Low repetition-rate, high-resolution femtosecond transmission electron microscopy

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ABSTRACT

The spatial and energy resolutions of state-of-the-art transmission electron microscopes (TEMs) have surpassed 50 pm and 5 meV. However, with respect to the time domain, even the fastest detectors combined with the brightest sources may only be able to reach the microsecond timescale. Thus, conventional methods are incapable of resolving myriad fundamental ultrafast (*i.e.*, attosecond to picosecond) atomic-scale dynamics. The successful demonstration of femtosecond (fs) laser-based (LB) ultrafast transmission electron microscopy (UEM) nearly 20 years ago provided a means to span this nearly 10-order-of-magnitude temporal gap. While nanometer-picosecond UEM studies of dynamics are now well established, ultrafast Å-scale imaging has gone largely unrealized. Further, while instrument development has rightly been an emphasis, and while new modalities and uses of pulsed-beam TEM continue to emerge, the overall chemical and materials application space has been only modestly explored to date. In this Perspectives article, we argue that these apparent shortfalls can be attributed to a simple lack of data and detail. We speculate that present work and continued growth of the field will ultimately lead to the realization that Å-scale fs dynamics can indeed be imaged with minimally modified UEM instrumentation and with repetition rates (f_{rep}) below – and perhaps even well below – 1 MHz. We further argue that the use of low f_{rep}, whether for LB UEM or for chopped/bunched beams, significantly expands the accessible application space. This calls for systematically establishing modality-specific limits so that especially promising technologies can be pursued, thus ultimately facilitating broader adoption as individual instrument capabilities expand.

I. BACKGROUND

In 2005, Ahmed Zewail and his group at Caltech published a paper demonstrating the feasibility of coupling a femtosecond (fs) pulsed laser to a commercial transmission electron microscope (TEM). This first system consisted of an FEI Tecnai T12 120 kV TEM with standard Wehnelt electrode, a custom 0.3 mm diameter LaB_6 source, and a 3W, 80 MHz Spectra-Physics Ti:sapphire fs laser oscillator.[1] The goal was to reach sub-picosecond scales while also preserving the base instrument capabilities and resolutions, and especially to enable coherent, *in-situ* fs optical specimen triggering for conducting ultrafast laser-pump/electron-probe measurements. They called this approach four-dimensional ultrafast electron microscopy (4D UEM), which aligned with their ultrafast gas/vapor-phase electron diffraction (UED) and ultrafast electron crystallography (UEC) work.[2-4] This first-generation 4D UEM instrument was dubbed UEM-1. Roughly two years later, the same group developed a second-generation instrument dubbed UEM-2. This instrument was based on an FEI Tecnai TF20 200 kV TEM equipped with a hybrid LaB_6 field-emission gun (FEG) coupled to a Clark-MXR Yb-doped fiber oscillator/amplifier.[5] Of particular note is that development of UEM-2 was motivated in large part by some of what was learned from working with UEM-1: the need to access lower repetition rates (f_{rep}) and higher pump pulse energies in order to expand the application space. See Baskin and Zewail (C. R. Phys., 2014) for an historical account of the development of fs laser-based (LB) UEM at Caltech.[6]

Prior to the developments at Caltech, efforts to improve TEM temporal resolution beyond detector limits by using a pulsed beam had occurred to some degree for decades, with significant contributions coming from Bostanjoglo and colleagues beginning in the 1970s, though Spivak, Petrov, and Pavlyuchenko appear to be the pioneers, reporting stroboscopic TEM experiments on magnetic domain wall motion at least as early as 1966.[7-11] These early efforts focused mainly on reaching nanosecond timescales *via* beam blanking or, later, with nanosecond pulsed lasers and photoemission.[12-14] Around the time fs LB UEM was being developed at Caltech, nanosecond LB single-shot TEM – dubbed dynamic TEM (DTEM) – was being further advanced at Lawrence Livermore National Lab (LLNL).[15,16] Members of the LLNL team later formed the company Integrated Dynamic Electron Solutions (IDES), which is now a wholly-owned subsidiary of JEOL. The technology

developed at LLNL for single-shot DTEM is now employed by several groups for fs LB UEM.[17-22]

