

Advanced Particle Imaging Techniques:
1986-2016 And Beyond

*Telluride Science Research Center
Telluride, Colorado*

August 8-12, 2016

David W. Chandler
Paul L. Houston
organizers

Schedule of Talks and Posters at the Telluride Meeting on Advanced Particle Imaging Techniques

Day	Start Time	End Time	Session	Number	Speaker	Title
Sunday, August 7:						
Sunday	5:00 PM	8:00 PM	Registration			
Monday, August 8:						
Monday	8:45 AM	8:50 AM	Announcements		David Chandler/Moderator	
	8:50 AM	9:20 AM	Photoelectrons	T1	Dan Neumark	Slow electron velocity-map imaging of cryogenically cooled anions
	9:20 AM	9:50 AM	Photoelectrons	T2	Lai-Sheng Wang	Photoelectron Imaging: From Multiply-Charged Anions to Ultracold Anions
	9:50 AM	10:20 AM	Coffee Break			
	10:20 AM	10:50 AM	Photoelectrons	T3	Andrei Sanov	Underemployed and looking for action: The plight of unpaired electrons in radicals and diradicals via anion photoelectron imaging
	10:50 AM	11:20 AM	Photoelectrons	T4	Toshinori Suzuki	Full observation of cascaded radiationless transitions from S ₂ (π,π*) state of pyrazine using ultrafast VUV photoelectron imaging
	11:20 AM	11:50 AM	Photoelectrons	T5	Christian Bordas	Recent Advances in Photoionization Microscopy
					Claire Vallance/Moderator	
	7:40 PM	8:00 PM	Photoelectrons	P4	Hot Topic: Samer Gozem	Photoelectron Spectra and Photoelectron Angular Distributions From Correlated Dyson Orbitals
	8:00 PM	8:30 PM	Photodissociation	T6	Michael Ashfold	Exploring photoinduced ring-opening
	8:30 PM	9:00 PM	Photodissociation	T7	William Jackson	Rotational dependence of the spin-orbit branching ratios of N(2D3/2) and N(2D5/2) states from the VUV photodissociation of state-selected N ₂
	9:00 PM	10:30 PM	Poster Session		Odd numbered posters, authors A-M	
Tuesday, August 9:						
Tuesday	9:00 AM	9:10 AM	Announcements		Michael Ashfold/Moderator	
	9:10 AM	9:40 AM	Photodissociation	T8	Simon North	Stereodynamics in Roaming Reactions: A New Window into the Study of Bimolecular Abstraction Reactions
	9:40 AM	10:20 AM	Coffee Break			
	10:20 AM	10:40 AM	New Instruments	P10	Hot topic: Chi-Kung Ni	An Old Dog with New Tricks: The Advantage of Spatial Map Ion Imaging
	10:40 AM	11:10 AM	Bimolecular Chemistry	T9	Andrew Orr-Ewing	VMI measurements and computational simulations of Cl-atom reactions with alkenes
	11:10 AM	11:40 AM	Bimolecular Chemistry	T10	Roland Wester	Dynamics of ion-molecule reactions by crossed-beam velocity map imaging
					George McBane/Moderator	
	7:40 PM	8:00 PM	New Instruments	P11	Hot Topic: Kasra Amini	Probing Ultrafast Chemical Dynamics by Time-Resolved Ion Imaging using the Pixel Imaging Mass Spectrometry (PImMS) camera
	8:00 PM	8:30 PM	New Instruments	T11	Claire Vallance	Multimass imaging with event-triggered sensors
	8:30 PM	9:00 PM	New Instruments	T12	Motoyoshi Nakano	Ion imaging study of photofragments from mass-selected cluster ions with double linear reflectron mass spectrometers
	9:00 PM	10:30 PM	Poster Session		Odd numbered posters, authors N-Z	
Wednesday, August 10:						
Wednesday	8:45 AM	8:50 AM	Announcements		Bob Continetti/Moderator	
	8:50 AM	9:20 AM	Clusters/Surfaces	T13	Marcel Drabbels	Imaging translational motion in superfluid helium nanodroplets
	9:20 AM	9:50 AM	Clusters/Surfaces	T14	Theofanis Kistopoulos	CO oxidation on Pt(111): Deciphering the second mechanism using Slice Imaging
	9:50 AM	10:20 AM	Coffee Break			
	10:20 AM	10:50 AM	Clusters/Surfaces	T15	David Parker	Imaging at Ice Surfaces
	10:50 AM	11:10 AM	Clusters/Surfaces	P16	Hot Topic: Frank Stienkemeier	Time-Resolved XUV-induced Electron Solvation Dynamics in Water Clusters
	11:10 AM	11:40 AM	Coincidence	T16	Itzik Ben-Itzhak	Coincidence three-dimensional momentum imaging of sequential (delayed) three-body fragmentation
					David Parker/Moderator	
	6:00 PM?	8:00 PM			BBQ Picnic/Cash Bar	
	8:00 PM	8:30 PM	Coincidence	T17	Robert Continetti	Coincidence Imaging Studies of Dissociation Dynamics with Fast Ion Beams
	8:30 PM	9:00 PM	Coincidence	T18	Balint Sztaray	Combustion Reactions Followed by Photoelectron Photoion Coincidence Spectroscopy: CRF-PEPICO
	9:00 PM	10:30 PM	Poster Session		even numbered posters, authors A-M	
Thursday, August 11:						
Thursday	8:45 AM	8:50 AM	Announcements		Arthur Suits /Moderator	
	8:50 AM	9:20 AM	Coincidence	T19	Thomas Weinacht	Strong Field Molecular Ionization Viewed with Coincidence Velocity Map Imaging
	9:20 AM	9:50 AM	Coincidence	T20	Wen Li	Attosecond spectroscopy with 3D coincidence imaging
	9:50 AM	10:20 AM	Coffee Break			
	10:20 AM	10:50 AM	High Resolution	T21	Bas Van Der Meerakker	Taming Molecular Collisions
	10:50 AM	11:20 AM	High Resolution	T22	Eckart Wrede	Imaging and trapping of cold SH/SD radicals produced via the photostop technique
	11:20 AM	11:50 AM	Alignment/Orientation	T23	Henrik Stapelfeld	Laser-induced alignment of molecules in He-nanodroplets: Revivals, long-time coherence and breaking-loose
					Mark Brouard /Moderator	
	7:40 PM	8:00 PM		P2	Hot Topic: E. Krishnakumar	Coherent excitation and symmetry breaking in dissociative electron attachment to molecular hydrogen
	8:00 PM	8:30 PM	High Energy/Intense Fields	T24	Luis Banares	A velocity map and slice imaging study of the photodissociation of the methyl radical from the 3s and 3pz Rydberg states
	8:30 PM	9:00 PM	Alignment/Orientaton	T25	Matt Costen	Polarization Resolved Stereodynamics of Rotational Energy Transfer in Collisions of NO(A) with Rare Gases and Molecules
	9:00 PM	10:30 PM	Poster Session		even numbered posters, authors N-Z	
Friday, August 12:						
Friday	8:45 AM	8:50 AM	Announcements		Paul Houston /Moderator	
	8:50 AM	9:20 AM	High Energy/Intense Fields	T26	Mark Vrakking	Ultrafast molecular imaging
	9:20 AM	9:50 AM	High Energy/Intense Fields	T27	Daniel Rolles	Imaging charge transfer and nuclear dynamics in polyatomic molecules
	9:50 AM	10:20 AM	Coffee Break			
	10:20 AM	10:50 AM	High Resolution	T28	Arthur Suits	FinA – A Reconstruction Method for Sliced Images and a Detailed Investigation of Slice Imaging Performance
	10:50 AM	11:20 AM	Alignment/Orientaton	T29	Vinod Kumarappan	Orientation Resolution from Rotational Coherence Spectroscopy
	11:20 AM	11:50 AM	Alignment/Orientaton	T30	Mark Brouard	Photo-induced dynamical studies using the fast imaging PImMS camera
	12:00 Noon		Conference Ends			

Posters

Hot Top ?	Number	Presenter	Institution	Title
	P1	Wei Kong	Oregon State U.	Electron diffraction of single molecules in superfluid helium droplets: a step towards single molecule diffraction
Thurs PM	P2	E. Krishnakumar	Tata Institute, Mumbai	Coherent excitation and symmetry breaking in dissociative electron attachment to molecular hydrogen
	P3	Thomas Luxford	Heriot-Watt U.	A Study of the Stereodynamics of the Collisions of NO(A22+) with Atomic and Molecular Partners using Crossed Molecular Beams
Mond AM	P4	Samer Gozem	U. Southern California	Photoelectron Spectra and Photoelectron Angular Distributions From Correlated Dyson Orbitals
	P5	George McBane	Grand Valley State U.	Status and current capabilities of the Imsim/Palfit programs for simulation and fitting of velocity-mapped crossed-beam scattering data
	P6	David Couch	U. Colorado, Boulder	Mass-specific photoelectron spectrum from electron-ion coincidence detection used to identify isomers formed from pyrolysis
	P7	Jingming Long	Max Born Institute, Berlin	Ion-ion coincidence imaging using an in-vacuum pixel detector
	P8	Kenichi Okutsu	Tohoku University	Development of an imaging apparatus for photofragment ions from mass selected ions using a linear-type double reflectron
	P9	Yuji Nakashima	Tohoku University	Ion imaging study using double linear reflectron mass spectrometers: application to photodissociation of Mg+Ar and Ca+Ar complex ions
Tues AM	P10	Chi-Kung Ni	IAMS, Taipei	An Old Dog with New Tricks: The Advantage of Spatial Map Ion Imaging
Tues PM	P11	Kasra Amini	U. Oxford	Probing Ultrafast Chemical Dynamics by Time-Resolved Ion Imaging using the Pixel Imaging Mass Spectrometry (PImMS) camera
	P12	Bernhard Dick	U. Regensburg	The photodissociation of dimethylnitrosamine studied with 3D-REMPI and VMI
	P13	Kellyn Patros	Indiana U.	Probing the electronic structure of O2-VOC using Anion Photoelectron Imaging Spectroscopy
	P14	Jeff Bartz	Kalamazoo College	Orientation and Alignment in the UV Photodissociation of Alkyl Nitrites
	P15	Ananya Sen	Argonne National Laboratory	Circular Dichroism of Angular Distributions (CDAD) by Using Velocity Map Photoelectron Imaging
Wed AM	P16	Frank Stienkemeier	U. Freiberg	Time-Resolved XUV-induced Electron Solvation Dynamics in Water Clusters
	P17	Do Hyung Kang	KAIST, Korea	Ultrafast Photodissociation Dynamics of Thiophenol revealed by Femtosecond Time-resolved Spectroscopic Measurements
	P18	Kyung Chul Woo	KAIST, Korea	Real-time Excited State Predissociation Dynamics of Thioanisole: the Role of $\pi\pi^*/n\pi\sigma^*$ Coupling in 'Resonance-in-Continuum'
	P19	Gary Lopez	CRF, Sandia	Multiphoton Ionization and Dissociation of H2 Molecule in Intense Laser Fields Using Velocity Mapping Imaging
	P20	Bethany Jochim (I. B.-I.)	Kansas State U.	Three-dimensional momentum imaging of delayed dissociation of metastable molecular ions
	P21	A. Gentleman, A. Iskra	U. Oxford	Velocity Map Imaging of Small d5 and d10 Transition Metal Molecules
	P22	Kevin Dorney	JILA/Physics, U. Colorado Boulder	Imaging and Controlling Electron Rescattering Dynamics in Bircircular Femtosecond Laser Fields
	P23	Suk Kyong Lee	Wayne State U.	Angle dependent single and double ionization dynamics of small molecules
	P24	Matthew Bain	Combustion Research Facility, Sandia	Multimass imaging of the ultraviolet photodissociation of toluene using the PImMS camera

Slow electron velocity-map imaging of cryogenically cooled anions

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Slow-electron velocity-map imaging of negative ions in combination with ion trapping and cryogenic cooling (cryo-SEVI) yields anion photoelectron spectra of complex anions with sub-meV resolution, enabling the observation of well-resolved vibrational structure that is obscured in more conventional photoelectron spectroscopy. Examples to be discussed will include polycyclic aromatic hydrocarbon radicals and transition metal oxide clusters. Applications to transition state spectroscopy of bimolecular and unimolecular reactions will also be covered.

