels of theoretical approximation.

	HF	MP2	CCSD	CCSD(T)	CCSD(T)-F12a	CCSD(T)-F12b	CCSD(T)-F12c
cc-pVDZ	-3.7	-3.5	-3.3	-3.4	-3.9	-3.8	-3.8
cc-pVTZ	-3.4	-3.4	-3.4	-3.4	-3.7	-3.7	-3.7
cc-pVQZ	-3.3	-3.5	-3.5	-3.5	-3.7	-3.6	-3.6
cc-pV5Z	-3.3	-3.5	-3.5	-3.5	-3.6	-3.6	-3.6
cc-pV6Z	-3.3	-3.5	-3.5	-3.6	-	-	-
aug-cc-pVDZ	-3.1	-3.0	-3.0	-3.0	-3.5	-3.5	-3.5
aug-cc-pVTZ	-3.2	-3.3	-3.3	-3.4	-3.6	-3.6	-3.6
aug-cc-pVQZ	-3.2	-3.4	-3.5	-3.5	-3.6	-3.6	-3.6
aug-cc-pV5Z	-3.3	-3.5	-3.5	-3.6	-3.6	-3.6	-3.6
cc-pVDZ-F12	-3.1	-3.0	-3.0	-3.0	-3.5	-3.5	-3.5
cc-pVTZ-F12	-3.3	-3.3	-3.4	-3.4	-3.6	-3.5	-3.6
cc-pVQZ-F12	-3.3	-3.4	-3.5	-3.5	-3.6	-3.6	-3.6

	B3LYP	B3LYP-D3	CAM-B3LYP	PBE0	M06-HF	M06-2X	M06
cc-pVDZ	-4.0	-4.4	-4.6	-4.1	-4.0	-4.3	-4.0
cc-pVTZ	-3.7	-4.1	-4.4	-3.8	-4.0	-4.3	-3.4
cc-pVQZ	-3.5	-3.9	-4.2	-3.7	-3.7	-4.0	-3.1
cc-pV5Z	-3.4	-3.8	-4.1	-3.6	-3.7	-3.9	-3.0
cc-pV6Z	-3.4	-3.7	-4.0	-3.5	-3.7	-3.9	-3.0
aug-cc-pVDZ	-3.2	-3.6	-3.8	-3.4	-3.5	-3.7	-3.2
aug-cc-pVTZ	-3.3	-3.7	-3.9	-3.4	-3.7	-3.9	-2.9
aug-cc-pVQZ	-3.3	-3.7	-4.0	-3.5	-3.6	-3.9	-2.9
aug-cc-pV5Z	-3.3	-3.7	-4.0	-3.5	-3.6	-3.9	-2.9

Table 2 The interaction energy and BSSE values [kcal/mol] calculated for the complexes formed between $(HF)_2$ and (4,4)CNT using different DFT functionals (step number -27). The carbon nanotubes have been represented by the cc-pVDZ or cc-pVTZ basis sets, whereas the HF dimer is described using aug-cc-pVDZ or aug-cc-pVTZ. Symbol CP refers to results obtained using the counterpoise correction scheme.

double-ζ quality

	$\Delta E_{(HF)_2@(4,4)CNT}$	$\Delta E^{CP}_{(HF)_2@(4,4)CNT}$	BSSE	$\Delta E^{in}_{HF\cdots HF}$	$\Delta E_{(HF)_2-(4,4)CNT}$	$\Delta E^{CP}_{(HF)_2-(4,4)CNT}$	BSSE	$\Delta E^{out}_{HF\cdots HF}$
B3LYP	23.6	30.7	7.1	-2.5	1.6	3.3	1.7	-3.1
B3LYP-D3	-0.5	6.5	7.0	-2.9	-3.2	-1.4	1.7	-3.5
CAM-B3LYP	14.4	21.1	6.8	-2.9	0.0	1.7	1.7	-3.8
PBE0	14.1	22.8	8.7	-2.6	0.3	1.9	1.6	-3.2
M06-HF	-10.0	-1.1	8.8	-2.0	-3.5	-1.6	1.9	-3.5
M06-2X	-9.1	-2.5	6.6	-3.1	-2.9	-1.4	1.5	-3.7
M06	0.2	8.1	7.9	-1.1	-1.8	-0.2	1.7	-3.4

