SUPPORTING INFORMATION

Introducing the new concept of *chiral-polaron giant-IRAV signature*.

Optical-active giant-response in vibrational circular dichroism.

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Index

Section 1

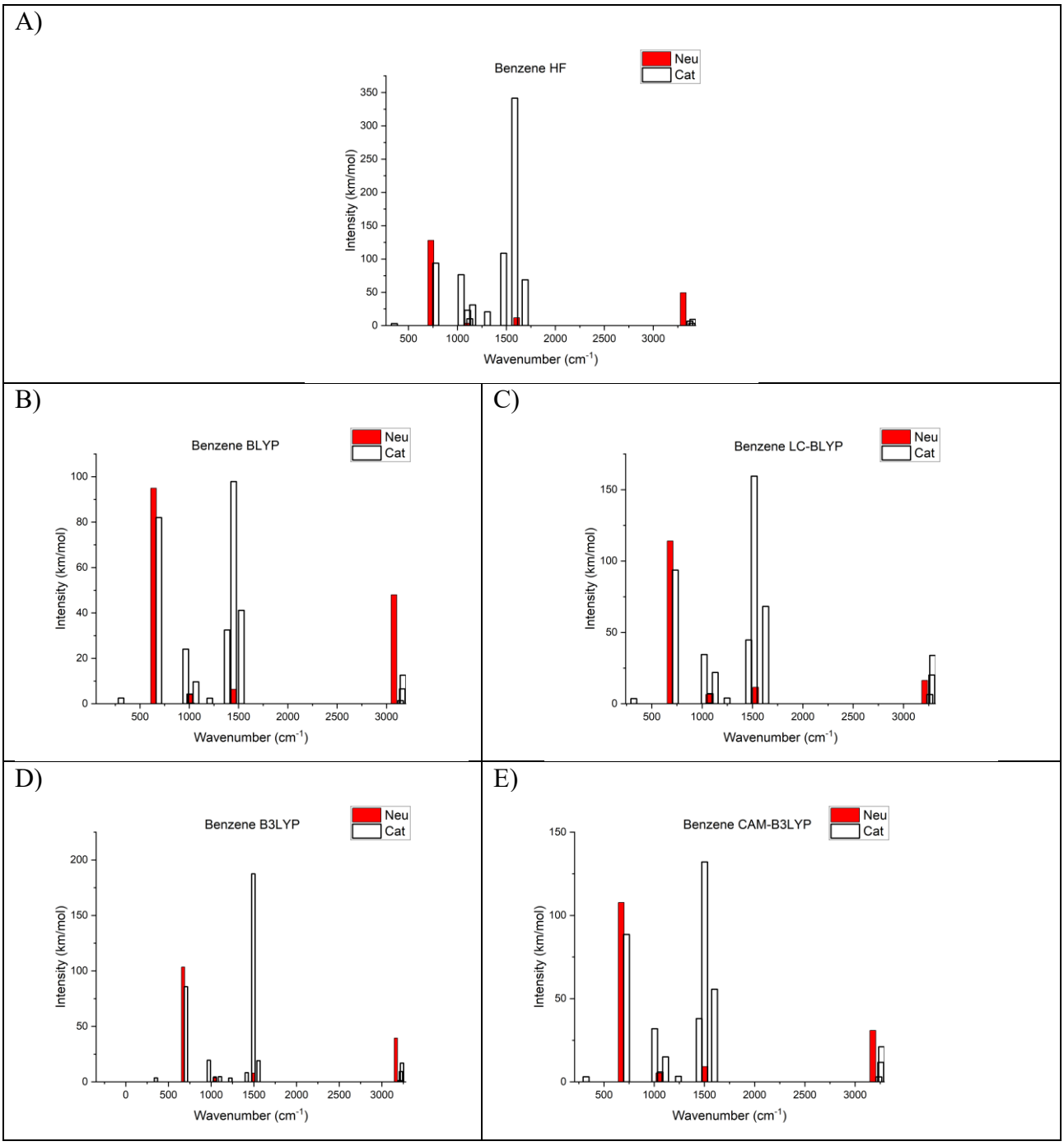

Figure S1.1. Benzene IR neutral (red bar) and cation (black bar) spectra. A) HF B) BLYP C) LC-BLYP D) B3LYP E) CAM-B3LYP.