Photoelectron Imaging: From Multiply-Charged Anions to Ultracold Anions

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Multiply charged anions are characterized by strong intramolecular Coulomb repulsions, which can have significant effects on the outgoing electrons in a photodetachment experiment [1]. We have used photoelectron imaging to probe the effects of the Coulomb repulsion on the outgoing electron trajectories. We have shown for a series of dicarboxylate dianions that photoelectrons detached from one end of the dianion preferentially emit along the axis of the molecule because of the presence of the negative charge on the opposite end [2]. For electron detachment from the center of a linear dianion, the outgoing electron tends to be emitted in the perpendicular directions [3]. We have also developed a velocity-map imaging system to conduct high-resolution photoelectron spectroscopy of singly charged anions produced using electrospray ionization and cooled in a cryogenic ion trap [4]. In our first experiment on phenoxide, we observed autodetachment resonances due to dipole bound excited states of the anion [5]. By tuning the detachment laser to the vibrational levels of the dipole-bound states, we obtained resonantly-enhanced photoelectron spectra that are highly non-Franck-Condon and yield much richer vibrational information [6]. We will show that resonant photoelectron spectroscopy via dipole bound states can also yield conformation-selective information [7], as well as information about electron-molecule interactions [8].

References:

- [1] "Probing Free Multiply Charged Anions Using Photodetachment Photoelectron Spectroscopy" (L. S. Wang and X. B. Wang), *J. Phys. Chem. A* **104**, 1978-1990 (2000).
- [2] "Imaging Intramolecular Coulomb Repulsions in Multiply Charged Anions" (X. P. Xing, X. B. Wang, and L. S. Wang), *Phys. Rev. Lett.* **101**, 083003-1-4 (2008).
- [3] "Guiding Electron Emissions by Excess Negative Charges in Multiply Charged Anions" (C. G. Ning, P. D. Dau, and L. S. Wang), *Phys. Rev. Lett.* **105**, 263001(4) (2010).
- [4] "Electrospray Photoelectron Spectroscopy: From Multiply-Charged Anions to Ultracold Anions" (L. S. Wang), *J. Chem. Phys.* **143**, 040901 (14 pages) (2015).
- [5] "Observation of Mode-Specific Vibrational Autodetachment from Dipole-Bound States of Cold Anions" (H. T. Liu, C. G. Ning, D. L. Huang, P. D. Dau, and L. S. Wang), *Angew. Chem. Int. Ed.* **52**, 8976-8979 (2013).
- [6] "Probing the Vibrational Spectroscopy of the Deprotonated Thymine Radical by Photodetachment and State-Selective Autodetachment Photoelectron Spectroscopy via Dipole-Bound States" (D. L. Huang, H. T. Liu, C. G. Ning, G. Z. Zhu, and L. S. Wang), *Chem. Sci.* **6**, 3129-3138 (2015).
- [7] "Conformation-Selective Resonant Photoelectron Spectroscopy via Dipole-Bound States of Cold Anions" (D. L. Huang, C. G. Ning, H. T. Liu, and L. S. Wang), *J. Phys. Chem. Lett.* **6**, 2153-2157 (2015).
- [8] "Resonant Photoelectron Imaging of Deprotonated Uracil Anion via Vibrational Levels of a Dipole-Bound Excited State" (D. L. Huang, H. T. Liu, C. G. Ning, P. D. Dau, and L. S. Wang), *Chem. Phys.* online. [doi:10.1016/j.chemphys.2016.06.003](https://doi.org/10.1016/j.chemphys.2016.06.003).

Underemployed and looking for action: The plight of unpaired electrons in radicals and diradicals via anion photoelectron imaging

Andrew Dixon, Tian Xue, and Andrei Sanov

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Elusive reactive intermediates and transient molecules are investigated by anion photoelectron imaging spectroscopy. We will present recent results focusing on the spectroscopy and electronic structure of several radical and diradical systems, including the “mysterious” (and—until recently—“hypothetical”) ethylenedione molecule, OCCO, and the related radical system involving the HOCCO and OHCCO species. Despite its apparent (yet misleading) simplicity and the straightforward closed-shell Kekulé structure $O=C=C=O$, ethylenedione is a transient diradical, which had eluded more than a century worth of prior attempts to synthesize or observe it. We report the first definitive spectroscopic fingerprint of this controversial species and analyze the electronic and geometric structures of its low-lying states using the photodetachment of the corresponding anion, $OCCO^-$. The OCCO diradical is further used as a starting point for discussion of the HOCCO and OHCCO radicals, which are also accessed and analyzed using the photodetachment of the corresponding anions. The comparative spectroscopy of these species sheds light on the differential effects of a hydrogen covalently bonded to different atoms within the OCCO diradical skeleton. In the same context, the effects of internal rotation of the methyl group in methylglyoxal are discussed in comparison to the unsubstituted glyoxal molecule using photoelectron imaging of the corresponding anions.

Full observation of ultrafast cascaded radiationless transitions from $S_2(\pi\pi^*)$ state of pyrazine using VUV photoelectron imaging

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and T. Suzuki

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⁺: visiting graduate student from University of Bristol

A photoexcited molecule undergoes multiple deactivation and reaction processes simultaneously or sequentially, which have been observed by combinations of various experimental methods. However, a single experimental method that enables complete observation of the photo-induced dynamics would be of great assistance for such studies. Here we report a full observation of cascaded electronic dephasing from $S_2(\pi\pi^*)$ in pyrazine ($C_4N_2H_4$) by time-resolved photoelectron imaging (TRPEI) using 9.3-eV vacuum ultraviolet (VUV) pulses with a sub-20 fs time duration. While we previously demonstrated a real-time observation of the ultrafast $S_2(\pi\pi^*) \rightarrow S_1(n\pi^*)$ internal conversion in pyrazine using TRPEI with UV pulses, this study presents complete observation of the dynamics including radiationless transitions from S_1 to S_0 (internal conversion) and $T_1(n\pi^*)$ (intersystem crossing). Also discussed is configuration interaction of the $S_2(\pi\pi^*)$ electronic wave function.

RECENT ADVANCES IN PHOTOIONIZATION MICROSCOPY

Christian BORDAS¹, Samuel COHEN², Panagiotis KALAITZIS², and Franck LÉPINE¹

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²*Atomic and Molecular Physics Laboratory, Physics Department, University of Ioannina, 45110 Ioannina, Greece*

Photoionization of an atom in the presence of a uniform static electric field provides the unique opportunity to expand and visualize the atomic wave function at a macroscopic scale. The development of advanced particle imaging techniques has allowed such observations and the thought experiment introduced by Fabrikant, Demkov, Kondratovitch and Ostrovsky [1-3] in the early eighties has become an actual field of experimental research almost fifteen years ago [4-6]. As compared to the simpler case of photodetachment, photoionization in the presence of an external electric field brings the additional complexity of the Stark effect in the continuum. Stark resonances above the ionization threshold present unique features allowing a direct connection between (quasi)bound states and the open ionization continua.

Photoionization microscopy offers the capability of revisiting this very fundamental problem under a new light. Indeed, the observation of the asymptotic electron wavefunction allows disentangling the contributions of various families of classical trajectories, and gives the clues to connect resonances in the continuum with the beating pattern resulting from interferences among various classical trajectories. Recent experimental results obtained on simple nonhydrogenic atoms will be presented to highlight this close link, with the support of semiclassical and quantum hydrogenic calculations. Classical scattering features will be discussed, more particularly the glory effect and the glory oscillations in the open continuum that will be demonstrated to be intimately connected with the well-known Freeman resonances.

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3. V. D. Kondratovich and V. N. Ostrovsky, J. Phys. B **17**, 1981 (1984); J. Phys. B **17**, 2011 (1984); J. Phys. B **23**, 21 (1990); J. Phys. B **23**, 3785 (1990).
4. C. Nicole, H.L. Offerhaus, M.J.J. Vrakking, F. Lépine and C. Bordas. Phys. Rev. Letters **88** (2002) 133001.
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Exploring photoinduced ring-opening

Michael N.R. Ashfold, Rebecca A. Ingle, Barbara Marchetti, Daniel Murdock

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Ion imaging and other photofragment translational spectroscopy (PTS) methods have enabled huge advances in our knowledge and understanding of photoinduced bond fission processes whereby a molecule dissociates into a pair of products.¹ There is another important family of bond fission processes – photoinduced ring opening reactions – which the gas phase dynamics community finds much harder to study. Early examples that revealed clear evidence of ring opening include studies of the deep UV photodissociations of 3-cyclopenteneone² and pyrrole.³

This presentation will summarise results of recent studies seeking evidence of near UV photoinduced ring-opening in several substituted thiophenes: 2-bromo- and 2-iodothiophene,⁴ using velocity map imaging methods, 2-thiophenethiol, using H Rydberg atom PTS⁵ and 2-thiophenone, using time resolved infrared absorption spectroscopy methods (in the solution phase).⁶

Acknowledgements: Funding from EPSRC through Programme Grants EP/G00224X and EP/L005913 is gratefully acknowledged.

¹ See, *e.g.* M.N.R. Ashfold, N.H. Nahler, A.J. Orr-Ewing, O.P.J. Vieuxmaire, R.L. Toomes, T.N. Kitsopoulos, I. Anton-Garcia, D. Chestakov, S.-M. Wu and D.H. Parker. *Phys. Chem. Chem. Phys.* **8** 26 (2006).

² R. Jiminez, S.H. Kable, J.C. Loison, C.J.S.M. Simpson, W. Adam and P.L. Houston, *J. Phys. Chem.* **96** 4188 (1992).

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⁴ B. Marchetti, T.N.V. Karsili, O. Kelly, P. Kapetanopoulos and M.N.R. Ashfold, *J. Chem. Phys.* **142** 224303 (2015).

⁵ R.A. Ingle, T.N.V. Karsili, G. Dennis, M. Staniforth, V.G. Stavros and M.N.R. Ashfold, *Phys. Chem. Chem. Phys.* **18** 11401 (2016).

