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Effect of hydrogen isotope

on plasma impedance and thermal pinching

induced by single aerosol droplets injected

into an inductively coupled plasma

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1   **Abstract**

2   The mass of the hydrogen isotope in micrometer-sized aqueous droplets introduced into

3   an ICP has been found to affect the degree of resulting plasma perturbation. Studied

4   plasma perturbations include local plasma cooling, plasma shrinkage due to thermal

5   pinching, and changes in plasma impedance. The local cooling effect caused by a

6   vaporizing aerosol droplet was found to be similar between H_2O and D_2O. This finding

7   is likely a result of the similar heat capacities and vaporization rates of H_2O and D_2O

8   droplets and of the comparable thermal conductivities and dissociation kinetics of H_2O

9   and D_2O vapor. In contrast, a clear isotope effect was observed for plasma shrinkage and

10   impedance change, with H_2O causing a considerably stronger effect. Plasma shrinkage,

11   gauged by the reduction in Ar emission at the edge of the plasma, was detected at all

12   observation heights within the load-coil region, with D_2O droplets causing as much as

13   30% less of an effect than H_2O. Likewise, D_2O droplets induce significantly less change

14   in plasma impedance than H_2O droplets. Depending on experimental conditions and the

15   probing method, changes in plasma impedance caused by monodisperse D_2O droplets

16   were only 52%−80% that of H_2O. The lower influence on plasma shrinkage and

17   impedance change for D_2O droplets is believed to be related to the much lower thermal

18   conductivity of atomic deuterium, around 70% that of atomic hydrogen (protium). The

19   time required for the plasma impedance to return to its original steady-state value was

20   comparatively long (~10 ms) and similar for H_2O and D_2O droplets.

21   **Keywords:**   inductively coupled plasma; aerosol perturbation; monodisperse droplets;

22   plasma pinch; plasma impedance; heavy water

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1

1.   Introduction

Although the inductively coupled plasma (ICP) is now regarded as a common workhorse for elemental analysis and despite many outstanding mechanistic studies that have been reported for processes occurring inside the plasma [1-5], there are still unsettled questions [6, 7].   One such question involves the influence of an introduced aerosol on the properties and behavior of the ICP. In addition, the burgeoning application of the ICP to single-particle analysis [8, 9] requires a better understanding of the interplay among introduced aerosol droplets and solute particles, the various plasma species, as well as energy coupling and flow in the plasma. The introduction of monodisperse droplets into an analytical flame [10, 11] or ICP [12-20], has long been recognized as a powerful means for gaining new insights into fundamental signal-production processes but also provides a useful tool to investigate these questions.

One particularly interesting question is what causes the observed change in plasma impedance and shrinkage of plasma size (thermal pinching) when a single micrometer-sized droplet is introduced into the ICP. We earlier reported a significant shift in plasma impedance when single aerosol droplets of 27 μm (i.e., ~ 10 pL in volume) are sent into the ICP [21]; others noted a shift in the radiofrequency delivered by a free-running generator upon injection of a single droplet into the plasma [22]. More recently, through the use of time-resolved two-dimensional monochromatic imaging, a sequence of plasma perturbations involving local cooling, plasma reheating and thermal pinching during single-droplet introduction was described [23].   The impedance change lasted a comparatively long time (~ 10 ms). Four transition points, based on the derivative (i.e.,

46   rate of change) of the impedance-probe signal, were unambiguously identified and found

47   to correlate qualitatively with particular stages of plasma perturbation [23]. Specifically,

48   the first and last transition points were correlated with the moments when the plasma

49   shrinkage became established and started to ease, respectively [23]. It was hypothesized

50   that plasma shrinkage during droplet introduction was the result of a thermal pinch effect

51   caused by hydrogen liberated from the decomposition of volatilized water. Because the

52   thermal conductivity of atomic hydrogen is over one order of magnitude higher than that

53   of argon [24, 25], the increased thermal conductivity of the bulk plasma accelerates heat

54   loss at the plasma periphery. Consequently, the plasma shrinks in size in response to the

55   increased heat loss.

56   The objective of the present follow-up work is to test the aforementioned hypothesis and

57   to verify the role of liberated hydrogen when a single aerosol droplet is introduced into

58   the ICP. A straightforward way to address this question is to compare the effect of

59   hydrogen (protium) with its isotope – deuterium. Because of the very large fractional

60   difference between the atomic masses of hydrogen and deuterium and the well-known

61   relationship between thermal conductivity of a monatomic gas and reciprocal of the

62   square root of its atomic mass (i.e., mass$^{-\frac{1}{2}}$) [26-28], a large difference would be expected

63   between H_2O and D_2O droplets if the hypothesis is correct that atomic hydrogen is the

64   dominant cause of plasma shrinkage and plasma impedance change. Accordingly,

65   changes in plasma impedance and thermal pinching during injection of single aerosol

66   droplets in the form of H_2O and D_2O were measured and compared.

3

2.   Experimental

The experimental setup (hardware) was identical to that previously described [23], with modifications in experimental conditions and procedures as noted below. The system consisted of an ICP generator, a set of entrance optics, a monochromatic imaging spectrometer equipped with an intensified and gated charged-coupled device (ICCD) detector, a commercial monodisperse microdroplet dispenser, an in-house-built trigger circuit to signal droplet introduction into the plasma, and two separate devices for measurement of any droplet-induced change in plasma impedance. A brief, yet self-contained account of the experimental setup is given below; more detail can be found in our previous publication [23].

2.1   Experimental setup

The ICP system and its operating conditions were common for this type of work [21, 23, 29]. The ICP generator (HFP-2500F, Plasma-Therm, Kresson, NJ, USA) was crystal-controlled at 27.12 MHz and was operated at a forward power of 1200 W. The inner diameter of the torch injector was 1.5 mm, and the torch was vertically mounted. The commercial monodisperse microdroplet dispenser (MD-K-150-010, Microdrop GmbH, Norderstedt, Germany) produced microdroplets with a nominal diameter of 50 μm (i.e., 65 pL). The dispenser was mounted vertically and directly onto the base of the ICP torch *via* a glass ball-joint adaptor, and introduced monodisperse droplets into the ICP at a user-selectable rate set here at 33 Hz. The droplet stream was entrained by a flow of argon and travelled vertically into the ICP. Three central-channel Ar flow rates of 0.155, 0.175 and 0.200 L/min were studied. These central-channel flows are much lower than

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89   those in typical solution nebulization but are common for microdroplet injection without

90   a desolvator [30].

91   A 1-m focal-length Czerny-Turner spectrometer was configured as a monochromatic

92   imaging spectrometer [31, 32].   This arrangement provided two-dimensional

93   monochromatic images of the ICP at selected wavelengths. The spectral bandpass was

94   ~0.8 nm, adequate for the emission lines employed in this work. Each monochromatic

95   image of the plasma was captured by a gated ICCD with its pixels binned in groups of

96   4×4 to give a final 256×256 image [23]. Forty sequential ICCD images were taken, at

97   each studied wavelength, at increasing delay times in steps of 100 μs, referenced to a

98   droplet-introduction event. The gate widths for all ICCD images were held constant at

99   100 μs.

100   The trigger signal for the ICCD was supplied from a photomultiplier tube, with a narrow-

101   bandpass interference filter selective for the H_α emission line (center $\lambda = 656.4$ nm,

102   $\Delta\lambda = 1$ nm, 656FS02-25, Andover Corp., Salem, NH, USA) placed in front of the

103   photocathode window. Because of its construction, this signal is termed H_α-PMT,

104   independent of the emission from the actual hydrogen isotopes (i.e., H or D) that was

105   measured. This emission was collected between the lowest and middle turns of the load

106   coil. The trigger signal actually fires several hundred microseconds before the intact

107   droplet enters into the plasma because solvent evaporation starts when the droplet leaves

108   the capillary of the droplet dispenser, and water vapor accelerates faster thus reaches the

109   plasma earlier than the droplet.

110   Two methods, both indirect, were used to gauge plasma impedance. The first was

111   through the voltage induced in a RF-probe coil placed inside the plasma-torch

112   compartment. The second means was through the signal from the phase detector of the

113   impedance-matching network of the ICP instrument. Signals from the RF-probe coil, the

114   phase detector, and the H$_\alpha$-PMT (i.e., the trigger) were simultaneously measured and

115   digitized by a multi-channel digital oscilloscope and saved for further processing.

116   **2.2   Experimental procedures and data processing**

117   Two samples were used in this work – deionized water and heavy water (deuterium oxide,

118   99 atom %D, Sigma-Aldrich, St. Louis, Missouri, USA). A spike of barium standard,

119   from a stock solution at a concentration of 100 mg/L prepared in 2% HNO$_3$ (ordinary

120   water), was doped into both the deionized and heavy-water samples to give a final

121   concentration of 2 mg/L Ba in each. For brevity, these two samples are referred to as

122   H$_2$O and D$_2$O in this study.

123   In one experiment involving separate introduction of H$_2$O and D$_2$O droplets, a set of three

124   images were obtained at wavelengths corresponding to emission of the Ba analyte (Ba II

125   at 455.4 nm), hydrogen (H I at 656.3 nm or D I at 656.1 nm), and argon (Ar I at

126   696.5 nm). The integrated exposure time for each ICCD image was 5 s (i.e., introduction

127   of 165 single droplets). Steady-state plasma background emission was corrected by

128   subtraction of an ICCD image taken with the same settings, but at a delay time of 25 ms,

129   well after any perturbation caused by a droplet event has dissipated.

3.   Results and Discussion

3.1   The effect of hydrogen isotope on plasma impedance during single-droplet introduction

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133   Figure 1 shows the temporal behavior of signals from the H_α-PMT, the RF-probe coil and

134   the phase-detector during repetitive introduction of single droplets into the ICP.   The

135   displayed temporal profiles are the averages of five oscilloscope traces, each comprising

136   the averaged responses from 1280 single-droplet introduction events.   As in our previous

137   studies [21, 23], the RF-probe coil and phase-detector signals were measured in ac-

138   coupling and dc-coupling modes, respectively.   For both isotopic forms of hydrogen –

139   protium and deuterium – in the introduced droplets, large excursions in plasma

140   impedance occurred, as reflected in the significant changes in RF-probe coil and phase-

141   detector signals.   However, D_2O droplets induced a clearly smaller change in plasma

142   impedance than H_2O.   Quantitatively, the peak height in the change of the RF-probe coil

143   signal for D_2O droplets was about 64% of that for H_2O.   Likewise, the dip in the phase

144   detector signal for D_2O was about 80% of that for H_2O.

