Spectroscopic Evidence for a Gold-Coloured Metallic Water Solution

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27 **Attempts to convert pure water from an insulator into a metal by**
28 **pressurizing the system remain in the realm of science fiction, since the estimated**
29 **required pressure¹ of 48 Mbar is an order of magnitude higher than what is feasible**
30 **in the laboratory nowadays and may only exist in cores of large planets or stars²⁻⁴.**
31 **Indeed, recent estimates show that at experimentally accessible pressures one can**
32 **reach at best superionic water with high protonic conductivity⁵, but not metallic**
33 **water with conductive electrons¹. Here, we show that a metallic water solution can**
34 **be prepared by massive doping by electrons liberated from alkali metals. Analogous**
35 **metallic solutions of liquid ammonia, which may serve in many respects as a proxy**
36 **to water, have been characterized previously⁶⁻⁹. However, it is a textbook knowledge**
37 **that dissolution of alkali metals in water leads to an explosive chemical reaction^{10,11},**
38 **thus aqueous solutions with only low (sub-metallic) electron concentrations have**
39 **been prepared so far¹²⁻¹⁴. We have now found a way around the explosive chemistry**
40 **by adsorbing water vapour at a pressure of about 10^{-4} mbar onto a train of liquid**
41 **sodium-potassium alloy drops ejected from a nozzle into a vacuum chamber. This**
42 **leads to a formation of a transient gold-coloured layer of water doped with $\sim 5 \times 10^{21}$**
43 **electrons/cm³, the metallic character of which is demonstrated by a combination of**
44 **optical reflection and synchrotron x-ray photoelectron spectroscopies.**

45

46 **Water adsorption on sodium-potassium alloy drops**

47 The current experiment is realized with a sodium-potassium (NaK) alloy, which is
48 liquid at room temperature^{15,16}, dripping at a rate of about one drop per 10 s from a
49 micro-nozzle into a vacuum chamber with a background water vapour pressure tunable
50 up to a fraction of a millibar. With no water vapour in the vacuum chamber the NaK
51 drops have no distinct colour, but only a silver metallic sheen (for a representative
52 snapshot see the top left panel of Figure 1). The lack of visible colour is due to the fact

53 that unlike transition metals, alkali metals have no *d* or *f* electrons subject to optical
54 excitations. Also, except for cesium, their plasmon frequency is far in the UV
55 region,^{9,16,17}.

56 When water vapour pressure in the vacuum chamber is increased to $\sim 10^{-4}$ mbar, a
57 sufficient amount of water adsorbs at the surface of the newly formed NaK drops such
58 that their surface layer turns almost immediately gold in colour (Figure 1). The golden
59 colour persists for up to ~ 5 s, after which, as water keeps adsorbing further, the colour
60 gradually turns into bronze for another 2–3 s (Figure 1). Eventually, the drop loses its
61 metallic sheen turning purple-blue and finally white - the latter due to formation of an
62 alkali hydroxide layer (Figure 1) as a product of the reaction of electrons with water. The
63 whole process lasts for about 10 s, within which the drop grows and reaches its final size
64 of ~ 5 mm in diameter, eventually falling off from the capillary end due to gravitational
65 force, with a new drop starting to evolve immediately afterwards. The transient formation
66 of a gold-coloured drop is completely reproducible for a “train” of hundreds of drops,
67 provided the water vapour pressure is kept in a relatively narrow range close to the
68 optimal values of about 10^{-4} mbar.

69 At this pressure, we can estimate using the Langmuir model¹⁸ that the aqueous
70 layer at the NaK drop grows at a rate of ~ 80 monolayers per second, i.e., it thickens by
71 about 24 nm/s. This estimate assumes that an impinging water vapour molecule has a
72 diameter of 0.3 nm and a surface sticking probability of unity (for a schematic picture see
73 Figure 2). The current situation differs from previous experiments where a single or a
74 very small number of water monolayers were grown on potassium (or by co-adsorption of
75 water with alkali metal on an inert metal substrate) at significantly lower water vapour
76 pressures of $\sim 10^{-6}$ mbar and at cryogenic substrate temperatures around 100 K^{19,20}. In
77 those studies, electrons liberated from the alkali metal into the water monolayer
78 transiently formed upon annealing individual partially hydrated electrons, which then

79 reacted toward hydrogen and hydroxide^{19,20}.

