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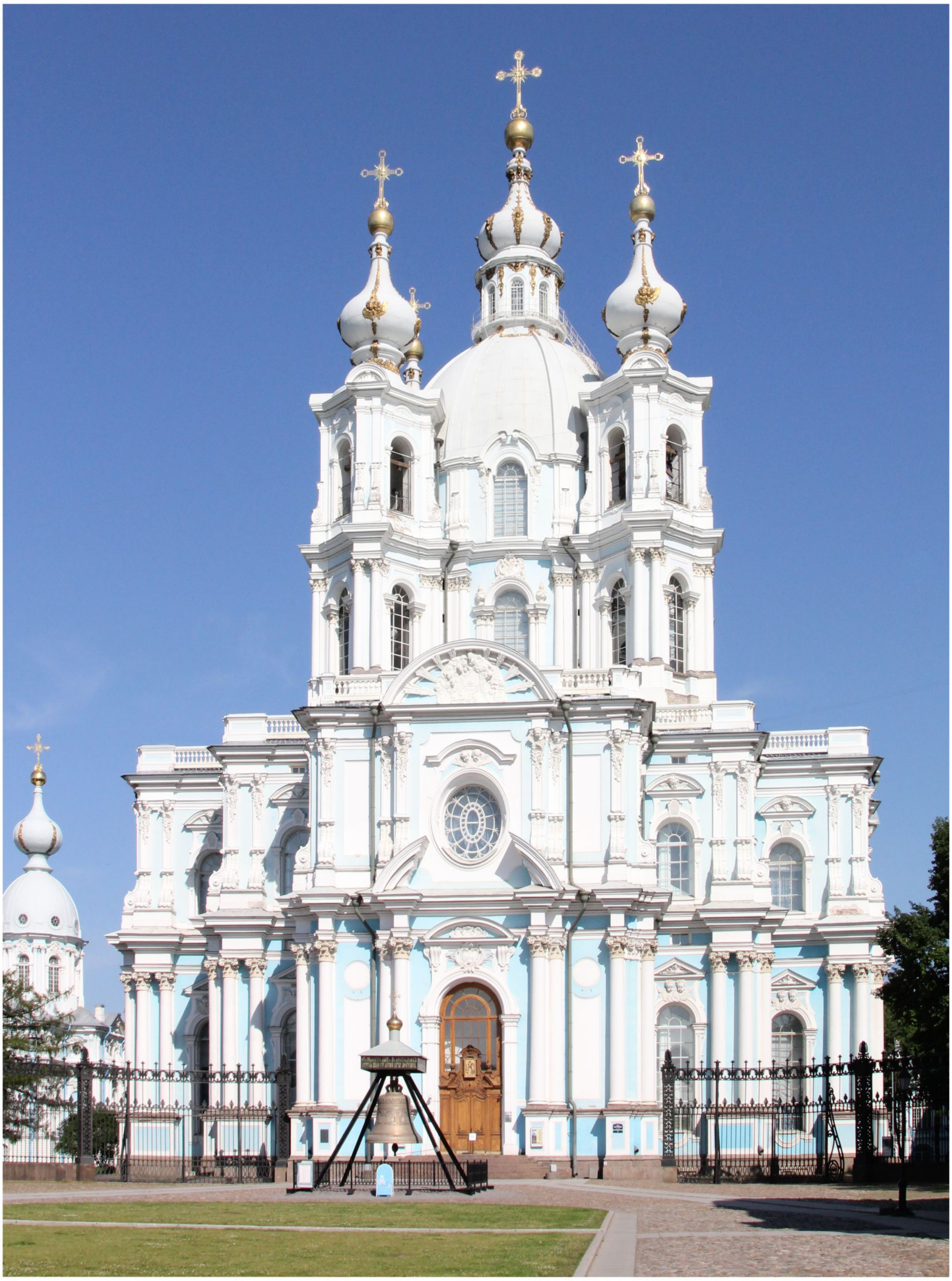
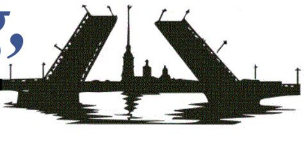
STEREODYNAMICS 2014



Russia, St. Petersburg,

August 17-22, 2014



STEREODYNAMICS 2014

St.Petersburg, Russia, 17-22 August, 2014

web-address: www.ioffe.ru/STD14/

The conference is organized by the Ioffe Institute, by St.Petersburg Scientific Center of the Russian Academy of Sciences, and by St.Petersburg Polytechnic University.

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The STEREODYNANICS 2014 meeting includes sessions on:

- Ultrafast photochemistry and real time dynamics of small molecules, clusters and biologically relevant molecules
- Cold molecules
- Surface scattering
- Reaction dynamics in the gas phase and in condensed media
- Photochemistry
- Chirality, Spin effects
- Chemical reaction control

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Richard B. Bernstein Award

The Award was established in the 12th edition of the Stereodynamics meeting (Dalian, China, 2008) in memory of Professor Richard Bernstein, one of the founding fathers of the field, for recognition of outstanding contributors in the area of steric properties of chemical reactions as one of the most fundamental aspects of reactions studied at the molecular level.
So far, the Award was granted to

2008: **Steven Stolte**, Vrije Universiteit, Amsterdam, The Netherlands

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The recipients of the Richard B. Bernstein Award 2014 are:

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Program of STEREODYNAMICS 2014

St. Petersburg, Russia, August 17-22, 2014

August 17th, 2014, Sunday

16:00-18:00 **Registration**

18:00 **Welcome Cocktail**

August 18th, 2014, Monday

9:00-9:10 **Opening**

Session: Chirality, Spin effects Chair: V. Aquilanti
9:10-9:50 **Martin Quack (ETH, Zürich, Switzerland)** p.12
Parity violation and stereodynamics in chiral molecules: Theory and spectroscopic experiments
9:50-10:30 **Arthur G. Suits (Wayne State University, Detroit, USA)** p.13
Probing spin-polarized hydrogen atoms with the high-n Rydberg time-of-flight technique
10:30-11:00 **T. Peter Rakitzis (IESL-FORTH, Heraklion-Crete, Greece)** p.27
Applications of chiral cavity ring down, and production of long-lived nuclear singlet states

11:00-11:20 **Coffee Break**

Session: Photochemistry I Chair: P. L. Houston
11:20-12:00 **King-Chuen Lin (National Taiwan University, Taipei, Taiwan)** p.14
Roaming as an Alternative Pathway in Molecular Photodissociation
12:00-12:30 **David H. Parker (Radboud University, Nijmegen, The Netherlands)** p.28
Polarization of nascent CO in photodissociation and inelastic scattering processes
12:30-13:00 **Alexey I. Chichinin (Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia)** p.29
Probabilities for 2-and 3-photon absorptions, ion pair channel ($H^+ + Cl^-$) in REMPI of HCl, and emission from metal surface of e^-, H^-, and HCl^- ions under the bombardment by H^+, Cl^+, and HCl^+ ions

13:00-14:30 **Lunch**

Session: Reaction dynamics in the gas phase I Chair: H.-J. Loesch
15:00-15:40 **Octavio Roncero (IFF-CSIC, Madrid, Spain)** p.15
Depolarizing collisions of neutral and singly ionized alkaline earths with hydrogen atoms
15:40-16:10 **Hirofumi Sakai (University of Tokyo, Tokyo, Japan)** p.30
Laser-field-free three-dimensional molecular orientation

16:10-16:40	**Steven Stolte (Vrije Universiteit, Amsterdam, The Netherlands)** *The modified Quasi-Quantum Treatment of rotationally inelastic NO(X)-He scattering*	p.31
16:40-17:00	**Coffee Break**	
	Session: Reaction dynamics in the gas phase II Chair: R.W.Anderson	
17:00-17:30	**Toshio Kasai (National Taiwan University, Taipei, Taiwan)** *A stereodynamical perspective on Arrhenius equation*	p.32
17:30-17:50	**Bethan A. Nichols (University of Oxford, Oxford , UK)** *Steric effects in collisions of NO(X) + Ar*	p.50

August 19th, 2014, Tuesday

	Session: Ultrafast real time dynamics Chair: A. G. Suits	
9:00-9:40	**Albert Stolow (University of Ottawa, Ottawa, Canada)** *Ultrafast non-adiabatic and laser-driven dynamics from the molecule's point of view*	p.16
9:40-10:20	**Luis Bañares (Universidad Complutense de Madrid, Madrid, Spain)** *Slice imaging stereodynamics for elucidation of photodissociation mechanisms*	p.17
10:20-10:50	**Bing Zhang (Chinese Academy of Sciences, Wuhan, China)** *Nonadiabatic dynamics in polyatomic molecules by femtosecond time-resolved photoelectron imaging*	p.33
10:50-11:10	**Coffee Break**	
	Session: Surface scattering I Chair: D.J. Nesbitt	
11:10-11:50	**Alec M. Wodtke (Max Planck Institute, Göttingen, Germany)** *Toward a dynamical understanding of chemistry at metal surfaces*	p.18
11:50-12:20	**Kenneth G. McKendrick (Heriot-Watt University, Edinburgh, UK)** *Steric aspects of gas-liquid interfacial collisions*	p.34
12:20-12:50	**Helen J. Chadwick (Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland)** *The role of vibrational symmetry and alignment in the dissociative chemisorption of methane on nickel*	p.35
13:00-14:30	**Lunch**	
	Session: Reaction dynamics in the gas phase III Chair: P. Villarreal	
15:00-15:30	**Simon Chefdeville (Université de Bordeaux, Bordeaux, France)** *Crossed-beam inelastic scattering experiments at energies approaching the cold regime*	p.36
15:30-16:00	**Shih-Huang Lee (NSRRC, Hsinchu, Taiwan)** *Crossed-beam reactions of C_nH (n = 1 – 6) radicals with propyne*	p.37
16:00-16:30	**Andrey K. Belyaev (Herzen University, St. Petersburg, Russia)** *What is wrong with the conventional Born-Oppenheimer approach for collision processes and how to handle it?*	p.38
16:30-17:00	**Coffee Break**	
17:00	**Poster Session**	

August 20th, 2014, Wednesday

	Session: Cold molecules I Chair: A. Wodtke	
9:00-9:40	**Andreas D. Osterwalder (Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland)** *Reactions of Polyatomic Molecules at Low Temperature*	p.19
9:40-10:10	**Jolijn Onvlee (Radboud University, Nijmegen, The Netherlands)** *Molecular collisions coming into focus*	p.39
10:10-10:40	**Alexey A. Buchachenko (Lomonosov Moscow State University, Moscow, Russia)** *Zeeman relaxation in cold atomic collisions: probing the interaction anisotropy*	p.40
10:40-11:00	**Coffee Break**	
	Session: Spin effects, Chemical Reaction control Chair: L. Bañares	
11:00-11:40	**Tamar Seideman (Northwestern University, Evanston, USA)** *New directions in coherent alignment. From spinning tops to ultrafast switches*	p.20
11:40-12:10	**Pavel G. Baranov (Ioffe Institute, St. Petersburg, Russia)** *Magnetic Resonance of Single Molecular, Single Defect Spins*	p.41
12:10-12:40	**Alberto Garcia-Vela (IFF-CSIC, Madrid, Spain)** *Achieving and probing quantum coherent control of the lifetime of a resonance state with laser pulses*	p.42
12:40-13:00	**Conference Photo**	
13:00-14:30	**Lunch**	
	Session: Cold molecules II Chair: K.G. McKendrick	
15:00-15:30	**Pablo Villarreal (IFF-CSIC, Madrid, Spain)** *Anionic Helium Species in He Clusters: Size Dependent Arrangements*	p.43
15:30-16:00	**Richard B. Bernstein Award Ceremony** ***Chairs: A. González-Ureña and S. Stolte***	
16:00-16:40	**Vincenzo Aquilanti (University of Perugia, Italy)** *Directions of chemical change*	p.21
16:40-17:20	**Kopin Liu (IAMS, Taipei, Taiwan)** *Steric control of polyatomic chemical reactions*	p.22

August 21th, 2014, Thursday

	Session: Photochemistry II Chair: D.H. Parker	
9:00-9:40	**Michael N.R. Ashfold (University of Bristol, Bristol, UK)** *Tuning molecular photochemistry: the roles of substituents*	p.23
9:40-10:10	**Yoshi-Ichi Suzuki (Kyoto University, Kyoto, Japan)** *Electronic dynamics of molecules and solutions studied by photoelectron spectroscopy*	p.44
10:10-10:40	**Vadim A. Bataev (Lomonosov Moscow State University, Moscow, Russia)** *Potential barriers and multimode nature of the internal rotation in aromatic and heterocyclic molecules*	p.45
10:40-11:00	**Coffee Break**	
	Session: : Surface scattering II Chair: K.-C. Lin	
11:00-11:40	**David J. Nesbitt (University of Colorado, Colorado, USA)** *Stereodynamics of Collisions at the Gas-Liquid Interface: A Quantum State-Resolved Approach*	p.24
11:40-12:00	**Arban Uka (Epoka University, Tirana, Albania)** *Hydrogen-Copper System Nonadiabatic Effects*	p.51
12:00-13:30	**Lunch**	
13:30-18:00	**Excursion**	
19:00	**Conference Dinner**	

August 22th, 2014, Friday

	Session: Photochemistry III ***Chair: T.P. Pakitzis***	
9:00-9:40	**Paul L. Houston (Institute of Technology, Atlanta, USA)** *NO Dissociation through ns, np, and nf Rydberg States: Angular Distributions*	p.25
9:40-10:10	**Alexey V. Baklanov (Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia)** *Singlet oxygen photogeneration from X-O_2 van der Waals complex. Double-spin flip vs. charge-transfer mechanism*	p.46
10:10-10:40	**Roger W. Anderson (University of California, Santa Cruz, USA)** *Discrete orthogonal transformations for Askey scheme polynomials*	p.47
10:40-11:00	**Coffee Break**	
	Session: Photochemistry IV ***Chair: T. Kasai***	
11:00-11:30	**Alexander V. Glushkov (Odessa State University, Odessa, Ukraine)** *Spectroscopy of cooperative laser electron-γ-nuclear processes in diatomic, multiatomic molecules and clusters*	p.48
11:30-11:50	**Alexander S. Bogomolov (Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia)** *Predissociation of High-Lying Rydberg States of Molecular Iodine via Ion-Pair States*	p.52
11:50-12:10	**Concluding remarks**	
13:00-14:30	**Lunch**	
15:00	**Departure**	

Keynote Lectures

KL-1

Parity violation and stereodynamics in chiral molecules: Theory and spectroscopic experiments

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The stereochemical behavior, structure and dynamics of chiral molecules has been and still is today a fundamental aspect of Chemistry, Biology and Chemical Physics [1-10]. It opens also a new window to look at fundamental symmetry violations in physics [6].

The investigation of parity violation in chiral molecules has been a major challenge for my research group in Zürich for several decades. Although some important questions could be answered, other problems have remained open [5-10]. Electroweak quantum chemistry predicts a small energy difference $\Delta_{\mathrm{pv}}E$ between the ground states of the enantiomers of chiral molecules, corresponding to a non-zero reaction enthalpy $\Delta_{\mathrm{pv}}H_0^{\ominus}$ for the stereomutation reaction of chiral molecules:

$$R = S \qquad \Delta_{\mathrm{pv}}H_0^{\ominus} = N_{\mathrm{A}}\,\Delta_{\mathrm{pv}}E \neq 0 \quad \text{(typical range: 1 to 1000 pJ/mol)} \tag{1}$$

With parity conserving ordinary quantum chemistry this reaction enthalpy would be exactly zero by symmetry. After our discovery in 1995 that $\Delta_{\mathrm{pv}}E$ is calculated to be typically by a factor of 10 to 100 larger than previously anticipated, theoretical results from many groups as well as ours have stabilized at these current values (see [6-8] and references cited therein). However, the experimental measurement of $\Delta_{\mathrm{pv}}E$ remains a challenge [10]. We shall in the lecture report on the current status of ongoing theory and experiments in our group, following the original proposal in [5-10] (see also [6] and refs. cited therein).

Our work is supported by ETH Zürich, SNF and an Advanced Grant from ERC.

[1] M. Quack, *Parity Violation and Stereodynamics in Chiral Molecules: Theory and Spectroscopic Experiments, Invited Lecture at Stereodynamics 2014, St. Petersburg, Russia, 17-22 August 2014.*

[2] M. Quack, *The Concept of Law and Models in Chemistry, European Review*, **2014**, *22*, S50-S86.

[3] M. Quack, *Structure and dynamics of chiral molecules, Angew. Chem. Int. Ed. Engl.*, **1989**, *28*, 571-586.

[4] M. Quack, *How important is parity violation for molecular and biomolecular chirality?, Angew. Chem. Int. Ed. Engl.*, **2002**, *41*, 4618-4630.

[5] M. Quack, *On the measurement of the parity violating energy difference between enantiomers, Chem. Phys. Lett.*, **1986**, *132*, 147-153.

[6] M. Quack, *Fundamental Symmetries and Symmetry Violations from High Resolution Spectroscopy,* in *Handbook of High Resolution Spectroscopy, Vol. 1*, Chapt. 18, pp. 659-722 (Eds.: M. Quack, F. Merkt), Wiley, Chichester, New York, **2011**, ISBN 978-0-470-06653-9.

[7] M. Quack, J. Stohner, M. Willeke, *High-resolution spectroscopic studies and theory of parity violation in chiral molecules, Annu. Rev. Phys. Chem.*, **2008**, *59*, 741-769.

[8] M. Quack, *Frontiers in Spectroscopy,* in *Faraday Discussions, Vol. 150,* pp. 533-565, **2011**.

[9] L. Horný, M. Quack, *On coupled cluster calculations of parity violating potentials in chiral molecules (Discussion contribution), Faraday Discuss.*, **2011**, *150*, 152-154.

[10] P. Dietiker, E. Miloglyadov, M. Quack, A. Schneider, G. Seyfang, *Two Photon IR-Laser Induced Population Transfer in NH_3 – First Steps to Measure Parity Violation in Chiral Molecules,* in *Proceedings of the 19th Symposium on Atomic, Cluster and Surface Physics 2014 (SASP 2014), Obergurgl, Austria, 8 to 14 February 2014,* pp. 226 - 229 (Eds.: D. Stock, R. Wester, P. Scheier), Innsbruck University Press (IUP), Innsbruck, **2014**, ISBN 978-3-902936-26-4.

KL-2

Probing spin-polarized hydrogen atoms with the high-n Rydberg time-of-flight technique

Bernadette M. Broderick[1], Vladimir Chernyak[1],
Oleg S. Vasyutinskii[2] and Arthur G. Suits[1]

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The production of spin-polarized hydrogen atoms in photodissociation has long been suspected[1], but it is only in recent years that this has been directly observed, first through inferences based on the co-fragment angular momentum polarization[2], and subsequently through probing of the H atom itself.[3] We have recently shown that by adapting the H atom Rydberg Time of Flight (HRTOF) technique, we can measure hydrogen atom spin polarization, and its velocity distribution, with the extraordinary resolution and sensitivity that this method affords.[4] The spin-sensitive probe scheme combines a linearly polarized Lyman-α laser, a circularly polarized tagging laser, and a photolysis laser. We illustrate this approach with a measurement of the coherent contributions to the H atom spin polarization in photodissociation of HBr and DBr at 212.8 nm. We will also discuss the means to adapt this method to detect the incoherent contribution to the photofragment spin polarization, and discuss our progress in applying the technique to dissociation of polyatomic molecules.

1. O. S. Vasyutinskii, *Sov. Phys. JETP Lett.* 31, 428 (1980).

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3. D. Sofikitis, L. Rubio-Lago, L. Bougas, A. J. Alexander, and T. P. Rakitzis, *The Journal of Chemical Physics* **129**, 144302 (2008).