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Rotational dependence of the spin-orbit branching ratios of $N(^2D_{3/2})$ and $N(^2D_{5/2})$ states from the VUV photodissociation of state-selected N_2

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Abstract

In an earlier study¹, we demonstrated that the VUV-VUV pump-probe apparatus could be used to determine the electronic state of the N atoms produced from the photodissociation of state-selected N_2 via,

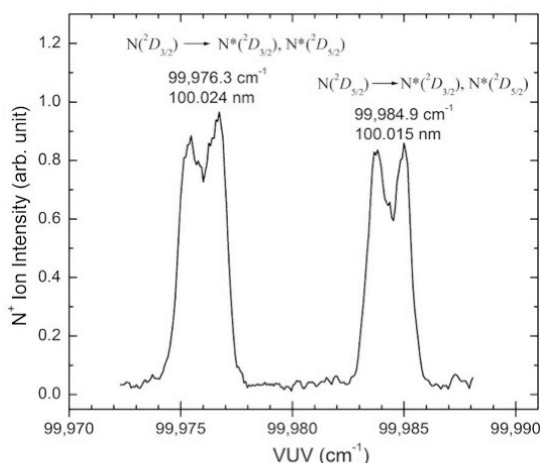
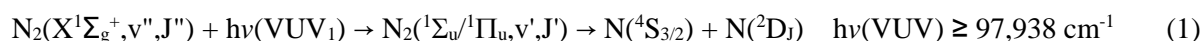


Fig. 1 Detection of the $N(^2D_{3/2})$ and the $N(^2D_{5/2})$ via degenerate autoionization states $N^*(^2D_{3/2}), N^*(^2D_{5/2})$ at $119,210 \text{ cm}^{-1}$.

by autoionization process. Using this autoionization level, we can now measure the spin-orbit state specific branching ratios as a function of the electronic, vibrational and rotational levels of the excited state of N_2 . This allows us to map out how these branching ratios vary with total angular momentum of the excited state.

This was accomplished by using a second VUV laser (VUV) to probe $N(^4S_{3/2})$ atom through (1+1') REMPI method, where the first photon is VUV photon and second photon is a visible photon. No attempt was made to separate the spin-orbit states of $N(^2D_J)$ in the observed images because the spacing between the levels is only 8.3 cm^{-1} . Thus, the measured branching ratios are the sum of the spin-orbit states that are formed along with the $N(^4S_{3/2})$ atom.

Recently, we have discovered two atomic transitions, which correspond to the direct excitation of the $N(^2D_{3/2})$ and $N(^2D_{5/2})$ states to the same intermediate level where they are subsequently ionized

¹ Yu Song, Hong Gao, Yih Chung Chang, D. Hammouténe, H. Ndome, M. Hochlaf, William M. Jackson, and C. Y. Ng, *Ap. J.*, **819**:23 (13pp), 2016; doi:10.3847/0004-637X/819/1/23

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“Stereodynamics in Roaming Reactions: A New Window into the Study of Bimolecular Abstraction Reactions”

Recent ion imaging studies and *ab initio* calculations on the photodissociation of the nitrate radical, NO_3 , have revealed two distinct pathways are responsible for the $\text{NO} + \text{O}_2$ channel and that both pathways involve ‘roaming dynamics’. The roaming mechanism avoids traditional ‘tight’ transition states normally associated with molecular elimination (*Science*, 355, 1075 (2012)). Instead, roaming bypasses these transition states and accesses the entrance channel connected to bimolecular abstraction. The observation of fragment vector correlations in the NO_3 system suggests the possibility of detailed study of bimolecular abstraction under well-defined initial conditions *via* judicious choice of roaming system. We are particularly interested in the correlation between fragment rotational angular momentum and velocity, the so-called v-J correlation, which is a result of exit channel torques and therefore a manifestation of anisotropy in the potential energy surface. For open shell systems vector correlations can also provide insight into the role of multistate dynamics. Our recent progress in these areas will be presented.

VMI measurements and computational simulations of Cl-atom reactions with alkenes

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Biogenic and anthropogenic sources emit a variety of hydrocarbons into the Earth's atmosphere. In the marine boundary layer and polluted coastal areas, chlorine atom reactions are an important initiator of oxidation chemistry that removes these volatile organic compounds. Propene, and the similar compounds isobutene and 2,3-dimethylbut-2-ene (DMB) serve as models for reactions of abundant atmospheric alkenes such as isoprene and higher terpenes. A Cl atom can either abstract a hydrogen atom from the methyl group or add to the C=C double bond of the alkene. Abstraction of an H atom makes HCl and a resonance-stabilized allyl ($\text{CH}_2\text{CHCH}_2^\bullet$) or methyl-substituted allyl radical. These abstraction reaction pathways are exothermic; for example, $\Delta_r H_{298\text{K}}^\circ = -63.1 \text{ kJ mol}^{-1}$ for $\text{Cl} + \text{CH}_3\text{CH}=\text{CH}_2 \rightarrow \text{HCl} + \text{CH}_2\text{CHCH}_2^\bullet$. We have observed the reaction dynamics in both the gas and liquid phases using the techniques of velocity map imaging (VMI)¹ and transient vibrational absorption spectroscopy (TVAS)² respectively. We have also simulated the dynamics in both gas and liquid phases with a newly developed global potential energy surface (PES). Our studies unravel the complex competing dynamics of addition and abstraction and reveal how the reaction mechanism is modified by a solvent.

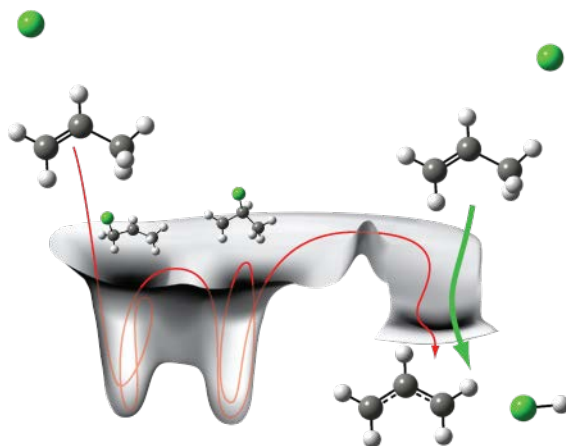


Figure 1: Schematic representation of the reaction pathways available to a Cl atom and a propene molecule. The arrows indicate addition-elimination and direct routes to HCl.

[1] T.J. Preston *et al.*, *J. Phys. Chem. A*, **2014**, *118*, 5595.

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Dynamics of ion-molecule reactions by crossed-beam velocity map imaging

Roland Wester

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In this talk I will present recent studies of the dynamics of nucleophilic substitution and elimination 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 nucleophilic substitution reactions of Cl^- , F^- and OH^- anions with CH_3I and a good agreement has been obtained with direct dynamics simulations [2-6]. The different mechanisms depend differently on the relative collision energy. Recently, we studied the influence of the leaving group on an $\text{S}_{\text{N}}2$ -reaction by comparing the reactants CH_3I and CH_3Cl 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_3I for CH-stretch excited reactant molecules. Both the $\text{S}_{\text{N}}2$ -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 $\text{S}_{\text{N}}2$ reaction when more than one carbon atom is present [9].

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Multimass imaging with event-triggered sensors

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The recent development of ultrafast CMOS imaging sensors with ‘intelligent’ pixels capable of storing timing information for recorded signals is opening up a number of opportunities in the arena of velocity-map imaging (VMI).

Firstly, as the domain of VMI experiments expands to include increasingly more complex molecules with multiple fragmentation pathways, the conventional approach of imaging a single product mass per experimental cycle becomes somewhat limiting. When studying small molecules, the scattering distribution of a single product often provides a considerable degree of insight into the dynamics of the overall process under study. However, this is often not the case when many product pathways are possible, with a single product only giving a partial picture of scattering or dissociation dynamics. Event-triggered imaging sensors record an (x,y,t) data point for each detected ion, allowing the complete scattering distribution of all scattered products to be recorded on each experimental cycle. This vastly increases the speed of data acquisition, as well as providing a broad-brush overview of the complete dynamics of the system within a single experiment.

Secondly, because multiple fragments from an individual photolysis or scattering event are detected within a given experimental cycle, appropriate statistical analysis of the data allows correlations between the scattering distributions of the two products to be explored. Known as covariance imaging, this approach allows ion-ion or ion-electron correlations to be studied, and is finding applications ranging from untangling complex multi-step fragmentation processes to elucidating information on molecular structure and dynamics from Coulomb explosion imaging data.

**A large number of researchers have contributed to the work that will be described in this talk. A full list of members of the Pixel Imaging Mass Spectrometry (PIImMS) Consortium can be found at <http://pimms.chem.ox.ac.uk/consortium.php>.*

Ion Imaging Study of Photofragments from Mass-Selected Cluster Ions with Double Linear Reflectron Mass Spectrometers

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We have been studying velocity and angular distributions of mass-analyzed fragment ions which were produced by photodissociation of mass-selected gas-phase complex ions using a reflectron time-of-flight (TOF) mass spectrometer combined with an imaging detector [1]. In the present study, velocity-map-imaging condition of the fragment ions was achieved by using a newly developed ion imaging apparatus with two linear reflectron mass spectrometers. Photofragment Ca^+ ion images have been examined by ultraviolet photodissociation of Ca^+Ar complex ions.

In the experimental setup, the two linear reflectrons were placed collinearly, both of which timing-controlled, high-voltage pulses were applied (Fig. 1).

The parent ions, Ca^+Ar , produced in the source first ran through a reflectron (2nd REF), and then they were reflected to the opposite direction by the next reflectron (1st REF). The ions were next irradiated with a linearly polarized photolysis laser (355 nm) at the middle of the two reflectrons. Photofragment ions,

Ca^+ , were then reflected by the 2nd REF and ran through the 1st REF. Finally the fragment ions were detected as velocity map ion images by microchannel plates with a phosphor screen as shown in Fig. 2. The images were obtained with changing the polarization direction (E) of the photolysis laser with respect to the ion beam direction (Z).

The electronic transition of Ca^+Ar at 355 nm has a localized nature of $\text{Ca}^+ 4p_z \leftarrow 4s$ excitation, in which the transition dipole moment is parallel to the bond (z) axis. The velocity and angular distributions of the produced $\text{Ca}^+(4p, ^2P_{3/2})$ ion were analyzed from the obtained images (Fig. 2). The binding energy of Ca^+Ar in the ground state was determined to be $760 \pm 210 \text{ cm}^{-1}$, which agreed well with the energies reported theoretically and by spectroscopic measurements [2]

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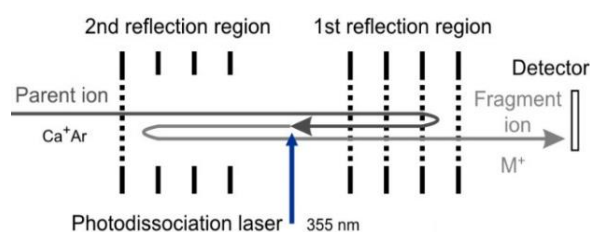


Figure 1: View of the imaging apparatus.

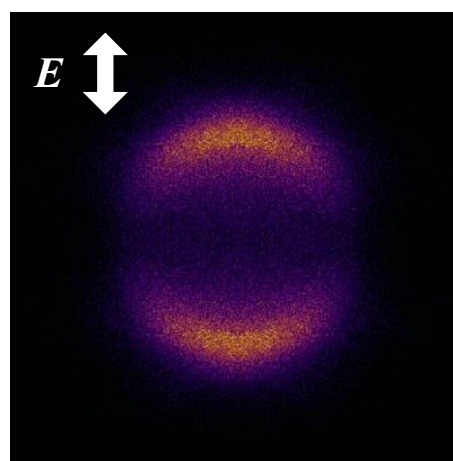


Figure 2: An observed image of the Ca^+ fragment ion from Ca^+Ar at 355 nm with $E \perp Z$.

