Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: Combining Multilevel Hartree Fock and Multilevel Coupled Cluster with Molecular Mechanics: a Study of Electronic Excitations in Solutions

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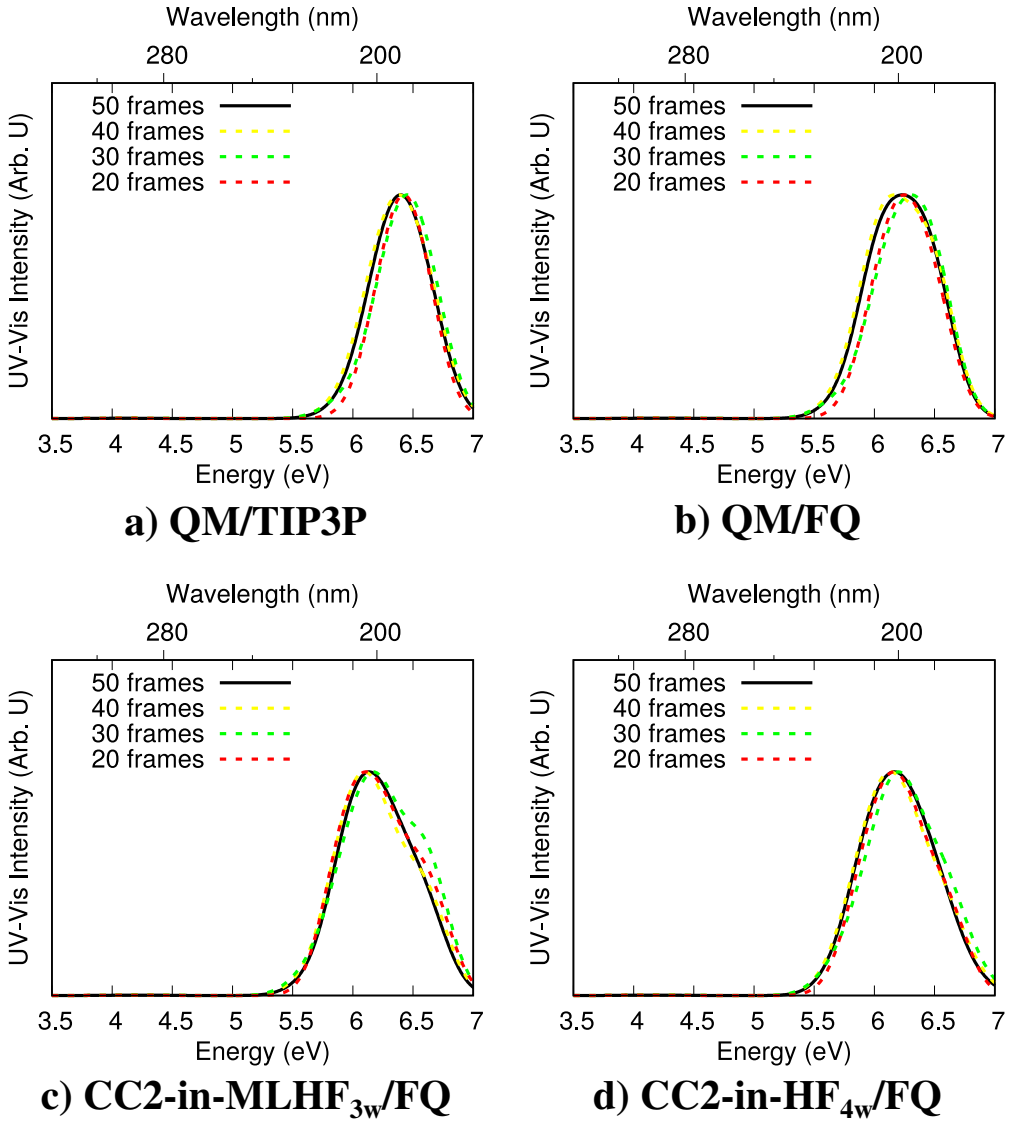

Figure S1: Absorption cross section of Acrolein in aqueous solution as a function of the number of frames.

