

# ChemPhysChem

Supporting Information

## Spectroscopic Study of the $\text{Br}^- + \text{CH}_3\text{I} \rightarrow \text{I}^- + \text{CH}_3\text{Br}$ $\text{S}_{\text{N}}2$ Reaction

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The supporting information presented here comprises of results from *ab initio* calculations of bromide-iodomethane and iodide-bromomethane gas-phase van der Waals complexes. Included are energies, vibrational data, and cartesian coordinates predicted at the CCSD(T) level of theory, with aug-cc-pVDZ, TZ and QZ basis sets. The aug-cc-pVXZ-PP basis sets were used for bromine and iodine. Collectively, these basis sets are referred to as AVXZ. Also attached is the mass spectrum of the dibromomethane-iodomethane-argon gas mixture with a complete putative assignment of the mass peaks.

Table S1: Energetics of the bare CH<sub>3</sub>Br and CH<sub>3</sub>I molecules, halide anions, and halogen radicals determined from CCSD(T) calculations.

	Basis Set	$E_{(\text{CCSD(T)})}$ [E <sub>h</sub> ]	zpe [kJ mol <sup>-1</sup> ]	VDE [eV]	Experimental SO* [eV]	Split VDE [eV]	Literature <sup>2</sup> P <sub>3/2</sub> VDE [eV]	Shift <sup>†</sup> [eV]
CH <sub>3</sub> Br	AVDZ	-455.4440699						
	AVTZ	-455.5984965	97.9					
	AVQZ	-455.6834034						
	CBS	-455.7358608						
CH <sub>3</sub> I	AVDZ	-334.5914504						
	AVTZ	-334.7348612	96.2					
	AVQZ	-334.8221599						
	CBS	-334.8753513						
Br <sup>-</sup>   Br <sup>•</sup>	AVDZ	-415.7264357   -415.6061898		3.272		3.120   3.577		+0.244
	AVTZ	-415.8364248   -415.7132791		3.351		3.199   3.656		+0.165
	AVQZ	-415.9123563   -415.7853280		3.457		3.305   3.762		+0.059
	CBS	-415.9599329   -415.8302313		3.529	-0.152   +0.305	3.377   3.834	3.364 <sup>a</sup>	-0.013
I <sup>-</sup>   I <sup>•</sup>	AVDZ	-294.8832580   -294.7690621		3.107		2.793   3.735		+0.266
	AVTZ	-294.9822876   -294.8654129		3.180		2.866   3.808		+0.193
	AVQZ	-295.0612417   -294.9399749		3.300		2.986   3.928		+0.073
	CBS	-295.1101148   -294.9859536		3.379	-0.314   +0.628	3.065   4.007	3.059 <sup>b</sup>	-0.006

\* A spin-orbit split which is applied to the simulated VDE. It accounts for the point at which two electronic states diverge based on the difference in their total angular momentum quantum number  $j$ , and is calculated from experimental values found at <https://www.nist.gov/pml/handbook-basic-atomic-spectroscopic-data>.

<sup>†</sup> Calculated as the difference between the literature <sup>2</sup>P<sub>3/2</sub> VDE and the simulated <sup>2</sup>P<sub>3/2</sub> VDE.

<sup>a</sup> C. Blondel, P. Cacciani, C. Delsart, R. Trainham, *Phys. Rev. A* **1989**, *40*, 3698-3701.

<sup>b</sup> R. J. Peláez, C. Blondel, C. Delsart, C. Drag, *J. Phys. B: At. Mol. Opt. Phys.* **2009**, *42*, 125001.

Table S2: Energetics of the bromide-iodomethane and iodide-bromomethane van der Waals complexes determined from CCSD(T) calculations.

