

5p and 4f photoabsorption in third-peak rapid-neutron-capture-process elements Ir, Pt, and AuEric Doyle^{✉,*}, Padraig Dunne^{✉,†} and Patrick Hayden[✉]*School of Physics, University College Dublin, Belfield, Dublin 4, Ireland*

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Photoabsorption spectra of ions of iridium, platinum, and gold have been recorded using the dual laser plasma technique in the spectral region between 48 and 126 eV. Features due to 5p and 4f excitation in neutral to four times ionized species lie in this region. Evidence of the rapid decay of the 5p hole following photoabsorption is provided by the widths of the spin-orbit split transition arrays, in contrast to the sharper and narrower features seen arising from 4f photoabsorption. The analysis of the iridium spectra is supported by atomic structure calculations and isoelectronic series analysis. Agreement with previous analysis of the spectra of platinum and gold is seen and some new identifications are also made. The significance of these *r*-process elements for astrophysical research is highlighted.

DOI: [10.1103/xk71-4n9b](https://doi.org/10.1103/xk71-4n9b)**I. INTRODUCTION**

Prior to 2017, binary neutron star (BNS) mergers had been suggested to account for the nucleosynthesis of roughly half of the quantity of elements heavier than iron ($Z=26$) in the universe via the rapid neutron capture process (*r* process) [1]. These merger events are followed by radioactively powered kilonova emission from the expanding merger ejecta. Watson *et al.* [2] identified spectral features attributable to the neutron-capture element, strontium, in the time-series spectra observed of the kilonova AT2017gfo, which followed the BNS merger detected as the gravitational wave event GW170817. Subsequent research from a broad community [3] supports the hypothesis that BNS mergers are a significant site for the *r* process. The increasing reach and localization capabilities of gravitational-wave detectors, the expansion of ground- and space-based instrumentation for detecting kilonova emission [4], and the progress in modeling BNS mergers and radiation transport in the kilonovae have collectively increased the significance of studying the atomic structure of *r*-process elements and ions.

Gillanders *et al.* [5] reported the number of spectral lines belonging to species and elements of interest in the study of the photospheric epoch of AT2017gfo. These data are essential for accurate modeling of both the kilonova and the BNS merger that preceded it, with a particular interest in *r*-process elements. Table 1 in that publication reports zero lines for the spectra of Pt^+ , Pt^{2+} , Au^+ , and Au^{2+} . More recently, Gillanders *et al.* [6] emphasized the need for more comprehensive atomic line transition data to interpret signals from the late

stages of the kilonova. They identified Ir, Ir^+ , Pt, Au, and Au^+ as candidate ions that may contribute to key spectral features in the post-photospheric epoch of AT2017gfo, thereby underscoring the demand for further research into these species. Additionally, McCann *et al.* [7] illustrated the sparsity of data available for the ions of gold beyond singly ionized systems.

The dual laser plasma (DLP) technique [8,9] uses the continuum generated by a laser-produced plasma (LPP) formed on a high-*Z* solid target to probe a second LPP containing the ions of interest. By increasing the time delay between the formation of the absorber plasma and the continuum-emitting backlighter plasma, it is possible to probe successively cooler plasmas containing lower ionization stages. The backlighter plasma is typically formed on a tungsten or hafnium target, which emits a smoothly varying continuum spectrum between 20 and 200 eV [10]. The extreme ultraviolet (EUV) continuum emission closely follows the temporal duration of the driving laser pulse, lasting typically 5–10 ns. This narrow temporal window, short compared to the timescale of the absorber plasma's evolution, enables selective probing of the dominant ion stages. Such selectivity greatly aids the analysis of spectra arising from multiple ion stages and from both ground and excited states within a particular ion stage. Time-resolved EUV photoabsorption spectra thus provide valuable insight into the evolution of the absorbing plasma, which is particularly useful in interpreting the often complex ultraviolet, visible, and infrared photoabsorption spectra of laser plasmas containing iridium and other elements contributing to the interpretation of kilonova spectra.

Photoionization cross-section measurements between 50 and 400 eV of iridium vapour under vacuum at 1×10^{-6} mbar were obtained by Cukier *et al.* [11] using direct photoabsorption of synchrotron radiation at the ACO storage ring (LURE) in Orsay, France. The observed spectra contained two strong features in the region of the O_2 (50 eV) and O_3 (63 eV) absorption edges with a cross section of 16–18 Mb, while between 80 and 400 eV the photoionization cross section measured less than 8 Mb. Simulated spectra were produced which provided agreement with experimental

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results in terms of absorption edge positions and the overall shape, but failed to account for the absolute cross section. The presence of peaks just below the O_2 and O_3 absorption edges were suggested to be due to $5p^65d^7 \rightarrow 5p^55d^8$ transitions, broadened by $5p^55d^7\epsilon d$ autoionization. Colarusso *et al.* [12] reported their photoionization threshold measurements of neutral iridium ($[Xe] 4f^{14}5d^76s^24F_{9/2}$) to be $72\,324 \pm 2\text{ cm}^{-1}$ using mass-analyzed optical-optical double-resonance spectroscopy, which provided close agreement with their theoretical calculations. The total atomic (binding) energy of the Ir ground state was calculated by Rodrigues *et al.* [13] using the Dirac-Fock approximation to be $-484\,754\text{ eV}$.

Single and double photoionization of atomic platinum were recorded at the BESSY storage ring in Berlin [14] in the range of $4f$ and $5p$ excitations using synchrotron radiation. The observed photoion yield spectra contain multiple Fano-type resonances, identified with the aid of shifted Hartree-Fock calculations [15]. As in many of the reported spectra of sixth row elements, electron correlations significantly influence the observed spectra. In their introduction, Sladeczek *et al.* give an excellent account of the influence of the $5p$, $4f$, and $5d$ orbitals, and the substantial overlap between them, on the observed spectra.

