

ABSTRACT

Measurement and Kinetic Analysis of Complex Ion-Molecule Reactions Influenced by Multiple Electronic Surfaces

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Energetically and temporally resolved gas phase studies of ion-molecule reactions, particularly those featuring open-shell transition metal ions, are fundamental to understanding complex chemical reactivity paradigms that can help shed light on the behavior of bulk and extended materials. Kinetic studies are particularly revealing as these elucidate mechanistic and dynamic features that would otherwise be impossible to determine. The unique single photon initiated dissociative rearrangement reactions (SPIDRR) technique measures the time dependence of product formation in ion-molecule reactions and is applied here to elucidate the mechanism of several ion-molecule systems. Moreover, the role of the transition metal /metal oxide ion's electronic structure toward chemical reactivity is determined.

Measurement and Kinetic Analysis of Complex Ion-Molecule Reactions Influenced by
Multiple Electronic Surfaces

by

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A Dissertation

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DEDICATION

To Lasien

ATTRIBUTIONS

The work detailed in Chapter Three has been entirely reproduced from a publication by multiple authors with permission from the Royal Society of Chemistry. As such it is appropriate to detail the contribution of each coauthor. Tucker Lewis contributed to the collection of experimental data, development of the kinetic model, and writing of the manuscript. Evan Mastin contributed to the collection of experimental data and data analysis. Dr. Zachry Theis contributed to the collection of experimental data. Dr. Michael Gutierrez calculated the vertical transition energies, and oscillator strengths of transitions. Dr. Darrin J. Bellert contributed to the analysis of the data and writing of the manuscript.

The work presented in Chapter Four is a draft for a manuscript that will likely be submitted soon. The draft features work from multiple authors, so it is appropriate to details each authors contribution. Tucker Lewis collected data with help from Evan Mastin and Zachry Theis. Data analysis was performed by Tucker Lewis. Dr. Gutierrez, Dr. Ellington, and Dr. Shuford performed the computational treatments. Tucker Lewis and Dr. Bellert authored the manuscript with some additions by Dr. Gutierrez and Dr. Ellington.

CHAPTER ONE

Introduction

Chemical Reaction Mechanisms

A primary goal of chemical research is gaining knowledge about the mechanism and energetics of a chemical reaction and attempting to generalize that mechanism for similar reactions. Reaction mechanisms describe the individual steps, each comprising one or several atomic motions, needed to transform reactants to products. However, it is not possible with current experimental techniques to confirm a reaction mechanism. Instead reaction mechanisms are probed through experimental study of individual reaction steps, which together can assist in the elucidation of a reaction mechanism.

The energetics and mechanism of a reaction can be experimentally investigated by studying reaction kinetics. Gas-phase kinetic studies offer an idealized environment where the reaction of interest is not perturbed by solvent effects or impurities. Several experimental techniques have been developed over the past five decades to study gas-phase kinetics. These include flowing afterglow, selected-ion flow tube (SIFT),¹⁻⁴ guided-ion beam (GIB),⁵⁻⁷ ion-cyclotron resonance (ICR) mass spectrometry,^{8,9} and others. These techniques are highly varied but attempt to measure the same properties: the reaction rate constant and product branching ratios. Product branching ratios provide information about

the relative competitions between reaction pathways. Rate constants describe the reaction probability per time and are explored below.

Microstates, States, and Phase Space

Degrees of Freedom of a Molecule

A single atom in cartesian space has three translational degrees of freedom (DOF) comprising of motion in the x,y and z directions. If a second atom is bound to the first, the three DOF of the second atom are converted into two rotational and one vibrational DOF. For any molecule there are $3N$ DOF, where N is the number of atoms. Three of the total DOF are translation. For linear systems, there will be two rotational and $3N-5$ vibrational DOF. Whereas for nonlinear molecules, there are three rotational and $3N-6$ vibrational DOF. Figure 1.1 illustrates the relative difference in energy levels expected for each DOF. In general translations have the smallest energy differences, followed by rotations, and then vibrations. The total energy of a molecule is divided statistically amongst these DOFs such that:

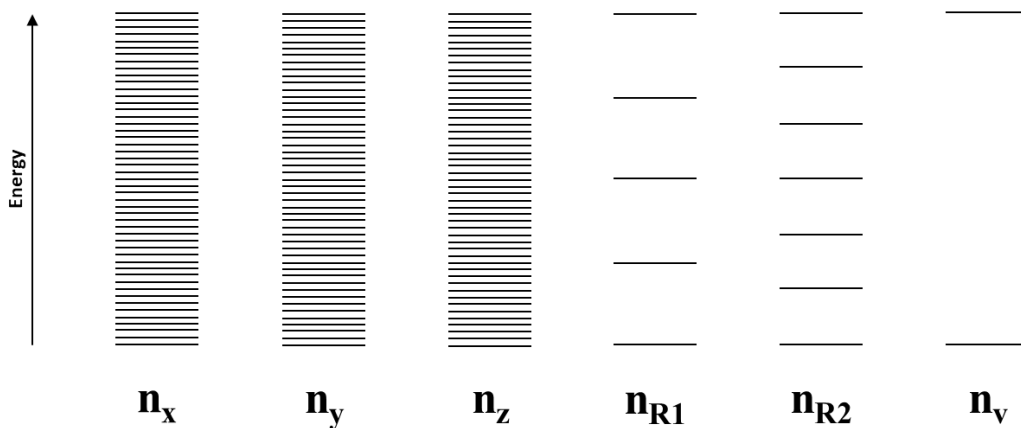


Figure 1.1. Cartoon of the relative energy states of translations, rotations, and vibrations.

$$E = \sum \epsilon_T + \epsilon_R + \epsilon_V \quad \text{Equation 1.1}$$

Where E is the total kinetic energy of the molecule, ϵ_T , ϵ_R and ϵ_V are the energy partitioned into translational, rotational, and vibrational states.

Microstates of a Molecule

The microstate of a molecule is given by a unique distribution of energy into the DOFs. Figure 1.2 is an example of three possible energetic distributions for a molecule with five indistinguishable DOF, and five quanta of energy equal to the energy level differences of each DOF. Each of these distributions will have some degree of degeneracy, the first has five, the second has 20, and the last only has one. Each distribution is one microstate of the molecule. Degenerate microstates will have the same geometric structure. The number of microstates of a molecule increases very rapidly with increasing energy and complexity. For the simple example in Figure 1.2 there are 126 possible microstates, if the number of DOF and quanta of energy are increased to nine, there are 24,310 microstates.

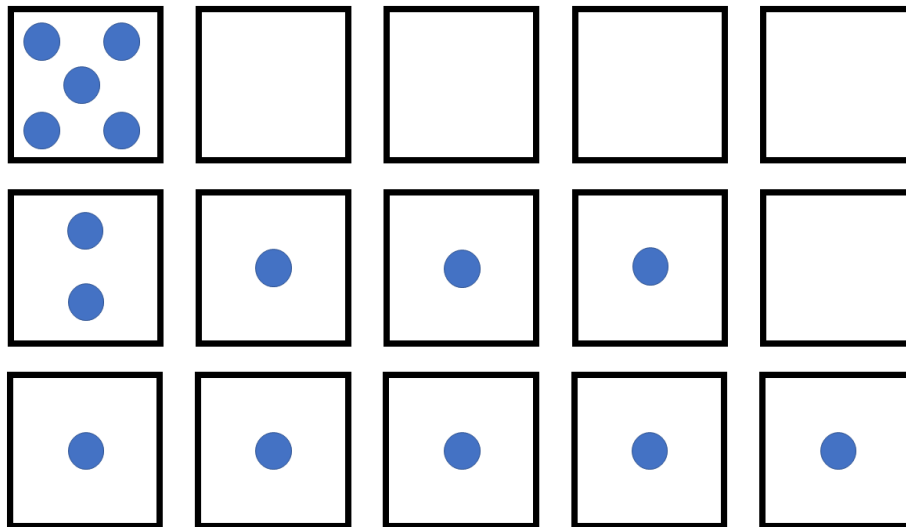


Figure 1.2. Possible distributions of five quanta of energy in five indistinguishable degrees of freedom.

Phase Space and Ensembles

A convenient way to keep track of the microstates of a molecule is through the employment of a phase space. The phase space of a molecule will have $2N$ axes. For each atom there is one axis for the position and another for its momentum. A point in phase space corresponds to a geometric structure of a molecule, given by degenerate microstates. A system consisting of a large number of indistinguishable molecules is called an ensemble. For the reactions studied here the energy content of the system is constant, referred to as a microcanonical ensemble. The microcanonical ensemble will statistically distribute population across the available microstates. The statistical distribution of energy is an assumption based on entropy, in that systems will distribute energy as much as possible between available microstates, with degenerate microstates consequently gaining more relative population. This is represented as many points in the phase space, with each point being a particular molecule in a particular microstate. The state of a system is described by a region of phase space corresponding to a geometric configuration of the molecule.

The Rate Constant

The rate constant is fundamental to chemical kinetics. For a reacting population undergoing the simple unimolecular Reaction 1.1:



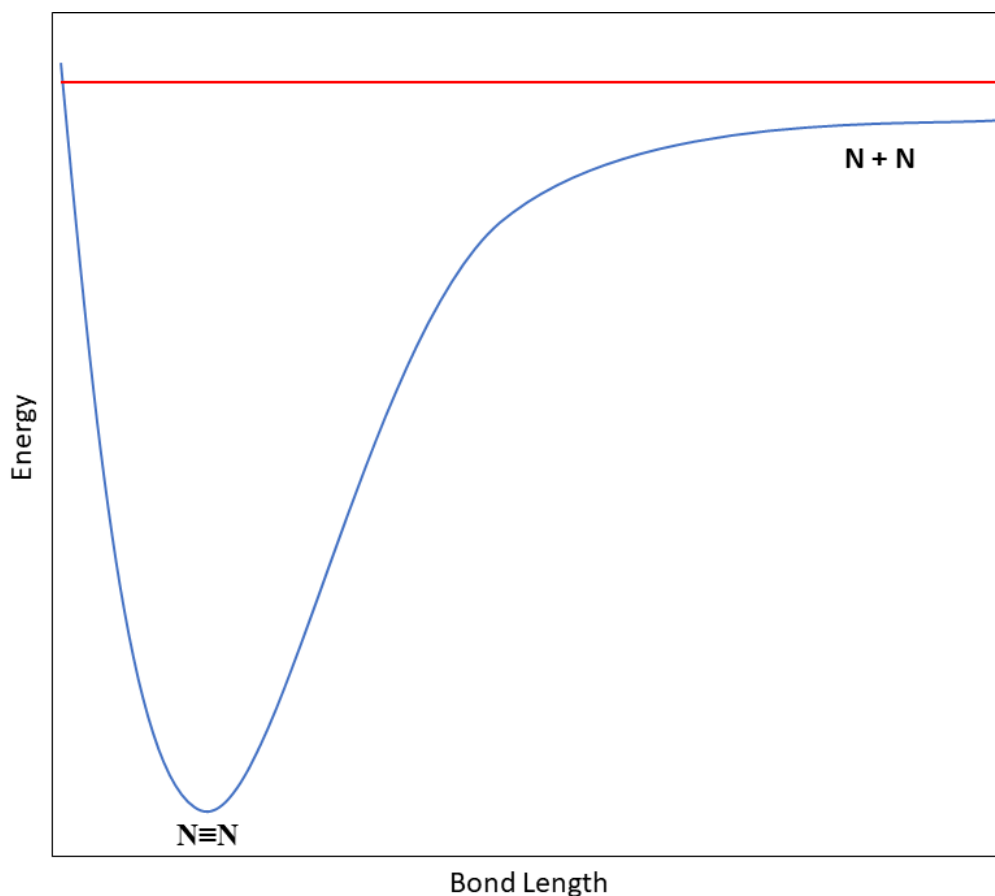


Figure 1.3. Cartoon of the potential energy of N_2 as a function of the N-N bond length. The red line is the system energy.

Where **A** is a reactant state and **B** is a product state. **A** and **B** each correspond to adjacent regions of phase space. The rate constant, k , describes the probability per unit time of **A** transitioning to **B**. The rate constant can therefore be conceptualized as the probability per unit time of a molecule that is in state **A** randomly redistributing energy, potentially resulting in structural changes, to become state **B**. In reactions that lack an activation barrier, this probability can be found by taking the ratio of all the states corresponding to **B** relative to the total number of available states, Equation 1.2, assuming the probability to randomly distribute energy into each state is equal.

$$k = P = \frac{S_B(E)}{S_A(E) + S_B(E)} \quad \text{Equation 1.2}$$

Where P is probability, and $S_A(E)$ and $S_B(E)$ are the available microstates of **A** and **B** at energy E . A simple example of this is the dissociation of N_2 . Figure 1.3 is a cartoon representation of the potential energy of $N_2 \rightarrow N + N$ as a function of the N-N bond length. The red line represents the total energy of the ensemble of N_2 molecules. Here N_2 is the reactant state, **A**, and $N + N$ is the product state, **B**. At energies in excess of the adiabatic bond energy of N_2 , Equation 1.2 can be used to calculate the rate constant for N_2 dissociation. However, as E decreases (the red line goes down), $S_B(E)$ will also decrease, along with the rate constant. As E decreases to or below the separated products, $N + N$, the rate constant goes to zero, Equation 1.3, as expected.

$$\lim_{S_B(E) \rightarrow 0} \left(\frac{S_B(E)}{S_A(E) + S_B(E)} \right) = 0 \quad \text{Equation 1.3}$$

For many reactions there is a potential energy barrier separating **A** from **B**, Figure 1.4. To transition from **A** to **B**, **A** must have a total kinetic energy, red line, in excess of the potential barrier separating **A** from **B**. Out of the total available states of **A**, a subset of those states will link **A** to **B**. These states are called transition states (TS) and they correspond to a geometric configuration typically called the activated complex (AC). The probability, the rate constant, of transitioning from **A** to **B** is given by the probability of **A** transitioning to the AC, and then the AC transitioning to **B**:

$$k = P = \frac{S_{TS}(E)}{S_A(E) + S_{AC}(E)} \frac{S_B(E)}{S_{AC}(E) + S_B(E)} \quad \text{Equation 1.4}$$

Once again, as the energy (red line) decreases below the TS energy, $S_{AC}(E)$ will decrease to zero.

Statistical Theories

Equation 1.2 and 1.4 are purposely derived in a general way to demonstrate how reaction rate constants are probabilistic and related to the properties of studied molecules. These derivations are not mathematically rigorous but are meant to provide a qualitative conceptual framework. A more complete picture of this relationship can be found in the derivations of Rice–Ramsperger–Kassel–Marcus (RRKM) theory,¹⁰ phase space theory,^{11,12} and statistical adiabatic channel model.^{13,14}

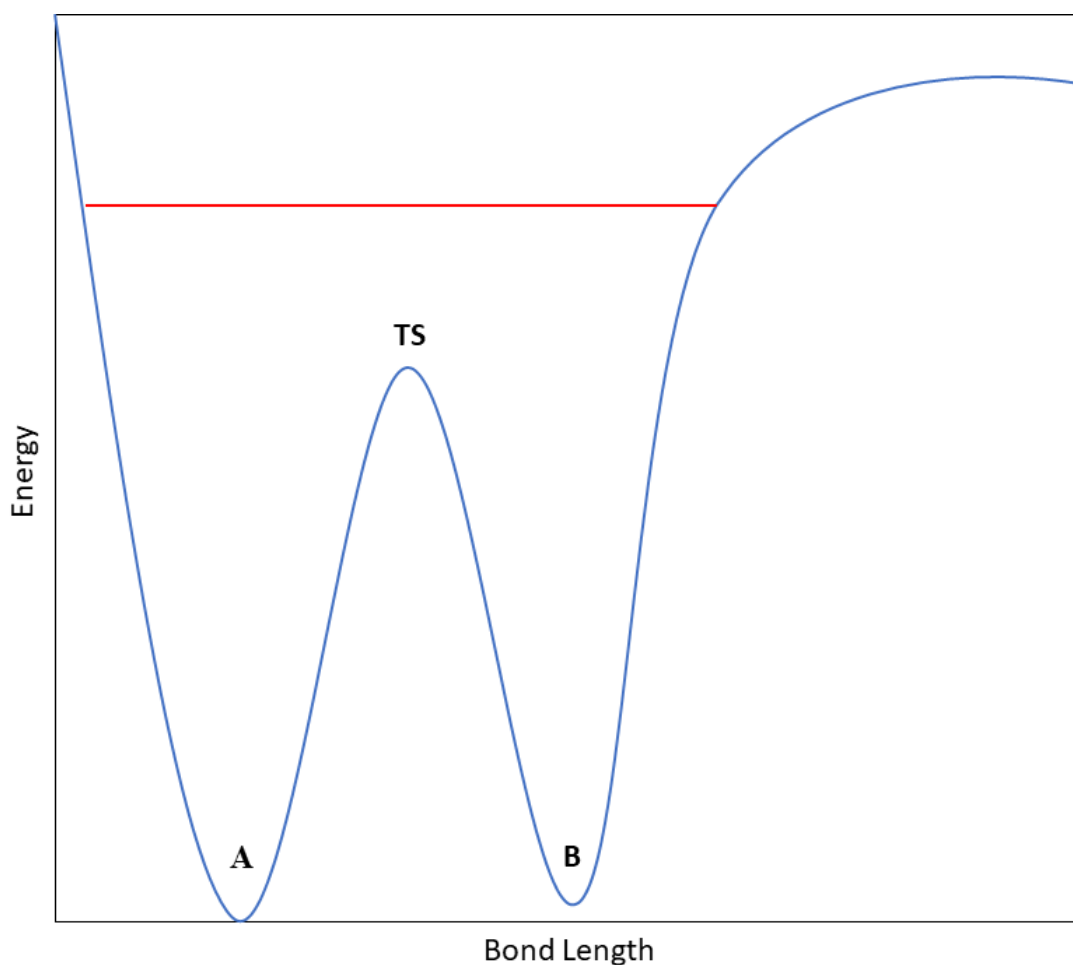


Figure 1.4. Cartoon representation of an A→B reaction featuring a transition state.

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CHAPTER TWO

Methods

Experimental Apparatus

The Single photon initiated dissociative rearrangement reactions (SPIDRR) instrument and technique were developed to study the kinetics of ion-molecule reactions. A detailed description of the instrument has been published previously,¹ and a summary of that description is provided here.

The SPIDRR instrument consists of two chambers. The first chamber is a 120 L stainless steel supersonic expansion chamber housing a laser vaporization (LAVA) source. The second chamber is a custom built orthogonally extracted time of flight mass spectrometer (TOFMS). Both chambers are differentially pumped maintaining pressures at $\sim 4 \times 10^{-6}$ Pa.

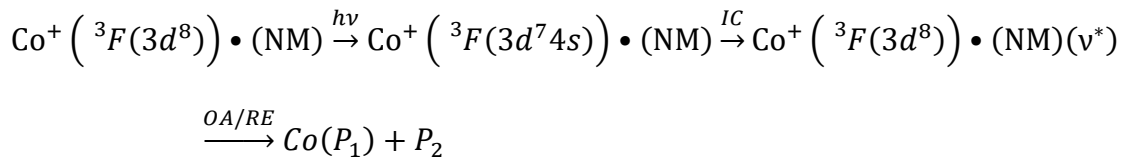
The LAVA source, located in the center of the expansion chamber, is similar to designs by Smalley² and Duncan.³ A Parker pulsed valve is bolted to an open source block, with a rotating metal target rod at its center. The pulsed output of a frequency doubled Nd³⁺ yttrium aluminum garnet (YAG) laser, the vaporization laser (VL), is focused on the metal target. The VL is timed to ablate the metal rod as the pulsed valve is triggered to open. A pulse of pressurized He gas ($\sim 5 \times 10^5$ Pa), entrained with the vapor pressure of a liquid neutral organic molecule of interest, expand into the vacuum of the expansion chamber. Numerous collisions occur between the He, metal plasma, and neutral molecule (NM), cooling the expanding beam. Metal cations form weakly bound complexes with the NM,

$M(NM)^+$. Heat released in the formation of the $M(NM)^+$ complex, referred to as the reactant complex (RC), is removed by further collisions with He.

The molecular beam carries the RC ions to the TOFMS at nearly the terminal velocity of He. The RC ions are extracted into the TOFMS by an orthogonal accelerator (OA). The OA consists of a series of metal plates each with a hole in their center. The plates are connected in series by resistors, with the last plate at instrument ground. A 2 kV voltage pulse is applied to the first plate, and is resistively divided to ground across the remaining plates. The resulting high and low electric fields accelerate and focus cations through the TOFMS onto the entrance of a hemispherical sector located 1.86 m away. The potential difference across the two halves of the sector is set to transmit the RCs to a Chevron microchannel plate (MCP) detector.

Photon Absorption and Excited Populations

The cooled RC lacks the energy needed to surmount potential energy barriers to rearrange and form products. The RC is activated by absorbing the output of a pulsed Nd^{3+} YAG pumped tunable dye laser, the activation laser (AL). An example sequence of the ensuing events for a Co^+ system is:



Where NM is a neutral organic molecule, $h\nu$ is a quantum of photon energy, IC is internal conversion, v^* indicates vibrational excitation, OA/RE is an oxidative addition/ reductive elimination reaction sequence, and P_1 and P_2 are neutral organic product fragments. The RC has a ground electronic state formed from the combination of the ${}^3F(3d^8)$ Co^+ cation

with the singlet NM ground state. The Co^+ cation acts as the chromophore, absorbing a photon to excite a 3d electron to a 4s state. The $s \leftarrow d$ transition is parity forbidden, but weakly allowed due to perturbations of the Co^+ electronic structure by the bound NM. Dissociation of the complex does not occur if the activating photon energy is below the complex bond dissociation energy. The RC is unlikely to relax through parity forbidden $s \rightarrow d$ emission because the oscillator strength is likely low. To relax, the electronically excited RC must internally convert energy to a high vibrational level of a lower electronic state. Entropic arguments suggest that the higher the vibrational level (and thus the lower in energy the associated electronic state) the higher the probability of IC. Thus, it is likely that IC will occur to a high vibrational level of the ground electronic state ($^3\text{F}(3d^8)$) of Co^+ . This significant increase in kinetic energy overcomes the potential barriers separating reactants and products, and so rearrangement will occur to yield product ions.

The SPIDRR Technique and the Acquisition of Reaction Kinetics

The AL is timed to activate the RC simultaneous with firing the OA. Upon activation, the RC will immediately begin to rearrange to form products. Product ions that are formed during or before the acceleration into the TOFMS will have a different arrival time to the detector than the RC. Product ions that are formed after acceleration will have the same arrival time to the detector, but a different kinetic energy. These product ions can be selectively transmitted to the detector by varying the potential difference across the hemispherical sector. Ions are transmitted through the sector when the kinetic energy of the ion matches the potential difference across the sector, measured in volts. The

transmission voltage of a product ion is proportional to the mass ratio of the product to the reactant and is given by:

$$V_P = V_R \frac{M_P}{M_R} \quad \text{Equation 2.1}$$

Where V_P , V_R , M_P , and M_R are the voltage and masses of the product and reactant ions. By monitoring the arrival time of the RC, while setting the potential difference across the sector to transmit a product ion, the relative yield of the RC into the product ion can be measured.

To obtain reaction kinetics, the RC is activated at successively earlier times prior to firing the OA. This difference in timing delay is denoted as τ . Increasing τ causes the RC to be activated at a further distance from the OA. During the travel time from activation to the OA, $|\tau|$, the activated RC will rearrange to form products, reducing the activated RC population that is extracted into the TOFMS. Product ions that are formed during the $|\tau|$ travel time will have a different arrival time to the detector and so don't contribute to the measured product signal. The decreased RC population yields fewer product ions as the RC travels through the TOFMS, yielding a smaller cumulative product signal. By decreasing τ in repeated experimental cycles, the signal will decay to 0 intensity.

Kinetic Modeling to Interpret SPIDRR Results

The SPIDRR technique is a powerful probe of ion-molecule kinetics and allows for the extraction of a wealth of kinetic information providing insight into reaction mechanisms. SPIDRR signals plot product formation versus τ , a negative number. The signals themselves can be directly analyzed by fitting exponential functions, Equation 2.2, to the signal to extract unimolecular rate constants.

$$A_0 e^{-k_1 t} \quad \text{Equation 2.2}$$

For simple reactions with a set of products that clearly result from a single reaction pathway, the product fragments stoichiometrically add to the NM, the fitting of a single or biexponential function is sufficient to extract most of the kinetic data. To extract all of the information, and to analyze more complicated reactions, a kinetic model is needed.

A kinetic model is a conceptual framework used to describe the relationship between stationary points in a reaction. In the kinetic models used in this dissertation, alphabetical letters denote successive species in a reaction. Arrows are used to show the flow of population from one species to the next. Rate constants, assigned one per arrow, describe the probability per unit time of population transitioning from one stationary state to the next. Kinetic models can be solved using matrix methods to give the time dependence of each species, rate constants, and the initial population. In the following sections several models will be proposed and evaluated to show the form of SPIDRR signals, and how the SPIDRR signals can be interpreted.

A → B Kinetic Model

The simplest model that is relevant to the studies in this dissertation is:



A is the first species in a reaction that has a kinetically important decay and is often the RC. In reactions that begin with one or more fast steps, **A** will be the first intermediate that has a rate limiting step following it. Transition metal mediated OA/RE reactions often yield two products $M(P_1)^+$ or $M(P_2)^+$ where P_1 and P_2 are stable organic fragments that

stoichiometrically add to **A** and are given by **C** and **D** from Model 2.1. The products form from a single product complex (PC = P₁-M⁺-P₂), **B**. For a M(NM)⁺ RC that forms M(P₁)⁺ and M(P₂)⁺ products, the PC contains both fully formed neutral fragments bound to the metal. Solving the model yields the time dependence of each species:

$$A(t) = A_0 e^{-k_1 t}$$

$$B(t) = \frac{A_0 k_1}{k_2 - k_1 + k_3} e^{-k_{123} t} (e^{k_{23} t} - e^{k_1 t})$$

$$C(t) = \frac{A_0 k_2}{k_{23} (k_2 - k_1 + k_3)} e^{-k_{123} t} (k_{23} e^{k_{23} t} - k_1 e^{k_1 t}) + (k_1 - k_2 - k_3) e^{k_{123} t}$$

$$D(t) = \frac{A_0 k_3}{k_{23} (k_2 - k_1 + k_3)} e^{-k_{123} t} (k_{23} e^{k_{23} t} - k_1 e^{k_1 t}) + (k_1 - k_2 - k_3) e^{k_{123} t}$$

Where A_0 is the activated RC population, $k_{23} = k_2 + k_3$, and $k_{123} = k_1 + k_2 + k_3$. The population of each species as a function of time is shown in the left two panels of Figure 2.1. The intensity of $A(t)$ exponentially decays to 0. **B** has little intensity, as the rate constants k_2 and k_3 are set to be much larger than k_1 . This is because dissociation of the PC, represented by **B** in Model 2.1, requires little rearrangement, is assumed to be fast, and is treated with large rate constants. The combined intensity of $C(t)$ and $D(t)$ at $t = \infty$ add to equal 1, the value used for A_0 . The ratio, $C(t)/D(t)$, is given by k_2/k_3 and is constant at all time. This is best illustrated in the lower left panel of Figure 2.1 by the overlapping signals of normalized $C(t)$ and $D(t)$ plotted versus time.

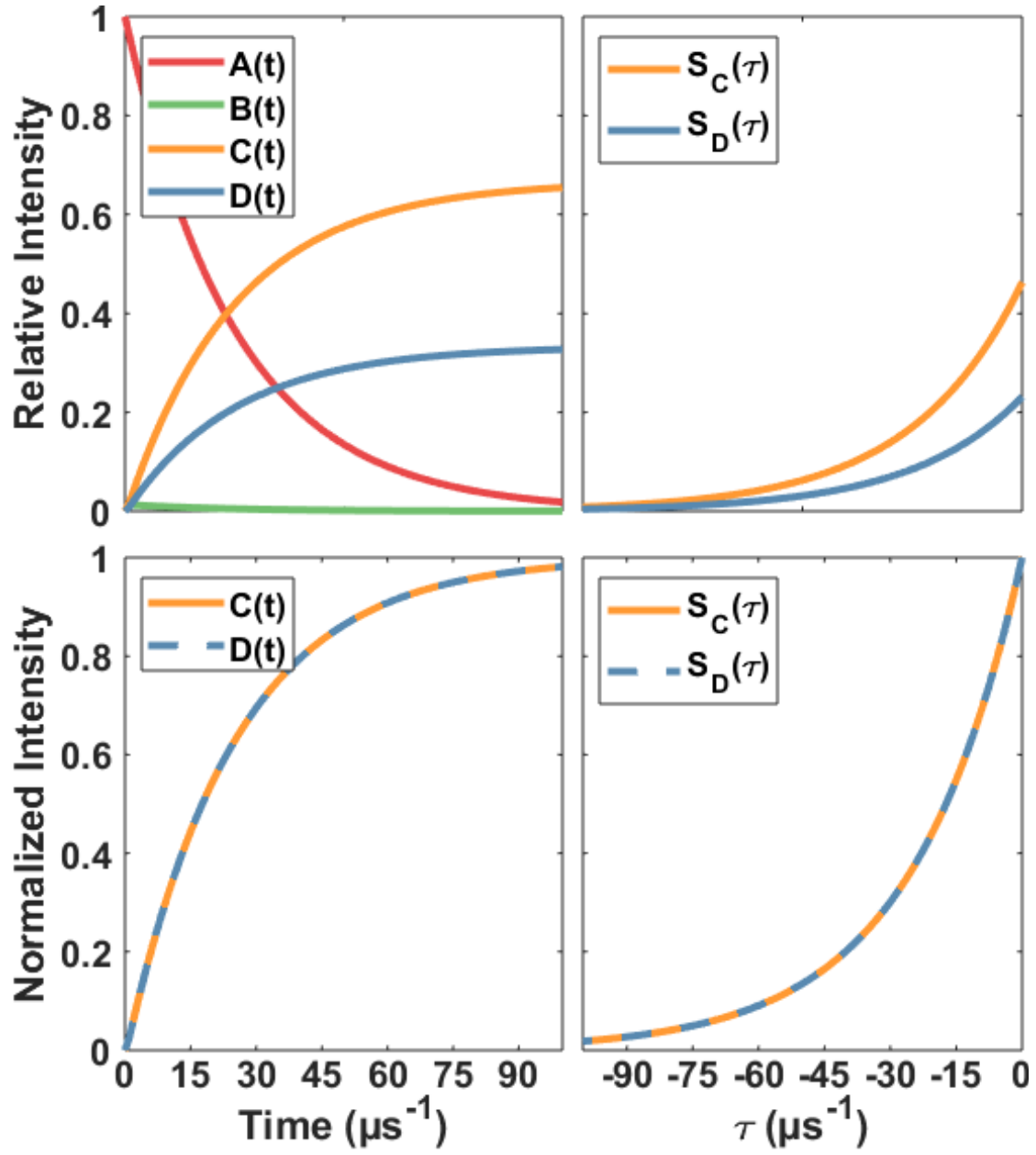


Figure 2.1: Time dependence of each species and SPIDRR product signals from Model 1. $A_0 = 1$, $k_1 = 0.04 \mu\text{s}^{-1}$, $k_2 = 2 \mu\text{s}^{-1}$, and $k_3 = 1 \mu\text{s}^{-1}$.

Integrating Model 2.1 to SPIDRR Signal and Rate Dependent Sampling

The SPIDRR technique samples products formed in the field-free TOFMS, after acceleration, and before the activated RC reaches the sector. This time window acts as integration limits for the formation of **C** and **D**.

Products formed prior to field-free flight in the TOFMS are not sampled. This early integration limit is defined by $|\tau|$, the flight time from activation to extraction, and α , the acceleration time ($\sim 3 \mu\text{s}$). Products formed from the RC population that survives field-free flight to the sector are not sampled. The surviving population decreases as the total time from activation to arrival to the sector increases. If the flight time through the TOFMS is Δ ($\sim 37 \mu\text{s}$), the RC population has, $|\tau| + \alpha + \Delta$, to react before further product formation is not sampled. Considering only the absolute value of τ , the SPIDRR signal of products **C** and **D** are:

$$S_C(\tau) = \int_{\tau+\alpha}^{\tau+\alpha+\Delta} \frac{dC}{dt} dt = \int_{\tau+\alpha}^{\tau+\alpha+\Delta} k_2 B_t = \int_{\tau+\alpha}^{\tau+\alpha+\Delta} \frac{A_0 k_1 k_2}{k_2 - k_1 + k_3} e^{-k_{123}t} (e^{k_{23}t} - e^{k_1 t})$$

$$S_D(\tau) = \int_{\tau+\alpha}^{\tau+\alpha+\Delta} \frac{dD}{dt} dt = \int_{\tau+\alpha}^{\tau+\alpha+\Delta} k_3 B_t = \int_{\tau+\alpha}^{\tau+\alpha+\Delta} \frac{A_0 k_1 k_3}{k_2 - k_1 + k_3} e^{-k_{123}t} (e^{k_{23}t} - e^{k_1 t})$$

Which evaluate and reduce to:

$$S_C(\tau) = \frac{A_0 k_2 (e^{-k_1(\alpha+\tau)} - e^{-k_1(\Delta+\tau)})}{k_2 - k_1 + k_3} - \frac{A_0 k_1 k_2 (e^{-(\alpha+\tau)k_{23}} - e^{-(\Delta+\tau)k_{23}})}{k_{23}(k_2 - k_1 + k_3)}$$

$$S_D(\tau) = \frac{A_0 k_3 (e^{-k_1(\alpha+\tau)} - e^{-k_1(\Delta+\tau)})}{k_2 - k_1 + k_3} - \frac{A_0 k_1 k_3 (e^{-(\alpha+\tau)k_{23}} - e^{-(\Delta+\tau)k_{23}})}{k_{23}(k_2 - k_1 + k_3)}$$

The SPIDRR signal corresponding to the formation of **C** and **D** is plotted in the right two panels of Figure 2.1. Comparing the top two panels of Figure 2.1, the SPIDRR technique significantly attenuates product intensity. The attenuation arises from rate dependent sampling (RDS). Two effects: products forming quickly prior to field-free flight

in the TOFMS, and activated RC not rearranging to products by the time the RC reaches the sector, together cause RDS. The portion of products that are formed during the α acceleration time into the TOFMS for Model 2.1 is given by Equation 2.3.

$$P = A_0 - A_0 e^{-k_1 \alpha} \quad \text{Equation 2.3}$$

Where P is product formed. Equation 2.3 increases with both increasing k_1 and α . Products formed during the acceleration event are not sampled by the SPIDRR technique because they arrive to the detector at a different time than the RC and have a different kinetic energy. In addition, when the activated RC reaches the sector any further product formation is not measured, as the RC will not be transmitted through the sector when set to transmit the measured product. The population that is not sampled due RC survival to the sector for Model 2.1 is given by Equation 2.4:

$$P = A_0 e^{-k_1(\Delta + \alpha)} \quad \text{Equation 2.4}$$

Where P is product formed. Equation 2.4 decreases with increasing k_1 , α , and Δ .

The bottom panel of Figure 2.1 plots normalized $S_c(\tau)$ and $S_D(\tau)$. Both product signals are superimposed, just as normalized $C(t)$ and $D(t)$ are superimposed. This demonstrates that RDS effects both products equally. Single exponential functions fit to $S_c(\tau)$ and $S_D(\tau)$ yield k_1 from Model 2.1. The ratio of k_2/k_3 can be extracted from the ratio of $S_c(\tau)/S_D(\tau)$.

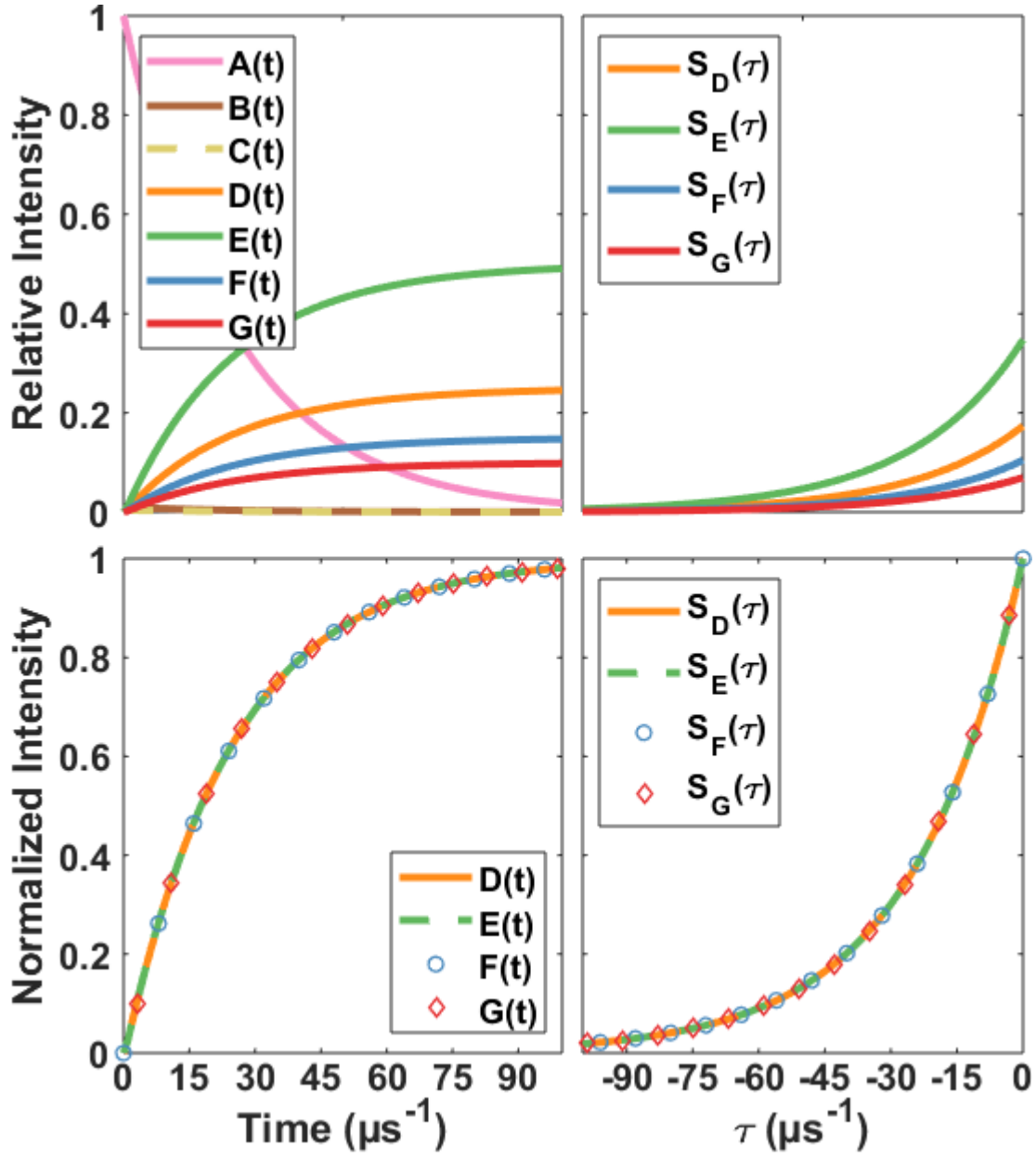


Figure 2.2: Time dependence of each species and SPIDRR product signals from Model 2 where $A_0 = 1$, $k_1 = 0.03 \mu\text{s}^{-1}$, $k_2 = 0.01 \mu\text{s}^{-1}$, $k_3 = 1 \mu\text{s}^{-1}$, $k_4 = 2 \mu\text{s}^{-1}$, $k_5 = 1.5 \mu\text{s}^{-1}$, $k_6 = 1 \mu\text{s}^{-1}$.