	Basis Set	$E_{\text{CCSD(T)}}$ [ $E_h$ ]	$D_0$ [kJ mol $^{-1}$ ]	VDE [eV]
Br $^-$ $\cdots$ H $_3$ CI (Min1)	AVDZ	-750.3358743		
	AVTZ	-750.5889156		
	AVQZ	-750.7525126		
	CBS	-750.8535433	47.6	3.841   4.298
Br $^-$ $\cdots$ HCH $_2$ I* (Min2)	AVDZ			
	AVTZ	-750.5882685	43.6	3.762   4.219
	AVQZ			
	CBS			
Br $^-$ $\cdots$ ICH $_3$ (Min3)	AVDZ	-750.3291600		
	AVTZ	-750.5839803		
	AVQZ	-750.7477629		
	CBS	-750.8486917	35.7	3.708   4.165
I $^-$ $\cdots$ H $_3$ CBr (Min4)	AVDZ	-750.3432191		
	AVTZ	-750.5966038		
	AVQZ	-750.7607204		
	CBS	-750.8621977	42.2	3.441   4.383
I $^-$ $\cdots$ BrCH $_3$ (Min5)	AVDZ	-750.3295673		
	AVTZ	-750.5838495		
	AVQZ	-750.7478782		
	CBS	-750.8492032	8.6	3.074   4.016

\* As was discussed in the main text, due to this complex lying in a region of the potential energy surface that changes due to the basis set used, only the AVTZ energies have been listed.

Table S3: Energetics of the transition structures along the back-side reaction coordinate determined from CCSD(T) calculations.

	Basis Set	$E_{(\text{CCSD(T)})}$ [ $E_h$ ]	$\Delta E_{\text{forward}}^\dagger$ [kJ mol $^{-1}$ ]	$\Delta E_{\text{reverse}}^\dagger$ [kJ mol $^{-1}$ ]
	AVDZ	-750.3246933		
[Br $\cdots$ CH $_3$ $\cdots$ I] $^-$ (TS1)	AVTZ	-750.5765710		
	AVQZ	-750.7396590		
	CBS	-750.8405848	32.6	53.6
	AVDZ			
Br $^-$ $\cdots$ HCH $_2$ I* (TS2)	AVTZ	-750.5882214	-0.4	2.0
	AVQZ			
	CBS			

\* As was discussed in the main text, due to this transition structure lying in a region of the potential energy surface that changes due to the basis set used, only the AVTZ energies have been listed.

$^\dagger$  Zero-point corrected.

Table S4: Vibrational frequencies, in cm $^{-1}$ , and zero point energies (zpe), in kJ mol $^{-1}$ , of the bare CH $_3$ Br and CH $_3$ I molecules, determined from CCSD(T)/AVTZ calculations.

	Symmetry	CH $_3$ Br	CH $_3$ I
$\omega_1$	A $_1$	3084	3085
$\omega_2$	A $_1$	1345	1290
$\omega_3$	A $_1$	625	556
$\omega_4$	E	3192	3196
$\omega_5$	E	3192	3196
$\omega_6$	E	1490	1481
$\omega_7$	E	1490	1481
$\omega_8$	E	973	896
$\omega_9$	E	973	896
zpe		98	96

Table S5: Vibrational frequencies, in  $\text{cm}^{-1}$ , and zero point energies (zpe), in  $\text{kJ mol}^{-1}$ , of the bromide-iodomethane and iodide-bromomethane van der Waals complexes determined from CCSD(T)/AVTZ calculations.

	$\text{Br}^- \cdots \text{H}_3\text{CI}$		$\text{Br}^- \cdots \text{HCH}_2\text{I}$		$\text{Br}^- \cdots \text{ICH}_3$		$\text{I}^- \cdots \text{H}_3\text{CBr}$		$\text{I}^- \cdots \text{BrCH}_3$	
	(Min1)		(Min2)		(Min3)		(Min4)		(Min5)	
	Symmetry	Frequency	Symmetry	Frequency	Symmetry	Frequency	Symmetry	Frequency	Symmetry	Frequency
$\omega_1$	$A_1$	3121	$A'$	3167	$A_1$	3050	$A_1$	3114	$A_1$	3058
$\omega_2$	$A_1$	1223	$A'$	3043	$A_1$	1245	$A_1$	1292	$A_1$	1320
$\omega_3$	$A_1$	477	$A'$	1467	$A_1$	516	$A_1$	552	$A_1$	609
$\omega_4$	$A_1$	70	$A'$	1296	$A_1$	86	$A_1$	62	$A_1$	52
$\omega_5$	E	3246	$A'$	889	E	3147	E	3235	E	3155
$\omega_6$	E	3246	$A'$	529	E	3147	E	3235	E	3155
$\omega_7$	E	1457	$A'$	105	E	1478	E	1470	E	1489
$\omega_8$	E	1457	$A'$	25	E	1478	E	1470	E	1489
$\omega_9$	E	860	$A''$	3197	E	840	E	939	E	947
$\omega_{10}$	E	860	$A''$	1489	E	840	E	939	E	947
$\omega_{11}$	E	56	$A''$	908	E	86	E	58	E	65
$\omega_{12}$	E	56	$A''$	135	E	86	E	58	E	65
zpe		96		97		96		98		98