triple-ζ quality

	$\Delta E_{(HF)_2@(4,4)CNT}$	$\Delta E^{CP}_{(HF)_2@(4,4)CNT}$	BSSE	$\Delta E^{in}_{HF\cdots HF}$	$\Delta E_{(HF)_2-(4,4)CNT}$	$\Delta E^{CP}_{(HF)_2-(4,4)CNT}$	BSSE	$\Delta E^{out}_{HF\cdots HF}$
B3LYP	28.8	30.2	1.4	-2.5	2.7	3.2	0.5	-3.3
B3LYP-D3	4.6	6.0	1.3	-2.9	-2.0	-1.5	0.5	-3.7
CAM-B3LYP	19.3	20.7	1.4	-3.0	1.1	1.6	0.5	-3.9
PBE0	20.9	22.3	1.4	-2.7	1.4	1.8	0.5	-3.3
M06-HF	-4.1	0.7	4.8	-2.2	-2.4	-1.2	1.2	-3.8
M06-2X	-5.2	-3.3	1.9	-3.4	-2.3	-1.8	0.5	-4.0
M06	2.2	5.5	3.3	-1.0	-1.5	-0.8	0.8	-3.3

Table 3 The interaction energy and BSSE values [kcal/mol] calculated for the complexes formed between $(HF)_2$ and (5,5)CNT using different DFT functionals (step number -27). The carbon nanotubes have been represented by the cc-pVDZ or cc-pVTZ basis sets, whereas the HF dimer is described using aug-cc-pVDZ or aug-cc-pVTZ. Symbol CP refers to results obtained using the counterpoise correction scheme.

double-ζ quality

	$\Delta E_{(HF)_2@(5,5)CNT}$	$\Delta E^{CP}_{(HF)_2@(5,5)CNT}$	BSSE	$\Delta E^{in}_{HF\cdots HF}$	$\Delta E_{(HF)_2-(5,5)CNT}$	$\Delta E^{CP}_{(HF)_2-(5,5)CNT}$	BSSE	$\Delta E^{out}_{HF\cdots HF}$
B3LYP	2.3	2.0	4.2	-3.4	-0.6	0.4	1.1	-3.3
B3LYP-D3	-16.5	-12.3	4.2	-3.8	-3.1	-2.1	1.1	-3.7
CAM-B3LYP	-6.1	-2.0	4.1	-3.9	-1.2	-0.2	1.0	-3.9
PBE0	-6.2	-1.2	5.0	-3.3	-1.2	-0.3	0.9	-3.4
M06-HF	-16.7	-12.0	4.7	-3.2	-2.3	-1.3	1.0	-3.5
M06-2X	-16.0	-12.1	4.0	-3.8	-2.2	-1.3	0.9	-3.7
M06	-16.3	-11.7	4.6	-3.6	-2.1	-1.1	1.0	-3.3

triple-ζ quality

	$\Delta E_{(HF)_2@(5,5)CNT}$	$\Delta E^{CP}_{(HF)_2@(5,5)CNT}$	BSSE	$\Delta E^{in}_{HF\cdots HF}$	$\Delta E_{(HF)_2-(5,5)CNT}$	$\Delta E^{CP}_{(HF)_2-(5,5)CNT}$	BSSE	$\Delta E^{out}_{HF\cdots HF}$
B3LYP	1.0	1.9	1.0	-3.5	0.1	0.4	0.3	-3.4
B3LYP-D3	-13.3	-12.3	0.9	-3.9	-2.4	-2.1	0.3	-3.8
CAM-B3LYP	-3.0	-2.0	1.0	-4.1	-0.6	-0.2	0.3	-4.0
PBE0	-2.1	-1.1	1.0	-3.4	-0.6	-0.3	0.3	-3.5
M06-HF	-13.8	-11.4	2.4	-3.4	-1.8	-1.3	0.5	-3.7
M06-2X	-13.9	-12.6	1.3	-4.3	-1.8	-1.5	0.3	-4.0
M06	-14.6	-12.5	2.2	–	-1.8	-1.4	0.4	-3.1