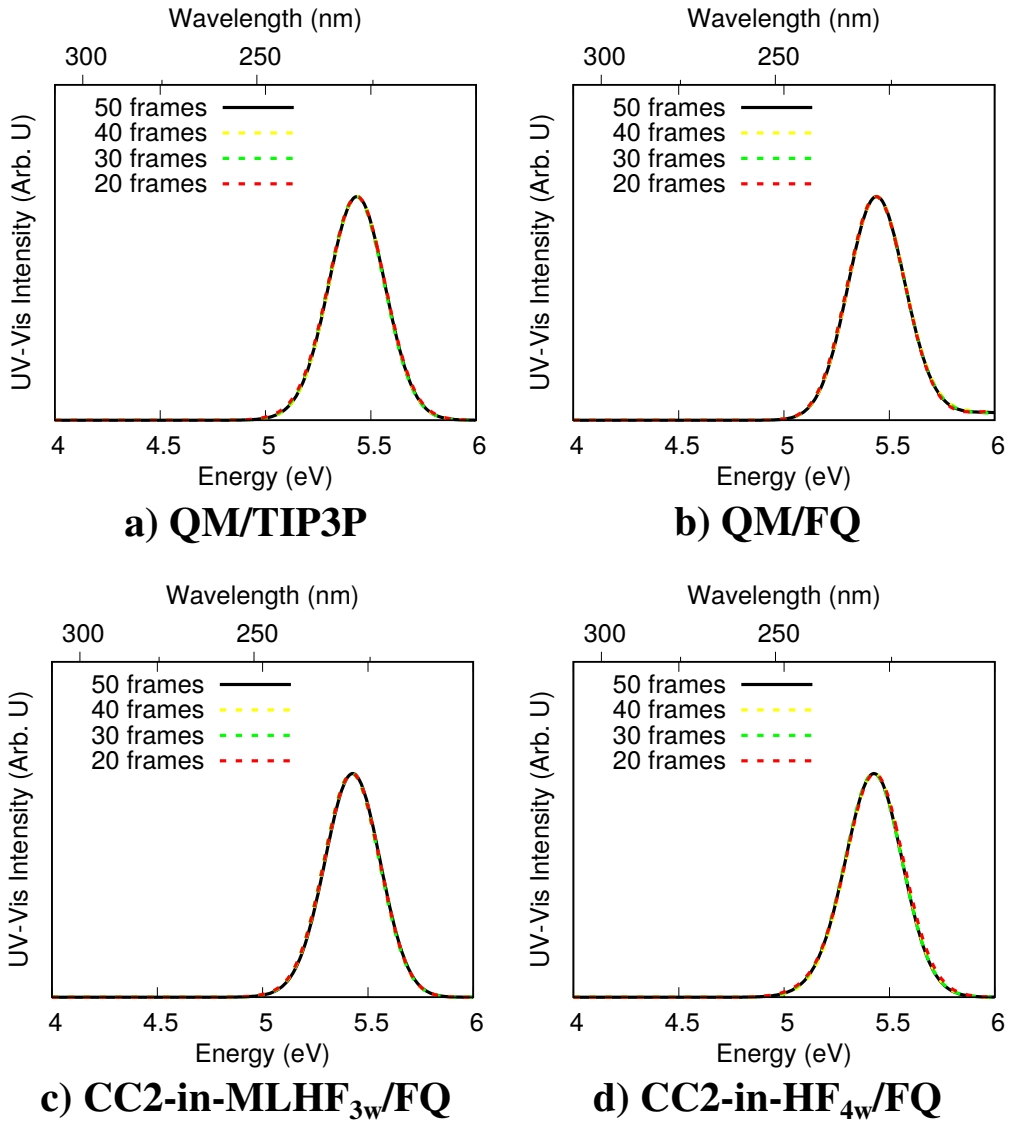

Figure S2: Absorption cross section of pyridine in aqueous solution as a function of the number of frames.