Early Bifurcation Model

Reactions with multiple PCs will often still have a single rate limiting step separating both sets of products from the RC. This is best represented by Model 2.2:



Where **D** and **E** are one set of products and **F** and **G** are a second set. **B** and **C** are two different PCs, each formed from a different reaction pathway from **A**. **A** is either the RC or the first intermediate with a kinetically important lifetime. Both k_1 and k_2 will be relatively small and rate limit the formation of **B** and **C**. Rate constants k_3 - k_6 correspond to the dissociation of the PCs, **B** and **C**, and are treated with large rate constants. The time dependence of each species and the integrated SPIDRR signals of the products are plotted in Figure 2.2. In the top left panel, the time dependence of each species is plotted. In the bottom left panel $D(t)$, $E(t)$, $F(t)$, and $G(t)$ are all normalized to 1, and their time dependencies superimpose. When the signals are sampled by SPIDRR, the products remain superimposable, as evidenced by the bottom right panel. The ratio of the initial intensities ($\tau = 0$) of $S_D(\tau)$, $S_E(\tau)$, $S_F(\tau)$, and $S_G(\tau)$ in the upper right panel of Figure 2.2 are equal to the ratio of the final product intensities ($t = \infty$) of $D(t)$, $E(t)$, $F(t)$, and $G(t)$ in the top left panel.

Single exponential functions fit to the SPIDRR signals in the top right panel extract the rate limiting rate constant, k_{RL} . Product formation will be rate limited at decay of **A**, which is equal to:

$$A(t) = A_0 e^{-(k_1+k_2)t} \quad \text{Equation 2.5}$$

Thus, $k_{RL} = k_1 + k_2$. The individual rate constants, k_1 and k_2 , can be extracted from the ratios of the two sets of product intensities from Equation 2.6:

$$\frac{k_1}{k_2} = \frac{S_D(\tau) + S_E(\tau)}{S_F(\tau) + S_G(\tau)} \quad \text{Equation 2.6}$$

The ratio of the intensity of product sums is determined by the ratio of the rate constants at bifurcation. Knowing the ratio k_1/k_2 , and the sum, $k_{RL} = k_1 + k_2$, the value of each rate constant is easily determined.

The following general solution is true for any reaction with a single rate limiting step to formation of any number of PCs:

$$\frac{k_n}{\sum_1^i k} = \frac{A_n}{A_0} \quad \text{Equation 2.7}$$

Where k_n is the rate constant leading to formation of the PC. A_n is the intensity of species n at $\tau = 0$, i is the number of PCs rate limited at the same step, and A_0 is the initial reacting population.

Biexponential Model

SPIDRR results can often be fit well to a biexponential function:

$$\gamma_1 e^{-k_1 t} + \gamma_2 e^{-k_2 t} \quad \text{Equation 2.8}$$

Where γ is a preexponential factor that determines the population that reacts through each rate constant. A biexponential response indicates that there are 2 pathways to form a single product. Model 2.3 is the simplest model that would result in a biexponential fit:



Where **C** is the PC, **B** is an intermediate, **F** and **G** are products, and **A** is either the RC or the first species to have a kinetically important decay. The first path, **A**→**B**→**C**, is rate limited at decay of **B**, such that $k_{RL} = k_3$. The second path, **A**→**C**, is rate limited at decay of **A**, to give $k_{RL} = k_1 + k_2$. The two paths cannot both be rate limited at decay of **A**, as that would reduce Model 2.3 to Model 2.1. The ratio of products D/E is given by k_4/k_5 . Finally, the ratio of products formed from the **A**→**B**→**C** pathway versus the **A**→**C** path is given by k_1/k_2 .

The SPIDRR signals of products **D** and **E**, as well as the time dependence of each species are plotted in Figure 2.3. A notable difference in the top left panel from previous models is the buildup in population of intermediate **B**. Rate limiting the top path of Model 2.3 at decay of **B** allows for the intermediate population to quickly increase from the decay of **A**, and then that population slowly decays to **C**. Both bottom panels of Figure 2.3 show the superimposable normalized products and product signals. This demonstrates that even in cases where the SPIDRR signals are more complicated, two products that are formed from a single PC will still be superimposable. Finally, the top right panel plots the intensities of $S_D(\tau)$ and $S_E(\tau)$.

Fitting a biexponential function to $S_D(\tau)$ and $S_E(\tau)$ yields $k_{RL} = k_3$ for the **A**→**B**→**C** pathway and $k_{RL} = k_1+k_2$ for the **A**→**C** path. However, the ratio of the preexponential factors, γ_1/γ_2 , does not recreate the expected k_1/k_2 ratio. This is caused by RDS affecting the two reaction pathways differently. The unsampled population along both pathways are:

$$P = A_0 - A_0 e^{-(k_1+k_2)\alpha} + A_0 e^{-(k_1+k_2)(\alpha+\Delta)} \quad \text{A} \rightarrow \text{C}$$

$$P = A_0 - B_t e^{-k_3\alpha} + B_t e^{-k_3(\alpha+\Delta)} \quad \text{A} \rightarrow \text{B} \rightarrow \text{C}$$

The unsampled population for the $\mathbf{A} \rightarrow \mathbf{C}$ pathway is a constant, while the unsampled population from the $\mathbf{A} \rightarrow \mathbf{B} \rightarrow \mathbf{C}$ path changes in time. Unlike Models 2.1 and 2.2, where RDS simply attenuates the product signals equally, in reactions that are represented well by Model 2.3 simply fitting a biexponential function is insufficient to extract all the kinetic information. Simultaneous fitting of both products with $S_D(\tau)$ and $S_E(\tau)$ corrects for this bias.

Model Selection

SPIDRR results are initially evaluated by fitting both single and biexponential functions. For simple systems with a single rate constant across all products and one or more pairs of products, Models 2.1 and 2.2 are sufficient to extract all the kinetic information. For more complex reactions, like the ones detailed in this dissertation, Model 2.3 or more complicated models are needed to replicate product time dependencies. Proposed models are solved for the time dependence of each species and the SPIDRR signal of product formation. The resulting functions are simultaneously fit to each measured SPIDRR result using a nonlinear least squares routine. Should the fitting routine provide rate constants that are sufficiently constrained by the data to give small errors, the model is considered a likely candidate to represent the product's time dependence. If the model is insufficiently constrained (too many steps), calculated curves will fit well to the data, but result in rate constants with large errors. If the model is too constrained (not enough steps) the model will not provide a good fit to the data. In general, the simplest possible model is first considered, Model 2.1, and then gradually more complicated kinetic models are invoked as needed to describe the SPIDRR results.

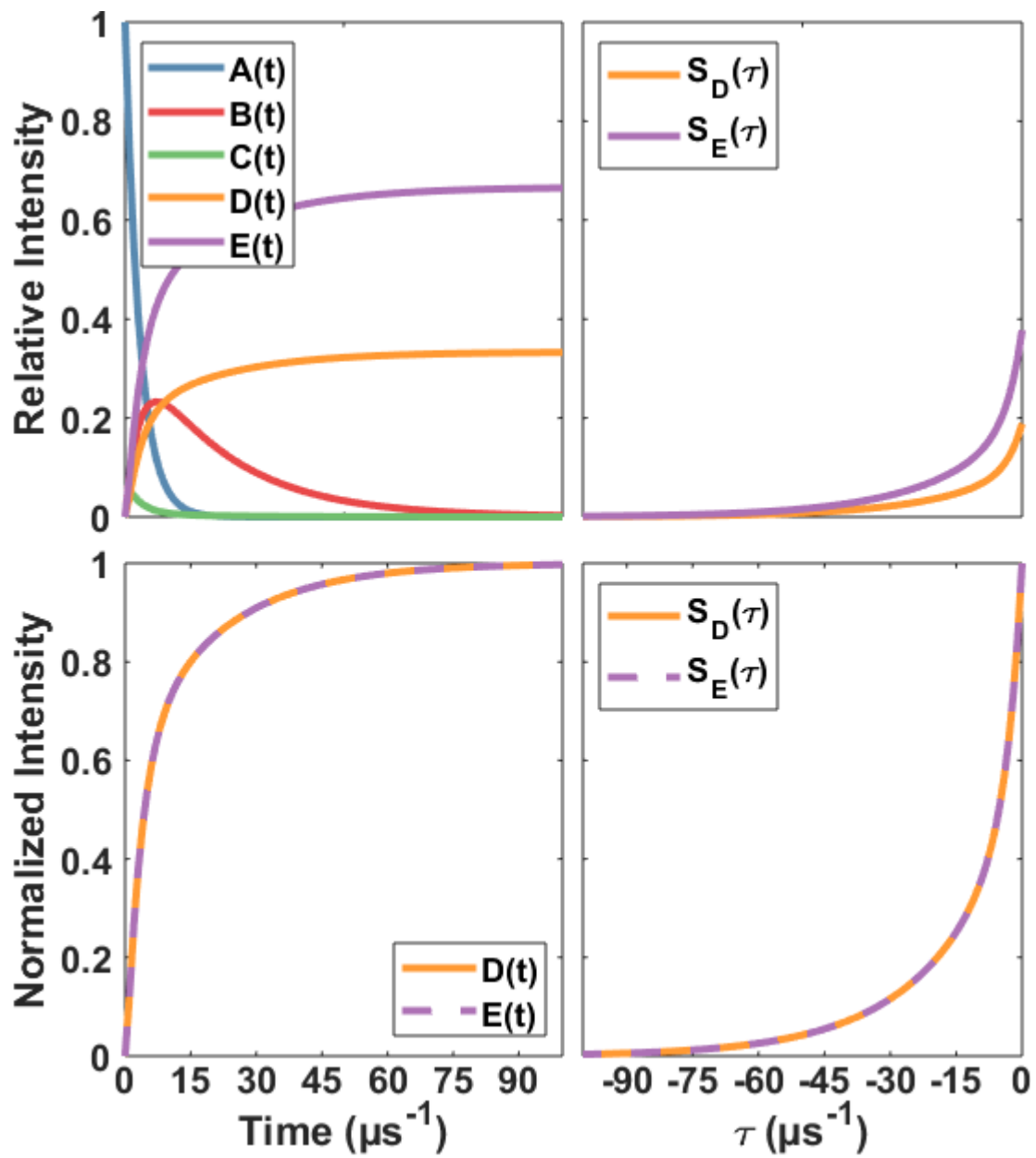


Figure 2.3: Time dependence of each species and SPIDRR product signals from Model 3. $A_0 = 1$, $k_1 = 0.1 \mu\text{s}^{-1}$, $k_2 = 0.2 \mu\text{s}^{-1}$, $k_3 = 0.05 \mu\text{s}^{-1}$, $k_4 = 1 \mu\text{s}^{-1}$, $k_5 = 2$.

A → B → C Model and Application to the Ni⁺ Mediated Decomposition of CH₃COOH

A → B → C Model

Reactions that require two sequential steps with same order of magnitude rate constants in each step are modeled well by Model 2.4:



Where **A** is the RC or the first intermediate to have a kinetically important decay, **B** is an intermediate, **C** is the PC, and **D** and **E** are products. The ratio of D/E is given by k_3/k_4 . Both k_1 and k_2 are kinetically important and serve to rate limit the reaction.

The time dependence of each species, as well as the SPIDRR signals of **D** and **E** are plotted in Figure 2.4. From the top left panel, intermediate **B** builds up population, like **B** in Model 2.3. The products, **D** and **E**, feature rounding at early times, as opposed to the sharper features of the product curves found in Figure 2.1 for Model 2.1. The rounding is a result of the fast dissociation of the PC causing the products, **D** and **E**, to follow the curve of **B**. This curvature is translated to early τ in $S_D(\tau)$ and $S_E(\tau)$ seen in the top right panel.

Ni⁺ Mediated Decomposition of CH₃COOH

Figure 2.5 is a mass spectrum where Ni⁺ is generated in the LAVA source and the vapor pressure of CH₃COOH is seeded into He. The Ni(CH₃COOH)⁺ reactant complex, as well as Ni(H₂O)⁺ and Ni(C₂H₂O)⁺ ions, likely formed from the unquenched Ni⁺ mediated decomposition of CH₃COOH in the high energy LAVA source, are labeled.

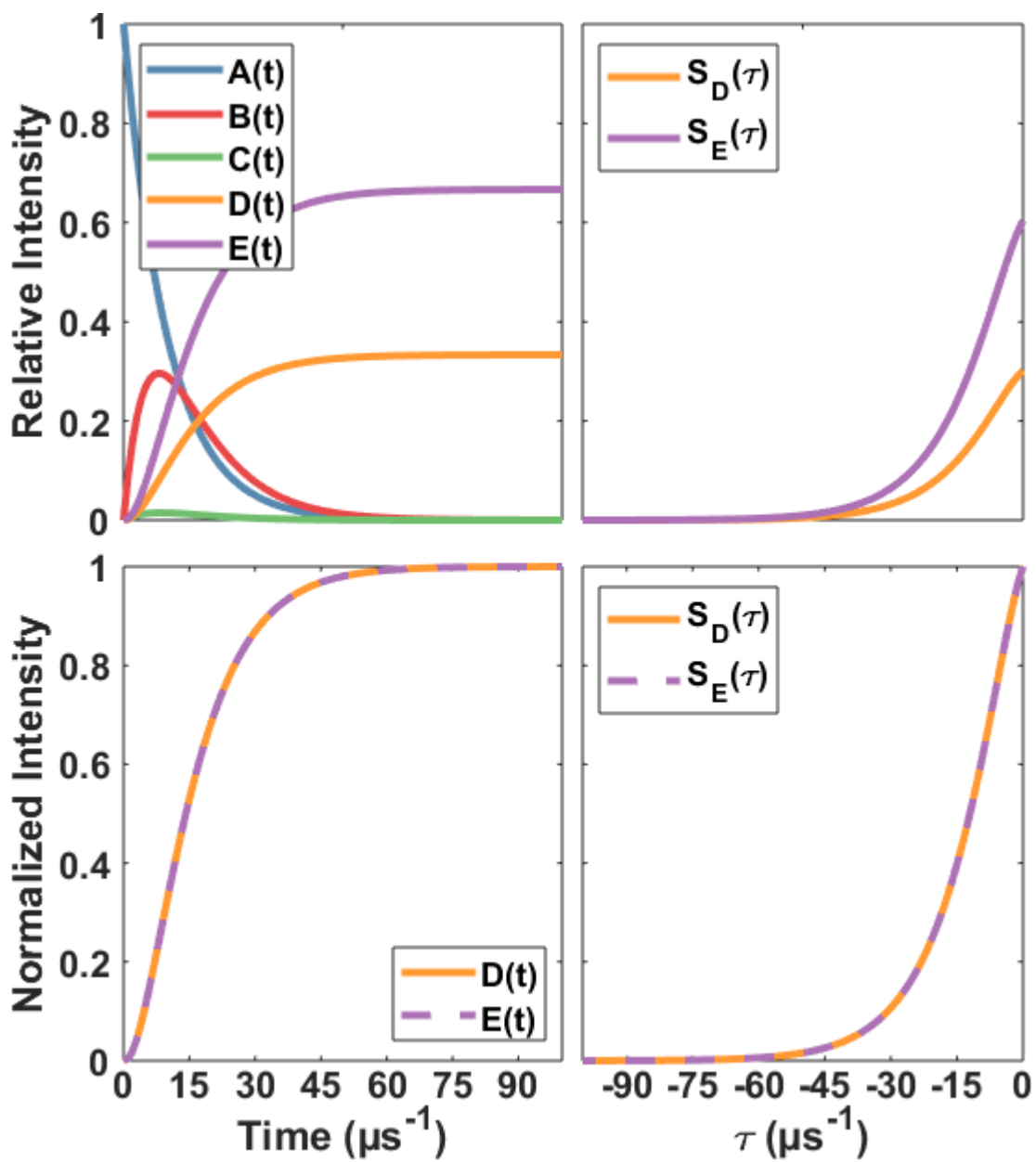


Figure 2.4. Time dependence of each species and SPIDRR product signals from Model 4. $A_0 = 1$, $k_1 = 0.1 \mu\text{s}^{-1}$, $k_2 = 0.15 \mu\text{s}^{-1}$, $k_3 = 1 \mu\text{s}^{-1}$, $k_4 = 2 \mu\text{s}^{-1}$.

The light induced dissociation (LID) products $\text{Ni}(\text{H}_2\text{O})^+$, $\text{Ni}(\text{C}_2\text{H}_2\text{O})^+$, and $\text{Ni}(\text{CH}_3\text{OH})^+$ were identified at $\tau = 0$ by scanning the potential difference across the sector halves. Product percent yields measured at an activating photon energy of $17,000\text{ cm}^{-1}$ are shown in Table 2.1.

Table 2.1: Product Branching Ratios for the Ni^+ mediated decomposition of CH_3COOH

$\text{Ni}(\text{CH}_3\text{COOH})^+ \rightarrow$	$\text{Ni}(\text{C}_2\text{H}_2\text{O})^+ + \text{H}_2\text{O}$	$\text{Ni}(\text{H}_2\text{O})^+ + \text{C}_2\text{H}_2\text{O}$	$\text{Ni}(\text{CH}_3\text{OH})^+ + \text{CO}$
Branching Ratio (%)	50	14	36

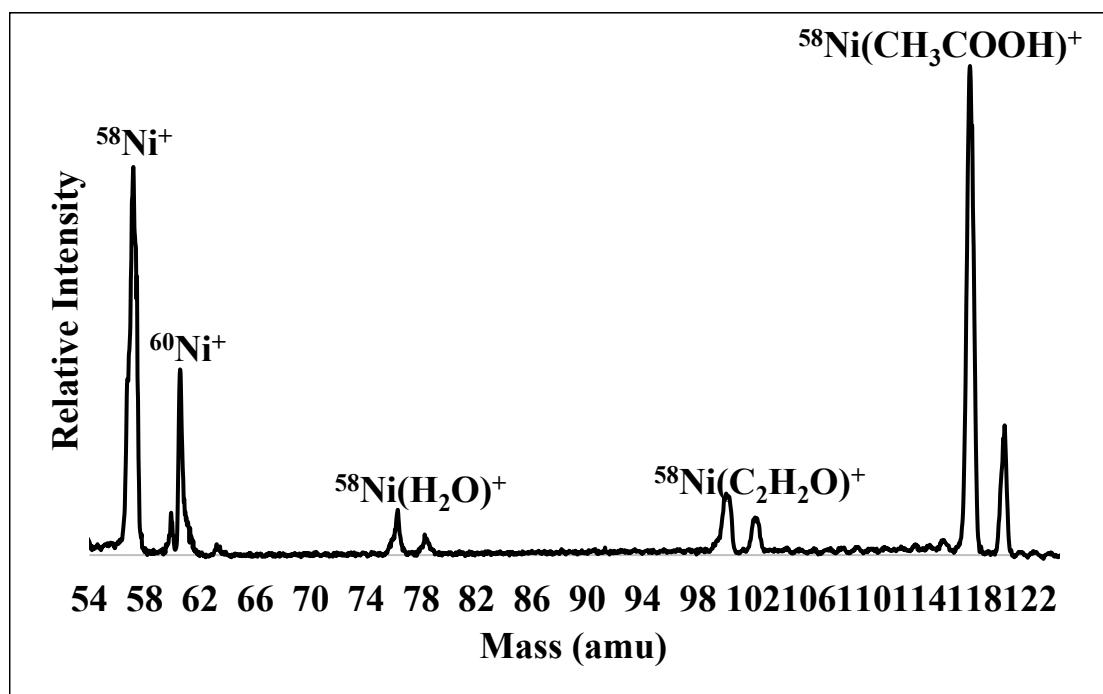


Figure 2.5: Precursor mass spectrum optimized for formation of $\text{Ni}(\text{CH}_3\text{COOH})^+$

A plot of the normalized intensity of $\text{Ni}(\text{H}_2\text{O})^+$, $\text{Ni}(\text{C}_2\text{H}_2\text{O})^+$, and $\text{Ni}(\text{CH}_3\text{OH})^+$ vs τ at an activating photon energy of $17,700\text{ cm}^{-1}$ is shown in panels B1, B2, and B3 of Figure 2.6. An analysis of the time dependence of the formation of each species revealed that

neither single nor biexponential fits sufficiently described the time dependence of all products. It was found that a kinetic model of the form $\mathbf{A} \rightarrow \mathbf{B} \rightarrow \mathbf{C}$, is needed to fit $\text{Ni}(\text{H}_2\text{O})^+$ and $\text{Ni}(\text{C}_2\text{H}_2\text{O})^+$ and this accounted for the rounding seen at early τ ($< 2 \mu\text{s}$). This type of model introduces an induction period that gives intermediate $\mathbf{B}$ time to build population as demonstrated in Figure 2.4. The $\mathbf{A} \rightarrow \mathbf{B} \rightarrow \mathbf{C}$ model requires that the first rate constant, k_1 , and the second rate constant, k_2 , each be nearly equal to account for the degree of curving shown in panels B1 and B2 of Figure 2.6. The similar temporal dependence of $\text{Ni}(\text{H}_2\text{O})^+$ and $\text{Ni}(\text{C}_2\text{H}_2\text{O})^+$ is expected, as both products likely are formed from a single product complex (PC), $\text{H}_2\text{O}-\text{Ni}^+-\text{C}_2\text{H}_2\text{O}$, where fast dissociation of an electrostatic bond generates the two observed products. In fact, the final dissociation of the PC merely serves to set the ratio of $\text{Ni}(\text{H}_2\text{O})^+$ to $\text{Ni}(\text{C}_2\text{H}_2\text{O})^+$. The temporal dependence of $\text{Ni}(\text{CH}_3\text{OH})^+$ product formation does not follow the ABC model, and instead is well represented by a single exponential function. This suggests that the reaction mechanism bifurcates early where two steps separate the RC from the $\text{H}_2\text{O}-\text{Ni}^+-\text{C}_2\text{H}_2\text{O}$ PC, and a single rate limiting step forms $\text{Ni}(\text{CH}_3\text{OH})^+$. The simplest model that provides these features, along with a simultaneous fit to all three products is Model 2.5.



Where $\mathbf{A}$ is first structure with a kinetically important decay, $\mathbf{D}$ is the $\text{Ni}(\text{CH}_3\text{OH})^+$ product, $\mathbf{C}$ is the $\text{H}_2\text{O}-\text{Ni}^+-\text{C}_2\text{H}_2\text{O}$ PC, and $\mathbf{E}$ and $\mathbf{F}$ are $\text{Ni}(\text{H}_2\text{O})^+$ and $\text{Ni}(\text{C}_2\text{H}_2\text{O})^+$. A key takeaway from Model 2.5 is that the observed rate constant for formation of $\text{Ni}(\text{CH}_3\text{OH})^+$ is a combination rate constant given by $k_1 + k_2$. The Ni^+ mediated decomposition of CH_3COOH was measured at a variety of activating photon energies, with Model 2.5 applied at each energy. There was insufficient signal to measure the minor $\text{Ni}(\text{CH}_3\text{OH})^+$ channel at the

lowest AL energies. This required using Model 2.4 to be simultaneously fit to the time dependence of the two measured product channels. The extracted rate constants from kinetic modeling and fitting are collected in Table 2.2. It is evident from the tabulated results that there is little change in the rate constants as a function of energy.

Table 2.2: Rate constants extracted from simultaneous fitting of the products from the Ni^+ mediated decomposition of acetic acid at varying activating photon energies

Energy cm^{-1}	A_0	k_1	k_2	k_3	R
15,500	1.708 ± 0.097	0.245 ± 0.012			1.28 ± 0.06
15,700	1.737 ± 0.074	0.268 ± 0.009			1.33 ± 0.04
16,000	1.663 ± 0.050	0.249 ± 0.006			1.40 ± 0.03
16,600	1.615 ± 0.074	0.245 ± 0.017	0.077 ± 0.022	0.640 ± 0.213	1.23 ± 0.04
17,100	1.577 ± 0.099	0.282 ± 0.024	0.103 ± 0.033	0.420 ± 0.071	1.34 ± 0.03
17,700	1.661 ± 0.055	0.281 ± 0.102	0.104 ± 0.018	0.466 ± 0.045	1.28 ± 0.02

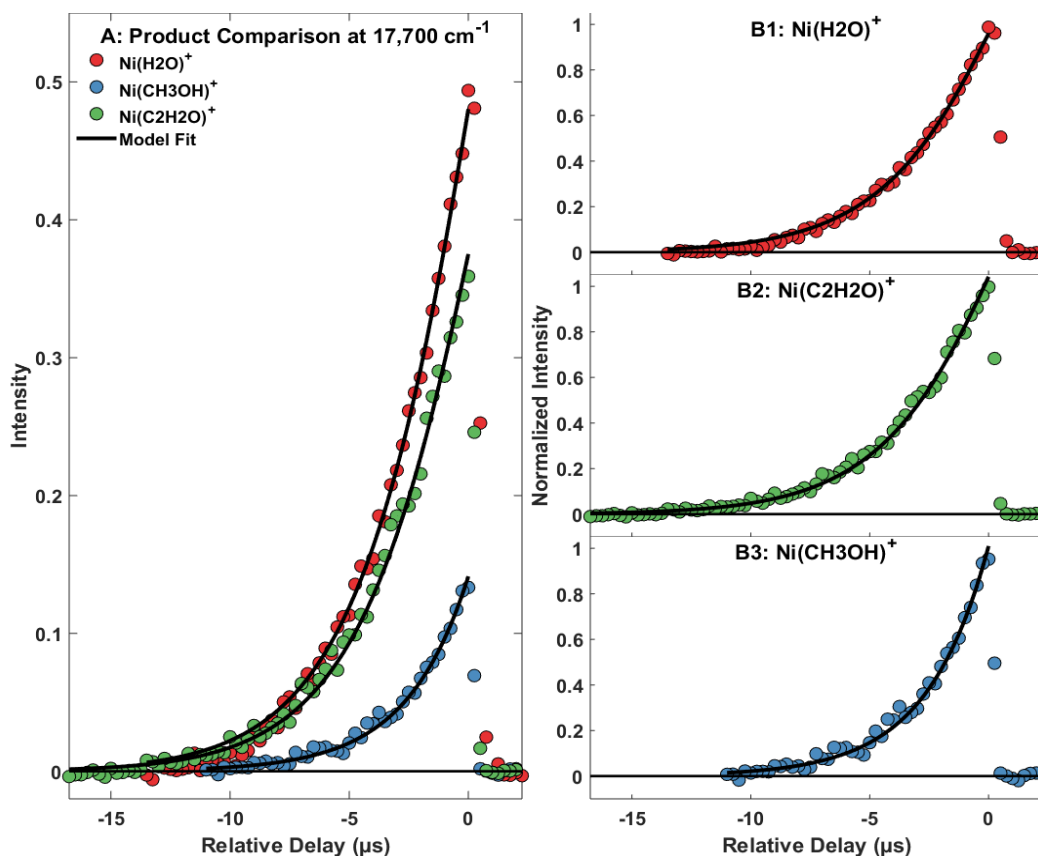


Figure 2.6: Comparison of the product channels, $\text{Ni}(\text{H}_2\text{O})^+$, $\text{Ni}(\text{C}_2\text{H}_2\text{O})^+$, and $\text{Ni}(\text{CH}_3\text{OH})^+$ rate of formation at an activating photon energy of $17,700 \text{ cm}^{-1}$.

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CHAPTER THREE

Measurement of Time Dependent Product Branching Ratios Indicates Two-State Reactivity in Metal Mediated Chemical Reactions.

Reproduced from T. Lewis, E. Mastin, Z. Theis, M. Gutierrez and D. Bellert, Measurement of Time Dependent Product Branching Ratios Indicates Two-State Reactivity in Metal Mediated Chemical Reactions, *Phys. Chem. Chem. Phys.*, 2022, **24**, 2300–2308. with permission from the Royal Society of Chemistry.

Abstract

For several decades, the influence of Two-State Reactivity (TSR) has been implicated in a host of reactions, but has lacked a stand-alone, definitive experimental kinetic signature identifying its occurrence. Here, we demonstrate that the measurement of a temporally dependent product branching ratio is indicative of spin inversion and is a kinetic signature of TSR. This is caused by products exiting different hypersurfaces with different rates and relative exothermicities. The composite measurement of product intensities with the same mass but with different multiplicities yield biexponential temporal dependences with the sampled product ratio changing in time. These measurements are made using the single photon initiated dissociative rearrangement reaction (SPIDRR) technique which identifies TSR but further determines the kinetic parameters for reaction along the original ground electronic surface in competition with spin inversion and its consequent TSR.

Introduction

A chemical reaction that initiates on the ground potential energy surface (PES) may transition to an excited surface to circumvent high transition barriers. The availability of excited surfaces is largely controlled by the energetic separation from, and degree of coupling to, the ground PES. If electronic couplings are weak, the reaction progresses on a single surface with reaction kinetics understood in terms of traditional statistical theories. However, as the strength of electronic surface couplings increase, the reacting population may transition between surfaces at spin inversion (SI) junctions to avoid the energetic costs of high transition barriers. Kinetic descriptions of such multi- (MSR) or two-state reactive (TSR) systems quantify product distributions, energetic costs, and reaction rates attributed to nonadiabatic chemical influences.

Early studies of SI utilized symmetry and MO theory to indicate SI's role toward product outcome during the decay of photo-excited organic molecules.¹⁻⁴ This successful employment led to the application of SI toward metal oxide cation reactivity and the consequent suggestion of TSR as a new paradigm in organometallic chemistry.⁵ Moreover, several landmark studies into the $\text{FeO}^+ + \text{H}_2$ reaction vaulted TSR into the modern research arena.⁶⁻⁸ Together these studies demonstrated that FeO^+ reactivity was strongly influenced by TSR leading Schröder, Shaik, and Schwarz to suggest that the TSR/MSR scope be widened to include condensed phase organo-metallic reactions.⁹ The notion that TSR/MSR reduces energetic costs and influences product selectivity in catalysis launched a significant number of theoretical investigations into systems that potentially exhibit SI and these continue today.⁷⁻³⁹

In contrast to the wealth of computational research that has gone into studying the influences of TSR/MSR toward chemical reactivity, experimental studies into this paradigm are far fewer.^{10,16,17,26,36,43} This is likely due to the lack of an easily measured experimental result that uniquely identifies TSR's influence over reaction progression. This elusive goal has been desired for two decades and recently forwarded by comparative studies between experimentally determined and computed hydrogen kinetic isotope effects (H-KIE) in a series of biomimetic complexes.⁴⁴ Specifically, tunneling corrected KIE values were computed for a reacting population's transmission through transition states of different multiplicities. Agreement between the measured and computed values identified the reactive transition state and its corresponding multiplicity. A multiplicity change from reactant complex to the reactive transition state indicates SI occurrence in a consequent TSR/MSR scenario. These studies show that the measured H-KIE value is a kinetic signature identifying the reactive spin state. However, such H-KIE measurements are most readily interpreted through comparative computational studies and a uniquely stand-alone experimental TSR measurement remains elusive, until now.

Here, we identify an easily measured, experimental kinetic signature indicating the competition between reactive spin states during metal mediated chemical reactions. This signature is a temporally dependent product branching ratio that confirms SI during chemical reaction. The confirmation of spin inversion, coupled with the measured competitive progression of the reacting population along each spin hypersurface, implicates the occurrence of TSR in the metal mediated chemistry. This study focuses on our observation and verification of TSR in the Co^+ mediated decomposition of CH_3CHO and demonstrates the feasibility of such determinations in the absence of supporting

theoretical calculations. These measurements are made using the single photon initiated dissociative rearrangement reaction (SPIDRR) technique, however similar measurements should be possible with other kinetic techniques with comparable temporal resolution.

Procedure

The SPIDRR technique has been described previously.⁴⁵ Instrumentation consists of a 120 L expansion chamber orthogonally coupled to a custom time of flight mass spectrometer (TOFMS) kept at vacuum. The TOFMS contains a pulsed orthogonal accelerator (OA) at its entrance and a hemispherical sector / microchannel plate detector assembly located at the TOF's end. The OA is pulsed from ground potential to accelerate ions into the TOFMS. The sector transmits ions with specific kinetic energy values to the detector which is controlled by selection of the potential difference across sector halves. The free field TOF region is 1.86 m in length. The TOF is maintained at $\sim 4 \times 10^{-6}$ Pa during experimentation.

Two different pulsed Nd³⁺ YAG lasers are used in the SPIDRR experiment. Both are frequency doubled to 532 nm. One is the vaporization laser (VL) which is focused to ablate a pure metal rod. The second pumps a dye laser to provide tunable pulsed radiation throughout the visible spectral region. The YAG pumped dye combination is considered the activation laser (AL).

A source block supports a rotating cobalt rod and pulsed valve assembly and is located at the center of the expansion chamber. Helium gas ($\sim 5 \times 10^5$ Pa), seeded with the vapor pressure of acetaldehyde, is maintained on the high-pressure side of the valve. The VL is timed to ablate the metal target as the valve is pulsed open, directing the vaporization

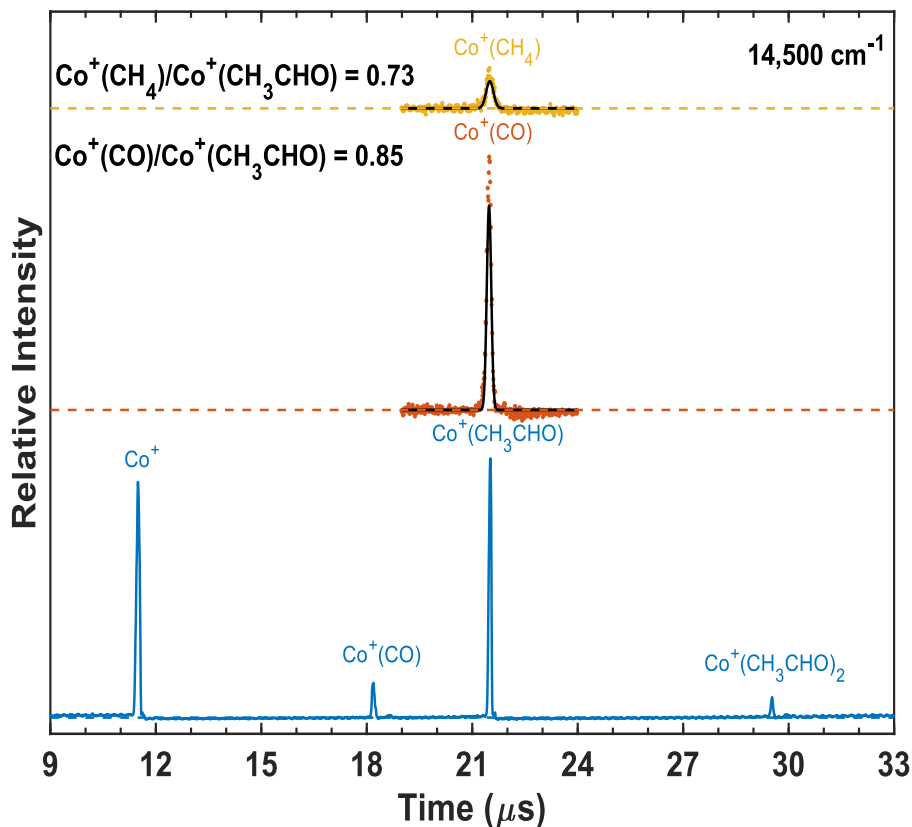


Figure 3.1. Precursor (bottom panel) and fragment (top panels) mass spectra. The fragments are products in a chemical reaction that are formed following acceleration into a TOFMS. Products have the same arrival times to the detector as does the precursor but with a fraction of the kinetic energy. Sector transmission voltages equal the product / precursor mass ratio. Top two panels are product intensities, measured at zero τ , following precursor absorption of a photon with energy $\tilde{\nu} = 14500 \text{ cm}^{-1}$.

products toward the OA. The numerous collisions form and cool the clusters in the expansion. The bottom panel of Figure 3.1 shows a typical precursor TOF mass spectrum where formation of the $\text{Co}(\text{CH}_3\text{CHO})^+$ cluster has been optimized.

