Supporting Information

Photoinduced Dissociation of Halobenzenes: Nonadiabatic Molecular Dynamics Simulations Reveal Key Pathways

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Normal mode analysis (NMA)

From the trajectories obtained through surface hopping simulations of PhBr, the normal mode activities were analyzed as follows. For each trajectory, the deviation $\Delta R_i(t)$ from the minimum geometry in the S_1 state of PhBr was calculated at every time step t in the ith trajectory, based on the following equation.

$$\Delta R_i(t) = \boldsymbol{Q}^{-1}\left(R_i(t) - R_{S_1 min}\right) \tag{S1}$$

Here, $\boldsymbol{Q}$ indicates the normal mode vector, R_i(t) indicates the geometries in the time step of t in ith trajectory and $R_{S_1 min}$ indicates the minimum geometry in the S_1 state of PhBr. The normal mode vector $\boldsymbol{Q}$ was determined using the harmonic frequencies calculated in the S_1 state of PhBr. After computing $\Delta R_i(t)$ for all trajectories based on Eq. S1, the average values $R_{avg}(t)$ were obtained by dividing the summation of $\Delta R_i(t)$ by N_{traj}, the total number of trajectories, as follows.

$$R_{avg}(t) = \frac{1}{N_{traj}} \sum_{i=1}^{N_{traj}} \Delta R_i(t) \tag{S2}$$

Notably, the averaging process cancels out random vibrational motions, leaving only the coherent modes along the trajectories. The standard deviation of $R_{avg}(t)$ for the time interval from k_i to k_f, representing the first and last steps of the selected time window was calculated using the following equation.

$$R_{\text{act}}^2 = \frac{1}{k_f - k_i} \sum_{K=k_i}^{k_f} \left(\Delta R_{\text{avg}}(K \cdot \Delta t)\right)^2 - \left(\frac{1}{k_f - k_i} \sum_{K=k_i}^{k_f} \Delta R_{\text{avg}}(K \cdot \Delta t)\right)^2 \tag{S3}$$

Here, K is the time step between k_i and k_f, and R_{act} is the coherent activity of normal mode. In this study, considering the time steps used in the surface hopping simulations, calculations were performed with a time step Δt of 0.5 fs.

Table S1. Characteristics of the excited states of PhI. The contributions of SF states to the composition of SO states are presented, along with their vertical excitation energies and oscillator strengths.

	State character	Energy (eV)	Oscillator strength (f)
State 1	S_0 99.4 %	0.00	-
State 2	T_1 97.2 %	3.98	-
State 3	T_1 99.1 %	3.98	0.00001
State 4	T_1 98.8 %	3.98	-
State 5	T_2 77.9 %, T_5 18.6 %	4.10	-
State 6	T_2 77.4 %, T_5 21.7 %	4.10	0.00004
State 7	T_2 93.1 %	4.15	0.00040
State 8	S_1 49.8 %, T_5 46.4 %	4.32	0.00227
State 9	T_3 96.0 %	4.48	0.00003
State 10	T_3 98.8 %	4.48	-
State 11	T_3 98.5 %	4.49	-
State 12	T_4 98.6 %	4.54	-
State 13	T_4 99.8 %	4.54	-
State 14	T_4 99.7 %	4.54	-
State 15	T_5 77.8 %, T_2 18.8 %	4.65	-
State 16	T_5 76.0 %, T_2 22.1 %	4.72	-
State 17	T_5 47.4 %, S_1 47.3 %	4.75	0.00204
State 18	S_2 99.5 %	4.76	0.00050

Table S2. Characteristics of the excited states of PhBr. The contributions of SF states to the composition of SO states are presented, along with their vertical excitation energies and oscillator strengths.

	State character	Energy (eV)	Oscillator strength (f)
State 1	S_0 100 %	0.00	-
State 2	T_1 100 %	3.95	-
State 3	T_1 100 %	3.95	-
State 4	T_1 100 %	3.95	-
State 5	T_2 100 %	4.43	-
State 6	T_2 100 %	4.43	-
State 7	T_2 100 %	4.43	-
State 8	T_3 100 %	4.51	-
State 9	T_3 100 %	4.51	-
State 10	T_3 100 %	4.51	-
State 11	S_1 100 %	4.60	0.01466
State 12	T_4 100 %	5.11	-
State 13	T_4 100 %	5.11	-
State 14	T_4 100 %	5.11	-
State 15	T_5 96.6 %	5.14	-
State 16	T_5 96.3 %	5.14	0.00004
State 17	T_5 99.1 %	5.15	0.00005
State 18	S_2 82.7 %, T_6 17.2 %	5.49	0.00250

Table S3. Structural parameters of PhI at the ground-state minimum. Key structural parameters are compared across various theoretical methods and the gas-phase diffraction experiment. We employed the ANO-RCC-VDZP basis set for all theoretical methods. Experimental values were obtained from Ref. S1.

	MP2	CASSCF	XMS-CASPT2	Exp.
r (C–I)	2.100	2.145	2.106	2.095
r (C1–C2)	1.399	1.395	1.394	1.394
r (C2–C3)	1.399	1.393	1.399	1.391
r (C3–C4)	1.399	1.397	1.397	1.393
∠(C2C1C6)	121.2	120.9	121.5	121.2

Table S4. Structural parameters of PhI at the ground-state minimum obtained with various theoretical methods and the gas-phase diffraction experiment. We employed the ANO-RCC-VDZP basis set for all theoretical methods. Experimental values were obtained from Ref. S2.

	MP2	CASSCF	XMS-CASPT2	Exp.
r (C–Br)	1.914	1.928	1.903	1.898
r (C1–C2)	1.397	1.397	1.397	1.394
r (C2–C3)	1.399	1.396	1.400	1.396
r (C3–C4)	1.399	1.403	1.401	1.394
∠(C2C1C6)	121.7	121.6	121.3	121.5

Table S5. Harmonic frequencies of PhBr in the S_1 state.

	Frequency (cm^{-1})
ν1	95.5
ν2	237.2
ν3	253.3
ν4	291.1
ν5	296.2
ν6	479.8
ν7	556.1
ν8	564.7
ν9	584.8
ν10	645.1
ν11	649.2
ν12	659.4
ν13	727.6
ν14	961.0
ν15	1001.2

	Frequency (cm^{-1})
ν16	1004.9
ν17	1072.7
ν18	1037.9
ν19	1248.1
ν20	1386.0
ν21	1495.2
ν22	1529.0
ν23	1640.8
ν24	1647.0
ν25	1873.9
ν26	3355.4
ν27	3366.9
ν28	3379.8
ν29	3399.4
ν30	3402.7

Table S6. The norm of spin-orbit coupling matrix element (|SOCME|) value between $^1(\pi,\pi^*)$ and $^3(n,\sigma^*)$ state of PhBr in certain C–Br distance of $\boldsymbol{Q} = 0$ and $\boldsymbol{Q} = 1$ geometries with respect to the *v*4 mode.