145   It is, of course, essential to determine that this difference is not due to an artifact.   We

146   earlier found [21] that both the RF-probe coil and phase-detector signal peaks are lower

147   for smaller droplets.   Accordingly, it is important to confirm that the D_2O and H_2O

148   droplets are the same size when they reach the base of the plasma.   For this evaluation, it

149   is tempting to use the H_α-PMT signal as a measure of droplet size; indeed, a quantitative

150   relationship between the two was assumed in our previous study [21].   However, this

151   proportionality might not hold for a comparison of H_2O and D_2O droplets because of a

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152   difference in transmission efficiency of the interference filter employed in the H_α-PMT

153   detection channel. First, the spectral bandpass of the H_α interference filter is 1 nm, and

154   the isotopic shift between the H_α (656.283 nm [33]) and D_α (656.093 nm [33]) lines is

155   0.19 nm. Although the half width of the heavily Stark-broadened H_α line is still only

156   around 0.1 to 0.2 nm [34], it is likely that not all of the H_α spectral profile can pass

157   through the H_α filter and also that the filter has dissimilar efficiencies for transmitting the

158   H_α and D_α emission lines. Second, for an interference filter to function properly, the

159   incoming beam needs to be collimated and to fall at normal incidence onto the filter

160   surface. If the incoming beam impinges at an angle onto the filter (i.e., tilted), the central

161   bandpass of the interference filter shifts to shorter wavelengths [35]. Because the original

162   intended purpose of the H_α-PMT signal was to generate a trigger signal, no collimating

163   optics was used in light collection. Instead, as previously outlined [21, 29], the collected

164   plasma emission was only partially collimated by passing it through a ~ 20 cm black-

165   painted glass tube with an internal diameter of 3 mm. As a result, it is plausible that our

166   H_α filter–PMT assembly favors the D_α line, which emits at a shorter wavelength [33].

167   Furthermore, the ion-dynamic effect is not the same for H and D because of the

168   substantial difference in reduced mass of the radiator (H or D)–perturber (presumably Ar^+)

169   system [36, 37]. As such, Stark profiles for H and D are also different. Compared to H_α,

170   reductions in Stark width (and hence increases in peak height) between 10% and 15% for

171   D_α have been experimentally reported [36, 38, 39] and calculated [36, 38, 40] for electron

172   densities and temperatures typical of an analytical ICP. Thus, although we consistently

173   observed stronger PMT signals from the D_2O samples, we are reluctant to interpret the

174   H_α and D_α signals quantitatively.

175   Because it is experimentally difficult to measure the size of droplets immediately before

176   they enter the plasma, we offer two arguments that D_2O droplets are *not* smaller than

177   their H_2O counterparts. The first argument is based on literature results involving droplet

178   production and evaporation, and the second is from acquired ICCD images to be

179   presented in the next section. The outcome is that the observed smaller change in plasma

180   impedance for D_2O droplets is real and not due to smaller droplet sizes.

181   In the literature, Lazar and Farnsworth [17] evaluated the influence of the physical

182   properties of liquids on droplet production by a pizeoelectric-based micropump similar to

183   the one used in the present study. Their (and our) micropump employs a glass tube with

184   a restriction at the inlet and surrounded by a pizeoceramic sleeve [12, 17]. When the

185   pizeoceramic is energized, a compression pulse squeezes the glass tube and expels a

186   droplet [17]. The restriction at the tube inlet reduces the backflow of liquid and

187   strengthens droplet ejection at the exit. The viscosity of the liquid governs the amount of

188   backflow through the restriction during the compressive pulse [17]; the lower the

189   viscosity, the greater the backflow, and the smaller the droplet size at the tip of the

190   micropump [17]. Lazar and Farnsworth [17] found a linear correlation between the

191   droplet volume and viscosity of water, methanol and xylene. Accordingly, the

192   volumetric ratio of D_2O to H_2O at the exit of our droplet dispenser can be estimated from

193   the corresponding ratio of the viscosities. The viscosities of D_2O and H_2O are 1.247 [41]

194   and 1.002 [42] mPa s at 20°C (i.e., a ratio of 1.24) and are 0.972 [41] and

195   0.797 [42] mPa s, respectively, at 30°C (i.e., a ratio of 1.22). Therefore, according to the

196   viscosity argument, D_2O droplets are expected to be about 20% *larger* in volume (or 7%

197   larger in diameter) than H_2O droplets. This difference is opposite from what would be

198   necessary for the observed effect on plasma impedance.

199   Even if the D_2O and H_2O droplets are initially of identical size, they might evaporate at

200   dissimilar rates. Only if the evaporation rate of D_2O is not higher than that of H_2O can

201   we persuasively argue that D_2O droplets are *not* smaller than those of H_2O when they

202   enter the plasma. The boiling point of D_2O is 101.4°C, slightly higher than that of H_2O.

203   From room temperature to their boiling points, the vapor pressure of H_2O is always

204   slightly higher than D_2O, by an amount between 17% (at room temperature) and 6% (at

205   the boiling point) [43]. From the viewpoint of vapor pressure, it is *not* expected that D_2O

206   droplets evaporate faster than H_2O droplets during their journey from the dispenser to the

207   plasma; nor, therefore, are D_2O droplets likely to be smaller than those of H_2O.

208   Of course, droplet evaporation inside the ICP injector is likely not in vaporization

209   equilibrium, so evaporation kinetics need to be considered.   The evaporation rates of

210   H_2O and D_2O droplets with diameters of 12 to 15 μm at temperatures between 3.6°C and

211   50.7°C injected into vacuum have been experimentally determined and were reported to

212   be nearly identical [44]. This finding agrees with a theoretical model based on competing

213   energetic and entropic effects [44]. Therefore, from arguments in the literature, we can

214   be confident that D_2O droplets are *not* smaller than those of H_2O when they enter the

215   plasma. An experimental inference is presented in the next section.

3.2 Monochromatic emission images of H and Ba showing height of complete droplet evaporation and initial solute-particle atomization

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218   Representative monochromatic emission images show that the heights of complete

219   vaporization of droplets from H_2O and D_2O are essentially identical, with a temporal

220   difference less than the exposure time of a single ICCD image frame (i.e., 100 µs).

221   Furthermore, through doping the droplets with Ba, it was found that the time for the first

222   appearance of Ba emission as well as the integrated Ba emission for H_2O and D_2O

223   droplets was indistinguishable. In all cases, the measured difference is not significant

224   compared to experimental uncertainties. If anything, evaporation of D_2O droplets is

225   marginally slower than H_2O droplets, suggesting that the D_2O droplets might be

226   marginally larger in size than those of H_2O.

227   Figure 2a shows the net (i.e., after background correction with an image taken at steady

228   state) monochromatic images, with a time stamp of 1.55 ms after the H_α-PMT trigger,

229   during single-droplet introduction into the plasma at H_α 656.3 nm and D_α 656.1 nm. The

230   exposure time of the ICCD was 100 µs, starting from 1.50 ms to 1.60 ms with respect to

231   the trigger. The scales marked on the *x*- and *y*-axes of the images represent the physical

232   size of the plasma. As detailed in several previous publications [23, 45, 46], because of

233   an optical artifact in the monochromatic imaging spectrometer, the vertical and horizontal

234   scales of the images are not identical but are correctable. Because a vaporizing droplet

235   serves as a local reservoir supplying hydrogen or deuterium atoms, the localized emission

236   in the image center (i.e., the red dot) pinpoints the location of the vaporizing droplet.

237   Also, as has been reported previously [23, 30], atomic hydrogen quickly diffuses

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238   throughout the whole plasma.   The positions of the hydrogen and deuterium atomic

239   clouds were at similar locations in the plasma – just above the second turn of the load coil,

240   counting from the bottom. A comparison of the two images reveals that the localized D_α

241   emission is stronger than that of H_α, suggesting that it took slightly longer for the D_2O

242   droplet to complete its evaporation in the plasma. In fact, the displayed H_α image is the

243   last one in the series in which a localized hydrogen emission cloud could be distinctly

244   identified.   In the subsequent ICCD image frame, with a time stamp of 1.65 ms (cf.

245   Figure 2b), no localized H_α emission could be seen although localized D_α emission was

246   still present.

247   Figure 3 displays net monochromatic images of Ba II 455.4 nm emission 1.65 ms after

248   the H_α trigger during H_2O and D_2O droplet introduction. This is the first frame in which

249   a distinct Ba emission cloud could be observed for either H_2O or D_2O; the images taken

250   at 1.55 ms (i.e., same time stamp as in Figure 2a, not shown) revealed no Ba emission.

251   Thus, although the last identifiable H_α and D_α emission clouds appeared respectively at

252   1.55 and 1.65 ms, the time lag between complete droplet evaporation for the H_2O and

253   D_2O was likely less than 100 μs, since the first appearance of analyte emission was at

254   1.65 ms in both cases.   The fact that D_α emission (cf. Figure 2b) and Ba II emission

255   clouds appeared simultaneously in the same ICCD frame with a gate width of only

256   100 μs clearly argues that the processes of analyte atomization, ionization and excitation

257   after complete solvent evaporation are very fast, in agreement with a previous report [14].

258   From the vertical time-dependent centroid of the H_α and D_α emission clouds, one can

259   readily follow the acceleration of the H_2O and D_2O droplets in the plasma (cf. Figure 4).

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260 This acceleration can be well represented by a quadratic function. The behavior in

261 Figure 4 is phenomenologically similar to that found in a chemical flame. Russo and

262 Hieftje [47] introduced monodisperse droplets of 68 μm diameter side-on into a chemical

263 flame and measured the vertical distance of the droplet in the flame as a function of its

264 residence time. Although a model of higher order (fourth order polynomial) was used

265 [47], the vertical height of the droplet in the flame can be adequately approximated with a

266 quadratic function. The bands in Figure 4 designated by horizontal dotted lines from -1.2

267 to -2.2 mm, from -7.5 to -8.5 mm, and from -13.8 to -14.8 mm denote three vertical

268 locations that will be discussed in detail in Section 3.4.

269 Spatial integration of emission from the Ba ion cloud (cf. Figure 3) could provide

270 additional insight into the relative sizes of the H_2O and D_2O droplets. To a first

271 approximation, if one assumes that the excitation environment is identical between H_2O

272 and D_2O droplet injection, the Ba emission will be directly proportional to the analyte

273 mass, which in turn is directly proportional to the initial droplet volume. Figure 5

274 displays the spatially integrated Ba emission with a window that runs laterally

275 between -2 mm and +2 mm of the plasma center and vertically from -9.73 mm to

276 +0.70 mm (i.e., all heights above the middle load coil, cf. Figure 3) at different delay

277 times. The small dip at ~1.4 ms before the appearance of the Ba emission spike is due to

278 local plasma cooling from the vaporizing droplet, causing a momentary drop in the

279 plasma continuum emission. The dip at ~1.9 ms is caused by part of the Ba emission

280 cloud being obscured by the load coil. Although the two Ba temporal profiles do not

281 overlap exactly, they are very close in shape and amplitude. In fact, if one further

282 integrates the temporal emission from 16 to 24 ms (i.e., from the time when Ba emission

13

283 started to when the Ba ion cloud moved out of the captured-image range), the difference

284 in the Ba emission between H_2O and D_2O droplets is smaller than the baseline noise (i.e.,

285 statistically insignificant).

286 Based on the experimental results discussed above, we are confident that the introduced

287 H_2O and D_2O droplets are very similar in size, and if there is a marginal difference, the

288 D_2O droplets could be slightly larger, but definitely *not* smaller than their H_2O

289 counterparts. This finding is critical, because as will be shown, plasma perturbations

290 induced by D_2O droplets are decidedly smaller than those by H_2O droplets.

291 **3.3   Monochromatic emission images of Ar showing plasma shrinkage**

292 Figure 6a shows the net absolute change in Ar I 696.5 nm emission during single-droplet

293 introduction. The time stamp for Figure 6a is 1.55 ms after the H_α-PMT trigger (same as

294 in Figure 2a). In this case, the droplet-induced change in Ar emission appears similar for

295 H_2O and D_2O. The most dramatic observation is the local cooling effect generated by the

296 droplets, which causes a substantial drop in argon emission in the center of the images.

297 In addition, H_2O and D_2O droplets both produce a sharp decline in Ar emission along the

298 two sides of the plasma. This plasma shrinkage is believed to be the result of thermal

299 pinching [48] due to a difference in thermal conductivity between the plasma gas (argon)

300 and the introduced foreign gas (in this case, the H_2O and D_2O droplets and/or their

301 dissociation products). The thermal pinching is not symmetrical, with a more prominent

302 effect found on the left side of the plasma images. As noted in our previous report [23],

303 the helical-shaped load coil likely causes the plasma asymmetry, especially within the

14

304   load-coil region. In addition, the curvature of the plasma torch tubing could induce

305   optical distortion in the collected plasma image, especially along the two sides [23].

