

Supporting information

Photochemistry of methyl hypobromite (CH₃OBr): excited states and photoabsorption spectrum

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S1. Cartesian Coordinates

The geometry of the ground state of CH₃OBr 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

S2. CASSCF and MRCI Details

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

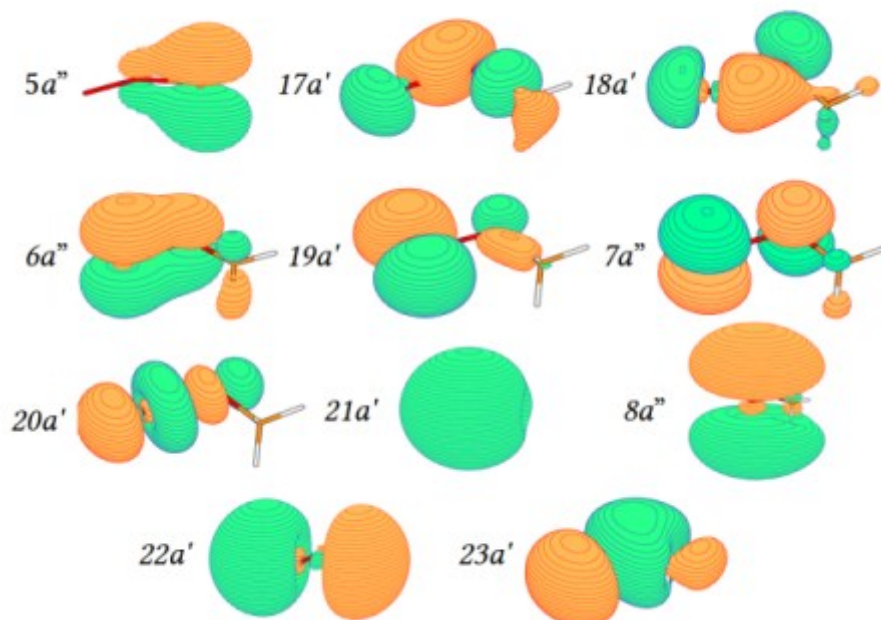


Table S1. The composition of SA-MCSCF(12,11) natural orbitals.

