Coulomb Explosion Imaging of CH_3I: **is non-adiabatic dynamics involved?**

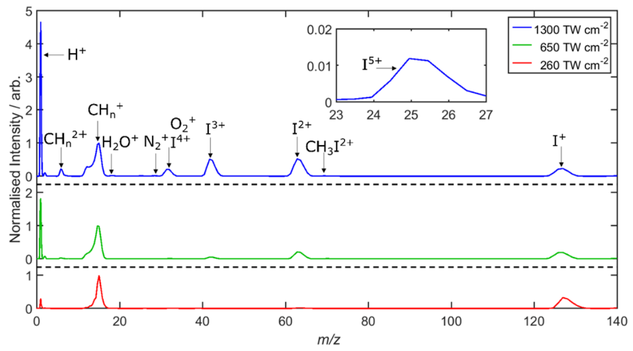
Lingfeng Ge, Stuart W. Crane, Graham A. Cooper, Ben P. Carwithen, Matthew Bain, James A. Smith, Christopher S. Hansen, Michael N. R. Ashfold

lingfeng.ge@bristol.ac.uk School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK, BS8 1TS

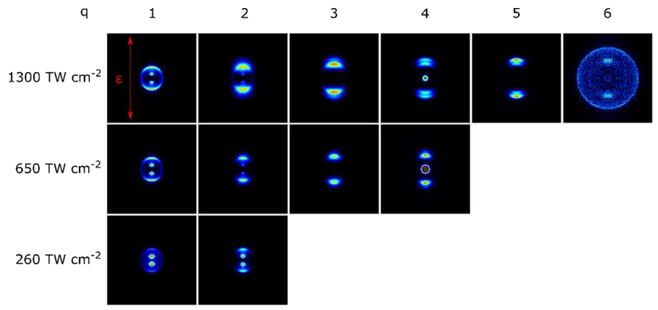
Experiments:

Jet-cooled molecular beam of CH_3I was intersected by a laser beam with ultrashort (40 fs) NIR (805 nm) pulses from a Ti:sapphire laser (1 kHz, 5 W). Three peak intensities of the laser pulses were chosen: 1300 TW cm^{-2}, 650 TW cm^{-2} & 260 TW cm^{-2}. ToF-MS and VMI were used to detect the fragment ions.

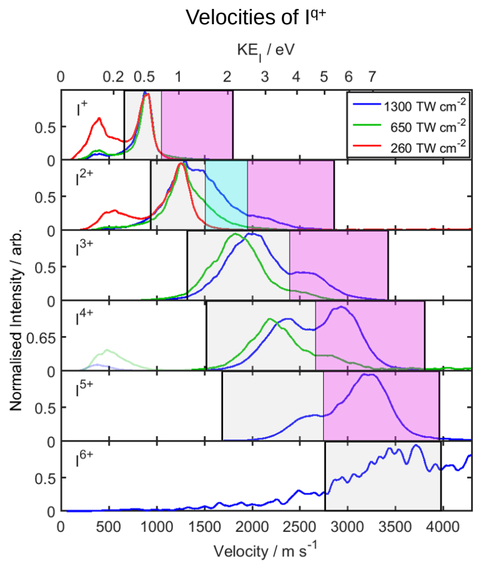
ToF mass spectra



Images of iodine ions (I^{q+})



Velocities of I^{q+}



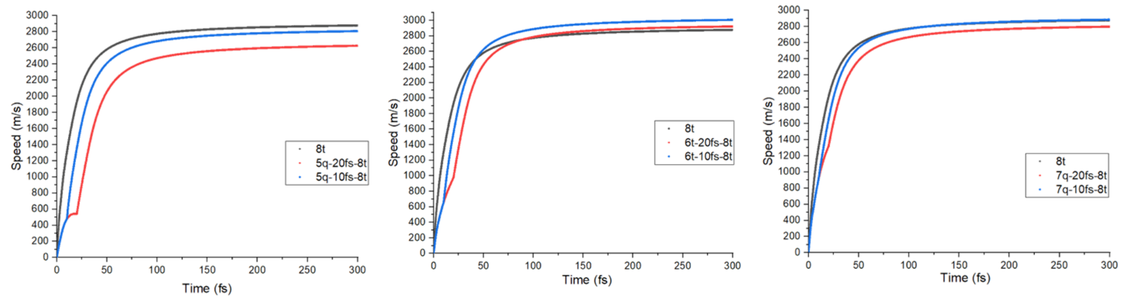
Simulations:

On-the-fly *ab initio* trajectories of Coulomb explosion dynamics of CH_3I were simulated. Simulation time is 300 fs, and step size is 0.1 fs. Electronic structure at each step was calculated at the Hartree-Fock level. (For more details of the simulation method, see *J. Chem. Phys. 153, 184201 (2020)*). Asymptotic fragmentation patterns, charges, and speeds from the simulation are shown in the table below. The superscript on the left of each charge value or molecular ion is the spin multiplicity of the ion.

