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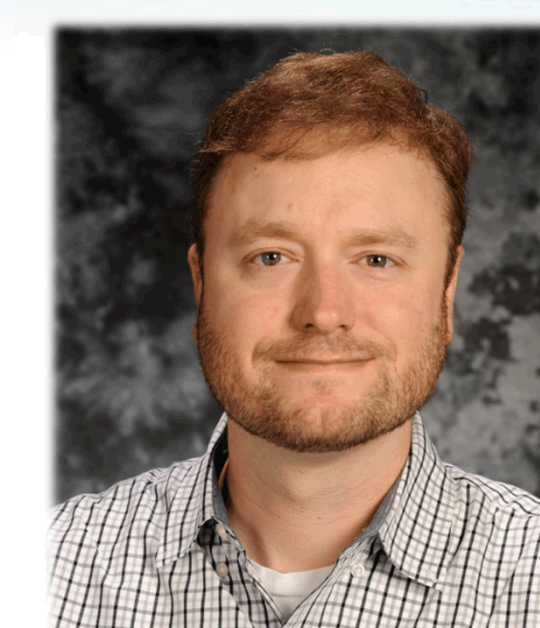
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Radiation-Induced Redox Chemistry of Californium-249

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Background

Lately, there is renewed interest in understanding the chemical behavior of complexes of the late actinides, due to their divergence in fundamental electronic (and thus bonding) properties as a result of relativist effects on electron distribution. While some attention has focused on investigating these fundamental properties, few studies have been performed on the inevitable effect of radiation chemistry on the late actinides, an understanding of which is critical for: (i) the design and development of innovative integrated nuclear fuel cycle technologies; (ii) actinide implementation in alternative energy solutions; and (iii) for rapid forensic analysis techniques.