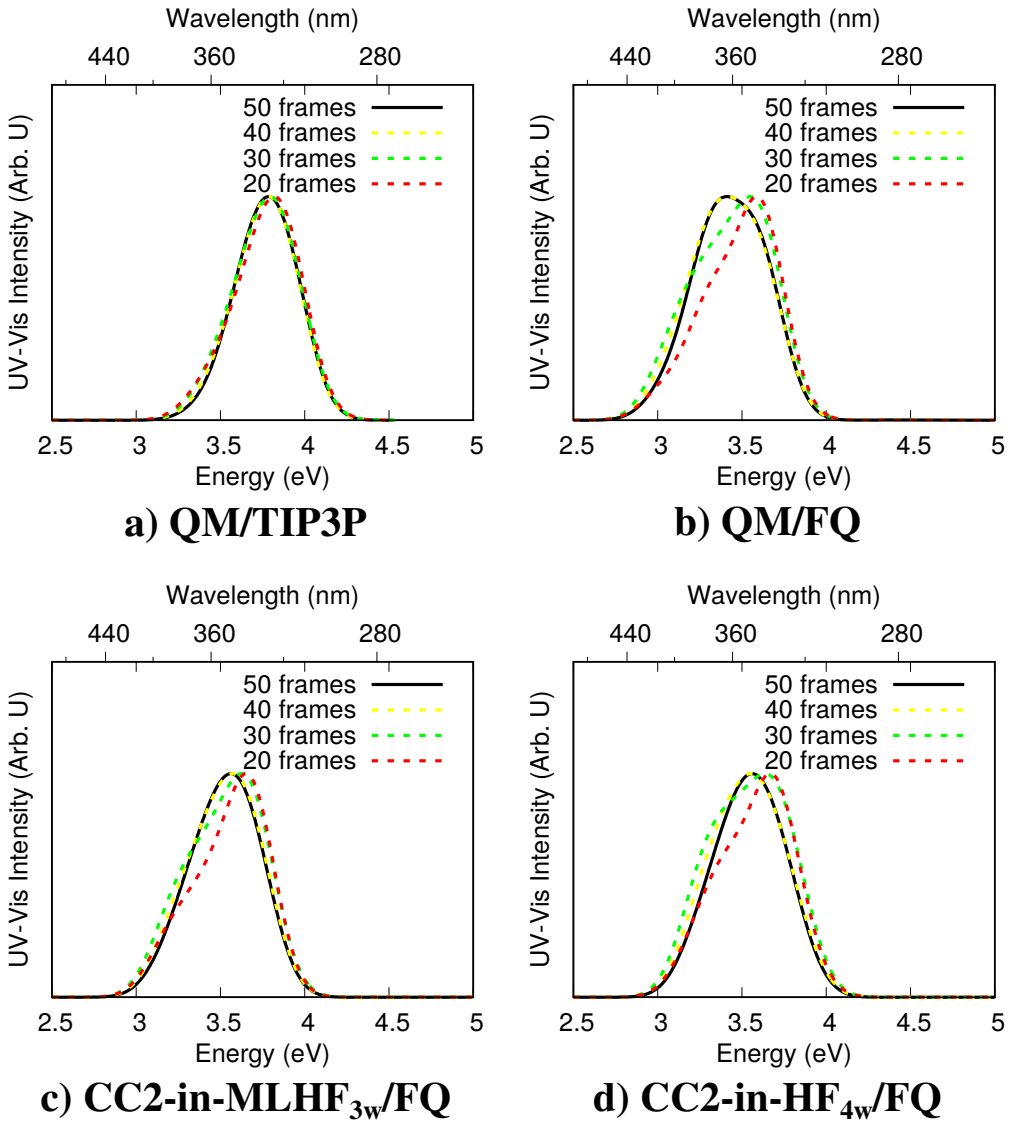

Figure S3: Absorption cross section of para-nitroaniline in aqueous solution as a function of the number of frames.

Table S1: The $n-\pi^*$ and $\pi-\pi^*$ excitation energies of the reduced snapshot of ACRO in aqueous solution (see Fig. 2 in the main text) computed at CC2/aug-cc-pVDZ level of theory, using different approaches to describe the reference state. The errors with respect to the reference CC2 results are also given. All data are reported in eV.