Table S6: Vibrational frequencies, in  $\text{cm}^{-1}$ , and zero point energies (zpe), in  $\text{kJ mol}^{-1}$ , of the transition structures along the back-side reaction coordinate determined from CCSD(T)/AVTZ calculations.

	$[\text{Br}\cdots\text{CH}_3\cdots\text{I}]^-$ (TS1)		$\text{Br}^- \cdots \text{HCH}_2\text{I}$ (TS2)	
	Symmetry	Frequency	Symmetry	Frequency
$\omega_1$	$A_1$	$418i$	$A'$	$35i$
$\omega_2$	$A_1$	3184	$A'$	3198
$\omega_3$	$A_1$	929	$A'$	3080
$\omega_4$	$A_1$	126	$A'$	1463
$\omega_5$	E	3378	$A'$	1273
$\omega_6$	E	3378	$A'$	860
$\omega_7$	E	1405	$A'$	520
$\omega_8$	E	1405	$A'$	77
$\omega_9$	E	884	$A''$	3209
$\omega_{10}$	E	884	$A''$	1477
$\omega_{11}$	E	161	$A''$	899
$\omega_{12}$	E	161	$A''$	102
zpe		95		97

Table S7: Cartesian coordinates, in  $\text{\AA}$ , of the bare  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$  molecules determined from CCSD(T)/AVTZ calculations.

Atom	$x$	$y$	$z$
C	1.61802988	0.00000000	0.00000000
H	1.94876298	-0.51702176	-0.89550797
H	1.94876298	-0.51702176	0.89550797
H	1.94876298	1.03404353	0.00000000
Br	-0.32069093	0.00000000	0.00000000
C	1.90493010	0.00000000	0.00000000
H	2.23256162	-0.51735931	-0.89609261
H	2.23256162	-0.51735931	0.89609261
H	2.23256162	1.03471862	0.00000000
I	-0.23331924	0.00000000	0.00000000

Table S8: Cartesian coordinates, in Å, of the bromide-iodomethane and iodide-bromomethane van der Waals complexes determined from CCSD(T)/AVTZ calculations.

Complex	Atom	$x$	$y$	$z$
Br <sup>-</sup> ···H <sub>3</sub> CI (Min1)	C	-0.10260222	0.00000000	0.00000000
	H	-0.42343898	-0.51673107	-0.89500447
	H	-0.42343898	-0.51673107	0.89500447
	H	-0.42343898	1.03346215	0.00000000
	Br	-3.30283991	0.00000000	0.00000000
	I	2.07373395	0.00000000	0.00000000
Br <sup>-</sup> ···HCH <sub>2</sub> I (Min2)	C	-0.11513498	-0.98448038	0.00000000
	H	-0.11009201	-1.59500824	-0.89763811
	H	-0.11009201	-1.59500824	0.89763811
	H	0.70940820	-0.27029630	0.00000000
	Br	3.20932327	0.07047297	0.00000000
	I	-1.98878636	0.07674706	0.00000000
Br <sup>-</sup> ···ICH <sub>3</sub> (Min3)	C	-3.17401844	0.00000000	0.00000000
	H	-3.52449990	0.51535049	-0.89261323
	H	-3.52449990	0.51535049	0.89261323
	H	-3.52449990	-1.03070098	0.00000000
	Br	2.22901699	0.00000000	0.00000000
	I	-1.00205966	0.00000000	0.00000000
I <sup>-</sup> ···H <sub>3</sub> CBr (Min4)	C	1.29720364	0.00000000	0.00000000
	H	0.96970005	-0.51611717	-0.89394116
	H	0.96970005	-0.51611717	0.89394116
	H	0.96970005	1.03223434	0.00000000
	Br	3.26936141	0.00000000	0.00000000
	I	-2.17888987	0.00000000	0.00000000
I <sup>-</sup> ···BrCH <sub>3</sub> (Min5)	C	-3.86933500	0.00000000	0.00000000
	H	-4.21676357	0.51552501	-0.89291552
	H	-4.21676357	0.51552501	0.89291552
	H	-4.21676357	-1.03105003	0.00000000
	Br	-1.92252107	0.00000000	0.00000000
	I	1.66190725	0.00000000	0.00000000



