Development of nanosecond time-resolved infrared detection at the LEAF pulse radiolysis facility

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ABSTRACT

When coupled with transient absorption spectroscopy, pulse radiolysis, which utilizes high-energy electron pulses from an accelerator, is a powerful tool for investigating the kinetics and thermodynamics of a wide range of radiation-induced redox and electron transfer processes. The majority of these investigations detect transient species in the UV, visible, or near-IR spectral regions. Unfortunately, the often-broad and featureless absorption bands in these regions can make the definitive identification of intermediates difficult. Time-resolved vibrational spectroscopy would offer much improved structural characterization, but has received only limited application in pulse radiolysis. In this paper, we describe in detail the development of a unique nanosecond time-resolved infrared (TRIR) detection capability for condensed-phase pulse radiolysis on a new beam line at the LEAF facility of Brookhaven National Laboratory. The system makes use of a suite of high-power, continuous wave external-cavity quantum cascade lasers as the IR probe source, with coverage from 2330-1051 cm^{-1} . The response time of the TRIR detection setup is ~ 40 ns, with a typical sensitivity of ~ 100 μOD after 4-8 signal averages using a dual-beam probe/reference normalization detection scheme. This new detection method has enabled mechanistic investigations of a range of radiation-induced chemical processes, some of which are highlighted here.

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I. INTRODUCTION

Developed over 50 years ago,¹⁻⁴ pulse radiolysis, which utilizes short, high-energy electron pulses generated by an accelerator, is a powerful method for the rapid production of radical ions, free radicals, and other transient species, after which their reaction kinetics can be followed by time-resolved absorption or emission spectroscopy on timescales ranging from picoseconds to seconds, generally in the ultraviolet (UV), visible (Vis), or near-infrared (NIR) regions.^{5, 6} It is therefore particularly useful for studying the kinetics and thermodynamics of various types of redox processes and electron transfer reactions, biological reactivity, and many other chemical processes that can be induced by ionizing radiation. In contrast to flash photolysis, in which a short pulse of light is directly absorbed by a dissolved solute to initiate a photochemical process, the energy from an electron pulse is mainly deposited in the medium itself. This typically results in the formation of either excited or ionized solvent molecules, followed by a rapid sequence of reactions that culminate in a homogeneous mixture of various ions and/or radicals derived from the solvent. Through the judicious addition of various reagents to the solution (particularly in aqueous solution), most of these primary products can be rapidly scavenged away, resulting in one major species that may act as either a strong reductant (e.g., the solvated electron) or a strong oxidant (e.g., the hydroxyl radical) toward dissolved solute molecules.⁷ In many ways, therefore, pulse radiolysis complements laser flash photolysis, and can often be advantageous, e.g., for molecules that lack any strong chromophores for the absorption of light, or which possess extremely short-lived photoexcited states that cannot lead to productive electron or energy transfer.

Identification of the transient species generated by pulse radiolysis is frequently an important aspect of this work. While there is a long history demonstrating the great utility of pulse

radiolysis using UV-Vis-NIR detection, condensed-phase absorption bands in these spectral regions are often broad and featureless, and not very sensitive to the details of the transient species' structure. In contrast, vibrational spectroscopy offers the possibility of much improved structural characterization.⁸ However, up to now the application of time-resolved vibrational spectroscopic methods to pulse radiolysis has been somewhat limited. For example, while some excellent research has been done using time-resolved resonance Raman (TR³) methods,^{e.g., 9-12} this is a difficult technique that is limited to select molecular species with appropriately strong electronic transitions. Time-resolved mid-infrared (TRIR) spectroscopy would have a much broader applicability but until recently,¹³ due to its own technical challenges with respect to implementation in a pulse radiolysis environment, it had been limited to only a handful of gas-phase studies on the microsecond timescale,^{e.g., 14-18} and an FTIR-based approach with ~30 s time resolution.¹⁹ Making use of high-power external-cavity quantum cascade lasers (EC-QCLs) as tunable IR sources, we previously demonstrated, for the first time, the feasibility of combining pulse radiolysis of condensed-phase samples with nanosecond time-resolved infrared (TRIR) spectroscopy,¹³ and have since begun to apply this powerful technique to the identification of transient intermediates in a diverse range of radiation-induced chemical processes.²⁰⁻²²

Since our initial feasibility study,¹³ significant changes and improvements have been made to the technique, and this paper describes in detail our development of dedicated nanosecond TRIR instrumentation for the study of condensed-phase samples that are subjected to pulse radiolysis on a new electron beam line at the BNL Laser-Electron Accelerator Facility (LEAF).²³ Construction and use of a dedicated TRIR experimental station enabled enormous progress in addressing technical challenges and improving the performance and sensitivity of the detection system. This apparatus has enabled enhanced mechanistic pulse radiolysis investigations, often

allowing the definitive identification of transient radicals, ions and molecules with nanosecond time resolution.

II. DESCRIPTION OF THE TRIR DETECTION APPARATUS AT LEAF

A. Accelerator and beam line

The LEAF accelerator and the general pulse radiolysis techniques employed at LEAF have been described in detail previously.^{23, 24} Briefly, a 266 nm laser pulse is directed onto a Mg photocathode inside an evacuated, four-cell, resonant cavity microwave gun about 30 cm long. The emitted photoelectrons are accelerated to 8.7 MeV within the length of the gun by a ~15 MW, 3 μ s pulse of microwave power. The electron pulse length is a function of the laser pulse width. LEAF was originally constructed with two beam lines for transient UV-Vis-NIR absorption and conductivity measurements. The initial proof-of-principle TRIR pulse radiolysis experiments¹³ were performed at the experimental station used for digitizer-based UV-Vis-NIR transient absorption detection (beam line “B”, Figure 1). However, due to the completely different optical requirements of TRIR detection and the disruption caused by switching back and forth, we recently added a third beam line (“IR”, Figure 1) dedicated to TRIR. The new beam line was designed and constructed by Advanced Energy Systems, Inc. (Medford, NY). The general design of the TRIR beam line is similar to the existing 90° line “A” used for the “Optical Fiber Single-Shot” experiment.²⁴ It branches off the main beam line with two consecutive 45° bending magnets, followed by a series of quadrupole focusing magnets and steering magnets, delivering electron pulses to a sample cell (see below) through a 0.0005” (12.7 μ m) thick aluminum window at the end of the beam line (Figure 1). The accelerator beam can be imaged for tuning and steering purposes by inserting a series of remote-controlled targets (“pop-ups”)

into the beam. The pop-ups are coated with a scintillator that produces a visible flash when struck by the electron pulse. The targets are viewed by digital video cameras (Allied Vision Technologies, Prosilica GC, Model: GC650), triggered to generate a frame when the accelerator fires. Single video frames are colorized and displayed on a PC for inspection.²⁵

FIG. 1. Schematic layout of the LEAF accelerator vault showing the electron gun (G), the existing beam lines A and B, and the recently-installed beam line dedicated to TRIR spectroscopy (red line, IR).