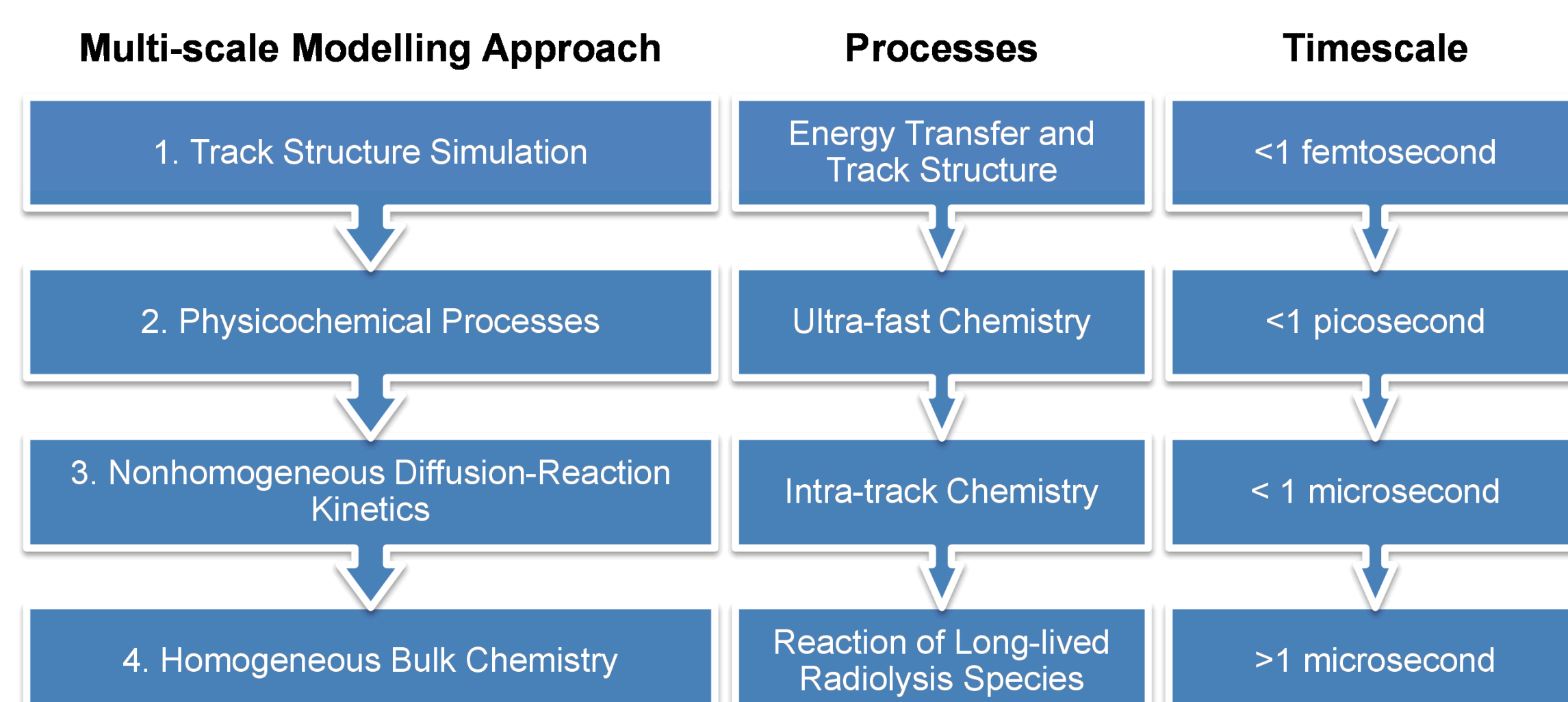


Irradiation of even simple solutions promotes the formation of numerous reactive species, both transient and steady-state, e.g.:



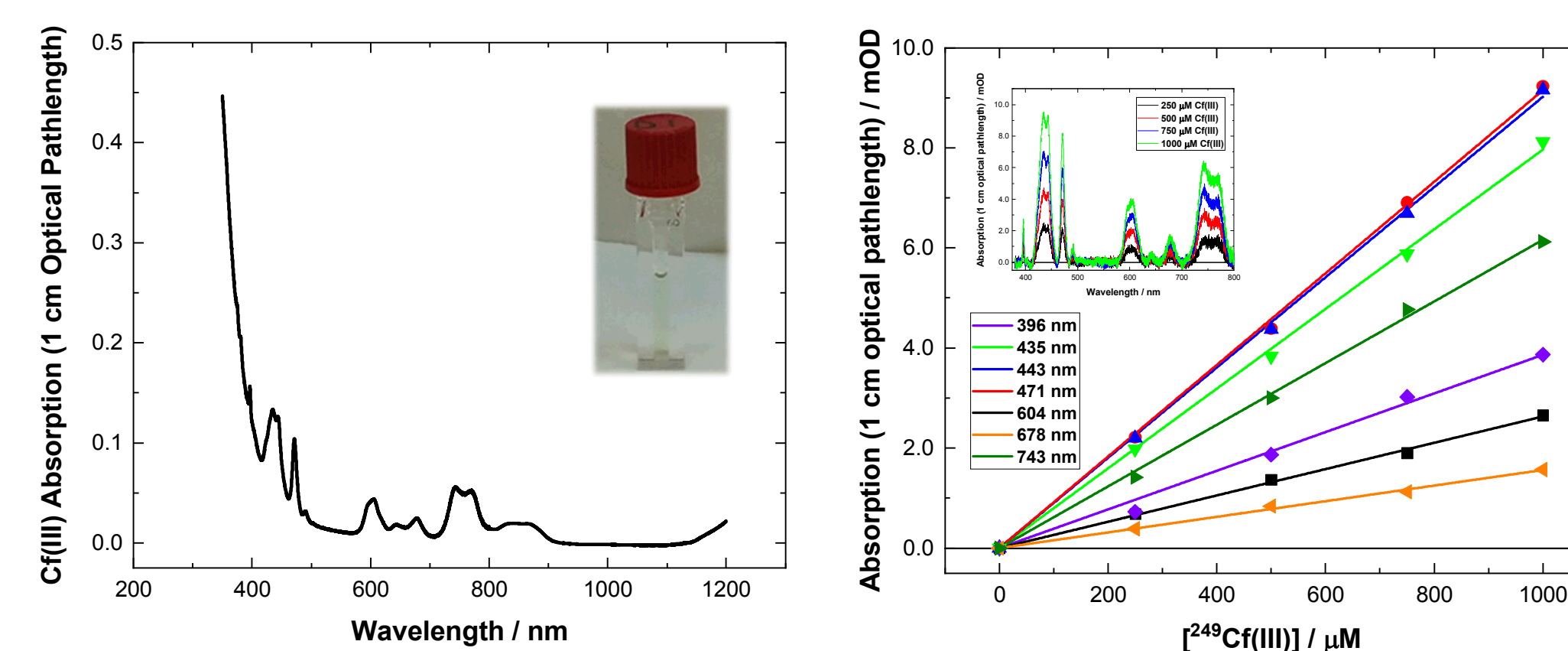
With respect to transients and the late actinide californium, rate coefficients have only been measured for the reduction of Cf(III) by the hydrated electron (e_{aq}^- , $k > 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), and subsequent decay of Cf(II) ($k = (7 \pm 1) \times 10^5 \text{ s}^{-1}$).^[1] However, there are a number of other important transient radiolysis products radiolytically generated in solutions pertinent to californium manipulations, e.g., the hydrogen atom (H^\cdot), and hydroxyl (OH^\cdot) and nitrate (NO_3^\cdot) radicals. These species are more than capable of influencing the redox behavior of californium and have been shown to do so with other actinides.^[2]

Here we present the first-ever time-resolved picosecond pulse radiolysis measurements for Cf(III) reaction kinetics, as part of an ongoing project to provide a comprehensive, quantitative, predictive mechanistic description for the radiation-induced chemistry of californium.



