

Theoretical and experimental study of $4f$ - $5d$ Fano resonances in EUV photoabsorption of Au I and Au II

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Fano-type resonances in neutral and singly ionized gold in the extreme ultraviolet spectral region have been investigated using both experimental and theoretical approaches. Absorption spectra were obtained using the dual laser plasma technique, observing variations in ion populations in the absorbing Au plasma at delays between 300 and 500 ns after formation. The theoretical work used atomic structure calculations, performed for Au I and Au II using the COWAN suite of codes, to identify the main features in the experimental spectrum between 79 and 83 eV. Synthetic spectra were produced using Boltzmann weighting and a collisional radiative model, which allowed for direct comparison with the experiment. The agreement between experiment and calculation was generally very good. Experimental features attributed to Au II that have not previously been identified have been assigned.

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I. INTRODUCTION

Gold is of significant interest across various areas of research. In the context of inertial confinement fusion plasmas, gold is commonly used as the hohlraum material due to its high atomic number ($Z = 79$). High- Z materials exhibit large x-ray conversion efficiencies arising from their complex atomic structure [1–3]. Laser irradiation heats the interior of the gold hohlraum, producing x-ray-emitting plasmas [4,5]. The x-rays greatly enhance the uniformity of the radiation driving the implosion of the fusion capsule, directly influencing the overall fusion yield [6]. Gold nanoparticles are also extensively researched for the development of therapeutic and diagnostic tools in medicine [7].

Furthermore, gold is of importance in an astrophysical context. It has been suggested that approximately half of the elements heavier than iron ($Z > 26$) are produced in binary neutron star (BNS) mergers via rapid neutron capture (r -process) [8]. Kilonova emission follows this process, in which neutron-rich ejecta emit primarily in the ultraviolet, optical, and near-infrared spectral regions [9]. Accurate atomic structure data for r -process elements are crucial for improving models of BNS mergers and radiation transport. Fontes *et al.* [10] demonstrated that open f -shell configurations, particularly lanthanides, play a dominant role in determining kilonova opacities. Sixth-row elements with $Z \geq 80$ possess filled p , d , and f shells; consequently, elements with $Z < 80$,

such as Au, provide an important test bed for studying open-shell dynamics relevant to r -process element modeling.

Nonlocal thermal equilibrium modeling has become increasingly important due to its relevance in kilonova ejecta, fusion plasmas, and stellar atmospheres [11–13]. Such models require extensive atomic data; however, there remains a lack of atomic data for elements with $Z \geq 75$ [14]. Recently, Bromley *et al.* showed that the ionization cross sections of Te I–Te III are significantly enhanced by autoionization from excited states near the ionization threshold [15]. This emphasizes the importance of spectroscopic studies in the extreme ultraviolet (EUV), where autoionization is a relevant ionization mechanism.

Early spectroscopic studies of Au by Köble *et al.* [16] identified the presence of $4f \rightarrow 5d$ transitions exhibiting Fano profiles in the (80–100)-eV region using dual laser plasma (DLP) techniques. This involves generating a plasma from the material of interest using a high-intensity laser. After a set time, a second laser ionizes a target to produce a continuum which is used to probe the plasma. This work highlighted the importance of configurations containing $6s^2$ terms. Building on these results, DLP techniques and Hartree-Fock calculations were employed to conduct a study of Au III–Au V spectra [4]. It was found that with decreasing ionization level, $4f \rightarrow 5d$ transitions are increasingly dominated by configurations containing $6s^2$ terms, in agreement with earlier findings by Köble *et al.* [16]. Su *et al.* also discussed the presence of $4f \rightarrow 6d$ transitions towards the higher-energy side of the $4f$ transition array. They found that these $4f \rightarrow 6d$ features appear at 95–120 eV and, with decreasing ionization level, the transitions appear at lower energies [4].

Related studies have observed similar behavior in neighboring elements. In Tm plasmas, Fano profiles resulting from $4d \rightarrow 4f$ transitions were discovered in the (140–230)-eV region [17]. Fano-like profiles in Pt and W have been attributed to $4f \rightarrow 5d$ transitions near 69 eV [18]. COWAN-code

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calculations have identified Fano resonances associated with $4f$ and $5p$ transitions in Ta, W, Re, and Os [19]. More recently, prominent $4f$ photoionization features in the (69–127)-eV energy range were observed in Pt ions from Pt^+ to Pt^{4+} , supported by COWAN-code and RTDLDA calculations [20].

Recently, Ir, Pt, and Au have been studied using the same experimental and theoretical approaches [21]. While $4f \rightarrow 5d$ transitions were identified for neutral through four-time-ionized species, additional spectral features in the (79–83)-eV region at longer time delays remained unidentified.