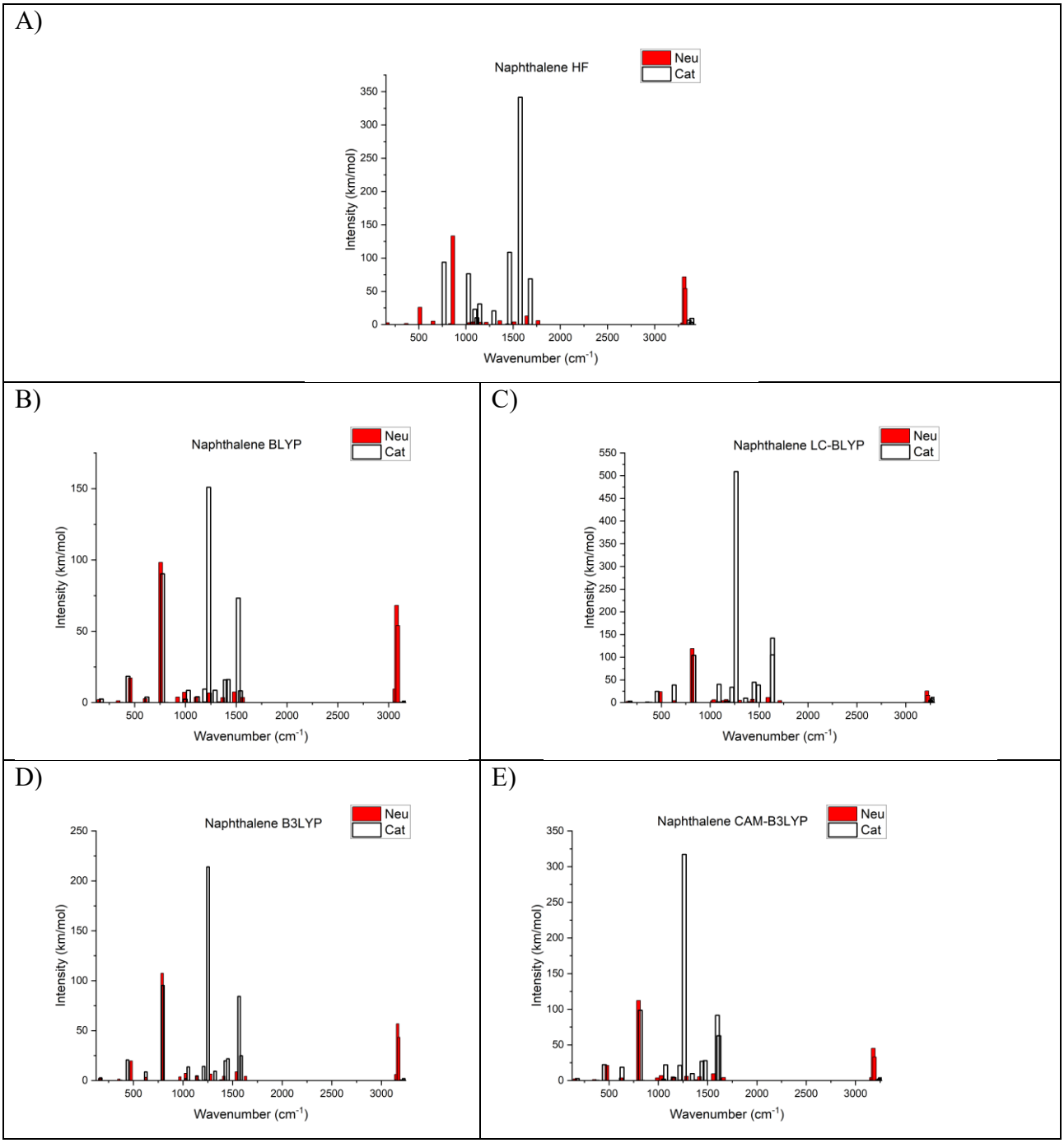

Figure S1.2. Naphtalene IR neutral (red bar) and cation (black bar) spectra. A) HF B) BLYP C) LC-BLYP D) B3LYP E) CAM-B3LYP.

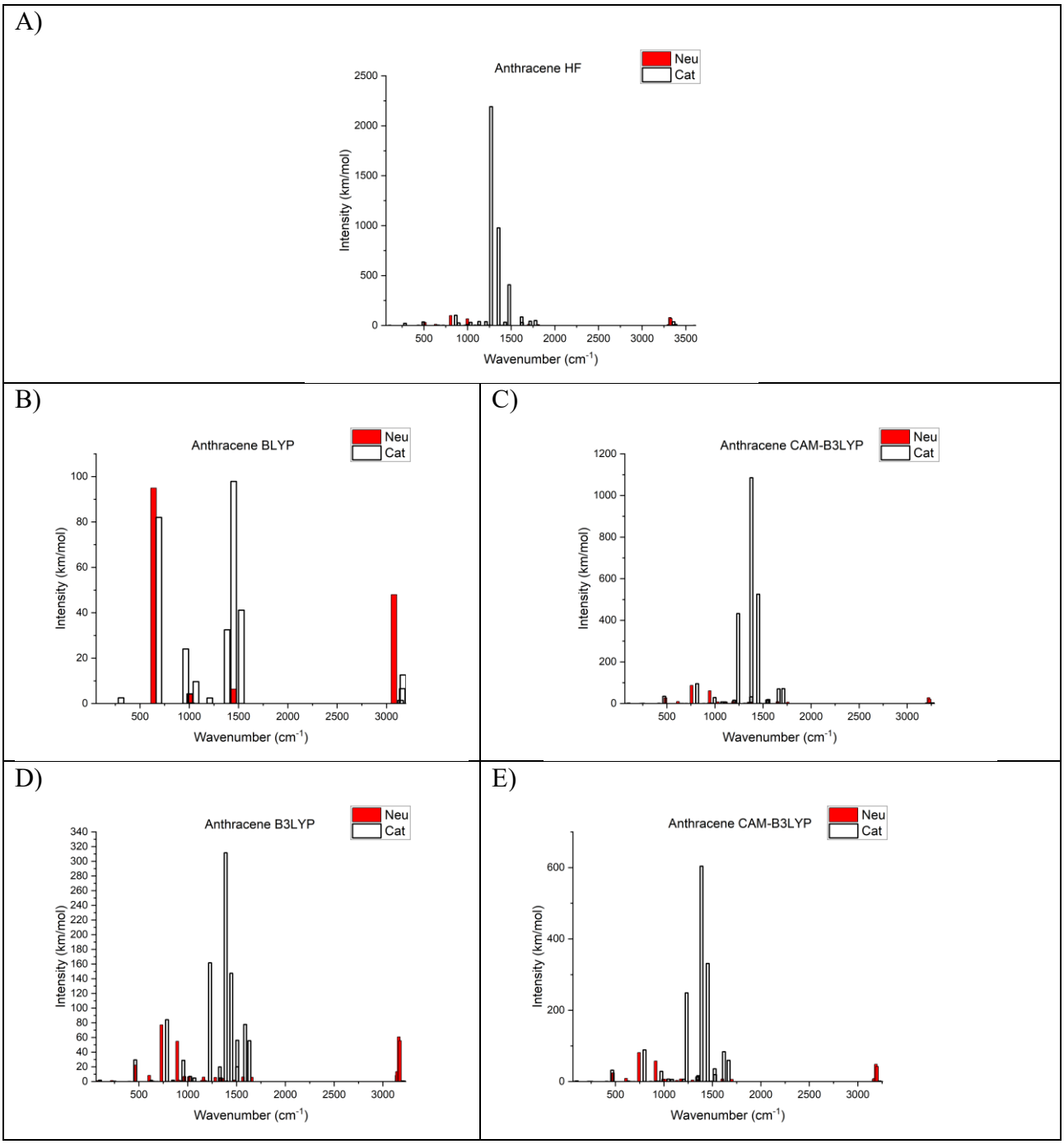

Figure S1.3. Anthracene IR neutral (red bar) and cation (black bar) spectra. A) HF B) BLYP C) LC-BLYP D) B3LYP E) CAM-B3LYP.