Photoionization cross-section measurements of Ir^+ and Ir^{2+} ions were conducted by Martins *et al.* [16] at the electron storage ring BESSY in Berlin. These data were obtained by probing the vapor of a thin iridium wire, Ohmic heated to 2600 K, with synchrotron radiation between 40 and 70 eV, and having $E/\Delta E \simeq 120$. The spectra contain a broad resonance at 47 eV attributed to $5p$ photoionization in Ir^+ , and weaker, narrower features at 59 and 62 eV due to $4f$ photoionization in Ir^+ and Ir^{2+} contributions. This interpretation was aided by $5p$ and $4f$ excitation calculations using the Hartree-Fock method provided by the COWAN code [15], which included configuration interaction of initial states $[Xe] 4f^{14}5d^76s^24F_{9/2}$ and $[Xe] 4f^{14}5d^86s^24F_{9/2}$ and had features broadened by overlapping resonance effects [17]. The calculated Ir^+ and Ir^{2+} photoionization cross sections closely match the observed $4f$ transitions located between 59 and 62 eV and show a wider structure centered at 50 eV which is similar in shape but is offset from the corresponding $5p$ resonance at 47 eV in the experimental data. In a follow-up work [18] Martins *et al.* conduct a survey on photoionization in $5d$ elements, supported by relativistic time-dependent local-density approximation (RTDLDA) calculations [19], enhanced by Hartree-Fock calculations using the COWAN codes. They comment that due to the proximity of the $4f$ and $5p$ subshells, interacting core resonances originating from different subshells can be investigated in the same spectral region.

Combining beams of tungsten ions extracted from an electron cyclotron resonance ion source with synchrotron radiation from the Advanced Light Source synchrotron enabled Müller *et al.* [20] and McLaughlin *et al.* [21] to measure absolute photoionization cross sections for W^+ and W^{2+} respectively, with 100 meV resolution. State-of-the-art R -matrix calculations [22] of the photoionization cross sections included about 400 target states. These were based on GRASP atomic structure calculations which were shifted to match known levels from the NIST Atomic Spectra Database [23], benchmarked with the experimental measurements. The

agreement between the experimental results and the calculations were remarkably good for such complex atomic systems.

Owing to their relevance for nuclear fusion studies, the ions of tungsten have been extensively studied, and the NIST database lists typically hundreds of known levels for each ion. In contrast, energy levels of many of the ions of iridium, platinum, and gold are not well known, with either one or no levels listed for Ir^{2+} , Pt^{2+} , Au^{2+} , and Au^{3+} . These ions are therefore less amenable to the atomic fine structure and cross-section calculations of the detailed type performed for tungsten ions.

In a DLP experiment, Su *et al.* [24] used a laser-produced plasma as a source of gold ions ranging from two to four times ionized. This was probed between 70 and 127 eV by the continuum emitted by a second laser-produced plasma, formed on a tungsten target. This study revealed $4f$ and $5p$ photoabsorption, interpreted with the aid of calculations using the COWAN suite of atomic structure codes [15], with configuration interactions. They obtained good agreement with the observed spectra and made predictions for the shape of the spectrum at energies below what they were able to observe. They predicted the photoabsorption cross sections for Au^{2+} , Au^{3+} , and Au^{4+} between 40 and 70 eV to be a decay of the $5p$ photoabsorption peak observed close to 70 eV, followed by another broad peak below 60 eV, which diminished towards 40 eV. This latter peak they predicted to be the lower-energy component of the spin-orbit split $5p \rightarrow 5d$ photoabsorption resonance. The height of this peak relative to its higher-energy companion decreased with increasing ionization, and some discrete structure was predicted to appear between the two peaks in the simulated spectrum of Au^{4+} . This work built on the earlier DLP study of atomic gold by Koble *et al.* [25], which reported both $5p$ and $4f$ photoabsorption, with two prominent Fano-type resonances [26] appearing over 200 ns after plasma formation. These profiles provided strong evidence of electron correlation effects between core- and valence-electron excitations.

In a later DLP experiment, with precise spatial control of the region probed by the tungsten continuum, Doyle *et al.* [27] studied platinum plasmas between 69 and 127 eV, obtaining $4f$ photoabsorption spectra in species ranging from singly to four times ionized. Analysis was facilitated by the COWAN suite of codes, with additional insight into quasicontinuous spectral features gained using the RTDLDA code of Liberman and Zangwill [19]. This work showed similar spectra to the study on gold by Su *et al.*, with broad $4f \rightarrow 5d$ resonances at lower energy and narrower features due to $4f \rightarrow 6d$ transitions at higher energies; $5p$ photoabsorption was absent from these spectra, as it is predicted to lie at energies below 69 eV [8].

In the present study, analysis of spectra from ions of all three elements enabled isoelectronic comparison between iridium, platinum, and gold ions. We have identified and analyzed new features due to $4f$ and $5p$ photoabsorption in iridium, observed $5p \rightarrow 5d$ absorption features previously predicted in the spectrum of gold by Su *et al.* [24], and extended the studies on platinum by Doyle *et al.* [27] to observe $5p$ photoabsorption at lower energies. This study may encourage more sophisticated, merged-beam experiments on the ions whose spectra are reported here.