Orbital	Composition	occupancy
5a''	$\sigma(\text{C-H})$	2
17a'	$\sigma(\text{O-Br}) + \sigma(\text{C-O}) (\sigma')$	2
18a'	$\sigma(\text{O-Br}) - \sigma(\text{C-O}) (\sigma'')$	2
6a''	$4p_z(\text{Br}) + 2p_z(\text{O}) (n')$	2
19a'	$4p_e(\text{Br}) (n_{\text{Br}})$	2
7a''	$4p_z(\text{Br}) - 2p_z(\text{O}) (n'')$	2
20a'	$\sigma^*(\text{O-Br})$	0
21a'	$5s(\text{Br})$	0
8a''	$5p_z(\text{Br})$	0
22a'	$5p_{xy}(\text{Br})$	0
23a'	$5p'_{xy}(\text{Br})$	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 ¹ A'	0.00	0.95 gs	62.3	--	0.00	0.89 gs	64.1	--	-7.56	0.00
2 ¹ A'	4.91	0.76 $n_{\text{Br}}\sigma^* + 0.14 n_{\text{Br}}p'_{xy} + 0.03 n_{\text{Br}}\sigma''\sigma^{*2}$	66.2	0.0055	4.77	0.74 $n_{\text{Br}}\sigma^* + 0.11 n_{\text{Br}}p'_{xy}$	67.4	0.0012	-7.70	4.70
3 ¹ A'	7.10	0.78 $n''p_z + 0.09 n_{\text{Br}}s + 0.03 n'\sigma''\sigma^*p_z$	131.6	0.0114	7.40	0.58 $n''\sigma^{*2} + 0.14 n''\sigma^*p'_{xy} + 0.10 n''\sigma^{*2} + 0.03 n'n''\sigma^{*2}$	68.3	0.0003	-7.26	7.39
4 ¹ A'	7.20	0.80 $n_{\text{Br}}s + 0.08 + n''p_z + 0.06 n_{\text{Br}}p_{xy}$	112.4	0.0840	7.88	0.46 $n''p_z + 0.27 n_{\text{Br}}s + 0.08 \sigma''\sigma^*$	116.9	0.0301	-6.88	8.01
5 ¹ A'	7.31	0.58 $n''\sigma^{*2} + 0.15 n''\sigma^*p'_{xy} + 0.13 n''\sigma^{*2} + 0.05 n''p_z$	70.4	0.0000	7.95	0.52 $n_{\text{Br}}s + 0.32 n''p_z + 0.03 n_{\text{Br}}p_{xy}$	118.6	0.0435	-6.92	8.08
6 ¹ A'	7.93	0.54 $n_{\text{Br}}p_{xy} + 0.18 \sigma''\sigma^* + 0.08 \sigma'\sigma^* + 0.05 n_{\text{Br}}s$	113.1	0.0566	8.14	0.42 $\sigma''\sigma^* + 0.15 \sigma'\sigma^* + 0.07 n''p_z + 0.07 n_{\text{Br}}s$	75.3	0.0636	-7.35	8.12
7 ¹ A'	8.05	0.34 $n_{\text{Br}}p_{xy} + 0.28 \sigma''\sigma^* + 0.14 \sigma'\sigma^* + 0.07 \sigma'p_{xy}'$	93.2	0.0563	8.77	0.81 $n_{\text{Br}}p_{xy} + 0.03 n_{\text{Br}}s$	137.5	0.0007	-6.83	8.92
1 ¹ A''	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 ¹ A''	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 ¹ A''	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 ¹ A''	7.05	0.89 $n''p_{xy} + 0.03 n''s$	139.3	0.0000	7.81	0.72 $n''p_{xy} + 0.09 n''n_{\text{Br}}\sigma^{*2}$	126.5	0.0000	-6.80	7.93
5 ¹ A''	7.77	0.59 $n_{\text{Br}}n''\sigma^{*2} + 0.13 n_{\text{Br}}n'\sigma^{*2} + 0.12 n_{\text{Br}}n''\sigma^*p_{xy}'$	67.5	0.0000	7.90	0.50 $n_{\text{Br}}n''\sigma^{*2} + 0.12 n''p'_{xy} + 0.10 n_{\text{Br}}n''\sigma^*p_{xy}' + 0.08 n_{\text{Br}}n''\sigma^{*2}$	77.9	0.0004	-7.43	7.89
6 ¹ A''	7.97	0.93 $n_{\text{Br}}p_z$	138.8	0.0066	8.82	0.88 $n_{\text{Br}}p_z$	137.2	0.0052	-6.70	9.00
7 ¹ A''	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 ³ A'	4.46	0.85 $n_{\text{Br}}\sigma^* + 0.06 n_{\text{Br}}s$	65.8	4.11	0.85 $n_{\text{Br}}\sigma^* + 0.03 n_{\text{Br}}s$	66.2	-7.90	3.97
2 ³ A'	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 ³ A'	7.15	0.34 $n_{\text{Br}}p_{xy} + 0.34 n_{\text{Br}}p'_{xy} + 0.25 n''p_z$	113.6	7.85	0.40 $n_{\text{Br}}p_{xy} + 0.46 n_{\text{Br}}p'_{xy}$	104.2	-6.87	7.98
4 ³ A'	7.17	0.64 $n''p_z + 0.16 n_{\text{Br}}p'_{xy} + 0.10 n_{\text{Br}}p_{xy}$	124.7	7.91	0.84 $n''p_z$	130.3	-6.82	8.05
5 ³ A'	7.94	0.50 $n_{\text{Br}}p_{xy} + 0.43 n_{\text{Br}}p'_{xy}$	133.1	8.69	0.79 $n''\sigma^{*2} + 0.09 n''\sigma^*s$	69.2	-6.81	8.72
6 ³ A'	8.43	0.85 $n_{\text{Br}}s + 0.06 n_{\text{Br}}\sigma^*$	125.8	8.70	0.47 $n_{\text{Br}}p_{xy} + 0.40 n_{\text{Br}}p'_{xy}$	130.5	-7.29	8.81
7 ³ A'	8.57	0.83 $n''\sigma^{*2} + 0.13 n''\sigma^*s$	70.3	9.02	0.83 $n_{\text{Br}}s + 0.03 n_{\text{Br}}\sigma^*$	131.2	-7.11	9.09
1 ³ A''	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 ³ A''	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 ³ A''	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 ³ A''	7.19	0.46 $n''p_{xy} + 0.44 n''p'_{xy}$	132.7	7.75	0.61 $n''n_{\text{Br}}\sigma^{*2} + 0.07 n''\sigma''\sigma s + 0.07 n'\sigma''\sigma^{*2} + 0.07 n''p'_{xy} + 0.06 n''p_{xy}$	76.7	-7.00	7.73
5 ³ A''	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 ³ A''	7.88	0.62 $n''n_{\text{Br}}\sigma^{*2} + 0.14 n''n_{\text{Br}}\sigma^{*2} + 0.13 n''n_{\text{Br}}\sigma^*s$	72.6	8.07	0.78 $n''s$	129.7	-7.36	8.11
7 ³ A''	8.07	0.93 $n_{\text{Br}}p_z$	132.4	8.85	0.88 $n_{\text{Br}}p_z$	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
$1^1\text{A}'$	0.00	--	A'	$^1\text{S}_0$	0.00	--
			A''	$^3\text{T}_{-1}$	2.97	0.0000
$1^3\text{A}''$	3.11	--	A'	$^3\text{T}_0$	2.98	0.0000
			A'	$^3\text{T}_1$	2.98	0.0000
$1^1\text{A}''$	3.71	0.0000	A''	$^1\text{S}_0$	3.73	0.0000
			A''	$^3\text{T}_{-1}$	4.11	0.0000
$1^3\text{A}'$	4.11	--	A'	$^3\text{T}_0$	4.11	0.0000
			A''	$^3\text{T}_1$	4.12	0.0000
$2^1\text{A}'$	4.77	0.0012	A'	$^1\text{S}_0$	4.93	0.0005
			A''	$^3\text{T}_{-1}$	5.74	0.0000
$2^3\text{A}''$	5.89	--	A'	$^3\text{T}_0$	5.75	0.0000
			A'	$^3\text{T}_1$	5.75	0.0000
$2^1\text{A}''$	6.25	0.0012	A''	$^1\text{S}_0$	6.23	0.0009
			A''	$^3\text{T}_{-1}$	6.79	0.0000
$2^3\text{A}'$	6.35	--	A'	$^3\text{T}_0$	6.79	0.0000
			A''	$^3\text{T}_1$	6.79	0.0000
			A'	$^3\text{T}_{-1}$	6.95	0.0000
$3^3\text{A}''$	6.99	--	A''	$^3\text{T}_0$	6.95	0.0000
			A'	$^3\text{T}_1$	6.95	0.0004
$3^1\text{A}''$	7.04	0.0439	A''	$^1\text{S}_0$	7.05	0.0432
$3^1\text{A}'$	7.40	0.0003	A'	$^1\text{S}_0$	7.44	0.0001
			A'	$^3\text{T}_{-1}$	7.73	0.0000
$4^3\text{A}''$	7.75	--	A''	$^3\text{T}_0$	7.73	0.0000
			A'	$^3\text{T}_1$	7.81	0.0000
			A''	$^3\text{T}_{-1}$	7.85	0.0000
$3^3\text{A}'$	7.85	--	A'	$^3\text{T}_0$	7.85	0.0000
			A''	$^3\text{T}_1$	7.85	0.0000
$4^1\text{A}'$	7.88	0.0301	A'	$^1\text{S}_0$	7.94	0.0075
			A'	$^3\text{T}_{-1}$	7.96	0.0000
$4^3\text{A}'$	7.91	--	A''	$^3\text{T}_0$	7.96	0.0001
			A''	$^3\text{T}_1$	7.97	0.0000
$4^1\text{A}''$	7.81	0.0000	A''	$^1\text{S}_0$	8.01	0.0000
			A'	$^3\text{T}_{-1}$	8.04	0.0110
$5^3\text{A}''$	7.88	--	A'	$^3\text{T}_0$	8.07	0.0000
			A''	$^3\text{T}_1$	8.07	0.0000