Assessment of the overall stroboscopic electron microscopy literature (including scanning electron microscopy, SEM), which again dates back decades, makes it apparent that the first use of a fs pulsed laser by Zewail and team to conduct ultrafast pump-probe experiments in the TEM (and later in the SEM in 2010)[23] was a watershed moment that catalyzed growth of the field and greatly expanded the materials, chemical, and solid-state physics application space. (It should be noted that Merano and colleagues first used a fs pulsed laser to generate ~10 ps photoelectron packets in a JEOL 6360 SEM in 2005, but they did not trigger the specimen with fs laser pulses.[24]) Indeed, since the seminal demonstration by Zewail and team, fs LB UEM has grown in use and in scope and is now being further developed, applied, and expanded by groups around the world.[17-21,25-38] Excitingly, pulsed-beam TEM is beginning to be used for new applications extending beyond time-resolved measurements, such as for the study of electron-beam radiation damage.[39-43] Other variants continue to emerge and be developed as well, including new takes on photon-induced near-field electron microscopy (PINEM) and new (or re-visited) forms of specimen triggering.[21,38,44-50]

II. HIGH-RESOLUTION (HR) UEM

A. Summary of HR-UEM images

Being a chemist, Zewail's ultimate vision for fs LB UEM was to be able to directly *image* (in real space) molecular bond dynamics.[4,25,51-54] He also had intense interest in imaging biomolecular dynamics with UEM, especially protein folding.[55] Realizing such a grand vision requires, at a minimum, combined Å-fs spatiotemporal resolutions and, thus, identification and quantification of the factors that impact resolution and define the limits. Beyond this, we argue that another important factor is having access to large ranges of instrument f_{rep} – especially below 1 MHz. This allows one to probe dynamics stemming from robust ground-state excitations, including relaxation dynamics, in the *largest possible* number of chemical and materials systems. Note that we are not suggesting that 1 MHz is a hard cut-off and that nothing useful can be done above this f_{rep} (quite the contrary). Instead, we chose this value based on previous experience with high laser f_{rep} in UEM-1 and also based on simulations of photothermal heating and dissipation in thin, electron-transparent specimens.[56-58]

Despite having been a significant motivation for the development of fs LB UEM, imaging dynamics at combined Å-fs scales has yet to be demonstrated with any UEM variant at any f_{rep}. In fact, only a few examples of sub-nm fs LB UEM *static* images have been reported, and none have been obtained with *in situ* fs specimen photoexcitation. Details of reported UEM lattice fringe images are compiled in Table I. While some examples are of lattice spacings larger than 1 nm, these are included so that a broader comparison can be made. Note that while fs LB UEM imaging has been shown to be sensitive to sub-nm dynamic changes in, for example, nanoparticle dimensions,[59] it has not been used to resolve sub-nm features, such as lattice spacings, during fs photoexcitation.

The first sub-nm, fs LB HR-UEM image was published in 2008 by Zewail and colleagues.[60] The team used UEM-2 to acquire an image of graphitized carbon with the 3.4 Å interlayer spacings resolved. Prior to this they used UEM-2 to acquire lattice fringe images of chlorinated copper phthalocyanine crystals (1.46 nm spacing with a fringe fwhm of 7 Å).[5] Unfortunately, no specific details were reported for either of these images [*e.g.*, f_{rep}, laser pulse duration (τ_{lp}), electrons per packet, or image acquisition time].

TABLE I. Compilation of fs LB HR-UEM imaging results. NR = not reported. SFEG = Schottky FEG. f_{rep} = laser repetition rate (pulses·s^{-1}). [a]Image not shown. [b]Claimed to have resolved CNT interlayer lattice spacings with f_{rep} = 200 kHz using LaB_6, but the image was not shown. [c]Calculated using $\sigma_{ep} \cong 400 n_e^{0.2}$ from Ref. 131, where σ_{ep} is the electron-packet temporal standard deviation, and n_e is the number of electrons per packet. Gaussian fwhm (τ_{ep}) is reported in the table.

PI/Country	f_{rep}	Spacing, specimen	Acquisition time	Mag.	e$^-$/packet	τ_{ep} (fwhm)	Source, gun, TEM	Pumped?	Year	Ref.
Zewail/USA	NR	1.46 nm, $C_{32}Cl_{16}CuN_8$	NR	NR	NR	NR	16 µm LaB_6, hybrid FEG, front illumination, FEI	No	2007	5
Zewail/USA	NR	3.4 Å, graphite	NR	NR	NR	NR	16 µm LaB_6, hybrid FEG, front illumination, FEI	No	2008	60
Li/China	80 MHz	3.4 Å, CNTs	NR	NR	NR	NR	LaB_6, Wehnelt, front illumination, JEOL	No	2015	61
Banhart/France	2 MHz	2.3 Å, Au	10 s, Binning NR	NR	NR	NR	0.9 mm Ta disk, biased Wehnelt + C0, front illumination, JEOL	No	2016	18
Houdellier/France	NR	9 Å[a], crocidolite	150 s, Binning NR	NR	NR	NR	W needle, cold FEG, side illumination, Hitachi	No	2018	29
Houdellier/France	2 MHz	8.65 nm, catalase	150 s, Binning 4	NR	11	NR	W needle, cold FEG, side illumination, Hitachi	No	2018	29
Li/China[b]	1 MHz	3.4 Å, CNTs	20 s, Binning 1	NR	33, 18	<1 ps	ZrO/W needle, SFEG, front illumination, JEOL	No	2020	34
Flannigan/USA	200 kHz	1.1 nm, $C_{32}Cl_{16}CuN_8$	10 s, Binning 1	150kx	811	3.6 ps[c]	100 µm LaB_6, unbiased Wehnelt, front illumination, FEI	No	-	this paper