II. EXPERIMENT

A line-focused LPP served as the absorbing medium for iridium, platinum, and gold species. These plasmas were probed by the continuum emission of a tungsten LPP focused to a point source in a series of DLP experiments conducted under vacuum conditions below 10^{-4} mbar. The absorber plasma was generated using a Continuum Surelite III-10 pulsed Nd:YAG laser with an average output of 560 ± 7 mJ at 1064 nm. A planoconvex cylindrical lens ($f = 50$ mm) focused the beam to an approximately 9×0.5 mm² region with the focal plane situated 4.20 ± 0.01 mm in front of the absorber target surface, yielding an average power density ϕ_a of approximately 10^9 W cm⁻². However, the Gaussian beam would have higher ϕ_a close to the center of the broad focal area, yielding higher ion stages. The backlighter plasma was produced using a Spectron SL805 laser with an average pulse energy of 800 ± 9 mJ, fired after absorber plasma formation, with a variable interplasma time delay Δt in the range 20–350 ns (± 1 ns) for each of the experimental spectra presented here.

EUV photons in the energy range 48–125 eV were diffracted by a Shimadzu model 30-003 grating with 1200 grooves/mm, housed within a custom-built 0.25-m spectrometer (resolving power $E/\Delta E = 195$). The resulting spectra were recorded photoelectrically using an Andor DX436-BN CCD camera, which features a 2048^2 pixel array with individual pixel dimensions of 13.5×13.5 μm^2 . The spectral profile I_0 of each backlighter plasma image was obtained by summing the illuminated pixel array perpendicular to the dispersion axis. The photoabsorption signal I was acquired by imaging the backlighter after it passed through the absorber plasma, followed by identical image processing. A predetermined absorber-only background signal I_a was subtracted from I to correct for self-emission from the absorber plasma. Each absorbance spectrum was subsequently calculated using Eq. (1). Calibration of the pixel-to-wavelength conversion, achieving average residuals below 0.1 eV, was performed using 49 spectral transition lines from the NIST Atomic Spectra Database [23], from reference spectra of aluminium, silicon, and iron:

$$\text{absorbance} = \ln \left(\frac{I_0}{I - I_a} \right). \quad (1)$$

A half-duplex RS-485 daisy chain of custom-designed electronic circuit boards, based on the STSPIN820 stepper motor driver and controlled by an Arduino Nano A000005, was employed as the driver system for Nema 8 captive linear actuators. Each actuator was mounted to a linear translation stage, enabling micron-precision positional control of beam optics and target materials. A second Arduino Nano was used to synchronize the timing of both laser flashlamps with the camera controller and a DG645 delay generator, which provided nanosecond-precision control over Δt .

The primary control parameters in these experiments were ϕ_a , Δt , and the spatial positioning of the absorber plasma relative to the backlighter plasma. For each species, datasets in which Δt varied between 20 and 350 ns were collected after selecting appropriate values for the remaining parameters. The absorber focusing conditions, the position of the absorber

plasma's central axis relative to the optic axis, and the distance of the absorber target's surface from the optic axis were each adjusted to optimize the spectral intensity ratio I_0/I , a key factor in ensuring optimal contrast of spectral features across the temporal range. For each spectrum, both the I_0 and I_a signals were recorded under fixed spatial alignment optimized to maximize intensity, followed by a focus adjustment that balanced total photon yield with a more uniform spectral continuum.

III. ATOMIC STRUCTURE CALCULATIONS

The EUV photoabsorption spectra of iridium, platinum, and gold ions are influenced by collective effects, absorption from low-lying excited states, the near degeneracy of $5d$ and $6s$ subshells, and autoionization due to the photon energies being greater than the ionization potentials in many cases. Thus the computation of synthetic spectra demands a careful choice of initial and final configurations, within the computational resources available. The calculations here were performed using Cowan's well-established suite of Hartree-Fock with configuration-interaction atomic structure codes [15]. The total effects of configuration interaction generally need to be further approximated by adjusting the Slater parameters F^k and G^k , typically reduced here to 85% of their *ab initio* values.

The set of input configurations, including continuum levels and decay mechanisms to compute autoionization widths, are given in Table I for iridium. Unfilled $5d$ subshells lead to bandlike energy-level distributions [27] and to substantial overlap of energy levels between neighboring configurations, resulting in significant configuration mixing. For example, in neutral Ir the configuration average energies of the [Xe] $4f^{14}5d^9$ and [Xe] $4f^{14}5d^76s^2$ configurations lie only 1.07 and 0.64 eV above that of the [Xe] $4f^{14}5d^86s^1$ configuration, respectively, while the lowest-lying level of [Xe] $4f^{14}5d^76s^2$ lies 0.17 and 3.1 eV below the lowest levels of [Xe] $4f^{14}5d^86s^1$ and [Xe] $4f^{14}5d^9$, respectively.

The configurations in Table I lead to 579 initial levels excitable to 131 600 final levels, which then may autoionize to 254 417 continuum levels across all the ion stages considered. Given the large number of levels and transitions involved, two calculations were performed for each ion stage. The first included all transitions of type $5p \rightarrow nd, ms$ and their appropriate decay channels, while the second included all $4f \rightarrow nd$ transitions along with suitable decay channels. The results of these calculations were parsed to extract the transition energies, absorption oscillator strengths, and decay widths for each family of transitions.

As the various levels in each configuration are thermally populated in the plasma, a Boltzmann distribution over the lower level of each transition was taken as a weighting factor. Each transition was then represented by a Lorentzian profile, where the half-width at half maximum intensity was taken as the calculated decay width, and the area was set to the oscillator strength multiplied by the Boltzmann weighting factor. This profile was further convolved with a Gaussian profile to account for the resolution of the spectrometer and compared to the experimental data to identify regions where the different transition types from different ion stages contribute to the observed spectra. Finally, the resulting spectra are shifted in

TABLE I. Initial- and final-state configurations in Ir-Ir⁵⁺. Here $x = 9 - q$, where q is the ionic charge, [Xe] represents the electronic configuration of xenon, n and m have values $n = \{5, 6, 7\}$ and $m = \{6, 7\}$, and δ is the ejection energy of a free electron of angular momentum p or f .

