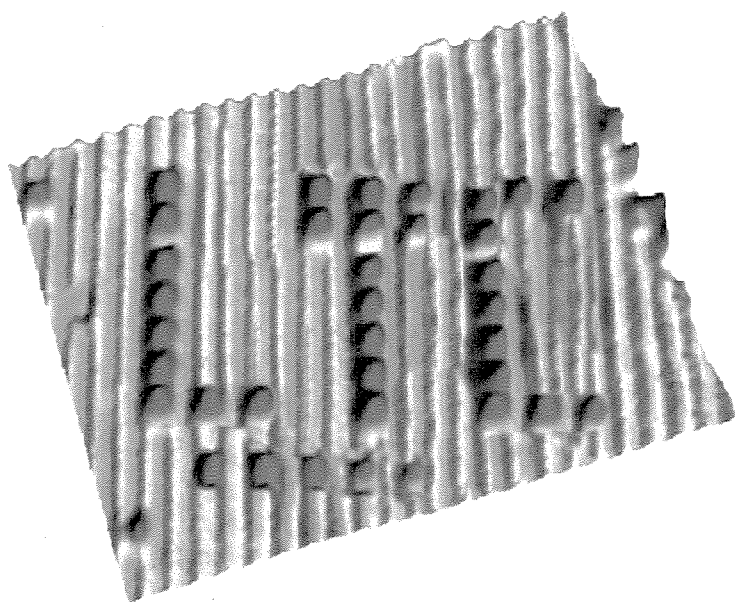


REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 20-09-2004		2. REPORT TYPE Conference Proceedings		3. DATES COVERED (From – To) 7 September 2004 - 10 September 2004	
4. TITLE AND SUBTITLE Fifth International Conference on Low Temperature Chemistry (LTC5). Held in Berlin-Dahlem, Germany on September 7-10, 2004. Final proceedings abstracts.				5a. CONTRACT NUMBER FA8655-04-1-5082	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Conference Committee				5d. PROJECT NUMBER	
				5d. TASK NUMBER	
				5e. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Freie Universität Berlin Arnimallee 14 14195 Berlin 14195 Germany				8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) EOARD PSC 802 BOX 14 FPO 09499-0014				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) CSP 04-5082	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited. (approval given by local Public Affairs Office). The U.S. Government has a non-exclusive royalty-free license in all copyrightable material herein.					
13. SUPPLEMENTARY NOTES See IC5 homepage @ http://www.physik.fu-berlin.de/ltc5/					
14. ABSTRACT The Final Proceedings for Fifth International Conference on Low Temperature Chemistry (LTC5), 7 September 2004 - 10 September 2004. The proceedings are abstracts only. Topics covered include: Quantum solid: hydrogens and condensates, Quantum liquid: helium and nanodroplets, Tunnelling and transport processes, Coherence and quantum chemical dynamics, Dynamics and femtochemistry, STM induced chemistry, Chemistry on surfaces and in nano materials, Reactions in clusters, Matrix isolation, Rare gas compounds, Cooled biomolecules, Astro- and stratospheric chemistry.					
15. SUBJECT TERMS EOARD, high energy density matter					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 125	19a. NAME OF RESPONSIBLE PERSON BARRETT A. FLAKE
a. REPORT UNCLAS	b. ABSTRACT UNCLAS	c. THIS PAGE UNCLAS			19b. TELEPHONE NUMBER (Include area code) +44 (0)20 7514 4285

Fifth International Conference on
Low Temperature Chemistry
(LTC5)



Berlin-Dahlem / Germany
September 7 - 10, 2004

Programme September 7 - 10, 2004

Tuesday, September 7

8:00 Registration additional early registration
monday evening

9:00 Opening
Chair: E. Savchenko

9:15 Cluster I **J. Eloranta**
9:55 **A. Lindinger**

10:35 *Coffee break*

11:00 **V. Buch**
11:40 **G.B. Sergeev**

12:20 *Lunch*
Chair: T. Shida

13:30 Matrix **M. Räsänen**
14:10 **B. Gerber**
14:50 **E. Misochko**

15:30 *Coffee break*

16:00 **M. Nakata**
16:40 **D.G. Eshchenko**
17:20 **T. Shabatina**

18:00 *Departure to boat trip*

19:30- 22:30 *Boat trip*

Thursday, September 9

Chair: T. Kumada

8:30 Hydrogen **M. Fajardo**

9:10 **D. Anderson**
9:50 **P. Percival**

10:30 *Coffee break*

11:00 Tunneling **G. Buntkowsky**
11:40 **O. Kühn**
12:20 Dynamics **V.A. Apkarian**

13:00 *Lunch*
Chair: M. Pettersson

14:00 **C. Crepin**
14:40 **D. Coker**
15:20 **M. Chergui**

16:00 *Coffee break*

16:30 **T. Kiljunen**
17:10 **I. Stienkemeier**

18:00 *Departure to Dinner*

19:00-22:00 *Conference Dinner*

Wednesday, September 8

Chair: V. A. Apkarian

8:30 Helium **I.P. Toennies**
9:10 **B. Whaley**
9:50 **R. Saykally**

10:30 *Coffee break*

11:00 **T. Momose**
11:40 **M. Strzhemechny**
12:20 **L.P. Mezhev-Deglin**

13:00 *Lunch*

14:00-19:00 **Poster Session**
Evening free for
excursion /tour

Friday, September 10

Chair: B. Gerber

8:30 Cluster II **M. Johnson**
9:10 **R. Wester**
9:50 Biomolecules **K. Kleinermanns**

10:30 *Coffee break*

11:00 **D. Clary**
11:40 Surfaces **F. Moresco**
12:20 **M. Wolf**

13:00 *Lunch*
Chair: G. Sergeev

14:00 Astrophysics **V. Storchak**
14:40 **G. Meijer**
15:20 **B. Rowe**

16:00 *Concluding remarks*

Preface

The series of International Low Temperature Chemistry Conferences started 1994 in Russia, went from the USA to Japan and reached a summit in Finland in 2002. The field develops on a border line between Physics and Chemistry. Condensed quantum systems like helium and hydrogen together with tunnelling and transport processes were central topics in the previous meetings. These subjects are once more broadly covered by invited speakers. Low Temperature Chemistry reaches a transition state and several topics obtain increasing momentum, new ones emerge. Rare gas chemistry develops on a fast pace. Femtochemistry, coherence, decoherence and chemical dynamics are going to play a major role. New tools like single molecule modifications by STM and high resolution spectroscopy of cooled biomolecules open new horizons. Reduced dimensionality in clusters, nano droplets, nano materials and on surfaces combined with advanced techniques lead us to new frontiers as will be exemplified by the invited speakers. The conference has enlarged and it attracted over 100 registered participants. A broad survey on the active branches of Low Temperature Chemistry will be provided by the 36 invited speakers and in the poster session with more than 65 contributions. The programme and the abstracts of the invited talks together with those for the posters are listed in the following pages.

Your visit to Berlin is the consequence of the LTC4 participants decision, expressing the preference for holding the next conference in Berlin in view of its central location and easy accessibility from east and west. Indeed, the majority of international participants originates from Russia, the Ukraine, Finland and Japan. The conference center is located in the pleasant housing area Dahlem in the south-west part of Berlin. The Harnack-Haus reflects the scientific history of Germany in the last century and its connection to international politics. It is surrounded by the historic scientific center formed by the Kaiser-Wilhelm-Gesellschaft, in which the most renowned German scientists worked. Now it is integrated in the lively campus of the Freie Universität and belongs to the the Max-Planck-Gesellschaft. A boat tour serves as a mixer and introduces the city from a special perspective. The conference dinner in "Berlin Mitte" reflects the cosmopolitan style of the city.

I take this opportunity to thank all my coworkers, coorganizers, and members of the Organizing Committee, whose names are listed on the next pages, for inventing an exciting programme. They all, and especially Ms Ingeborg Twesten, worked very hard to prepare the conference. Grants by the Deutsche Forschungsgemeinschaft and the Air Force and financial support by the Freie Universität allowed to gather a high rank international scientific community. I thank all participants for coming to Berlin. Your stimulating contribution will determine the success of the meeting. I wish you an exciting conference and a pleasant stay in Berlin.

Berlin, August 2004

Nikolaus Schwentner

Fifth International Conference on Low Temperature Chemistry (LTC5)

International Programm Committee

V.A. Apkarian (Irvine, USA)
M. Fajardo (Florida, USA)
B. Gerber (Jerusalem/Irvine, Israel/USA)
M. Gudipati (NASA, USA)
A. Jezowski (Wroclaw, Poland)
H. Kunttu (Jyväskylä, Finland)
L.P. Mezhov-Deglin (Chernogolovka, Russia)
T. Miyazaki (Nagoya, Japan)
E. Savchenko (Kharkov, Ukraine)
G.B. Sergeev (Moscow University, Russia)
V.G. Storchak (Moscow Kurchatov, Russia)

Local Organizing Committee

M. Fushitani	N. Owschimikow
M. Gühr	S. Riemann
H. Ibrahim	M. Soltwisch
T. Kiljunen	I. Twesten

Email: ltc5@physik.fu-berlin.de

Homepage: <http://www.physik.fu-berlin.de/ltc5>

Chair

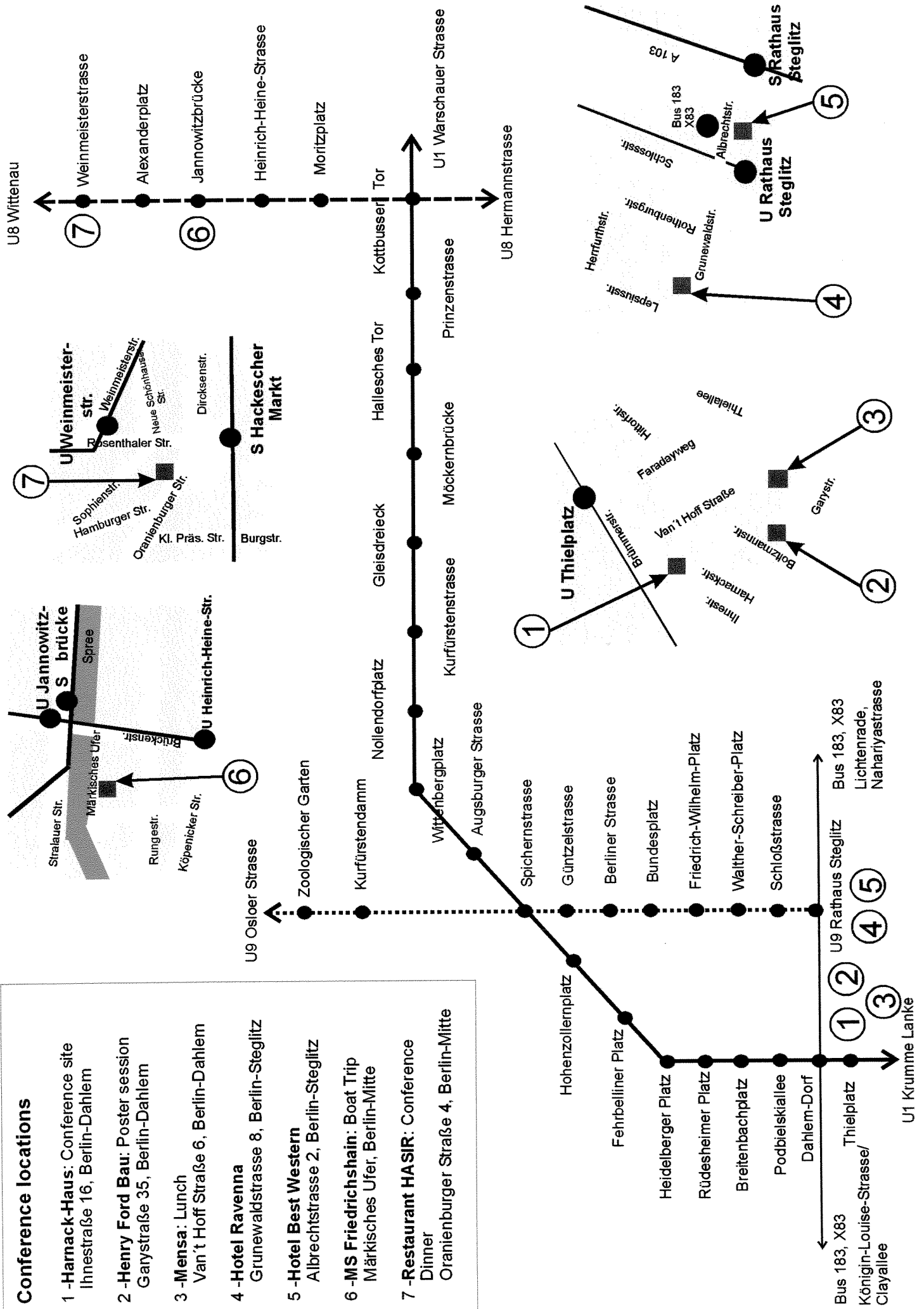
N. Schwentner
Arnimallee 14, D 14195 Berlin
Tel. +49-30-838 56035
FAX+49-30-838 75502

Email:

nikolaus.schwentner@physik.fu-berlin.de

Conference locations

- 1 -Harnack-Haus: Conference site
Innestraße 16, Berlin-Dahlem
- 2 -Henry Ford Bau: Poster session
Garystraße 35, Berlin-Dahlem
- 3 -Mensa: Lunch
Van't Hoff Straße 6, Berlin-Dahlem
- 4 -Hotel Ravenna
Grunewaldstrasse 8, Berlin-Steglitz
- 5 -Hotel Best Western
Albrechtstrasse 2, Berlin-Steglitz
- 6 -MS Friedrichshain: Boat Trip
Märkisches Ufer, Berlin-Mitte
- 7 -Restaurant HASIR: Conference
Dinner
Oranienburger Straße 4, Berlin-Mitte



General Information

Early Registration: Monday 18:00 – 20:00 in Harnack-Haus and Monday 18:00 – 20:00 in Hotel Ravenna for those with accommodation in Hotel Ravenna or Hotel Best Western. Please pay conference fee in cash if you did not prepay.

Registration

Tuesday 8:00 – 9:00 and at Coffee Breaks in Harnack-Haus
Please pay conference fee in cash if you did not prepay.

Conference Location:

Harnack-Haus, Ihnestr. 16-20, 14195 Berlin

Tel.+49 30 84133800 or 84133804 FAX 49 30 8413801

Take U-Bahn U1 in direction Krumme Lanke and exit at Thielplatz. Walk 200 m to Ihnestraße according to map.

From Hotels Ravenna and Best Western:

Take Bus 183 or X83, exit in Dahlem Dorf and take U1 to Thielplatz (one station) or walk Brümmerstraße according to map.

From Tegel Airport

Bus 109 or X9 to Jacob-Kaiser-Platz, enter U7 in direction to Rudow and change at Fehrbelliner Platz to U1. Go on as described before.

From Station Zoologischer Garten

Take U9 in direction to Rathaus Steglitz and change at Spichernstraße to U1. Go on as described before.

Poster Session is arranged Wednesday afternoon in:

Henry Ford Bau of the Freie Universität Berlin, Main Lobby. Boltzmannstraße at corner to Garystraße, 5 min walk from Harnack-Haus

Instructions for talks and posters

Talks 40 min. including discussion, overhead projection and computer presentation provided; please contact technical assistance before beginning of previous session.

Posters: size 90 cm broad, 120 cm long. Material for mounting will be provided. Put up 13:00 on Wednesday, to be removed 19:00 on Wednesday.

Conference Office

In Harnack-Haus during Coffee Breaks

Transportation

With your registration you receive a conference tag, which is a valid ticket for all public transportation (BVG: U-Bahn, S-Bahn, Bus, Tram and BVG Ferry) in greater Berlin (ABC) during the conference, i.e. Tuesday, Wednesday, Thursday, Friday.

Lunch

With registration, you receive prepaid tickets for four complete meals at the FU Mensa I, Van't-Hoff-Straße 6 about 7 minutes walk according to map.

Conference events

Boat Tour with guide: Tuesday evening with MS-Friedrichshain of Stern- und Kreisschiffahrt GmbH.

Boat and a meal plate are complimentary with registration, drinks have to be paid.

Departure 19:30 sharp from station Märkisches Ufer, return around 22:30

Take U1 in direction to Warschauerstraße, switch at Kottbusser Tor to U8 in direction Wittenau, exit at Jannowitzbrücke and cross the bridge to Märkisches Ufer according to map until you reach the Stern- und Kreisschiffahrt station.

Conference Dinner: Thursday evening, 19:00 – 22:00 at the

HASIR Restaurant, Oranienburgerstr. 4, 10178 Berlin, Tel. 49 30 28041616

Complimentary with registration.

Take U1 in direction Warschauerstr., switch at Kottbusser Tor to U8 direction Wittenau, exit at Weinmeisterstraße and walk along Rosenthalerstraße to Oranienburgerstraße according to map. Restaurant is close to Hackescher Markt.

Information on

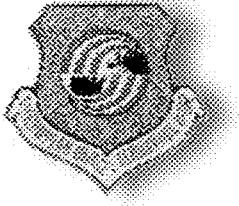
Sightseeing, concerts, theatre, laboratory visits will be provided during the conference and arrangements are on demand.

Sponsors

The conference is strongly supported by a grant of the Deutsche Forschungsgemeinschaft. Funds are provided also by the 'Fachbereich Physik' of the Freie Universität and by the 'Sonderforschungsbereich' 450.



We wish to thank the following for their contribution to the success of this conference: European Office of Aerospace Research and Development, Air Force Office of Scientific Research, United States Air Force Research Laboratory.



Our industrial sponsors Leybold Vacuum and VTS-Createc will present their products during the conference.