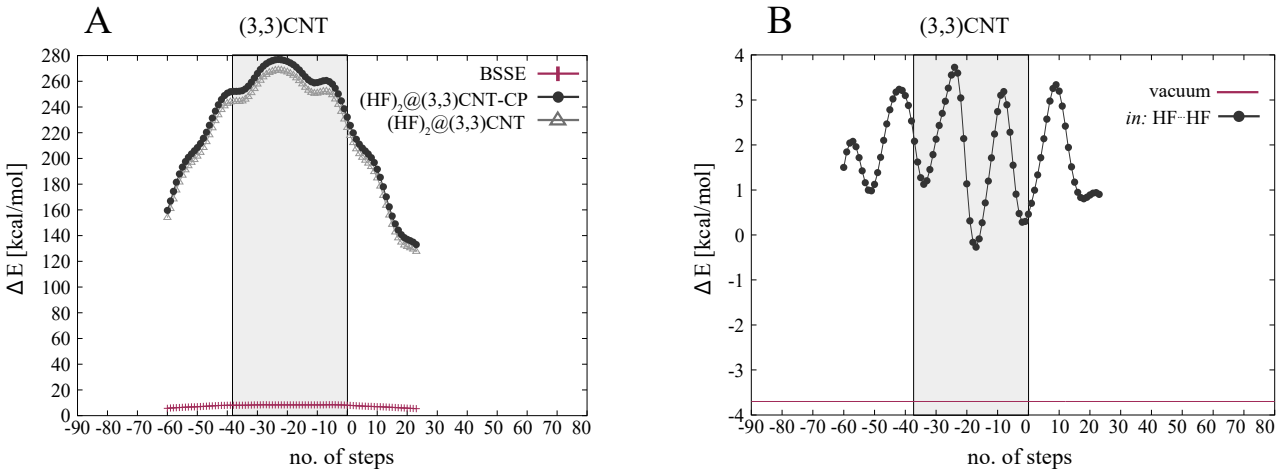

Figure 1 (A) The interaction energy values calculated for the endohedral complexes formed between the HF dimer and (3,3)CNT. (B) The influence of spatial confinement, represented by (3,3)CNT, on the intermolecular interaction energy of the hydrogen fluoride dimer. All calculations have been performed using the M06-2X method and the Dunning's basis sets of double-ζ quality. Symbol CP refers to results obtained using the counterpoise correction scheme. The region highlighted in gray, between steps -38 to 0, corresponds to the situation when the entire hydrogen fluoride dimer is located inside the (3,3) carbon nanotube. The value of $\Delta E_{HF\cdots HF}$ in vacuum equals -3.7 kcal/mol (M06-2X/aug-cc-pVDZ).

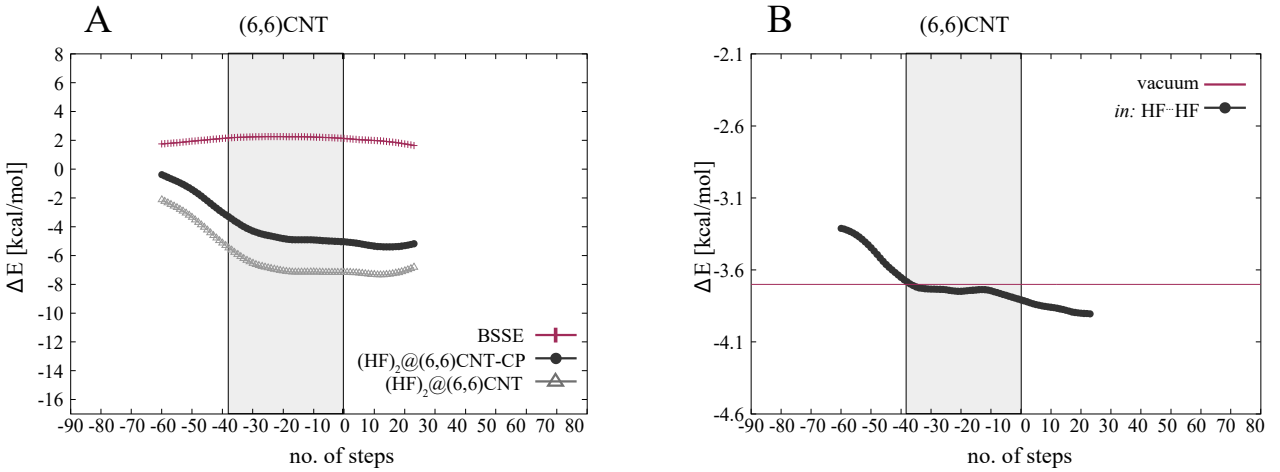

Figure 2 (A) The interaction energy values calculated for the endohedral complexes formed between the HF dimer and (6,6)CNT. (B) The influence of spatial confinement, represented by (6,6)CNT, on the intermolecular interaction energy of the hydrogen fluoride dimer. All calculations have been performed using the M06-2X method and the Dunning's basis sets of double-ζ quality. Symbol CP refers to results obtained using the counterpoise correction scheme. The region highlighted in gray, between steps -38 to 0, corresponds to the situation when the entire hydrogen fluoride dimer is located inside the (6,6) carbon nanotube. The value of $\Delta E_{HF\cdots HF}$ in vacuum equals -3.7 kcal/mol (M06-2X/aug-cc-pVDZ).