Initial states	Final states	
	Discrete	Continuous
[Xe] 4f ¹⁴ 5d ^x	[Xe] 4f ¹³ 5d ^x nd	[Xe] 4f ¹⁴ 5d ^{x-2} nd + $\delta(p, f)$
	[Xe] 4f ¹⁴ 5p ⁵ 5d ^x nd	[Xe] 4f ¹⁴ 5d ^{x-2} nd + $\delta(p, f)$
	[Xe] 4f ¹⁴ 5p ⁵ 5d ^x ms	[Xe] 4f ¹⁴ 5d ^{x-1} + $\delta(p, f)$
[Xe] 4f ¹⁴ 5d ^{x-1} 6s	[Xe] 4f ¹³ 5d ^{x-1} 6s nd	[Xe] 4f ¹⁴ 5d ^{x-2} ms + $\delta(p, f)$
		[Xe] 4f ¹⁴ 5d ^{x-2} nd + $\delta(p, f)$
	[Xe] 4f ¹⁴ 5p ⁵ 5d ^{x-1} 6s nd	[Xe] 4f ¹⁴ 5d ^{x-3} 6s nd + $\delta(p, f)$
		[Xe] 4f ¹⁴ 5d ^{x-2} nd + $\delta(p, f)$
	[Xe] 4f ¹⁴ 5p ⁵ 5d ^{x-1} 6s ms	[Xe] 4f ¹⁴ 5d ^{x-3} 6s nd + $\delta(p, f)$
[Xe] 4f ¹⁴ 5d ^{x-2} 6s ²	[Xe] 4f ¹³ 5d ^{x-2} 6s ² nd	[Xe] 4f ¹⁴ 5d ^{x-1} + $\delta(p, f)$
		[Xe] 4f ¹⁴ 5d ^{x-2} 6s + $\delta(p, f)$
	[Xe] 4f ¹⁴ 5p ⁵ 5d ^{x-2} 6s ² nd	[Xe] 4f ¹⁴ 5d ^{x-3} 6s ² + $\delta(p, f)$
		[Xe] 4f ¹⁴ 5d ^{x-1} + $\delta(p, f)$
		[Xe] 4f ¹⁴ 5d ^{x-2} 6s + $\delta(p, f)$
		[Xe] 4f ¹⁴ 5d ^{x-3} 6s ms + $\delta(p, f)$
		[Xe] 4f ¹⁴ 5d ^{x-2} 6s + $\delta(p, f)$
		[Xe] 4f ¹⁴ 5d ^{x-3} 6s ² + $\delta(p, f)$

energy to best match the observed spectra: +0.15 eV to $5p \rightarrow nd$, +0.7 eV to $5p \rightarrow ms$, and +1.5 eV to $4f \rightarrow nd$ transitions, for each ion stage.

IV. RESULTS AND DISCUSSION

Spectra were observed over a range of time delays for each element. Increments in the delay were 5 ns up to 100 ns, and 50 ns for delays longer than 100 ns. A selection of

these spectra between 48 and 125 eV, recorded at time delays ranging from 35 to 350 ns, is shown in Fig. 1. The maximum absorbances in the iridium spectra, as calculated in Eq. (1), increased from 0.8 at 20 ns to 5 at 200 ns, decreasing to 1.5 at 350 ns. The spectra share common features and are seen to evolve in a regular way at delays past 15 ns. Distinct absorption features emerge and fade with increasing time delay, reflecting the evolving ion stage composition of the plasma, and trends are evident along both isonuclear and isoelectronic

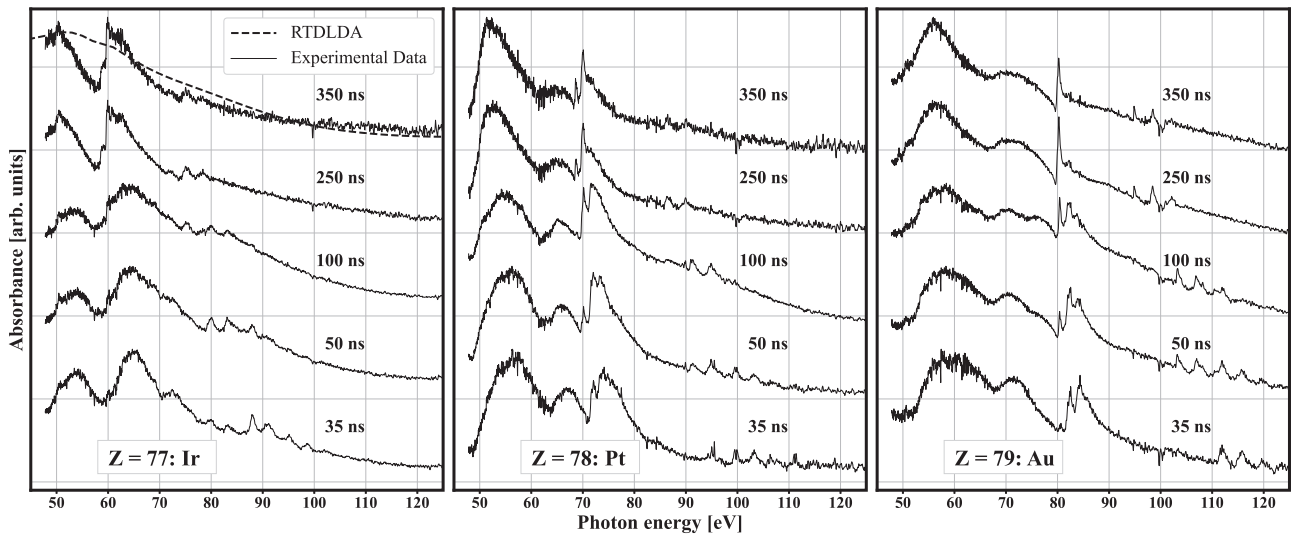


FIG. 1. Photoabsorption spectra of iridium, platinum, and gold laser-produced plasmas, recorded between 35 and 350 ns after their formation. Plots are scaled with respect to each other to cover a similar vertical range in the figure. An RTDLDA calculated cross section is shown for Ir at 350 ns delay.

