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# Toward Å–fs–meV resolution in electron microscopy: systematic simulation of the temporal spread of single-electron packets

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Though efforts to improve the temporal resolution of transmission electron microscopes (TEMs) have waxed and waned for decades, with relatively recent advances routinely reaching sub-picosecond scales, fundamental and practical challenges have hindered the advance of combined Å–fs–meV resolutions, particularly for core-loss spectroscopy and real-space imaging. This is due in no small part to the complexity of the approach required to access timescales upon which electrons, atoms, molecules, and materials first begin to respond and transform – attoseconds to picoseconds. Here we present part of a larger effort devoted to systematically mapping the instrument parameter space of a TEM modified to reach ultrafast timescales. With General Particle Tracer, we studied the statistical temporal distributions of single-electron packets as a function of various fs pulsed-laser parameters and electron-gun configurations and fields for the exact architecture and dimensions of a Thermo Fisher Tecnai Femto ultrafast electron microscope. We focused on easily-adjustable parameters, such as laser pulse duration, laser spot size, photon energy, Wehnelt aperture diameter, and photocathode size. In addition to establishing trends and dispersion behaviors, we identify regimes within which packet duration can be 100s of fs and approach the 300 fs laser limit employed here. Overall, the results provide a detailed picture of the temporal behavior of single-electron packets in the Tecnai Femto gun region, forming the initial contribution of a larger effort.

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## Introduction

Four-dimensional ultrafast electron microscopy (UEM) with femtosecond/picosecond (fs/ps) temporal resolution<sup>1–4</sup> has been used to inform a diverse and growing set of chemical, materials, and biological problems, such as phonon behaviors at atomic-to-nanoscale dimensions,<sup>5–17</sup> the spatiotemporal evolution of photoinduced phase transitions,<sup>18–23</sup> and the interaction of free electrons with photons at nanomaterial and biointerfaces.<sup>24–35</sup> High temporal resolution (*i.e.*, 100 fs to 1 ns) in UEM is typically achieved by interfacing a modified transmission electron microscope (TEM) with a fs pulsed laser such that stroboscopic photon-pump/electron-probe experiments can be conducted, though incorporation of an electromagnetic cavity or beam blander into the column provides a laser-free (or hybrid) option with comparable temporal resolution.<sup>36–47</sup> With laser-driven UEM, however, spatial and temporal coherence of the probe electron packets quickly degrade with increasing density due to deleterious electron–electron interactions,<sup>48–50</sup> in addition to broadening effects imposed by electric and

magnetic fields specific to the base TEM platform. This poses practical challenges to achieving high combined spatial, energy, and temporal resolutions for this form of ultrafast TEM, as a balance must be struck between signal acquisition time, electrons per packet and packets per unit time (*i.e.*, beam current), and specimen relaxation time ( $\tau_{\text{relaxation}}$ ).

Methods for overcoming the resolution-limiting effects of electron–electron interactions in UEM focus on either undoing the broadening, as in proposed approaches employing pulse compression schemes,<sup>51,52</sup> or avoiding it altogether, as with conventional beams that are chopped or blanked (mentioned above), or by reducing the photoelectron packet density by simply using a lower pulsed-laser fluence.<sup>1</sup> Indeed, instrument-limited  $\sim 2$  Å real-space resolution and sub-eV energy resolution have been demonstrated with both laser-free and laser-driven pulsed electron beams.<sup>41,53,54</sup> However, photoexcitation (or any type of triggering event) for stroboscopic study of dynamics requires extremely precise and highly robust spatial and temporal specimen reversibility. Accordingly, Å-resolved fs/ps real-space imaging of structural dynamics has yet to be demonstrated, despite the pulsed beams having sufficient coherence under certain operating conditions. As importantly, the high repetition rates ( $f$ ) used to offset low packet densities and to reduce data acquisition times (true for both laser-driven and

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laser-free approaches) relegates such high- $f$  approaches to studies employing weak excitations (*i.e.*, small perturbations) or to events having approximately nanosecond or shorter lifetimes; more generally, to events where  $\tau_{\text{relaxation}} < f^{-1}$ .<sup>4</sup> Ideally, and especially for chemical and nanomaterials systems, one would identify an experimental parameter space where combined Å–fs–meV resolutions can be reached and preserved while being applied to the largest-possible set of phenomena and compositions (*i.e.*, the widest range of  $\tau_{\text{relaxation}}$  for triggered events).

For fs laser-driven UEM, settings that lead to the (statistical) generation of a single photoelectron at the source (which is ideally collected into the illumination system<sup>55</sup>) should produce the most coherent beam at the highest beam current for a given  $f$  owing to the absence of electron–electron interactions.<sup>1,56–58</sup> Under such conditions, resolutions are then dictated by the fs laser-pulse properties and by space-charge-independent broadening effects inherent to the base TEM (*i.e.*, by fields specific to the instrument architecture, dimensions, materials, and geometries).<sup>57–61</sup> Accordingly, it would be useful to systematically study and quantify the impact of laser-pulse properties, electric and magnetic fields, and – importantly – specific instrument specifications on single-electron-packet resolutions, coherence, and collection efficiency in order to: (i) define theoretical limits, (ii) identify simple, low-cost approaches to tunable optimization, and (iii) begin to build-up a knowledge-base to better establish cause-effect relationships and to address unfounded dogma that has emerged where key data is missing.

Here, our contribution to a necessarily larger, multifaceted effort is a systematic set of simulations of single-electron-packet temporal distributions ( $\tau_{\text{electron}}$ ) as a function of fs laser-pulse properties for the specific gun/accelerator architecture and dimensions of an FEI Tecnai Femto UEM (Thermo Fisher). Using the General Particle Tracer software package in tandem with field maps calculated using Poisson Superfish,<sup>62,63</sup> we studied the effects of easily-tunable laser-pulse properties and electron-gun dimensions on the temporal duration of single-electron packets. Adjustable parameters included the Wehnelt aperture diameter ( $D_{\text{W}}$ ), the photoelectron emission spot size (*i.e.*, the fs UV probe-laser spot size on a truncated LaB<sub>6</sub> cathode), the laser photon energy ( $h\nu$ ), the laser pulse duration ( $\tau_{\text{laser}}$ ), and the diameter of the cathode emitting surface ( $D_{\text{tip}}$ ). In addition to identifying trends and uncovering unexpected behaviors, the goal here was to establish a foundation for additional systematic studies of increasing complexity for an entire laser-driven UEM system so as to ultimately generate an operational phase diagram for better targeting specific applications. While the simulations and results are specific to the Tecnai Femto system, the insights uncovered here are expected to be at least qualitatively applicable to other base TEM models and UEM systems.