In this work, we experimentally and theoretically study EUV photoabsorption in Au in the (79–83)-eV region. Experimental spectra were obtained using the DLP technique, and theoretical analysis was performed using COWAN's suite of Hartree-Fock atomic structure codes. Previous work in this region focused on Au I [16] and Au III–Au V [4]. In Au I, Köble *et al.* [16] presented strong evidence for the $[\text{Xe}]4f^{14}5d^96s^{2,2}D_{5/2} \rightarrow [\text{Xe}]4f^{13}5d^{10}6s^{2,2}F_{7/2}$ transition and its manifestation as a Fano profile. They also observed the $[\text{Xe}]4f^{14}5d^96s^{2,2}D_{3/2} \rightarrow [\text{Xe}]4f^{13}5d^{10}6s^{2,2}F_{5/2}$ transition at 82 eV but, due to its relative weakness, commented on the poor quality of the experimental evidence for this assignment. Su *et al.* [4] focused on Au III–Au V and did not study Au II.

The focus here is on Au I and Au II in the same region, using a combination of experimental and theoretical evidence. Strong overlapping resonances corresponding to a combination of Au I and Au II transitions align with an experimental feature observed at 80.3 eV. These are due to Au III $J = 2 \rightarrow 3$ and $J = 3 \rightarrow 4$ transitions from the $[\text{Xe}]4f^{14}5d^96s^{1,3}D$ state. When combined with the Au I Fano resonance due to the $[\text{Xe}]4f^{14}5d^96s^{2,2}D_{5/2} \rightarrow [\text{Xe}]4f^{13}5d^{10}6s^{2,2}F_{7/2}$ transition, these reproduce the 80.3-eV feature very well. In addition, we provide evidence for assigning an experimental feature at 82.3 eV to overlapping Au II transitions: $J = 1 \rightarrow 2$ transitions from the $[\text{Xe}]4f^{14}5d^96s^{1,3}D_1$ state and $J = 4 \rightarrow 5$ transitions from the $[\text{Xe}]4f^{14}5d^86s^{2,3}F_4$ state. Combined with the Au I Fano profile due to the $[\text{Xe}]4f^{14}5d^96s^{2,2}D_{3/2} \rightarrow [\text{Xe}]4f^{13}5d^{10}6s^{2,2}F_{5/2}$ transition, these reproduce the 82.3-eV feature very well. We also find contributions from an Au I feature previously identified by Köble *et al.* [16].

II. EXPERIMENT

Spectra were recorded using the DLP technique [18], as outlined in Ref. [20]. The output of a Q -switched neodymium yttrium garnet (Nd:YAG) laser (1064 nm, 10 Hz, average energy equal to 570 ± 7 mJ in 6 ns) was focused through a cylindrical plano-convex lens onto a planar Au target. The focused spot measured 0.5×9 mm², yielding a power density of approximately 10^9 W cm⁻², which generated a plasma containing the ions of interest. After some predetermined time Δt later (0–500 ns), a second Nd:YAG laser, delivering 800 ± 9 mJ in 15 ns, was focused to its maximum intensity (approximately 10^{12} W cm⁻²) on a tungsten target. The plasma thus formed emits a relatively featureless continuum in this region of the spectrum [22], used to probe the Au absorbing plasma. The targets and their respective lenses were mounted on xyz precision motorized stages with accuracy on the order of 10^{-6} m. Varying their position with respect to the optical axis

of the spectrometer as well as varying the interplasma time delay facilitated isolating populations of different ions within the absorbing plasma.

Spectra gathered using shorter interplasma time delays and closer to the optical axis of the target surface revealed structure associated with the higher ion stages and conversely spectra gathered using longer delays and further from the optical axis generated information about the lower ion stages. Spectra were recorded on a 0.25-m grazing incidence spectrograph that housed a Shimadzu 30-002 flat field grating with 1200 grooves per millimeter, diffracting the XUV light onto a 2048×2048 pixel charged couple device (CCD) camera that was kept cooled at -20°C for the duration of the experimental run. Both the laser plasma chamber and the spectrograph were kept under a vacuum of 10^{-4} mbar or better for the duration of the experiment such that atmospheric absorption effects on XUV photons were minimized.

Spectra were captured between 48 and 184 eV, with the data recorded by the CCD array with a resolving power $E/\Delta E$ of approximately 800. The resulting accuracy of the system was therefore approximately 0.05 eV, or an uncertainty on the order of a single pixel of the CCD. The emission from the backlighting tungsten plasma, intensity I_0 , and the same emission having passed through the absorbing Au plasma, intensity I , were acquired and allowed for the relative absorbance to be determined from $\ln(I_0/I)$. An average intensity of the emission intensity was computed over ten shots for the backlighting plasma to account for shot-to-shot fluctuations in intensity and spectral variation arising from ion populations within the plasma.

Optimization of the absorption signal was completed by varying the position of the focusing lenses and targets, to maximize emission intensity from the backlighting plasma while not saturating absorption due to strong transitions within the Au plasma. Generally, absorbance values between 0.1 and 2 provided the optimum dynamic range in which to view absorption features while maintaining a satisfactory signal-to-noise ratio. The absorbing Au plasma was probed with either 0.6 or 0.75 mm between the optical axis of the spectrometer and the target surface. The energy axes for I and I_0 were calibrated separately, before the relative absorbances were determined. Spectra were recorded at a range of interplasma time delays from 0 to 100 ns in steps of 5 ns and from 50 to 500 ns in steps of 50 ns. Spectra recorded between 300 and 500 ns after plasma formation are presented here as we expect these spectra to be dominated by absorption features associated with transitions in Au I and Au II.