	C–Br distance (Å)	|SOCME| (cm^{-1})
$\boldsymbol{Q} = 0$	1.94	0.71
	1.96	0.93
	1.98	1.15
	2.00	1.43
$\boldsymbol{Q} = 1$	2.04	24.0
	2.06	166.1
	2.08	24.8
	2.10	18.7

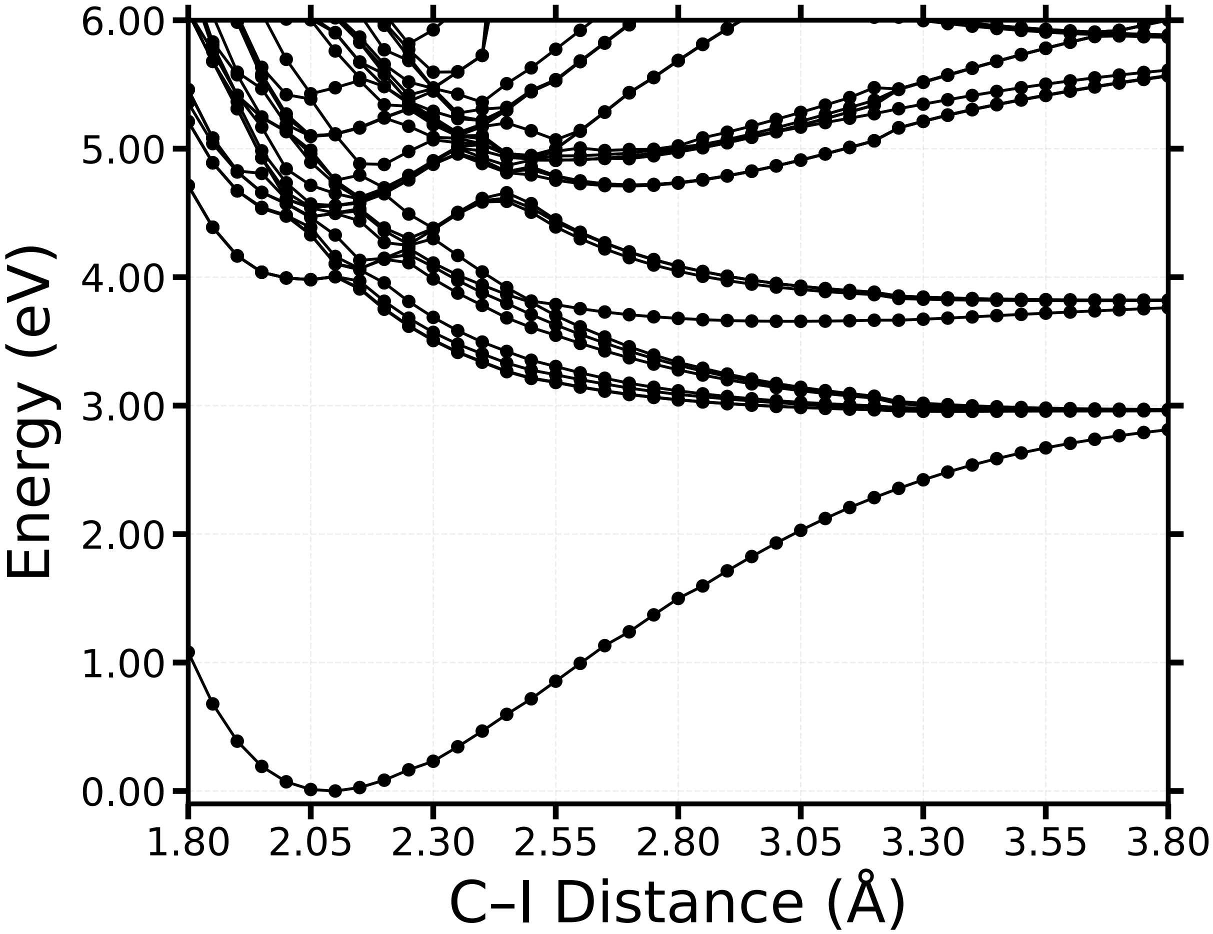


Figure S1. Adiabatic PECs for SO states of PhI with respect to the C–I distance.