## Experimental

### Elements of the simulations

General Particle Tracer (GPT, Pulsar Physics) was used to map particle trajectories through the electron gun and the

electrostatic accelerator of a Thermo Fisher/FEI Tecnai Femto UEM (Fig. 1a).<sup>63</sup> To reduce computation time, simulations of  $n = 50\,000$  non-interacting electrons simultaneously generated from the cathode were performed. In the gun region, a series of dynodes comprise the accelerator and raise the electron energy to 200 keV. Once fully accelerated, the beam impinges upon an X-ray aperture, which here is the final element of the simulated electron gun. Two-dimensional, cylindrically-symmetric electrostatic field maps were calculated for the specific architecture and dimensions of the Tecnai Femto UEM (base instrument is Tecnai T20 G2)† using Poisson Superfish.<sup>62</sup>

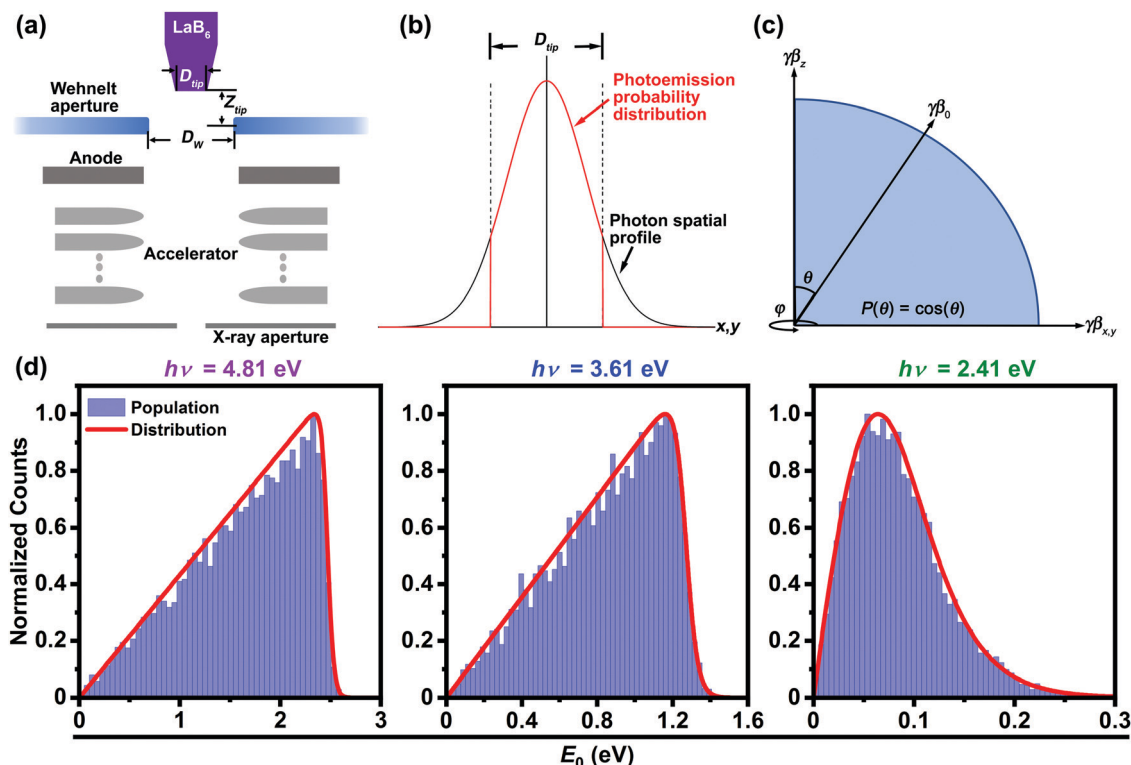
In UEM mode, the electron gun consists of an unbiased Wehnelt triode with an aperture of diameter  $D_{\text{W}}$  and a truncated LaB<sub>6</sub> cathode with an emitting surface of diameter  $D_{\text{tip}}$  and a work function of  $\Phi = 2.4$  eV. The aperture can be variably positioned relative to the emitting surface at a distance  $Z_{\text{tip}}$  in the Wehnelt assembly. Here, a fixed  $Z_{\text{tip}}$  of 0.35 mm was used, as previous simulations of the Tecnai Femto indicated that this is the optimal position for maximizing electron collection efficiency in single-electron mode for  $D_{\text{W}} = 0.7$  mm.<sup>55</sup> Further, a fixed  $Z_{\text{tip}}$  was used in order to specifically study the effects of photoemission spot size (*i.e.*, assumed to be the fwhm size of the laser spot on the LaB<sub>6</sub> surface) and  $D_{\text{W}}$  on  $\tau_{\text{electron}}$ . As with previous simulations on minimally-modified TEMs for ultrafast operation,<sup>55</sup> the effects of emission spot size and  $D_{\text{W}}$  are of interest because they are readily adjustable and tunable.

Single-electron packets were approximated by generating a set of non-interacting particles having momentum distributions and spatial coordinates specific to the photoemission characteristics under consideration. This approximates a series of single-electron photoemission events. Note the distinction between photoemission spot size and  $D_{\text{tip}}$ , which manifests in the emission probability ( $P$ ) for a Gaussian laser-spot spatial profile (Fig. 1b). Further, LaB<sub>6</sub> shank emission was not considered, as the laser spot can be trained entirely on the flat cathode surface.<sup>54,58</sup> This is experimentally achieved by encircling the LaB<sub>6</sub> with a high  $\Phi$  material such that  $h\nu < \Phi$  and by simply focusing the laser-spot size such that it is smaller than  $D_{\text{tip}}$ .<sup>1,8,58</sup>

The probability of photoemission ( $P$ ) was varied as the cosine of the initial emission angle,  $\theta$  [*i.e.*,  $P(\theta) = \cos(\theta)$ ] (Fig. 1c).<sup>55,64</sup> Note that different approaches to treating the angular photoemission distribution in UEM and ultrafast electron diffraction (UED) simulations have been adopted. One common approach is to assume a uniform distribution of photoemission probabilities within the hemisphere subtended by the photocathode emitting surface.<sup>57,59,65</sup> Compared to the  $\cos(\theta)$  approach, uniformly-distributed trajectories will produce photoelectron packets with increased temporal distortions due to the larger fraction of off-axis emission events. Only the  $\cos(\theta)$  distribution was employed here. Following this, the product of the Lorentz factor ( $\gamma$ ) and the normalized relativistic velocity ( $\beta$ ) was used as the momentum factor ( $\gamma\beta$ ) to initialize the GPT simulations.

