Mechanisms of PAH growth and oxidation in combustion

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The presentation will overview results of ab initio calculations of potential energy surfaces combined with RRKM-Master Equation calculations of reaction rate constants, carried out in order to unravel reaction mechanisms of the growth of polycyclic aromatic hydrocarbons (PAHs) as well as oxidation of their radicals with molecular oxygen at temperatures and pressures relevant to combustion. In particular, we will compare the oxidation mechanism and rate constants of the phenyl and naphthyl radicals with those for the pyrenyl radical, which reacts consequently with two O_2 molecules oxidizing a six-member ring first and a five-member ring second. We will also describe our recent efforts directed toward the development of a comprehensive mechanism of PAH growth in combustion and will consider possible formation routes to two-ring PAHs, naphthalene and indene. The reactions potentially leading to naphthalene involve $C_{10}H_x$ (x = 6-11) surfaces and include variations of the HACA mechanism, recombination of two cyclopentadienyl radicals, C_6H_5 (phenyl) + C_4H_4 (vinylacetylene)/C_4H_6 (1,3-butadiene), C_9H_7 (indenyl) + CH_3, and C_7H_7 (benzyl) + C_3H_3 (propargyl). Alternatively, the reactions leading to indene occur on C_9H_x (x = 6-11) potential energy surfaces and include C_6H_5 + C_3H_4 (allene and propyne), benzyl + C_2H_2 (acetylene), C_6H_5 + C_3H_6 (propene), C_6H_5 + C_3H_5 (allyl), and C_6H_5 + C_4H_6 (1,2-butadiene). While modeling is required to compare contributions of different reactions to the formation of naphthalene and indene, a number of interesting qualitative conclusions on the role of various mechanisms will be presented based on the computed temperature and pressure-dependent rate constants.

Quantum Chemical Treatment of SFG-Electronic Transition

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Sum-frequency generation spectroscopies have become very popular to study the structures of molecules on the surface and in the interface of condensed phases. The principle of SFG will be discussed. In this talk, two types of electronic Sum-frequency generations, that is, symmetry-allowed and symmetry forbidden transitions will be presented. Temperature effect on band shapes of SFG will be discussed by using carbonyl compounds as examples.

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Chemistry of reactive intermediates in combustion and tropospheric oxidation systems

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The oxidation of hydrocarbons is an important process in the troposphere and in combustion systems, and investigators in both these arenas seek predictive models of hydrocarbon oxidation chemistry. Especially in complex environments, a predictive model often requires understanding the role of reactive intermediate species in the overall oxidation process. For example, radical chain branching in autoignition relies on the reaction of hydroperoxyalkyl ("QOOH") radicals, and oxidation of unsaturated hydrocarbons by ozone creates carbonyl oxide "Criegee intermediates." I will describe recent investigations that aim to isolate and interrogate the reactivity of these often unstable species.

Spectroscopy and Reactions of Criegee Intermediates

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The Criegee intermediates, a carbonyl oxide proposed to be produced in reactions of ozone with unsaturated hydrocarbons, play important roles in formation of OH and organic acids in the atmosphere but have eluded its direct detection until recently [1] when the reaction of $CH_2I + O_2$ was employed to produce CH_2OO. We reported previously the transient IR absorption spectrum of CH_2OO using a step-scan FTIR spectrometer [2], [3]. Here, we report the IR absorption spectra of CH_2OO at resolution 0.25 cm^{-1}, showing partially rotationally resolved structures [4]. With the analysis of the vibration-rotational spectra, we provide a definitive assignment of these bands to CH_2OO. Previously assigned v_5 mode near 1330 cm^{-1} turned out to be $2v_9$ at 1233.5 cm^{-1}, and the true v_5 mode lies at 1213.0 cm^{-1}. At high pressure (P>100 Torr) four bands near 1233.8, 1221, 1087, and 923 cm^{-1} were identified as ICH_2OO, the adduct of $CH_2I + O_2$. With direct detection of both CH_2OO and ICH_2OO, we determined the pressure dependence of the yield of CH_2OO; the value near one atmosphere is greater than previous reports and might have significant impact in atmospheric chemistry.