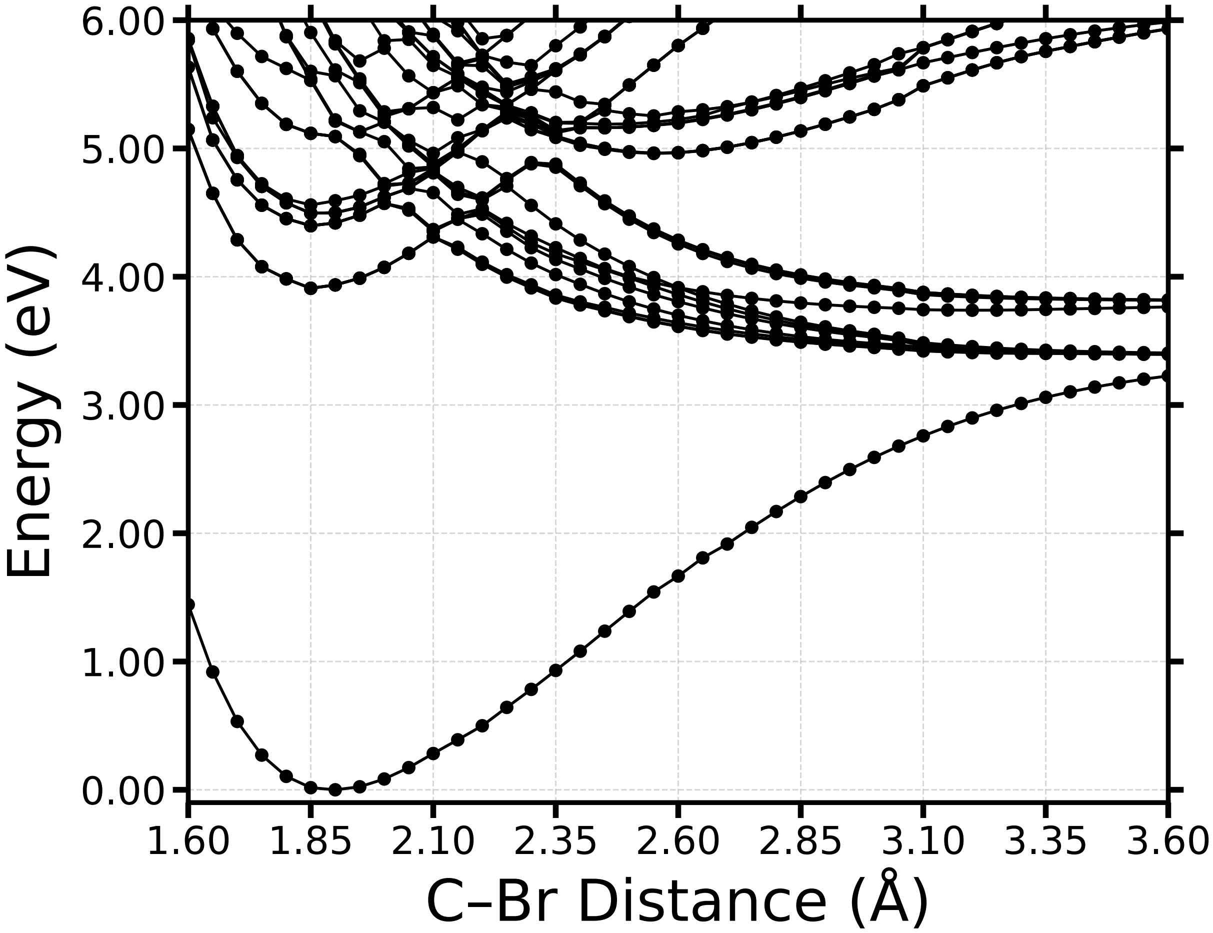


Figure S2. Adiabatic PECs for SO states of PhBr with respect to the C–Br distance.

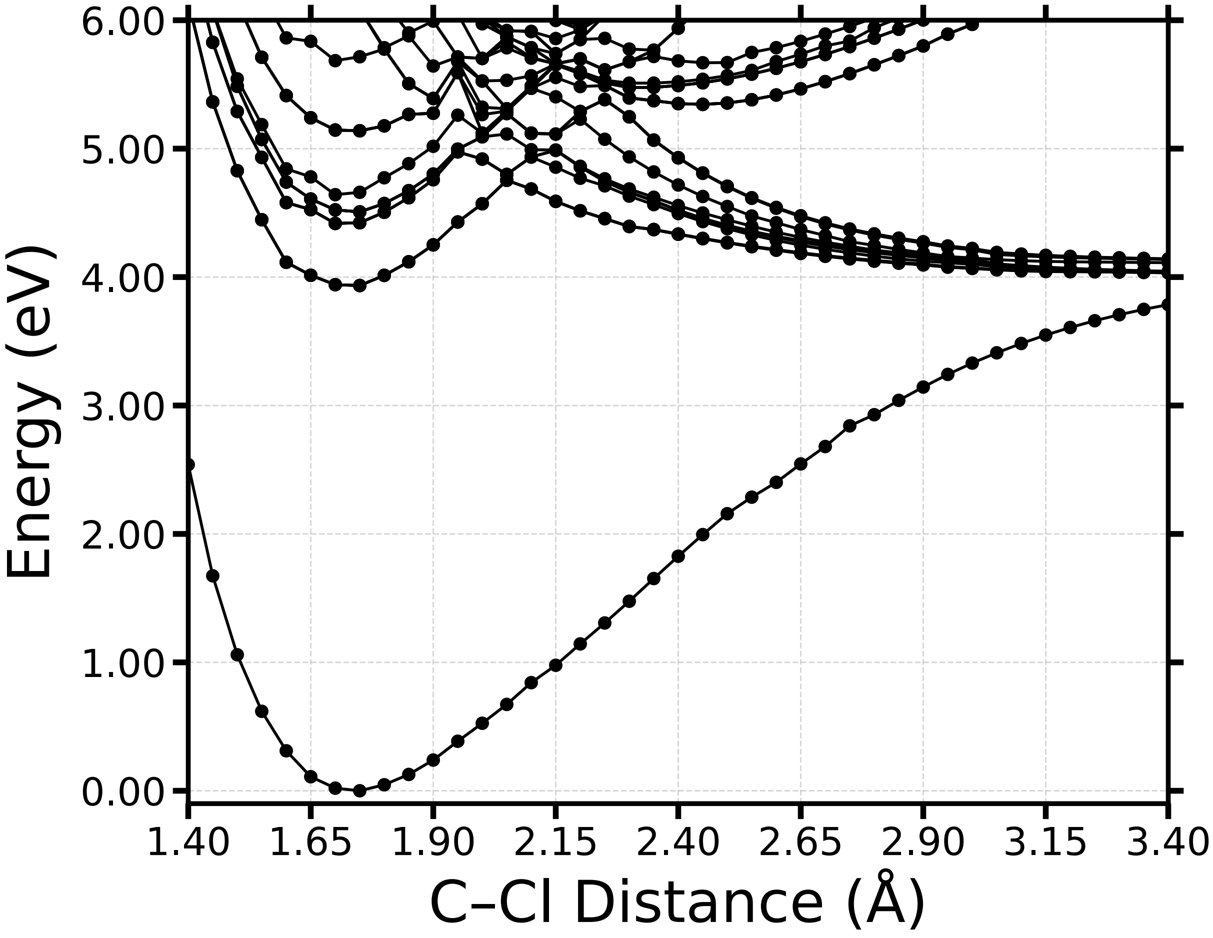


Figure S3. Adiabatic PECs for SO states of PhCl with respect to the C–Cl distance.