Imaging translational motion in superfluid helium nanodroplets

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The best-known property of superfluid helium is the vanishing viscosity that objects experience while moving through the liquid with speeds below the so-called critical Landau velocity. This critical velocity is generally considered to be a macroscopic property since it is related to the collective excitations of the helium atoms in the liquid. Here I will report experiments that show the existence of a critical Landau velocity in nanometer scale, finite-size helium systems. The experiments use a direct approach to probe the superfluid character of helium nanodroplets by determining the vanishing viscosity embedded atoms and molecules experience as they are being accelerated out of the droplets following optical excitation. By recording the speed distributions of the ejected species using imaging techniques we find that a critical Landau velocity exists in these systems, even for nanodroplets consisting of less than a thousand helium atoms. We furthermore find that the creation of roton pairs is at the origin of this critical velocity, and that the mean speed and the width of the speed distributions are in quantitative agreement with predictions based on the dispersion curve of superfluid helium. The experimental conclusions find further support in theoretical simulations based on a time-dependent density functional description of the helium bath.

CO oxidation on Pt(111): Deciphering the second mechanism using Slice Imaging

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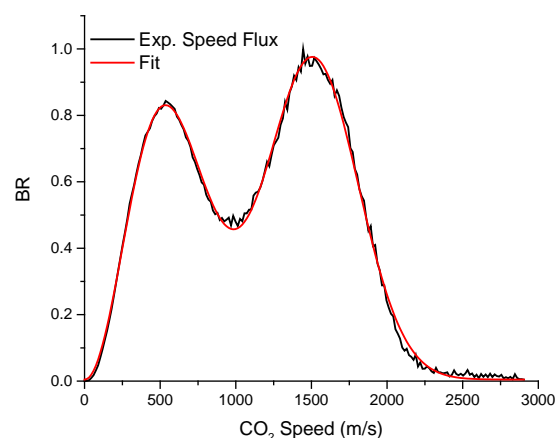
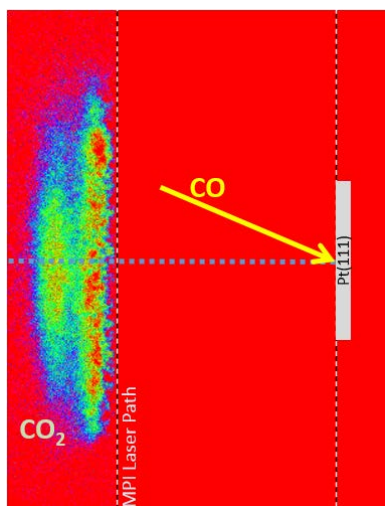
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Abstract

This study elucidates the underlying mechanism in the catalytic oxidation of CO on Pt(111), revealing a second reaction pathway that involves the reaction between weakly bound “physisorbed” CO molecules (CO_p) with adsorbed oxygen atoms. This reaction pathway is significant and dominates the oxidation process at high oxygen coverage and consequently under industrially relevant conditions. By implementing slice imaging to measure the kinetics we determine the rate constants for all reaction steps. The two reaction pathways have distinct CO_2 product velocity distributions which are identified in our experiment and allow for branching ratios to be extracted. The branching ratios are in perfect agreement with the rate constants reported we determine independently thus ensuring the self-consistency of our measurements. Our observations suggest a new mechanism for surface catalyzed exothermic reactions which in a way bridges the gap between the two generally accepted mechanisms, i.e., those of Langmuir-Hinshelwood and Eley-Rideal. Our results indicate that the formation of a *weakly bound physisorbed state* results in the adsorbed atom desorbing and colliding with the physisorbed atoms (*reverse Eley-Rideal*) that consequently releases most of the reaction exothermicity into the reaction products, in our case CO_2 translational and internal energy. The formation of these physisorbed states are favored by appropriate mass ratios such as a *relatively-heavy-gas* reactant collides with a *light-mass-adsorbed* molecule on a very *heavy surface* (*heavy-light-heavy*). As in gas phase reaction dynamics, this combination is very favorable for the formation of long lived complexes, our work presented here seems to indicate for the first time its relevance to surface catalyzed reactions.



“Imaging at Ice Surfaces”

Roy Scheidsbach and David H. Parker, Radboud University Nijmegen, The Netherlands

Most of the photochemistry in our Universe takes place at ice-covered grain particles in interstellar space irradiated by star light. In an effort to contribute to the understanding of these processes we have combined velocity mapped ion imaging detection with a typical laboratory astrochemistry setup using laser desorption or molecular beam scattering at an ice surface capable of being cooled down to 5K. Ice layer growth is characterized by thermal programmed desorption monitored by a quadrupole mass spectrometer. Our first results will be described in this talk where we detect O(³P) atoms and O₂ molecules desorbed at 320 and 250 nm from an 80 monolayer thick O₂-ice surface. The extra information provided by detection with velocity map imaging will be illustrated; we show, for example, that following desorption at the relatively long wavelength of 320 nm, surprisingly large amounts of singlet a¹Δ_g molecules are formed along with vibrationally excited O₂. This work is supported by the Dutch National Sciences grant NWO-CW-TOP, and is done in collaboration with H. Cuppen (Theoretical Chemistry, Nijmegen) and H. Linnartz (Leiden).

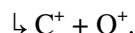
Coincidence three-dimensional momentum imaging of sequential (delayed) three-body fragmentation

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Advances in imaging techniques have led to better understanding of molecular fragmentation induced by photons or collisions. Experimental distinction between concerted and sequential (sometimes called “stepwise”) fragmentation mechanisms in polyatomic molecules is a long-standing goal. Key to its achievement is the coincidence detection of all fragments, although alternatives without coincidence measurements have been suggested [1].

The sequential breakup of triply-charged triatomic molecules may involve an intermediate dication – later undergoing unimolecular dissociation, for example $\text{OCS}^{3+} \rightarrow \text{S}^+ + \text{CO}^{2+}$



In particular we focus on metastable dication states which survive much longer than their rotational period, i.e. $\tau \gg T_R$. This “delayed” sequential breakup has been invoked to explain a circular feature in a Newton diagram showing the momenta of the three final fragments measured in coincidence [2-4]. This example demonstrates the strong link between the method used to visualize the multi-parameter data and the conclusions one can draw from it about the underlying fragmentation mechanism.

We further explore the identity of these metastable states by analyzing the coincidence three-dimensional momentum imaging data of the three fragment ions in two frames of reference associated with each of the breakup steps. This method allows the clear identification of sequential breakup of states with $\tau \gg T_R$, separating them from the other competing breakup mechanisms, and thus providing branching ratios. More importantly, the evaluated kinetic energy release (KER) during each step opens the door to

pinpointing the specific electronic, or with improved resolution, vibrational states. Our method is demonstrated using ionization of OCS and CO_2^+ targets by ultrashort intense laser pulses. However, it is applicable for other processes leading to three-body breakup as long as the momenta for the three fragments are detected in coincidence.

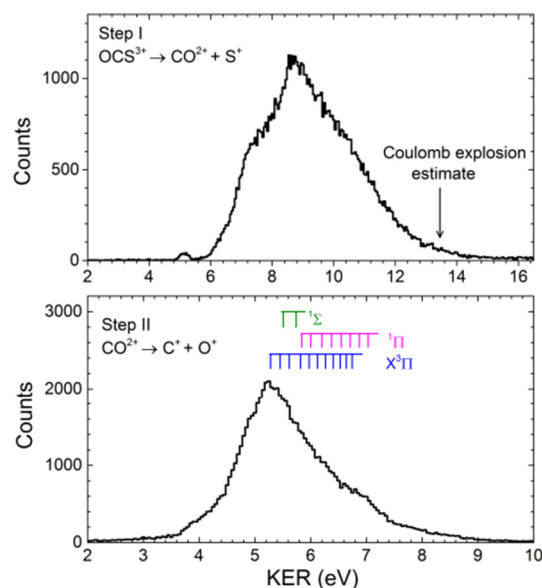


Figure 1 – Kinetic energy release distribution for the first step (top) and second step of OCS^{3+} fragmentation. The ticks indicate the expected KER for unimolecular dissociation of CO^{2+} .

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We acknowledge support by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.

Title: 'Coincidence Imaging Studies of Dissociation Dynamics with Fast Ion Beams'

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Coincidence imaging techniques can be effectively coupled with fast ion beam experiments to provide kinematically complete measures of a range of physical processes. Studies of the dynamics of neutral bimolecular reactions using dissociative photodetachment of negative ion beams will be reviewed, along with three-body dissociation dynamics of neutrals using charge exchange neutralization of positive ion beams. Finally, the current state of the art, using cryogenic buffer gas cooling accumulator traps in concert with electrostatic ion beam traps will be presented.

This work was supported by the US Department of Energy under grant DE-FG03-98ER14879

Combustion Reactions Followed by Photoelectron Photoion Coincidence Spectroscopy: CRF-PEPICO

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Photoionization mass spectrometry is a powerful detection method in gas-phase physical chemistry. Tunable synchrotron light enables isomer separation based on unique photoionization (PI) spectra; however, mixtures of several isomers can be difficult to resolve. By measuring the photoelectron spectrum corresponding to each cation m/z ratio, Photoelectron Photoion Coincidence Spectroscopy (PEPICO) provides a more detailed spectral fingerprint and higher isomer selectivity than PI spectra. We have demonstrated the power of PEPICO detection in proof-of-concept experiments and constructed a prototype laser-photolysis flow-tube PEPICO experiment for the VUV beamline of the Swiss Light Source. This new instrument features a velocity map imaging (VMI) setup for both the photoelectrons and the photoions and allowed us to extend the utility of the PEPICO method in several new ways.

Traditionally, the false coincidence background of PEPICO limited its dynamic range, largely precluding its use as a gas-phase detection technique. We have developed a novel solution to this problem. Combining velocity mapped photoions with a position-sensitive ion detector and a temporal deflection scheme, we can effectively suppress the false coincidence background, increasing the dynamic range in the PEPICO TOF mass spectrum by 2–3 orders of magnitude. As an example, when cold argon clusters are ionized, false coincidence suppression allowed us to observe species up to Ar_9^+ , whereas Ar_4^+ is the largest observable cluster under traditional operation.

This new experiment, called *Combustion Reactions Followed by Photoelectron Photoion Coincidence (CRF-PEPICO)*, features a “slow-flow” quartz reactor tube, where reactions are photolytically initiated using a pulsed Nd-YAG laser. In the first successful kinetic time resolved PEPICO experiments, CH_2I radical formation and its reaction with O_2 were studied. The reaction was initiated by photolysis of CH_2I_2 at 355 nm, producing CH_2I radicals. Decay of the CH_2I radical was monitored in time-resolved measurements to obtain the rate coefficient, which was in good agreement with literature determinations. The product of the above reaction, the Criegee intermediate CH_2OO was also detected, but so far in concentrations too low to obtain a full photoelectron spectrum.

In separate experiments, the mass-selected threshold photoelectron spectrum (ms-TPES) of the methylperoxy radical was measured and analyzed using Frank-Condon spectral simulations. The PEPICO experiment also collects dissociative photoionization data for the CH_3OO species. The heat of formation of the methylperoxy radical was derived from the 0-K appearance energy of CH_3^+ daughter ion, and is in good agreement with the literature value.

Lastly, the utility of PEPICO as a selective detection tool to understand complex photochemical reaction mechanisms is illustrated with our ongoing study on acetyl acetone, where mass-selected threshold photoelectron spectra allowed unambiguous identification of several key photofragments, including traces of allene next to its dominant isomer, propyne.

Strong Field Molecular Ionization Viewed with Coincidence Velocity Map Imaging

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& Thomas Weinacht

Strong field molecular ionization plays an important role in imaging molecules and following their dynamics on attosecond timescales. However, there are many aspects which are not understood, such as the competition between different electronic continua and the variation of ionization yields with molecular geometry and orbital shape. This talk will describe experiments carried out with velocity map imaging of electrons and ionic fragments in coincidence as a function of pulse duration from multicycle pulses down to the impulsive limit ($\tau_{\text{pulse}} < \tau_{\text{vibration}}$). We interpret our measurements with the help of electronic structure calculations and a simple model of strong field ionization with competing electronic continua.