Methyl substitution of CH_2OO induces two conformers of CH_3CHOO and consequently complicates the infrared spectrum. We report the transient infrared spectrum of both *syn-* and *anti-*CH_3CHOO, produced from $CH_3CHI + O_2$ in a flow reactor, using a step-scan Fourier-transform spectrometer [5]. Guided and supported by high-level full-dimensional quantum calculations, rotational contours of the four observed bands are simulated successfully and provide definitive identification of both conformers. Furthermore, a*nti-*CH_3CHOO shows a reactivity greater than *syn-*CH_3CHOO toward NO/NO_2; at the later period of reaction, the spectrum can be simulated with only *syn-*CH_3CHOO. Without NO/NO_2, a*nti-*CH_3CHOO also decays much faster than *syn-*CH_3CHOO.

If time permits, results of IR spectra of $(CH_3)_2CHOO$ and reaction products of CH_2OO + SO_2 and CH_2OO + H_2O will also be presented.

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Structure Dependent Reactivity of Criegee Intermediates and the Implications in Atmospheric Chemistry

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Ozonolysis of alkenes produces highly reactive Criegee intermediates, which are thought to play an important role in atmospheric chemistry, in particular, the oxidation of SO_2. The SO_3 product would further react with water to form H_2SO_4, an important constituent of aerosols and acid rain. However, the impact of such oxidation reactions is affected by the reactions of Criegee intermediates with water vapor, because of high water concentrations in the troposphere. We have studied a few simple Criegee intermediates at near atmospheric conditions by using transient UV absorption. We found the CH_2OO and *anti*-CH_3CHOO react with water dimer very quickly, such that their steady-state concentrations would be low in the troposphere [1]. On the other hand, we demonstrated that water vapor does not react with dimethyl substituted Criegee intermediate $(CH_3)_2COO$, at least not fast enough to significantly consume $(CH_3)_2COO$ in the troposphere. And $(CH_3)_2COO$ reacts with SO_2 three times faster than CH_2OO does, indicating Criegee intermediates of a structure similar to $(CH_3)_2COO$ are potential candidates for an efficient oxidant in the atmospheric SO_2 oxidation. In addition, a significant pressure dependence was observed for the reaction of $(CH_3)_2COO$ with SO_2, suggesting the use of low pressure rate may underestimate the impact of this reaction [2]. Our works show that the reactivity of a Criegee intermediate towards water vapor strongly depends on its structure, which will influence the main decay pathways and steady-state concentrations for various Criegee intermediates in the atmosphere.

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# Towards Polanyi rules for polyatomics: Vibrational dynamics at Conical Intersections

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Conical intersections play a role in excited state reaction dynamics very similar to that of the transition state in ground state dynamics. As such, one might hope that there should emerge, for excited state polyatomic dynamics, a set of notions analogous to the Polanyi rules for ground states which guide our thinking about the topography and location of conical intersections relative to potential gradients, barriers and thresholds. Will there be notions such as "early" or "late"? Do the "velocity" and "direction" of passage through a conical intersection affect diabatic versus adiabatic branching? We experimentally probe excited state dynamics using time-resolved photoelectron spectroscopy [1] (TRPES), a method sensitive to both vibrational and electronic degrees of freedom. We combine TRPES with 'on the fly' ab initio Full Multiple Spawning (FMS) trajectory calculations wherein we additionally compute the excited state photoelectron spectrum 'on the fly' during each trajectory. Using a phenomenological approach, we vary methyl substitution on unsaturated hydrocarbons [2]-[6] so as to 'tune' trajectory motions near conical intersections.
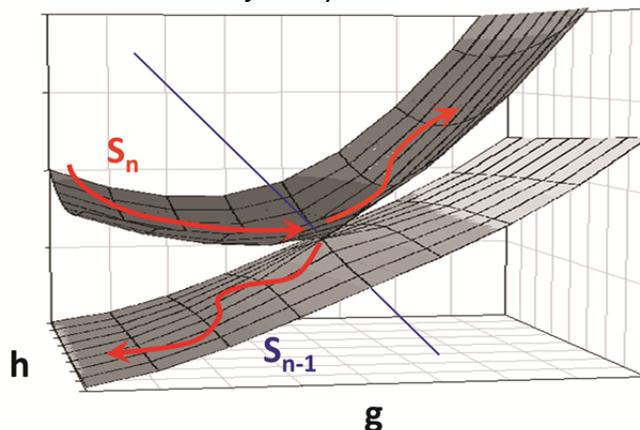
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A first principle study of THz vibrational spectroscopy of molecular crystals

