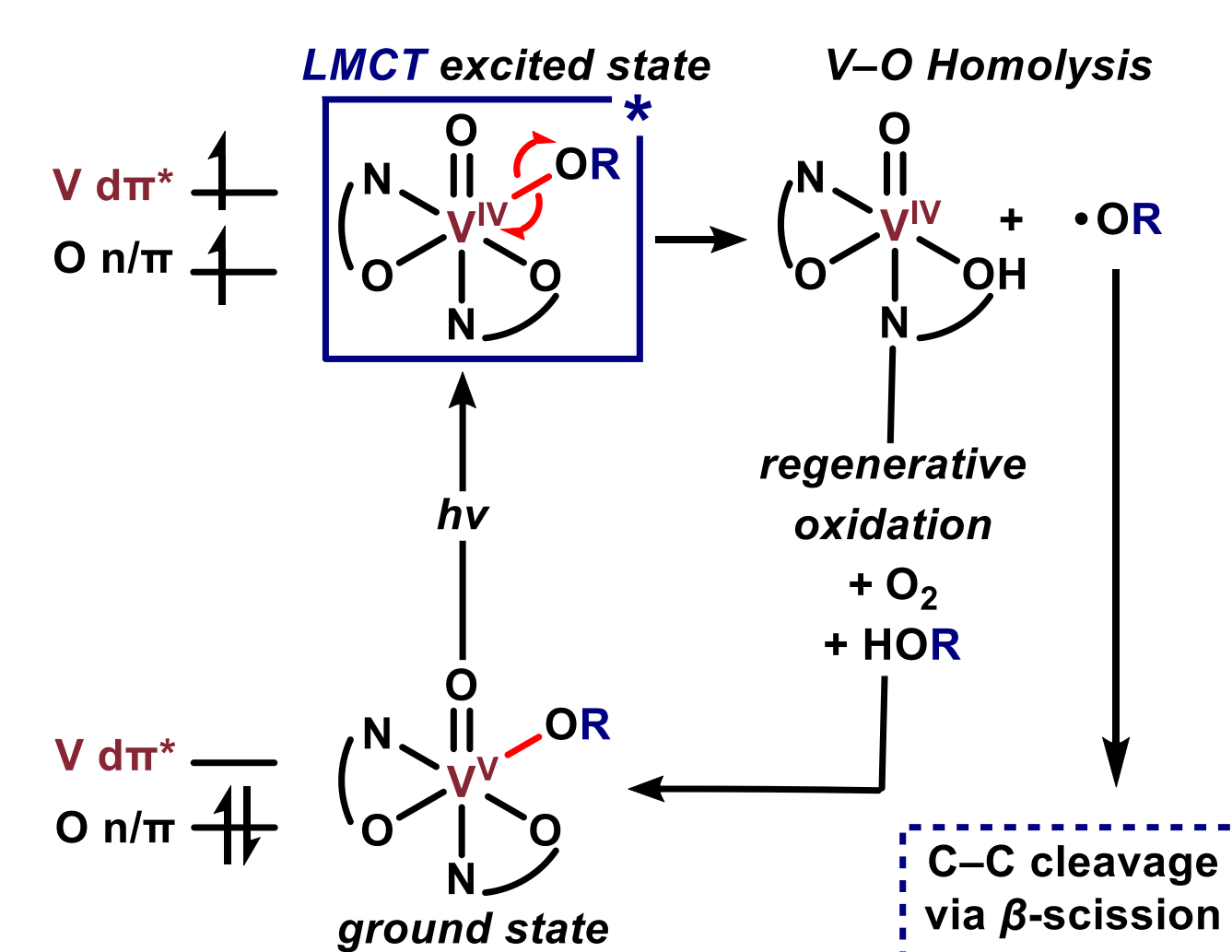


Motivation: Exploiting Ligand-To-Metal Charge Transfer for Bond Homolysis

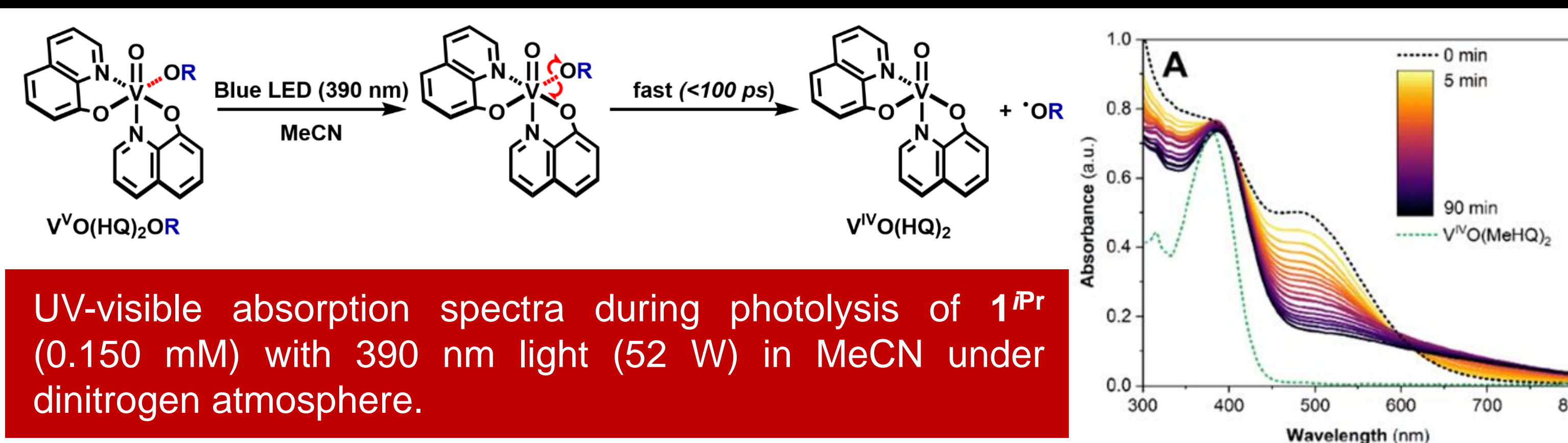
LMCT photoredox catalysts employ inner-sphere bond homolysis to generate reactive open-shell species. Several features differentiate unimolecular LMCT mechanisms from bimolecular MLCT single-electron transfer:

- (1) short-lived (~picoseconds) excited states participate in catalysis to circumvent diffusional limitations;
- (2) metal and substrate bind directly to enable chemoselective bond homolysis;