Attosecond spectroscopy with 3D coincidence imaging

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Attosecond spectroscopy holds great promise as a time-resolved general probe of electron correlation dynamics, which is central to important many-body phenomena from superconductivity to chemical bond formation. Double ionization processes are envisioned to be a direct probe of electron correlation by studying the time-resolved momentum correlation of two electrons. However, the time delay between two photoelectrons arising from double ionization has not been measured directly in the attosecond time domain, so it remains to be seen what such measurements can reveal concerning the details of electron correlation. Recently, using a newly developed three-dimensional (3D) electron-electron coincidence imaging technique and an attosecond two-electron angular streaking method, we show the emission time delay between two electrons can be measured from zero attoseconds to more than one femtosecond. Surprisingly, in benzene, the double ionization rate decays as the time delay between the first and second electron emission increases during the first femtosecond. With this new method, pump-probe studies of electron correlation dynamics at the attosecond time-scale have become a reality. In this talk, I will describe the development and some applications of this new method.

Taming Molecular Collisions

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The study of molecular collisions with the highest possible detail has been an important research theme in physical chemistry for decades. Over the last years we have developed methods to get improved control over molecules in a molecular beam [1]. With the Stark decelerator, a part of a molecular beam can be selected to produce bunches of molecules with a computer-controlled velocity and with longitudinal temperatures as low as a few mK. The molecular packets that emerge from the decelerator have small spatial and angular spreads, and have almost perfect quantum state purity. These tamed molecular beams are excellent starting points for high-resolution crossed beam scattering experiments [2,3].

I will discuss our most recent results on the combination of Stark deceleration and velocity map imaging. The narrow velocity spread of Stark-decelerated beams results in scattering images with an unprecedented sharpness and angular resolution. This has facilitated the observation of diffraction oscillations in the state-to-state differential cross sections for collisions of NO with rare gas atoms [4,5], and the observation of scattering resonances at low-energy inelastic NO-He collisions that reveal the influence of individual partial waves to the scattering dynamics [6].

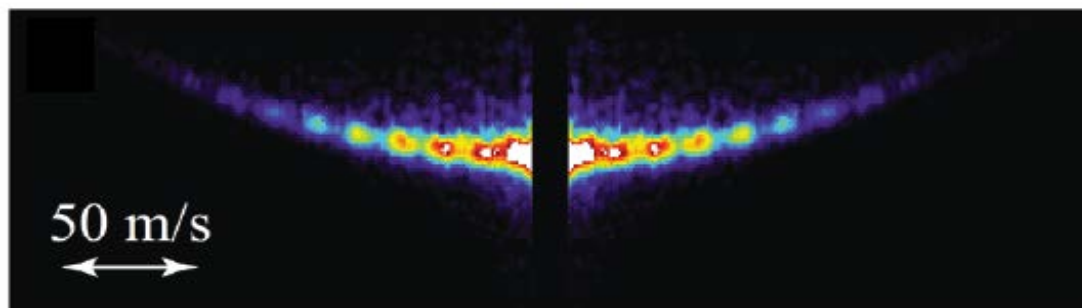


Fig. 1 Velocity mapped ion image for inelastic NO-Ar collisions, featuring a rich diffraction oscillation pattern. Adapted from Ref. [5].

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Imaging and trapping of cold SH/SD radicals produced via the photostop technique

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We have demonstrated that photofragments can be produced at rest in the laboratory frame after the photodissociation of a precursor molecule—a technique we call photostop. If the recoil speed of the photodissociation event is matched to the speed of the precursor molecules in a supersonic molecular beam, photofragments that recoil opposite to the precursor velocity will be created at zero velocity in the laboratory frame. Molecular and atomic fragments (NO from NO₂ dissociation [1] and Br from Br₂ dissociation [2]) have been successfully stopped and their free evaporation from the probe volume monitored using velocity-map imaging (VMI). Recently, the tapping of photostopped Br atoms has been demonstrated [3].

We will present our progress towards trapping of cold SH and SD radicals produced with the photostop technique. The collapse of the velocity distribution of the stopped fraction of fragments inside the probe volume has been monitored via VMI. We will present the latest results from our new, purpose-built trapping experiment including a comparison with simulations of the photodissociation and evaporation processes in free space and within the trap.

Acknowledgments: This work is funded by EPSRC.

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Laser-induced alignment of molecules in He-nanodroplets: Revivals, long-time coherence and breaking-loose

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High resolution infrared and microwave spectra of molecules dissolved in liquid helium nanodroplets display discrete rotational structure – a unique feature explained as the result of frictionless rotation of molecules adiabatically followed by a local solvation shell of He atoms [1].

The frictionless behavior did, however, not manifest itself in recent time-resolved experiments, based on femtosecond laser-induced molecular alignment techniques. In particular, the transient recurrences of alignment characteristic of freely rotating gas phase molecules was absent and the rotational dynamics was much slower than that expected from spectroscopy [2,3].

In this talk we present new experiments on femtosecond laser-induced alignment of iodine molecules embedded in helium nanodroplets showing striking new phenomena:

- 1) At low to moderate fluences the alignment pulse sets the molecule and a non-superfluid fraction of the He droplet into coherent motion. The coherence, although decaying, persists for many hundreds of picoseconds – long enough to allow the composite molecule-He-shell system to exhibit rotational revivals.
- 2) At larger fluences of the alignment pulse the molecule is accelerated to such large angular velocities that the binding to the surrounding He atoms in the droplet is broken due to the centrifugal force. Hereafter, the molecule rotates essentially freely for a few ps until the interaction with He atoms sets in again and slows the molecule down.

Our experimental observations are rationalized by classical and two-body time-dependent quantum simulations.

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A velocity map and slice imaging study of the photodissociation of the methyl radical from the $3s$ and $3p_z$ Rydberg states

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The relevance of the methyl radical spans across both applied and fundamental areas of Chemistry. It is of great importance in processes like hydrocarbon combustion, the formation of complex hydrocarbons in the interstellar medium, troposphere chemistry and chemical vapour deposition for diamond growth. As the simplest alkyl radical, it has been considered as a benchmark system in molecular orbital theory for the photochemistry of larger open-shell hydrocarbons and still many questions relating to its spectroscopy and excited state dynamics remain unanswered. Since the methyl radical is planar, many excited states cannot be observed by one-photon spectroscopy and only by multiphoton spectroscopy these excited states are accessible. Both the first excited state, the $3s$ Rydberg state, which is accessible by one-photon absorption at about 216 nm, and the $3p_z$ Rydberg state, which is accessible by two-photon absorption at about 330 nm, are predissociative. In this work, we have studied the photodissociation dynamics of the methyl radical from these two $3s$ and $3p_z$ Rydberg states by one-photon and two-photon excitation, respectively, using a combination of femtosecond [1] and nanosecond [2] laser pulses and the velocity map and slice ion imaging techniques. A great deal of details about the time-resolved predissociation dynamics of the $3p_z$ state and of the photodissociation dynamics to the final photofragments $\text{CH}_2 + \text{H}$ from the two excited states, have been obtained and the experimental results explained by high level *ab initio* calculations of the potential energy curves involved in the photodissociation process.

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Polarization Resolved Stereodynamics of Rotational Energy Transfer in Collisions of NO(A) with Rare Gases and Molecules

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We have used crossed-molecular beam scattering with velocity-map imaging, combined with optical state-selection, to study the stereodynamics of rotational energy transfer of electronically excited NO($A^2\Sigma^+$, $v = 0$, $N = 0$, $j = 0.5$) with both rare gas and molecular colliders.[1,2] We extract state-to-state resolved differential cross sections, and scattering angle-resolved rotational alignment moments. Comparison to the results of QS calculations enables us to provide high-quality tests of *ab initio* potentials for the rare gas colliders, and to make predictions about the hitherto unknown molecular collider potentials. We will present results for a variety of rare gas and molecular colliders. We will demonstrate how the angular momentum polarization in these systems systematically deviates from the classical, hard-shell, behaviour observed in NO(X) collisions, and relate these to the differences in the respective potentials.

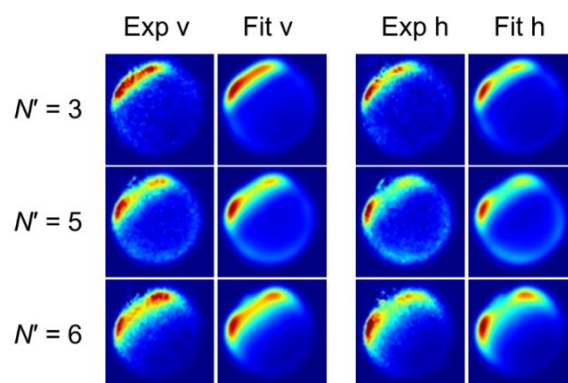


Figure: Example experimental and fit images for NO(A)+D₂ scattering for product states $N' = 3, 5$ & 6 , acquired with probe polarization in-plane (h) or orthogonal (v).

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Ultrafast molecular imaging

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In the last few years two novel XUV/x-ray sources have acquired an important role within atomic and molecular physics research, namely high-harmonic generation (HHG) and a new generation of free electron lasers (FELs). These two sources are of significant interest for at least two reasons. On the one hand, the short optical period of XUV/x-ray light allows the synthesis of attosecond laser pulses that can be used to study electronic processes on their natural timescale. On the other hand, the availability of very energetic photons provides opportunities for the development of novel spectroscopic techniques that are based on diffraction and/or the use of atom-specific inner shell excitation.

In many experiments that are performed with the novel XUV/X-ray sources, the use of electron/ion detection methods that permit a recording of angle-resolved kinetic energy distributions is vitally important. Accordingly, velocity map imaging has become a widely used. In my talk I will present some examples of the use of velocity map imaging in ultrafast, XUV/X-ray based studies of molecular physics, and will moreover discuss how the use of velocity map imaging complements that of other detection techniques based on a measurement of covariant or coincident signals.

Imaging charge transfer and nuclear dynamics in polyatomic molecules

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The combination of various electron and ion imaging schemes, such as Velocity Map Imaging and Coincident Electron and Ion Momentum Imaging, with femtosecond light sources ranging from the near-infrared to the hard X-ray regime has allowed us to systematically study ultrafast dynamics in polyatomic gas-phase molecules. I will report on a series of time-resolved experiments on halogenated hydrocarbons performed with femtosecond near-infrared lasers as well as with soft and hard X-ray free-electron lasers, where we can directly observe nuclear dynamics in bound and dissociating molecular systems and image charge transfer between the molecular constituents.

FinA – A Reconstruction Method for Sliced Images and a Detailed Investigation of Slice Imaging Performance

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Abstract

Since the advent of ion imaging, one of the key issues in the field has been creating methods to reconstruct the initial 3D spherical distribution of particles from its 2D projection. This has led to development of a number of different numerical methods and fitting techniques to solve this fundamental issue in imaging. In recent years, slice-imaging methods have been developed that permit direct recording of the 3D distribution, i.e., a thin slice of the recoiling fragment distribution. In this approach, the standard imaging detector is gated over the region of the central slice of the incoming ion distribution so only ions resulting from the central region of the spherical particle distribution are detected. However, in practice, most slice imaging experiments achieve a slice width of around 10 – 25% around the center of the distribution. This still carries significant out-of-plane elements that can blur the spectrum, lose fine resolution and distort the product distributions for the slowest fragments.

