

PRF# 58742-UNI6

Investigating the Nonadiabatic Chemical Transformations of Nitric Oxide Radicals with Molecular Partners using State-Resolved Imaging

Nathanael M. Kidwell, The College of William & Mary, Department of Chemistry

Laser-induced fluorescence on the NO ($A^2\Sigma^+-X^2\Pi$) band system is widely implemented in the petroleum combustion community to probe the efficiency and performance of fuels with spectroscopic accuracy. However, precise fluorescence quantum yields and thus concentration measurements require knowledge of the electronic quenching of NO ($A^2\Sigma^+$) for predictive modeling. Indeed, combustion models rely upon accurate theoretical predictions, therefore necessitating experimental benchmarks for their refinement. The goals of this project are to utilize velocity map imaging to characterize the reactive and nonreactive electronic quenching channels of NO ($A^2\Sigma^+$) with molecular partners prevalent in petroleum combustion to improve predictive combustion models and to inform strategic optimization of next-generation engine technologies.

Implementing a Dual-Flow Nozzle to Conduct NO ($A^2\Sigma^+$) Electronic Quenching Experiments

During the initial stages of the funding period of this ACS PRF UNI award, we focused on finding signal due to electronic quenching of NO ($A^2\Sigma^+$) with O_2 using a single gas line. However, it was quickly evident from imaging that the NO products were primarily generated from photolysis of NO_2 , which is the reaction product of NO and O_2 . In order to resolve this issue, we constructed and implemented a novel dual-flow pulse valve shown in Figure 1 that facilitates the two reagent gases converging only at the exit of the pulse valve to limit contribution from NO and O_2 reaction. In particular, O_2 flows through the main sample line, whereas NO is streamed through a parallel sample line and through a ‘v-channel’.

We first studied collisional quenching of NO ($A^2\Sigma^+$) radicals with O_2 , in which either the reactive (chemical transformation) or nonreactive (energy exchange) nonradiative pathways are accessible. The reactive channel includes formation of NO_2 and O-atom from quenching, and nonreactive quenching results in the available energy being distributed to rovibronic states of NO and O_2 . Selected as an Editor’s Pick in *J. Chem. Phys.* and accepted as a part of the JCP Emerging Investigators Special Collection, we published

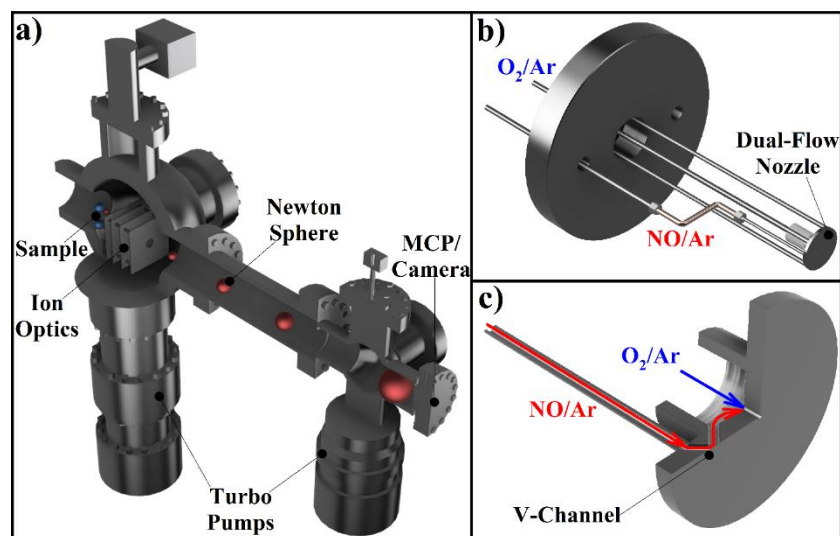


Figure 1: (a) Schematic of the velocity map imaging apparatus used to study electronic quenching dynamics. (b) NO and O_2 flow through separate gas lines to limit reaction to NO_2 . (c) Close-up of the dual-flow pulse nozzle, in which NO flows through a ‘v-channel’ and NO only encounters O_2 at the pulse valve exit. Both reagent gases are injected into a high-vacuum chamber with supersonic jet cooling prior to interaction with the pump and probe laser pulses.

our results describing the nonreactive collisional quenching of NO ($A^2\Sigma^+$) with O_2 ($X^3\Sigma_g^-$) using velocity map imaging. Figure 2 shows the temporal decay profile obtained while scanning the time delay between the pump and probe lasers and monitoring the probe ion signal enhancement. The pump laser prepares NO with purely electronic excitation in the $v'=0$, $N'=0$ level of the excited $A^2\Sigma^+$ state using the $Q_1(J''=0.5)$ line, and the decay profile is obtained while the probe laser measures signal in the NO ($X^2\Pi$, $v''=0$, $R_1(J''=50.5)$) level due to collisions with O_2 . The quenched lifetime ($\tau \sim 132$ ns) is greatly reduced from the natural radiative lifetime of NO ($A^2\Sigma^+$) ($\tau \sim 205$ ns).