Activation of the $\text{Co}(\text{CH}_3\text{CHO})^+$ precursor cluster occurs along the expansion axis at various values of τ . τ is time in the laboratory frame and is defined as the relative delay between firing the OA and AL which are programmatically controlled to within 12.5 nanoseconds. Zero τ is the coincident firing of the AL and OA indicating absorption of

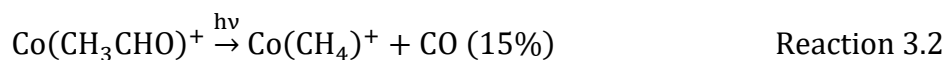
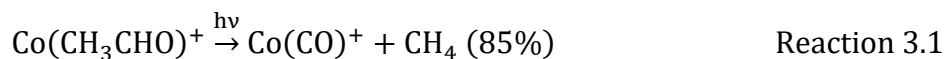
pulsed laser radiation by the precursor $\text{Co}(\text{CH}_3\text{CHO})^+$ just as the ion packet is orthogonally accelerated into the TOF. All precursor clusters that dissociate after exiting the OA, but before entering the sector (defined as the free flight time within the TOF), form fragment ions that have the same velocity as the accelerated precursor but with a fraction of the kinetic energy. Thus, time gating over the precursor arrival time, while maintaining a sector potential difference that transmits a specific fragment ion, provides the precursor's yield into that fragment channel while guaranteeing that the fragment results from a specific precursor. The ratio of sector voltages that transmit the fragment is equal to the fragment : precursor mass ratio. Thus, assignment of mass peaks in the precursor mass spectrum and measurement of sector transmission voltages determines fragment masses. Values of τ are then decreased from zero while monitoring fragment yields. This physically places precursor photon absorption at locations along the expansion axis with the absolute value of $|\tau|$ providing the photo-excited precursor travel time to the OA. Furthermore, unimolecular decay begins at the time of photon absorption resulting in a portion of the excited population not surviving the $|\tau|$ travel time to the OA. The surviving population, after pulsed acceleration into the TOF, forms fragments within the free flight time which are detected with intensity plotted vs. τ . All negative values of τ indicate some degree of precursor survival whereas all positive values of τ yield zero fragment intensity since the AL fires after the ions have been orthogonally accelerated from the expansion axis. The collection of fragment intensities plotted vs. τ values is considered the SPIDRR result. This features a sharp interface between positive and negative τ followed by an exponentially decreasing function of fragment intensity as τ decreases from zero.

Oscillator strengths between the ground state of the $\text{Co}(\text{CH}_3\text{CHO})^+$ precursor and low-lying excited states are determined using the CASSCF/CASPT2/SO-RASSI method.⁴⁶ The OpenMolcas electronic structure package was used for these calculations.⁴⁷

Results and Discussion

(a) Product distributions. Precursor preparation. Photon absorption. Excited populations.

Figure 3.1 shows the precursor (bottom panel) and fragment (top two panels) mass spectra measured at different sector potential differences. The fragment mass spectra are monitored following precursor absorption of a 14500 cm^{-1} energy quantum. The detector is operated at a higher gain when measuring fragment mass spectra. The precursor arrival time to the detector is the same for each fragment, indicating that the precursor dissociates into both observed fragments and yields are not contaminated by fragment ions formed in the source nor from the dissociation of other clusters. Each top trace is labeled by the voltage ratio that permits maximum fragment transmission through the sector and identifies the fragment masses. The products of the photon-initiated Co^+ mediated decay of CH_3CHO are:



with fragment partitioning indicated. The obvious relationship between Reactions 3.1 and 3.2 suggest that the photon-initiated reaction bifurcates late in the reaction progression to eliminate neutral fragments which stoichiometrically add to acetaldehyde. The formation of such products suggests a rearrangement reaction where the Co^+ cation oxidatively adds to a covalent bond and then facilitates the reductive elimination of products.

A gaussian function is fit to each fragment signal in the top panels of Figure 3.1 and are shown as the solid curves plotted through the observations. Areas under each curve determine relative partitioning into each product. The $\text{Co}(\text{CO})^+$ and $\text{Co}(\text{CH}_4)^+$ are the only fragments that result from single photon absorption of the precursor at the laser energies used in this study. Elimination of neutral CH_4 relative to CO occurs at an 85:15 fraction, measured at zero τ . Thereby, Figure 3.1 demonstrates SPIDRR's ability to identify fragments and their corresponding ratio measured at a specific time following precursor photon absorption.

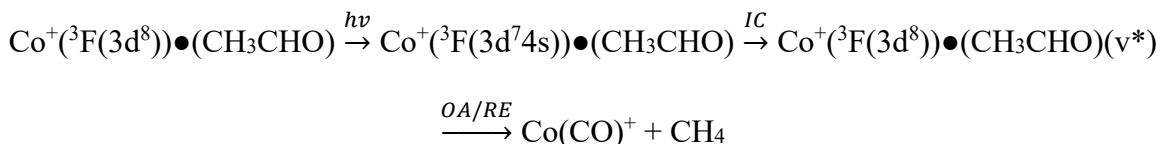
The SPIDRR technique forms the Co^+ and CH_3CHO reactants into a cluster under jet-cooled conditions. Spectroscopic studies of simpler Co^+ -ligand species have demonstrated the effectiveness of helium collisions in a supersonic expansion to reduce electronic, vibrational, and rotational internal energy within the precursor.^{48,49} In those studies, similar laser-driven helium expansions formed these simpler species in the lowest spin-orbit component of the vibrationless ground state as confirmed through spectroscopic measurements of resolved electronic transitions. However, for the larger systems studied here, the increased vibrational congestion, higher cluster bond strengths, and lowered symmetry render resolved spectroscopic measurements impossible. Still, the production of those simpler species suggests methods to produce these larger $\text{Co}(\text{organic})^+$ clusters with reduced internal energies. We have learned that it is easier to cool ionic species in a supersonic expansion, relative to neutrals, presumably due to their long-range, inverse r^4 attractive potential causing greater numbers of collisions with the bath gas. The system studied here, $\text{Co}(\text{CH}_3\text{CHO})^+$, approaches the terminal velocity of helium, $1.77 \times 10^3 \text{ ms}^{-1}$, in the molecular beam suggesting that the system is translationally cold. Moreover,

roughly 1-2% CH₄ gas is often doped into the carrier gas to provide additional collisions with the clusters as similar dopants have shown to further reduce vibrational excitation in a supersonic expanding population, presumably, by providing collision partners that can more readily accept the transfer of vibrational energy.⁵⁰ Replicate SPIDRR measurements are made where the collisional environment is modified by adding such collision partners to the bath gas. However, the same SPIDRR result is measured whether the expansion gas is pure helium or doped with CH₄. This suggests that the vibrational temperature of the CoCH₃CHO⁺ cluster in the supersonic beam is sufficiently low such that additional cooling collisions make a negligible impact to the precursor's thermal population following expansion. Together, these suggest that the ground electronic state of the precursor is preferentially formed and with reduced vibrational energy.

The electronic ground state of the precursor is formed from the combined ground states of the Co⁺ cation and acetaldehyde. The NIST⁵¹ database indicates the ground atomic state of the Co⁺ cation is ³F(3d⁸). Thus, the ground state of the cluster is Co⁺(³F(3d⁸))•(CH₃CHO). The electronic properties of each species within the cluster are primarily retained but slightly modified through interaction with the bonding partner. The Co⁺ cation has a rather dense low-lying electronic structure whereas CH₃CHO has only electronic transitions in the UV region. The Co⁺ cation is therefore the chromophore within the cluster, absorbing a visible photon, with excitation to atomic-centered electronic states. The likely transitions are spin-allowed with probable Co⁺(³F(3d⁷4s))•(CH₃CHO) and/or Co⁺(³P(3d⁸))•(CH₃CHO) excited states.⁵¹ These s ← d and d ← d transitions are parity forbidden in the isolated atom but are weakly allowed in the cluster with oscillator strengths calculated 0.00334 and 0.00387, respectively, using the CASSCF/CASPT2/SO-RASSI

method. Spin-forbidden transition to the lowest singlet state, $\text{Co}^+(\text{}^1\text{D}(3\text{d}^8))\bullet(\text{CH}_3\text{CHO})$, has an oscillator strength less than 1×10^{-5} and is not likely populated during photon absorption. It is noteworthy that spin-orbit coupling in the light transition metals is expected to be insufficient to allow direct absorption to the singlet surface and that the above conclusion may be surmised without computational support.

The $\text{Co}^+\text{-CH}_3\text{CHO}$ cluster bond strength can be approximated by the charge/dipole attractive potential and an assumed $\text{Co}^+\text{-CH}_3\text{CHO}$ bond length. A cluster bond length of 200 pm results in an electrostatic cluster bond energy of $\sim 15000 \text{ cm}^{-1}$. This value is a lower limit to the cluster bond strength since chemical interactions between the bonding partners are not considered. Thus, single photon absorption of quanta less than 15000 cm^{-1} is insufficient to break the $\text{Co}^+\text{-CH}_3\text{CHO}$ cluster bond indicating that the excited precursor cannot relax by simple cluster bond dissociation. Moreover, relaxation through emission is unlikely due to the low oscillator strengths of the electronic transitions. Rather, the system likely relaxes by coupling to nearby electronic states and depositing the energy of electronic excitation into high vibrational levels of a lower energy electronic state. Statistic or entropic arguments suggest that the probability of populating lower states should scale with the density of vibrational states on each lower energy surface at the AL's photon energy. The ratio of the density of vibrational states between the ground triplet and lowest singlet is $\sim 10^6$ at the photon energies used in this study. Thus, the probability of internally converting (IC) the photon's energy into vibrational energy on the ground triplet surface is significantly greater than populating an excited singlet through intersystem crossing (ISC). This suggests the following sequence is the most probable scenario to energize the triplet $\text{Co}^+\text{-CH}_3\text{CHO}$ cluster toward a dissociative rearrangement reaction:



Where v^* indicates vibrational excitation. Thus, the energy of electronic excitation is converted into vibrational energy in the ground state triplet which powers a reaction through an OA/RE sequence. We assume that the reaction kinetics measured in this study are due to the relatively slow nuclear motion attributed to the OA/RE steps following photo-activation.

Electrostatic arguments suggest that the entrance channel to this reaction has a relatively deep potential well attributed to the charge-dipole interaction within the $\text{Co}^+(\text{}^3\text{F}(3\text{d}^8))\bullet(\text{CH}_3\text{CHO})$ reactant complex (^3RC). Upon photo-activation, the Co^+ cation oxidatively adds to a covalent organic bond and then facilitates the reductive elimination of products. Products are eliminated from the product complex, PC. The PC structure, $\text{CH}_4\text{-Co}^+\text{-CO}$, has CH_4 and CO neutral species bound primarily through electrostatic forces to the Co^+ cation. Product elimination is simple dissociation of one of the electrostatic bonds in the PC. The PC structure resides in a deep potential well that results from such electrostatic attractions. The intermediate structures that occur between RC and PC generally have shallow potential energy wells separated by transition states. During cluster formation, it is possible to form $\text{Co}^+\text{CH}_3\text{CHO}$ isomers other than the RC. The structures of such isomers will be those of the intermediates, or minima, within the PES. The RC and PC are the most probable isomers formed in the molecular beam as these have structures associated with the deep wells along the PES. Photon absorption by either the RC or PC will result in the products given in Reactions 3.1 and 3.2, however, at significantly different rates. The RC undergoes an OA/RE sequence whereas the PC experiences simple bond

fissure without significant rearrangement. RRKM calculations predict that this electrostatic bond breakage in the PC occurs on the nanosecond time scale. Products formed this fast are formed in the OA, receive the full kinetic energy imparted by the OA, and are not transmitted through the sector. Thus, despite the possibility of forming the PC isomer during cluster formation, its consequent fast photo-induced dissociation does not add to measured fragment yields.

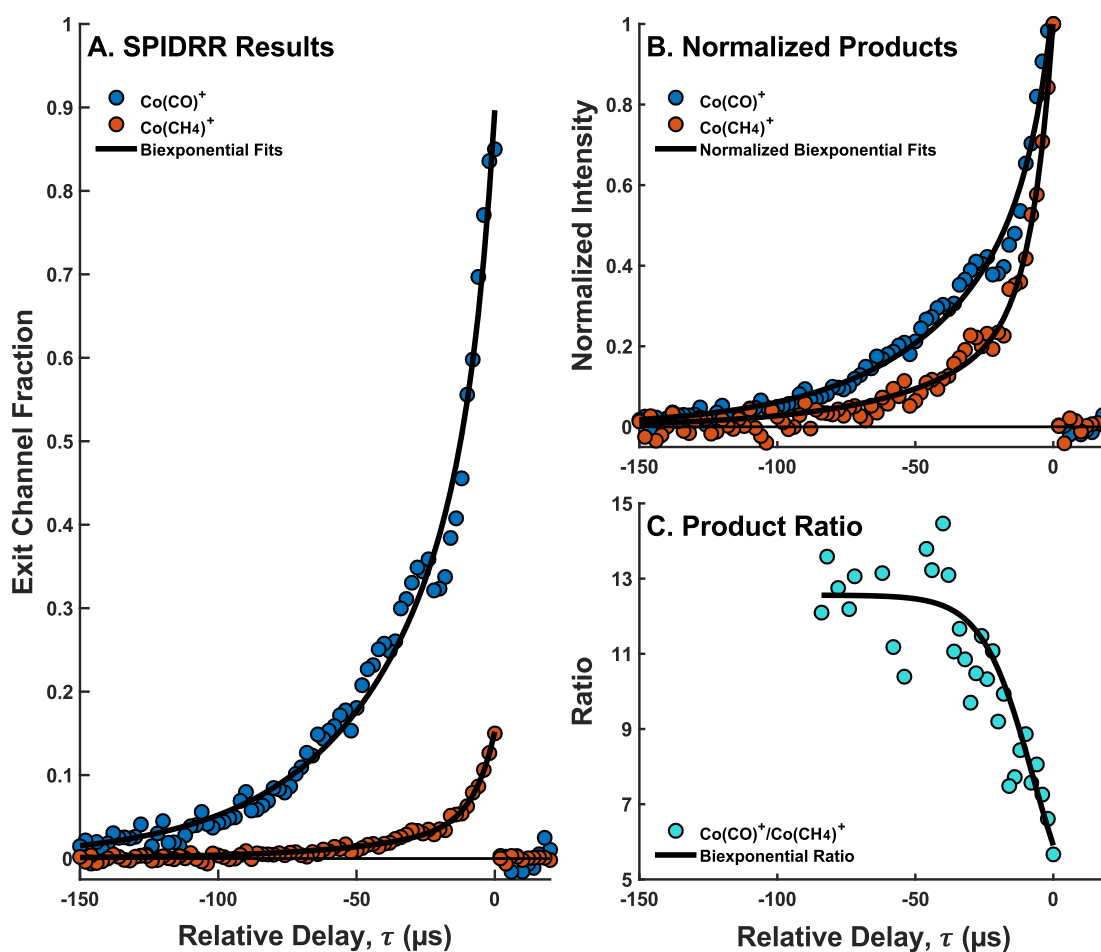


Figure 3.2. Results of the Co^+ mediated decomposition of CH_3CHO following precursor absorption of a 14700 cm^{-1} quantum. (A) SPIDRR results showing the measured relative intensities of the major and minor products. (B) The SPIDRR results of panel A normalized to one. Note that the biexponential temporal dependences of each product's formation is nonsuperimposable. (C) The ratio of product intensities measured in panel A truncated at $\tau = -80\text{ }\mu\text{s}$.

(b) *TSR Identification.*

Figure 3.2 presents SPIDRR results measured in the Co^+ mediated decomposition of CH_3CHO resulting from the absorption of a single photon at 14700 cm^{-1} . Multi-photon absorption of the precursor does not contribute to fragment yields as demonstrated by linear AL power dependent studies (Figure 3.3). Panel A of Figure 3.2 shows precursor dissociation into each product ion (Reactions 3.1 and 3.2) where the sum of the product ions is normalized to one at $\tau = 0\text{ }\mu\text{s}$. Effectively, the intensity of each datum point in Figure 3.2 results from averaged mass spectra as those presented in Figure 3.1, but measured at sequentially decreasing values of τ . Collectively, the data represent the temporal development of the $\text{Co}(\text{CO})^+$ and $\text{Co}(\text{CH}_4)^+$ product yields following $\text{Co}(\text{CH}_3\text{CHO})^+$ absorption of a 14700 cm^{-1} quantum. Activation of the precursor at this energy yields SPIDRR results that are biexponentially dependent on τ . SPIDRR results in Figure 3.2 are simultaneously fit to:

$$I_{\text{CoCO}^+} = A e^{k_f\tau} + B e^{k_s\tau} \text{ and } I_{\text{CoCH}_4^+} = C e^{k_f\tau} + D e^{k_s\tau} \quad \text{Equation 3.1}$$

using a residual minimization routine where I is intensity, k_f and k_s are rate constants determining the fast and slow biexponential components, and A - D are preexponential factors indicating quantities of the reacting population along the fast and slow pathways. The calculated curves (solid lines) in Panels A and B are the results of these simultaneous fits.

Table 3.1. Constants extracted from the fit of Equation 3.1 to the SPIDRR results in panel B of Figure 3.2.

	$\text{Co}(\text{CO})^+$	$\text{Co}(\text{CH}_4)^+$
$k_f (\mu\text{s}^{-1})$	0.13 ± 0.02	
A/C	0.35 ± 0.08	0.70 ± 0.06
$k_s (\mu\text{s}^{-1})$	0.024 ± 0.002	
B/D	0.70 ± 0.06	0.32 ± 0.05

Panel B of Figure 3.2 re-plots Panel A's data but with the intensity of each product ion normalized to one at $\tau = 0$. Equation 3.1 fit to the data in Panel B results in the constants provided in Table 3.1 reported at the lambda 95 confidence interval. The fast and slow components of the biexponential temporal dependence appear similar in each product channel but the normalized SPIDRR results are nonsuperimposable. This is interesting because the formation of each product ion occurs from the fast dissociation of the PC into CoCO^+ (P_1) and CoCH_4^+ (P_2). The formation rate of each product is,

$$\frac{d[P_1]}{dt} = k_{p1}[PC]_t, \quad \frac{d[P_2]}{dt} = k_{p2}[PC]_t \quad (\text{Equation 3.2})$$

with the ratio of product intensities constant in time:

$$\frac{d[P_1]/dt}{d[P_2]/dt} = \frac{k_{p1}}{k_{p2}} \quad (\text{Equation 3.3})$$

Thus, the normalized temporal dependence of each product's formation should be identical, rate-limited by transition barriers preceding PC, and yielding superimposed normalized SPIDRR results. This is clearly not the case observed in panel B of Figure 3.2. Moreover, the systematic deviation from this expected behavior cannot be attributed to signal to noise arguments as these measurements are within the temporal resolving power of this technique. It is apparent that the nonsuperimposable, biexponentially dependent SPIDRR results of Panel B in Figure 3.2 require a more complex mechanistic description than the single state scenario offered by Equations 3.2 and 3.3.

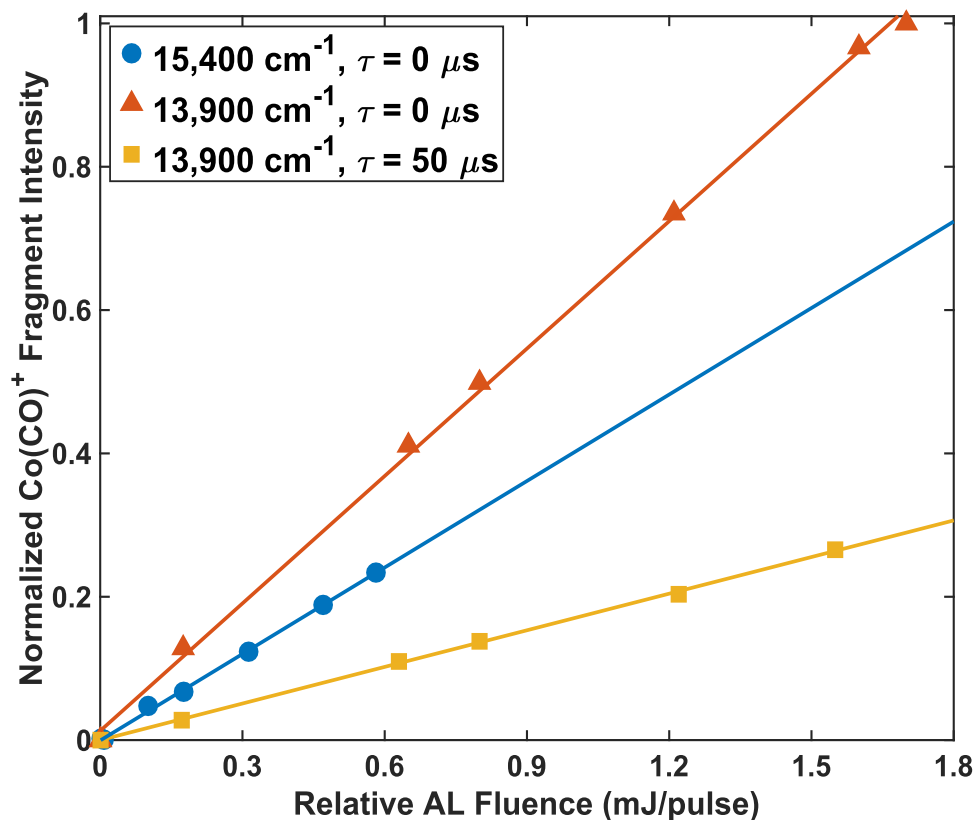


Figure 3.3. Product intensities are linearly dependent on laser fluence with zero intercept. Laser fluence was measured by directing an AL back reflection into a power meter with output recorded simultaneously with product intensity.

Panel C of Figure 3.2 offers insight into the mechanistic features required to describe these observations. Here, ratios of the measured product intensities, $I_{\text{CoCO}^+}/I_{\text{CoCH}_4^+}$, and their biexponential temporal dependences from Panel A are plotted vs. τ . This plot is truncated at $\tau = -80 \mu\text{s}$ because the signal to noise in the minor channel is too low to take product ratios confidently as τ is further decreased. A steadily increasing product ratio is observed as τ is decreased from zero to $-40 \mu\text{s}$. This is followed by the product ratio acquiring a constant value at τ is further decreased. Thus, the product branching ratio is initially time dependent only to become constant at long time. This can only happen if there are two PC structures, each formed at different rates, with each

dissociating into the same mass products but with different ratios. The product ratio is governed by the relative energy differences between each product and therefore, unique ratios require that each product pair is formed with unique relative exothermicities. This can only occur if product pairs have different spin multiplicities ($2S+1$) and exit on different spin hypersurfaces. Thus, a time dependent product branching ratio, as observed in Panel C of Figure 3.2, indicates that PC structures of different multiplicities are populated and dissociate to form products along unique spin hypersurfaces with different reaction rates.

Modification of Equations 3.2 to incorporate dissociation from a second PC yields:

$$\begin{aligned} \frac{d[P_1]}{dt} &= {}^{2S_1+1}k_{P1}[{}^{2S_1+1}PC] + {}^{2S_2+1}k_{P1}[{}^{2S_2+1}PC] \\ , \frac{d[P_2]}{dt} &= {}^{2S_1+1}k_{P2}[{}^{2S_1+1}PC] + {}^{2S_2+1}k_{P2}[{}^{2S_2+1}PC] \end{aligned} \quad (\text{Equation 3.4})$$

with the $d[P_1]/dt : d[P_2]/dt$ ratio given by:

$$\frac{d[P_1]/dt}{d[P_2]/dt} = \frac{{}^{2S_1+1}k_{P1}[{}^{2S_1+1}PC] + {}^{2S_2+1}k_{P1}[{}^{2S_2+1}PC]}{{}^{2S_1+1}k_{P2}[{}^{2S_1+1}PC] + {}^{2S_2+1}k_{P2}[{}^{2S_2+1}PC]} \quad (\text{Equation 3.5})$$

Where $d[P_1]/dt$ and $d[P_2]/dt$ represent the combined sampling of P_1 and P_2 products of all multiplicities, and S_1 and S_2 are the spin quantum numbers of the interacting hypersurfaces. The ratio of the two time differential expressions predicts time dependent exit channel fractioning as observed.

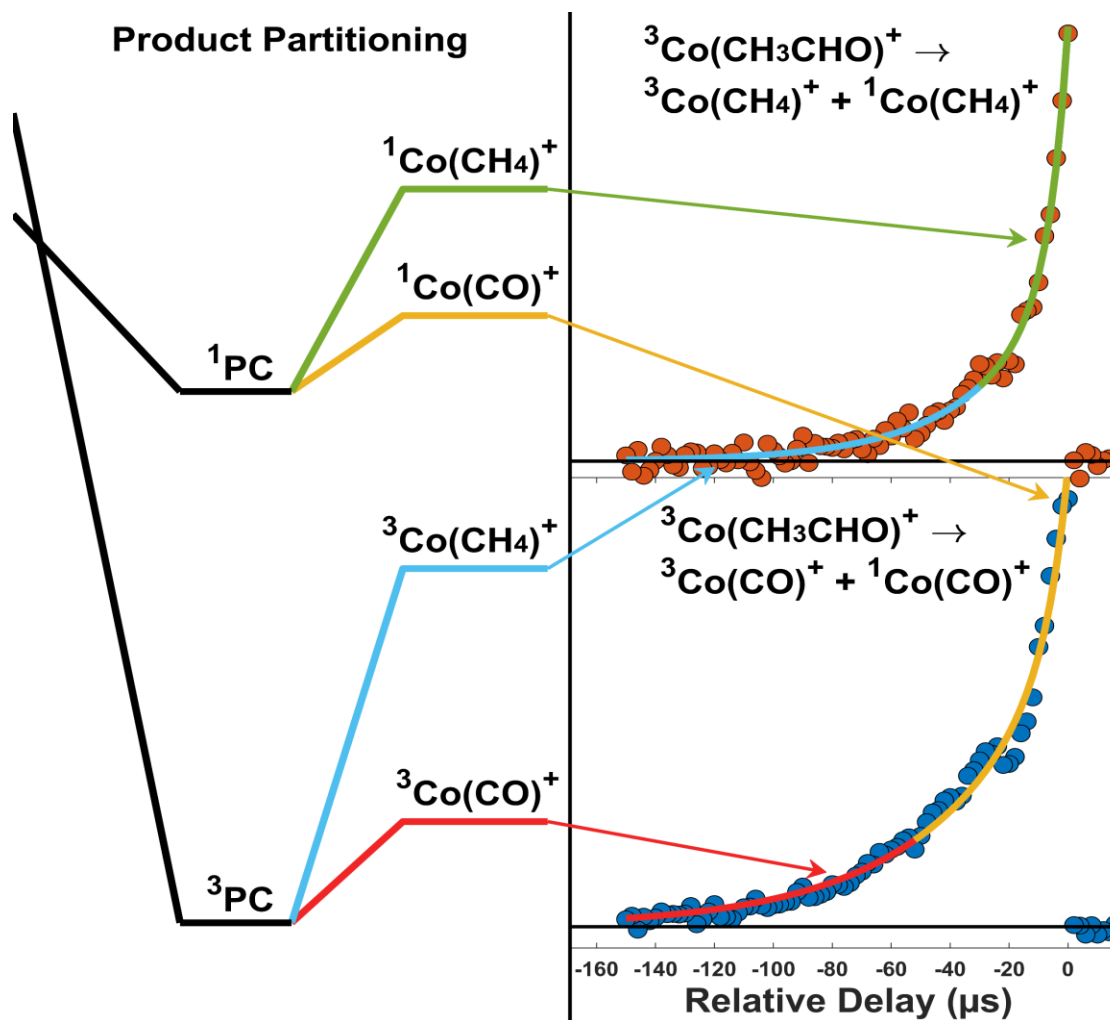


Figure 3.4. The form of the SPIDRR result indicates features of the reaction PES. Right panel: Normalized SPIDRR results following $\text{Co}(\text{CH}_3\text{CHO})^+$ absorption of a 14700 cm^{-1} quantum. Left panel: PES features that account for the observations in the right panel.

Figure 3.4 demonstrates the relationship between our measurements and the PES. The left panel of Figure 3.4 is a representative diagram demonstrating the features that must be present in the PES to account for the SPIDRR measurements in the right panel. The biexponential curve plotted through the measurements is color-coded to correlate PES features with the observations made in this study. The constants extracted from the simultaneous fits of the SPIDRR results in Figure 3.2 and provided in Table 3.1 can now

be interpreted to provide molecular-level details of this decomposition reaction. The fast (green and yellow) and slow (blue and red) components of each biexponential temporal response are associated with travel along a single spin hypersurface. The measured rate constants are $k_f = (0.13 \pm 0.02) \mu\text{s}^{-1}$ and $k_s = (0.024 \pm 0.002) \mu\text{s}^{-1}$, indicating that rate-limiting travel along one surface is ~ 5.5 x faster than travel along the other. The A and C preexponential factors from Equation 3.1 determine the relative population exiting on the singlet surface as shown by the green and yellow curves in Figure 3.4. Correspondingly, the B and D preexponential factors represent the triplet exit channel ratio indicated by the blue and red curves of Figure 3.4. The ratio $(A+C) / (B+D) \approx 1$, indicates that an equal population exits on each spin hypersurface. The low oscillator strength of spin forbidden transitions indicates that direct absorption to other spin states at the encounter complex cannot account for this high observed probability. Nor can this large spin inverting population be accounted for by ISC, as described above. The only remaining mechanism to transfer large populations between spin hypersurfaces is SI and its consequent TSR. Therefore, the measurement of a temporal dependent product branching ratio, as seen in Panel C of Figure 3.2, immediately indicates SI and strongly implies TSR as a mechanistic feature in a chemical reaction.

In the specific case of the Co^+ mediated decomposition of CH_3CHO , the electronic ground state at the RC is a triplet, ^3RC . The triplet must spin invert along the reaction coordinate bifurcating with nearly equal populations progressing along each hypersurface. Assuming that the description of the $\text{Co}(\text{CH}_3\text{CHO})^+$ system is typical, in the sense that the inverting state is of lower multiplicity and the population inverts to avoid high barriers on the original surface, then $S_1 = 0$ and $S_2 = 1$ in Equation 3.5. There exists a competition in

this system between adiabatic reaction along the triplet surface with the nonadiabatic reaction progression along the singlet surface populated through SI in a two-state reactive scenario. Moreover, the ^1PC structure forms at a faster rate than the ^3PC consistent with barrier avoidance along the triplet hypersurface.

Conclusion

The measurement of time dependent product branching ratios is an experimental kinetic signature indicating TSR. This was measured using the SPIDRR technique but should be extendable to other experimental methods with similar temporal resolution. Transition oscillator strengths and RRKM styled vibrational level density calculations were the only theory used to support the presence of TSR within this metal mediated reaction. However, the rather low spin-orbit coupling of the light transition metals and simple entropic arguments could be leveraged to support such claims even in the absence of these supporting calculations. Thus, such a measurement represents a stand-alone experimental determination of a TSR kinetic signature.

It is noteworthy that nonsuperimposable normalized SPIDRR results, such as those in Panel B of Figure 3.2, is a straightforward measurement using the SPIDRR technique. Outside of signal averaging, very little processing of the temporally dependent results is required to assess TSRs presence in the measured metal mediated chemistry. We look forward to continued studies of deuterium labeled systems as such measurements may further assess the viability of measured H-KIE values as another experimental kinetic signature of TSR.⁴⁴

Conflicts of interest

There are no conflicts of interests to declare.

Acknowledgments

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CHAPTER FOUR

Two State Reactivity (TSR) and Hydrogen Tunneling Reaction Kinetics Measured in the Co^+ Mediated Decomposition of CH_3CHO

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Introduction

Metal catalyzed chemical transformations are important to research laboratories, industrial processes, and biochemistry, and are so pervasive that they influence all aspects of life. Transition metals are particularly useful as these both accept and donate electrons, allowing reacting populations to explore alternate oxidative addition / reductive elimination (OA/RE) reaction pathways. It is interesting that industrially catalyzed processes,^{1,2} as well as organic synthetic laboratories,³ often use the platinum group elements as the active site in various processes, whereas bio-catalysts have capitalized on earth-abundant transition metals to perform their remarkable chemistry.⁴⁻⁶ Indeed, synthesizing biomimetic complexes that utilize earth abundant 3d transition metals as alternatives to precious metal catalysis is of ongoing interest.⁷⁻¹¹

Understanding rate-limiting nuclear motions in OA/RE, oxygen atom transfer, or metal catalyzed rebound reactions reveal key transition state structures that occur during chemical transformations. Synthesizing a mimetic compound which forces substrates into such transition structures clearly reduces energy requirements, as introduced by Pauling,¹² and is a common goal in catalytic kinetic studies. However, reaction dynamics also influence catalytic ability, and while mechanistic studies appear more prevalent,

establishing the conditions where reaction dynamics can be logically inferred is a desired experimental feature. Here we demonstrate that two-state reactivity (TSR)^{13,14} and hydrogen tunneling are nonadiabatic dynamic features controlling the low energy conversion of CH₃CHO into CO + CH₄ mediated by the Co⁺ cation.

Single state reactivity, SSR, occurs when a reacting population remains fixed on a single adiabatic potential energy surface (PES). Likewise, in TSR, a population is energized with initial reaction progression along the ground surface. However, the reacting population transitions to another electronic surface, avoiding high barriers on the original PES, allowing the reaction to progress faster and with lower energy requirements. Generally, in a TSR scenario, the ground surface is of a higher multiplicity than the excited surface. Transition barrier magnitudes are influenced by electron spin and the corresponding covalent bonding required to preserve the multiplicity, resulting in different barrier heights along each surface.¹³

Recently, a definitive experimental kinetic signature was identified as a temporally dependent product branching fraction in the Co⁺ mediated decay of CH₃CHO.¹⁵ This was accomplished using the single photon initiated dissociative rearrangement reaction (SPIDRR) technique which selectively measures the temporal dependence of product formation in a mass spectrometer. We continue this study and present the energy dependent reaction kinetics of the Co⁺ mediated decay of CH₃CHO, a system controlled by the nonadiabatic influences of TSR and hydrogen tunneling at low internal energies. Here, we highlight the changing TSR/SSR competition with energy. Moreover, we present multi-reference calculations of the two reaction pathways where minimum energy crossing points (MECPs) have been determined.

Procedure

(a) Experimental

The SPIDRR technique and our ability to detect TSR's kinetic signature has been described previously.¹⁶ Here, we reinforce how our measurements suggest kinetic models which in turn imply reaction mechanism. We therefore highlight the relationship between our measurements and deterministic kinetics while only providing a short description of the SPIDRR technique.

SPIDRR studies are conducted in a 120 L high-vacuum source chamber orthogonally coupled to a ~ 2 m time of flight mass spectrometer (TOFMS). A pulsed valve bolted onto a laser vaporization (LAVA) source is centrally located in the source chamber. High-pressure helium gas, doped with acetaldehyde's vapor pressure, is pulsed through a plume of laser vaporized cobalt. Collisions between Co^+ and CH_3CHO form the reactant complex, $\text{RC} = \text{Co}(\text{CH}_3\text{CHO})^+$, which is cooled through collisions with helium gas during supersonic expansion. Similar helium expansions have generated electronically and vibrationally cold clusters as demonstrated through electronic spectroscopy.

Species created in the LAVA source travel at the terminal velocity of helium to arrive at a pulsed orthogonal accelerator in a time of flight mass spectrometer (TOFMS). Cations are extracted by voltage pulse and directed through the TOMS toward the entrance of a hemispherical sector. The potential difference across the sector halves transmits ions of a specific kinetic energy to a Chevron microchannel plate detector which records fragment intensity.

Clusters within the molecular beam are activated by pulsed laser photon absorption. The activation laser (AL) is a Nd^{3+} YAG pumped dye laser with 10 ns pulsed output at a

12.5 ns timing resolution. Photon absorption by the $\text{Co}(\text{CH}_3\text{CHO})^+$ cluster occurs along the expansion axis at various values of τ . τ is defined as the time delay between pulsed cation extraction and the AL photon absorption, with zero τ representing photon absorption simultaneous with acceleration into the TOFMS. All precursor clusters that dissociate after extraction, but before entering the sector (defined as the free flight time within the TOFMS), form fragment ions that have the same velocity as the accelerated precursor but with a fraction of the kinetic energy. Thus, time gating over the precursor arrival time, while maintaining a sector potential difference that transmits a specific fragment ion, provides the precursor's yield into that product channel while guaranteeing that the fragment results from a specific precursor.

Reaction kinetics are obtained by measuring the charged product's intensity while scanning the pulsed AL to times prior to the orthogonal extraction voltage pulse. Unimolecular decay begins at the time of photon absorption resulting in a portion of the excited population decaying within the l_{rf} travel time to the extraction region of the TOFMS. Precursors that dissociate within the TOF's free flight time form products with intensity plotted vs. τ . All negative values of τ indicate some degree of precursor survival whereas all positive values of τ yield zero fragment intensity since the AL fires after ion extraction. The collection of fragment intensities plotted vs. τ values is considered the SPIDRR result. Given that the precursor ions are supersonically expanded into vacuum,

the absorbed quantum of photon energy approximates the internal energy of the clusters prior to dissociation.