	$n-\pi^*$		$\pi-\pi^*$	
	Exc. Ene.	Error	Exc. Ene.	Error
QM/TIP3P	3.87	-0.02	6.33	0.44
QM/FQ	3.92	0.03	6.26	0.37
CC2-in-MLHF	3.95	0.06	6.21	0.32
CC2-in-MLHF$_{2w}$	3.93	0.04	6.05	0.16
CC2-in-MLHF$_{3w}$	3.92	0.03	5.99	0.10
CC2-in-MLHF$_{4w}$	3.92	0.03	5.98	0.09
CC2-in-MLHF$_{5w}$	3.91	0.02	5.97	0.08
CC2-in-MLHF-AB	3.97	0.08	6.34	0.45
CC2-in-MLHF-AB$_{2w}$	3.94	0.05	6.10	0.21
CC2-in-MLHF-AB$_{3w}$	3.93	0.04	6.01	0.12
CC2-in-MLHF-AB$_{4w}$	3.93	0.04	6.00	0.11
CC2-in-MLHF-AB$_{5w}$	3.92	0.03	5.98	0.09
CC2-in-HF	3.96	0.07	6.19	0.30
CC2-in-HF$_{2w}$	3.93	0.04	6.03	0.14
CC2-in-HF$_{3w}$	3.93	0.04	5.97	0.08
CC2-in-HF$_{4w}$	3.92	0.03	5.97	0.08
CC2-in-HF$_{5w}$	3.92	0.03	5.95	0.06
MLCC2$_{25CNTOs}$	3.91	0.02	5.98	0.09
MLCC2$_{30CNTOs}$	3.91	0.02	5.97	0.08
MLCC2$_{35CNTOs}$	3.90	0.01	5.96	0.07
CC2	3.89	–	5.89	–

Table S2: The $n-\pi^*$ and $\pi-\pi^*$ excitation energies of the full snapshot of ACRO in aqueous solution (see Fig. 6 in the main text) computed at CC2/aug-cc-pVDZ level of theory, using different approaches to describe the reference state. The FQ force field is used to represent the long-range interactions. The errors with respect to the reference CC2-in-HF_{15w} are given, together with the shifts with respect to the data in Tab. S1. All data are given in eV.

	$n-\pi^*$			$\pi-\pi^*$		
	Exc. Ene.	Error	Shift	Exc. Ene.	Error	Shift
QM/FQ	4.04	0.05	0.12	6.18	0.38	-0.08
CC2-in-MLHF/FQ	4.07	0.08	0.12	6.14	0.34	-0.07
CC2-in-$MLHF_{2w}$/FQ	4.06	0.07	0.13	5.91	0.11	-0.14
CC2-in-$MLHF_{3w}$/FQ	4.03	0.04	0.11	5.88	0.08	-0.11
CC2-in-$MLHF_{4w}$/FQ	4.02	0.03	0.10	5.88	0.08	-0.10
CC2-in-$MLHF_{5w}$/FQ	4.00	0.01	0.09	5.88	0.08	-0.09
CC2-in-MLHF-AB/FQ	4.09	0.10	0.12	6.26	0.46	-0.08
CC2-in-MLHF-AB_{2w}/FQ	4.07	0.08	0.13	5.95	0.15	-0.15
CC2-in-MLHF-AB_{3w}/FQ	4.04	0.05	0.11	5.90	0.10	-0.11
CC2-in-MLHF-AB_{4w}/FQ	4.03	0.04	0.10	5.90	0.10	-0.10
CC2-in-MLHF-AB_{5w}/FQ	4.01	0.02	0.09	5.90	0.10	-0.08
CC2-in-HF/FQ	4.07	0.08	0.11	6.14	0.34	-0.05
CC2-in-HF_{2w}/FQ	4.04	0.05	0.11	5.90	0.10	-0.13
CC2-in-HF_{3w}/FQ	4.04	0.05	0.11	5.88	0.08	-0.09
CC2-in-HF_{4w}/FQ	4.04	0.05	0.12	5.87	0.07	-0.10
CC2-in-HF_{5w}/FQ	4.03	0.04	0.11	5.86	0.06	-0.09
$MLCC2_{25CNTOs}$/FQ	4.02	0.03	0.11	5.89	0.09	-0.09
$MLCC2_{30CNTOs}$/FQ	4.02	0.03	0.11	5.88	0.08	-0.09
$MLCC2_{35CNTOs}$/FQ	4.01	0.02	0.11	5.82	0.02	-0.14
CC2-in-HF_{15w}	3.99	–	0.10	5.80	–	-0.09