Initial photoelectron kinetic-energy distributions were modeled as calculated transmission coefficients for free electrons

† Provided by Dr Erik Kieft of Thermo Fisher Scientific.



**Fig. 1** Elements of the simulations. (a) Simplified schematic of the FEI Tecnai Femto electron gun and accelerator with key components and dimensions labeled.  $D_{tip}$  is the diameter of the LaB<sub>6</sub> emitting surface,  $Z_{tip}$  is the distance from the LaB<sub>6</sub> surface to the plane of the Wehnelt aperture (here, fixed at 0.35 mm), and  $D_w$  is the diameter of the Wehnelt aperture. (b) Spatial photoelectron emission probability (red curve) from the LaB<sub>6</sub> emitting surface for a Gaussian laser-spot shape (black curve). The probability is set to zero for  $x,y > D_{tip}$ . (c) Photoelectron emission probability ( $P$ ) as a function of emission angle ( $\theta$ ) relative to the center of the illuminated LaB<sub>6</sub> surface. The full probability distribution subtended by the LaB<sub>6</sub> emitting surface parallel to the  $x,y$  plane is generated by sweeping azimuthally over  $\varphi$  to establish cylindrical symmetry.  $\gamma$  and  $\beta$  are the Lorentz factor and the normalized relativistic velocity, respectively. The product  $\gamma\beta$  is the rest-mass-normalized particle momentum used in GPT. (d) Calculated initial probe photoelectron kinetic-energy ( $E_0$ ) distributions (red curves) for LaB<sub>6</sub> with work function  $\Phi = 2.4$  eV and select photon energies  $h\nu = 4.81$  (left), 3.61 (center), and 2.41 eV (right) (i.e., harmonics of the Yb:KGW fs laser in the UEM lab at Minnesota).

encountering a step potential (Fig. 1d). Photoemission was approximated by shifting the Fermi–Dirac distribution by the amount of the incident photon energy  $h\nu$ ; the three photon energies studied here (2.41, 3.61, and 4.81 eV) are harmonics (2nd–4th, respectively) of the UEM laser system at Minnesota (Yb:KGW,  $h\nu_{\text{fundamental}} = 1.2$  eV). Note that this approach is an approximation for near-threshold photoemission from the surface of LaB<sub>6</sub>.<sup>66</sup> All reported single-electron-packet properties are those that are present 2.5 ns after photoemission. This ensured that all packets were fully increased to 200 keV and had reached the X-ray aperture, regardless of initial trajectory. Finally,  $\tau_{\text{electron}}$  (single-electron temporal distribution for  $n$  individual, integrated non-interacting particles) was calculated by dividing the root-mean-square longitudinal packet length by the average longitudinal velocity.

## Results and discussion

### Dependence of $\tau_{\text{electron}}$ on photoemission spot size and $E_0$ for key values of $D_w$

To establish a baseline behavior for  $\tau_{\text{electron}}$ , three discrete values of  $E_0$  were first simulated (0.10, 1.76, and 2.40 eV) for

two Wehnelt aperture diameters (0.7 and 1.0 mm, Fig. 2). These  $E_0$  values were selected because 0.10 and 2.4 eV are near the extremes of the full range of  $E_0$  for the oft-used  $h\nu = 4.8$  eV and  $\Phi = 2.4$  eV for generating photoelectrons in UEM experiments, while 1.76 eV is the average value of the calculated distribution for  $h\nu = 4.81$  eV (Fig. 1d, left panel). The two values of  $D_w$  were chosen because they are standard (0.7 mm) and optimum (1.0 mm) diameters used in thermionic and single-electron UEM modes (per simulation), respectively.<sup>55</sup> Because the particles in each bunch are non-interacting, one can separate the space-charge-independent broadening effects for different values of  $E_0$ . Further, the use of single, discrete values of  $E_0$  at this stage, rather than the distributions shown in Fig. 1d, provides direct insight into the degree of influence of those effects.

The simulations indicate that a strong dependence of  $\tau_{\text{electron}}$  on photoemission spot size exists for  $D_w = 1.0$  mm as compared to the standard 0.7 mm aperture, which instead shows very little variation across the entire range of spot sizes investigated (0–180  $\mu\text{m}$ ). In particular, the two larger  $E_0$  values (i.e., larger initial kinetic energies due to larger  $h\nu$  values) for  $D_w = 1.0$  mm show a large drop in  $\tau_{\text{electron}}$  to near the

laser-pulse duration ( $\tau_{\text{laser}} = 300$  fs) with decreasing spot size. This is intriguing because it suggests that experimental parameter space exists wherein one can overcome degraded temporal resolution for cases where  $h\nu > \Phi$  when using a tightly-focused laser. Further, the simulated value of  $\tau_{\text{electron}}$  is approximately the same for all values of  $E_0$  at spot sizes smaller than  $\sim 20$   $\mu\text{m}$  (Fig. 2, bottom panel). This suggests that one might be able to both preserve optimum temporal resolution while also increasing photoemission probability when operating in the single-electron regime. However, it is important to note that the behaviors and thus optimum settings will change when each laser pulse produces multiple photoelectrons and electron-electron interactions are present. Again, throughout this study we focused solely on the idealized single-electron regime, but work is needed to better understand the behaviors of packets with increasing density generated with fs laser pulses. It should be noted that the general increase in  $\tau_{\text{electron}}$  with  $E_0$  (*i.e.*,  $h\nu$ ), which is especially apparent for  $D_W = 0.7$  mm, is a well-known effect in UED experiments. The simulations here indicate this effect is also present in UEM, despite the more complex instrument architecture. However, this increased complexity may also offer additional flexibility for offsetting negative effects with simple adjustments to key components once the parameter space is mapped, as suggested by the results in Fig. 2.

