Supporting information

Photochemistry of methyl hypobromite (CH_3OBr): excited states and photoabsorption spectrum

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S1. Cartesian Coordinates

The geometry of the ground state of CH_3OBr molecule optimized at MP2/aug-cc-pVTZ level. The geometry is given in standard XYZ format in Ångstroms.

```
H     0.000000     0.000000     0.000000
C     0.000000     0.000000     1.087887
O     1.386054     0.000000     1.441569
Br    1.569589     0.000000     3.251889
H    -0.501661    -0.892598     1.462312
H    -0.501661     0.892598     1.462312
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S2. CASSCF and MRCI Details

Figure S1. The molecular orbitals comprising the active space in the SA-MCSCF(12,11) computations.

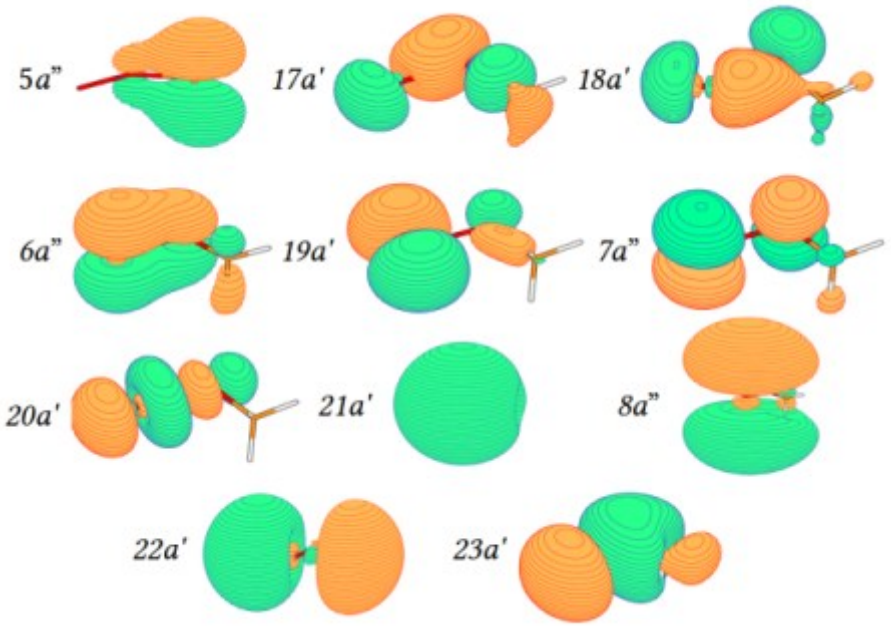


Table S1. The composition of SA-MCSCF(12,11) natural orbitals.

Orbital	Composition	occupancy
5a"	σ(C-H)	2
17a'	σ(O-Br) + σ(C-O) (σ')	2
18a'	σ(O-Br) - σ(C-O) (σ")	2
6a"	$4p_z$(Br) + $2p_z$(O) (n')	2
19a'	$4p_e$(Br) (n_{Br})	2
7a"	$4p_z$(Br) – $2p_z$(O) (n")	2
20a'	σ*(O-Br)	0
21a'	5s(Br)	0
8a"	$5p_z$(Br)	0
22a'	$5p_{xy}$(Br)	0
23a'	$5p'_{xy}$(Br)	0

Table S2. SA-MCSCF, MRCI-SD, and MRCI-SD+Q results for vertical excitation energies (E_v in eV), spatial extent ($\langle r^2 \rangle$ in a_0^2), configuration weights, and oscillator strengths (*f*) of the ground and excited singlet electronic states.