Invited Lectures

- D. Anderson**, Univ. Wyoming: *Infrared spectroscopy of reactive species trapped in solid hydrogen.*
- A. Apkarian**, UCI Irvine: *Quantum coherent dissipation - a glimpse of the "CAT"*
- V. Buch**, Dep. Phys. Chem. Hebrew Univ. Jerusalem: *Solid phase solvation of acids.*
- G. Buntkowsky**, Inst. of Chem., FU Berlin: *Low temperature chemistry in metal hydrides: from coherent tunnelling to incoherent chemical exchange.*
- M. Chergui**, EPFL Lausanne: *Ultrafast structural dynamics in solid Hydrogen.*
- D. Clary**, Univ. Oxford: *Quantum simulation of biomolecules.*
- D. Coker**, Dep. Chemistry, Boston University: *Modeling vibrational and electronic relaxation of photoexcited radical reactions in condensed phases.*
- C. Crepin**, Univ. Paris-Sud: *Vibrational coherence of weakly bonded molecular systems probed by IR one color DFWM experiments.*
- J. Eloranta**, University of Jyväskylä: *Time domain analysis of electronic spectra in superfluid ^4He .*
- D.G. Eshchenko**, Paul Scherrer Inst. Villingen: *Electron capture by muons in rare gas solids and liquids.*
- M. Fajardo**, AFRL, Florida: *Rovibrational dynamics and nuclear spin conversion of water monomers and water complexes in solid parahydrogen.*
- B. Gerber**, Dep. Phys-Chem. Hebrew Univ. Jerusalem: *The surprising chemistry of noble gas atoms: new reactions, new molecules and new materials.*
- M. Johnson**, Dep. Chem. Yale Univ.: *How water networks accommodate an excess electron: structure and dynamics of the binding site.*
- T. Kiljunen**, Dep. Phys. FU Berlin: *Control of molecular photodynamics by strong-field alignment in solids.*
- K. Kleinerhanns**, Univ. Düsseldorf: *Photochemistry of nucleobases in beams.*
- O. Kühn**, Inst. of Chem., FU Berlin: *Multidimensionality and cooperativity of intramolecular hydrogen bond dynamics.*
- A. Lindinger**, Inst. Exp. Phys., FU Berlin: *Optimal control of multi-photon ionization processes in alkali dimers: Learning from the optimized pulse shapes.*
- G. Meijer**, Fritz-Haber-Inst., Berlin: *Cold molecules.*
- L. Mezhev-Deglin**, Inst. Sol. State Phys., Chernogolovka: *A new nanocluster system - impurity-helium condensate (impurity gel) in liquid helium.*
- E. Misochko**, Inst. of Prob. of Phys., Chernogolovka: *In situ synthesis and internal stability of the simplest ketocarbene (formylmethylene) in solid argon.*
- T. Momose**, Div. of Chem., Kyoto Univ.: *Spectroscopy of molecules in solid parahydrogen, solid He, and He nanodroplet matrices.*
- F. Moresco**, Dep. Phys., FU Berlin: *Modifications of molecules by low temperature STM.*
- M. Nakata**, Agric. and Tech., Tokyo Univ.: *Hydrogen-atom moving in low-temperature rare-gas matrices.*
- P. Percival**, Chem. Dep., Simon Fraser Univ. Vancouver: *Hydrogen atom chemistry studied via its isotope muonium.*
- M. Räsänen**, Dep. Chem., Univ. Helsinki: *Frontiers of rare gas chemistry.*
- B. Rowe**, Univ. Rennes: *Radical-molecule reaction down to 10 K and interstellar implications.*
- R. Saykally**, Dep. Chem. UC Berkeley: *Terahertz spectroscopy of water clusters: progress towards a universal water potential.*
- G.B. Sergeev**, Chem. Dep., Moscow State Univ.: *Low temperature chemistry of nanomaterials.*

- T. Shabatina**, Chem. Dep., Moscow State Univ.: *Metastable complexes formation and their reactions in low temperature mesogenic matrices.*
- F. Stienkemeier**, Univ. Bielefeld: *Spectroscopy of doped helium droplets: matrix isolation of PTCDA nanostructures and real-time measurements.*
- V. Storchak**, Kurchatov Inst. Moscow: *Hydrogen atom in gigantic magnetic and electric fields: conditions of a neutron star in a lab.*
- M. A. Strzhemechny**, Verkin Inst. Kharkov: *Hydrogen-impurity gels: preparation and identification.*
- J.P. Toennies**, Max-Planck-Inst. für Strömungsforschung Göttingen: *Magic numbers of neutral ^4He and para- H_2 clusters.*
- R. Wester**, Phys. Inst. Univ. Freiburg: *Laser-induced reactions in traps: A road to quantum-controlled chemistry?*
- B. Whaley**, Dep. Chem. UC Berkeley: *Evolution of superfluidity in nanoscale clusters of helium and hydrogen.*
- M. Wolf**, Dep. Phys. FU Berlin: *Ultrafast dynamics of photoinduced electron transfer and solvation processes at the ice/metal interface.*

INFRARED SPECTROSCOPY OF REACTIVE SPECIES TRAPPED IN SOLID HYDROGEN

David T. Anderson

*Department of Chemistry, University of Wyoming, 1000 E. University Ave, Laramie, WY 82071
danderso@uwyo.edu*

Since its inception matrix isolation has been used to store spectroscopically detectable concentrations of reactive species in an inert matrix [1]. The use of solid molecular hydrogen as a matrix host presents an interesting twist on this technique. The matrix is no longer chemically inert and thus can react with the dopant species. In addition, solid molecular hydrogen is a very weakly perturbing matrix host owing to the quantum mechanical nature of molecular hydrogen. This makes it a unique environment to study low temperature chemistry. The Momose group has demonstrated that the methyl radical (CH_3) can be stored in solid parahydrogen for up to weeks [2], and have studied the tunneling reactions of deuterated methyl radical with the surrounding H_2 matrix host in detail [3]. Part of our research efforts are focused on studying how atoms and molecules that would react with hydrogen at room temperature and pressure can be metastably trapped in solid parahydrogen (99.97% $J=0$) at liquid helium temperatures. We are interested in trapping highly reactive species and in investigating the low temperature chemistry of these species in solid parahydrogen. Our approach has been to isolate stable precursor molecules in solid hydrogen using the rapid vapor deposition technique developed by Fajardo and coworkers [4] and then use lasers to photochemically generate the reactive species *in situ*. We characterize the chemically doped solid parahydrogen samples in the infrared region using a high resolution interferometric spectrometer [5]. We will discuss recent progress (and failures) in this area for three precursor molecules: (i) Cl_2 , (ii) NH_3 , and (ii) $\text{W}(\text{CO})_6$.

This research is sponsored in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society and by the National Science Foundation.

References:

- [1] E. Whittle, D. A. Dows and G. C. Pimentel, *J. Chem. Phys.* **22**, 1943 (1954).
- [2] T. Momose, M. Miki, M. Uchida, T. Shimizu, I. Yoshizawa, and T. Shida, *J. Chem. Phys.* **103**, 1400 (1995).
- [3] H. Hoshina, M. Fushitani, T. Momose and T. Shida, *J. Chem. Phys.* **120**, 3706 (2004).
- [4] M. E. Fajardo and S. Tam, *J. Chem. Phys.* **108**, 4237 (1998).
- [5] K. Yoshioka and D. T. Anderson, *J. Chem. Phys.* **119**, 4731 (2003).

QUANTUM COHERENT DISSIPATION – A GLIMPSE OF THE “CAT”

V. Ara Apkarian

*Department of Chemistry, UCI, Irvine 92697
aapkaria@uci.edu*

Abstract

The absence of interference between macroscopically distinct states, or Schroedinger's cats, is ascribed to decoherence. A cat state may be defined as the coherent evolution of N , nearly orthogonal states in superposition. This situation is realized in strongly coupled system-bath dynamics, where the system is prepared in superposition $\chi(o) = (|s\rangle + |s'\rangle)|b\rangle$ and after unitary time evolution each system packet generates its own history in the bath $\chi(t) = |s,b;t\rangle + |s',b';t\rangle$. This sets the entanglement between system and bath coordinates. The coherently evolved macro-system, can quite generally be decomposed into an orthogonal representation, $\chi(t>t) = |s(t)\rangle|b(t)\rangle + |s'(t)\rangle|b'(t)\rangle$. A projective measurement over the system would then interrogate the quantum interference term $(|s'(t)\rangle \langle s(t)|)(|b'(t)\rangle \langle b(t)|)$, as the coherence of entangled states.

I will report on such measurements using three-color and four-color four-wave mixing, in which two energetically distinct vibrational wavepackets are prepared on the electronically excited state of the chromophore. The classical coherence (with diagonal bath) and quantum coherence (evolution in two distinct baths) is measured after extensive dissipation via pump-probe and four-waves, to uniquely extract the bath/bath coherence. From simulations, we can estimate that the coupled coherent bath consists of $N>12$ active orthogonal modes, *i.e.* $|b\rangle = \Pi_i^N |i\rangle$, demonstrating a rather formidable “cat”.

Solid phase solvation of acids

Victoria Buch¹, J. P. Devlin², J. Sadlej³, F. Mohammed⁴, M. Parrinello⁴

¹*Physical Chemistry Department, the Hebrew University, Jerusalem, Israel*

²*Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, USA*

³*Department of Chemistry, Warsaw University, Warsaw, Poland*

⁴*ETH-Zurich, Switzerland*

The nature of solid phase solvation is quite different than that in the liquid phase, since in the solid, the acid and the solvent combine in well defined ratios. A joint spectroscopic - computational study is presented for mixed solids of HX (X=Cl,Br) with water, methanol and ethers (DME and THF). HX:water ionic solids combine in 1:1, 1:2, 1:3 and 1:6 ratios; the corresponding infrared spectra are discussed and analyzed. Spectroscopic signatures due to Zundel and hydronium ions are observed, depending on composition. The closely related HX:methanol ionic solids form in 1:1, 1:2 and 1:3 ratios and display similar spectra. A new and striking family of HX:ether solids is presented, with ratios ranging from 6:1 to 1:2. The spectra indicate proton sharing with ether, rather than proton transfer, and solvation of the asymmetric Zundel units by excess acid. The 1:1 HCl:DME structure, dynamics and spectroscopy was investigated with the help of on-the-flight molecular dynamics simulations.

LOW TEMPERATURE CHEMISTRY IN METAL HYDRIDES: FROM COHERENT TUNNELLING TO INCOHERENT CHEMICAL EXCHANGE.

Gerd Buntkowsky, Hans-Heinrich Limbach

Department of Physical Chemistry, FU Berlin, Takustr. 3, 14195 Berlin, Germany;
eMail: bunt@chemie.fu-berlin.de

In many transition metal dihydrides and dihydrogen complexes the hydrogens are relatively weakly bound and exhibit a fairly high mobility, in particular with respect to their mutual exchange[1-6]. Part of this high mobility is due to the exchange symmetry of the two hydrogens, which causes an energy splitting into even and odd spatial energy eigenfunctions, resulting in the typical coherent tunneling of a two-level system. Owing to the quantum mechanical symmetry selection principles the eigenfunctions are connected to the possible nuclear spin states of the system. If the tunneling frequency is in the proper frequency window it is thus possible to observe these tunneling transitions by NMR at very low temperatures, where no thermally induced exchange reactions overshadow the tunneling.

The first part of the talk reports results of a ^2H solid state NMR spectroscopy and T_1 relaxatiometry study of trans-[Ru(D₂)Cl(PPh₂CH₂CH₂PPh₂)₂]PF₆, in the temperature regime from 5.4K to 320K. In the Ru-D₂ sample coherent tunneling and incoherent exchange processes on the time scale of the quadrupolar interaction are observed. From the spectra and T_1 -data the height of the tunneling barrier is determined. The second part reports results of ^2H -spin-lattice relaxation measurements for a selectively η^2 -D₂ labeled isotopomer of the complex W(PCy₃)₂ (CO)₃ (η^2 -D₂). The relaxation measurements are analyzed in terms of a simple one dimensional Bell tunnel model and comparison to INS data from the H₂ complex. The comparison reveals a strong isotope effect of 2×10^3 for the exchange rates of the deuterons versus hydrons.

Literature

- [1]. F. Wehrmann, J. Albrecht, E. Gedat, H. -H. Limbach, G. J. Kubas, G. Buntkowsky, *J.Phys.Chem.A*, **106**, 2855 (2002)
- [2]. G. Facey, S. Macholl, R.H. Morris, G. Buntkowsky, *Phys.Chem. Chem. Phys.*, **2**,935,(2000)
- [3]. F. Wehrmann, T. P. Fong, R. H. Morris, H. -H. Limbach, G. Buntkowsky, *Phys.Chem. Chem. Phys.*, **1**, 4033, (1999)
- [4]. H. -H. Limbach, S. , S. Gründemann, G. Buntkowsky, S. Sabo-Etienne, B. Chaudret, G. J. Kubas, J. Eckert, *J. Am. Chem. Soc.* **120**, 7929, (1998)
- [5]. G. Buntkowsky, H. -H. Limbach, F. Wehrmann, I. Sack, H. M. Vieth, R. H. Morris, *J. Phys. Chem. A*, **101**, 4679, (1997)
- [6]. G. Buntkowsky, J. Bargon, H. -H. Limbach, *J. Am. Chem. Soc.* , **118**, 8677, (1996)

Ultrafast structural dynamics in solid Hydrogen.

M. Chergui

*Laboratoire de Spectroscopie Ultrarapide, ISIC-BSP, Ecole Polytechnique Fédérale de
Lausanne, CH-1015 Lausanne-Dorigny, Switzerland*

The ultrafast dynamics of electronic bubble formation upon excitation of the A ($3s\sigma$) Rydberg state of NO impurity trapped in solid para- H_2 has been studied by femtosecond pump-probe spectroscopy. The evolution of the spherical bubble is followed in real time by means of a probe pulse, which maps the transient configurations via transitions to higher lying Rydberg states. The NO A $\leftarrow$ X transition (6eV) is achieved by a non resonant two-photon process, which improves the time resolution of the experiment to about 100 fs.

A first ultrafast expansion of the cage boundaries around the photoexcited impurity takes place in around 200 fs, corresponding to a net energy flow of approx. 0.5 eV from the excited center to the lattice. The medium undergoes then to a slower structural rearrangement on a time scale of few picoseconds. The dynamical structural information, extracted directly from experimentally measured quantities, is compared with the results of molecular dynamics simulations, in which a temperature correction is used to mimic the quantum fluctuations. The MD simulations indicate that the initial dynamics can be safely associated to the expansion of the first shell of solvent neighbors, while a successive slower expansion (continuing up to 1 ps) should be associated to the collective motion of many shells.

Quantum simulation of biomolecules

David C. Clary

Department of Physical and Theoretical Chemistry
University of Oxford
South Parks Rd
Oxford, UK

david.clary@chem.ox.ac.uk

This lecture will describe calculations that we have done recently on the simulations of clusters and biomolecules. Particular emphasis will be placed on a description and application of the torsional path integral simulation method that has been developed in our group by Thomas Miller. This allows for the quantum description of the torsional degrees of freedom in a macromolecule and readily yields important thermodynamic quantities such as free energies of molecules. The method also allows for the prediction of the populations of conformations of biomolecules as a function of temperature that can be compared with experiment. Application to some small biomolecules will be described at the conference.

MODELING VIBRATIONAL AND ELECTRONIC RELAXATION OF PHOTOEXCITED RADICAL REACTIONS IN CONDENSED PHASES

David F. Coker and Jing Zhang

Department of Chemistry, Boston University, 590 Commonwealth Avenue, Boston, MA 02215, coker@bu.edu

The competition between electronic and vibrational relaxation, and radical bond cleavage and formation is explored in photoexcited reactions of polyatomic molecules in condensed phase environments. A combination of semi-empirical excited state electronic structure methods, mixed quantum-classical, and semi-classical molecular dynamics techniques are used to study model excited state reactions of I_2 and ICN in a variety of environments, from simple rare gas matrices and liquids, to model aluminosilicate zeolites. We explore how environmental factors can be manipulated to control photoexcited radical reaction pathways.

VIBRATIONAL COHERENCE OF WEAKLY BONDED MOLECULAR SYSTEMS PROBED BY IR ONE COLOR DFWM EXPERIMENTS

M. Broquier^a, C. Crépin^a, A. Cuisset^a, H. Dubost^a, J.-P. Galaup^b

Laboratoire PPM, CNRS, Bât 210, Université Paris-Sud, 91405 Orsay, France
Laboratoire Aimé Cotton, CNRS, Bât 505, Université Paris-Sud, 91405 Orsay, France
e-mail : claudine.crepin-gilbert@ppm.u-psud.fr

The investigation of vibrational dynamics for molecules trapped in the condensed phase gives direct information on dynamic processes in the electronic ground state and on the effect of environment on these processes. We focus our attention on model systems : diatomic molecules (CO, H(D)Cl) embedded in van der Waals solids, at low temperature. Vibrational dephasing times (T_2) are deduced from time-resolved Degenerated Four Wave Mixing (DFWM) experiments performed with the Free Electron Laser of Orsay (CLIO) or with an OPO laser. Relaxation times (T_1) of isolated CO or H(D)Cl molecules are in the microsecond range, hence T_2 measures the pure dephasing time, due to the interaction with the solid. We observe IR accumulated photon echoes and the specific time structure of our experiment gives access to different vibrational processes occurring in very different timescales [1] : dephasing process in the picosecond time scale and spectral diffusion in the nanosecond time scale.

The dephasing time of CO in N_2 is found to be extremely long (> 120 ns) : the vibrational transition of CO in solid nitrogen has the narrowest homogeneous bandwidth ever observed in matrices [1]. The study of H(D)Cl embedded in nitrogen or rare gas matrices allows the observation of the behavior of both van der Waals interactions between isolated molecules and the matrix, and weak hydrogen bonds involved in dimers or complexes trapped in the same sample. A dependence of T_2 on the strength of the hydrogen bond is clearly shown in the investigation of H(D)Cl dimers involving two stretching modes perturbed in different ways by the hydrogen bond (figure 1a). A dependence of this time on the lattice host and on deuteration is also observed.

In solid nitrogen, spectral diffusion due to energy transfer between isolated DCl molecules is a very rapid process. This efficiency is explained by an enhancement of the vibrational transition dipole moment of the molecule in this peculiar host [2]. In particular, vibrational energy transfers between isotopic species result in the observation of “quantum beats” in DFWM signals which are induced by spectral diffusion between independent two-level systems [3] (figure 1b).