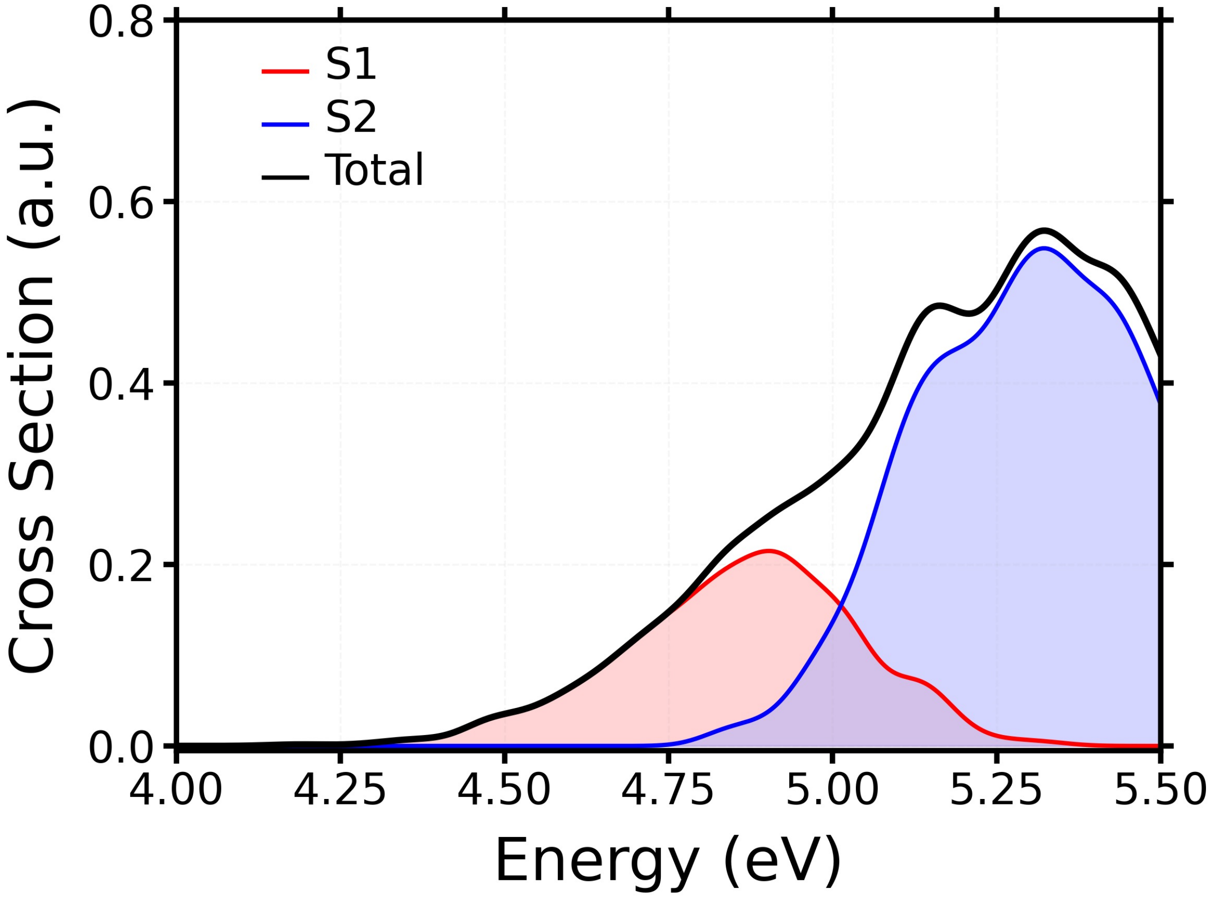


Figure S4. The absorption cross-section spectrum of PhI. The spectrum was calculated using excitation energies and oscillator strengths obtained from 500 geometries sampled via 0 K Harmonic Wigner distribution. A Gaussian broadening of 0.15 eV was applied to calculation for the spectrum. The nomenclature of excited states is presented in SF notation.

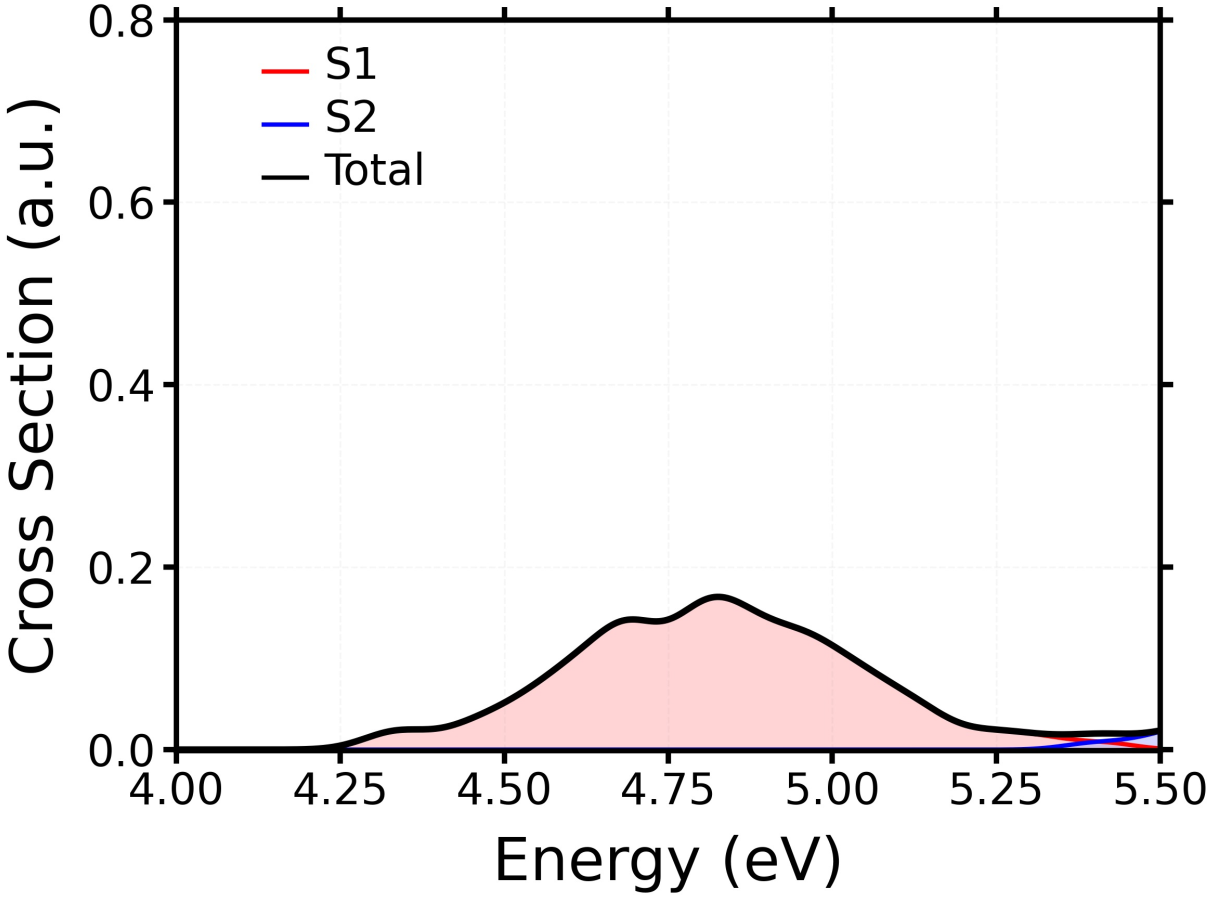


Figure S5. The absorption cross-section spectrum of PhBr. The spectrum was calculated using excitation energies and oscillator strengths obtained from 2000 geometries sampled via 0 K Harmonic Wigner distribution. A Gaussian broadening of 0.15 eV was applied to generate the spectrum. For clarity in visualization, the nomenclature of excited states is shown in SF notation.