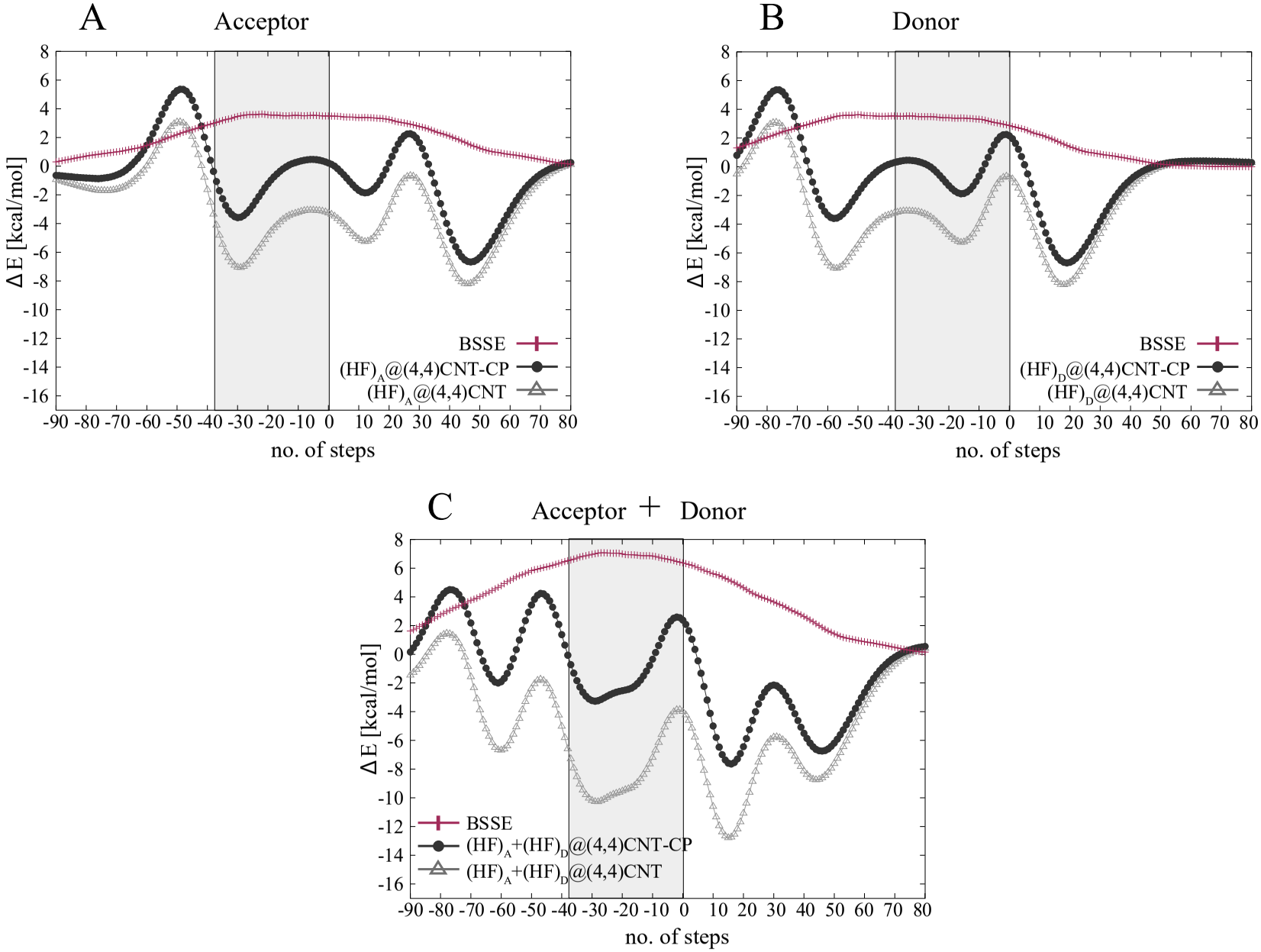

Figure 3 The interaction energy values calculated for the endohedral complexes formed between (4,4)CNT and: *i*) the proton acceptor molecule as well as *ii*) the proton donor molecule (B). In panel (C) the interaction energy values obtained as a sum of the data computed for $(HF)_A$ and $(HF)_D$ molecules interacting with (4,4)CNT have been presented. All calculations have been performed using the M06-2X method and the Dunning's basis sets of double-ζ quality. Symbol CP refers to results obtained using the counterpoise correction scheme. The region highlighted in gray, between steps -38 to 0, corresponds to the situation when the entire hydrogen fluoride dimer is located inside (4,4)CNT.