The effect of photoemission spot size on  $\tau_{\text{electron}}$  shown in Fig. 2 is due in part to the precise trajectories of the

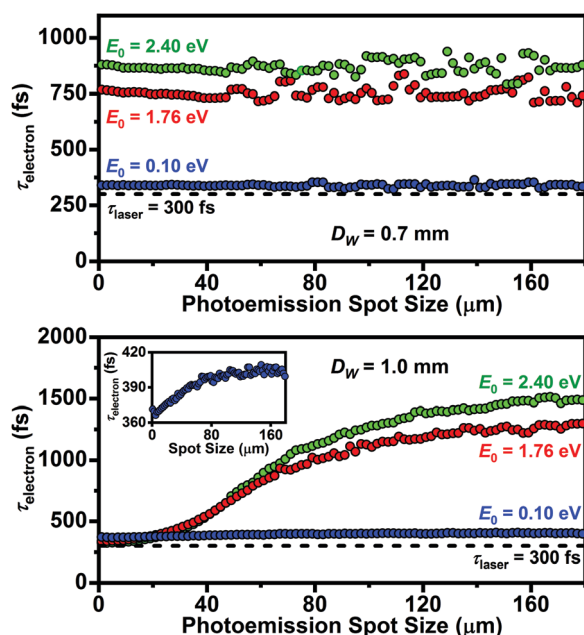


Fig. 2 Single-electron-packet duration ( $\tau_{\text{electron}}$ ; fwhm) as a function of LaB<sub>6</sub> photoemission spot size for  $D_W = 0.7$  mm (top) and  $D_W = 1.0$  mm (bottom). Note that three discrete initial photoelectron kinetic energies ( $E_0 = 0.10, 1.76$ , and  $2.40$  eV) were compared (*i.e.*, here, the full distributions shown in Fig. 1d were not yet used in order to first focus on the effect of photoemission spot size and  $D_W$ ). The horizontal black dashed line in each panel ( $\tau_{\text{laser}}$ ) represents the selected probe laser-pulse duration of 300 fs (fwhm) typical of the current system at Minnesota. The inset (bottom panel) is the 0.10 eV plot for  $D_W = 1.0$  mm with the y-axis rescaled to visualize the subtle response of  $\tau_{\text{electron}}$ .

photoelectrons in the gun region. Integrated over  $n$  electrons, larger emission spot sizes will have a larger fraction of off-optical-axis particles, which then leads to broadening of the temporal distribution. Photoelectrons emitted from surface regions that are far from the optical axis, as well as those that are not parallel to the axis when emitted, will contribute to the broadening due to prolonged dwell times and delays in acceleration. Importantly, the Wehnelt aperture is the main electrostatic component affecting tip-region dwell time, with the diameter ( $D_W$ ) strongly impacting overall behavior and thus serving as a source of tunability and optimization. This is intuitively straightforward to understand. Decreasing  $D_W$  effectively moves the associated electrostatic field closer to the optical axis, thus impacting a larger fraction of the total (integrated) emitted population and increasing the sensitivity of  $\tau_{\text{electron}}$  to off-axis and non-parallel photoelectrons. The  $D_W = 1.0$  mm data in Fig. 2 further illustrate this effect; photoemission spots below a certain diameter dictated by the specific  $D_W$  will have minimally-impacted populations. Thus, the onset of an increase in  $\tau_{\text{electron}}$  will move to larger spot sizes as  $D_W$  is also increased.

Unlike the 1.0 mm aperture, the standard 0.7 mm aperture appears to impact all photoelectrons regardless of emission spot size. Practically, this may be beneficial, as one need not worry about carefully controlling spot size in order to have a consistent  $\tau_{\text{electron}}$ . However, it does not provide for simple tunability or for reaching resolutions close to  $\tau_{\text{laser}}$  beyond using lower  $h\nu$  (at the expense of beam current for a given  $f$ ). Relatedly, temporal distortions of electron packets have been indirectly observed for UEM systems having independent control over Wehnelt bias and for photoelectrons emitted from shank regions of conical cathodes for reasons similar to those here, though differences in magnitude are potentially due to differing geometries and to the absence of electron-electron interactions in the simulations.<sup>54,60</sup> Such distortions are also not unlike those introduced by magnetic lenses.<sup>65,67,68</sup>

The increase in  $\tau_{\text{electron}}$  with  $h\nu$  (Fig. 2) can be explained as follows. One contribution comes from the distribution of initial trajectories, which will create an effective dispersion in the longitudinal velocities. This will result in a general statistical broadening of the temporal distribution due to electron acceleration.<sup>57,59</sup> However, the effect will diminish with decreasing  $E_0$  due to the lower initial velocities. Another related contribution comes from the resulting variation in electron-gun dwell times (*i.e.*, the time needed for each electron to reach a fixed position after the final electron-gun element). Importantly, the difference in dwell time between the extremes in initial trajectory ( $\theta = 0$  and  $\frac{\pi}{2}$ , Fig. 1c) increases with increasing  $E_0$ . For example, for  $E_0 = 0.10$  eV the spread in dwell time increases 500 fs for  $\theta$  increasing from 0 to  $\frac{\pi}{2}$ , but over the same trajectory range, it increases by 2.6 ps for  $E_0 = 2.40$  eV (Fig. 3). More generally, electron packets with larger  $E_0$  will, on average, have a shorter dwell time (*i.e.*, shorter arrival time) relative to smaller  $E_0$  at any given trajectory within the relevant range despite the non-linear behavior. It is important to note

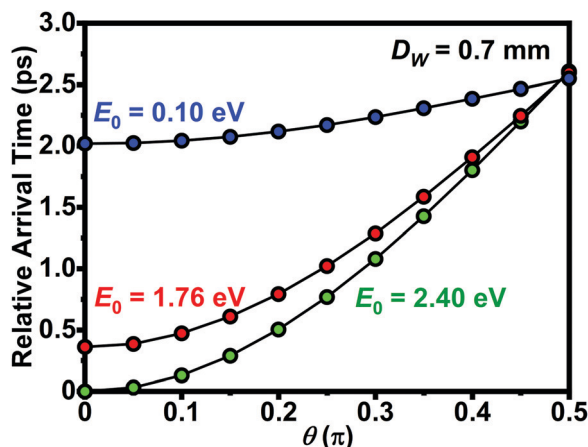


Fig. 3 Relative photoelectron arrival time at a fixed position after the final electron-gun element as a function of initial photoemission angle from the LaB<sub>6</sub> surface ( $\theta$ ) for  $D_W = 0.7$  mm and  $E_0 = 0.10$ , 1.76, and 2.40 eV. The photoemission spot size was fixed at 5  $\mu$ m diameter for all data, and all photoelectrons had the same initial momentum. All arrival times are relative to  $\theta = 0$  (i.e., parallel to the optical axis) and  $E_0 = 2.40$  eV, the specific condition for which the shortest transit time to the aperture occurs.

that the dwell-time delay is not due to electrostatic accelerator-induced broadening, because all electrons are emitted with identical longitudinal velocities. Instead, it is a result of the increased interactions of large-angle trajectories with the Wehnelt aperture for larger  $E_0$ .