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KL-3

Roaming as an Alternative Pathway in Molecular Photodissociation

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An alternative photodissociation pathway other than the conventional transitional state mechanism for formaldehyde (H_2CO) leading to CO + H_2 was first found early in 1990, [1] then followed by a detailed characterization and interpretation using ion imaging detection of CO that was accompanied by an elaborate quasi-classical trajectory (QCT) calculations on a full dimensional potential energy surface of H_2CO.[2,3] Since then, the so-called roaming atom and radical processes were extended to other molecules, involving in direct dissociation paths or isomerization routes of intermediates. We present two molecules, methyl formate ($HCOOCH_3$) and propionaldehyde (C_2H_5CHO),[4,5] that carry roaming signature in their photodissociation. Photodissociation of methyl formate at photolysis wavelengths from 225 to 255 nm has been probed using ion imaging techniques. With the aid of the quasiclassical trajectory (QCT) calculations, insight into the photodissociation dynamics can be gained. The translational energy distributions of CO were acquired, showing a bimodal feature that is composed of three channels, triple fragmentation, roaming and transition state processes, depending on the photolysis wavelength. It is noticeable to find that the branching to roaming process is enhanced at the expense of triple fragmentation,.H + CO + CH_3O.

Among the aldehydes, formaldehyde and acetaldehyde (CH_3CHO) were found to carry roaming signature in the photodissociation.[1-3,6-9] In this work, we employed time-resolved FTIR emission spectroscopy in photolysis of CH_3CH_2CHO at 248 nm to characterize the role of roaming pathway. A roaming saddle point was found containing two far separated moieties of HCO and CH_3CH_2 with a weak interaction between them. QCT calculations on this configuration yielded the CO energy flow behavior consistent with the experimental findings.

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4. P-Y. Tsai, M-H. Chao, T. Kasai, K-C. Lin, A. Lombardi, F. Palazzetti, and V. Aquilanti, *Phys. Chem .Chem. Phys.* **16**, 2854 (2014).
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9. K-C. Hung, P-Y. Tsai, H-K. Li, and K-C. Lin, *J. Chem. Phys.* **140**, 064313 (2014).

KL-4

Depolarizing Collisions of Neutral and singly ionized alkaline earths with Hydrogen Atoms

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Depolarizing rates on the lowest levels of neutral and singly ionized alkaly-earths Mg I, Sr I, Ba I, Mg II, Ca II, and Ba II, due to collisions with Hydrogen atoms are presented. We compute ab initio potential curves of the atom-H system and solve the quantum mechanical dynamic using a close-coupling time-independent approach in a space-fixed frame. From the scattering amplitudes we calculate the depolarizing rates for Maxwellian distributions of colliders at temperatures T<10000 K. A comparative analysis of our results and previous calculations in the literature is done [1]. We discuss the effect of these rates on the formation of scattering polarization patterns of resonant lines of alkali-earths in the solar atmosphere, and their effect on Hanle effect diagnostics of solar magnetic fields.

For non-zero nuclear spin, as some isotopes of Ba I and Ba II, the rates in the hyperfine basis set is obtained using a recoupling technique [2,3] directly from the rates obtained in the fine representation.

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KL-5

Ultrafast non-adiabatic and laser-driven dynamics from the molecule's point of view

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The dynamics of polyatomic molecules exhibit the coupling of vibrational modes, leading to vibrational energy flow and structural rearrangements within molecules and conical intersections which involve the ultrafast non-adiabatic coupling of electronic and vibrational motions, leading to charge rearrangements within molecules. Ideally, one would like to observe these ultrafast processes from the molecule's point of view - the Molecular Frame - thereby avoiding loss of information due to orientational averaging. This can be achieved by Time-Resolved Coincidence Imaging Spectroscopy (TRCIS) which images 3D recoil vectors of both photofragments and photoelectrons, in coincidence and as a function of time. This permits direct Molecular Frame imaging of valence electronic dynamics during a chemical reaction [1]. Laser induced diploes can be used for field-free 1D alignment of linear molecules and field-free 3D alignment of asymmetric top molecules [2]. Using laser alignment, we can transiently fix a molecule in space, yielding a more general approach to direct Molecular Frame imaging of valence electronic dynamics during a chemical reaction [3, 4].

The emerging field of Attosecond Science, which offers direct observation of purely electronic dynamics, emerged out of the physics of Strong Field Ionization (SFI) and High Harmonic Generation (HHG). In strong fields, a new laser-matter physics emerges for polyatomic systems [5] wherein both the single active electron picture and the adiabatic electron response, both implicit in the standard models, can fail dramatically. This has important consequences for all strong field spectroscopies of polyatomic molecules, including HHG. For example, multiple electronic continua have been implicated in the HHG spectroscopy of polyatomic molecular dynamics [6]. We discuss an experimental method, Channel-Resolved Above Threshold Ionization (CRATI), which directly unveils the electronic continua participating in the attosecond molecular SFI response [7]. The implications for probing excited state dynamics and 'attosecond chemistry' will be discussed.

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7. Science 335, 1336 (2012); Physical Review Letters 110, 023004 (2013)

KL-6

Slice imaging stereodynamics for elucidation of photodissociation mechanisms

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In this contribution, stereodynamics in combination with the slice imaging technique is fully exploited to disentangle photodissociation mechanisms in polyatomic molecules. The stereodynamical information is extracted from fragment ion images measured at different polarization geometries of the pump and probe lasers in the form of Dixon's bipolar moments, following the treatment by Grubb et al. [1]. These bipolar moments contain information about the relevant vector correlations in the photodissociation process. The treatment includes some approximations dealing with fragment detection by (2+1) REMPI [2]. A particularly significant case is the photodissociation of methyl iodide in the onset of the *B*-band. We have studied the stereodynamics of the photodissociation of this molecule between 199 and 214 nm using slice imaging of both $CH_3(\nu=0)$ and $I^*(^2P_{1/2})$ photoproducts. The anisotropy β parameter extracted from the stereodynamical analysis of the $I^*(^2P_{1/2})$ ion images settles the *B*-band origin (0^0_0 vibronic transition to the $^3R_1$ state) at 201.11 nm with an accuracy of ±0.12 nm. In addition, a depolarization factor due to parent molecule rotation during the predissociation process is estimated to be 0.29±0.06. Analysis of the Dixon's bipolar moments extracted from the CH_3^+ images indicates that direct excitation to the *A*-band $^3A_1(4E)$ repulsive state is enhanced, even at the maximum of the *B*-band origin, by vibrational coupling between the two involved surfaces at the conical intersection, through in-plane vibrational motion.

1. M. P. Grubb, M. L. Warter, C. D. Freeman, N. A. West, K. M. Usakoski, K. M. Jonhson, J. A. Bartz, and S. W. North, J. Chem. Phys. 135, 094201 (2011).
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KL-7

Toward a dynamical understanding of chemistry at metal surfaces

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One of our most fundamental scientific challenges is to develop predictive theories of chemistry rigorously grounded in the laws of physics. In 1929, Dirac identified the problem famously in a comment about the importance of quantum mechanics to chemistry… *“The underlying physical laws necessary for the mathematical theory of... ...the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”* Despite electrifying advances in computational power, Dirac is still right. The theory of chemistry requires approximate methods for practical computations.

For the theory of surface chemistry, three central approximations are made, involving the use of: 1) classical mechanics for describing nuclear motion, 2) density functionals for calculating electronic states and the Born-Oppenheimer approximation to separate electronic and nuclear degrees of freedom.

The growing importance of computational surface chemistry motivates us to design rigorous experimental tests of these assumptions. Many fundamental questions arise. Can we trust the Born-Oppenheimer approximation for calculating potential energy surfaces for reactions at metal surfaces? Can we characterize and overcome the weaknesses of density functional theory, for example by developing new wave-function based methods for the solid-state? For all of these reasons, it is important to carefully design experimental tests of the capabilities of modern computational surface chemistry.

Using modern molecular beams methods in state-to-state scattering experiments, we obtain a wealth of observational data characterizing the interactions of molecules with metal surfaces. Emphasizing quantitative comparison to first principles theories, we find that energy conversion can occur by unexpected mechanisms, where the electronically adiabatic approximation separating the time scales of electronic and nuclear motion is found to be invalid. The simplicity of the systems under study provides opportunities for developing new theories that go beyond the Born-Oppenheimer approximation. One important outcome of this is the realization that Born-Oppenheimer breakdown can be induced by simple electron transfer events that are common in surface chemistry. Among other things, we see that electron transfer events occurring between molecules and metal surfaces exhibit an interesting stereochemistry.

KL-8

Reactions of Polyatomic Molecules at Low Temperature

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We have developed an experiment to study gas-phase reactions between polar molecules and paramagnetic particles in a temperature range 0.1 K-200 K. For this we bend two supersonic molecular beams, one in an electrostatic guide and one in a magnetic guide such that they overlap and move in parallel. By adjusting the conditions of the supersonic expansions we can set the two beam velocities to be equal, resulting in very low relative velocities of particles from the two beams.

This experiment has been used to study a variety of polyatomic reactions. Mass-selective detection of products allows to separately monitor reaction channels that lead to products with different masses. The observation of nearly temperature dependent branching ratios is used in attempts to explain the reaction dynamics and in some cases elucidate stereodynamical aspects, or the absence thereof, of the reaction.

KL-9

New directions in coherent alignment.
From spinning tops to ultrafast switches

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Nonadiabatic alignment is a coherent approach to control over the spatial properties of molecules, wherein a short, moderately-intense laser pulse is applied to populate a broad rotational wavepacket with fascinating properties. In the limit of small isolated molecules, nonadiabatic alignment has evolved during the past 17 years into an active field of theoretical and experimental research with a rich variety of applications.

In the present talk we extend the alignment concept to complex systems, including large polyatomic molecules, dissipative media, nonrigid systems, molecular assembly, molecular conduction junctions and dense molecular ensembles. Following a review of the essential physics underlying alignment, we consider the case of asymmetric top molecules, where alignment overcomes the mechanisms that render the rotations unstable in the classical limit. Next we focus on dissipative media, and illustrate the application of rotational wavepackets as a probe of the decohering properties of the environment. We extend alignment to control the torsional motions of polyatomic molecules, and apply torsional control to manipulate charge transfer events in solutions, suggesting a potential route to light controlled molecular switches. Turning to interfaces, we introduce a route to guided molecular assembly, wherein laser alignment is extended to induce long-range orientational order in molecular layers. Combining the nonadiabatic alignment concept with recent research on nanoplasmonics and on conductance via molecular junctions, we develop an approach to coherent control of transport in the nanoscale [1]. Finally, we explore the case of dense molecular ensembles, where alignment generalizes into a collective phenomenon that gives rise to formation of molecular assembly with long range translational and orientational order, suggesting intriguing potential applications in material design.

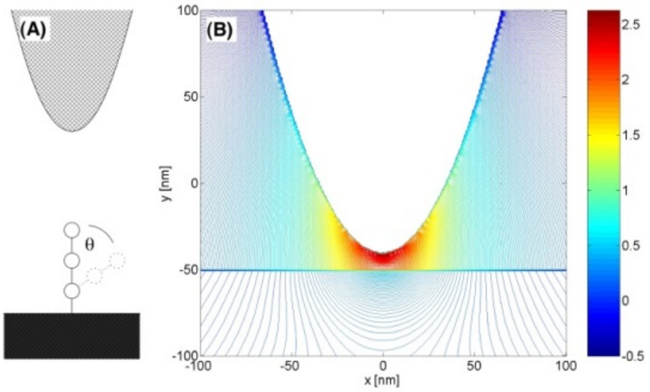

Figure 1: An ultrafast, nanoscale molecular switch based on combination of the of nonadiabatic alignment with nanoplasmonics

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KL-10

Directions of chemical change

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Stereodynamics is the science that investigates spacial aspects of molecular evolution.This presentation is given with the aim of drawing the attention to the versatility of current experimental investigations [1] on the leading rôle that molecular orientation and alignment [2] play on the outcomes of reactive and photodissociation processes. Crucial is the accompanying theoretical and computational progress in quantum mechanical and molecular dynamics techniques [3,4] .

Advanced molecular beams methods, together with a combination of modern tools for specific preparation, selection and detection, permits us to discover new trends on reactivity in the gas phase as well as at surfaces. Experimental evidence on novel paths in reaction dynamics and photodissociation [5] is described; additionally, we also consider specific topics recently entered into the focus of stereodynamicists: (i) chirality effects in collisions [6,7]; and (ii) the non-linear Arrhenius behavior in the temperature dependence [8,9] of chemical and biophysical processes.

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KL-11

Steric control of polyatomic chemical reactions

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The concept of preferred collision geometry in chemical reactivity is at the heart of reaction dynamics [1]. Exemplified by a series of crossed molecular beam studies on the reactions of a C-H stretch-excited $CHD_3(v_1=1)$ with F, Cl, and $O(^3P)$ atoms, two types of steric control of bimolecular collisions will be highlighted. The *passive* control is governed in a reaction with strong anisotropic entry valley that can significantly steer the incoming trajectories. This disorientation effect exerted by the long-range interaction potential is illustrated by the F and $O(^3P) + CHD_3(v_1=1)$ reactions. In the former case, the long-range anisotropic interaction acts like an optical "negative" lens by deflecting the trajectories away from the favored transition-state geometry, and thus inhibits the bond rupture of the stretch-excited CHD_3 [2,3]. On the contrary, the interaction between $O(^3P)$ and $CHD_3(v_1=1)$ behaves as a "positive" lens by pulling the large-impact-parameter collisions into the cone-of-acceptance, and thereby enhances the reactivity and substantially changes the dynamical outcomes [4,5].

On the other hand, for reactions with relatively weak anisotropic interactions in the entry valley, the *active* control can be performed by polarizing the reactants in space, as demonstrated in the reaction of Cl with a pre-aligned $CHD_3(v_1=1)$ reactant [6-10]. The experiment exploited the polarization property of the infrared (IR) excitation laser when preparing the C-H stretch-excited $CHD_3(v_1=1)$, and a time-sliced, velocity-map-imaging method for probing the products [7,11]. A set of product images under judiciously chosen molecular-beam and IR-polarization configurations provide all necessary ingredients to unravel, for the first time, a complete set of polarization-dependent differential cross sections (PDDCS) [9,12], from which the full three-dimensional stereo aspects of a reactive encounter are revealed [8,10].

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KL-12

Tuning molecular photochemistry: the roles of substituents

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Azoles and phenols are key components of the chromophores in nucleobases and aromatic amino-acids, which dominate the near-UV absorption spectra of many biological molecules. $\pi^* \leftarrow \pi$ transitions are responsible for these strong UV absorptions, but these molecules also possess excited states formed via $\sigma^* \leftarrow \pi$ electron promotions. These $\pi\sigma^*$ excitations have much smaller absorption cross-sections, but are currently attracting much detailed attention. Photofragment translational spectroscopy experiments and complementary *ab initio* theory have been applied to the study of H atom loss following UV photoexcitation of many such heteroaromatic molecules in the gas phase [1]. These studies reveal that X–H bond fission (X = heteroatom) following direct excitation to the $1^1\pi\sigma^*$ state (or, in phenols, by tunneling under the conical intersection between the $1^1\pi\pi^*$ and $1^1\pi\sigma^*$ potential energy surfaces) is often an important non-radiative decay channel. The radical products are formed in the ground and/or first excited electronic states, and in a very limited sub-set of the possible vibrational states. Identifying these latter states can provide detailed insights into the non-adiabatic couplings that enable the evolution from photoexcited parent molecule to eventual fragments, *i.e.* the sterodynamics of the dissociation process.

This presentation will (i) summarise the state of knowledge derived from such gas phase studies, (ii) highlight ways in which substitution, at sites remote from the dissociating bond, can be used to 'tune' both the rate of X–H bond fission and the electronic branching in the resulting radical fragments [2,3] and (iii) illustrate the extent to which such knowledge can inform our interpretation of ultrafast pump-probe studies of the UV photofragmentation of similar molecules (*e.g.* (thio)phenols, anisoles and ethers) in solution [4,5].

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KL-13

Stereodynamics of Collisions at the Gas-Liquid Interface: A Quantum State-Resolved Approach

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Liquids are by far the least well understood phase of matter, with a detailed understanding of the very outermost “skin” of such liquids representing an ongoing and outstanding challenge to the chemical physics community. This talk will highlight recent results from our group using a novel combination of i) supersonically cooled molecular beams and ii) high resolution IR/UV lasers to permit detailed stereodynamical study of hypersonic collisions at the gas-liquid interface by probing the final quantum state distributions. Time permitting, this talk will address work in two areas. 1) Jet cooled CO_2 molecules in ($J = 0$, $M_J = 0$) at 15 kcal/mol are collided at surfaces of liquid perfluorinated polyethers, with both the alignment and orientation of the resulting scattered CO_2 probed by shot noise limited, polarization modulated IR laser absorption spectroscopy. Interestingly, results from circularly polarized laser studies indicate a strong stereodynamical propensity for the scattered CO_2 molecules to acquire *positive* orientation (i.e., “top spin”) for glancing collisions with the liquid surface. Furthermore, the degree of M_J orientation is found to grow continuously from zero as a function of final J state, in agreement with correspondence principle predictions. 2) These state-to-state collision methods have been extended substantially with laser induced fluorescence (LIF), resonance enhanced multiphoton ionization (REMPI) with velocity-map imaging (VMI) to yield *quantum-state* and *vector momentum* resolved distributions in the scattered molecular flux. This part of the talk will focus on low energy ($E_{inc} = 2.7$ kcal/mol) and hyperthermal ($E_{inc} = 21$ kcal/mol) scattering of jet cooled NO (A’ $^2\Pi$) at gas-room temperature ionic liquid (RTIL) interfaces, for which the final A’ and A” electronic spin-orbit state distributions reveal intriguing sensitivity to stereodynamical effects in the entrance/exit channel to the gas-liquid collision event. Interestingly, facile spin orbit changes in the scattered flux unambiguously identify a strongly non-adiabatic component to the gas-liquid collision dynamics. Most importantly, the spin-orbit electronic temperatures are found to be surprisingly sensitive to RTIL anion identity, which therefore suggests the importance of *transient electron transfer* to the antibonding NO Π^* molecular orbital in the immediate vicinity of the gas-liquid interface.

KL-14

NO Dissociation through *ns*, *np*, and *nf* Rydberg States: Angular Distributions

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Quantum mechanical calculations of photofragment angular distributions have been performed as a function of the frequency of excitation, the lifetime of the dissociative state, the rotational level and the rotational constant . In the limit of high *J* values and white, incoherent excitation, the general results are found to agree exactly with both those of Mukamel and Jortner and those of Jonah. Example calculations describe how the anisotropy is dependent on the degree of broadening, the rotational constant, the initial rotational level, and the frequency of excitation. Applications are also made to explain experimental results on the photodissociation of ClO via the 10-0 and 6-0 bands of the *A* doublet Pi 3/2 - *X* doublet Pi 3/2 transition and on the photodissociation of molecular oxygen via the 0-0 band of the *E* triplet Sigma minus (u) - *X* triplet Sigma minus (g) transition.

Velocity-mapped imaging and theoretical calculations have been used to study the angular distribution of the products of NO predissociation following its excitation to the *11s*, *10p*, *11p* and *9f* Rydberg levels based on the NO^+ ($X\ ^2\Sigma^+$) core. The Rydberg states were reached from the NO ($A\ ^2\Sigma^+$, $v = 0$, $N = 2$, $J = 1.5$) level prepared with strong alignment by excitation with linear polarization from NO ($X\ ^2\Pi$, $v = 0$, $N = 1$, $J = 0.5$). Ion dip spectra of the Rydberg states were recorded along with velocity-mapped images at the major peaks. The results are compared to calculations based on a previous theoretical approach modified to include transitions to states of Hund's case (d) coupling. The reasonable agreement shows the predictive value of the theory. The theory has also been used to reassess and explain previous results and to understand variations in the rate of photodissociation with components of the*10p* and *11p* Rydberg states.