Table S3: The $n-\pi^*$ and $\pi-\pi^*$ excitation energies of the full snapshot of ACRO in aqueous solution (see Fig. 6 in the main text) computed at CC2/aug-cc-pVDZ level of theory, using different approaches to describe the reference state. The TIP3P force field is used to represent the long-range interactions. The errors with respect to the reference CC2-in-HF_{15w} are given, together with the shifts with respect to the data in Tab. S1. All data are given in eV.

	$n-\pi^*$			$\pi-\pi^*$		
	Exc. Ene.	Error	Shift	Exc. Ene.	Error	Shift
QM/TIP3P	3.95	-0.04	0.08	6.29	0.49	-0.04
CC2-in-MLHF/TIP3P	4.03	0.04	0.08	6.18	0.38	-0.03
CC2-in-$MLHF_{2w}$/TIP3P	4.01	0.02	0.08	5.98	0.18	-0.07
CC2-in-$MLHF_{3w}$/TIP3P	3.99	0.00	0.07	5.94	0.14	-0.05
CC2-in-$MLHF_{4w}$/TIP3P	3.98	-0.01	0.06	5.94	0.14	-0.04
CC2-in-$MLHF_{5w}$/TIP3P	3.96	-0.03	0.05	5.94	0.14	-0.03
CC2-in-MLHF-AB/TIP3P	4.05	0.06	0.08	6.30	0.50	-0.04
CC2-in-MLHF-AB_{2w}/TIP3P	4.02	0.03	0.08	6.03	0.23	-0.07
CC2-in-MLHF-AB_{3w}/TIP3P	4.00	0.01	0.07	5.96	0.16	-0.05
CC2-in-MLHF-AB_{4w}/TIP3P	3.99	0.00	0.06	5.96	0.16	-0.04
CC2-in-MLHF-AB_{5w}/TIP3P	3.97	-0.02	0.05	5.96	0.16	-0.02
CC2-in-HF/TIP3P	4.02	0.03	0.06	6.16	0.36	-0.03
CC2-in-HF_{2w}/TIP3P	4.00	0.01	0.07	5.97	0.17	-0.06
CC2-in-HF_{3w}/TIP3P	3.99	0.00	0.06	5.94	0.14	-0.03
CC2-in-HF_{4w}/TIP3P	3.99	0.00	0.07	5.93	0.13	-0.04
CC2-in-HF_{5w}/TIP3P	3.99	0.00	0.07	5.92	0.12	-0.03
$MLCC2_{25CNTOs}$/TIP3P	3.97	-0.02	0.06	5.95	0.15	-0.03
$MLCC2_{30CNTOs}$/TIP3P	3.97	-0.02	0.06	5.94	0.14	-0.03
$MLCC2_{35CNTOs}$/TIP3P	3.97	-0.02	0.06	5.89	0.09	-0.07
CC2-in-HF_{15w}	3.99	–	0.10	5.80	–	-0.09