80 The key point regarding water adsorption on the alkali metal in the current
81 experiment (Figure 2) is that dissolution of electrons and alkali cations in water^{11,21} is a
82 much faster process than the growth of the aqueous layer^{18,22}. What is being built up on
83 the NaK drop is thus not pure water but rather an aqueous layer doped with electrons, as
84 well as with alkali cations. Unlike pure water, multiple layers of such an aqueous solution
85 can apparently be grown under the current experimental conditions. This is a dynamical
86 process, within which the formed layer is unlikely to be fully homogeneous. While in
87 future studies it would be challenging to investigate in detail the spectroscopic signatures
88 of all the stages of the evolution of the aqueous surface of the NaK drop, including the
89 metal-to-electrolyte transition^{6,9} and the accompanying chemical transformations; here,
90 we focus on the early phase characterized by the golden colour of the surface of the drop.

91 **Optical and photoelectron spectra**

92 For the gold-coloured drops, we recorded optical reflectance and x-ray
93 photoelectron (PE) spectra and compared them to those of pure NaK drops (Figure 3).
94 For optical spectroscopy, we imaged the reflected light from a $\sim 1 \text{ mm}^2$ spot at the NaK
95 drop surface and recorded reflection spectra using a commercial UV/VIS spectrometer
96 (for details including calibration see Methods and SI). As mentioned above, pure NaK is
97 colourless and the corresponding reflection-mode optical spectrum thus reflects the
98 distribution of spectral intensity of the incandescent lightbulb used for illuminating the
99 sample (black line in Figure 3a). With water vapour in the chamber the formation of the
100 gold-coloured aqueous layer on the NaK drop is manifested in the spectrum by
101 occurrence of a prominent broad absorption feature at a wavelength range of 400 – 600
102 nm, see Figure 3a,b. A fully quantitative Lorentzian fit to these measured data in energy
103 units is presented in Figure 4a yielding a peak at 2.74 eV (corresponding to 452 nm) with
104 a full width at half maximum (FWHM) of 0.59 eV.

105 Analogously to metallic alkali metal – liquid ammonia solutions⁹, we can connect
106 the observed metallic golden colour to the plasmon frequency pertinent to the free
107 electron gas²³ of the metallic water solution. However, unlike the bulk metallic solutions
108 of alkali metals in liquid NH₃, which reflect light below the plasmon frequency and are
109 transparent to light at higher frequencies⁹, here we additionally observe absorption of
110 light around the plasmon frequency. Note that in bulk systems light as transverse
111 electromagnetic radiation is from symmetry reasons unable to excite plasmons, which are
112 longitudinal waves²³. The key point here is that metallic water solution is formed in the
113 current experiments as a thin layer in which optical excitation of a plasmon becomes
114 feasible at around the plasmon frequency²⁴ (see SI for further details).

115 An interesting feature in the spectrum is that the reflectivity at frequencies above
116 the plasmon absorption band increases again (Figure 3a,b). The metallic water solution,
117 like any other simple metal, becomes transparent for radiation of frequencies higher than
118 the plasmon frequency and hence its reflectivity would not be expected to recover.
119 However, in the current case of a thin metallic water layer, high-frequency radiation
120 which is transmitted through it is in fact reflected from the underlying pure NaK, which
121 has its plasmon frequency only at around 275 nm (corresponding to 4.5 eV).