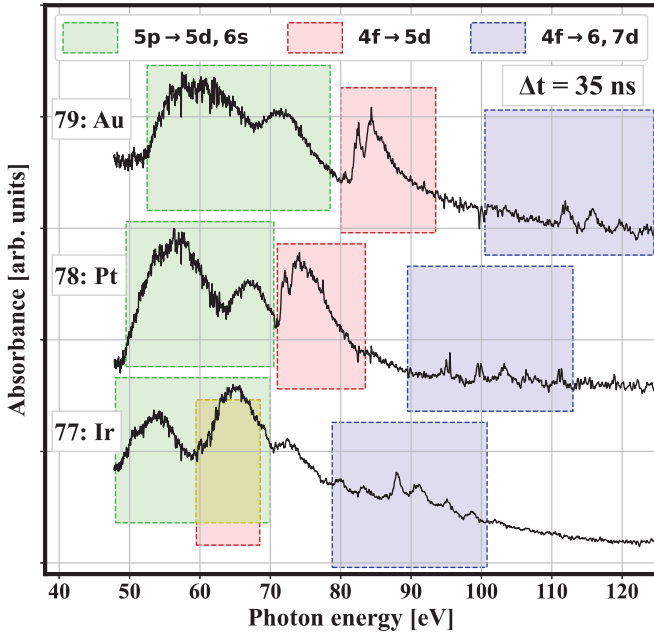


FIG. 2. Photoabsorption spectra of plasmas of iridium, platinum and gold, between 48 and 125 eV, recorded at a time delay of 35 ns. The shaded areas indicate regions where named transition arrays contribute strongly to each spectrum. Each spectrum is normalized to the maximum absorbance.

series. At the earliest times Ir^{5+} is present in the plasma, while after 300 ns has elapsed, the plasma contains mainly neutral and singly ionized species. The ~ 5 -ns duration of the continuum pulse that probes the plasmas gives a reasonable degree of ion stage selectivity. It should be noted that the continuum probe effectively integrates the signal along the long axis of the plasma, thereby combining absorption from regions of the plasma with varying temperature and density. A steady-state collisional-radiative model [28] was employed to estimate ion stage distributions, and the Boltzmann equation was used to populate the lower states, to best fit the simulated spectra to the observed spectra for each reported time delay. A consistent plasma electron temperature was used for both the CR model and the Boltzmann fit for each spectrum.

Figure 2 presents the spectra of plasmas formed on iridium, platinum, and gold targets at a time delay of 35 ns. The spectra of the three elements show broad transition arrays due to $5p \rightarrow 5d$ and $5p \rightarrow 6s$ transitions, with narrower features due to $4f \rightarrow 5d$ and $4f \rightarrow 6d$ transitions at higher energies, as reported previously in the spectra of platinum and gold plasmas [24,27]. In general, the transition arrays are situated at lower energies with increasing time delay. The $4f \rightarrow 5d$ transitions, which are merged with the $5p \rightarrow 5d$ transitions between 59 and 68 eV in iridium, are observed at relatively higher energies with increasing atomic number and are well isolated in the gold spectrum.

A. Iridium spectra

Analysis of iridium spectra above 75 eV, based on calculations using the COWAN suite of codes [15], identifies a number of $4f \rightarrow 6d$ transition arrays. The mean energies of