- (3) and reactivity is dictated by bond dissociation free energy (BDFE) values, independent of metal and substrate redox potentials.

LMCT activation enables targeted bond homolysis photochemistry of first-row earth-abundant elements, cleaving σ or $\sigma+\pi$ donor interactions of substrates. Alkoxy radicals cleave C-C bonds via β -scission for use in chemical synthesis and biomass valorization.



Steady-State Kinetic Analysis and Photochemical Quantum Yields



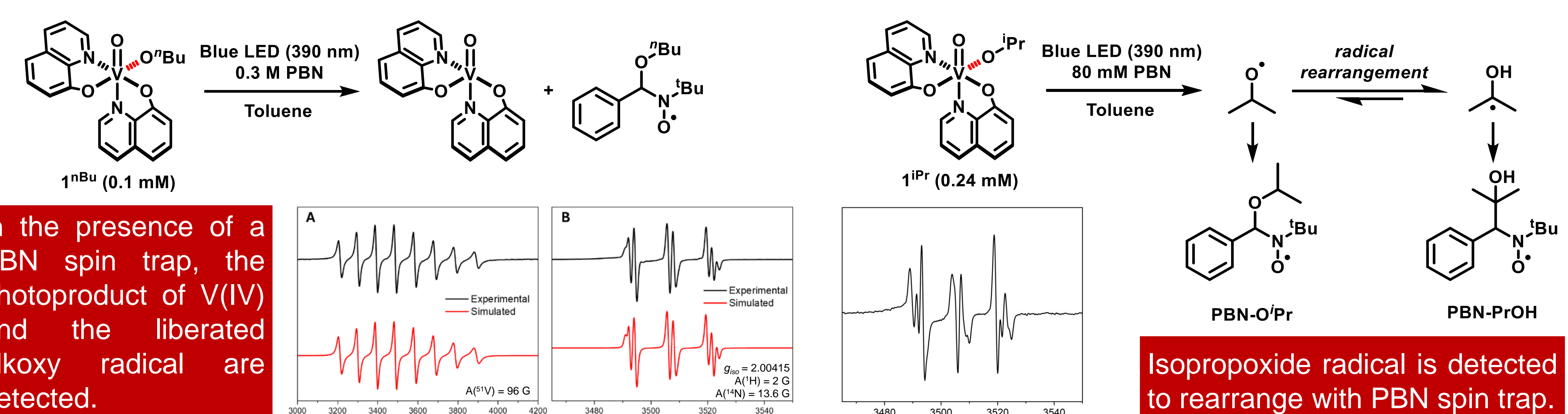
UV-visible absorption spectra during photolysis of **1Pr** (0.150 mM) with 390 nm light (52 W) in MeCN under dinitrogen atmosphere.