306   Although the net change in Ar emission for H_2O and D_2O droplets appears similar in

307   Figure 6a, a considerable difference can be noted if the change is expressed as a

308   percentage (cf. Figure 6b). Here, percentage change in emission refers to the net change

309   (i.e., after subtraction of steady-state emission) relative to the steady-state emission. The

310   local cooling effect (i.e., the decrease in Ar emission close to the center of the image) is

311   similar for H_2O and D_2O whereas H_2O was found to induce a noticeably stronger plasma

312   pinching effect than D_2O; the percentage reduction in Ar emission, in particular on the

313   left edge of the plasma, is larger for H_2O. If one defines a threshold of 10% drop in Ar

314   emission to assess the degree of plasma shrinkage, the estimated size reduction was

315   2.3 mm and 1.8 mm, respectively, on the left side of the plasma for the introduction of

316   H_2O and D_2O droplets. The corresponding size decreases on the right side of the plasma

317   were 1.5 mm and 1.1 mm for H_2O and D_2O, respectively.

318   **3.4   Temporo-spatial change in Ar emission during single-droplet introduction**

319   In this section, the temporo-spatial change in relative argon emission upon H_2O and D_2O

320   droplet introduction will be compared. As already depicted in Figure 6b, two regions of

321   the plasma, its center and edge, are particularly affected by the droplets. Accordingly, the

322   average change in Ar emission within a radius of 0.9 mm of the plasma center and also in

323   a region within 0.8 mm from the left-hand edge of the plasma was calculated at three

324   vertical ±0.5 mm-high windows, centered at -14.3, -8.0, and -1.7 mm with reference to

325   the top of the load coil.

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326   Figure 7a shows the droplet-induced fractional change in Ar emission close to the bottom

327   of the load coil at a vertical height of -14.3 mm with reference to the top of the load coil.

328   In the center of the plasma, a similar change in Ar emission was observed for H_2O and

329   D_2O droplets, indicating that the local cooling effect caused by the droplet is independent

330   of the identity of the hydrogen isotope. There was a slight delay between the time when

331   the droplets were present within the observation volume and the moment when the

332   greatest Ar depression occurred. As noted in Figure 4, the droplet velocity was

333   comparatively low in the bottom part of the load coil and the droplet virtually stayed at

334   this observation height from about 0.45 to 0.65 ms whereas the maximum dip in Ar

335   emission occurred later, from 0.65 to 0.95 ms. At the left edge of the plasma, a more

336   pronounced depression in Ar emission was found, induced by plasma shrinkage. The

337   maximum percentage drop in Ar emission was ~12% at the edge, compared to ~7% in the

338   plasma center. Furthermore, the plasma shrinkage, as reflected by the percentage drop in

339   Ar emission at the edge, is sensitive to the isotopic form of hydrogen in the droplets. A

340   lesser effect, roughly by a factor of one-third, was observed with the D_2O droplets.

341   Moreover, the maximum plasma shrinkage happened around 1.0 to 1.5 ms, a time by

342   which the droplet had already moved quite far above the observation height (cf. Figure 4).

343   The cause for this significant delay was not determined, but could be due to the finite

344   transport time of the species (presumably atomic hydrogen or deuterium) responsible for

345   the plasma shrinkage, likely through recirculation, from the plasma center to its periphery.

346   The percentage change in Ar emission in the middle of the load-coil region (-8.0 mm) is

347   illustrated in Figure 7b. Similar to the case at -14.3 mm (cf. Figure 7a), H_2O and D_2O

348   droplets induced the same extent of local cooling in the plasma center. In addition, the

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349 percentage drop in Ar emission in the plasma center is very comparable at the two

350 heights (~7 to 8%), despite the fact that the droplet is certainly becoming smaller during

351 its upward passage in the ICP. Similar unexpected observations have been reported

352 elsewhere [23]. It took roughly ~1.6 ms, with reference to the H_α trigger (cf. Figure 4),

353 for the droplets to reach this vertical region of the plasma, which coincides with the time

354 of the maximum dip in Ar emission in the plasma center (cf. Figure 7b). At the edge of

355 the plasma, the hydrogen isotope effect again is apparent, with the influence of D_2O

356 droplets significantly weaker than that of the H_2O droplets. The maximum decrease in

357 Ar emission at the edge is ~16%, larger than the ~12% decrease at -14.3 mm.

358 Figure 7c shows the change in Ar emission even higher, in the upper part of the load-coil

359 region at an observation height centered at -1.7 mm. In the center of the plasma, here as

360 at other heights, the decline in Ar emission is similar for H_2O and D_2O droplets.

361 However, compared to lower positions (cf. Figures 7a and 7b) in which the drops in Ar

362 emission are about 7 to 8%, the dips here are only about 5%. The reduced effect is likely

363 because the droplets are completely vaporized at this vertical height (cf. Figure 4), so any

364 cooling effect is no longer created locally but is carried from upstream locations (lower

365 positions in the plasma) by the argon gas flow and is therefore diluted. The greatest dips

366 were at 1.55 ms and 1.95 ms, respectively, for observations at -8.0 mm and -1.7 mm,

367 giving an averaged velocity of about 16 m/s, which is about right for the linear gas

368 velocity in the upper part of the load-coil region [49, 50]. As reflected by the change in

369 Ar emission at the edge of the plasma, the plasma shrinkage effect continues to climb

370 from the bottom to the top of the load coil. Even at 0.6 ms, when the droplets are still

371 within the bottom part of the load coil (cf. Figure 4), plasma shrinkage at higher locations

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372   could unambiguously be detected, suggesting rapid diffusion of the effect throughout the

373   plasma. Generally speaking, whenever plasma shrinkage is clearly detected, the effect

374   induced by H_2O droplets is larger than that by D_2O droplets, although the difference was

375   smaller compared to the behavior in lower regions of the load coil (cf. Figures 7a and 7b).

376   **3.5   Rate of change of plasma impedance**

377   Sections 3.1 and 3.4 compared changes in plasma impedance and plasma shrinkage that

378   resulted when monodisperse H_2O and D_2O droplets were introduced into the plasma. The

379   present section examines the rate of change in plasma impedance, which better reflects

380   the kinetics of whatever process causes the changes. Figure 8a displays the rate of

381   change (first derivative) of the RF-probe and phase-detector signals (collectively termed

382   plasma-impedance signals) as a function of time upon H_2O and D_2O droplet introduction.

383   Because the absolute changes in plasma impedance signals are smaller for D_2O droplets,

384   the rate of change for D_2O is also lower. In addition, slight delays were observed

385   between the temporal profiles of H_2O and D_2O. For instance, the minimum in the first

386   derivative for the phase-detector signal occurred at 0.63 and 0.83 ms, respectively, for

387   H_2O and D_2O. Likewise, the phase-detector signals reached their respective minimum

388   (i.e., when derivatives equal zero) at 1.61 ms for H_2O and 1.75 ms for D_2O. The RF-

389   probe signals exhibited slightly longer delays due to the slower circuit response [21, 23],

390   but yielded the same conclusion. Because the phase-detector circuit offered wider

391   bandwidth and hence better temporal accuracy and resolution, the phase-detector signal

392   was used as the primary reference to pinpoint the temporal change in plasma impedance.

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393   The bandwidths of the RF-probe coil and phase-detector circuits were previously

394   determined to be 1,300 and 15,000 Hz, respectively [21].

395   Apart from the slight delay between the responses for H_2O and D_2O (i.e., slight

396   horizontal shift in the time axis), the overall shapes of the temporal profiles for the rate of

397   change are similar, which is even more apparent if the temporal profiles of the plasma-

398   impedance signals are normalized before their derivatives are taken (cf. Figure 8b).

399   Notice that decay of the droplet-induced effect on plasma impedance is similar for H_2O

400   and D_2O and that it takes a comparatively long time (~10 ms) for the plasma impedance

401   to return to its steady-state value for both. The similar restoration time for H_2O and D_2O

402   supports our previous hypothesis [23] that to re-establish the energy-coupling equilibrium,

403   not only must hydrogen (protium or deuterium) be completely flushed from the system

404   but also the temperature distribution among plasma species needs to be restored. It is

405   reasonable that complete flushing and replacement of protium or deuterium takes a

406   similar length of time. Furthermore, slow thermal diffusion and ambipolar diffusion [51]

407   constitute the rate-limiting step for temperature redistribution in the ICP. As a result, the

408   time taken for the plasma impedance to return to its steady-state value is independent of

409   the isotopic form of hydrogen in the introduced water droplets.

410   In our previous study [23], we identified four important transitions in the droplet-induced

411   plasma-impedance change, which were further found to correlate with distinct stages of

412   plasma perturbation. The four transition points are evidenced by either a change of sign

413   or slope in the rate of change of the phase-detector signals. The present experiment

414   revealed one distinctly different condition from our previous report [23]. In that earlier

415   work, the droplet did not undergo complete evaporation in the load-coil region and we

416   observed localized H atomic and OH molecular emission continuously travelling upward

417   from -15 mm to +1 mm in height (referenced to the top of the load coil) in the captured

418   monochromatic images [23]. In contrast, in the present study, complete solvent

419   evaporation was accomplished around midway within the load coil region.

420   The use of conditions so that droplet vaporization was complete within the load coil

421   region was intentional here for two reasons. First, if droplet evaporation is not complete,

422   it would be difficult to gauge the relative sizes of the H_2O and D_2O droplets. Only if the

423   hydrogen emission cloud disappeared and the analyte cloud emerged at the same height

424   for H_2O and D_2O droplets, can one assess the relative sizes of the two aerosols. An

425   added complication of incomplete evaporation is that it would then be difficult to gauge

426   the relative amount of protium and deuterium released in the load-coil region by the H_2O

427   and D_2O droplets, respectively. Consequently, it would be difficult to compare the

428   change in plasma impedance and plasma shrinkage induced by H_2O and D_2O droplet

429   introduction, as it would have been impossible to rule out the possibility of different

430   amounts of hydrogen being released in the load-coil region. Second, if complete

431   evaporation occurs inside the load-coil region, one can validate the previously observed

432   correlation between transition points and different stages of plasma perturbation and

433   provide additional experimental basis to revise the correlation, if needed.

434   The first transition point (arrow I in Figure 8) occurs when the phase-detector signal

435   shows its maximum rate of change; this point occurs at the trough of the first derivative

436   because the phase-detector signal moves negative when the plasma is perturbed by an

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437   aerosol droplet. The first transition points were around 0.63 and 0.73 ms for H_2O and

438   D_2O droplets, respectively (cf. Figure 8b). The first transition point was previously found

439   [23] to correspond to the moment when the thermal pinch and plasma shrinkage became

440   established in the load-coil region of the plasma. Figure 7c supports this observation;

441   argon emission clearly drops at the edge of the plasma (i.e., thermal pinch and plasma

442   shrinkage) at ~0.7 ms. Therefore, the same conclusion applies in the present case in

443   which droplet evaporation is complete within the load coil region.

444   The second transition point (arrow II in Figure 8) is defined as the instant when the

445   induced change in phase-detector signal is at its maximum (i.e., zero derivative), which

446   occurred at 1.61 and 1.75 ms for H_2O and D_2O droplets, respectively (cf. Figure 8b).

447   This transition point corresponds to the time when the microdroplet was close to the

448   center of the load-coil region (cf. Figure 4), in excellent agreement with previous findings

449   [23].

450   The third transition (arrow III in Figure 8) happens when the rate of change in phase-

451   detector signal attains its maximum in the direction opposite to that of the first transition,

452   and before it begins to return to the baseline [23]. For H_2O and D_2O droplets, the third

453   transition arose at ~2.0 and ~2.4 ms, respectively. In our previous work [23], this

454   transition was found to correlate with the time when the droplet moved out of the load-

455   coil region. Clearly, this interpretation needs to be revised here because the droplets were

456   completely vaporized within the load coil. From Figure 7c, the reduced Ar emission in

457   the plasma center exhibited sharp recoil from 2.0 to 2.4 ms. Therefore, it is reasonable to

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458 revise our interpretation of the third transition as the time when the localized cooling

459 effect of a droplet in the plasma center moves out of the load-coil region.