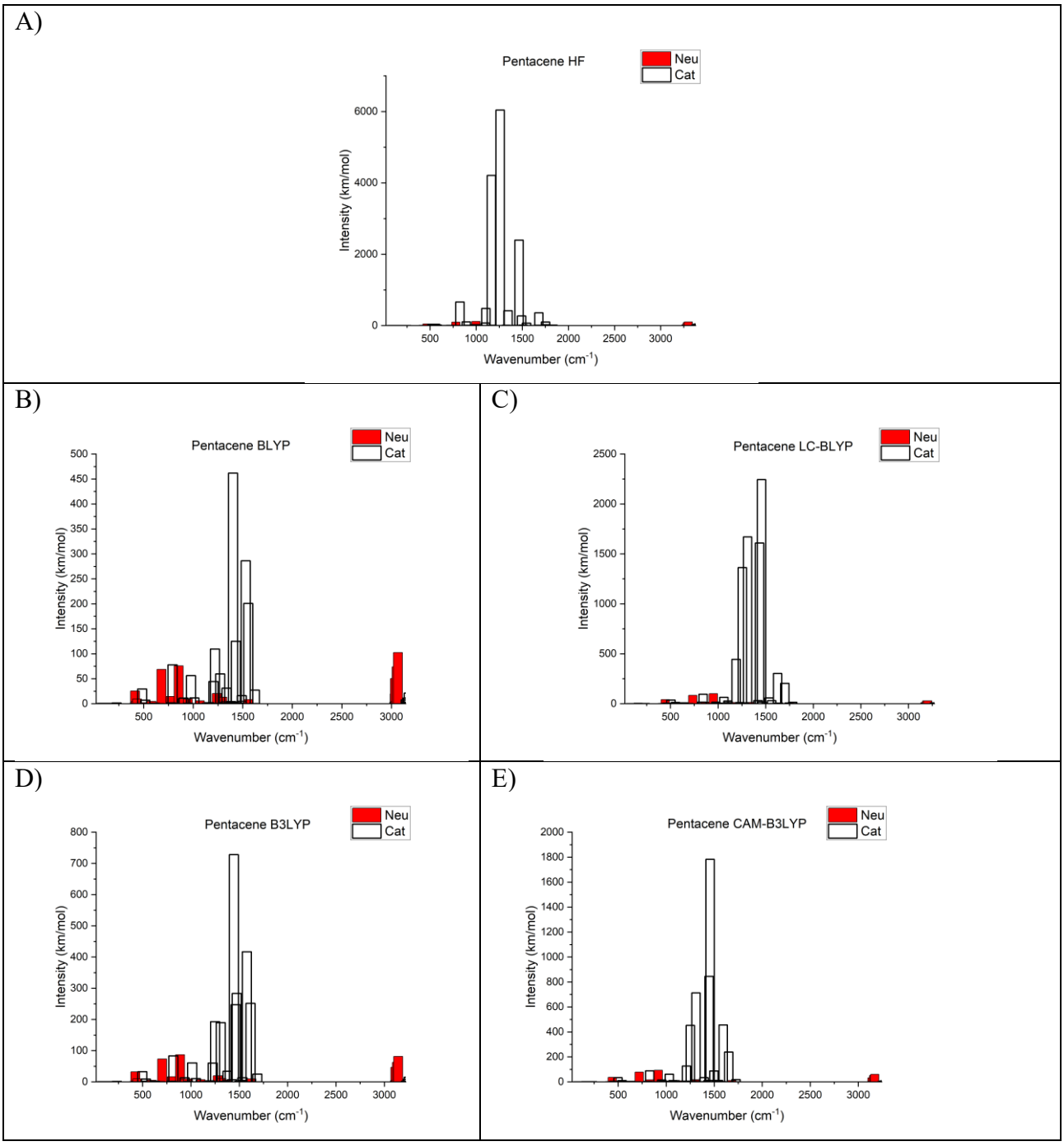

Figure S1.4. Pentacene IR neutral (red bar) and cation (black bar) spectra. A) HF B) BLYP C) LC-BLYP D) B3LYP E) CAM-B3LYP.

