Supplementary material: Wavefunction embedding for molecular polaritons

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I. REACTION ENERGY BARRIER AND REACTION ENERGY FOR METHYL TRANSFER IN PYRIDINE WITH METHYL BROMIDE INSIDE AN OPTICAL CAVITY WITH CAVITY PARAMETERS $\lambda = 0.1$ A.U. AND $\omega = 3$ EV

TABLE I: Reaction energy barrier (TS)[a] and reaction energy (ΔE)[b] (in kcal/mol) for methyl transfer in pyridine with methyl bromide inside an optical cavity.

method	outside cavity		x direction		y direction		z direction	
	TS	ΔE	TS	ΔE	TS	ΔE	TS	ΔE
QED-HF	13.63	-18.65	14.02	-19.49	13.41	-20.53	18.63	-17.64
QED-PBE	7.37	-16.06	9.00	-15.68	7.19	-17.81	12.75	-23.91
QED-PBE0	7.79	-19.07	8.65	-19.58	7.41	-21.08	15.86	-21.45
QED-B3LYP	6.74	-19.54	7.80	-19.84	6.39	-21.48	14.24	-22.64
QED-CCSD	10.46	-21.17	9.96	-22.72	10.08	-22.55	13.91	-23.58
QED-CCSD-in-HF	10.25	-23.95	10.03	-25.29	9.83	-25.65	13.94	-26.04
QED-CCSD-in-PBE	11.56	-18.86	10.91	-20.75	11.11	-20.58	16.23	-20.05
QED-CCSD-in-PBE0	11.58	-19.80	11.16	-21.43	11.17	-21.46	15.63	-21.68
QED-CCSD-in-B3LYP	11.90	-19.27	11.43	-20.93	11.47	-20.97	15.99	-21.01
QED-CCSD-in-PBE0[c]	12.38	-17.94	12.29	-18.92	12.05	-19.38	16.74	-18.91
QED-CCSD-in-PBE0[d]	10.22	-21.56	-	-	-	-	-	-

[a]Reaction energy barrier is calculated as the energy difference between the transition state and the reactant.
[b]Reaction energy is calculated as the energy difference between the product and the reactant.
[c]CL calculation performed with one CL shell.
[d]Embedding domain that include additional two adjacent CH groups.

II. REACTION ENERGY BARRIER AND REACTION ENERGY FOR PROTON TRANSFER IN AMINOPROPENAL INSIDE AN OPTICAL CAVITY WITH CAVITY PARAMETERS $\lambda = 0.1$ A.U. AND $\omega = 3$ EV

TABLE II: Reaction energy barrier (TS)[a] and reaction energy (ΔE)[b] (in kcal/mol) for proton transfer in aminopropenal inside an optical cavity.

method	outside cavity		x direction		y direction		z direction	
	TS	ΔE	TS	ΔE	TS	ΔE	TS	ΔE
QED-HF	16.65	8.63	18.65	9.57	17.24	9.00	16.64	8.69
QED-PBE	3.93	6.26	6.14	7.07	4.08	6.08	3.83	6.26
QED-PBE0	6.09	6.62	8.36	7.45	6.45	6.59	6.02	6.63
QED-B3LYP	7.32	6.80	9.58	7.62	7.64	6.73	7.25	6.81
QED-CCSD	9.65	4.54	10.72	4.67	9.71	4.32	9.32	4.34
QED-CCSD-in-HF	10.43	5.49	11.75	5.59	10.43	5.07	10.16	5.16
QED-CCSD-in-PBE	11.06	6.38	12.78	6.07	11.04	6.08	10.77	6.18
QED-CCSD-in-PBE0	10.74	5.95	12.29	5.80	10.71	5.63	10.46	5.74
QED-CCSD-in-B3LYP	11.29	5.87	12.93	5.66	11.26	5.53	11.01	5.65
QED-CCSD-in-PBE0[c]	10.69	6.21	12.34	6.20	10.58	5.73	10.41	5.97

[a]Reaction energy barrier is calculated as the energy difference between the transition state and the reactant.
[b]Reaction energy is calculated as the energy difference between the product and the reactant.
[c]CL calculation performed with one CL shell.