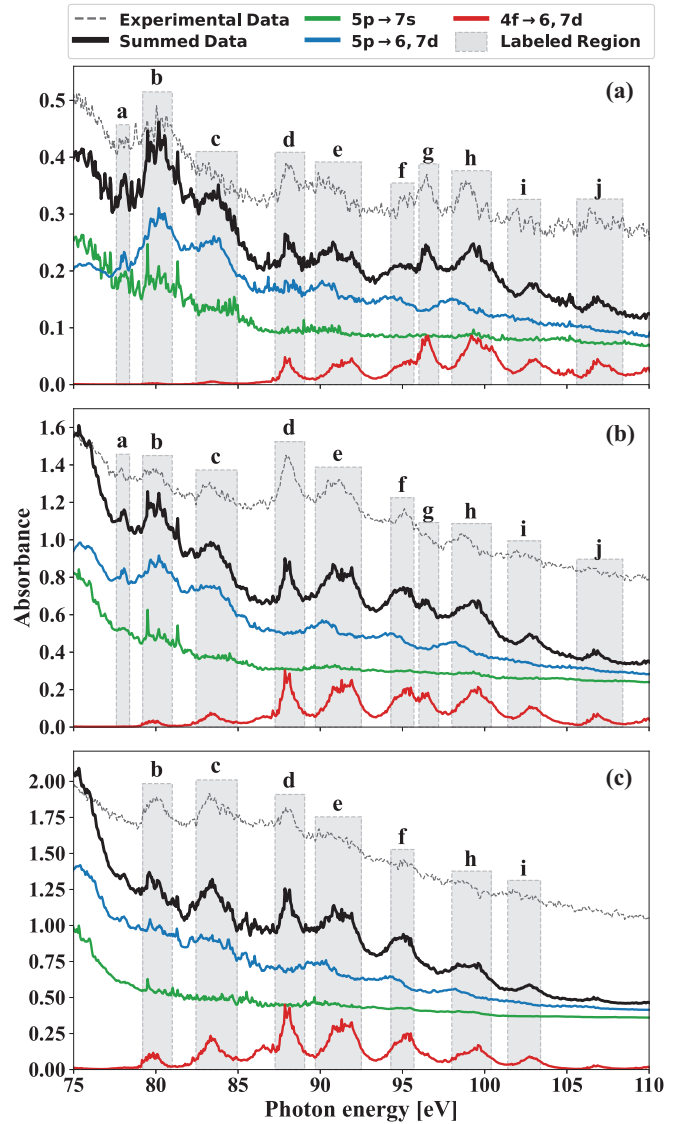


FIG. 3. Photoabsorption spectra of iridium LPPs at three time delays (a) $\Delta t = 20$ ns, (b) $\Delta t = 35$ ns, and (c) $\Delta t = 50$ ns, compared with corresponding synthetic spectra in the energy range 75–110 eV. Experimental absorbance was calculated using Eq. (1), and labeled regions indicate identified transition arrays as defined in Table III. The synthetic spectra, calculated from CR model-weighted COWAN transitions, are shown alongside their three constituent families for each case (a) $T_e = 9.0$ eV, (b) $T_e = 7.5$ eV, and (c) $T_e = 6.4$ eV. All simulated spectra have been scaled in intensity to best match the experimental data and shifted in energy as described in the text.

these arrays are located at 76.3 eV in Ir^+ , 85.6 eV in Ir^{2+} , 91.1 eV in Ir^{3+} , 102.5 eV in Ir^{4+} , and 108 eV in Ir^{5+} . This separation in energy of the $4f \rightarrow 6d$ arrays from different ion stages allows us to identify the ions contributing to the merged, broader features at lower energies in the same spectra. Figure 3 shows experimental iridium spectra, between 70 and 115 eV, recorded at delays of 20, 35, and 50 ns, along with synthetic spectra for plasma electron temperatures of 9.0, 7.5, and 6.4 eV. Good agreement is seen between the summed simulated and the experimental spectra. The distributions of ion stages at plasma temperatures ranging from 20 to 300 ns,

TABLE II. Percentage Ir ion compositions that best reproduce experimental spectra at various interplasma time delays Δt and their corresponding electron temperature T_e (assuming an electron density of 10^{21} cm^{-3}) according to the CR model used [28].

Δt (ns)	T_e (eV)	Ir ion compositions (%)					
		Ir	Ir ⁺	Ir ²⁺	Ir ³⁺	Ir ⁴⁺	Ir ⁵⁺
20	9.0	0.0	0.1	4.0	29.4	54.6	11.4
35	7.5	0.0	1.0	17.0	50.9	29.7	1.3
50	6.4	0.1	4.2	38.6	48.1	8.9	0.1
100	4.3	3.3	38.5	53.8	4.4	0.0	0.0
150	3.1	20.6	66.9	12.4	0.1	0.0	0.0
200	2.5	45.0	53.1	1.9	0.0	0.0	0.0
250	2.2	62.3	37.3	0.4	0.0	0.0	0.0
300	2.0	74.2	25.7	0.1	0.0	0.0	0.0

based on the CR model, are given in Table II. Details of labeled identified transition arrays are shown in Table III, including peak energy, contributing ion stages, number of transitions N , and the sum of weighted transition oscillator strengths gf values. Some features are comprised of contributions from adjacent ion stages and the number of $4f \rightarrow 6d$ arrays varies with the occupancy of the $5d$ subshell.

Below 70 eV the spectra of iridium plasmas show two broad features, comprising many thousands of transitions and making identification of individual transitions impossible. As seen in Fig. 4, $5p \rightarrow 5d$, $5p \rightarrow 6s$, and $4f \rightarrow 5d$ transition arrays are responsible for these two spectral features. The $5p$ spin-orbit splitting remains relatively constant at approximately ~ 11 eV from neutral to five times ionized iridium. The mean energy of transitions resulting in a $5p_{3/2}$ vacancy ranges from 55 eV at 20 ns, when the plasma is dominated by Ir³⁺ and Ir⁴⁺, to 51 eV at 350 ns, when the plasma mainly comprises neutral species. Likewise, the transitions resulting

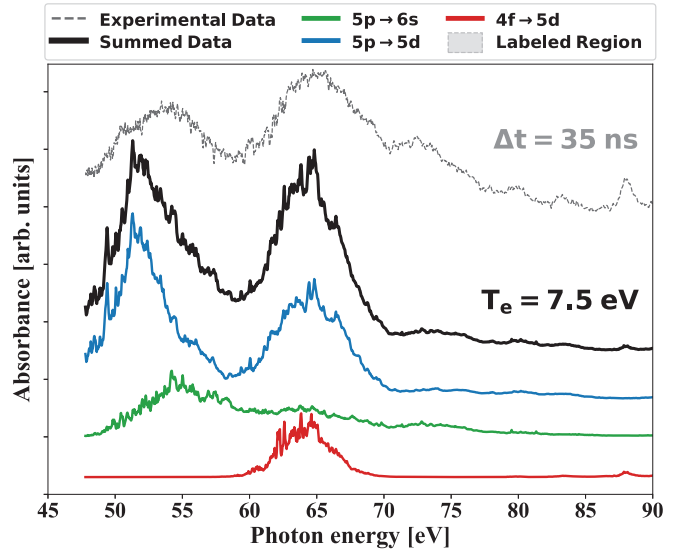


FIG. 4. Experimental photoabsorption spectrum of an iridium plasma at $\Delta t = 35$ ns in the energy range 48–90 eV, compared with a synthetic spectrum and its constituent transition families. The synthetic spectrum was calculated from CR model-weighted COWAN transitions at an electron temperature of $T_e = 7.5$ eV, scaled in intensity to best match the experimental data and shifted in energy as described in the text.