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Terahertz (THz) vibrational spectroscopy provides direct access to molecular phonons in the optical branch in the vicinity of the center of the Brillouin zone. Typical observable frequency region is 0.1 THz ~ 10 THz (3 cm^{-1} ~ 300 cm^{-1}) in which the intermolecular interaction plays an important role. The phonons at Gamma point, of course, provide valuable information on the characteristics of the crystal structures and dynamics. Moreover, vibrational spectroscopy techniques can easily be performed in the laboratory.

A great deal of progress has been made by several groups at identifying and characterizing the mixing of the intra-molecular vibrational motions with inter-molecular vibrations in the THz frequency region. However, a success of these attempts relies heavily on the accurate assignment of the vibrational modes. In particular, for the case in which non-trivial mixing of the intra- and inter-molecular vibrations exists, the mode assignment becomes formidable.

In this report, we will discuss the origin of the difficulty in mode assignment of THz-vibrational modes of molecular crystals and recent development of mode analysis methods in our groups. We will provide perspective of its application of THz vibrational spectroscopy to crystalline polymers by addressing the relationship between the packing and staking configurations of polymers and the characteristics of the THz vibrational spectroscopy.

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Characterization for Diabatic States for Singlet Fission Rates

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In the simulation of dynamics with curve-crossing, the states involved are close in energy, and the Born-Oppenheimer approximation breaks down. The dynamics is better described with diabatic states, which generally require additional conditions in their definition and description. Even though diabatic states are originally defined as the eigenstates of the kinetic energy operator, they are over-determined for systems with more than two atoms [1]. Thus, an alternative definition is necessary. Diabatic states are often defined as a state that retains certain key properties when the system moves along the reaction coordinate [2]. For example, the generalized Mulliken-Hush scheme, a useful method for for electron transfer, retains the dipole moment in the diabatic states [3]. The fragment excitation difference scheme is a similar method for energy transfer problems, in which the excitation population is localized to each fragment [4].

The electronic coupling for singlet fission, an important parameter for determining the rate, has been found to be too small unless charge-transfer (CT) components were introduced in the diabatic states, mostly through perturbation or a model Hamilto- nian. In the present work, the Fragment Spin Difference (FSD) scheme was generalized to calculate the singlet fission coupling. The largest coupling strength obtained was 14.8 meV for two pentacenes in a crystal structure, or 33.7 meV for a transition-state structure, which yielded singlet fission lifetime of 239 or 37 fs, generally consistent to experimental result (80 fs). Test results with other polyacene molecules are similar. We found that the charge on one fragment in the S1 diabatic state correlates well with FSD coupling, indicating the importance of the CT component. The FSD approach is a useful first-principle method for singlet fission coupling, without the need to include the CT component explicitly [5].