For most UV-Vis-NIR experiments, the LEAF photocathode is illuminated by a 7-15 ps pulse of 266 nm radiation, generating a 5-10 nC, 8.7 MeV electron pulse of similar duration. However, fast HgCdTe detectors used for mid-IR detection typically provide a time response of a few tens of nanoseconds, making excitation by picosecond electron pulses superfluous. For this reason, LEAF is operated in its so-called “macropulse” mode for TRIR detection: the short UV laser pulse on the photocathode is replaced by a ~ 7 ns 266 nm pulse derived directly from a Quanta Ray GCR-170 Nd:YAG laser, resulting in a ~ 7 ns, 8.7 MeV electron pulse (more specifically a train of 20 pulses, each separated by 0.35 ns). Depending on the needs of a particular experiment, these long electron pulses may carry as much as 100 nC of charge, which can be conveniently manipulated by simply changing the energy of the 266 nm laser pulse. An additional advantage

of the higher macropulse radiation dose for TRIR detection is that it results in a higher concentration of transient species. This partially compensates for (i) the decrease in signal intensity that results from the necessity to use much shorter cell pathlengths (by a factor of $\geq 10\times$) when working in the mid-IR compared to the UV-Vis-NIR regions, due to often-strong solvent IR absorptions, and (ii) the fact that mid-IR absorption bands generally exhibit lower molar absorptivities than UV-Vis bands. However, the picosecond electron pulse is still available for TRIR experiments, for example if a sample is extremely radiation-sensitive.

As with any typical TRIR detection setup, we require a tunable source of mid-IR radiation for probing the IR absorptions of transient species, a suitable sample cell for housing the solution under investigation, fast rise-time IR detectors, and an appropriate digitizer to record the signals from the detectors. Each of these components is discussed in more detail in the following sections.

B. Quantum cascade lasers as an IR probe source

In UV-Vis-NIR experiments at LEAF, light for probing the absorptions of transient species is provided by an essentially white, pulsed Xe arc lamp or a flashlamp, synchronized in time with the electron pulse, with wavelengths for analysis being selected by sets of narrow bandpass filters.²³ However, such a source does not provide sufficient intensity in the mid-IR portion of the spectrum. Traditionally, continuous wave (CW) mid-IR sources for nano- to millisecond TRIR spectroscopy have been limited to either globars^{26, 27} and tunable lead-salt diode lasers,²⁸ both of which require the use of a monochromator to select a single probe wavelength, or line-tunable CO or CO₂ gas lasers^{28, 29} (see Table I for a list of the advantages and disadvantages of these sources for use with pulse radiolysis). Each of these has proved to be extremely useful in different forms of TRIR spectroscopy when coupled with laser flash photolysis. However, for

several reasons, including: (i) pulse radiolysis often produces lower concentrations of transient species than laser flash photolysis, (ii) probe beams typically need to be transported over long distances in a pulse radiolysis experiment in order to locate sensitive detection apparatus away from electromagnetic and ionizing radiation, (iii) a pulse radiolysis environment is typically noisier in terms of electrical and electromagnetic noise than a laser flash photolysis environment, and (iv) for the technique to be applicable to a wide range of samples, broad coverage across much of the mid-IR is required; none of the traditional IR sources were deemed to be suitable for high signal-to-noise (S/N) nanosecond TRIR measurements in a pulse radiolysis environment. For example, although globars and lead-salt diode lasers offer coverage throughout the mid-IR, they are too low power for sufficient S/N, and while CO and CO₂ lasers are extremely high power devices, their limited tuning ranges render them unsuitable for many interesting chemical systems that will be investigated with pulse radiolysis-TRIR.

TABLE I. The advantages and disadvantages of potential CW IR probe sources for nanosecond TRIR detection in pulse radiolysis experiments.

IR Source	Advantages	Disadvantages
Globalar	<ul style="list-style-type: none"> • Cheap and very reliable. • Coverage across entire mid-IR region. 	<ul style="list-style-type: none"> • Very low power, especially when used with a monochromator. • Non-coherent source, difficult to transmit over long distances.
Lead-Salt Diode Laser	<ul style="list-style-type: none"> • Proven technology. • Wide wavelength availability (3 – >20 μm). • Narrow linewidth. • Continuous tuning. • Reasonable cost. 	<ul style="list-style-type: none"> • Narrow tunable range for each diode ($\leq 100 \text{ cm}^{-1}$). • Low power ($\leq 1 \text{ mW}$). • Requires a monochromator for mode separation. • Cumbersome cryogenic cooling.
CO / CO ₂ Lasers	<ul style="list-style-type: none"> • Proven technology. • Very high power (up to kW). • Narrow linewidth. • Grating tuning for single line operation eliminates need for monochromator. 	<ul style="list-style-type: none"> • Limited tuning ranges in specific regions of the mid-IR. • Non-continuous tuning. • Large size and bulky power supply.
CW Mode-Hop-Free External-Cavity Quantum Cascade Laser (CW-MHF EC-QCL)	<ul style="list-style-type: none"> • High power (~100 – 400 mW). • Can often exhibit fairly wide tuning ranges (up to 100-200 cm^{-1}). • Wide wavelength availability (4.3 – 10.5 μm). • Narrow linewidth. • Continuous tuning. • No monochromator required. • Room temperature operation. • Extremely compact. 	<ul style="list-style-type: none"> • Fairly new technology that is still developing. • Expensive. • Often exhibit synchronous and random beam intensity fluctuations that requires dual-beam probe/reference normalization for very high S/N.