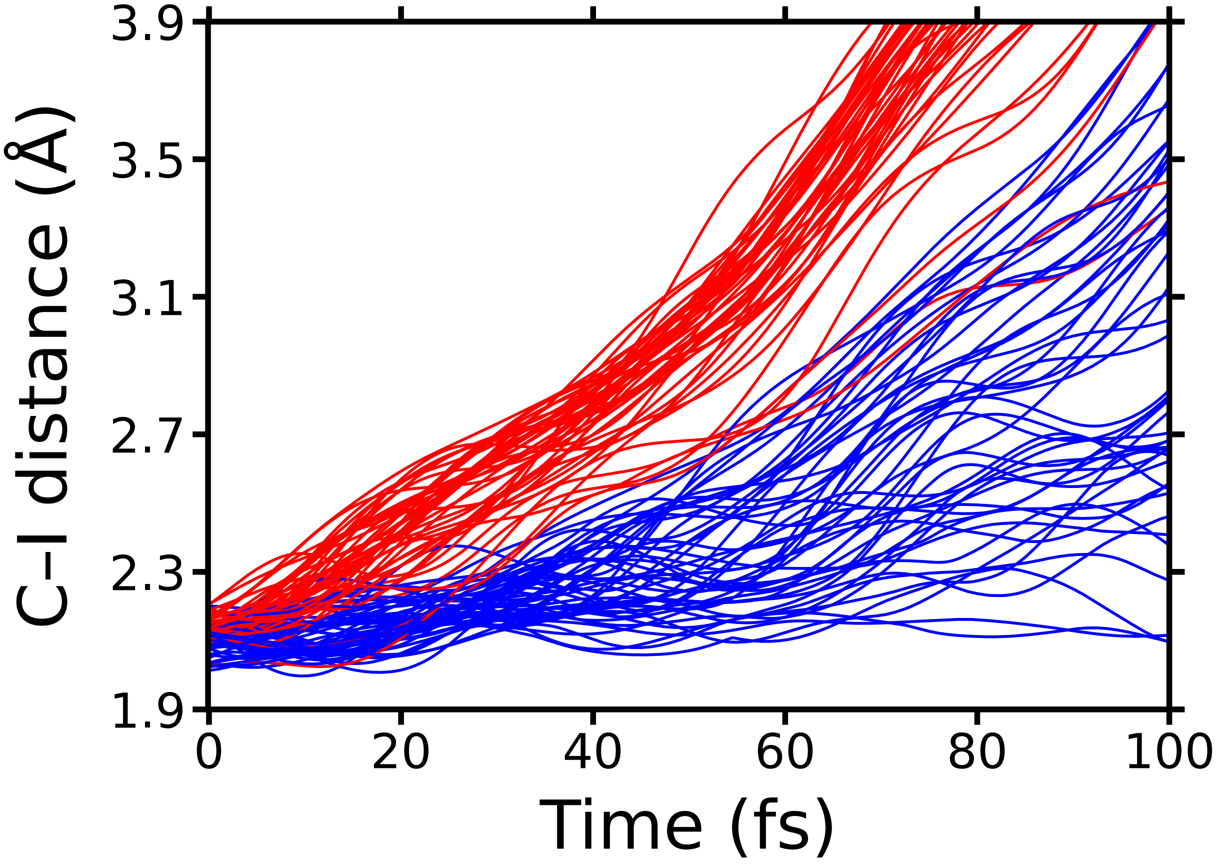
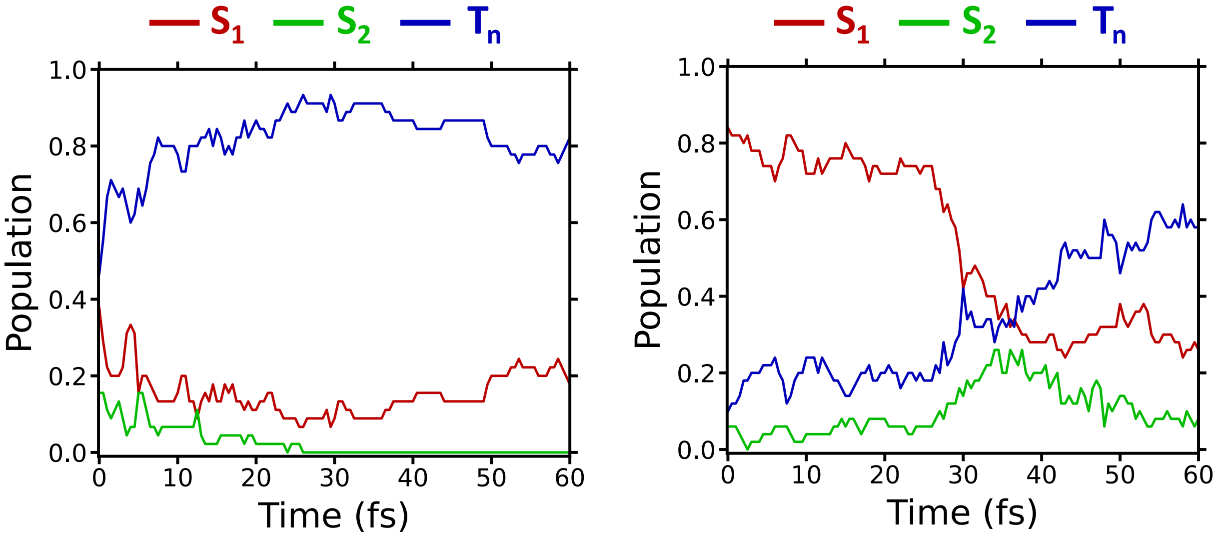


Figure S6. Individual trajectories of PhI in the first 100 fs, categorized into direct and indirect dissociation.



Direct dissociation

Indirect dissociation

Figure S7. State population of two types of PhI trajectories within the first 60 fs: direct dissociation (left panel) and indirect dissociation (right panel).