Quantum Yields of Bond Homolysis for VO(HQ)₂(OR)

Species	$\Phi_{390\text{ nm}}^b$
1Pr	5.23×10^{-4}
1Cy	3.08×10^{-3}
1nBu	1.64×10^{-3}

^aDetermined using a frequency doubled Ti:Sapphire pulsed laser ($\lambda_{\text{irr}} = 390\text{ nm}$, 30 mW) in MeCN solvent. ^bEvaluated from the ratio of the number of photolysis events divided by the absorbed photons.

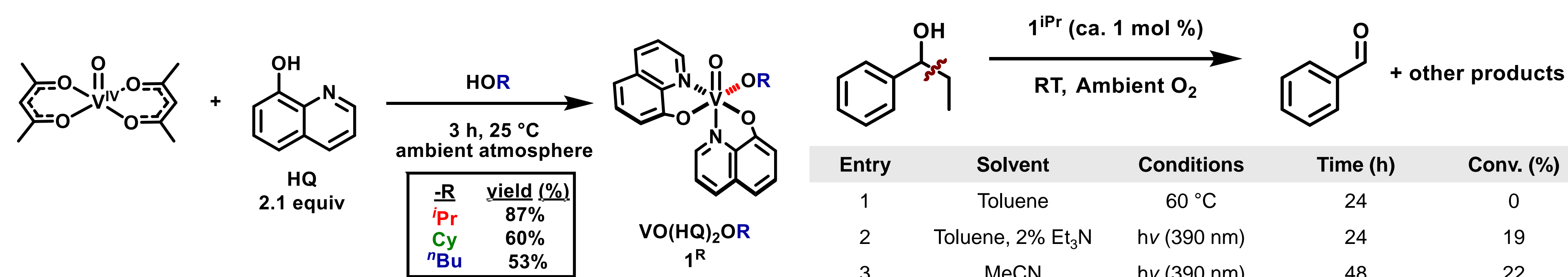
Identifying Photoproducts using EPR Spectroscopy



In the presence of a PBN spin trap, the photoproduct of V(IV) and the liberated alkoxy radical are detected.

Isopropoxide radical is detected to rearrange with PBN spin trap.