Lectures

L-1

Applications of chiral cavity ring down, and production of long-lived nuclear singlet states

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Sensing chirality is of fundamental importance to many fields. The most widely used methods for optical chiral sensing are the traditional methods of circular dichroism and optical rotation. However, these chiral signals are typically very weak, and their measurement is limited by larger time-dependent backgrounds (such as spurious birefringence) and by imperfect and slow subtraction procedures. We discuss proposals [1] and demonstrations [2] of a pulsed-laser bowtie-cavity-ringdown polarimeter with counter-propagating beams, which solves these background problems: the chiral signals are enhanced by the number of cavity passes (typically $>10^3$); the effects of linear birefringence are suppressed by a large induced intracavity Faraday rotation; and rapid signal reversals are effected by reversing the Faraday rotation and subtracting signals from the counter-propagating beams. These advantages allow measurements of absolute chiral signals in environments where background subtractions are not feasible. Specifically, we measure optical rotation from of (+)-α-pinene and (−)-α-pinene in open air, as well as from chiral liquids in the evanescent wave produced by total internal reflection at a prism surface. Evanescent-wave optical rotations of various (+)-maltodextrin and (−)-fructose solutions confirm the Drude-Condon model for Maxwell's equations in isotropic optically active media. We discuss the limits of this polarimeter for chiral sensing, and also the application to the measurement of parity nonconserving optical rotation in atomic gases [1,3,4].

On a separate topic, we also discuss a method for the production of nuclear singlet states, for polyatomic molecules with two nearly identical (but distinct) nuclear spins, such as for $^{15}N_2O$. The method is based on careful state-preparation in a molecular beam, followed by the hyperfine interaction between the molecular rotation and the nuclear spin, resulting quantum beats for a specific period of time, before ending the interaction by sticking the molecules to a cold surface [5,6]. Such long-lived singlet states have potential application for the enhancement of NMR signals.

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L-2

Polarization of nascent CO in photodissociation and inelastic scattering processes

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In this talk we describe preliminary results from our current velocity map imaging measurements of nascent CO arising from the photodissociation of CO_2 and COS in the vacuum ultraviolet, and of rotationally excited CO from crossed-beam scattering with Helium or Argon. We show that laser ionization in the vacuum ultraviolet is well-suited for CO detection in terms of overall sensitivity and in particular to the CO rotational angular momentum polarization. In both the photodissociation and scattering studies the simplest picture is that the angular momentum vector of CO is directed perpendicular to the scattering or half-collision recoil vector. We observe strong polarization effects in both systems, the angular momentum directionality revealed from these measurements is compared with the simple model prediction. For the He-CO inelastic scattering process *ab initio* theory calculations of the CO product angular momentum moments by Song and van der Avoird[1] will be compared with the imaging data. Results from similar studies of collision induced polarization in the NO-Ar system by, for example, Brouard *et al* [2] are described. For the photodissociation studies, comparison with theoretical predictions for product polarization following non-axial photodissociation by, for example, Kuznetsov et al, will be presented.

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L-3

Probabilities for 2-and 3-photon absorptions, ion pair channel (H^+ + Cl^-) in REMPI of HCl, and emission from metal surface of e^-, H^-, and HCl^- ions under the bombardment by H^+, Cl^+, and HCl^+ ions

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The main objective of the present study was to understand the mechanism of the ion pair formation channel in the resonance enhanced multi-photon ionization (REMPI) of HCl occuring in the spectral region from 230 to 245 nm. In order to study the process, a new "twin" three-dimensional (3D) imaging setup was constructed. The reconstructed set-up differs from the former versions primarily by the presence of two time-of-flight (TOF) spectrometers in the vacuum chamber, being the mirror reflection one of another and having common symmetry axis, two detectors and the centered pulsed nozzle. As a result, both positive and negative ions can be observed, both separately and simultaneously.

The HCl ion-pair photodissociation mechanism is assumed to be

$$\mathrm{HCl}\,(X^1\Sigma^+) \xrightarrow{2h\nu} \mathrm{HCl}^*(\mathrm{IS}_1) \xrightarrow{h\nu} \mathrm{HCl}^{**}(\mathrm{IS}_2) \rightarrow \mathrm{HCl}^{**}(V^1\Sigma^+) \rightarrow \mathrm{H}^+ + \mathrm{Cl}^-.$$

In the present work, the 3D velocity distributions of Cl^- ions are registered via excitation of intermediate states $IS_1 = V^1\Sigma^+(v=8\text{-}15,\ J=0)$, $E^1\Sigma^+(v=0,1,\ J=0)$, and $g^3\Sigma^-(0+, v=0,\ J=0)$ states. In all cases, the speed distributions, β parameters of anisotropy, and the dependencies of [Cl^-] vs squared laser intensity ($\langle I_2 \rangle$) were determined. Such dependencies were obtained for the H^+, HCl^+, and Cl^+ ions also. All observed β parameters are close to 2, indicating the symmetry of the second intermediate state IS_2 to be $^1\Sigma^+$.

The analysis of this mechanism consists of comparison between the results of quantum chemical *ab initio* modeling of the processes and experimental two-photon and three-photon absorption cross-sections. Determination of these cross-sections includes theoretical description and experimental measurements. The theoretical analysis gives us detailed expressions for the proportionality factors P_2 and P_3 in the expressions $N(Cl^-)=P_2E^2$ and $N(Cl^-) =P_3E^3$, where $N(Cl^-)$ denotes amount of the Cl^- ions, and E is the laser radiation power.

In the analysis of our detection system we found an interesting subject: the secondary electron and negative-ion emission from metal surface under the bombardment by positive ions (H^+, Cl^+, HCl^+). Absolute values for secondary electron and negative ion (HCl^-, H^-) yields resulting from positive ions impacting steel wire have been measured as a function of kinetic energy of the positive ions (200--750 eV). The experiment allows to measure the probabilities of both the forward and the backward scattering. The information on the angular distributions of the ions was obtained from TOF profiles of the secondary negative particles. It was found that diatomic ion HCl^+ produces HCl^- more efficiently than atomic ions H^+ and Cl^+ produce H^- and Cl^- respectively. The TOF profile of HCl^- consists of one broad and one strong sharp structures, indicating unknown resonant process.

L-4

Laser-field-free three-dimensional molecular orientation

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Molecular alignment and orientation techniques based on laser technologies have been extensively studied over the last 15 years since the first experimental demonstration of the adiabatic molecular alignment with an intense nonresonant laser field [1,2]. Molecular alignment techniques are well established and used in many applications [3].

Nowadays, researchers are interested in the development of various molecular orientation techniques and their applications. Based on the theoretical proposal by Friedrich and Herschbach [4], our group has demonstrated both one- [5,6] and three-dimensional molecular orientation [7] with a linearly- and elliptically-polarized laser field, respectively, in the presence of a weak electrostatic field. After that, laser-field-free molecular orientation with combined electrostatic and rapidly-turned-off laser fields was proposed [8], and demonstrated [9] by rapidly turning off a nanosecond laser pulse at its peak intensity with the plasma shutter technique. On the other hand, all-optical molecular orientation with intense nonresonant two-color laser field was proposed [10], and demonstrated [11]. The research and development of molecular orientation techniques is becoming more and more active.

Recently, we have achieved laser-field-free orientation of state-selected asymmetric top iodobenzene molecules with higher degrees of orientation with combined electrostatic and shaped laser fields with a slow turn on and rapid turn off [12]. We find that higher degrees of orientation is maintained in the laser-field-free condition for 5-10 ps, which is long enough to study electronic stereodynamics in molecules with femtosecond pulses [13], after the rapid turn off of the laser pulse. After that, with combined weak electrostatic and elliptically polarized shaped laser fields with a 6-ns turn off and a 150-fs turn off, we have also achieved laser-field-free three-dimensional orientation of state-selected asymmetric top 3,4-dibromothiophane molecules with higher degrees of orientation. It is confirmed that higher degrees of orientation are maintained for ~5 ps. Three-dimensional molecular orientation means the perfect control of spatial directions of asymmetric top molecules.

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L-5

The modified Quasi-Quantum Treatment of rotationally inelastic NO(X)-He scattering

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A Modified Quasi-Quantum Treatment (MQQT) of the rotationally inelastic scattering problem has been developed to improve on the so-called Regular QQT (RQQT), in which the potential energy surface (PES) $V(R,\gamma_R)$ is replaced by its hard shell contour $V(R,\gamma_R)=E_{col}$. The MQQT presented here overcomes the limitations imposed by a single contour PES. It is replaced by $V(R,\gamma_R)=E_{col}\cdot\cos^2\beta$, so that the potential is equal to the collision energy E_{col} provided by the component of the incoming momentum vector ***k*** directed anti parallel to the shell surface normal ***n***. Consequently the component of ***k*** parallel to the shell surface at the moment of impact remains conserved and the full range $0\le V(R,\gamma_R)\le E_{col}$ of repulsive PES contours is taken into account. The MQQT rotationally inelastic state-to-state DCSs and ICSs of He + NO(X) at $E_{col}=508\ cm^{-1}$ have been compared with those resulting from RQQT and from numerically exact QM calculations. The MQQT DCSs resemble the QM DCSs more closely than the RQQT DCSs for $j'\le 5.5$ up to a scattering angle of $\theta\approx 60°$. The MQQT and RQQT inelastic DCSs are quite similar for all other inelastic transitions and θ ranges. These results have been attributed to the specifics of the anisotropic Legendre expansion coefficients $C_n(\cos\beta)$ of the contours of the He + NO(X) V_{sum} PES. In the particular case for which the bond length or geometry of a molecular collider changes with the proximity of the collision partner due to charge transfer, the short range anisotropic terms will depend strongly onto the intermolecular distance, which can be accounted for by MQQT but not by RQQT.

L-6

A stereodynamical perspective on Arrhenius equation

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Chemists for a long time have recognized that energy is not the only factor affecting the rate of chemical reaction and the branching ratios to product channels.[1] The steric factor may be such a factor as we traditionally describe in Arrhenius equation 1.

$$k = \rho Z \exp(-E_a/RT) \qquad (1)$$

where ρ is the steric factor, Z the collision frequency, E_a activation energy, R the gas constant, and T is the absolute temperature.

At the molecular level, we find, for instance, an experimental example on the electron transfer in the $K+CF_3Br \rightarrow KBr+CF_3$ reaction.[2] As for more complex four-center reactions of the type AB+CD, stereodynamical understanding due to collisional geometry becomes more versatile and interesting.[3-5] For instance, the potential energy surface of the $HCl + OH \rightarrow Cl+H_2O$ reaction, which involves a relatively deep pre-barrier van der Waals well, leads to unexpected pathways that involve strong reorientation of the reagents. The quasi-classical trajectory method suggests that for the previous process, the traditional "cone of acceptance" picture of the steric effect is no longer valid.[3] For clarifying such stereodynamical aspects, experimental studies under the control of reactant mutual orientations with the aid of theory are necessary.

As for common macroscopic understanding of chemical reactions such as overall reaction rates and their temperature dependence, there must be some manifestation even there of the steric effect which we have observed at the molecular level.[6] In this talk, we explore and try to find out any link between the microscopic and macroscopic view for understanding stereodynamical behaviors in chemical reactions. It is expected that such comparison regarding especially based on the link of these views would lead us a novel aspect of reaction dynamics.[7]

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L-7

Nonadiabatic dynamics in polyatomic molecules by femtosecond time-resolved photoelectron imaging

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Using femtosecond time-resolved mass spectrometry (fs-MS), photofragment imaging (fs-PFI), and photoelectron imaging (fs-PEI), we have studied the non-adabatic dynamics of some polyatomic molecules. Work focus on fs-PEI with the aim to track the temporal populations of relevant optically bright and dark states populated and depopulated by ultrafast non-radiative transitions via conical intersections. The followings are some examples of research works.

The laser induced predissociation dynamics of the *B* Rydberg state of CH_3I following two-photon absorption of a pump pulse was studied. The predissociation lifetime was measured to be 1.55 ps induced by the crossing between the *B* state and the repulsive *A*-band. Two possible predissociation channels were observed originating from (a) direct coupling between the *B* state and the repulsive $^3Q_0$ state and (b) a second crossing between the $^3Q_0$ and $^1Q_1$ states after the coupling between the *B* and $^3Q_0$ states, respectively.

The electron dephasing mechanism of S_1 (B_2) state of *p*-bromofluorobenzene is determined to be the intersystem crossing (ISC) from the S_1 (B_2) to the T_1 (B_2) state and predissociation S_1 (B_2) *via* T_1 (B_1) state. The lifetime of S_1 (B_2) and T_1 (B_2) is determined to be 40ps and 33ps from the decay of the photoelectron signal.

The intramolecular vibrational energy redistribution (IVR) induced by a Fermi resonance in the S_1 low energy regime of *p*-difluorobenzene has been experimentally observed for the first time. The corresponding photoelectron angular distributions (PADs) clearly reflect each Fermi component character of the resonance $5^1 \cdots 6^2$. The oscillation period for the IVR is estimated to be less than 20 ps.

Nonadiabatic alignment of the asymmetric molecule on excited state by femtosecond laser pulse was observed on real time via time-resolved photoelectron angular distributions (TRPAD). Surprisingly, the molecular-axis alignment revival at as long as 296 ps of S_1 o-dichlorobenzene was observed.

Combining the merits of the femtosecond and nanosecond lasers, we use a pump-control-probe scheme to investigate and control the nonadiabatic process in polyatomic molecules. The femtosecond lasers work as the pump and control pulses, and nanosecond laser as the probe beam to detect the products with REMPI scheme. Now, by introducing AC Stark shift with an IR fs laser as the control beam, we have succeed in controlling the branching ratio of iodine atoms from the photodissociation of iodobenzene.

L-8

Steric aspects of gas-liquid interfacial collisions

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Building on our earlier work on the fundamental mechanisms of collisions of gas-phase radicals with model hydrocarbon liquid and related surfaces, we are developing selective reactions of gas-phase projectiles as a new method to determine the composition and structure of the extreme outer layers of ionic liquids. The properties of these materials can be varied selectively by modifying the structure of the typically large organic cation and by pairing it with a wide range of anions. In many of their potential applications as "green" solvents in, for example, multiphase catalysis and gas separation, the composition of the ionic-liquid surface layer is crucial.

We use complementary experimental approaches based on either laser photolysis or laser detonation to produce $O(^3P)$ atoms with medium[1] or high[2] kinetic energies, respectively. In the medium-energy experiments, the relative yields, internal state distributions and translational energies of the nascent OH products that escape the surface are characterized by laser-induced fluorescence. In the high-energy experiments, mass spectrometric detection provides highly resolved kinetic energy and angular scattering distributions of the reactive OH and other potential products and of inelastically scattered O atoms.

These experiments yield both fundamental insight into the stereodynamics of the collisions and detailed information on the composition and organization of the liquid surface. We are able to quantify, in particular, the extent to which alkyl chains on the organic cation are exposed to attack by the incoming atoms. We have investigated systematically the family of liquids based on 1-alkyl-3-methylimidazolium cations. A very non-linear increase in fractional surface coverage is observed with increasing alkyl chainlength. More subtle changes as a function of the identity of the anion are detected with high sensitivity. Smaller, compact anions allow more efficient, cooperative packing of cationic alkyl chains. However, comparative OH yields from a reference pure hydrocarbon liquid and the dynamical attributes of the reactive product OH and inelastically scattered $O(^3P)$ atoms all point to incomplete surface coverage for alkyl chains up to C_{12}.

The interpretation of the experiments is enhanced by comparison with molecular-dynamics simulations of liquid-surface structures and on-going QM/MM scattering calculations.

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L-9

The role of vibrational symmetry and alignment in the dissociative chemisorption of methane on nickel

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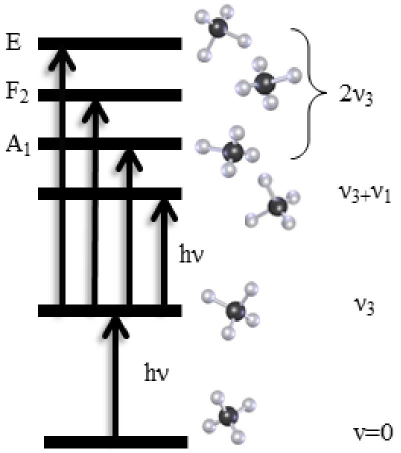
Quantum state resolved reactivity measurements have been performed to probe the role of vibrational symmetry and alignment on the dissociative chemisorption of CH_4 on Ni(111). IR-IR double resonance excitation in a molecular beam is used to prepare CH_4 in all three different vibrational symmetry components A_1, E, and F_2 of the $2\nu_3$ antisymmetric stretch overtone vibration, and in the $\nu_1+\nu_3$ combination band. Carbon atoms on the Ni(111) surface are detected via Auger electron spectroscopy as the products of the dissociative chemisorption at a surface temperature of 475K. We observe strong mode specificity for the prepared vibrational states, which can be related to the differences in the localization of the C-H stretch amplitude in each state.



Schematic energy level diagram for the double resonance transitions used in the current study

We also explore the role that the vibrational alignment has on the reactivity of CH_4 for the overtone and combination bands considered above, building on previous work investigating the effect for single resonance excitation [1,2]. By rotating the linear polarization of the IR excitation, the C-H stretch amplitude can be prepared to be either parallel or perpendicular to the plane of the surface. A significant vibrational alignment dependence is observed for the E and F_2 vibrational symmetries, whereas no alignment effect is seen for the totally symmetric A_1 vibration, and the $\nu_1+\nu_3$ combination band. The alignment effects for the E and F_2 symmetries are seen to be opposite, with the E symmetry being the most reactive when the laser polarization is perpendicular to the surface, and the F_2 symmetry when the laser polarization is parallel to the surface.

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L-10

Crossed-beam inelastic scattering experiments at energies approaching the cold regime

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I will present recent results in the study of inelastic scattering at collision energies approaching the cold regime, defined by temperatures below 1 K. Theoretical calculations predict that the dynamics of rotational energy transfer to small molecules, such as CO or O_2, by collisions with H_2, is dominated by quantum resonances, which can only be revealed at very low energies. Their experimental observation provides a stringent test for theoretical models.

Experiments were performed using a crossed molecular beam apparatus with variable intersection angle and cryogenically cooled fast-pulsed valves. The integral cross sections (ICS) were determined as a function of the relative translational energy down to a few wavenumbers, below the thresholds of the $\{j = 0 - 1\}$ CO transition at 3.85 cm^{-1} and the $\{(N = 1; j = 0) - (N = 1; j = 1)\}$ O_2 transition at 3.96 cm^{-1}. The experimental ICS exhibit behaviors characteristic of resonances and are compared to quantum mechanical scattering calculations. The results obtained for $O_2 + H_2$ show that this $\{(N = 1; j = 0) - (N = 1; j = 1)\}$ collision-induced transition, which is classically forbidden, occurs exclusively in a pure quantum regime *via* shape and Feshbach resonances arising from definite partial waves [1]. The complete assignment of the observed resonances is allowed by the very good agreement between experimental and theoretical ICS. An excellent agreement between experimental ICS for CO + *para*-H_2 and theoretical ICS calculated with a recent potential energy surface (PES) [2] is also obtained. This PES was also used for comparison with our recent experimental studies of inelastic scattering of CO with *normal*-H_2, *ortho*-D_2 and *normal*-D_2.

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L-11

Crossed-beam reactions of C_nH (n = 1 – 6) radicals with propyne

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Carbon is the fourth most abundant element in our solar system and in the universe. Hydrocarbon chemistry plays an important role in planetary atmospheres, interstellar environments, and fuel combustions. Thus, the study of dynamics of hydrocarbon reactions can facilitate the understanding of stellar evolution, air pollution, *etc*. A crossed molecular-beam apparatus combined with synchrotron vacuum-ultraviolet ionization has been demonstrated to be a powerful tool in the investigation of dynamics of elementary chemical reactions [1]. Recently, we have explored the dynamics of C/H and C/X exchanges in the reactions of ^{3}P carbon atoms with ethene (C_2H_4) [2], vinyl fluoride (C_2H_3F) [3], vinyl chloride (C_2H_3Cl) [4], and propene (C_3H_6) [5] using the crossed molecular-beam apparatus established at *NSRRC*; X = F, Cl or CH_3. The success encourages us to investigate the reactions of hydrocarbon radicals (e.g., CH, C_2H, C_3H, C_4H, C_5H, and C_6H) with unsaturated hydrocarbons (e.g. C_3H_4). Those free radicals were produced from a mixture of 1% ethyne (C_2H_2) seeded in He by pulsed high-voltage discharge [6]. We will present some of the experimental results of the reactions of C_nH (n = 1 – 6) radicals with propyne (C_3H_4) leading to product $C_{n+3}H_4$ + H. The mechanisms of production of methylpolyynes were investigated by interrogating translational-energy distributions, angular distributions, and photoionization spectra of products $C_{n+3}H_4$. Furthermore, the potential-energy surfaces of reactions $C_nH + C_3H_4 \rightarrow C_{n+3}H_4 + H$ were established with *ab-initio* methods. The combination of crossed-beam experiments and quantum-chemical calculations gives an outline for the mechanisms of reactions of C_nH radicals with propyne.