Fortunately, the relatively new technology of tunable, CW mode-hop-free, mid-IR external-cavity quantum cascade lasers (CW-MHF EC-QCLs) was commercialized several years ago by Daylight Solutions, Inc. (San Diego, CA). These lasers offer a key advantage for pulse radiolysis-TRIR in that they have very high CW output powers, typically in the range of ~100-400 mW. It is this high power that helps overcome the first three concerns highlighted in the

previous paragraph, providing excellent S/N in pulse radiolysis-TRIR experiments. EC-QCLs can be individually grating-tuned over a wavenumber range as wide as $\sim 100\text{-}220\text{ cm}^{-1}$, with the output power varying as a function of wavenumber, typically dropping to zero at the edges of the tuning range and peaking near the center. When tuned to a particular wavenumber, the linewidth of a CW-MHF EC-QCL beam is extremely small (typically $<0.0002\text{ cm}^{-1}$), rendering these lasers essentially monochromatic for the purposes of condensed-phase TRIR spectroscopy. The beam from a CW-MHF EC-QCL has a typical spot size of $<2.5\text{ mm}$ and a low divergence ($<5\text{ mrad}$). The wavelength range covered by our current set of twelve lasers spans $4.29\text{-}9.51\text{ }\mu\text{m}$ ($2330\text{-}1051\text{ cm}^{-1}$) with only a few tuning gaps (see Table II), giving us access to a wide range of molecular vibrations. The laser heads are compact (nominally $16.5 \times 11.0 \times 9.5\text{ cm}$) and each is mounted on an $8 \times 10''$ baseplate with its own pair of alignment mirrors, allowing for kinematic mounting and rapid exchange to select new wavelengths with virtually no realignment required in the apparatus. The temperature of the EC-QCL laser chip is maintained by thermoelectric cooling, typically just a few degrees below room temperature. Thus, the laser head requires only moderate cooling with a smooth flow of $20\text{ }^{\circ}\text{C}$ water. Due to the narrow linewidth and continuous tunability of EC-QCLs, when working in regions of the mid-IR that are heavily obscured by atmospheric water vapor absorptions (e.g., $1900\text{-}1300\text{ cm}^{-1}$), one can simply tune in-between the water vapor lines, completely eliminating absorption of the IR probe beam by water vapor, which often plagues IR spectroscopy measurements. Eventually though, we plan to install nitrogen-purged tubing and enclosures along the IR beam path to minimize this inconvenience.

TABLE II. Our suite of twelve CW-MHF EC-QCLs^a for pulse radiolysis-TRIR showing their full tuning ranges and maximum CW output powers, which are typically achieved near the center of the tuning ranges.

	Nominal Wavelength (μm)	Wavenumber Range (cm^{-1})	Maximum CW Power (mW)
1	4.3	2330-2160	105
2	4.5	2235-2105	125
3	4.7	2230-2020	180
4	4.9	2180-1970	275
5	5.2	1981-1873	80
6	5.4	1903-1774	145
7	5.8	1900-1675	210
8	6.2	1670-1536	100
9	6.8 ^a	1685-1445	370
10	7.4	1395-1306	100
11	8.4	1258-1181	85
12	9.0	1135-1051	160

^aThe 6.8 μm laser is not a CW-MHF model. It is actually a CW/Pulsed model, which can be subject to small mode hops. However, the size of these hops is small ($<0.5 \text{ cm}^{-1}$), and the dual-beam probe/reference detection scheme described below eliminates any noise associated with mode hopping.

Another advantage of EC-QCLs as a probe source is that they may lead to more routine TRIR measurements of aqueous-based systems. Although a major focus of our work on pulse radiolysis-TRIR so far has been in organic solvents, such as acetonitrile (CH_3CN) and tetrahydrofuran (THF), water is a very commonly-used solvent in pulse radiolysis and radiation chemistry in general, and it would be desirable to be able to perform TRIR measurements on aqueous systems also. Water is a difficult solvent for transmission IR spectroscopy due to its

extremely strong absorbance throughout most of the mid-IR, necessitating the use of very short pathlengths (typically <10-80 μm , depending on the region) that result in small signal intensities. However, the high output power of QCLs has led to their use in steady-state IR studies of aqueous systems with pathlengths as long as 140 μm .³⁰ Therefore, it is our hope that the use of EC-QCLs as an IR probe source will open the door to more facile pulse radiolysis-TRIR measurements of aqueous systems.

C. Custom IR flow cell and flow system

For optimum S/N, one wants the absorption of probe radiation to be sufficiently large so that the amplitude of the transient absorption is larger than all noise sources, but not so large that all the probe radiation is absorbed. For many UV-Vis-NIR experiments in transparent solvents with μM -mM solute concentrations, appropriate absorption pathlengths are on the order of 5-20 mm. However, due to significant absorptions by solvent IR bands, the pathlength for the mid-IR needs to be much shorter, on the order of <0.1-2 mm, depending on the solvent. In addition, the choice of cell window material presents a number of challenges. The cell windows must not significantly absorb probe light over a wide range of wavelengths. Also, the window material must not give rise to spurious signals or color centers when the radiolysis electrons pass through. Finally, the cell windows must have sufficient structural strength to withstand compression seals and the pressure of pumping solution flow. After testing many crystal windows, thin (0.35 mm thick $\times$ 10 mm dia.) IR-grade polished CaF_2 windows met these criteria (Crystran Ltd., Poole, UK). These windows are sufficiently thin that they exhibit excellent transmission of mid-IR radiation all the way to the 9-10 μm sensitivity limit of the IR detectors. Provided that care is taken when handling the windows (since they are quite fragile), they can be used repeatedly in multiple experiments.

A miniaturized, air-tight, custom flow cell was designed at BNL and manufactured by Gamma Technologies, Inc. (Morrisville, NC). The design is loosely based on that of a commercial demountable liquid IR cell but with several changes, including a removable back insert that allows for easier assembly/disassembly and cleaning of the cell. A cross-section of the cell is shown in Figure 2. The body is 316 stainless steel and the spacers that separate the windows and define the optical pathlength are either polyether ether ketone (PEEK) or polytetrafluoroethylene (PTFE). The window sealing o-rings are made of Kalrez[®] for chemical resistance, and these render the cell completely air-tight, which is critical since the majority of the samples under investigation are gas-saturated, e.g., with argon or CO₂. Assembly of the cell is facile and rapid. The back metal insert that holds the back o-ring against the back window is held in place by a back plate that is wedged to prevent interference effects (see below). The front metal insert, which pushes on the front o-ring and window is pressed down by screwing the outer knurled metal cap onto the external thread of the cell body until it is finger tight. Liquids are flowed into and out of the cell by means of PEEK tubing (0.010" ID × 1/16" OD) and miniature HPLC fittings (IDEX, M-660). The internal volume of the cell is low, allowing small quantities of samples to be studied, and reducing waste during flow experiments. For example, with a 1.93 mm pathlength (a typical pathlength that we have used with CH₃CN samples), the internal cell volume is only 34 μL.