III. EXPERIMENTAL RESULTS

Experimental photoabsorption spectra of laser-produced Au plasma are shown in Fig. 1, with the dominant transition types in each energy region indicated. The natural absorbance of the plasma decreases as the time delay increases, due to the expansion and cooling of the Au plasma. The focus here is specifically on the (79–83)-eV region which is dominated by $4f \rightarrow 5d$ transitions. The feature at 80 eV has been studied by Köble *et al.* for Au I [16] and Su *et al.* have studied Au III–Au V [4]. However, the dynamics of this feature in Au II is still unexplored. References [20,21] indicate that at

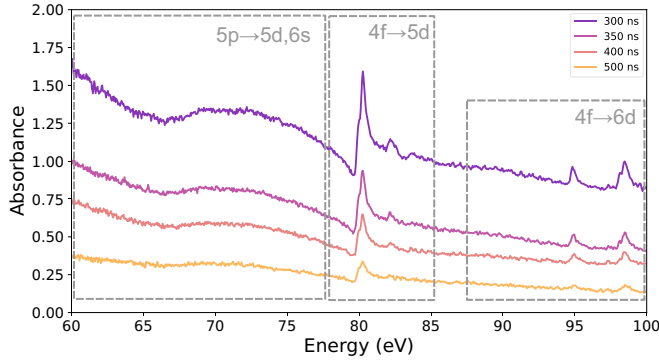


FIG. 1. Experimental photoabsorption spectra of laser-produced plasmas dominated by Au I and Au II, recorded at different time delays. The natural absorbance decreases with increasing time delay. The dominant transition types in each energy region are indicated.

time delays beyond 400 ns, Ir and Pt plasmas formed under similar conditions are dominated by singly ionized and neutral species, and at larger time delays the plasmas are increasingly dominated by neutrals. Comparing the relative strengths of spectral features over time provides evidence for the ion stages involved. Figure 2 labels the features of interest in the (79–83)-eV region. Since higher ion stages should recombine over time, we expect that the strength of features arising from higher ion stages to shrink relative to those from lower ions. This qualitative picture of the plasma dynamics serves as a useful first guide for the more detailed analysis presented later.

With increasing time delay the feature at 82.3 eV (R_3) decays rapidly. The peak at 80.3 eV (R_1) also decays, while the shoulder at 80 eV (R_2) grows in strength relative to the peak. This implies that both R_3 and R_1 have strong contributions from Au II transitions. The relative growth in strength of R_2 implies that there is a significant Au I contribution. However, as discussed below, the evolution of the shape of R_2 can be

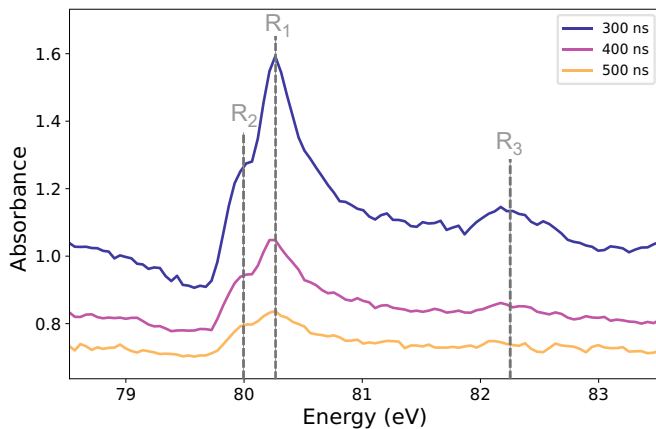


FIG. 2. Experimental photoabsorption spectra showing $4f \rightarrow 5d$ transitions in laser-produced plasmas dominated by Au I and Au II, recorded at time delays of 300–500 ns. The 400- and 500-ns spectra are shifted vertically by +0.4 and +0.5, respectively, for ease of comparison. The feature around 80 eV consists of a sharp peak at 80.3 eV (R_1) with a left-hand shoulder at 80 eV (R_2). There is also a strong feature (R_3) at 82 eV.

explained by the presence of both Au I and Au II contributions whose relative strengths change with time. Figure 2 indicates that the combination of the R_1 and R_2 features has an asymmetric line profile and, coupled with the presence of a strong continuum, we look at the possibility of these being Fano profiles.

Asymmetric (Fano) line shapes emerge when discrete states are coupled to a continuum of states and the Fano q parameter is used to characterize and quantify the asymmetry [23,24].

IV. ATOMIC STRUCTURE CALCULATIONS

The COWAN suite of atomic structure codes [25–27] was used to identify the transitions in the unknown experimental features. In doing so, Fano q parameters for the resonances of interest were calculated. The Slater scaling parameters were scaled to 99% of their *ab initio* values to give the best agreement with the value of the q parameter of the $[\text{Xe}]4f^{14}5p^65d^96s^2D_{5/2} \rightarrow [\text{Xe}]4f^{13}5p^65d^{10}6s^2F_{7/2}$ Fano profile determined by Köble *et al.* [16]. This led to a q parameter of 2.5, which differs by a small amount from the 2.2 obtained by Köble *et al.* The discrete and continuum configurations included in the Au I and Au II calculations are given in Table I. In addition to the dominant $4f \rightarrow 5d$ transitions, open $5p$ shells have been included in the calculations due to strong configuration mixing [19].