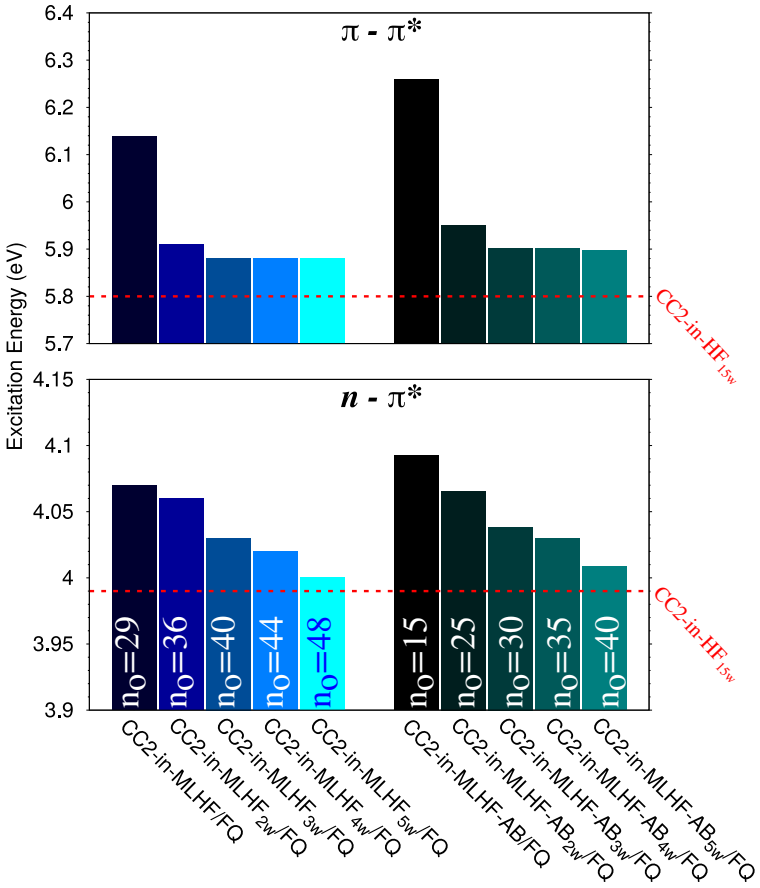

Figure S4: The $n-\pi^*$ and $\pi-\pi^*$ excitation energies of the full snapshot of ACRO in aqueous solution computed at the CC2/aug-cc-pVDZ level, using the MLHF (left) and MLHF-AB (right) reference states. The FQ force field is used to represent the long-range interactions.

