

Formation of $^{238}\text{U}^{16}\text{O}$ and $^{238}\text{U}^{18}\text{O}$ observed by time-resolved emission spectroscopy subsequent to laser ablation

David G. Weisz*, Jonathan C. Crowhurst, Wigbert J. Siekhaus, Timothy P. Rose, Batikan Koroglu, Harry B. Radousky, Joseph M. Zaug, Michael R. Armstrong, Brett H. Isselhardt, Michael R. Savina

Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA

Magdi Azer

Illinois Applied Research Institute, University of Illinois at Urbana-Champaign, Champaign, IL 61820, USA

Mikhail S. Finko, Davide Curreli

Department of Nuclear, Plasma, and Radiological Engineering, University of Illinois at Urbana-Champaign, Champaign, IL 61801, USA

* Corresponding author. Glenn T. Seaborg Institute, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA Tel.: + 1 925 422 0971

Email address: weisz3@llnl.gov

19 Abstract

20 We have measured vibronic emission spectra of an oxide of uranium formed after laser ablation
21 of the metal in gaseous oxygen. Specifically, we have measured the time-dependent relative
22 intensity of a band located at approximately 593.6 nm in $^{16}\text{O}_2$. This band grew in intensity
23 relative to neighboring atomic features as a function time in an oxygen environment, but was
24 relatively invariant with time in argon. In addition, we have measured the spectral shift of this
25 band in an $^{18}\text{O}_2$ atmosphere. Based on this shift, and by comparison with earlier results obtained
26 from free-jet expansion and laser excitation, we can confirm that the oxide in question is UO,
27 consistent with recent reports based on laser ablation in $^{16}\text{O}_2$ only.

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Laser ablation offers a simple and inexpensive means to produce plasma environments in

41 which to study the high temperature emission spectra of atoms and molecules. In laser-induced
42 breakdown spectroscopy (LIBS), a pulsed laser focused at or near sample surface produces an
43 ablation plasma and the resultant emission spectrum of atomic de-excitation is typically used to
44 determine the elemental composition of the ablated material¹⁻³. Emission spectra are also
45 routinely used to study simple molecular species that form in the condensing plasma. The use of
46 ultrafast methods to collect spectral data permits the study of spatially- and temporally-resolved
47 in-growth of molecular species in the evolving ablation plume⁴⁻⁹. Recent work in this area has
48 stimulated the development of models to describe rovibronic transitions of diatomic species that
49 can be used to evaluate molecular temperatures⁴, local thermodynamic equilibrium conditions⁷,
50 and chemical kinetics pathways⁹ in the plasma plume.

51 Most of these recent molecular emission studies of laser-induced plasmas have focused
52 on low-Z elements, where the discrimination of atomic and molecular emission lines is relatively
53 straightforward. There is considerable interest in the application of LIBS technology to study
54 uranium-bearing materials¹⁰⁻¹⁵. A better understanding of uranium oxide formation during laser
55 plasma condensation would be beneficial to both nuclear forensics and non-proliferation
56 monitoring. However, comparatively little has been done to explore the molecular emission of
57 uranium oxide species due to the complexity of the spectra. The use of molecular emission
58 spectra to understand uranium oxidation chemistry requires the accurate assignment of uranium
59 oxide emission bands.

60 Recently, laser ablation molecular isotopic spectrometry (LAMIS) has been proposed as a
61 means by which the isotopic composition of samples can be determined, as the isotopic shifts in
62 rovibrational transitions in diatomic molecules are larger and hence more easily resolved, in at

65 In some cases, than isotope shifts in atomic emissions^{16,17}. Recent LAMIS studies, have
64 identified a uranium oxide line and measured the isotopic shift between the ^{235}U and ^{238}U
65 substituted species^{18,19,20}. Hartig *et al.*, (2017a) and Mao *et al.*, (2017), independently identify a
66 uranium oxide emission peak at approximately 593.6 nm with an isotopic red shift of 50 pm and
67 35 pm respectively between the ^{235}U and ^{238}U substituted species^{18,19}. Their basis for identifying
68 this peak as uranium oxide was its growth in intensity (relative to nearby atomic lines) as a
69 function of time after laser impingement (thus suggesting molecular formation as temperature
70 decreases in the expanding plasma). They further correlated the peak's spectral position with at
71 least one known transition previously reported for UO identified in thermal emission²¹, free-jet
72 expansion, and laser excitation experiments²¹⁻²⁴. Hartig *et al.*, (2017a) did not positively identify
73 the peak as due to UO but rather more generally as a uranium oxide species (U_xO_y) because of
74 differences in position and shape from the previous reports. However, Hartig *et al.*, (2017b) and
75 Mao *et al.*, (2017) did positively identify the peak as due to UO, aided in this identification by
76 the pressure dependence of the relative atomic and molecular emission intensities²⁰, and the
77 observation of two additional, although less distinct, bands at 594.57 nm and 595.22 nm¹⁸.

