High-sensitivity and multi-species detection in the gas phase: techniques, performance, and applications

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Sensitive and quantitative detection of gas-phase molecules is essential in fields ranging from atmospheric chemistry and combustion to astrochemistry and molecular physics. A wide range of experimental techniques is available, offering different combinations of sensitivity, selectivity, spectral coverage, resolution, and acquisition speed. Choosing the most appropriate approach depends on the molecular species of interest, the experimental conditions, and the information to be retrieved.

This talk will review established and emerging laser-based spectroscopic techniques for highsensitivity and multi-species detection. Approaches based on direct absorption, cavity enhancement, saturated absorption, photoacoustic detection, and broadband spectroscopy will be discussed, including developments enabled by optical frequency combs. Their demonstrated performance, practical advantages, and limitations will be compared, with particular attention to the trade-offs between detection sensitivity, spectral bandwidth, resolution, measurement time, and quantitative accuracy.

Examples from the literature and our own research will illustrate the capabilities of these techniques in different experimental contexts, including recent developments in broadband, high-resolution spectroscopy and its application to cold molecular gases produced in supersonic expansions. The discussion will also address the requirements for reliable quantification, including accurate spectroscopic parameters, line-shape modelling, and characterization of the molecular sample, as well as the challenges associated with measurements in complex or transient environments.

Multidimensional Detection of Chemical Reactions: A New TimeResolved Photoelectron Photoion Coincidence Spectrometer

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We present a new apparatus that provides a multi-dimensional view of unimolecular and bimolecular chemical reactions through time-resolved photoelectron photoion coincidence (PEPICO) spectroscopy. Coupled with tunable vacuum ultraviolet radiation for single photon ionization, our TR-PEPICO spectrometer breaks new ground in time- and mass-resolution while also providing isomer-resolved species identification through mass-selected photoelectron spectra. We interrogate the gas expansion dynamics of a side-sampled chemical reactor tube, revealing clear evidence for viscous flow in the expansion before ionization. Cation imaging can be used to restrict detected signal to only the direct molecular beam, removing contributions from background and reflected gases. We demonstrate mass resolution of $m/\Delta m$ = 3200 – 11000 depending on conditions, with mass accuracy of 3 ppm, sufficient to unambiguously define empirical formulas in C/H/O systems. We quantify the temporal instrument response function and show that velocity map imaging of cations may be used to eliminate the transit time delay and reduce the temporal blurring inherent in *ex situ* sampling geometries. The resulting upper bound of time resolution is 7 μs, a significant improvement compared to previous instruments. We discuss methods to quantify and address the ubiquitous problem of background electrons ejected from metal surfaces in photoelectron spectrometers. Finally, we compare variants of photoion mass-selected photoelectron spectroscopy, provide an example of quantitative analysis using PEPICO, and present evidence for unexpected products in the 193 nm photodissociation of CH_3OH that underscores the value of universal imaging approaches.

Low Temperature Radical Kinetics and Signal Estimation by Millimeter Wave Spectroscopy

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We investigate the vinoxy (CH_2CHO) + O_2 reaction at 70 and 100 K using chirped-pulse millimeter-wave rotational spectroscopy in a uniform supersonic flow. Vinoxy will be generated by 193 nm photolysis of ethyl vinyl ether, and repeated excitation pulses will monitor vinoxy decay and vibrationally excited formaldehyde formation under pseudo-first-order conditions. Matched filtering of the molecular free-induction decays will provide complex amplitudes for kinetic analysis and extraction of bimolecular reaction rate coefficients. The reaction is faster at low temperature than at room temperature, motivating comparison with multireference electronic-structure calculations, variable-reaction-coordinate transition-state theory, and master-equation modeling. These calculations support barrierless oxygen addition, with an outer transition state important below approximately 60 K and a tight inner transition state imposing entropic constraints at higher temperatures.

A complementary study will assess signal estimators using CH_3CN measurements and HCO signals, including the HCO + O_2 reaction. Fourier-transform magnitude estimators will be compared with matched filtering and multicomponent time-domain analysis to evaluate noise bias, interference from neighboring transitions, and sensitivity to the analysis window. Baseline measurements and excitation normalization will help separate instrumental effects from molecular signals. The comparison will examine how estimator choice affects detection sensitivity, kinetic profiles, and recovered reaction rate coefficients, particularly as radical signals weaken during the reaction.

Precision molecular spectroscopy applications in semiconductor industry diagnostics

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We report on the applications of cavity ring-down spectroscopy (CRDS) and direct frequency comb spectroscopy (DFCS) to metrology research and development challenges facing the semiconductor industry. This talk will discuss ongoing research from two collaborative NIST projects. The first aims to apply mid-infrared CRDS to quantify trace impurities in semiconductor gases, towards ultra-sensitive optical diagnostics and new gas reference materials. The second aims to apply mid-infrared DFCS to the real-time monitoring of chemical transformations in plasma etching processes.

Direct Optical Measurements of Transient Species and Particles in Atmospheric and Combustion Systems

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Reactive intermediates and micron-scale particles often govern the chemistry and energy release of complex reacting systems, yet their transient nature makes direct quantitative measurement challenging. Here, two complementary optical approaches are presented for probing short-lived species in atmospheric chemistry and rapic micron-scale combustion.

In the first study,[1] near-UV cavity ring-down spectroscopy was used to directly detect **Criegee intermediates** formed during **isoprene ozonolysis**. Isoprene is the most abundant alkene in troposhpere, yet the critical Criegee intermediates during its ozonolysis have never been measured previously. The observed vibronic absorption features were assigned to CH_2OO and further confirmed by selective scavenging with SO_2. *In situ* concentration time profiles enabled direct kinetic analysis of the reaction network. At low pressure, CH_2OO dominates the stabilized Criegee intermediate population, with a stabilization yield of approximately 21%, whereas stabilization of larger C_4 Criegee intermediates is negligible under the same conditions. These measurements provide direct constraints on branching and pressure-dependent stabilization in isoprene ozonolysis.

