

Supporting Information

Low-lying excited states of model proteins:

Performances of the CC2 method versus multireference methods

Nadia Ben Amor^{1,2}, Sophie Hoyau², Daniel Maynau^{1,2}, Valérie Brenner³

¹*CNRS, UPS, LCPQ (Laboratoire de Chimie et Physique Quantiques), IRSAMC, 118, rte de Narbonne F-31062 Toulouse Cedex. France.*

²*Université de Toulouse, UPS, LCPQ (Laboratoire de Chimie et Physique Quantiques), IRSAMC, 118, rte de Narbonne F-31062 Toulouse Cedex. France.*

³*Laboratoire Interactions, Dynamiques et Lasers, LIDYL, CEA, CNRS, Université Paris-Saclay, 91191 Gif-sur-Yvette Cedex, France*

Appendix S1: Cartesian coordinates of all the geometries of the NAPA B conformer.

Table S1-1: Cartesian coordinates of the B97-D2/TZVPP optimized ground state geometry (Å).

C	2.1012809	2.8012753	-0.7962777
H	2.6829063	2.8102244	-1.7245541
H	2.5283087	3.5605002	-0.1314497
C	2.2623085	1.4411635	-0.1341555
O	3.3725270	0.9987098	0.1749704
N	1.1086496	0.7565672	0.0869590
H	0.2393554	1.1443544	-0.2536865
C	1.0243877	-0.5231547	0.7911005
H	1.8269094	-0.5134581	1.5407075
C	1.3400483	-1.7462516	-0.1295981
O	0.5981846	-2.7152051	-0.2351044
C	-0.3343449	-0.6562608	1.5214627
H	-0.4399299	-1.7064709	1.8095437
H	-0.2778540	-0.0512285	2.4333322
C	-1.5369592	-0.2132956	0.7138013
C	-2.1280013	-1.0502808	-0.2454252
H	-1.7207727	-2.0451963	-0.3957499
C	-2.0613549	1.0770206	0.8942465
H	-1.6167840	1.7278717	1.6457609
C	-3.2139170	-0.6036792	-1.0020174
H	-3.6629927	-1.2651954	-1.7394558
C	-3.1467592	1.5269869	0.1356274
H	-3.5416242	2.5279347	0.2943963
C	-3.7254001	0.6854571	-0.8175615
H	-4.5712026	1.0289782	-1.4085182
N	2.5389948	-1.6466053	-0.7580640
H	3.1694248	-0.8769566	-0.5480749
H	1.0590375	3.0589417	-1.0161458
H	2.8460937	-2.4248093	-1.3223449

Table S1-2: Cartesian coordinates of the CC2/cc-pVDZ optimized $M_{\pi\pi^*}$ excited state geometry (Å).

C	-2.1252717	-1.1546159	-0.2226251
C	-1.4713441	-0.2826615	0.7293417
C	-1.9349089	1.0883775	0.8621547
C	-3.0483759	1.5583897	0.0760321
C	-3.6857968	0.6814654	-0.8690932
C	-3.2248664	-0.6720585	-1.0206385
C	-0.2951474	-0.7452156	1.5369858
C	1.0498089	-0.5759332	0.7973685
C	1.2975704	-1.7314188	-0.2001655
O	0.5385732	-2.7046127	-0.3087644
N	1.1010772	0.7390793	0.1722200

C	2.2692556	1.4061498	-0.0572559
C	2.1185112	2.8033248	-0.6258816
N	2.4460980	-1.5724348	-0.9158344
O	3.3857242	0.8992651	0.1719711
H	0.2109399	1.1618115	-0.0921014
H	1.8863566	-0.6115673	1.5215295
H	-0.2436729	-0.1626483	2.4735101
H	-0.3952562	-1.8139177	1.7858947
H	-1.4967595	1.7307338	1.6337328
H	-3.4106788	2.5826595	0.2023664
H	-4.5254285	1.0463043	-1.4671186
H	-3.7060896	-1.3379560	-1.7416317
H	-1.7538018	-2.1751941	-0.3353733
H	2.7395599	-2.3517642	-1.4963761
H	3.1136449	-0.8520683	-0.6304265
H	2.5028856	2.8104427	-1.6577124
H	1.0781531	3.1613156	-0.6236561
H	2.7442935	3.4879346	-0.0348836