In 2016, Banhart and colleagues published a fs LB HR-UEM image of the (111) lattice spacing of Au (2.3 Å), and they also saw hints of the (002) spacing (2.0 Å) in the FFT.[18] This was done using an f_{rep} of 2 MHz and a remarkable 10 s acquisition time with an independently-biased, Wehnelt-based thermionic electron gun (TEG) and an additional condenser lens (C0) incorporated into the column. Again, however, some key details were not reported. Further, given that the resolution is roughly the same as that specified for the base TEM, additional details about the repeatability and robustness of the measurement would have been especially informative. In 2018, another group in France, Houdellier, Arbouet, and colleagues, stated that they resolved the 9 Å lattice spacings of a crocidolite crystal using a side-illuminated cold-FEG tungsten needle.[29] Unfortunately, no image was shown, and no other specific experimental details were given. They did, however, show an image of a catalase crystal with the 8.65 nm spacings resolved.

Finally, in 2015, Li and colleagues reported an image of resolved 3.4 Å interlayer spacings in multi-walled carbon nanotubes (CNTs).[61] This was reportedly accomplished with an f_{rep} of 80 MHz and a front-illuminated LaB_6 source, but no additional information connected to the image was provided. In 2020, the same group claimed to have resolved the 3.4 Å interlayer lattice spacings of CNTs with a LaB_6 source but this time with a much lower f_{rep} of 200 kHz, a τ_{lp} of 300 fs, and a remarkable ~5,000 electrons per packet.[34] Unfortunately, no image was shown. They did, however, report an image claiming to show the 3.4 Å interlayer spacings resolved using a ZrO/W Schottky FEG [SFEG; f_{rep} = 1 MHz, τ_{lp} = 190 fs, 33 and 18 electrons per packet, and a 20 s acquisition time – this is the entry in Table I]. However, it is difficult to determine from the image and the FFT if the spacings are clearly resolved. Further, none of the other several claimed sub-nm images were shown.

B. Critical need for details and systematic studies

An oft-stated hypothesis is that imaging sub-nm, fs dynamics with HR-UEM will not be possible until the deleterious effects of photothermal accumulation are minimized, and the photomechanical stability is robust, such that pulse-to-pulse whole-specimen spatial variation is smaller than the feature of interest. This is intuitive and was indeed commented on by Zewail and team at least as early as 2007 and was also a factor in the design and development of UEM-2 at Caltech and of the UEM at Minnesota.[5,26,60] Unfortunately, little in the way of systematic studies aimed at establishing spatiotemporal image resolution limits and trends have been reported for any UEM modality. Indeed, even basic specifications remain ill-defined, such as how *static* HR-UEM image resolution varies with f_{rep} (all else being the same, lower f_{rep} would require longer acquisition times to reach the same signal level). We argue that such work is critical to advancement and growth of the field, as the results could be used to guide data-driven optimization efforts and would inform future designs and configurations. The dearth of data is itself a compelling reason to systematically explore the limits of HR-UEM.

Because of the lack of data, proposed limitations to imaging sub-nm dynamics with UEM – no matter how intuitive – are supported by one-off measurements and shared anecdotes; trends are often absent, and measurements are often not repeated (or are perhaps not easily repeatable). That is, statements about what presently limits the realization of HR-UEM imaging dynamics are speculative and have not yet been rigorously tested. Thus, the *degree* to which each (speculated) factor is limiting is unknown. To illustrate this, the lattice spacings that have been resolved with HR-UEM imaging, for which (1) an image was shown and (2) an associated f_{rep} was reported, are compiled in Figure 1. As can be seen, the data is sparse, there are large areas of the resolution-f_{rep} space that are empty, and no trends are obvious. Indeed, one could argue that these measurements cannot be directly compared, because it is not clear if they represent the instrument/lab limits. It is also entirely unknown how fs photoexcitation would quantitatively impact these limits. We argue in particular that it is critically important to establish the resolution-f_{rep} limit-trend below ~1 MHz (illustrated with speculative red-dashed trendlines in Figure 1), for which there is presently only one data point (Figure 2). (As noted in the Table I caption, Li and team claimed to have resolved 3.4 Å lattice fringes with f_{rep} = 200 kHz and ~5,000 electrons per packet, but no image was shown.) There are many open questions, and, as we argue here, the answers can be found by simply conducting the measurements and providing all the critical details so that comparisons across instruments and labs can be made.

