Electronic Supplementary Material for PCCP

SUPPORTING INFORMATION

A direct ab-initio molecular dynamics (MD) study on the

Benzophenone-Water 1:1 complex

Hiroto TACHIKAWA,* Tetsuji IYAMA and Kohich KATO

Division of Materials Chemistry, Graduate School of Chemistry

Hokkaido University, Sapporo 060-8628, JAPAN

Table S1. Optimized geometrical parameters of benzophenone (Bp). Bond lengths and angles are in Å and in degrees, respectively.

	B3LYP/6-31G(d)	B3LYP/6-311G(d,p)	B3LYP/6-311++G(d,p)
r(C=O)	1.2264	1.2192	1.2004
r(C-C_1)	1.5010	1.5016	1.5007
r(C-C_1')	1.5010	1.5016	1.5007
r(C_1-C_2)	1.4035	1.4006	1.4008
r(C_2-C_3)	1.3955	1.3930	1.3935
r(C_3-C_4)	1.3956	1.3928	1.3935
ϕ	50.1	52.1	54.2
θ_1	120.7	120.3	120.1
θ_2	119.7	119.8	120.0
θ_3	119.7	119.8	120.0

Table S2. Optimized geometrical parameters of benzophenone H_2O 1:1 complex Bp(H_2O). Bond lengths and angles are in Å and in degrees, respectively.

parameter	B3LYP/6-31G(d)	B3LYP/6-311G(d,p)	B3LYP/6-311++G(d,p)
r(C=O)	1.2323	1.2252	1.2265
r(C-C_1)	1.4950	1.4959	1.4950
r(C-C_1')	1.4985	1.4990	1.4975
r(C_1-C_2)	1.4054	1.4024	1.4026
r(C_2-C_3)	1.3942	1.3918	1.3923
r(C_3-C_4)	1.3960	1.3932	1.3939
ϕ	51.3	53.0	55.0
θ_1	120.7	120.4	120.2
θ_2	120.7	120.7	120.7
θ_3	118.6	118.9	119.1
r(O-O_W)	2.8820	2.8869	2.8703
r(O-H_{W1})	1.9532	1.9756	1.9157
r(O_W-H_0)	2.3531	2.3528	2.4711
r(Ow-H_1)	0.9759	0.9691	0.9714
r(Ow-H_2)	0.9690	0.9623	0.9611
∠(C-O-O_W)	131.5	130.5	133.5
∠(H_{W1}-O_W-H_{W2})	102.8	103.0	105.3

Table S3. Total energies of Bp, Bp(H_2O) and H_2O (in au), and solvation energy (ΔE_{solv} in kcal/mol). Solvation energy corrected with the basis set superposition error (BSSE) is given in parenthesis (in kcal/mol).

Method	Bp	Bp(H_2O)	H_2O	ΔE_{solv}
HF/3-21G(d)	-569.78756	-645.39423	-75.58596	13.0
B3LYP/6-31G(d)	-576.63227	-653.05484	-76.40895	8.5
B3LYP/6-311G(d,p)	-576.77441	-653.23565	-76.44745	8.7
B3LYP/6-311++G(d,p)	-576.78217	-653.25048	-76.45853	6.1 (5.5)
PW91PW91/6-311++G(d,p)	-576.55589	-652.9981393	-76.4304982	7.4

Table S4. Excitation energies (in eV) of Bp calculated at the B3LYP/6-311++G(d,p) level and experimental excitation energies.

Assignment	B3LYP/6-311++G(d,p)	Experiment	INDO/CIS (Ref.25)
nπ*	3.60 (0.0013)	3.58 (weak)	3.15
ππ*(1)	4.53 (0.0147)	4.46 (shoulder)	4.48
ππ*(2)	4.61 (0.0438)		4.50
ππ*(3)	4.71 (0.2464)	5.01 (strong and broad)	4.93
ππ*(4)	4.87 (0.0383)		5.04

Table S5. Excitation energies (in eV) of Bp and Bp(H_2O), and energy shifts (ΔE_{shift} in eV) caused by 1 : 1 complex formation

Method	Excitation	Bp	Bp(H_2O)	ΔE_{shift}
TD-B3LYP/6-311++G(d,p)// B3LYP/6-31G(d)				
	nπ*	3.55	3.66	+0.11
	ππ*(1)	4.48	4.34	-0.14
	ππ*(2)	4.55	4.43	-0.12
	ππ*(3)	4.64	4.53	-0.11
TD-PW91PW91/6-311++G(d,p)// PW91PW91/6-311++G(d,p)				
	nπ*	3.12	3.25	+0.13
	ππ*(1)	3.91	3.36	-0.55
	ππ*(2)	3.98	3.88	-0.11
	ππ*(3)	4.05	3.88	
TD-B3LYP/6-311++G(d,p)// B3LYP/6-311++G(d,p)				
	nπ*	3.60	3.75	+0.15
	ππ*(1)	4.53	4.37	-0.16
	ππ*(2)	4.61	4.50	-0.11
	ππ*(3)	4.71	4.58	-0.13
Expl.[a]				
	nπ*	3.58	3.85	+0.27
	ππ*	5.01	4.81	-0.20

[a]Experimental values are cited from Reference 32. The excitation energies of Bp in bulk water.

Table S6. Mulliken atomic charges, bond populations, and dipole moments (in Debye) calculated by SE-CI/6-31G(d) calculations.

		S_0	$n\pi^*(S_1)$	$\pi\pi^*$ (S_2)	$\pi\pi^*$ (S_3)
Bp					
	charge				
	O	-0.557	-0.298	-0.600	-0.588
	C	+0.538	+0.264	+0.496	+0.520
	bond population				
	C=O	0.581	0.318	0.557	0.570
	dipole moment				
	μ [a]	3.41	1.52	3.95	3.88
Bp-H_2O					
	charge				
	O	-0.606	-0.351	-0.653	-0.642
	C	+0.565	+0.286	+0.511	+0.535
	bond population				
	C=O	0.541	0.301	0.509	0.522
	O--H_{w1}	0.023	0.009	0.028	0.026
	H_0--O_w	0.016	0.045	0.017	0.016

[a] Experimental values of dipole moment of Bp are 2.98 D for S_0 state and 1.50 D for S_1 state.

Table S6. Formation energies of water dimer (ΔE_{dimer} in kcal/mol) calculated at the B3LYP/6-311++G(d,p)// B3LYP/6-31G(d) level.

Method	H_2O	$(H_2O)_2$	ΔE_{dimer}
B3LYP/6-311++G(d,p)	-76.45853	-152.9263403	5.8
PW91PW91/6-311++G(d,p)	-76.4304982	-152.8718132	6.8

Co

Table S7. Excitation energies of BpH_2O calculated at the B3LYP/6-311++G(d,p)// B3LYP/6-31G(d) level.

	nπ*	ππ*(1)	ππ*(2)	ππ*(3)	ππ*(4)
B3LYP/6-311++G(d,p)	3.664	4.336	4.426	4.528	4.748
//B3LYP/6-31G(d)	0.00131	0.0163	0.0453	0.2783	0.0502