Table S1-3: Cartesian coordinates of the CC2/cc-pVDZ $CI_{\pi\pi^*/n\pi^*co(2)}$ geometry connecting the two CC2/cc-pVDZ optimized equilibrium geometries of $M_{\pi\pi^*}$ and $M_{n\pi^*co(2)}$ excited states (Å).

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4312773
C	1.2391763	0.0000000	2.1599976
C	2.4796286	-0.0080348	1.4262933
C	2.4748325	0.0057958	-0.0058128
C	1.2359834	0.0033726	-0.7178467
C	1.2578136	-0.0536430	3.6614461
C	1.1350762	-1.4933553	4.2003383
N	2.0850246	-2.3611405	3.5209949
C	2.5855665	-3.4925577	4.1062350
O	2.2510507	-3.8589728	5.2486638
C	-0.3098479	-2.0014229	4.0938291
N	-0.4697529	-3.3215271	4.4758722
O	-1.2970638	-1.1985291	3.9749218
C	3.5697526	-4.2744402	3.2584141
H	2.2817155	-2.1512616	2.5424468
H	1.3995750	-1.5163068	5.2760373
H	2.2023650	0.3755308	4.0378391
H	0.4154747	0.5224126	4.0786254
H	3.4271446	0.0508287	1.9734036
H	3.4216053	0.0229433	-0.5538155
H	1.2363642	0.0103754	-1.8115672
H	-0.9492037	-0.0031297	-0.5429853
H	-0.9385859	-0.0125117	1.9915155
H	-1.4361344	-3.6306501	4.5583056
H	0.2581229	-3.7212198	5.0779238
H	3.0752606	-5.1881297	2.8924693
H	3.9457162	-3.6994674	2.3989321
H	4.4119887	-4.5817866	3.8945851

Table S1-4: Cartesian coordinates of the CC2/cc-pVDZ optimized $M_{n\pi^*co}(2)$ excited state geometry (Å).

C	-2.0710079	-1.0323881	-0.2022098
C	-1.5678491	-0.1272217	0.7592886
C	-2.1114537	1.1725455	0.8201167
C	-3.1397784	1.5646740	-0.0575728
C	-3.6349389	0.6568083	-1.0086910
C	-3.0996247	-0.6434017	-1.0756759
C	-0.4173462	-0.5278243	1.6501587
C	0.9184000	-0.4323210	0.8960325
C	0.9368428	-1.4163059	-0.2450883
O	0.7860441	-2.7549114	0.0447886
N	1.1586968	0.9208466	0.4339294
C	2.4444299	1.3482369	0.1783934
C	2.5338368	2.6961717	-0.5110960
N	2.0533078	-1.3447090	-1.1472043
O	3.4441780	0.6827201	0.4898223
H	0.3913168	1.3706418	-0.0635912
H	1.7523961	-0.6911897	1.5819539
H	-0.3695385	0.1180135	2.5422971
H	-0.5315591	-1.5738024	1.9843057
H	-1.7336468	1.8775548	1.5700987
H	-3.5562588	2.5750893	0.0071629
H	-4.4376838	0.9568293	-1.6893331
H	-3.4857796	-1.3567780	-1.8107803
H	-1.6542363	-2.0450905	-0.2529732
H	2.0729734	-2.1822416	-1.7380872
H	2.9431410	-1.2352645	-0.6336886
H	2.5656000	2.5342368	-1.6010837
H	1.6751686	3.3427689	-0.2752528
H	3.4679020	3.1886045	-0.2095565

Table S1-5: Cartesian coordinates of the CC2/cc-pVDZ partially optimized M^{\prime}_{CT} excited state geometry with the NH(1) bond length constrained to 1.216 Å (Å).