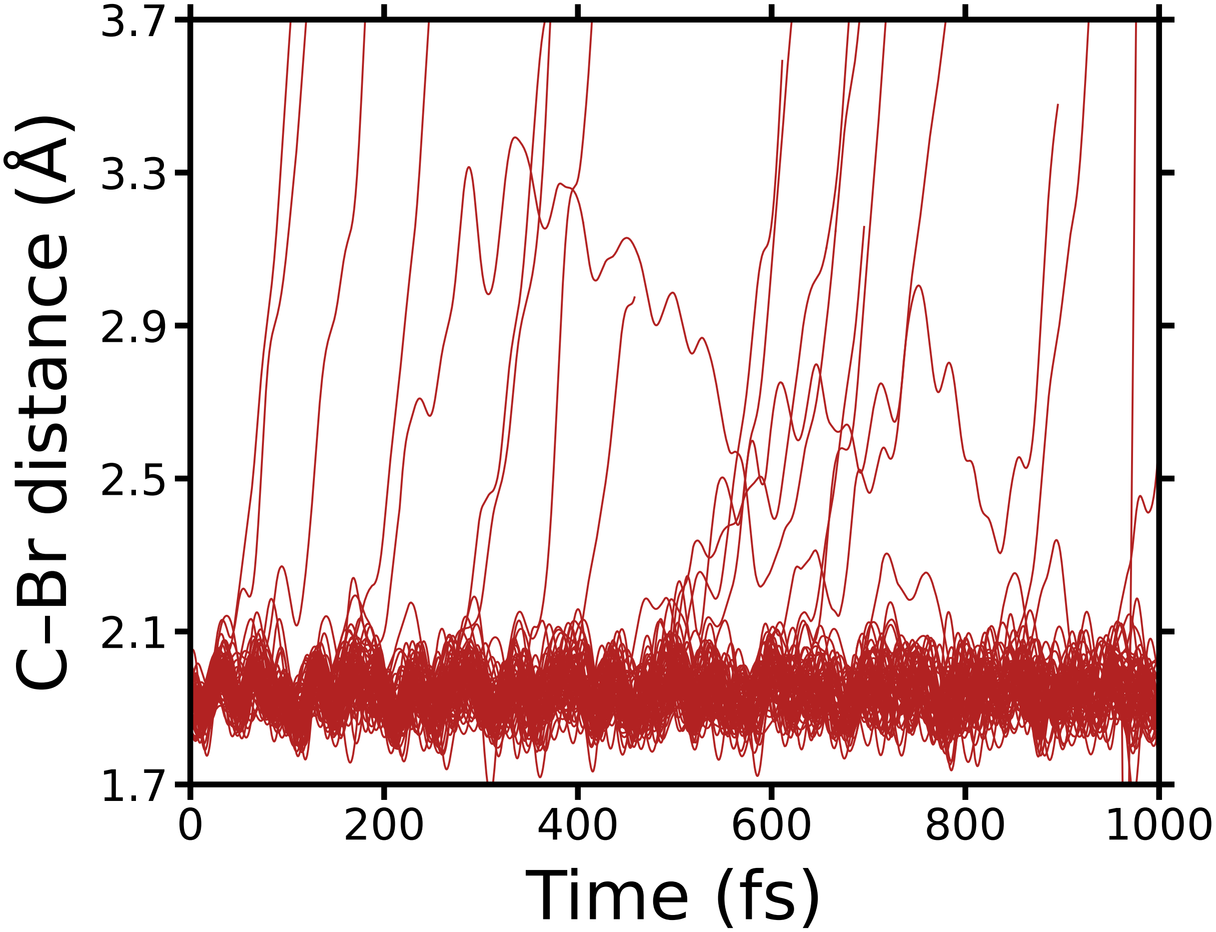


Figure S8. The C–Br distances of PhBr up to 1 ps from all trajectories.

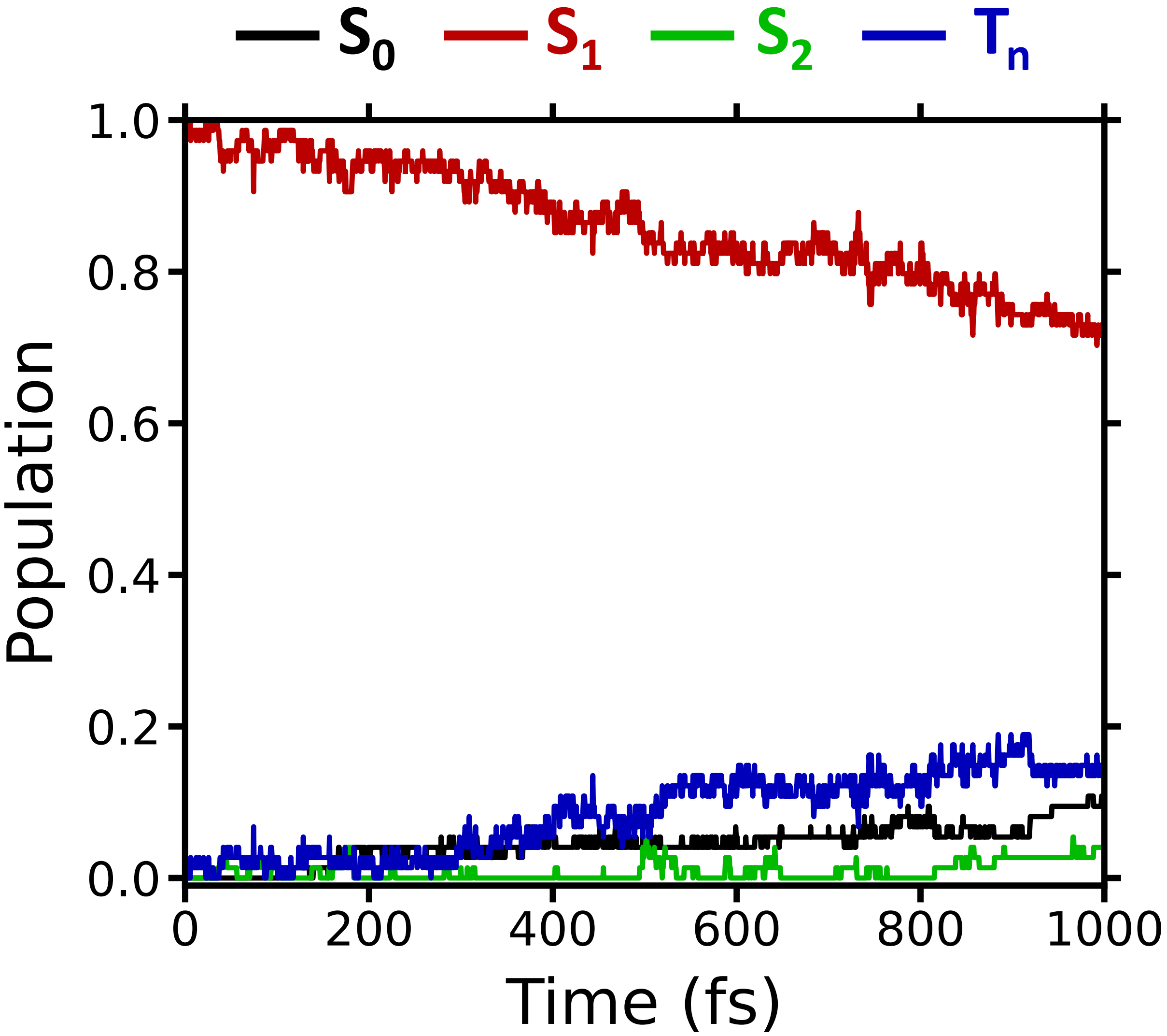


Figure S9. State populations of PhBr trajectories obtained from surface hopping simulations.