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L-12

What is wrong with the conventional Born-Oppenheimer approach for collision processes and how to handle it?

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The Born-Oppenheimer approach is the most widely used approach in theoretical studies of different reactions including collision processes. The approach treats a process in two steps: (i) a quantum-chemical treatment of electrons at fixed nuclei, and (ii) a nuclear dynamical study based on fixed-nuclei potentials and nonadiabatic couplings. Nowadays quantum-chemical calculations can be performed with high accuracy by means of well developed theoretical methods and computer codes, and this give a challenge to a (nonadiabatic) nuclear dynamical treatment with the same level of accuracy. For bound molecules the Born-Oppenheimer approach has been proved to provide accurate results, but in studying collision processes one faces a paradoxical situation: An approximate study, e.g., a model study, might yield reasonable results, but an accurate calculations based on high-accurate quantum-chemical data might lead to unphysical results such as infinite inelastic cross sections.

The matter of the fact is that although the conventional applications of the Born-Oppenheimer approach looks straightforward, it encounters severe difficulties. The problems are two-fold: (i) Many nonadiabatic couplings remain nonzero in the asymptotic region (where the internuclear distance goes to infinity) and this is a fundamental feature of the Born-Oppenheimer approach; and (ii) the Born-Oppenheimer asymptotic nuclear wave functions (expressed via exponential, sine and cosine, or Bessel functions depending on the internuclear distance) are not correct. This results in nonadiabatic transitions between molecular states at arbitrary large internuclear distances and at all total angular momentum quantum numbers. Finally, this leads to divergences of inelastic cross sections.

The situation can be handled by the reprojection method [1-4] which will be presented at the conference.

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L-13

Molecular collisions coming into focus

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Molecular scattering processes play an important role in the interstellar medium, atmospheres and combustion. To fully understand these processes, accurate theoretical models are required, which have to be tested extensively. In this joint experimental and theoretical project, high resolution scattering experiments are used to test the quality of state-of-the-art theory.

Experimentally, a Stark decelerator is used to form a beam of state-selected and velocity-controlled NO molecules to study collisions of these radicals with He, Ne and Ar atoms in the gas phase. The resulting state-to-state differential cross sections are measured using velocity map imaging. The narrow velocity distribution of the NO beam results in an unprecedented resolution in the scattering images and the corresponding cross sections [1]. In this way, we can fully resolve quantum diffraction oscillations, as shown in Figure 1 for collisions between NO and Ne.

Quantum close-coupling scattering calculations are performed using different intermolecular potential energy surfaces. The resulting differential cross sections are compared to experimental data and they are in excellent agreement with each other. The observation of the rapid diffraction oscillations provides a sensitive test for the accuracy of the potentials used.

Calculations have shown that, especially at low collision energies, scattering resonances – due to quantum interference effects – occur, which result in peaks in collision cross sections. Experimentally, it is challenging to reach these low collision energies and to obtain the extremely high energy resolution that is required to resolve these resonances. In the future, the combination of Stark deceleration and velocity map imaging will be used to overcome these problems and to study how scattering resonances affect the angular distributions of the scattered molecules. This will provide additional information on the quantum character of molecular collisions and it will be an excellent test for the quality of the potential energy surfaces used in the calculations.

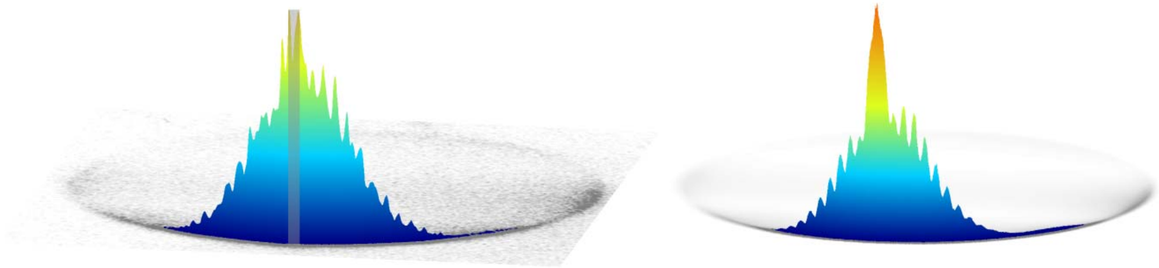

Figure 1. Experimental (left) and simulated (right) three-dimensional representations of the angular scattering distribution for NO radicals scattered with Ne atoms, showing diffraction oscillations. The simulation is based on a theoretical prediction of the differential cross section.

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L-14

Zeeman relaxation in cold atomic collisions: probing the interaction anisotropy

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Degeneracy of magnetic sublevels in isotropic space makes the experimental study of the orientation and alignment effects in atomic collisions difficult. External magnetic field allows one to discriminate magnetic sublevels in energy, but Zeeman splitting is normally small comparing to thermal collision energy or its spread. However, at low temperatures the situation reverses. Cold collisions in magnetic field can be therefore used to probe the cross sections of the transitions *inelastic* in the magnetic quantum number and, in turn, underlying effects of interatomic interaction anisotropy, the same as stipulate orientation and alignment in free space. In particular, collision-induced Zeeman relaxation of the low-field seeking magnetic states is the dominant source of losses in the buffer gas loading into the magnetic trap. Measurements of the relaxation rates supplemented by thorough theoretical analysis greatly enhance our understanding of the nature of interaction anisotropy for different open-shell atoms.

In the non-relativistic picture, the only source of interaction anisotropy is the orbital electronic angular momentum, which introduces the dependence of interatomic interaction potential matrix elements on its projection onto the collision axis. The next important effect is represented by the vectorial spin-orbit (SO) coupling. The first-order (intra-multiplet) SO coupling rearranges the magnetic sublevels according to the total (orbital plus spin) electronic angular momentum *J* eventually suppressing the interaction anisotropy for some *J* levels. For instance, an atom in the $^2P_{1/2}$ level interacts with the He atom isotropically, whereas anisotropic interaction takes place for the same atom in the $^2P_{3/2}$ level. Previous and recent experiments with the Al, Ga and In atoms at the temperatures close to or below 1 K [1] provide clear indication of the suppressed Zeeman relaxation in the ground $^2P_{1/2}$ level, in full accord with the theoretical predictions based on the rigorous quantum scattering calculations with accurate *ab initio* interaction potentials. By contrast, the second-order (inter-multiplet) SO coupling may induce the interaction anisotropy. This is the case for the atoms in S state with the spin $S > 1/2$ interacting with excited states of P symmetry. SO interaction effectively “transfers” excited-state anisotropy to the ground state. An example is the pnictogen atoms (N-Bi) in their $^4S^o$ states. For heavy Sb-He and Bi-He collision complexes with very strong SO coupling, theoretical calculations predicted large interaction anisotropy – the splitting of the ground $^4\Sigma^-$ state into $\Omega = 1/2$ and 3/2 components [2]. It largely enhances Zeeman relaxation making magnetic trapping hardly possible. The measurements fully confirmed this prediction.

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L-15

Magnetic Resonance of Single Molecular, Single Defect Spins

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Magnetic-resonance of single molecules, single defects represent the final limit in sensitivity of electron paramagnetic resonance (EPR) - the detection of a single spin. This sensitivity is reached by combining single molecule, single defect spectroscopy and optically detected magnetic resonance (ODMR). ODMR is a "trigger detection" in that the absorption of a resonance microwave photon triggers a change in emission of an optical photon. The detection of photons is thus displaced from the microwave domain to the far more sensitive optical domain. Two independently working groups performed the first magnetic-resonance experiments on single molecules (pentacene) embedded in a host crystal and demonstrated that the sensitivity of ODMR is limited only by the spin-dependent photophysical properties of the system under study [Koehler et al., Wrachtrup et al., Nature, 1993].

The nitrogen–vacancy (NV) defects in diamond have wonderful properties which make it the pet subject of modern research and applications. NV defect consisting of a nitrogen atom (N) and a vacancy (V) in adjacent lattice sites is the only known solid-state system where there exist possibility of detecting and manipulating the spin states (S = 1) of a single localized electron at room temperature [Gruber et al., Science, 1997]. Coupling between the NV and N spins in NV –N pair due to a cross-relaxation gives rise to new possibilities for spin manipulation. Paramagnetic defects in diamond and nanodiamonds open up an avenue to practical quantum computing.

The unique quantum properties of the nitrogen–vacancy defect in diamond have motivated efforts to find defects with similar properties in silicon carbide (SiC), which is a material with highly developed device technologies and can extend the functionality of such systems not available to the diamond. Depending on the defect type, temperature, SiC polytype, and crystalline position, two opposite schemes have been observed for the optical alignment of the ground state spin sublevels population of the Si-vacancy related defects upon irradiation with unpolarized light [Baranov et al., PRB, 2011]. Optically induced spin polarization of the ground-state spin sublevels (S = 3/2) of a family of Si-vacancy related defects in SiC has been shown to persist up to the room temperature and spin ensemble can be prepared in a long-lived coherent superposition of the spin states at room temperature. Optically detected magnetic resonance shows the possibility to manipulate of the ground state spin population by applying radiofrequency field. The unique properties of the defects make them a promising quantum system for single-defect and single-photon spectroscopy in the infrared region. These properties can be used to implement high-power masers and low-noise radio-frequency amplifiers with optical or electrical pumping [Kraus, Soltamov, et al., Nature Physics, 2013]. SiC light-emitting diode is shown to be a perspective room temperature source of single photons and electrically driven alignment of the ground state spin sublevels with inverse population at room temperature. As these defects can potentially be generated at a low or even single defect level, electrically driven single photon source for quantum telecommunication and information processing can be realized.

These altogether make the Si-vacancy related defects in SiC very favourable candidate for spintronics, quantum optics, quantum information processing, nanoscale magnetometry, biolabelling.

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L-16

Achieving and probing quantum coherent control of the lifetime of a resonance state with laser pulses

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Quantum coherent control of the lifetime of a specific target resonance state has been recently achieved by creating a coherent superposition of resonances overlapping with the target resonance [1-3]. Such a superposition is prepared by using one [1], two [2,3], or even three [3] pump laser pulses. The control scheme is based on exploiting the interference effects that occur between overlapping resonances that are excited simultaneously [1]. Performance of the control schemes is illustrated by three-dimensional wave packet simulations of resonance decay in the Br_2(B)-Ne complex. More specifically, in the simplest case of preparing a superposition of only two overlapping resonances by exciting each resonance with a different pump pulse, enhancement of the lifetime of the target resonance by a factor of three is achieved when the amplitude ratio and the time delay between the two pulses is varied [2]. A most relevant aspect of the above control schemes is their experimental realization, and this point has been investigated by carrying out simulations applying an experimentally realistic and feasible time-resolved pump-probe scheme [4]. Such simulations show that indeed experimental detection of the signature and effects of control on the survival probability of the target resonance is possible by selective resonant excitation with the probe laser pulse.

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L-17

Anionic Helium Species in He Clusters: Size Dependent Arrangements

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We present variational calculations (T=0 K) on small $He_N...He^{*-}$ and $He_N...He_2^{*-}$ metastable clusters ($N\leq4$), as well as Path Integral Monte Carlo simulations (T=0.4 K) on larger species. They have been carried out assuming additive parwise-like potential surfaces. The underlying $He(^1S)$-$He^{*-}(^4P)$ potential curve and the $He(^1S)$-$He_2^{*-}(^4\Pi_g)$ anisotropic interaction have been recently estimated through accurate CCSD(T) calculations[1], while the He-He interaction is described by a Aziz-Slaman semiempirical potential[2].

For the atomic anion case, the interaction with helium presents a deep well near 1 Å followed by a small barrier and then a shallow minimum, see left panel in Figure 1. Accordingly, as He atoms are added, a marked preference to form a bi-pyramid charged core He_7^-, with the rest of He atoms surrounding it, is observed (right panel in that figure). In turn, the molecular anion He_2^{*-}, considered as a rigid rotor, tends to point towards a set of packed helium atoms which are placed at long distance from the anion.

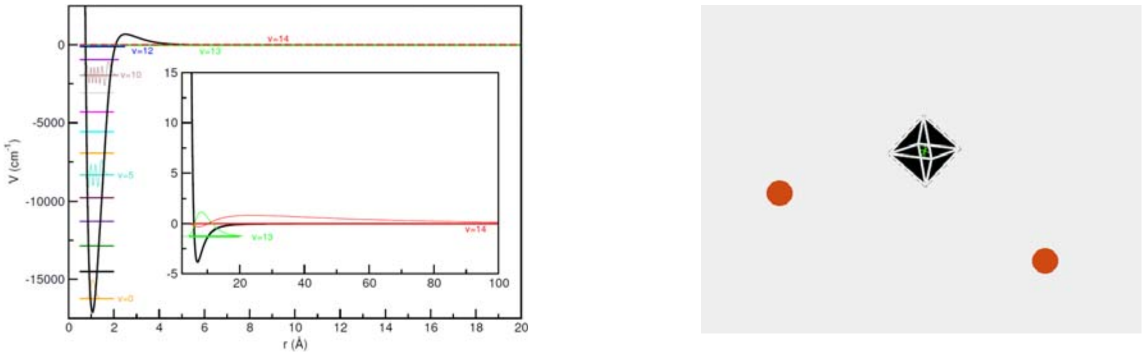

Figure 1. He-He^{*-} potential curve supporting 15 bound states, the last two ones being depicted in the inset (left panel), and structure of $(He)_8$-He^{*-} cluster as predicted by a genetic algorithm (right panel).

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L-18

Electronic dynamics of molecules and solutions studied by photoelectron spectroscopy

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We present results of time- and angle resolved photoemission spectroscopy applied to aqueous solutions and a new strategy to investigate electronic structure of molecules.

I. Liquid water is indispensable for life, and the intriguing properties and dynamics of liquid water due to strong hydrogen bonding of great interest. The electronic structure of liquid water is regarded as a wide-gap semiconductor, in which an electron can be trapped in the forbidden band assisted by reorganization of hydrogen bonding around the electron. The electron binding energy (eBE) of this trapped state (a hydrated electron) is 3.4 eV with respect to the vacuum level. In addition to a hydrated electron in bulk water, it has been speculated that an electron is also trapped on the surface of water. Our results indicate that photoemission from the ground state of a hydrated electron at 260 nm is found to be isotropic, while anisotropic photoemission is observed for the excited states of DABCO and I^- in aqueous solutions; and that surface and subsurface species create hydrated electrons in the bulk side [Fig. (I)]. No signature of a surface-bound electron has been observed [1].

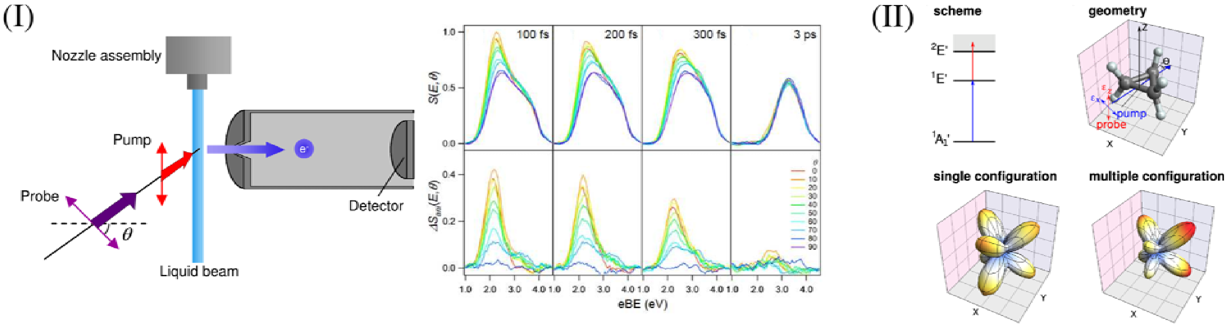

Figure. (I) Experimental setup and Photoelectron spectra of aqueous 0.5M DABCO solution as a function of the delay time and the polarization angle of the probe pulse θ with respect to the electron detection axis. (II) Excitation scheme of cyclopropane molecule and its molecular frame photoelectron angular distributions.

II. Inclusion of electron correlation is a major objective of the theory of molecular electronic structure and computational chemistry. However, few methods have been proposed to detect such a multi-electron effect. To find experimental observables that are sensitive to electron correlation, we focus on the geometrical aspect upon photoionization. The molecular orbitals and their symmetries are defined in the Hatree-Fock theory, but not in accurate theories. Photoionization processes depend on the orbital symmetry and the light polarization. We show that the symmetry of molecular frame photoelectron angular distributions can be broken due to the electron correlation [Fig. (II)], and there are signatures of electron correlation in the laboratory frame photoelectron angular distributions of aligned molecules.

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L-19

Potential barriers and multimode nature of the internal rotation in aromatic and heterocyclic molecules

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The large discrepancy of the potential barrier to internal rotation values of the benzaldehyde molecule within the experimental and quantum chemical approaches is analyzed on the basis of the *ab initio* potential energy surface calculations. The observed difference in 1.5-2 times is well known in literature for a large number of experimental and theoretical studies. The discrepancy seems be too stable to variations of the level of *ab initio* calculations to be ignored. The possible ways to understand the nature of this essential difference are presented here on the basis of the systematic study of some direct and inversed vibrational problems.

There exist at least two reasons for the difference mentioned. In our opinion a part of problems is closely connected with the assignment of some bands in experimental spectra of the torsion transitions of the benzaldehyde molecule, though there is no doubt in assignment of the fundamental torsion transition. This is resulted in instability of the inversed spectral problem when the experimental value of the potential barrier is estimated. The second essential problem is a result of the multimode nature of internal rotation that is usually ignored under solution of the traditional one-dimensional inverse problem. The multimode nature of the internal rotation means not only the complex form of the potential energy surface or the essential curvature of the "reaction path" of the torsion motion. The changes in the non-diagonal matrix elements of the kinematical energy also ensure strong correlations of vibrational mode for internal rotation and that one for non-planar distortion of the aldehyde CHO-group. The variational solution of the corresponding two-dimensional vibrational problem on the basis of *ab initio* potential energy surfaces gives excellent agreement of quantum chemical and experimental data for low lying vibrational energy levels.

Similar complex nature of the internal rotation was also found in a number of aromatic and heterocyclic aldehydes. The illustrations based on the non-empirical analysis of a series of substituted benzaldehydes and heterocyclic aldehydes (furfural, thienaldehyde, selenophene carbaldehyde, tellurophene carbaldehyde, etc.) are presented.

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L-20

Singlet oxygen photogeneration from X-O_2 van der Waals complex. Double-spin flip vs. charge-transfer mechanism.

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Recently it was shown that UV-photoexcitation of van der Waals complexes is followed by the formation of oxygen in the first excited singlet state $O_2(^1\Delta_g)$ [1]. In the current work the mechanism of singlet oxygen photogeneration from a variety of van der Waals complexes X-O_2 is investigated experimentally with the use of velocity map imaging technique. In Figure 1 the images of $O(^3P_0)$ atom appearing after photoexcitation of several van der Waals complexes X-O_2 as well as of unbound O_2 are shown. The channels indicating formation of singlet oxygen are shown by the arrows.