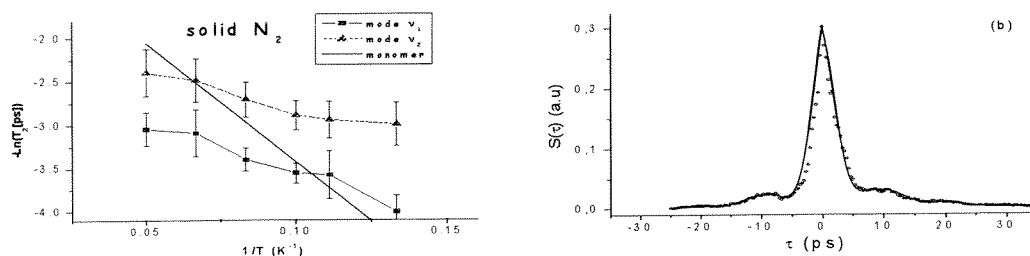


Figure 1 : (a) dephasing times of the two stretching modes of $(DCl)_2$ in solid nitrogen versus temperature ; (b) time-resolved DFWM signal (dots) of isolated DCl molecules in solid nitrogen showing quantum beats in the tens of picoseconds ; the fit (solid line) is obtained using expressions given in references [2,3].

[1] C. Crépin et al., *Phys. Rev. Lett.*, **85**, 964 (2000).

[2] M. Broquier et al., *J. Chem. Phys.* **118**, 9582 (2003).

[3] C. Crépin, *Phys. Rev. A*, **67**, 013401 (2003).

Time-domain analysis of electronic spectra in superfluid ^4He

J. Eloranta ^a, H. Ye. Seferyan ^b, and V. A. Apkarian ^b

^a Department of Chemistry, University of Jyväskylä, Surfontie 9, 40500 Jyväskylä, Finland

^b Department of Chemistry, University of California, Irvine, California 92697
e-mail: eloranta@jyu.fi

Optical absorption spectroscopy of atoms and molecules (e.g. chromophores) has been successfully implemented in both superfluid helium droplets [1] and in bulk helium [2]. Of particular interest is the case of weak electron-phonon coupling, where the observed phonon sidebands accompanying a sharp zero-phonon line interrogate the elementary excitations of the fluid [3, 4, 5, 6]. The absorption spectrum of glyoxal in helium droplets is prototypical [3]. A sharp zero-phonon line defines the electronic origin of the $S_1 \leftarrow S_0$ transition, followed by a +6 K spectral gap, and phonon wings with two broad maxima at *ca.* +8 K and +14 K. Depending on the molecule, the gap region contains a number of additional sharp lines.

A theoretical model, which can be used to calculate the phonon sidebands in the electronic absorption spectra, is described in this work. The electronic degrees of freedom are reduced to a two-level system, which is subject to a time dependent potential due to the surrounding superfluid bath. The bath dynamics is obtained using time dependent density functional theory for superfluid helium [7] whereas the two-level system is treated using a combination of quantum adiabatic theorem and time dependent perturbation theory. More detailed description of this model has been submitted for publication [8].

The calculations are able to reproduce the experimentally observed maxon-roton bands in both helium droplets and bulk helium. In the latter case these bands are predicted to be well resolved. Bulk helium bath is also predicted to display information on the solvent cavity radial breathing mode. Spectra in helium droplets at 0 K is predicted to show sharp progression close to the zero phonon line because emitted waves form a standing wave pattern between the inner and outer droplet boundaries. However, at finite temperatures and with given droplet size distribution, inhomogeneous broadening must smear out this structure and hence it does not constitute as an experimentally observable feature.

[1] Toennies J.P., Vilesov A.F., *Ann. Rev. Phys. Chem.*, **49**, 1 (1998).

[2] Q. Hui and M. Takami, *J. Low Temp. Phys.*, **119**, 393 (2000).

[3] M. Hartmann, F. Mielke, J. P. Toennies, A. F. Vilesov, and G. Benedek, *Phys. Rev. Lett.*, **76**, 4560 (1996).

[4] M. Hartmann, M. Lindinger, J. P. Toennies, A. F. Vilesov, *Chem. Phys.*, **239**, 139 (1998).

[5] S. Grebenev, M. Hartmann, A. Lindinger, N. Pörtner, B. Sartakov, J. P. Toennies, A. F. Vilesov, *Physica*, B **280**, 65 (2000).

[6] F. Stienkemeier and A. F. Vilesov, *J. Chem. Phys.*, **115**, 10119 (2001).

[7] F. Dalfovo, A. Lastri, L. Pricapenko, S. Stringari, and J. Treiner, *Phys. Rev. B*, **52**, 1193 (1995).

[8] J. Eloranta, H. Ye. Seferyan, and V. A. Apkarian, Submitted to *Chem. Phys. Lett.* (2004).

ELECTRON CAPTURE BY MUONS IN RARE GAS SOLIDS AND LIQUIDS

D.G. Eshchenko

*Physik-Institut der Universität Zürich, CH-8057 Zürich, Switzerland and
Laboratory for Muon Spin Spectroscopy, PSI, CH-5232 Villigen PSI, Switzerland
email: dimitry.eshchenko@psi.ch*

Experimental studies of excess electron transport in solid and liquid phases of Ne and Ar are presented and compared with those for He. The technique of muon spin relaxation in frequently reversed electric fields was used to study the phenomenon of delayed muonium formation, whereby excess electrons liberated in the μ^+ ionization track converge upon the positive muons and form μ^+e^- atoms. This process is shown to be crucially dependent upon the electron's interaction with its environment (*i.e.* whether it occupies the conduction band or becomes localized) and upon its *mobility* in these states. The characteristic lengths involved are 10^{-6} to 10^{-4} cm; the characteristic times range from nanoseconds to tens of microseconds. Such a microscopic length scale sometimes enables the electron to spend its entire free lifetime in a state which may not be detected by conventional macroscopic techniques. The end-of-track processes are compared in: (i) liquid and solid helium [where the electron is known to be localized in a bubble in the liquid phase and is thought to behave in a similar manner in the solid]; (ii) liquid and solid neon [where both localized and bandlike electrons are found in the liquid phase while most are delocalized in the solid]; and (iii) liquid and solid argon [where most electrons are bandlike in both phases]. This scaling from light to heavy rare gases enables us to demonstrate new features of excess electron localization on the microscopic scale and provides insight into the structure of the end of the muon track in condensed rare gases.

ROVIBRATIONAL DYNAMICS AND NUCLEAR SPIN CONVERSION OF WATER MONOMERS AND WATER COMPLEXES IN SOLID PARAHYDROGEN

MARIO E. FAJARDO

*AFRL/MNME, Energetic Materials Branch, Ordnance Division,
U.S. Air Force Research Lab, 2306 Perimeter Rd., Eglin AFB, FL 32542-5910
mario.fajardo@eglin.af.mil*

Analysis of the rovibrational infrared (IR) absorption spectra of water (H_2O , D_2O , HDO) molecules isolated in solid parahydrogen (pH_2) reveals their existence as very slightly hindered rotors, with rotational constants reduced by only 2-5% from their gas phase values. Clustering of residual orthohydrogen (oH_2) molecules with water monomers results in the appearance of several new IR absorption features. For Type B water monomer bands (e.g. ν_1 , ν_2) most of the new features appear near the vibrational origin, and were originally interpreted as indicating the presence of “non-rotating” water molecules.^a However, for Type A bands (e.g. ν_3 , $\nu_2 + \nu_3$, $2\nu_2 + \nu_3$, $\nu_1 + \nu_3$) very little IR activity is observed near the vibrational origin, refuting this appealingly simple explanation. Here we propose a new interpretation which assumes a semi-rigid C_{2v} structure for the ground state of the oH_2 -water complexes, with the oH_2 acting as a proton donor to the water oxygen atom. In this picture, the oH_2 -water complex spectra can be understood as parallel and perpendicular bands of an asymmetric top near the prolate symmetric top limit.^b Thus, the features bunching near the Type B vibrational band origins arise from the $\Delta K = 0$ selection rule for parallel bands, while the more widely separated features in the Type A bands arise from the $\Delta K = \pm 1$ selection rule for perpendicular bands.

We report and assign a number of water dopant-induced IR absorption features of the pH_2 host, along with cooperative water- pH_2 transitions in which the vibrational excitation of the pH_2 solid is accompanied by a pure rotational transition of the water dopant. Comparison of the linewidths of the cooperative transitions with those of the water monomer rovibrational transitions indicates that rotational dephasing is the dominant line broadening mechanism.

The nuclear spin conversion (NSC) of metastable $J = 1$ ortho- H_2O (oH_2O) and para- D_2O (pD_2O) molecules follow first order kinetics, with single exponential decay lifetimes at $T = 2.4$ K of 1900 ± 100 s, and 860 ± 50 s, respectively. Surprisingly, NSC of oH_2 -water complexes proceeds at very nearly the same rate as for the corresponding water monomer. We report unassigned spectra of larger $(\text{oH}_2)_n$ -water clusters, and the even more surprising observation of the apparent prolonged survival (!) of oH_2O and pD_2O molecules clustered with several oH_2 molecules.

^aM.E. Fajardo, 57th International Symposium on Molecular Spectroscopy, paper MF01 (2002).

^bM.E. Fajardo, S. Tam, and M.E. DeRose, J. Mol. Struct. **695-696**, 111 (2004).

THE SURPRISING CHEMISTRY OF NOBLE-GAS ATOMS: NEW MOLECULES AND NEW MATERIALS

R.B. Gerber, A. Cohen, Z. Bihary and E. Brown

*Department of Physical Chemistry and Fritz Haber Research Center, The Hebrew University,
Jerusalem 91904, Israel*

And

Department of Chemistry, University of California, Irvine, CA 92697

Abstract of Lecture

A range of new compounds with chemically-bound noble- gas elements are explored theoretically, using methods that include ab initio computations, Transition State rate calculations and Molecular Dynamics simulations. The focus is on formation mechanisms and dynamics and on the prediction of new molecules and their condensed phases (neat crystals). The molecules discussed in the talk are motivated by the compounds of the type of HRgY (where Rg denotes noble-gas atom and Y is an electronegative group), pioneered by Räsänen and his group and prepared by photolysis of HY in rare-gas solids. However, the systems predicted have new characteristics that open novel directions in the field. The main results are:

- (1) Neat crystalline phases of several HRgY compounds such as HXeH and HXeCCH are predicted to be stable. Crystal structures are proposed for these solids.
- (2) Polymeric xenon acetylide, being a linear, periodic and extended polymer with the repeat unit - (CCXe) - is predicted to be stable. Transition State calculations suggest high kinetic stability of the polymer, once formed.
- (3) Several new "Organo-Rare" compounds are predicted, including xenon dialkynides, R-CCXeCC-R. These diacetylides may be stable also outside the cryogenic range.
- (4) Monte Carlo transition State calculations are carried out for the formation of HArF in an Ar matrix, for a preparation where HF is photolyzed in solid Ar, followed by thermal annealing. The computed threshold temperature for HArF formation is in good accord with experiment.

HOW WATER NETWORKS ACCOMMODATE AN EXCESS ELECTRON: STRUCTURE AND DYNAMICS OF THE BINDING SITE

Nathan I. Hammer, Joong-Won Shin, Jeffrey Headrick, Eric G. Diken, Gary H. Weddle,
and Mark A. Johnson

*Sterling Chemistry Laboratory
Yale University
P.O. Box 208107
New Haven, CT 06525
Mark.johnson@yale.edu*

The deformation of water molecules that reside near a hydrated electron has remained elusive since the discovery of this species over forty years ago. Here we quantify the local electron-molecule interactions in a gas phase, argon “nanomatrix” cluster study, where sharp vibrational bands are reported for both H and D isotopomers of the small water cluster anions, $(\text{H}_2\text{O})_{4-6}^-$. Analysis of these band patterns reveals a detailed picture of the diffuse electron binding site. The dominant bands are traced primarily to the hydrogen atom stretches on a single water molecule attached to the supporting network with a double H-bond acceptor motif. Several bands appear dramatically distorted because the excited vibrational levels are strongly coupled to the electron continuum, and lineshape analysis is used to quantify the vibration-to-electronic energy transfer rates. These rates are found to be both mode-specific and remarkably fast, with the symmetric stretching mode only surviving for about 8 vibrational periods.

CONTROL OF MOLECULAR PHOTODYNAMICS BY STRONG-FIELD ALIGNMENT IN SOLIDS

T. Kiljunen,^a B. Schmidt,^b and N. Schwentner^a

^a*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany,*

^b*Institut für Mathematik II, Freie Universität Berlin, Arnimallee 2-6, 14195 Berlin, Germany*
Toni.Kiljunen@physik.fu-berlin.de

Molecular response to intense nonresonant laser field is studied theoretically, in terms of alignment of a molecule with field polarization. The oscillating field induces an anisotropic polarization, and the energy gain in the field then leads to a formation of pendular states, i.e., directional hybridizations of free molecular rotations. Two qualitatively different time scales can be interrogated in the process: adiabatic regime, where populations on the excited molecular rotational states follow the laser pulse envelope, and ultrafast regime, where a post-pulse alignment occurs due to the formation of a rotational wave packet. [1]

The effect of a condensed phase surrounding, such as a solid rare gas hindering the induced molecular rotation, is here assessed by incorporation of highly symmetric model potentials in the time-dependent Schrödinger equation. The main goal of the research is to attain optical control on molecular photophysics and –chemistry by affecting the product yields of photoprocesses, such as dissociation and recombination, via suitable preorientation in condensed phase conditions.

We present the above ideas and apply the computational scheme for a specific matrix-isolation case of CIF molecule in solid Ar host. This system is recently characterized by both theory and experiments.[2] In particular, the attempt in the present case is to steer the dissociative dynamics selectively in or out of the lattice cage.

[1] J.Ortigoso, M.Rodriquez, M.Gupta, and B. Friedrich, *J. Chem. Phys.* **110**, 3870 (1999).

[2] T.Kiljunen, M.Bargheer, M.Gühr, B.Schmidt, and N.Schwentner, *PCCP* **6**, 2932 (2004), and references therein.

Photochemistry of nucleobases in beams

Chr. Plützer, I. Hünig, K.A. Seefeld, D. Löwenich, M. Nispel, K. Kleinermanns
Heinrich Heine Universität, Universitätsstr.26.43.02, D-40225 Düsseldorf

Intrinsic properties of isolated biomolecules and large parts of their energy landscape can be investigated by high resolution laser spectroscopy in molecular beams and directly compared to theory. Different electronic states of Adenine as well as Adenine-Thymine and Adenine-Adenine base pairs and their methyl substituted derivatives are observed and assigned based on resonant two photon ionisation and IR-UV and UV-UV double resonance experiments in a supersonic jet. Expansion conditions were chosen to preferentially form small clusters. The IR-UV spectrum in the range of the NH stretch vibrations fits cluster structures with $\text{HNH}\cdots\text{O}=\text{C}/\text{N}\cdots\text{HN}$ hydrogen bonding based on the comparison with the A and T monomer IR spectra and with *ab initio* calculated vibrational spectra of the most stable A-T isomers. The Watson-Crick A-T base pair is not the most stable A-T pair at different *ab initio* levels and its vibrational spectrum is not in agreement with the observed experimental spectrum. The Adenindimer shows $\text{HNH}\cdots\text{N}/\text{N}\cdots\text{HN}$ hydrogen bonding. 9-Methyladenine – adenine has a stacked structure and exhibits extremely efficient hydrogen transfer upon electronic excitation. Adenine shows H atom dissociation upon UV excitation as exhibited by 2+1-REMPI at 243 nm. The photochemical stability of the DNA bases and GC and AT base pairs are compared and their mechanism of conversion of electronic excitation to the ground state is critically discussed based on our experimental results of hydrogen transfer and N-H photodissociation.

References:

1. Pairing of isolated nucleic-acid bases in the absence of the DNA backbone, Eyal Nir, Karl Kleinermanns & Mattanjah S. de Vries NATURE, Vol. 408, 21/28 December 2000
2. Pairing of the nucleobase adenine studied by IR-UV double-resonance spectroscopy and *ab initio* calculations, Chr. Plützer, I. Hünig, K. Kleinermanns, Phys. Chem. Chem. Phys., 2003, 5, 1158 - 1163).
3. Photostability of Isolated and Paired Nucleobases. 1. N-H Dissociation of Adenine and Hydrogen Transfer in its Base Pairs examined by Laser Spectroscopy., I. Hünig, C. Plützer, K. A. Seefeld, D. Löwenich, M. Nispel and K. Kleinermanns, accepted for publication in ChemPhysChem (2004)

MULTIDIMENSIONALITY AND COOPERATIVITY OF INTRAMOLECULAR HYDROGEN BOND DYNAMICS

Oliver Kühn

*Institut für Chemie, Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustr. 3, D-14195
Berlin, ok@chemie.fu-berlin.de*

The reaction path motion of a Hydrogen atom across an intramolecular Hydrogen bond is often characterized by a simultaneous rearrangement of the molecule's heavy atoms. Thus, a rigorous theoretical description faces the challenges of generating a multidimensional potential energy surface and solving the respective Schrödinger equation for the nuclear wave function.

As a compromise between accuracy and feasibility reaction surface concepts have been established. Here an accurate treatment of the large amplitude reactive motion of the Hydrogen atom is combined with a harmonic approximation for the skeleton degrees of freedom. An all Cartesian formulation [1] was shown to be particularly convenient because it contains all couplings between the coordinates in the potential energy operator [2]. Besides having an approximate but full-dimensional Hamiltonian this approach has the additional advantage that the latter has a form which is separable in most degrees of freedom. This facilitates an effective numerical solution of the time-dependent Schrödinger equation by using the Multiconfiguration Time-Dependent Hartree method [3,4].

In this contribution a number of examples for multidimensional nuclear quantum dynamics of Hydrogen bonds will be discussed. Emphasis will be put on the interpretation of complex spectral lineshapes in terms of time dependent wave packets and related ultrafast infrared spectroscopies. Besides single Hydrogen bond dynamics the issue of cooperative motion of double Hydrogen bonds will be addressed.

- [1] B. A. Ruf, W. H. Miller, *J. Chem. Soc. Faraday Trans. 2*, **84**, 1523, (1988).
- [2] H. Naundorf, J. A. Organero, A. Douhal, O. Kühn, *J. Chem. Phys.* **110**, 11286 (1999).
- [3] H. Naundorf, G. A. Worth, H.-D. Meyer, O. Kühn, *J. Phys. Chem. A* **106**, 719 (2002).
- [4] M. Petković, O. Kühn, *J. Phys. Chem. A* **107**, 8458 (2003).