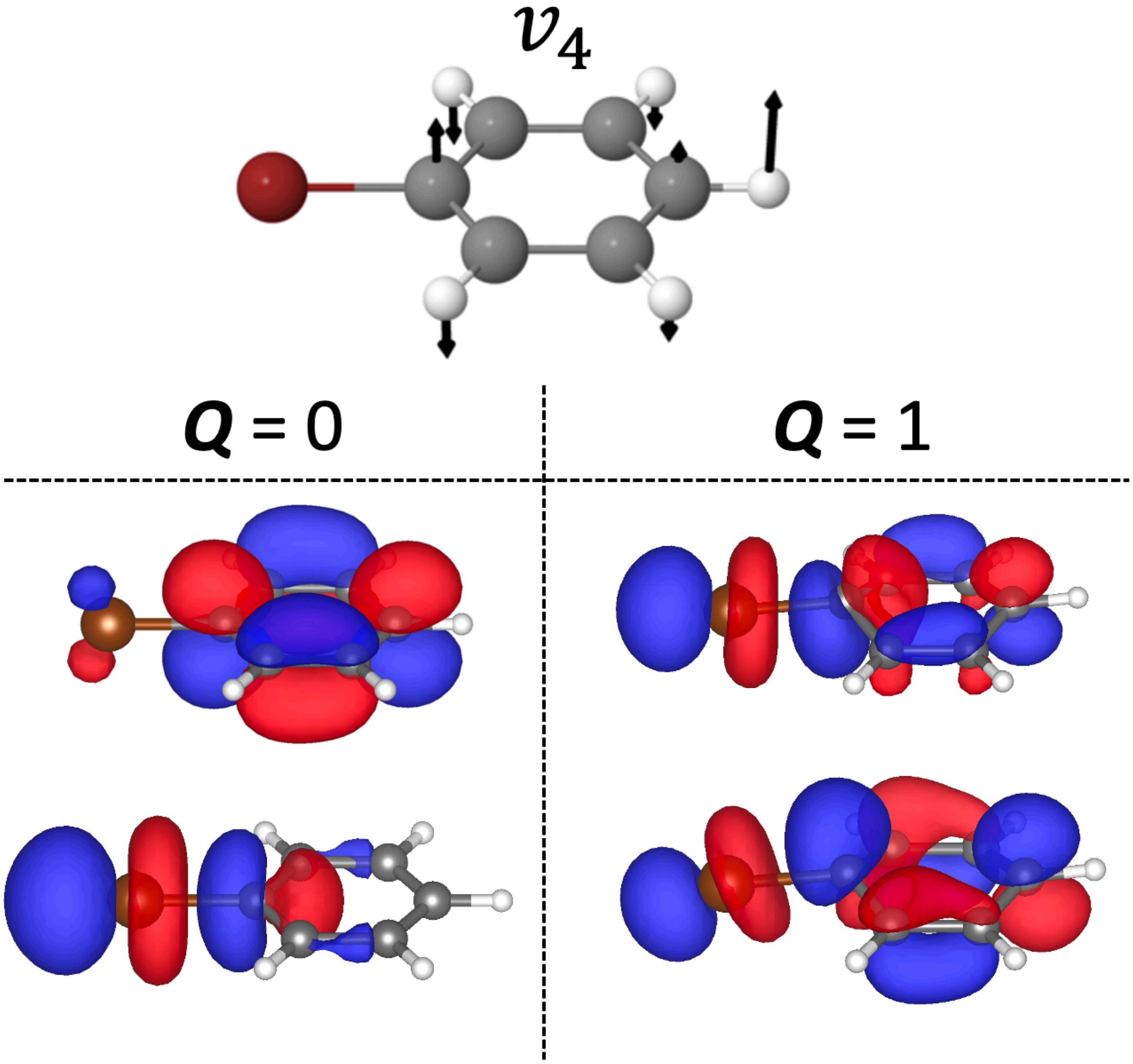
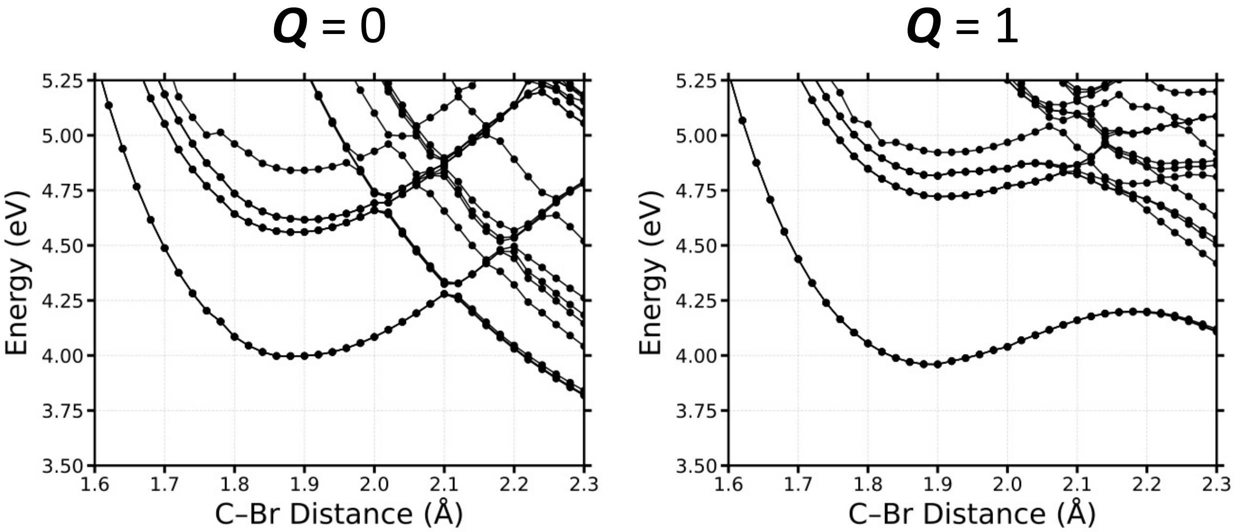


Figure S10. Two representative active spaces of the $\boldsymbol{Q}$ = 0 and $\boldsymbol{Q}$ = 1 geometries shifted with respect to the *ν*4 vector.


Q = 0

Q = 1

Figure S11. 1D PECs of PhBr along the C–Br coordinate, calculated at the $\boldsymbol{Q} = 0$ and $\boldsymbol{Q} = 1$ geometries, shifted along the *v*4 normal mode vector.