Parent ion charge	parent ion spin multiplicity	IP/eV	fragment ions and their charges						speeds / m s^{-1}						
			C	I	H	H	H		I^+	I^{2+}	I^{3+}	I^{4+}	I^{5+}	I^{6+}	I^{7+}
2+	singlet	25.34		^{1}1				$^1(CH_3)^+$	800						
	triplet	24.81		^{3}1				$^1(CH_3)^+$	800						
	quintet	30.76		^{3}1		0		$^2(CH_2)^+$	730						
3+	doublet	50.94			1			$^2(CH_2I)^{2+}$							
	quartet	50.55		^{4}2				$^1(CH_3)^+$		1320					
4+	singlet	84.14			0	1	1	$^2(CI)^{2+}$							
	triplet	84.47	^{2}1	^{3}1	0	1	1		1320						
	quintet	84.63	^{2}1	^{3}1	1	1	0		1500						
5+	doublet	126.09	^{2}1	^{1}1	1	1	1		1300						
	quartet	126.07	^{2}1	^{3}1	1	1	1		1200						
6+	singlet	176.11	^{2}1	^{2}2	1	1	1			1880					
	triplet	175.53	^{2}1	^{4}2	1	1	1			2010					
	quintet	176.28	^{2}1	^{4}2	1	1	1			1900					
7+	doublet	234.89	^{1}2	^{2}2	1	1	1			2400					
	quartet	233.91	^{1}2	^{4}2	1	1	1			2400					
8+	singlet	304.51	^{1}2	^{1}3	1	1	1				3000				
	triplet	303.61	^{1}2	^{3}3	1	1	1				2900				
	quintet	306.49	^{3}2	^{3}3	1	1	1				3000				
9+	doublet	384.96	^{1}2	^{2}4	1	1	1					3400			
	quartet	386.68	^{3}2	^{2}4	1	1	1					3400			
10+	singlet	478.66	^{2}3	^{2}4	1	1	1					3900			
	triplet	479.68	^{2}3	^{2}4	1	1	1					4000			
	quintet	484.90	^{2}3	^{4}4	1	1	1					4000			
11+	doublet	583.39	^{2}3	^{1}5	1	1	1						4600		
	quartet	588.40	^{2}3	^{3}5	1	1	1						4600		
12+	singlet	700.22	^{1}4	^{1}5	1	1	1						5000		
	triplet	705.22	^{2}3	^{2}6	1	1	1							5100	
	quintet	752.82	^{2}3	^{4}6	1	1	1							5000	
13+	doublet	834.55	^{1}4	^{2}6	1	1	1							5700	
	quartet	879.09	^{1}4	^{4}6	1	1	1							5600	
14+	singlet	987.68	^{1}4	^{1}7	1	1	1								6300
	triplet	1019.35	^{1}4	^{3}7	1	1	1								6200
	quintet	1071.69	^{1}4	^{5}7	1	1	1								6100

Does it mean that the ions went through sequential ionisation during the duration of a laser pulse rather than were ionised to a high charge state instantaneously?

Sequential ionisation dynamics were then simulated, and the results are shown in the three pictures below: the speeds of I^{3+} versus time for sequential ionisation from the neutral molecule to the 5+ quintet, 6+ triplet, and 7+ quartet parent ions and then to the 8+ triplet parent ion, compared with the instantaneous ionisation to the 8+ triplet parent ion.



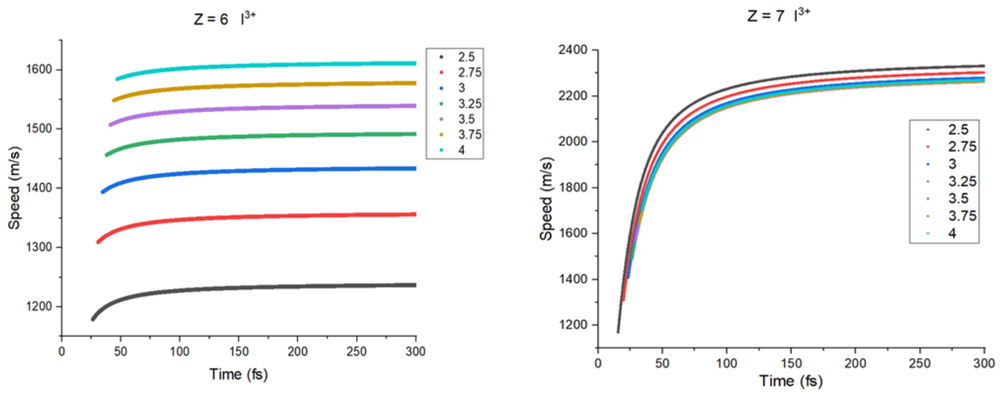
By comparing the experimental and the simulated iodine ion speeds, we can see that the two are roughly in agreement for 2+ and 3+ parent ions but in disagreement for q ≥ 3, where the simulated speeds are higher than the experimental ones.

And we can see the resultant speeds are still higher than the ones from the experiments.

Or did non-adiabatic effects take place during the dissociations?

There may have been a charge transfer within the parent ion in the early stages of its dissociation. The I^{3+} ions may have been I^{2+} which received an extra charge from the carbon ion. The 6+ parent ion may have switched from C^+ and I^{2+} to a neutral C and I^{3+}; the 7+ parent ion may have switched from C^{2+} and I^{2+} to C^+ and I^{3+}.

The two pictures below show the simulated speeds of I^{3+} in the 6+ and 7+ parent ions, resulted from charge transfers happening at a range of different C-I bond lengths (2.5 – 4 angstroms).



This seems to be able to explain why the I^{3+} speeds in the experiments are lower than the original simulation results, which assume all the dissociation dynamics are adiabatic.

So what about q > 3, namely I^{4+} and I^{5+}? Similar non-adiabatic simulation results have been obtained, but there's no more space to show the pictures on this poster. If you are interested to see them, you may see them later this year in a paper we're currently preparing – keep your eyes peeled 😜

If you have questions, feel free to Zoom me or email me!