In the Fano formalism of coupling discrete to continuum states [23], the total wave function is represented as a superposition of discrete and continuum wave functions

$$|\Psi_E\rangle = a|\phi\rangle + \sum_k \int dE' b_{k,E'} |\psi_{k,E'}\rangle, \quad (1)$$

where $|\phi\rangle$ is the discrete state wave function, $|\psi_{k,E'}\rangle$ is the continuum state wave function of a given channel k , and E' is the free-electron energy. This results in the Fano q parameter for a resonant transition, given by

$$q_{ij} = \frac{D_{ij}}{\pi \sum_k M_{jk} D_{ik}}, \quad (2)$$

where $M_{jk} = V_{jk}/\sqrt{\sum_k V_{jk}^2}$, D_{ij} is the dipole matrix element corresponding to the discrete state $|i\rangle \rightarrow |j\rangle$ with resonance energy E_r , and D_{ik} are continuum dipole matrix elements which correspond to transitions from initial discrete states to continuum states $|k\rangle$. In addition, V_{jk} are configuration-interaction matrix elements [16,23]. Finally, the cross section is given by

$$\sigma(E) = \frac{\left(\frac{q\Gamma}{2} + E - E_r\right)^2}{\left(\frac{\Gamma}{2}\right)^2 + (E - E_r)^2}, \quad (3)$$

where Γ is the linewidth and E_r is the resonance energy. In this paper the formalism is extended following Mies' work [28], which modifies the calculated cross sections. The key difference between the two formalisms is that Mies' treatment allows for an arbitrary number of bound resonance states, rather than the single discrete state assumed by Fano.

TABLE I. Configurations included in the Au I and Au II COWAN calculations.

Calculation	Initial	Final Discrete	Final Continuum
Au I	[Xe] $4f^{14} 5d^{10} 6s^1$	[Xe] $4f^{13} 5d^{10} 6s^2$	[Xe] $4f^{14} 5d^{10} \rightarrow \varepsilon(p, f, h)$
	[Xe] $4f^{14} 5d^9 6s^2$	[Kr] $4d^{10} 5s^2 5p^5 4f^{14} 5d^{10} 6s^2$	[Xe] $4f^{14} 5d^9 6s^1 \rightarrow \varepsilon(p, f, h)$ [Xe] $4f^{14} 5d^8 6s^2 \rightarrow \varepsilon(p, f, h)$
Au II	[Xe] $4f^{14} 5d^{10}$	[Xe] $4f^{13} 5d^{10} 6s^1$	[Xe] $4f^{14} 5d^9 \rightarrow \varepsilon(p, f, h)$
	[Xe] $4f^{14} 5d^9 6s^1$	[Xe] $4f^{13} 5d^9 6s^2$	[Xe] $4f^{14} 5d^8 6s^1 \rightarrow \varepsilon(p, f, h)$
	[Xe] $4f^{14} 5d^8 6s^2$	[Kr] $4d^{10} 5s^2 5p^5 4f^{14} 5d^{10} 6s^1$	[Xe] $4f^{14} 5d^7 6s^2 \rightarrow \varepsilon(p, f, h)$
		[Kr] $4d^{10} 5s^2 5p^5 4f^{14} 5d^9 6s^2$	

In the Mies formalism, the total wave function is given by the superposition of discrete and continuum states

$$|\Psi_{\alpha,E}\rangle = \sum_n b_{n,\alpha} |\phi_n\rangle + \sum_{\beta} \int dE' c_{\beta,E'} |\psi_{\beta,E'}\rangle, \quad (4)$$

where Greek indices refer to scattering channels and $|\psi\rangle$ and $|\phi\rangle$ have the same meaning as in the Fano picture.

The modified cross section is then given by

$$\sigma(E) = \tilde{\mathbf{t}}^* \cdot \mathbf{t}, \quad (5)$$

where $\tilde{\mathbf{t}} = G\mathbf{t}$, with G a matrix described further in the Appendix. The vector $\mathbf{t}$ is defined as

$$\mathbf{t} = Z \left[1 + \tilde{\nu} \left(\frac{\pi \mathbf{q}}{\mathbf{E} - \delta} \right) \nu \right]. \quad (6)$$

Here $\frac{\pi \mathbf{q}}{\mathbf{E} - \delta}$ is a diagonal matrix with elements $\frac{\pi q_n}{\mathbf{E} - \delta_n} \delta_{m,n}$, where q_n and δ_n are the Fano q parameter and the resonance energy of state n , respectively. The vectors ν and $\tilde{\nu}$ are related to the configuration-interaction matrix, and Z is a scattering quantity described further in the Appendix.