Adding to the difficulties described above is the general trend illustrated in Table I of not clearly and thoroughly reporting critical details or performing direct comparison experiments to conventional TEM (*e.g.*, resolution at the same dose rate and total accumulated dose). Further, as more

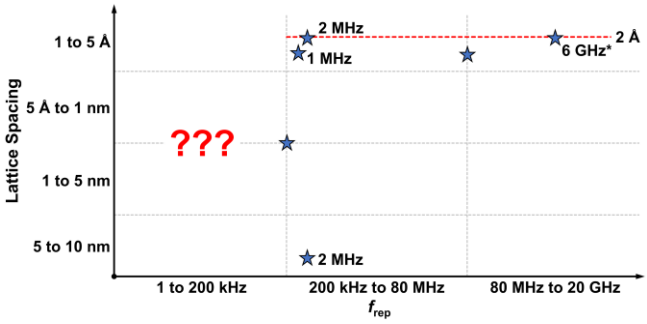

FIG 1. Illustration of some of the static fs LB HR-UEM measurements compiled in Table I that show an image and that report an associated f_{rep}. The 200 kHz, 1.1 nm image obtained in this lab is shown in Figure 2. The 6 GHz* image was obtained with a radio frequency chopped beam and is included for comparison. The red dashed line represents an apparent limit at those f_{rep} values, while the resolutions limits below ~1 MHz are unknown.

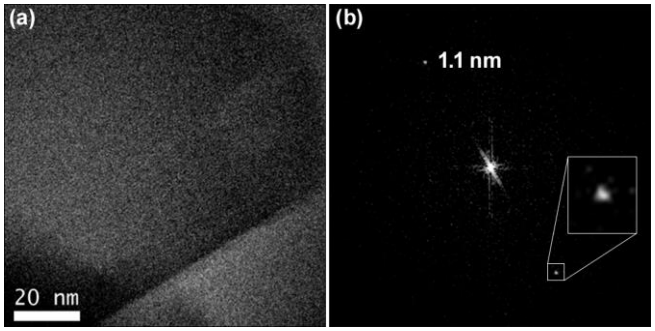

FIG 2. (a) Contrast-enhanced UEM bright-field image of a $C_{32}Cl_{16}CuN_8$ crystal with 1.1 nm lattice spacings resolved. Details: f_{rep} = 200 kHz, τ_{lp} = 240 fs (measured), τ_{ep} = 3.6 ps (calculated), 811 electrons per packet (measured at the detector), 150kx magnification, 10 s acquisition time, binning 1, specimen unpumped, TEM column not floated. (b) Contrast-enhanced FFT of (a) showing the 0.91 nm^{-1} spatial frequency, with the lower-right spot magnified.

results ultimately are generated, it will be critical to know what the lab conditions and the baseline instrument performance were *during* data acquisition. This will be an additional means with which to glean what factors impact performance. For example, the UEM Lab at Minnesota has typical steady-state temperature control of ±0.2 ˚C. Indeed, without key details, evaluation and benchmarking within and across different approaches, instruments, and labs is impossible. This is also potentially problematic to growth of the field, as a lack of clearly defined performance metrics based on validated and reproducible studies could be perceived as high-risk with respect to investment by industry, funding agencies, and universities.

C. High f_{rep} chopped/bunched beam TEM

As mentioned above, another pulsed-beam approach – laser-free stroboscopic UEM based on beam blanking – has been developed and applied since at least the 1960s and is now making an exciting re-emergence in the configuration of a radio-frequency (RF) module paired with an aperture for beam chopping and bunching.[8,9,11,62-87] Perhaps owing to very high f_{rep} (*e.g.*, 100s of MHz to 10s of GHz) and laser-free probe operation, such pulsed-beam TEMs have recently been shown to resolve deep sub-nm features.[88] Thus, background is provided here for qualitative comparison to fs LB UEM. (Note that several laser-free variants have been developed and explored, including line sampling, combination chopped beam and signal gating, and gating of the secondary electron signal.[89-94])