C	-2.4030317	-0.8977387	0.1859705
C	-1.4668265	-0.1348730	0.8751197
C	-1.2910596	1.3273539	0.6039599
C	-2.3001929	1.8955076	-0.3096010
C	-3.2288935	1.1064093	-0.9659611
C	-3.3164430	-0.3027639	-0.7247173
C	-0.3567674	-0.7512422	1.6775734
C	0.9596593	-0.6674531	0.8698808
C	0.8992366	-1.8114093	-0.3029468
O	0.0960084	-2.7301264	-0.2093568
N	1.0911097	0.6132648	0.3090830
C	2.3376747	1.1563660	-0.0575722
C	2.2772910	2.6462432	-0.2817687
N	1.8202098	-1.6192598	-1.2693289

O	3.3655615	0.4684626	-0.1771118
H	0.0037979	1.1547614	0.2609467
H	1.8786188	-0.9756284	1.4151467
H	-0.1812596	-0.1971147	2.6205915
H	-0.5406372	-1.8128072	1.9123216
H	-1.1385370	1.9258629	1.5373266
H	-2.2913194	2.9786670	-0.4954559
H	-3.9311051	1.5736053	-1.6679871
H	-4.0738825	-0.9109348	-1.2296265
H	-2.4360459	-1.9815602	0.3579954
H	1.9668960	-2.3988960	-1.9076839
H	2.6122350	-1.0095121	-1.0416360
H	3.2489672	3.0094273	-0.6402510
H	1.4841348	2.8743662	-1.0115153
H	2.0083962	3.1503138	0.6600804

Appendix S2: Dependence of the excitation energy and reference weight of the zeroth-order wave function on the level shift in CASPT2 calculations of the excited states