FIG. 2. A 3D cross-sectional diagram of the custom flow cell that is used for pulse radiolysis-TRIR experiments at LEAF. A: cell body; B: 6-32 threaded flat-bottom port; C: front insert; D: back insert; E: knurled screw cap; F: 8° wedged back plate; G: Kalrez[®] o-ring; H: PEEK or PTFE spacer with holes for liquid flow; I: 10 mm dia. × 0.35 mm thick polished CaF₂ window; J: plate for mounting inside sample block. A–E are 316 stainless steel. F and J are aluminum. The wedged plate F is 1×1" in size.

Since pulse radiolysis results in the formation of permanent products, it is necessary to frequently refresh the solution under investigation. For this purpose, we have chosen to make use of a remotely-operated syringe pump flow system. The solution is typically prepared inside an inert atmosphere glovebox, where it is placed inside a glass sample reservoir bottle equipped with a GL32-threaded cap that contains three ¼-28 threaded ports and valves (Omnifit, 00932Q-3V). The valves are closed and the reservoir bottle is then placed inside a nitrogen-purged Plexiglas[®] box that contains a remotely-operated syringe pump (Hamilton Company, Microlab 500 series). A gas-tight syringe (e.g, Hamilton Company, 2.5 mL, P/N: 81420) is attached to the pump head, which in turn is connected to both the sample reservoir bottle and the IR flow cell by

0.060" ID and 0.010" ID PEEK tubing, respectively, and standard PEEK HPLC tube fittings. The exit tube from the IR flow cell is connected to a waste bottle with more 0.010" ID PEEK tubing. The solution inside the reservoir bottle is continuously bubbled with any desired gas (e.g., argon, CO₂, etc.), that has first been passed through a pre-bubbler containing pure solvent (to prevent evaporation of solvent from the reservoir bottle). After priming and filling the syringe from the reservoir bottle, an aliquot of solution is flowed through the IR cell for a TRIR measurement. This is repeated after every few electron pulses. The volume of each aliquot is typically set to approx. 3× the cell volume so that it almost completely refreshes the solution inside the cell. For example, with the 1.93 mm pathlength spacer (34 μL cell volume) we use 100 μL aliquots. Once the syringe is empty, it is remotely refilled and the experiment continued. A useful feature of this flow system is that the syringe pump can be equipped with two separate reservoir bottles and syringes. Thus, two solutions can be flowed simultaneously through a simple Y-connector mixer (e.g., IDEX, P/N: P-512). By varying the flow rate of each syringe, one can vary the mixing ratio and therefore vary the concentration of solutes or dissolved gases (if different gases are bubbled into each reservoir vessel).

D. Optical layout for the pulse radiolysis-TRIR experiments

Figure 3 shows the optical layout of the pulse radiolysis-TRIR experiment at LEAF. All of the reflective optics (apart from two aluminum mirrors and a CaF₂ beamsplitter, discussed below) have protected silver coatings to ensure a high throughput of the IR beam. The flow cell is mounted inside an aluminum sample block and held by a rail mount similar to the cell mount in a conventional IR spectrophotometer. The cell is mounted as close as possible to the beam line window to maximize the radiation dose, since the electron beam begins to scatter upon passing through the window and in the air. The electrons pass through fixed 45° aluminum-coated

mirrors (made of thin (0.5 mm) fused silica substrate to minimize electron scatter) that are located in front of and behind the cell. These mirrors reflect the IR laser beam in a zigzag path through the sample block and the cell, anti-collinear with the accelerator beam. If the cell is mounted with the windows perfectly normal to the laser beam, noise artifacts can appear on the detector signal associated with back-reflection of the IR laser beam into the laser cavity. Therefore, the cell is mounted $\sim 8^\circ$ off the laser beam axis (Figure 2), and is slightly vertically translated to assure unencumbered passage of electrons and the laser beam. In fact, due to the extreme sensitivity of the EC-QCLs to optical feedback, all optical elements in the beam path that might reflect the laser beam back to the cavity are mounted at 45° or slightly off-normal to the beam.

FIG. 3. Schematic of the optical layout at the pulse radiolysis-TRIR beam line at LEAF. Al: 0.5 mm thick aluminum-coated mirror; BL: Electron beam line (electron beam shown with gray shading); BS: 0.5 mm thick CaF_2 beamsplitter on rotation stage; C: Lead/KirksiteTM cave; CH: remotely-removable chopper for alignment; D: HgCdTe IR detector; FC: Faraday cup; HST: heat-sensitive target on 90° flip mount; LD: red laser diode; M: plane silver mirror; M_R : plane silver mirror on rotation/translation stage; ND: remote-controlled ZnSe circular variable ND filter wheel; OAP: off-axis parabolic silver mirror; PBS: kinematically-mounted pellicle beamsplitter; QCL: EC-QCL laser head; S: shutter; SB: aluminum sample block; SC: sample cell.

One caveat that comes with the high output power of the EC-QCLs is that their CW laser output is often subject to random and synchronous amplitude fluctuations, especially near the edges of the tuning ranges. These fluctuations are often particularly evident when recording data on long timescales (tens of microseconds to seconds), and can severely obscure the data (see below). For this reason, we have implemented real-time dual-beam normalization of signals for data acquisition with the new TRIR beam line, which virtually eliminates the amplitude fluctuation noise in the normalized data. The EC-QCLs are capable of sufficient intensity that there is no effective penalty for reducing the beam amplitudes by beamsplitting. Thus, the vertically-polarized IR laser beam is split into two beams (probe and reference) by directing it onto a 0.5 mm thick $\times$ 25 mm dia. CaF_2 beamsplitter (AR-coated on the back side) mounted on a rotation stage. Taking advantage of the dependence of the front surface Fresnel reflectivity on the angle of incidence, rotation of the beamsplitter allows the IR beam to be divided into probe and reference beams with varying intensity ratios (see below). The probe beam is transmitted by the CaF_2 beamsplitter, after which it is directed to the sample block where it is focused into the sample under investigation and recollimated by a pair of 4" reflected focal length off-axis parabolic (OAP) mirrors (Thorlabs, MPD254508-90-P01). We chose to focus the IR beam to a small spot size (<0.5 mm) inside the sample to eliminate signal artifacts that may result from sample disturbances such as shock waves and/or local heating during the electron pulse. After the sample block, the IR probe beam is focused onto a HgCdTe fast rise-time IR detector (Kolmar Technologies, Inc., KMPV9-0.5-J2, DC-20 MHz, 0.5 mm detector element) by another OAP mirror. A remotely-operated ZnSe circular variable neutral density (ND) IR filter wheel (Reynard Corporation, R05610-40, ND = 0-4) is situated immediately before the detector, allowing attenuation of the IR beam to avoid driving the detector into saturation. Rotation of the