State	SA-MCSCF				MRCI-SD					MRCI-SD+Q
	E_v	Weights	$\langle r^2 \rangle$	*f*	E_v	Weights	$\langle r^2 \rangle$	*f*	E_{corr} (MRCI-SD)	E_v
$1^1A'$	0.00	0.95 gs	62.3	--	0.00	0.89 gs	64.1	--	-7.56	0.00
$2^1A'$	4.91	0.76 $n_{Br}\sigma^*$ + 0.14 $n_{Br}p'_{xy}$ + 0.03 $n_{Br}\sigma''\sigma^{*2}$	66.2	0.0055	4.77	0.74 $n_{Br}\sigma^*$ + 0.11 $n_{Br}p'_{xy}$	67.4	0.0012	-7.70	4.70
$3^1A'$	7.10	0.78 $n''p_z$ + 0.09 $n_{Br}s$ + 0.03 $n'\sigma''\sigma^*p_z$	131.6	0.0114	7.40	0.58 $n''^2\sigma^{*2}$ + 0.14 $n''^2\sigma^*p'_{xy}$ + 0.10 $n'^2\sigma^{*2}$ + 0.03 $n'n''\sigma^{*2}$	68.3	0.0003	-7.26	7.39
$4^1A'$	7.20	0.80 $n_{Br}s$ + 0.08 + $n''p_z$ + 0.06 $n_{Br}p_{xy}$	112.4	0.0840	7.88	0.46 $n''p_z$ + 0.27 $n_{Br}s$ + 0.08 $\sigma''\sigma^*$	116.9	0.0301	-6.88	8.01
$5^1A'$	7.31	0.58 $n''^2\sigma^{*2}$ + 0.15 $n''^2\sigma^*p'_{xy}$ + 0.13 $n'^2\sigma^{*2}$ + 0.05 $n''p_z$	70.4	0.0000	7.95	0.52 $n_{Br}s$ + 0.32 $n''p_z$ + 0.03 $n_{Br}p_{xy}$	118.6	0.0435	-6.92	8.08
$6^1A'$	7.93	0.54 $n_{Br}p_{xy}$ + 0.18 $\sigma''\sigma^*$ + 0.08 $\sigma'\sigma^*$ + 0.05 $n_{Br}s$	113.1	0.0566	8.14	0.42 $\sigma''\sigma^*$ + 0.15 $\sigma'\sigma^*$ + 0.07 $n''p_z$ + 0.07 $n_{Br}s$	75.3	0.0636	-7.35	8.12
$7^1A'$	8.05	0.34 $n_{Br}p_{xy}$ + 0.28 $\sigma''\sigma^*$ + 0.14 $\sigma'\sigma^*$ + 0.07 $\sigma'p_{xy}'$	93.2	0.0563	8.77	0.81 $n_{Br}p_{xy}$ + 0.03 $n_{Br}s$	137.5	0.0007	-6.83	8.92
$1^1A''$	3.69	0.80 $n''\sigma^*$ + 0.12 $n''p'_{xy}$ + 0.03 $n'\sigma''\sigma^{*2}$	65.6	0.0016	3.71	0.76 $n''\sigma^*$ + 0.10 $n'\sigma\sigma^*$	66.3	0.0000	-7.54	3.68
$2^1A''$	6.21	0.64 $n''\sigma^*$ + 0.10 $n'p_{xy}$ + 0.09 $n''p_{xy}$ + 0.09 $n''s$	70.5	0.0000	6.25	0.70 $n'\sigma^*$ + 0.09 $n''p_{xy}$ + 0.07 $n''\sigma''\sigma^{*2}$	66.4	0.0012	-7.52	6.20
$3^1A''$	6.34	0.81 $n''s$ + 0.08 $n'\sigma^*$ + 0.03 $n'\sigma''\sigma^*s$	105.5	0.0766	7.04	0.84 $n''s$ + 0.03 $n'\sigma\sigma^*s$	107.2	0.0439	-6.87	7.16
$4^1A''$	7.05	0.89 $n''p_{xy}$ + 0.03 $n''s$	139.3	0.0000	7.81	0.72 $n''p_{xy}$ + 0.09 $n''n_{Br}\sigma^{*2}$	126.5	0.0000	-6.80	7.93
$5^1A''$	7.77	0.59 $n_{Br}n''\sigma^{*2}$ + 0.13 $n_{Br}n'\sigma^{*2}$ + 0.12 $n_{Br}n''\sigma^*p_{xy}'$	67.5	0.0000	7.90	0.50 $n_{Br}n''\sigma^{*2}$ + 0.12 $n''p'_{xy}$ + 0.10 $n_{Br}n''\sigma^*p'_{xy}$ + 0.08 $n_{Br}n''\sigma^{*2}$	77.9	0.0004	-7.43	7.89
$6^1A''$	7.97	0.93 $n_{Br}p_z$	138.8	0.0066	8.82	0.88 $n_{Br}p_z$	137.2	0.0052	-6.70	9.00
$7^1A''$	9.00	0.85 $n's$ + 0.07 $n''\sigma''\sigma^*s$	110.4	0.0385	9.55	0.77 $n's$ + 0.04 $n''\sigma''\sigma^*s$	107.2	0.0113	-7.01	9.58

Table S3. SA-MCSCF, MRCI-SD, and MRCI-SD+Q results for vertical excitation energies (E_v in eV), spatial extent ($\langle r^2 \rangle$ in a_0^2), configuration weights, and oscillator strengths (*f*) of the excited triplet electronic states.