To overcome these limitations we developed a new numerical method to reconstruct the sliced image. The FINite sliced Analysis (FinA) method models the off axis elements of the 3D particle distribution through the use of radial basis functions. Once subtracted, this function reconstructs the true central slice of the 3D particle distribution, without fitting or smoothing the data and reproduces the true intensity distribution. The program can accommodate any degree of slicing as well as unsliced data with the same algorithm. We demonstrate this reconstruction approach with a broad range of synthetic and experimental data that allow us to examine the impact of finite slicing on the recovered distributions in detail.

Vinod Kumarappan
Kansas State University

Title: Orientation Resolution from Rotational Coherence Spectroscopy

Abstract: For asymmetric top molecules, fully orientation-resolved measurements require control or coincident measurement of at least two Euler angles that characterize the molecule's orientation in space. Such experiments currently feasible only with multi-particle coincidence measurements, which limits them to processes involving multiple ionization and rely on the axial recoil approximation. I will discuss how we can use time-domain measurements from a impulsively excited rotational wave-packet to extract the angle dependence of strong-field non-dissociative ionization and fragmentation of asymmetric top molecules. These measurements require neither three-dimensional alignment nor the axial recoil approximation, and illustrate the power of the method.

Photo-induced dynamical studies using the fast imaging PImMS camera

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Keywords: Photodissociation, Imaging mass spectrometry, fast CMOS imaging camera, PImMS

Recent work on the development of a fast imaging camera, known as the Pixel Imaging Mass Spectrometry (or PImMS) camera will be described¹⁻³. This camera has been developed in collaboration between the Physics and Chemistry Departments at Oxford University, and the Rutherford Appleton Laboratory, Science and Technology funding Council, UK.

The talk will principally focus on example applications of the PImMS camera to photo-induced dynamical studies⁴, including studies of molecular photofragmentation using two- and three-fold covariance methods⁵ and applications of three-dimensional imaging techniques. Applications involving Coulomb explosion imaging will be described in detail. Future developments and applications will also be discussed.

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**Electron diffraction of single molecules in superfluid helium droplets:
a step towards single molecule diffraction**

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Electron diffraction of oriented molecules offers a solution to the crystallization problem in biomolecule structure determination. A critical issue in this approach is molecular orientation. Electric field induced alignment and/or orientation relies on effective suppression of thermal rotation, thus superfluid helium droplets with an equilibrium temperature of 0.4 K offer the desired cooling effect. However, the droplet matrix also introduces a diffraction background. Here we demonstrate the practicality of electron diffraction of single molecules inside superfluid helium droplets. By reducing the background from pure undoped droplets via multiple doping, with small corrections for dimers and trimers, clearly resolved diffraction rings of CBr_4 similar to those of gas phase molecules can be observed. By taking advantage of the velocity slip in a pulsed droplet beam and adjusting the doping condition, diffraction from singly doped ferrocene can also be observed. Possible extensions of this approach to macromolecular ions will be discussed.

Coherent excitation and symmetry breaking in dissociative electron attachment to molecular hydrogen

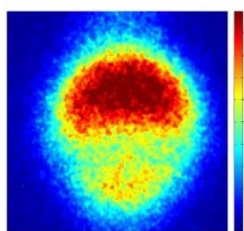
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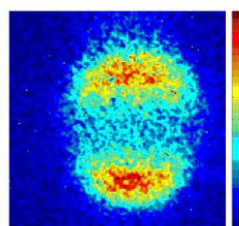
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Quantum coherence induced interference effects have been shown to break the inversion symmetry in the photoionization of homonuclear diatomic molecules [1, 2]. Such an asymmetry arises from the entanglement of the *gerade* and *ungerade* states and the subsequent loss of inversion symmetry. While these coherence induced effects have been identified in electron emission processes, such effects in electron attachment have not been observed till now. Our measurements using velocity slice imaging of H^- ions show strong asymmetry in the forward – backward direction for the 14 eV resonance in H_2 , while this asymmetry is significantly less in D^- from D_2 for the same resonance.

The experiment consists of a velocity slice imaging spectrometer and comprises of a pulsed electron beam of 200 ns duration incident on an effusive jet of molecular hydrogen. The ions formed in the interaction region are extracted into a time of flight region after a delay of 200 ns using a pulsed extraction field [3, 4]. The ions are detected using three 75 mm diameter microchannel plates in Z-stack geometry followed by a phosphor screen and a CCD camera. The central slice of the Newton sphere is captured by applying a 2 kV pulse of 100 ns duration to the detector bias. The slice images of H^- from H_2 and D^- from D_2 at 14.5 eV are given below. In these images the electron beam direction is from top to bottom.



H^- from H_2 at 14.5 eV



D^- from D_2 at 14.5 eV

We explain the results in terms of coherent excitation of two resonances of Σ_u^+ and Σ_g^+ symmetries and the ensuing quantum interference as they take two different paths to the same dissociation limit. The difference between H_2 and D_2 is explained in terms of the larger time for dissociation of D_2 and subsequent faster decay of one of the states as compared to the other one, resulting in rather weak interference. Detailed analysis will be presented at the meeting.

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A Study of the Stereodynamics of the Collisions of $\text{NO}(A^2\Sigma^+)$ with Atomic and Molecular Partners using Crossed Molecular Beams

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Using crossed molecular beams in combination with velocity mapped ion imaging, the state-resolved stereodynamics of the collision of $\text{NO}(A^2\Sigma^+)$ with atomic and molecular collision partners are studied. Experimentally measured differential-cross-sections and angle-resolved rotational polarisation moments are presented for the collisions of $\text{NO}(A)$ with He and D_2 , along with the results of quantum scattering calculations using an *ab-initio* potential energy surface for the $\text{NO}(A)$ -He system. Good agreement is seen between the experimental results and the quantum scattering calculations, supporting the accuracy of the $\text{NO}(A)$ -He potential energy surface. By comparison of these results to those of the kinematically identical $\text{NO}(A)$ - D_2 scattering system, it is possible to gain insights into several aspects of the currently uncalculated $\text{NO}(A)$ - D_2 potential energy surface. Additionally, experimental and calculated results are presented for the $\text{NO}(A)$ -Ne and Ar scattering systems, which display strikingly non-hard-shell behaviour, and experimental results are presented for the collisions of $\text{NO}(A)$ with atmospherically relevant molecular colliders N_2 , O_2 and CO.

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Photoelectron Spectra and Photoelectron Angular Distributions From Correlated Dyson Orbitals

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Photoelectron spectroscopy and photoelectron imaging are powerful techniques for probing the electronic structure of molecules and ions, but their interpretation is often largely aided by theoretical modeling. However, the accurate modeling of photoionization/photodetachment phenomena requires a correct description of the wave functions of the initial N-electron system, the final N-1-electron system, as well as the final wave function of the ejected photoelectron. All the necessary information related to the N and N-1 electron wave functions is embodied in a Dyson orbital. The Dyson orbital is a correlated analogue of a Hartree-Fock orbital describing the initial state of the ionized electron within Koopmans' theorem, and can be computed from equation-of-motion coupled-cluster (EOM-CC) wavefunctions. EOM-CC Dyson orbitals include correlation and orbital relaxation effects missing in Koopmans' framework, and different flavors of EOM-CC can be used to describe photoionization in correlated systems such as diradicals, triradicals, and electronically excited states. We will present the theoretical framework for computing photoelectron spectra and photoelectron angular distributions from EOM-CC Dyson orbitals and for how to treat the photoelectron wave function, as well as a comparison with experimental spectra.

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Status and current capabilities of the Imsim/Palfit programs for simulation and fitting of velocity-mapped crossed-beam scattering data

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May 16, 2016

Abstract

Imsim and Palfit are programs that can be used for image simulations, fitting, and density to flux transformations of velocity-mapped data from crossed beam experiments. They are based on deterministic rather than Monte Carlo quadratures, so they do not introduce statistical noise into basis images used for fitting. They were first written over fifteen years ago but are still being developed and used in several laboratories. The current capabilities of the programs will be described.

Mass-specific photoelectron spectrum from electron-ion coincidence detection used to identify isomers formed from pyrolysis

David Couch, William Peters, Grant Buckingham, Barney Ellison, Henry Kapteyn, and Margaret Murnane

The invention of new effective fuels and catalysts for efficient combustion relies upon accurate models and simulations of combustion processes. However, these simulations must include hundreds of possible chemical intermediates, many of which have never been experimentally confirmed. Here, photoelectron-photoion coincidence detection offers a mass spectrum and mass-specific photoelectron spectra, which allows identification of most molecules present including isomer identification. A flash pyrolysis microreactor creates radicals and unstable molecules important to combustion reactions. A tabletop source of line-tunable VUV light is used to ionize pyrolysis products. The ions and electrons are captured in coincidence using a COLTRIMS reaction microscope. The resulting mass-specific photoelectron spectra allow identification of isomers with differing ionization potentials in spite of the simultaneous presence of other pyrolysis products. Additionally, our uniform-field spectrometer resolves ion momentum, distinguishing pyrolysis products in the molecular jet from ions caused by fragmentation after ionization (dissociative ionization). These tools for identifying unstable molecules are useful in determining the primary intermediates involved in combustion and for determining the energy necessary to create them. As our understanding of combustion chemistry improves, we can develop new technology to help reduce carbon emissions and preserve our global climate.

Ion-ion coincidence imaging using an in-vacuum pixel detector

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The ionization and fragmentation of molecules by intense laser fields has been the subject of intense research for the last three decades. Over the years, experimental techniques have been developed to record the momentum distribution of the charged particles generated from strong field ionization. Among them, two techniques are widely used: on one hand the velocity map imaging spectroscopy that allows recording the 2D momentum distribution of the charged fragments produced by a laser excitation and on the other hand the 3D coincidence imaging family [1]. In a typical VMI experiment, only the momentum distribution of a single, either positively or negatively, charged fragment is recorded at a time. The 3D momentum vectors of all participating fragments can be measured in coincidence using a reaction microscope (REMI) [2] or a cold target recoil ion momentum spectrometer (COLTRIMS) [1]. In such device, the charged fragments are mapped onto a position- and time- sensitive detector that allows reconstructing the momentum distribution of those fragments. In 3D coincidence experiment, the common position- and time- sensitive detector is composed of a microchannel plate detector (MCPs) in combination with delay-line-anodes. The position is given by measuring the charge distribution from the delay-line-anode whereas the timing information is extracted directly from the MCPs and can reach below 50 ps resolution.

Recently, we have implemented a new in-vacuum pixel detector device, the so-called Timepix, as a replacement of traditional delay-line-anodes. This new 3D detector has been tested for ion-ion coincidence experiments showing the possibility to reach sub-pixel spatial resolution ($<55 \mu\text{m}$) and a 25 ps temporal resolution, at a 1 kHz frame readout rate. Combined with a high repetition rate (400 kHz) laser, our ion-ion coincidence imaging spectrometer can achieve an event rate faster than 10^4 ion events per second, and can be a powerful tool in studies of ultrafast nuclear dynamics in strong laser fields.

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Development of an imaging apparatus for photofragment ions from mass selected ions using a linear-type double reflectron

Kenichi Okutsu, Yuji Nakashima, Keita Fujimoto, Motoyoshi Nakano, Keijiro Ohshimo, and Fuminori Misaizu

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Reflectron-type time-of-flight mass spectrometer is useful as a tandem mass spectrometer for the study of photodissociation of cluster ions. In the present study, we have developed an apparatus using a linear-type double reflectron, for imaging measurements of photofragment ions produced from mass-selected ions. Ultraviolet photodissociation of Ca^+Ar was examined in order to check the performance of the apparatus.