122 Optical measurements were complemented in an analogous setup by synchrotron
123 radiation x-ray PE spectroscopy. PE spectra at photon energy of 330 eV were acquired in
124 the so-called fixed-mode that allows simultaneous recording of a 9 eV wide spectral
125 window with a sampling rate of ~0.6 Hz, i.e., every 1.6 s a spectrum is recorded (for
126 more details see Methods and SI). The spectrum collected from NaK drops ejected into
127 the vacuum chamber in the absence of water vapour (black line in Figure 3c) is almost
128 identical to that obtained from a pure NaK microjet previously⁹ (see also SI). The main
129 PE spectral features of pure NaK are a ~2 eV wide conduction band, with a sharp Fermi
130 edge defining here zero binding energy, and a Lorentzian-shaped plasmon peaking at

131 around 4.5 eV (Figure 3c and Ref. 9).

132 Due to water vapour adsorption on the NaK drops, the PE spectrum (golden line
133 in Figure 3c) changes in three distinct ways. First, an additional peak appears at 2.7 eV
134 with FWHM of ~ 0.6 eV on a rather shallow spectral background (Figures 3c and 4b),
135 which quantitatively matches the value of the metallic water plasmon energy observed in
136 the optical spectrum (Figure 3a,b). Second, there appears a new feature near the Fermi
137 edge²³, which we interpret as a narrow (~ 1.1 eV) conduction band of the metallic water
138 solution on top of a wider (~ 2 eV) conduction band of pure NaK (Figure 3c). It is
139 important to reiterate here that the drop is a dynamic system that grows and spins during
140 the measurement. Typically, only part of the region on the drop's surface that is probed
141 by x-rays consists of a metallic water layer, with the remainder being pure NaK alloy.
142 Therefore, the recorded PE spectrum is a sum of contributions from the metallic water
143 solution and pure NaK (Figure 3c). Third, a strong signal rises at higher binding energies
144 with an onset around 5.3 eV from the Fermi level. The limited energy window within the
145 fixed-mode data acquisition did not allow for simultaneous measurement of PE peaks of
146 all the species present (i.e., excess electrons, water, alkali cations, and hydroxide anions),
147 nevertheless we clearly see water signal in the PE spectra acquired in the sweep-mode
148 integrated over the drop lifetime (see SI for more details). Also, the observed onset of the
149 spectra in Figure 3c occurs in the spectral region where signal from hydroxide, both
150 aqueous²⁵ and solid²⁶, should start to appear. As the drop matures, we observe a shift of
151 about 0.3 eV of this onset toward higher binding energies (see SI). An analogous shift
152 was noticed previously for aqueous hydroxide upon increasing its concentration²⁵. This
153 indicates that before a visible crust of solid alkali hydroxide is formed at the later stages
154 of the drop's development, hydroxide is dissolved in the thin layer of metallic water.

155 The decomposition of the PE spectrum into contributions from the metallic water
156 solution and NaK, with conduction bands and plasmons fitted using the free electron gas

157 model, assuming a Lorentzian shape of the plasmon peaks, is presented in Figure 4b (see
158 SI for more details). Given the simplicity of the model, where the only parameter is the
159 density of free electrons, it is remarkable how well it fits the experimental data. The value
160 of the obtained free electron density is about $5 \times 10^{21} \text{ cm}^{-3}$, which corresponds to a
161 concentration of ~ 18 MPM. This estimated value for the metallic aqueous solutions of
162 sodium and potassium is likely to be close to the saturation limit, being consistent with
163 solubilities of these alkali metals in liquid ammonia reaching ~ 20 MPM (with the
164 electrolyte-to-metal transition occurring at around $1 - 5$ MPM)⁶. Also note that the free
165 electron density of the metallic water solution is about three times lower than that of pure
166 NaK⁹, which is in line with the UV-to-visible shift of the plasmon peak and a conduction
167 band of about half the width when comparing the former with the latter system (Figure
168 4b).