ND wheel is achieved by use of a stepper motor that is controlled by an Arduino Uno board and custom LabVIEW software (National Instruments, Inc.). Finally, an AR-coated germanium window (Edmund Optics, P/N: 83-349) is placed on the front surface of the probe detector to eliminate the pickup of spurious signal artifacts arising from radiation-induced Cerenkov emission in the sample. We should note that in some cases (e.g., when using THF as a solvent), we have found that attenuating the IR probe beam after the sample is not ideal since focusing the full intensity of the probe beam into the sample can sometimes induce oscillating fluctuations on the transient signal in regions of the IR where the solvent strongly absorbs. In these cases, we insert a remotely-operated linear variable ND IR filter (Reynard Corporation, R0232Z-20, ND = 0-2) between the CaF₂ beamsplitter and the first OAP focusing mirror before the sample. This allows pre-attenuation of the IR probe beam before it is focused into the sample, and eliminates the signal oscillations. In a future iteration of the apparatus, we may replace the linear variable ND filter with the circular variable ND filter wheel from in front of the probe detector, so that there is only ever one ND filter in the probe beam path.

The reference beam is reflected off the front surface of the CaF₂ beamsplitter onto a plane mirror that is also mounted on a rotation stage at the same angle as the beamsplitter. In order to adjust the beamsplitting ratio, both the CaF₂ beamsplitter and the mirror on the rotation stage must be rotated to the same angle, while the mirror must also be horizontally translated in order to receive the reflected beam again due to its change in angle. In practical terms, based on the geometry of our setup, we can adjust the probe/reference intensity ratio from ~50/50 to ~96/4, which is useful for very strongly absorbing samples. The reference beam bypasses the sample cell and is focused onto a second, identical HgCdTe fast rise-time IR detector (Kolmar Technologies, Inc., KMPV9-0.5-J2, DC-20 MHz, 0.5 mm detector element) by an OAP mirror.

Again, a remotely-operated ZnSe circular variable ND IR filter wheel (Reynard Corporation, R05610-40, ND = 0-4) is situated immediately before the reference detector for beam attenuation. For protection of the detectors, a remotely-operated shutter (Vincent Associates, Uniblitz), placed immediately after the EC-QCL, is always closed before tuning the laser to a new wavelength and is only opened once both ND filter wheels have been reset to their maximum ND positions.

Since the EC-QCL beams are invisible, alignment of the optics is more challenging than for UV-Vis beams. Initial alignment is achieved with a compact red laser diode module (Thorlabs, CPS180, $\lambda = 635$ nm) that is introduced into the beam path by means of a kinematically-mounted pellicle beamsplitter (Thorlabs, BP108) and set to be collinear with the EC-QCL beam (Figure 3). The pellicle is removed for the TRIR measurements. The paths that the probe and reference IR beams follow are then defined by several heat-sensitive targets (labeled as HST in Figure 3). These targets are circular discs cut from a temperature-sensitive liquid crystal sheet (Edmund Optics) with a small hole punched in the center, that are mounted in 90° flip mounts (Thorlabs, TRF90). This is an excellent method for locating the EC-QCL IR beams since brief exposure of the liquid crystal sheet to the beam results in an immediate color change. A small strip of the liquid crystal sheet can also be used to check the position of the IR beam on any of the optics. Once the IR beams have been aligned onto the centers of all the heat-sensitive targets, the targets are flipped out of the beam path. Since all of the EC-QCL heads are mounted identically on individual 8×10" breadboards equipped with two alignment mirrors, and their beam paths have all been pre-aligned to be collinear with one another, very little additional alignment is required when exchanging laser heads. This can be checked by flipping the heat-sensitive targets back into the beam path and making any necessary adjustments. An optical chopper, situated

immediately after the EC-QCL, is used for final alignment of the OAP mirrors in front of the detectors since it helps to visualize the detector signal on an oscilloscope, and also the shape of the chopped detector signal can be used to determine if the IR beam is focused properly onto the small IR detector element. The chopper is removed from the beam path before TRIR measurements commence.

E. Signal acquisition with dual-beam probe/reference normalization

As discussed above, we have adopted a dual-beam probe/reference normalization detection scheme to eliminate random and synchronous EC-QCL beam intensity fluctuations from the TRIR transient signals. The two beams, collected simultaneously from a single experimental shot, constitute a probe (I) and reference (I_0) pair for absorbance calculation, removing the laser noise. This procedure results in signals with extremely high S/N, typically with the average of only four shots, which also helps to minimize radiation degradation of samples. The IR detectors that we use are equipped with both AC- and DC-coupled outputs from their built-in pre-amplifiers. In contrast to our earlier preliminary TRIR experiments at LEAF,¹³ we now make exclusive use of the DC-coupled outputs in order to avoid distorting low-frequency components in the transient signals, and to record the magnitude of I_0 in a straightforward manner. Before each measurement, the EC-QCL is tuned to a particular wavenumber, the shutter is opened, and the ND filter wheels are rotated to set both DC detector signals as close as possible to 3 V (detector saturation occurs at ~ 4.5 V). In regions where the sample and/or solvent absorb strongly or the EC-QCL output is weak, it may not be possible to achieve a nominal 3 V probe signal level, and in these cases, the reference signal level is dropped to match that of the probe. After the electron pulse, the DC-coupled signals from the two IR detectors are digitized by two channels of a 12-bit digital oscilloscope (Teledyne LeCroy HRO 66Zi, 600 MHz with the input

channels bandwidth-limited to 20 MHz to reduce high-frequency noise), and automatically transferred to custom LabVIEW software for analysis. Since the magnitude of the transient signal on the probe channel is typically only 10-100 mV riding on the incident beam intensity of ~3 V, to take full advantage of the 12-bit resolution of the oscilloscope and to fill the screen with the transient, the oscilloscope must permit a several volt (at least up to 3 V) offset, and the 66Zi does this. A major advantage of the 12-bit resolution of this oscilloscope is that when the EC-QCL beam intensity is fluctuating too much to allow the signal to remain on the screen at high vertical gain settings, the gain can simply be reduced to accommodate the fluctuations while still retaining a more than adequate digitization of the signal.