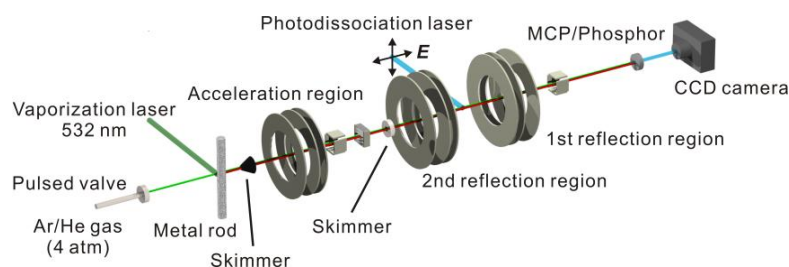


Figure. Schematic view of the imaging apparatus

As shown in the figure, cluster ions produced by laser vaporization were accelerated with pulsed electric fields at the acceleration region. The mass-selected ions were dissociated with a linearly polarized laser after reflecting with the 1st reflection region. The fragment ion images were finally obtained after the reflection at the 2nd reflection region. Both of the 1st and 2nd reflection regions were controlled by pulsed voltages. Stainless steel meshes were attached on the holes of all electrodes in the 1st reflection region, in order to avoid electrostatic lens effects, which influence the sizes of the fragment ion images. By contrast, the velocity map imaging condition was optimized by using the electrostatic lens effect in the 2nd reflection region, because the electrodes in this region were used without metal meshes.

**Ion imaging study using double linear reflectron mass spectrometers:
application to photodissociation of Mg^+Ar and Ca^+Ar complex ions**

Yuji Nakashima, Kenichi Okutsu, Keita Fujimoto, Motoyoshi Nakano, Keiji Ohshimo, and Fuminori Misaizu

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Ion imaging technique was applied to photodissociation reactions of Mg^+Ar and Ca^+Ar complex ion in ultraviolet region. The experimental apparatus consists of double linear reflectron time-of-flight (TOF) spectrometers and a position sensitive detector (PSD), which enables not only the mass selection of parent ions but also the mass analysis and velocity map imaging of fragment ions. Cluster ions M^+Ar_n ($\text{M} = \text{Mg}, \text{Ca}$) were produced by laser vaporization, and they were introduced into the TOF mass spectrometers. After mass selection, the 1:1 parent ion M^+Ar was irradiated with a linearly-polarized photodissociation laser at the wavelength of 266 nm for Mg^+Ar or 355 nm for Ca^+Ar . The fragment ion, Mg^+ or Ca^+ , was mass-analyzed and finally detected by the PSD.

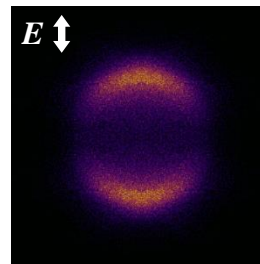


Fig. 1 Observed image of fragment ions Ca^+ from Ca^+Ar at 355 nm for $E \perp Z$

For Ca^+Ar , the 355 nm laser induces electronic excitation $E \ ^2\Sigma^+ \leftarrow X \ ^2\Sigma^+$, which leads to direct dissociation into Ca^+ ($^2P_{3/2}$) + Ar. Fig. 1 shows the image of fragment ion Ca^+ for $E \perp Z$, where E refers to the polarization direction and Z the ion beam direction. From the velocity distribution, binding energy of Ca^+Ar in the ground state was determined to be $760 \pm 210 \text{ cm}^{-1}$, which well reproduces the results of previous studies. Anisotropy parameter β at the most probable velocity was also obtained to be 1.70 ± 0.21 , which deviate from the value for the pure parallel transition, $\beta = 2$. This deviation can be discussed by correlation between total kinetic energy release and rotational motion before dissociation.

An Old Dog With New Tricks: The Advantage of Spatial Map Ion Imaging

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The original ion imaging, based on spatial map, has low velocity resolution. Since the invention of velocity map ion imaging, most of the studies of photodissociation were investigated using the new technique. In this study, we use the photodissociation of phenol as an example to demonstrate one important advantage of spatial map ion imaging. When phenol are excited by UV photons, $C_6H_5OH(S_0) + h\nu$ (pump) $\rightarrow C_6H_5OH(S_n)$, they undergo dissociation on the excited state, $C_6H_5OH(S_n) \rightarrow C_6H_5O + H$, or undergo internal conversion, $C_6H_5OH(S_n) \rightarrow C_6H_5OH^*(S_0)$, followed by the dissociation on the electronic ground state, $C_6H_5OH^*(S_0) \rightarrow C_6H_5O + H$. In typical velocity map ion imaging, these dissociation products are then ionized by probe laser beam, $H + h\nu$ (probe) $\rightarrow H^+$ and detected by ion imaging. The pump-probe delay time is around 10 ns for most velocity map ion imaging experiments. However, the lifetime of dissociation on the ground state can be several hundred nanoseconds or up to several hundred microseconds, depending on the excitation photon energy. Most of the excited phenol in the ground state do not dissociate into products when probe laser pulse arrives. They might absorb photons from the probe laser pulse and dissociate into ionic products by dissociative ionization, $C_6H_5OH^*(S_0) + h\nu$ (probe) $\rightarrow C_6H_5O + H^+$. The ion image of the products from dissociation might overlap with the image from dissociative ionization when velocity map ion imaging is used. This causes the difficulty in the determination of signal and background. We demonstrate that they can be distinguished easily by using the multimass ion imaging technique based on spatial map. The results suggest the slow component in the photofragment translational energy distribution obtained using velocity map ion imaging (and Rydberg tagging) is mainly from background.

Probing Ultrafast Chemical Dynamics by Time-Resolved Ion Imaging using the Pixel Imaging Mass Spectrometry (PIImMS) camera

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Femtosecond pump-probe experiments provide opportunities to investigate and understand changes in molecular structure and photochemical reaction dynamics in unprecedented detail^{1,2}. Here, we study and compare the UV-induced photodissociation of a tightly-bound simple aliphatic molecule, iodomethane (CH₃I), with an aromatic molecule, 2,6-difluoriodobenzene (DFIB), in a pump-probe arrangement using two complementary probe schemes, either an 800 nm (near-IR) Ti:Sa laser or the FLASH free-electron laser (FEL) tuned to 11.6 nm (XUV).

The absorption of multiple near-IR photons results in strong-field ionization that can occur anywhere in the molecule leading to subsequent Coulomb explosion. The XUV photon on the other hand induces inner-shell ionization and Auger cascade that is initially strongly spatially localized at the iodine atom in the molecule, before the charge is spread to the rest of the molecule and leads to a Coulomb explosion.

In order to detect all ions produced in the Coulomb explosion, we coupled the Pixel Imaging Mass Spectrometry (PIImMS) camera³⁻⁵, a time-stamping device that records the hit position and arrival time for up to four ions per pixel, with velocity-map ion-imaging. To enhance the effects of momentum correlation in our ion images and to help us probe changes in molecular structure, the molecules were constrained in one- or three-dimensional space⁶ through adiabatic alignment pulses from a nanosecond Nd:YAG laser.

We compare and contrast the two different fragmentation processes of CH₃I and DFIB probed with either 800 nm laser photons or 11.6 nm FEL photons. We then investigate time-dependent effects in UV-FEL pump-probe experiments, in particular comparing and contrasting the onset of charge transfer^{1,7} in both CH₃I and DFIB.

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The photodissociation of dimethylnitrosamine studied with 3D-REMPI and VMI

Manuel Schneider, Uwe Kensy, Bernhard Dick, Universität Regensburg, Germany;

Whereas the ground state chemistry of nitrosamines has been studied for more than three decades and is mostly well understood, much less is known on their photochemistry, in particular photodissociation. We employed velocity map imaging (VMI) and the 3D-REMPI technique to obtain detailed insight into the photodissociation dynamics of Dimethyl-Nitrosamin (DMN) following excitation into either its S_1 or S_2 state.

Our results indicate a direct dissociation from the S_1 level on a purely repulsive potential energy surface, in good agreement with previous studies on this molecule¹⁻³. We also investigated the influence of additional vibrational excitation within the S_1 state, measuring the relative population and angularly resolved velocity distribution for many rovibrational states of the NO fragment. We present evidence that this extra vibrational energy remains in the $N(CH_3)_2$ -fragment. The corresponding vibration must hence be assigned to an internal vibration of the aminyl fragment rather than the N-N or N-O stretching modes as suggested in earlier studies³.

In the case of dissociation from the S_2 level, the observed data also indicate a fast and direct dissociation. Apparently two distinct dissociation channels exist, which differ in the amount of kinetic energy released. One channel produces the aminyl radical in the electronically excited state 2A , the other produces the electronic ground state 2B . This second channel was theoretically proposed by Peláez *et al.*⁴ and observed for N-nitrosopyrrolidine (NNPy) by Wenge *et al.*⁵ in our group.

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Probing the electronic structure of O₂·VOC using Anion Photoelectron Imaging Spectroscopy

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Anion photoelectron imaging was used to measure the effect of volatile organic compounds (VOC = hexane, isoprene, benzene, benzene-d₆, and ethanol) on the low-lying electronic structure of O₂⁻ and O₂. Photodetachment of the anion is expected to prepare the neutral on a modestly repulsive part of the O₂ – VOC intermolecular potential energy surface. The spectra exhibit a VOC-dependent shift in the electron binding energy of O₂⁻, in addition to slight variations in the relative energies of the O₂ (³Σ_g⁻)·VOC and O₂ (¹Δ_g)·VOC electronic states. No vibrational structure was observed in transitions to the ground O₂ (³Σ_g⁻)·VOC states, however, the O₂ (¹Δ_g)·isoprene and O₂ (¹Δ_g)·benzene bands exhibit partially-resolved O₂ stretch progressions, suggesting that for these two complexes, the O₂ (¹Δ_g)·VOC state is longer-lived. In addition, these O₂ (¹Δ_g)·VOC transitions are more intense with more isotropic photoelectron angular distributions for isoprene and benzene compared to hexane and ethanol as complex partners. Similar effects are observed in the photoelectron imaging spectra of O₄⁻·VOC complexes. Overall, the results underscore how the symmetry of the O₂ π_g orbitals is broken by different collision partners, which may have implications for atmospheric photochemistry and models of solar radiation absorption that include collision induced absorption.

Orientation and Alignment in the UV Photodissociation of Alkyl Nitrites

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The photodissociation of alkyl nitrites provides a view of fundamental processes in chemical dynamics. A primary product in the photodissociation, NO, is readily amenable to 1+1' REMPI, allowing for a detailed view of the translational, vibrational, and rotational energy in the products. Further information on alignment and orientation of the NO product is determined using polarized lasers.

We have studied the photodissociation of methyl nitrite, CH₃ONO, and t-butyl nitrite, (CH₃)₃CONO, from the S₂ state in a velocity-mapped ion imaging apparatus to determine the vector correlations in the photodissociation events. Since the photodissociation from the S₂ state occurs promptly, it is not surprising that the NO products are highly oriented and preferentially aligned after the dissociation event. What is surprising is the difference in the degree of orientation between methyl nitrite and t-butyl nitrite, hinting at the differences in initial conformation and details of the photodissociation event.