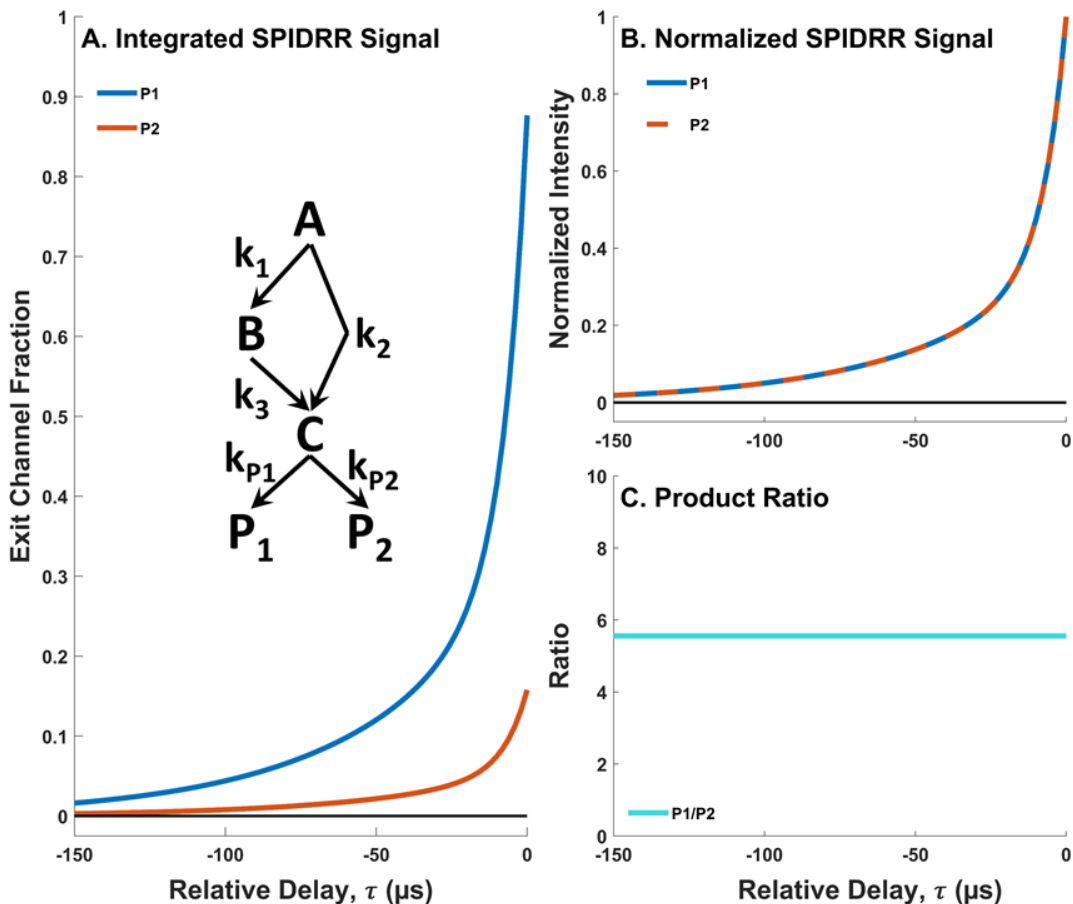


Figure 4.1. Panel A shows simulated SPIDRR results based on rate equations from a deterministic interpretation of the imbedded model. Here, the decay of species A and B both influence the reaction rate resulting in biexponential SPIDRR results. Panel B shows the normalized SPIDRR results from panel A. Panel C shows the time dependence of the product P1/ P2 ratio.

The form of a SPIDRR result is interpreted in terms of chemical kinetic rate laws from a unimolecular reaction mechanism. Each species shown in the model in Figure 4.1 has an associated temporal dependence. The SPIDRR technique collects product ions formed throughout the TOF free flight. We define $\alpha = 3 \mu\text{s}$ as the time required for

CoCH₃CHO⁺ precursors to exit the OA (enter the TOF free flight), $\Delta = 37 \mu\text{s}$ as the time required to enter the sector (leave the TOF free flight), and consider only *lrl*. The SPIDRR signal $S(\tau)$ is the collection of fragments produced over the TOF free flight and is expressed as a definite integral. The SPIDRR signal for product 1, $S_{P1}(\tau)$, is:

$$S_{P1}(\tau) = \int_{(\tau+\alpha)}^{(\tau+\alpha+\Delta)} \frac{d[P1]}{dt} dt = \int_{(\tau+\alpha)}^{(\tau+\alpha+\Delta)} k_{P1}[C] dt \quad \text{Equation 4.1}$$

which evaluates to:

$$S_{P1}(\tau) = A_0 k_{P1} \left[\frac{k_2}{(k_{P1P2} - k_{12})} \left(\frac{\gamma_1}{k_{12}} e^{-k_{12}\tau} + \frac{\gamma_2}{k_{P1P2}} e^{-k_{P1P2}\tau} \right) + \frac{k_1 k_3}{(k_3 - k_{12})} \left[\frac{1}{k_{P1P2} - k_{12}} \left(\frac{\gamma_1}{k_{12}} e^{-k_{12}\tau} + \frac{\gamma_2}{k_{P1P2}} e^{-k_{P1P2}\tau} \right) - \frac{1}{k_{P1P2} - k_3} \left(\frac{\gamma_3}{k_3} e^{-k_3\tau} + \frac{\gamma_2}{k_{P1P2}} e^{-k_{P1P2}\tau} \right) \right] \right] \quad \text{Equation 4.2}$$

where A_0 is the number of photo-excited precursors and k represents the rate constants associated with the various reaction steps in the model of Figure 4.1. The values k_{12} and k_{P1P2} are the summed rate constants, $(k_1 + k_2)$ and $(k_{P1} + k_{P2})$, respectively. The three γ constants in Equation 4.2 are:

$$\gamma_1 = (1 - e^{-k_{12}\Delta})(e^{-k_{12}\alpha}) \quad \text{Equation 4.3}$$

$$\gamma_2 = (e^{-k_{P1P2}\Delta} - 1)(e^{-k_{P1P2}\alpha}) \quad \text{Equation 4.4}$$

$$\gamma_3 = (1 - e^{-k_3\Delta})(e^{-k_3\alpha}) \quad \text{Equation 4.5}$$

Often in SPIDRR studies, intermediate **C** in Figure 4.1 is the product complex, PC, a structure composed of fully formed neutral products electrostatically bound to a metal cation. Simple fissure of an electrostatic bond is a fast mechanistic step since little rearrangement is required for product formation. Thus, rate constants k_{P1} and k_{P2} are significantly larger than rate constants k_1 , k_2 , and k_3 . Under this condition, γ_2 in Equation

4.4 becomes negligibly small and if k_{12} and k_3 have comparable magnitudes, Equation 4.2 reduces to a biexponential function of τ , as seen in $S_{P1}(\tau)$ in Panel A of Figure 4.1. Indeed, assuming forward reaction progression, the model in Figure 4.1 is the simplest to yield a biexponential temporal response.

A_0k_{P2} simply replaces A_0k_{P1} in Equation 4.2 to form $S_{P2}(\tau)$. Thus, the temporal dependence of each species is identical resulting in the $S_{P1}(\tau) / S_{P2}(\tau)$ ratio equal to the k_{P1} / k_{P2} fraction at all time, as seen in Panel C of Figure 4.1. Plotting the normalized $S_{P1}(\tau)$ and $S_{P2}(\tau)$ responses yields superimposed SPIDRR results as seen in Panel B. This treatment is completely general in that the results of panels B and C are unchanged regardless of the rate constant values used in the model, and the complexity of the reaction prior to dissociation of the PC.

(b) Theory

Density functional theory (DFT) was used to locate stationary points on the $\text{Co}(\text{CH}_3\text{CHO})^+$ ground state triplet and first excited singlet potential energy surfaces at the (u)PBE0/aug-cc-pVTZ level of theory. Calculated stationary points were characterized via harmonic analysis. Single point energy corrections to the DFT structures were then performed at the CASSCF/CASPT2 level of theory.

In addition, minimum energy crossing points (MECPs) between the triplet and singlet PESs were also computed at the (u)PBE0/aug-cc-pVTZ level of theory. Single point energy corrections to MECP structures were then performed using SA-CASSCF/CASPT2 with equal weight ascribed to the ground state triplet and first excited singlet states, and with the energy of the MECP structures being reported as the average

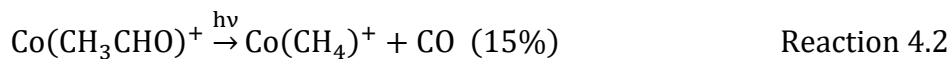
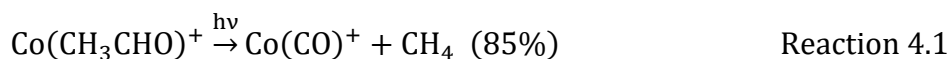
energy of these states. Spin orbit coupling at the MECPs was evaluated using the SA-CASSCF orbitals and the Breit-Pauli Hamiltonian.

DFT calculations of the triplet and singlet PESs were performed using the Gaussian16 electronic structure program.¹⁷ MECP optimization and spin orbit coupling calculations were performed using the GAMESS electronic structure program.¹⁸ CASSCF/CASPT2 calculations were performed using the Orca electronic structure program.¹⁹ Molecular structures and orbital visualization were performed with Gaussview 6 and Avogadro.²⁰⁻²²

Results and Discussion

(a) Two-State Reactivity and Kinetic Model

The peak area of each product in a fragment mass spectrum provides the product's relative intensity at a specific value of τ in a chemical reaction. Two products have been identified in the Co^+ mediated decomposition of CH_3CHO with 85% and 15% yields at $\tau = 0$:



$\text{Co}(\text{CH}_3\text{CHO})^+$ is the reactant complex, RC, of Reactions 4.1 and 4.2 and has triplet multiplicity. It is formed from the combined ground states of the $3d^8\ ^3\text{F}$ atomic Co^+ cation and the singlet state of acetaldehyde. The Co^+ cation is the chromophore and photon absorption likely prepares a metastable triplet excited state with $3d^74s\ ^3\text{F}$ or $3d^8\ ^3\text{P}$ character. The prepared state's energy is below the adiabatic bond energy of the $\text{Co}^+ + \text{CH}_3\text{CHO}$ separated reactants making relaxation by simple cluster bond breakage

impossible. Moreover, emission from the excited state is forbidden. Rather, entropic arguments suggest that relaxation of the prepared RC's metastable state is likely through internal conversion of the photon's quantum into ground state vibrational levels at a sufficiently high energy to power Reactions 4.1 and 4.2 to products.

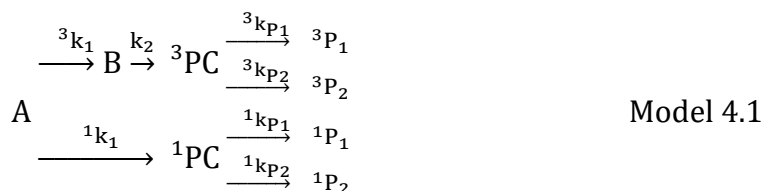
Figure 4.2 provides SPIDRR results obtained for the major CoCO^+ and minor CoCH_4^+ products in the Co^+ mediated decomposition of CH_3CHO following absorption of a $14,700\text{ cm}^{-1}$ photon. Panel A of Figure 4.2 plots CoCO^+ and CoCH_4^+ SPIDRR results where the sum of the product intensities is normalized to one at $\tau = 0\text{ }\mu\text{s}$. Panel B plots SPIDRR results for both the major and minor product channels, each normalized to one. Panel C provides the $\text{CoCO}^+ / \text{Co}(\text{CH}_4)^+$ intensity ratio from Panel A plotted from $\tau = 0$ to $-80\text{ }\mu\text{s}$. The signal to noise in the minor channel at τ less than $-80\text{ }\mu\text{s}$ is too low to confidently take ratios.

There are clear similarities and differences when comparing Figures 4.1 and 4.2. In both, products are formed with a biexponential temporal dependence suggesting that the mechanism followed by the $\text{Co}(\text{CH}_3\text{CHO})^+$ RC is likely similar to the kinetic model in Figure 4.1. However, the normalized SPIDRR results do not superimpose in panel B nor is Panel C's product ratio constant in time. At $\tau = 0$ the $\text{CoCO}^+ / \text{Co}(\text{CH}_4)^+$ product ratio is $85/15 = \sim 5.7$. This fraction initially increases as τ decreases only to assume a constant limiting value of ~ 12.5 as seen in panel C. These observations are systematic in that SPIDRR measurements made at other activating photon energies deviate from Figure 4.1 in the same way- the temporal dependence of the product ratio increases with decreasing τ acquiring a constant value at long $|\tau|$. Figure 4.1's kinetic model is incapable of describing the measured reaction kinetics.

The nonsuperimposable normalized SPIDRR results in Panel B and the time dependent product branching fraction of Panel C in Figure 4.2 can only be accounted if two separate PCs are competitively formed at different rates. Moreover, each PC must dissociate into the same mass products but with different relative intensities. This only occurs if each PC has a different multiplicity and dissociates into products with different relative exothermicities. Since the reaction initiates on the ground triplet surface, the results in Panels B and C indicate spin inversion (SI) has occurred during the reaction. For atomic mediated reactions that initiate on the ground electronic surface with intermediate spin-orbit coupling, the nonsuperimposable SPIDRR results of panel B and the temporally dependent product branching ratio of Panel C is TSR's kinetic signature as previously reported.

We indicate multiplicity as a left superscript and label the ground hypersurface as ^3PES . Minima and maxima energies along the potential energy surface are influenced by how multiplicity effects bonding. Nuclear motion in this reaction initiates by the addition of the Co^+ cation to an acetaldehyde bond. Maintaining triplet multiplicity requires forming a covalent two-electron bond where the electrons have parallel spins. Such bonding is unfavorable as electrons are localized on each fragment and the resulting lack of electron delocalization causes higher energy structures for all covalently bound species on the ^3PES . Covalent bonding in structures along the ^1PES features traditional two-electron bonds formed by anti-parallel spin electrons. This allows electrons to delocalize in a bonding molecular orbital (MO) lowering the structure's energy. This suggests that the TSR scenario is for the reacting population to spin invert from the ^3PES to the ^1PES which allows population to circumvent the higher transition barriers on the triplet surface.

The kinetic model that describes these nuclear motions is a modification of Figure 4.1's model and provided in Model 4.1.



Here, the reacting population bifurcates early in the reaction. This bifurcation is through a triplet/singlet SI junction with reaction competition given by the ${}^1k_1 / {}^3k_1$ ratio. The population remaining on the triplet hypersurface must overcome a subsequent rate-limiting barrier to form 3PC . The inverted population circumvents such barriers, forming 1PC . Each PC structure contains neutral CO and CH₄ bound to a Co⁺ cation of either singlet or triplet multiplicity. The PC's lifetime is fleeting since little rearrangement is required to form the observed products. Pairs of same-mass products with different multiplicities are formed at different rates but detected simultaneously causing the observed biexponential temporal dependence. Each same-mass product is formed with different relative intensities since the exothermicity of spin product pairs is different with respect to 3PC and 1PC . This causes the temporal dependence in the product ratio observed in Panel C of Figure 4.2.

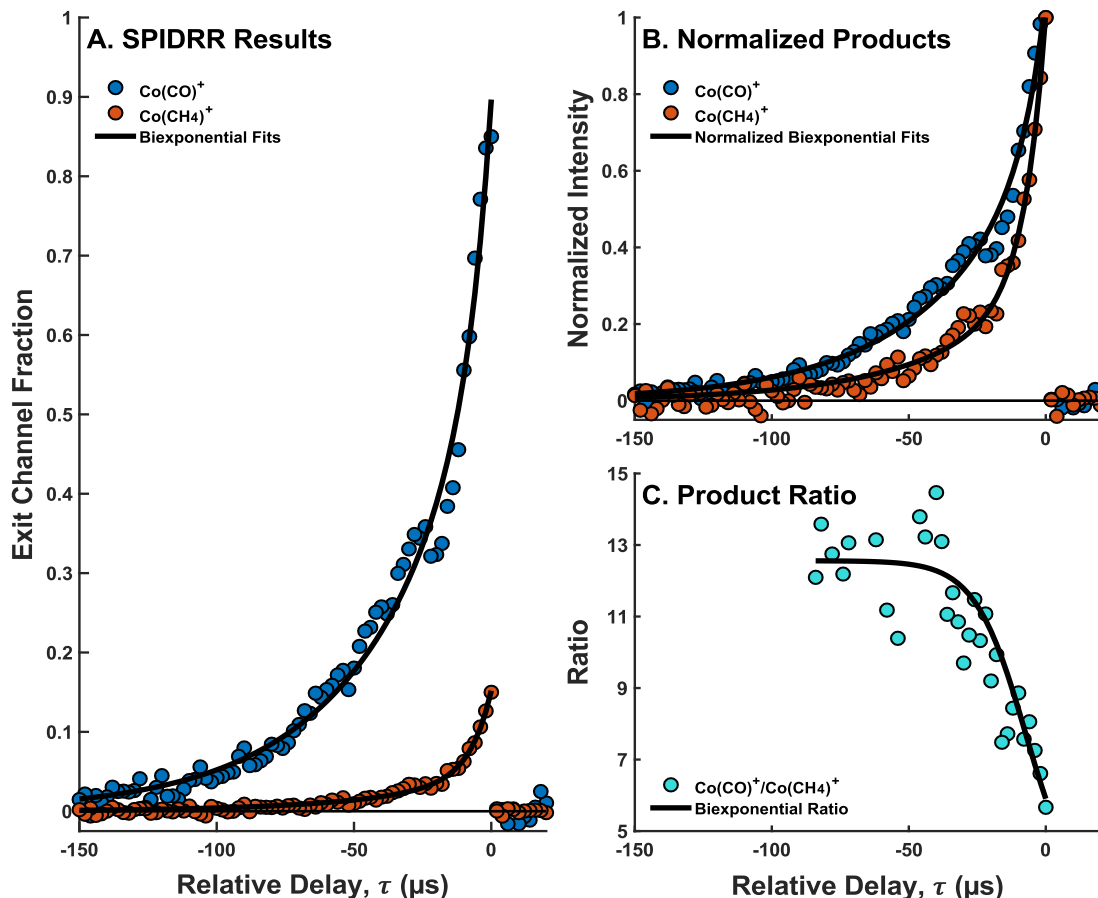


Figure 4.2. Results of the Co^+ mediated decomposition of CH_3CHO following precursor absorption of a 14700 cm^{-1} quantum. (A) SPIDRR results showing the measured relative intensities of the major and minor products. (B) The SPIDRR results of panel A normalized to one. Note that the biexponential temporal dependences of each product's formation is nonsuperimposable. (C) The ratio of product intensities measured in panel A but truncated at $\tau = -80\text{ }\mu\text{s}$.

Model 4.1 is exactly solvable to yield integrated rate equations similar to Equation 4.2. The adjustable parameters in the model are the rate constants k_1 and k_2 , the ratios $^3k_{P1} / ^3k_{P2}$ and $^1k_{P1} / ^1k_{P2}$, as well as the initial photo-excited population. The integrated rate equations are simultaneously fit to the CoCO^+ and $\text{Co}(\text{CH}_4)^+$ SPIDRR results in a squared residual minimization routine. Simultaneous fitting significantly constrains the model yielding rate constants with narrow confidence intervals (Table 4.1). The resulting fits are the solid curves through the data points in each panel of Figure 4.2.

(b) Reaction Mechanism, Energetics, and Dynamics Suggested by the Kinetic Model

Model 4.1 is the simplest kinetic model that captures the salient features in the measured reaction kinetics. The kinetic model indicates that the $\text{Co}(\text{CH}_3\text{CHO})^+$ decay mechanism contains three structures that bifurcate the reacting population. Spin inversion is one of those bifurcations occurring early in the reaction. The remaining two are PCs with structures $\text{CH}_4 - \text{Co}^+ - \text{CO}$ where each species is differentiated by the Co^+ atomic term. The model also indicates that the decay of two structures in the reaction mechanism rate limits product formation. The reaction mechanism is likely an OA/RE sequence and, assuming that the reaction can be reduced to these steps, places SI at the oxidative addition side of the PES.

We believe that the ground and interacting excited hypersurfaces are of triplet and singlet multiplicity, respectively. The lowest energy Co^+ singlet state is $3d^8\ ^1\text{D}_2$ at 11651.28 cm^{-1} above the ground $3d^8\ ^3\text{F}_4$ atomic state.²³ The ^1RC is therefore formed from this $^1\text{D Co}^+$ cation bound to the ground singlet state of acetaldehyde. The ^1RC potential well may be deeper than ^3RC as suggested by resolved electronic spectroscopy of simpler systems. This suggests a higher probability of triplet / singlet interaction given their energetic separation at the RC is likely less than the 11651.28 cm^{-1} difference at the separated reactant limit.²³

Table 4.1. Rate constants extracted from a deterministic kinetic model based on Model 4.1. Energies are in cm^{-1} and rate constants are in μs^{-1} . Uncertainties are calculated at the 95% confidence interval.

AL Photon Energy (cm^{-1})	3k_1	1k_1	$^1k_1/^3k_1$	$^1k_{\text{RL}} = (^1k_1 + ^3k_1)$	$^3k_{\text{RL}} (\mu\text{s}^{-1})$	$^3\text{Co}(\text{CO})^+ / ^3\text{Co}(\text{CH}_4)^+$	$^1\text{Co}(\text{CO})^+ / ^1\text{Co}(\text{CH}_4)^+$
16000	0.2 ± 0.2	0.7 ± 0.5	4 ± 4	0.9 ± 0.5	0.27 ± 0.06	NA	NA
15700	0.1 ± 0.2	0.3 ± 0.1	2 ± 3	0.4 ± 0.2	0.16 ± 0.04	NA	NA
15600	0.08 ± 0.03	0.27 ± 0.05	3 ± 1	0.35 ± 0.06	0.08 ± 0.01	NA	NA
15500	0.07 ± 0.05	0.19 ± 0.03	3 ± 2	0.26 ± 0.06	0.085 ± 0.016	NA	NA
15400	0.09 ± 0.08	0.20 ± 0.04	2 ± 2	0.29 ± 0.09	0.10 ± 0.02	NA	NA
15200	0.047 ± 0.006	0.076 ± 0.005	1.6 ± 0.2	0.124 ± 0.008	0.022 ± 0.001	9 ± 2	5 ± 1
14900	0.072 ± 0.006	0.102 ± 0.007	1.4 ± 0.2	0.174 ± 0.008	0.0245 ± 0.0008	8 ± 1	5 ± 1
14700	0.067 ± 0.007	0.084 ± 0.005	1.2 ± 0.1	0.150 ± 0.008	0.0274 ± 0.0008	12 ± 1	5 ± 0.5
14500	0.10 ± 0.03	0.074 ± 0.016	0.8 ± 0.3	0.17 ± 0.03	0.024 ± 0.001	7 ± 1	5 ± 1
14200	0.050 ± 0.009	0.073 ± 0.009	1.5 ± 0.3	0.12 ± 0.01	0.017 ± 0.002	7 ± 2	5 ± 1
13900	0.06 ± 0.01	0.046 ± 0.006	0.7 ± 0.2	0.11 ± 0.01	0.015 ± 0.008	11 ± 2	3.8 ± 0.7

Photon absorption ultimately forms vibrationally excited ^3RC states following the internal conversion of the photon's quantum. SI junctions, transition barriers (neglecting tunneling), and all product channels must be exothermic with respect to the prepared ^3RC states with its consequent internal energy approximately equal to the absorbed photon's energy. The SI junction appears to be on the entrance side of ^3PES . The reductive elimination is the aldehyde hydrogen transfer to form CH_4 and CO neutral products. This must be rate-limiting for the triplet reaction else the observed SPIDRR results would be

single exponentially dependent on time. The transition to ^1PES circumvents the higher triplet barrier suggesting that the fast portion of the biexponential decay is caused by formation of excited singlet products. The slow portion is due to the continuation of the reacting population's progression on the ^3PES to form ground state products.

The kinetic model is only sensitive to rate-limiting transformations and may only suggest the corresponding mechanistic structures responsible for such rate-determining behavior. For example, the model guarantees the existence of one rate controlling triplet maximum following SI but cannot preclude the possibility of several transition maxima. Nor can the model rule out the possibility of a rate-limiting barrier following SI on ^1PES . Although these additional considerations would change some interpretations of our observations, the most important aspects of this study are rate-determining behaviors and the spin inverting population ratio. These properties are insensitive to such subtleties and we therefore progress with Model 4.1 realizing that modifications to our interpretation are possible.

Thus, a likely mechanism begins with an activated ^3RC . An SI junction occurs either on route to the Co^+ C-C bond activation of acetaldehyde or shortly thereafter. The portion of the reacting population that transitions onto ^1PES is given by the $^1k_1 / ^3k_1$ ratio. The population remaining on ^3PES will transition the rate limiting aldehyde hydrogen transfer barrier, given by $^3k_{\text{RL}}$, to form ^3PC , $\text{CH}_4 - \text{Co}^+ (3d^8, ^3\text{F}) - \text{CO}$. Fast decay of ^3PC forms the observed products with triplet multiplicity. The SI junction may be at an energy greater than any remaining barriers on the ^1PES allowing the spin inverted population to travel unhindered to ^1PC , $\text{CH}_4 - \text{Co}^+ (3d^8, ^1\text{D}) - \text{CO}$. Formation of the singlet products is rate limited by the decay of ^3RC with $^1k_{\text{RL}}$ equal to $^1k_1 + ^3k_1$. Each PC structure rapidly

dissociates into the products of Reactions 4.1 and 4.2, albeit with different multiplicities and relative exothermicities.

(c) Reaction Energy Dependence and Hydrogen Tunneling

SPIDRR results were acquired over a range of AL photon energies and Figure 4.3 presents the CoCO^+ product channel at these various energies. The integrated rate equations used to model the SPIDRR results in Figure 4.2 were simultaneously fit, when possible, to each CoCO^+ and CoCH_4^+ SPIDRR result measured at the AL photon energy. This yielded a set of optimized rate constants that are reported in Table 4.1 at the 95% confidence interval and were used to generate the solid curves plotted through the observations in each panel of Figure 4.3. The intensity of SPIDRR results in this study decreased as the photon energy increased. Thus, signal to noise in the minor channel at AL energies greater than 15400 cm^{-1} was too low to confidently measure the time dependence of CoCH_4^+ product formation. In these cases, the model was fit only to the CoCO^+ SPIDRR result, removing constraints, and widening confidence intervals.

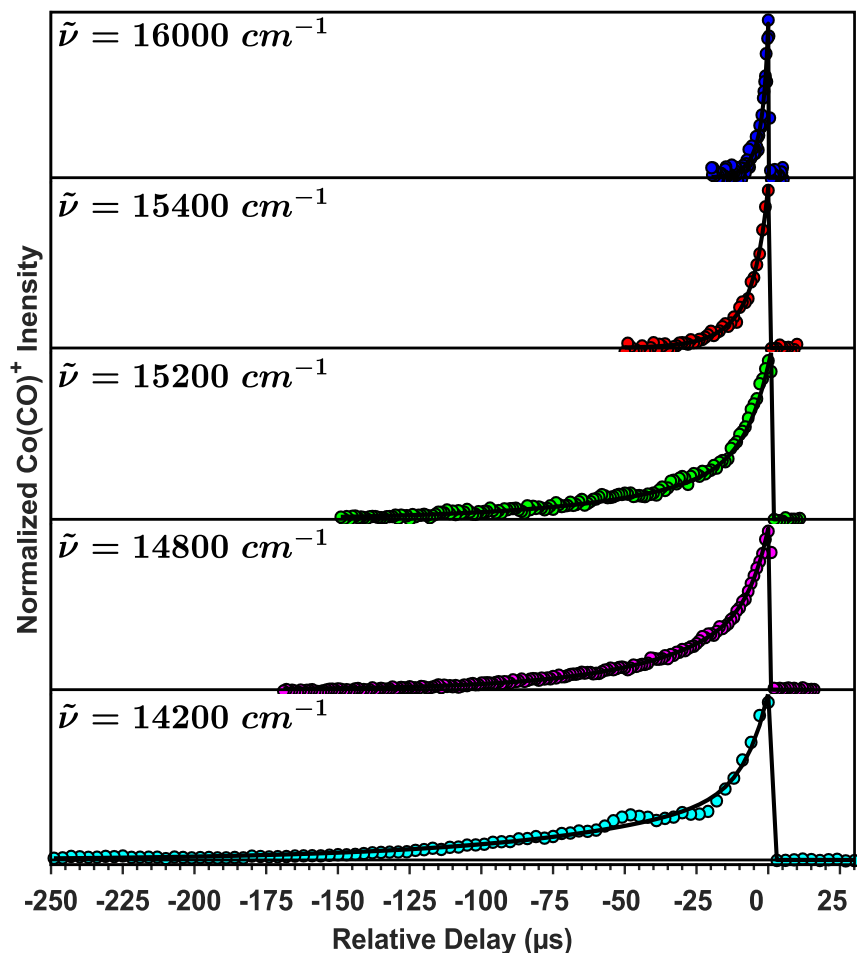


Figure 4.3. $\text{Co}(\text{CH}_3\text{CHO})^+ \rightarrow \text{Co}(\text{CO})^+ + \text{CH}_4$ SPIDRR results measured at various AL photon energies.

The reaction rates and rate constants generally increase with AL photon energy. This is more clearly seen in Figure 4.4 which plots the extracted rate constant values and their ratios against AL energy. We first note the negligible energy dependence of $^3k_{\text{RL}}$, the rate constant describing the rate limiting aldehyde hydrogen transfer on ^3PES , measured in the 13900 cm^{-1} to 15200 cm^{-1} range. This behavior is ubiquitous to hydrogen tunneling where the width, as opposed to the energy, of a transition barrier is the primary factor determining the reaction rate constant. Transition barrier widths generally decrease

slightly as the reaction energy is increased and we measure a very gradual increase in $^3k_{\text{RL}}$ within this energy range. Beyond this limit, the $^3k_{\text{RL}}$ reaction rate constants increase rapidly from 15400 cm^{-1} to 16000 cm^{-1} consistent with AL energies near or greater than the Eyring transition barrier for the aldehyde hydrogen transfer. These observations suggest that the energy of this rate-limiting barrier on ^3PES is $15250 \pm 500\text{ cm}^{-1}$.

The $^1k_1 / ^3k_1$ ratio describes the TSR / SSR competition in this reaction. At low AL energies, these rate constants have similar values and roughly equal portions of the reacting population progress on the ground and excited PESs toward products. However, as the reaction energy is increased, Figure 4.4 shows that the $^1k_1 / ^3k_1$ ratio also increases, indicating that increasingly larger portions of the reacting population spin inverts onto the singlet surface. The rate limiting rate constants in the right panel also increase with increasing energy, however, $^1k_{\text{RL}}$ appears to grow at a faster rate relative to the $^3k_{\text{RL}}$. This is due to the 1k_1 contribution to $^1k_{\text{RL}}$. It appears that nonadiabatic chemistry dominates this reaction over the energy range studied.

Thus, the Co^+ cation adiabatically reduces the decomposition energy of CH_3CHO into $\text{CO} + \text{CH}_4$ products by providing a source and sink of the electrons required for an OA/RE sequence. This may be considered the typical behavior of transition metal active sites in catalytic transformations. However, these energy requirements are further lowered by the nonadiabatic influences of TSR and hydrogen tunneling. For TSR, it is the low-lying electronic structure of the active site that is responsible for such energy reductions in chemical transformations.

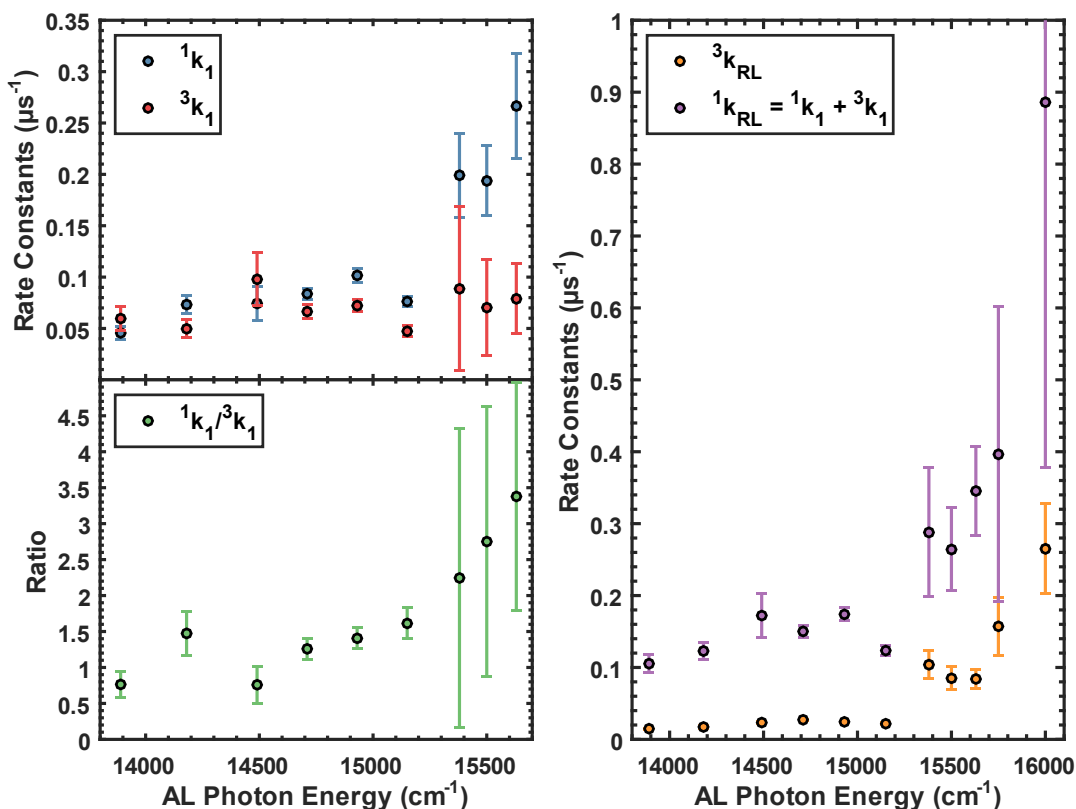


Figure 4.4. Energy dependence of the rate limiting rate constants measured in the Co^+ mediated decay of CH_3CHO . Rate constant uncertainties are at the 95% confidence interval. The time dependence of the minor channel cannot be confidently measured at higher photon energy, preventing simultaneous fitting, and widening the 95% confidence intervals of the extracted rate constants.

(d) CASSCF Calculations

Various elements of the two state $\text{Co}(\text{CH}_3\text{CHO})^+$ reaction PES must be in place as determined by experimental observations. These were used as standards by which to determine the accuracy of calculation at the various levels of theory employed. These metrics included (i) A rough replication of the known $\text{Co}^+ (3d^8, {}^1\text{D}) \leftarrow (3d^8, {}^3\text{F})$ atomic promotion energy at the separated reactant limit. (ii) Similar ${}^3\text{RC}$ and ${}^1\text{RC}$ bond energies. (iii) Transition barriers and product energies that are submerged, or endothermic, with respect to the separated ground $\text{Co}^+ (3d^8, {}^3\text{F}) + \text{CH}_3\text{CHO}$ reactant limit.

The structures featured on the two-state reaction surface of $\text{Co}(\text{CH}_3\text{CHO})^+$ were first based on chemical intuition and were then generated using density functional theory (DFT) computations. Although this approach is fairly straightforward and effective in qualitatively identifying the correct stationary points, it failed to capture the required features of the $\text{Co}(\text{CH}_3\text{CHO})^+$ potential energy surface. Moreover, the pure density functionals, BLYP and M06L, incorrectly classified several minima as transition states and other higher-order saddle points. Subsequent computations using hybrid DFT confirmed that the lack of electron correlation was the likely culprit behind the anomalous calculated behavior. Therefore B3LYP, M06-2X, and wB97XD were employed. These did predict a consistent set of minima ($n_i = 0$) and transition states ($n_i = 1$) of the $\text{Co}(\text{CH}_3\text{CHO})^+$ PES. However, regardless of identity of the hybrid DFT, each technique led to dramatically overbound complexes exothermic with respect to the separated $\text{Co}^+ + \text{CH}_3\text{CHO}$ reactants. To account for these issues and to avoid others commonly associated with using DFT to describe weakly bound clusters (e.g., self-interaction), the RC and their isolated constituents were characterized with the MP2 and CCSD(T) *ab initio* methods. The optimized structures identified with these techniques were nearly identical to their B3LYP counterparts; however, the corresponding relative electronic energies were only slightly improved. This result is somewhat surprising given that CCSD(T) has been demonstrated to provide accurate results for weakly bound clusters. Although energy corrections from explicitly correlated CCSD(T)-F12 did help the situation, they led to the same overall result.

