SUPPLEMENTARY INFORMATION

Fragmentation of pure and hydrated clusters of 5Br-Uracil by low energy carbon ions: observation of hydrated fragments

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SI.1 Experimental Details

The experiments have been performed on crossed-beam apparatus where an atomic ion projectile beam cross collides with a neutral molecular target beam. This collision device has been described previously[1]. The ion beam is produced by an electron cyclotron resonance ion source at the low-energy ion beam ARIBE facility of the GANIL in Caen[2]. The projectile beam is chopped in bunches of 500 ns temporal width, transported and focused in the interaction zone of the apparatus where they collide with the beam of the target molecules/clusters. The cationic products of the interaction are extracted into a modified Wiley-McLaren time-of-flight spectrometer. A Daly-type detector is used to keep the detection efficiency constant over a wide mass range. After the field-free region of the spectrometer, the cations are post-accelerated and impact on a plate leading to the emission of secondary electrons. These secondary electrons are then deflected by a weak magnetic field towards a stack of microchannel plates and their detection gives the time-of-flight signal. This signal is digitised with a time precision of 1 ns (FAST ComTec P788).

Two different types of target beams can be produced: i) an effusive beam of isolated molecules obtained by heating a Molybdenum oven, ii) a cluster beam formed in a gas aggregation cluster source (see Fig.SI.1). The latter source is now further described. An oven filled with commercial powder of 5BrU is resistively heated (250°C) in 1 mbar atmosphere of He buffer gas. The flow carries the 5BrU vapour into the liquid nitrogen cooled condensation channel, where the molecules aggregate. The produced cluster distribution depends on different parameters[3]. In the present experiment, we control the He flow, regulated by a mass flow controller, and the 5BrU vapour pressure, i.e. the temperature of the oven monitored by a K-type thermocouple and regulated by a power supply. Two skimmers define a differential pumping stage and help to collimate the cluster beam through the interaction zone.

In order to produce hydrated species, a water reservoir is connected to the gas line through a needle valve. Thus, a mixture He/H_2O flows into the condensation channel with the 5BrU molecules. The vapour pressure is produced by heating at 40°C purified water under primary vacuum (three vacuum distillation cycles have been performed before the experiments). The mixture He/H_2O is regulated by the needle valve and in order to avoid the water condensation in the gas line, it is heated at 55-60°C.