169 **Discussion and Conclusions**

170 We have shown here that exposing NaK drops to vapor pressure of $\sim 10^{-4}$ mbar
171 leads to an almost immediate formation of a gold-coloured layer of a metallic water
172 solution. The gold colour cannot be due to interference effects since it appears already
173 when the layer is more than an order of magnitude thinner than the corresponding
174 wavelength region of 400 - 600 nm. Moreover, we do not observe any red-to-blue colour
175 shift that would be characteristic to interference from a layer growing to a thickness
176 approaching wavelengths of the blue edge of the visible spectrum. The gold colour with
177 its characteristic sheen is instead a signature of a metallic character of the surface layer.

178 The relatively long lifetime of several seconds of the metallic water layer is partly
179 due to the presence of the underlying alkali metal providing excess electrons in a quasi-
180 steady state manner; this is similar to our earlier experiments, where putting sodium-
181 potassium alloy next to a water drop led to transient formation of a blue electrolyte layer
182 of hydrated electrons at elevated temperature¹³. In addition, it is plausible that hydrated

183 electrons become less reactive and thus longer-lived upon delocalization in the metallic
184 regime. This effect could be rationalized by the fact that for localized hydrated electrons
185 there is a better chance to react with adjacent water molecules than for delocalized
186 electrons in the conduction band of the metallic solution. The lifetime of dilute localized
187 hydrated electrons is sub-millisecond²⁷, while in the current experiments the metallic
188 water layer persists for seconds. Still, chemistry starts early on as evidenced by the
189 presence of a signal from hydroxide in the PE spectra. The metallic water solution should
190 thus be understood as a dynamically evolving system of a high concentration of excess
191 electrons forming a conduction band and alkali metal cations. Moreover, as chemistry
192 proceeds during the drop development, hydroxide anions and hydrogen form, leading to
193 an increasingly concentrated aqueous hydroxide solution as well as to solid hydroxide.
194 Consistent with earlier observations of a blue colour of electrons in strongly alkaline
195 amorphous ices^{28,29}, this effect together with further water adsorption is likely causing
196 the change of colour to purple/blue as the drop matures (Figure 1).

197 In conclusion, by adsorbing water vapour on a NaK drop rather than dissolving
198 alkali metals in liquid water, we managed to keep the vigorous (even explosive) chemical
199 reactivity temporarily at bay in a manner sufficient for spectroscopic characterization of
200 the formed gold-coloured layer of a metallic water solution. In this way, we were able to
201 bypass the need for employing unrealistically high pressures¹ for metallization of water.

202
203

204 **Methods**

205 Liquid sodium-potassium alloy (NaK) was made by mixing solid sodium and
206 solid potassium (1:1 mol-ratio, 99.8% Sigma-Aldrich). Details are provided in Ref. ¹¹ and
207 in the SI. For acquiring both optical and PE spectra we used our modified microjet setup
208 described in Ref. ³⁰ to produce drops (as well as micro-sized jets) of NaK and we added a
209 water supply line to transfer water vapor at pressures varying from 10^{-5} to 2×10^{-4} mbar
210 into our vacuum chamber. By reducing the argon pressure above the NaK reservoir, the

211 continuous NaK jet turns into a periodic drop train, which was essential for tracking
212 formation of the metallic water solution on the drop surface.

213 ***Optical reflection measurements***

214 The optical reflection measurements, described in more detail in the SI and in a
215 Supplementary Video, were conducted at IOCB Prague. In a typical experiment, we
216 created NaK drops at a rate of one drop every ~ 10 s with spectra recorded with the
217 AvaSpecULS 2048 spectrometer every 0.1–0.3 s. We synchronized the saving of the time
218 stamp of each spectrum by recording a video where the image of the drop taken with a
219 CCD camera is shown together with the current time to directly relate the sampled
220 spectra to the size and colour of the NaK drop at a given moment in time.