Table S9: Cartesian coordinates, in Å, of the transition structures along the back-side reaction coordinate determined from CCSD(T)/AVTZ calculations.

Structure	Atom	$x$	$y$	$z$
[Br $\cdots$ CH $_3\cdots$ I] $^-$ (TS1)	C	-0.60812386	0.00000000	0.00000000
	H	-0.62942076	-0.53632137	-0.92893587
	H	-0.62942076	-0.53632137	0.92893587
	H	-0.62942076	1.07264275	0.00000000
	Br	-3.09053131	0.00000000	0.00000000
	I	1.99441444	0.00000000	0.00000000
Br $^- \cdots$ HCH $_2$ I (TS2)	C	-0.03590686	-0.72732770	0.00000000
	H	0.67646441	0.09328675	0.00000000
	H	0.06274930	-1.32775737	0.89807778
	H	0.06274930	-1.32775737	-0.89807778
	Br	3.28714497	0.05450385	0.00000000
	I	-2.04715690	0.05522939	0.00000000

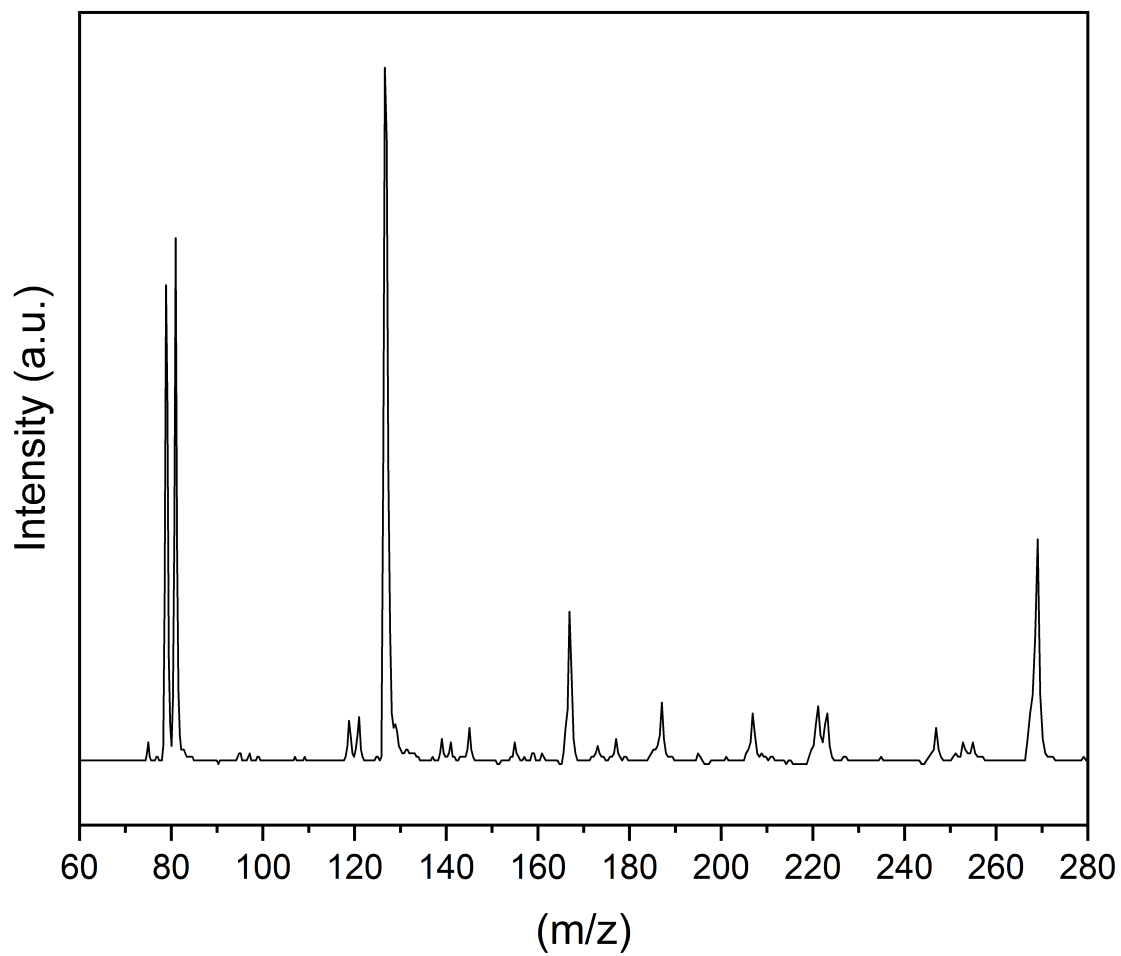


Figure S1: Negative ion mass spectrum recorded from a gas mixture containing dibromomethane, iodomethane and argon, which was used to form the  $S_N2$  reaction intermediates observed at 221 m/z and 223 m/z.

Table S10: Putative peak assignments of dibromomethane-iodomethane-argon gas mixture.

Position ( $m/z$ )	Assignment
74.98	$^{35}\text{Cl}^- \dots \text{Ar}$
76.89	$^{37}\text{Cl}^- \dots \text{Ar}$
78.89	$^{79}\text{Br}^-$
80.93	$^{81}\text{Br}^-$
94.96	$^{35}\text{Cl}^- \dots \text{OCS}$
97.01	$^{37}\text{Cl}^- \dots \text{OCS}, ^{79}\text{Br}^- \dots \text{H}_2\text{O}$
98.89	$^{81}\text{Br}^- \dots \text{H}_2\text{O}$