5 ¹ A'	7.95	0.0435	A'	¹ S ₀	8.11	0.0433
5 ¹ A"	7.90	0.0004	A"	¹ S ₀	8.13	0.0032
			A'	³ T ₋₁	8.64	0.0000
5 ³ A'	8.69	--	A"	³ T ₀	8.65	0.0000
			A"	³ T ₁	8.65	0.0000
			A"	³ T ₋₁	8.98	0.0000
6 ³ A"	8.07	--	A'	³ T ₀	8.98	0.0000
			A'	³ T ₁	8.98	0.0002
6 ¹ A"	8.82	0.0052	A"	¹ S ₀	9.00	0.0014
			A'	³ T ₋₁	9.19	0.0000
6 ³ A'	8.70	--	A"	³ T ₀	9.19	0.0000
			A"	³ T ₁	9.19	0.0002
6 ¹ A'	8.14	0.0636	A'	¹ S ₀	9.25	0.0100
			A'	³ T ₋₁	9.51	0.0001
7 ³ A"	8.85	--	A"	³ T ₀	9.51	0.0000
			A'	³ T ₁	9.51	0.0003
7 ¹ A"	9.55	0.0113	A"	¹ S ₀	9.60	0.0178
7 ¹ A'	8.77	0.0007	A'	¹ S ₀	10.35	0.1020
			A'	³ T ₋₁	10.36	0.0000
7 ³ A'	9.02	--	A"	³ T ₀	10.36	0.0000
			A"	³ T ₁	10.36	0.0000