In the second study,[2] synchronized digital in-line holography and three-color pyrometry were developed to simultaneously resolve the morphology, three-dimensional motion, and temperature of micron-scale particles generated during combustion of 3D-printed composites. Increasing fuel richness produces longer surface residence times, larger droplets, and lower ejection velocities.

Together, these studies demonstrate how high-sensitivity spectroscopy and high-speed microscopic imaging can directly capture transient chemical species and rapid particle dynamics, linking microscale processes to atmospheric reaction mechanisms and macroscale combustion behavior.

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An all-optical determination of calcium isotope ratios

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Calcium isotope ratios are valuable tracers in biomedical and geochemical systems, providing insight into processes such as bone metabolism and paleoenvironmental change. Conventional calcium isotope measurements rely on mass spectrometry, which requires extensive sample preparation, large instrumentation, and often indirect access to the most abundant calcium isotope due to isobaric interferences.

Here, we present a laser-based approach for determining calcium isotope ratios using high-resolution laser-induced fluorescence spectroscopy of CaF isotopologues (^{40}CaF, ^{42}CaF, and ^{44}CaF). Measurements are performed in a cold molecular beam, enabling well-controlled rotational populations and reduced spectral congestion. Rotationally resolved transitions in the $A^2\Pi - X^2\Sigma^+$ band of CaF ($Q_1(3)$ and $^{Q}R_{12}(3)$) are probed for each isotopologue.

Isotope ratios are extracted by integrating the fluorescence signals and applying corrections for rotational population distributions and Franck-Condon factors calculated using LEVEL. Comparisons with reference materials and external measurements indicate that remaining deviations likely arise from systematic effects that are not yet characterized.

This work demonstrates the potential to adapt molecular beam spectroscopy, a technique traditionally used for high-resolution spectroscopic studies, into a platform for quantitative analytical measurements. These results highlight the viability of laser-based isotope ratio analysis with reduced sample preparation and improved experimental control.

Theory and Experiment Working Hand-in-Hand to Develop Predictive Models for Complex Chemically Reactive Environments

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The development of physically-correct high-fidelity models for the kinetics of sequences of chemical reactions is a primary goal of fundamental research in chemical kinetics. Such models are an important companion to the optimization and control of complex chemical environments. They are best developed through the direct collaboration of theory and experiment, with the synergy aiding in interpreting the experiments, testing the theoretical foundations, and ensuring the breadth, precision, and correctness of the model. We will review a number of our recent theory-experiment collaborations to illustrate the various roles of theory in this synergy. We will also discuss the growing role of automation and machine learning in the process.

The specific synergies and questions to be considered are

a) Isopentane derived QOOH dissociations – What isomers and conformers are produced and probed by the experiment? (with Marsha Lester and Sarah Elliott)
b) Testing RRKM theory – (i) Criegee Intermediates, (ii) QOOHs, and (iii) propenal. Can we predict barrier energies? Can we implement RRKM theory accurately? Are statistical assumptions valid for transient species? Are statistical assumptions valid in a multi-step dissociation? How do you connect time decays to channel specific rate constants in a multistep process? (with Marsha Lester and with Floyd Davis)
c) Physical dimerization – What is required to accurately predict rates for this process? How important are anharmonicities? How do you calculate energy transfer in a weakly bound molecule? Are internal modes involved in the low-T energy transfer process? (with Ian Sims,
   Alberto Farto, Ahren Jasper)
d) Ramifications of multiple transition states – (i) Importance of roaming in Criegee Intermediate dissociation (with Marsha Lester, Rebecca Caravan, Craig Taatjes, David Osborn, Carl Percival, Lenny Sheps, Frank Winiberg, and Sarah Elliott) (ii) Exploring the transition from the long-range to the short-range transition state in $CH_2CHO + O_2$ radicalradical reactions – Are there barrier for the recombination of two resonantly stabilized radicals? Can we predict the kinetics across a broad temperature range? (with Arthur Suits)
e) Non-thermal effects in QOOH + O_2 for tetrahydrofuran – What do the simultaneous observations of OH, HO_2, and other transient species across a broad range of initial conditions tell us about the dynamics? Can we optimize conditions for directly demonstrating the importance of non-thermal effects? (with Lenny Sheps, Raghu Sivaramarkishnan)

Coupled Cluster Theory for Open-Shell Species: Efficient Implementations in CFOUR

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Coupled cluster theory has long been recognized as a powerful and systematically improvable method for capturing dynamical correlation in molecular systems; however, the availability of optimized open-shell implementations has typically lagged that of closed-shell counterparts, and in most cases has relied on automatic equation generation and factorization. We present new, efficient, "hand-coded" implementations of a variety of coupled cluster methods for arbitrary open-shell references, leveraging the TBLIS framework embedded in the NCC module of CFOUR. Efficient calculation of energies (and in many cases, gradients) for a variety of approximate and full coupled cluster models ranging from CCSD to EOMEE-CCSDTQ are now possible. A particular emphasis will be placed on advancements in the "spin-flip" and "double spin-flip" sector for treatment of electronically complex species.

Constraining collisional energy transfer with time-resolved experiments and advanced modelling

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Pressure-dependent gas-phase reactions are typically modeled by the chemical master equation (ME), which uses simplified treatments of the collisional energy transfer (CET), e.g., the single-exponential-down model. The CET parameters in master equation modeling are often uncertain, and we therefore wish to experimentally validate and compare them with the CET parameters from first-principles calculations.