State	SA-MCSCF			MRCI-SD				MRCI-SD+Q
	E_v	Weights	$\langle r^2 \rangle$	E_v	Weights	$\langle r^2 \rangle$	E_{corr} (MRCI-SD)	E_v
$1^3A'$	4.46	0.85 $n_{Br}\sigma^*$ + 0.06 $n_{Br}s$	65.8	4.11	0.85 $n_{Br}\sigma^*$ + 0.03 $n_{Br}s$	66.2	-7.90	3.97
$2^3A'$	6.13	0.89 $\sigma''\sigma^*$ + 0.03 $\sigma''s$	64.7	6.35	0.85 $\sigma''\sigma^*$ + 0.03 $\sigma''s$	64.8	-7.34	6.37
$3^3A'$	7.15	0.34 $n_{Br}p_{xy}$ + 0.34 $n_{Br}p'_{xy}$ + 0.25 $n''p_z$	113.6	7.85	0.40 $n_{Br}p_{xy}$ + 0.46 $n_{Br}p'_{xy}$	104.2	-6.87	7.98
$4^3A'$	7.17	0.64 $n''p_z$ + 0.16 $n_{Br}p'_{xy}$ + 0.10 $n_{Br}p_{xy}$	124.7	7.91	0.84 $n''p_z$	130.3	-6.82	8.05
$5^3A'$	7.94	0.50 $n_{Br}p_{xy}$ + 0.43 $n_{Br}p'_{xy}$	133.1	8.69	0.79 $n'n''\sigma^{*2}$ + 0.09 $n'n''\sigma^*s$	69.2	-6.81	8.72
$6^3A'$	8.43	0.85 $n_{Br}s$ + 0.06 $n_{Br}\sigma^*$	125.8	8.70	0.47 $n_{Br}p_{xy}$ + 0.40 $n_{Br}p'_{xy}$	130.5	-7.29	8.81
$7^3A'$	8.57	0.83 $n'n''\sigma^{*2}$ + 0.13 $n'n''\sigma^*s$	70.3	9.02	0.83 $n_{Br}s$ + 0.03 $n_{Br}\sigma^*$	131.2	-7.11	9.09
$1^3A''$	3.30	0.88 $n''\sigma^*$ + 0.05 $n''s$	65.5	3.11	0.85 $n''\sigma^*$ + 0.03 $n''s$	65.5	-7.75	3.02
$2^3A''$	6.10	0.78 $n'\sigma^*$ + 0.10 $\sigma''n''\sigma^{*2}$ + 0.05 $n's$	67.3	5.89	0.79 $n'\sigma^*$ + 0.05 $\sigma''n''\sigma^{*2}$	66.0	-7.76	5.76
$3^3A''$	6.37	0.44 $n''p_{xy}$ + 0.45 $n''p'_{xy}$	104.8	6.99	0.42 $n''p_{xy}$ + 0.40 $n''p'_{xy}$	103.0	-6.94	7.11
$4^3A''$	7.19	0.46 $n''p_{xy}$ + 0.44 $n''p'_{xy}$	132.7	7.75	0.61 $n''n_{Br}\sigma^{*2}$ + 0.07 $n''\sigma''\sigma s$ + 0.07 $n'\sigma''\sigma^{*2}$ + 0.07 $n''p'_{xy}$ + 0.06 $n''p_{xy}$	76.7	-7.00	7.73
$5^3A''$	7.51	0.83 $n''s$ + 0.05 $n''\sigma^*$	125.6	7.88	0.37 $n''p_{xy}$ + 0.37 $n''p'_{xy}$ + 0.09 $n''\sigma''\sigma^{*2}$	124.0	-7.20	7.94
$6^3A''$	7.88	0.62 $n''n_{Br}\sigma^{*2}$ + 0.14 $n'n_{Br}\sigma^{*2}$ + 0.13 $n''n_{Br}\sigma^*s$	72.6	8.07	0.78 $n''s$	129.7	-7.36	8.11
$7^3A''$	8.07	0.93 $n_{Br}p_z$	132.4	8.85	0.88 $n_{Br}p_z$	132.0	-6.78	9.01

S3. SPIN-ORBIT COUPLING

Table S4. Vertical excitation energies (eV) and oscillator strengths for pure spin states and for spin-orbit coupled states.