78 Here, we present molecular emission spectra of uranium oxide substituted with ^{16}O and
79 ^{18}O to provide additional evidence that the spectral feature positioned at ~ 593.6 nm is from UO
80 emission. While free-jet expansion and laser excitation data for the isotopic shift between U^{16}O
81 and U^{18}O have been shown^{21,22}, uranium emission spectra from laser ablation plumes have not
82 been previously reported in an $^{18}\text{O}_2$ environment. Our data show an isotopic shift between the
83 ^{16}O and ^{18}O substituted isotopomers that is very consistent with that observed in free-jet
84 expansion and laser excitation experiments.

In our experiments, a New Wave Polaris II Nd:YAG (1064 nm wavelength, ~ 5 ns pulse

86 length, 2.75 mm output beam diameter) was used to generate 1.4 mJ pulses, which were focused
87 onto the surface of a depleted uranium (<0.72% ^{235}U) metal target using a planoconvex lens (5
88 cm focal length) to create an ablation plasma. Emission spectra were collected using a Shamrock
89 SR-303i spectrometer equipped with an 1800 lines/mm grating and coupled to an Andor iSTAR
90 intensified CCD (1024x1024 pixels, 13 μm pixel size). Spectra were collected at either 300 ns,
91 550 ns, 800 ns, 1050 ns, or 1300 ns after the arrival of each laser pulse. A 250 ns gate-width was
92 selected in each case. Spectra were collected as the sum of 500 shots at 20 Hz, with a spectral
93 window of 20 nm (580-600 nm for this study). The wavelength was calibrated using a Ne
94 standard lamp, and the Ne atomic emission lines had a measured FWHM of 0.09 nm. The
95 measured spectral intensities were corrected for the instrumental response using a standard lamp.

96 The atmosphere around the uranium metal target was controlled in an air-tight chamber with
97 sapphire windows that are transparent to the incident ablation laser and emitted light. To achieve
98 $^{16}\text{O}_2$, $^{18}\text{O}_2$, and Ar environments, the chamber was evacuated to ~0.03 atm using a roughing
99 pump and then filled with 1 atm of either isotopically purified $^{16}\text{O}_2$ (99.98% purity), $^{18}\text{O}_2$ (97.4%
100 $^{18}\text{O}_2$, 1.7% $^{17}\text{O}_2$), or Ar (99.99%).

101 Figure 1 shows time-resolved spectra for uranium ablation in 1 atm $^{16}\text{O}_2$ (Fig. 1a) and 1
102 atm $^{18}\text{O}_2$ (Fig. 1b) over the range of 590 nm to 594 nm. The intensities are shown in log-scale, to
103 emphasize the change in intensity of key features in the spectra. In Figure 1a, the evolution of
104 three features as a function of delay time is highlighted in the spectra: the atomic emission lines
105 at 591.54 nm and 593.38 nm, and another prominent emission peak at 593.56 nm. In the $^{16}\text{O}_2$
106 environment, the feature at 593.56 nm is difficult to discern at early delay times (300 ns), while
107 at late times (1300 ns) it is more prominent than the atomic line at 593.38 nm. Notably, as delay

108 The signal increases (as shown moving from the top spectrum to the bottom spectrum in Figure 1a,
109 light to dark), the feature grows in intensity relative to its neighboring atomic lines even though
110 there is an overall decrease in spectral intensity. In the $^{18}\text{O}_2$ environment shown in Figure 1b, the
111 peak at 593.56 nm is absent (or much reduced in intensity) and a prominent feature is seen at
112 593.74 nm that grows in relative intensity as delay time increases. The atomic lines at 591.54 nm
113 and 593.38 nm are present at roughly the same intensities in both experiments. In the spectra
114 obtained in an Ar environment, shown in Figure 1c, the overall intensity is lower by at least a
115 factor of 2 at all delay times. Further, in the Ar environment, the relative change in absolute
116 intensity from 300 ns to 1300 ns is significantly less than in either O_2 environment: in Ar the
117 signal decreases by a factor of 2, while in O_2 the signal decreases by nearly an order of
118 magnitude. Most notably, there is no prominent peak at either 593.56 nm or 593.74 nm in Ar,
119 although there may be minimal contribution to the 593.56 nm peak due to residual $^{16}\text{O}_2$ in the
120 chamber, or the oxide layer on the uranium metal.