As early as 1978, Hosokawa and colleagues demonstrated electron packet durations as short as 200 fs in an SEM using a combination chopper/buncher, though they resolved relatively slow dynamics (100s of picoseconds).[72,95,96] More recently, Kruit and colleagues proposed beam deflection for electron microscopes based on photoconductive switches predicted to reach 100 fs and better than 10 nm resolutions. Note that SEM beam blankers are currently being explored for a number of applications, including time-resolved cathodoluminescence.[97-102] Early work to develop stroboscopic electron microscopes was motivated by the desire to probe cyclic integrated circuit operation or cyclic magnetic responses using oscillatory, phase-shifted specimen driving signals.[63,65-68,78] This specific specimen driving mechanism (oscillatory electric or magnetic waveforms) was also employed for chopped-beam TEMs by Bostanjoglo and colleagues but at much lower frequencies, and recent work has improved the spatial resolution of such an approach to slightly better than 1.2 Å (no dynamics) by using phase locking (10 kHz but with long 12.5 μs electron pulses).[11,47] Early chopped-beam SEMs could be operated with an f_{rep} of 100s of kHz up to 64 GHz with custom aperture wheels; 100s of nanometer spatial resolutions and picosecond time resolutions were routinely reached.[66,67,103] (Note that while SEM beam blankers are still under active study, and much more could be described, TEMs are the primary focus of this Perspectives article.[99,100])

As previously noted, recent work on laser-free pulsed-beam TEM has focused on using GHz RF modules paired with apertures for reaching 10s of picoseconds to 100s of fs. The instruments now in service have shown promise for reaching nm-ps resolutions, with potential for going below this barrier. For example, a team from Lawrence Berkeley National Lab and University of California, Berkeley, TU Eindhoven, Dow Chemical, and Thermo Fisher Scientific reported packet durations in an RF stroboscopic TEM as short as 2 ps, though they did not explicitly report a pulsed-beam real-space resolution, and no dynamics were studied.[39] Members of this team have worked on RF cavity pulsers for UEM and UED for years and have suggested that this approach may be able to reach 100 fs temporal resolution at f_{rep} >> 1 MHz.[104-109]

Another team comprised of researchers from Brookhaven National Lab, NIST, and Euclid Labs recently reported resolving 2 Å lattice fringes (Au, no dynamics) using a frequency-tunable RF strip-line pulser with an effective f_{rep} of 6 GHz (tunable from 100 MHz to 12 GHz) and with τ_{ep} = 60 ps (acquisition time was not reported for the lattice fringe image).[88,110,111] They also reported imaging dynamics (RF-driven mechanical oscillations) at 1200x magnification with ~10 ps temporal resolution and a 1.5 s acquisition time.[50] This again is conceptually similar to time-resolved SEM sampling of voltage- or RF-driven microcantilever beams, wherein nm-ns displacements can be resolved, or to cyclic ultrasonic excitation and sampling with TEM.[11,93,94,112,113] For example, Gopinath and Hill reported 300 nm and 10 ps resolutions of potential-field dynamics (~1 μm domains propagating at ~100 $nm \cdot ps^{-1}$) in a Gunn device with a stroboscopic SEM operated at 9.1 GHz.[66,67] There are many other examples.[62,63,65,68,70-75,78] Interestingly, this particular application (carrier contrast dynamics) has also been explored with LB scanning UEM (S-UEM) for some time, beginning at IBM in the 1980s with picosecond lasers

(again for testing integrated circuits) and currently continued by several groups using fs lasers, beginning with a group at EPFL in 2005 for probing carrier dynamics (τ_{lp} = 200 fs, f_{rep} = 80.7 MHz, as low as 1 electron per packet, 50 nm and 10 ps spatiotemporal resolution).[23,24,114-127] Note that the early LB S-UEM at IBM had demonstrated resolutions of (up to) 4 ps and 100 nm.[114]