S4. TDA-DFT

Table S5. TDA-CAM-B3LYP and TDA- ω B97XD 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.

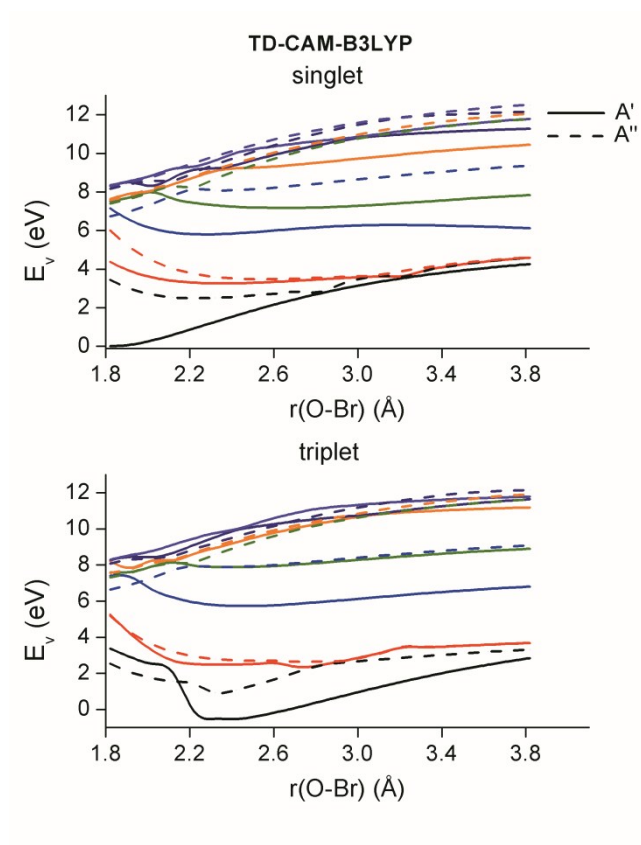
State	TD-CAM-B3LYP			TD- ω B97XD			TDA-CAM-B3LYP			TDA- ω B97XD		
	E_v	weights	f	E_v	weights	f	E_v	weights	f	E_v	weights	f
1 ¹ A'	0.00	gs	--	0.00	gs	--	0.00	gs	--	0.00	gs	--
2 ¹ A'	4.37	0.98 n σ^*	0.0010	4.43	0.98 n σ^*	0.0009	4.47	0.97 n σ^*	0.0013	4.52	0.97 n σ^*	0.0012
3 ¹ A'	7.14	0.92 $\sigma\sigma^*$	0.1297	7.19	0.92 $\sigma\sigma^*$	0.1321	7.26	0.82 $\sigma\sigma^*$	0.1471	7.32	0.81 $\sigma\sigma^*$	0.1474
4 ¹ A'	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 ¹ A'	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 ¹ A'	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 ¹ A'	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 ¹ A''	3.45	0.98 n σ^*	0.0000	3.49	0.98 n σ^*	0.0000	3.53	0.97 n σ^*	0.0001	3.57	0.97 n σ^*	0.0001
2 ¹ A''	6.01	0.96 n σ^*	0.0003	6.03	0.95 n σ^*	0.0003	6.05	0.95 n σ^*	0.0005	6.08	0.95 n σ^*	0.0005
3 ¹ A''	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 ¹ A''	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 ¹ A''	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 ¹ A''	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 ¹ A''	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- ω B97XD results for vertical excitation energies (E_v in eV) and configuration weights of excited triplet electronic states.