121 The spectral differences between the $^{16}\text{O}_2$ and $^{18}\text{O}_2$ ablation environments are emphasized in
122 Figure 2 for early (550 ns, Fig. 2a,b) and late (1300 ns, Fig. 2c,d) delay times. The most
123 prominent peak in Figure 2a is the neutral atomic emission line at ~ 593.38 nm (also seen in
124 Figure 1), with two other neighboring atomic emission lines labeled at 592.55 nm and 592.93
125 nm. While the intensities of individual atomic lines are slightly different, the main features
126 observed in the $^{16}\text{O}_2$ and $^{18}\text{O}_2$ environments are the same at the earlier delay time of 550 ns. The
127 $^{16}\text{O}_2$ and $^{18}\text{O}_2$ spectra show a clear difference at the late delay time of 1300 ns with distinct
128 features at 593.56 nm (in $^{16}\text{O}_2$) and 593.74 nm (in $^{18}\text{O}_2$), as shown in Figure 2d. Figures 2b and
129 2d show magnified views (from 593 nm to 594 nm) of the spectral features in Figure 2a and 2c,
130 respectively. These respective features are only present at any appreciable intensity in their

unique oxygen isotope environments. Though the features at 593.56 nm and 593.74 nm are
132 observable at the 550 ns delay time (Fig. 2b), they become significantly more intense than the
133 neighboring 593.38 nm atomic line at later delay (Fig. 2d). Further, the relative intensity of the
134 line at 593.56 nm (in $^{16}\text{O}_2$) is roughly 2-fold higher in absolute intensity than the 593.74 nm line
135 (in $^{18}\text{O}_2$) at identical delay times.

In Figure 3, the intensities of the 593.56 nm and 593.74 nm peaks are compared with the
136 intensity of the neighboring atomic line at 592.55 nm (as shown in Fig. 2a), taken as ratios to the
137 strong atomic line at 591.54 nm (labeled in Fig. 1) in oxygen (both $^{16}\text{O}_2$ and $^{18}\text{O}_2$, Figure 3a), and
138 argon (Figure 3b). In the 1 atm oxygen environment, the atomic line ratios (blue triangles)
139 remain relatively time-invariant for delay times exceeding 500 ns (decreased by roughly 25%
140 from the value at 300 ns delay), while the peaks at 593.56 nm (black circles) and 593.74 nm (red
141 squares), taken as ratios to the atomic line at 591.54 nm, increase by more than 2-fold. However,
142 in the 1 atm Ar environment, all of these ratios become relatively constant after 300 ns.
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The time-dependent in-growth of the 593.56 nm peak relative to the neighboring atomic
144 emission lines (Fig. 3a) in the $^{16}\text{O}_2$ experiment suggests this is the same feature reported in recent
145 studies by Mao *et al.*¹⁸ (593.55 nm) and Hartig *et al.*^{19,20} (593.57 nm), which were assigned as
146 U_xO_y ¹⁹ or UO ^{18,20}. The absence of a peak at 593.56 nm in $^{18}\text{O}_2$ is evidence that this is due to the
147 emission from an oxide of uranium; in fact, there appears to be a local minimum in the spectrum
148 at this position in the $^{18}\text{O}_2$ ablation environment. The in-growth of the 593.74 nm peak in the
149 $^{18}\text{O}_2$ environment provides further evidence that these features are associated with uranium oxide
150 emission, particularly as it has a similar time dependence to that of the 593.56 nm peak in $^{16}\text{O}_2$
151 (Fig. 3a), and neither peak shows a relative increase in the Ar environment (Fig. 3b).
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It is important to note that there are weak atomic emission lines reported at 593.55 nm and 593.74 nm²⁵. Further, the shoulder at 593.74 nm shown in Figure 2b in the spectrum acquired in ¹⁶O₂ could lead to the conclusion that the peak in ¹⁸O₂ is due to atomic emission. However, the spectra shown in Figure 2 and the high-resolution time-resolved spectra of Mao *et al.*¹⁸ both show there is never a time when the intensity at 593.74 nm exceeds the intensity of the atomic emission line identified at 593.38 nm. This is not the case in the ¹⁸O₂ experiment, where the peak at 593.74 nm becomes the dominant feature in the spectrum (Figure 2d). Given the clear increase in intensity of the peaks at 593.56 nm and 593.74 nm at late delay times relative to the atomic line intensities, it is unlikely that either of these peaks are solely the result of atomic emission, especially considering their notable absence in Ar. Nevertheless, the presence of atomic emission interference could explain the aberrant increase in all the ratios shown in Figure 3 at early delay (300 ns), when atomic emission has been shown to dominate molecular emission^{7,17}.