Without spin-orbit			With spin-orbit			
State	E_v	*f*	Sym	State	E_v^{SOC}	*f*
1^1A'	0.00	--	A'	$^1S_0$	0.00	--
			A"	$^3T_{-1}$	2.97	0.0000
1^3A"	3.11	--	A'	$^3T_0$	2.98	0.0000
			A'	$^3T_1$	2.98	0.0000
1^1A"	3.71	0.0000	A"	$^1S_0$	3.73	0.0000
			A"	$^3T_{-1}$	4.11	0.0000
1^3A'	4.11	--	A'	$^3T_0$	4.11	0.0000
			A"	$^3T_1$	4.12	0.0000
2^1A'	4.77	0.0012	A'	$^1S_0$	4.93	0.0005
			A"	$^3T_{-1}$	5.74	0.0000
2^3A"	5.89	--	A'	$^3T_0$	5.75	0.0000
			A'	$^3T_1$	5.75	0.0000
2^1A"	6.25	0.0012	A"	$^1S_0$	6.23	0.0009
			A"	$^3T_{-1}$	6.79	0.0000
2^3A'	6.35	--	A'	$^3T_0$	6.79	0.0000
			A"	$^3T_1$	6.79	0.0000
			A'	$^3T_{-1}$	6.95	0.0000
3^3A"	6.99	--	A"	$^3T_0$	6.95	0.0000
			A'	$^3T_1$	6.95	0.0004
3^1A"	7.04	0.0439	A"	$^1S_0$	7.05	0.0432
3^1A'	7.40	0.0003	A'	$^1S_0$	7.44	0.0001
			A'	$^3T_{-1}$	7.73	0.0000
4^3A"	7.75	--	A"	$^3T_0$	7.73	0.0000
			A'	$^3T_1$	7.81	0.0000
			A"	$^3T_{-1}$	7.85	0.0000
3^3A'	7.85	--	A'	$^3T_0$	7.85	0.0000
			A"	$^3T_1$	7.85	0.0000
4^1A'	7.88	0.0301	A'	$^1S_0$	7.94	0.0075
			A'	$^3T_{-1}$	7.96	0.0000
4^3A'	7.91	--	A"	$^3T_0$	7.96	0.0001
			A"	$^3T_1$	7.97	0.0000
4^1A"	7.81	0.0000	A"	$^1S_0$	8.01	0.0000
			A'	$^3T_{-1}$	8.04	0.0110
5^3A"	7.88	--	A'	$^3T_0$	8.07	0.0000
			A"	$^3T_1$	8.07	0.0000

5^1A'	7.95	0.0435	A'	$^1S_0$	8.11	0.0433
5^1A"	7.90	0.0004	A"	$^1S_0$	8.13	0.0032
			A'	$^3T_{-1}$	8.64	0.0000
5^3A'	8.69	--	A"	$^3T_0$	8.65	0.0000
			A"	$^3T_1$	8.65	0.0000
			A"	$^3T_{-1}$	8.98	0.0000
6^3A"	8.07	--	A'	$^3T_0$	8.98	0.0000
			A'	$^3T_1$	8.98	0.0002
6^1A"	8.82	0.0052	A"	$^1S_0$	9.00	0.0014
			A'	$^3T_{-1}$	9.19	0.0000
6^3A'	8.70	--	A"	$^3T_0$	9.19	0.0000
			A"	$^3T_1$	9.19	0.0002
6^1A'	8.14	0.0636	A'	$^1S_0$	9.25	0.0100
			A'	$^3T_{-1}$	9.51	0.0001
7^3A"	8.85	--	A"	$^3T_0$	9.51	0.0000
			A'	$^3T_1$	9.51	0.0003
7^1A"	9.55	0.0113	A"	$^1S_0$	9.60	0.0178
7^1A'	8.77	0.0007	A'	$^1S_0$	10.35	0.1020
			A'	$^3T_{-1}$	10.36	0.0000
7^3A'	9.02	--	A"	$^3T_0$	10.36	0.0000
			A"	$^3T_1$	10.36	0.0000

S4. TDA-DFT

Table S5. TDA-CAM-B3LYP and TDA-ωB97XD results for vertical excitation energies (E_v in eV) and configuration weights of the ground and excited singlet electronic states compared to the corresponding full TD-DFT results.