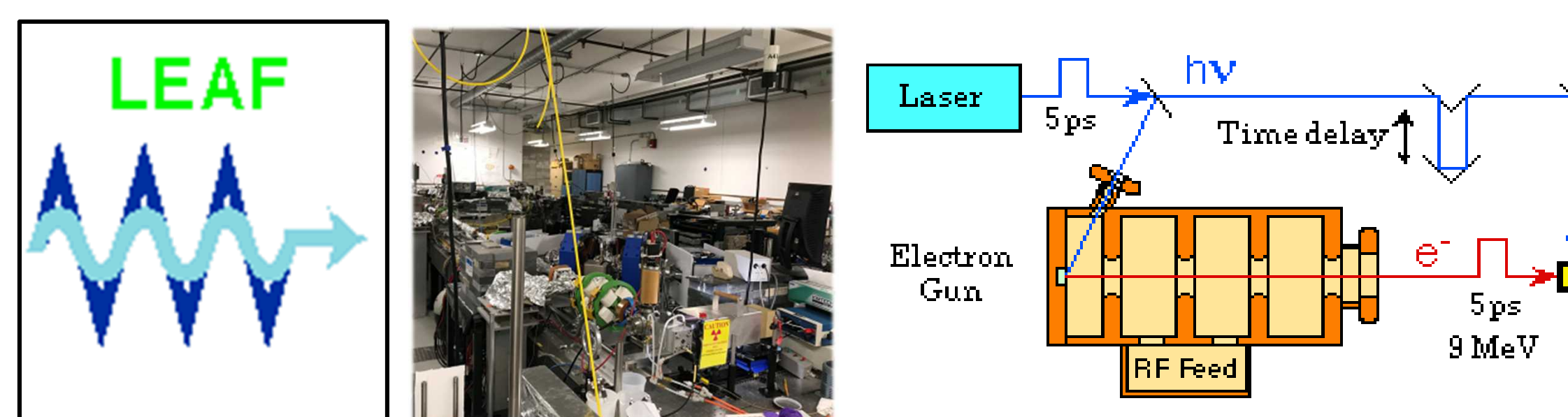
Methods

All experiments were performed using $^{249}\text{CfCl}_3$ as received from Oak Ridge National Laboratory (ORNL). The californium salt was then converted into specific media via metathesis and distillation. Samples comprised varying concentrations of solute in 1.00 cm optical pathlength cuvettes sealed with Teflon screw-caps:



Transient	Solvent	Sample Conditions	Measurement
e_{aq}^-	1 mM HClO_4	0.5 M tBuOH, N_2 sparge	direct decay
H^\cdot	0.1 M HClO_4	100 μM parachlorobenzoic acid, 20 mM tBuOH, N_2 sparge	competition
NO_3^\cdot	6 M HNO_3	N_2O sparge	direct decay
OH^\cdot	10 mM HClO_4	0.1 mM KSCN, N_2O sparge	competition

Reaction kinetics were measured using the picosecond pulsed electron radiolysis/transient absorption system at the Brookhaven National Laboratory Laser Electron Accelerator Facility (LEAF).^[3] Decay kinetics of the transient species were followed at 365, 470, 635, & 720 nm over 200-900 ns using a FND-100 silicon diode detector, and digitized by a LeCroy WaveRunner 640Zi oscilloscope (4 GHz, 8 bit). Interference filters (~10-nm bandpass) were used for wavelength selection of the analyzing light. Radiation dose was measured using the thiocyanate method: KSCN, $\lambda_{\text{max}} = 472 \text{ nm}$ ($G = 5.2 \times 10^{-4} \text{ m}^2 \cdot \text{J}^{-1}$).



Results

Future Work

Measured rate coefficients will be combined with upcoming γ & α irradiation studies to develop a comprehensive multi-scale model for the radiation chemistry of californium. This model will determine lifetimes of transient species that cannot be experimentally observed in addition to predicting the redox speciation of californium under a variety of conditions.



References

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