460 The fourth transition (arrow IV in Figure 8) arises when the rate of change in phase-

461 detector signal begins to asymptotically approach its original, unperturbed level [23]. It

462 was previously reported [23] that plasma shrinkage started to ease near the fourth

463 transition. In the present study, this transition occurred around 4.8 ms for both H_2O and

464 D_2O droplets. Although no monochromatic image was taken after 4 ms in the present

465 study, the H_α-PMT signal sheds some light on this transition point. Comparing Figures 1

466 and 8b, one can see that the fourth transition point coincides with the time when the H_α-

467 PMT signal approaches a horizontal line. Although it had not been explicitly pointed out,

468 a similar correlation between the final transition points of the phase-detector and H_α-

469 PMT signals also existed in our previous work [23]. Therefore, the decay of the H_α-PMT

470 signals should serve as an effective indicator for recovery of the plasma to its steady-state

471 conditions. This hypothesis is reasonable if one assumes that the plasma shrinkage and

472 change in impedance are caused by atomic hydrogen present in the plasma.

473 **3.6   Repeatability of change in plasma impedance**

474 In our experiments, changing between H_2O and D_2O involves removing and re-installing

475 the monodisperse droplet generator from the base of the plasma torch. As a result, it was

476 always a concern whether an observed change in plasma impedance between H_2O and

477 D_2O might be an artifact caused by different mounting positions of the droplet generator.

478 This concern arose because the Farnsworth group [17, 19] reported that in their

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479   experience with the MDMI (monodisperse dried microparticulate injector), which can be

480   viewed as a monodisperse droplet generator coupled to a laminar-flow oven, the

481   measurement results were very sensitive to the positioning of the micropump at the base

482   of the oven. Specifically, removal and reinsertion of the pump could cause significant

483   changes in the position of the droplet stream with respect to the plasma [19]. Our present

484   experimental setup differed from the MDMI work in the way that the droplet dispenser

485   (micropump) was directly mounted onto the base of the ICP torch and that no oven was

486   involved. Our arrangement, without an oven, significantly reduces the travel distance for

487   the droplet, and we did not observe a noteworthy change in signal response when the

488   micropump was removed and reinstalled on the ICP torch. Nevertheless, an experiment

489   was performed to evaluate the effect on our results of removing the micropump, changing

490   the solution from H_2O to D_2O and vice versa, and reinstalling the micropump.

491   Figures 9a and 9b show the change in RF-probe and phase-detector signals, respectively,

492   for four sample-switch cycles. Each temporal trace represents the average of 512

493   individual droplet-introduction events. For each sample (H_2O or D_2O), clear differences

494   exist in the amplitude of the temporal profiles of plasma impedance, which could result

495   from either an irreproducibility in the micropump position or a drift in plasma conditions.

496   For reasons given in the next paragraph, the variation is more likely caused by drift.

497   Regardless, the key feature in Figures 9a and 9b is that the several traces for either H_2O

498   or D_2O are more similar to each other than to the traces from the other sample type.

499   Clearly, H_2O droplets induce a larger change in plasma impedance than D_2O.

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500 Two experiments were performed with the sequence of micropump removal, sample

501 change and micropump re-installation after each measurement; a third experiment did not

502 involve any sample change and micropump removal during the five repetitive

503 measurements of the plasma impedance signals. Table 1 compiles ratios of the change in

504 RF-probe and phase-detector signals for D_2O to those for H_2O samples. Clearly, D_2O

505 induces a significantly and consistently smaller change in plasma impedance than H_2O.

506 Specifically, the range is about 0.52 to 0.80, depending on the experimental conditions

507 and the probing method. The quoted uncertainties in Table 1 represent the standard

508 deviations obtained through error propagation between the several measurements taken

509 with H_2O and D_2O samples. Because the measurement uncertainties were similar for all

510 three experiments, it is likely that the observed irreproducibility was caused by drift in

511 the plasma rather than by a change in micropump position during its removal and re-

512 installation. Further, the three experiments whose results are presented in Table 1 were

513 performed under slightly different conditions so that droplet evaporation was incomplete,

514 complete near the top of the load coil, or complete midway in the load-coil region.

515 Overall, the ratios are comparable, suggesting that the smaller plasma-impedance change

516 induced by D_2O droplets than H_2O droplets is a general observation not related to the

517 position of complete droplet evaporation.

518 **3.7   Species responsible for plasma shrinkage and change in plasma impedance**

519 From the foregoing discussion, it is unambiguous that the impact from introduction of

520 H_2O droplets is considerably larger than that from D_2O. Such a difference is not

521 surprising. Plasma shrinkage has been widely reported in situations when a foreign

522 substance (e.g., organic solvent [48, 52] or molecular gas [25, 53-55]) is introduced into

523 the plasma. Because such substances have a higher thermal conductivity than the plasma

524 gas (argon), it is reasonable to link plasma shrinkage and impedance change observed

525 here to the species that are known to have the highest thermal conductivity: atomic

526 hydrogen [56], from decomposition of water. Conveniently, atomic hydrogen (protium

527 or deuterium) is monatomic, so the thermal conductivity of the two isotopes can be

528 readily compared since they vary as mass$^{-\frac{1}{2}}$ [26-28]. This means that thermal

529 conductivity of atomic deuterium is about 71% of that of atomic protium, which agrees

530 well with the ratios of the change in plasma impedance induced by D_2O to H_2O droplets

531 (cf. Table 1). Although this correlation is strong, the present experiment provides only

532 indirect support that atomic hydrogen is the species mainly responsible for the strong

533 thermal pinch and change in plasma impedance. Accordingly, we should consider and

534 eliminate other possibilities as much as possible in order to establish greater confidence

535 in assigning the role of atomic hydrogen.

536 The first possibility to be considered is the thermal conductivity of H_2O and D_2O

537 molecules. After all, the thermal conductivities of gaseous H_2O and D_2O are also higher

538 than that of argon. For example, the thermal conductivities of gaseous D_2O and Ar at

539 2500 K are, respectively, 0.31 [57] and 0.08 [58] W m^{-1} K^{-1}. However, the thermal

540 conductivity ratios of D_2O to H_2O are very close to unity and range only from 0.95 to

541 1.05, depending on temperature [57, 59]. For polyatomic molecules such as H_2O and

542 D_2O, thermal conductivity can no longer can be approximated by the mass$^{-\frac{1}{2}}$ relationship

543 as the internal energy-storage modes of the molecule also play an important role [60].

544 Because the difference in thermal conductivities between H_2O and D_2O is only a few

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545 percent, it is unlikely that thermal conductivity of the intact molecules would cause a

546 change in plasma impedance as large as observed.

547 Another possible alternative explanation is a difference in the decomposition kinetics of

548 H_2O and D_2O. If the dissociation kinetics are very different, the dissimilar release rates

549 of atomic H and D into the plasma would make data interpretation difficult. The

550 decomposition kinetics of H_2O and D_2O were studied in an argon environment at a

551 temperature of 5000 K and no difference was found within experimental error [61].

552 Therefore, it seems that the thermal pinching effect and the large difference in plasma

553 response to H_2O and D_2O droplet introduction is most confidently attributable to atomic

554 hydrogen released from decomposition of water.

555 **4. Conclusion**

556 The introduction of a single micrometer-sized water droplet causes a significant

557 perturbation in an ICP. By means of the isotope effect, specifically through the

558 introduction of single H_2O and D_2O droplets, the role of hydrogen in plasma

559 perturbations was clarified. Specific perturbations explored here include local plasma

560 cooling, plasma shrinkage due to thermal pinching, and changes in plasma impedance.

561 Several specific conclusions arise from the study. First, based on both theoretical

562 arguments and experimental inference, H_2O and D_2O droplets produced by a piezo-

563 electric-based on-demand monodisperse droplet generator are very similar in size; the

564 D_2O droplets might be marginally larger, but definitely are *not* smaller than those of H_2O.

565 Second, a strong isotope effect was experimentally confirmed in governing the extent of

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566   plasma shrinkage and changes in plasma impedance. In all cases, D_2O droplets induce

567   significantly less plasma shrinkage and a smaller shift in plasma impedance.

568   Quantitatively, changes in plasma-impedance signals caused by D_2O droplet introduction

569   ranged from 52% to 80% of those generated by their H_2O counterparts. As the thermal

570   conductivity of deuterium is only about 70% of that for atomic hydrogen (protium),

571   atomic hydrogen is believed to play an important role in the thermal-pinch effect in the

572   plasma. In marked contrast, no isotope effect was found in the local cooling caused by an

573   evaporating droplet. Third, decay of the droplet-induced effect on plasma impedance was

574   similar for H_2O and D_2O and it takes a comparatively long time (~10 ms) for the plasma

575   impedance to return to its steady-state value for both.

576   As was reported in our earlier study [23], the droplet-induced change in plasma

577   impedance correlates qualitatively with four specific stages of plasma perturbation. This

578   correlation was confirmed in the present study even though, here, complete vaporization

579   of the droplet occurred in the middle of the load coil.

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744 Table 1 Ratio of the change in RF-probe and phase-detector signals induced by

745 D_2O droplet introduction to change induced by H_2O droplets. Listed

746 uncertainties obtained through error propagations of the standard

747 derivations of the individual measurements.

	Area[†] of RF-probe signal	Peak height of RF-probe signal	Area[†] of phase-detector signal	Peak height of phase-detector signal
Sample change[*] between individual measurements; droplet evaporation was incomplete in the load-coil region (conditions very similar to our previous work [23]); temporal profiles are shown in Figures 9a and 9b; $n = 4$	0.56±0.07	0.52±0.07	0.63±0.12	0.65±0.09
Sample change[*] between individual measurements; droplet evaporation was likely complete near the top of the load-coil region; $n = 4$	0.59±0.11	0.58±0.09	0.71±0.09	0.72±0.05
No sample change[*] between individual measurements; complete droplet evaporation was midway in the load-coil region; temporal profiles are shown in Figure 1; $n = 5$	0.63±0.15	0.64±0.07	0.80±0.09	0.80±0.06

748 [†]Area is defined as the baseline-corrected integrated signal from 0 ms to end of the
749 captured temporal profile, typically at ~8.5 ms.
750 [*]"Sample change" is defined as the sequence of micropump removal, sample change of
751 H_2O–D_2O, and micropump re-installation.
752

753 **Figure Captions**

754 Figure 1 Averaged ($n = 5 \times 1280$) oscilloscope traces of the signals from the H_α-

755 PMT, the RF-probe coil and the phase detector during repetitive H_2O and

756 D_2O single-droplet introduction into the ICP. The RF-probe and phase-

757 detector signals were measured in ac- and dc-coupling modes, respectively.

758 The error bars represent the standard deviations from the five

759 measurements. Because the temporal traces contain 2500 data points, for

760 clarity of the figure, error bars are shown only for every 75 data points.

761 Figure 2 Net monochromatic images (i.e., after subtraction of steady-state plasma

762 emission) of the ICP load-coil region at H I 656.3 nm for H_2O and D I

763 656.1 nm for D_2O (as marked), during repetitive introduction of

764 monodisperse microdroplets into the ICP. The vertical and horizontal

765 scales marked on the four edges of the images are in units of millimeters.

766 Time stamps: (a) 1.55 ms, and (b) 1.65 ms after the H_α-PMT trigger.

767 Figure 3 Net monochromatic images (i.e., after subtraction of steady-state plasma

768 emission) of the ICP load-coil region at Ba II 455.4 nm during repetitive

769 introduction of monodisperse H_2O and D_2O (as marked) microdroplets

770 into the ICP. The vertical and horizontal scales marked on the four edges

771 of the images are in units of millimeters. Time stamp: 1.65 ms after the

772 H_α-PMT trigger.

773 Figure 4 Vertical positions of the H_2O and D_2O droplets in the ICP as a function of

774 time. The data are fitted with a quadratic function. The three regions

775 denoted by dotted lines represent the three selected vertical heights at

35

776   which spatio-temporal responses were discussed in detail (see text for

777   discussion). The measurement is limited by the size of the binned ICCD

778   pixels, which contributed an uncertainty of 0.07 mm.

779   Figure 5   Temporal profile of spatially integrated Ba II emission over all vertical

780   locations and between ±2 mm of the plasma center. The dip at ~1.9 ms

781   was caused by obstruction of part of the Ba emission cloud by the load

782   coil.