#### Systematic study of the effect of $D_W$ on $\tau_{\text{electron}}$ for an $h\nu$ -driven distribution of $E_0$

The results discussed above, which provide a foundation upon which to increase the complexity of the simulations, have significant implications for  $n$  photoelectrons comprising a temporally-integrated packet consisting of a range of  $E_0$  (Fig. 1d) rather than a single discrete value. Accordingly, Fig. 4

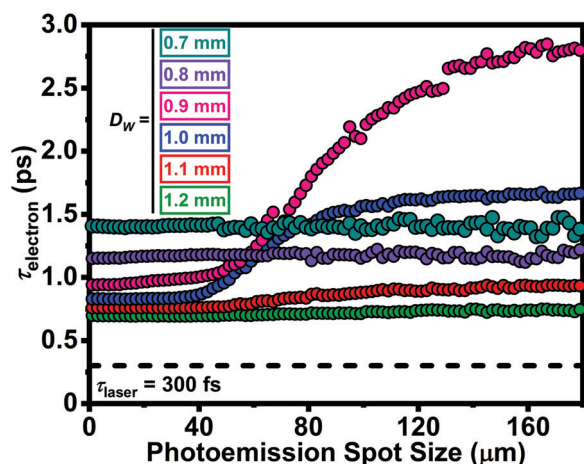


Fig. 4 Single-electron packet duration ( $\tau_{\text{electron}}$ , fwhm) as a function of photoemission spot size for  $D_W$  ranging 0.7–1.2 mm. The LaB<sub>6</sub>  $D_{\text{tip}}$  was 180  $\mu$ m. The horizontal black dashed line ( $\tau_{\text{laser}}$ ) represents the selected probe laser-pulse duration of 300 fs (fwhm). The  $h\nu = 4.81$  eV distribution in Fig. 1d was used as the  $E_0$ .

summarizes the results of such simulations, where the  $E_0$  distribution for the  $h\nu = 4.81$  eV case shown in Fig. 1d was used instead of the discrete value  $E_0 = 2.40$  eV (Fig. 2 and 3). Further, the simulations were performed for six different  $D_W$  ranging 0.7–1.2 mm, all as a function of the photoemission spot size.

Several notable behaviors emerge from the simulations summarized in Fig. 4. Perhaps the most notable is that, for spot sizes smaller than  $\sim 50$   $\mu$ m,  $\tau_{\text{electron}}$  decreases with increasing  $D_W$ , reaching a value of  $\sim 700$  fs (fwhm) for the largest aperture (again, for the broadest  $E_0$  distribution generated from  $h\nu = 4.81$  eV with  $\tau_{\text{laser}} = 300$  fs). This again indicates that  $D_W$  is an adjustable parameter for optimizing temporal resolution of minimally-modified thermionic UEM systems that lack independent control over Wehnelt bias. As is the case for discrete values of  $E_0$  (Fig. 2), this effect is due to a reduction in the influence of Wehnelt electrostatic fields on off-axis photoelectrons [emphasizing again the  $P(\theta) = \cos(\theta)$  distribution used here]. Interestingly, there is a rather abrupt onset of aperture influence on  $\tau_{\text{electron}}$  dispersion with photoemission spot size when increasing from  $D_W = 0.8$  to 0.9 mm, with a nearly similarly-abrupt relaxation when increasing from 1.0 to 1.1 mm (though a relatively modest dispersion of  $\sim 100$  fs is still seen for  $D_W = 1.1$  mm). At least with respect to  $\tau_{\text{electron}}$ , the simulations indicate that a  $D_W$  larger than  $\sim 1$  mm provides the highest temporal resolution (for a given  $D_W$ ) combined with the least sensitivity to photoemission spot size. Further, the sensitivity of  $\tau_{\text{electron}}$  to spot size for  $D_W = 0.9$  and 1.0 mm is connected to the cosine functional form of emission probability (Fig. 1c) and, therefore, the precise (integrated) distribution of photoelectron kinetic energies (Fig. 1d).

Compared to data shown in Fig. 2 (i.e., compared to  $E_0 = 2.40$  eV for each  $D_W$ ), the single-electron packets generated from a distribution of  $E_0$  shown in Fig. 4 are generally further temporally broadened. This is due to a further increase in longitudinal-velocity spread and broadening of the associated distribution in electron-gun dwell times (see Fig. 3 for the case of discrete values of  $E_0$ ). Such broadening typically manifests in energy and longitudinal-velocity distributions of single electrons propagating in accelerating fields.<sup>59,61</sup> Here, however, the effect appears to also emerge in non-accelerating fields due to the electrostatic forces imposed by an unbiased Wehnelt aperture and the portion of the  $E_0$  distribution that dominates the overall behavior for specific combinations of non-zero photoemission spot sizes and  $D_W$ . Indeed, the effect becomes quite deleterious in terms of  $\tau_{\text{electron}}$  for standard  $D_W$  aperture sizes (e.g., 0.7 mm), regardless of spot size; here,  $\tau_{\text{electron}}$  is broadened to 1.4 ps from the laser limit, despite the general shortened dwell time for higher-energy photoelectrons (Fig. 3).