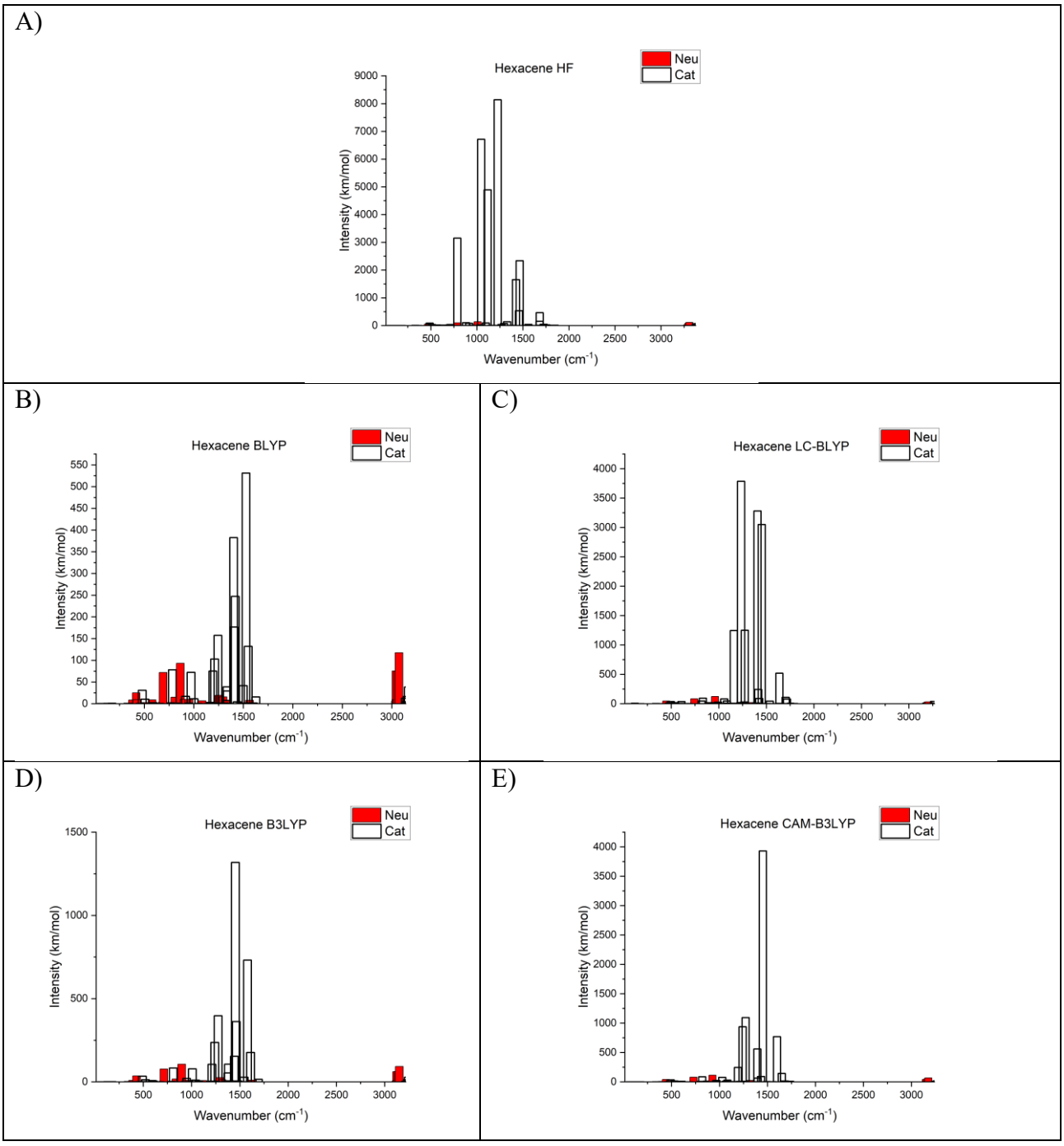

Figure S1.5. Hexacene IR neutral (red bar) and cation (black bar) spectra. A) HF B) BLYP C) LC-BLYP D) B3LYP E) CAM-B3LYP.

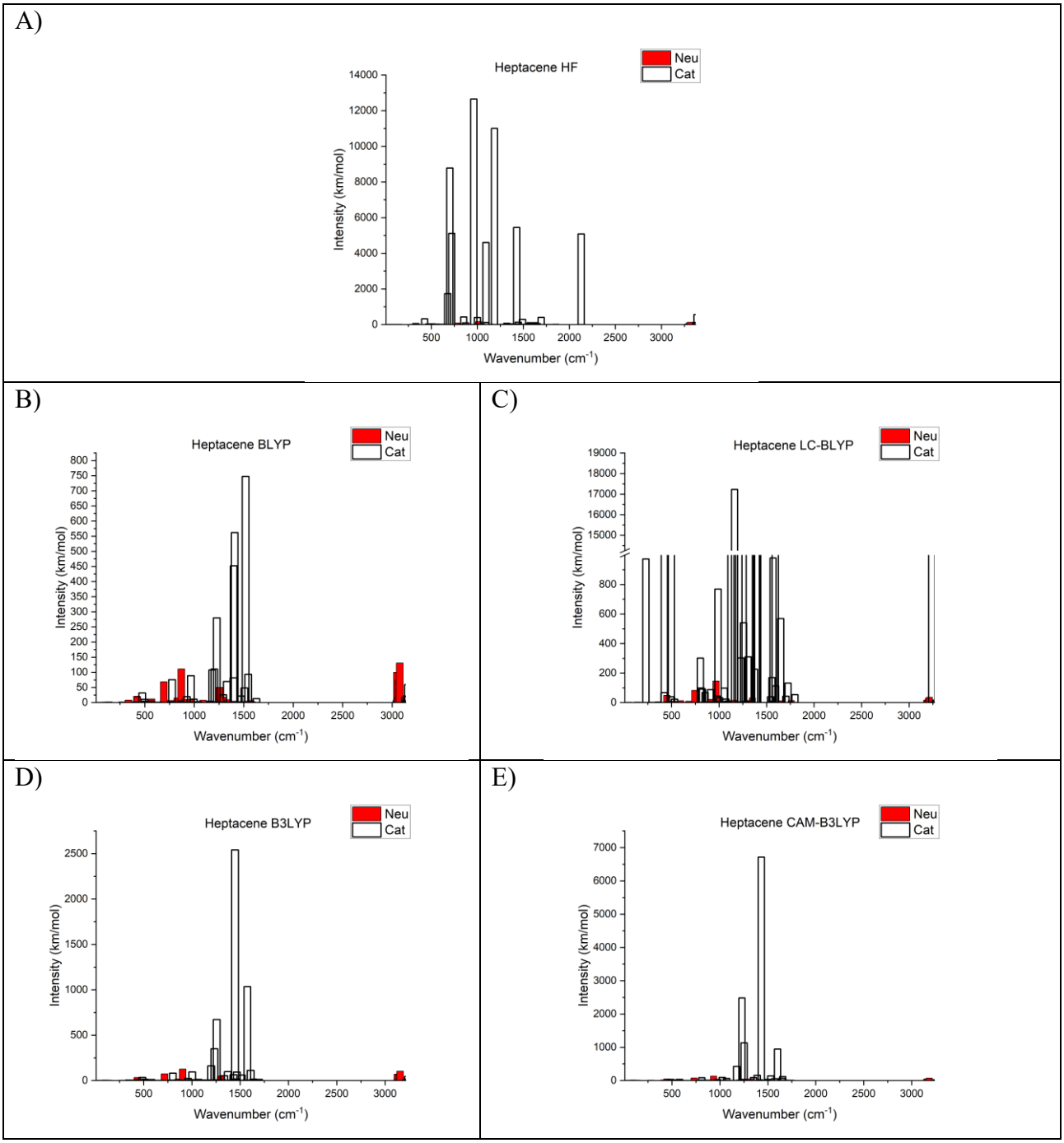

Figure S1.6. Heptacene IR neutral (red bar) and cation (black bar) spectra. A) HF B) BLYP C) LC-BLYP D) B3LYP E) CAM-B3LYP.