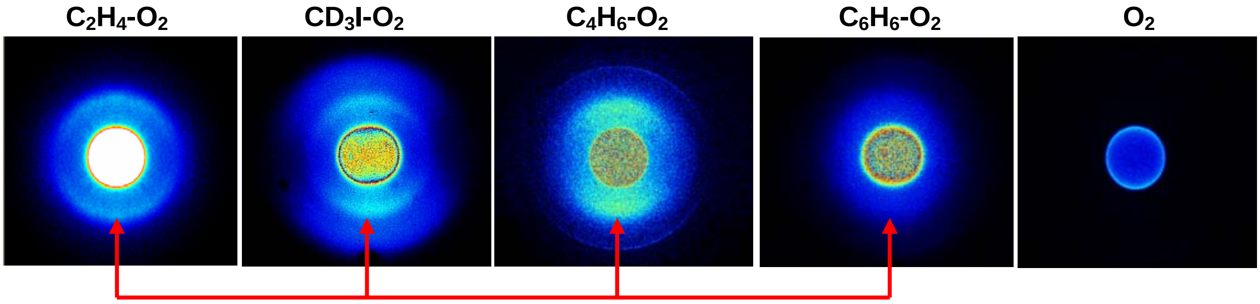

Figure 1.

The data obtained are considered via comparison of two possible mechanisms. One mechanism based on double-spin flip transition was suggested recently by Vidma et al. [1]. Another mechanism based on the charge-transfer (CT) transition was suggested earlier for "contact" complexes of oxygen X-O_2 in condensed phase by Scurlock and Ogilby [2].

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L-21

Discrete orthogonal transformations for Askey scheme polynomials

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This work presents discrete transforms that correspond to the discrete polynomials of the Askey Scheme. The Racah [1] and Hahn [2] transforms have been studied before, but the transforms corresponding to Krawtchouk, Gram, Meixner, and Charlier polynomials are new [3]. The transforms corresponding to Racah and Hahn polynomials have been shown to be important as discrete representations in quantum mechanical calculations, and historically as the transformations that connect different coupling schemes in quantum mechanics. We expect that the new transforms corresponding to Krawtchouk, Gram, Meixner, and Charlier polynomials will also have important applications. All of the transforms (including those for Racah and Hahn polynomials) can be easily obtained by diagonalization of a symmetric tridiagonal matrix, and they have the property that $\boldsymbol{U}^T\boldsymbol{U} = \boldsymbol{U}\boldsymbol{U}^T = \boldsymbol{I}$. For all of the transforms the classical and non-classical regions of the square screens are obtained. Discrete representations of Wigner *d* functions, Legendre polynomials, and anharmonic oscillator wave functions are found. A truncation procedure is used to obtain finite size square screens for Meixner and Charlier polynomials that have an infinite range for the *x* variable. Braun Potential functions provide important insight about the transforms and the accuracy of the truncation procedure. Some properties of symmetric tridiagonal matrices are used to find the desired transformations.

Here the transform are Rank 2 matrices where the columns and rows are the discrete values of a function with given discrete variable and order. These transforms form complete sets of discrete functions that have important applications in molecular quantum mechanics, data smoothing and compression. The connections of the transforms with the Askey scheme has been a goal for many years of Coletti, Aquilanti, and coworkers [see 4].

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L-22

Spectroscopy of cooperative laser electron-γ-nuclear processes in diatomic, multiatomic molecules and clusters

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In the modern molecular spectroscopy and dynamics it is intensively studied a new class of problems, connected with the cooperative laser-electron-γ-nuclear processes. It includes a calculation of the probabilities and energies of the mixed γ-optical transitions in molecules, intensities of the complicated γ-transitions due to the changing of the molecular excited state population due to the laser field effect. The first qualitative estimates of the cooperative effects parameters were earlier presented (see [1,2] and refs. therein). We present an advanced quantum approach to calculation of the electron-γ-transition spectra (e-vibration satellites) of nucleus in diatomics, multiatomic molecules and clusters , based on density functional (DF; one version) and model potential (second version) methods and energy approach [3]. Decay and excitation probability are linked with imaginary part of the molecule - field system. New data on the electron-nuclear γ-transition spectra of the nucleus in some multiatomics are presented for a number of molecules: 3-atomic XY_2 ($D_{\infty h}$), 4-atomic $XY_3(D_{3h})$, 5-atomic $XY_4(T_d)$, 7-atomic $XY_6(O_h)$ ones. As example, in figure 1 the theoretical emission (solid curve) and absorption spectrum of nucleus ^{127}I in H^{127}I is presented. In table 1 our data on probabilities of the first several vibrational-nuclear transitions in a case of the emission and absorption spectrum of ^{188}Os ($E^{(0)}_{\gamma}$= 155 keV) linked with molecule *OsO₄* are listed.

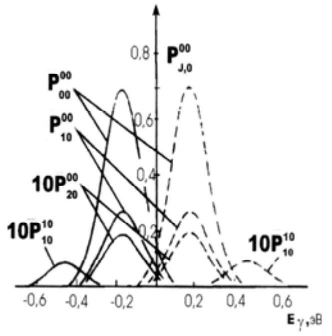

Figure 1. Emission and absorption spectrum of ^{127}I in H^{127}I (init. state: νa=0,

Table 1 . Probabilities of vibration-nuclear transitions for molecule OsO_4

Vibration transition	Probability
$v_3^a, v_4^a - v_3^b, v_4^b$	$\overline{P}(v_3^a, v_4^a - v_3^b, v_4^b)$
0,0 – 0,0	0.795
1,0 – 0,0	0.018
0,1 – 0,0	0.074
1,0 – 1,0	0.750
0,1 – 0,1	0.673

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Hot Topics

HT-1

Steric effects in collisions of NO(X) + Ar

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Inelastic scattering measurements have been made for collisions of oriented NO(X) with Ar using a crossed molecular beam apparatus coupled with velocity mapped ion imaging, for a selection of spin-orbit conserving and spin-orbit changing transitions. The initial state of the NO(X) was selected using a hexapole field and the final state by (1+1') REMPI, allowing full Λ-doublet resolution of both the initial and final quantum state. The bond axis of the NO molecule was oriented prior to the collision using a static electric field generated by a four rod setup. Fast switching between the orientation field and velocity mapping conditions is needed to be able to image the scattered NO after the collision [1].

The state to state oriented differential cross-sections for scattering of NO with Ar have been measured, building on previous work on the steric asymmetry [2-3]. Complementary quantum mechanical calculations have also been performed and the agreement between the experimental and theoretical differential cross-sections is good. The normalised difference between the two oriented DCSs varies with scattering angle, and can be qualitatively reproduced by model calculations that consider the interferences between four limiting scattering paths [4].

Preliminary measurements of the product rotational angular momentum alignment following collisions of oriented NO(X) with argon have also been performed experimentally. These measurements contain information about the "full" four vector correlation between the bond vector and relative momenta (or between rotational and relative momenta). The difference in the product rotational alignment for the two bond orientations is not as pronounced as for the oriented differential cross sections. The results obtained can be explained classically by considering a simple kinematic apse model, in which the projection of $\boldsymbol{j}$ onto the apse is conserved throughout the collision. Again, the polarisation parameters obtained from the experimental data are in good agreement with those obtained theoretically.

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HT-2

Hydrogen-Copper System Nonadiabatic Effects

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Dynamics of molecules in the vicinity of a surface has been studied extensively as it provides a platform to understand the intermediate steps in heterogeneous catalysis, gas-grain interactions in astronomical systems. Complexities that may be observed in experiments because of the different structures of the surface such as locally stepped, corrugated or disordered ones have been tried to solve by using well ordered surfaces. Molecules inherently have many degrees of freedom (DOF) and each of them would affect the experimental outcome in a different way. To identify the relative importance of DOF on the interaction we need to do quantum state resolved measurements. Even after considerable work by both experimentalists and theoreticians on relatively simpler systems - metal-hydrogen system – still the interaction theories are not complete. Many theoreticians have employed Born-Oppenheimer approximation in their work. Recently there has been experimentalists have questioned the validity of this approximation both directly and indirectly. Direct evidence is the observation of the chemicurrents (1) and the e- emission from a metal surface as vibrationally excited molecues are scattered (2) and the indirect evidence is the study of the vibrational relaxation of H_2 and D_2 on copper (3). Here we report scattering measurement on copper-hydrogen system and the questions that we try to answer are: (i) is the process adiabatic or not?, (ii) relative role of translational and vibrational energy and (iii) surface temperature dependence. Results suggest that the energy loss in the elastic scattering is a nonadiabatic process.

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HT-3

Predissociation of High-Lying Rydberg States of Molecular Iodine via Ion-Pair States

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The photodissociation of the two-photon excited molecular iodine in the energy range 73500-74500 cm^{-1} covering the bands of high-lying *gerade* Rydberg states $[^2\Pi_{1/2}]_c6d;0_g^+$ and $[^2\Pi_{1/2}]_c6d;2_g$ has been studied with velocity map imaging technique. The ion signal was dominated by the atomic fragment ion I^+. Up to 5 dissociation channels yielding I^+ ions with different kinetic energy were observed when the I_2 molecule was excited within discrete peaks of Rydberg states and their satellites in this region. One of these channels gives rise to images of I^+ and I^- ions with equal kinetic energy indicating predissociation of I_2 via ion-pair states. The contribution of this channel was up to about 50% of the total I^+ signal. The four other channels correspond to predissociation via lower lying Rydberg states giving rise to excited iodine atoms providing I^+ ions by subsequent one-photon ionization by the same laser pulse. The ratio of these channels varied from peak to peak in the spectrum but their total ionic signal was always much higher than the signal of (2+1) REMPI of I_2, which was previously considered to be the origin of ionic signal in this spectral range. The first-tier $E0_g^+$ and $D'2_g$ ion-pair states are concluded to be responsible for predissociation of Rydberg states $[^2\Pi_{1/2}]_c6d;0_g^+$ and $[^2\Pi_{1/2}]_c6d;2_g$, respectively. Further predissociation of these ion-pair states via lower lying Rydberg states gives rise to excited $I(5s^25p^46s^1)$ atoms responsible for major part of ion signal. The isotropic angular distribution of the photofragment recoil directions observed for all channels indicates that the studied Rydberg states are long-lived compared with the rotational period of the I_2 molecule (1).

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Poster Session

P-1

Photoelectron-photoion spectroscopy of $Xe.CF_4$, $Kr.CF_4$, and $Xe.SF_6$ vdW molecules

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This contribution reports on observation of $Xe.CF_4$, $Kr.CF_4$, and $Xe.SF_6$ vdW molecules and corresponding ions. Experiments were performed on the DESIRS beamline at SOLEIL [1]. The clusters were formed in a supersonic expansion and recorded using the DELICIOUS photoelectron-photoion coincidence spectrometer [2]. For all three studied vdW molecules the ionization potential was found ≈ 0.05 eV below that of the monomer (Xe or Kr atom). The threshold photoelectron spectrum of $Xe.CF_4$ is shown in Figure 1 as an example. The neutral clusters are assumed to be vibrationally cold and ionization takes place at the equilibrium geometry of the ground state. The part of $Xe.CF_4^+$ potential energy surface accessible for such vertical transitions may be significantly shifted from the $(Xe.CF_4)^+$ PES minimum. The experimental ionization energies may thus be considered as a lower bound estimate. The equilibrium geometry and dissociation energy of Rg.M ions (Rg=Kr, Xe; M=CF4, SF_6) may be obtained using *ab initio* methods. Some work in this direction is planned and results will be reported elsewhere.

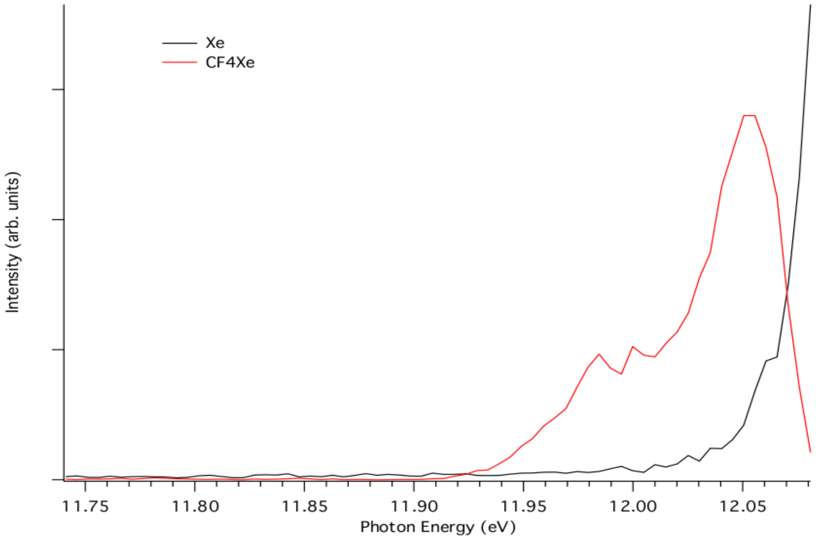

Figure 1. Threshold photoelectron spectra of $Xe.CF_4$ (red) and Xe (black). The total resolution is ≈ 17 meV.

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P-2

Ion-pair states of halogens and rare gas halides

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Molecules containing at least one fragment with positive electron affinity have ion-pair (IP) states diabatically dissociating onto two oppositely charged ions. Typically IP states are severely perturbed due to crossing with potentials of Rydberg and strongly repulsive valence states. Because of large electron affinity of halogen atom and absence of excited valence states (except spin-excited X $^2P_{1/2}$ state) halogens and rare gas halides are among very few molecules which have nonperturbed IP states. Aim of this contribution is to report a summary of recent *ab initio* studies of these molecules with an emphasis on the IP states..

Calculations were performed on the CASSCF/CASPT2 level with inclusion of the spin-orbit interaction. For rare gas halides calculations were performed for all 10 experimentally observed RgX/Rg_2X pairs. Because of bound-free character of optical transitions in the RgX molecules accurate spectroscopic constants of the IP states *B*, *C* and *D* are known only for very few molecules. Special attention was given to the lowest strongly bound $4^2\Gamma$ state of Rg_2X molecules. For this state we report $R_{Rg\text{-}Rg}$ and $R_{Rg\text{-}X}$ equilibrium bond lengths, dissociation energy, radiative lifetime and frequencies of three vibrational modes.

In contract to rare gas halides, IP states of halogens molecules are known with spectroscopic accuracy allowing a systematic comparison of *ab initio* results with experiment. As an example, Figure 1 compares IP potentials of the benchmark I_2 molecule. Results of a comparable accuracy have been obtained for other homo and heteronuclear halogens. Besides potentials, we also report dipole moment functions of some transitions between IP states, correlating to a common and different dissociation asymptotes. These dipole moment functions are of interest in the context of experimental studies of the amplified spontaneous emission effect on transitions between IP states.

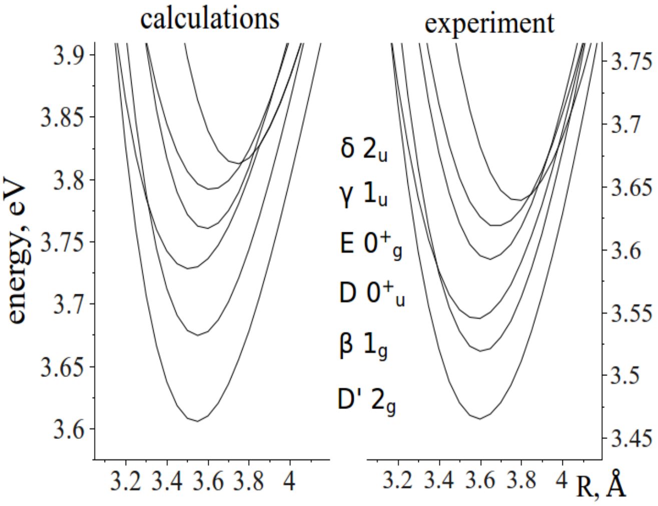

Figure 1. Comaprison of experimental and *ab initio* potentials of the I_2 molecule correlating with $I^+(^3P_2) + I^-(^1S_0)$. Position of the *D* 0^+_u is strongly affected by interaction with a high lying state correlating with $I^+(^1D_2) + I^-(^1S_0)$. The *D* 0^+_u state of Br_2 and Cl_2 is above *E* 0^+_g. The amplified spontaneous emission effect has been observed for the *E* → *D*, and γ → β transitions [3, 4].

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P-3

Fourier-transform spectroscopy of Xe/CF_4 mixtures in the Vac UV region

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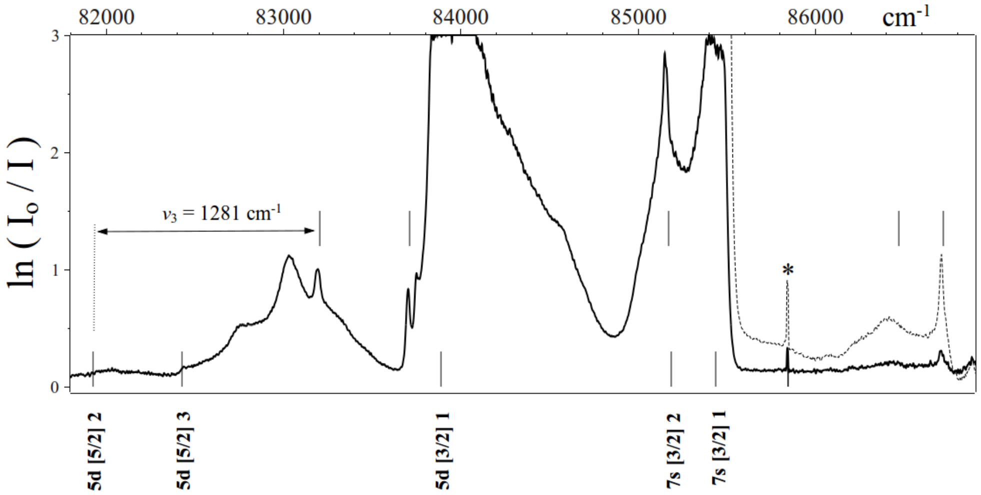
It has been reported that Vac UV spectra of Xe/CF_4 mixtures display collisional satellites induced by the IR active ν_3 mode of CF_4 [1]. The corresponding photoprocess may be written as follows $Xe(G) + CF_4(\nu_3=0) + h\nu \rightarrow Xe(DF) + CF_4(\nu_3=1)$,where *G* and *DF* denote respectively the ground and dipole-forbidden states of the Xe atom. The satellite energies are close to energies of the Xe(*DF*) states increased by ν_3 quantum energy.

In the present work the Xe+CF_4 system was studied using Vac UV Fourier-transform spectrometer on the DESIRS beamline at SOLEIL [2]. Spectra of the vibrationally induced satellite bands were recorded with high resolving power provided by this instrument. The studied region spanned from the first Xe resonance line at λ=146.9 nm and up to MgF_2 window cutoff at λ ~ 115 nm. An example of spectra showing collisionally broadened resonance transitions and vibrationally induced satellites is given below.



Absorption spectra in the region of the Xe 5*d*[3/2]$_1$ and the Xe 7*s*[3/2]$_1$ resonances: solid line - Xe (10 mbar) + CF_4 (1 bar), dotted line - Xe (75 mbar) + CF_4 (1 bar). The lower sticks mark the energy positions indicate energies of the Xe Rydberg states and the upper sticks indicate energies of these states increased by the ν_3 quantum energy. The feature marked by * is due to Kr admixture.

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P-4

Ab-initio modeling of an anion C_{60}^{-} pseudopotential for molecular dynamics purpose

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Fullerene-based compounds are often used as an acceptor [1, 2] in donor-acceptor composite with polymers in order to obtain volumetric heterojunction that is very effective for realization of organic solar photoelectric sell (OSPS). To search new promising compounds it is necessary to develop effective method of specification of geometry and stability of composite system, for example by means of molecular dynamics. As far as C_{60} acts as an acceptor in such systems, it is important to determine form of pseudopotential of anion C_{60}^{-}.

It is clear that pseudopotential of C_{60}^{-} could be presented as a sum of two summands: the potential of ion core, which depends on positions of 60 ions C^{4+}, determined by optimal geometry of object, and the potential created by electron density of 241 valence electrons. The shape of pseudopotential near the fullerene radius should depend significantly on electron density profile, thus, we have to estimate it accurately.