A consequence of the modified Mies cross section is that there is no longer a single q parameter; when all scattering channels are included, our cross section instead consists of a number of interacting Fano profiles. Going forward in this paper, we refer to asymmetric line shapes as Fano profiles; however the calculations are performed using the Mies formalism.

V. RESULTS

Synthetic spectra were obtained using

$$\sigma_{\text{synth}}(E) = \sum_{Z,i} w_z \frac{g_i^Z}{g_g^Z} e^{-E_i^Z/k_B T} \sigma_i^Z(E), \quad (7)$$

where w_z are ion weights derived from a modified version of a collisional radiative (CR) model by Colombant and Tonon [29,30], $\sigma_i^Z(E)$ is the calculated Fano cross section with lower energy level E_i^Z of a given transition of ion stage Z , and g_i^Z is the corresponding degeneracy. The ground-state energy levels are taken to be 0 eV with degeneracy g_g^Z .

Synthetic spectra were produced using Eq. (7) and the ion stage weights w_z were determined by selecting those which resulted in the most accurate representation of the experimental spectra. From these weights, the temperature of the plasma at different time delays was derived.

The plasma temperatures and ion stage percentages for the five different time delays of interest here are summarized in Table III.

Figure 3 shows the comparison of these calculations with the experimental spectra. The characteristic asymmetry of Fano profiles is clear in all of the spectra. The main transitions are listed in Table II. The table includes the labels $R_1 \rightarrow R_3$, introduced above, which will be used in the following discussion. All of these transitions originate in metastable levels, at energies E_i above the relevant ground state. The relative population of these initial levels was determined by assuming a Boltzmann distribution. The absorbances of the calculated Au I and Au II spectra in Fig. 3 have been individually scaled and vertically shifted to match experiment, with a universal 0.74-eV shift applied to both spectra to align with experimental energies. The agreement between experiment and calculation is generally very good.

As shown in Table II, in Au I the discrete transitions result from two pairs of upper and lower levels, and the continuum contributions primarily come from p and f decay channels. Channels with larger angular momentum make negligible contributions. The Mies formalism used here, which accounts for multiple overlapping resonances for a given transition [27,28], is particularly important for the Au II calculations. Overlapping resonances refer to the coupling of multiple resonance states to different continua. Further details of the Mies formalism can be found in the Appendix. As a result of these complex interactions, there is not a single q parameter associated with each feature in the cross section; rather there are multiple q parameters associated with each contributing resonance. For completeness, a list of the calculated contributions to each observed profile is given in Table II. The information detailed in Table II was used to calculate absorbances, shown in Fig. 3.

To compare the Mies and Fano formalisms, we also calculated cross sections using the Fano formalism, Eq. (3), and the parameters of the resonances in Table II which lie closest to experimental features. For example, we used [Xe] $4f^{13} 5d^{10} 6s^1 {}^3F_4$ resonances with $E_r = 80.23$ eV for the R_1 feature. The positions of the peaks obtained from the two formalisms line up exactly but differ significantly in strength and in the shape of the continuum. Across all calculations performed, the Mies profile is stronger than the Fano profile, likely due to the overlapping resonances' interactions with the continuum. Therefore, even in the case where these closest-lying resonances dominate the profile, the

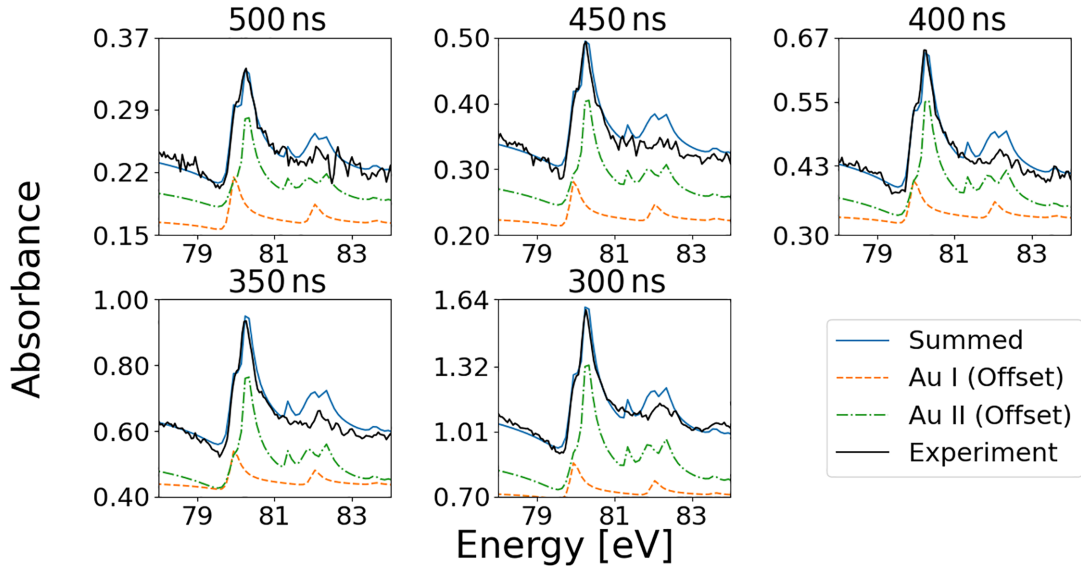


FIG. 3. Scaled and shifted Boltzmann and CR-weighted profiles for Au I and Au II, compared to experimental spectra. Each panel displays the total theoretical cross section (blue solid line) alongside the individual contributions from Au I (orange dashed line) and Au II (green dash-dotted line), and the experimental spectrum (black solid line) at the indicated time delay. The assignments of the spectral features are discussed in the text.