As stated above, the relative intensity change in peaks alone is not sufficient to identify this emission as a UO band. Kaledin and Heaven²¹ reported molecular band centers for ²³⁸U¹⁶O by free-jet expansion and laser excitation at 593.52 nm and 593.66 nm at low-resolution, and 593.48 nm at high-resolution (shown as filled black circles, Figure 2d) – assigned to a $7s\sigma \rightarrow 7p\pi$ metal-centered transition²⁶. That study also reports bandheads for ²³⁸U¹⁶O at 593.48 nm, 593.55 nm, and 593.68 nm in thermal emission spectra (shown as open black circles, Figure 2d). The peak we measured at 593.56 nm in ¹⁶O₂, and the positions reported by Hartig *et al.* (2017a), Hartig *et al.* (2017b), and Mao *et al.* (2017), are approximately in the same location as those reported by Kaledin and Heaven (1997), and could potentially be the convolution of multiple bands.

As seen in Figure 2d, the apparent 593.56 nm peak width encompasses the positions of at least three peaks observed in the published free-jet expansion and emission data. Interestingly,

free-jet expansion data recorded at 130 K show the most intense peak at 593.48 nm, while the
177 emission data (recorded at 2500 K) show the most intense peak at 593.52 nm, in contrast to the
178 peak position of 593.56 nm measured in the high-resolution spectra shown in Mao *et al.*, (2017).
179 Given that laser ablation plumes are initially much hotter (up to 10000 K or more)¹, it is possible
180 that this observed shift in the $^{238}\text{U}^{16}\text{O}$ peak position is due to differences in the temperature at
181 which the data were acquired. While a temperature-based attribution is speculative, it plausibly
182 accounts for the 0.04-0.08 nm longer wavelength reported in the studies by Hartig *et al.*, (2017a),
183 Hartig *et al.* (2017b), Mao *et al.*, (2017), and this study.

184 For $^{238}\text{U}^{18}\text{O}$, only free-jet expansion data are available in the study by Kaledin and Heaven
185 (1997), seen as red circles in Figure 2d. While an intense band center is reported at 593.74 nm
186 (the same location as the peak measured in the present study), the free-jet expansion data show a
187 very intense peak at 595.69 nm, a position which did not exhibit any notable shift or intensity
188 change in our spectra (see Supporting Materials). We also note that, in the free-jet expansion
189 data of Kaledin and Heaven for $^{238}\text{U}^{16}\text{O}$, a peak was observed at 581.38 nm that was slightly
190 more intense than that at 593.48 nm. This peak was not apparent (or at least much less intense) in
191 our spectra and it was not reported in either of the two recent emission studies^{18,19}. It is possible
192 that the intensity-ratios observed in free-jet expansion and laser induced fluorescence studies are
193 not necessarily indicative of what might be observed in ablation spectra due to vastly different
194 experimental conditions in temperature (130 K for free-jet expansion vs. thousands of kelvins for
195 emission studies) and pressure. Particularly, the effect of pressure could affect the intensity ratios
196 by kinetically favoring one vibronic transition over another.