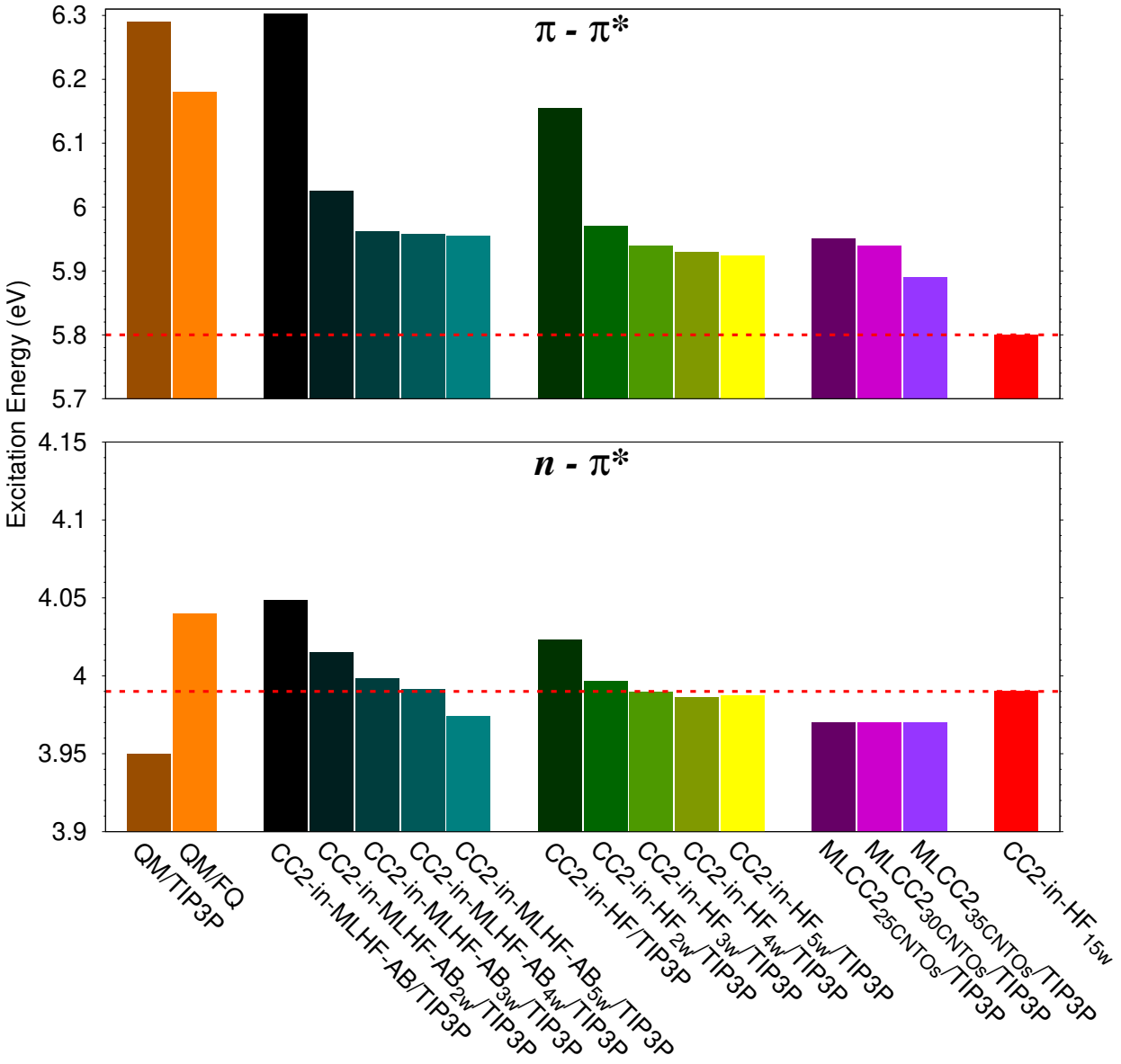

Figure S5: The $n - \pi^*$ and $\pi - \pi^*$ excitation energies of the full snapshot of ACRO in aqueous solution computed at CC2/aug-cc-pVDZ level of theory, using different approaches to describe the reference state. The TIP3P force field is used to represent the long-range interactions.