We have recently completed a study of the ethyl (C_2H_5) + O_2 reaction, in which we investigated the prompt (well-skipping) and thermal formation of the products, C_2H_4 + HO_2. We quantified HO_2 at pressures up to 10 bar of He, Ar, and N_2, and temperatures up to 700 K using a high-pressure time-resolved fluorescence assay by gas expansion (FAGE) apparatus. The experiments produced accurate measurements of the prompt product fraction via the reaction $C_2H_5 + O_2 \rightarrow C_2H_5O_2^{\ddagger} \rightarrow C_2H_4 + HO_2$, and subsequent ME modeling showed that these prompt yields were highly sensitive to the CET dynamics of the activated peroxy radical intermediate, $C_2H_5O_2^{\ddagger}$. Furthermore, we constrained the ME model parameters for this system using our new automated workflow, KiMecO, and compared the CET parameters in all three bath gases to those calculated from high-level, trajectory-based simulations. The results show that the average energy transferred per collision with the bath gas, $\langle \Delta E_{\text{down}} \rangle$, should be reduced by a factor of 2 - 3 from the trajectory-based values when using the single-exponential-down model, in agreement with an earlier theoretical prediction.

What Should We Be Looking For? Guiding Detection with Automated Kinetics and Machine-Learned Potentials

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Quantitative detection of reactive intermediates and products increasingly relies on theory to determine which species are expected and how fast they form. For all but the simplest systems, the answer requires exploring potential energy surfaces (PESs), which are often far larger than chemical intuition can cover. KinBot locates stationary points on reactive PESs, connects them into kinetic networks, and feeds them to master-equation calculations of temperature- and pressure-dependent rate coefficients and branching fractions.

Through recent collaborations with experimental groups, I will show how KinBot reveals chemistry in a systematic manner and how this impacts experimental interpretation. In an early example, I will show how theory motivated using a new detection technique in the study of the reaction of triplet sulfur with alkenes.[1] In the cyclopentadienyl + propargyl reaction, we found that dihydropentalenes form instead of styrene, because styrene formation is blocked by a tight isomerization barrier, while the dihydropentalene isomers are linked by low barriers to each other.[2] In the reaction of methylhydroxycarbene with acetaldehyde, a carbonyl-ene pathway through a deep prereactive complex and a submerged saddle point explains why acetoin is the only product seen by photoionization mass spectrometry.[3] Finally, in photoexcited norbornadiene, the products are C_7H_8 isomers with five- and six-membered rings rather than quadricyclane, the isomer expected from [2+2] cycloaddition.[4]

I will also discuss how KinBot is evolving to make such studies faster and more reliable. We benchmarked the UMA foundation machine-learned potential within KinBot on twelve combustion and atmospheric systems, covering about 1700 stationary points.[5] It reproduces its parent DFT method to within 0.6 kcal/mol and recovers all known reaction channels. I will show characteristic failure modes, such as "hallucinated" minima. This motivates a hybrid strategy in which MLIPs drive exploration and sampling while more accurate methods are reserved for the kinetically relevant regions of the PES. Two further developments will also be discussed. The first is an automated high-level energy correction layer. The second is a stereochemistry update that distinguishes stereoisomers and follows distinct stereochemical pathways. Together, these steps aim to make automated, high-accuracy kinetics a routine partner for quantitative detection of gas-phase intermediates.

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Isomer-Resolved Detection of Vinoxylic Radicals

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Vinoxylic radicals are resonance-stabilized open-shell molecules with a delocalized electron partially on the oxygen atom of a carbonyl group. In the gas phase, vinoxylic radicals can be formed through hydroxyl radical (OH) reactions with unsaturated carbonyl compounds. We investigated the reaction of OH with cyclopentenone derivatives between 323 K and 523 K using multiplexed photoionization mass spectrometry. Time-resolved soft ionization allows for the direct detection of transient vinoxylic radicals formed under multiple collision conditions. We compared experimental photoion spectra to normalized integrated Franck–Condon factors to estimate the branching ratios between the different detected product channels and determine their isomeric distribution. We found that reactions of OH with cyclopent-2-en-1-one proceeded via addition to the conjugated C=C bond (Pathways A and B in Figure 1) and abstraction of a hydrogen atom from a saturated carbon (Pathways C and D). Near room temperature, the branching ratio between the two mechanisms is ~1:3 in favor of OH-addition, with the contribution from H-abstraction increasing as the temperature increases. We also found that 70% of the addition entrance channel proceeded via OH addition to the carbon in *β*-position (Pathway A), forming the 3-hydroxy-cyclopentanone-2-yl vinoxylic intermediate, of which a small fraction was stabilized by collision and detected under our experimental conditions.

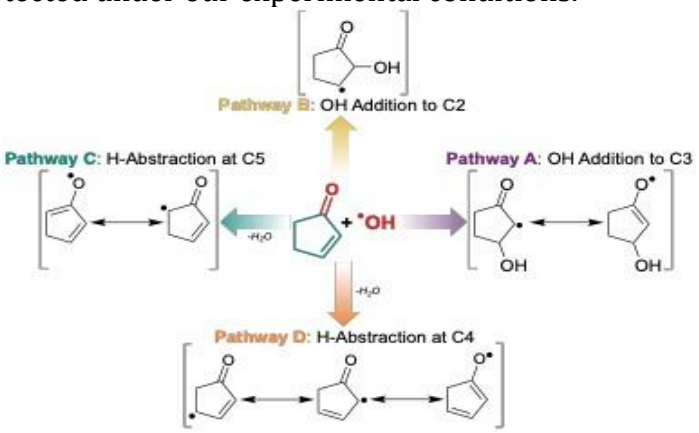


Figure 1. Formation of vinoxylic radical by reaction of OH with cyclopentenone

Probing Low-Temperature Fuel Oxidation by Proton-Transfer Reaction Mass Spectrometry

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The transition toward more sustainable combustion technologies requires the development of renewable fuels together with a detailed understanding of their oxidation chemistry. Biomassderived fuels are particularly attractive candidates, but their oxygenated molecular structures give rise to complex low-temperature reaction kinetic networks involving a wide variety of intermediates [1,2]. Identifying and quantifying these species is essential for constraining and validating detailed chemical kinetic models, ultimately providing a predictive chemical basis for CFD simulations of practical combustion systems.