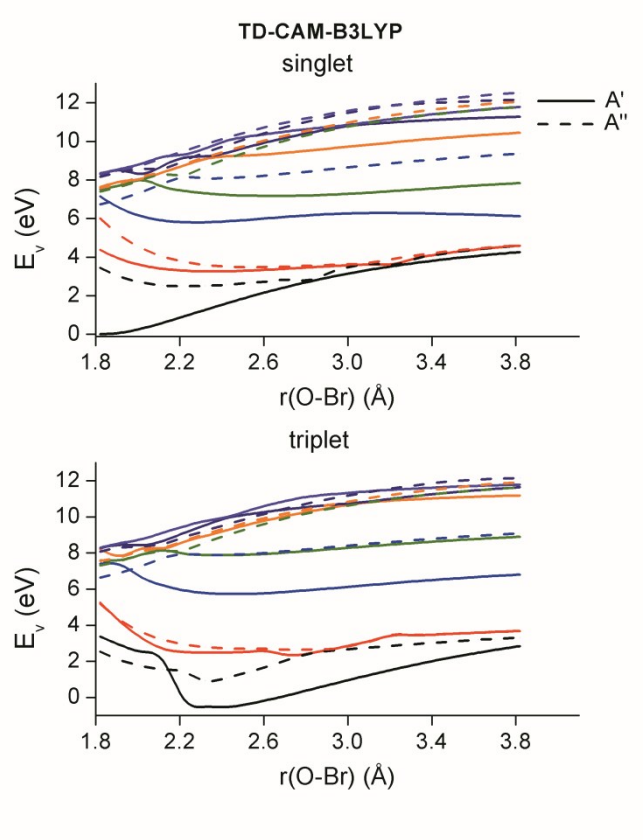
State	TD-CAM-B3LYP			TD-ωB97XD			TDA-CAM-B3LYP			TDA-ωB97XD		
	E_v	weights	*f*	E_v	weights	*f*	E_v	weights	*f*	E_v	weights	*f*
$1^1A'$	0.00	gs	--	0.00	gs	--	0.00	gs	--	0.00	gs	--
$2^1A'$	4.37	0.98 nσ*	0.0010	4.43	0.98 nσ*	0.0009	4.47	0.97 nσ*	0.0013	4.52	0.97 nσ*	0.0012
$3^1A'$	7.14	0.92 σσ*	0.1297	7.19	0.92 σσ*	0.1321	7.26	0.82 σσ*	0.1471	7.32	0.81 σσ*	0.1474
$4^1A'$	7.524	ns + np	0.0550	7.60	ns + np	0.0486	7.53	ns + np	0.0583	7.61	ns + np	0.0542
$5^1A'$	7.64	ns + np	0.0111	7.62	ns + np	0.0195	7.65	ns + np	0.0122	7.64	ns + np	0.0164
$6^1A'$	8.30	ns + np	0.0040	8.37	ns + np	0.0211	8.31	ns + np	0.0070	8.37	ns + np	0.0288
$7^1A'$	8.34	ns + np	0.0380	8.38	ns + np	0.0190	8.35	ns + np	0.0377	8.39	ns + np	0.0122
$1^1A''$	3.45	0.98 nσ*	0.0000	3.49	0.98 nσ*	0.0000	3.53	0.97 nσ*	0.0001	3.57	0.97 nσ*	0.0001
$2^1A''$	6.01	0.96 nσ*	0.0003	6.03	0.95 nσ*	0.0003	6.05	0.95 nσ*	0.0005	6.08	0.95 nσ*	0.0005
$3^1A''$	6.74	ns + np	0.0563	6.83	ns + np	0.0591	6.74	ns + np	0.0603	6.84	ns + np	0.0613
$4^1A''$	7.40	ns + np	0.0005	7.51	ns + np	0.0000	7.40	ns + np	0.0006	7.51	ns + np	0.0000
$5^1A''$	7.58	ns + np	0.0093	7.59	ns + np	0.0065	7.58	ns + np	0.0100	7.59	ns + np	0.0068
$6^1A''$	8.17	ns + np	0.0000	8.20	ns + np	0.0007	8.17	ns + np	0.0000	8.21	ns + np	0.0008
$7^1A''$	8.30	ns + np	0.0091	8.32	ns + np	0.0091	8.30	ns + np	0.0095	8.33	ns + np	0.0092

Table S6. TDA-CAM-B3LYP and TDA-ωB97XD results for vertical excitation energies (E_v in eV) and configuration weights of excited triplet electronic states.