#### Simulations of $E_0$ ( $h\nu$ ) distributions for select $D_W$

As Fig. 4 summarizes the behavior of  $\tau_{\text{electron}}$  as a function of photoemission spot size for various  $D_W$  and for the  $h\nu = 4.81$  eV distribution of  $E_0$  (Fig. 1d), a systematic approach dictates that simulations for the other two select  $E_0$  distributions (again, as specified by the available laser harmonics) also be performed and compared. Accordingly, Fig. 5 summarizes the results for

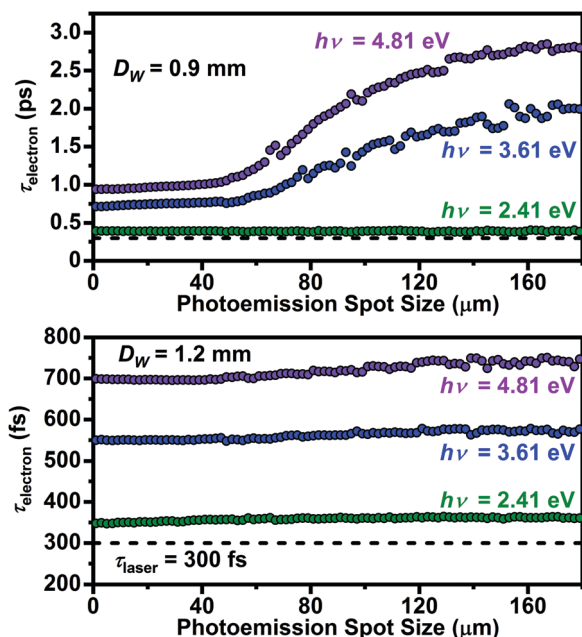


Fig. 5 Single-electron packet duration ( $\tau_{\text{electron}}$ , fwhm) as a function of photoemission spot size for discrete laser photon energies ( $h\nu = 2.41, 3.61$ , and  $4.81$  eV) for  $D_W = 0.9$  mm (top) and  $1.2$  mm (bottom). The LaB<sub>6</sub>  $D_{\text{tip}}$  was  $180$   $\mu\text{m}$ . The horizontal black dashed line ( $\tau_{\text{laser}}$ ) in each panel represents the selected probe laser-pulse duration of  $300$  fs (fwhm). The  $E_0$  distributions shown in Fig. 1d were used for each corresponding photon energy.

$D_W = 0.9$  and  $1.2$  mm for all three  $E_0$  distributions. These aperture values were chosen because they show (for the  $E_0 = 2.41$  eV distribution; Fig. 4) the strongest dispersion, in the case of the  $0.9$  mm aperture, and the weakest and mostly-insensitive temporal broadening (*i.e.*, the best temporal resolution that is robust across all spot sizes), in the case of the  $1.2$  mm aperture.

As can be seen, the trend for  $E_0 = 2.41$  eV (*i.e.*,  $h\nu = 4.81$  eV) generally continues for the other distributions with some notable and important variations. Photoexcitation with  $h\nu$  closer to the LaB<sub>6</sub>  $\Phi$  value (here, fixed at  $2.4$  eV) produces an overall improvement in  $\tau_{\text{electron}}$  for both values of  $D_W$ , regardless of photoemission spot size. Further, the strong dispersion seen for  $D_W = 0.9$  mm and  $h\nu = 4.81$  eV is also observed for  $h\nu = 3.61$  eV (scales approximately linearly) but is relaxed across all spot sizes for  $h\nu = 2.41$  eV (*i.e.*,  $h\nu$  approximately equivalent to  $\Phi$ ). Indeed,  $\tau_{\text{electron}}$  for  $h\nu = 2.41$  eV is broadened by  $\sim 50$  fs (17%) relative to  $\tau_{\text{laser}}$  across all spot sizes for both values of  $D_W$  (again, however, such a condition would introduce practical challenges with beam current and thus  $f$ ).

Generally, a decrease in  $\tau_{\text{electron}}$  as  $h\nu$  approaches  $\Phi$  is expected, as both the total integrated energy and the overall energy spread of the photoelectron distribution are reduced (see Fig. 1d).<sup>61,67</sup> Despite the differing architectures, dimensions, and field strengths, such an effect also exists in dedicated UED instruments and arises from the dependence on the longitudinal velocity spread and the average field strength of the accelerating cavity (which here is  $1.7$  kV mm<sup>-1</sup>).<sup>59</sup> Further, the longitudinal velocity spread depends upon  $E_0$  and the angular distributions of the photoelectrons. Here the

specific accelerator-induced temporal broadening was calculated to be  $650$  fs for  $h\nu = 4.81$  eV,  $474$  fs for  $h\nu = 3.61$  eV, and  $171$  fs for  $h\nu = 2.41$  eV. Convoluting this with  $\tau_{\text{laser}}$  (root sum square), the minimum  $\tau_{\text{electron}}$  for  $D_W = 1.2$  mm was found to be  $716$ ,  $561$ , and  $345$  fs (fwhm) for  $h\nu = 4.81$ ,  $3.61$ , and  $2.41$  eV, respectively (spot size =  $0$ , Fig. 5 bottom panel). For  $D_W = 0.9$  mm, the minimum  $\tau_{\text{electron}}$  increases by  $\sim 200$  fs for  $4.81$  and  $3.61$  eV and by  $\sim 50$  fs for  $2.41$  eV due to increased interactions with the Wehnelt aperture for a larger fraction of the overall integrated photoelectron distribution.

Though not the subject of this particular study, it is worth briefly emphasizing that one must also consider the impact of the laser-pulse properties and instrument architecture on beam coherence and beam current (*i.e.*, photoelectron collection efficiency) for studying ultrafast dynamics with Å-fs-meV TEM (in addition to  $\tau_{\text{relaxation}}$  and reversibility). For example, using  $h\nu = \Phi$  may generally provide the highest coherence and shortest  $\tau_{\text{electron}}$  (*i.e.*, best temporal resolution), but it will also result in the lowest photoelectron yield and the lowest beam current.<sup>69</sup> This poses a challenge, as long acquisition times and/or high repetition rates must be used in order to minimize signal acquisition times and the deleterious impacts of lab and instrument instabilities. To offset the low beam current, one can use a higher laser fluence when  $h\nu$  is close to  $\Phi$ , but this introduces other challenges due to electron–electron interactions and associated reductions in coherence and  $\tau_{\text{electron}}$  and will negate any gains achieved by matching  $h\nu$  to  $\Phi$ . The view here is that  $\tau_{\text{electron}}$  is one of three important parameters that need to be quantitatively understood, the other two being coherence and current, and they are all interwoven with one another. Thus, generation of operational phase diagrams for these parameters for specific instruments should be coupled with specific lab conditions in order to define ultimate resolution limits. This is likely to require multiple systematic studies of increasing complexity, which are then tested with careful experimentation under optimal conditions.