As a point of reference, fs LB UEM (TEM-based) has demonstrated τ_{ep} = 200 fs (τ_{lp} = 50 fs) and better than 100 fs sensitivities.[27,44,128] We have conducted simulations of electron trajectories in the FEI Tecnai Femto UEM that indicate τ_{ep} may become laser limited (τ_{lp} = 300 fs), which is interesting considering the instrument has a standard Wehnelt TEG.[129,130] Experiments on this system also indicate the temporal resolution can be laser limited, at least for laser pulse durations of 100s of fs.[131] Near laser-limited τ_{ep} has been reported for a side-illuminated cold-FEG source by Houdellier and colleagues (τ_{lp} = 350 fs, τ_{ep} = 360 fs, 20 electrons per packet, Hitachi HF2000).[29] Other claims of τ_{ep} becoming laser limited at low packet density have been made,[132] though additional systematic studies based on various combinations of laser and instrument configurations still need to be performed in order to establish robust trends. Regardless of modality, current thinking based on the relationship between laser parameters and beam current, and on fundamental electron-beam physics (*e.g.*, electron-electron repulsion), is that a balance must be struck between coherence, beam current, and acquisition time for achieving robust and routine Å-fs imaging of the broadest-possible range of phenomena and materials. This balance can be appreciated by inspecting Equation 1 for the LB UEM photoelectron beam current (I_{pe}) reaching the detector.

$$I_{pe} = \left[\left(\frac{E_p}{h\nu} \cdot \eta\right) \cdot CE\right] \cdot e \cdot f_{\text{rep}} \qquad (1)$$

Here, E_p is the pulse energy of the probe laser striking the electron source, $h\nu$ is the photon energy, η is the photoelectron quantum efficiency, CE is the collection efficiency (*i.e.*, the ratio of the number of photoelectrons reaching the detector to the number generated at the source), and e is the fundamental charge.

III. THE CASE FOR LOW f_{rep} HR-UEM

The challenges associated with using high f_{rep} LB UEM for studying fs-ps dynamics have been known since at least the development of UEM-1 at Caltech.[5,56,133,134] Myriad nanomechanical, energy, and quantum materials phenomena are either not accessible or are obscured when using high f_{rep} owing to relatively long-lived excited states or high quality-factor oscillatory relaxations. For example, while carrier recombination times in thin films of pristine ferroelectric materials span nanoseconds to microseconds, the creation of gap states by defects can lead to trapping and long lifetimes, thus producing long-lived incoherent and coherent lattice responses and protracted relaxation times.[135-137] Further, using high f_{rep} can hinder full dissipation of photothermal energy prior to the next pump event, thus activating or enhancing thermally driven mechanisms that produce atomic displacements and plastic (inelastic) morphological changes (*e.g.*, mass diffusion, melting, ablation, dislocation motion, fracture, and solid-solid structural transformations). A schematic illustrating timescales of select chemical and materials dynamics is shown in Figure 3 and is meant to

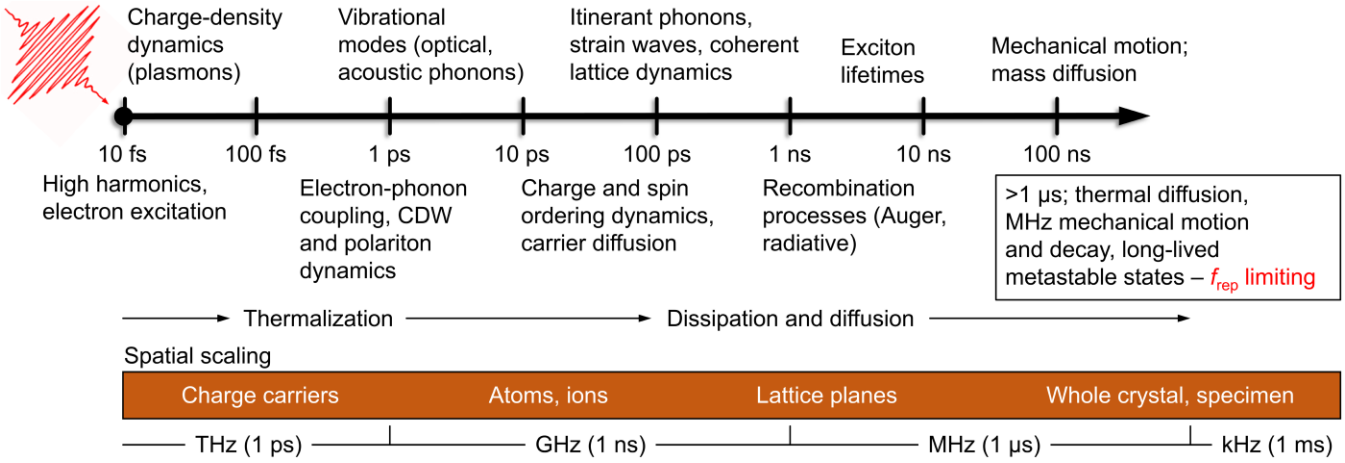

FIG 3. Select zoology of ultrafast photoinduced dynamics and their approximate timescales. Boundary conditions become increasingly important to energy dissipation with increasing time owing to dynamics encompassing the entire specimen (*i.e.*, initiating with charge-carrier dynamics and increasing in scale to whole-crystal/specimen motion and thermal diffusion). Relatively long-lived states and dissipation channels will limit the UEM operational f_{rep} if full recovery is desired, which can take microseconds or longer. For comparison, the f_{rep} (and the associated time between packets) needed to capture full recovery of the discrete examples is shown in relation to the overall chain of events, further illustrating the need for f_{rep} < MHz for full recovery of the broadest range of chemical and materials phenomena.

convey how the use of low f_{rep} UEM can generally expand the application space.