in a $5p_{1/2}$ vacancy center on approximately 66 eV at 20 ns, moving to 62 eV at 350 ns. The spectra are similar in appearance to the photoionization spectra recorded by Martins *et al.* [16], with one key difference. Martins *et al.* reported that they observed weak photoionization resulting in a $5p_{1/2}^{-1}$ state, due to the forbidden $5p_{1/2} \rightarrow 5d_{5/2}$ transitions. In [18] they note that filling the $5d$ subshell, along the elements of the sixth row, reduces the influence of the $5p_{1/2}$ contribution. The reverse effect is observed in our spectra of Ir plasmas: With increasing

TABLE III. Transition array statistics corresponding to the regions labeled in Fig. 4, for an iridium plasma recorded 35 ns after formation and containing Ir²⁺–Ir⁵⁺ ions. The displayed values were computed from COWAN code output for the specified families of transitions, within the indicated energy ranges and incorporating the energy shifts described in the text.

Label	Energy range (eV)	Ion	Transition array	N	$\sum gf$	$\sum \Gamma$ (eV)
<i>a</i>	77.6–78.4	Ir ⁴⁺	$5p \rightarrow 6d$	2370	3.40	353.82
<i>b</i>	79.2–81.0	Ir ⁴⁺	$5p \rightarrow 6d$	8049	23.57	1336.14
<i>c</i>	82.44–84.94	Ir ⁴⁺	$5p \rightarrow 6d$	14701	45.25	2808.71
			$4f \rightarrow 6d$	45678	7.28	119.91
			$5p \rightarrow 6d$	7791	10.14	375.02
<i>d</i>	87.25–89.05	Ir ³⁺	$4f \rightarrow 6d$	22252	4.29	130.54
<i>e</i>	89.7–92.5	Ir ³⁺	$4f \rightarrow 6d$	59885	12.81	355.01
			$5p \rightarrow 6d$	12131	15.81	8711.37
			$4f \rightarrow 7d$	12197	1.80	23.58
<i>g</i>	96.0–97.2	Ir ⁴⁺	$4f \rightarrow 6d$	12508	5.15	427.95
<i>h</i>	98.0–100.4	Ir ⁴⁺	$4f \rightarrow 6d$	37705	10.56	1093.96
			$4f \rightarrow 7d$	52111	5.12	82.07
			$4f \rightarrow 6d$	34915	9.49	714.46
<i>i</i>	101.4–103.4	Ir ³⁺	$4f \rightarrow 7d$	44522	4.14	51.73
			$4f \rightarrow 6d$	28659	3.18	64.91
			$4f \rightarrow 6d$	18784	9.19	136.40

ionization, the reduced occupancy of the $5d$ subshell causes $5p_{1/2} \rightarrow 5d$ transitions to grow in influence, shown by the relative increase of the feature centered around 65 eV. A second factor contributing to this difference is the relatively low vapor temperature above the Ohmic heated wire, on the order of 0.4 eV, compared to the temperature of the laser plasma, typically 2 eV after 300 ns. The laser plasma has a higher population in excited states which also have a reduced occupancy of the $5d$ subshell. This allows more transitions resulting in a $5p_{1/2}^{-1}$ state, further enhancing photoabsorption around 65 eV, as observed in the laser plasma spectra.

The $4f \rightarrow 5d$ resonances also contribute between 62 and 66 eV, as identified by our calculations and in photoionization studies [16,18]. The bulk of these transitions form a broad band approximately 7 eV wide, the center of which shifts from 61 eV at 350 ns to 65 eV at 20 ns, reflecting the increase in $4f$ binding energy with increasing ionization. As reported for platinum spectra in [27], the transition arrays above approximately 70 eV, overlay a continuumlike absorption feature which falls off with increasing energy up to around 110 eV. A many-body RTDLDA calculation [19] reproduces this feature when $5p$, $5d$, and $4f$ channels are included. The calculated cross section has a value of approximately 13 Mb at 90 eV. The RTDLDA calculations account for collective electronic behaviours not treated by COWAN codes.

B. Platinum spectra

The series of photoabsorption spectra of platinum plasmas recorded between 48 and 125 eV in Fig. 1 show good agreement at energies above 69 eV with the $4f$ photoabsorption reported by Doyle *et al.* [27]. In the spectrum recorded at 350 ns in Fig. 1, the resonances at 51 and 70 eV and the shoulder evident in the region of 64 eV reported by Sladeczek *et al.* [14] are clearly evident.

The spectra show the evolution of $5p$ photoabsorption in singly, doubly, and triply ionized platinum with decreasing time delay. The peak at 51 eV becomes more symmetric and moves towards 56 eV, while the feature between 60 and 70 eV grows in amplitude and moves by 2 eV to higher energies. Sladeczek *et al.* [14] reported that in neutral platinum, relativistic COWAN-code calculations ascribed the feature at 51 eV to $5p$ resonances and that at 70 eV to $4f$ resonances, excited from both $5d^9 6s$ and $5d^8 6s^2$ initial states. The photoionization from $5p$ excited states showed two resonances, associated with the spin-orbit split $5p_{3/2}$ and $5p_{1/2}$ hole states, separated by about 13 eV. The features due to $4f$ excitation were seen to overlap with and dominate the $5p_{1/2}$ resonance. In addition, the shoulder at 64 eV observed in the experimental cross sections, was far weaker in their calculations, even after shifting the *ab initio* calculations. In a similar argument to that raised by Martins *et al.* [18], they attributed this to the low probability of transitions between the $5p_{1/2}$ hole states and the vacant states in the more than half-filled $5d$ subshell, which would be predominantly $j = 5/2$ in character.