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Nucleophilic substitution dynamics by crossed-beam ion imaging

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In this talk I will present recent studies of the dynamics of nucleophilic substitution reactions, which we have performed using crossed-beam velocity map ion imaging [1]. By analysing the differential scattering cross sections, we have identified several distinct reaction mechanisms for the reactions of Cl$^-$, F$^-$ and OH$^-$ anions with CH$_3$I and a good agreement has been obtained with direct dynamics simulations [2]-[6]. The different mechanisms depend differently on the relative collision energy. This will be discussed with respect to the role of the energetics and the geometrical structure of the entrance channel complex. Recently, we studied the influence of the leaving group on an S$_N$2-reaction by comparing the reactants CH$_3$I and CH$_3$Cl and observed a profound difference for the two - in good agreement with dynamics simulations. This is explained by subtle differences in the interaction in the entrance channel [7].

In order to clarify the influence of spectator vibrational modes on the reaction dynamics we studied the reaction of F$^-$ with CH$_3$I for CH-stretch excited reactant molecules. Both the S$_N$2-product and the proton transfer product were observed. For the latter a strong effect of the infrared excitation was manifest, whereas the former is only marginally affected by the vibrational excitation, which indicates spectator-like dynamics [8]. In crossed-beam experiments with larger alkyl halides we recently found evidence for the bimolecular elimination reaction (E2), which competes with the S$_N$2 reaction when more than one carbon atom is present [9].

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Carbon Chain Ion Reaction with D_2: Differences between Cation and Anion

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Due to flexible balance of s and p orbitals, carbon species are found in many different geometrical forms: linear chains, planar graphene, and three dimensional fullerene. Due to interest in astrophysics and combustion communities, many studies were performed on carbon clusters with focus on the effect of geometric structure towards the reactivity.   In this paper we concentrated on the small ionic species and studied the difference/similarities of reactivities of linear $C_n^{+/-}$ (n = 4–9) and D_2.

In the first part I present results on linear C_n^+ (n = 4–9) and D_2, studied using ion mobility mass spectrometry techniques and quantum chemical calculations.   Only linear C_nD^+ product was observed for the odd (n=5, 7, 9) linear clusters, while $C_nD_2^+$ was the main product for the even clusters.   As for the reaction rate constants determined for these two channels, we have obtained the following two features: (1) the rate constant decreases with the size n, and (2) even-sized clusters have lower rate constants than neighboring odd-sized clusters.   In the theoretical calculations using the CCSD(T) and B3LYP methods with the cc-pVTZ basis, we found that a low lying $^2\Sigma$ state in odd clusters may play an important role for these reactions.   This is opposed to the previous interpretations that the $^2\Pi_{g/u}$ state is the dominant electronic state for linear C_n^+ (n = 4–9) clusters.   We showed that a barrierless radical abstraction forming C_nD^+ occurs through direct head on approach for the $^2\Sigma$ state C_n^+. In contrast, a carbene-like insertion forming $C_nD_2^+$ occurs through a sideways approach for the $^2\Pi_{g/u}$ state C_n^+. We have concluded that the higher rate constants for the odd clusters come from the existence of symmetry broken $^2\Sigma$ states which are absent in even linear clusters.

In the latter half, I will present results on the reaction of linear C_n^- (n = 4–9) and D_2. Our simulations showed very small reactivity, $<10^{-17}$ cm^3 sec^{-1}, and this is consistent with the fact that it was not possible to detect the reaction in the room temeprature experiments.   Analysis concerngin the difference in the cation and anion reaction will also be discussed.

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Dissection of Polyatomic Reaction Dynamics:
X + H$_2$O → HX + OH (X=F, Cl, O(^{3}P))