Collisional Quenching of NO ($A^2\Sigma^+$) with O₂ ($X^3\Sigma_g^-$)

Shown in Figure 3, the isotropic ion image of NO ($X^2\Pi$, $v''=0$, $R_1(J''=50.5)$) reveals that the NO-O₂ system evolves through a long-lived NO₃ collision complex prior to formation of products. Additional ion images for the $Q_1(J''=40.5)$, $R_2(J''=30.5)$, and $Q_2(J''=20.5)$ levels also appeared isotropic, which is consistent with collisional quenching occurring on a longer timescale compared to the rotational period of NO ($\tau > 1$ ps). Statistical Phase Space Theory (PST) simulations were also carried out to predict the energy partitioning to relative translational energy between the NO ($X^2\Pi$, $v''=0$, J'') + O₂ co-fragments for comparison with the experimental TKER distributions (black trace). The PST simulated ion image and corresponding TKER distribution (red trace) support that the O₂ collision co-products are formed primarily in the $c^1\Sigma_u^-$ electronic state with NO ($X^2\Pi$, $v''=0$, J'' , F_n , Λ), resolving an issue in the literature. The deviations between experimental results and statistical Phase Space Theory simulations illustrate the key role that the conical intersection plays in the quenching dynamics to funnel population to product rovibronic levels. Furthermore, the product state distributions also indicate that NO ($X^2\Pi$) is generated with a propensity to occupy the $\Pi(A'')$ Λ -doublet state, which is consistent with the NO π^* orbital aligned perpendicular to nuclear rotation. Coupled with high-level theory, we are currently quantifying the branching ratios for NO ($A^2\Sigma^+$) quenching by collecting ion images and product state distributions for NO ($X^2\Pi$, $v''>0$, J'' , F_n , Λ) and O₂ (v'' , J''). We also observe signal when detecting O-atoms from quenching,

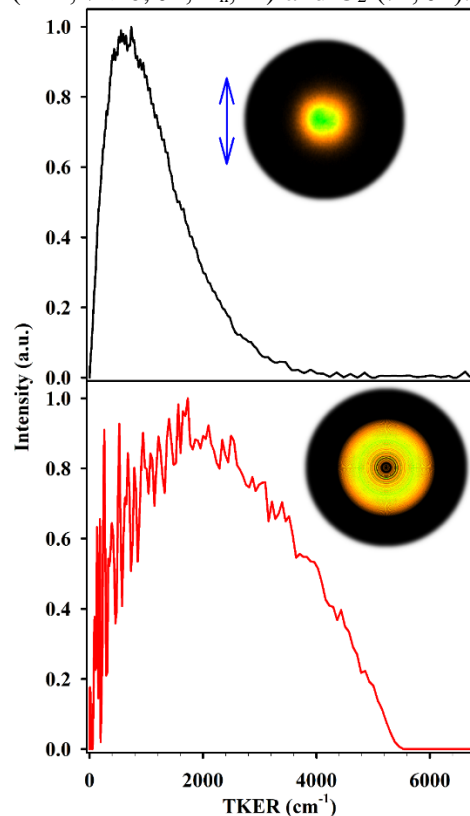


Figure 3: (Top) Total kinetic energy release (TKER) of NO ($X^2\Pi$, $v''=0$, $R_1(J''=50.5)$) and O₂ products from collisional quenching (black line), where the inset shows the experimental ion image revealing an isotropic distribution. The pump laser is parallel to the detector indicated by a blue arrow. (Bottom) The ion image and TKER distribution (red line) from a Phase Space Theory simulation are shown for comparison using O₂ ($c^1\Sigma_u^-$) as the collisional co-product.

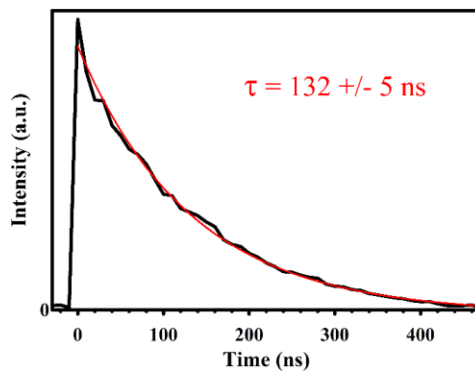


Figure 2: Temporal decay profile of NO ($A^2\Sigma^+$) while monitoring the NO ($X^2\Pi$, $v''=0$, $R_1(J''=50.5)$) level populated from electronic quenching. The best-fit NO ($A^2\Sigma^+$) quenched lifetime is $\tau = 132 \pm 5$ ns while recording the NO probe ion signal enhancement.

which reports on the dynamical outcomes from the reactive pathway. By characterizing the collisional quenching signatures of NO ($A^2\Sigma^+$) with O₂ (and other molecular partners), this may open up new research avenues for the theoretical and modeling communities to explore molecule-molecule quenching dynamics.

Impact on the PI and Supported Students

The grant support has enabled a total of 7 undergraduates and 1 M.S. student to conduct research during the funding period. During this time, students gained proficiency in project design of the dual-flow nozzle, carrying out experiments, and interpreting the results. The PI, M.S. student, and 3 undergraduates attended the Spring 2019 National ACS Meeting in Orlando to present our results. While at the conference, our M.S. student participated in a career development session to explore alternative chemistry careers, and an undergraduate student was selected for the ACS Travel Bridge Award to present her work. The M.S. student has graduated, and his thesis contains a significant amount of PRF-funded work. Furthermore, our collaborations with theoretical chemistry groups have provided a complementary understanding of NO ($A^2\Sigma^+$) collisional quenching. Our continued investigations will form the basis of a collaborative proposal to study NO dynamics in the excited and ground states.