**Circular Dichroism of Angular Distributions (CDAD) by Using Velocity Map
Photoelectron Imaging**

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Photoelectron angular distributions (PAD) recorded following ionization with polarized light can be used to probe the orientation and alignment of excited atoms and molecules, and provide insight into the details of the photoionization dynamics.¹ In particular, the circular dichroism of photoelectron angular distributions (CDAD) can be used to perform “complete” photoionization experiments, allowing the extraction of all of the dynamical parameters required to describe the process. In CDAD experiments performed before the development of velocity map imaging, a linear polarized pump beam was followed by a left- or right circular polarized probe beam, and the difference in signal for the two circular polarized beams was monitored as a function of the angle between the pump polarization and the detection angle. The resulting experiments require photoelectron spectra at many angles, and are difficult and time consuming. Here we explore the possibility of using a circular polarized pump beam and left and right circular polarized probe beams, along with velocity map photoelectron imaging along the axis perpendicular to the laser propagation axes. We have employed this technique to study the (1+1') photoionization of NO via the $A^2\Sigma^+$ ($v=0$, N) state and the (2+1') ionization of Xe(1S_0) via the $(2P_{1/2})6p^1[3/2]_2$ Rydberg state. Our results are compared with theoretical CDAD spectra calculated by using the previously determined dynamical parameters.

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Time-Resolved XUV-induced Electron Solvation Dynamics in Water Clusters

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The solvation of electrons in aqueous solutions plays a nearly ubiquitous role in biological and chemical systems. That being said, a fundamental understanding of the solvation properties (e.g. solvation time, binding energies, solvation shells, and binding motifs) has yet to be attained. Here, we report the first observed XUV-induced electron solvation in water clusters where subsequent to ionization the electron is recaptured in the cluster. The binding energy of the electron is measured by means of velocity map imaging in a pump-probe scheme where we find different solvation states occurring at different times in the femtosecond to picosecond range. The slower dynamics of deuterated water clusters has also been investigated as comparison. XUV femtosecond pulses were provided by the seeded free electron laser FERMI. Results are discussed in connection with experiments on water cluster anions, liquid jets and corresponding theory.

Ultrafast Photodissociation Dynamics of Thiophenol revealed by Femtosecond Time-resolved Spectroscopic Measurements

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Abstract: By employing femtosecond time-resolved spectroscopy, ultrafast photodissociation dynamics of thiophenol (PhSH) on the S_1 state has been investigated in the time-domain. Excited state lifetime of sub-100 fs was obtained from our time-resolved ion yield measurement, giving excellent agreement with the previous value indirectly measured from homogeneously broadened linewidth in the photofragment (H/D) excitation spectra [You *et al.* *J. Phys. Chem. Lett.* vol. 6, 3202 (2015)]. Ultrashort excited state lifetime indicates that the wavepacket prepared on the S_1 state undergoes the S-H bond dissociation very rapidly under the influence of a quite shallow potential well. Effect of the deuterium substitution (PhSD) was also studied in order to unravel the possible tunneling mechanism implicated in the dissociation pathway. Kinetic isotope effect (KIE) on the reaction rate ($k_{\text{PhSH}}/k_{\text{PhSD}}$) is measured to be about 1.4. This may indicate that the dissociation takes place with no significant barrier along the tunneling coordinate. Experiment could not be explained by one-dimensional mode calculation based on the WKB approximation. This might be only rationalized by invoking multi-dimensional tunneling pathway where the adiabatic reaction barrier is dynamically varied by the geometrical distortion along S-H torsional coordinate, for instance. Time-resolved photoelectron imaging (TR-PEI) also assured ultrafast S_1/S_2 coupling.

Real-time Excited State Predissociation Dynamics of Thioanisole: the Role of $\pi\pi^*/n\sigma^*$ Coupling in ‘Resonance-in-Continuum’

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Abstract: Relaxation dynamics involving $\pi\pi^*$ and $n\sigma^*$ excited states of thioanisole ($\text{C}_6\text{H}_5\text{SCH}_3$) in the gas phase has been investigated by time-resolved ion yield (TR-IY) and time-resolved photoelectron imaging (TRPEI) methods. Both parent-ion decay and methyl fragment rise transients show biexponential behavior with two distinct time constants. This implies that two predissociating channels co-exist in the excitation energy region where S_1 and S_2 are strongly mixed. Relative portions of fast and slow components in transients are quite sensitive to the excitation energy, which may be correlated with the previously reported ‘dynamic resonance’ behavior observed from the energy-domain experiments [Lim *et al. Nat. Chem.* vol. 2, 627 (2010)].

Multiphoton Ionization and Dissociation of H₂ Molecule in Intense Laser Fields Using Velocity Mapping Imaging

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Velocity mapping imaging is used to study the photophysics and photochemistry of the 532 nm nonresonant multiphoton dissociation of H₂ molecules and the 532 nm photodissociation following the 2+1 resonance enhanced multiphoton ionization (REMPI) throughout the E,F electronic state of H₂ molecule. Photoelectron and photofragment images have been recorded at laser intensities in the ranges of 4.8×10^{13} to 1.5×10^{14} W/cm² and 1.27×10^{11} to 1.96×10^{14} W/cm², respectively. Many nonlinear and perturbative effects in the molecule are observed due to the high laser intensities producing unique photophysics (bond softening). The photodissociation of H₂ (E,F state) $v=0$, $J=0$ has a strong alignment effect of the molecule to the laser polarization ($\sin^2(\theta)$ distribution) at low 532 nm laser intensities (1.27×10^{11} W/cm²) compared to high laser intensities (1.96×10^{14} W/cm²) where a $\cos^2(\theta)$ distribution is observed whereas in the case of the $J=1$ state a strong effect is not observed.

Three-dimensional momentum imaging of delayed dissociation of metastable molecular ions

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Coincidence three-dimensional momentum imaging has been a powerful technique in studies of molecular fragmentation following ionization by ultrashort intense laser pulses, fast ion or electron impact, etc. Sometimes, the fragmentation of an intermediate molecular ion can be delayed by a significant fraction of its flight time to the detector due to the presence of metastable states. We examine in detail the signatures of delayed dissociation into ion pairs observed in coincidence spectra measured using cold target recoil ion momentum spectrometry (COLTRIMS). Moreover, we present a method for recovering the complete 3D momenta of the fragments as well as the time delay of the dissociation, t_d , which can be used to extract the lifetime(s) of the metastable state(s) involved. We also discuss inherent challenges in evaluating t_d and possible ways to address them. Laser-induced dissociation of hydrocarbon dications, for

example, $\text{C}_2\text{H}_4^{2+} \rightarrow \text{H}^+ + \text{C}_2\text{H}_3^+$, is highlighted to demonstrate this method. Studying the corresponding channel in C_2D_4 , we also find an isotopic effect in the obtained lifetimes.

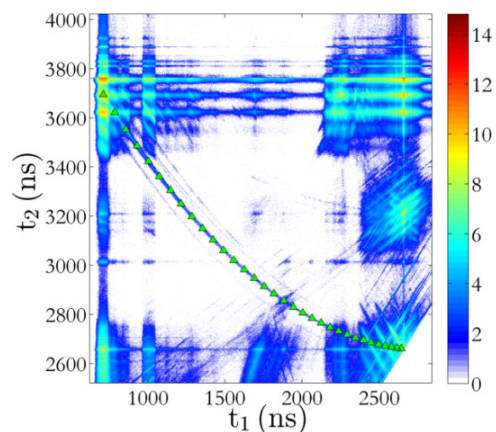


Figure 1 – Coincidence time-of-flight map zoomed in on the $\text{C}_2\text{H}_4^{2+} \rightarrow \text{H}^+ + \text{C}_2\text{H}_3^+$ delayed dissociation channel. The curve predicted by Newton's equations, indicated by the green triangles, agrees well with the measured data.

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Velocity Map Imaging of Small d^5 and d^{10} Transition Metal Molecules

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Velocity Map Imaging (VMI) is a powerful technique enabling, among other things, direct measurement of dissociation energies. It has been used previously by the Mackenzie group on a variety of systems, including small Cu and Au molecules.^{1,2} Other uses have included direct imaging of the vibrational wavefunctions of Xe₂ molecules during photodissociation.³

The current work presented in this poster builds on this previous group expertise by turning our attention to molecules containing d^5 transition metals (molybdenum and chromium, specifically), and silver, the only d^{10} transition metal we did not investigate previously. In particular, we have investigated the photodissociation dynamics of MoO, CrO, and Ag-RG (RG = Ar, Kr, Xe) complexes using VMI. These experiments have allowed for the direct measurement of the dissociation energies of these species, including: (i) allowing for the direct measurement of the dissociation energy of MoO, which was previously determined using a thermodynamic cycle consisting of the ionization potentials of MoO and Mo and the dissociation energy of MoO⁺ (*i.e.* $D_0(\text{MO}) = \text{IP}(\text{MO}) - \text{IP}(\text{M}) + D_0(\text{MO}^+)$),⁴ and (ii) improving upon the known value for the dissociation energy of CrO, which was previously determined using Knudsen cell mass spectrometry and guided ion and crossed molecular beam techniques.^{5,6}

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Imaging and Controlling Electron Rescattering Dynamics in Bicircular Femtosecond Laser Fields

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Laser-driven electron-ion rescattering has recently emerged as a powerful tool for the self-interrogation of atomic and molecular structure with sub-Angstrom spatial and sub-femtosecond temporal resolution. However, the accurate retrieval of structural information from the rescattered electron wavepackets requires a detailed understanding of the electron rescattering dynamics in the presence of a strong-field laser. In these studies, we investigate electron-ion rescattering in bichromatic, bicircular, femtosecond laser fields, which allow electrons to be steered in two-dimensions before recolliding with the parent ion. Using a velocity map imaging spectrometer and tomographic reconstruction techniques, we reconstruct the full three-dimensional photoelectron distributions resulting from strong-field ionization of argon atoms. We find that we can control the kinetic energy and flux of rescattered electrons by changing the relative intensity ratio of the bicircular field. Additionally, we observe the intensity ratio that leads to optimal high energy electron-ion rescattering (i.e., “hard” rescattering) is roughly when the pondermotive energy of the two fields are equal. Furthermore, we show that the kinetic energy spectra of the photoelectrons as they return to the parent ion have narrow energy bandwidth for a wide range of intensity ratios. These findings, plus the fact that the electrons can be steered in two-dimension before returning to the parent ion, provide an optimal source for rescattering-based atomic and molecular imaging applications.

Angle dependent single and double ionization dynamics of small molecules

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We report the results of angle dependent single and double ionization rates of methane and methyl chloride in strong laser fields using 3D double-, triple- and quadruple- coincidence imaging techniques. Employing a circularly polarized light and angular streaking method, recoil frame ionization rates were recorded to identify ionizing orbitals in both single and double ionization processes. In the double ionization experiments, ultrafast nuclear and electronic dynamics were observed following the removal of the first electron.

Multimass imaging of the ultraviolet photodissociation of toluene using the PImMS camera

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The multimass imaging capabilities of the PImMS camera on a unimolecular velocity map imaging experiment were characterised by studying the dissociative multiphoton ionisation of toluene around 266 nm at various concentrations and at different laser powers. Toluene was chosen due to its intense $\pi\pi^*$ absorption bands and multiple product fragments. The resulting images were somewhat surprising and we've complemented this study with photoelectron images to help further elucidate the mechanism by which this photofragmentation proceeds. Two pathways for the ionisation were hypothesised. Firstly, the ionisation of the toluene followed by decomposition due to absorbing further photons. Alternatively, dissociation of the toluene on the excited state followed by ionisation of the resulting photofragments.

We've measured the growth of the different photofragments as a function of laser intensity and concentration and then looked at similar trends in the photoelectron images.