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We discuss recent advances in theoretical characterization of reaction dynamics involving polyatomic molecules. Specifically, we focus on the hydrogen abstraction reactions of water by several atomic radicals, as indicated in the title [1]. Thanks to recent advances in electronic structure theory and potential energy surface fitting, it has become possible to construct chemically accurate global potential energy surfaces for polyatomic reactive systems such as the ones discussed here. These accurate potential energy surfaces enable detailed dynamical (both quantum and quasi-clssical) studies of the reaction dynamics. We report here interesting (and sometimes surprising) dynamical effects revealed by these theoretical studies, focusing on mode specificity and product energy disposal. A simple transition state based model is proposed to explain the observed dependence of reactivity on the initial rotational and vibrational excitations of the reactants and the internal state excitations in the products, some of which are in clear violation of the venerable Polanyi's Rules. This so-called Sudden Vector Projection (SVP) model, which attributes the mode specificity and product energy disposal to the coupling of reactant/product modes with the reaction coordinate at the transition state [2], is shown to successfully predict most observed mode specificity and product energy disposal.

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Effects of Some Roaming-type Transition States on Unimolecular Decomposition Reactions

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There have been numerous examples on the existence of roaming or roaming-like transition states since the term was coined by Suits, Harding, Bowman and coworkers (Sci., 306, 1158, 2004). Many of these very loose transition states do affect product distributions. In this presentation, several of examples studied in our group at NCTU relevant to combustion and atmosphere chemistry will be discussed; these include the production of CO (v) from highly excited CH_3O, the hydrolyses of N_2O_4 to HNO_2 + HNO_3, the hypergolic reaction of $(CH_3)_3Al$ in air, among others.

Strong field photoelectron holography

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The application of velocity map imaging for the detection of photoelectrons resulting from atomic and molecular ionization allows the observation of interferometric, and in some cases holographic structures that contain detailed information on the atomic and molecular targets from which the photoelecrons are extracted.

In my talk I will present several recent examples of the use of photoelectron velocity map imaging in experiments where atoms and molecules are exposed to strong optical and dc electric fields. I will discuss (i) observations of the nodal structure of Stark states of hydrogen and helium measured in a dc electric field, (ii) the appearance of holographic structures in mid-infrared strong-field ionization of metastable Xe atoms, (iii) the application of photoelectron holography towards the determination of (time-dependent) molecular structures, and (iv) the application of photoelectron holography in attosecond pump-probe experiments.
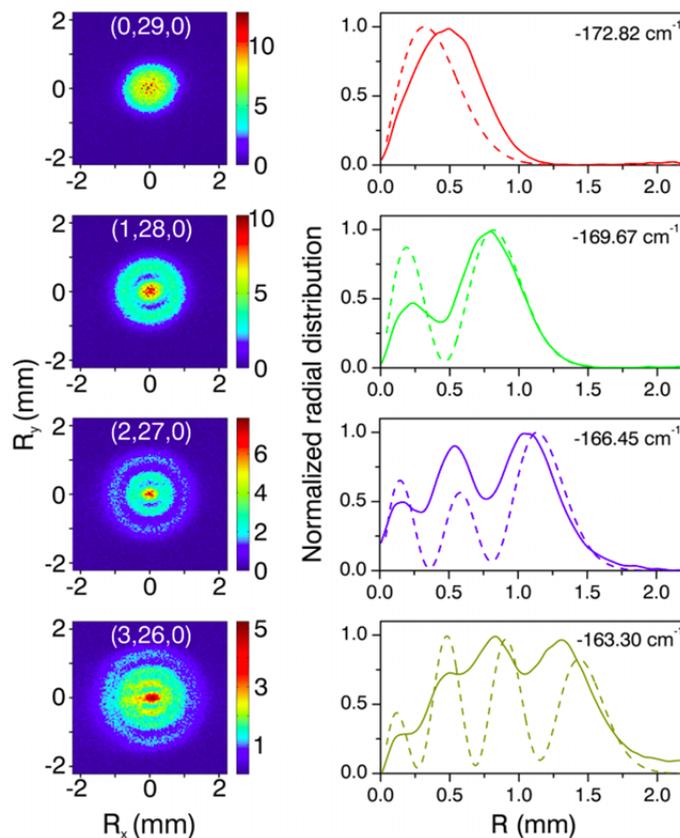
Nodal structure of 4 hydrogen Stark states, recorded by performing a photoelectron velocity map imaging experiment (A. Stodolna et al., Physical Review Letters 2013. 110(21): p. 213001.)