State	TD-CAM-B3LYP		TD-ωB97XD		TDA-CAM-B3LYP		TDA- ωB97XD	
	E_v	weights	E_v	weights	E_v	weights	E_v	weights
1^3A'	3.38	0.96 nσ*	3.45	0.96 nσ*	3.47	0.96 nσ*	3.55	0.96 nσ*
2^3A'	5.26	0.96 σσ*	5.37	0.94 σσ*	5.50	0.88 σσ*	5.60	0.88 σσ*
3^3A'	7.40	ns + np	7.48	ns + np	7.41	ns + np	7.48	ns + np
4^3A'	7.57	ns + np	7.52	ns + np	7.57	ns + np	7.53	ns + np
5^3A'	8.21	ns + np	8.23	ns + np	8.22	ns + np	8.23	ns + np
6^3A'	8.28	ns + np	8.26	ns + np	8.29	ns + np	8.26	ns + np
7^3A'	8.29	ns + np	8.38	ns + np	8.38	ns + np	8.44	ns + np
1^3A"	2.54	0.97 nσ*	2.62	0.96 nσ*	2.64	0.96 nσ*	2.71	0.96 nσ*
2^3A"	5.18	0.92 nσ*	5.23	0.92 nσ*	5.24	0.92 nσ*	5.29	0.92 nσ*
3^3A"	6.64	ns + np	6.76	ns + np	6.65	ns + np	6.76	ns + np
4^3A"	7.33	ns + np	7.42	ns + np	7.33	ns + np	7.43	ns + np
5^3A"	7.55	ns + np	7.54	ns + np	7.56	ns + np	7.54	ns + np
6^3A"	8.08	ns + np	8.10	ns + np	8.09	ns + np	8.11	ns + np
7^3A"	8.26	ns + np	8.26	ns + np	8.27	ns + np	8.26	ns + np

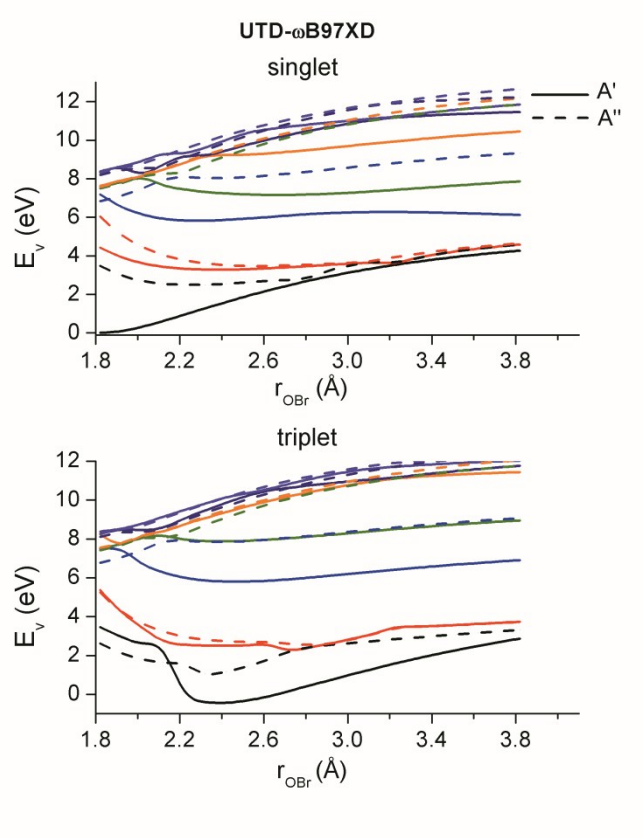
S5. TD-CAM-B3LYP

Figure S2. Potential energy curves for the excited singlet (top) and triplet (bottom) states along O-Br coordinate computed with TD-CAM-B3LYP method.