III. ENERGY CONTRIBUTIONS BREAKDOWN

TABLE III: Effect of the cavity[a] on the energy contributions for the proton binding energy (in kcal/mol) for MeOH in gas phase and in solvent calculated with the QED-HF and QED-CCSD methods.

energy contributions	MeOH	MeOH-in-5H_2O
	QED-HF	
electronic	0.07	0.09
dipole self energy	0.45	0.86
total	0.52	0.95
	QED-CCSD	
electronic	0.48	0.39
dipole self energy	1.01	1.28
dipolar coupling	0.06	0.04
total	1.55	1.71

[a] Effect of the cavity on the PBEn is calculated as the difference between the PBEn obtained with the QED method and the corresponding conventional electronic structure method.

Table III shows effect of the cavity on the energy contributions for the proton binding energy of MeOH in the gas phase and in the explicit solvent calculated with the QED-HF and QED-CCSD (QED-HF + QED-correlation) methods. The energy contributions for the QED-HF method are electronic $\left(\langle 0^{\mathrm{e}}0^{\mathrm{ph}}|\,\hat{H}^{\mathrm{e}}\,|0^{\mathrm{e}}0^{\mathrm{ph}}\rangle)\right)$, and dipole self energy $\left(\langle 0^{\mathrm{e}}0^{\mathrm{ph}}|\,\frac{1}{2}(\boldsymbol{\lambda}\cdot\Delta\boldsymbol{d})^2\,|0^{\mathrm{e}}0^{\mathrm{ph}}\rangle\right)$. The energy contributions for the QED-CCSD methods are electronic $\left(\langle 0^{\mathrm{e}}0^{\mathrm{ph}}|\,\hat{H}^{\mathrm{e}}\,|0^{\mathrm{e}}0^{\mathrm{ph}}\rangle + \bar{g}^{ab}_{ij}\times(0.25\cdot t^{ij,0}_{ab} + 0.5\cdot t^{i,0}_{a}t^{j,0}_{b})\right)$, dipole self energy $\left(\langle 0^{\mathrm{e}}0^{\mathrm{ph}}|\,\frac{1}{2}(\boldsymbol{\lambda}\cdot\Delta\boldsymbol{d})^2\,|0^{\mathrm{e}}0^{\mathrm{ph}}\rangle + ((\boldsymbol{\lambda}\cdot\boldsymbol{d})^2)^{ab}_{ij}\times(0.25\cdot t^{ij,0}_{ab} + 0.5\cdot t^{i,0}_{a}t^{j,0}_{b})\right)$, and dipolar coupling $\left((\boldsymbol{\lambda}\cdot\boldsymbol{d})^{a}_{i}\times(t^{i,1}_{a} + t^{i,0}_{a}t^{0,1})\right)$. In the case of the QED-HF method, the total (electronic + dipole self energy) corresponds to the cavity effect at the QED-HF level, whereas for the QED-CCSD method, the total (electronic + dipole self energy + dipolar coupling) corresponds to the cavity effect at the QED-CCSD level. The calculations employ cavity parameters $\lambda = 0.1$ a.u. and $\omega = 3$ eV.

IV. CARTESIAN COORDINATES OF THE OPTIMIZED GEOMETRIES

Optimized with the MP2/6-31G(d) method:
Pyridine with methyl bromide reactant (number of imaginary frequencies=0)

C	1.13759681	-0.05477211	-2.19306978
H	0.24449380	0.44574240	-2.55396116
H	1.13314176	-1.09244459	-2.51982225
H	2.01600197	0.44796781	-2.58556594
Br	1.08790491	-0.22514853	-5.15588397
N	1.16435647	-0.00324395	-0.68355764
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38825264
C	1.21359614	0.00000000	2.07545441
C	2.40191143	-0.00274236	1.34538743
C	2.35238160	-0.00267165	-0.04196715
H	1.23297434	0.00214095	3.16119421
H	-0.90284719	-0.00066197	-0.60145425
H	-0.94822464	0.00436088	1.91541110
H	3.36834811	-0.00056812	1.83838151
H	3.23316883	-0.00536202	-0.67529613