Ultrafast Ion Chemistry

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In this talk we will discuss the applications of femtosecond time-resolved photofragmentation spectroscopy [1], [2] to ultrafast photoionization-induced uni- and bi-molecular ion chemistry. In this method, a femtosecond pump pulse first produces an ensemble of positive ions via photoionization of the neutrals. Owing to the structural difference between the ionic and neutral ground states, vertical femtosecond photoionization can prepare an initial wave packet far away from the global equilibrium structure of the cation. The initial wave packet then evolves on the ionic surface and may undergo rearrangement (reaction) and dissociation, depending on the deposited energy and the nature of the ionic surface. A delayed probe pulse then brings the evolving cationic system to higher ionic states that ultimately undergo fragmentation. The ionic dynamics can be detected by monitoring either the parent-ion depletion or fragment-ion formation as a function of the pump-probe delay time, provided that the probing transition varies along the reaction coordinate. This fs-pump-probe photoionization-photofragmentation scheme is simply the time-domain version of ion photofragmentation spectroscopy and is most suitable for studying photoionization induced ultrafast ion chemistry. It is based on the general fact that the molecular nuclear and electronic structures often exhibit significant changes upon removal of an electron. In well-designed molecular systems, these changes may correspond to important elementary steps, including isomerization, proton transfer, and charge transfer.

Applications of this technique to photoionization-induced azobenzene cation twisting isomerization [1] and proton transfer (PT) between phenol cation and ammonia [2] will be discussed. In the case of the PT system, [2] neutral PhOH-NH$_3$ complexes prepared in a free jet were photoionized by femtosecond 1+1 REMPI using phenol as the chromophor, and the subsequent dynamics occurring in the cations was probed by

delayed pulses that result in ion fragmentation. The experiments revealed that PT in [PhOH-NH$_3$]$^+$ cation proceeds in two distinct steps: an initial impulsive wave-packet motion in ~70 fs followed by a slower relaxation of about 1 ps that stabilizes the system into the final PT configuration. These results indicate that for a barrierless PT system, even though the initial PT motions are impulsive and ultrafast, the reaction may take a much longer time scale to complete.

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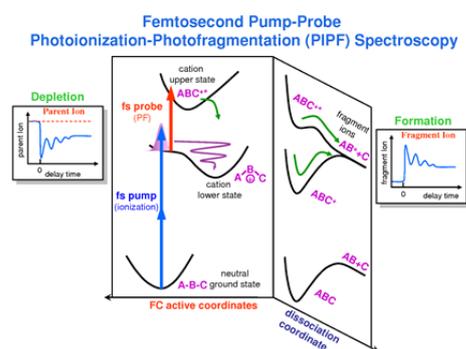
CPUF: Chirped-pulse Microwave Spectroscopy in Pulsed Uniform Supersonic Flows
Probing Reaction Dynamics with Rotational Spectroscopy

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We describe development and application of a new instrument combining two powerful techniques: chirped-pulse Fourier-transform microwave spectroscopy and pulsed uniform supersonic flows.   The objective is to join the virtues of microwave spectroscopy: quantitative, near universal detection affording structural information, with Laval flows offering thermalized conditions at low temperature and high density, to study reaction dynamics of polyatomic molecules with unprecedented detail in product characterization. This combination, which we term "CPUF" (chirped-pulse/uniform flow), delivers broad-band rotational spectra with MHz resolution and allows monitoring, on the μs timescale, of the appearance of transient reaction products with quantitative determination of product branching, yielding isomer and in some cases vibrational level specificity. We have applied this technique to study multichannel product branching in the reaction of CN radicals with unsaturated hydrocarbons at low temperature as well as a number of photochemical systems. The approach will be described and recent examples of the capabilities of the technique will be presented.   If time permits, other new directions in the probe of polyatomic reaction dynamics will be presented.