783   Figure 6   (a) Net absolute, and (b) percentage change in Ar I 696.5 nm emission,

784   relative to steady state, at 1.55 ms after the H_α-PMT trigger, caused by

785   repetitive introduction of monodisperse H_2O and D_2O microdroplets into

786   the ICP.

787   Figure 7   Temporal profiles of the relative change in Ar I 696.5 nm emission at the

788   left edge (within 0.8 mm) and center (±0.9 mm) of the plasma during

789   repetitive introduction of monodisperse H_2O and D_2O microdroplets into

790   the ICP. Vertical heights were (a) -14.3, (b) -8.0, and (c) -1.7 mm with

791   reference to the top of the load coil. Note different vertical scales in plots

792   for center and left edge of plasma.

793   Figure 8   Rates of change (first derivatives) of (a) originally measured, and (b)

794   normalized H_α-PMT, RF-probe coil and phase-detector signals during

795   repetitive H_2O and D_2O single-droplet introduction into the ICP. Four

796   notable transitions in the temporal profiles and their derivatives are

797   marked as Arrows I, II, III and IV (see text for discussion). The error bars

798   represent the standard deviations from the five measurements. Because

36

799   the temporal traces for the derivatives contain 100 data points, for clarity

800   of the figure, error bars are shown only for every 3 data points.

801   Figure 9   Temporal profiles of (a) RF-probe, and (b) phase-detector signals during

802   repetitive H_2O and D_2O single-droplet introduction into the ICP. Four

803   individual measurement cycles between the H_2O and the D_2O samples

804   were acquired. The sequence of micropump removal, sample change

805   between H_2O and D_2O, and micropump re-installation was performed

806   between trials in each set of measurements.
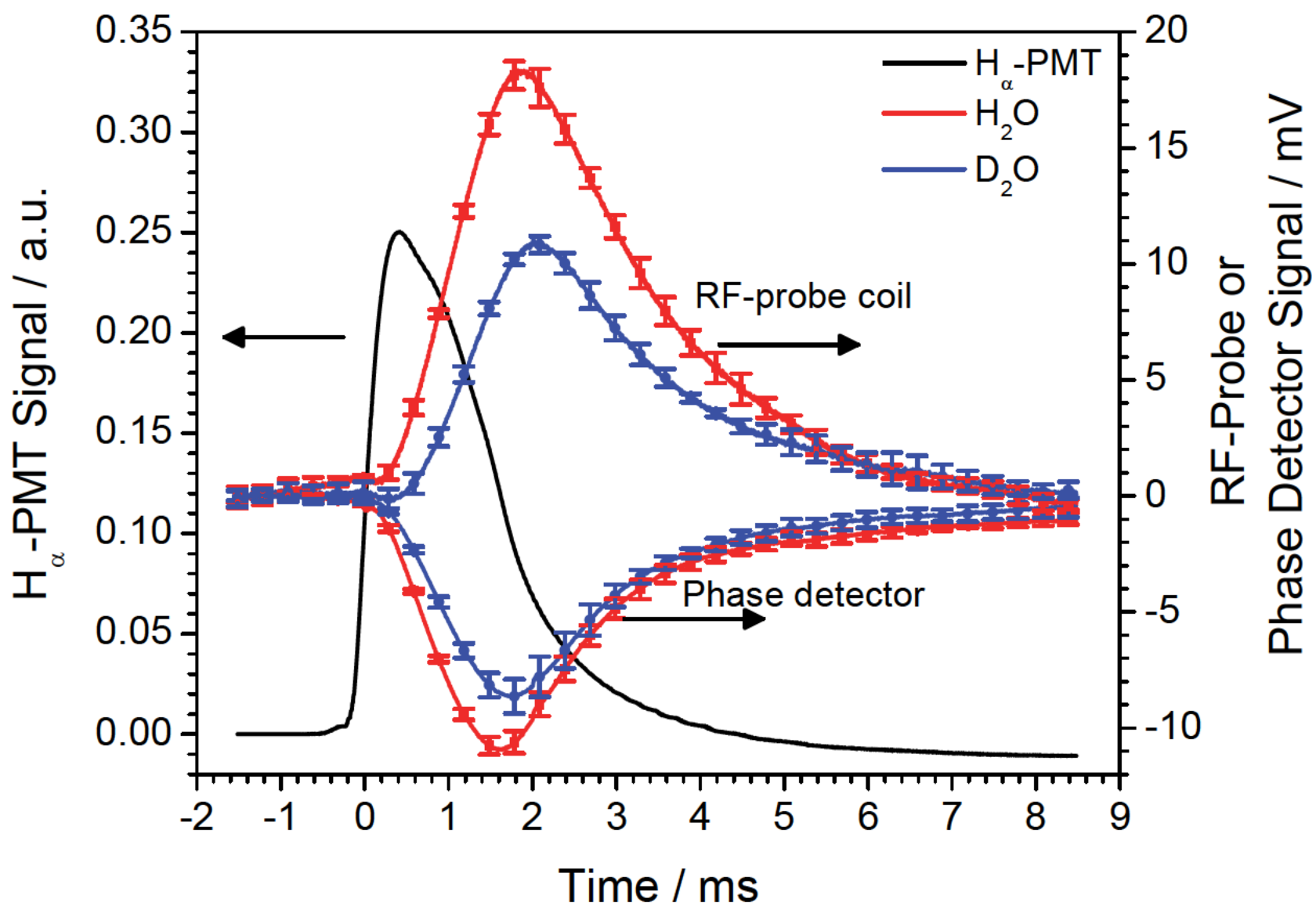
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Figure 1

H₂O Droplet

D₂O Droplet

H₂O Droplet **D₂O Droplet**

Figure 3

H₂O Droplet **D₂O Droplet**

Figure 4

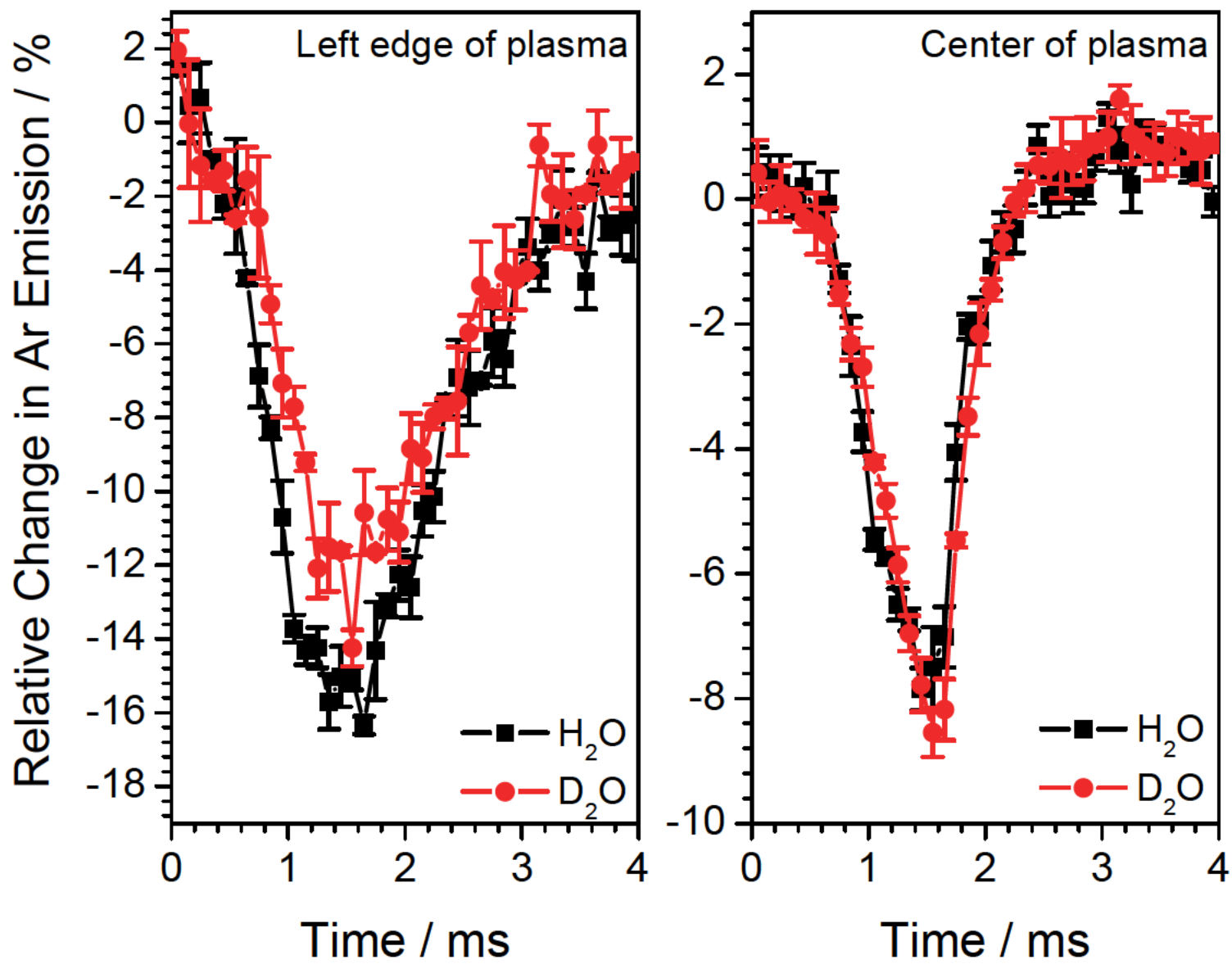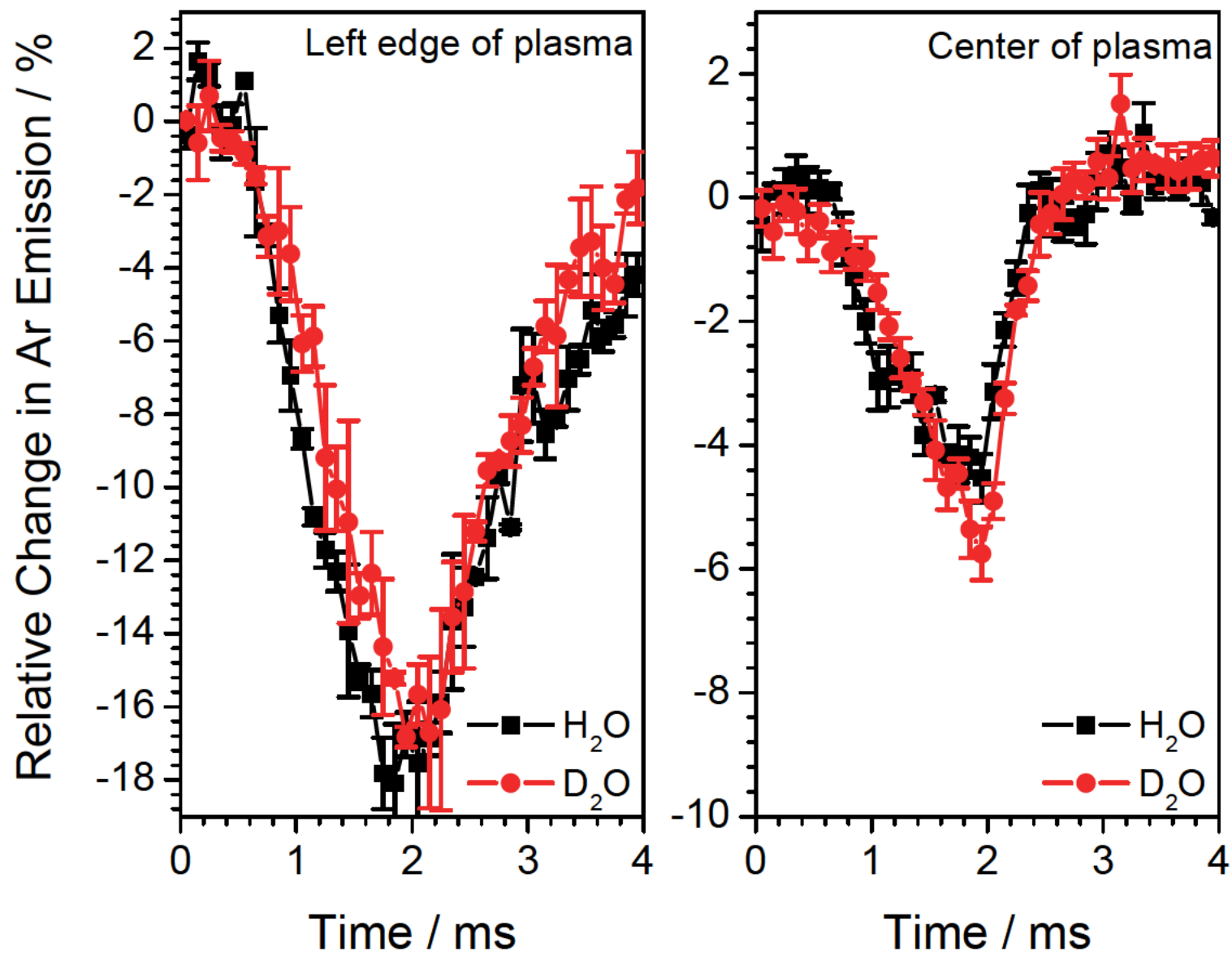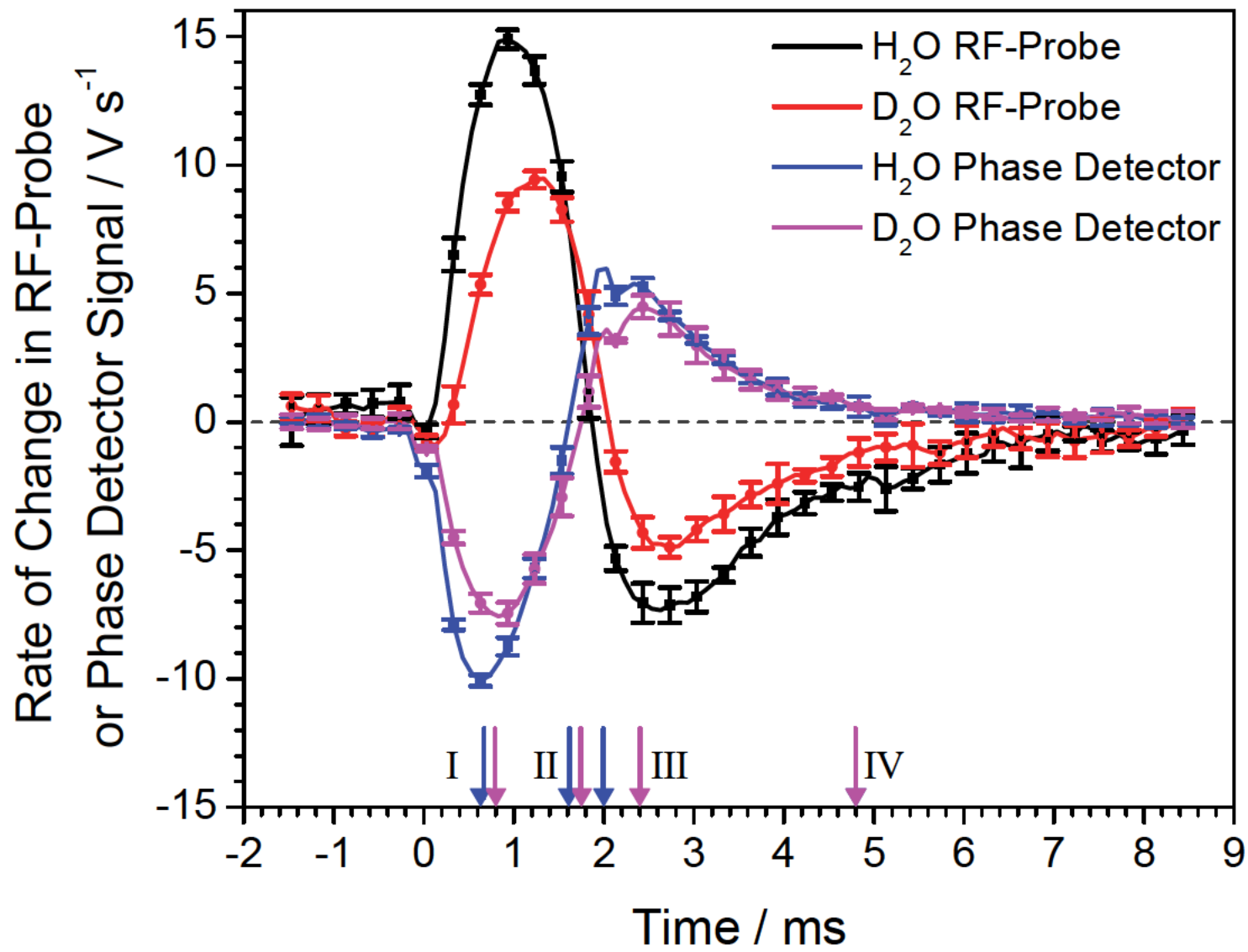**Figure 5**