221 First, we took as reference the reflection spectra of pure NaK drops, the surface of
222 which is highly reflective in the infrared and visible parts of the electromagnetic spectrum
223 (up to its plasmon frequency of ~ 4.5 eV). Next, water vapor was transferred into the
224 vacuum chamber via a tube from a water reservoir with the amount of vapour being
225 controlled using a needle valve. We found the NaK drop to turn golden for several
226 seconds within a pressure range of 6×10^{-5} - 2×10^{-4} mbar with an optimal performance at
227 $\sim 10^{-4}$ mbar. The spectra taken at this water vapour pressure were normalized using the
228 reflection spectra of pure NaK.

229 ***Synchrotron-based photoelectron spectroscopy measurements***

230 X-ray PE spectroscopy measurements were performed using the SOL³PES setup²⁷
231 connected to the U49-2_PGM-1 beamline²⁸ of the synchrotron radiation facility BESSY
232 II in Berlin (see SI for more details). Similarly to the optical measurements, experiments
233 were performed under vacuum conditions (10^{-5} mbar) with or without the presence of
234 water vapour at a pressure of $\sim 10^{-4}$ mbar, with a NaK drop rate of 0.1 Hz. Drops were

235 irradiated on the upper part by horizontally polarized soft x-ray light. Water vapour was
236 directed onto the same surface spot where the x-ray photons hit the NaK drop. The
237 emitted photoelectrons were detected by a ScientaOmicron R4000 HiPP-2 hemispherical
238 electron analyzer mounted in the same plane as the polarization axis. Valence PE spectra
239 were measured at a photon energy of 330 eV using a pass energy of 100 eV. This large
240 pass energy allowed us to detect within the fixed-mode setting of the electron analyzer a
241 9-eV wide kinetic energy window in one shot, which was enough to record the
242 conduction band with its Fermi edge and the plasmon features, as well as the onset of the
243 hydroxide peak.

244 A sampling rate of ~0.6 Hz (with a spectrum being recorded for 0.4 s followed
245 by 1.2 s of a dead time due to saving the data) was chosen to guarantee a sufficient time
246 resolution as well as a good enough signal-to-noise ratio. Details of this data acquisition
247 mode and the corresponding data analysis and fitting procedures are described in the SI.

248 ***Data availability***

249 The data sets generated during the current study are available as Supplementary
250 Data or are available from the corresponding author upon reasonable request.

251 ***Code availability***

252 Data-processing and fitting results can be generated using numerical methods
253 described in Methods and Supplementary Information and developed computer codes that
254 are available upon reasonable request.

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346 **Supplementary information** is linked to the online version of the paper at www.nature.com/nature .

347 **Acknowledgments**

348 P.J. acknowledges support from the European Regional Development Fund (project
349 ChemBioDrug no. CZ.02.1.01/0.0/0.0/16_019/0000729). D.M.N. and C.L. acknowledge support from the
350 Director, Office of Basic Energy Science, Chemical Sciences Division of the U.S. Department of Energy
351 under Contract No. DE-AC02-05CH11231 and the Alexander von Humboldt Foundation. S.E.B., T.B.,
352 and R.S.M. are supported by the US National Science Foundation (CHE-1665532). P.E.M. acknowledges
353 support from the viewers of his YouTube popular science channel. C.T. acknowledge support from the
354 Charles University in Prague and from the International Max Planck Research School in Dresden. S.T.
355 acknowledges support from the JSPS KAKENHI Grant No. JP18K14178. RS acknowledges the German
356 Research Foundation for an Emmy-Noether Young-Investigator stipend (DFG, project SE 2253/3-1). F.T.
357 and B.W. acknowledge support by the MaxWater initiative of the Max-Planck-Gesellschaft. All authors
358 thank the staff of the Helmholtz-Zentrum Berlin for their support during the beamtimes at BESSY II.