Within the context of the OXIBIO3 project, we developed a new experimental setup dedicated to fuel oxidation under controlled low-temperature conditions. The setup combines a flow reactor operated between 300 and 800 K using a tubular furnace at atmospheric pressure with online chemical-ionization mass spectrometry. Detection is performed using Proton-TransferReaction Mass Spectrometry (PTR-MS), whose soft H_3O^+ chemical ionization provides high sensitivity toward a broad range of oxygenated species. Although PTR-MS is a well-established analytical technique in atmospheric chemistry, its application to the direct investigation of fundamental fuel oxidation chemistry remains scarce [3].

Here, we present the first results obtained with this new setup. The low-temperature oxidation of *n*-heptane was selected as a reference system to validate the reactor and PTR-MS measurements. Both O_2 oxidation and O_3-assisted oxidation were investigated, the latter exploiting the ability of O_3 to promote fuel reactivity at low temperature [4]. The oxygenatedproduct mole fraction profiles were compared with predictions from a kinetic model of the literature. Finally, preliminary results will be presented for the oxidation of furan, a prototypical oxygenated heterocycle of relevance to biomass-derived fuels, combustion chemistry, and atmospheric chemistry [5,6].

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Probing the Frontiers of Interstellar Chemistry Through Cold and Controlled Ion-Molecule Experiments

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Ion-molecule reactions drive much of the chemistry in the interstellar medium, yet few have been measured under conditions that truly reflect the cold, dilute environment of space. We use techniques from atomic physics to study ion-molecule reactions under well-controlled conditions that replicate key aspects of the interstellar environment.

Our focus is on understanding how reactions involving small, carbon-containing molecules can drive molecular growth toward the complex organic species observed in space. Of particular interest are polycyclic aromatic hydrocarbons (PAHs), which are relatively abundant in the interstellar medium, yet the chemical pathways responsible for their formation remain poorly understood. One possible route is bottom-up molecular growth, in which sequential reactions of small carbon-containing species progressively build larger and more complex molecules.

To investigate these processes, we experimentally study sequential ion-molecule reactions initiated by the protonation of small hydrocarbons under single-collision conditions. By following these reactions, we identify pathways that promote carbon growth, as well as those that terminate and do not undergo further reaction. These measurements allow us to test proposed routes toward molecular complexity and provide new insights into the chemical processes that may contribute to the bottom-up formation of PAHs in the interstellar medium.

High-Resolution Spectroscopy of Elusive Molecular Ions

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With the recent development of leak-out spectroscopy (LOS) [1], high-resolution spectra of bare molecular ions can now be recorded in the laboratory with unprecedented sensitivity. In LOS, the internal energy of vibrationally excited ions stored in a 22-pole cryogenic ion trap is partially converted into kinetic energy through inelastic collisions with a neutral atomic or molecular partner inside the trap. This process allows the ions to escape from the trap and be detected as a function of the excitation frequency. In this talk, the method will be briefly introduced along with some recent applications.

I will present both rotationally resolved infrared and pure rotational spectra of astrophysically relevant cations, ranging from small hydrocarbons to protonated forms of abundant complex organic molecules, such as protonated methanol. Because the energy associated with a pure rotational transition is typically insufficient to induce the leak-out process, the pure rotational transitions of these ions are usually measured using millimeter-wave–infrared double-resonance spectroscopy [2]. Recently, however, we recorded a pure rotational LOS transition of OH^+ at 2 THz without the need for a double-resonance scheme [3]. Several of the ions featured in this talk have been discovered in space recently based on the newly laboratory data.

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Low-Temperature Kinetics of the C_2 Molecule

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Dicarbon, C_2, is one of the most abundant molecules in the universe, detected in a variety of astrochemical environments including: the interstellar medium, comets, diffuse clouds and stars (1). Unusually, the first electronically excited state, $a^3\Pi_u$, sits only 610 cm^{-1} above the ground state, $X^1\Sigma_g^+$, with both states populated over a wide range of temperatures, including those relevant to astrochemical conditions (2). This study reports the generation of $^1C_2$ and $^3C_2$ via 213 nm photolysis of tetrachloroethylene, C_2Cl_4. Detection was via laser-induced fluorescence (LIF) spectroscopy of $^1C_2$ using excitation of the $D^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ (0,0) transition of the Mulliken bands at ~ 231 nm and of $^3C_2$ using excitation of the $d^3\Pi_g \leftarrow a^3\Pi_u$ (0,0) transition of the Swan band system at ~ 516 nm. A Cinétique de Réaction en Ecoulement Supersonique Uniforme (CRESU) apparatus, specifically a pulsed Laval nozzle which generates a collimated uniform supersonic flow of gas with a defined temperature and pressure via an isentropic expansion, was used to monitor the reaction of C_2 with ethylene (C_2H_4) over the temperature range of 36 127 K. Results from $^3C_2$ kinetics were used to constrain the global biexponential fitting of the $^1C_2$ LIF traces. The five determined rate coefficients for $^1C_2 + C_2H_4$ exhibited a negative temperature dependence when compared to higher temperature literature data. Here we also present preliminary calculations of the potential energy surface of the reaction of $^1C_2$ with acetonitrile (CH_3CN), for which five stationary points have been identified and optimised at the B3LYP/6311G(d,p) level of theory. The proposed products of the $C_2 + CH_3CN$ reaction (3-cyano propargyl radical, CH_2C_3N, and 1-cyano propargyl radical, HC_3HCN) have been detected in the dark cloud TMC-1, with both isomers hypothesised to play an important role in the synthesis of larger organic N-bearing molecules and nitrogen heterocycles (3). However, the kinetics of the reaction between C_2 and CH_3CN have never been studied, and the modelled chemical processes in TMC-1 rely on estimated rate coefficients. Experimental and theoretical studies of the kinetics of $C_2 + CH_3CN$ are currently underway.