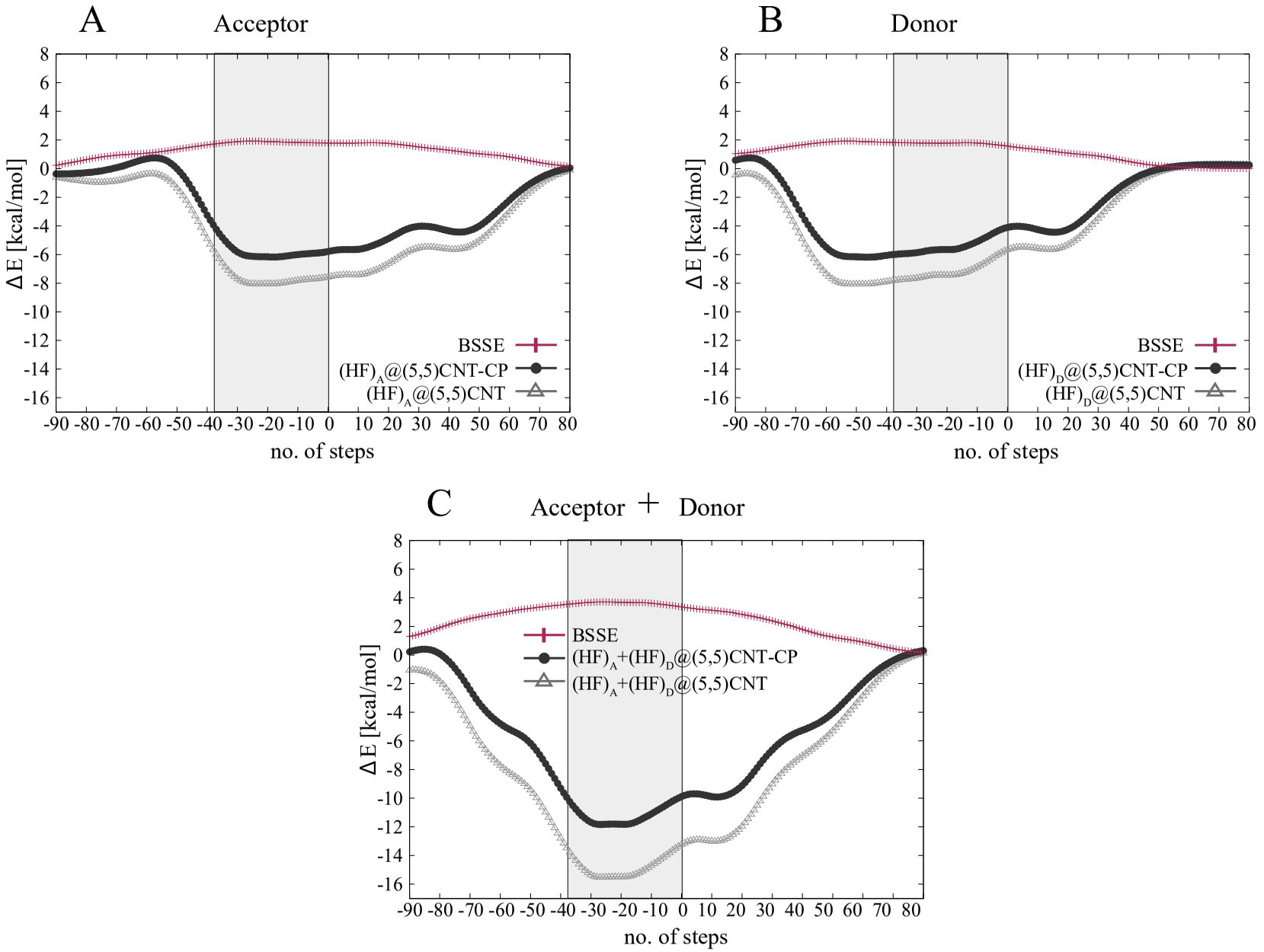

Figure 4 The interaction energy values calculated for the endohedral complexes formed between (5,5)CNT and: *i*) the proton acceptor molecule as well as *ii*) the proton donor molecule (B). In panel (C) the interaction energy values obtained as a sum of the data computed for $(HF)_A$ and $(HF)_D$ molecules interacting with (5,5)CNT have been presented. All calculations have been performed using the M06-2X method and the Dunning's basis sets of double-ζ quality. Symbol CP refers to results obtained using the counterpoise correction scheme. The region highlighted in gray, between steps -38 to 0, corresponds to the situation when the entire hydrogen fluoride dimer is located inside (5,5)CNT.