#### Effect of $\tau_{\text{laser}}$ on $\tau_{\text{electron}}$

In addition to  $h\nu$ , the laser-pulse duration ( $\tau_{\text{laser}}$ ) for photoelectron-generation was a specific parameter studied here. As optimization and trends of  $\tau_{\text{electron}}$  were the focus, values of  $\tau_{\text{laser}} < 300$  fs were studied, as it was hypothesized that shorter  $\tau_{\text{laser}}$  will generally lead to shorter  $\tau_{\text{electron}}$ . Indeed, as noted above, in the single-electron regime, temporal resolution is expected to be directly impacted by laser parameters, including  $\tau_{\text{laser}}$ . Accordingly, Fig. 6 summarizes the results for  $\tau_{\text{laser}}$  ranging  $50$  to  $300$  fs at  $50$  fs steps. Otherwise identical conditions to those for Fig. 4 were used, where the  $E_0$  distribution for  $h\nu = 4.81$  eV was simulated (Fig. 1d).

The immediate and most important result shown in Fig. 6 is that, even for the shortest  $\tau_{\text{laser}} = 50$  fs, the minimum  $\tau_{\text{electron}}$  observed is broadened by several hundred fs (*e.g.*,  $\tau_{\text{electron}} = 625$  fs at  $\sim 20$   $\mu\text{m}$  spot size for  $D_W = 1.2$  mm, Fig. 6c). This suggests that simply using a shorter fs laser pulse is insufficient for significantly improving UEM temporal resolution in the single-electron regime. This stems from the influence the

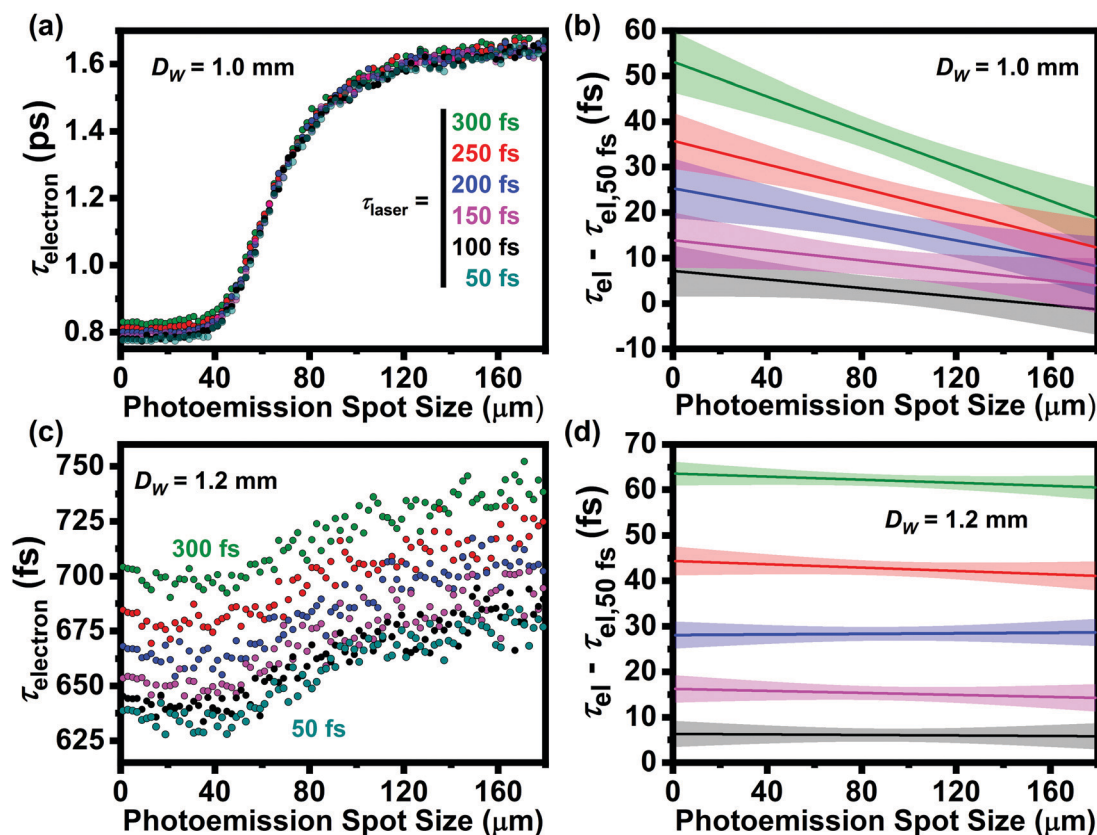


Fig. 6 Single-electron packet duration ( $\tau_{\text{electron}}$ , fwhm) as a function of photoemission spot size for laser-pulse durations ( $\tau_{\text{laser}}$ , fwhm) spanning 50 to 300 fs (panel a legend for  $\tau_{\text{laser}}$  applies to all panels) for  $D_W$  of 1.0 mm (a and b) and 1.2 mm (c and d).  $D_{\text{tip}} = 180 \mu\text{m}$  and the  $E_0$  distribution for  $h\nu = 4.81 \text{ eV}$  (Fig. 1d) were used for all simulations. Panels (b and d) show linear fits to the difference between  $\tau_{\text{electron}}$  (i.e.,  $\tau_{\text{el}}$ ) for  $\tau_{\text{laser}} = 50 \text{ fs}$  ( $\tau_{\text{el}} - \tau_{\text{el},50 \text{ fs}}$ ) and all other laser-pulse durations for  $D_W = 1.0$  and  $1.2 \text{ mm}$ , respectively. The shaded bands around each line represent the 95% confidence level.

Wehnelt aperture and electrostatic interactions have on  $\tau_{\text{electron}}$ , as observed when comparing the results for  $D_W = 1.0$  and  $1.2 \text{ mm}$  (e.g., much larger dispersion for the smaller aperture). This dispersion seems to be a general limitation to  $\tau_{\text{electron}}$ , despite the complete absence of electron–electron interactions in the single-electron regime.<sup>67</sup> Fig. 6 also shows that, while improvement in  $\tau_{\text{electron}}$  occurs when reducing  $\tau_{\text{laser}}$  from 300 to 50 fs (regardless of  $D_W$ ), shorter laser-pulse durations result in diminishing returns in temporal resolution. For example, for  $D_W = 1.2 \text{ mm}$ , the minimum  $\tau_{\text{electron}}$  is  $\sim 690 \text{ fs}$  for  $\tau_{\text{laser}} = 300 \text{ fs}$ , compared to  $625 \text{ fs}$  for  $\tau_{\text{laser}} = 50 \text{ fs}$ . One must also contend with larger spectral bandwidths at shorter  $\tau_{\text{laser}}$  and the associated impacts on  $\tau_{\text{electron}}$ , in addition to challenges imposed by electrostatic effects. The effect of diminishing returns when going to shorter  $\tau_{\text{laser}}$  is summarized in Fig. 6b and d, where the difference between  $\tau_{\text{laser}} = 50 \text{ fs}$  and all other durations is plotted as a function of the photoemission spot size.