State	TD-CAM-B3LYP		TD- ω B97XD		TDA-CAM-B3LYP		TDA- ω B97XD	
	E_v	weights	E_v	weights	E_v	weights	E_v	weights
1 ³ A'	3.38	0.96 n σ^*	3.45	0.96 n σ^*	3.47	0.96 n σ^*	3.55	0.96 n σ^*
2 ³ A'	5.26	0.96 $\sigma\sigma^*$	5.37	0.94 $\sigma\sigma^*$	5.50	0.88 $\sigma\sigma^*$	5.60	0.88 $\sigma\sigma^*$
3 ³ A'	7.40	ns + np	7.48	ns + np	7.41	ns + np	7.48	ns + np
4 ³ A'	7.57	ns + np	7.52	ns + np	7.57	ns + np	7.53	ns + np
5 ³ A'	8.21	ns + np	8.23	ns + np	8.22	ns + np	8.23	ns + np
6 ³ A'	8.28	ns + np	8.26	ns + np	8.29	ns + np	8.26	ns + np
7 ³ A'	8.29	ns + np	8.38	ns + np	8.38	ns + np	8.44	ns + np
1 ³ A''	2.54	0.97 n σ^*	2.62	0.96 n σ^*	2.64	0.96 n σ^*	2.71	0.96 n σ^*
2 ³ A''	5.18	0.92 n σ^*	5.23	0.92 n σ^*	5.24	0.92 n σ^*	5.29	0.92 n σ^*
3 ³ A''	6.64	ns + np	6.76	ns + np	6.65	ns + np	6.76	ns + np
4 ³ A''	7.33	ns + np	7.42	ns + np	7.33	ns + np	7.43	ns + np
5 ³ A''	7.55	ns + np	7.54	ns + np	7.56	ns + np	7.54	ns + np
6 ³ A''	8.08	ns + np	8.10	ns + np	8.09	ns + np	8.11	ns + np
7 ³ A''	8.26	ns + np	8.26	ns + np	8.27	ns + np	8.26	ns + np