Alcohol Prefunctionalization and β -Scission of Secondary Alcohols

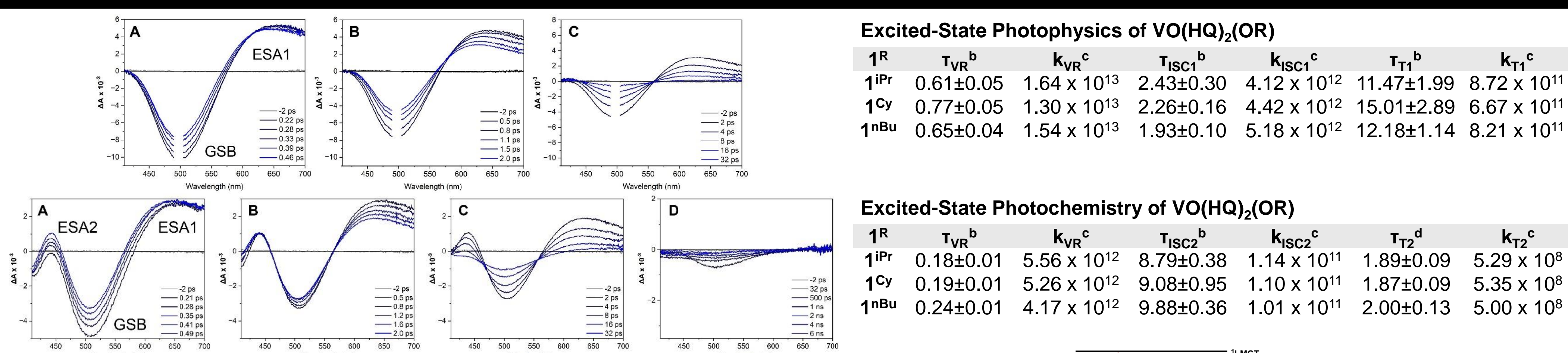


Vanadium(V) complexes are readily accessed by *in situ* oxidation of the vanadium(IV) acetylacetonate precursor under aerobic conditions, affording a six-coordinate product with coordinated alkoxide groups.¹

Upon UV-A photoactivation, these complexes catalyze the β -scission of secondary alcohols. We aim to understanding the photoactivation mechanism that initiates V-O homolysis photochemistry in these molecules.

¹ Blair, A. J.; Pantony, D. A.; Minkoff, G. J. *J. Inorg. Nucl. Chem.* 1958, 5, 316–331.

Assign Excited State Dynamics from Transient Absorption Spectroscopy



Excited-State Photophysics of VO(HQ)₂(OR)

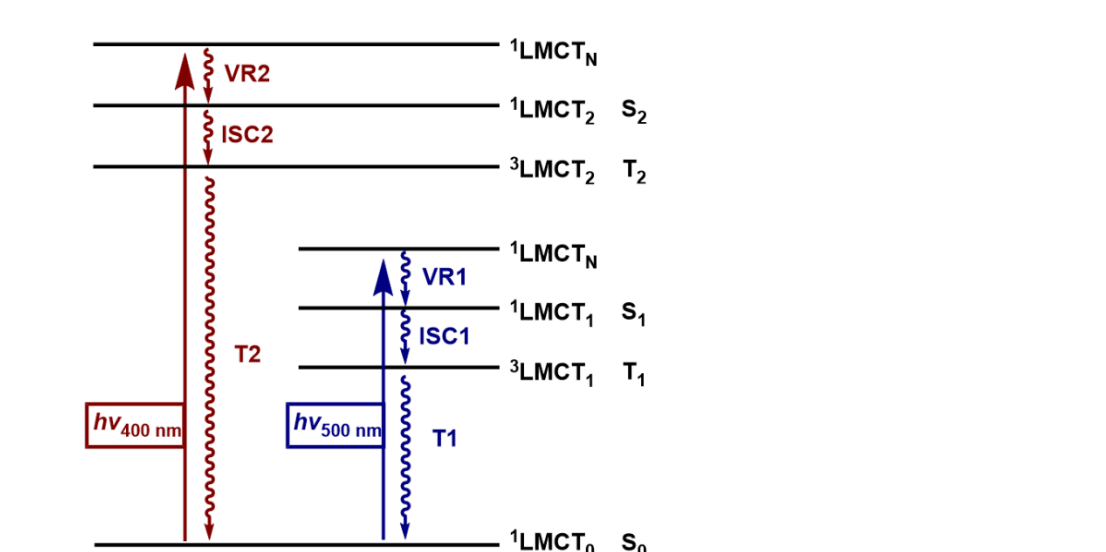
1R	T_{VR}^b	k_{VR}^c	T_{ISC1}^b	k_{ISC1}^c	T_{T1}^b	k_{T1}^c
1Pr	0.61 ± 0.05	1.64×10^{13}	2.43 ± 0.30	4.12×10^{12}	11.47 ± 1.99	8.72×10^{11}
1Cy	0.77 ± 0.05	1.30×10^{13}	2.26 ± 0.16	4.42×10^{12}	15.01 ± 2.89	6.67×10^{11}
1nBu	0.65 ± 0.04	1.54×10^{13}	1.93 ± 0.10	5.18×10^{12}	12.18 ± 1.14	8.21×10^{11}

Excited-State Photochemistry of VO(HQ)₂(OR)