The recent calculations [3] showed that the application of simple and widely used jellium model doesn't bring data into accordance with results of more complicated but accurate *ab initio* calculations. Therefore in this paper we use *ab initio* approach to determine electron density profile. Figure 1 demonstrates the electron density profiles of valence electrons of C_{60} и C_{60}^{-} averaged over angles of spherical coordinate system. The Hartree-Fock method was used for self-consistent calculations in all three cases. As Fig.1 indicates, the results of *ab initio* calculations for fullerene and anion are close, but substantially differ from the results of jellium model calculations for C_{60}, which makes this approach non applicable to solving a problem of determination of C_{60}^{-} pseudopotential.

In present paper the pseudopotential of C_{60}^{-} anion has been simulated in terms of *ab initio* methods, in order to use this pseudopotential in molecular dynamics modeling.

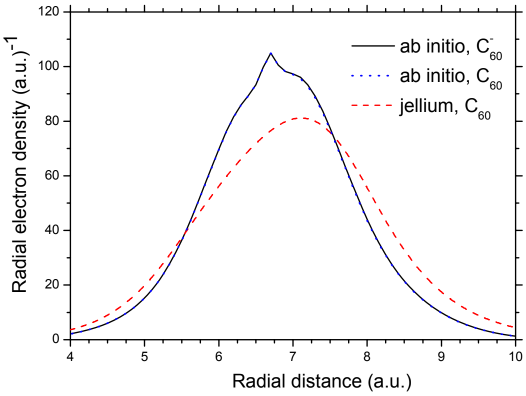

Figure1. Radial electron density of C_{60} and C_{60}^{-} calculated by ab-initio method and within the jellium model.

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P-5

Quantum mechanical modeling of electronic structure and photoabsorption of anion C_{60}^{-}

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Since the discovery of fullerene C_{60} researches of properties of carbonic clusters, their electronic structure and interaction with external fields attract much attention both experimentalists and theorists. High degree of symmetry of C_{60} and the arrangement of its molecular orbits create some special chemical and physical properties. C_{60} is good electron acceptor; its three-fold degenerate lowest valence orbit (1.5-2.0 eV above its top occupied valence state) enables reversible addition of up to six extra electrons [1, 2]. It's necessary to note that recombination of charge in such systems is slower than transfer of photoinduced electrons. That leads to relatively long-lived states with split charge. Because of this property donor-acceptor systems containing fullerenes were offered as models for photosynthesis and as systems for energy storage [3]. Thus the investigation of complex organic molecules containing fullerenes (which act as acceptor in compounds) and different functional groups is of a big interest.

Calculations of electronic structure and photoabsorption processes were held before using the simple models, for example the jellium model. Such calculations explain basic fullerene properties: its shell structure, photoabsorption cross-section behavior near the giant plasmon resonance. Yet the jellium model gives inaccurate result in description of ionization potential and fine structure near threshold of photoabsorption cross-section, while for study of optical response it's important to describe the absorption profile in boundary of visible and infrared spectrum highly accurate. Recently the calculations of structure and photoabsorption cross-section behavior of C_{60} were executed in terms of *ab initio* methods [4].

As far as C_{60} acts as an acceptor in complex organic molecules containing fullerenes and different functional groups, in order to study optical response of the system as whole in the present work we studied ion C_{60}^{-}. Ion calculations in terms of *ab initio* methods contain a number of complications (multiplicity of atoms, correct representation of extra charge). All calculations were made with *ab initio* quantum chemistry methods of electronic-structure calculation, using the Quantum ESPRESSO computer code package [5]. Calculations were based on the Density Functional Theory, plane wave basis sets, and pseudopotentials.

In present work we compare results of calculation obtained using different methods of representation of C_{60}^{-} ion, in order to select correct and less computer-intensive method. Besides we calculate optical response of C_{60}^{-} and compare it with optical response of neutral molecule.

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P-6

Chirality change in collisions: A hyperspherical approach

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Hydrogren peroxide, H2O2, and hydrogen persulphyde, H2S2, are among the simplest chiral molecules. The passage between the two mirror forms is due to the overcoming of a torsional barrier; for this reason they are also called *floppy molecules*. It is of particular interest inastrobiology and in the study of the origin of chiral discrimination (1). The hyperspherical harmonics expansion is a suitable method for the representation of the H2O2 – and H2S2 – raregas- atom interaction potentials (2-5): it ensures compactness, a full account of the symmetry of the system and its analytical expression is appropriate for applications in dynamics simulations.Classical trajectory simulations on the binary interaction floppy-molecule – rare-gas-atom unveil the importance of the molecular orientation in enantioselective collisional processes (6): as widely discussed, oriented chiral molecules show chiral effects although they do not interact with a chiral species (in this case the rare-gas-atom). Similar effects could be obtained in the interaction of chiral molecules with light, by using unpolarized lasers (non chiral) instead of circularly polarized lasers (chiral) (7).

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P-7

$(H_2O)_n$-O_2 complex, with n=1-2

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Molecular oxygen presents a challenge for the spectroscopists and it is the second most abundant component in the atmosphere. One can question if the association of O_2 with H_2O can interfere with the optical transition among several O_2 excited states. In this work, we present the $(H_2O)_n$-O_2 complexes for ground state and the lowest singlet and quintet state, with n=1-2. It will be discussed the interaction energy among several states of O_2 and $(H_2O)_n$ presented here. The calculation was performed using the MOLPRO code at CCSD(T)/aug-cc-pVTZ. All geometries are optimized at MP2(full)/aug-cc-pVTZ including the BSSE correction. The first observation is the O-O distance at the complex that keeps closeted to the distance of the O-O for each state considered here. The O-O distance from the one of the oxygen molecule in the O_2 molecule to the H_2O molecules are, also, close for all clusters.

	O_2			$(H_2O)_2$	$(H_2O)_3$	H_2O-O_2			$(H_2O)_2$-O_2		
	S	T	Q	S	S	S	T	Q	S	T	Q
OO	1.259	1.233	1.890			1.261	1.230	1.889	1.261	1.233	1.900
OO(H2O)				2.977	2.854	3.239	3.591	3.319	3.227	3.199	3.311
OO(H2O)					2.805				3.563	3.229	3.316
E_{int} [cm^{-1}]				20.140	43.871	5.939	3.651	94.147	11.205	86.629	112.796

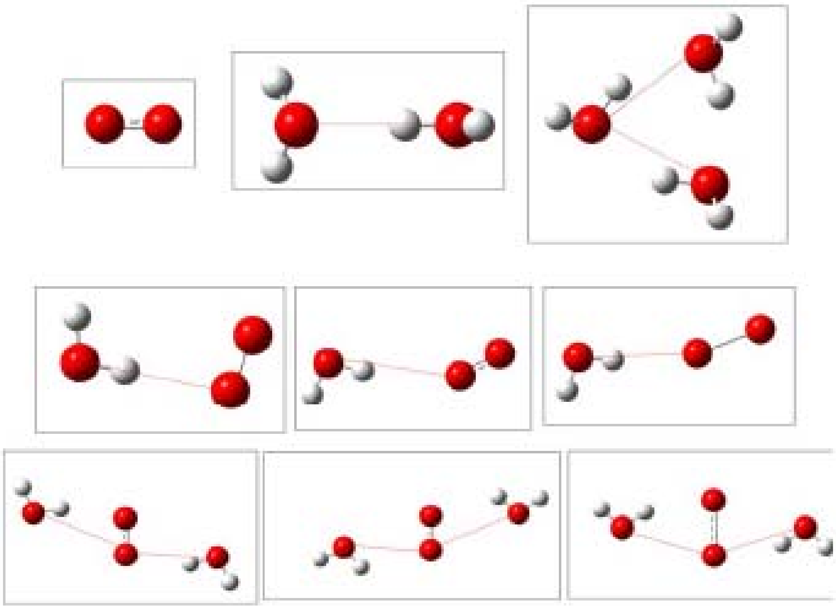

Figura 1: $(H_2O)_n$-O_2 Clusters, with n=1,2

P-8

Fragmentation of biologically significant molecules at their collisions with ions.

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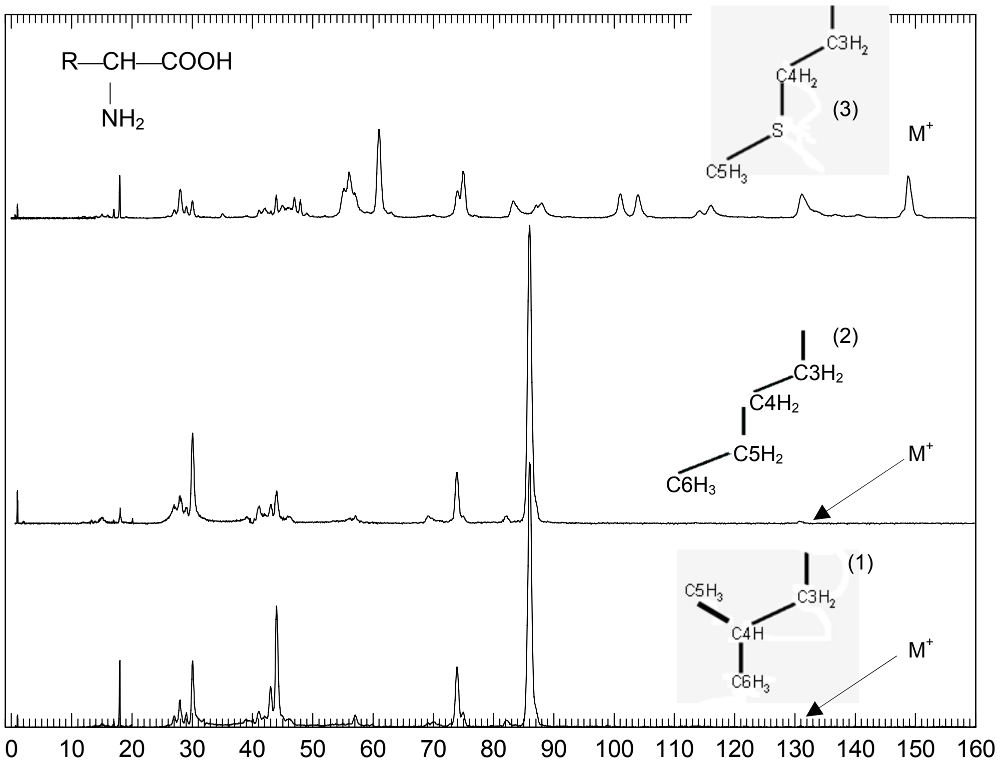
Fragmentation processes of molecules of some organic species including α-amino acids have been studied at one electron capture processes in collisions of single target molecule with different keV-energy projectiles. The structural scheme of these molecules is shown on the left of figure, where R is a side-chain. The mass-spectra of charged molecular fragments formed at single electron capture process by He^{2+} ions from D- and L-leucine (1 on the fig.), D-norleucine (2) and D- and L-methionine (3) are shown in figure (all spectra normalized on the same integral). As one could expect the scalar interaction leads to identical fragmentation of D and L stereoisomers.

The replace of linear side-chain ($R = C_4H_9$) in norleucine by ramified one leucine leads to slightly higher fragmentation probability of forming molecular ion.

The replace of $C5H_2$ group in side-chain of norleucine by sulphure atom (methionine) leads to more diverse outline of forming molecular ion fragmentation at considerably higher probability of nondissociated molecular ion M^+ formation.

This work has been supported by Russian Foundation for Basic Research grant #14-03-00367.



P-9

Optical population of the states correlating with the I(^{2}P$_{1/2}$) + I(^{2}P$_{1/2}$) dissociation limit and mixed by hyperfine interaction

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Optical population of the iodine molecule 0_g^+, 1_u and 0_u^- states, correlating with the third I(^{2}P$_{1/2}$) + I(^{2}P$_{1/2}$), (*bb*), dissociation limit, in a two-step scheme via the $B\,0_u^+$ intermediate state has been investigated. An additional third step has been also utilized to populate ion-pair states of different parities to probe population of the (*bb*) states, so the excitation scheme in use for the I$_2$($\beta 1_g$), e.g., is as follows:

$$\mathrm{I}_2(\beta 1_g, v_\beta, J_\beta \xleftarrow{h\nu_2} 1_\mathrm{u}(bb), v_{1\mathrm{u}}, J_{1\mathrm{u}} \xleftarrow{h\nu_f} B\,0_u^+, v_B, J_B \xleftarrow{h\nu_1} X\,0_g^+, v_X, J_X)$$

The $1_u\,(bb) \leftarrow \mathrm{B}\,0_u^+$ transition occurs, though the *u* ↔ *u* transition is strongly forbidden as electric dipole one in homonuclear molecules.

It has been experimentally shown that mechanisms leading to the selection rule violation such as strong electric field influence, formation of colliding pairs as well as magnetic dipole and electric quadrupole characters of transitions are unable to explain all observed features.

To explain the excitation scheme, we assume that the *g* ↔ *u* selection rule is violated since the molecular rovibronic levels of the 0_g^+, 1_u and $0_u^-(bb)$ states are mixed due to hyperfine interaction, and the $1_u\,(bb) \leftarrow B\,0_u^+$ transition in fact occurs between the $B\,0_u^+$ state and an admixture of the 0_g^+ (*bb*) state to the 1_u one.

We have analyzed wavenumbers of the transitions involved in optical population of the ion-pair states of different parities via the 0_g^+, $1_u\,(bb)$ states and shown that both upper states are populated via *the same* rovibronic levels of the lower states mixed by hyperfine interaction, though energy gaps between interacting rovibronic states are huge, ≥ 0.7 cm^{-1}, and far exceed those published earlier.

Absorption dichroism experiments have been also carried out to verify the three-step excitation mechanism suggested and to obtain information on the transition symmetry. Experimental values of absorption dichroism degree are in a good agreement with calculated using the spherical tensor approach ones.

Obtained results are of interest since the states correlating with the third dissociation limit turn out to be a good subject for hyperfine interaction investigations.

P-10

Detection of nonradiative relaxation in singlet oxygen molecules by digital holography

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The most direct and commonly used methods aimed for detection of excited molecules are based on the recording of fluorescence resulting from their radiative relaxation. However if the transition under study is forbidden the fluorescence signal is weak and most of the energy is released through nonradiative relaxation. This relaxation channel can be monitored by recording temperature gradients formed in the vicinity of the excited molecule.

In this communication we report on the application of this approach for detection of nonradiative transitions in singlet oxygen molecules. Excited oxygen molecules were produced in aqueous solutions of Radachlorin® photosensitizer by 405-nm laser irradiation at various exposures.

Temperature gradients formed by nonradiative relaxation of singlet oxygen molecules were recorded using digital holography technique which allows one to reconstruct both the phase and amplitude of the wave front passed through the sample. The applied algorithm [1] of wave front reconstruction requires a single off-axis fringe pattern only, allowing thus to study fast dynamic processes. Assuming the cylindrical symmetry of the formed temperature gradient and applying the inverse Abel transform radial temperature distributions for different photosensitizer concentrations have been obtained (fig 1).

The financial support from Russian Science Foundation, project # 14-13-00266, is gratefully acknowledged.

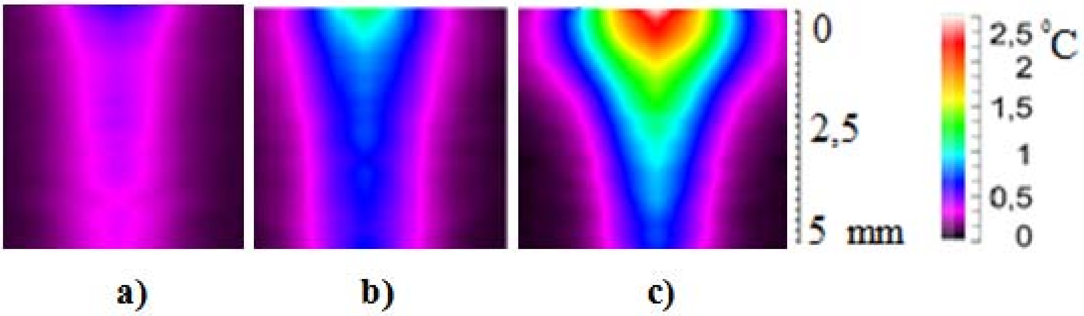

Fig.1. Radial temperature distributions in 0.16% (a); 0.33% (b); 0.66% (c) photosensitizer solutions in water after 5-second laser irradiation (405 nm, 50mW).

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P-11

Holographic interferometry of non-radiative transitions in singlet oxygen in water.

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The research on photodynamic generation of singlet oxygen is very important in different areas of science, from photo-oxidation processes, DNA destruction, photodynamic therapy of cancer to polymer science. The most widely used methods of detection of singlet oxygen are based on the deactivation of excited molecular states to the ground state. Time-resolved monitoring of the $a^1\Delta_g \rightarrow X^3\Sigma_g$ phosphorescence at 1270 nm provides the most direct information on singlet oxygen [1] in a system. However this transition is forbidden and the phosphorescence intensity is very low.

Non-radiative mechanisms play a dominant role in the deactivation of singlet oxygen. These mechanisms result in formation of local temperature gradients in a medium and can be detected using photothermal and photoacoustic techniques [2]. Detection of non-radiative transitions in molecules by holographic interferometry has recently been suggested by the authors of this communication [3]. The major advantage of the holographic method is an opportunity to obtain two-dimensional, time-dependent spatial distributions of refractive index variations with high temporal and spatial resolution.

In our experiments singlet oxygen was generated in the Radachlorin® photosensitizer solution in distilled water by a diode laser (405 nm, 50 mW). Holographic interferograms were recorded using a pulsed ruby laser (694 nm, 20 ns) at different excitation durations. Phase distributions were reconstructed from interferograms by means of the «Fringe Analyzer» software developed at St.Petersburg University ITMO and the software package Mathcad 14. As a result of the processing the temperature maps of the recorded area were reconstructed. Examples of the results obtained are shown in Figure 1.

The financial support from Russian Science Foundation, project # 14-13-00266, is gratefully acknowledged.

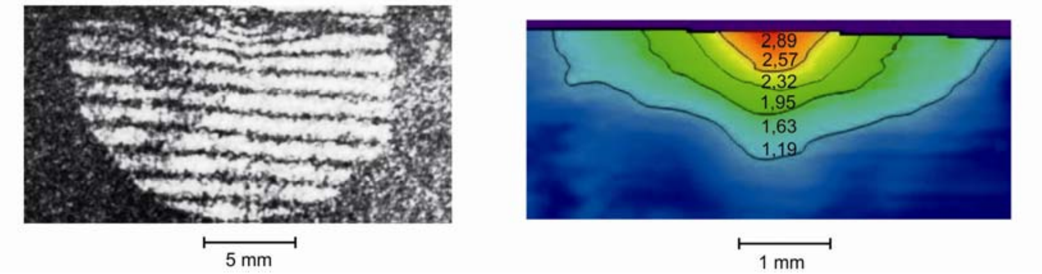

Figure 1. Holographic interferogram and the corresponding reconstructed temperature map for 20s excitation.

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P-12

Effect of the intermolecular excitation in the vibrational predissociation dynamics of van der Waals complexes and the implications for control

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The effect of intermolecular excitation on the vibrational predissociation lifetime is investigated systematically for the first time for four different vdW complexes Rg-X_2(B,v') (Rg=He, Ne, X=Cl_2, Br_2, I_2) by means of wave packet simulations. The lifetime as a function of intermolecular excitation displays a pattern of maxima and minima, with a similar shape for the different Rg-X_2(B,v') complexes [1]. The pattern is consistent with previous experimental findings involving lifetimes of intermolecular excitations in similar systems [2,3]. The structure of the lifetime pattern is found to be determined by the shape of the resonance wave functions in the two van der Waals degrees of freedom (stretching and orientation), and more specifically by the magnitude of the overlap between the wave function and the coupling responsible for predissociation. Lifetime maxima and minima are associated with minima and maxima of this overlap, respectively. Implications for control of the complex lifetime are discussed.

