

Halogen-atom effect on the ultrafast photodissociation dynamics of the dihalomethanes CH₂ICl and CH₂BrI[†]

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Supplementary Information

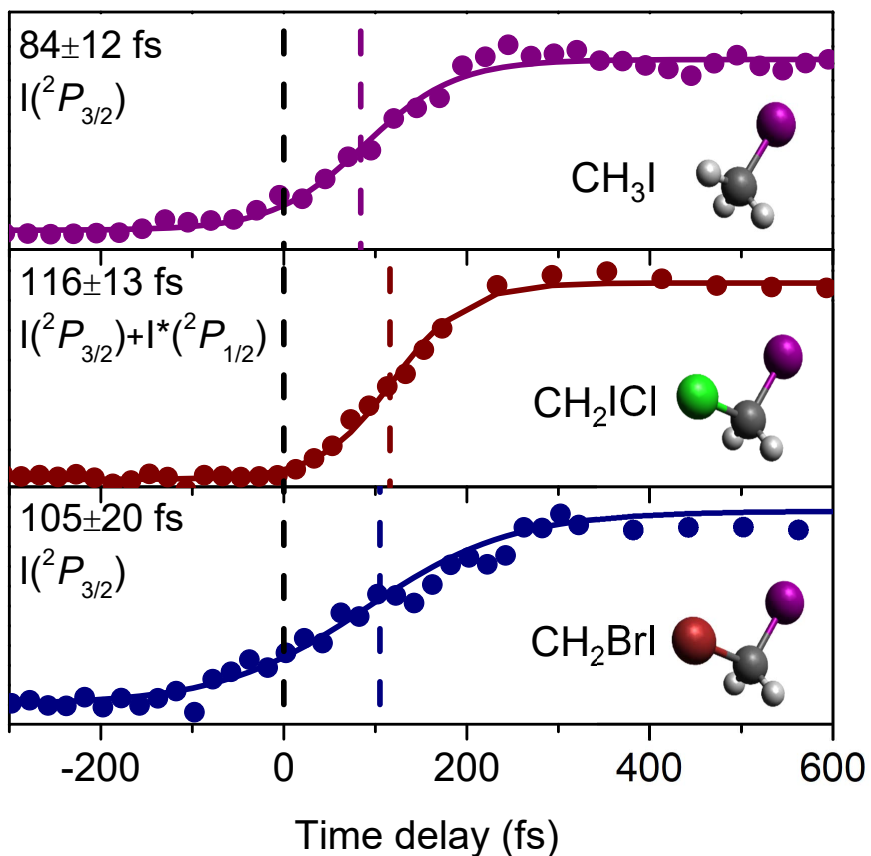


Fig. S1 Transients measured for CH₃I (top), CH₂ICl (middle) and CH₂IBr (bottom) for the I(²P_{3/2}) channel (top,bottom) and I(²P_{3/2})+I(²P_{1/2}) channels (middle) fitted using a Boltzmann sigmoidal function (solid line). The reaction (clocking) times are referred to the time zero found in situ by measuring the 1 + 1' ionization signal in xenon. Time zero is indicated in each panel by means of a vertical dashed line in black. The reaction time is defined as the time between time zero and the time corresponding to the middle of the rise of the transient (indicated by vertical dashed lines in each panel). The reaction times obtained as a mean value of several measurements along with the standard deviations are indicated in each panel.