#### Effect of LaB<sub>6</sub> tip size ( $D_{\text{tip}}$ ) on $\tau_{\text{electron}}$

Finally, the diameter of the emitting surface of the truncated LaB<sub>6</sub> cathode ( $D_{\text{tip}}$ ) was another adjustable parameter explored here owing to the hypothesized influence different tip sizes will have on the electrostatic fields in the gun region. The effects of four commonly-used  $D_{\text{tip}}$  on  $\tau_{\text{electron}}$  as a function of photoemission

spot size were investigated (Fig. 7). For each simulation,  $D_W$  was fixed at  $1.0 \text{ mm}$ , the  $E_0$  distribution for  $h\nu = 4.81 \text{ eV}$  was used (Fig. 1d), and  $\tau_{\text{laser}}$  was fixed at  $300 \text{ fs}$  (fwhm). It was found that  $D_{\text{tip}}$  generally has a significant effect on  $\tau_{\text{electron}}$ , though the magnitude and sensitivity strongly depend on the photoemission spot size. Indeed, at a spot size of  $\sim 10 \mu\text{m}$ ,  $\tau_{\text{electron}}$  is roughly identical for all  $D_{\text{tip}}$  ( $\sim 850 \text{ fs}$ ), but increasing to  $16 \mu\text{m}$  (the limit of the smallest tip) causes  $\tau_{\text{electron}}$  for  $D_{\text{tip}} = 50 \mu\text{m}$  to increase to nearly  $1.25 \text{ ps}$ . Further,  $\tau_{\text{electron}}$  varies by nearly a factor of two for the three largest tip sizes at a fixed spot size of  $35 \mu\text{m}$ . This behavior supports the hypothesis that the tip size itself impacts the electrostatic fields in the gun region, which in turn influences  $\tau_{\text{electron}}$ . This is practically important, as it indicates  $\tau_{\text{electron}}$  may significantly change if the tip size is changed (e.g., by changing cathodes) but the laser spot size is not (e.g., by changing the focal spot size). Moving to larger spot sizes, the dispersion behavior is such that  $\tau_{\text{electron}}$  plateaus to a single value, as observed for many cases above, suggesting a relatively poor but consistent temporal resolution can be expected for  $D_{\text{tip}} > \sim 150 \mu\text{m}$ . In general, the results indicate the dispersion behavior is such that variations in  $\tau_{\text{electron}}$  are initially small for tight laser focus which then passes through a strongly-dispersive regime before again plateauing an elevated but consistent and robust value for large spot sizes. The trend in Fig. 7 also suggests that the strongly-dispersive regime will shift to larger spot sizes for

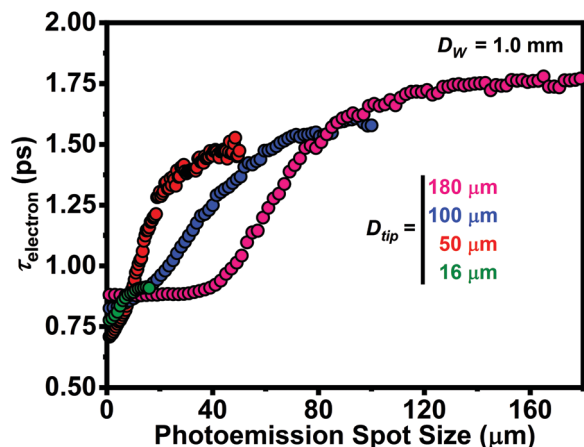


Fig. 7 Dependence of  $\tau_{\text{electron}}$  (fwhm) on photoemission spot size for four LaB<sub>6</sub> emitting surface diameters ( $D_{\text{tip}} = 16, 50, 100$ , and  $180 \mu\text{m}$ ). Wehnelt diameter was fixed at  $D_W = 1.0 \text{ mm}$ , the incident laser-pulse duration was fixed at  $\tau_{\text{laser}} = 300 \text{ fs}$  (fwhm), and the  $E_0$  distribution for  $h\nu = 4.81 \text{ eV}$  shown in Fig. 1d was used each  $D_{\text{tip}}$ . Photoemission spot sizes were limited to the available emitting surface (*i.e.*, shank emission for spot sizes larger than  $D_{\text{tip}}$  were ignored, as justified by the reasons given above).

larger  $D_{\text{tip}}$  (compare the 100 and  $180 \mu\text{m}$  simulations). This suggests that a practical approach to preserving high temporal resolution while having a somewhat forgiving spot-size requirement would be to use a large cathode and a laser spot size that is smaller than that at which the dispersion sets in (*i.e.*, smaller than the tip-dependent threshold dispersion value).

In summary, we have systematically explored the impact of various laser-pulse and electron-gun conditions and parameters on the duration of single-electron packets using GPT simulations and properties specific to the FEI Tecnai Femto UEM. We have identified a number of simple, adjustable parameters for optimizing the temporal resolution, and we have also identified operating phase spaces of both low and high sensitivity to those parameters. This work constitutes one part of a larger effort aimed at quantifying the ultimate spatial, temporal, and energy resolutions of ultrafast TEMs such that combined Å-fs-meV operating conditions might be achieved and experimentally demonstrated. This foundational effort, wherein temporal resolution under space-charge-free conditions was explored, will complement studies focused on understanding beam coherence and beam current in order to conduct multi-dimensional parameter-space mapping. An additional hope is that this work will continue to spur significant efforts into expanding TEM temporal resolution at levels comparable to spatial and energy resolutions.

## Author contributions

W. A. C. contributions were data curation, formal analysis, investigation, methodology, software, validation, visualization, writing – original draft, writing – review and editing. D. J. F. contributions were conceptualization, data curation, funding acquisition, methodology, project administration, resources, supervision, visualization, writing – original draft, writing –

review and editing. See the NISO CRediT taxonomy for definitions of contributing roles ([credit.niso.org](https://credit.niso.org)).

## Conflicts of interest

There are no conflicts to declare.

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