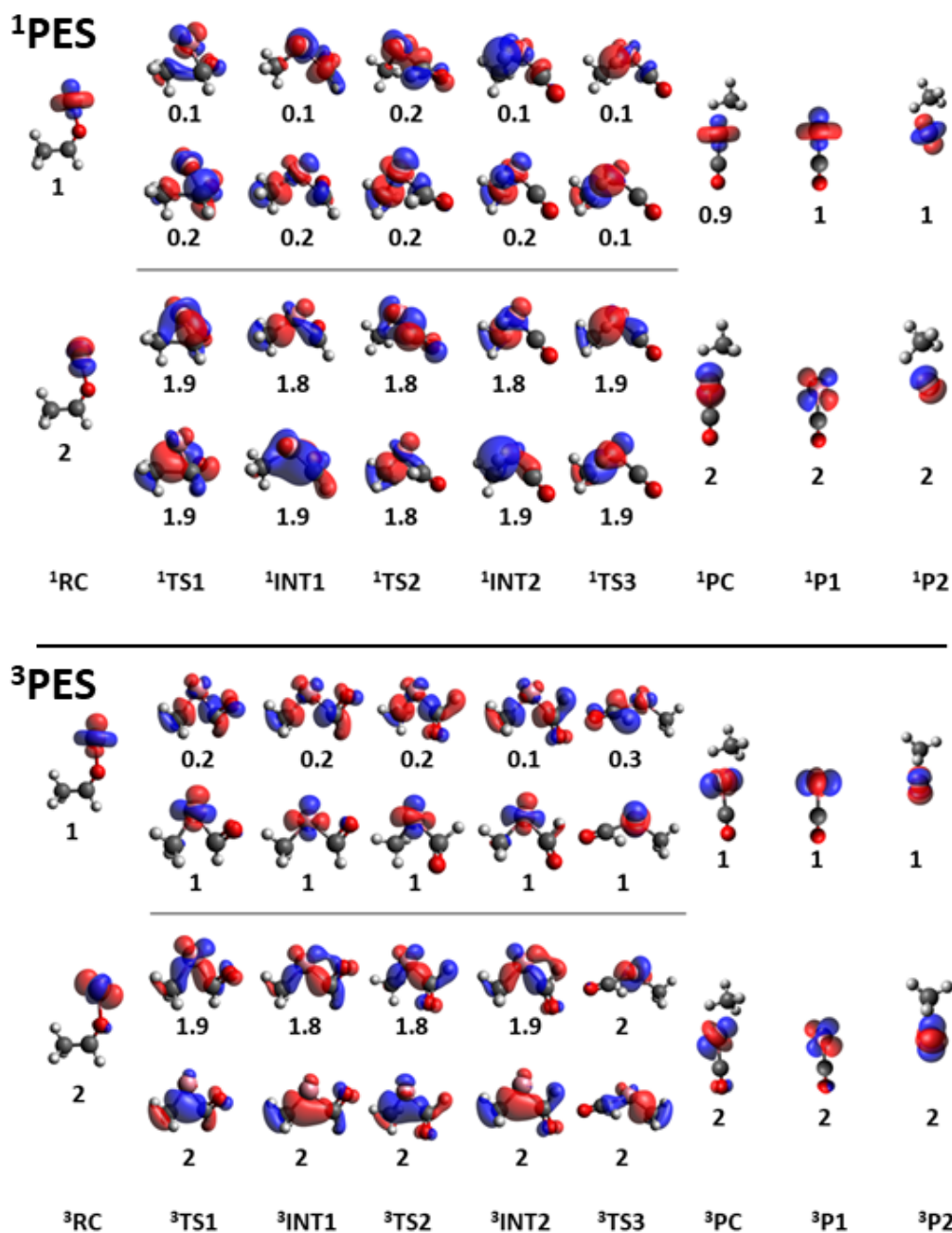


Figure 4.5. The Co^+ mediated decomposition of CH_3CHO reaction progression and molecular orbitals on the triplet (lower panel) and singlet (top panel) hypersurfaces. MOs were calculated at the CASSCF/CASPT2/aug-cc-pVTZ//PBE0/aug-cc-pVTZ level of theory with electron occupancy indicated. Bonding in the RC, PC, and Product structures is primarily atomic and two representative MOs are presented here, one fully and one half occupied. Bonding and antibonding MOs (portrayed below and above each thin grey line, respectively) are displayed for the structures associated with the OA/RE sequence on each hypersurface.

The most significant improvement to the overall energetics of the $\text{Co}(\text{CH}_3\text{CHO})^+$ structures along each PES is realized through CASSCF-NEVPT2 computations. Here, with a multiconfigurational method and quantum tunneling corrections, the theory did predict a more accurate atomic promotion energy as well as similar bond energies for ^3RC and ^1RC . Moreover, the product energies were primarily exothermic with respect to the ground state separated reactants. However, despite these successes and the computational effort that was put forth, this approach again computed overbound structures exothermic with respect to the $\text{Co}^+ (3d^8, ^3F) + \text{CH}_3\text{CHO}$ separated reactant limit. As such, only qualitative aspects of our theoretical results (i.e., structures, molecular orbitals, etc.) will be discussed in subsequent sections.

Figure 4.5 shows the Co^+ mediated decomposition of CH_3CHO reaction progression along both triplet and singlet hypersurfaces. There are three calculated TS structures that represent maxima along each PES while the remaining structures are minima. Theory predicts that the Co^+ cation oxidatively adds to the C-C bond of acetaldehyde to progress from RC to INT1. The $\text{Co}^+\text{-C}$ bond then rotates to place the aldehyde hydrogen in a position to transfer across the cation as seen in the INT2 structure. However, a minimum energy crossing point, MECP1, located in the $^3\text{INT1}$ potential well allows the reacting population to transition between PESs. The aldehyde hydrogen transfer onto the methyl group is calculated to be the highest barrier on ^3PES . There is a second computed crossing point, MECP2, that follows $^1\text{TS3}$ and $^3\text{TS3}$ on route to formation of each PC. Each PC eliminates Co^+ , either in the 3F or 1D state, bound to natural water or methane products.

Representative molecular orbitals, MOs, are calculated at the CASSCF/CASPT2/aug-cc-pVTZ//PBE0/aug-cc-pVTZ level of theory and presented in Figure 4.5 for both hypersurfaces. The valence MOs in the RC, PC, and products are primarily composed of atomic d-orbitals indicating their electrostatic nature and are effectively noncovalently bound to the corresponding organic molecule. The designation of bonding or antibonding is reserved for the covalently bound species associated with the oxidative addition and the steps leading to elimination. These structures are separated by a thin line in each panel of Figure 4.5. Orbital occupancies are indicated as numbers below each structure. The MOs presented for each electrostatic complex were chosen so that one of the d-orbital MOs is full and one is half filled.

The successful application of Model 4.1's kinetic model, combined with the observed hydrogen tunneling indicated in Figure 4.4, agrees with calculation that the highest barriers along the triplet surface is due to the aldehyde hydrogen transfer. Moreover, this rate determining step must be preceded by the competitive progression of the reacting population through the SI junction.

Conclusion

The energy dependence of the Co^+ mediated decomposition of CH_3CHO has been studied by the SPIDRR technique with results presented here. The open-shell nature of the Co^+ cation adiabatically reduces the energy requirements for CH_3CHO decomposition into $\text{CH}_4 + \text{CO}$ to $\sim 15250 \text{ cm}^{-1}$. This barrier is additionally reduced through hydrogen tunneling facilitated by the hydrogen transfer across the cation. The Co^+ electronic structure further reduces the decomposition energy nonadiabatically through TSR. We believe that this is

the first experimental study where the kinetic influences of two dynamic nonadiabatic features, TSR and hydrogen tunneling, are shown to dominate the low energy regime of a chemical transformation.

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CHAPTER FIVE

Two-State Reactivity in the TiO^+ Mediated Decomposition of CH_3COCH_3 and CD_3COCD_3

Introduction

The TiO^+ mediated decomposition of CH_3COCH_3 and CD_3COCD_3 was originally studied to explore the superatom phenomenon. TiO^+ and Ni^+ are isoelectronic featuring $^2\Delta$ and 2D ground states, and studies by Castlemann¹⁻⁴ found that there were similar reactivity patterns between transition metal oxides and their isoelectronic bare transition metal analogs. The Bellert group has previously published the Ni^+ mediated decomposition of CH_3COCH_3 and CD_3COCD_3 where Ni^+ decarbonylates acetone following an $\mathbf{A} \rightarrow \mathbf{B} \rightarrow \mathbf{C}$ type model.⁵ Here we demonstrate the very different reactivity of TiO^+ .

Methods

The SPIDRR technique and instrument has been reported in detail⁶ but will be briefly summarized here. The instrument is composed of a 120 L expansion chamber coupled to a time of flight mass spectrometer (TOFMS). The instrument is maintained at $\sim 4 \times 10^{-6}$ Pa by differentially pumping the two chambers. The expansion chamber contains a custom laser vaporization source, featuring a Ti metal rod, that is functionally similar to the original design by Smalley.⁷ Focused laser light from a pulsed Nd^{3+} YAG laser is timed to ablate the Ti target as a pulsed valve is triggered to open. A pulse of gas containing the vapor pressure of either CH_3COCH_3 or CD_3COCD_3 entrained in He expands into the vacuum chamber. Numerous collisions between Ti^+ cations and acetone vapor produce

TiO^+ . The TiO^+ ion undergoes further collisions with acetone to form the supersonically cooled $\text{TiO}(\text{CH}_3\text{COCH}_3)^+$ reactant complex (RC). The RC ions entrained in the expanding molecular beam travel $\sim 1\text{m}$ along the expansion axis and are extracted into the TOFMS by a voltage pulse from an orthogonal accelerator (OA). The extracted cations travel 1.86 m through the field-free region of the TOFMS to a kinetic energy selective hemispherical sector. Cations of a specific kinetic energy are then selectively transmitted to a microchannel plate detector.

The time dependence of product formation is measured following activation of the RC through photon absorption. A Nd^{3+} YAG pumped tunable dye laser, dubbed the activation laser (AL), is timed to pulse as the RC is extracted into the TOFMS by the OA. The RC absorbs the AL photon and is promoted to an excited electronic state. Internal conversion converts the energy to high vibrational levels on the ground electronic state. This provides the RC sufficient kinetic energy to surmount potential barriers to rearrange into product ions.

Product ions originating from the RC that are formed in the field-free region of the TOFMS will have the same arrival time to the detector as the RC but possesses a kinetic energy consistent with its mass. These products are selectively transmitted to the detector through the hemispherical sector. The experiment is repeated at successively larger relative delays between firing the AL and OA, τ . Firing the AL before the OA, negative τ , intersects the RC earlier along the expansion axis, leading to a decrease in the surviving population to the OA. Consequently, fewer product ions are formed in the field-free region of the TOFMS and are sampled. This results in decreased product yields as a function of τ , providing the time-dependence of product formation.

Oscillator strengths and optimized geometries of the ground state of $\text{TiO}(\text{CH}_3\text{COCH}_3)^+$ and $\text{TiO}(\text{CD}_3\text{COCD}_3)^+$ and their low-lying excited states are calculated using time-dependent density functional theory (TDDFT) with the B3LYP functional and aug-cc-pVTZ basis set. The OpenMolcas package was employed for these calculations.⁸

Results

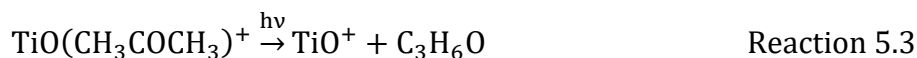
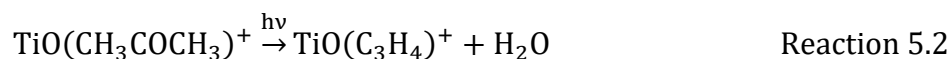
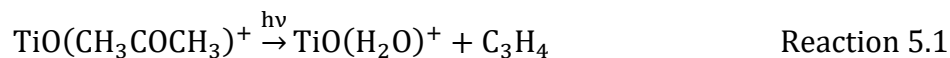
RA. Product Identification:

Products are identified by scanning the potential difference across the hemispherical sector halves while monitoring ion transmission to confirm product masses. This is referred to as a sector voltage scan. Scanning the potential difference across the instrument's sector, while monitoring the $\text{TiO}(\text{CH}_3\text{COCH}_3)^+$ RC arrival time to the detector, allows for the exclusive transmission of product ions formed from the RC. The transmission voltage of a product ion is proportional to the ratio of the product ion and reactant ion masses, provided in Equation 5.1.

$$V_P = V_R \frac{M_P}{M_R} \quad \text{Equation 5.1}$$

Where V_P , V_R , M_P , and M_R are the transmission voltages and masses of the product and reactant ions. Collisions between accelerated RC and trace He energize the RC, leading to product formation. In contrast with this collision induced dissociation (CID), laser induced dissociation (LID) occurs when a photon is absorbed to drive the reaction to products. Careful sector voltage scans of CID and LID products were performed for both the $\text{TiO}(\text{CH}_3\text{COCH}_3)^+$ and $\text{TiO}(\text{CD}_3\text{COCD}_3)^+$ RCs. Analysis of these sector voltage scans indicated that there are three different massed LID products for each precursor

isotopologue. These masses are consistent with the product assignments of TiO^+ , $\text{TiO}(\text{H}_2\text{O})^+$, and $\text{TiO}(\text{C}_3\text{H}_4)^+$, as seen in Table 5.1. These products are formed (Equations 5.1-5.3) from dissociative rearrangement of the $\text{TiO}(\text{CH}_3\text{COCH}_3)^+$ RC.



Where $h\nu = 16,000 \text{ cm}^{-1}$. The mediated decomposition of the deuterium labeled isotope agrees with expected product mass changes resulting from the degree of deuterium labeling, ie. the water and organic products increased by 2 and 4 amu while there was no change in the TiO^+ product channel. Products percent yields, originating from the TiO^+ mediated decomposition of CH_3COCH_3 and CD_3COCD_3 are measured at $\tau = 0$ and shown in Table 5.1.

The major product was initially assigned as $\text{TiO}(\text{H}_2\text{O})^+$ because the neutral ligands from Reactions 5.1 and 5.2, H_2O and C_3H_4 , stoichiometrically add to form CH_3COCH_3 . This implies that there is a common product complex ($\text{PC} = \text{H}_2\text{O}-\text{TiO}^+-\text{C}_3\text{H}_4$), where both ligands are fully formed with TiO^+ bound between them. The isobaric products, $\text{TiO}_2(\text{H}_2)^+$

and $\text{Ti}(\text{OH})_2^+$, would not have the same complementary nature, as $\text{C}_3\text{H}_4\text{-TiO}_2(\text{H}_2)$ and $\text{C}_3\text{H}_4\text{-Ti}(\text{OH})_2$ dissociation would likely yield products with unobserved masses.

Figure 5.1 is the precursor mass spectra for both the TiO^+ mediated decomposition of CH_3COCH_3 and CD_3COCD_3 . The precursor mass spectrum includes not only the reactant $\text{TiO}(\text{CH}_3\text{COCH}_3)^+$ and $\text{TiO}(\text{CD}_3\text{COCD}_3)^+$ complexes, but also ions that were formed under high-energy LAVA source conditions. CID sector voltage scans were performed while monitoring the arrival time of $\text{TiO}(\text{H}_2\text{O})^+$ and $\text{TiO}(\text{C}_3\text{H}_4)^+$ in the precursor mass spectrum to determine each ions subsequent dissociation products. The products were determined to dissociate by Reactions 5.4 and 5.5,

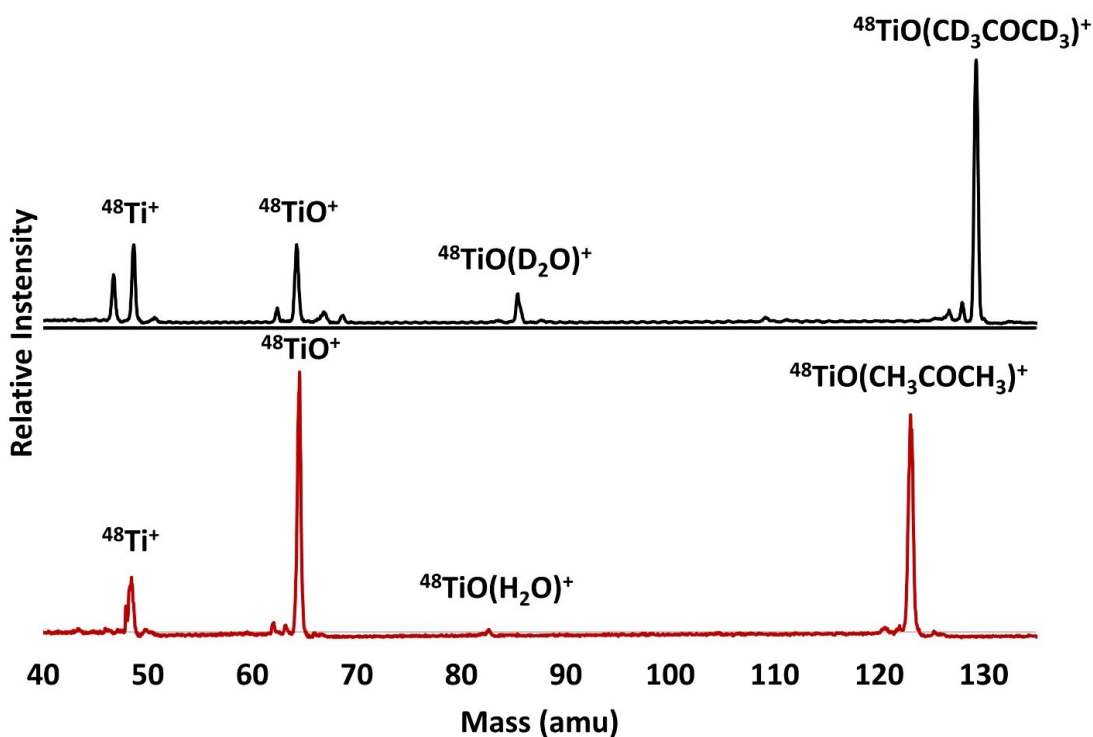
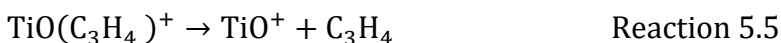


Figure 5.1: Mass spectra optimized for formation of $\text{TiO}(\text{CH}_3\text{COCH}_3)^+$ (bottom) and $\text{TiO}(\text{CD}_3\text{COCD}_3)^+$ (top).

suggesting the identity of the major product is TiO^+ bound to an intact H_2O molecule. The structure of the C_3H_4 ligand is likely propadiene or propyne.

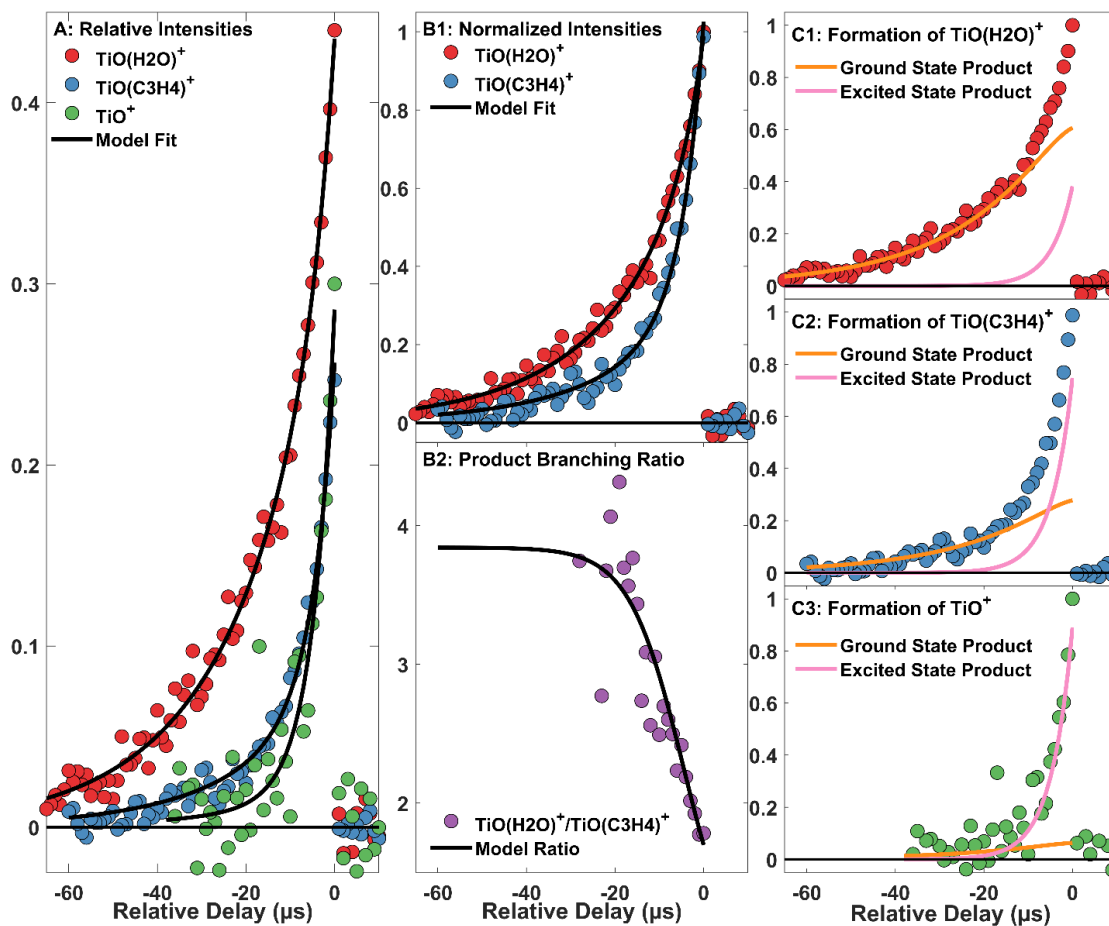


Figure 5.2: Time dependence of product formation for the TiO^+ mediated decomposition of CH_3COCH_3 with an activating photon energy of $16,000\text{ cm}^{-1}$. (A) Plot of the relative intensities of each product ion vs the relative delay between firing the AL and OA. (B1) The results shown in panel A, normalized to 1. (B2) The ratio of $\text{TiO}(\text{H}_2\text{O})^+/\text{TiO}(\text{C}_3\text{H}_4)^+$ intensities from panel A. (C1,C2 and C3) Intensities of $\text{TiO}(\text{H}_2\text{O})^+$, $\text{TiO}(\text{C}_3\text{H}_4)^+$, and TiO^+ normalized to 1 and plotted with their ground state and excited state contributions.

Table 5.1: Product masses and product branching ratios measured at $\tau = 0$ for the TiO^+ mediated decomposition of CH_3COCH_3 and CD_3COCD_3

Reactant Ion	$\text{TiO}(\text{H}_2\text{O})^+ + \text{C}_3\text{H}_4$	$\text{TiO}(\text{C}_3\text{H}_4)^+ + \text{H}_2\text{O}$	$\text{TiO}^+ + \text{C}_3\text{H}_6\text{O}$
$\text{TiO}(\text{CH}_3\text{COCH}_3)^+ \rightarrow$	44%	25%	30%
Reactant Ion	$\text{TiO}(\text{D}_2\text{O})^+ + \text{C}_3\text{D}_4$	$\text{TiO}(\text{C}_3\text{D}_4)^+ + \text{D}_2\text{O}$	$\text{TiO}^+ + \text{C}_3\text{D}_6\text{O}$
$\text{TiO}(\text{CD}_3\text{COCD}_3)^+ \rightarrow$	43%	20%	37%

RB. TiO^+ Mediated Decomposition of CH_3COCH_3 and CD_3COCD_3 Reaction Kinetics at an Activating Photon Energy of $16,000 \text{ cm}^{-1}$

The time dependencies of $\text{TiO}(\text{H}_2\text{O})^+$, $\text{TiO}(\text{C}_3\text{H}_4)^+$, and TiO^+ formation from the TiO^+ mediated decomposition of CH_3COCH_3 at an activating photon energy of $16,000 \text{ cm}^{-1}$ are plotted in Figure 5.2. Panel A plots the measured relative intensity of each product's formation vs τ .

Panel B1 plots the normalized intensities of $\text{TiO}(\text{H}_2\text{O})^+$ and $\text{TiO}(\text{C}_3\text{H}_4)^+$ vs τ . These products must share a common PC which quickly bifurcates to form $\text{TiO}(\text{H}_2\text{O})^+$ and $\text{TiO}(\text{C}_3\text{H}_4)^+$. The dissociation of the PC is assumed to be fast because dissociation of the PC requires little rearrangement of the molecule. For SSR reactions it is expected that the $\text{TiO}(\text{H}_2\text{O})^+ / \text{TiO}(\text{C}_3\text{H}_4)^+$ ratio will be a constant given by Equation 5.2.

$$\frac{\text{TiO}(\text{H}_2\text{O})^+}{\text{TiO}(\text{C}_3\text{H}_4)^+} = \frac{k_{p_1}}{k_{p_2}} \quad \text{Equation 5.2}$$

Where k_{p_1} and k_{p_2} are the rate constants for dissociation of the PC into $\text{TiO}(\text{H}_2\text{O})^+$ and $\text{TiO}(\text{C}_3\text{H}_4)^+$ respectively. A constant product ratio of $\text{TiO}(\text{H}_2\text{O})^+/\text{TiO}(\text{C}_3\text{H}_4)^+$ will result in superimposed normalized products, as demonstrated previously for single state reactions.⁹ Panel B2 of Figure 5.2 plots the ratios of the relative intensities of $\text{TiO}(\text{H}_2\text{O})^+$ and $\text{TiO}(\text{C}_3\text{H}_4)^+$ products from panel A vs τ . If the products formed on a single surface, the product ratio would be constant with respect to τ , resulting in a horizontal line with its

magnitude given by Equation 5.2. The products are neither superimposable in B1 or at a constant ratio in B2, implying that the reaction does not occur on a single electronic surface.

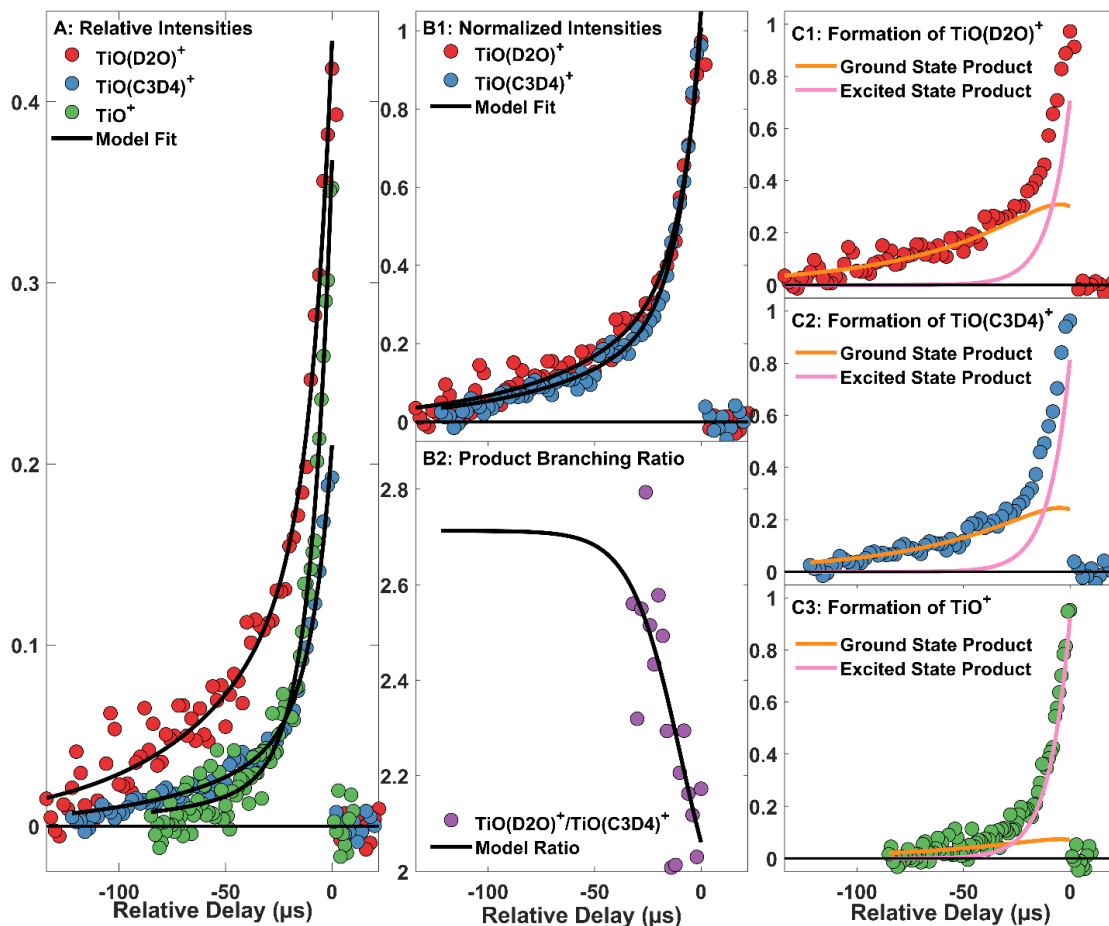


Figure 5.3: SPIDRR results for the TiO^+ mediated decomposition of CD_3COCD_3 at an activating photon energy of $16,000\text{ cm}^{-1}$. (A) Plot of the relative intensities of each product vs τ . (B1) Intensities of each product from panel A, normalized to 1. (B2) Ratio of relative intensities of $\text{TiO}(\text{D}_2\text{O})^+/\text{TiO}(\text{C}_3\text{D}_4)^+$ from panel A. (C1, C2, and C3) Intensities of $\text{TiO}(\text{D}_2\text{O})^+$, $\text{TiO}(\text{C}_3\text{D}_4)^+$, and TiO^+ normalized to 1 and plotted with the individual ground and excited state contributions.

The time dependence of $\text{TiO}(\text{D}_2\text{O})^+$, $\text{TiO}(\text{C}_3\text{D}_4)^+$, and TiO^+ production for the $\text{TiO}(\text{CD}_3\text{COCD}_3)^+$ reaction at an activating photon energy of $16,000\text{ cm}^{-1}$ is shown in Figure 5.3. A difference between the CH_3COCH_3 and CD_3COCD_3 reactions is shown in panel B1 where the similar normalized intensities of $\text{TiO}(\text{D}_2\text{O})^+$ and $\text{TiO}(\text{C}_3\text{D}_4)^+$ are plotted versus τ . However, the product ratio increases at early τ and approaches a constant value at long τ , consistent with the results in panel B2 of Figure 5.2. Once again this suggests that products are forming on multiple surfaces.

It was previously demonstrated that the observations made in panels B1 and B2 of Figures 5.2 and 5.3 can only be explained by TSR.⁹ The model shown in the left panel of Figure 5.4 was proposed to account for our measured observations for the reaction of TiO^+ with both acetone isotopologues. This model suggests, as supported by previously published results,⁹ that the three observed product ions from the reactions of both isotopologues are each composed of two same-massed, but different TiO^+ electronic configuration, product ions. Total yields in each channel result from a convolution of ground and excited state products that are measured at a common arrival time to the detector. In Figure 5.4 the two sets of products are given by $\mathbf{E}_1 + \mathbf{E}_2 = \text{TiO}(\text{H}_2\text{O})^+$ and $\mathbf{F}_1 + \mathbf{F}_2 = \text{TiO}(\text{C}_3\text{H}_4)^+$.

Product integrated rate equations were derived and simultaneously fit to the measured temporal dependence of the three convoluted products. These fits are shown as the solid black curves in Figures 5.2 and 5.3. Extracted unimolecular rate constants for the reaction of each isotopologue are collected in Table 5.2. The modeled contributions from

the ground state and excited state products are shown in panels C1, C2, and C3 of Figures 5.2 and 5.3.

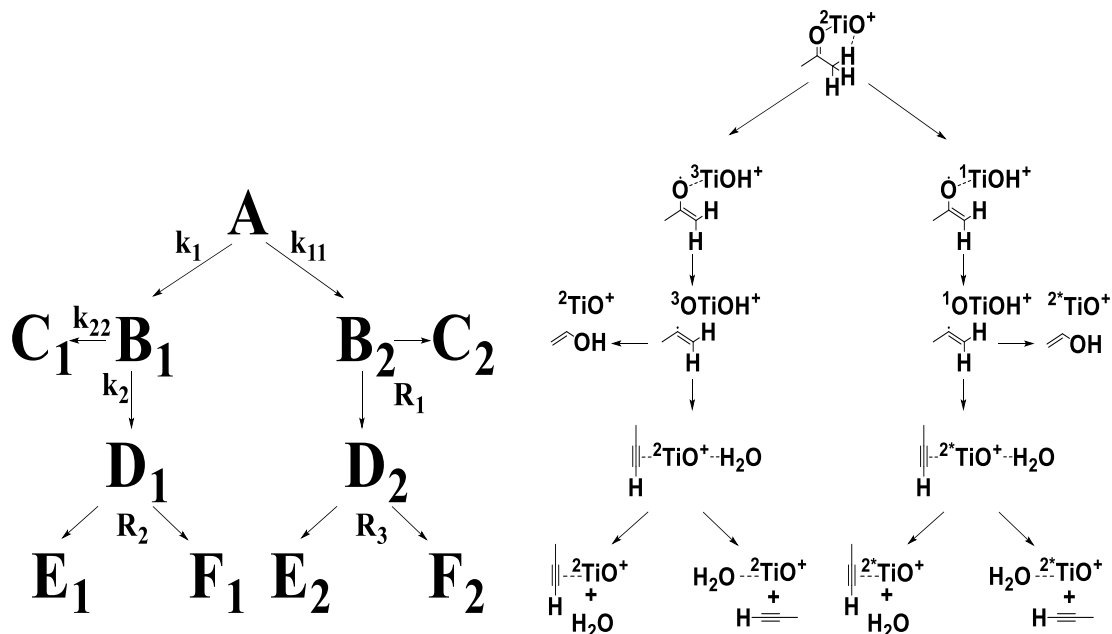


Figure 5.4. The proposed kinetic model (left) and mechanism (right).

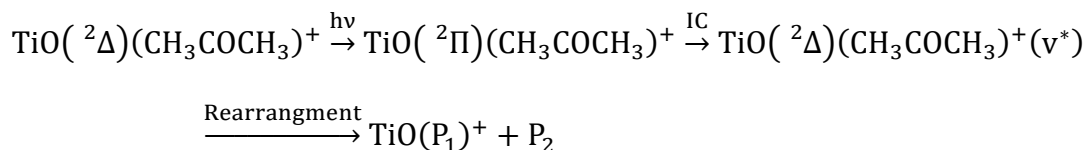
In the proposed model there are two steps that are treated with rate limiting rate constants. These steps are the initial reaction bifurcation from **A**, and the subsequent bifurcation from **B₁**. Fitting these steps with relatively small rate constants allows for a quality fit of the model to the measured temporal dependence. The bifurcation of **B₂**, **D₁**, and **D₂** are each treated with a ratio of rate constants. It is assumed that dissociation of the **D₁** and **D₂** PCs will be fast, as little rearrangement is required. A quality fit requires large rate constants to describe bifurcation at **B₂**. In each of these cases a ratio of rate constants

is used as these steps only serve to set the ratio of products. The model given in Figure 5.4 is the simplest model that yields quality fitting results with narrow confidence intervals.

Table 5.2: Rate constants extracted from the simultaneous fitting of the time dependence of formation of all three products to the proposed model given in Figure 5.4 Errors are reported at the lambda-95 confidence intervals.

Reactant Ion	k_1	k_{11}	k_2	k_{22}	R_1	R_2	R_3
$\text{TiO}(\text{CH}_3\text{COCH}_3)^+$	0.063 ± 0.017	0.145 ± 0.021	0.044 ± 0.004	0.0025 ± 0.0021	1.284 ± 0.231	3.842 ± 0.719	0.900 ± 0.226
$\text{TiO}(\text{CD}_3\text{COCD}_3)^+$	0.031 ± 0.004	0.071 ± 0.005	0.016 ± 0.002	0.0023 ± 0.0006	1.354 ± 0.103	2.713 ± 0.358	1.869 ± 0.212
H/D KIE	~ 2	~ 2	~ 2.75	~ 1	~ 1	~ 1	~ 2

The agreement of the model presented in Figure 5.4, with $\mathbf{E}_1 + \mathbf{E}_2 = \text{TiO}(\text{H}_2\text{O})^+$ and $\mathbf{F}_1 + \mathbf{F}_2 = \text{TiO}(\text{C}_3\text{H}_4)^+$, suggests that the results from Figures 5.2 and 5.3 can only be explained by the production of two same-massed products. Reaction pathways to produce the same products would be identical unless there is a difference in electronic structure between the two pathways. Thus, the reaction does not exit onto a single electronic state and instead exhibits both ground state and excited state reactivity. This poses the question: How does reacting population access the excited state? SPIDRR initiates with photon absorption which provides access to an excited state, so calculations must be performed to determine if photon absorption populates the reacting state. TiO^+ is the chromophore because TiO^+ has known transitions at $16,000 \text{ cm}^{-1}$, while CH_3COCH_3 has only transitions in the UV. TDDFT calculations predict a $^2\Delta$ ground state with two low-lying $^2\Sigma$ states at $3,800$ and $10,300 \text{ cm}^{-1}$ above the ground state and a $^2\Pi$ at $14,100 \text{ cm}^{-1}$ above the ground state. The $^2\Pi \leftarrow ^2\Delta$ transition is calculated to have the highest oscillator strength by an order of magnitude. The following sequence is likely to occur upon photon absorption:



Where $h\nu$ is a quantum of photon energy = 16,000 cm^{-1} , IC is internal conversion, v^* are excited vibrational levels, rearrangement denotes RC rearrangement to products, and P_1 and P_2 are neutral product fragments. Photo-exciting to the ${}^2\Sigma$ state is predicted to be weak. Upon excitation to the ${}^2\Pi$ state, population internally converts to high vibrational levels on the ${}^2\Delta$ ground state. Calculations predict the $\text{TiO}^+-\text{CH}_3\text{COCH}_3$ bond strength to be greater than 16,000 cm^{-1} , so relaxation of the excited population occurs through chemical reaction and not through simple dissociation of the RC. The significant increase in kinetic energy on the ground surface allows for reacting population to surmount potential barriers and rearrange to products.

Discussion

The TiO^+ mediated decomposition of CH_3COCH_3 and CD_3COCD_3 is likely exiting onto two different electronic surfaces while initiating on a single surface, consistent with TSR. Chemical intuition, combined with the suggested framework provided by the model, suggest a mechanism for the reaction.

The mechanism, the right panel of Figure 5.4, initiates with the fast abstraction of a hydrogen atom from acetone by the highly reactive ${}^2\text{TiO}^+$ vibrationally excited ground state. This step is assumed to be fast, leading to formation of TiOH^+ and an alpha keto radical, **A**, in the model (left panel of Figure 5.4). The electronic structure of TiOH^+ has been calculated to have a ${}^3\Delta$ ground state with ${}^3\Sigma^-$, ${}^3\Phi$, ${}^3\Pi$, ${}^1\Sigma^+$, and ${}^1\Gamma$ low lying excited states within $\sim 7000 \text{ cm}^{-1}$.¹⁰ The spin conserved reaction between ${}^2\Delta \text{TiO}^+$ and ${}^1\text{CH}_3\text{COCH}_3$

will yield the ${}^2\text{TiOH}(\text{CH}_3\text{COCH}_2\bullet)^+$ intermediate structure composed of ${}^1\text{TiOH}$ and ${}^2\text{CH}_3\text{COCH}_2\bullet$ radical. The likely candidates for the excited singlet state of TiOH^+ are a ${}^1\Sigma^+$ and ${}^1\Gamma$ calculated between 5500 and 7000 cm^{-1} above the ${}^3\Delta$ ground state of TiOH^+ .