Optimal control of multi-photon ionization processes in alkali dimers: Learning from the optimized pulse shapes

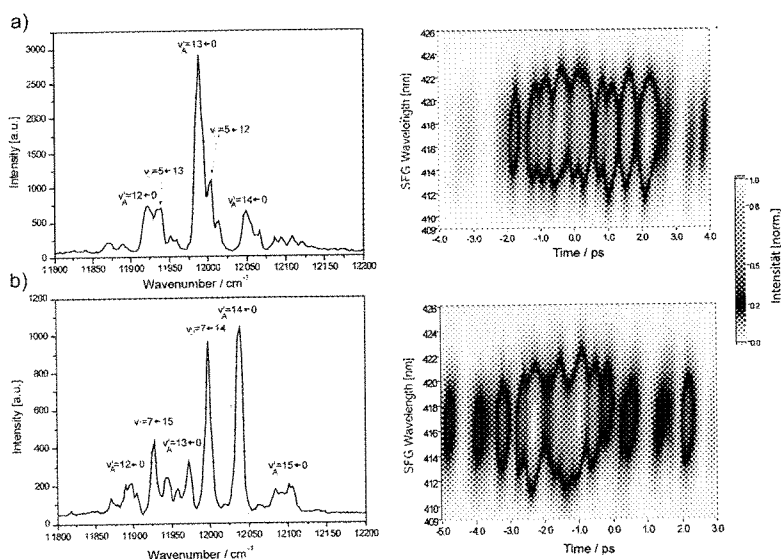
A. Lindinger, M. Plewicky, F. Vetter, S. M. Weber, C. Lupulescu, A. Merli, and L. Wöste

Institut für Experimentalphysik, FU Berlin, Arnimallee 14, 14195 Berlin; e-mail: lindin@physik.fu-berlin.de

The controllability of three-photon ionization pathways by shaped fs-pulses is investigated for alkali dimers. A feedback loop using evolutionary algorithms is applied in order to optimize a chosen objective. The acquired optimized pulse shapes reveal intrinsic information about the molecule and the chosen ionization pathways. For the ionization of NaK a comparison with theoretical results achieved by using optimal control theory shows a good agreement [1]. This aids the interpretation and can be seen as a tool for identification of the responsible processes.

In particular, selective optimization of different isotopomers in an ionization process is investigated, demonstrated for $^{39,39}\text{K}_2$ and $^{39,41}\text{K}_2$ [2]. A surprisingly high enhancement of one isotope compared to the other and vice versa is achieved (in total by about 140). Information about the dynamics on the optimally chosen vibrational states within the ionization path could be extracted from the acquired pulse shapes. This provides a new spectroscopical approach of yielding temporal information of distinct frequency pattern on fs-time scales. It reveals how the algorithm precisely addresses the vibrational wave functions by coherent interaction with the corresponding spectral pulse components. The presented isotopomer selection method should, in principle, be generally feasible for all molecules.

Moreover, experimental realizations of novel methods in coherent control are presented. One approach is the implementation of pulse cleaning where extraneous control field features are removed by applying genetic pressure on the spectral components using appropriate cost functions. The other new approach being demonstrated is the introduction of parametric optimization in the time or frequency domain in order to reduce the searching space for the algorithm. Choosing intuitively accessible parameters like intensities, spacings, and chirps of subpulses aids the understanding of the involved molecular processes.



Pulse spectra and corresponding XFROG-traces for the maximization (a) and minimization (b) of the K_2 isotope ratio. The labeling at the peaks in the spectra denote the vibrational levels of the electronic transitions $A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ and $2^1\Pi_g \leftarrow A^1\Sigma_u^+$ of $^{39,39}\text{K}_2$ for maximization and of $^{39,41}\text{K}_2$ for minimization. In the XFROG-traces half oscillation periods of the wavepacket in the excited $A^1\Sigma_u^+$ state ($T_{1/2} = 250$ fs) can be identified.

- [1] B. Schäfer-Bung, R. Mitrić, V. Bonačić-Koutecký, A. Bartelt, C. Lupulescu, A. Lindinger, Š. Vajda, S. M. Weber, and L. Wöste, J. Phys. Chem. A **108**, 4175-4179 (2004).
- [2] A. Lindinger, C. Lupulescu, M. Plewicky, F. Vetter, A. Merli, S. M. Weber, and L. Wöste, Phys. Rev. Lett. **93**, 033001-1-4 (2004).

Cold molecules

Gerard Meijer

*Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany
e-mail: meijer@fhi-berlin.mpg.de*

Getting full control over both the internal and external degrees of freedom of molecules has been an important goal in molecular physics during the last decades. This control is essential in the presently very active field of Cold Molecules. Trapped samples of neutral molecules have been created by means of buffer gas cooling in a magnetic trap, by using deceleration of a molecular beam in combination with an electrostatic trap, and by pairing cold atoms to form molecules in optical or magnetic traps. Recently, spectacular progress has been made with association of ultra-cold atoms assisted by magnetically induced Feshbach resonances, resulting in the first molecular Bose-Einstein condensates. In the field of Cold Molecules there is a particular interest in cold dipolar molecules which stems from the presence of the anisotropic, long-range dipole-dipole interaction in these samples, which is predicted to lead to interesting physics and novel applications.

In this presentation I will give an overview of the various experiments that we have performed during the last few years to explore the possibilities of manipulating neutral polar molecules with electric fields [1]. Arrays of time-varying, inhomogeneous electric fields have been used to reduce in a stepwise fashion the forward velocity of molecules in a beam. With this so-called 'Stark decelerator', the equivalent of a LINear ACcelerator (LINAC) for charged particles, one can transfer the high phase-space density that is present in the moving frame of a pulsed molecular beam to a reference frame at any desired velocity; molecular beams with a computer-controlled (calibrated) velocity and with a narrow velocity distribution, corresponding to sub-mK longitudinal temperatures, can be produced. These decelerated beams offer new possibilities for collision studies, for instance, and enable spectroscopic studies with an improved spectral resolution; first proof-of-principle high-resolution spectroscopic studies have been performed. These decelerated beams have also been used to load ground-state OH radicals in an electrostatic trap at a density of (better than) 10^7 mol/cm³ and at temperatures of around 100 mK. In another experiment, a decelerated beam of ammonia molecules is injected in an electrostatic storage ring. The package of molecules in the ring can be observed for more than 50 distinct round trips, corresponding to 40 meter in circular orbit and almost 0.5 sec. storage time. By miniaturizing the electrode geometries, high electric fields can be produced using only modest voltages. A micro-structured mirror for neutral molecules that can rapidly be switched on and off has been constructed and used to retro-reflect a beam of ammonia molecules with a forward velocity of about 30 m/s. This holds great promise for miniaturizing the whole decelerator, trap and storage ring for future applications.

[1] H.L. Bethlem and G. Meijer, Int. Rev. Phys. Chem. 22, 73 (2003)

A new nanocluster system — impurity-helium condensate (impurity gel) in liquid helium

L.P.Mezhov-Deglin, V.B.Efimov, A.A.Levchenko, G.V.Kolmakov, M.Yu.Brazhnikov

ISSP RAS, Chernogolovka, Moscow region, Russia
e-mail: mezhov@issp.ac.ru

A new form of condensed matter — high porous impurity-helium condensate (gel) soaked with superfluid He-II can be prepared by condensation of a flow of gaseous ^4He with admixture of the impurity on the surface of He-II cooled below 1.6 K. It is supposed that the gel samples formed of nanoparticles of heavy water or deuterium and cooled below a few mK could be used for accumulation and storage of ultracold neutrons, and the gel samples containing the mixture of molecules and atoms (free radicals) of the molecular impurity could be used for storage of the energy at low temperatures.

IN-SITU SYNTHESIS AND INTERNAL STABILITY OF THE SIMPLEST KETOCARBENE (FORMYLMETHYLENE) IN SOLID ARGON

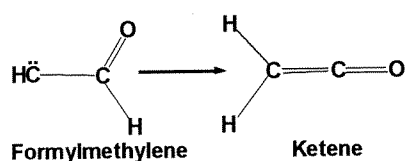
E.Ya. Misochko, A.V. Akimov, I.U. Goldschleger

Institute of Problems of Chemical Physics RAS, Chernogolovka, Moscow Region, 142432 Russia

C.A. Wight

Department of Chemistry, University of Utah, Salt Lake City, UT, 84112 USA

The ketocarbenes are generally considered as important intermediates entrained in a various types of chemical reactions. Lifetimes of ketocarbenes are controlled by reaction of the intramolecular rearrangement leading to production of ketene:



Formylmethylene has been postulated as one of the key intermediates in $[\text{C}_2\text{H}_2\text{O}]$ molecular system, but only ethynol and oxiranylidene have been experimentally observed previously.

Here we report the first spectroscopic observation of formylmethylene in its ground state and show how the triplet intermediate undergoes facile rearrangement to singlet ketene. We obtained infrared spectra of five different deuterium and ^{18}O formylmethylene isotopomers in solid argon, and we measured the rate constants of their conversion into ketene.

The new intermediate was generated by chemical reaction of mobile oxygen atoms with acetylene molecules in solid samples $\text{Ar}/\text{O}_3/\text{C}_2\text{H}_2 = 3000/1/1$ at 15 K. It was observed that UV photolysis of ozone leads to the growth of infrared bands assigned to ketene. A new series of bands appears in the spectrum simultaneously. After completion of photolysis the new intermediate converts spontaneously to ketene with a characteristic time of 180 s (for $\text{C}_2\text{H}_2\text{O}$). The following sequence for rate constant K_r in various isotopomers is observed:

$$K_r(\text{HCCOD}) < K_r(\text{DCCOD}) < K_r(\text{HCCOH}) < K_r(\text{DCCOH}).$$

The measured vibrational spectra were compared with density functional calculations [B3LYP/6-311++G(3df,2p)] for various structural isomers of $[\text{C}_2\text{H}_2\text{O}]$. Comparison of the observed and the calculated infrared spectra provides convincing evidence that the intermediate species is the *trans* isomer of triplet formylmethylene. Calculations predict that the ground state of this simplest ketocarbene has triplet multiplicity and a planar molecular structure.

This work was supported by the U.S. National Science Foundation (Grant CHE-99700320) and the Russian Foundation for Basic Research (Grant 04-03-32599).

Spectroscopy of molecules in solid parahydrogen, solid He, and He nanodroplet matrices

Takamasa Momose

Department of Chemistry, Graduate School of Science, Kyoto University, Japan

momose@kuchem.kyoto-u.ac.jp

Quantum matrices such as solid hydrogen and He nanodroplets are the useful and convenient matrices for the study of molecules at very low temperatures. Because of the weakness of perturbation from surroundings, molecules in these quantum matrices rotate almost freely as in the gas phase. Moreover, spectral linewidths in these quantum matrices are extremely narrow, so that high-resolution spectroscopy can be performed. One of the examples is given in Figure 1.[1] The narrow spectral linewidths in these quantum matrices allow us to study physical and chemical properties of molecules at low temperatures in various aspects. In this talk, we would like to compare properties of molecules in solid parahydrogen, He nanodroplets, and solid helium based on the data of high-resolution spectroscopy.

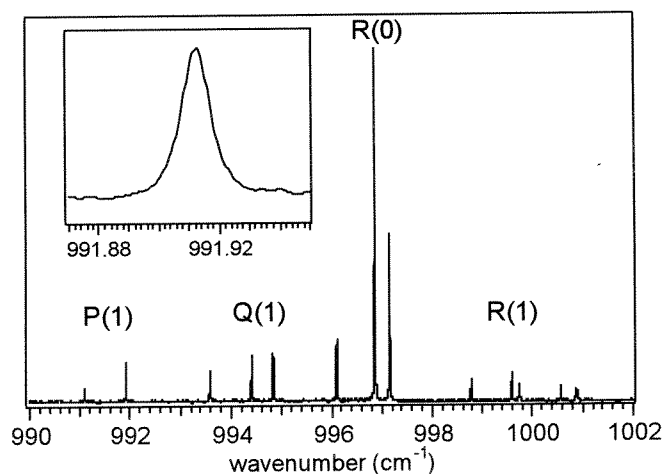


FIGURE 1. The ν_4 transition of CD_4 in solid parahydrogen.

[1] T. Momose, H. Hoshina, M. Fushitani, and H. Katsuki, *Vib. Spectrosc.* **34**, 95 (2004).

MODIFICATIONS OF MOLECULES BY LOW TEMPERATURE STM

Francesca Moresco¹, Leo Gross¹, Leohnard Grill¹, Micol Alemani¹, André Gourdon²,
Christian Joachim², and Karl-Heinz Rieder¹

¹ Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

² CEMES-CNRS, 29 rue J. Marvig, P.O. Box 4347, F-31055 Toulouse Cedex, France
francesca.moresco@physik.fu-berlin.de

The ability of Low Temperature Scanning Tunneling Microscope to manipulate atoms and to build nanostructures with atomic precision can be extended to the manipulation of larger molecules and to selectively modify their internal degrees of freedom. Manipulation experiments on individual molecules show an exciting diversity of physical, chemical, and electronic phenomena. They permit a deeper insight into the quantum electronics of molecular systems and provide important information on the conformational and electronic properties of single complex molecules.

In this talk, some examples of recent manipulation experiments performed on single molecules will be presented. Single Porphyrin based molecules (TBPP) and model systems for molecular wires (Lander) have been manipulated on copper surfaces by means of their interaction with the STM tip.

The principle of a conformational molecular switch working under the action of a STM tip have been realized with a single TBPP molecule [1] and the small intramolecular changes of the molecule during its lateral movement on the surface have been recorded [2].

Moreover, the reproducible contact and de-contact of a Lander molecule to a metallic step edge have been investigated and controlled by lateral manipulation. The interaction of the terminal part of the wire with the 2D surface electron gas on Cu(111) notably modifies the electronic standing wave patterns at the contact position [3]. The standing wave pattern of a single Lander on a terrace show that specific information concerning the electronic interaction of the different internal groups of the molecule with the surface can be obtained [4].

[1] F. Moresco, G. Meyer, K.-H. Rieder, H. Tang, A. Gourdon, C. Joachim
Phys. Rev. Lett. **86**, 672 (2001).

[2] F. Moresco, G. Meyer, K.-H. Rieder, H. Tang, A. Gourdon, C. Joachim
Phys. Rev. Lett. **87**, 88302 (2001).

[3] F. Moresco, L. Gross, M. Alemani, H. Tang, A. Gourdon, C. Joachim, K.-H. Rieder
Phys. Rev. Lett. **91**, 03660 (2003).

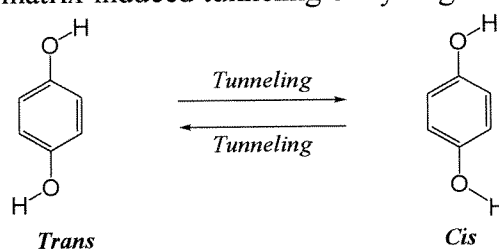
[4] L. Gross, F. Moresco, L. Savio, A. Gourdon, C. Joachim, K.-H. Rieder
Phys. Rev. Lett., in press.

HYDROGEN-ATOM MOVING IN LOW-TEMPERATURE RARE-GAS MATRICES

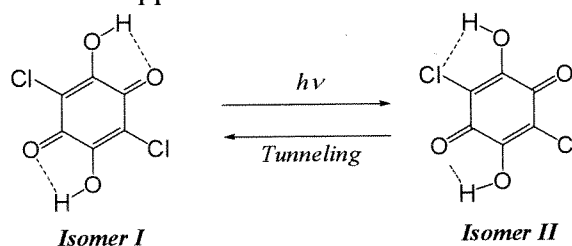
Munetaka NAKATA

Graduate School of BASE, Tokyo University of A & T, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan
(necom@cc.tuat.ac.jp)

Hydrogen-atom moving in hydroquinone and its derivatives in low-temperature rare-gas matrices has been studied by Fourier transform infrared spectroscopy (FTIR) with an aid of density-functional-theory (DFT) calculations [1-4]. In the case of hydroquinone [1], the *cis/trans* population ratio changed reversibly in conformance with the Boltzmann distribution law when the temperature of Xe matrix was changed between 16 and 75 K, despite the high torsional barrier, 10.8 kJ mol⁻¹. The *cis-trans* isomerization equilibrium at low temperature is accounted for in terms of the matrix-induced tunneling of hydrogen atoms.



A similar hydrogen-atom tunneling was found in the torsional isomerization around the two C-O bonds of 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone [2]. The infrared spectrum of the most stable isomer, *Isomer I*, was observed, while that of *Isomer II*, which is 22 kJ mol⁻¹ less stable than *Isomer I*, was observed as a transient species during UV-visible irradiation. Isomerization from the less stable isomer to the most stable one occurred immediately by tunneling after the irradiation was stopped.



- [1] N. Akai, S. Kudoh, M. Takayanagi, M. Nakata, *Chem. Phys Letters*, **356**, 133 (2002).
- [2] N. Akai, S. Kudoh, M. Takayanagi, M. Nakata, *J. Phys. Chem.*, **106**, 11029 (2002).
- [3] N. Akai, S. Kudoh, M. Nakata, *J. Phys. Chem.*, **107**, 2635 (2003).
- [4] N. Akai, S. Kudoh, M. Nakata, *J. Phys. Chem.*, **107**, 3655 (2003).
- [5] N. Akai, S. Kudoh, M. Nakata, *J. Photochem. Photobiol. A*, in press (2004).