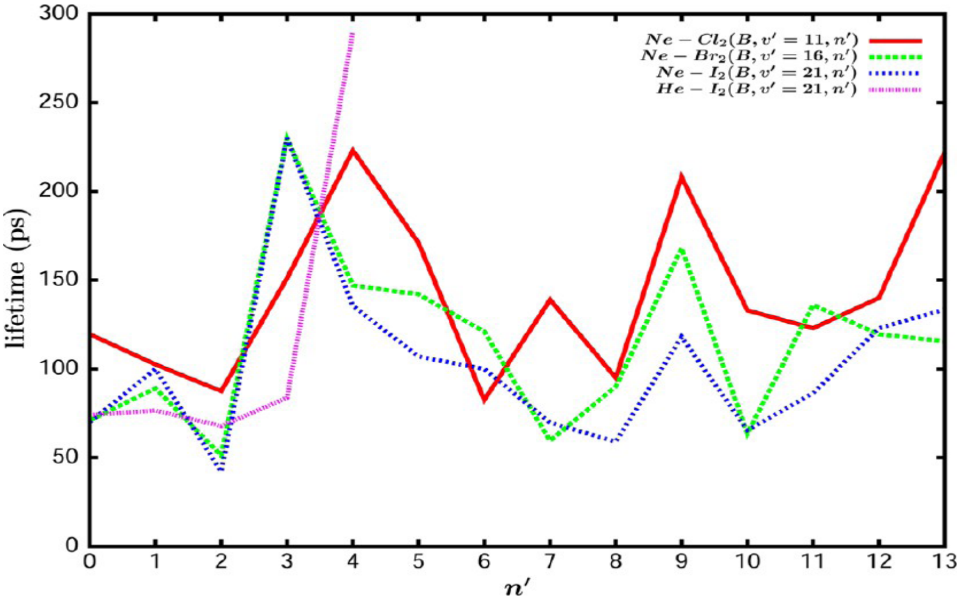

Figure1. Lifetimes for different Rg-X_2(B,v',n') vdW complexes vs the n' level of intermolecular excitation.

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P-13

Detection of singlet oxygen by two-photon excited fluorescence on the c → b transition

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Monitoring of singlet oxygen molecules in their $a^1\Delta_u$ and $b^1\Sigma_g^+$ states in biological environment with high temporal and spatial resolution is a very important problem because of the outstanding role plaid by singlet oxygen in biochemistry, life science and medicine [1]. In this work we present a new experimental technique allowing for direct monitoring of the singlet oxygen state $O_2(b^1\Sigma_g^+)$ dynamics with extremely high temporal resolution up to a few picoseconds using the pump-and-probe scheme. The technique is based on the direct excitation of the ground state oxygen molecule by two femtosecond laser pulses at 760 nm. The first (pump) pulse populated the $b^1\Sigma_g^+$ (v_1=0) singlet state and the second (probe) pulse which was delayed from the first pulse by several picoseconds initiated two-photon excitation from the $b^1\Sigma_g^+$ (v_1=0) state to the upper-laying $c^1\Sigma_u^-$ (v_2 = 12) state. Fluorescence from the relaxed $c^1\Sigma_u^-$ (v_2 = 0) state to the vibrationally excited $b^1\Sigma_g^+$ (v_1) state at about 1000 nm which was proportional to $b^1\Sigma_g^+$ (v_1=0) state population was experimentally detected by a sensitive avalanche photodiode used in the photon count regime. Varying the delay between the first and the second laser pulses we were able to study the relaxation dynamics of singlet oxygen $O_2(b^1\Sigma_g^+)$ in water with picoseconds temporal resolution.

The paper presents the experimental apparatus and experimental results obtained. The sensitivity of the experimental method used and the singlet oxygen relaxation mechanisms are considered.

The research was supported by the Russian Science Foundation under the grant # 14-13-00266.

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Computational modelling structural properties of biogene amines (serotonine, histamine,γ-amino oil acid) with laser and neutron capture effects

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Paper is devoted to the Monte-Carlo [1,2] computational studying the structural, spectroscopic and biochemical properties for the biogene amines: the serotonine (ST), histamine (HM), γ-amino oil acid (AC) and the laser and neutron capture action on the structural and biochemical properties of the molecules. The ST (5-hydroxitriptamine, 5-HT) is produced by means of the hydroxciliration of essencial amine acid of the triptophane [1]. ST influences mainly in a place of its appearance and calls for blood vessel narrowing in places of the trombocites decay. Probably, serotonine ST is the mediator for transition of the nervous pulses in some branch of the brain. HM is produced in cells (mastocides) from the histidine amino acid and plays a role of the nervous transfer mediator in some regions of nervous system. Many biomolecules (BM) are composed not only by hydrophilic, but also by hydrophobic groups, in the vicinity of which the water-water (or blood plasma) interaction is expected to be present even in the zeroth approximation. We present results of the Monte-Carlo calculating the cluster consisting of the serotonine ST (histamine HM) molecules and 100 molecules of water. All relevant interaction potentials are obtained by means of the quantum calculation. The water-water interaction potential was found by Matsouka etal by CI method. The BM-water interaction potential was obtained in the SCF approximation Calculation is carried out at T=300K; All molecules are treated as rigid. As an example, the results for interaction energies are listed in table:

Potential, $kJmol^{-1}$	Neutral molecule	zwitterion
Water-water	-27.7 ± 0.8	-27.2 ± 0.7
ST-water	-59.5 ±2.0	-348.5 ± 15.0
HM-water	-37,8 ±2.0	-178,4 ± 15.0

The zwitterion appears as expected to be strongly favoured with respect to neutral molecule. This result is similar to one for system: glycine-water [3]. The HM in the “zwitterion” more intensively (on the order) catalyses the gastric juice secretion and secretion from other endocrine glands. The similar situation is with action of the HM in the inflammatory and allergic reactions with further increasing vessel walls permeability and appearance of the edema phenomena and action of the ST with further blood-vessel narrowing in places of the trombocites decay. We at first consider the possibilities of laser and neutron capture action on different of molecules, including an analysis of Szilard-Chalmers (n,γ), (n,n), Mössbauer and cooperative [2] effects.

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P-15

Laser spectroscopy and photodissociation dynamics of H_2^-

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An anion beam apparatus has been set up in our laboratory whose main parameters and details have been described in a recent publication (Rudnev et al Review of Scientific Instruments 84, 124102(2013)) .To demonstrate the capability of the developed experimental technique we have applied it to investigate the spectroscopy of the H_2^- anion.

It should be noted that H_2^- is the simplest molecular anion which consists of only two protons and three electrons. It is thought to play a key role in relevant reactions as, for example, the dissociative attachment $e + H_2 \rightarrow H_2^- \rightarrow H + H^-$, or its reverse, the so-called associative attachment. The latter process is believed to be the dominant formation mechanism of H_2 in the early Universe.
A serious difficulty of the H_2^- investigation relies in its elusive nature as it is unstable relative to auto-detachment into the $H_2 + e$ continuum for internuclear distances of about 3 a_0 (note that $a_0 \equiv 0.0529$ nm), and below. In fact, only recently it was proven experimentally that a long-lived rovibrational state of H_2^- does unambiguously exist.
Using the cited anion beam technique the photodetachment cross-section of H_2^- (v=0,26) has been measured in absolute values following laser excitation at λ_{exc} = 565 nm. In addition, the photo-fragmentation spectrum of the mentioned anion was measured over the 17600 cm^{-1} - 17750 cm^{-1} energy range . These data will be presented and discussed at the Conference

P-16

Three Vector Correlations In NO(X) Rare Gas Inelastic Scattering

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Inelastic scattering measurements have been made for the NO(X) Ar, Kr and Xe (Rg) systems using a crossed molecular beam apparatus [1] coupled with velocity mapped ion imaging[2]. The initial state of the NO(X) was selected using hexapole focussing and the final state by (1+1') REMPI. This scheme allows for fully Λ-doublet resolved transitions to be observed [3], heightening the experiment's sensitivity to the attractive and repulsive forces that govern the collision dynamics.

The experimental apparatus also facilitates the determination of various polarisation moments (*fig. 1*) [4-5]. Measurements have recently been completed of both the alignment (plane of rotation) of the NO after collision and the orientation [6](sense) of rotation of NO(X) after collision. These measurements are extremely sensitive to the NO(X)—Rg PES [6] and provide insights into the interplay between the attractive and repulsive terms in the NO(X)-Rg potential and hence the observed dynamics.

We have also completed a theoretical study of the NO(X)—Kr alignment and have shown that although the collision system can be rationalised classically by the kinematic apse model[7], only by using a full quantum treatment can one reproduce all the features observed in the experimental data.

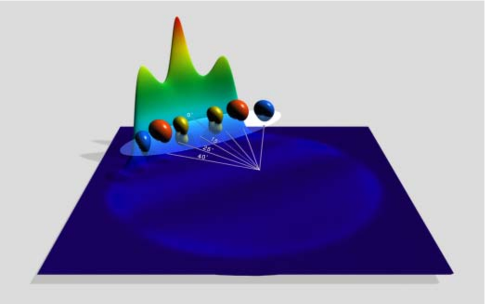

Fig. 1 Quantum mechanically predicted angular momentum polarisation for the NO(X)—Kr collision with *j'=3.5f*. Only quantum mechanics reproduces the observed experimental polarisation. The background shows the theoretical angular distribution for the transition.

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P-17

On the imaging of the hydrogen fragment electronic state in photodissociation: A proposal for experiment

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Polarization of atomic fragments carries a wealth of information on the dynamics of molecular photodissociation. The polarization (density matrix) of the fragment is extracted from polarization and angular distribution of the fragment fluorescence, polarization dependence of the fragment photoabsorption, cross sections of its resonant multiphoton ionization (REMPI) and by other methods [1]. Pump-probe experiments, combining intense VUV/X-ray and optical radia-tion, allow advancing to higher frequencies and using atto- and femtosecond pulses with a time delay to study the dynamics of the process in time. In this contribution we propose a method of monitoring the density matrix of the fragment suitable for the atomic hydrogen fragment H*. The density matrix elements are extracted from the photoelectron angular distribution in ionization of H* by probe radiation with variable polarization. An essential point is that exact photoionization amplitudes of the hydrogen atom are known at least within the first-order, which allows to concentrate on other aspects of the process. Furthermore, using exactly known wave functions of the hydrogen atom, the electron density and the electron current in the H* fragment are easily restored from the density matrix. The latter procedure has been applied to the beam-foil experiments [2] and to the proton-atom collisions [3]. In the proposed method the variable time delay may provide snapshots of the electron density and the electron current in the hydrogen fragment. An excited hydrogen atom is unique because of the degeneracy of its Coulomb levels. Thus, in general, H* possesses electric dipole moment, which is described by coherent mixing of states with opposite parity. This dipole moment is an additional vivid parameter characterizing the process of the fragment formation, which can be found from the density matrix.

The method looks suitable literally for all hydric molecules widespread in nature. The H_2 photodissociation producing H*(n=2) fragment is the ideal case for the first such study: the molecule has a simple structure and the H* atoms in the H_2 photodissociation have already been observed in a pump-probe experiment at FEL with the 90.5 eV photons [4]. The experiment indicated high population of the H*(n=2) states after the dissociation. Further discussion of the proposed method will be presented at the conference on the example of the H*(n=2) fragment after photodissociation of H_2 at the photon energies above 60 eV.

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P-18

Velocity-map imaging studies of OH(A)+Rg collision dynamics

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An extensive range of experiments has been carried out to investigate the collision dynamics of the OH(A)+Rg system (where Rg is a rare gas species) using laser-induced fluorescence with the application of Zeeman Quantum Beat Spectroscopy[1]. A recent emphasis of this work has been to quantify the role of electronic quenching, a non-adiabatic process that plays a significant role in the dynamics of the OH(A)+Kr and OH(A)+Xe systems[2].

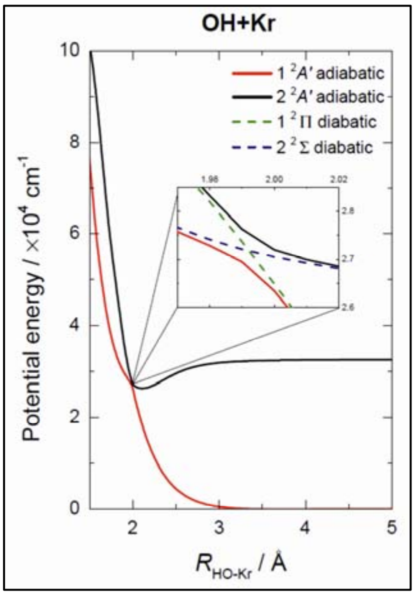

Fig. 1. Cross-sections through PESs[1] of OH+Kr in the near linear HO-Rg geometry showing a conical intersection

Since *non-adiabatic* electronic quenching[3] and *adiabatic* energy transfer and angular momentum depolarisation all occur in the same region of the OH(A)+Rg potential energy surfaces (PESs), it is particularly interesting to study the competitive interaction of these three processes.

A compact crossed-molecular beam apparatus[4] will be used to further study OH(A) radical dynamics using velocity-map imaging techniques[5]. Both existing and novel REMPI schemes will be used to detect quenched OH(X) and OH(A).

The use of VMI-REMPI techniques will allow for a determination of the $\boldsymbol{k}$–$\boldsymbol{k}'$ (velocity vector) differential cross-sections (DCSs) that will complement the information already obtained on the $\boldsymbol{j}$–$\boldsymbol{j}'$ (angular momentum vector) correlation from previous work[1,2]. The results of these new experiments will also be compared closely with both *quasi*-classical trajectory (QCT) and full quantum mechanical calculations with the aim of assessing the appropriateness of the QCT method and of introducing new surface-hopping[6] algorithms to model the experimentally observed non-adiabatic effects.

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P-19

Role of many-body effects in stability of electron-positron droplets

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Recently a novel type of a matter-antimatter compound system, an electron-positron droplet (EPD), has been predicted theoretically [1]. This is a finite quantum object similar to an atomic cluster. It consists of an equal number of electrons and positrons coupled together due to strong Coulomb and mutual polarization forces. The main goal of this work is to take into account the many-particle correlations in the calculation of the total energy of EPD.

The first calculations the EPD energies had been performed within the local density approximation (LDA) [1]. The negative value of the energy per an electron-positron pair obtained led to the conclusion that the bound state of the EPD can exist. The obtained absolute value of the energy per pair was lower than the same value for dipositronium molecule [2] (Fig.1). Up to date, several attempts have been undertaken to improve the stability of EPD against decay into the system of dipositroniums, in particular within the Hartree-Fock approximation [3].

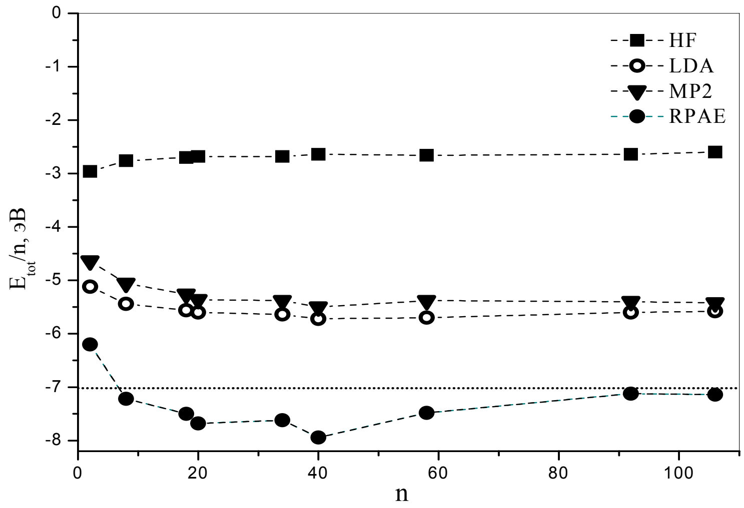

Figure.1.Total energy of the EPD per electron-positron pair number *n* calculated within different theoretical approaches. The dotted line is the same energy for dipositronium.

The perturbation theory within the Møller-Plesset second order (MP2) approach predicts the better values, than HF and LDA [4], but is not so good as the Random Phase Approximation with Exchange (RPAE) approach, that provided the lowest values of the energy per electron-positron pair (see Fig.1). So far, the crucial role of dynamical many-particle correlations for the EPD stability is manifested.

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P-20

Low-energy deposition of microscopic sodium clusters on an insulating surface

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The theoretical study of the deposition of small sodium clusters Na_6 on insulating NaCl crystal substrate is presented. The NaCl substrate surface is taken as inert acting on the cluster through its interface potential [1]. The time-evolution of the system is described using the microscopic model based on the Time-Dependent Local Density Approximation (TDLDA) and Molecular dynamics (MD) [2]. The dependences of the cluster attachment on different initial cluster velocities and different initial orientations relative to the surface are studied.

It was found that the low-energy cluster in its deposition process undergoes center of mass oscillations in the vicinity of the equilibrium position. The attachment process arised to be sensitive to the initial cluster orientation with respect to the surface as well as whether the deposition occurs over a Cl^- or Na^+ site of the substrate lattice. The kinetic energy loss of the projectile cluster and its post-collision behavior depends on the collision conditions. The numerical simulations show that there is an energy threshold for initial kinetic energy of a cluster that can be attached by the surface. It was found that extremely slow initial velocities are necessary to ensure a cluster deposition without damaging the original cluster. Deposition process with initial cluster kinetic energy above the attachment threshold results in inelastic reflection of the cluster, that leads to its fragmentation due to the excitation of internal ionic degrees of freedom.

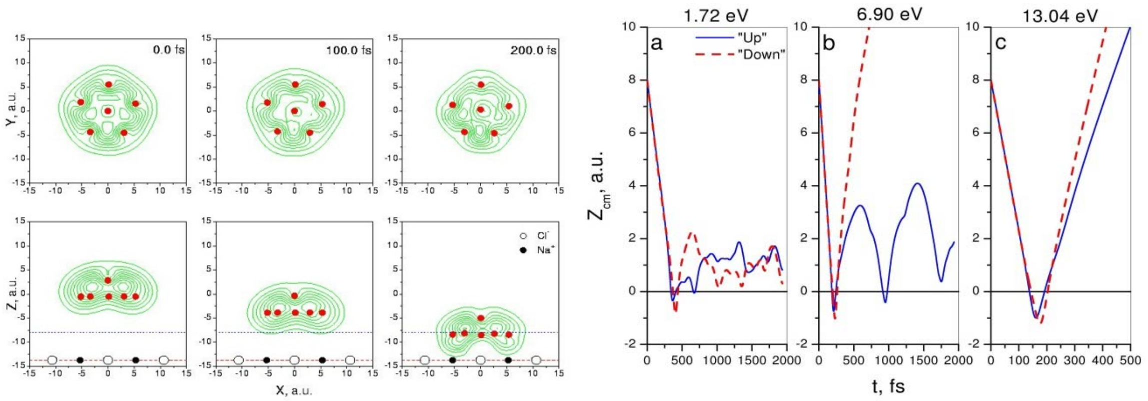

Figure: a) Snapshots of the electron charge density and ionic positions in different time of the cluster deposition with initial kinetic energy 6.9 eV; b) time evolution of the cluster center of mass during the deposition on the surface for different initial kinetic energies

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P-21

Penning ionization of polyatomic molecules at very low collision energies

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A novel merged-beam technique for neutral molecules has been employed in the study of Penning ionization of polyatomic molecules at collision energies spanning the range of 10 μeV to 20 meV. Polar molecules that exhibit a favorable linear Stark effect, e.g. NH_3/ND_3, CH_3F, CHF_3, have been merged with a beam of electronically excited neon atoms, Ne($^3P_2$), bent by means of a magnetic hexapole guide. The production rate of charged molecular fragments has been recorded as a function of relative velocity between two molecular beams. The resulting relative reaction cross sections are described well by the Langevin capture model at low collision energies, wherein the reaction is dominated by long-range part of the potential energy surface. We see evidence of short-range chemical forces' contribution to the reaction rate at higher collision energies. Simultaneous detection of all charged reaction products has enabled us to measure the sought-after branching ratios between different reactive channels.

P-22

Topochemical transformations in carbon nanotubes: fracture-induced defect, and ad-dimer welding.