H$_2$O Droplet

D$_2$O Droplet

H₂O Droplet　　　　　D₂O Droplet
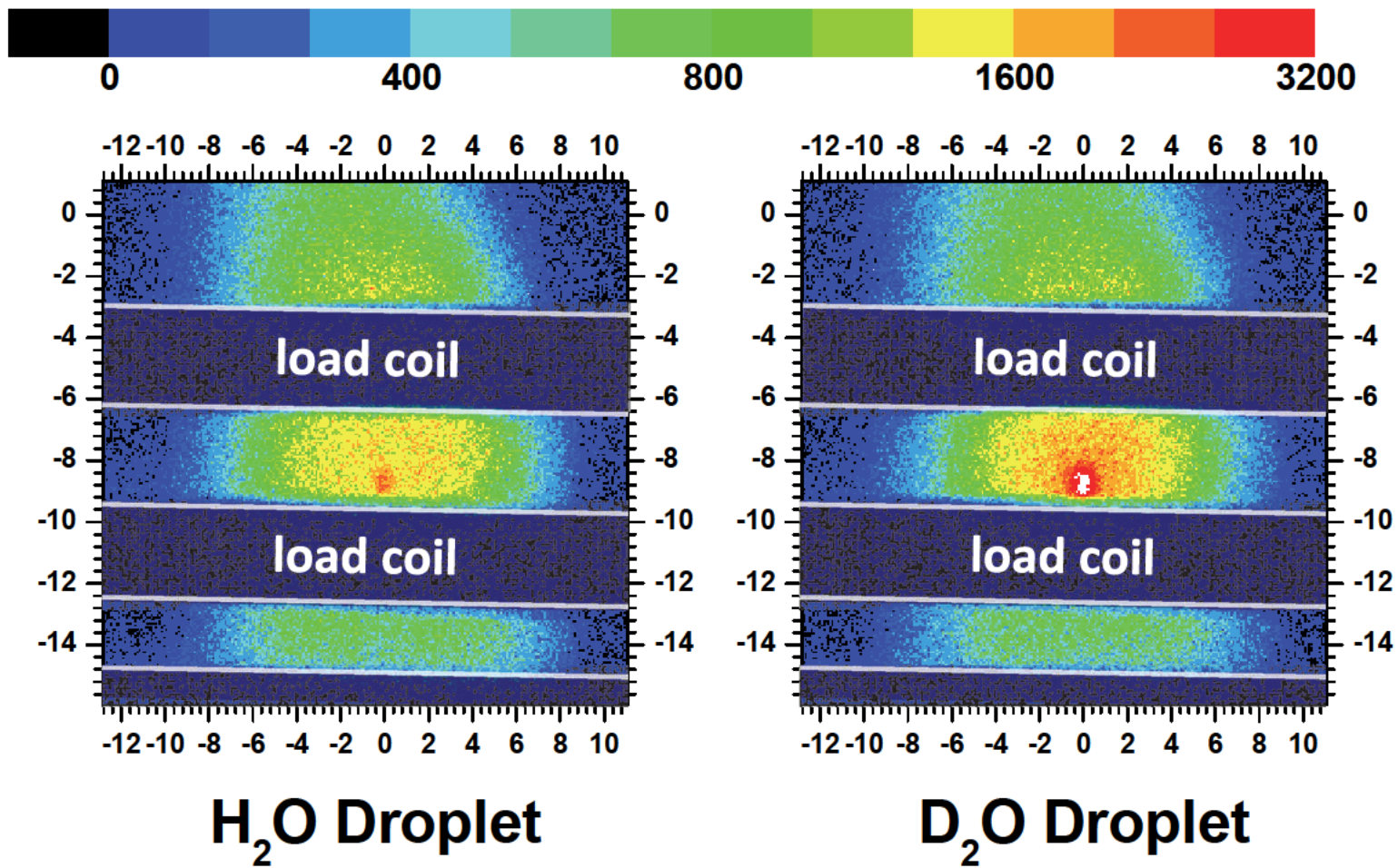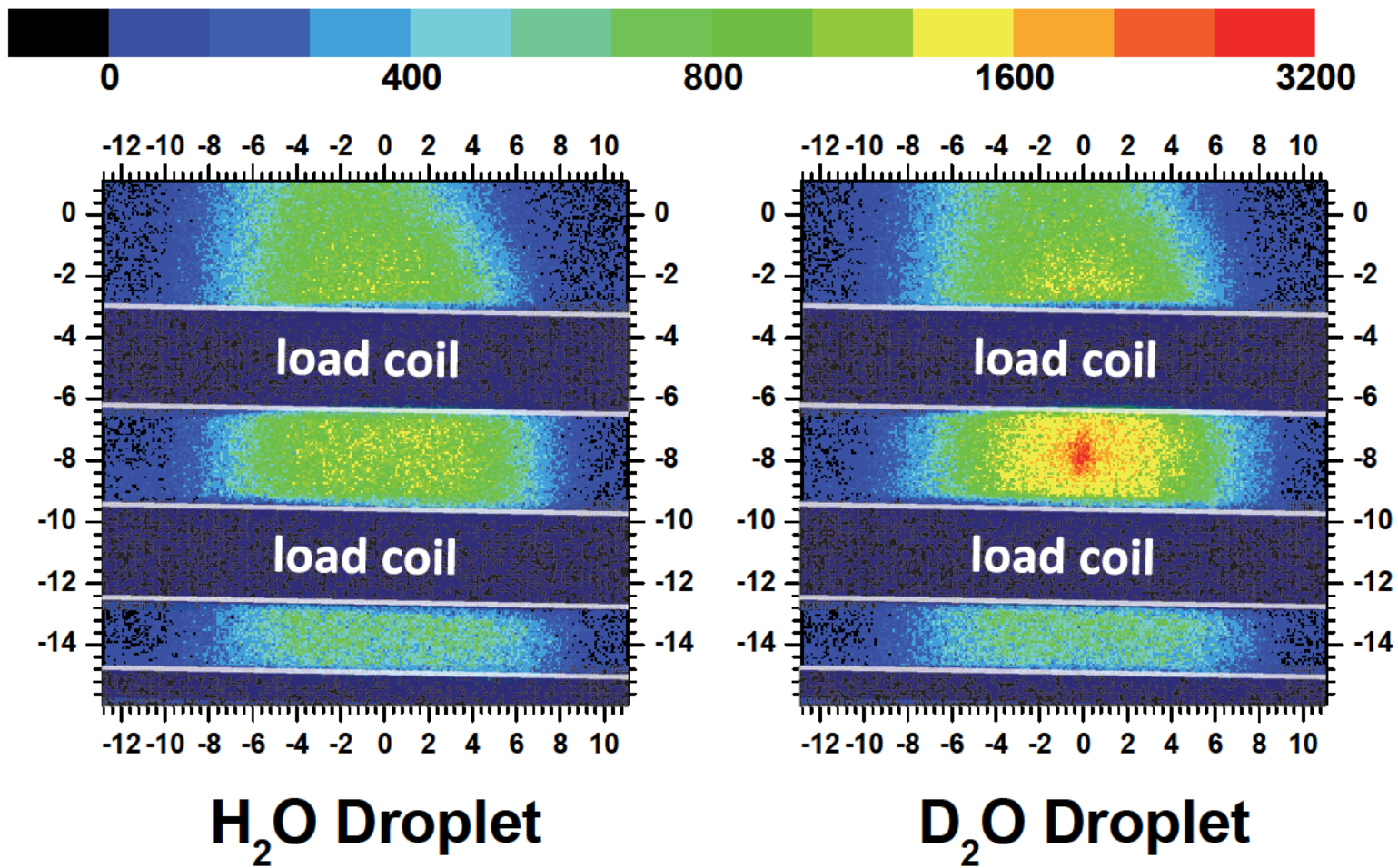