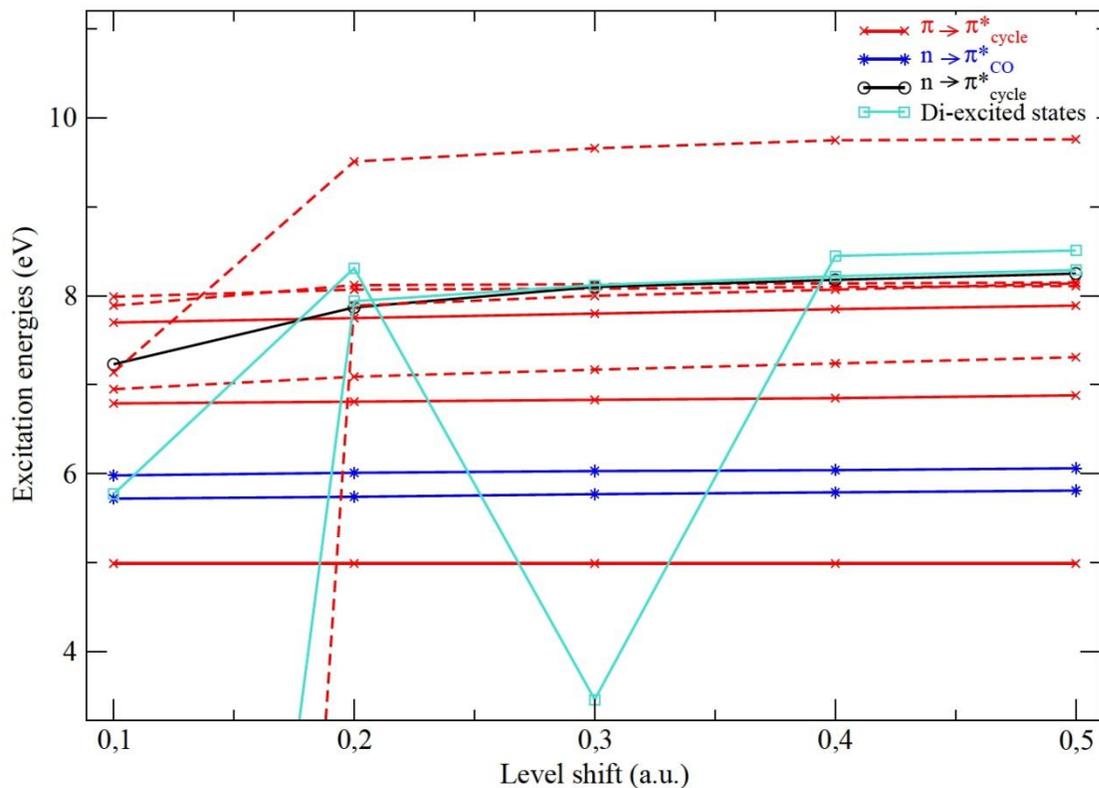


Figure S2-1: CASPT2 excitation energy as a function of the level shift (IPEA default value 0.25).

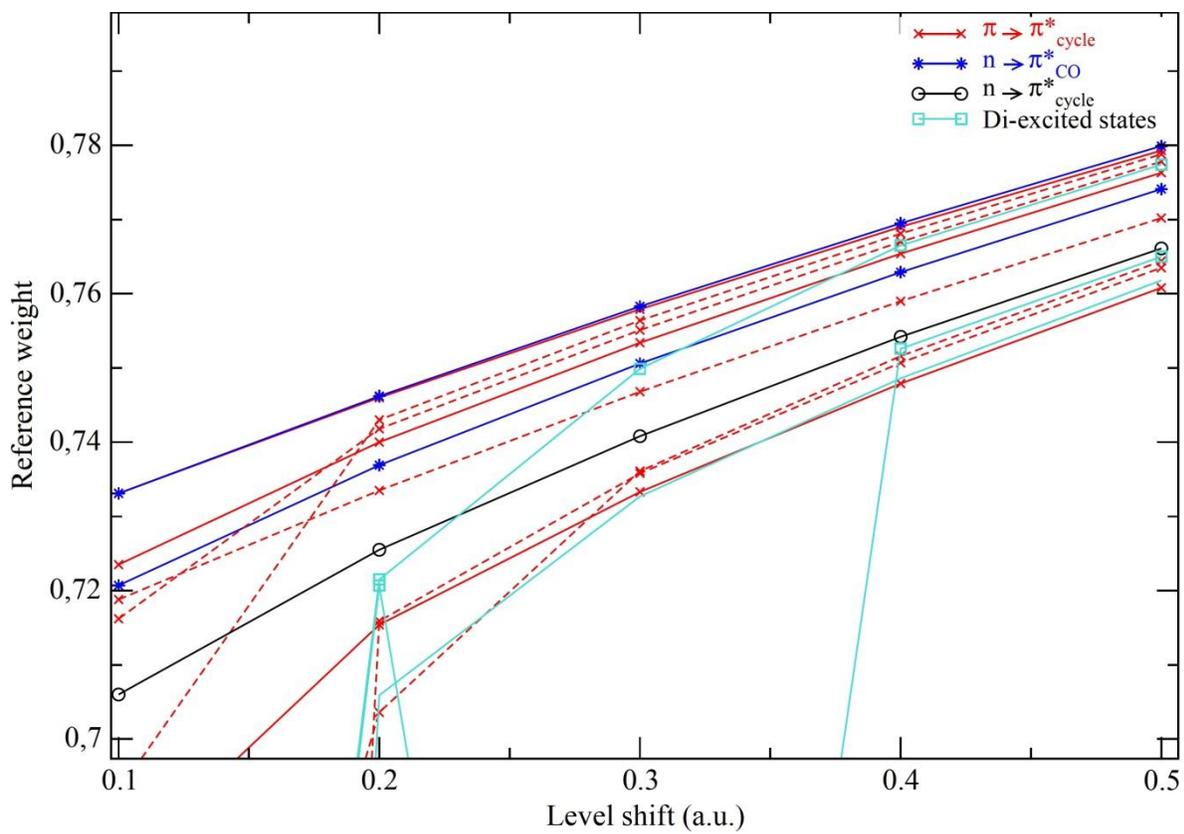


Figure S2-2: Reference weight of the zeroth-order wave function as a function of the level shift (IPEA default value 0.25).