HYDROGEN ATOM CHEMISTRY STUDIED VIA ITS ISOTOPE MUONIUM

Paul W. Percival

Department of Chemistry, Simon Fraser University, Burnaby, B.C. V5A 1S6, Canada. percival@sfu.ca

Muonium ($\text{Mu} \equiv \mu^+e^-$) is the single-electron atom with a positive muon as its nucleus. Although the muon mass is only $\sim 1/9^{\text{th}}$ that of the proton, it is still much heavier than the electron; thus the *reduced* mass of Mu is close to that of H, and key atomic properties (size and ionization energy) are similar. Accordingly, Mu may be thought of as a light isotope of hydrogen. Just like deuterium and tritium, Mu can be used as a spin or radioactive tracer to explore the chemistry of H atoms, as well as to extend the mass range of isotope studies. An obvious barrier to muonium chemistry studies is the limited availability of muons, which are produced in beams at particle accelerators, such as TRIUMF in Canada and PSI in Switzerland. However, given a suitable muon source, it turns out to be relatively easy to use Mu to study H atoms and free radicals. Indeed, the ease of use of this exotic probe has resulted in its application to study H chemistry under extreme conditions where conventional spectroscopic techniques are not practical. Among the factors favouring Mu are: (1) A beam of muons can be fired into any sample container, without the need for optical windows. (2) Mu is formed in most materials when muons thermalize. (3) Muons are studied by magnetic resonance methods (collectively known as μSR), but since beam muons are highly spin polarized there is no need for radio-frequency or microwave radiation. (4) The detectors are simple devices (plastic scintillators) outside the controlled sample environment. (5) Given the short lifetime of the muon ($\tau = 2.2 \mu\text{s}$), μSR is inherently suited to the study of transients.

The versatility of this exotic atom has resulted in the ironic situation that in many materials Mu has been studied over a wider range of conditions than H. Taking water as an example, Mu has been studied from below 10 K up to the melting point of ice, and in liquid water up to supercritical conditions. The μSR techniques are not limited to study of the atom; they can also provide valuable information on the free radical products of muonium addition to unsaturated compounds. Hyperfine constants (hfc) can be determined for other nuclei with spin, in addition to the muon. For example, a study of $^{13}\text{C}_{60}\text{Mu}$ has provided unique information on the unpaired electron spin distribution in the C_{60}H radical. The temperature dependence of hfc can often be interpreted in terms of intramolecular dynamics, such as methyl rotation in ethyl, propyl and tert-butyl radicals, all of which have been studied over the full liquid range of the parent alkenes. The most recent work in this area involves the muoniated methyl radical, CH_2Mu , and revealed an interesting isotope effect. The proton hfc of the unsubstituted CH_3 is known to fall with temperature, consistent with increasing population of excited vibrational levels of the out-of-plane bending. In contrast, the muon and proton hfc in the muoniated radical have negligible temperature dependence. This can be rationalized in terms of the higher zero-point vibrational frequency for CH_2Mu . At a given temperature there is much less population of excited states in the muoniated isotopomer. Or, to put it another way, the muoniated radical mimics the behaviour of the heavier isotopomer at a much lower temperature.

Frontiers of rare gas chemistry

Leonid Khriachtchev¹, Jan Lundell¹, Hanna Tanskanen¹, Antti Lignell¹, Mika Pettersson² and Markku Räsänen^{1,3}

¹Laboratory of Physical Chemistry, PO Box 55, FIN-00014 University of Helsinki, Finland

²Department of Chemistry, University of Jyväskylä, PO Box 35, FIN-40014 Jyväskylä, Finland

³E-mail address: markku.rasanen@helsinki.fi

At the present time the family of noble-gas containing hydrides of common structure HNgY amounts 20, including the first argon molecule, HArF [1]. Both inorganic and organic Y fragments are involved in such molecules, the organic acetylenic and diacetylenic species being recently synthesized [2-5]. These examples suggest that new such molecules will be found in future. The HNgY molecules have very characteristic properties as suggested by computational methods: linear bonding is involved around the noble gas atom, the (HNg)⁺Y⁻ structure plays a central role in stabilisation, and they possess very high dipole moments. The practical consequences of the properties of these molecules are versatile, and will be discussed. First, the H-Ng stretching absorption intensity is quite large, and the formation of the HNgY molecules upon hydrogen atom mobilisation can be monitored with great sensitivity yielding reliable measures for the H/D mobility [6]. Secondly, exceptionally large matrix site effects due to their large dipoles are found for these molecules, giving tools to probe experimentally the local environments of the embedded molecules [7]. Furthermore, these molecules show strong complexation with various impurities [8, 9], and such solvation effects may lead to their stabilization in other media than solid noble gases. Finally, first examples of reactions of noble gas hydrides with other species are available, and will be discussed.

- [1] L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell, and M. Räsänen, *Nature (London)* **406**, 874 (2000).
- [2] L. Khriachtchev, H. Tanskanen, J. Lundell, M. Pettersson, H. Kiljunen, and M. Räsänen, *J. Am. Chem. Soc.* **125**, 4696 (2003).
- [3] V. I. Feldman, F. F. Sukhov, A. Y. Orlov, and I. V. Tyulpina, *J. Am. Chem. Soc.* **125**, 4698 (2003).
- [4] L. Khriachtchev, H. Tanskanen, A. Cohen, R. B. Gerber, J. Lundell, M. Pettersson, H. Kiljunen, and M. Räsänen, *J. Am. Chem. Soc.* **125**, 6876 (2003).
- [5] H. Tanskanen, L. Khriachtchev, J. Lundell, H. Kiljunen, and M. Räsänen, *J. Am. Chem. Soc.* **125**, 16361 (2003).
- [6] L. Khriachtchev, H. Tanskanen, M. Pettersson, M. Räsänen, V. Feldman, F. Sukhov, A. Orlov, and A. F. Shestakov, *J. Chem. Phys.* **116**, 5708 (2002).
- [7] L. Khriachtchev, M. Pettersson, A. Lignell, and M. Räsänen, *J. Am. Chem. Soc.* **123**, 8610 (2001).
- [8] A. Lignell, L. Khriachtchev, M. Pettersson, and M. Räsänen, *J. Chem. Phys.* **117**, 961 (2002).
- [9] A. V. Nemukhin, B. L. Grigorenko, L. Khriachtchev, H. Tanskanen, M. Pettersson, and M. Räsänen, *J. Am. Chem. Soc.*, **124**, 10706 (2002).

Radical-molecule reactions down to 10 K and interstellar implications.

B.R. Rowe

*UMR 6627 CNRS-Université de Rennes 1, Bâtiment 11C, campus de Beaulieu, 35042 Rennes Cedex, France.
Bertrand.rowe@univ-rennes1.fr*

The kinetics of many gas-phase reactions between neutral species follow the Arrhenius expression:

$$k(T) = A(T) \exp(-E_a/T)$$

where the activation energy E_a (here in K) comes from an activation energy barrier. Reactions with such barriers play no role in the cold chemistry of diffuse and dense interstellar clouds where the typical temperature range is 10-100K. It has been recognized for a long time however that radical-radical reactions often occur at room temperature with a rate approaching the so-called collision limit i.e. with zero activation energy. A few reactions of this kind were included in the early models of interstellar chemistry [1] but, owing to the lack of experimental data, the dependence of the rate coefficient was assumed positive with the square root of the temperature. The gas phase network was therefore mainly based on ion-molecule and ion-electron reactions.

This view has radically changed in the last ten years due to the finding that reactions of radicals with “stable” molecules can be fast at 300 K and remain fast down to 10 K exhibiting a variety of behaviours and very often a negative temperature dependence [2]. Most of the experimental data concerning the kinetics have been obtained with the so-called CRESU technique (Cinétique de Réaction en Ecoulement Supersonique Uniforme) [2] and a few have been confirmed by crossed beams experiments at low collision energy [3] and by theoretical calculations. These findings have raised great difficulties for gas-phase modelling of interstellar chemistry as the exact behaviour of neutral-neutral reactions is far more difficult to predict than that of ion-molecule reactions. Therefore models have to rely on “educated guesses” which can, in the end, result in order of magnitude differences for the predicted abundances [4]. It is therefore vital for interstellar chemistry to extend the chemical data base at very low temperature.

In this presentation I will concentrate on two new developments of the CRESU technique. The first one developed at Birmingham university allows radical-atom reactions, such as $\text{OH} + \text{O}$, to be studied. These are key reactions in the interstellar gas phase reaction network [4]. The difficulty here is to create the reactant atom in large and known quantity. The second development deals with the problem of complex reacting species of low vapour pressure such as Polycyclic Aromatic Hydrocarbons (PAHs) which are thought to be an important component of the interstellar medium. Results for reactions of anthracene with respectively OH and CH down to 50 K will be presented.

[1] Y.P. Viala, *Astron. Astrophys. Suppl. Ser.*, **64**, 391, (1986).

[2] I.W.M. Smith and B.R. Rowe, *Acc. Chem. Res.*, **33**, 261, (2000).

[3] W.D. Geppert et al, *Physical Chemistry Chemical Physics*, **2**, 2873, (2000).

[4] I.W.M. Smith, E. Herbst, and Q. Chang, *Mont. Not. R. Astron. Soc.*, **350**, 323, (2004).

TERAHERTZ SPECTROSCOPY OF WATER CLUSTERS: PROGRESS TOWARDS A UNIVERSAL WATER POTENTIAL

Richard J. Saykally

Department of Chemistry, University of California, Berkeley, CA 94720-1460, U.S.A.
saykally@uclink4.berkeley.edu

Great progress has been achieved in the quest to understand the intriguing properties of water (e.g. 15 forms of ice, density maximum, diverging heat capacity of supercooled liquid...) through the use of effective force fields in computer simulations. However, despite the construction of literally hundreds of such effective potentials, none can accurately describe water in all of its forms, viz. clusters, liquid, solid. Following initial studies of the water dimer by microwave spectroscopy, the development of Terahertz VRT spectroscopy led to the first highly detailed studies of the water clusters through the hexamer via their intermolecular vibrations, yielding structures, hydrogen bond rearrangement dynamics, and vibrational frequencies. These data provide a route to determining a "universal force field" for water of unprecedented accuracy. Major advances in theoretical methods for computing spectra of such highly nonrigid systems have led to the determination of "spectroscopic" water potential surfaces by direct inversion of spectroscopic results for the dimer.

The latest such potential surface, called VRT(ASP-W)III, has been tested against data for water clusters up to hexamer as well as for the room temperature liquid, and found to give excellent results. Thermodynamic properties of the dimer have been computed, leading to accurate predictions of dimer concentrations in the atmosphere as a function of temperature and humidity. Further refinements in "spectroscopic" water force fields will be described.

Reference:

- [1] N. Goldman, and R.J. Saykally, "Elucidating the role of many-body forces in liquid water. I. Simulations of water clusters on the VRT(ASP-W) potential surfaces," *J. Chem. Phys.* **120**, 4777-4789 (2004).
- [2] N. Goldman, C. Leforestier, and R.J. Saykally, "A 'First Principles' Potential Energy Surface for Liquid Water from VRT Spectroscopy of Water Clusters," *Proceedings of The Royal Society Discussion Meeting, Configurational energy landscapes and structural transitions in clusters, fluids and biomolecules*, Philosophical Transactions A, London, UK (submitted 5/26/2004).
- [3] F.N. Keutsch, and R.J. Saykally, "Water Clusters: Untangling the mysteries of the liquid, one molecule at a time," *PNAS* **98**, 10533-10540 (2001).

LOW TEMPERATURE CHEMISTRY OF NANOMATERIALS

Gleb B. Sergeev

Department of Chemistry Moscow State University, 119992 Moscow Russia
gbs@kinet.chem.msu.ru

Production of nanoparticles of different chemical elements and their organization in functional materials can be considered nowadays as highly promising new inter-science direction. These fundamental problems are actively developed by chemical, physical and material chemistry scientific groups from the world.

It is established that the properties of the materials obtained are strongly depended on particle size (the number of atoms which formed particles). The most promising results were obtained for the investigations of size effects for chemical reactions in the gas phase.

Using low and superlow temperatures, combination of matrix isolation methods with preparative cryochemistry also allows to carry out the production and stabilization of nanoparticles of different chemical elements. The processes of co-condensation and further annealing of the samples led to unusual chemical reactions of metal nanoparticles, synthesis of new substances and nanomaterials with the unique combination of physical and chemical properties.

The unusual reaction of magnesium atoms and higher clusters with polyhalogen methanes were analysed by using of IR- and UV-spectroscopy combining with the results of quantum-chemistry modeling of the reactive system. The mechanism of the reaction of magnesium species with carbon tetrachloride in temperature range 12-77 K was proposed.

Cryoformation of nanosystems based on lead nanoparticles and nanofilms was studied using AFM-spectroscopy. The control of their electrical and physical properties by interaction with water and ammonia vapors was proposed. It was shown the existence of size effects for condensation process of water films revealed through measuring of mechanical stresses in growing sample during its cryoformation. Some problems of cryochemical production of new functional materials are discussed.

References.

- [1] G.B.Sergeev .Nanochemistry, Moscow Univ.Publ., 2003, p.288
- [2] G.B.Sergeev .Cryochemistry of metal nanoparticles. J.Nanopart.Research , 2003, 5, 529-537.
- [3] S.P.Michalev, V.N.Soloviev, G.B.Sergeev. Cryoreactions of magnesium atoms, clusters and nanoparticles with polyhalomethanes. Mendeleev Commun, 2004, 48.
- [4] V.E.Botchenkov, P.Karageorgiev, L.Brehmer, G.B.Sergeev. Quenched growth of nanostructured lead thin films on insulating substrates, Thin Films, 2004, 458, 303-307.

METASTABLE COMPLEXES FORMATION AND THEIR REACTIONS IN LOW TEMPERATURE MESOGENIC MATRICES

T.I.Shabatina

*Department of Chemistry, Moscow State University, 119992 Moscow, Russia,
<tsh@kinet.chem.msu.ru>*

The new metal-mesogenic systems have been obtained via low temperature co-deposition of d-block metals (Ag, Cu) and f-block metals (Sm, Eu) atoms with mesogenic alkylcyanobiphenyls (CB) and alkylcyanophenylpyridines (CPhPy). Their thermal evolution from low temperatures up to the ambient temperatures was studied via different spectroscopic (IR-, UV-, ESR) techniques.

Metal atom and small cluster containing mesogenic film samples ($l=20-50\text{ }\mu\text{m}$) were obtained by reagent's vapor co-condensation on the cooled surfaces of quartz, KBr or CaF_2 or polished copper under molecular beam conditions. The systematic studies of the specific interactions in low temperature co-condensates were carried out using special cryostats [1-2]. The spectroscopic data combining with the results of quantum chemistry calculations showed the formation of metastable sandwich-like complexes at low temperatures and the structure with head-to-tail arrangement of two ligand molecules was proposed [1-2].

The spectroscopic study of Sm(Eu)/CB and Sm(Eu)/CPhPy systems at 90-180 K showed the solid phase transformation of mononuclear biligand complex structure to dimeric complexes including two lanthanide atoms in their structure [2].

The metastable complexes possess thermal degradation at 150-200 K. Aggregation of metal atoms at room temperature led to formation of nanosize metal particles. TEM data for silver-cyanobiphenyl systems show two kinds of metal particles stabilised in mesogenic matrix: globes of 15-30 nm in size and highly anisometric rod-like particles of 0,5-1 μm in length [3, 4].

The kinetics of complex thermal degradation and metal cluster's growth were studied by ESR technique. It was shown the retarded character of kinetic curves revealed the existence of activation energy distribution for complex thermal degradation. The main value of process activation energy was estimated as 30 kJ/mole. The silver cluster formation was shown also for UV-irradiation of the samples at low temperatures [4].

Acknowledgements. The work was partially supported by RFBR grant 04-03-32748 and INTAS grant 2000-00-911.

[1] T.I.Shabatina. Reactions in mesogenic cyanophenyls at low temperatures and cryoformation of metallomesogenic nanosystems.// Moscow University Chemistry Bulletin, 2003, v.57, N5, pp.20-36.

[2] T.I.Shabatina, G.B. Sergeev. Reactions at low temperatures in the chemistry of nanosystems // Russ.Chem.Rev., 2003, v.72, №7, c.643-663..

[3] T.I.Shabatina, V.A.Timoshenko, Yu.N.Morosov, G.B.Sergeev Material Science and Engineering, 2002, v. C22, p.219-222.

[4] Shabatina T.I., Timoshenko V.A., Morosov Yu.N., Sergeev G.B., Colloids and surfaces, A: Physicochemical and Engineering Aspects, 2002, 198-200, 255-259.

SPECTROSCOPY OF DOPED HELIUM DROPLETS: MATRIX ISOLATION OF PTCDA NANOSTRUCTURES AND REAL-TIME MEASUREMENTS

O. Bünermann, P. Claas, G. Droppelmann, M. Wewer, and F. Stienkemeier

*Fakultät für Physik, Universität Bielefeld, Universitätsstr. 25, D-33615 Bielefeld, Germany
Email: franks@physik.uni-bielefeld.de*

C.P. Schulz

Max-Born-Institut, Max-Born-Str. 2A, D-12489 Berlin, Germany

Nano-structured organic semiconductors are of applied interest for new developments in the field of electronics and opto-electronics. In particular, 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and its derivatives are studied in connection with organic light emitting devices as well as thin film transistors and solar cells. We use a beam of superfluid helium nanodroplets as a low temperature matrix to study molecules and larger complexes at temperatures of 380 mK. Laser-induced fluorescence is applied to examine electronic properties of PTCDA and MePTCDI [1,2]. For the first time, vibrational resolved fluorescence spectra are obtained of single molecules as well as selected isomers of molecular dimers. Furthermore, in sandwich-like structures of complexes, clearly exciton transitions can be separated from molecular excitations. Results are discussed in comparison with spectra obtained in films and molecules probed in organic solvents.

The second part of the talk will present recent results on femtosecond pump-probe spectroscopy of doped helium droplets [3]. The formation of alkali-helium exciplexes is followed in real-time. In particular a comparison between superfluid ^4He droplets and their normalfluid ^3He counterparts will be discussed. Moreover, quantum interference structures are observed upon ionisation of exciplex molecules, providing a novel approach to characterize the vibrational structure and dynamics of transient species.

References

- [1] M. Wewer and F. Stienkemeier, *Phys.Rev. B* **67**, 125201 (2003).
- [2] M. Wewer and F. Stienkemeier, *J.Chem.Phys.* **120**(3), 1239 (2004).
- [3] G. Droppelmann, O. Bünermann, C.P. Schulz, and F. Stienkemeier, *Phys.Rev.Lett.* **93**, 023402 (2004).

HYDROGEN ATOM IN GIGANTIC MAGNETIC AND ELECTRIC FIELDS: CONDITIONS OF A NEUTRON STAR IN A LAB

V.G. Storchak

*Kurchatov Institute, Moscow 123182, Russia
email: storchak@stor.polyn.kiae.su*

The problem of atoms in extremely large magnetic and electric fields has attracted a great deal of attention in both atomic physics and astrophysics. The reason is that neutron stars can produce magnetic and electric fields close to those of atomic scale. Therefore, the importance of a shallow donor state goes beyond semiconductor physics since it imitates the hydrogen atom in giant magnetic and electric fields.