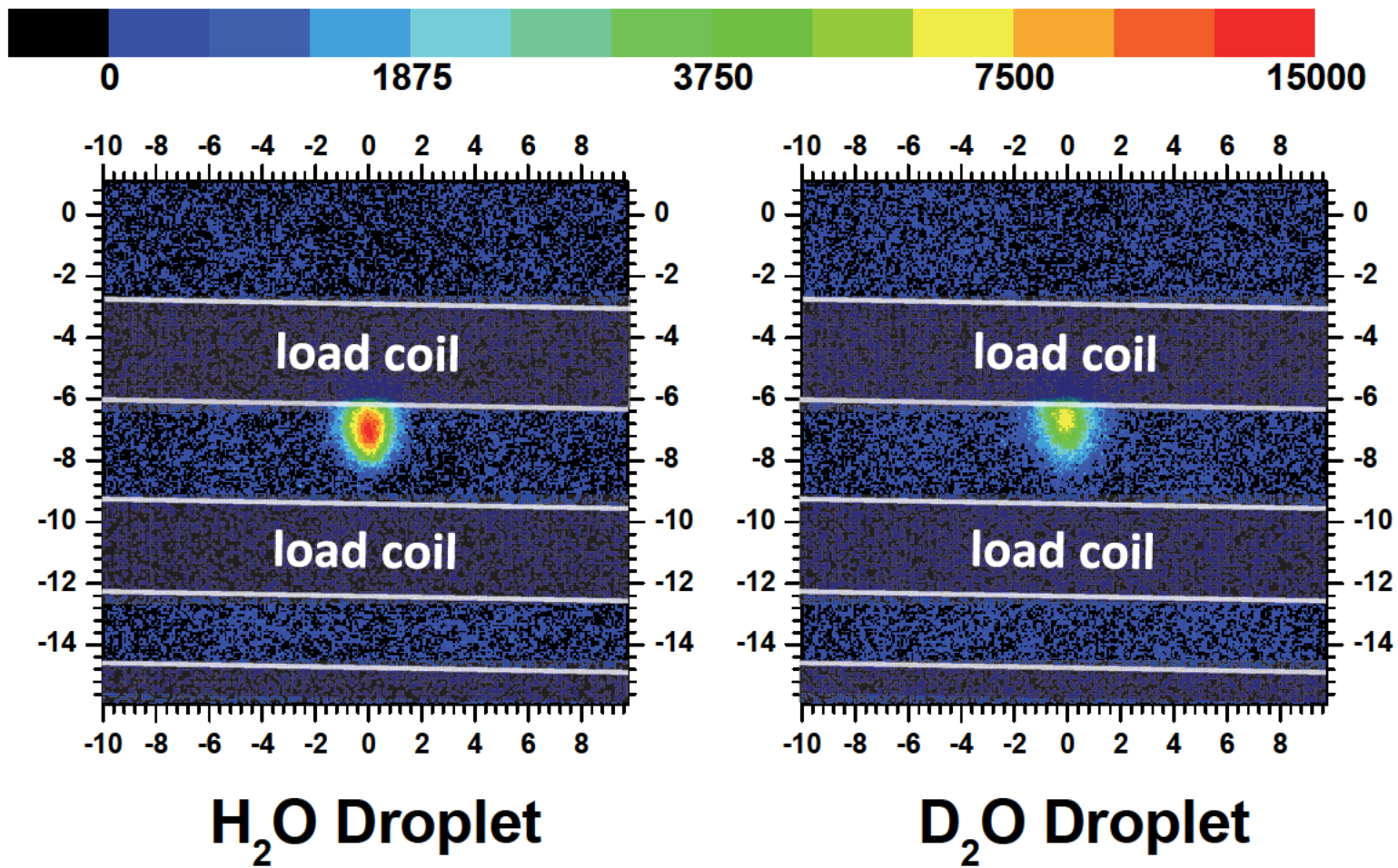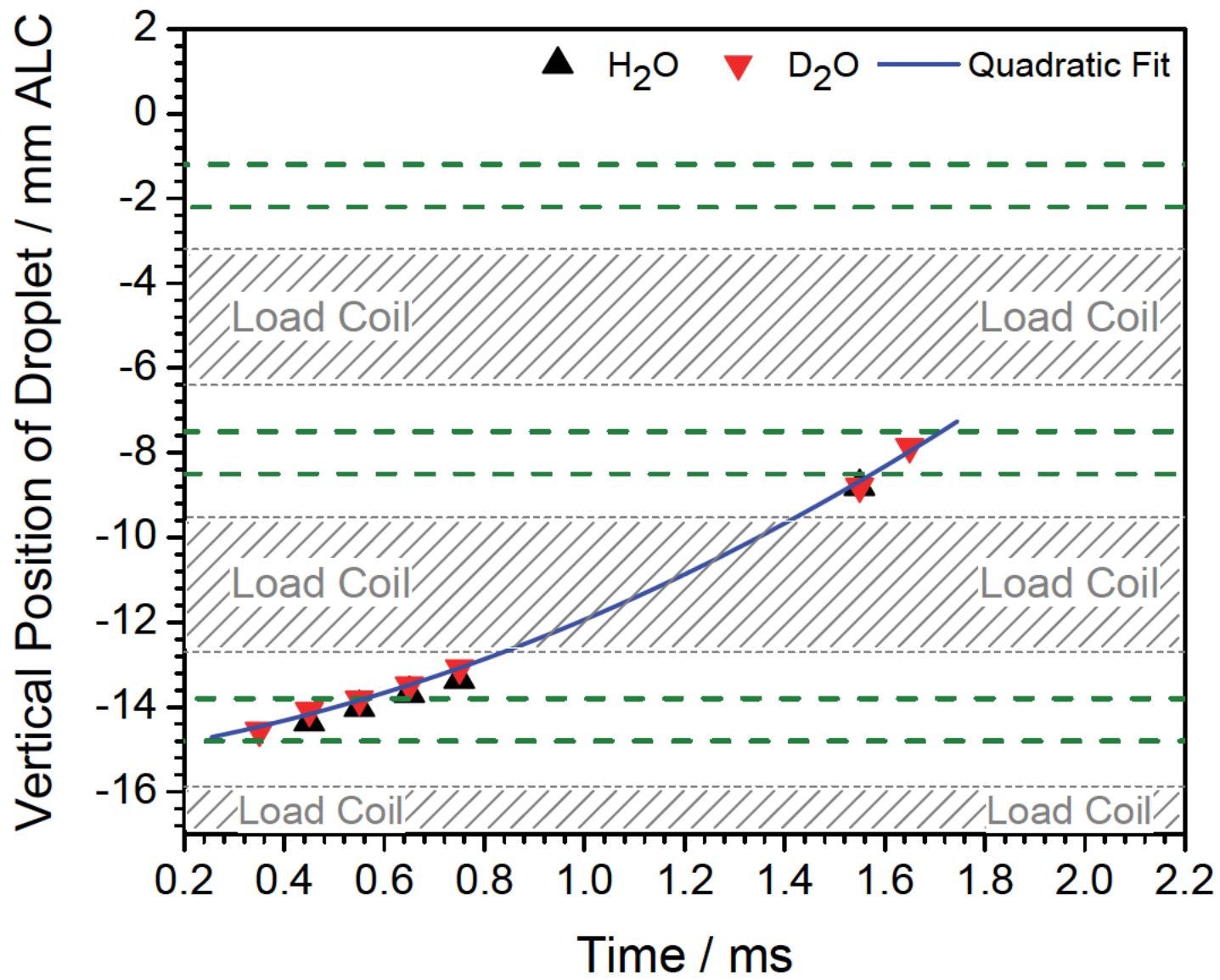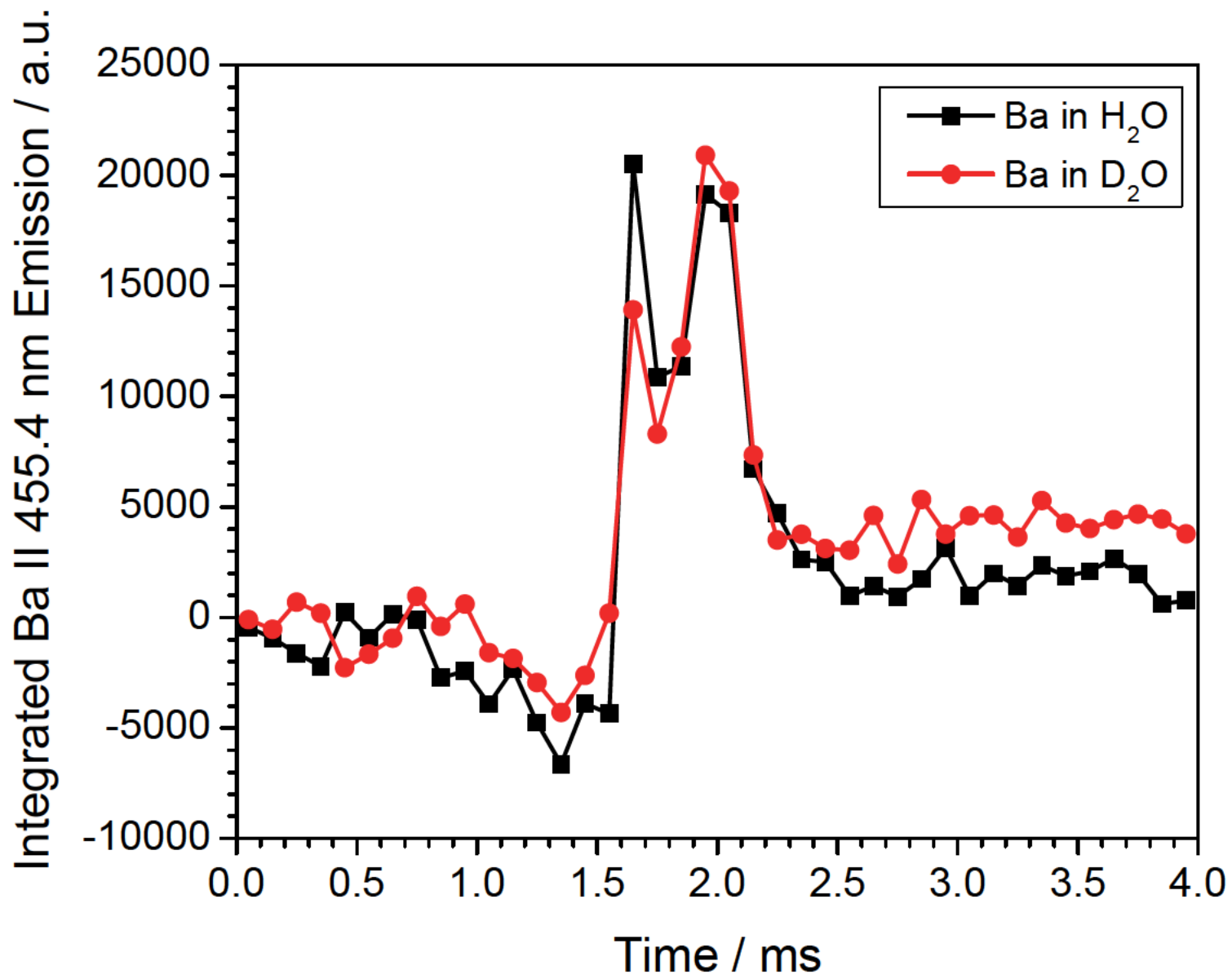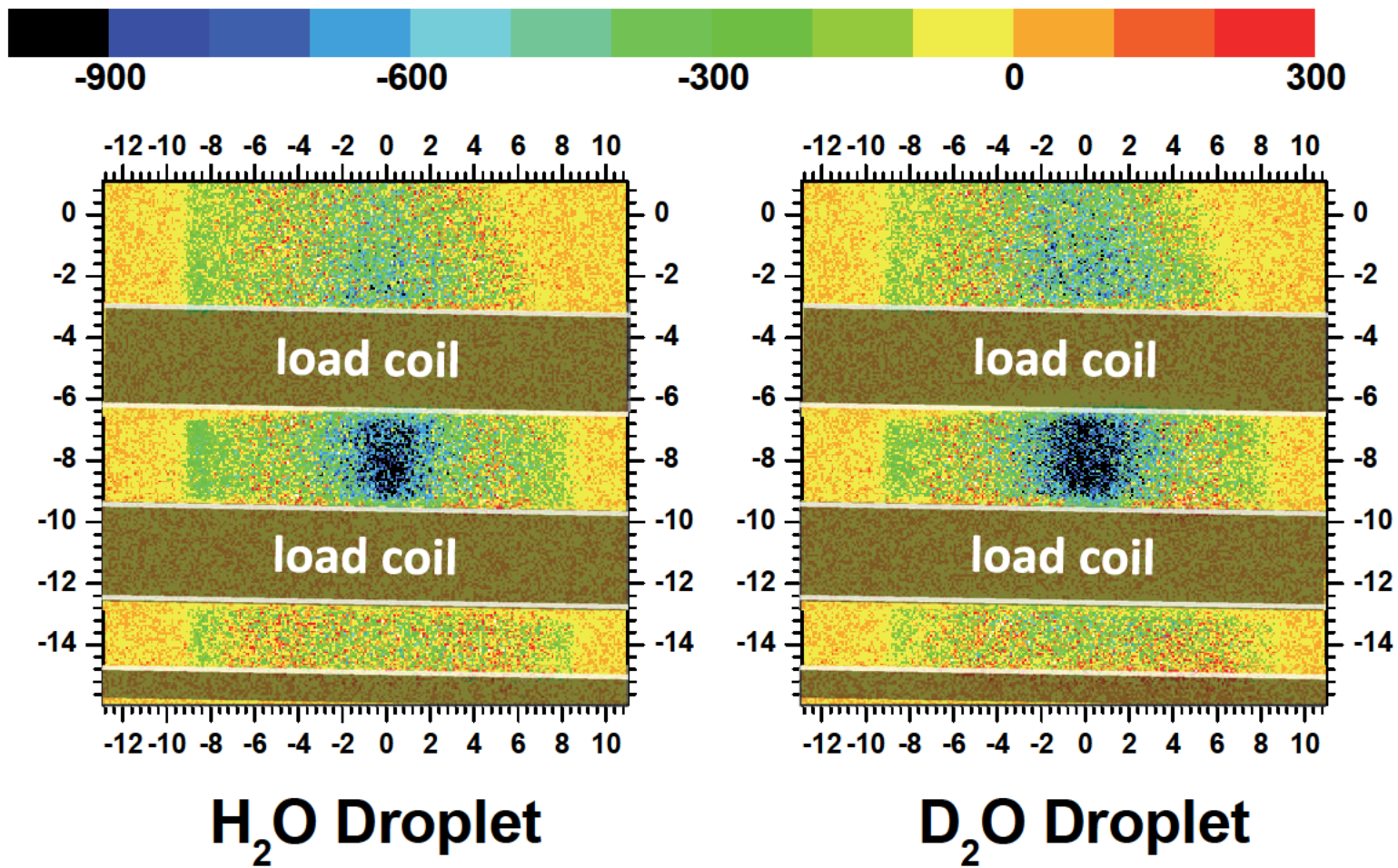