Optimized with the MP2/6-31G(d) method:
pyridine with methyl bromide transition state (number of imaginary frequencies=1)

C	1.10026781	-0.05950199	-2.53988699
H	1.09727598	-1.13283765	-2.63133480
H	2.02255209	0.47277974	-2.70410122
H	0.17128876	0.47383242	-2.65586161
Br	1.03462545	-0.13090326	-5.05746718
N	1.14831147	-0.00003940	-0.69694831
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.39173587
C	1.22030589	0.00000000	2.06832316
C	2.40375234	-0.00091860	1.32915551
C	2.33133285	-0.00089199	-0.06069652
H	1.24857876	0.00072777	3.15428244
H	-0.91605046	-0.00071297	-0.58576567
H	-0.94245073	0.00142231	1.93058869
H	3.37296670	-0.00022807	1.81823783
H	3.21566118	-0.00228926	-0.69333534

Optimized with the MP2/6-31G(d) method:
pyridine with methyl bromide product (number of imaginary frequencies=0)

C	1.02368319	0.05729769	-3.88264194
H	0.14367313	0.58843316	-3.53298410
H	1.02352551	-0.96949641	-3.53110392
H	1.93068036	0.57179520	-3.58034422
Br	0.97146917	0.02891100	-5.84054942
N	1.12024672	0.00002885	-0.74573812
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.39525820
C	1.22336316	0.00000000	2.06448953
C	2.39439815	-0.00016595	1.30740911
C	2.29212447	-0.00016307	-0.08409104
H	1.26322069	-0.00005113	3.15080347
H	-0.93752389	-0.00055095	-0.55341536
H	-0.93952305	-0.00007929	1.94067080
H	3.37136483	-0.00038187	1.78250172

H	3.18659424	-0.00087954	-0.70471099

Optimized with the CCSD/cc-pVDZ method:
Aminopropenal reactant (number of imaginary frequencies=0)

H	0.00000000	0.00000000	0.00000000
C	0.00000000	1.09163906	0.00000000
C	1.26822472	1.80690645	0.00000000
N	-1.33404678	3.10992888	0.00000000
O	1.39279087	3.03379031	0.00000000
H	-0.48254004	3.66582880	0.00000000
H	-2.24599052	3.54003736	0.00000000
C	-1.19931821	1.76513995	0.00000000
H	2.18220599	1.16371496	0.00000000
H	-2.14055701	1.20128576	0.00000000

Optimized with the CCSD/cc-pVDZ method:
Aminopropenal transition state (number of imaginary frequencies=1)

H	0.00000000	0.00000000	0.00000000
C	0.00000000	1.08943910	0.00000000
C	1.19187861	1.82073020	0.00000000
N	-1.15503519	3.15085322	0.00000000
O	1.23956085	3.10723950	0.00000000
H	0.06714025	3.42106531	0.00000000
H	-2.03971004	3.65182794	0.00000000
C	-1.21230682	1.83679656	0.00000000
H	2.16133262	1.29142618	0.00000000
H	-2.18458586	1.32025952	0.00000000

Optimized with the CCSD/cc-pVDZ method:
Aminopropenal product (number of imaginary frequencies=0)

H	0.00000000	0.00000000	0.00000000
C	0.00000000	1.09138840	0.00000000
C	1.19000326	1.75971354	0.00000000
N	-1.29869978	3.11237163	0.00000000
O	1.33369004	3.08569523	0.00000000
H	0.41141507	3.45367072	0.00000000
H	-2.26092059	3.46346742	0.00000000
C	-1.27014745	1.81619151	0.00000000
H	2.14625767	1.22260226	0.00000000
H	-2.19412100	1.21051211	0.00000000