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Native point defects of graphene and carbon nanotubes are related to C—C dimer. The first type is a topochemical turn of a single honeycomb C—C bond around its centre (SW defect, introduced in 1986 by A. J. Stone & D. J. Wales). The second one is incorporation of adsorpted dimer molecule (ad-dimer) into honeycomb carbon net (grafted ad-dimer, or di-interstitial).

1) Recently we have solved the problem of generation of SW in small-diameter tubes under mechanical fracture-type deformation, when mechanical stress is concentrated in a small area of the tube [1]. Fracture of zigzag (8,0) and armchair (5,5) tubes was considered by means of quantum chemistry. The SW on the compressed side of the tube is energetically favourable in comparison with the stretched side. At a fracture angle above critical value –

yield point: 1.7 degrees for (8,0), and 2.7 degrees for (5,5),

– the formation of SW decreases total energy of deformed defectless tube. Thus, fracturing deformation of the tube «turns on a plasticity channel» in the form of mechanical generation of the Stone–Wales defect. Deformations above yield point were experimentally studied only with large-diameter multiwalled tubes [2]. Kink of such a sample obeys continuous-media mechanics, perhaps the honeycomb structure of the tube is preserved in the kink area. Thus, a topochemical phenomenon of SW generation in small-radii tubes waits for experimental support.

2) Covalent chemical bonding between a pair of kriss-kross nanotubes should be achieved, if we could align tubes carefully, in order to make two parallel C—C bonds, one of each tube, come into [2+2] cyclo-addition. A reliable bonding – welding – can be achieved with the help of ad-dimer, that shifts and rotates adjusting to neighbour chemical bonds. Versatile chemical behaviour of ad-dimer (di-interstitial) in graphite has been analyzed theoretically [3].

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P-23

Effect of the electronic degeneracy and spin-orbit interaction in complex-forming collisions at low energies

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Formation of a long-lived complexes very often represent a first, and rate determining, step in exothermal chemical reactions. This event is usually preceded by inelastic processes occurring on the way to the region where chemical forces, responsible for a tight bonding, become operative. At low collision energies, the full dynamical treatment of the capture is simplified by introducing the adiabatic approximation with respect to properly defined states of the collision partners, such as adiabatic channel (AC) approach (known also under other acronyms) or axially-nonadiabatic (ANC) approximation. These approaches are well defined when the capture occurs on a single electronic Born-Oppenheimer potential energy surface (BO-PES) and when the adiabatic approximation with respect to rotational and vibrational motion of the collision partners transforms a multidimensional PES into a set of one-dimensional adiabatic potential curves. If collision partners are in degenerate electronic states and if the spin-orbital (SO) interaction is comparable to spacing between rotational states of the partners, the definition of adiabatic states, that evolve across AC potentials, becomes obscure. This talk discusses one way to introduce AC potentials which obviates the determination of multiplicity of electronic BO states (as a first step), with subsequent construction of AC vibrational-rotational states (as a second step). Here, the AC potentials are defined as eigenvalues of the Hamiltonian of the partners at a fixed interfragment distance with the electronic part, the spin-orbital interaction and the rotational motion of the collision partners treated simultaneously on the same footing within the rotronic (rotational-electronic) basis. This approach is exemplified by the calculation of the AC potentials and state-specific rate coefficients for the capture of OH molecule in a given rotational state from *e* and *f* ladders of the $X^2\Pi$ electronic state (*a-b* intermediate Hund coupling case) by an atom in a ${}^3P_j$ state (carbon, with a regular SO structure, and oxygen, with an inverted SO structure). The temperature dependence of the capture rate coefficient, calculated within the rotronic basis, differs markedly from that obtained from the capture dynamics on the lowest electronic PES weighted by the thermal population of the ground spin-orbit state.

Molecular angular momentum polarization in the chemical reactions Li+HF and F+HD

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The modern quantum-mechanical approach [1] is applied for the investigation of the molecular product and reagent polarization in the Li+HF and F+HD reactions. For these reactions accurate scattering information has become recently available through time-dependent and time-independent approaches [2, 3]. We consider two important cases: a) the first is reaction between polarized reagents; b) the second is reaction between unpolarized reagents. In the first case, it is shown that the role of the angular momentum alignment is large, particularly when the angular momentum is perpendicular to the reaction scattering plane. In the second case, the orientation and alignment of the product angular momentum was found to be significant and strongly dependent on the scattering angle. The calculation also present significant differences between the vector correlation properties of the two reactions under study which are due to difference in the reaction mechanisms. Moreover, the isotopic effect in F+HD reaction is analyzed and explained. Finally, we describe the geometrical arrangement for the experimental determination of the product angular momentum orientation and alignment based on REMPI 2+1, the compact and convenient spherical tensor expression for the intensity of the REMPI 2+1 signal is presented.

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P-25

Two- and three-photon absorption cross section measurement in case of HCl photoionization and photodissociation by means of 3D-imaging method

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The absorption of the laser radiation by HCl molecule in the spectral region from 230 to 245 nm results in [2+1] resonance enhanced multi-photon ionization (REMPI) or in three-photon photodissociation via several channels [1]. The photoionization or each photodissociation channel starts from a resonant two-photon absorption to an intermediate state IS_1. A third photon excites a higher state IS_2, which can be the ground state of HCl molecular ion or another excited state of the HCl molecule, from which the system directly dissociates or undergoes a nonadiabatic transition to a lower state and dissociates from it.

To characterize quantitatively the efficiency of the process of two-photon absorption as well as the processes of photoionization and photodissociation the concepts of two-photon and three-photon absorption cross-sections have been introduced. A theoretical study of three-photon processes, describing the photoionization and photodissociation has been performed to obtain the exact expression for the proportionality factor between the number of products and the cube or square (the case of the saturation of third photon absorption) of the laser radiation power.

The experimental dependences of products number on the laser radiation power have been measured by means of three-dimensional imaging based on a position-sensitive delay-line anode assembly [2] in case of excited intermediate states $IS_1=V^1\Sigma^+(v=8,9,10,11,12,13,14,15,16,\ J=0)$, $E^1\Sigma^+(v=0,1,\ J=0)$, and $g^3\Sigma^-(0^+,v=0,\ J=0)$. The values of two-photon and three-photon absorption cross-section exhibit large difference of about one order of magnitude depending on the nature of the intermediate excited state IS_1. The largest cross-sections were observed for $IS_1 = V^1\Sigma^+(v=12, J=0)$.

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P-26

Surface scattering of H^- and HCl^- ions, resulting from the recharge of H^+ and HCl^+

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The surface scattering of recharged H^- and HCl^- ions has been studied by means of a specially configured three-dimensional ion imaging experimental set-up providing negative ion trapping conditions.

To produce the recharged ions a two-step procedure has been used. In the first step the electronically excited state HCl^*(V, v=12, J=0) has been prepared by two-photon resonant absorption of ground state HCl via the Q(0) transition at 236.000 nm. The consequent one-or two-photon excitation at the same wavelength results in the production of H^+, Cl^+, and HCl^+ ions. In the second step these ions were accelerated to energies in the range from 250 to 750 eV and subsequently hit the surface of the grid. As a result of the impacts the recharge of H^+ and HCl^+ ions to H^- and HCl^- as well as the emission of the electrons from the grid has been observed. The recharged Cl^- ions have not been detected, whereas the impacts of Cl^+ on the grid produced the electrons.

Combining the special configuration of the 3D imaging set-up with the normal configuration, used to detect positive photoions, a comparison of the number of produced photoions and the number of recharged ions and emitted electrons at identical conditions has been performed. As a result the absolute probabilities to produce the recharged ion as well as to produce the electron on the grid surface have been calculated. These probabilities increase with the increase of the positive ion kinetic energy.

In case of HCl ions two possible mechanisms of recharged ion scattering have been observed. The first mechanism results in scattering with broad angular distribution, whereas the second one exhibits a resonance-like behavior characterized by a sharp angular distribution.

P-27

Fast dynamic transition Carbon nanotubes – Graphene

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It is known that active impact of strong electric fields in carbon nanotubes (CNTs), can lead not only to S-type electric instability but also to structural transformations of various types, in particular [1] to nanotubes transforming into graphene planes. It is possible that study of current with short (ns) duration of the electric field can reveal such nanotubes transforming into graphene planes and, as a consequence, appearance of additional grids in the percolation array. In recent years, we have performed first investigations of nanosecond voltage–current (VI) characteristics in the electric instability mode for arrays of multi (MWCNTs) and single walled carbon nanotubes (SWCNTs) [2]. The aim of this work to show that such graphene analogs as carbon nanotubes can be a convenient target for SOC experimental studies in the case of their transformation into graphene plane. In the conditions of our experiment the current flow threshold can be achieved in one of two ways. The first one is to change voltage of the control pulse. The last weakest link, which is tangle nanotube self-intersection area of the basic grid, disappears since corresponding voltage U_{c1} is reached (Fig.1). The second option is based on creating conditions for the sample conductivity relaxation mode, well known earlier as high-resistance state recovery mode [3]. The last weakest link, which is tangle nanotube self-intersection area of the new grid, disappears since corresponding voltage U_{c2} is reached (Fig.1). Let us note that given explanation can provide the role of various “tangled’ grid graphene chains during percolation process.

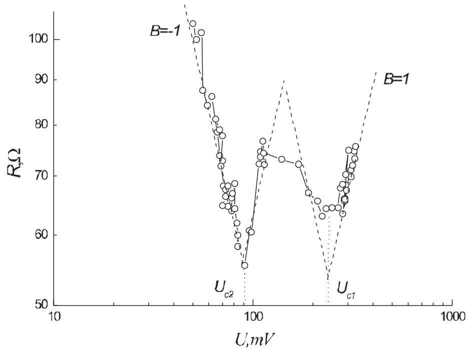

Figure 1. Generalized nanosecond R(U) dependency for SWCNT sample. The slope index- B

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P-28

Polarized Two-color Two-photon Excited Fluorescence in Indole: Determination of Molecular Parameters.

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We present the results of the experimental and theoretical study of indole using the time-resolved femtosecond laser spectroscopy. We analyze the polarized fluorescence of indole dissolved in propylenglycole and excited by two photons of different wavelengths. The excitation is made by the laser pulses with tunable wavelength range at about 400 nm and 800 nm which allowed for reaching of variable excitation energy corresponding to one-photon excitation wavelength range of 266—294 nm. Utilizing different polarization geometries of all three photons involved in the process we were able to infer the wavelength-dependent molecular M-parameters which are important quantities containing all information about the underline molecular excitation dynamics [1]. It is shown that the interplay of the two first electronic excited states ^1L_a and ^1L_b and their vibrational structure result in the non-trivial wavelength dependence of the M-parameters. Similar technique was already used elsewhere for analysis of fluorescence of p-terphenyl dissolved in cyclohexane/paraffin [2].

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P-29

Dynamics of Two-Photon Two-Color Transitions in DMQ Excited by Femtosecond Laser Pulses

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The excitation of polyatomic molecules with multiple photons have the advantages compared with the one-photon excitation regarding the investigation of complex molecular characteristics such as the molecular structure and dynamics. Due to the femtosecond laser spectroscopy and its non-invasive methods of examination of biologically-relevant molecules in the real time-domain.

We present the results of theoretical and experimental studies of the polarized fluorescence in 2-methyl-5-t-butyl-p-quaterphenyl (DMQ) excited by two-photon two-color (2P2C) femtosecond laser pulses. A two-color two-photon excitation by two femtosecond laser pulses at 800 and 400 nm has been used in combination with the time-resolved detection of polarized molecular fluorescence for DMQ molecules dissolved in cyclohexane/paraffin. The fluorescence decay was found to be two-exponential resulting in the molecular excited state lifetime of 753 ± 10 ps and the rotational correlation time of 724 ± 45 ps. We have used the temporal- and polarization-dependent 2C2P excited fluorescence technique as a powerful tool for determination of the full structure of the two-photon excitation tensor in DMQ. Thus, control over the excited and fluorescent photons polarization has been used for determination from experiment of seven independent molecular parameters. The experimental data was analyzed on the basis of the recent theoretical approach [1, 2] supported *ab initio* computations of the DMQ electronic structure and transition dipole moments. As result, all elements of the two-photon absorption tensor **S** have been determined and analyzed. As shown, the two-photon excitation preferably occurs through the d_z d_z components of the transition dipole moment which are parallel to the molecular long axis Z. However, there is also evidence for the symmetry-mixing two-photon transitions related to the dipole moment components d_x d_z and d_yd_z in the conditions of our measurements.

The equilibrium geometries, excitation energies and transition dipole moments between the ground and excited states in DMQ and p-quaterphenyl molecules have been computed. Results of calculation shows that the first three excited state energies for the twisted conformer of C_2 symmetry of p-quaterphenyl are significantly larger than the corresponding excited state energies for two other conformers. Full geometry optimization for the ground and the first excited relaxed electronic states in DMQ has been performed for vacuum condition and for DMQ dissolved in cyclohexane and paraffin. In both cases the optimized values of the dihedral angles were found to be practically the same. The first excited state geometry in DMQ is almost planar. Comparing the data for DMQ and p-quaterphenyl one can conclude that adjoining of the methyl and t-butyl groups to p-quaterphenyl results in losing the molecular state symmetry and shifts down the first excited state energy by only about 0.12 eV, however dramatically shifts down the energy of highly excited states making the energy structure much more dense.

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P-30

Photodissociation Dynamics in DBr

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The photodissociation of hydrogen halides and deuterium halides is important in the study of stellar objects and the atmospheric chemistry of the planets. The deuterium provides information on massdependent effects in the molecular level structure. Moreover, a combined studies of the photodissociation of the hydrogen molecular compounds and deuterium molecular compounds provides the more detail information on the dynamics of molecular dissociation. Thus, Alexander M.H. et al. [1] research the dynamics of the photofragmentation of HCl and DCI.

We report time-dependent wave packet calculations [2,3,4], to study the photodissociation dynamics of the molecule DBr. The branching fraction for the formation of excited state bromine atoms Br(^{2}P_{1/2}), total and partial integral cross sections, and the anisotropy parameters for both ground and excited state bromine are calculated as a function of photolysis energy. Higher order anisotropy parameters are computed for the first time for DBr molecule. The theoretical calculation of the photodissociation process involves two important parts: the determination of the underlying electronic structure and the dynamical calculations. *Ab initio* potential energy curves (PECs), dipole moments, transition dipole moments, and non-adiabatic couplings are computed in our paper [4]. In paper [4] we tests the quality of our *ab initio* calculations by comparing the computed scalar photodissociation properties, such as the total cross section and the Br(^{2}P_{1/2}) branching fraction, with experimentally determined quantities. We also compute the vector correlation and anisotropy parameters and compare these with measured quantities. The good agreement is obtained between the theoretical predictions and the experimental measurements. In this work, we present analogous dynamic calculations for the molecule DBr. The results of dynamic calculation for the molecules HBr and DBr are compared and discussed. Our result is the first which reports a comparison of the dynamic of the photodissociation for the molecules HBr and DBr. In particular, we found that the contribution of the a^{3}Pi_{1} partial cross section to the total cross section have approximately same magnitude as the A^{1}Pi_{1} partial cross section for DBr in contrast to HBr molecule where the a^{3}Pi_{1} partial cross section is dominant. As may be seen from the calculated anisotropy parameter beta, the photon energy at which the photodissociation process to produce Br(^{2}P_{1/2}) changes from parallel to perpendicular is smaller in the HBr molecule. The branching fraction for the formation of excited state bromine atoms Br(^{2}P_{1/2}) and anisotropy parameters also have the essential distinction in values for the photodissociation of the molecule DBr and HBr.

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P-31

Photodissociation of SiO molecule

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The SiO molecule belongs to a set of molecules of great astrophysical interest. Its photodissociation can be important in the research of the molecular balance in stellar envelopes of the Mira-type variable stars where the SiO molecule is a source of maser emission at the frequencies of ro-vibrational transitions J=2-1 (v=1,2,3) [1]. There is no experimental data regarding SiO photodissociation and only a single paper [2] on the calculation of the SiO photodissociation cross section based on the ground and first excited $^1\Sigma^+$ potentials and their transition dipole momentum calculated using the multireference configuration interaction (MRCI) method with the aug-cc-pVTZ basis set.

We have applied the MRCI with the aug-cc-pVQZ basis set to obtain the ground state and excited $^1\Sigma^+$ potential curves that seemed to be a proper candidate of the photodissociation process. Ten molecular orbitals were used in the active configuration space. The calculated ground and excited states were found to possess deeper wells than those computed with aug-cc-pVTZ basis set. The depth of the wells were approximately 2.4 and 0.4 eV respectively, while the transition dipole connecting the two states the previous one around twice. The time-dependent wave packet method [3] was applied to compute the photodissociation cross sections from the ground state with v=0 and j=0. We found that the calculated cross sections were several orders of magnitude less than the same cross section calculated with data based on the aug-cc-pVTZ basis set. This fact can be well explained by the computed well depth of the excited potential curve using the two different basis sets. We have computed photodissociation cross sections from different initial vibrational quantum states, and the results show a fast growth of the cross sections with increasing the vibrational quantum number. This can be explained by the width of the initial wave packet in coordinate space and the shape of the upper electronic state potential.

The photodissociation from the $X^1\Sigma^+$ via the $^1\Sigma^-$ and $^1\Delta$ electronic states is forbidden, The two $^1\Pi$ states have well depths even deeper than the excited $^1\Sigma^+$ one thus we may expect to find a similar behavior in the photodissociation through these excited states as well.

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Fluorescence excitation spectrum and excited state dynamics of jet-cooled propanal

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Propanal (CH_3CH_2CHO) is a conformationally non-rigid molecule and in its ground (singlet, S_0) electronic state (in the gas-phase) there are two conformers: *cis*, CCCO angle is 0°, and *gauche*, CCCO angle is 128.2°, with the energy difference ΔE (*gauche* – *cis*) is about 400 cm^{-1}, *cis* energy is lower. Our quantum chemical calculations (CASSCF/6-31G**) [1] of the propanal structure in the S_0 and first excited singlet electronic state (S_1) predicted the significant conformational changes being in result of $S_1 \leftarrow S_0$ electronic excitation: the rotation of ethyl (C_2H_5) group and the pyramidalization of the carbonyl fragment (CCHO), planar in the S_0 state. These changes are shown in the Newman projections (see figure):

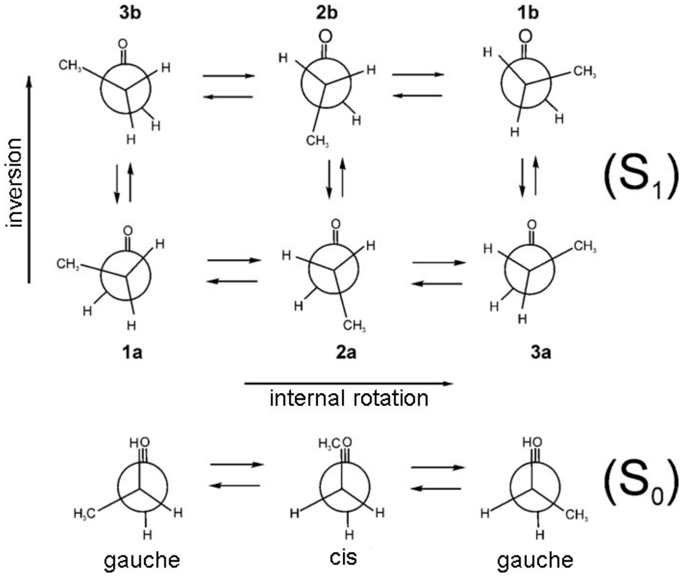

Figure. Newman projections of the conformers of the propanal molecule in the S_0 and S_1 states.

One can see that there are three pairs of mirror-symmetry conformers in the S_1 state. According to our calculations [1] the probabilities of vibronic transitions (in the region of 0_0^0) for *gauche* conformer are higher than for *cis*. And in agreement with it the bands in our propanal gas-phase absorption spectrum could be assigned to the vibronic transitions of *gauche* conformers [2]. In the present work we investigated the jet-cooled propanal and only *cis* conformer vibronic transitions could be observed. As a result the experimental values could be found for all propanal conformers in S_1 state and compared with the corresponding theoretical data. All of them are in the reasonable agreement.

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