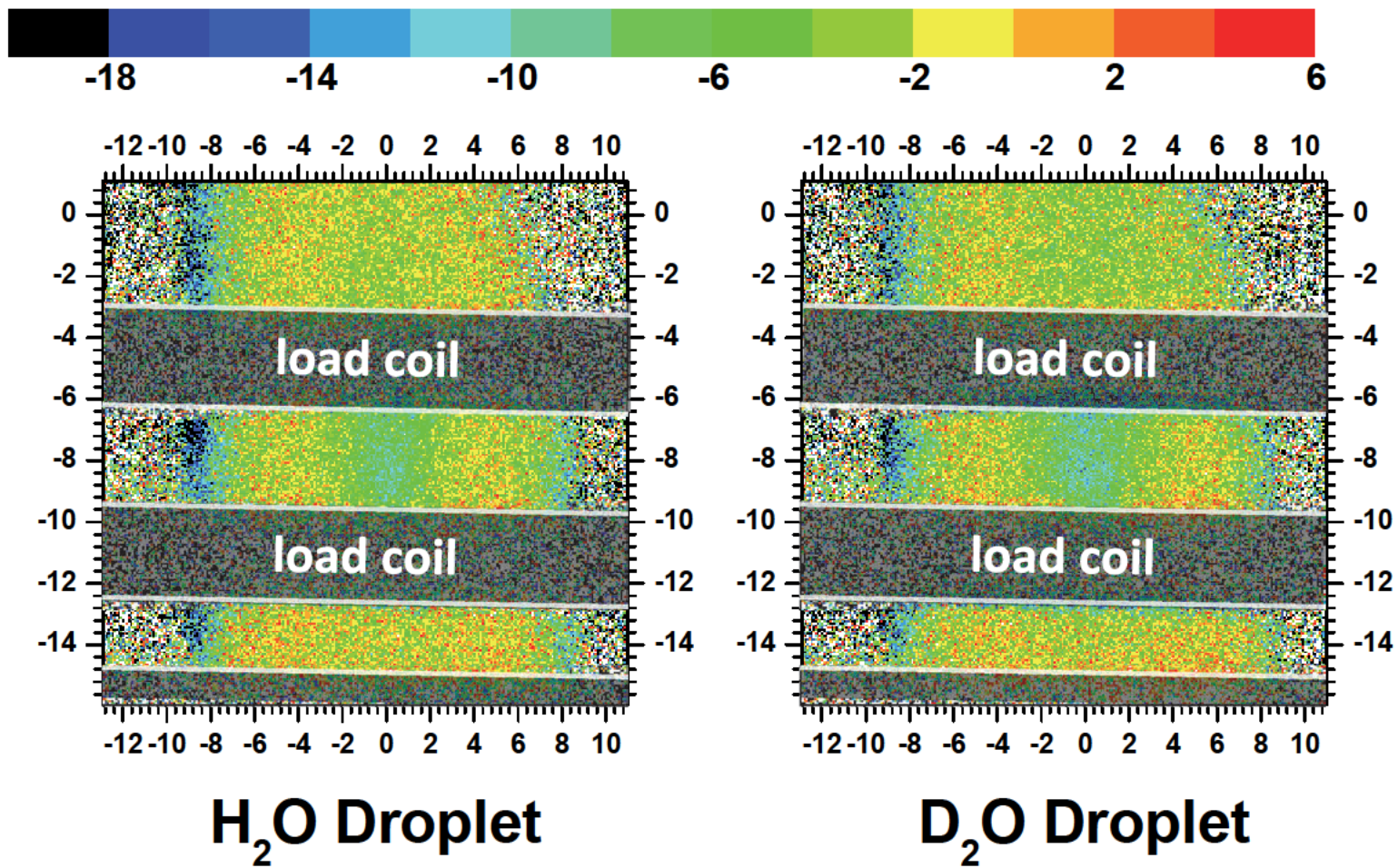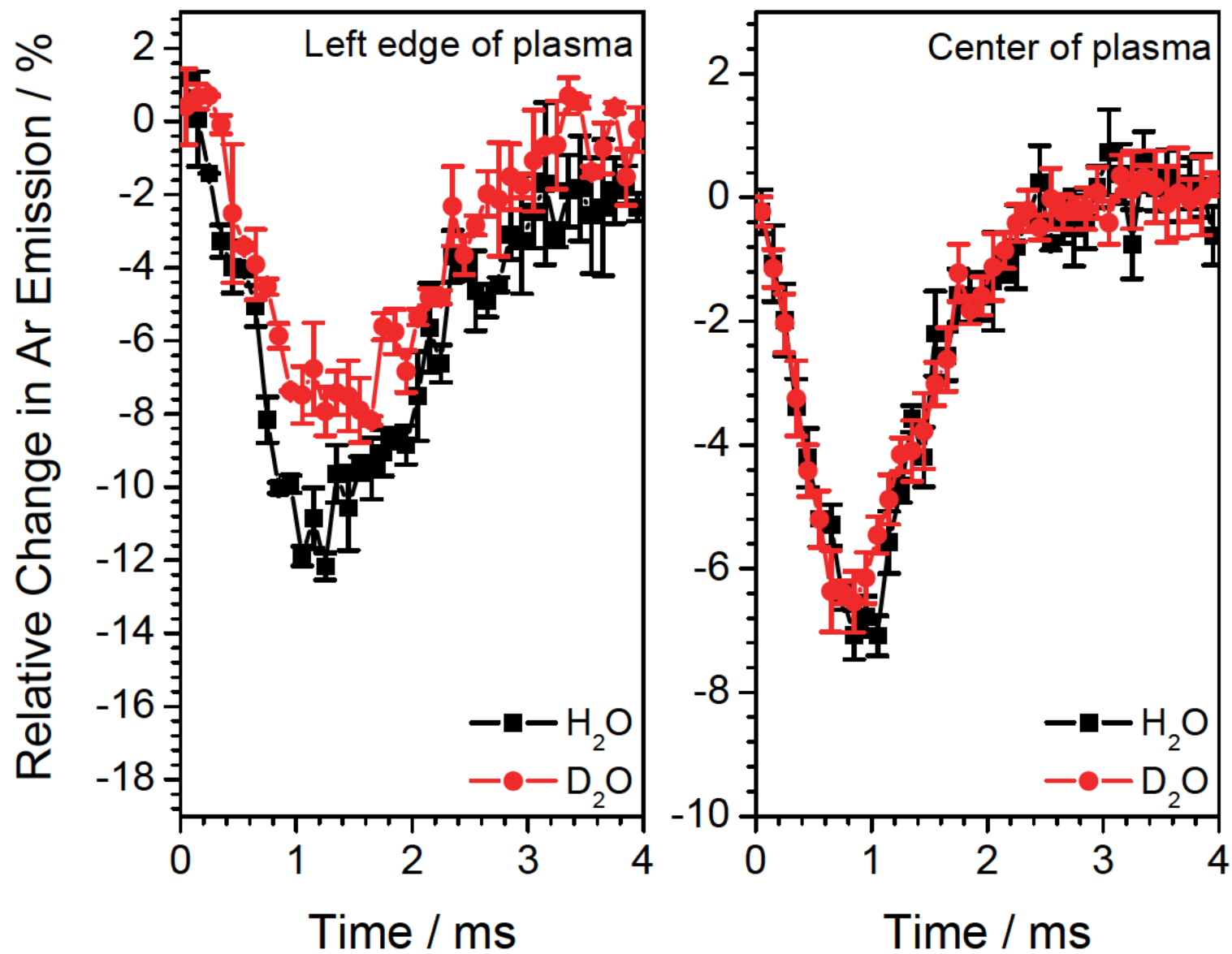
Figure 7b

Figure 7c

Figure 8b

Figure 9a

Figure 9b