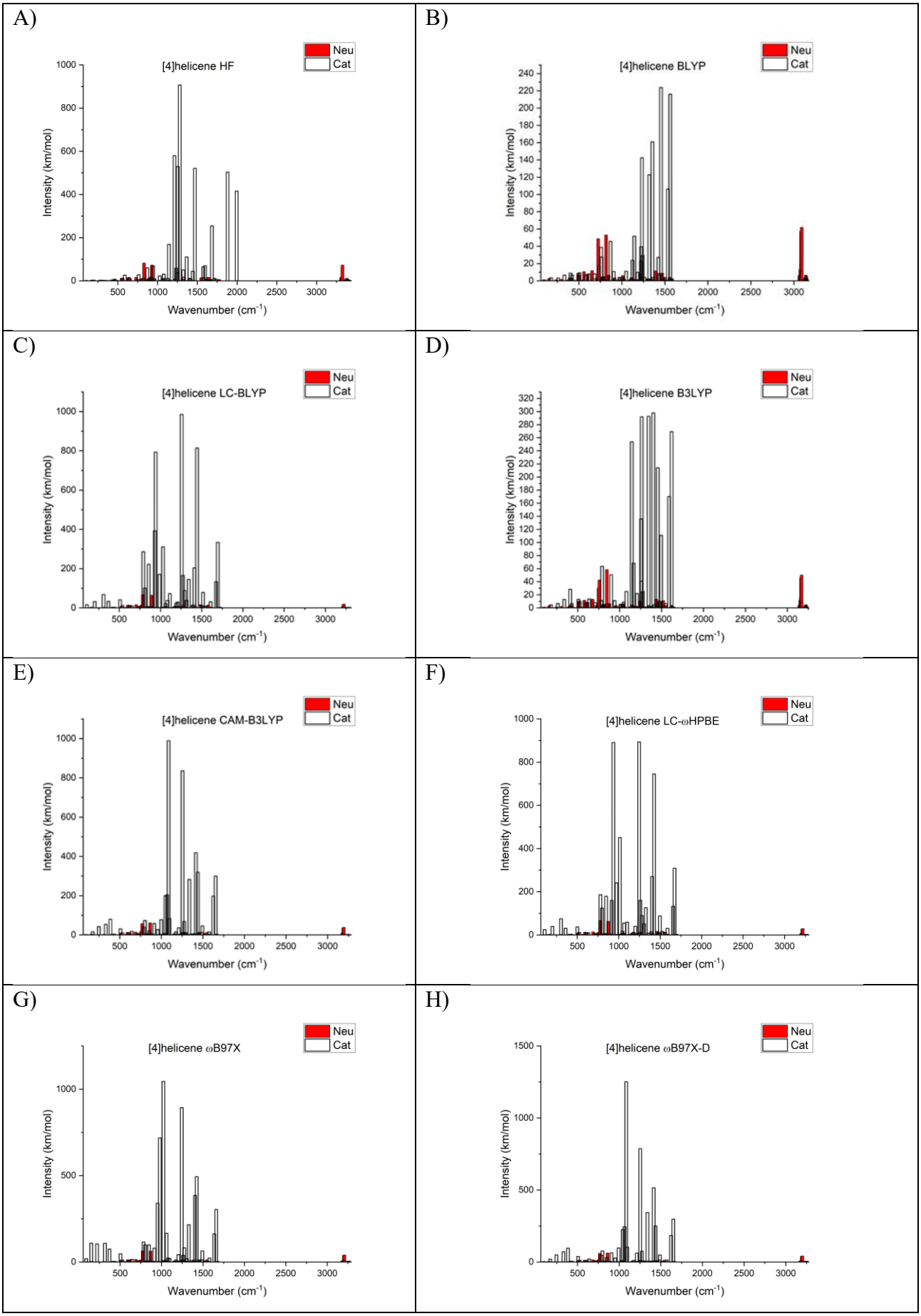

Figure S1.7. [4]helicene IR neutral (red bar) and cation (black bar) spectra. A) HF B) BLYP C) LC-BLYP D) B3LYP E) CAM-B3LYP.

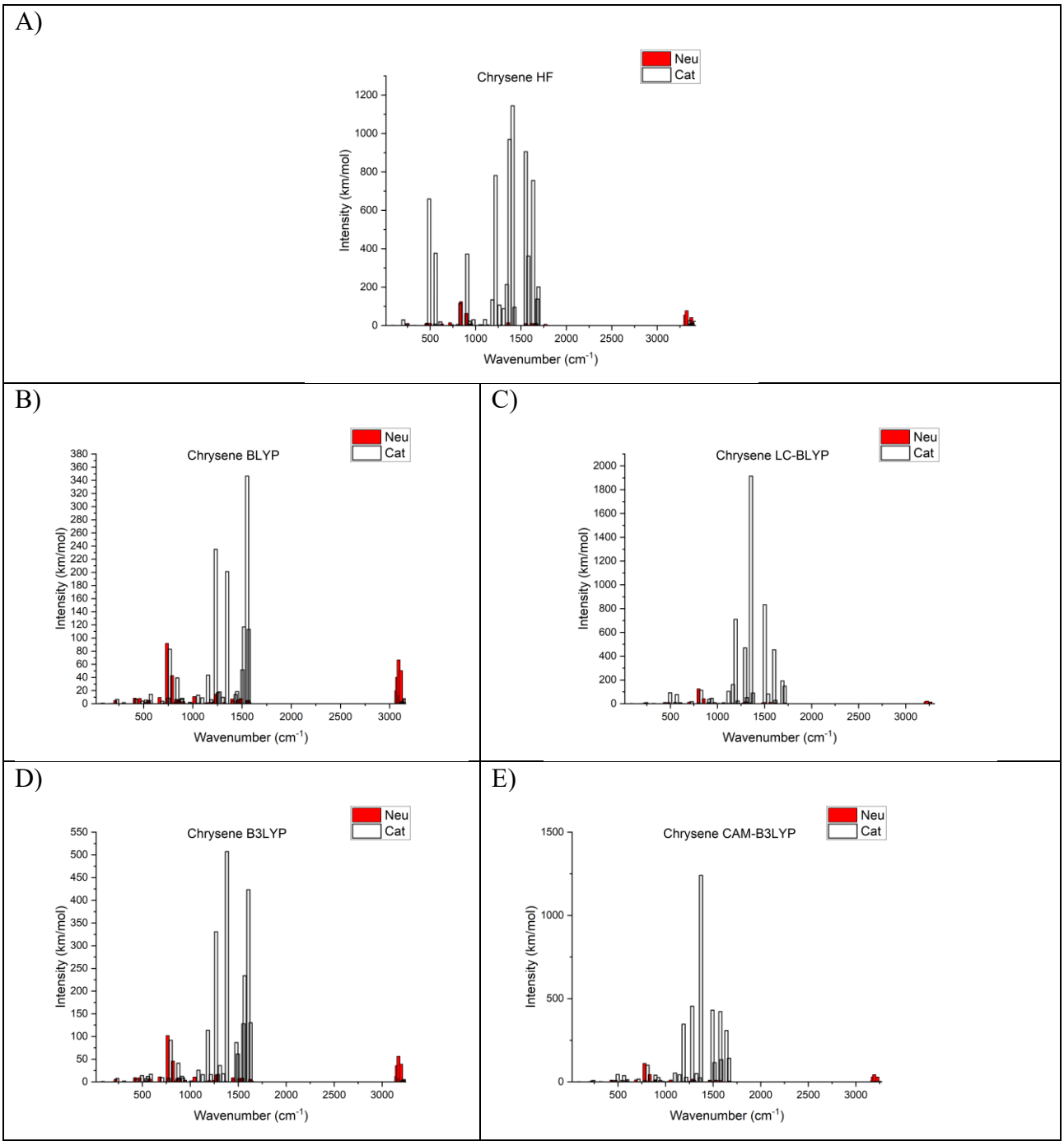

Figure S1.8. Chrysene IR neutral (red bar) and cation (black bar) spectra. A) HF B) BLYP C) LC-BLYP D) B3LYP E) CAM-B3LYP.