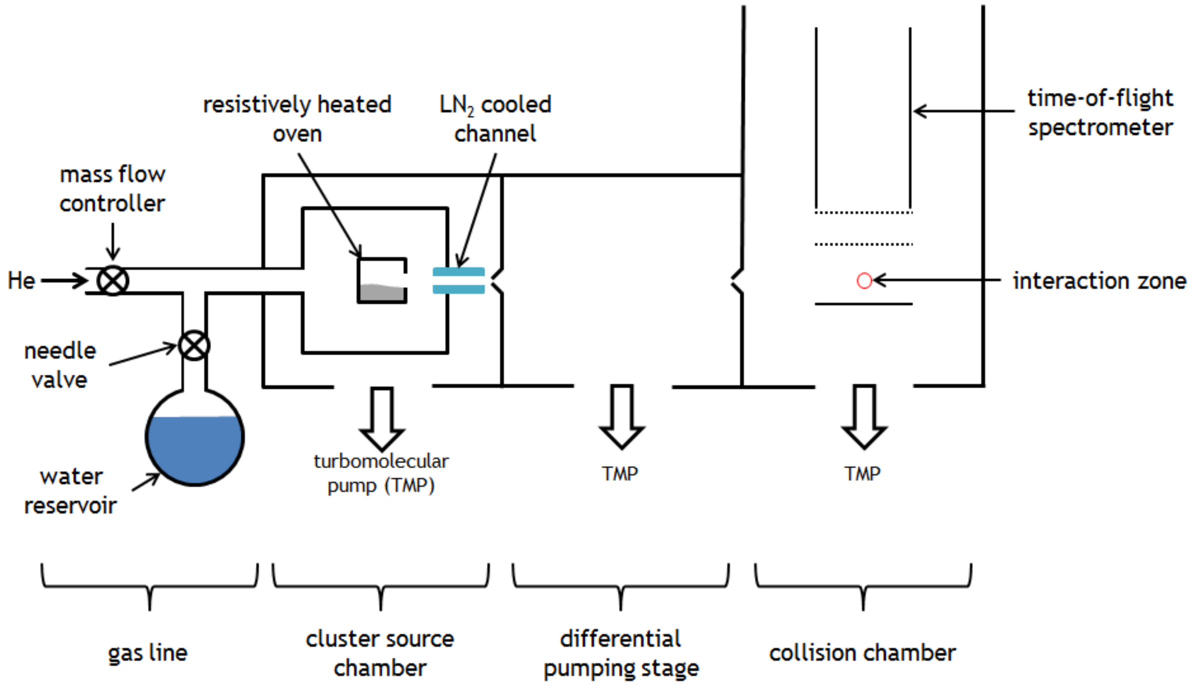

Fig.SI.1 *Scheme of the experimental set-up.The ion beam provided by the ARIBE facility in GANIL is perpendicular to the cluster beam.*

SI.1 The role of the environment: formation of hydrated fragments

The comparison between the fragmentation mass spectrum of 5BrU homogeneous and hydrated clusters is presented in Fig.SI.2 and briefly reviewed in this section. The present section aims to describe the complete list of hydrated fragments obtained by the fit procedure up to a value of mass such that the assignment was unambiguous. For this reason the mass region between 85 and 235 is shown. The series of hydrated fragments in Fig.SI.2 starts from value of n=0, it means that no water molecules are bound to the fragment for that value of mass, and in that case both the contribution of the fragment and its protonated have been taken into account as explain in the main text. The contribution of the protonated structure for each fragment is listed in Table SI.1 the together with the complete list of all the protonated hydrated series.