1R	T_{VR}^b	k_{VR}^c	T_{ISC2}^b	k_{ISC2}^c	T_{T2}^d	k_{T2}^c
1Pr	0.18 ± 0.01	5.56×10^{12}	8.79 ± 0.38	1.14×10^{11}	1.89 ± 0.09	5.29×10^8
1Cy	0.19 ± 0.01	5.26×10^{12}	9.08 ± 0.95	1.10×10^{11}	1.87 ± 0.09	5.35×10^8
1nBu	0.24 ± 0.01	4.17×10^{12}	9.88 ± 0.36	1.01×10^{11}	2.00 ± 0.13	5.00×10^8

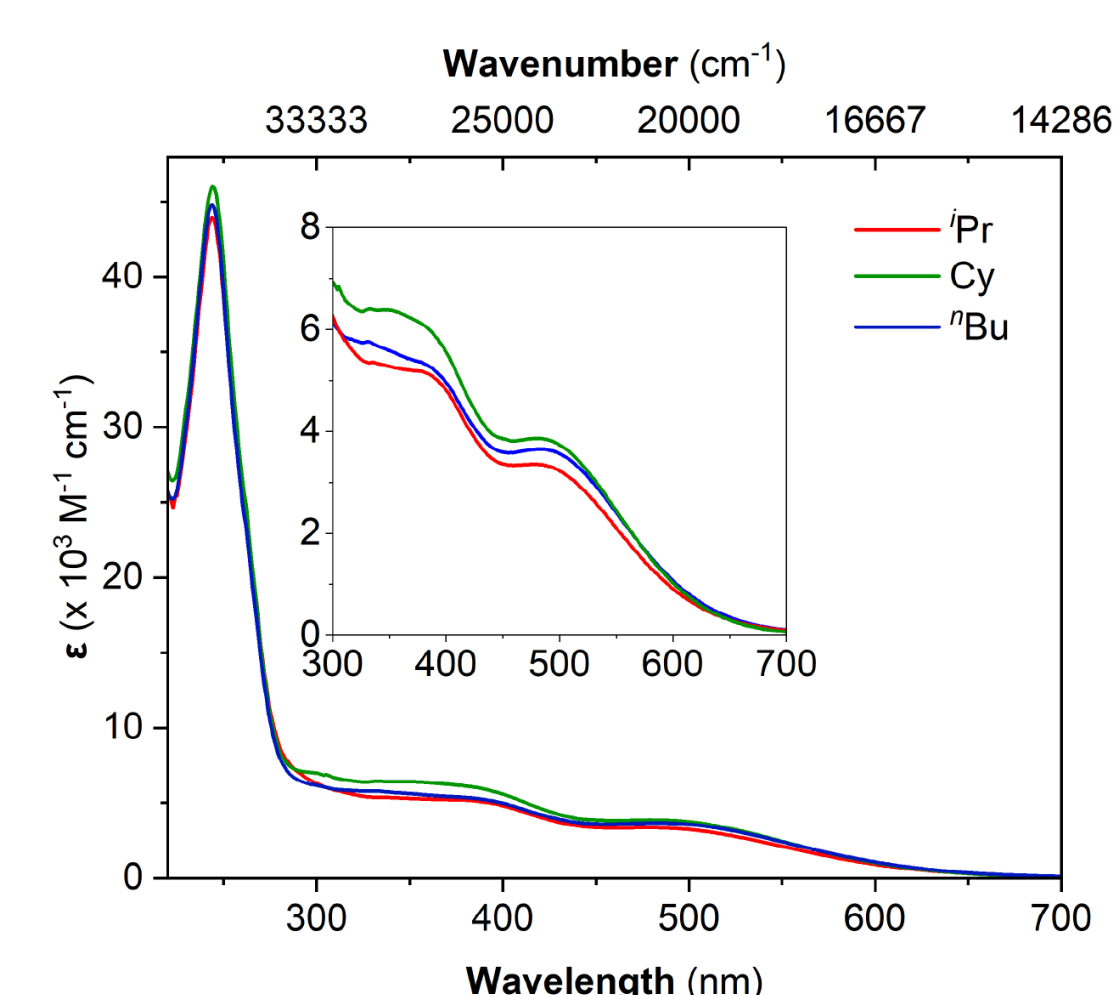
Ultrafast TA difference spectra of **1R** complexes in MeCN upon 500 nm (top) or 400 nm (bottom) pulsed laser excitation (1.00 μJ per pulse, 100 fs fwhm).