Appendix S3: Diffuse orbital effects on the excitation energy in CC2 and MS-CASPT2 calculations.

ΔE (eV)	CC2 <i>{cc-pVDZ/aug-ccpVDZ}</i>	CC2 <i>{cc-pVTZ/aug-ccpVTZ}</i>	MS-CASPT2 20R/ <i>{cc-pVDZ/aug-ccpVDZ}</i>
$\pi_{\text{cycle}} \rightarrow \pi_{\text{cycle}}^*$	5.22 [0.89]	5.14 [0.85]	5.17 [0.74]
$n \rightarrow \pi_{\text{CO}}^*$	5.50 [0.63]	5.44 [0.53] +CT [0.10]	5.81 [0.54] + LE $\pi_{\text{CO}}\pi_{\text{CO}}^*$ [0.19]
$n \rightarrow \pi_{\text{CO}}^*$	5.79 [0.73]	5.72 [0.73]	6.07 [0.501] + LE $\pi_{\text{CO}}\pi_{\text{CO}}^*$ [0.18]
$\pi_{\text{cycle}} \rightarrow \pi_{\text{cycle}}^*$	6.36 [0.74]	6.27 [0.72]	6.45 [0.86]
<i>MR</i>			6.69 LEπ [0.22] + LE π_{pep} [0.18] + CT [0.11]
<i>MR</i>			6.86 CT [0.28] + LE $\pi_{\text{CO}}\pi_{\text{CO}}^*$ [0.24] + LE π_{pep} [0.21] + LE π [0.12]
$\pi_{\text{cycle}} \rightarrow \pi_{\text{cycle}}^*$	6.44[0.48]+ CT[0.33]		6.95 [0.63] + CT [0.10]
$n \rightarrow \pi_{\text{cycle}}^*$	6.53 [0.43]+ LE π_{pep} [0.20]	6.34 [0.29] + LE π [0.27] + LE π_{pep} [0.13]	7.15 [0.53] + LE π [0.17]
$\pi_{\text{cycle}} \rightarrow \pi_{\text{cycle}}^*$	6.59 [0.38]+ CT[0.37]		
$n \rightarrow \pi_{\text{cycle}}^*$	6.69 [0.48] + LE π [0.11]	6.44 [0.38] + LE π_{pep} [0.15] + LE π [0.14]	7.21 [0.34] + LEπ [0.39]

Table S3: CC2 and MS-CASPT2 excitation energy (eV) of the excited states of the NAPA B conformer at its DFT-D optimized ground state geometry (Figure 1(a) and Table S1-1) calculated within adapted basis sets (see text). All states up to the two first CT states are reported. For the definition of the values in bracket, see captions of Tables 2 and 3.

Appendix S4: First CASSCF excited states for the ground state geometry as a function of the number of roots.

14 roots	20 roots
Ground state energy: -683.673225 a.u.	Ground state energy: -683.670317 a.u.
state 2: 4.81 eV $\pi \rightarrow \pi^*$ 0.71	state 2: 4.82 eV $\pi \rightarrow \pi^*$ 0.57
state 3: 6.08 eV $n_{\text{pept1}} \rightarrow \pi^*_{\text{pept1}}$ 0.57 $n_{\text{pept1}} \rightarrow \pi^*_{\text{pept2}}$ 0.12	state 3: 5.66 eV $n_{\text{pept2}} \rightarrow \pi^*_{\text{pept2}}$ 0.52 $n_{\text{pept2}} \rightarrow \pi^*$ 0.14
state 4: 6.11 eV $n_{\text{pept2}} \rightarrow \pi^*_{\text{pept2}}$ 0.40 $\pi_{\text{pept1}} \rightarrow \pi^*_{\text{pept2}}$ 0.11 $n_{\text{pept2}} \rightarrow \pi^*_{\text{pept1}}$ 0.18	state 4: 6.14 eV $n_{\text{pept1}} \rightarrow \pi^*_{\text{pept1}}$ 0.36 $\pi \rightarrow \pi^*_{\text{pept1}}$ 0.24
state 5: 7.87 eV $\pi \rightarrow \pi^*$ 0.77	state 5: 7.91 eV $\pi \rightarrow \pi^*$ 0.72
state 6: 8.00 eV $\pi \rightarrow \pi^*$ 0.42 $\pi \pi \rightarrow \pi^* \pi^*$ 0.26	state 6: 8.00 eV $\pi \rightarrow \pi^*$ 0.31 $\pi \pi \rightarrow \pi^* \pi^*$ 0.34