TRIR kinetic traces in units of ΔOD vs. time are constructed from the raw probe and reference oscilloscope traces using equation 1. The second term in equation 1 is used to correct for the fact that the DC signal levels from the probe and reference detectors will never be absolutely identical. It essentially applies a vertical offset that results in a mean pre-trigger ΔOD of zero in the final kinetic trace. All of these manipulations are performed automatically by LabVIEW and/or Igor Pro software (Wavemetrics, Inc.).

$$\Delta OD = -\log_{10} \left(\frac{\text{probe signal}}{\text{reference signal}} \right) + \log_{10} \left(\frac{\text{mean pre-trig level}_{\text{probe}}}{\text{mean pre-trig level}_{\text{ref.}}} \right) \quad (1)$$

An example of the power of the dual-beam probe/reference normalization signal acquisition method is shown in Figure 4, which depicts two TRIR kinetic traces that were obtained by processing the data recorded after a single electron pulse by two different methods. The kinetic process under investigation in this experiment was recorded at 1976 cm^{-1} after pulse radiolysis of

a 1.5 mM solution of *fac*-Mn(OCHO)(4,4'-^tBu₂-bpy)(CO)₃ (bpy = 2,2'-bipyridyl) in argon-saturated CH₃CN containing 50 mM tetrabutylammonium formate. It shows the formation of a ν(CO) absorption of the Mn–Mn dimer, [Mn(4,4'-^tBu₂-bpy)(CO)₃]₂ that is formed after one-electron reduction of the Mn monomer and subsequent dissociation of the formate ligand.²⁰ Trace (a) was obtained from only the probe channel data, and both high-frequency oscillations and longer-timescale undulations are clearly evident and are deteriorating the data. Trace (b) was obtained from the probe and reference channel data, using the normalization equation discussed above. It is clear from this that the dual-beam normalization detection scheme virtually eliminates the majority of the laser intensity fluctuations, resulting in high-quality TRIR kinetic traces. With 4 to 8 signal averages, we can generally achieve a baseline noise on the order of ~100 μOD. It should be noted that Figure 4 represents a single case, and depending on which EC-QCL is being used and even the particular wavenumber setting, the noise fluctuations are often less than those depicted in Figure 4(a) but they can also be worse, which is when the power of the dual-beam detection scheme really comes into play. Another advantage of the dual-beam detection is that high-quality kinetic traces can be recorded on significantly long timescales, with long-term drifting of the laser beam intensity being perfectly compensated for. Acquisitions on the order of several minutes are possible, as shown below near the end of the discussion (Figure 6).

FIG. 4. TRIR kinetic traces (offset for clarity) recorded at 1976 cm^{-1} after pulse radiolysis of a 1.5 mM solution of *fac*- $\text{Mn}(\text{OCHO})(4,4'\text{-}^t\text{Bu}_2\text{-bpy})(\text{CO})_3$ (bpy = 2,2'-bipyridyl) in argon-saturated CH_3CN containing 50 mM tetrabutylammonium formate. The traces were recorded after a single electron pulse and were processed in different ways. Trace (a) makes use of only the probe channel data, while trace (b) makes use of both the probe and reference channels using dual-beam probe/reference normalization signal processing, as discussed in the main text.

In typical condensed-phase TRIR experiments, the EC-QCLs are tuned in steps of $\sim 2\text{-}4\text{ cm}^{-1}$ over the region of interest, recording IR transient absorption kinetic traces at each wavelength. These kinetic traces are then collated by home-written macros in Igor Pro software, and a time slice can be taken at any desired time delay after the electron pulse in order to generate a TRIR spectrum, plotted as a series of points as change in absorbance after the electron pulse (ΔOD) vs. wavenumber (cm^{-1}). An example of such a point-by-point TRIR spectrum is given in Figure 5, obtained 40 ns after pulse radiolysis of the solution described in Figure 4. Shot-to-shot variations in signal amplitude due to intensity fluctuations of the electron pulses are corrected by measuring the charge in each electron pulse with a copper Faraday cup mounted inside the sample block (see Figure 3), which collects the high-energy electrons that have passed through the sample cell. (The cell configurations used here are not thick enough to entirely stop the 8.7 MeV electron

beam.) The average Faraday cup reading for a set of shots is recorded with the corresponding kinetic trace. The absorbance values at each point in the spectrum are then normalized to the same Faraday cup reading to produce data such as those shown in Figure 5.

FIG. 5. (Bottom) FTIR spectrum of a 1.5 mM solution of *fac*-Mn(OCHO)(4,4'-^tBu₂-bpy)(CO)₃ (bpy = 2,2'-bipyridyl) in argon-saturated CH₃CN containing 50 mM tetrabutylammonium formate. (Top) TRIR spectrum recorded 40 ns after pulse radiolysis of this solution.²⁰ The bands at 2004 and 1892 cm⁻¹ are the ν(CO) vibrations of the one-electron reduced complex, *fac*-[Mn(OCHO)(4,4'-^tBu₂-bpy^{•-})(CO)₃]⁻, while the two peaks marked with an asterisk show that partial formation of the neutral Mn-based radical, *fac*-Mn[•](4,4'-^tBu₂-bpy)(CO)₃ that results from formate dissociation from the one-electron reduced species has already occurred 40 ns after the electron pulse. The smooth line is the result of multiple Gaussian peak curve fitting of the data points. Reprinted with permission from *J. Am. Chem. Soc.* **136**, 5563 (2014). Copyright 2014 American Chemical Society.

The response time of the IR detectors (10 – 90% rise) was measured to be ~40 ns. This is due to a combination of their 20 MHz bandwidth and the long length of the signal cables connecting them to the oscilloscope (Midisco MDC8141 50 Ω cable, 29.3 pF/ft capacitance, 30 ft length). Long cables are required since the oscilloscope is located inside the operator control room, far from the beam line. In principle, a faster time resolution on the order of ~15-20 ns could be achieved if the oscilloscope was placed inside the accelerator vault close to the detectors.