Distinct excited state events are detected upon excitation at 400 nm and 500 nm. Irradiation at 500 nm induces a reversible photocycle of the low-lying LMCT, relaxing to the ground state within 30 ps. Conversely, excitation at 400 nm leads to a persistent excited state with a lifetime of approximately 2 ns, which is identified as the homolytic excited state species.

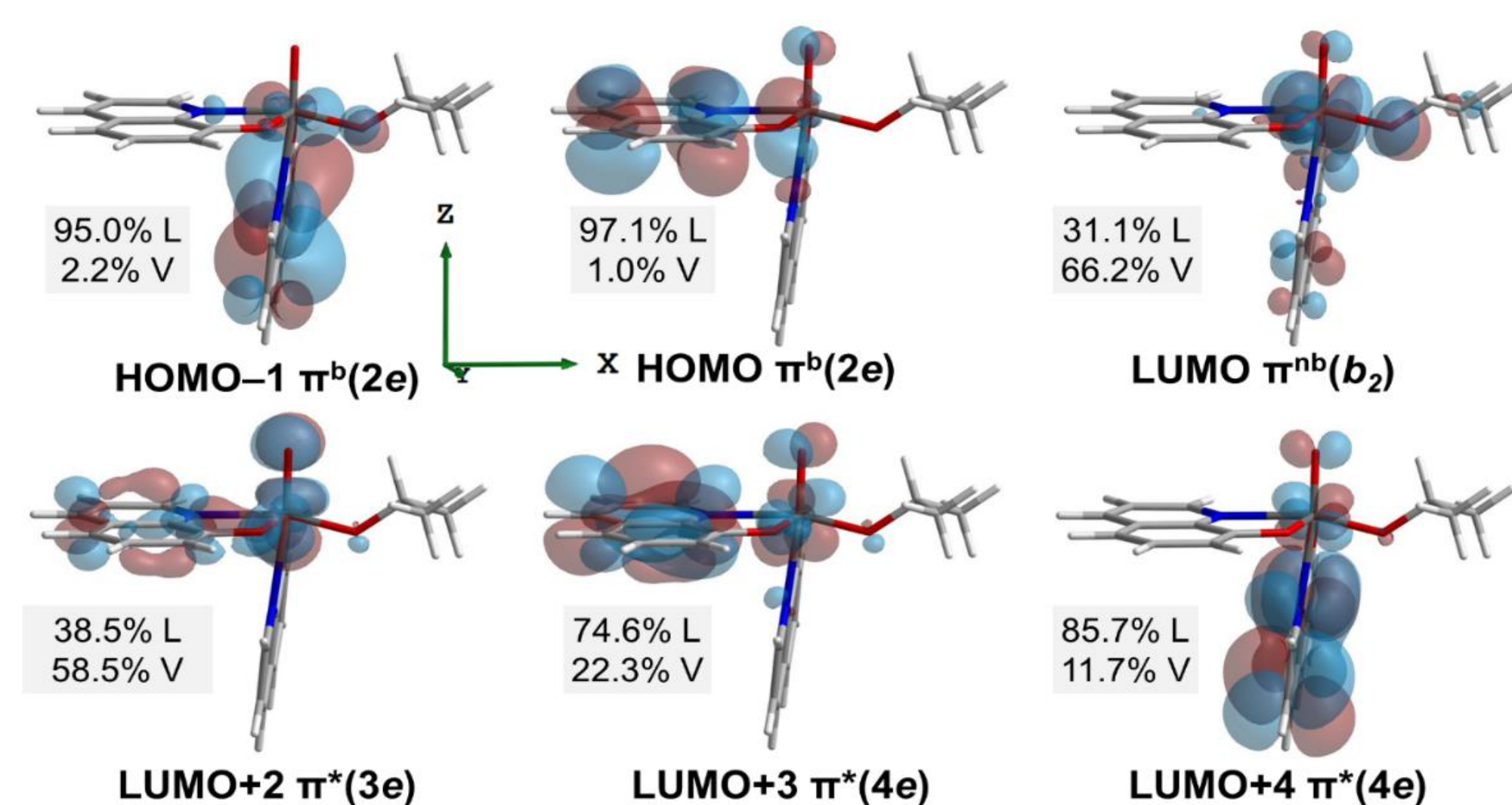


Proposed potential energy landscape for the photodissociation of alkoxy radicals from **1R** complexes.