It is evident in Fig. 1 that the shoulder at approximately 64 eV in the spectrum recorded at 350 ns becomes stronger at shorter time delays, which probe more highly ionized plasmas. We can identify the dominant ion stage in each spectrum by comparing the features between 85 and 115 eV in Fig. 1

with analysis in [27]. At 250 ns the spectrum contains significant contributions from Pt^{2+} and Pt^+ , at 100 ns the spectrum is dominated by Pt^{3+} , and at 50 ns by Pt^{3+} and Pt^{4+} . As in the iridium case, the explanation for the rise in the $5p_{1/2}$ resonance is that with increasing ionization, vacant $j = 3/2$ states arise in the $5d$ subshell, permitting photoabsorption to occur from $j = 1/2$ states. The spin-orbit splitting of the $5p$ subshell does not change significantly along the isonuclear sequence from Pt^+ to Pt^{4+} .

Bilodeau *et al.* [29] observed photodetachment from negative platinum ions (Pt^-) at the Advanced Light Source synchrotron, with ion-frame photon energies up to 90 eV. This allowed for the removal of up to four electrons, generating species up to Pt^{3+} . Broad resonances associated with $5p$ excitation and strong, narrow Feshbach resonances due to $4f$ excitation were observed, at energies in agreement with previous studies [14] and more recent photoabsorption studies [27]. The evolution of $4f \rightarrow 5d$ transitions in Fig. 1 between 67 and 75 eV is consistent with these previous works.

C. Gold spectra

Spectra of laser-produced gold plasmas were recorded over a similar range of time delays to both iridium and platinum. As seen in Fig. 1, the evolution of spectral features and ion stages in gold plasmas over time is consistent with that of the Ir and Pt spectra observed in this series of experiments. Many of the features reported by Koble *et al.* [25] and Su *et al.* [24] have been observed in this experiment, in addition to new observations across the spectra.

At time delays of 250 and 350 ns we have seen features at 94 and 98 eV that are due to $4f \rightarrow 6d$ photoabsorption in neutral gold. They are also seen at a delay of 450 ns, confirming this suggestion in [25] from a spectrum observed at 600 ns delay. At time delays between 100 and 250 ns, features are seen at 103 and 107 eV that can be identified as arising from $4f \rightarrow 6d$ transition arrays in Au^+ . This identification is supported by calculations using the COWAN code and consistent isonuclear and isoelectronic trends.

These identifications augment those reported by Su *et al.* [24], where similar features between 110 and 130 eV at a time delay of 50 ns were attributed to $4f \rightarrow 6d$ transitions in Au^{2+} to Au^{4+} . The transition arrays due to Au^{4+} are seen in our spectra of gold plasmas recorded at a 35-ns time delay and those due to Au^{3+} are seen at a 50-ns time delay.

This consistency allows us to interpret the broader resonances seen in gold spectra between 47 and 85 eV, at time delays from 100 ns down to 35 ns. The first conclusion is that some of the structure between 82 and 85 eV, seen at a time delay of 100 ns in [25], can be attributed to $4f \rightarrow 5d$ absorption in excited states in singly ionized gold. The energy of this structure highlights the tighter binding of the $4f$ orbital in gold, as compared to platinum or iridium, and merits further analysis in the future. A second conclusion is that there is reasonable qualitative agreement between the simulated $5p \rightarrow 5d$ cross sections for Au^{2+} , Au^{3+} , and Au^{4+} below 80 eV reported in [24] and the observed photoabsorption cross sections at time delays decreasing from 100 ns to 25 ns in this work. In particular, the evolution of the ratio of the heights of the broad peaks at 58 and 73 eV with time delay is in

broad agreement with the corresponding feature ratios in the simulated cross sections for these gold ion stages presented in [24].

V. CONCLUSION

Photoabsorption spectra of laser-produced plasmas containing iridium, platinum, and gold have been recorded using the dual laser plasma technique for time delays ranging from 25 to 500 ns. Many features in the iridium spectra, plus some in the platinum and gold spectra, have been identified with the aid of atomic structure calculations. We observed consistent evolution of spectra along isonuclear and isoelectronic series and noted good agreement with previously reported spectra where available. We identified spectral contributions from neutral to four time ionized species with decreasing time delay for each element. The narrow $4f$ photoabsorption resonances contrast with the broad spin-orbit pair of features due to $5p$ photoabsorption. The proximity of $5d$ and $6s$ energy levels required inclusion of excited states in calculations of the synthetic spectra.

We have presented detailed temporal evolution of iridium laser-produced plasmas, detailing which ions are dominant between 30 and 300 ns after plasma formation. The visible and infrared spectra of plasmas containing near-neutral species of interest for kilonova studies, particularly r -process

elements such as Ir, Pt, and Au, and Sr, Y, and Zr, are frequently complex, containing hundreds of lines. The temporal mapping of ion stage evolution presented here may motivate further merged-beam photoionization experiments and detailed calculations. It will also aid analysis of visible and near-infrared photoabsorption spectra recorded in future dual laser plasma experiments, supporting analysis of kilonova observations [30].

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DATA AVAILABILITY

The data that support the findings of this article are openly available [31].

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