TABLE II. Experimental features R_{1-3} at energies E_e are shown together with their assigned calculated lower levels, energies E_i above the relevant ground state, and term labels, as well as each upper level contribution to the Mies formalism of the cross section. These data include the resonance energies E_r , which have been shifted by 0.74 eV to match experiment, the autoionizing width Γ , and the Fano q parameter.

Feature	E_e (eV)	Ion	E_i (eV)	Lower Term	Upper Term	E_r (eV)	Γ (eV)	q
R_1	80.3	II	1.8	$[\text{Xe}]4f^{14}5d^96s^1\ ^3D_3$	$[\text{Kr}]4d^{10}5s^25p^54f^{14}5d^96s^2\ ^3F_4$	58.13	4.37	3.90
					$[\text{Xe}]4f^{13}5d^{10}6s^1\ ^3F_4$	80.23	0.28	2.13
					$[\text{Xe}]4f^{13}5d^96s^2\ ^3F_4$	84.78	0.14	0.60
					$[\text{Xe}]4f^{13}5d^96s^2\ ^1G_4$	86.74	0.25	0.35
					$[\text{Xe}]4f^{13}5d^96s^2\ ^3G_4$	88.61	0.31	0.22
					$[\text{Xe}]4f^{13}5d^96s^2\ ^3H_4$	90.83	0.02	0.07
R_2	80.0	I	1.4	$[\text{Xe}]4f^{14}5d^96s^2\ ^2D_{5/2}$	$[\text{Xe}]4f^{13}5d^{10}6s^2\ ^2F_{7/2}$	79.87	0.28	2.50
R_2	80.0	II	2.2	$[\text{Xe}]4f^{14}5d^96s^1\ ^3D_2$	$[\text{Kr}]4d^{10}5s^25p^54f^{14}5d^96s^2\ ^3F_3$	60.87	7.49	5.68
					$[\text{Kr}]4d^{10}5s^25p^54f^{14}5d^96s^2\ ^3D_3$	64.52	8.15	-1.30
					$[\text{Kr}]4d^{10}5s^25p^54f^{14}5d^96s^2\ ^1F_3$	79.08	6.08	-26.18
					$[\text{Xe}]4f^{13}5d^{10}6s^1\ ^1F_3$	79.93	0.44	3.05
					$[\text{Xe}]4f^{13}5d^{10}6s^1\ ^3F_3$	83.57	0.28	2.42
					$[\text{Xe}]4f^{13}5d^96s^2\ ^3D_3$	85.43	0.45	0.21
					$[\text{Xe}]4f^{13}5d^96s^2\ ^3F_3$	86.84	0.33	-1.93
					$[\text{Xe}]4f^{13}5d^96s^2\ ^3G_3$	88.59	0.38	0.08
					$[\text{Xe}]4f^{13}5d^96s^2\ ^1F_3$	90.53	0.46	-0.46
R_3	82.3	I	3.0	$[\text{Xe}]4f^{14}5d^96s^2\ ^2D_{3/2}$	$[\text{Xe}]4f^{13}5d^{10}6s^2\ ^2F_{5/2}$	81.96	0.27	2.73
R_3	82.3	II	3.4	$[\text{Xe}]4f^{14}5d^96s^1\ ^3D_1$	$[\text{Kr}]4d^{10}5s^25p^54f^{14}5d^{10}6s^1\ ^3P_2$	55.09	8.73	1.44
					$[\text{Kr}]4d^{10}5s^25p^54f^{14}5d^96s^2\ ^1D_2$	57.89	7.46	3.92
					$[\text{Kr}]4d^{10}5s^25p^54f^{14}5d^96s^2\ ^3D_2$	61.24	9.05	6.02
					$[\text{Kr}]4d^{10}5s^25p^54f^{14}5d^96s^2\ ^3F_2$	74.94	4.40	10.16
					$[\text{Kr}]4d^{10}5s^25p^54f^{14}5d^96s^2\ ^3P_2$	76.00	6.94	-8.50
					$[\text{Xe}]4f^{13}5d^{10}6s^1\ ^3F_2$	82.28	0.27	2.86
					$[\text{Xe}]4f^{13}5d^96s^2\ ^1D_2$	84.03	0.23	3.77
					$[\text{Xe}]4f^{13}5d^96s^2\ ^3P_2$	86.57	0.43	6.72
					$[\text{Xe}]4f^{13}5d^96s^2\ ^3D_2$	87.60	0.27	-2.00
					$[\text{Xe}]4f^{13}5d^96s^2\ ^3F_2$	89.23	0.23	0.74
					$[\text{Xe}]4f^{13}5d^96s^2\ ^3G_5$	81.81	0.47	2.81
					$[\text{Xe}]4f^{13}5d^96s^2\ ^3H_5$	84.23	0.13	3.09
					$[\text{Xe}]4f^{13}5d^96s^2\ ^1H_5$	86.48	0.42	3.58

contributions from the other resonances are non-negligible, and so the attribution of resonant contributions to the ionization features cannot be entirely conclusive.