F. The accelerator noise environment

Due to the intrinsic strength of mid-IR absorption bands generally being lower than those in the UV-Vis regions, and the fact that solvent absorption bands require the use of much shorter cell pathlengths in the mid-IR, TRIR absorption signals are often quite small. On the other hand, RF-driven accelerators include many noise sources: the high-voltage modulator radiates noise into the facility electrical ground synchronous with the current pulses through the klystron; the electron beam radiates microwave and terahertz frequencies when it passes through the beam window and through the open air before hitting the Faraday cup; and x-rays are generated when high-energy electrons are scattered. When the x-rays strike the detectors and amplifiers, they generate spurious signals. The myriad of ancillary electronic instruments required to run the accelerator send noise back into the AC lines powering them, which can also appear on signal channels. The solution to most of these problems was to enclose the EC-QCLs and the detectors inside Kirksite™ (Zn:Al/Cu/Mg alloy) and/or lead brick “caves” for electromagnetic- and ionizing-radiation shielding (see Figure 3), and to power the detector pre-amplifiers and the EC-QCLs not from the AC lines, but from lead-acid gel cell batteries. With this arrangement, most of the noise sources external to the signal-generating circuits have been reduced to acceptable levels. The cave for the EC-QCLs is mounted on linear bearings, making it very easy to move when exchanging laser heads. Similarly, a side wall of the detector cave is on a linear slide, allowing easy access for mirror alignment and filling the detectors with liquid nitrogen. An additional advantage to placing the detectors close to the sample cell is to greatly reduce sensitivity to atmospheric water vapor absorptions from long-distance laser beam propagation that would be necessitated by placing the detectors outside the accelerator vault (as they are in conventional UV-Vis-NIR LEAF experiments), although as discussed above, the tunability and

narrow linewidth of EC-QCLs largely overcomes the issue of water vapor absorption. Despite the fact that the EC-QCLs and the IR detectors are located inside the vault fairly close to the sample cell, the total IR beam path and number of optical components are still quite high compared with typical laser flash photolysis-TRIR setups, and this highlights another advantage of the high output power of the EC-QCL lasers.

III. SCIENTIFIC INVESTIGATIONS WITH PULSE RADIOLYSIS-TRIR AT LEAF

The combination of pulse radiolysis with TRIR spectroscopy opens up many possibilities for detailed mechanistic investigations of a wide variety of radiation-induced processes, many of which would have proved extremely difficult or even impossible with traditional transient absorption detection in the UV-Vis-NIR regions. Below, we summarize some of the work we have already completed with this new technique, and then discuss some future investigations that we plan to undertake.

A. Previous investigations

Following our original feasibility tests of TRIR detection at LEAF, in which we studied the one-electron reduction of *fac*-[Re(bpy)(CO)₃(CH₃CN)]⁺ in argon-saturated CH₃CN, probing its $\nu(\text{CO})$ stretching vibrations,¹³ we installed a new electron beam line dedicated to TRIR, as described above. In a recent study using the new apparatus,²⁰ we probed the kinetics and mechanism of the formation of a Mn–Mn dimer complex, [Mn(4,4'-^tBu₂-bpy)(CO)₃]₂ upon one-electron reduction of a mononuclear precursor, *fac*-Mn(OCHO)(4,4'-^tBu₂-bpy)(CO)₃ in CH₃CN. This precursor, along with other similar compounds,^{31, 32} is a precatalyst for the electrocatalytic reduction of CO₂ to CO. It was already known that one-electron reduction results in the formation of the Mn–Mn dimer, which is a key species in the catalytic reduction reaction.

However, none of the intermediate species involved in the process of formation of the dimer had ever been directly observed. Using the pulse radiolysis-TRIR technique, we successfully observed all of these species on timescales ranging from 40 ns to 2 ms, i.e., the initial one-electron reduced product, *fac*-[Mn(OCHO)(4,4'-^tBu₂-bpy^{•-})(CO)₃]⁻, the neutral Mn-based radical, *fac*-Mn[•](4,4'-^tBu₂-bpy)(CO)₃ that is formed after rapid formate dissociation from the reduced metal complex, and the Mn–Mn dimer that is generated by dimerization of two of the radicals. We were also able to determine that the neutral radical remained as a five-coordinate species before dimerization, with no solvent molecule binding to the metal center at the vacant coordination site.²⁰ Figure 5 shows one of the TRIR spectra from this experiment, recorded 40 ns after pulse radiolysis, and Figure 4 shows the kinetics of formation of the Mn–Mn dimer complex, [Mn(4,4'-^tBu₂-bpy)(CO)₃]₂ on a timescale of several hundred microseconds.

For the pulse radiolysis-TRIR technique to be widely applicable to a range of different chemical systems, it must be capable of detecting transient absorptions of vibrational bands that are significantly weaker than strong metal carbonyl $\nu(\text{CO})$ absorption bands, such as those discussed above. One example of this is our recent investigation of the mechanism of radiolytic decomposition of a choline-based ionic liquid (IL) in collaboration with Dr. Ilya Shkrob of Argonne National Laboratory.²¹ There is great interest in ILs and deep eutectic mixtures that are based on choline ((2-hydroxymethyl)trimethylammonium), betainium (1-carboxy-*N,N,N*-trimethylmethanaminium), and other derivatized natural amino compounds as diluents in metal ion separations,³³ including nuclear separations where the constituent ions would be exposed to ionizing radiation that is emitted by decaying radionuclides.³⁴ Thus, it is critical to investigate the radiation stability of such ILs, particularly since they are compositionally similar to radiation hypersensitive solids such as choline chloride, which decomposes significantly upon irradiation.

Upon pulse radiolysis of argon-saturated choline NTf₂ at 50 °C (NTf₂ = bis(trifluoromethylsulfonyl)imide), we successfully monitored the prompt formation of vinyl alcohol and acetaldehyde via their C=C and C=O vibrational bands at 1649 and 1733 cm⁻¹, respectively.²¹ These products cannot be detected by transient UV-Vis pulse radiolysis since their signals in the UV are weak (e.g., acetaldehyde,³⁵ $\epsilon_{290\text{nm}} = 13 \text{ M}^{-1} \text{ cm}^{-1}$) and obscured by the background absorption of the IL. Conversely, the acetaldehyde C=O stretch at 1733 cm⁻¹ ($\epsilon = 189 \text{ M}^{-1} \text{ cm}^{-1}$) can be easily resolved from the IL background absorption.²¹ Based on the observed kinetics, our results suggested that most of the radiolytically induced C₁–N fragmentation in choline NTf₂ occurs promptly (within 40 ns), and that there is a further ~40% increase in the yield of vinyl alcohol over the following 400 μs . These results, combined with other data using different techniques, led to a revision of the previously-accepted Symons mechanism of radiation hypersensitivity in choline chloride and a demonstration that the conditions that lead to hypersensitivity do not exist in ILs.