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The Influence of Resonance Stabilization on β-Hydroxyalkyl Radical Reactivity with O_2

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During daylight hours, tropospheric oxidation of unsaturated volatile organic compounds (VOCs) occurs primarily through reactions with OH. The addition of OH to an alkene generates a β-hydroxylalkyl radical, which rapidly reacts with oxygen to form a β-hydroxyalkylperoxy radical. Such reactions are key initial steps in the oxidation of VOCs that can lead to secondary organic aerosol formation. We have investigated the influence of functionalization on βhydroxyalkylperoxy radical formation by measuring rate coefficients for a series of βhydroxylalkyl + O_2 reactions at the high-pressure limit, spanning C_2-C_6 radicals. For nonconjugated radicals, the rate coefficients correlate with the ionization potential of the radical, indicating ionic contributions to the entrance channel. In contrast, resonance-stabilized radicals exhibit much lower reactivity. These results reveal the influence of electronic structure on R + O_2 association reactions and provide insight into atmospheric oxidation of important VOCs, including isoprene.

UV Absorption Cross Sections of 1,2-ISOPOOH and Kinetics of Its Reaction with Criegee Intermediates

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Isoprene is the most abundantly emitted non-methane hydrocarbon. Its oxidation under lowNOx conditions, where peroxy radical chemistry is dominated by HO_2, yields 1,2-ISOPOOH as a major first-generation product. 1,2-ISOPOOH is in turn a key intermediate in the formation of secondary organic aerosol (SOA), which influences climate and public health. However, the peroxide's low volatility and strong affinity for surfaces make its gas-phase concentration difficult to quantify. As a result, accurate absorption cross sections are difficult to measure, which limits gas-phase kinetic studies. To address this challenge, we constructed a sample delivery system consisting of a continuous-flow injector and a custom heated disseminator head. The thermal injection system delivers a constant flow of 1,2-ISOPOOH, allowing the concentration to be determined as a function of injection rate, liquid density, and pressure. Using this system, we have obtained preliminary UV absorption cross sections at 185 nm and from 200 to 310 nm. These measurements have in turn enabled initial bimolecular rate coefficients for the reaction of 1,2-ISOPOOH with the simplest Criegee intermediate (CI), CH_2OO. Together, these results help constrain the CI-mediated loss of 1,2-ISOPOOH, improving estimates of its atmospheric lifetime and its contribution to SOA formation.

Reaction of Methane and UV-activated Perchlorate: Relevance to Heterogeneous Loss of Methane in the Atmosphere of Mars

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The absence of significant detectable signatures of organic molecules in the atmosphere and on the surface of Mars is a major unsolved puzzle. One possible explanation is that perchlorate‐rich Martian soils, activated by solar ultraviolet (UV) radiation, create an environment favorable for the rapid oxidation of organics such as alkanes (including methane or CH_4). In this paper, we measured product formation rates from the methane-perchlorate-UV system at room temperature. Our results show that magnesium perchlorate ($Mg(ClO_4)_2 \bullet 6H_2O$) surfaces exposed to UV light at wavelengths reaching the Mars' surface accelerate the decomposition of methane (CH_4), resulting in the formation of carbon dioxide (CO_2), carbon monoxide (CO), and volatile chlorine oxides. The production rates for CO_2 and CO on UV-activated perchlorate surfaces are accelerated by a factor of 2.5 and 4.5, respectively, compared to those in the absence of perchlorate. In addition, with UV radiation exposure, perchlorate (ClO_4^-) decomposes to chlorate (ClO_3^-) and chlorine oxides. These results are incorporated into a simple box model to estimate the near-surface atmospheric methane lifetime. The model gives a lower bound of the lifetime on the order of hours to days, substantially shorter than ~300 yrs calculated from methane loss by gas-phase chemistry alone.

Rotational Strong Coupling and Molecular Thermometry in the Gas Phase

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Strong coupling between molecular rotations and cavity photons offers a platform for probing coherent light–matter interactions under well-defined conditions. We demonstrate collective rotational strong coupling of gas-phase N_2O and OCS in tunable millimeter-wave Fabry–Pérot cavities using complementary frequency- and time-domain measurements. N_2O transmission spectra show an avoided crossing and a Rabi splitting of 1.98 MHz, exceeding the cavity linewidth. For OCS, coherent beating during cavity ring-up and ring-down reveals consistent polariton frequencies and a collective splitting of 5.72 MHz. Room-temperature measurements agree with the predicted density dependence of collective coupling without an adjustable scale factor. We further use the splitting of two OCS rotational transitions to determine rotational temperatures of 20–34 K throughout a pulsed expansion. The results establish rotational polaritons as a platform for resolving coherent cavity–molecule dynamics and extracting timedependent rotational temperatures and monomer densities in molecular expansions.

Temperature-Dependent Kinetics of the OH + Ethylene Oxide Reaction

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Ethylene oxide (EtO, C_2H_4O), designated a Class 1 carcinogen by the EPA, has widespread industrial use (e.g., medical equipment sterilization, polyester production). The primary removal pathway of EtO in the gas phase is oxidation by the hydroxyl radical (OH). To assess EtO exposure risks for communities near emission sources across regional climates, the atmospheric lifetime of EtO with respect to OH-initiated oxidation should be determined. Using a pressureand temperature-controlled chamber with a Pulsed Laser Photolysis-Laser Induced Fluorescence (PLP-LIF) apparatus, time-resolved OH decay signals were measured under pseudo-first-order conditions. OH radicals were generated by photolyzing HNO_3 ($h\boldsymbol{\nu}$ = 248 nm), with decays measured over 288 - 353 K at 50 Torr. The derived two-parameter Arrhenius (cm^3 $molecule^{-1}$ s^{-1}), k = (4.06 ± 0.30) * 10^{12} exp[(-1063 ± 24)/T], suggests faster rates over the entire temperature range compared to current recommended values. Observed rate coefficients were 47% and 14% higher at 288 K and 353 K, respectively, compared to previous literature, corresponding to a 37% and 17% decrease in the estimated atmospheric lifetime of EtO at these temperatures.