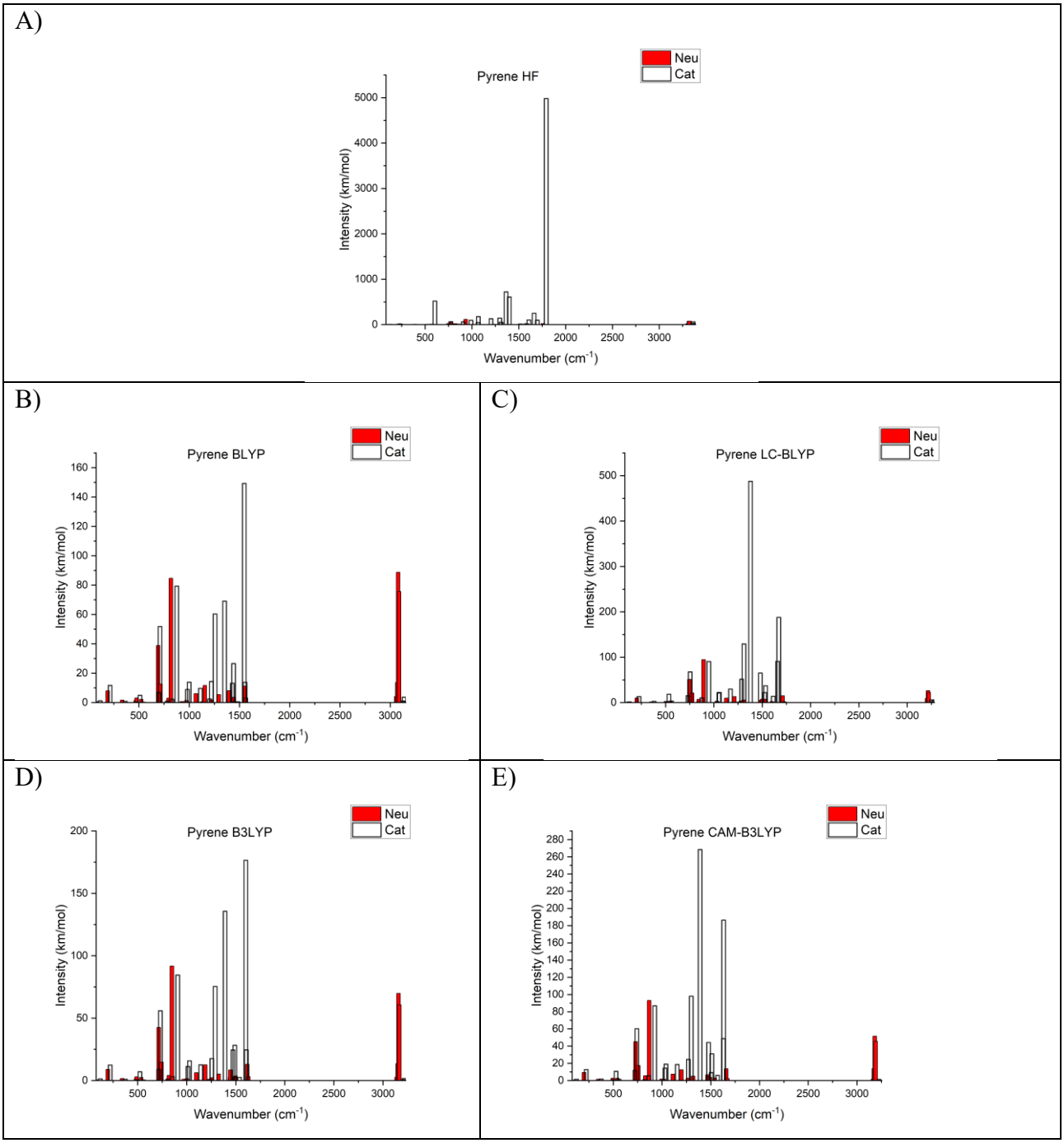

Figure S1.9. Pyrene IR neutral (red bar) and cation (black bar) spectra. A) HF B) BLYP C) LC-BLYP D) B3LYP E) CAM-B3LYP.

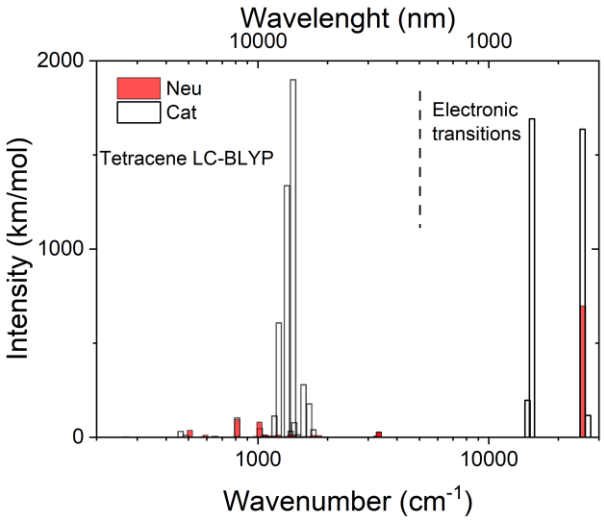

Figure S1.10. LC-BLYP/cc-pVTZ Tetracene IR and UV-Vis spectra neutral (red bar) and cation (black bar) species shown in the same graph, the dashed vertical line marks the boundary between vibrational (left of the dashed vertical line) and electronic (right of the dashed vertical line) spectra.