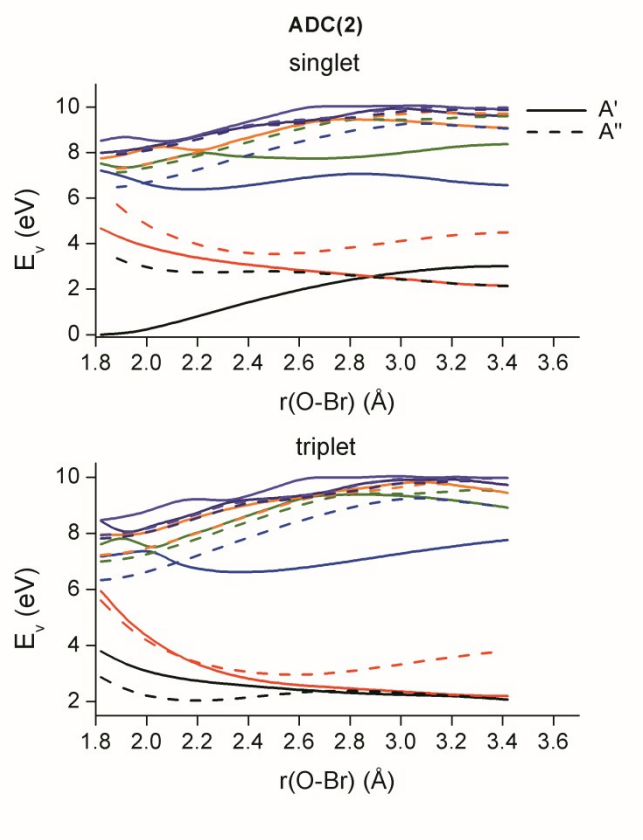
S6. Unrestricted DFT

Figure S3. Potential energy curves for the excited singlet (top) and triplet (bottom) states along O-Br coordinate computed with spin-unrestricted TD-ωB97XD method.



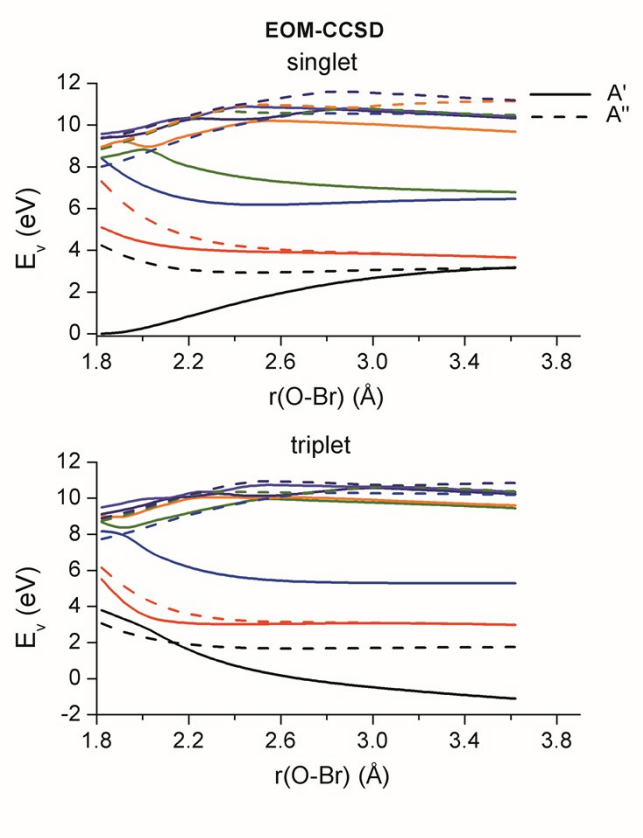
S7. ADC(2)

Figure S4. Potential energy curves for the excited singlet (top) and triplet (bottom) states along O-Br coordinate computed with ADC(2) method.



S8. EOM-CCSD

Figure S5. Potential energy curves for the excited singlet (top) and triplet (bottom) states along O-Br coordinate computed with EOM-CCSD method.



S9. D_1 diagnostics

Figure S6. The computed D_1 values for the MP2 and CC2 ground states. The recommended limits for D1 values are represented by the black dashed line for MP2, and by the red dashed line for CC2 method.