106.98	$^{79}\text{Br}^- \dots \text{N}_2$
109.01	$^{81}\text{Br}^- \dots \text{N}_2$
118.79	$^{79}\text{Br}^- \dots \text{Ar}$
120.93	$^{81}\text{Br}^- \dots \text{Ar}$
126.80	$^{127}\text{I}^-$
138.97	$^{79}\text{Br}^- \dots \text{OCS}$
141.01	$^{81}\text{Br}^- \dots \text{OCS}$
145.02	$^{127}\text{I}^- \dots \text{H}_2\text{O}$
154.97	$^{127}\text{I}^- \dots \text{N}_2$
158.97	$^{79}\text{Br}^- \dots (\text{Ar})_2$
160.93	$^{81}\text{Br}^- \dots (\text{Ar})_2$
166.89	$^{127}\text{I}^- \dots \text{Ar}$
173.11	$^{127}\text{I}^- \dots \text{N}_2(\text{H}_2\text{O})$
177.02	$^{35}\text{Cl}^- \dots \text{CH}_3\text{I}$
179.09	$^{37}\text{Cl}^- \dots \text{CH}_3\text{I}$
187.06	$^{127}\text{I}^- \dots \text{OCS}$
194.96	$^{127}\text{I}^- \dots \text{N}_2(\text{Ar})$
206.88	$^{127}\text{I}^- \dots (\text{Ar})_2$
221.11	$^{79}\text{Br}^- \dots \text{CH}_3\text{I}$
223.15	$^{81}\text{Br}^- \dots \text{CH}_3\text{I}$
246.88	$^{127}\text{I}^- \dots (\text{Ar})_3$
250.98	$^{79}\text{Br}^- \dots \text{CH}_2(^{79}\text{Br})_2$
252.76	$^{79}\text{Br}^- \dots \text{CH}_2(^{79}\text{Br})(^{81}\text{Br}), ^{81}\text{Br}^- \dots \text{CH}_2(^{79}\text{Br})_2$
254.88	$^{79}\text{Br}^- \dots \text{CH}_2(^{81}\text{Br})_2, ^{81}\text{Br}^- \dots \text{CH}_2(^{79}\text{Br})(^{81}\text{Br})$
256.87	$^{81}\text{Br}^- \dots \text{CH}_2(^{81}\text{Br})_2$
269.02	$^{127}\text{I}^- \dots \text{CH}_3\text{I}$