Table S4: CASSCF total and excitation energy of the NAPA B conformer at its DFT-D optimized ground state geometry (Figure 1(a) and Table S1-1) and weights of the different excitations in the wave function as a function of the number of roots.

Appendix S5: Characteristic structural parameters of the different studied NAPA B geometries.

Geometry	Ac-Phe-NH2			NAPA B		
	Φ	Ψ	χ	ω_2	$d_{\text{NH}(2)\cdots\text{O}}$	$d_{\text{NH}(1)\cdots\text{C}\pi}$
Ground state	-83	55	44	-172	2.02	2.57
$M_{\pi\pi^*}$	-83	53	45	-167	1.95	2.35
$CI_{\pi\pi^*/n\pi^*\text{co}(2)}$	-82	52	49	-143	2.00	2.42
$M_{n\pi^*\text{co}(2)}$	-80	49	60	-90	2.28	2.66
M'_{CT}	-85	44	45	-159	1.87	1.35

Table S5-1: Characteristic structural parameters of the ground state, $M_{\pi\pi^*}$, $M_{n\pi^*\text{co}(2)}$, $CI_{\pi\pi^*/n\pi^*\text{co}(2)}$ and M'_{CT} geometries. Ramachandran Φ , Ψ , side chain orientation χ and second peptide bond flatness ω_2 angles are in degrees and bond length in Å.

Geometry	Ac-Phe-NH2				NAPA B				
	θ_{N1}	θ_{N2}	θ_{N3}	$\sum\theta_{\text{Ni}}$	θ_{C1}	θ_{C2}	θ_{C3}	$\sum\theta_{\text{Ci}}$	d_{CO}
Ground state	118	119	121	358	124	113	123	360	1.23
$M_{\pi\pi^*}$	117	119	121	357	124	113	123	360	1.24
$CI_{\pi\pi^*/n\pi^*\text{co}(2)}$	115	117	121	353	122	114	122	358	1.28
$M_{n\pi^*\text{co}(2)}$	110	111	111	332	105	117	118	340	1.38
M'_{CT}	116	117	119	352	128	113	120	361	1.22

Table S5-2: Characteristic geometrical parameters of the second peptide bond deformation. θ_{Ni} and θ_{Ci} ($i=1-3$) angles (see Figure S5-3 for the definition) are in degrees and bond length in Å.

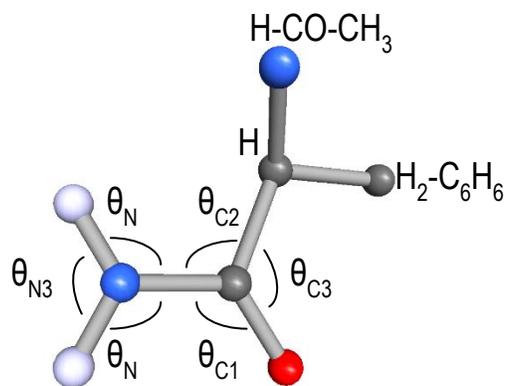


Figure S5-3: Definition of the angles characteristic of the pyramidalization of the NH₂ group and the COCH group.