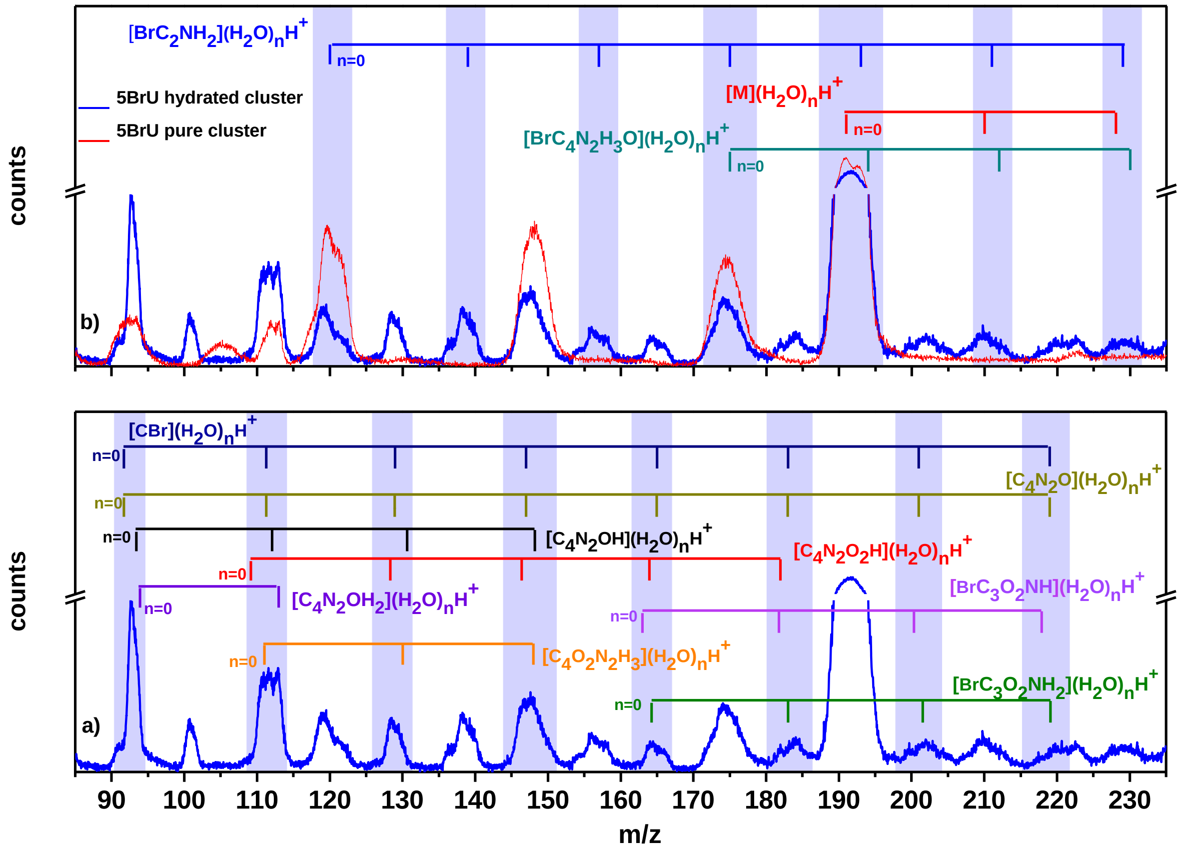

Fig.SI.2 The 36 keV $^{12}C^{4+}$ ion induced mass spectrum of the hydrated (blue) and pure (red) 5BrU clusters in (b) and only hydrated 5BrU clusters in (a) in the m/z region between 85 and 235. The peaks belonging to hydrated series are highlighted in blue in both the spectra. All the hydrated fragments considered in the fit procedure and do not reported in the main article are labelled.

Table SI.1 *Complete list of all the hydrated fragments observed in the mass spectrum of hydrated clusters of 5BrU. The fragments are listed according the series they are assigned to. The protonated species of each fragment considered in the fit procedure are also listed in the table.*

m/z (amu)	**Assignment**
18	**$(H_2O)^+$**
19	$(H_2O)H^+$
37	$(H_2O)_2H^+$
55	$(H_2O)_3H^+$
73	$(H_2O)_4H^+$
91	$(H_2O)_5H^+$
28	**$[HCNH]^+$**
29	$(HCNH)H^+$
47	$(HCNH)\,(H_2O)H^+$
65	$(HCNH)\,(H_2O)_2H^+$
83	$(HCNH)\,(H_2O)_3H^+$
101	$(HCNH)\,(H_2O)_4H^+$
119	$(HCNH)\,(H_2O)_5H^+$
91(93)	**$[CBr]^+$**
92(94)	$(CBr)H^+$
110(112)	$(CBr)\,(H_2O)H^+$
128(130)	$(CBr)\,(H_2O)_2H^+$
146(148)	$(CBr)\,(H_2O)_3H^+$
164(166)	$(CBr)\,(H_2O)_4H^+$
182(184)	$(CBr)\,(H_2O)_5H^+$
200(202)	$(CBr)\,(H_2O)_6H^+$
218(220)	$(CBr)\,(H_2O)_7H^+$
92	**$[C_4N_2O]^+$**
93	$(C_4N_2O)H^+$
111	$(C_4N_2O)\,(H_2O)H^+$
129	$(C_4N_2O)\,(H_2O)_2H^+$
147	$(C_4N_2O)\,(H_2O)_3H^+$
165	$(C_4N_2O)\,(H_2O)_4H^+$
183	$(C_4N_2O)\,(H_2O)_5H^+$
201	$(C_4N_2O)\,(H_2O)_6H^+$
219	$(C_4N_2O)\,(H_2O)_7H^+$
93	**$[C_4N_2OH]^+$**
94	$(C_4N_2OH)H^+$
112	$(C_4N_2OH)\,(H_2O)H^+$
130	$(C_4N_2OH)\,(H_2O)_2H^+$
148	$(C_4N_2OH)\,(H_2O)_3H^+$
94	**$[C_4N_2OH_2]^+$**
95	$(C_4N_2OH_2)H^+$
113	$(C_4N_2OH_2)\,(H_2O)H^+$
109	**$[C_4N_2O_2H]^+$**
110	$(C_4N_2O_2H)H^+$
128	$(C_4N_2O_2H)\,(H_2O)H^+$
146	$(C_4N_2O_2H)\,(H_2O)_2H^+$
164	$(C_4N_2O_2H)\,(H_2O)_3H^+$
182	$(C_4N_2O_2H)\,(H_2O)_4H^+$