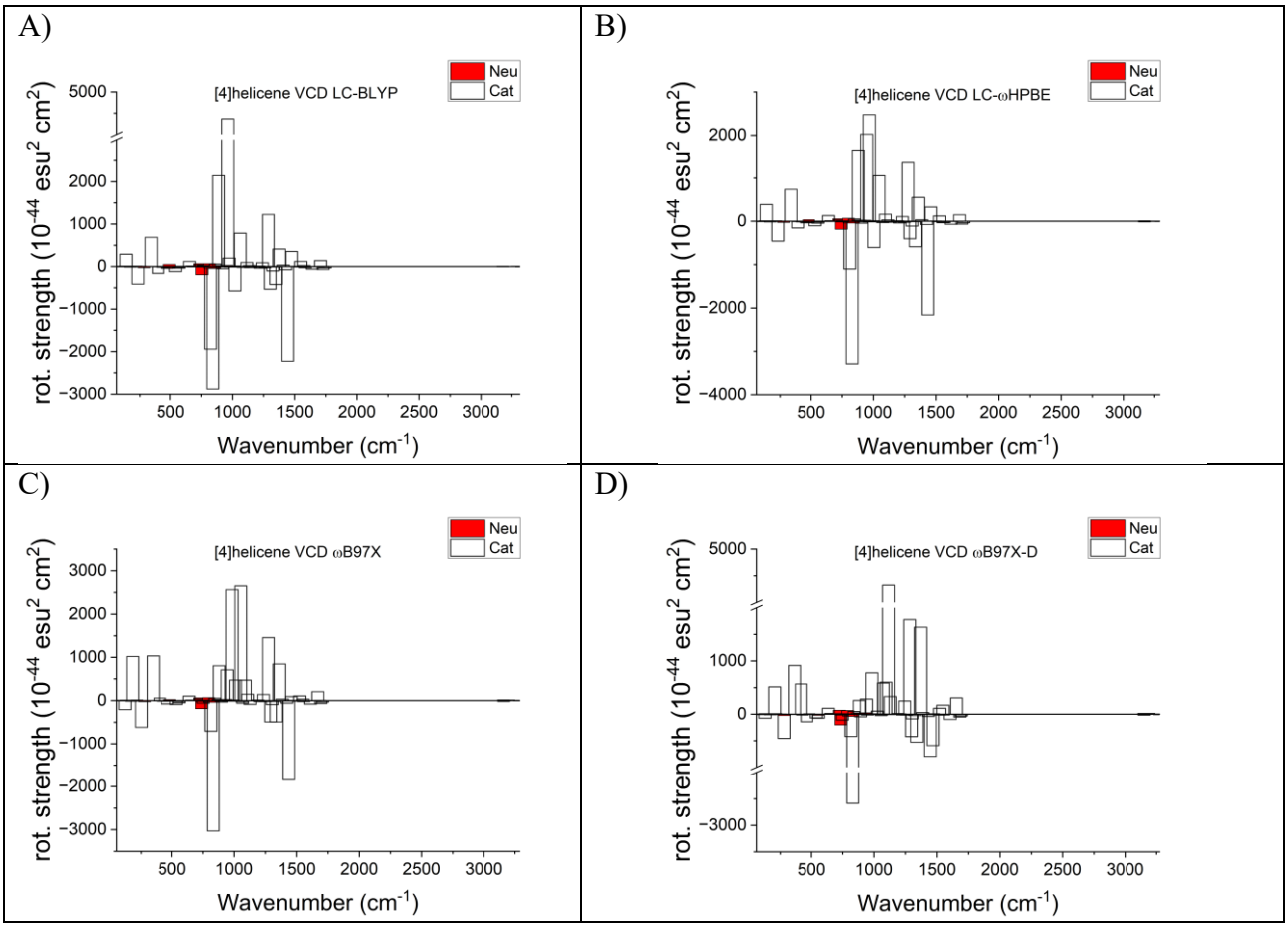

Figure S1.11. [4]helicene VCD neutral (red bar) and cation (black bar) spectra. A) LC-BLYP B) LC-ωHPBE C) ωB97X D) ωB97X-D.

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Section 2

Table S2.1. Summary of ρIR related to linear PAHs at different exchange and correlation functionals.

Species	x/cc-pVTZ	ρIR
Benzene	CAM-B3LYP	1.23
-	B3LYP	1.81
-	LC-BLYP	1.40
-	BLYP	1.03
-	HF	2.67
Naphthalene	CAM-B3LYP	2.83
-	B3LYP	1.99
-	LC-BLYP	4.28
-	BLYP	1.54
-	HF	2.56
Anthracene	CAM-B3LYP	7.44
-	B3LYP	4.04
-	LC-BLYP	12.48
-	BLYP	2.48
-	HF	22.13
Tetracene	CAM-B3LYP	11.64
-	B3LYP	6.81
-	LC-BLYP	20.51
-	BLYP	3.8
-	HF	46.13
Hexacene	CAM-B3LYP	34.53
-	B3LYP	12.43
-	LC-BLYP	30.76
-	BLYP	4.52
-	HF	58.14
Heptacene	CAM-B3LYP	49.90
-	B3LYP	20.17
-	LC-BLYP	119.48
-	BLYP	5.71
-	HF	76.49

Table S2.2. Summary of ρIR, symmetry, HOMO-LUMO and HOMO-SOMO delta related to four ringed PAHs at different exchange and correlation functionals.

Species	x/cc-pVTZ	ρIR	delta HOMO LUMO	delta SOMO LUMO	Symmetry
Tetracene	CAM-B3LYP	11.64	0.18465	0.12988	D2h
-	B3LYP	6.81	0.10154	0.05132	D2h
-	LC-BLYP	20.51	0.2646	0.20507	D2h
-	BLYP	3.8	0.05975	0.01268	D2h
-	HF	46.13	0.28377	0.25198	D2h
Pyrene	CAM-B3LYP	2.88	0.22721	0.13678	D2h
-	B3LYP	1.92	0.14128	0.05578	D2h
-	LC-BLYP	5.15	0.31018	0.21545	D2h
-	BLYP	1.76	0.09593	0.01465	D2h
-	HF	42.72	0.33069	0.26748	D2h
Chrysene	CAM-B3LYP	11.17	0.24595	0.13071	C2h
-	B3LYP	4.96	0.1561	0.04999	C2h
-	LC-BLYP	15.37	0.33182	0.21041	C2h
-	BLYP	3.78	0.10781	0.01106	C2h
-	HF	9.21	0.35301	0.2601	C2h
4-Helicene	CAM-B3LYP	16.20	0.24373	0.13231	C2
-	B3LYP	5.10	0.1544	0.0518	C2
-	LC-BLYP	14.62	0.32837	0.2095	C2
-	BLYP	4.22	0.10653	0.01208	C2
-	HF	11.04	0.34832	0.24033	C2

Table S2.3. Summary of tetracene ρIR, at varying the omega parameter in LC-BLYP and CAM-B3LYP functionals.