The model predicts that **A**, ${}^2\text{TiOH}(\text{CH}_3\text{COCH}_2\bullet)^+$ bifurcates to two electronic surfaces. The Ti-OH bond is calculated to be approximately 1700 cm^{-1} weaker on the excited singlet surfaces versus the triplet ground surface.¹⁰ This relatively weakened interaction with the hydroxyl group reduces the energetic requirements for further oxidation of the Ti atom. The lower potential barrier on the singlet surface likely leads to crossing with the ground triplet surface to give an MECP. Entropy compels population to explore all energetically accessible states and so population transitions from ${}^1\text{TiOH}^+$ to ${}^3\text{TiOH}^+$, despite the likely higher triplet surface potential barriers. This is significant because TSR is typically considered to be enthalpically driven, where the formally forbidden spin inversion occurs so that reacting population can access lower potential barriers.

Reaction along both the singlet and triplet surfaces likely proceed with the oxygen of the alpha keto radical attacking TiOH^+ to yield ${}^1\text{OTiOH}^+$ and ${}^3\text{OTiOH}^+$, each bound to the propyne radical. Formation of ${}^1\text{OTiOH}^+$ is modeled by **A**→**B**₂, with rate constant k_{11} from Figure 5.4. Formation of ${}^3\text{OTiOH}^+$ is modeled by **A**→**B**₁, where the rate constant k_1 is smaller than rate constants for either the oxygen attack or the spin inversion to the triplet surface. The modeled H/D KIEs for formation of ${}^3\text{OTiOH}^+$ and ${}^1\text{OTiOH}^+$ are both approximately 2, consistent with a secondary KIE.

The model then predicts that the reaction bifurcates again along both surfaces from **B**₁ and **B**₂. Along one path the mechanism suggests that OTiOH^+ abstracts a second

hydrogen to form $\text{C}_3\text{H}_4\text{-}^2\text{TiO}^+\text{-OH}_2$, **D**₁ in the model, and $\text{C}_3\text{H}_4\text{-}^{2*}\text{TiO}^+\text{-OH}_2$, **D**₂, product complexes (PC). Two doublet PCs, ^2PC and $^{2*}\text{PC}$, must form to explain the time dependent product branching ratio observed in Figures 5.2 and 5.3. $\text{C}_3\text{H}_4\text{-}^2\text{TiO}^+\text{-OH}_2$ is formed with rate constant k_2 , and $\text{C}_3\text{H}_4\text{-}^{2*}\text{TiO}^+\text{-OH}_2$ is predicted by the model to form quickly.

Alternatively, the OTi-OH bond will break and the OH group transfers onto the organic fragment to form TiO^+ bound to a primary alcohol. This reaction pathway cannot be dissociation to separated reactants because the RC has been supersonically cooled such that after photon absorption the RC lacks the energy required to separate into $\text{CH}_3\text{COCH}_3 + \text{TiO}^+$. Thus, rearrangement to lower energy separated products is required to form the TiO^+ product.

Along the ground triplet surface, the second hydrogen abstraction, **B**₁→**D**₁, has a modeled H/D KIE of approximately 2.75, suggesting that hydrogen motion is important in this step. Progression along the singlet surface is rate limited at oxygen atom attack, **A**→**B**₂, (KIE = 1), with subsequent steps fit by large magnitude rate constants where only the ratio of rate constants is used to describe the competition between bifurcation along each pathway. The competition along the singlet surface for hydrogen abstraction versus OTi-OH bond breakage is given by R_1 and is unaffected by deuteration.

The PC formed from the hydrogen abstractions from either the triplet or singlet pathway will both yield ^2TiO . However, due to the observation of time-dependent product branching ratios shown in Panel B2 of Figures 5.2 and 5.3, both ground state $^2\text{TiO}^+$, ^2PC , and excited $^{2*}\text{TiO}^+$, $^{2*}\text{PC}$, must be formed to account for these observations. Both ^2PC and $^{2*}\text{PC}$ will then dissociate to products quickly modeled by the ratios, R_2 and R_3 . R_2 and R_3 describe the relative product branching of $\text{TiO}(\text{H}_2\text{O})^+$ and $\text{TiO}(\text{C}_3\text{H}_4)^+$, **E** and **F**. The R_2

ratio does not change upon deuteration, however the R_3 ratio doubles in favor of $\text{TiO}(\text{D}_2\text{O})^+$ formation. Breaking of the OTi-OH bond yields the isomerization products, presumably $\text{TiO}^+ + \text{C}_3\text{H}_5\text{OH}$. The ground state contribution to this product channel has a very small rate constant that is unaffected by deuteration, consistent with this proposed step not exhibiting hydrogen motion.

Conclusions

The TiO^+ mediated decomposition of CH_3COCH_3 and CD_3COCD_3 was measured at an activating photon energy of $16,000\text{ cm}^{-1}$ using the SPIDRR technique. Three different massed products were identified: TiO^+ , $\text{TiO}(\text{H}_2\text{O})^+$, and $\text{TiO}(\text{C}_3\text{H}_4)^+$. Modeling the time-dependence of formation of each product indicated that each mass product is the convolution of two same-massed but different electronic configuration products. Theory suggests that under the instrumental conditions of this study the reaction should initiate on a single electronic surface. The observation of different spin-surface products indicates the reaction is likely exhibiting TSR. A mechanism, informed by chemical intuition and the kinetic modeling, was proposed where the TSR is caused by an entropic redistribution of the excited singlet population of a formed intermediate into a lower energy, and vibrationally more dense triplet state.

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CHAPTER SIX

Rate-Limiting Hydrogen Transfers in the Ni^+ Mediated Decomposition of Diethyl Ether

Abstract

Energy-resolved kinetics of the Ni(I) mediated decomposition of diethyl ether has been characterized by the single photon initiated dissociative rearrangement reaction (SPIDRR) technique, in combination with high-level theory. The presence of the transition metal cation lowers the activation energy required to rearrange the precursor into daughter fragments. This reaction features two competitive pathways affording different products and with different rates, each measured at a $\text{Ni}((\text{C}_2\text{H}_5)_2\text{O})^+$ precursor activation energy equal to $16,000\text{ cm}^{-1}$. One path follows an immediate α hydride transfer, neutralizing the cation, and characterized by precursor dissociation into $\text{NiH} + \text{C}_4\text{H}_9\text{O}^+$ fragments. The rate constant controlling this concerted hydride transfer/charge transfer process at $16,000\text{ cm}^{-1}$ is $k_{\text{HTCT}} = 0.15 \pm 0.02\text{ }\mu\text{s}^{-1}$. The second path features an oxidative addition/reductive elimination sequence producing neutral ethene and ethanol fragments. The rate constant values measured for these steps when the precursor is energized to $16,000\text{ cm}^{-1}$ are $k_{\text{OA}} = 0.21 \pm 0.02\text{ }\mu\text{s}^{-1}$ and $k_{\text{RE}} = 0.082 \pm 0.003\text{ }\mu\text{s}^{-1}$. Both pathways are rate-limited by the hydride transfer step with different transfer rates.

Introduction

Gas-phase ion chemistry has substantially contributed to the understanding of organometallic reaction mechanisms and, more significantly, to the fundamental role of the

metal center in transition metal mediated catalysis.¹⁻⁵ Isolation of metal ions in the gas-phase removes environmental effects which facilitates a greater understanding of the transformations mediated by the catalytic active site. Moreover, computational studies of new or novel reaction mechanisms are often conducted on reactants isolated in the gas phase. Such studies provide atomistic details of reaction progression and, when in agreement with resolved experimentation, provides substantial physical insight into metal mediated catalytic transformations. Our recent efforts have focused on Ni(I) mediated chemical transformations where we have found several interesting hydrogen transfer mechanisms facilitated by the Ni^+ active site, some of which represent the rate limiting step in a decomposition reaction.⁶

Nickel metal is relatively abundant in earth's crust and is known to catalyze a host of chemical reactions. A few examples include carboxylation, transamidation, and amide alkylation reactions. Nickel also catalyzes C-H activation processes, additions to unsaturated compounds, and cross coupling reactions to name just a few. This versatile metal has thus received considerable attention and has been the subject of numerous investigations. Helmut Schwarz has recently published an article reviewing the gas-phase chemistry of nickel mediated transformations.⁷

Pioneering studies into the decomposition of organic ethers mediated by iron cations were conducted by Freiser and co-workers in the 1980s.⁸ A rather complete and more recent study of the Fe^+ mediated decomposition of dimethyl ether was conducted by

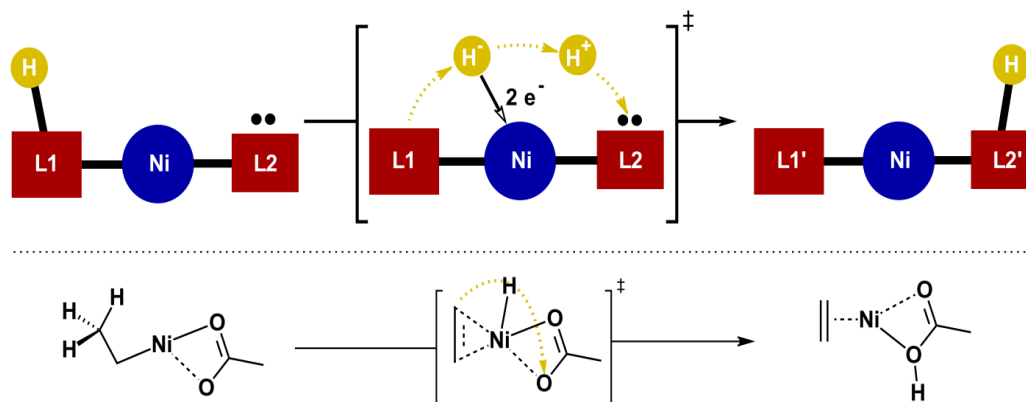


Figure 6.1: Schematic of the nickel mediated, orbit-like hydride transfer observed in precedent work.

Schwarz and co-workers.⁹ Here, unimolecular and collision induced reactions in a mass spectrometer, in conjunction with selective isotopic labelling, yielded exit channel fractions which in turn provided the hydrogen kinetic isotope effect. The authors definitively showed that the dissociative mechanism involved a rate-limiting Fe^+ activation of a C-O bond that was followed by a hydrogen shift to produce neutral methane and Fe^+ bound formaldehyde as products. Interestingly, in the present study we find that the chemistry of the Ni^+ cation acting on a similar substrate, diethyl ether, also involves C-O bond activation followed by hydrogen motion, but the hydrogen shift is shown to be rate determining.

McCarren *et. al.* have recently computed the free energy surface for the $\text{Ni}(0)$ catalyzed reductive coupling of acetylene and acetaldehyde.¹⁰ Their study demonstrated that an oxidative cyclization step rate limited the coupling reaction and this step occurred shortly after acetaldehyde replaces a phosphine ligand in an alkyne(bisphosphane) $\text{Ni}(0)$ precursor. Complexation with triethylborane formed an intermediate which underwent low-energy nickel mediated ethyl and hydrogen shifts leading to the elimination of the final

product. Of particular interest, a transition state where a beta-hydrogen atom appears to be escorted by the nickel center from a distant ethyl group to be subsequently deposited onto the opposite side of the molecule to form the elimination products. Interestingly, we have found similar large amplitude hydrogen transfers in two studies involving the chemistry of Ni(I) complexes.

Three distinct hydrogen transfers were computed to occur in the Ni(I) mediated decomposition of ethyl acetate, each with different degrees of Ni(I) involvement and with each eliminating different products.⁶ The most intense exit channel, as verified through the experimentation described below, involved large amplitude hydrogen motion where, again, the metal center appeared to escort a hydrogen atom during its transfer between distant portions of the molecule to ultimately eliminate final products. In the decomposition of ethyl acetate, the Ni(I) atom first oxidatively adds to a C-O bond forming Ni(III). The transfer step cleaves a hydride from an ethyl moiety resulting in an orbit-like motion on the surface of the nickel center depositing the hydride's two electrons to the metal thereby reducing Ni(III) it to its initial Ni(I) state. The resulting proton adds to a lone pair on a distant oxygen atom forming the elimination products (Figure 6.1).

The Ni(I) mediated decomposition of diethyl ether is the subject of the present study. Experimentally, energy-resolved reaction kinetics and exit channel fractions are measured using the gas-phase single photon initiated dissociative rearrangement reaction (SPIDRR) technique.¹¹ The potential energy surface is then calculated for the decomposition reaction which reveals two types of rate-limiting large amplitude hydride transfers, each concomitant with nickel reduction. The associated mechanistic steps may be broadly described as a charge transfer in one case while the other as a reductive

elimination. Both pathways are competitive with significantly different reaction rates. The prevalence of such large-scale hydride motions in nickel mediated chemistry suggests that this may be a more general mechanistic feature in nickel-based catalysis.

Methods

Experimental

Rate constants and exit channel fractions have been measured for the Ni^+ mediated decomposition of diethyl ether using the SPIDRR technique. The SPIDRR method has recently been described in detail and only a brief description is provided here.¹¹ Ni^+ , generated through laser vaporization in a high vacuum chamber, is entrained in a pulsed helium expansion doped with the vapor pressure of liquid diethyl ether. Collisions between the metal cation and neutral organic molecule form ionic complexes which are cooled in supersonic expansion. Cations formed in the ion source are ultimately pulsed into a time of flight mass spectrometer where their mass/charge ratio is detected.

Exit channel products resulting from the laser induced decomposition of the $\text{Ni}((\text{C}_2\text{H}_5)_2\text{O})^+$ precursor are determined by directing a pulsed laser beam to intersect the precursor along the expansion axis just prior to orthogonal extraction into the TOFMS. Complexes that absorb a single photon are energized to a level below the adiabatic $\text{Ni}^+ - ((\text{C}_2\text{H}_5)_2\text{O})$ bond energy but above requirements for the relatively slow rearrangement and dissociation into fragments. Precursor dissociation that occurs within the field-free region of the TOF yields fragments that travel with the same velocity as the precursor (and thus have the same arrival time to the detector) but carry only a fraction of the precursor kinetic energy. These fragments are selectively transmitted through a hemispherical electrostatic

sector to a microchannel plate detector. Fragment transmission voltage is proportional to the fragment to precursor mass ratio and a scan of the potential difference across the halves of the hemispherical sector permits the selective detection and identification of each fragment.

Energy-resolved kinetics are measured by monitoring the intensity of a unique dissociative fragment during temporal scans of the activation laser. The laser is timed to fire prior to the pulse which charges the orthogonal accelerator (OA) activating the precursor at locations between the OA and the expansion orifice of the source. The location and the relative timing of the activation event are well known. The triggers required to coincidentally charge the OA and to fire the YAG-pumped dye laser is defined as $\tau = 0 \text{ } \mu\text{s}$. Activation of the precursor complex at negative τ values (corresponding to a location along the expansion axis) allows a portion of the photo-populated precursor to decay into fragments prior to orthogonal extraction. These fragments are not collected as they travel through the TOF with a velocity different than that of the precursor. Rather the precursor population that survives right angle abstraction by the OA, but dissociates prior to selection by the sector, are collected and add to the fragment yield recorded at the relative τ timing value. At positive τ values, pulsed laser radiation arrives at the interaction region after the precursors have been accelerated into the TOF. Intensities of the detected fragment decrease with decreasing τ values since the survival probability of the photo-activated precursor decreases with laser activation at greater distances from the OA. Essentially, the absolute value of τ represents the time that the precursor decays prior to forming fragments and these are detected at the same arrival time to the detector as the precursor. Monitoring fragment intensities in this way is directly related to precursor unimolecular decay by

integrating the rate equations derived from unimolecular reaction kinetics over the TOF flight time. For the mechanism $A \xrightarrow{k} B$ the precursor decays by

$$\frac{dA}{dt} = -kA_t \quad \text{Equation 6.1}$$

Integration yields

$$A_t = A_0 e^{-kt} \quad \text{Equation 6.2}$$

SPIDRR experiments sample the product ions that are formed, and for this case are:

$$\frac{dB}{dt} = kA_t = kA_0 e^{-kt} \quad \text{Equation 6.3}$$

The observed SPIDRR signals are an integration over the decay that occurs during Δ , the field free flight time of the TOF. Consequently, any decay that occurs for a value of τ , and during the acceleration time, α , is not measured. The SPIDRR signal can then be expressed as

$$S_\tau = \int_{\alpha+\tau}^{\alpha+\tau+\Delta} kA_0 e^{-kt} dt = A_0 (e^{-k\alpha}) (1 - e^{-k\Delta}) e^{-k\tau} \quad \text{Equation 6.4}$$

The SPIDRR technique forms complexes in supersonic expansion which reduces the thermal energy contribution to the precursor internal energy. Thus, the energy of the absorbed laser photon approximates the internal energy of the precursor complex.

Computational

Throughout this work the Kohn-Sham formulation of the density functional theory was employed.^{12,13} The parameter free functional from Perdew, Burke and Ernzerhof (PBE)¹⁴ was used along with the correlation consistent double- ζ quality cc-pVDZ basis set.^{15,16} This density functional has been tested in previous work and provided reliable results for Ni(I) chemistry.⁶ The wavefunction stability for each optimized structure has

also been checked at this level of theory.¹⁷ Analysis of the normal modes obtained via diagonalization of the Hessian matrix was used to confirm the topological nature of each stationary point. Normal mode analysis and thermochemistry was obtained applying the rigid rotor and harmonic oscillator models.

Given the multireference character found in some structures involving Ni(I) catalysis we decided to employ methodology that can accurately describe non-dynamic correlation.¹⁸ CASSCF wavefunctions can describe appropriately this multireference character, but they only include a limited and undetermined amount of non-dynamic correlation.¹⁹ Given the importance of dynamic correlation in electronic structure calculations, a balanced amount of both are desirable.²⁰ To consider both electronic components at a reasonable computational cost we included the treatment of dynamic correlation in the multireference scheme via perturbational theory, MRMP, as implemented by Nakano.^{21–23} Single point calculations at PBE/CC-pVDZ geometries were performed at the MRMP(5,5)/CC-pVDZ. The resulting level of theory is usually noted as MRMP(5,5)/CC-pVDZ//PBE/CC-pVDZ. This strategy relies on the fact that density functional theory geometries are often accurate even when the electronic structure of the species under study exceeds the capability of this single determinant method. We have already employed this approach successfully for organic molecules with strong diradical character.^{24,25} All DFT calculations have been performed with Gaussian 09²⁶ and all MRMP energy refinement calculations were run with the GAMESS^{27,28} package.

Results

Figure 6.2 shows a typical mass spectrum where the $n = 1,2$ complexes of $\text{Ni}((\text{C}_2\text{H}_5)_2\text{O})^+$ are identified. Additionally, peaks with m/z ratios = 104 and 73 are observed and assigned as $\text{Ni}(\text{C}_2\text{H}_5\text{OH})^+$ and $\text{C}_4\text{H}_9\text{O}^+$. These likely result from the decomposition of the binary precursor $\text{Ni}((\text{C}_2\text{H}_5)_2\text{O})^+$ prior to supersonic cooling in the ion source. Both ^{58}Ni and ^{60}Ni isotopes are clearly observed in each nickel containing mass peak. The peak labelled $\text{C}_4\text{H}_9\text{O}^+$ is assigned as an oxocarbenium. The intensity of the $\text{C}_4\text{H}_9\text{O}^+$ peak dominates the mass spectrum, saturating the detector and causing the baseline to drop following detection of this mass peak. The mass assignments of each peak with appreciable intensity have been corroborated using collision induced dissociation experiments.

Figure 6.3 plots fragment intensity resulting from the laser induced dissociation

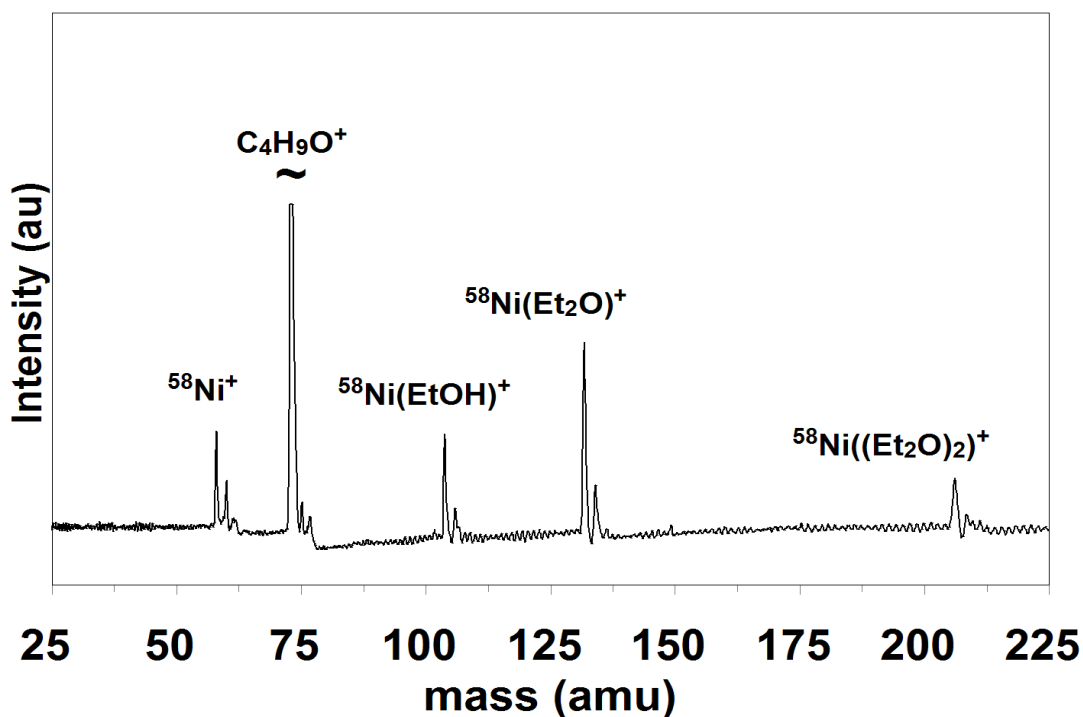


Figure 6.2: Typical TOF mass spectrum resulting from vaporization of nickel metal in a pulsed helium expansion doped with the vapor pressure of diethyl ether.

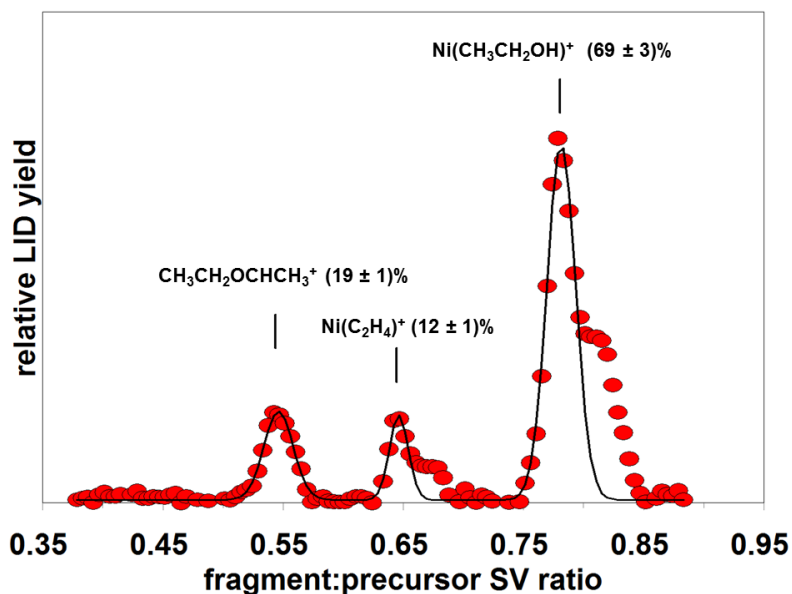
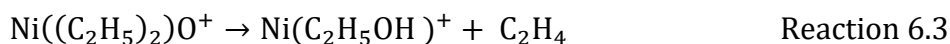
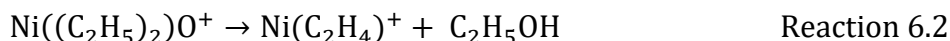
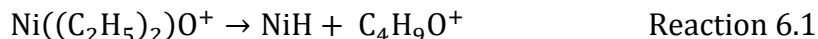


Figure 6.3: Transmission profile for each observed fragment in the Ni^+ mediated rearrangement dissociation of diethyl ether. Exit channel fractions provided in the figure require correction to account for the rate dependent sampling of the SPIDRR technique. Corrected exit channel fractions are provided in Table 6.1.

(LID) of the $\text{Ni}((\text{C}_2\text{H}_5)_2\text{O})^+$ precursor energized with an activating photon energy equal to $16,000\text{ cm}^{-1}$. Fragment yields are plotted against their fragment to precursor sector voltage ratio and each peak is assigned based on the known mass and sector transmission voltage of the precursor. The shoulder on the high mass ratio side of each of the heavier fragment peaks is due to $^{60}\text{Ni}(\text{fragment})^+$ isotope and is an artefact of how the sector is voltage scanned. A Gaussian function is fit to the experimental intensities of each fragment peak which is given by the solid curve in Figure 6.3. The exit channel fractions provided in Figure 6.3 are determined directly from these Gaussian fits and represents the peak's fractional integrated area relative to the total integrated fragment yield. Exit channel fractions measured in this way require corrections, described below, due to the rate dependent sampling of the SPIDRR technique. The three peaks observed in Figure 6.3

result from the relatively slow Ni^+ mediated rearrangement decomposition of diethyl ether when activated with a photon of energy equal to $16,000\text{ cm}^{-1}$. Interestingly, this energy is significantly less than that required for the thermal decomposition of $(\text{C}_2\text{H}_5)_2\text{O}$ and it is the presence of the bare Ni^+ cation that opens the low-energy pathways for decomposition into the products shown in Figure 6.3 and in Reactions 6.1-6.3.



Reactions 6.1-6.3 are the exit channels available to the $\text{Ni}((\text{C}_2\text{H}_5)_2)\text{O}^+$ following absorption of a quantum of energy equal to $16,000\text{ cm}^{-1}$. Reaction 6.1 proceeds through a hydride transfer/charge transfer sequence (HT/CT) while Reactions 6.2 and 6.3 follow an oxidative addition/reductive elimination (OA/RE) sequence. Clearly, there is the suggestion of rather interesting competitive reaction kinetics and dynamics associated with the decay of the photo-excited $\text{Ni}((\text{C}_2\text{H}_5)_2)\text{O}^+$ precursor.

Energy-resolved reaction kinetics were measured for rearrangement Reactions 6.1-6.3 at a precursor activation energy = $16,000\text{ cm}^{-1}$. Normalized fragment intensity is plotted against τ in the three traces of Figure 6.4. The HT/CT, Reaction 6.1, occurs at a rate that is roughly five times greater than the OA/RE sequence of Reactions 6.2 and 6.3. The faster reaction was therefore scanned at a 250 ns resolution whereas the slower processes were measured at a 1 μs temporal resolution. We have previously demonstrated that SPIDRR kinetic signals of the type shown in Figure 6.4, where the intensity of each fragment is plotted as a function of the relative delay between firing the OE and dye laser, is directly related to the rate law governing precursor decay. The SPIDRR kinetic signals

in Figure 6.4 were fit to a single exponential function (solid curve through the data) with the extracted rate constant provided in each trace. The signals in the lower two traces, elimination of neutral ethanol/ethene fragments (Reactions 6.2 and 6.3) display the same decomposition kinetics within the error of the measurements. This suggests that the reaction that forms these fragments initiates along a single path that bifurcates following the rate determining step in the dissociative mechanism.

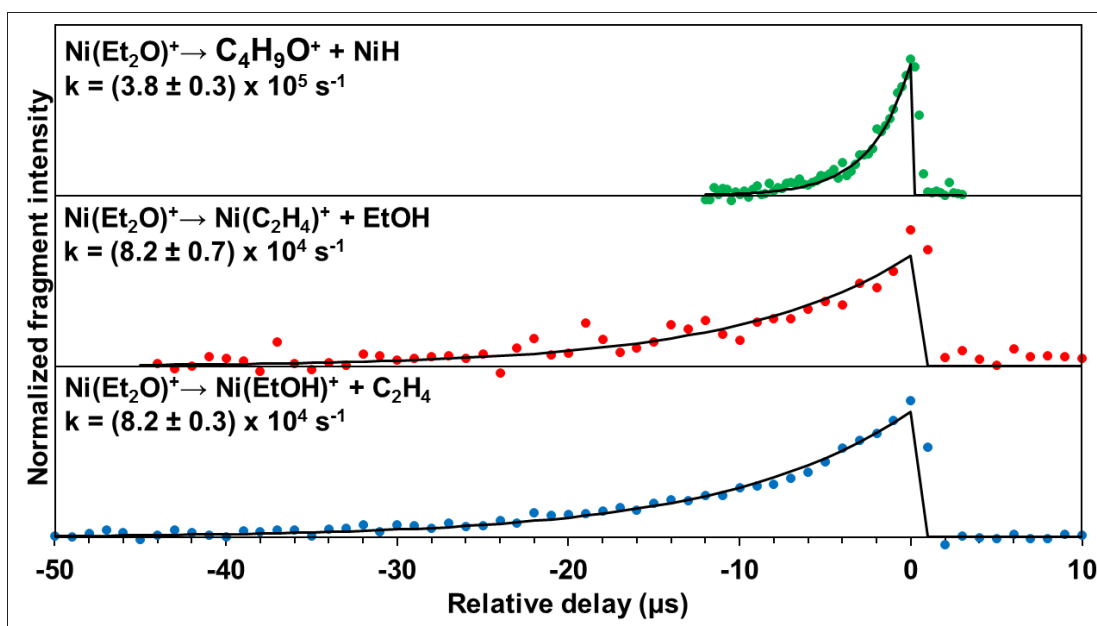


Figure 6.4: Normalized SPIDRR fragment intensities plotted against τ , or the relative time delay between precursor absorption of a quantum of photon energy = $16,000 \text{ cm}^{-1}$ and pulsed extraction into the TOF. Uncertainties are reported to a $\pm$ one standard deviation obtained from single exponential fits.

Table 6.1. Rate constants and corrected product branching ratios measured in the Ni⁺ mediated decomposition of (C₂H₅)₂O at an activating energy of 16,000 cm⁻¹.

Reaction	Exit Channel	k (s ⁻¹)	Exit Channel %
6.1	C ₄ H ₉ O ⁺ + NiH	3.8 ± 0.3 x 10 ⁵	40 ± 2
6.2	Ni(C ₂ H ₄) ⁺ + C ₂ H ₅ OH	8.2 ± 0.7 x 10 ⁴	9 ± 2
6.3	Ni(C ₂ H ₅ OH) ⁺ + C ₂ H ₄	8.2 ± 0.3 x 10 ⁴	51 ± 4

Again, relative exit channel intensities measured by sector scan in the SPIDRR technique (Figure 6.3) are dependent on the reaction rates governing their formation. This technique exclusively samples fragments formed in the field-free region of the TOF. However, the reaction is initiated through photon absorption while the precursor ions are within the plates of the orthogonal extractor. Thus, the precursor must exit the acceleration field (~3 μs required to accelerate through the grid) before producing detectable fragments. The portion of the fragment signal produced by precursor decay within the OA remains unsampled. When each product channel has the same formation kinetics, as is the case for Reactions 6.2 and 6.3, the exit channel fractions measured by sector scan represent an unbiased measurement of relative intensities. However, in those cases where the precursor decay rate into the various channels is different, as indicated in Figure 6.4 for Reaction 6.1 relative to Reactions 6.2 and 6.3, then the measured exit channel fractions need correction to account for the unsampled precursor decay that occurs within the acceleration field. This correction is accounted for in a straight-forward fashion.¹¹ Table 6.1 provides the energy-resolved rate constants and corrected exit channel fractions for the Ni⁺ mediated decay of diethyl ether.

Potential energy profiles computed for the Ni^+ mediated decomposition of diethyl ether were secured at various levels of theory. Each computed profile features a single transition state (TS) separating the encounter complex (EC) from the $\text{C}_4\text{H}_9\text{O}^+ + \text{NiH}$ products. Each profile computes two TS barriers along the OA/RE pathway, one associated with oxidative addition and the other with reductive elimination. The difference between the various computed PESs is the relative TS barrier heights and the energy of the exit channel products. Figure 6.5a provides the potential energy surface that we feel best represents the Ni^+ mediated decay of diethyl ether and is computed at the MRMP(5,5)/CC-pVDZ//PBE/CC-pVDZ level. The reaction initiates in the deep well of the EC. There are two viable pathways to product formation with the competition between these paths occurring at the first transition state (TS1). Reaction 6.1, the HT/CT, is the yellow pathway while the blue path shows the OA/RE sequence of Reactions 6.2 and 6.3. The TS1 energy difference between these two pathways is 1010 cm^{-1} . The red dashed path leads to unobserved products that are discussed below.

Following Reaction 6.1 the precursor surmounts TS_{AC} as a hydride is transferred to the Ni^+ neutralizing the cation while leaving the remaining organic fragment charged. The resulting intermediate thus features a neutral NiH bound to the oxocarbenium cation which travels a featureless energy barrier to separate into the $\text{NiH} + \text{C}_4\text{H}_9\text{O}^+$ fragments at $14,500\text{ cm}^{-1}$ relative to the EC. Reactions 6.2 and 6.3 follow the Ni^+ cation adding to the ether C-O bond, further oxidizing the metal center. TS_{AB} separates the EC from the Ni^+ inserted intermediate **B** and represents the lowest energy barrier on the PES. A β -hydride elimination ensues as a hydride is transferred to the cation, depositing its electrons, and reducing the metal to its initial +1 charge state. The hydrogen motion continues as the

proton binds to an electron pair on the oxygen atom forming ethanol. This transfer mimics the near orbital hydrogen motion that was observed in the rate determining step in the Ni^+ mediated decay of ethyl acetate (Figure 6.1).

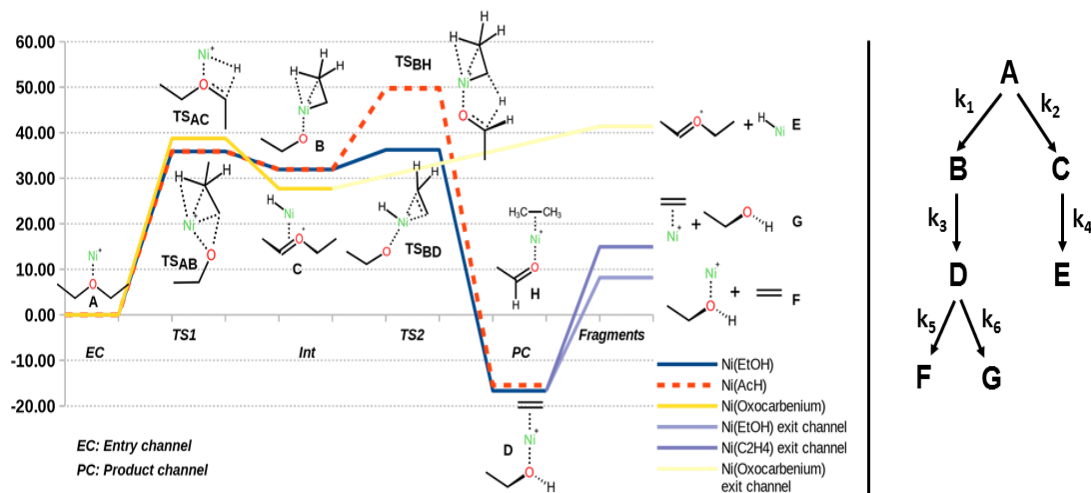


Figure 6.5: (a) Energy profiles for the different pathways considered in the Ni^+ mediated decomposition of diethyl ether computed at the MRMP(5,5)/CC-pVDZ//PBE/CC-pVDZ level (relative Gibbs free energies in kcal/mol). (b) Labels showing structure equivalents in the left panel that are connected through rate constants (k_1 - k_6). This scheme is the kinetic model used to generate integrated rate equations.

For completeness, the pathway for the reverse hydrogen transfer following intermediate **B** (Figure 6.5) was also computed. This reverse transfer would produce acetaldehyde and ethane, instead of ethanol and ethene. The relatively high activation energy for this process, 4200 cm^{-1} vs. $12,700\text{ cm}^{-1}$ computed for TS_{BH} and TS_{BD} suggests why these products are not observed in the SPIDRR experiment.

The profile of Figure 6.5a suggests that the HT/CT of Reaction 6.1 occurs in a single concerted step while the OA/RE of Reactions 6.2 and 6.3 occur in discernible two step sequences. These processes reduce to the simpler mechanism provided in Figure 6.5b

which associates a rate constant with surmounting each specific barrier. Time differential equations are determined from Figure 6.5b for the decay of the photo-excited EC or precursor, formation and decay of each intermediate, and production of final product. These differential equations are exactly integrated to yield a series of rate equations that detail the temporal development of each species. We have previously demonstrated that SPIDRR signals of the types provided in each trace of Figure 6.4 result from evaluating a definite integral over the time differential equations detailing the production of a specific fragment. Thus, the SPIDRR results provided in Figures 3 and 4 can be combined and modelled by a single kinetic model based on the integrated rate equations. Figure 6.6 shows these results.