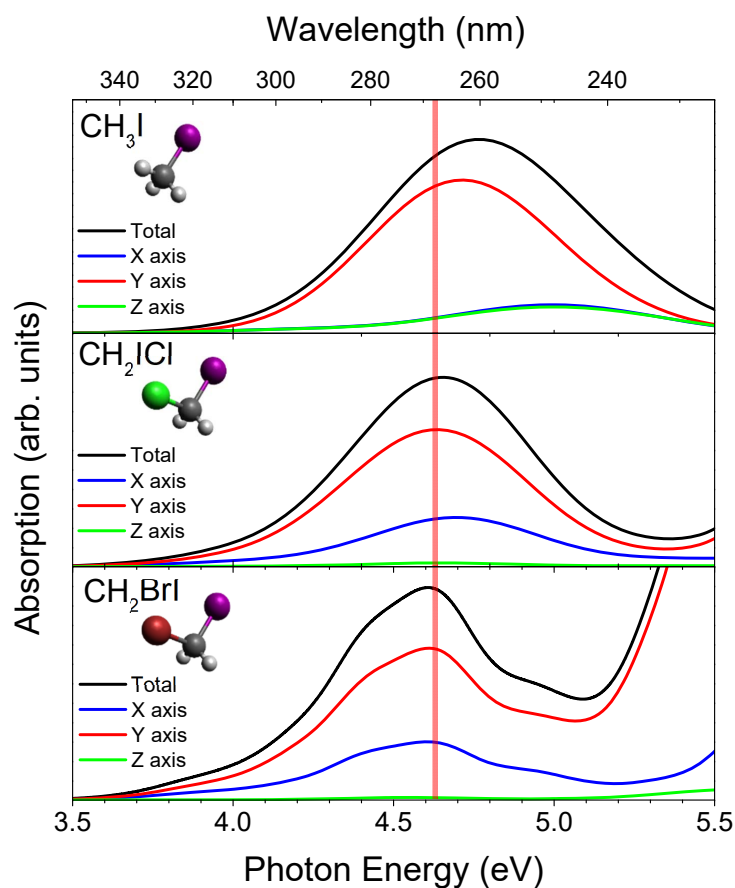


Fig. S2 Computed absorption spectra for CH_3I (top), CH_2ICl (b) and CH_2IBr (c) as a function of the transition dipole moment axis. X axis represents a perpendicular orientation with respect to the C-I bond (in the I-C-Cl plane for CH_2ICl and in the I-C-Br plane for CH_2IBr), Y axis represents a parallel orientation to the C-I bond and Z axis represents a perpendicular orientation with respect to the C-I bond and perpendicular to the I-C-Cl plane for CH_2ICl and in the I-C-Br plane for CH_2IBr . The vertical arrows indicate the excitation wavelengths of 268 nm used in the present experiments.

Table S1 *Ab initio* energy at the Franck-Condon (FC) geometry of the CH₃I, CH₂ICl and CH₂BrI molecules, symmetry in the C_s and C_{3v} groups as well as the transition dipole moment (TDM) – total and for each axis – of the computed electronic state. X axis is located in the I-C-Ω plane, perpendicular to the C-I bond, Y axis in the I-C-Ω plane, along the C-I bond and the Z axis perpendicular to the I-C-Ω plane, where Ω= H, Cl or Br. The table has been truncated up to the 5A' (¹Q₁) state. Complete list of computed states in Table 2.

State number	Franck-Condon energy (eV)	Symmetry (C _s)	Correlated symmetry (C _{3v})	TDM	X	Y	Z
CH ₃ I molecule							
1	0		–	0.66193	0.00013	0.66193	0.00000
2	4.20		³ Q ₂	0.00067	0.00066	0.00009	0.00001
3	4.20		³ Q ₂	0.00060	0.00001	0.00000	0.00060
4	4.36		³ Q ₁	0.02046	0.00000	0.00000	0.02046
5	4.36		³ Q ₁	0.02046	0.02046	0.00005	0.00000
6	4.71		³ Q _{0–}	0.00000	0.00000	0.00000	0.00000
7	4.79		³ Q ₀₊	0.12158	0.00028	0.12158	0.00000
8	5.07		¹ Q ₁	0.05258	0.05258	0.00004	0.00000
9	5.07		¹ Q ₁	0.05255	0.00000	0.00000	0.05255
10	6.53		² A ₂	0.00000	0.00000	0.00000	0.00000
11	6.55		4E	0.01528	0.01528	0.00002	0.00001
12	6.55		–	0.01529	0.00001	0.00000	0.01529
CH ₂ ICl molecule							
1	0	1A'	–	0.51543	0.434820	0.276770	0.000000
2	3.92	1A''	³ Q ₂	0.00042	0.000000	0.000000	0.000421
3	3.92	2A'	³ Q ₂	0.00679	0.000250	0.006780	0.000000
4	4.06	2A''	³ Q ₁	0.01131	0.000000	0.000000	0.011310
5	4.07	3A'	³ Q ₁	0.06245	0.042500	0.045760	0.000000
6	4.38	3A''	³ Q _{0–}	0.00120	0.000000	0.000000	0.001193
7	4.49	4A'	³ Q ₀₊	0.15119	0.062330	0.137750	0.000000
8	4.70	4A''	¹ Q ₁	0.02766	0.000000	0.000000	0.027661
9	4.76	5A'	¹ Q ₁	0.19746	0.122770	0.154660	0.000000
10	5.47	5A''	² A ₂	0.00136	0.000000	0.000000	0.001360
11	5.50	6A''	4E	0.01352	0.000000	0.000000	0.013521
12	5.51	6A'	–	0.06060	0.043330	0.042370	0.000000
13	6.09	7A'	–	0.04810	0.019330	0.044050	0.000000
14	6.09	7A''	–	0.00335	0.000000	0.000000	0.003352
15	6.09	8A'	–	0.05187	0.020330	0.047720	0.000000
CH ₂ BrI molecule							
1	0	1A'	–	0.48635	0.439920	0.207390	0.000000
2	3.83	1A''	³ Q ₂	0.00241	0.000000	0.000000	0.002411
3	3.83	2A'	³ Q ₂	0.00330	0.003140	0.001030	0.000000
4	3.96	2A''	³ Q ₁	0.01134	0.000000	0.000000	0.011340
5	4.00	3A'	³ Q ₁	0.11854	0.068830	0.096510	0.000000
6	4.28	3A''	³ Q _{0–}	0.00054	0.000000	0.000000	0.000540
7	4.39	4A'	³ Q ₀₊	0.13841	0.052570	0.128040	0.000000
8	4.60	4A''	¹ Q ₁	0.03196	0.000000	0.000000	0.031960
9	4.62	5A'	¹ Q ₁	0.34889	0.188250	0.293740	0.000000
10	5.01	5A''	² A ₂	0.00498	0.000000	0.000000	0.004976
11	5.05	6A'	4E	0.1049	0.061870	0.084710	0.000000
12	5.16	A''	–	0.00884	0.000000	0.000000	0.008831
13	5.17	7A'	–	0.08522	0.013610	0.084130	0.000000
14	5.25	7A''	–	0.00077	0.000000	0.000000	0.000770
15	5.27	8A'	–	0.02185	0.004100	0.021460	0.000000