Functional	ω	ρIR
CAM-B3LYP	0	6.81
CAM-B3LYP	0.15	8.45
CAM-B3LYP	0.33	11.64
CAM-B3LYP	0.55	12.83
LC-BLYP	0	3.8
LC-BLYP	0.15	6.63
LC-BLYP	0.25	10.72
LC-BLYP	0.35	16.83
LC-BLYP	0.47	20.51
LC-BLYP	0.55	19.3
LC-BLYP	0.65	19.59
LC-BLYP	0.75	19.97

Section 3

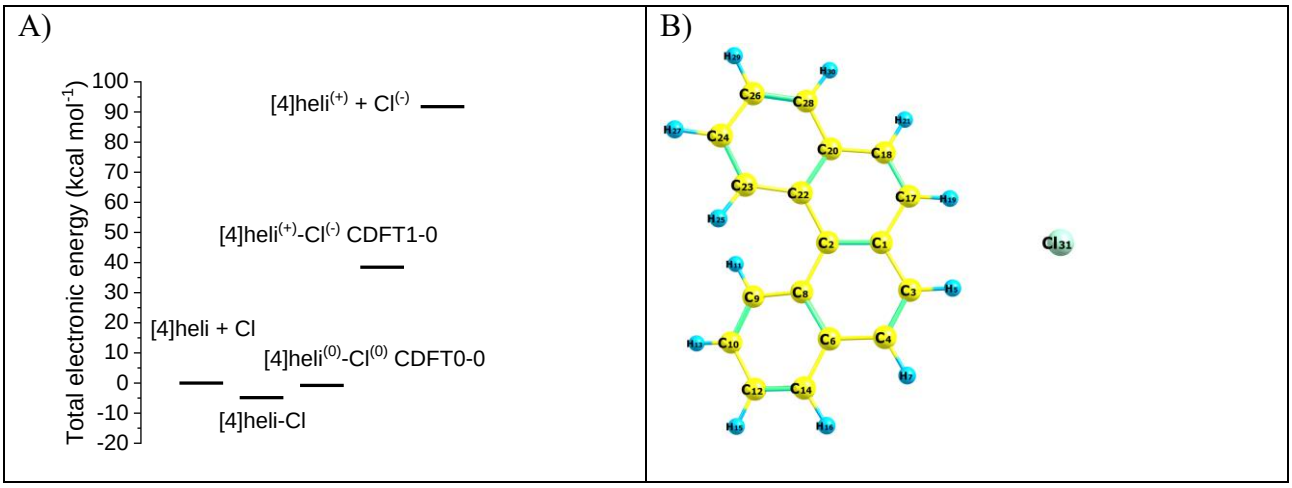

Figure S3.1. A) potential energy surface projection of points in energy corresponding to the following molecular systems, from left to right: *[4]helicene + Chlorine* atom at infinite distance, selected as zero energy; *[4]helicene−Chlorine* molecular adduct, with a C2−Cl31 distance of 0.6029 nm. B) *[4]helicene(0)−Chlorine(0)* molecular adduct, CDFT calculation imposing zero net charge on both [4]helicene and chlorine; *[4]helicene(+1)−Chlorine(-1)* molecular adduct, CDFT calculation imposing [4]helicene cation and chlorine anion; *[4]helicene(+1)+Chlorine(-1)* at infinite distances, [4]helicene cation and chlorine anion

Section 4

Equation 2: Energy vs. box length parameter L (compare equation (2) in the main text. Plotted just as an example $E(L) = 1/L^2 - 1/L$

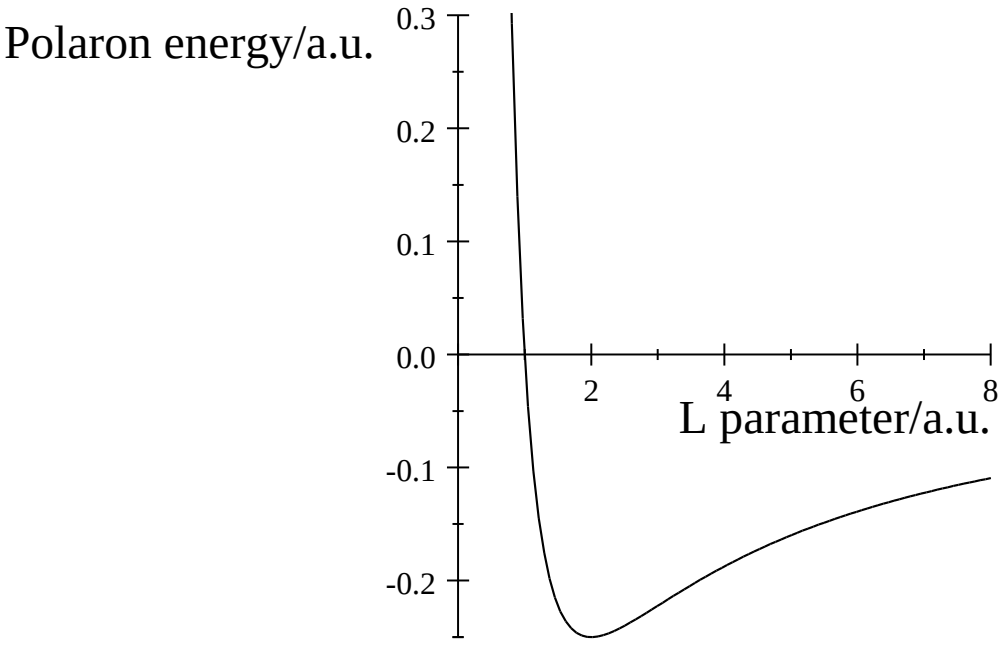

Figure S4.1. Plot of the 1D polaron energy as a function of the model box length (copare equation (2) main text for further details)