A final example of the power of pulse radiolysis-TRIR for detailed structural identification of radiation-induced transient intermediates comes from our recent study of the formation of ion pairs in THF in the presence of electrolytes, in collaboration with Drs. Mani and Miller of BNL.²² When a solution of 9,9-dihexyl-9*H*-fluorene-2-carbonitrile (F1CN) in neat THF was subjected to pulse radiolysis, prompt formation of the free radical anion, F1CN^{•-} was observed by a red-shift of the $\nu(\text{CN})$ IR absorption band from 2224 to 2110 cm⁻¹. However, when the experiment was repeated in the presence of 100 mM of an electrolyte (tetrabutylammonium tetrafluoroborate), the radical anion band further red-shifted to 2096 cm⁻¹, and was identical to that observed by IR spectroelectrochemistry under the same conditions. This further red-shifted band was assigned to the ion-paired form of F1CN^{•-}, in which the anion is closely associated

with a tetrabutylammonium cation. The direction of the shift of the ion-paired $\nu(\text{CN})$ band in relation to that of the free ion can be explained in terms of the Vibrational Stark Effect, indicating that the cation is located next to the CN group of the $\text{F1CN}^{\bullet-}$ anion. By repeating the TRIR experiment in the presence of varying amounts of electrolyte, we were able to estimate the reduction potential of F1CN in electrolyte-free THF to be -3.03 V vs. $\text{Fc}^{+/0}$ (cf. -2.74 V vs. $\text{Fc}^{+/0}$ in the presence of 100 mM electrolyte). This is important information in relation to future applications in organic solar photovoltaics. These experiments would have been impossible to perform without TRIR detection, since the UV-Vis absorption bands of the free ions and ion pairs are too similar.

B. Future investigations

The possibilities for future pulse radiolysis-TRIR investigations are numerous, and here we briefly highlight some of our planned investigations with the technique. A core focus of our research is the mechanistic investigation of catalytic processes related to solar energy conversion, examples of which were discussed above for Mn and Re complexes.^{13, 20} We therefore intend to extend these pulse radiolysis-TRIR studies, attempting to access and identify various proposed intermediates in the catalytic cycles of photo- and electro-catalytic CO_2 reduction in CH_3CN . Since many of the reactions will involve CO_2 as a reactant, it is important that we more fully understand the radiation chemistry of CO_2 in CH_3CN , since under CO_2 -saturated conditions, the primary reduction product will be the radical anion of CO_2 , i.e., $\text{CO}_2^{\bullet-}$ which should behave as a reducing agent toward transition metal complexes. We have already begun preliminary investigations and have definitively identified the TRIR band of $\text{CO}_2^{\bullet-}$ in CH_3CN .

We also feel that the new TRIR pulse radiolysis detection system has important applications in unraveling the kinetics and mechanisms of radiation-induced polymerization reactions. For example, we recently performed a demonstration experiment in collaboration with Mr. Hiro Minamimoto and Profs. Susumu Kuwabata and Tetsuya Tsuda of Osaka University on the radiation-induced polymerization of 1-butyl-3-vinylimidazolium NTf₂ (BuVym NTf₂). They have an interest in using electron and focused ion beams to fabricate nanostructures by polymerization of allyl- and vinyl-functionalized ILs,^{36, 37} and they observed that while focused ion beams could write high-resolution 3-dimensional structures in 1-allyl-3-ethylimidazolium NTf₂, the use of BuVym NTf₂ resulted in very irregular shapes, suggesting uncontrolled polymerization.³⁷ We therefore examined the pulse radiolysis-initiated polymerization kinetics of BuVym NTf₂ via TRIR spectroscopy by monitoring the consumption of the BuVym⁺ cation monomer through the bleaching of its characteristic vinyl C=C double bond stretch at 1656 cm⁻¹. Figure 6 shows the progressive consumption of vinyl monomer over a time course of >7 minutes. The kinetic trace clearly indicates that, after an initial rapid phase ($\tau \approx 6$ s) the polymerization of BuVym NTf₂ continues unabated for many minutes after irradiation. Indeed, the sloping baseline before the electron pulse at time zero reflects ongoing polymerization from previous shots. We observed separately that a dose of only 60 Gy was more than sufficient to turn liquid BuVym NTf₂ into a rubbery gel. These preliminary results demonstrate the power of the TRIR pulse radiolysis system to monitor polymerization kinetics in a wide range of systems, owing largely to the high output power of the EC-QCLs and the dual-beam probe/reference normalization detection scheme.

FIG. 6. Single-shot TRIR pulse radiolysis trace of argon-saturated BuVym NTf₂ measured at 1656 cm⁻¹. Pathlength: 30 μm. Dose: 400 Gy.

IV. CONCLUSIONS

We have developed new instrumentation for high signal-to-noise nanosecond time-resolved mid-infrared (TRIR) spectroscopy pulse radiolysis measurements of condensed-phase samples at the BNL LEAF facility. The system is based on the use of CW mode-hop-free external-cavity quantum cascade lasers as an IR probe source, taking advantage of their high output power and wide tunability when compared with other potential CW mid-IR sources. Our current suite of twelve EC-QCLs covers the region of 2330-1051 cm⁻¹ with relatively few tuning gaps. Using a dual-beam probe/reference normalization detection scheme, we are able to record very high quality TRIR kinetic traces with only a moderate number of signal averages (typically 4-8), resulting in a sensitivity level on the order of ~100 μOD, with a time resolution of ~40 ns. TRIR spectra are built-up on a point-by-point basis by tuning the EC-QCLs in discrete steps and recording TRIR kinetic traces at each wavelength. The routine availability of TRIR detection for pulse radiolysis now opens up many possibilities for the structural identification of transient

intermediates that would otherwise have proven difficult or impossible to identify by other methods. We have demonstrated the power of this new technique for detailed mechanistic investigations on a wide range of chemical systems, and have plans for many more studies in the future.

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