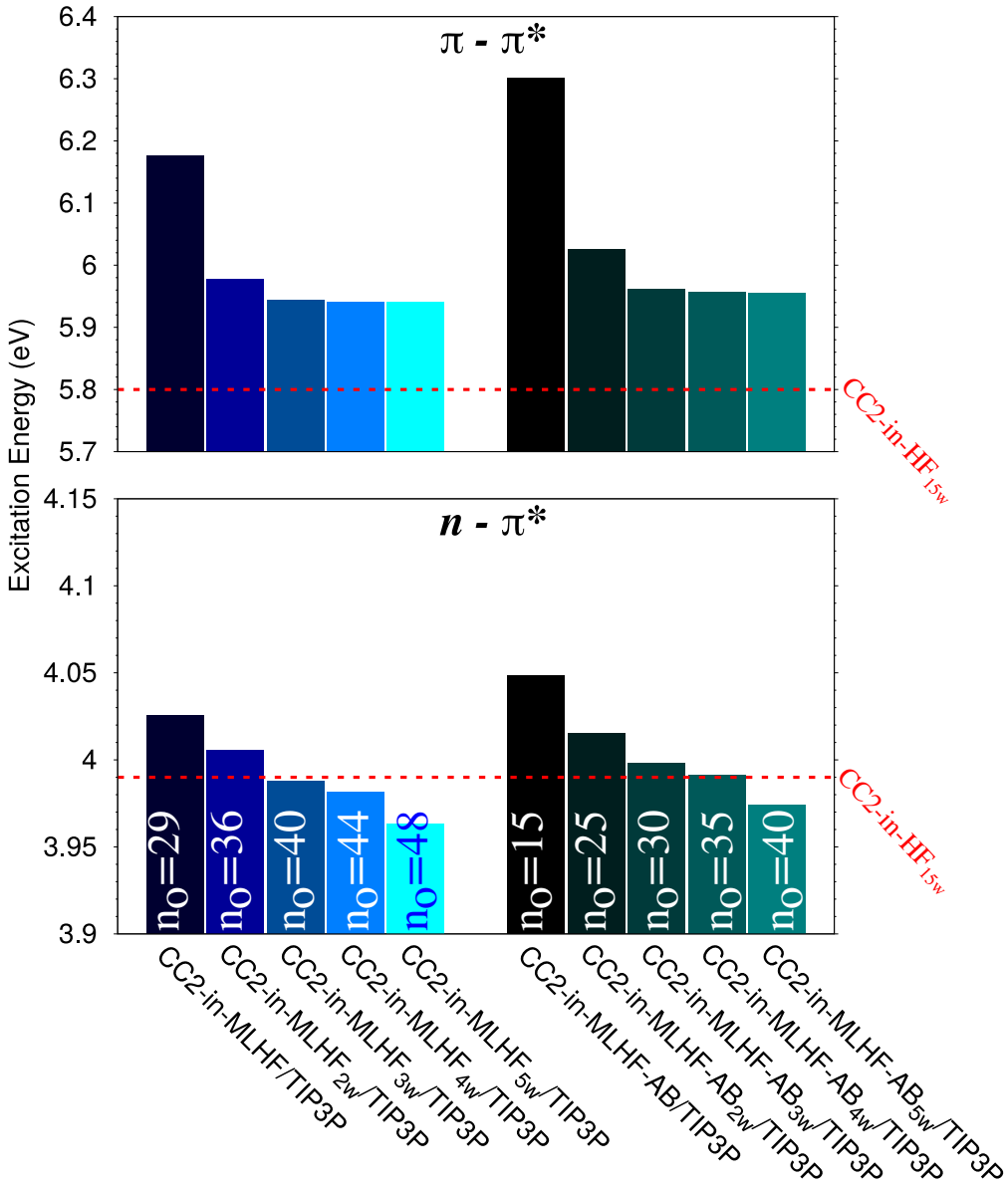

Figure S6: The $n-\pi^*$ and $\pi-\pi^*$ excitation energies of the full snapshot of ACRO in aqueous solution computed at the CC2/aug-cc-pVDZ level, using the MLHF (left) and MLHF-AB (right) reference states. The TIP3P force field is used to represent the long-range interactions.

Table S4: $n-\pi^*$ and $\pi-\pi^*$ excitation energies and vacuo-to-solvent solvachromic shifts of ACRO in vacuo and in aqueous solution. Theoretical solvatochromic shifts are calculated with respect to the vacuo value, which is computed as an average from the structures extracted from the MD by removing the water molecules. Computed standard errors at the 68% confidence interval are also given. Experimental data are reproduced from Ref. 1.

	$n-\pi^*$		$\pi-\pi^*$	
Method	Exc. Ene. (eV)	Shift (eV)	Exc. Ene. (eV)	Shift (eV)
$<$vacuo$>_{MD}$	3.87 ± 0.02	–	6.74 ± 0.01	–
exp (vac)	3.69	–	6.42	–
QM/TIP3P	4.11 ± 0.02	-0.24 ± 0.02	6.39 ± 0.03	0.35 ± 0.03
QM/FQ	4.26 ± 0.02	-0.39 ± 0.02	6.23 ± 0.03	0.51 ± 0.03
CC2-in-MLHF$_{3w}$/FQ	4.13 ± 0.02	-0.26 ± 0.02	6.19 ± 0.03	0.55 ± 0.03
CC2-in-MLHF-AB$_{3w}$/FQ	4.16 ± 0.02	-0.29 ± 0.02	6.26 ± 0.03	0.48 ± 0.03
CC2-in-HF$_{4w}$/FQ	4.17 ± 0.02	-0.30 ± 0.02	6.21 ± 0.03	0.53 ± 0.03
MLCC2$_{30CNTOs}$/FQ	4.12 ± 0.02	-0.25 ± 0.02	6.14 ± 0.03	0.60 ± 0.03
exp (wat)	3.94	-0.25	5.90	0.52

References

(1) Aidas, K.; Møgelhøj, A.; Nilsson, E. J.; Johnson, M. S.; Mikkelsen, K. V.; Christiansen, O.; Söderhjelm, P.; Kongsted, J. On the performance of quantum chemical methods to predict solvatochromic effects: The case of acrolein in aqueous solution. *J. Chem. Phys.* **2008**, *128*, 194503.