197 While the Kaledin and Heaven (1997) study do not report emission data in an $^{18}\text{O}_2$
198 environment, their free-jet expansion data signal a band center at 593.74 nm attributed to $^{238}\text{U}^{18}\text{O}$

200 a prominent emission feature in the ^{18}O ablation environment, which was not observed in Ar.
201 Further, they report an isotopic shift of 0.197 nm between the $^{238}\text{U}^{16}\text{O}$ and $^{238}\text{U}^{18}\text{O}$ in this
202 position from the same assigned transition. In our study, the ~ 0.18 nm shift between the 593.56
203 nm and 593.74 nm peaks in $^{16}\text{O}_2$ and $^{18}\text{O}_2$, respectively, is (given our spectral resolution)
204 indistinguishable from the value reported by Kaledin and Heaven (1997), acquired from free-jet
205 expansion experiments. While there is an obvious difference in intensity between the peaks we
206 measured at 593.56 nm in $^{16}\text{O}_2$ and 593.74 nm in $^{18}\text{O}_2$ (the $^{238}\text{U}^{16}\text{O}$ peak is roughly 2-fold higher
207 in intensity), dramatic changes in relative intensity with isotopic substitution are shown in many
208 of the transitions reported from free-jet expansion experiments by Kaledin and Heaven (1997).

209 The growth in relative intensity we observed in oxygen ablation environments, and lack
210 thereof in argon, are compelling evidence that the peak at 593.56 nm is a uranium oxide emission
211 band. Further, the spectral shift in the peak from 593.56 nm in $^{16}\text{O}_2$ to 593.74 nm in $^{18}\text{O}_2$
212 corresponds to the shift shown by free-jet expansion/laser excitation between $^{238}\text{U}^{16}\text{O}$ and
213 $^{238}\text{U}^{18}\text{O}$. This affirms conclusions drawn from other recent laser ablation experiments.
214 Considering the easily resolvable isotopic shift, this substitution technique may be useful for
215 identifying (and assigning) future U_xO_y emission lines for exploring high-temperature uranium
216 chemistry as well as for use in analytical techniques such as LAMIS.

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234 Supporting Material

235 See supporting Figure S1 for a comparison of the band positions published by Kaledin and
236 Heaven (1997) and the full emission spectrum we recorded at 1300 ns in both $^{16}\text{O}_2$ and $^{18}\text{O}_2$.

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286 Figure captions

287 Figure 1. Time-resolved emission spectra obtained upon laser ablation of depleted uranium in
288 (A) $^{16}\text{O}_2$, (B) $^{18}\text{O}_2$, and (C) Ar. Each spectrum was collected at 250 ns delay increments, starting
289 with 300 ns delay (top spectrum) to 1300 ns delay (bottom spectrum), with a 250 ns gate at each
290 increment. The uranium atomic emission lines at 591.54 (highlighted in blue on the left) and
291 593.38 nm (indicated by blue arrows) are evident in $^{16}\text{O}_2$, $^{18}\text{O}_2$, and Ar. Molecular emission peak

positions are highlighted in blue on the right-hand side of each spectrum, at 593.56 nm for $^{238}\text{U}^{16}\text{O}$ and 593.74 nm for $^{238}\text{U}^{18}\text{O}$.

Figure 2. Emission spectra for uranium ablation in $^{16}\text{O}_2$ and $^{18}\text{O}_2$ at 550 ns delay, panels (A) and (B), and 1300 ns delay, panels (C) and (D). The spectra in both $^{16}\text{O}_2$ and $^{18}\text{O}_2$ are dominated by atomic emission lines at early delay times (550 ns), though in the magnified spectrum in panel (B), U^{16}O and U^{18}O emission lines can be observed. At later delay times (1300 ns), these peaks become the dominant features in the spectra. In panel (D), the UO band positions from Kaledin and Heaven (1997) are plotted as red circles (free-jet expansion and laser excitation, $^{238}\text{U}^{18}\text{O}$), filled black circles (free-jet expansion and laser excitation, $^{238}\text{U}^{16}\text{O}$), and open black circles (emission, $^{238}\text{U}^{16}\text{O}$).

Figure 3. (A) Molecular emission and uranium atomic emission (at 592.55 nm) intensities as a function of delay time, taken as ratios to the intense uranium atomic emission line at 591.54 nm. The atomic emission ratio is relatively constant in comparison to the molecular emissions, which increase by a factor of more than 2 from 550 ns delay to 1300 ns delay. The earliest delay time (300 ns) show a marked increase in molecular emission intensity, particularly for the $\text{U}^{18}\text{O}/\text{U}$ ratio (marked by a red asterisk). This may be due to interference by atomic emission lines, or high plasma-continuum emission. (B) The same ratios are shown from the spectra collected in 1 atm Ar. Here, all the ratios are shown to be relatively invariant, in contrast to the relative increases shown for the molecular emission peaks in oxygen (A).