Muonium centers in semiconductors have been studied extensively for more than four decades. The typical justification for these studies comes from the idea that using the muonium atom as a light hydrogen isotope one can model the dynamics of the *isolated* H atom, whose observation is restricted because of its high reactivity.

Our recent studies of muonium atom formation in semiconductors provide an idea of how hydrogen atom would behave in magnetic and electric fields of atomic scale. Experiments in GaAs, GaP and CdS suggest that the electron is initially captured into a highly excited state, from which the cascade down to the muonium ground state goes through an intermediate weakly bound state (shallow donor state) determined by the electron effective mass. The electronic structure of this weakly bound state is shown to be hydrogenic. The nature of the final muonium state depends on the energy releasing mechanisms in the cascade process. We suggest that muonium dynamics in semiconductors (including the effects of electric and magnetic fields and temperature) reflect the electron dynamics in weakly bound muonium state(s) in which the electron is delocalized over distances of about 100 Angstroms.

HIGROGEN-IMPURITY GELS: PREPARATION AND IDENTIFICATION

M. A. Strzhemechny

*Verkin Institute for Low Temperature Physics and Engineering, Kharkov, Ukraine
National Academy of Sciences of Ukraine,
E-mail: strzhemechny@ilt.kharkov.ua*

Successes in the preparation of self-supporting mixtures of helium with many non-metal species (atoms and simpler molecules in the ground and excited states, simple radical, ions) have been reached owing to the specific properties of liquid (superfluid) [1,2] or solid [3] helium. Subsequent investigations (cf. [4] for an overview) showed that those states of condensed matter, called helium-impurity mixtures, are gels, i.e., agglomerates of separate particles and small clusters, irregularly interspaced with helium. Being highly metastable, these states break down with increasing temperature in an explosion-like manner. The critical temperature is rather sensitive to the species employed: the stronger helium-species interaction, the higher is the critical temperature above which a particular gel does not exist.

To produce similar gels with hydrogen instead of helium, we tried fast quenching of hydrogen-containing gas mixtures with rare gases. We were actually able to vary only the gas deposition flow density. In those gas mixes we used rare gases from neon to xenon and normal hydrogen. Characterization of the deposited samples was performed by powder x-ray diffraction. The most interesting results have been obtained, Kr-H₂ mixtures [5], the nominal hydrogen concentration X in the gas mix varying from 0 to 50%. The x-ray patterns from samples with $X \geq 10\%$ did not show any signs of reflections that could be attributed to solid krypton while reflections from a hydrogen-rich phase were distinct. On warming, the hydrogen reflections went away first and at a still higher, critical temperature T_c (which is substantially sensitive to X in on) the sample underwent an abrupt transformation and good Kr reflections appeared. In as-prepared Ar-H₂ mixtures, only a broad (111) argon reflection was detected together with hydrogen ones. As the temperature was raised, first hydrogen lines disappeared and then an abrupt recrystallization of the argon-rich fraction occurred.

The neon-containing mixtures behaved upon quench deposition in a different way. With $X \geq 2\%$ the diffraction patterns contained three reflections, which belong to two phases, *fcc* and *hcp*, both with the lattice parameters close to those of solid neon. Reliably attributable hydrogen lines appeared only when X exceeded about 85%.

- [1] E.B. Gordon, L.P. Mezhev-Deglin, and O.F. Pugachev, *Pisma ZhETF*, **19**, 103 (1974).
- [2] E.B. Gordon, V.V. Khmelenko, A.A. Pelmenov, E.A. Popov, and O.F. Pugachev, *Chem. Phys. Lett.*, **155**, 301 (1989).
- [3] E.B. Gordon, *Fiz. Nizk. Temp.* (2004, to appear).
- [4] V.V. Khmelenko, S.I. Kiselev, D.M. Lee, and C.Y. Lee, *Physica Scripta*, **T102**, 118 (2003).
- [5] M. A. Strzhemechny, N. N. Galtsov, and A. I. Prokhvatilov, *Fiz. Nizk. Temp.* **29**, 699 (2003) [*Low Temp. Phys.* **29**, 522 (2003)].

MAGIC NUMBERS OF NEUTRAL ^4He AND para- H_2 CLUSTERS

Anton Kalinin, Oleg Kornilov and J. Peter Toennies

*Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-37073 Göttingen, Germany
jtoenni@gwdg.de*

With improved angular resolution the diffraction of cluster beams from transmission nano-gratings now provides information on cluster size distributions up to $N \cong 60$ (^4He) and $N = 40$ (H_2) [1]. Although not predicted by theory the measured size distributions of ^4He exhibit up to five magic numbers. The ^4He magic numbers correlate with the successive stabilization of single collective excitation levels calculated by the Diffusion Monte Carlo (DMC) method. A modified liquid drop model can explain the ^4He excitation levels and provides a new improved method for determining the size dependence of the surface tensions of small droplets [2]. pH_2 clusters have also been investigated in Madrid using Raman spectroscopy with a spatial resolution of several microns [3]. With this technique clusters with up to 8 molecules are resolved and their growth in the early stages of the expansion is observed. Magic numbers are found at $N = 13$, which is also observed in the diffraction experiments suggesting an icosahedral structure. DMC calculations explain the $N = 13$ pH_2 magic number in terms of an increased stability despite evidence that the clusters are fluid [3].

- [1] R. Brühl, R. Guardiola, A. Kalinin, O. Kornilov, J. Navarro, T. Savas and J.P. Toennies, Phys. Rev. Lett. **92**, 185301-1 (2004)
- [2] O. Kornilov, J.P. Toennies, R. Guardiola and J. Navarro, accepted Journal of Low Temperature Physics
- [3] G. Tejeda, J.M. Fernandez, S. Montero, D. Blume and J.P. Toennies, Phys. Rev. Lett. **92**, 223401-1 (2004)

Laser-induced reactions in traps: A road to quantum-controlled chemistry?

Roland Wester

Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

The ability to cool and trap ultracold atoms has led to tremendous progress in the manipulation of atomic interactions. Based on these techniques laser-induced formation of molecules by photoassociation [1] as well as molecule formation using Feshbach resonances or three-body collisions has opened the field of ultracold molecular physics, which recently culminated in the formation of molecular Bose-Einstein condensates [2]. While these molecules are translationally and rotationally in their lowest quantum states, they occupy highly excited vibrational levels. How to transfer such molecular ensembles into their absolute ground state is currently a major open question. In our group we study photoassociation of cesium dimers inside an optical dipole trap. Due to the controlled conditions in the optical trap we can extract absolute photoassociation rate coefficients and directly investigate weak photoassociation transitions that form molecules in the triplet ground state potential. Also saturation of the photoassociation process at the unitarity limit was observed. The created molecules are expected to stay trapped in our optical trap together with the atomic cloud. A recently installed detection system for ground state molecules by multi-photon ionization will soon put us in the position to study interactions or even chemical reactions of this ultracold atom-molecule mixture.

Controlled cooling of charged molecules and clusters into their lowest rovibrational states by thermalization in buffer gas at a few Kelvin benefits significantly from the advent of high-order multipole traps such as the temperature-variable 22-pole trap [3]. Recently we observed the laser-induced reaction of H_3^+ with argon by vibrational overtone excitation and determined the H_3^+ internal and translational temperature. We have set out to employ cold ions and clusters to study the quantum dynamics of reactive collisions, such as nucleophilic substitution reactions [4], and to explore routes to their manipulation. Embedding reactant ions inside clusters of a few water molecules, will furthermore enable us to switch-on the solution phase interactions in a clean way, while retaining the means to study and manipulate quantum dynamical properties.

- [1] J. D. Miller *et al.*, Phys. Rev. Lett. **71**, 2204 (1993).
A. Fioretti *et al.*, Phys. Rev. Lett. **80**, 4402 (1998).
- [2] S. Jochim *et al.*, Science **302**, 2101 (2003).
M. Greiner *et al.*, Nature **426**, 537 (2003).
M. Zwierlein *et al.*, Phys. Rev. Lett. **91**, 250401 (2003).
- [3] D. Gerlich, Physica Scripta **T59**, 256 (1995).
- [4] S. Schmatz, ChemPhysChem, **5**, 600 (2004).

Evolution of superfluidity in nanoscale clusters of helium and hydrogen

K. B. Whaley

Department of Chemistry and Kenneth Pitzer Center for Theoretical Chemistry
University of California
Berkeley, CA 94720-1460

I shall present recent theoretical work on nanoscale clusters of helium and hydrogen that shows the development of nanoscale superfluid behavior at small cluster sizes. Zero and finite temperature calculations providing evidence for a transition from van der Waals type clusters to superfluid solvation around small molecules in doped clusters will be presented, including results for the molecules OCS, N₂O and CO₂. The nature of the coupling between an impurity molecule and the quantum fluid will be discussed in the context of dynamical renormalization of the molecular mass, and a distinction between light and heavy molecule renormalization made. Finally, we present evidence for a supersolid state of molecular hydrogen within a solvated nanocluster.

Ultrafast dynamics of photoinduced electron transfer and solvation processes at the ice/metal interface

Martin Wolf

Fachbereich Physik, Freie Universität Berlin, Germany

Electron transfer across interfaces is of fundamental importance in diverse areas such as electrochemistry, surface photochemistry and charge injection in dye sensitized solar cells and organic semiconductor devices. We have studied the dynamics of photoinjected electrons in ultrathin layers of ice grown on single crystal metal surfaces using femto-second time- and angle resolved two-photon-photoemission (2PPE). Photo-injection of electrons into the conduction band of amorphous D_2O layers on Cu(111) is followed by ultrafast localization and solvation of the excess electron within the first 100 fs [1]. Subsequent energetic stabilization of these solvated electrons due to nuclear rearrangements of the polar molecular environment is accompanied by an increasing degree of localization as evidenced by angle resolved measurements of the dispersion and 2PPE intensity [2,4]. The solvation dynamics is found to be strongly dependent of the structure of the ice, which can be controlled by the growth conditions and the choice of different substrates as a template [3]. In particular, for crystalline ice we find exceptionally long lived solvated electrons which provide insight in various time scales and dependence on temperature of the solvation process.

Acknowledgement: This work was performed in collaboration with U. Bovensiepen, C. Frischkorn, C. Gahl, P.A. Loukakos, M. Mehlhorn, K. Morgenstern, J. Stähler, (FU Berlin) and I. Adrianov, T. Klamroth, P. Saalfrank (Uni Potsdam).

References:

- [1] C. Gahl, U. Bovensiepen, C. Frischkorn, and M. Wolf, **Ultrafast dynamics of electron localization and solvation in ice layers on Cu(111)**, Phys. Rev. Lett. **89**, 107402 (2002).
- [2] U. Bovensiepen, C. Gahl and M. Wolf, **Solvation Dynamics and Evolution of the Spatial Extent of Photoinjected Electrons in D_2O /Cu(111)**, J. Phys. Chem. B **107**, 8706 (2003).
- [3] U. Bovensiepen, C. Gahl, J. Stähler, P.A. Loukakos, and M. Wolf, **Femtosecond dynamics of electron transfer, localization and solvation processes at the ice-metal interface**, Israel. J. Chem. (in press).
- [4] I. Adrianov, T. Klamroth, P. Saalfrank, U. Bovensiepen, C. Gahl, and M. Wolf, **Quantum theoretical study of electron solvation dynamics in ice layers on a Cu(111) surface**, J. Chem. Phys. (submitted).

Poster Contributions

ordered according to presenting person, alphabetically

Photodissociation of formyl fluoride in rare gas matrices

Jussi Ahokas, Kari J. Vaskonen and Henrik M. Kunttu

PHOTOREACTION MECHANISM OF CHLOROHYDROQUINONE IN A LOW-TEMPERATURE ARGON MATRIX

Nobuyuki AKAI and Munetaka NAKATA

ESR spectroscopy of XEF^{*} in solid argon. Relativistic effects in chemical bonding of heavy noble gas atom.

A.V. Akimov, I.U. Goldschleger, E.Ya. Misochko, D.A. Tyurin

VIBRATIONAL DEPHASING OF MOLECULES IN CRYOGENIC CRYSTALS

Daisuke Ando, Yuki Miyamoto, and Takamasa Momose

HEAT CAPACITY OF p-H₂-p-D₂-Ne SOLID SOLUTION: EFFECT OF (p-D₂)Ne CLUSTERS

M.I. Bagatskii, I.Ya. Minchina, B.M. Bagatskii.

Struktural identification of gas-phase biomolecules using IR spectroscopy

Joost M. Bakker, Isabelle Compagnon, Gert von Helden, Jos Oomens and Gerard Meijer

Towards magnetic trapping of ultracold neutral molecules

Joost M. Bakker, Michael Stoll, Dennis Weise, Oliver Vogelsang, Gerard Meijer and Achim Peters

LONG TERM STABILITY OF H ATOMS IN HD-D₂-He SOLIDS

E.P. Bernard, R.E. Boltnev, V.V. Khmelenko, D.M. Lee

APPLICATIONS OF PULSE ESR TO THE INVESTIGATION OF ATOMS IN IM-He SOLIDS

E.P. Bernard, P.P. Borbat, V.V. Khmelenko, D.M. Lee and J.H. Freed

Low temperature structural and optical properties of thin film nano-materials buildt from mono-disperse metal clusters

Thorsten M. Bernhardt, T. Gleitsmann, B. Stegemann, M. Vaida, L. Wöste

REACTION MECHANISMS OF GAS PHASE HYDRATED ELECTRONS (H₂O)_n⁻ WITH SMALL MOLECULES

Martin K. Beyer, O. Petru Balaj, Iulia Balteanu, Vladimir E. Bondybey

Theoretical Analysis of Guest-Host Dynamics After Photoexcitation of Cl₂ in an Argon Matrix

M. Schröder, A. Borowski, O. Kühn

Ultrafast Dynamics of F₂ Photodissociation in Ar Matrix

Arik Cohen, Masha.Y.Niv and R.B.Gerber

KINETICS AND MECHANISMS OF ICE AND HYDRATE NANOPARTICLE INTERCONVERSIONS

J. Paul Devlin, Carmi Yinnon and Victoria Buch

Detection of methyl radicals in low-temperature reactions of astrophysical interest

Yu. A. Dmitriev, R. A. Zhitnikov

INFRARED SPECTRA AND AB INITIO CALCULATIONS OF NO:CH₃Cl IN SOLID NEON AND SOLID ARGON

Nadia DOZOVA, Lahouari KRIM, Esmail ALIKHANI and Nelly LACOME.

FAST ELECTRON IRRADIATION OF ORGANIC MOLECULES IN A XENON MATRIX: FORMATION OF NOVEL-TYPE SPECIES

Vladimir Feldman, Fedor Sukhov, Aleksei Orlov, Irina. Tyulpina, Elizaveta Logacheva and Daniil Tyurin

ORGANIC RADICAL CATIONS PRODUCED BY FAST ELECTRON IRRADIATION IN SOLID ARGON:

EPR SPECTRA, STABILIZATION AND FRAGMENTATION

Vladimir Feldman, Fedor Sukhov, Aleksei Orlov and Irina. Tyulpina

Charge Transfer States of C₂ Doped Krypton Solids

S.L. Fiedler, H. Kunttu, J. Eloranta

PROTONATED AND FRAGMENT IONS OF ACETONITRILE MASS-SELECTIVE MATRIX-ISOLATION STUDY

Marcin Frankowski, Alice M. Smith-Gicklhorn, Zheng Sun, Alexey N. Ponomaryov and Vladimir E. Bondybey

WAVEPACKET DYNAMICS IN CONDENSED PHASE: Cl₂ IN Ar

Mizuho Fushitani, Matias Bargheer, Markus Gühr, and Nikolaus Schwentner

X-ray studies of pH₂-nD₂ solid solutions

Galtsov N.N., Prokhvatilov A.I., Strzhemechny M.A.

Nature of electronic states in CdSe nanocrystals studied by Stark spectroscopy

G.Giraud, M.Mohamed, L.Heinen, M.Chergui and F. Van Mourik

**Probing Molecular Metal Contacts by Scattering
of Surface State Electrons**

Leo Gross, Francesca Moresco, Micol Alemani, André Gourdon, Christian Joachim, and
Karl-Heinz Rieder

**Generation of Coherent Zone Boundary Phonons by Impulsive Excitation of
Molecules**

M. Gühr and N. Schwentner

**Laser-induced recombination of self-trapped holes with electrons
in preirradiated solid Ar.**

G.B. Gumenchuk, M.A. Bludov, A.G. Belov.