The normalized intensity of the SPIDRR signals of Figure 6.4 are multiplied by the relative exit channel fractions determined by the sector voltage transmission profiles in Figure 6.3. These are plotted as symbols against τ in the top panel of Figure 6.6. The solid curve through the symbols is calculated from the kinetic model based on the integrated rate equations and using the rate constant values provided in Figure 6.6. Elimination of the final Ni^+ bound ethanol and ethene products are governed by rate constants k_5 and k_6 . However, the fit is dependent only on the k_5/k_6 ratio and this value optimized to roughly equal the $\text{Ni}(\text{CH}_3\text{CH}_2\text{OH})^+/\text{Ni}(\text{C}_2\text{H}_4)^+$ exit channel ratio measured in Figure 6.3. Rate constant values were optimized by minimizing the squared residuals to the simultaneous fit of all three SPIDRR waveforms (symbols, top panel of Figure 6.6) with the only constraint that the rate constants remain positive values. The lower panel of Figure 6.6 shows the temporal dependence of the precursor, each intermediate, and the three observed products. Reaction 6.1, the formation of the oxocarbenium cation product, is rate limited

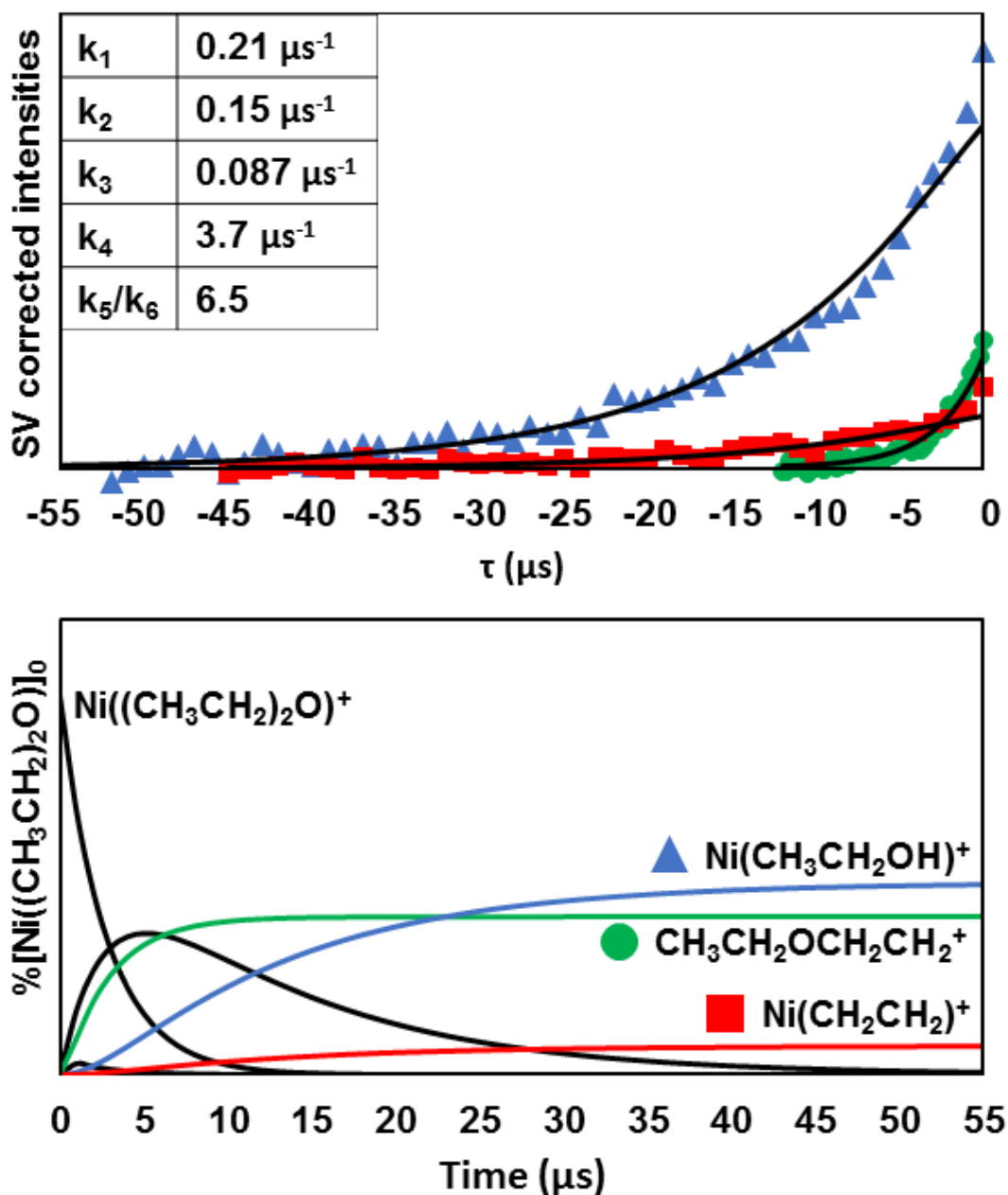


Figure 6.6: (top panel) Sector voltage corrected fragment intensities (symbols) plotted against τ (the relative delay between firing the OA and activation laser). This represents an accurate relative rendering of the fragment intensities. The solid curve through the symbols is calculated from the kinetic model using the rate constant values in the inset. (lower panel) The temporal decay of the precursor, the build-up and decay of each intermediate, and the formation of each fragment ion as determined from the kinetic model. The horizontal axes show the relationship between τ and time.

by precursor decay as is evident by the black and green traces in the lower panel of Figure 6.6. The $\text{Ni}((\text{C}_2\text{H}_5)_2\text{O})^+$ precursor decays competitively along two pathways when energized to $16,000\text{ cm}^{-1}$. This occurs with a composite rate constant given by the sum of the individual rate constants ($k_1 + k_2$) required to overcome TS_{AB} and TS_{AC} . The composite rate constant is the experimentally measured observable and has a value equal to $0.38 \pm 0.03\text{ }\mu\text{s}^{-1}$ (Figure 6.4 and Table 6.1). The kinetic model, however, separates this composite rate constant and quantifies each value along each competitive path. The model predicts that the k_1 and k_2 rate constants required to surmount TS_{AB} and TS_{AC} are $0.21 \pm 0.02\text{ }\mu\text{s}^{-1}$ and $0.15 \pm 0.02\text{ }\mu\text{s}^{-1}$, respectively. Their sum, $0.36\text{ }\mu\text{s}^{-1}$, compares favourably with the individual measurement, $0.38 \pm 0.03\text{ }\mu\text{s}^{-1}$. The error limits on k_1 and k_2 are propagated from the standard deviation on the composite rate constant combined with the uncertainty in the exit channel fractions (Figure 6.3).

Demanding that the kinetic model simultaneously fit the observed reaction rates and the relative exit channel intensities significantly limits the possible acceptable rate constant combinations. Moreover, this limits the acceptable calculated potential energy profiles as well. Formation of the oxocarbenium cation product must be rate limited by precursor decay. Each calculated profile agrees that this dissociative pathway contains a single transition state located just past the reaction entrance channel and motion along this path is essentially concerted. Since the HC/CT path is rate limited by precursor decay, the remaining OA/RE dissociative pathway must be rate limited by the reductive elimination step of this sequence, otherwise, the rate constant for formation of each measured product would be identical, but this is not observed. Thus, formation of the elimination products, loss of neutral ethene and ethanol, is rate limited by the decay of reaction INT-**B** to INT-**D**

through TS_{BD}. This is the hydride transfer step along the OA/RE sequence (see Figure 6.5a). Simultaneously fitting each SPIDRR waveform to the results of the integrated rate equations optimizes this rate constant value as $k_3 = 0.087 \mu\text{s}^{-1}$. The measured value for the rate limiting step along the OA/RE sequence from Figure 6.4 is $0.082 \pm 0.003 \mu\text{s}^{-1}$. Overall, there is agreement (within 2 standard deviations) between the rate constants extracted from simultaneously fitting the measured kinetic responses and the values extracted from the individual fits of Figure 6.4.

Discussion

SPIDRR experiments in combination with computational theory suggest that there exist two low energy dissociative pathways to form the observed products. Both pathways are active when the $\text{Ni}((\text{C}_2\text{H}_5)_2)\text{O}^+$ precursor is energized with an activating photon energy of $16,000 \text{ cm}^{-1}$. This is well below the energy required to break isolated C-O bonds ($30,000 \text{ cm}^{-1}$) and thus the Ni^+ cation lowers activation requirements and in doing so, acts in similar fashion to a catalytic active site during the decomposition reaction.

The competitive pathways are described as HT/CT and OA/RE sequences each involving a rate limiting hydride transfer with different transfer rates. The rate constant describing the rate of hydride transfer along the charge transfer pathway is $k_2 = k_{\text{HTCT}} = 0.15 \pm 0.02 \mu\text{s}^{-1}$ which occurs when the $\text{Ni}((\text{C}_2\text{H}_5)_2)\text{O}^+$ precursor is energized to $16,000 \text{ cm}^{-1}$. This value was extracted from the measured composite rate constant for the formation of the oxocarbenium cation, $k = 0.38 \pm 0.03 \mu\text{s}^{-1}$. The rate constant describing the hydride transfer along the remaining pathway is associated with the reductive elimination step along the OA/RE sequence. This value was directly measured via formation of the

$\text{Ni}(\text{CH}_3\text{CH}_2\text{OH})^+$ and $\text{Ni}(\text{C}_2\text{H}_4)^+$ fragments as $k_3 = k_{\text{RE}} = 0.082 \pm 0.003 \text{ } \mu\text{s}^{-1}$. The k_{RE} rate constant value is $\sim 2\times$ smaller than k_{HTCT} .

Figure 6.5a suggests that the competition to enter the OA/RE and HT/CT pathways occurs at the first transition state that the energized $\text{Ni}((\text{C}_2\text{H}_5)_2)\text{O}^+$ precursor experiences. Again, the rate constant associated with oxidative addition is extracted from the composite rate constant for formation of $\text{C}_4\text{H}_9\text{O}^+$ and has the value $k_1 = k_{\text{OA}} = 0.21 \pm 0.02 \text{ } \mu\text{s}^{-1}$ at an activating energy of $16,000 \text{ cm}^{-1}$. The competition between entering the different pathways is given by the $k_{\text{OA}}/k_{\text{CTHT}}$ ratio (≈ 1.5) which is equal to the 60/40 exit channel ratio provided in Table 6.1 (sum of product integrated areas from Reactions 6.2 and 6.3 relative to Reaction 6.1). Once the path is selected, the $\text{Ni}((\text{C}_2\text{H}_5)_2)\text{O}^+$ precursor will either dissociate into $\text{NiH} + \text{C}_4\text{H}_9\text{O}^+$ fragments in a concerted fashion or the Ni^+ cation will oxidatively add into a CO bond and reductively eliminate neutral ethene and ethanol fragments. Reductive elimination is the rate limiting barrier along this sequence. The rate limiting motion is computed to be a hydride atom transfer from the beta position of the CH_2CH_3 fragment across the Ni^+ cation and onto the oxygen atom lone pair of electrons. This large amplitude, orbit-like motion has been previously observed in the Ni^+ mediated decay of ethyl acetate.⁶ In this earlier study, a β -hydride was transferred following the oxidative addition of the Ni^+ cation into a C-C bond. The transferring hydride travelled from an organic CH_2CH_3 fragment, across the Ni^+ cation while depositing electron density into the cation, to finally protonate an oxygen lone pair of electrons eliminating ethene and acetic acid products. Such transfers are appearing to be a more prevalent motif in Ni^+ mediated decomposition reactions.

Conclusions

Experimentation has been complimented by computation to provide a dynamic picture of the reaction kinetics in the low energy, Ni^+ mediated decomposition of diethyl ether. The SPIDRR technique has measured energy-resolved rate constants for the decomposition of $\text{Ni}((\text{C}_2\text{H}_5)_2\text{O})^+$ at an activation energy = $16,000\text{ cm}^{-1}$. The reaction is complicated by the presence of two types of dissociative pathways, each with competing kinetics. One is an immediate alpha hydride transfer onto the Ni^+ , neutralizing the cation, and characterized by precursor dissociation into $\text{NiH} + \text{C}_4\text{H}_9\text{O}^+$ fragments. The energy-resolved rate constant controlling this hydride transfer/charge transfer process at an activating energy of $16,000\text{ cm}^{-1}$ is $k_{\text{HTCT}} = 0.15 \pm 0.02\text{ }\mu\text{s}^{-1}$. The second type of reaction features an oxidative addition/reductive elimination two-step sequence with rate constant values $k_{\text{OA}} = 0.21 \pm 0.02\text{ }\mu\text{s}^{-1}$ and $k_{\text{RE}} = 0.082 \pm 0.003\text{ }\mu\text{s}^{-1}$. Analysis of the experimental results in the context of the computed reaction profile indicates that the reductive elimination step rate limits the reaction while the ratio of $k_{\text{OA}} / k_{\text{HTCT}}$ controls partitioning along each dissociative pathway.

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CHAPTER SEVEN

Conclusions

This dissertation has been dedicated to the investigation of complex ion-molecule reactions. Each of the systems studied in Chapters 3-6 had at least two competitive reactions proceeding with different rates. In addition, the first study of a metal oxide's reactivity investigated with the SPIDRR technique is reported here. Previous single photon initiated dissociative rearrangement reactions (SPIDRR) technique studies had not addressed these more complicated reactive scenarios and I have learned that significant care must be taken in the analysis of these systems, due to the unique sampling of SPIDRR distorting the observed product partitioning of complicated reactions, as described in Chapter 2. Application of such has unveiled unprecedented mechanistic and dynamic information in metal and metal oxide mediated chemistries.

It is difficult to overstate the value of the SPIDRR technique's unique ability to measure the time-dependence of product formation directly, rather than merely obtain rate constants through measurement of mass spectral peak intensities. This dissertation has hopefully proven that an incredible amount of detailed information exists in the kinetic signatures obtained by SPIDRR. This is most readily demonstrated by the identification of a unique experimental signature of two-state reactivity (TSR), an achievement that has been sought since its inception over two decades ago.

Significant progress in kinetic modeling has been made. MatLab scripts have been developed that allow for analytical solutions of the time dependence of all species in

virtually any kinetic model. Analytic solutions allow for the extraction of convoluted kinetic information from SPIDRR signals. In addition, more advanced methods of error analysis have been employed that significantly improve our ability to evaluate the quality of fit of a kinetic model to SPIDRR signals. This ability removes certain chemical interpretations from consideration while accelerating others, which aides in the elucidation of a reaction mechanism.

Moving forward, future work should focus on studying other reactive systems that are likely to feature TSR. These include reactions of transition metal cations that feature a dense electronic structure, such as Co^+ and Fe^+ , with simple organic molecules. The energy dependence of the TiO^+ mediated decomposition of CH_3COCH_3 should be investigated. Further studies of transition metal oxides mediated decompositions also show promise of featuring TSR and interesting reactive paradigms that can be investigated in unique detail using SPIDRR.

Finally, the kinetic modeling is now mature enough to be integrated with statistical theories such as RRKM. The integration of computational chemistry, statistical theory, kinetic modeling, with experimental SPIDRR signals will provide an unprecedented set of tools to investigate reaction dynamics and mechanisms.

The End

APPENDICES

APPENDIX A

MatLab Scripts for Kinetic Modeling

Several simple scripts are presented here that were developed for the models used in Chapter Two. Each of these scripts can be copy/pasted or typed into MatLab versions R2019a or newer. At the beginning of each script are several adjustable parameters that determine the plotted curves. The method used to analytically solve for the time dependence of each species in a model is based on common matrix methods. An excellent explanation of these methods is provided in the second chapter of: J. I. Steinfeld, J. S. Francisco and W. L. Hase, Chemical Kinetics and Dynamics (2nd Edition), 1998.

$A \rightarrow B$ (Model 2.1)

```
% Symbolic Kinetics with Reversibility and SPIDRR %  
%%  
clear;  
  
A_0 = 1;      % intial value of A  
k_1 = 0.04;  
k_2 = 2;  
k_3 = 1;  
alpha = 3;  
delta = 37;  
  
% Solving  
% All symbols being used %  
syms A0 k1 k2 k3 t  
  
% Rate Constant Matrix %  
k = [-k1 0 0 0;  
      k1 -(k2+k3) 0 0;  
      0 k2 0 0;  
      0 k3 0 0;];  
% Initial Concentration Matrix %  
Conc_0 = [A0;  
          0;
```

```

0;
0];

% Solving for eigenvecs/vals %
evals = eig(k);
[x, ~] = eig(k);
lambda = exp(evals*t);
diag_evals = diag(lambda);

% Calculation %
Conc = x*diag_evals/x*Conc_0;
A(t) = Conc(1,1);
B(t) = Conc(2,1);
C(t) = Conc(3,1);
D(t) = Conc(4,1);

t_int = 0:1:100; % time interval

simplify(A);
simplify(B);
simplify(C);
simplify(D);

P1 = k2*B;
P2 = k3*B;

P1_s = int(P1,t+alpha,t+delta);
P2_s = int(P2,t+alpha,t+delta);

P1_s = simplify(P1_s);
P2_s = simplify(P2_s);

A_fun = matlabFunction(A);
B_fun = matlabFunction(B);
C_fun = matlabFunction(C);
D_fun = matlabFunction(D);

P1_fun = matlabFunction(P1_s);
P2_fun = matlabFunction(P2_s);
%-----
%plotting. Settings

fig = figure;
fig.Position = [2307 94 1077 900];

%setting axis
xlims = [0 100];
sxlims = [-100 0];
ylims = [0 1];
ylims_2 = [0 1];
%colors and settings
colors = linespecer(4);

```

```

fontsize = 14;
axisfontsize = 14;
markersize = 6;
axispos = -148;
start_ratio = 46;
stop_ratio = 62;

data_settings = {'LineStyle', 'none', 'Marker', 'o', 'MarkerEdgeColor',
'k', 'MarkerSize', 10};
fit_settings = {'LineWidth', 3, 'Color', 'k'};
manydata_settings = {'LineStyle', 'none', 'Marker', 'o', 'MarkerSize',
5, 'MarkerEdgeColor', 'k'};
axis_settings = {'YLim', ylims, 'fontsize', 15, 'fontweight', 'bold',
'XLim', xlims};
signal_axis_settings = {'YLim', ylims_2, 'XLim', xlims, 'fontsize',
15, 'fontweight', 'bold'};
font_settings = {'FontSize', 15, 'FontWeight', 'bold'};
ann_settings = {'FitBoxToText', 'on', 'EdgeColor', 'k', 'FontSize', 10,
'FontWeight', 'bold'};

% Plotting
close all;

Ay = A_fun(t_int,A_0,k_1);
By = B_fun(t_int,A_0,k_1,k_2,k_3);
Cy = C_fun(t_int,A_0,k_1,k_2,k_3);
Dy = D_fun(t_int,A_0,k_1,k_2,k_3);

P1y = P1_fun(A_0,k_1,k_2,k_3,t_int);
P2y = P2_fun(A_0,k_1,k_2,k_3,t_int);
%-----
fig1 = figure();
fig1.Position = [800 300 550 620];

plot_all = subplot(2,2,1,axis_settings{:});
plot_all.XAxis.TickLabels = '';
plot_all.Position = [0.11 0.56 0.43 0.43];
hold on
plot_all.Box = 'on';

plot(t_int,Ay, fit_settings{:}, 'Color', colors(2,:));
plot(t_int,By, fit_settings{:}, 'Color', colors(3,:));
plot(t_int,Cy, fit_settings{:}, 'Color', colors(4,:));
plot(t_int,Dy, fit_settings{:}, 'Color', colors(1,:));

ylabel('Relative Intensity');
legend("A(t)", "B(t)", "C(t)", "D(t)", 'Location', 'NorthWest');
%-----
plot_all_norm = subplot(2,2,3,axis_settings{:});

```

```

plot_all_norm.Position = [0.11 0.09 0.43 0.43];
hold on
plot_all_norm.Box = 'on';

plot(t_int,Cy/(2/3), fit_settings{:}, 'Color', colors(4,:));
plot(t_int,Dy/(1/3), fit_settings{:}, 'Color',
colors(1,:), 'LineStyle', '--');

plot_all_norm.XRuler.TickLabelGapOffset = -4;
plot_all_norm.XTick = [0 15 30 45 60 75 90];
xlab1 = xlabel('Time ( $\mu\text{s}^{-1}$ )');
xlab1.Position = [50 -0.07 -1];

ylabel('Normalized Intensity');
%xlim([0 10]);
legend('C(t)', 'D(t)', 'Location', 'NorthWest');
%-----
plot_signal = subplot(2,2,2,signal_axis_settings{:});
plot_signal.Position = [0.56 0.56 0.43 0.43];
plot_signal.XAxis.TickLabels = '';
plot_signal.YAxis.TickLabels = '';
hold on
plot_signal.Box = 'on';

plot(-t_int,P1y, fit_settings{:}, 'Color', colors(4,:));
plot(-t_int,P2y, fit_settings{:}, 'Color', colors(1,:));

legend("S_{C}(\tau)", "S_{D}(\tau)", 'Location', 'NorthWest');
%-----
plot_signal_norm = subplot(2,2,4,signal_axis_settings{:});
plot_signal_norm.Position = [0.56 0.09 0.43 0.43];
plot_signal_norm.YAxis.TickLabels = '';
hold on
plot_signal_norm.Box = 'on';

plot(-t_int,P1y/P1y(1), fit_settings{:}, 'Color', colors(4,:));
plot(-t_int,P2y/P2y(1), fit_settings{:}, 'Color',
colors(1,:), 'LineStyle', '--');

legend("S_{C}(\tau)", "S_{D}(\tau)", 'Location', 'NorthWest');

plot_signal_norm.XRuler.TickLabelGapOffset = -4;
plot_signal_norm.XTick = [-90 -75 -60 -45 -30 -15 0];
xlab2 = xlabel('\tau ( $\mu\text{s}^{-1}$ )');
xlab2.Position = [-50 -0.07 -1];

```

$A \rightarrow B \rightarrow C$ (Model 2.4)

```

% Symbolic Kinetics with Reversibility and SPIDRR %
%%
clear;

```

```

A_0 = 1;      % intial value of A
k_1 = 0.1;
k_2 = 0.15;
k_3 = 1;
k_4 = 2;
k_5 = 2;
k_6 = 1;
alpha = 3;
delta = 37;

% Solving
% All symbols being used %
syms A0 k1 k2 k3 k4 k5 k6 t

% Rate Constant Matrix %
k = [ -k1  0      0 0 0;
      k1 -k2    0 0 0;
      0  k2 -(k3+k4) 0 0;
      0  0      k3 0 0;
      0  0      k4 0 0];

% Initial Concentration Matrix %
Conc_0 = [A0;
          0;
          0;
          0;
          0];

% Solving for eigenvecs/vals %
evals = eig(k);
[x, ~] = eig(k);
lambda = exp(evals*t);
diag_evals = diag(lambda);

% Calculation %
Conc = x*diag_evals/x*Conc_0;
A(t) = Conc(1,1);
B(t) = Conc(2,1);
C(t) = Conc(3,1);
D(t) = Conc(4,1);
E(t) = Conc(5,1);

t_int = 0:1:100;    % time interval

simplify(A);
simplify(B);
simplify(C);
simplify(D);
simplify(E);

P1 = k3*C;
P2 = k4*C;

```

```

P1_s = int(P1,t+alpha,t+delta);
P2_s = int(P2,t+alpha,t+delta);

P1_s = simplify(P1_s);
P2_s = simplify(P2_s);

A_fun = matlabFunction(A);
B_fun = matlabFunction(B);
C_fun = matlabFunction(C);
D_fun = matlabFunction(D);
E_fun = matlabFunction(E);

P1_fun = matlabFunction(P1_s);
P2_fun = matlabFunction(P2_s);

%-----
%plotting. Settings

fig = figure;
fig.Position = [2307 94 1077 900];

%setting axis
xlims = [0 100];
sxlims = [-100 0];
ylims = [0 1];
ylims_2 = [0 1];
%colors and settings
colors = linespecer(5);
%colors = flip(colors);

fontsize = 14;
axisfontsize = 14;
markersize = 6;
axispos = -148;
start_ratio = 46;
stop_ratio = 62;

data_settings = {'LineStyle', 'none', 'Marker', 'o', 'MarkerEdgeColor',
'k', 'MarkerSize', 10};
fit_settings = {'LineWidth', 3, 'Color', 'k'};
manydata_settings = {'LineStyle', 'none', 'Marker', 'o', 'MarkerSize',
5, 'MarkerEdgeColor', 'k'};
axis_settings = {'YLim', ylims, 'fontsize', 15, 'fontweight', 'bold',
'XLim', xlims};
signal_axis_settings = {'YLim', ylims_2, 'XLim', sxlims, 'fontsize',
15, 'fontweight', 'bold'};
font_settings = {'FontSize', 15, 'FontWeight', 'bold'};
ann_settings = {'FitBoxToText', 'on', 'EdgeColor', 'k', 'FontSize', 10,
'FontWeight', 'bold'};

% Plotting

```

```

close all;

Ay = A_fun(t_int,A_0,k_1);
By = B_fun(t_int,A_0,k_1,k_2);
Cy = C_fun(t_int,A_0,k_1,k_2,k_3,k_4);
Dy = D_fun(t_int,A_0,k_1,k_2,k_3,k_4);
Ey = E_fun(t_int,A_0,k_1,k_2,k_3,k_4);

P1y = P1_fun(A_0,k_1,k_2,k_3,k_4,t_int);
P2y = P2_fun(A_0,k_1,k_2,k_3,k_4,t_int);

%-----
fig1 = figure();
fig1.Position = [2345 241 550 620];

plot_all = subplot(2,2,1,axis_settings{:});
plot_all.XAxis.TickLabels = '';
plot_all.Position = [0.11 0.56 0.43 0.43];
hold on
plot_all.Box = 'on';

plot(t_int,Ay, fit_settings{:}, 'Color', colors(1,:));
plot(t_int,By, fit_settings{:}, 'Color', colors(2,:));
plot(t_int,Cy, fit_settings{:}, 'Color', colors(3,:));
plot(t_int,Dy, fit_settings{:}, 'Color', colors(4,:));
plot(t_int,Ey, fit_settings{:}, 'Color', colors(5,:));

ylabel('Relative Intensity');
legend("A(t)", "B(t)", "C(t)", "D(t)", "E(t)", 'Location', 'NorthWest');
%-----
plot_all_norm = subplot(2,2,3,axis_settings{:});
plot_all_norm.Position = [0.11 0.09 0.43 0.43];
hold on
plot_all_norm.Box = 'on';

plot(t_int,Dy/(1/3), fit_settings{:}, 'Color', colors(4,:));
plot(t_int,Ey/(2/3), fit_settings{:}, 'Color',
colors(5,:), 'LineStyle', '--');

plot_all_norm.XRuler.TickLabelGapOffset = -4;
plot_all_norm.XTick = [0 15 30 45 60 75 90];
xlabel = xlabel('Time ( $\mu s^{-1}$ )');
xlabel.Position = [50 -0.07 -1];

ylabel('Normalized Intensity');
%xlim([0 10]);
legend("D(t)", "E(t)", 'Location', 'SouthEast');
%-----
plot_signal = subplot(2,2,2,signal_axis_settings{:});
plot_signal.Position = [0.56 0.56 0.43 0.43];
plot_signal.XAxis.TickLabels = '';

```

```

plot_signal.YAxis.TickLabels = '';
hold on
plot_signal.Box = 'on';

plot(-t_int,P1y, fit_settings{:}, 'Color', colors(4,:));
plot(-t_int,P2y, fit_settings{:}, 'Color', colors(5,:));

legend("S_{D}(\tau)", "S_{E}(\tau)", 'Location', 'NorthWest');
%-----
plot_signal_norm = subplot(2,2,4,signal_axis_settings{:});
plot_signal_norm.Position = [0.56 0.09 0.43 0.43];
plot_signal_norm.YAxis.TickLabels = '';
hold on
plot_signal_norm.Box = 'on';

plot(-t_int,P1y/P1y(1), fit_settings{:}, 'Color', colors(4,:));
plot(-t_int,P2y/P2y(1), fit_settings{:}, 'Color',
colors(5,:), 'LineStyle', '--');

legend("S_{D}(\tau)", "S_{E}(\tau)", 'Location', 'NorthWest');

plot_signal_norm.XRuler.TickLabelGapOffset = -4;
plot_signal_norm.XTick = [-90 -75 -60 -45 -30 -15 0];
xlab2 = xlabel('\tau (\mu s^{-1})');
xlab2.Position = [-50 -0.07 -1];

```

Early Bifurcation (Model 2.2)

```

% Symbolic Kinetics with Reversibility and SPIDRR %
%%
clear;

A_0 = 1;      % initial value of A
k_1 = 0.03;
k_2 = 0.01;
k_3 = 1;
k_4 = 2;
k_5 = 1.5;
k_6 = 1;
alpha = 3;
delta = 37;

% Solving
% All symbols being used %
syms A0 k1 k2 k3 k4 k5 k6 t

% Rate Constant Matrix %
k = [-(k1+k2) 0 0 0 0 0 0;
      k1 -(k3+k4) 0 0 0 0 0;
      k2 0 -(k5+k6) 0 0 0 0;

```

```

        0 k3 0 0 0 0 0;
        0 k4 0 0 0 0 0;
        0 0 k5 0 0 0 0;
        0 0 k6 0 0 0 0];
% Initial Concentration Matrix %
Conc_0 = [A0;
          0;
          0;
          0;
          0;
          0;
          0];

% Solving for eigenvecs/vals %
evals = eig(k);
[x, ~] = eig(k);
lambda = exp(evals*t);
diag_evals = diag(lambda);

% Calculation %
Conc = x*diag_evals/x*Conc_0;
A(t) = Conc(1,1);
B(t) = Conc(2,1);
C(t) = Conc(3,1);
D(t) = Conc(4,1);
E(t) = Conc(5,1);
F(t) = Conc(6,1);
G(t) = Conc(7,1);

t_int = 0:1:100;    % time interval

simplify(A);
simplify(B);
simplify(C);
simplify(D);
simplify(E);
simplify(F);
simplify(G);

P1 = k3*B;
P2 = k4*B;
P3 = k5*C;
P4 = k6*C;

P1_s = int(P1,t+alpha,t+delta);
P2_s = int(P2,t+alpha,t+delta);
P3_s = int(P3,t+alpha,t+delta);
P4_s = int(P4,t+alpha,t+delta);

P1_s = simplify(P1_s);
P2_s = simplify(P2_s);
P3_s = simplify(P3_s);
P4_s = simplify(P4_s);

A_fun = matlabFunction(A);

```

```

B_fun = matlabFunction(B);
C_fun = matlabFunction(C);
D_fun = matlabFunction(D);
E_fun = matlabFunction(E);
F_fun = matlabFunction(F);
G_fun = matlabFunction(G);

P1_fun = matlabFunction(P1_s);
P2_fun = matlabFunction(P2_s);
P3_fun = matlabFunction(P3_s);
P4_fun = matlabFunction(P4_s);
%-----
%plotting. Settings

fig = figure;
fig.Position = [2307 94 1077 900];

%setting axis
xlims = [0 100];
sxlims = [-100 0];
ylims = [0 1];
ylims_2 = [0 1];
%colors and settings
colors = linspace(7);
colors = flip(colors);

fontsize = 14;
axisfontsize = 14;
markersize = 6;
axispos = -148;
start_ratio = 46;
stop_ratio = 62;

data_settings = {'LineStyle', 'none', 'Marker', 'o', 'MarkerEdgeColor',
'k', 'MarkerSize', 10};
fit_settings = {'LineWidth', 3, 'Color', 'k'};
manydata_settings = {'LineStyle', 'none', 'Marker', 'o', 'MarkerSize',
5, 'MarkerEdgeColor', 'k'};
axis_settings = {'YLim', ylims, 'fontsize', 15, 'fontweight', 'bold',
'XLim', xlims};
signal_axis_settings = {'YLim', ylims_2, 'XLim', sxlims, 'fontsize',
15, 'fontweight', 'bold'};
font_settings = {'FontSize', 15, 'FontWeight', 'bold'};
ann_settings = {'FitBoxToText', 'on', 'EdgeColor', 'k', 'FontSize', 10,
'FontWeight', 'bold'};

% Plotting
close all;

Ay = A_fun(t_int,A_0,k_1,k_2);
By = B_fun(t_int,A_0,k_1,k_2,k_3,k_4);
Cy = C_fun(t_int,A_0,k_1,k_2,k_5,k_6);
Dy = D_fun(t_int,A_0,k_1,k_2,k_3,k_4);
Ey = E_fun(t_int,A_0,k_1,k_2,k_3,k_4);

```

```

Fy = F_fun(t_int,A_0,k_1,k_2,k_5,k_6);
Gy = G_fun(t_int,A_0,k_1,k_2,k_5,k_6);

P1y = P1_fun(A_0,k_1,k_2,k_3,k_4,t_int);
P2y = P2_fun(A_0,k_1,k_2,k_3,k_4,t_int);
P3y = P3_fun(A_0,k_1,k_2,k_5,k_6,t_int);
P4y = P4_fun(A_0,k_1,k_2,k_5,k_6,t_int);
%-----
fig1 = figure();
fig1.Position = [2345 241 550 620];

plot_all = subplot(2,2,1,axis_settings{:});
plot_all.XAxis.TickLabels = '';
plot_all.Position = [0.11 0.56 0.43 0.43];
hold on
plot_all.Box = 'on';

plot(t_int,Ay, fit_settings{:}, 'Color', colors(1,:));
plot(t_int,By, fit_settings{:}, 'Color', colors(2,:));
plot(t_int,Cy, fit_settings{:}, 'Color', colors(3,:), 'LineStyle', '--');
plot(t_int,Dy, fit_settings{:}, 'Color', colors(4,:));
plot(t_int,Ey, fit_settings{:}, 'Color', colors(5,:));
plot(t_int,Fy, fit_settings{:}, 'Color', colors(6,:));
plot(t_int,Gy, fit_settings{:}, 'Color', colors(7,:));

ylabel('Relative Intensity');
legend("A(t)", "B(t)", "C(t)", "D(t)", "E(t)", "F(t)", "G(t)", 'Location', 'NorthWest');
%-----
plot_all_norm = subplot(2,2,3,axis_settings{:});
plot_all_norm.Position = [0.11 0.09 0.43 0.43];
hold on
plot_all_norm.Box = 'on';

plot(t_int,Dy/(1/3)/0.75, fit_settings{:}, 'Color', colors(4,:));
plot(t_int,Ey/(2/3)/0.75, fit_settings{:}, 'Color',
colors(5,:), 'LineStyle', '--');
plot(t_int(1:8:end),Fy(1:8:end)/(3/5)/0.25, fit_settings{:}, 'Color',
colors(6,:), 'LineStyle', 'none', 'Marker', 'o', 'LineWidth', 1);
plot(t_int(4:8:end),Gy(4:8:end)/(2/5)/0.25, fit_settings{:}, 'Color',
colors(7,:), 'LineStyle', 'none', 'Marker', 'd', 'LineWidth', 1);

plot_all_norm.XRuler.TickLabelGapOffset = -4;
plot_all_norm.XTick = [0 15 30 45 60 75 90];
xlabel1 = xlabel('Time ( $\mu s^{-1}$ )');
xlabel1.Position = [50 -0.07 -1];

ylabel('Normalized Intensity');
%xlim([0 10]);
legend("D(t)", "E(t)", "F(t)", "G(t)", 'Location', 'SouthEast');
%-----
plot_signal = subplot(2,2,2,signal_axis_settings{:});
plot_signal.Position = [0.56 0.56 0.43 0.43];
plot_signal.XAxis.TickLabels = '';

```

```

plot_signal.YAxis.TickLabels = '';
hold on
plot_signal.Box = 'on';

plot(-t_int,P1y, fit_settings{:}, 'Color', colors(4,:));
plot(-t_int,P2y, fit_settings{:}, 'Color', colors(5,:));
plot(-t_int,P3y, fit_settings{:}, 'Color', colors(6,:));
plot(-t_int,P4y, fit_settings{:}, 'Color', colors(7,:));

legend("S_{D}(\tau)",
"S_{E}(\tau)", "S_{F}(\tau)", "S_{G}(\tau)", 'Location', 'NorthWest');
%-----
plot_signal_norm = subplot(2,2,4,signal_axis_settings{:});
plot_signal_norm.Position = [0.56 0.09 0.43 0.43];
plot_signal_norm.YAxis.TickLabels = '';
hold on
plot_signal_norm.Box = 'on';

plot(-t_int,P1y/P1y(1), fit_settings{:}, 'Color', colors(4,:));
plot(-t_int,P2y/P2y(1), fit_settings{:}, 'Color',
colors(5,:), 'LineStyle', '--');
plot(-t_int(1:8:end),P3y(1:8:end)/P3y(1), fit_settings{:}, 'Color',
colors(6,:), 'LineStyle', 'none', 'Marker', 'o', 'LineWidth',1);
plot(-t_int(4:8:end),P4y(4:8:end)/P4y(1), fit_settings{:}, 'Color',
colors(7,:), 'LineStyle', 'none', 'Marker', 'd', 'LineWidth',1);

legend("S_{D}(\tau)",
"S_{E}(\tau)", "S_{F}(\tau)", "S_{G}(\tau)", 'Location', 'NorthWest');

plot_signal_norm.XRuler.TickLabelGapOffset = -4;
plot_signal_norm.XTick = [-90 -75 -60 -45 -30 -15 0];
xlab2 = xlabel('\tau (\mu s^{-1})');
xlab2.Position = [-50 -0.07 -1];

```

Biexponential Model (Model 2.3)

```

% Symbolic Kinetics with Reversibility and SPIDRR %
%%
clear;

A_0 = 1;      % intial value of A
k_1 = 0.1;
k_2 = 0.2;
k_3 = 0.05;
k_4 = 1;
k_5 = 2;
k_6 = 1;
alpha = 3;
delta = 37;