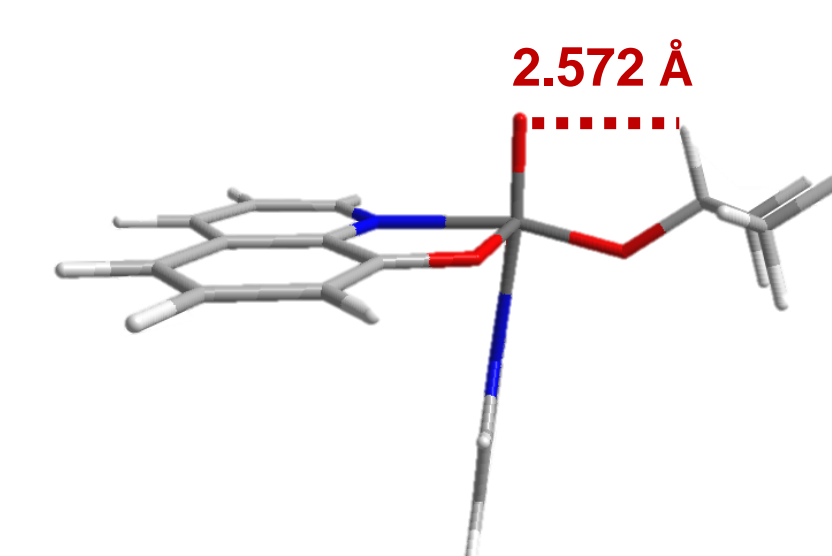
Evaluate the Ground State Electronic Structure



$a_1 (d_{z^2} \sigma^*)$
 $b_1 (d_{x^2-y^2} \sigma^*)$
 $4e (Ar \pi^*)$
 $3e (d_{xz}, d_{yz} \pi^*)$
 $b_2 (d_{xy} \pi^*)$
 $2e (O \pi^*)$
 $1e (Ar \pi^*)$



Electronic structure calculations enable assignment of the UV-visible absorption spectra (B3LYP/def2-TZVP).



Optimized structures have a hydrogen bonding interaction at the substrate α -carbon, which matches downfield shifts in ¹H NMR spectra.

Species	$^1(1e \rightarrow 3e)$		$^1(2e \rightarrow 4e)^b$		$^1(2e \rightarrow 3e)^b$		$^1(2e \rightarrow b_2)^b$	
	$\epsilon_{\lambda, \text{max}}^c$	$\lambda_{\text{abs, max}}^d$	$\epsilon_{\lambda, \text{max}}^c$	$\lambda_{\text{abs, max}}^d$	$\epsilon_{\lambda, \text{max}}^c$	$\lambda_{\text{abs, max}}^d$	$\epsilon_{\lambda, \text{max}}^c$	$\lambda_{\text{abs, max}}^d$
1Pr	43380	242	6046	5200	369	3080	510	
1Cy	45202	242	6848	305	6223	369	3560	511
1nBu	44272	242	6016	304	5435	366	3460	508

^aCollected at 295K in MeCN solvent. ^bLMCTs deconvoluted using Gaussian fits of the energy-linearized absorption spectrum. ^c $\text{M}^{-1} \text{cm}^{-1}$ ^dIn nm.

Absorption spectra in MeCN (295 K) resolves as two low-lying LMCT transitions and two intraligand transitions.

Conclusions and Future Directions

Steady-state and ultrafast transient absorption spectroscopy provide electronic structure assignment of the ground and excited state electronic structure of V(V) photocatalysts for metal-substrate bond homolysis. Future work will elucidate the scope of alkoxy radical substrates amenable to β -scission over competing 1,5-hydrogen atom transfer.

Acknowledgements and Financial Support

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