LASER INDUCED WATER DESORPTION FROM SILVER NANOPARTICLES

A. Hotzel, S. Kwiet, D. Starr*, A. Grujic, M. Wolf

Vibrational Coherence and fractional Revivals in Br₂:Ar

M. Gühr, H. Ibrahim and N. Schwentner

Microwave spectroscopy of molecules in bulk liquid Helium

Masazumi Ishiguro and Yasuyuki Aratono

**PHOTOCHEMISTRY OF PROPYLIC ACID AND ITS ISOMERS IN SOLID
ARGON.**

Esa Isoniemi, Leonid Khriachtchev, Maarit Makkonen, and Markku Räsänen

**Electron trap-related low temperature relaxation
in preirradiated Ne matrix**

I.V. Khyzhniy, E.V. Savchenko, A.G. Belov, E.M. Yurtaeva, M. Frankowski,
M.K. Beyer, A.M. Smith-Gicklhorn, and V.E. Bondybey

**TIME RESOLVED CARS MEASUREMENTS OF I₂ IN SOLID Kr:
VIBRATIONAL STATE DEPENDENT DEPHASING TIMES
BETWEEN 2.6 - 32 K**

Tiina Kiviniemi, Jukka Aumanen, Pasi Myllyperkiö and Mika Pettersson

**HEAT TRANSFER IN THE NONIDEAL CRYSTAL AND IMPURITY
PARAHYDROGEN**

O. A. Korolyuk, A. I. Krivchikov, B. Ya. Gorodilov, P. Stachowiak, A. Jezowski.

**NEON CLUSTERS IN NANOPOROUS CONFINEMENT OF AMORPHOUS
CARBON FILMS**

N.V. Krainyukova

Stark deceleration and cooling of large molecules

Jochen Küpper, Kirstin Wohlfart, Hendrick L. Bethlem, Henrik Haak and Gerard Meijer

Time-resolved CARS studies of vibrational coherences in the condensed phase: I₂ in solid krypton

Michael Karavitis, Ilya Goldschleger, V. Ara Apkarian, and Takayuki Kumada

THE CONFORMATIONAL BEHAVIOR OF SERINE: AN EXPERIMENTAL MATRIX-ISOLATION FT-IR AND THEORETICAL DFT(B3LYP)/6-31++G STUDY**

Bert Lambie, Riet Ramaekers and Guido Maes

3-Hydroxyflavone: An Example for Photochemistry in Superfluid Helium Droplets

Rudolf Lehnig, Alkwin Slenczka

Theoretical modelling of electronic spectroscopy in superfluid ⁴He

Lauri Lehtovaara*, Jussi Eloranta

INTERACTION OF CHARGE CENTERS WITH ORTHOMOLECULES IN PARAHYDROGEN

V.A.Lykah, E.S. Syrkin, T.V.Svitenko-Krasnokutskaya

Phase Separation and Homogenization of ³He-⁴He Solid Mixtures

V.Grigor'ev, V.Maidanov, A.Penzev, A.Polev, S.Rubets, E.Rudavskii, A.Rybalko, E.Syrnikov

Isotope control of K₂- and NaK-Dimers

Franziska Vetter, Andrea Merli, Albrecht Lindinger, Mateusz Plewicki, Cosmin Lupulescu, Stefan Weber, and Ludger Wöste

Nuclear spin relaxation of methane in solid parahydrogen.

Yuki Miyamoto, Mizuho Fushitani, Daisuke Ando, and Takamasa Momose

STRUCTURE AND PHOTOCHEMICAL TRANSFORMATIONS OF AMIDOESTER RADICAL CATIONS WITH METHYLENE "BRIDGE" IN LOW-TEMPERATURE FREON MATRIXES

Kirill Nuzhdin, Vladimir Feldman, Mikhail Melnikov

Matrix Isolation and Ab Initio Study of the H₂O₂...SO₂ complex

Susanna Pehkonen, Jan Lundell, Leonid Khriachtchev, Mika Pettersson and Markku Räsänen

EMISSION SPECTROSCOPY OF ATOMIC (H, HE, N, O) AND DIATOMIC (H₂, HE₂, N₂, O₂, NO) IMPURITIES INJECTED INTO SUPERFLUID HELIUM*.

Jussi Ahokas, Jussi Eloranta, Henrik Kunttu, Evgeny A. Popov

CORRELATION BETWEEN THE THERMAL PRESSURE AND ISOCHORIC THERMAL CONDUCTIVITY OF SOLIDS CO₂ AND NH₃

O. I. Pursky and V. A. Konstantinov

Elementary stages of relaxation processes in ion-containing cryomatrices as probed by activation spectroscopy.

E.V. Savchenko, O.N. Grigorashchenko, G.B. Gumenchuk, I.V. Khyzhniy, M. Frankowski, M.K. Beyer, A.M. Smith-Gicklhorn, V.E. Bondybey.

COHERENT SPIN CONTROL FOR DIHALOGENS IN ARGON

M.V. Korolkov, O. Kühn, J. Manz, M. Schröder

GAS-PHASE KINETICS AND DYNAMICS AT VERY LOW TEMPERATURES: OBTAINING DATA FOR ASTROCHEMISTRY

David Carty, André Canosa, Andrew Goddard, Sven Köhler, Sébastien D. Le Picard, Alejandra Pàramo, Ian R. Sims and Ian W.M. Smith

LOW TEMPERATURE COMPLEXES OF SAMARIUM AND EUROPIUM WITH 4-PENTHYL-4'-CYANOBIPHENYL

T.I. Shabatina, A.V. Vlasov, A.Yu. Ivanov, G.G. Sheina, G.B. Sergeev

Low temperature synthesis and spectroscopic (IR, UV, ESR) characterisation of paramagnetic copper atom complexes with mesogenic cyanobiphenyl ligands

A.A. Belyaev, A.A. Bogdanova, V.A. Timoshenko, T.I. Shabatina

CRYOCHEMICAL STABILIZATION AND THERMAL EVOLUTION OF ACTIVE SILVER AND COPPER SPECIES IN ADAMANTANE MATRIX

Yu.N.Morozov, N.Sogoshi, V.A.Timoshenko, T.I.Shabatina, G.B.Sergeev

THE ESR STUDY OF CHEMICAL INTERACTIONS IN TRIPLE SOLID SILVER - CARBON TETRACHLORIDE - MESOGENIC CYANOBIPHENYL CO-CONDENSATE SYSTEM

V.A.Timoshenko, Yu.N.Morosov, A.A.Belyaev, T.I.Shabatina, G.B.Sergeev

The comparison of conformational structures of pyrimidine nucleosides isolated in the low temperature Ar matrices.

A.Yu. Ivanov, G. Sheina

The peculiarities of vibrational spectra of 1-methyl-uracil--Sm complexes isolated in Ar matrices.

A.Yu. Ivanov, G.Sheina, T.Shabatina, G.Sergeev

The vibrational spectra of complexes of 1-methyl-uracil with metal chlorides

A.Yu. Ivanov, G.Sheina

LABILE ALUMINUM CHLORIDE COMPLEXES IN THE HYDROCARBON MATRICES

M.I. Shilina, R.V. Bakharev, V.V. Smirnov

PREDICTIONS OF NOVEL Xe COMPOUNDS WITH BN

Alice M. Smith-Gicklhorn, Marcin Frankowski, Alexey N. Ponomaryow
and Vladimir E. Bondybey

Structure and transitions of condensed oxygen films

A.A.Solodovnik, V.V.Danchuk, M.A.Strzemechny

**Chemical Compounds Formed from Diacetylene and Noble-Gas Atoms: HKrC₄H
and HXeC₄H**

Hanna Tanskanen, Leonid Khriachtchev, Jan Lundell, Harri Kiljunen, Markku Räsänen

SOLVATION OF HCl BY METHANOL AND DIMETHYL ETHER

N. Uras-Aytemiz, O. Boylu, J. Sadlej, J. P. Devlin, V. Buch

Photodissociation of formaldehyde in rare gas matrixes

Kari J. Vaskonen and Henrik M. Kunttu

Fragmentation of ionised neon clusters in superfluid helium nanodroplets

David Bonhommeau, Alexandra Viel and Nadine Halberstadt

**Coherent Control Experiments Employing Pulse Cleaning and Parameterization
Techniques**

S. M. Weber, A. Lindinger, F. Vetter, M. Plewicky, A. Merli, and L. Wöste

**CO₂ NANO-PARTICLE AGGREGATION AND COALESCENCE STUDIED BY IR
SPECTRA AND MOLECULAR DYNAMICS SIMULATIONS.**

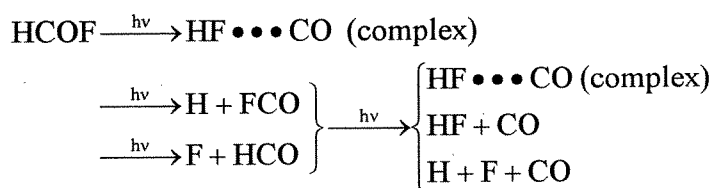
Carmi Yinnon, Victoria Buch, Paul Devlin

Photodissociation of formyl fluoride in rare gas matrices

Jussi Ahokas, Kari J. Vaskonen and Henrik M. Kunttu

*NanoScience Center, Department of Chemistry, P.O. Box 35, FIN-40014
University of Jyväskylä, Finland
E-Mail: jusahok@cc.jyu.fi*

The photodissociation process of formyl fluoride has been studied in rare gas matrices at two distinct wavelengths, 248 nm and 193 nm. These wavelengths are used to excite the molecule electronically causing dissociation. Different reaction channels (see Reaction scheme) are subsequently reached by this electronic excitation and the different reaction channels lead to various products which are seen in the spectrum. IR spectroscopy and electron paramagnetic resonance have been used as tool for approaching this problem. We attempt to quantify these reaction channels through kinetic measurements correlated with other spectroscopic information. Additionally, we relate the excess energy of photoproducts effects to the final distribution. The underlying aim of this study is to understand matrix effect on dissociation process.



Reaction scheme: Possible photodissociation channels of formyl fluoride.

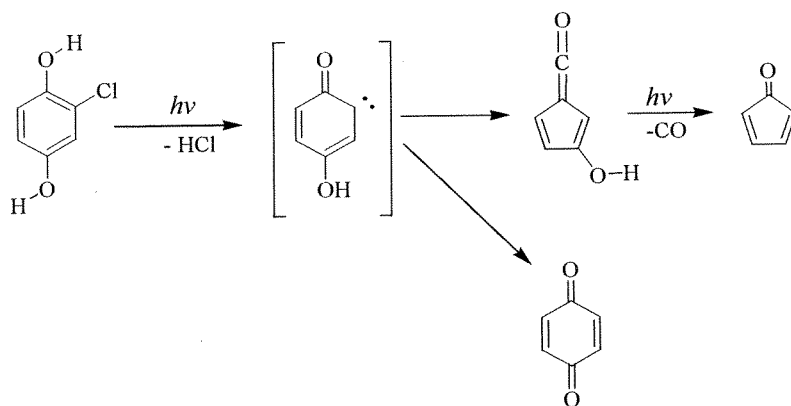
PHOTOREACTION MECHANISM OF CHLOROHYDROQUINONE IN A LOW-TEMPERATURE ARGON MATRIX

Nobuyuki AKAI¹ and Munetaka NAKATA²

¹Center for Quantum Life Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima, Hiroshima 739-8530, Japan (rosso@hiroshima-u.ac.jp)

²Graduate School of Science, BASE, Tokyo University of A & T, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan

Photolysis of chlorohydroquinone in a low-temperature argon matrix was investigated by Fourier transform infrared spectroscopy with an aid of hybrid density-functional-theory calculation. The new photoreaction pathways via a ketocarbene intermediate produced by dissociation of hydrogen chloride upon UV irradiation were found, where a five-membered ring ketene and *p*-benzoquinone were produced from the ketocarbene by Wolff rearrangement and intramolecular hydrogen-atom migration, respectively. The large H/D isotope effect in the branching ratio for the final products, ketene and *p*-benzoquinone, was found in the analysis of the growth behavior of the infrared bands, implying that the hydrogen-atom migration occurs by tunneling effect. The further photolysis of five-membered ring ketene produced cyclopentadienone by dissociation of CO and migration of hydrogen atom of the hydroxyl group. The photoreaction mechanism is compared with those of 2-chlorophenol,¹ 2-bromophenol,² and 2-iodophenol.³



- [1] N. Akai, S. Kudoh, M. Takayanagi, M. Nakata, *J. Photochem. Photobiol., A*, **146**, 49 (2001).
- [2] N. Akai, S. Kudoh, M. Takayanagi, M. Nakata, *Chem. Phys. Letters*, **363**, 591 (2002).
- [3] M. Nagata, Y. Futami, N. Akai, S. Kudoh, M. Nakata, *Chem. Phys. Letters*, **392**, 259 (2004).

ESR SPECTROSCOPY OF XeF[•] IN SOLID ARGON. RELATIVISTIC EFFECTS IN CHEMICAL BONDING OF HEAVY NOBLE GAS ATOM.

A.V. Akimov, I.U. Goldschleger, E.Ya. Misochko

Institute of Problems of Chemical Physics RAS, Chernogolovka, Moscow Region, 142432 Russia

D.A. Tyurin

Moscow MV Lomonosov State Univ, Moscow 119899, Russia

Xenon fluoride radicals were generated by solid-state chemical reactions of mobile fluorine atoms with xenon atoms trapped in an argon matrix. Highly resolved ESR spectra of XeF[•] were obtained in the temperature range 5 – 25 K. The anisotropic hyperfine parameters of ESR spectra were obtained for magnetic nuclei ¹⁹F, ¹²⁹Xe and ¹³¹Xe using the naturally occurring and isotopically enriched xenon. Signs of the hyperfine components were established from analysis of temperature changes in the spectra and from numerical solutions of spin-Hamiltonian for two nonequivalent magnetic nuclei. Thus, the complete set components of axial symmetric hyperfine- and g- tensors of XeF[•] are determined.

	A(¹²⁹ Xe), MHz				A(¹⁹ F), MHz			
	A	A _⊥	A _{iso}	A _{dip}	A	A _⊥	A _{iso}	A _{dip}
Nonrelativistic DFT			-617	-315			315	1053
Relativistic DFT,			-1409	-586			362	1047
Experiment (Spin-orbit corrected)	-2217	-969	-1385 (-1340)	-416 (-485)	2934	-814	435.3	1249

Comparison of the measured hyperfine parameters with those predicted by quantum-chemical DFT calculations shows, that the relativistic DFT gives true electron spin distribution in the ²Σ⁺ ground-state, increasing significantly the electron-nuclear contact Fermi (A_{iso}) and magnetic-dipole interactions (A_{dip}) of Xe nuclei in comparison with nonrelativistic theory. The other relativistic feature is follows from considerable anisotropy of g-tensor (g_{||} = 1.9822, g_⊥ = 2.0570) which results from spin-orbital interaction. The orbital contribution appears due to mixing of the ionic ²Π states with the ²Σ⁺ ground-state, and, as it follows from recent quantum-chemical predictions, it plays a significant role in chemical bonding of XeF.

This work was supported by the Russian Foundation for Basic Research (Grant 04-03-32599) and by Russian Academy of Sciences in frame of subprogram “Theoretical and experimental study of chemical bonding and mechanisms of chemical reactions and processes”. A.V.A. thanks the Russian Science Support Foundation for support.

VIBRATIONAL DEPHASING OF MOLECULES IN CRYOGENIC CRYSTALS

Daisuke Ando, Yuki Miyamoto, and Takamasa Momose

Division of Chemistry Graduate School of Science, Kyoto University, JAPAN

e-mail: adaisuke@kuchem.kyoto-u.ac.jp

A number of theoretical studies on the temperature dependence of the homogeneous linewidth of impurity molecules in crystals have been reported. Especially two typical models have been discussed; one is the Debye model for dephasing by acoustic phonons, and another is local-mode model for dephasing by pseudolocal phonons. The Debye model predicts that the homogeneous linewidth depends on the 7th power of temperature, while the local-mode model predicts that the temperature dependence of the width obeys an Arrhenius-type function.

We have been studying vibrational dephasing of CD₄ molecules trapped in parahydrogen crystals [1]. Solid parahydrogen is an ideal system for the study of dephasing, because there is no inhomogeneous broadening. In the previous paper [1], we reported the temperature dependence of the dephasing of the both the ν_3 and ν_4 modes of CD₄ in solid parahydrogen in the range between 4 and 8K. Unfortunately, the temperature range was not wide enough to judge which mechanism governs the dephasing in solid parahydrogen. In this work, we extend the measurement to much lower temperatures. The temperature dependence of the FWHM of the R(0) ($J = 1 \leftarrow 0$, $M = \pm 1 \leftarrow 0$) transition of the ν_4 mode is plotted in Fig. 1. It turned out that the Debye model fits the experimented data better than the local-mode model. However, the temperature dependence was not $\sim T^7$ but $\sim T^5$. Detail of the experimental data together with the analysis will be presented.

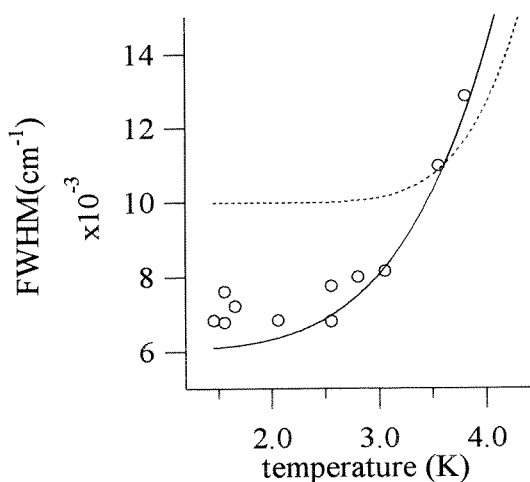


Fig. 1. Temperature dependence of the linewidth

— Debye model: $\Delta\nu = 0.00634 + 1.03 \times 10^{-5} \times T^{4.81}$
..... local-mode model: $\Delta\nu = 0.0103 + 19.0 e^{-35.5/T}$
○ experiments

[1] H. Katsuki, and T. Momose, Phys. Rev. Lett. **84**, 3286 (2000).

HEAT CAPACITY OF p-H₂-p-D₂-Ne SOLID SOLUTION: EFFECT OF (p-D₂)Ne CLUSTERS

M.I. Bagatskii, I.Ya. Minchina, B.M. Bagatskii.

*B. Verkin Institute for Low Temperature Physics & Engineering, National Academy of Sciences of Ukraine,
47, Lenin Ave., 61103, Kharkov, Ukraine, e-mail: bagatskii@ilt.kharkov.ua*

Heavy impurities in quantum crystals of hydrogen isotopes cause strong disturbance of (quantum) zero-point vibrations and rotational motion of the matrix molecules. In the vicinity of heavy impurities, local changes in the lattice structure are also possible leading to the formation of new quantum objects – clusters and complex of molecules [1]. This affects considerably the physical properties of crystals. These phenomena are being studied intensively.

In this study the contribution of the rotational motion of the p-D₂ molecules in the clusters (p-D₂)Ne to the heat capacity of the solid 1% p-D₂ - p-H₂ solution doped with 0.25% Ne has been investigated in the interval $\Delta T = 0.5 - 4$ K. The choice of the impurity concentrations and the temperature interval was dictated by the following. (i). Neon is a quasi-isotopic impurity with a high mass ratio ($m'/m \sim 10$) of the impurity particles (m') and the matrix (m). (ii). Quantum diffusion of the p-D₂ molecules in the p-H₂ lattice is impossible [2] and the conversion of the p-D₂ molecules during the time of the experiment is negligible. (iii). The heat capacity of the 1% p-D₂ – solid p-H₂ solution ($\Delta T = 0.4-6$ K) has already been investigated [2]. This permits direct separation of the contribution made by the p-D₂ rotation in the (p-D₂)Ne – type clusters.