Though the relatively high beam currents afforded by using high f_{rep} ease difficulties associated with obtaining HR-UEM images, the tradeoff is that the accessible application space becomes limited. This is of course not to say that high f_{rep} UEM should not be pursued (see the next paragraph). Rather, our perspective is that the reach and impact of a characterization tool is dependent not only upon the insights that can be gathered but also upon how broadly it can be applied. Thus, we argue that growth of UEM requires broader adoption, and that broader adoption will come about by expanding the application space. Additionally, considering the high barrier to entry, we have long advocated for development of user-friendly instruments that are fully operational as both a pulsed-beam UEM and a conventional, HR analytical TEM. This would increase the attractiveness of installing such instruments in a university user facility, owing to the typical reliance on hourly fees.

In light of the points raised thus far, having access to a large range of f_{rep} – from 1 kHz to 1 GHz, for example – together with fs specimen photoexcitation in one instrument would be extremely enabling. Indeed, the relatively recent emergence of new applications for pulsed-beam TEM have shown that there are numerous compelling reasons to pursue high f_{rep} UEM. Some of these include the study of cyclic waveform excitations with high spatial resolution, electron-photon quantum effects (PINEM), and damage-reduced (or even damage-free) probing, as being pursued, for example, in optical near-field electron microscopy (ONEM).[44,50,138] Ultimately, large-scale development will be driven by the emergence of critical need areas, as has occurred with quantum and energy materials research. For these specific applications, a range of f_{rep} is needed, though the issue of beam coherence is also critical.

As noted above, nature often requires a balance to be struck and compromises to be made. For example, side-illuminated cold-FEG and SFEG sources have high coherence and high brightness at the expense of electrons per packet (as well as long-term stability), which therefore also requires high f_{rep} in order to increase beam current and reduce acquisition time.[27,29,128,139] As such, the reasons put forth for using sharp-tip emitters and (S)FEGs for fs LB UEM are essentially the same as those for conventional TEM – higher brightness and better spatial coherence. However, one might glean from the discussion thus far that much is still unknown about the effects of laser and electron-source parameters for front-illuminated flat photocathodes, and especially for conventional Wehnelt-based TEGs. For example, as noted above, Li and team claim to have resolved 3.4 Å interlayer spacings in CNTs using a LaB_6 emitter and an astounding ~5,000 electrons per packet and τ_{ep} <1 ps.[34] If correct, this seems to clearly indicate that the electron trajectories are behaving in a way that is yet to be fully understood – it is remarkable that packets of that size would retain coherence such that τ_{ep} <1 ps and 3.4 Å spacings could be resolved.

Some of our own recent work on large, front-illuminated flat cathodes and unbiased Wehnelt electrodes suggests that such UEM beam properties may in fact not be so far fetched. The image shown in Figure 2 is one example, which was obtained with over 800 electrons per packet. Clearly, if the measurements are correct, there are differences that must be reconciled between this and the measurement by Li and team (*e.g.*, our calculated τ_{ep} is 3.6 ps for 811 electrons per packet). This aside, we feel there is enough evidence to suggest that there are new electron-packet behaviors waiting to be discovered and new, clever instrument configurations that can be designed that will allow for the HR-UEM f_{rep} limit to be pushed well below the MHz regime. In this regard, some of the new insights we have recently gathered through simulations have indeed been surprising. For example, we found that improvements in coherence and temporal resolution are seen when photoelectron emission occurs from a region centered on the optic axis, the size of which is dictated by the (unbiased) Wehnelt aperture.[129,130] We note that this is strictly for single-electron packets; in addition to experimental testing, the simulations need to be extended to multi-electron packets incorporating particle-particle interactions.