MALDI Ionization Mechanism

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In past studies, mistakes in determining the ionization mechanism in MALDI were made because an inappropriate ion-to-neutral ratio was used. We begin by describing the properties of ion-to-neutral ratios and review the past experimental measurements. A discussion of the errors committed in previous theoretical studies and a comparison of recent experimental measurements follow. We describe a thermal proton transfer model and demonstrate how the model appropriately describes ion-to-neutral ratios and the total ion intensity. We demonstrate arguments raised to challenge thermal ionization are not valid and conclude that thermal proton transfer must play a crucial role in the ionization process of MALDI. We then describe the formation of metaliated ions and the decomposition of glucose and sucrose, and explain the low detection sensitivity of carbohydrates in MALDI. Potential methods to increase the detection sensitivity are proposed.

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Reactions of C_mH (m = 1 – 8) Radicals with Ethyne and Some Related Reactions

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The dynamics of reactions of $C + C_2H_4$ [1], $C_2 + C_2H_4$ [2], $C_2 + C_6H_2$ [3], and $C_3 + C_2H_2$ [4] have been investigated in our laboratory. Recently, we are interested in the reactions of hydrocarbon radicals with unsaturated hydrocarbons such as ethyne (C_2H_2) and propyne (C_3H_4). The reactions of C_mH (m = 1 – 8) radicals with C_2H_2 were investigated in crossed-molecular beams by interrogating products $C_{m+2}H_2$. The C_mH radicals were synthesized from 1% C_2H_2/He by pulsed high-voltage discharge. Time-of-flight (TOF) spectra and photoionization-efficiency spectra of $C_{m+2}H_2$ were measured using tunable synchrotron vacuum-ultraviolet (VUV) ionization. Product's translational-energy and angular distributions of the hydrogen-loss channels were derived from the global fitting to product TOF spectra recorded at various laboratory angles. The C_mH (m = 1 – 8) + C_2H_2 reactions can be classified into two types of reactions $C_{2n-1}H + C_2H_2$ and $C_{2n}H + C_2H_2$; n = 1 – 4. In the $C_{2n-1}H + C_2H_2 \rightarrow C_{2n+1}H_2 + H$ reaction, singlet c-$HC_{2n-1}(C)CH$ and triplet $HC_{2n+1}H$ are the most-possible product isomers justified by the maximal translational-energy release and the photoionization threshold. This work implies the formation of $C_{2n+1}H_2$ from the $C_{2n-1}H + C_2H_2$ reaction though $C_{2n+1}H_2$ (n ≥ 2) has yet been discovered in interstellar space and in combustion processes. In the $C_{2n}H + C_2H_2 \rightarrow C_{2n+2}H_2 + H$ reaction, the product $C_{2n+2}H_2$ has an ionization threshold in good agreement with the ionization energy of polyyne ($HC_{2n+2}H$, sometimes called polyacetylene). This work verifies that the $C_{2n}H + C_2H_2$ reaction is a major source for the formation of various polyacetylenes, e.g., di-, tri-, tetra-, and penta-acetylene, observed in the interstellar medium and in combustion processes. Furthermore, the complementary quantum-chemical calculations indicate that the reactions $C_mH + C_2H_2 \rightarrow C_{m+2}H_2 + H$ have small or negligible entrance barriers in accord with the experimental observations. The reactions of $C_4H + C_4H_2 \rightarrow C_8H_2 + H$, $C_3H + C_6H_2 \rightarrow C_9H_2 + H$, and $C_4H + C_6H_2 \rightarrow C_{10}H_2 + H$ will also be stated in the talk.