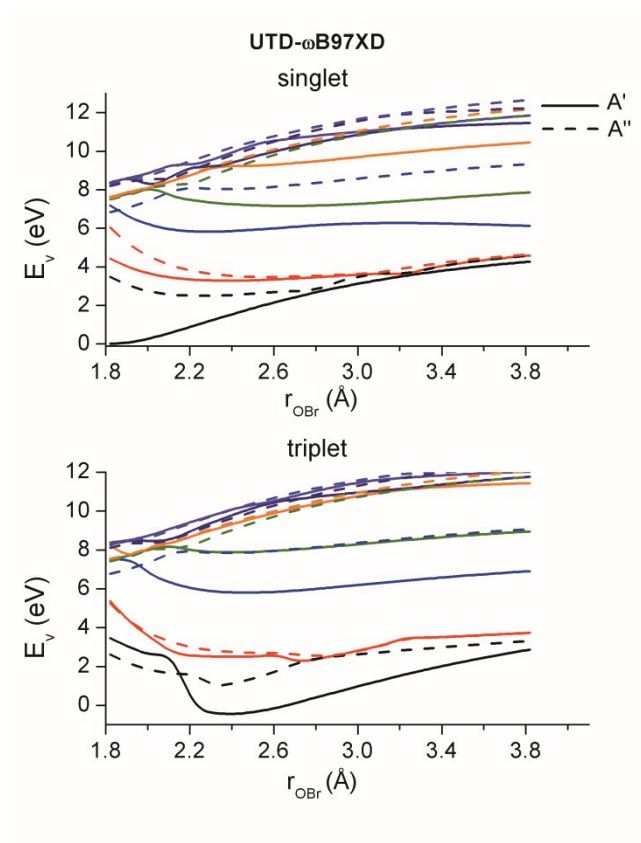
S5. TD-CAM-B3LYP

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



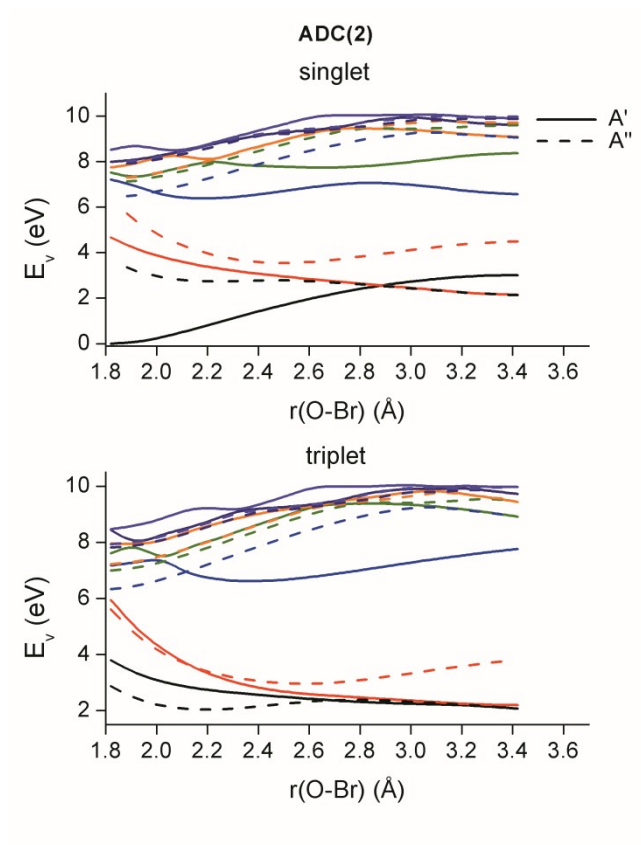
S6. Unrestricted DFT

Figure S3. Potential energy curves for the excited singlet (top) and triplet (bottom) states along O-Br coordinate computed with spin-unrestricted TD- ω B97XD method.



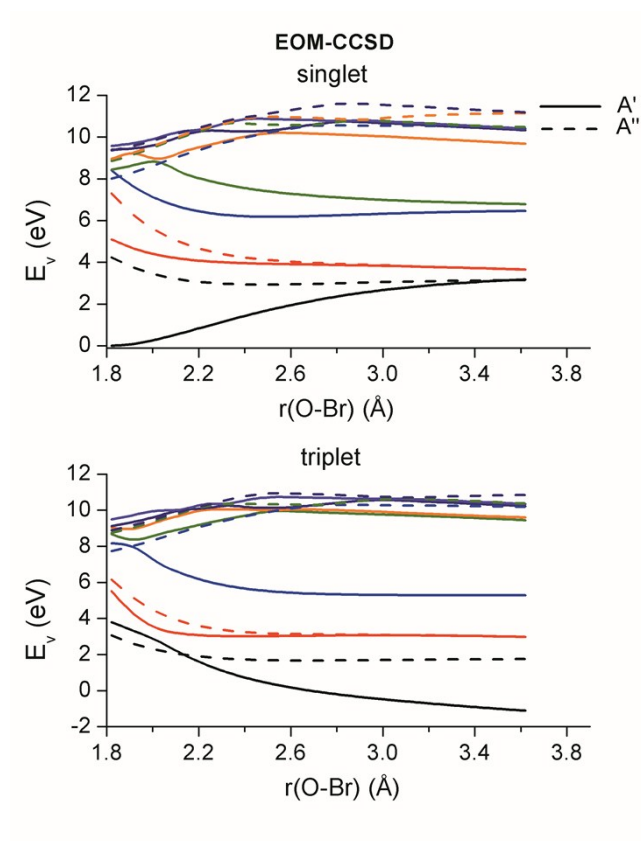
S7. ADC(2)

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. D₁ diagnostics

Figure S6. The computed D₁ 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.