Study of NH + NO_2 Under Conditions Representative of Hot Exoplanet Atmospheres

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Interpretation of spectra collected of exoplanet atmospheres by JWST and other modern observation platforms relies on the modeling of the complex chemical systems in those atmospheres. Often these atmospheric retrieval models assume these environments to be close to thermodynamic equilibrium, disregarding disequilibria processes, such as photochemistry and transport-induced quenching which have been shown to have substantial impacts on the derived results. In sub-Neptune to Jupiter sized exoplanets, modelers expect there to be enough NH_3 that these disequilibria processes can greatly alter the spectroscopic signatures of these bodies. Though the importance of these effects is recognized by the community, there is a scarcity of chemical kinetics and product branching ratio data for NH_x (NH and NH2) chemistry for models to include over temperatures ranging from 300-800 K and pressures from 10 — 800 Torr, which are representative of exoplanet atmospheres.

The abundance of molecules such as NH_3 in an exoplanet atmosphere can yield valuable information regarding the physical processes occurring such as convection and transport. Currently, the NH_3 mixing ratio in hot exoplanets such as HD 189733b can vary by as much as an order of magnitude due to the uncertainty in the kinetics data used in the models. The work shown here aims at reducing the uncertainty of such data by providing new reaction rate coefficients for NH_x reactions.

The work presented here discusses the observation of the NH + NO_2 reaction over a temperature range of 300 — 800 K at a pressure of 50 Torr using NH (A ← X) Laser Induced Fluorescence. This work represents one of the first modern measurements of the reaction and the extension into conditions relevant to exoplanet atmospheres. Additionally, these experiments highlight the ability of a newly constructed High Temperature Laser Induced Fluorescence instrument designed to target exoplanet atmospheric chemistry. Experimental results and the potential impact on the understanding of exoplanet atmospheres will be discussed.

In Situ Cavity Ring Down Spectroscopy for the Detection of Reactive Gas Phase Species in Electron-Enhanced Atomic Layer Deposition

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Electron-enhanced atomic layer deposition (EE-ALD) is a thin film deposition technique that uses low-energy electrons to stimulate thermally inaccessible reactions for monolayer-precise, next-generation nanomaterials. In the gas phase, electron-impact dissociation generates radical species, while electron flux at the surface stimulates the desorption of unwanted precursor ligands. However, detecting these sparse, transient species remains challenging, motivating the development of sensitive, species-selective spectroscopic techniques.

To investigate the chemistry of EE-ALD reactions, we are developing an in-situ cavity ring-down spectroscopy (CRDS) system integrated into an EE-ALD chamber for operando measurements of thin film deposition processes. The high-finesse optical cavity enables detection of trace methyl and amino group overtone stretches in the near infrared. Current efforts focus on detecting methyl radicals and characterizing other plasma-generated gas-phase species in a DC hollow cathode discharge.

Our goal is to apply this spectroscopic diagnostic to EE-ALD, where monitoring gas-phase intermediates and volatile reaction products will provide insight into precursor decomposition, plasma chemistry, and surface reaction mechanisms during thin-film growth.

Spectroscopic Interrogation of Chemical Reaction Dynamics from Molecular to Planetary Scales

Dedicated to Stan Sander

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The quantum nature of matter imparts a unique spectroscopic signature to each atom or molecule based on its rotational, vibrational, and electronic energy levels and the allowed transitions between these energy levels. These spectroscopic 'fingerprints' can be used to quantify molecular abundances with high confidence, determine the rates of chemical reactions and characterize their products, and identify previously unknown molecules on scales from individual reactions to planetary atmospheres.

Stan Sander was a master of developing state of the art spectroscopic technologies and harnessing them to investigate Grand Challenge problems related to the chemical kinetics of planetary atmospheres. This presentation is inspired by Stan's legacy and the projects on which we worked together to make measurements in the laboratory, in the field, and from space.

CO_2 - easy to measure to 1% but that is nowhere good enough to be useful

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The first measurements of CO_2 in ambient air that were sufficiently precise and accurate to observe the small differences in time and space were made at Caltech in the early 1950s by David Keeling. Keeling went on to establish the first set of in situ measurement sites in the late 1950s – measurements that detailed the increasing CO_2 levels driven by fossil fuel combustion. In 2014, OCO-2 was launched to take the Keeling curve globally – mapping CO_2 from space. This fall, Caltech has taken over the OCO-2 and OCO-3 missions and will operate them going forward. The OCO missions' record of CO_2 observations from orbit are truly amazing providing new insight into the impact of climate on the biosphere and how El Nino alters the carbon cycle dynamics across the globe. Stan brought these techniques to Mt. Wilson creating a similar but much more dense set of observations of CO_2 (and CH_4) across the Los Angeles Basin.

Experimentally Reassessing the Spectroscopic and Kinetic Properties of the HO_2 Radical

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The hydroperoxy radical (HO_2) is one of the most important free radicals in the atmosphere, and quantitative characterization of its spectroscopic and kinetic properties is essential for both fundamental physical chemistry and atmospheric chemistry. High-resolution spectroscopic measurements and absolute line-strength determinations of HO_2 using mid-infrared timeresolved dual-comb spectroscopy will be presented [1,2]. The resulting absolute intensities of individual transitions and integrated band strengths, with typical uncertainties of 4–8%, provide reliable experimental reference data for validating computational methods and refining existing HO_2 spectroscopic databases. Building on these experimentally determined HO_2 line strengths, the kinetics of the HO_2 self-reaction are further re-examined using a collinear photolysis-probe configuration that integrates flash photolysis, time-resolved UV absorption spectroscopy, and high-resolution mid-infrared dual-comb spectroscopy. The resulting parameterization of the HO_2 self-reaction rate coefficients is derived from measurements spanning tropospherically relevant temperatures and pressures and varying concentrations of methanol and water vapor, with potentially significant implications for laboratory kinetic studies involving HO_2 radicals and for the prediction of HO_2 and H_2O_2 concentrations in atmospheric chemistry models [3].