As mentioned previously, the evolution of the spectra suggests that the shoulder R_2 can partially be attributed to Au I since it grows with increasing time delay (corresponding to increased amounts of Au I). The Au II contributions to R_2 are discussed later in the paper. The COWAN calculations confirm this, from Fig. 3, and R_2 can be attributed to $[\text{Xe}]4f^{14}5p^65d^96s^2D_{5/2} \rightarrow [\text{Xe}]4f^{13}5p^65d^{10}6s^2F_{7/2}$ transitions in Au I. This feature was also studied by Köble *et al.* [16] at a longer time delay of 600 ns leading to a plasma comprising predominantly of Au I species. The lower level of this transition is the first metastable relative to the ground state and is significantly thermally populated at these plasma temperatures.

Table II details the calculated contributions to the Fano profile using the Mies formalism. Taking R_1 as an example, we can examine how the various resonances contribute to the feature. The average autoionizing width is $\langle\Gamma\rangle \approx 0.90$ eV, and there are energy differences between resonance energies within this width, meaning these resonances will overlap with each other. Since there are multiple resonances for each transition, from here on we will just refer to them using their J values: $J_i \rightarrow J_j$.

Figure 3 shows that both Au I and Au II transitions contribute to R_2 . Table II indicates that the dominant Au II contribution to this feature arises from an initial $[\text{Xe}]4f^{14}5d^96s^1D_1$ configuration with overlapping resonances formed from $J = 2 \rightarrow 3$ transitions. Similarly, transitions in Au II contribute to R_1 , with $J = 3 \rightarrow 4$ transitions arising from the $[\text{Xe}]4f^{14}5d^96s^1D_3$ state being the most significant ones. All of these metastable states are close to the ground state and are likely to be significantly thermally populated from 300 to 500 ns.

At short time delays (300 ns) the feature at 82 eV (R_3) becomes stronger. Table II indicates R_3 is a result of overlapping $J = 1 \rightarrow 2$ transitions coming from the $[\text{Xe}]4f^{14}5d^96s^1D_1$ state and $J = 4 \rightarrow 5$ transitions originating in the $[\text{Xe}]4f^{14}5d^96s^1F_4$ state in Au II. While the dynamics of R_3 appears to be dominated by Au II transitions, there is a weak Au I contribution $[\text{Xe}]4f^{14}5d^96s^2D_{3/2} \rightarrow [\text{Xe}]4f^{13}5d^{10}6s^2F_{5/2}$ to R_3 which appears to get stronger at the later time delays and may contribute to the overestimation of R_3 at these times. In this case, these lower levels are significantly higher than the ground state, and thus the population of these levels is highly dependent on the thermal properties of the plasma: They are most significant when the plasma is hot enough to sustain these levels. It can be seen from Fig. 3 that the R_3 feature is overestimated by the calculated cross sections. One potential reason for this is that the CR model may not fully capture the ion stage dynamics. Specifically, the thermal populations of the initial levels for the transitions may be overestimated by the model. Table II indicates that the initial states responsible for R_3 are the most energetic in the table.

It can be seen from the estimated abundances (Table III) that the populations of Au I and Au II change very slowly with time delay. When compared with similar studies in Ir and Pt [20,21], which have two and one fewer electron than Au,

TABLE III. Au species abundances and plasma temperatures T_e derived from the experimental data at different time delays using a collisional radiative model [29,30]. These calculations used an electron density of $n_e \approx 1 \times 10^{21} \text{ cm}^{-3}$.

Δt (ns)	T_e (eV)	Au I (%)	Au II (%)
500	2.21	58	42
450	2.34	50	50
400	2.40	47	53
350	2.43	45	55
300	2.51	41	59

respectively, the recombination of the Au plasma is much slower at later times. At 300 ns and a temperature of approximately 2.0 eV, the total amount of Ir I has been estimated to be 74% [21], while for Pt, a rapid change in abundances between 300 and 400 ns is observed: The Pt II population decreases by approximately 17% as the temperature changes from 4.2 eV to 3.6 eV [20]. This is similar to the total decrease observed in this work for Au II between 300 and 500 ns.

Given that the pulse-to-pulse energy stability of the lasers deployed in this work is better than $\pm 2\%$, and the positions of the cylindrical lens and the absorber target are reproducible to $\pm 1 \mu\text{m}$, the absorbing plasmas, which are typically formed at power densities close to 10^9 W/cm^2 , are highly reproducible. The timing jitter between the pump and probe lasers is typically ± 2 ns. The plasma conditions probed over a range of time delays are thus closely comparable, and differences in temporal evolution between plasmas of different elements may perhaps be ascribed to the effects of atomic structure on plasma dynamics. The origins of these differences are currently unknown but warrant further study.