359 **Author contribution**

360 P.E.M., H.C.S., T.B., B.W., S.E.B., and P.J. designed the experiments, P.E.M., H.C.S., T.B., B.W., H.A.,
361 V.K., M.V., F.T., C.L., D.M.N., R.S., and P.J performed the experiments, and P.E.M., H.C.S., T.B.,
362 B.W., S.E.B., R.S.M., C.L., R.S., S.T., and P.J analyzed the obtained data. P.J. wrote the main paper,
363 while H.C.S. and P.J. wrote the Supplementary Information, both with critical feedback from all the co-
364 authors. P.E.M. produced the Supplementary Video.

365 **Competing Interests statement**

366 The authors declare that they have no competing financial interests.

367 **Additional information**

368 **Supplementary information** The online version contains supplementary material available at ...

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373 **Figure captions:**

374 **Figure 1: A pure NaK drop in vacuum vs. time evolution of a NaK drop exposed to**
375 **water vapour.** A fresh drop of sodium-potassium alloy ejected from a quartz capillary
376 into the vacuum chamber without the presence of water vapour (top left). This silver
377 drop lacks any distinct colour. Next, we show eight snapshots recording the second-by-
378 second time evolution of a sodium-potassium alloy drop ejected from a micro-nozzle
379 into the vacuum chamber with a background water vapor pressure of $\sim 10^{-4}$ mbar. The
380 snapshots demonstrate an early formation of a gold-coloured layer of a metallic water
381 solution, which due to further water adsorption turns within several seconds into bronze
382 and blue losing eventually its metallic sheen, with visible white patches of the formed
383 alkali hydroxide. At the end of the ~ 10 s cycle, the drop reaches a final diameter of
384 about 5 mm, after which it detaches from the capillary and a new drop starts forming.

385 **Figure 2: A schematic picture demonstrating formation of a thin gold-coloured**
386 **metallic water layer by water vapour adsorption on a NaK drop.** The dynamical
387 process is characterized by a much faster dissolution of electrons and alkali cations^{11,21}
388 than is the growth of the aqueous layer^{18,22}, which ensures high concentration of
389 electrons throughout the system. At the same time, chemistry is taking place, leading to
390 formation of hydroxide and hydrogen.

391 **Figure 3: Spectroscopic signatures of metallic water solution from optical and x-**
392 **ray photoelectron spectroscopies.** a,b) Optical reflection spectra and c) photoelectron
393 spectra of the gold-coloured layer of a metallic water solution (partially) covering the
394 NaK drop and analogous spectra of a pure sodium-potassium alloy drop. a) The
395 reflection spectrum of the colourless pure NaK drop reflects the spectral characteristics
396 of the illuminating lamp, which when subtracted b) yields for this system a flat

397 spectrum, while exemplifying a prominent plasmonic absorption of the metallic water
398 layer. c) A typical photoelectron spectrum of a metallic water solution compared to a
399 pure sodium-potassium alloy. The emerging spectral features upon exposure to $\sim 10^{-4}$
400 mbar of water vapour encompass occurrence of a new plasmon peak and of a narrow
401 conduction band next to the Fermi edge. At the same time, we observe signal from
402 hydroxide as a product of the chemical reaction between alkali metals and water.

403 **Figure 4: Fits to the experimental data employing a free electron gas model.** a) A
404 Lorentzian fit to the plasmonic absorption feature in the optical reflection spectrum
405 yielding a broad peak at 2.74 eV. b) Fits to averaged photoelectron spectra of NaK
406 drops exposed to $\sim 10^{-4}$ mbar of water vapour, namely to the plasmon peaks (by
407 Lorentzian functions) and conduction bands of both NaK and a metallic water solution
408 using the free electron gas model. Formation of the gold-coloured metallic water layer
409 is accompanied with an appearance of a plasmon peak at ~ 2.7 eV and a 1.1 eV wide
410 conduction band with a sharp Fermi edge at 0 eV (on top of a broader
411 conduction band of pure NaK).

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413 Figure 1

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424 Figure 3

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426 Figure 4