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Rate Constant of the Self-Reaction of Methyl Peroxy Radicals

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The self-reaction of peroxy radicals is a major removal path for radicals in environments with low NO-concentrations where the cycling of peroxy radicals to HO_2 and back to OH through reaction with NO is slowed down. Different products are possible for methyl peroxy, CH_3O_2:

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2 \quad (R1)$$
$$\rightarrow 2\ CH_3O + O_2 \quad (R2)$$
$$\rightarrow CH_3OOCH_3 + O_2 \quad (R3)$$

This reaction can become a major sink for CH_3O_2 and thus the rate constant and product branching has non-negligible impact on the overall radical budget.

The branching ratio has been measured several times from stable end product measurements and it is agreed that (R1) is the major path with a branching of around 63% and (R2) the minor path with the remaining 37%, while (R3) seems negligible. The rate constant has been measured many times in the 1990's, mostly through laser-photolysis/UV absorption, and IUPAC recommendation was for a long time $k_{298K}=3.5\times10^{-13}$ cm^3s^{-1}. In 2022 a new measurement from Onel *et al.* [1] revised this value down by 40% through new measurements using FAGE detection coupled to the HIRAC simulation chamber. This motivated the IUPAC team in 2025 to decrease the recommended value down to $k_{298K}=3.23\times10^{-13}$ cm^3s^{-1}.

Due to the importance of this reaction, especially in remote marine environments, we have recently carried out new measurements using simultaneous CH_3O_2 and HO_2 detection by cwCRDS in the near IR, coupled to laser photolysis, for another determination of the rate constant. The results will be presented.

KEYWORDS

Methylperoxy radicals, rate constant, self-reaction, CRDS, laser photolysis

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Direct generation of a prototypical n-pentyl peroxy radical reveals how mixed-fate chemical regimes shape product distributions

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Organic peroxy radicals (RO_2) are key branch points in atmospheric oxidation with competing fates in the troposphere: reaction with NO, reaction with HO_2, self-/cross-reaction with another RO_2, and isomerization. RO_2 often react in mixed-fate regimes, yielding product distributions with a complex dependence on reactivity conditions. In traditional environmental chamber experiments, not all RO_2 fates are equally accessible, and chemical regimes favoring RO_2 self-/cross-reactions and isomerizations are poorly characterized. Here, we access these conditions in an environmental chamber via 1-iodopentane photolysis, monitoring product distributions with NH_4^+ chemical ionization mass spectrometry. We tune the relative importance of these reaction pathways by varying the initial conditions, spanning bimolecular lifetimes from ~100-2000 s. Across conditions, the major observed C5 product, $C_5H_{10}O_3$ (~4060% yield), requires at least one RO_2 isomerization to form, demonstrating the importance of downstream RO_2 unimolecular reactions even if they are not the major fate of upstream RO_2. Model mechanisms partially reproduce observed product distributions but cannot quantitatively capture variations with changing RO_2 fate. Discrepancies suggest poorlyunderstood RO_2 cross-reactions substantially influence product distributions. Conditions favoring RO_2 isomerization unintuitively enhance both fragmentation and accretion via downstream functionalized alkoxy and peroxy radical chemistry. Results illuminate important gaps in existing atmospheric reaction mechanisms when predicting product distributions in mixed-fate chemical regimes.

The never-ending pursuit of OH radical: Its formation via carbonyl photolysis and reactions with SO_2 and HNO_3.

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The hydroxyl radical is arguably one of the most important free radical in the atmosphere. Even though the major source of this radical is the reaction of $O(^1D)$ with H_2O in Earth's atmosphere, other minor sources contribute and can be important in certain regions. I will describe laboratory studies that aim to quantify the role of carbonyls in producing OH.

A large number of chemicals in the atmosphere are removed by reaction with OH. I will describe some recent experimental and theoretical studies that examine the role of pre-reaction complexes in determining the rate coefficients for OH reactions with SO_2 and HNO_3.

Aromatic growth in dense molecular clouds: What we know and open challenges

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Recent radio-astronomical detections of aromatic molecules and small PAHs in dense molecular clouds, particularly TMC-1, have revealed abundances far higher than standard astrochemical models predict. This talk reviews what we know and the challenges that remain, organized around three questions.

First, how do aromatics form in cold, dense clouds? Ion–molecule and neutral–neutral chemistry can explain benzene and cyclopentadiene, but fail for larger species. We propose that barrierless atomic carbon addition followed by hydrogenation provides an efficient bottom-up growth sequence with minimal carbon loss. This network, supported by quantum chemical calculations and implemented in the Nautilus gas–grain code, reproduces the observed abundances of C_6H_5CN, $C_6H_5C_2H$, C_9H_7 and $C_{10}H_7CN$.

Second, are cyano-PAHs reliable proxies for their radio-invisible parent PAHs? We will compare predicted and observed abundances for species where both the bare molecule and its cyano derivative have been detected.

Third, can we trust the derived abundances, and why do they remain nearly flat with increasing molecular size, as both observations and our model suggest? We will contrast this behavior with the well-known decline in carbon-chain abundances with increasing size.

Addressing these questions is key to understanding the aromatic inventory of TMC-1 and other cold interstellar environments.