VI. CONCLUSION

Gold photoabsorption spectra were recorded over a (48–184)-eV energy range using the DLP technique. These experimental results revealed unidentified features arising from Au II in the region of 79–83 eV. The spectra revealed Fano-like profiles for the unknown features.

Atomic structure calculations were performed for Au I and Au II using the COWAN suite of codes to identify the unknown features. Calculated absorbances and the Fano q parameters of Au I were compared with the literature to benchmark our calculations. Fano profiles from Au I and Au II were calculated for transitions in the (79–83)-eV region. Synthetic spectra were produced using Boltzmann weighting and a CR model, which allowed for direct comparison with the experiment. The agreement between experiment and calculation was generally very good, although the calculations did overestimate contributions from more highly excited initial states. Au I features studied by Köble *et al.* were confirmed and previously unidentified features in Au II assigned.

Furthermore, the study revealed that Au plasmas are observed to recombine more slowly at later time delays when compared to similar Ir and Pt plasmas. This warrants further study into the ionization and recombination mechanisms of Au, relevant for kilonova studies due to the increased interest in autoionization. This will also be useful for spectroscopic

experiments mapping ion stage dynamics in the plasmas, aiding the analysis of experiments relevant to kilonovae.

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DATA AVAILABILITY

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

APPENDIX: DETAILS OF THE MIES FORMALISM

Here we describe the terms stated in the Mies formalism that were not detailed in the main text. We strictly follow the presentation and the symbols used by Mies [28]. We begin by defining G , an orthogonal matrix defined by

$$F = \tilde{G} \mathcal{E} G, \quad (\text{A1})$$

where $\mathcal{E}$ is the diagonal matrix of resonance energies and F has the form

$$F_{n,m} = E_n \delta_{n,m} + \mathcal{P} \left(\int_0^\infty dE' \sum_\beta \frac{V_{n,\beta} V_{m,\beta}}{E - E'} \right), \quad (\text{A2})$$

where $\mathcal{P}(\cdot)$ denotes the principal value of the integral. Therefore, G is an orthogonal matrix which diagonalizes F .

Using the transformation matrix G , the modified configuration-interaction matrix coupling resonance n to continuum β is

$$v_{n,\beta} = \sum_m G_{n,m} V_{m,\beta}. \quad (\text{A3})$$

The term Z in the expression for the vector t from which the cross section is determined is given by

$$Z = (\tilde{A}^0)(1 + i\kappa)^{-1}, \quad (\text{A4})$$

where A^0 is a matrix associated with the scattering matrix $S = \tilde{A}A$. The superscript 0 denotes the unperturbed (zeroth-order) resonance states, before their coupling to the continua. Finally, κ has the form

$$\kappa = \pi \tilde{v}(E - \mathcal{E})^{-1} v. \quad (\text{A5})$$

To quantify the effects of overlapping resonances, Mies [28] defines the overlap matrix between continua. For each resonance n , the interaction between the resonance and the set of continua is given by

$$\Psi_{\alpha=1,E}^n = \left(\frac{2\pi}{\Gamma_n} \right)^{1/2} \sum_\beta v_{n,\beta} \Psi_{\beta,E}^0, \quad (\text{A6})$$

where $\Gamma_n = \sum_\beta \Gamma_{\beta,n}$ is the total autoionizing width, $\Gamma_{\beta,n} = 2\pi |v_{n,\beta}|^2$ is the partial autoionizing width into continuum β , and $\Psi_{\beta,E}^0$ is a continuum state β at energy E . Here $\alpha = 1$ represents a continuum and its interaction with the rest of the continua. The remaining continua are orthonormal to α and orthogonal to n . If the continua associated with each resonance are mutually orthogonal, there is no interaction between the resonances due to configuration interaction, and each may be treated as an isolated resonance embedded in its own continuum. In general, however, these continua are not orthogonal, introducing overlap effects.

Mies defines the overlap matrix as the matrix elements of different resonances coupling to the same continua:

$$\mathcal{O}_{n,m} \delta(E - E') = \langle \Psi_{1,E}^n | \Psi_{1,E'}^m \rangle \quad (\text{A7})$$

or

$$\mathcal{O}_{n,m} = \left(\frac{(2\pi)^2}{\Gamma_n \Gamma_m} \right)^{1/2} \sum_\beta v_{n,\beta}^* v_{m,\beta}. \quad (\text{A8})$$

The general case, when $\mathcal{O}_{n,m} \neq 1$, is referred to by Mies [28] as “overlapping,” indicating nonvanishing off-diagonal terms between resonances n and m , i.e., their associated continua are neither orthogonal nor identical. When $\mathcal{O}_{n,m} = 1$, the resonances couple to the same continuum. Mies [28] referred to this case as the resonances being “superimposed” to a single continuum $\alpha = 1$. The resonances can be considered as separate when the mean width of the overlapping resonances $\langle \Gamma \rangle \ll |E_n - E_m|$. Combining these two cases recovers Fano’s original form, with one resonance and one continuum [23].

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