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Moving the ocean into the laboratory for studies of sea spray aerosol impacts on clouds and climate

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The ocean plays a large but highly uncertain role in affecting clouds and climate, generating sea spray aerosols that can directly impact climate by scattering solar radiation and indirectly through nucleating clouds. A tremendous amount has been learned about these interactions over decades of marine studies, however the goal of establishing robust relationships between seawater composition and sea spray climate properties has remained elusive. Much of the impediment stems from difficulties associated with unraveling the impacts of nascent sea spray and background marine aerosols which have been shown to dominate field measurements. In an effort to advance our understanding of nascent sea spray properties, we have developed a new approach for studying this issue in a newly developed ocean-atmosphere facility equipped with breaking waves. After establishing extremely low background aerosol concentrations (< 1 per cc), studies have probed the size distribution and chemical mixing state of sea spray aerosols produced by breaking waves in natural seawater. The critical importance of using bubble size distributions representative of real breaking waves to generate sea spray aerosol (SSA) is discussed. Using a combination of techniques probing individual particle composition and morphology including aerosol time-of-flight mass spectrometry (ATOFMS), scanning tunnel x-ray microscopy (STXM), and electron microscopy, four major sea spray particle types are prevalent in all studies, consisting of sea salt, mixed sea salt and biogenic organic species, biogenic organic species, and primary biological aerosol particles (PBAP). Results from studies aimed at probing how changes in seawater composition due to biological activity impact sea spray aerosol composition and climate properties will be discussed.

Ultrafast Photoelectron Spectroscopy of Non-Adiabatic Dynamics in Gas and Liquid Phases

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State-resolved differential cross-section measurments have enabled elucidation of unprecedented details of photodissociation and bimolecular reaction dynamics. On the other hand, the quest for understanding electronic non-adiabatic dynamics and nuclear motions prior to bond dissociation and rearangements has stimulated development of ultrafast spectroscopy.

In my lecture, I describe time- and angle-resolved photoelectron spectroscopy of gases and liquids to illustrate how this method is utilized to understand photo-induced dynamics of polyatomic molecules or aggregates such as a hydrated electron in water.
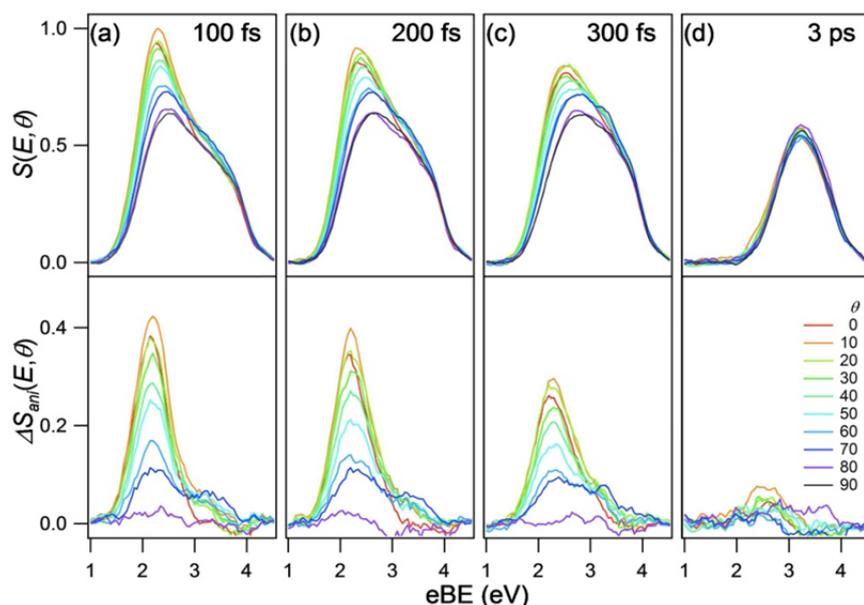
Photoemission from aqueous 0.5M DABCO [1,4-diazabicyclo[2,2,2]octane] solution occurs from the Rydberg state of DABCO at short time delays with strong anisotropy, whereas photoemission at 3 ps occurs from a hydrated electron in the ground state with negligible anisotropy.

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