```

```

% Solving
% All symbols being used %
syms A0 k1 k2 k3 k4 k5 k6 t

% Rate Constant Matrix %
k = [-(k1+k2) 0 0 0 0;
      k1 -k3 0 0 0;
      k2 k3 -(k4+k5) 0 0;
      0 0 k4 0 0;
      0 0 k5 0 0];

% Initial Concentration Matrix %
Conc_0 = [A0;
           0;
           0;
           0;
           0];

% Solving for eigenvecs/vals %
evals = eig(k);
[x, ~] = eig(k);
lambda = exp(evals*t);
diag_evals = diag(lambda);

% Calculation %
Conc = x*diag_evals/x*Conc_0;
A(t) = Conc(1,1);
B(t) = Conc(2,1);
C(t) = Conc(3,1);
D(t) = Conc(4,1);
E(t) = Conc(5,1);

t_int = 0:1:100; % time interval

simplify(A);
simplify(B);
simplify(C);
simplify(D);
simplify(E);

P1 = k4*C;
P2 = k5*C;

P1_s = int(P1,t+alpha,t+delta);
P2_s = int(P2,t+alpha,t+delta);

P1_s = simplify(P1_s);
P2_s = simplify(P2_s);

A_fun = matlabFunction(A);

```

```

B_fun = matlabFunction(B);
C_fun = matlabFunction(C);
D_fun = matlabFunction(D);
E_fun = matlabFunction(E);

P1_fun = matlabFunction(P1_s);
P2_fun = matlabFunction(P2_s);

%-----
%plotting. Settings

fig = figure;
fig.Position = [2307 94 1077 900];

%setting axis
xlims = [0 100];
sxlims = [-100 0];
ylims = [0 1];
ylims_2 = [0 1];
%colors and settings
colors = linspace(5);

fontsize = 14;
axisfontsize = 14;
markersize = 6;
axispos = -148;
start_ratio = 46;
stop_ratio = 62;

data_settings = {'LineStyle', 'none', 'Marker', 'o', 'MarkerEdgeColor',
'k', 'MarkerSize', 10};
fit_settings = {'LineWidth', 3, 'Color', 'k'};
manydata_settings = {'LineStyle', 'none', 'Marker', 'o', 'MarkerSize',
5, 'MarkerEdgeColor', 'k'};
axis_settings = {'YLim', ylims, 'fontsize', 15, 'fontweight', 'bold',
'XLim', xlims};
signal_axis_settings = {'YLim', ylims_2, 'XLim', sxlims, 'fontsize',
15, 'fontweight', 'bold'};
font_settings = {'FontSize', 15, 'FontWeight', 'bold'};
ann_settings = {'FitBoxToText', 'on', 'EdgeColor', 'k', 'FontSize', 10,
'FontWeight', 'bold'};

% Plotting
close all;

Ay = A_fun(t_int,A_0,k_1,k_2);
By = B_fun(t_int,A_0,k_1,k_2,k_3);
Cy = C_fun(t_int,A_0,k_1,k_2,k_3,k_4,k_5);
Dy = D_fun(t_int,A_0,k_1,k_2,k_3,k_4,k_5);
Ey = E_fun(t_int,A_0,k_1,k_2,k_3,k_4,k_5);

P1y = P1_fun(A_0,k_1,k_2,k_3,k_4,k_5,t_int);
P2y = P2_fun(A_0,k_1,k_2,k_3,k_4,k_5,t_int);

```

```

%-----
fig1 = figure();
fig1.Position = [2345 241 550 620];

plot_all = subplot(2,2,1,axis_settings{:});
plot_all.XAxis.TickLabels = '';
plot_all.Position = [0.11 0.56 0.43 0.43];
hold on
plot_all.Box = 'on';

plot(t_int,Ay, fit_settings{:}, 'Color', colors(1,:));
plot(t_int,By, fit_settings{:}, 'Color', colors(2,:));
plot(t_int,Cy, fit_settings{:}, 'Color', colors(3,:));
plot(t_int,Dy, fit_settings{:}, 'Color', colors(4,:));
plot(t_int,Ey, fit_settings{:}, 'Color', colors(5,:));

ylabel('Relative Intensity');
legend("A(t)", "B(t)", "C(t)", "D(t)", "E(t)", 'Location', 'NorthWest');
%-----
plot_all_norm = subplot(2,2,3,axis_settings{:});
plot_all_norm.Position = [0.11 0.09 0.43 0.43];
hold on
plot_all_norm.Box = 'on';

plot(t_int,Dy/(1/3), fit_settings{:}, 'Color', colors(4,:));
plot(t_int,Ey/(2/3), fit_settings{:}, 'Color',
colors(5,:), 'LineStyle', '--');

plot_all_norm.XRuler.TickLabelGapOffset = -4;
plot_all_norm.XTick = [0 15 30 45 60 75 90];
xlabel = xlabel('Time ( $\mu s^{-1}$ )');
xlabel.Position = [50 -0.07 -1];

ylabel('Normalized Intensity');
%xlim([0 10]);
legend("D(t)", "E(t)", 'Location', 'SouthEast');
%-----
plot_signal = subplot(2,2,2,signal_axis_settings{:});
plot_signal.Position = [0.56 0.56 0.43 0.43];
plot_signal.XAxis.TickLabels = '';
plot_signal.YAxis.TickLabels = '';
hold on
plot_signal.Box = 'on';

plot(-t_int,P1y, fit_settings{:}, 'Color', colors(4,:));
plot(-t_int,P2y, fit_settings{:}, 'Color', colors(5,:));

legend("S_{D}(\tau)", "S_{E}(\tau)", 'Location', 'NorthWest');
%-----
plot_signal_norm = subplot(2,2,4,signal_axis_settings{:});

```

```

plot_signal_norm.Position = [0.56 0.09 0.43 0.43];
plot_signal_norm.YAxis.TickLabels = '';
hold on
plot_signal_norm.Box = 'on';

plot(-t_int,P1y/P1y(1), fit_settings{:}, 'Color', colors(4,:));
plot(-t_int,P2y/P2y(1), fit_settings{:}, 'Color',
colors(5,:), 'LineStyle', '--');

legend("S_{D}(\tau)", "S_{E}(\tau)", 'Location', 'NorthWest');

plot_signal_norm.XRuler.TickLabelGapOffset = -4;
plot_signal_norm.XTick = [-90 -75 -60 -45 -30 -15 0];
xlab2 = xlabel('\tau (\mu s^{-1})');
xlab2.Position = [-50 -0.07 -1];

```

APPENDIX B

Data Analysis Scripts

Single Exponential Analysis

```
clear;
[filename, filepath] = uigetfile('*.txt; *.csv', 'Select One or More
Files', 'MultiSelect', 'on', 'C:\Users\Tucker_Lewis1\Box Sync\Bellert
Group 2021\Data by system\FE-Acetone\H6\2021\02_February\020121');
Scan = importdata(fullfile(filepath, filename));
%%
Channel = 1;
BLC = 0;
logfile = 'Ni (DEE)_14500.xlsx';

Tstep = Scan(:,3); %creates a vector of the time column
mov = min(diff(Scan(:,4))); %find the value where max overlap occurs
time = find(diff(Scan(:,4))==mov)+1; %find the index of max overlap
[n,p] = size(Scan); %finds the number of time steps
x = 1:n; %creates a vector of the time steps from 0 to n by 1
xcor = minus(x,time); %subtracts the index of max overlap from all time
steps
tstep = Tstep(1,1)-Tstep(2,1); %find the actual scan rate
xaxis = -(xcor * tstep); %multiplies the corrected time steps by the
actual scan rate to give the corrected relative delay time

Y = -Scan(:,Channel+4); % Inverts the data to positive values
BL = mean(Y(1:time-1-BLC)); % Use this line for normal baseline
%BL = mean(Y((end-BaselinePoints):end)); % Use this line for backend
baseline
CY = Y - BL; % Subtracts baseline average from data
ND = CY/max(CY); % Normalize data
truncND = ND(time:end); % Define normalized data as vector without the
BL
truncx = xaxis(time:end);
truncx = -truncx';
xaxis = xaxis';

%start = rand(1,2);
start = [1 0.3];
[fitbi, gof] = fit(truncx, truncND, 'exp1', 'StartPoint', start,
'Upper', [100 0]);

%plotting -----
hold on

plot(xaxis,ND);
plot(xaxis(time:end),fitbi(truncx));
confid = confint(fitbi);
```

```

aerr = fitbi.a - confid(1,1);
kerr = fitbi.b - confid(1,2);

apara = ['a0: ', num2str(fitbi.a), ' ', num2str(aerr)];
kpara = ['b0: ', num2str(abs(fitbi.b)), ' ', num2str(kerr)];

label = [num2str(fitbi.a), ' ± ', num2str(aerr),
'*exp(', num2str(fitbi.b), ' ± ', num2str(kerr), '*t)'];
text(xaxis(end-2),0.9,label);

xlabel('Relative Delay (\mus)');
ylabel('Relative Intensity');
set(gca, 'FontSize', 20);
xlim([xaxis(end) xaxis(1,1)]);

newfilename = [filename(1:end-4), ' Channel ', num2str(Channel)];
title(gca,newfilename(1:end-7));

%output
output = {newfilename,'exp1', fitbi.a, aerr, abs(fitbi.b),kerr, '0',
'0', '0', '0', gof.sse};

print(newfilename,'-dpng', '-r600');

```

Biexponential Analysis

```

clear;
[filename, filepath] = uigetfile('*.txt; *.csv', 'Select One or More
Files', 'MultiSelect', 'on', 'C:\Users\Tucker_Lewis1\Box Sync\Bellert
Group 2021\Data by system\FE-Acetone\H6\2021\02_February\020121');
Scan = importdata(fullfile(filepath, filename));
%%
Channel = 1;
BLC = 0;
logfile = 'Fe(acetone) H6 16000';

Tstep = Scan(:,3); %creates a vector of the time column
mov = min(diff(Scan(:,4))); %find the value where max overlap occurs
time = find(diff(Scan(:,4))==mov)+1; %find the index of max overlap
[n,p] = size(Scan); %finds the number of time steps
x = 1:n; %creates a vector of the time steps from 0 to n by 1
xcor = minus(x,time); %subtracts the index of max overlap from all time
steps
tstep = Tstep(1,1)-Tstep(2,1); %find the actual scan rate
xaxis = -(xcor * tstep); %multiplies the corrected time steps by the
actual scan rate to give the corrected relative delay time

Y = -Scan(:,Channel+4); % Inverts the data to positive values
BL = mean(Y(1:time-1-BLC)); % Use this line for normal baseline

```

```

%BL = mean(Y((end-BaselinePoints):end)); % Use this line for backend
baseline
CY = Y - BL; % Subtracts baseline average from data
ND = CY/max(CY); % Normalize data
truncND = ND(time:end); % Define normalized data as vector without the
BL
truncx = xaxis(time:end);
truncx = -truncx';
xaxis = xaxis';

start = rand(1,4);
[fitbi, gof] = fit(truncx, truncND, 'exp2', 'StartPoint', start);

%plotting -----
hold on

plot(xaxis,ND);
plot(xaxis(time:end),fitbi(truncx));
confid = confint(fitbi);

aerr = fitbi.a - confid(1,1);
klerr = fitbi.b - confid(1,2);
berr = fitbi.c - confid(1,3);
k2err = fitbi.d - confid(1,4);

apara = ['a0: ', num2str(fitbi.a), ' ', num2str(aerr)];
klpara = ['b0: ', num2str(abs(fitbi.b)), ' ', num2str(klerr)];

label1 = [num2str(fitbi.a), ' ± ', num2str(aerr),
'*exp(',num2str(fitbi.b), ' ± ', num2str(klerr), '*t) + '];
text(xaxis(end-2),0.9,label1);

label2 = [num2str(fitbi.c), ' ± ', num2str(berr), '*exp(',
num2str(fitbi.d), ' ± ', num2str(k2err), '*t)'];
text(xaxis(end-2),0.85,label2);

xlabel('Relative Delay (\mus)');
ylabel('Relative Intensity');
set(gca, 'FontSize', 20);
xlim([xaxis(end) xaxis(1,1)]);

newfilename = [filename(1:end-4), ' CH ', num2str(Channel)];
title(gca,newfilename(1:end-7), 'FontSize', 15);

%output
output = {newfilename,'exp1', fitbi.a, aerr, abs(fitbi.b),kerr, '0',
'0', '0', '0', gof.sse};

print(newfilename, '-dpng', '-r600');

```

All Analysis

All_analysis is designed to automatically analyze a large set of data. When you run the script you select many kinetic scans at once and all_analysis will analyze each and save them automatically.

```
close all
clear
[filenames, filepath] = uigetfile('*.txt; *.csv', 'Select One or More
Files', 'MultiSelect', 'on', 'C:\Users\Tucker_Lewis1\Box
Sync\Backup\Documents\analysis\Ni (AcOH)\Data');

KSindex = find(contains(filenames, "KS"));
filenames = filenames(KSindex);

Scans = cell(1,length(KSindex));

for n = 1:length(KSindex)
    import = fullfile(filepath, filenames{n});
    Scans{n} = importdata(import);
end

%%
close all
system = 'Ni (AcOH)';
isotope = 'H4';
energy = 566;
SV = 595;

font_settings = {'FontSize', 15, 'FontWeight', 'bold'};
ann_settings = {'FitBoxToText', 'on', 'EdgeColor', 'k', 'FontSize', 10,
'FontWeight', 'bold'};

% data handling -----

for n = 1:length(KSindex)
    Scan = Scans{n};
    filename = filenames{n};

    SV = Scan(16,2);
    numchannels = find(Scan(16,:) == 0);
    numchannels = numchannels(1) - 5;
    BLC = 0;

    for Channel = 0:numchannels
        close all
        Tstep = Scan(:,3); %creates a vector of the time column
```

```

mov = min(diff(Scan(:,Channel+4))); %find the value where max overlap
occurs
time = find(diff(Scan(:,Channel+4))==mov)+1; %find the index of max
overlap
[j,p] = size(Scan); %finds the number of time steps
x = 1:j; %creates a vector of the time steps from 0 to n by 1
xcor = minus(x,time); %subtracts the index of max overlap from all time
steps
tstep = Tstep(1,1)-Tstep(2,1); %find the actual scan rate
xaxis = -(xcor * tstep); %multiplies the corrected time steps by the
actual scan rate to give the corrected relative delay time

Y = -Scan(:,Channel+4); % Inverts the data to positive values
BL = mean(Y(1:time-1-BLC)); % Use this line for normal baseline
%BL = mean(Y((end-BaselinePoints):end)); % Use this line for backend
baseline
CY = Y - BL; % Subtracts baseline average from data
ND = CY/max(CY); % Normalize data
truncND = ND(time:end); % Define normalized data as vector without the
BL
truncx = xaxis(time:end);
truncx = -truncx';
xaxis = xaxis';

% fitting -----
[fitsin, gof1] = fit(truncx, truncND, 'exp1', 'Upper', [100 0]);

confid = confint(fitsin);
sin_aerr = round(fitsin.a - confid(1,1),3);
sin_kerr = round(fitsin.b - confid(1,2),3);

sin_a = round(fitsin.a,3);
sin_k = round(fitsin.b,3);

[fitbi, gof2] = fit(truncx, truncND, 'exp2', 'Upper', [100 0 100 0]);

confid = confint(fitbi);
bi_aerr = round(fitbi.a - confid(1,1),3);
bi_klerr = round(fitbi.b - confid(1,2),3);
bi_berr = round(fitbi.c - confid(1,3),3);
bi_k2err = round(fitbi.d - confid(1,4),3);

bi_a = round(fitbi.a,3);
bi_k1 = round(fitbi.b,3);
bi_b = round(fitbi.c,3);
bi_k2 = round(fitbi.d,3);

% plotting -----

fig = figure;
fig.Position = [2400 240 820 660];

data_settings = {'LineStyle', 'none', 'Marker', 'o', 'MarkerEdgeColor',
'k', 'MarkerSize', 10, 'MarkerFaceColor', '#0072BD'};
fit_settings = {'LineWidth', 3, 'Color', 'k'};

```

```

% single exponential plotting -----
plot1 = subplot(2,1,1);

plot(xaxis,ND, data_settings{:});
hold on
plot(xaxis(time:end),fitsin(truncx), fit_settings{:});
plot(xaxis,zeros(length(xaxis)), 'LineWidth', 1.5, 'Color', 'k');

sin_apara = string(['A_{0}: ', num2str(sin_a), ' ± ',
num2str(sin_aerr)]);
sin_kpara = string(['k_{1}: ', num2str(abs(sin_k)), ' ± ',
num2str(sin_kerr)]);

sin_label = [sin_apara; sin_kpara];
txt_ann1 = text(xaxis(end-2), 0.7, sin_label, font_settings{:},
'EdgeColor', 'k');

plot1.XAxis.TickLabels = "";
xlim([round(xaxis(end),-1) round(xaxis(1,1),-1)]);
plot1.XAxis.MinorTick = 'on';

ylabel('Normalized Intensity', font_settings{:});
plot1.YAxis.FontSize = 15;
plot1.YAxis.FontWeight = 'bold';
plot1.YAxis.Limits = [-0.05 1.1];
plot1.YAxis.TickValues = 0:0.2:1;

sin_title = join([filename(1:end-4), ' Channel ',num2str(Channel), "
Single Exponential"]);
title(gca,sin_title, font_settings{:}, 'Interpreter', 'none');

% bi exponential plotting -----
plot2 = subplot(2,1,2);

plot(xaxis,ND, data_settings{:});
hold on
plot(xaxis(time:end),fitbi(truncx), fit_settings{:});
plot(xaxis,zeros(length(xaxis)), 'LineWidth', 1.5, 'Color', 'k');

bi_apara = string(['A_{0}: ', num2str(bi_a), ' ± ', num2str(bi_aerr)]);
bi_k1para = string(['k_{1}: ', num2str(abs(bi_k1)), ' ± ',
num2str(bi_k1err)]);
bi_bpara = string(['B_{0}: ', num2str(abs(bi_b)), ' ± ',
num2str(bi_berr)]);
bi_k2para = string(['k_{2}: ', num2str(abs(bi_k2)), ' ± ',
num2str(bi_k2err)]);

bi_label = [bi_apara; bi_k1para; bi_bpara; bi_k2para];
txt_ann2 = text(xaxis(end-2), 0.7, bi_label, font_settings{:},
'EdgeColor', 'k');

xlim([round(xaxis(end),-1) round(xaxis(1,1),-1)]);
plot2.XAxis.MinorTick = 'on';
plot2.XAxis.FontSize = 15;
plot2.XAxis.FontWeight = 'bold';

```

```

xlabel('Relative Delay (\mus)', font_settings{:});
plot2.XAxis.TickValues =
plot2.XAxis.Limits(1):10:plot2.XAxis.Limits(2);

ylabel('Normalized Intensity', font_settings{:});
plot2.YAxis.FontSize = 15;
plot2.YAxis.FontWeight = 'bold';
plot2.YAxis.Limits = [-0.05 1.1];
plot2.YAxis.TickValues = 0:0.2:1;

bi_title = join([filename(1:end-4), ' Channel ', num2str(Channel), ": Bi-
Exponential"]);
title(gca, bi_title, font_settings{:}, 'Interpreter', 'none');

% output -----
output = {filename(1:end-4), SV, Channel, tstep, 'exp1', sin_a,
sin_aerr, abs(sin_k), sin_kerr, 'exp2', bi_a, bi_aerr, abs(bi_k1),
bi_k1err, bi_b, bi_berr, abs(bi_k2), bi_k2err};
nanindex =
find(cell2mat(cellfun(@(x) any(isnan(x)), output, 'UniformOutput', false)))
;

output = fixnan(output);

newpath = ['C:\Users\Tucker_Lewis1\Box
Sync\Backup\Documents\analysis\', system, '\', isotope, '\',
num2str(energy), '\', num2str(SV), '\', num2str(Channel), '\'];
[status, msg] = mkdir(newpath);

newfilename = [filename(1:end-4), '_ch', num2str(Channel)];
fullfilename = fullfile(newpath, newfilename);
print(fullfile, '-dtiffn', '-r300');

logpath = ['C:\Users\Tucker_Lewis1\Box
Sync\Backup\Documents\analysis\', system, '\', isotope, '\',
num2str(energy), '\'];
logfile = [system, '_', isotope, '_', num2str(energy), '_', 'log.xlsx'];
fulllogfile = fullfile(logpath, logfile);

end
end

function x = fixnan(x)
%will work no matter how many levels, including if cells are not
consistent types
    if isnumeric(x)
        x(isnan(x)) = 0;
    elseif iscell(x)
        x = cellfun(@fixnan, x, 'uniform', 0);
    %else other types do nothing, return unchanged
    end
end

```

Averager

Averager can take a set of unprocessed kinetic scans and average them together.

```
close all
clear
[filenames, filepath] = uigetfile('*.txt; *.csv', 'Select One or More
Files', 'MultiSelect', 'on', 'C:\Users\Tucker_Lewis1\Box
Sync\Backup\Documents\analysis\Ni (AcOH) \Data\D4');

KSindex = find(contains(filenames, "KS"));
filenames = filenames(KSindex);
Scans = cell(1,length(filenames));

for n = 1:length(KSindex)
    import = fullfile(filepath, filenames{n});
    Scans{n} = importdata(import);
    Scans{n} = Scans{n}(:,1:find(Scans{n}(16,:) == 0)-1);
end

includedscans = Scans;
includednames = char(filenames);
allfilenames = char(filenames);
totalscans = length(KSindex);

%%
close all
system = 'Ni (AcOH) ';
isotope = 'H4';
energy = 566;
SV = 565;

channels = zeros(1,length(KSindex));
channeloffset = input("What Channel do you want to start at? ");
channels = channels + channeloffset;
bli = 0;
adjt = 0;
menuinput = 0;
SNO = 0;
%-----
%-----
while menuinput ~= 6
    close all;
    % first check the scan rates for agreement, allow remove if no agree

    numscans = length(includedscans);
    namesrates = strings(1,numscans);
    scanrates = zeros(1, numscans);
    scanrates(1) = 1;
    chkrate = unique(scanrates);
```

```

while length(chkrate) ~= 1
    numscans = length(includedscans);
    namesrates = strings(1,numscans);
    scanrates = zeros(1, numscans);
    scanrates(1) = 1;

    for n = 1:numscans
        scandiff = diff(includedscans{n}(:,3));
        scanrates(n) = scandiff(1);
        namesrates(n) = join([num2str(n), ". ", includednames(n,:), '
', num2str(scandiff(1))], "");
    end

    chkrate = unique(scanrates);

    if length(chkrate) ~= 1
        disp('*****Different Scan
Rates*****');
        disp("           Scans           Time Step");
        disp(namesrates');
        removeindex = input('Select Which Scans to Remove: ');
        includedscans(removeindex) = [];
        includednames(removeindex,:) = [];
        numscans = length(includedscans);
        channels(removeindex) = [];
        chkrate = unique(scanrates);
    end
end

%loop starts here
% second find the overlapping time axis of all included scans
startt = min(cellfun( @(a,b,c) a(1,3), includedscans));
endt = max(cellfun( @(a,b,c) a(end,3), includedscans));

startindex = cellfun(@(a) find(a(:,3) == startt), includedscans);
endindex = cellfun(@(a) find(a(:,3) == endt), includedscans);

newscans = zeros(endindex(1) - startindex(1)+1, 2, numscans);
for n = 1:numscans
    newscans(:, :, n) = includedscans{n}(startindex(n):endindex(n), [3
channels(n)+4]);
end

% third average together the signal values at each overlapped time,
also
% normalize the data and include a S/N bias value that can be toggled
% later

[~, peakindex] = min(newscans(:,2,:), [], 1);
[noneed, mostchn] = min(diff(newscans(:,2,:)));
BLstart = min(peakindex, mostchn) - 1 - bli;

BLcorrscans = zeros(endindex(1) - startindex(1) + 1, 1, numscans);
for n = 1:numscans

```

```

        BLcorrscans(:,1,n) = newscans(:,2,n) -
mean(newscans(1:BLstart(n),2,n));
end
[peakval, peakindex] = min(BLcorrscans(:,1,:), [], 1);
normdata = BLcorrscans(:,1,:)./peakval;
BLcorrnormscans = [newscans(:,1,:) -BLcorrscans normdata]; %this
contains 3 columns: 1. uncorrected time axis, 2. BL corrected scans, 3.
normalized scans

Signalnoise = abs(peakval)./(max(BLcorrscans(end-9:end,1,:)) -
min(BLcorrscans(end-10:end,1,:))); %S'N factor for later bias
Signalnoise = squeeze(Signalnoise);

if SNO == 1
    for i = 1:numscans
        BLcorrnormscans(:,2,i) = BLcorrnormscans(:,3,i)*Signalnoise(i);
    end
end

avgdata = mean(BLcorrnormscans(:, [2 3], :), 3);
avgscan = [newscans(:,1,1) avgdata]; %this contains 3 columns: 1.
uncorrected time axis, 2. BL corrected scans, 3. normalized scans

%fourth find peak max and adjust time axis to corrected time, include
an
%adjustment paramenter for the "adjust time axis" option

[~,maxt] = max(avgscan(:,3));
avgscan(:,1) = avgscan(:,1) - avgscan(maxt,1) + adjt;

%-----
%fit single and biexponential to the time corrected averaged data
% norm fitting -----
[fitsin1, gof11] = fit(avgscan(maxt:end,1), avgscan(maxt:end,3),
'exp1', 'Upper', [100 100], 'Lower', [0 0]);

confid = confint(fitsin1);
sin_aerr1 = round(fitsin1.a - confid(1,1),3);
sin_kerr1 = round(fitsin1.b - confid(1,2),3);

sin_a1 = round(fitsin1.a,3);
sin_k11 = round(fitsin1.b,3);

start = [0.36 0.1 0.6 0.02];

[fitbil, gof21] = fit(avgscan(maxt:end,1), avgscan(maxt:end,3),
'exp2', 'Upper', [100 100 100 100], 'Lower', [0 0 0 0], 'StartPoint',
start);

confid = confint(fitbil);
bi_aerr1 = round(fitbil.a - confid(1,1),3);
bi_klerr1 = round(fitbil.b - confid(1,2),3);
bi_berr1 = round(fitbil.c - confid(1,3),3);
bi_k2err1 = round(fitbil.d - confid(1,4),3);

```

```

bi_a1 = round(fitbi1.a,3);
bi_k11 = round(fitbi1.b,3);
bi_b1 = round(fitbi1.c,3);
bi_k21 = round(fitbi1.d,3);

% BLcorr/SNB fitting

[fitsin2, gof12] = fit(avgsin(maxt:end,1),
avgsin(maxt:end,2)./max(avgsin(:,2)), 'exp1', 'Upper', [100 100],
'Lower', [0 0]);

confid = confint(fitsin2);
sin_aerr2 = round(fitsin2.a - confid(1,1),3);
sin_kerr2 = round(fitsin2.b - confid(1,2),3);

sin_a2 = round(fitsin2.a,3);
sin_k12 = round(fitsin2.b,3);

[fitbi2, gof22] = fit(avgsin(maxt:end,1),
avgsin(maxt:end,2)./max(avgsin(:,2)), 'exp2', 'Upper', [100 100 100
100], 'Lower', [0 0 0 0], 'StartPoint', start);

confid = confint(fitbi2);
bi_aerr2 = round(fitbi2.a - confid(1,1),3);
bi_k1err2 = round(fitbi2.b - confid(1,2),3);
bi_berr2 = round(fitbi2.c - confid(1,3),3);
bi_k2err2 = round(fitbi2.d - confid(1,4),3);

bi_a2 = round(fitbi2.a,3);
bi_k12 = round(fitbi2.b,3);
bi_b2 = round(fitbi2.c,3);
bi_k22 = round(fitbi2.d,3);

%-----
%plot single and bi fit, and an overlay of all the scans so you can see
%which are included, have both a normalized and not normalized view
xlims = [avgsin(end,1) avgsin(1,1)];

colors = linspace(numscans);
colors2= linspace(9);

data_settings = {'LineStyle', 'none', 'Marker', 'o', 'MarkerEdgeColor',
'k', 'MarkerSize', 10};
fit_settings = {'LineWidth', 3, 'Color', 'k'};
manydata_settings = {'LineStyle', 'none', 'Marker', 'o', 'MarkerSize',
5, 'MarkerEdgeColor', 'k'};
axis_settings = {'YLim', [-0.2 1.05], 'fontsize', 15, 'fontweight',
'bold', 'XLim', xlims};
if SNO == 0
    axis_settings2 = {'fontsize', 15, 'fontweight', 'bold', 'XLim',
xlims, 'YLim', [-1 max(max(-BLcorrscans(:,1,:)))+0.1]};
else

```

```

axis_settings2 = {'fontsize', 15, 'fontweight', 'bold', 'XLim',
xlims, 'YLim', [-1 max(Signalnoise)]};
end
font_settings = {'FontSize', 15, 'FontWeight', 'bold'};
ann_settings = {'FitBoxToText', 'on', 'EdgeColor', 'k', 'FontSize', 10,
'FontWeight', 'bold'};

%normalized plots
fig = figure;
fig.Position = [2288 152 1101 774];
plot1 = subplot(2,3,[1,2], axis_settings{:});
plot1.Position = [0.035 0.525 0.6 0.425];

hold on
for n = 1:numscans
    plot(avgscan(:,1),BLcorrnormscans(:,3,n),manydata_settings{:},
'MarkerFaceColor', colors(n,:))
end

plot(avgscan(:,1),avgscan(:,3),fit_settings{:});

plot(avgscan(:,1),zeros(length(avgscan(:,1))), 'LineWidth', 1.5,
'Color', 'k');

leg1 = legend(plot1, [join([string(includednames(:,1:end-4))
num2str(channels(:))], " CH: "); "-AVG Data-"], 'Location',
'NorthWest', 'interpreter', 'none', 'FontSize', 12);

%norm fit plot
plot2 = subplot(2,3,3, axis_settings{:});
plot2.Position = [0.67 0.525 0.32 0.425];
hold on

plot(avgscan(:,1),avgscan(:,3), data_settings{:}, 'MarkerFaceColor',
colors2(2,:));
plot(avgscan(maxt:end,1),fitsin1(avgscan(maxt:end,1)),fit_settings{:},
'Color', colors2(1,:));
plot(avgscan(maxt:end,1),fitbi1(avgscan(maxt:end,1)),fit_settings{:},
'Color', colors2(4,:));

plot(avgscan(:,1),zeros(length(avgscan(:,1))), 'LineWidth', 1.5,
'Color', 'k');

sin_apara1 = string(['A_{0}: ', num2str(sin_a1), ' ± ',
num2str(sin_aerr1)]);
sin_kpara1 = string(['k_{1}: ', num2str(abs(sin_k11)), ' ± ',
num2str(sin_kerr1)]);
sin_labell1 = [sin_apara1; sin_kpara1];

bi_apara1 = string(['A_{0}: ', num2str(bi_a1), ' ± ',
num2str(bi_aerr1)]);
bi_klpara1 = string(['k_{1}: ', num2str(abs(bi_k11)), ' ± ',
num2str(bi_klerr1)]);
bi_bpara1 = string(['B_{0}: ', num2str(abs(bi_b1)), ' ± ',
num2str(bi_berr1)]);

```

```

bi_k2para1 = string(['k_{2}: ', num2str(abs(bi_k21)), ' ± ',
num2str(bi_k2err1)]);
bi_label1 = [bi_apara1; bi_k1para1; bi_bpara1; bi_k2para1];

annotation('textbox', [0.7 0.85 0.1162579 0.07235142], 'String',
[sin_label1; ""; bi_label1], ann_settings{:});

%BLcorr/SNB plots
plot3 = subplot(2,3,[4,5], axis_settings2{:});
plot3.Position = [0.035 0.05 0.6 0.425];
hold on

for n = 1:numscans

plot(avgsan(:,1),BLcorrnormscans(:,2,n),manydata_settings{:}, 'MarkerFaceColor', colors(n,:))
end

plot(avgsan(:,1),avgsan(:,2),fit_settings{:});

plot(avgsan(:,1),zeros(length(avgsan(:,1))), 'LineWidth', 1.5,
'Color', 'k');

SN = num2str(round(squeeze(Signalnoise),1));
SNstr = string(SN);

legend(plot3, [SNstr; 'AVG'], 'Location', 'NorthWest', 'interpreter',
'none', 'FontSize', 12);

%Blcorr/SNB fit plots
plot4 = subplot(2,3,6, axis_settings{:});
plot4.Position = [0.67 0.05 0.32 0.425];
hold on

plot(avgsan(:,1),avgsan(:,2)./max(avgsan(:,2)), data_settings{:},
'MarkerFaceColor', colors2(2,:));
plot(avgsan(maxt:end,1),fitsin2(avgsan(maxt:end,1)),fit_settings{:},
'Color', colors2(1,:));
plot(avgsan(maxt:end,1),fitbi2(avgsan(maxt:end,1)),fit_settings{:},
'Color', colors2(4,:));

plot(avgsan(:,1),zeros(length(avgsan(:,1))), 'LineWidth', 1.5,
'Color', 'k');

sin_apara2 = string(['A_{0}: ', num2str(sin_a2), ' ± ',
num2str(sin_aerr2)]);
sin_kpara2 = string(['k_{1}: ', num2str(abs(sin_k12)), ' ± ',
num2str(sin_kerr2)]);
sin_label2 = [sin_apara2; sin_kpara2];

bi_apara2 = string(['A_{0}: ', num2str(bi_a2), ' ± ',
num2str(bi_aerr2)]);
bi_k1para2 = string(['k_{1}: ', num2str(abs(bi_k12)), ' ± ',
num2str(bi_k1err2)]);

```

```

bi_bpara2 = string(['B_{0}: ', num2str(abs(bi_b2)), ' ± ',
num2str(bi_berr2)]);
bi_k2para2 = string(['k_{2}: ', num2str(abs(bi_k22)), ' ± ',
num2str(bi_k2err2)]);
bi_label2 = [bi_apara2; bi_k1para2; bi_bpara2; bi_k2para2];

ann1 = annotation('textbox', [0.7 0.37 0.1162579 0.07235142], 'String',
[sin_label2; ""; bi_label2], ann_settings{:});

%-----
if SNO == 1
    SN1 = annotation(fig, 'textbox', [0.635/2-0.05 0.475-0.035 0.1
0.035], 'String', "S/N Corrected", ann_settings{:});
    SN2 = annotation(fig, 'textbox', [0.7 0.475-0.03 0.1 0.03],
'String', "S/N Corrected", ann_settings{:});
end

%-----
-----
--
%display menu:
% 1. Add or remove scans
% 2. Change channels
% 3. Adjust time axis
% 4. S/N bias
% 5. Output
% 6. Exit

menustr = ["Menu:", "1. Add or Remove Scans", "2. Change Channels", "3.
Adjust Time Axis", "4. S/N Bias", "5. Output", "6. Exit"];
disp(menustr);
menuinput = input('Please Select An Option: ');

%scan menu
off = find(0 == ismember(allfilenames,includednames, 'rows'));

    menu1 = '          Scans      Channels   S/N   Status';
    menu2 = strings(totalscans,1);
    for n = 1:numscans
        menu2(n,:) = join([num2str(n) ". " includednames(n,1:end-4) "
" num2str(channels(n)) "          " num2str(SN(n,:)) "          " '!'], '');
    end
    for i = 1:length(off)
        n = n+1;
        [~, width] = size(SN);
        offphrase = join([num2str(n) ". " allfilenames(off(i),1:end-4)
"          blanks(width) "          " '?'], '');
        menu2(n) = offphrase;
    end

if menuinput == 1
    disp(menu1);
    disp(menu2);
    toggle = input("Enter Scan You Would Like To Toggle: ");
    if toggle > numscans

```

```

        newchannel = input("What Channel Would You Like to Use: ");
        channels = [channels newchannel];
        for i = 1:totalscans
            letter = allfilenames(i,7);
            if 1 == contains(menu2(toggle),letter)
                newname = allfilenames(i,:);
                newscan = Scans{i};
            end
            end
            includednames = [includednames; newname];
            includedscans{length(includedscans)+1} = newscan;
        else
            includednames(toggle,:) = '';
            channels(toggle) = [];
            includedscans(toggle) = [];
        end
    end
end

if menuinput == 2
    disp(menu1);
    disp(menu2(1:numscans));
    toggle = input("Enter Scan To Change: ");
    newchannel = input("Enter New Channel: ");
    channels(toggle) = newchannel;
end

if menuinput == 3
    display(join(["The Current adjustment is:" num2str(adjt)]));
    adjt = input("Enter Time Axis Adjustment (Positive Numbers Move 0
To The Right): ");
end

if menuinput == 4
    if SNO == 0
        SNO = 1;
    else
        SNO = 0;
    end
end

if menuinput == 5

    dates = string(unique(includednames(:,1:6), 'rows'));
    letterdates = strings(1,length(dates));

    for i = 1:length(dates)
        letterdates(i) = join([dates(i,:)
string(includednames(string(dates(i,:)) ==
string(includednames(:,1:6)),7)')], '_');
    end
    outputname = join(letterdates, '_');
    display(outputname);
    version = input("Version of this average? ");
    outputname = join([outputname version], '_');

```

```

    newpath = join(['C:\Users\Tucker_Lewis1\Box
Sync\Backup\Documents\analysis\', system, '\', isotope, '\',
num2str(energy), '\', num2str(SV), '\', 'Averages'], '');
    [status, msg] = mkdir(newpath);
    fullfilename = fullfile(newpath, outputname);
    print(fullfilename, '-dtiff');
    %print(fullfilename, '-dsvg');
end

end

function x = fixnan(x)
%will work no matter how many levels, including if cells are not
consistent types
    if isnumeric(x)
        x(isnan(x)) = 0;
    elseif iscell(x)
        x = cellfun(@fixnan, x, 'uniform', 0);
    %else other types do nothing, return unchanged
    end
end

```

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