m/z (amu)	**Assignment**
110	**$[C_4N_2O_2H_2]^+$**
111	$(C_4N_2O_2H_2)H^+$
129	$(C_4N_2O_2H_2)\,(H_2O)H^+$
147	$(C_4N_2O_2H_2)\,(H_2O)_2H^+$
165	$(C_4N_2O_2H_2)\,(H_2O)_3H^+$
183	$(C_4N_2O_2H_2)\,(H_2O)_4H^+$
201	$(C_4N_2O_2H_2)\,(H_2O)_5H^+$
219	$(C_4N_2O_2H_2)\,(H_2O)_6H^+$
111	**$[C_4N_2O_2H_3]^+$**
112	$(C_4N_2O_2H_3)H^+$
130	$(C_4N_2O_2H_3)\,(H_2O)H^+$
148	$(C_4N_2O_2H_3)\,(H_2O)_2H^+$
147(149)	**$[BrC_3ONH_2]^+$**
148(150)	$(BrC_3ONH_2)H^+$
166(168)	$(BrC_3ONH_2)\,(H_2O)H^+$
184(186)	$(BrC_3ONH_2)\,(H_2O)_2H^+$
202(204)	$(BrC_3ONH_2)\,(H_2O)_3H^+$
162(164)	**$[BrC_3O_2NH]^+$**
163(165)	$(BrC_3O_2NH)H^+$
181(183)	$(BrC_3O_2NH)\,(H_2O)H^+$
199(201)	$(BrC_3O_2NH)\,(H_2O)_2H^+$
217(219)	$(BrC_3O_2NH)\,(H_2O)_3H^+$
163(165)	**$[BrC_3O_2NH_2]^+$**
164(166)	$(BrC_3O_2NH_2)H^+$
182(184)	$(BrC_3O_2NH_2)\,(H_2O)H^+$
200(202)	$(BrC_3O_2NH_2)\,(H_2O)_2H^+$
218(220)	$(BrC_3O_2NH_2)\,(H_2O)_3H^+$
222	**$[D\text{-}2Br]^+$**
223	$[D\text{-}2Br]H^+$
118(120)	**$[BrC_2NH]^+$**
119(121)	$(BrC_2NH)H^+$
137(139)	$(BrC_2NH)\,(H_2O)H^+$
155(157)	$(BrC_2NH)\,(H_2O)_2H^+$
173(175)	$(BrC_2NH)\,(H_2O)_3H^+$
191(193)	$(BrC_2NH)\,(H_2O)_4H^+$
209(211)	$(BrC_2NH)\,(H_2O)_5H^+$
227(229)	$(BrC_2NH)\,(H_2O)_6H^+$
m/z (amu)	**Assignment**
117(119)	**$[BrC_2N]^+$**
118(120)	$(BrC_2N)H^+$
136(138)	$(BrC_2N)\,(H_2O)H^+$
154(156)	$(BrC_2N)\,(H_2O)_2H^+$
172(174)	$(BrC_2N)\,(H_2O)_3H^+$
190(192)	$(BrC_2N)\,(H_2O)_4H^+$

119(121)	**$[BrC_2O]^+$** **$[BrC_2NH_2]^+$**
120(122)	$(BrC_2O)H^+$ $(BrC_2NH_2)H^+$
138(140)	$(BrC_2O)\,(H_2O)H^+$ $(BrC_2NH_2)\,(H_2O)H^+$
156(158)	$(BrC_2O)\,(H_2O)_2H^+$ $(BrC_2NH_2)\,(H_2O)_2H^+$
174(176)	$(BrC_2O)\,(H_2O)_3H^+$ $(BrC_2NH_2)\,(H_2O)_3H^+$
192(194)	$(BrC_2O)\,(H_2O)_4H^+$ $(BrC_2NH_2)\,(H_2O)_4H^+$
210(212)	$(BrC_2O)\,(H_2O)_5H^+$ $(BrC_2NH_2)\,(H_2O)_5H^+$
228(230)	$(BrC_2O)\,(H_2O)_6H^+$ $(BrC_2NH_2)\,(H_2O)_6H^+$
173(175)	**$[BrC_4N_2H_2O]^+$**
174(176)	$(BrC_4N_2H_2O)H^+$
192(194)	$(BrC_4N_2H_2O)\,(H_2O)H^+$
210(212)	$(BrC_4N_2H_2O)\,(H_2O)_2H^+$
228(230)	$(BrC_4N_2H_2O)\,(H_2O)_3H^+$
174(176)	**$[BrC_4N_2H_3O]^+$**
175(177)	$(BrC_4N_2H_3O)H^+$
193(195)	$(BrC_4N_2H_3O)\,(H_2O)H^+$
211(213)	$(BrC_4N_2H_3O)\,(H_2O)_2H^+$
229(231)	$(BrC_4N_2H_3O)\,(H_2O)_3H^+$
190(192)	**M^+**
191(193)	MH^+
209(211)	$M\,(H_2O)H^+$
227(229)	$M\,(H_2O)_2H^+$

1 T. Bergen et al., *Rev. Sci. Instrum.,* 1999, 70, 3244-3253.
2. V. Bernigaud et al., *Publ. Astron. Obs. Belgrade,* 2008, 84, 83-86.
3. U. Zimmermann et al., *Z. Physik. D*, 1994, 31, 85-93.