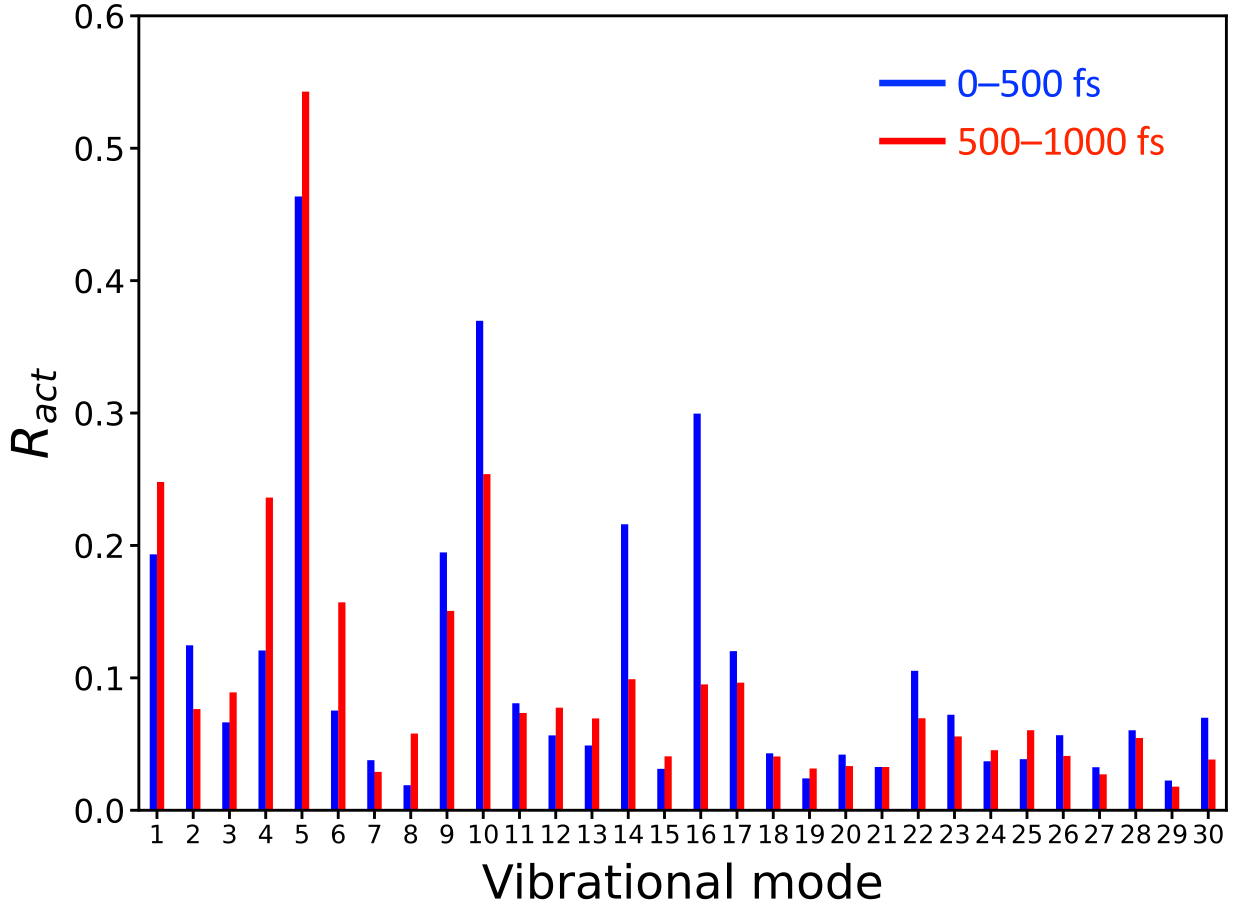


Figure S12. Activities of all vibrational modes of the S_1 state of PhBr, analyzed during the first 500 fs and between 500 fs and 1000 fs.

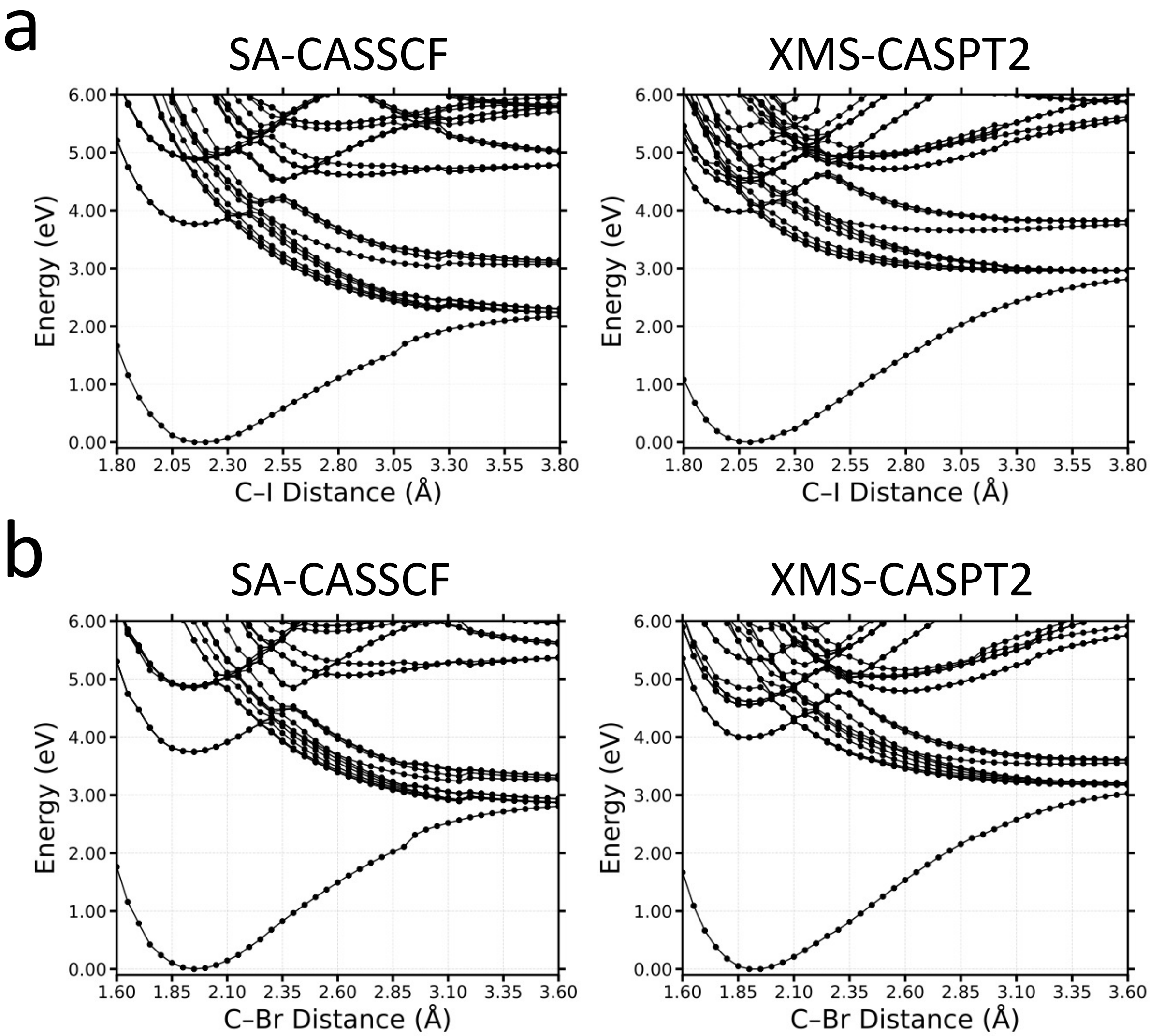


Figure S13. Comparison of the PECs of PhI (a) and PhBr (b) with respect to the C–I (Br) distances, calculated with SA-CASSCF and XMS-CASPT2 level of theory.

References

(S1) Brunvoll, J.; Samdal, S.; Thomassen, H.; Vilkov, L. V.; Samdal, S. The Molecular Structure of Iodobenzene and *p*-Iodonitrobenzene in the Gaseous State. *Acta Chem. Scand*. **1990**, *44*, 23–30 https://doi.org/10.3891/acta.chem.scand.44-0023

(S2) Almenningen, A.; Brunvoll, J.; Popik, M. V.; Sokolkov, S. V.; Vilkov, L. V.; Samdal, S. The molecular structure of gaseous monobromobenzene. *J. Mol. Struct.* **1985**, *127* (1–2), 85–94. https://doi.org/10.1016/0022-2860(85)80152-6.