Lastly, we again note that fs specimen photoexcitation may indeed pose a challenge to reaching Å-fs imaging dynamics, though systematic studies are still needed. It is thus worth considering other potentially less spatially disruptive forms of excitation. However, in our view, there are strong and compelling reasons to use fs photoexcitation for HR-UEM, and thus to establish the limits through systematic experimentation. First, the use of a fs pulsed laser to coherently trigger dynamics *in situ* provides significant versatility and flexibility – for example, it enables polarization-dependent near-UV to near-IR excitation, above-gap carrier excitation, resonant and non-resonant excitation of electron density and vibrational/phonon modes, and both strong and weak excitations of large-gap semiconductors (*e.g.*, the oxide perovskites). Ultrafast photoexcitation is also coherent, in that it is a temporally well-defined trigger occurring on timescales commensurate with charge-carrier responses, as explained by Zewail for molecular ensembles.[140] Importantly, the ability to directly probe these processes with high spatiotemporal resolutions (and with small probe sizes on chosen, well-characterized specimen regions), as well as coupling them to ultrafast X-ray spectroscopies (for example),[51,141,142] will enable development of a comprehensive understanding of ultrafast dynamics spanning charge carriers to nanomechanics and without temporal gaps. This encompasses generation, coupling, conversion, transport, and decay and the associated influences of structure, morphology, geometry, and boundary conditions.

Second, the practical use of mechanical delay stages to select the time delay for fs LB UEM means the fundamental laser-pulse properties may dictate the ultimate resolution limits if the microscope pinch points can be identified and

optimized. Indeed, mechanical delay stages have resolutions better than 1 fs, calibrated accuracies better than ±5 fs, and bidirectional repeatabilities of better than ±2 fs. Further, the full range of typical delay stages spans nanoseconds, thus providing access to initial relaxation dynamics. This again provides significant flexibility, versatility, and tunability. Third, owing to the thin specimens and large accelerating voltages, arguments pertaining to confounding factors arising from differences in electron and photon penetration depths in fs LB UEM are unfounded – the large body of quantifiable and readily-modeled published fs LB UEM data attests to the accessibility of the approach. Further, claimed limitations due to laser-beam pointing stabilities are also unfounded and have not been quantifiably demonstrated to limit performance at any magnification when applied in a stable lab environment. Fourth and finally, using a fs pulsed laser is often simply cited as "challenging", but we have operated a UEM lab for nearly 8 years primarily with a group of 5 to 10 graduate and undergraduate students and without technical staff. Growing the field requires moving beyond anecdotes and addressing dogma with data and detail, so it is paramount that the limits of fs LB UEM be determined, and that the entire experimental parameter space be systematically and quantitatively mapped so that a clear delineation of the limits can be made and so that the chemical and materials application space can be expanded.

IV. CONCLUSIONS

The sub-nm HR-UEM images that have been published to date have typically been obtained with $f_{rep} \geq 1$ MHz and never with photoexcitation. However, the number of experimentally accessible ultrafast chemical and materials phenomena drops as the instrument lower-bound f_{rep} goes up owing to insufficient energy dissipation between excitation pulses. Speculative predictions are that the requirement of high spatial repeatability and efficient thermal dissipation between pulses for stroboscopic fs LB UEM will limit the resolution to ~1 nm for coherently triggered specimens, regardless of f_{rep} or the base instrument. *However, such conceptions are not based on the results of systematic studies – the spatial resolution and f_{rep}-limits of fs LB UEM have yet to be quantitatively, rigorously, and systematically established for any UEM modality, and no information on achievable resolutions with in-situ fs photoexcitation has been published.*

Though fs LB UEM has been touted as a viable path to reaching Å-fs real-space imaging, as well as being uniquely positioned to probe dark states (*i.e.*, sensitive to all elements and structures), to probe individual defect dynamics, and to probe complex heterogeneous behaviors, only a tiny fraction of the expansive parameter space has been explored and characterized. This is especially true for a minimally modified, TEG-based UEM, which may in fact be well-suited for low f_{rep} HR-UEM studies of the broadest range of chemical and materials phenomena. Further, there is a need to determine the resolution limits for such instruments so that comparisons across different configurations and modalities can be made. As can be gleaned from Figure 1, the dearth of information on fs UEM operation below 1 MHz – regardless of instrument configuration – illustrates a significant opportunity to establish new development directions and to greatly expand the application space.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

D. J. Flannigan: Conceptualization, data curation, funding acquisition, methodology, project administration, resources, supervision, visualization, writing – original draft, writing – review and editing. **W. A. Curtis:** Data curation, investigation, methodology, validation. **E. J. VandenBussche:** Conceptualization, writing – original draft. **Y. Zhang:** Conceptualization, writing – original draft. See the NISO CRediT taxonomy for definitions of contributing roles (credit.niso.org).

DATA AVAILABILITY

Data is available upon request from the corresponding author.

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