Applications of CPICE as a new spectroscopic instrument for studying interstellar ice analogues and sublimation dynamics

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Chirped-Pulse ICE (CPICE) couples buffer gas cooling and broadband millimeter wave spectroscopy as an approach to interrogate molecules following thermal desorption from an ice. Additionally, CPICE utilizes Reflection Absorption Infrared Spectroscopy (RAIRS) for further understanding of condensed phase mechanisms that occur before and during heating. This allows for a complete investigation of complex organic molecules within both phases. CPICE employs both a vacuum ultraviolet photolysis lamp and high-energy electron gun to compare the effects of various energetic processing sources on the final product ratios. This talk will first discuss the results of irradiating both methyl and ethyl cyanide (CH_3CN and CH_3CH_2CN) with each energy source and key observations of distinct tautomerization pathways per energy source will be discussed.[1]

In addition to observing chemical reactions within the condensed phase, CPICE also has the unique ability to investigate phase change dynamics of large, Astrophysically relevant species. Propyl cyanide (PrCN, C_3H_7CN) has a complex conformer and isomer landscape which have all been detected within the interstellar medium and have accessible, low energy vibrationally excited states.[2,3] Following the warmup of neat normal or iso-PrCN ices, distinct nonequilibrium populations for these low lying vibrationally excited states were detected.[4] These distributions cannot be characterized by energy differences, so a new framework is proposed to quantitatively answer the key question: how is the internal energy distribution of a molecule modified as it crosses the surface-gas interface? **References:**

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Spectroscopy and predissociation dynamics of SH/SD radical via the $A^2\Sigma^+$ state

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The spectroscopy and predissociation dynamics of rovibrational levels of SH ($A^2\Sigma^+$, v' = 0–7) and SD ($A^2\Sigma^+$, v' = 0–8) are studied using the high-n Rydberg atom time-of-flight (HRTOF) technique. By measuring the photoproduct translational energy distributions as a function of excitation wavelength, contributions from overlapping $A^2\Sigma^+$ (v') ← $X^2\Pi$ (v'') transitions can be separated, and the H/D + S(^3P_J) photofragment yield (PFY) spectra are obtained across various rovibrational levels (SH v' = 0-7 and SD v' = 0-8) of the $A^2\Sigma^+ \leftarrow X^2\Pi$ bands. The upper $A^2\Sigma^+$ state vibrational levels v' = 5-7 of SH and v' = 3-8 of SD are determined for the first time, providing vibrational origins and linewidths of these rovibrational levels. The linewidths ($\geq$ 1.5 cm^{-1}) of the SH $A^2\Sigma^+$ v' = 3-7 and SD $A^2\Sigma^+$ v' = 2-8 states are characterized, demonstrating that these levels undergo rapid predissociation with lifetimes on the order of picosecond. The measured spin-orbit branching fractions of the H/D(^2S) + S($^3P_{J=2,1,0}$) product channels provide insights into the predissociation dynamics of the SH/SD $A^2\Sigma^+$ state, which vary dramatically as the vibrational level v' increases. The $A^2\Sigma^+$ v' = 0 state of SH/SD predissociates predominantly via adiabatic coupling to the $^4\Sigma^-$ repulsive state. As the vibrational level v' increases, predissociation dynamics change drastically, with all three repulsive states ($^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$) involved in the dissociation. Nonadiabatic interactions and quantum interferences among these dissociation pathways affect the fine-structure state distributions of the S($^3P_{J=2,1,0}$) products.

Integrating entangled photons into spectroscopy: Where does it work?

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Entangled photons have been slower to integrate into optical spectroscopy than into quantum computing and quantum information. The low flux of entangled photon sources often makes classical techniques faster and more precise for a given measurement time. In this talk, I'll introduce how entangled photons are used in linear optical spectroscopy and their newer use in ultrafast spectroscopy. We will focus on the information available from correlated photon pairs and the challenges posed by source brightness and photon-counting detectors. For example, we have achieved practicality by developing custom thin-film lithium niobate and lithium tantalate photonic integrated circuits. These entangled photon sources are specialized for spectroscopy, spanning the UV to IR and offering flux levels that make spectroscopy practical. The goal of this talk is to both introduce entangled photon spectroscopy and discuss its practical applications and future directions in the chemical sciences.

Engineered Molecular Clocks for Quantum Sensing

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Precision measurements in molecules have enabled sensitive probes of fundamental physics beyond the Standard Model, and are currently exploring areas beyond the reach of particle accelerators. Looking forward, several directions remain where significant improvements are yet to be realized: adding modern quantum precision measurement tools, performing deeper probes of the nucleus, and accessing exotic species with significant amplification of intrinsic sensitivity. Realizing these goals will impact a wide range of areas in particle, nuclear, chemical, and astronomical physics I will discuss our research in these directions via engineered molecules with exotic nuclei, and efforts to dramatically speed up their spectroscopic study.

Spectroscopy of CP violation-sensitive states on a nonlinear molecule: $SrNH_2$

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Heavy, polar molecules are sensitive detectors of new symmetry-violating particles and electromagnetic moments. Leading precision experiments increasingly exploit rich molecular degrees of freedom to enhance the sensitivity, tunability, and robustness of measurements. Nonlinear molecules, in particular, contain highly polarizable, long-lived rotational *K*-states are useful for symmetry violation metrology. In this work, we identify and characterize CP violation (CPV)-sensitive states and transitions on a prototypical system – the asymmetric top molecule strontium monoamide ($SrNH_2$). Using resonant laser spectroscopy on a cold molecular beam, we perform high-resolution field-free, Stark and Zeeman, studies on the 0^0_0 vibronic band of the $\tilde{C}\ ^2A_1$–$\tilde{X}\ ^2A_1$ system of $SrNH_2$. An effective Hamiltonian was used to extract fine parameters, molecular frame electric dipole moments and magnetic g-factors. These measurements elucidate the electromagnetic tuning of optical cycling and CPV-sensing transitions – which is critical to science state preparation, interrogation, and control on $SrNH_2$ – and enable the calculation of field-insensitive metrology conditions. Our results illustrate a realistic pathway towards a potentially broad class of CPV experiments utilizing heavy, nonlinear molecules.