The heat capacity (C_{rot}) caused by the p-D₂ rotation in the (p-D₂)Ne clusters has been detected and analyzed.

It is found experimentally that the number of (p-D₂)Ne clusters is dependent on the conditions of preparation of solid samples. The sample prepared by condensation of a gas mixture to the solid phase has more clusters – than the sample prepared from the liquid phase.

The level splitting Δ of the (p-D₂) molecules in the (p-D₂)Ne clusters found from the analysis of the temperature dependence of heat capacity $C_{rot}(T)$ is consistent with the theoretical estimate [3].

[1] A.S. Barylnik, A.I. Prokhvatilov, and G.N. Shcherbakov, *Low. Temp. Phys.* **21**, 530 (1995).

[2] A.I. Krivchikov, M.I. Bagatskii, V.G. Manzhelii, I.Ya. Minchina, and P.I. Muromtsev, *Sov. J. Low. Temp. Phys.*, **15**, 1 (1989).

[3] V.B. Kokshenev, *Sov. J. Low. Temp. Phys.*, **2**, 118, (1976).

STRUCTURAL IDENTIFICATION OF GAS-PHASE BIOMOLECULES USING IR SPECTROSCOPY

Joost M. Bakker, Isabelle Compagnon, Gert von Helden, Jos Oomens and Gerard Meijer

FOM Institute for Plasma Physics Rijnhuizen, Nieuwegein, The Netherlands

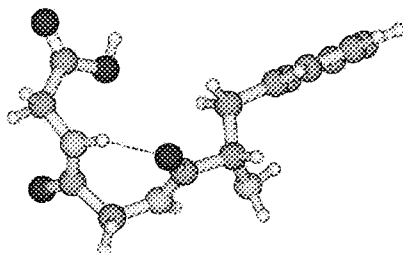
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

email: jmbakker@fhi-berlin.mpg.de

For biologically relevant molecules, such as proteins and saccharides, the primary structure can nowadays be obtained in a rather routine fashion, making use of techniques such as mass spectrometry and electrophoresis. The secondary and higher orders structures, i.e. the three dimensional structure, of such systems are much harder to obtain, however. Since the secondary structure is a decisive factor in the biological function of the species, it is of great interest to study the fundamental interactions that determine the shape of the molecule. In gas-phase experiments the influences of a solvating medium are eliminated, so a careful study of these inter- and intramolecular interactions is possible.

Unfortunately, where for molecules in solution one can use nuclear magnetic resonance (NMR) spectroscopy to obtain the secondary structure, for gas-phase species such techniques are rare. One technique that may fill this gap is Infrared (IR) absorption spectroscopy. Using a double-resonance technique, IR spectra of cold, well defined structural conformers can be measured. IR excitation of the molecules of interest is performed with mid-IR radiation (5–40 μm) produced by the Free-Electron Laser for Infrared eXperiments (FELIX) in Nieuwegein, the Netherlands, followed by UV ionization. As different conformations can have different excitation energies to the first electronically excited state, IR spectra of specific conformations can be measured.

We here present IR absorption spectra for several small systems of biological relevance. Data will be presented for the amino acid tryptophan, the tripeptide phe-gly-gly, for the nucleobase pair of guanine and cytosine and for a synthetic disaccharide. A comparison of the experiments with results from quantum-chemical calculations allows for a rather solid structural assignment for the different conformers.



Calculated structure of phe-gly-gly

TOWARDS MAGNETIC TRAPPING OF ULTRACOLD NEUTRAL MOLECULES

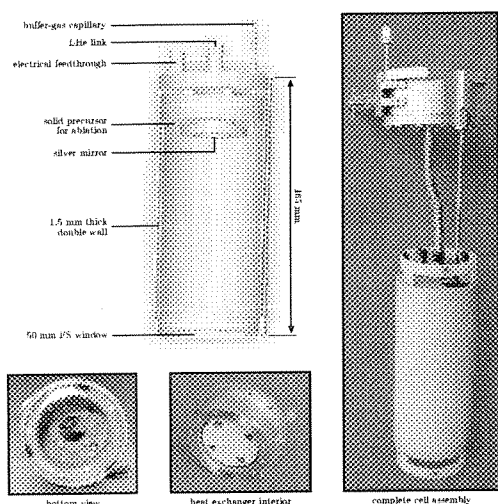
Joost M. Bakker, Michael Stoll, Dennis Weise, Oliver Vogelsang, Gerard Meijer and Achim Peters

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany
Department for Quantum Optics and Metrology, Humboldt-Universität zu Berlin
email: jmbakker@fhi-berlin.mpg.de*

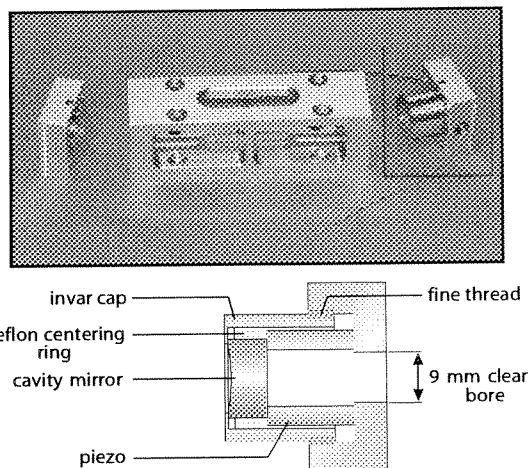
The buffer gas loading and subsequent magnetic trapping of neutral molecules is a powerful tool for the creation of dense samples of ultracold molecules and is applicable to a great variety of paramagnetic species. Up to now the buffer-gas loading technique has yielded the highest initial numbers and densities of cold molecules, and it therefore provides excellent initial conditions for evaporative cooling. Such dense samples of ultracold molecules can form a starting point for the performance of a large variety of experiments, such as the formation of a molecular quantum gas, ultra-high resolution spectroscopic measurements to test fundamental physics or interactions between ultracold molecules.

In this project we aim to create dense samples of neutral paramagnetic molecules by means of buffer-gas loading and trapping inside a superconducting quadrupole magnet using a ^3He - ^4He dilution refrigerator. Introduction of the particles to be trapped into the experimental cell can be done by means of ablation of a solid target or by capillary injection.

We report on the progress of the experiment and present preliminary data on the injection and subsequent thermalization of atomic Chromium, and of studies into the feasibility of high-quality optical resonators at cryogenic temperatures for detection purposes.



Experimental cell



Cryogenic optical resonator

LONG TERM STABILITY OF H ATOMS IN HD-D₂-He SOLIDS

E.P. Bernard (1), R.E. Boltnev (2), V.V. Khmelenko (1), D.M. Lee (1)

(1) *Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY, 14853 USA*
(epb22@cornell.edu)

(2) *Branch of Institute of Energy Problems of Chemical Physics, Chernogolovka, Moscow region,*
142432, Russia

We employed an electron spin resonance (ESR) technique for investigating the long-term behavior of hydrogen and deuterium atoms in HD-D₂ impurity helium solids. These solids were created by sending a gas mixture [H₂]:[D₂]:[He] = 1:4:100 through a radio-frequency electrical discharge into a volume of superfluid ⁴He at T=1.5 K. H and D atoms were stabilized inside nanoclusters of impurity molecules. The exchange tunneling reactions $D + H_2 \rightarrow HD + H$ and $D + HD \rightarrow D_2 + H$ proceeded to eliminate D atoms and increase the concentration of H atoms in the HD-D₂ impurity-helium solids. Local concentrations of H atoms inside the molecular nanoclusters of order 10²⁰ cm⁻³ were achieved. The high concentration of H atoms was stable during ≈ 40 hours storage of the sample at $T = 1.35$ K. These solids are possible candidates for quantum “supersolid”-like behavior of atomic hydrogen if the Bose-Einstein degeneracy regime can be attained.

APPLICATIONS OF PULSE ESR TO THE INVESTIGATION OF ATOMS IN IM-He SOLIDS

E.P. Bernard (1), P.P. Borbat (2), V.V. Khmelenko (1), D.M. Lee (1) and J.H. Freed (2)

*(1) Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY, 14853 USA
(epb22@cornell.edu)*

*(2) Advanced ESR Technology Research Center (ACERT), B28 Baker Laboratory,
Cornell University, Ithaca, NY 14853 USA*

An X-band pulse ESR spectrometer has been designed and assembled to investigate atomic and molecular radicals concentrated within Impurity-Helium solids. Pulse instrumentation allows for several measurements that are difficult or impossible with CW ESR spectroscopy. Rapid acquisition of spectra allows the study of the dynamics of fast hydrogen-deuterium tunneling reactions within the solid impurity clusters. These studies give information about the mobility of the atoms within the impurity clusters. The distribution of the radicals within the clusters can be studied through their dipolar interactions using the solid echo refocusing technique. Spin echo and free induction decay measurements provide a means of distinguishing between homogeneous, inhomogeneous, and dipole-dipole broadening mechanisms. Time-domain analysis of free induction decays may allow the observation of exchange narrowing in the most concentrated samples, if the concentration of the radicals approaches 10^{21} cm^{-3} . Pulse ESR spectroscopy also offers the possibility of using electron spin echo envelope modulation to study interactions with the nuclei surrounding the radicals, providing information about their local environment.

Low temperature structural and optical properties of thin film nano-materials built from mono-disperse metal clusters

Thorsten M. Bernhardt, T. Gleitsmann, B. Stegemann, M. Vaida, L. Wöste

Institut für Experimentalphysik, Freie Universität Berlin,

Arnimallee 14, 14195 Berlin, Germany

On a nanometer scale the physical and chemical properties of a metal particle are critically determined by its dimension. Below a certain size even the addition or removal of just one atom can change the material properties by orders of magnitude making also matter with completely new characteristics conceivable. This is the regime where material design by cluster size engineering is most effective. Our experimental approach therefore starts from well defined atomic metal clusters in the gas phase. These mass-selected clusters are guided toward the surface and soft-landed at low energies and low temperatures avoiding decomposition. The resulting nano-scale cluster materials and thin-films are preserving the characteristics of the cluster constituents. As one example a new allotropic modification of antimony consisting of Sb_4 cluster units will be presented [1]. Furthermore the optical and electronic properties of silver clusters on various substrates will be discussed and a new method for silver cluster generation on silver oxide thin films by femtosecond laser irradiation will be demonstrated. Such photoactivated thin films show strong luminescent properties and are proposed to be promising substrates for optical data storage [2].

[1] T. M. Bernhardt, B. Stegemann, B. Kaiser, K. Rademann: *Crystalline structures of Sb_4 molecules in antimony thin films*, Angew. Chem. Int. Ed. **42**, 199 (2003).

[2] T. Gleitsmann, B. Stegemann, T. M. Bernhardt: *Femtosecond laser activated fluorescence from silver oxide nano-particles*, Appl. Phys. Lett. **84**, 4050 (2004).

REACTION MECHANISMS OF GAS PHASE HYDRATED ELECTRONS $(\text{H}_2\text{O})_n^-$ WITH SMALL MOLECULES

Martin K. Beyer, O. Petru Balaj, Iulia Balteanu, Vladimir E. Bondybey

*Department Chemie, Lehrstuhl 2 für Physikalische Chemie, Technische Universität München,
Lichtenbergstraße 4, 85747 Garching, Germany; email: martin.beyer@ch.tum.de*

The reactivity of hydrated electrons $(\text{H}_2\text{O})_n^-$ with small molecules is studied by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The ionic nanodroplets are generated by laser vaporization of a solid zinc target and supersonic expansion of the hot plasma into high vacuum in a helium/water mixture. In bulk solution, hydrated electrons are short lived due to a variety of recombination processes, e.g. with protons to form hydrogen atoms. In the nanodroplet, no species are available for recombination. If the droplet is sufficiently large, i.e. $n > 30$, hydrated electrons are stable on the time scale of seconds. The only decay channel is loss of individual water molecules due to heating by black body radiation [1], while smaller species may also exhibit electron detachment. Upon collisions with small molecules, one can classify at least three different reaction mechanisms: a) Ligand exchange, where e.g. a methanol molecule replaces water; b) core switching, where a hydrated radical anion is formed, e.g. O_2^- or CO_2^- ; c) chemical reactions, where e.g. a hydrogen atom is transferred to acetonitrile, forming CH_3CHN and $\text{OH}(\text{H}_2\text{O})_n^-$ [2]. Since the nanodroplet is constantly cooled by the evaporation of water molecules, the reactions proceed at thermal energies in the gas phase. This experimental approach probes the chemistry of the hydrated electron in neat water, and with its mass spectrometric detection provides complementary information to pulsed radiolysis studies.

- [1] M. K. Beyer, B. S. Fox, B. M. Reinhard, V. E. Bondybey, *J. Chem. Phys.* **115**, 9288 (2001).
- [2] O. P. Balaj, I. Balteanu, B. S. Fox-Beyer, M. K. Beyer, V. E. Bondybey, *Angew. Chem.* **115**, 5675 (2003); *Angew. Chem. Int. Ed.* **42**, 5516 (2003).

Theoretical Analysis of Guest-Host Dynamics After Photoexcitation of Cl_2 in an Argon Matrix

M. Schröder, A. Borowski, O. Kühn

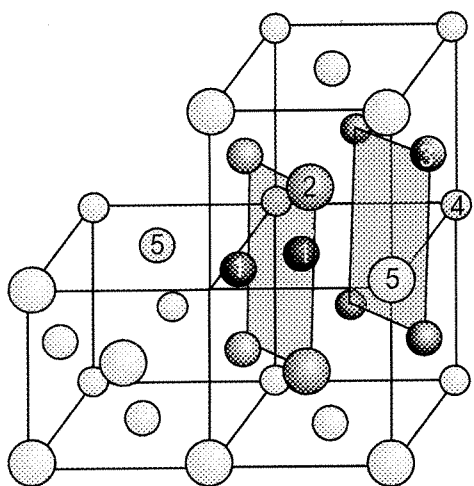
*Institut für Chemie, Physikalische und Theoretische Chemie, Freie Universität Berlin
Takustr. 3, D-14195 Berlin*

Dihalogen molecules embedded in low temperature rare gas matrices serve as prototypes for chromophore-environment systems in both experimental and theoretical studies.

In the present contribution we will focus on the case of Cl_2 in a solid argon matrix which is shown in the figure. For the theoretical investigation we combined the diatomics-in-molecules (DIM) approach with Molecular Dynamics simulations of representative classical trajectories to account for the chromophore-matrix interactions on the different electronic states.

The dynamics of the matrix-isolated chlorine molecule (atoms labelled 1 in the figure) after photoexcitation to the B or C state can be characterized by the local interactions with four different groups of lattice atoms, that is, belt (2), window (3), collision (4), and “phonon” atoms (5). A typical scenario of host-guest dynamics as characterized by these

interaction partners may look as follows:



After excitation of the chlorine molecule (1) it stretches and induces a motion of the surrounding belt (2) atoms towards the molecule's axis in order to fill the emptied space caused by the proceeding intramolecular separation. The chlorine atoms might then pass through the rectangle of window atoms (3) to hit two collision atoms (4) on a straight line. Thereby most of the kinetic energy of the chlorine atoms (1) is transferred to the collision atoms (4) that in turn trigger a shockwave spreading through the lattice. Finally, after having pushed the belt atoms outwards again the recombination of the chlorine atoms (1) can occur.

As a second example of coupled guest-host dynamics the interaction between the molecule and phonons of the host lattice was considered. For the exemplification of this phenomenon the so-called “phonon” atoms (5) are of particular interest. Those atoms might provide a link to the experimentally observed impulsively excited coherent phonon vibration [1]. To unravel the origin of the coherent phonons we investigated the response of the matrix to the sudden change of the chromophore's electron density taking place upon excitation of the B or C state.

[1] M. Gühr, M. Bargheer, N. Schwentner, *Phys. Rev. Lett.*, **91**, 085504 (2003)]

Ultrafast Dynamics of F₂ Photodissociation in Ar Matrix

Arik Cohen, Masha.Y.Niv and R.B.Gerber

*Department of Physical Chemistry, the Fritz-Haber Center for
Molecular Dynamics, The Hebrew University of Jerusalem, 91904, Israel*

The photodissociation dynamics of F₂ in solid argon are studied by semiclassical Molecular Dynamics simulations that include multiple electronic states and the non-adiabatic transitions between them.

This work is done in cooperation with the laser femtosecond experiments of the N.Schwentner group (FU Berlin), and with the quantum studies of J.Manz and his group (FU Berlin) and of M.Korolkov, which control strategies for this and related systems (FCl in Ar).

The simulation is done for a slab of F₂ surrounded by 255 argon atoms, using periodic boundary conditions. The results are compared with previous calculations for F₂ embedded in a cluster of 54 argon atoms.

The 36 relevant potential energy surfaces are generated by the DIM (Diatomic in Molecules) method. The simulations use the 'Surface Hopping' method of Tully for computing nonadiabatic transitions between different electronic states. The initial excitation is to a singlet Π , the relation between the electronic state and the occurrence of cage-exit events by F atoms was explored. A very interesting result is the rapid formation of triplet-state populations, the weak spin-orbit coupling for F atoms. Large population is found for the $^3\Pi_0$ state after less than 100 fs. This corresponds to the "Ultrafast Spin-Flip effect" observed experimentally by Schwentner et al. for FCl, in the framework of this joint project.

The new simulation results show that

- (1) Also the other triplet states, $^3\Pi_1$ and $^3\Pi_2$ are substantially populated already within very short time scales (appreciable populations are found in the range from 60fs to 250 fs). The populations of the different triplet states are, however, not identical.
- (2) The triplets $^3\Pi_1$ and $^3\Pi_2$ seem to have a higher propensity for cage exit than $^3\Pi_0$. This is interpreted in terms of the effective interaction potentials between F and Ar that differ for the different states.
- (3) $^3\Pi_0$ is the dominant triplet for the caged molecules, at least for the first 300fs.
- (4) Also the populations of different singlet states are found to be very different.
- (5) The rates of singlet-to triplet transitions are on the average of the same magnitude than for the spin-allowed transitions.

These results are helpful in designing control strategies for specific electronic states, and Manz and Korolkov were able to design methods for coherent control of spin states, motivated in part by these findings. Cooperation with the Manz and the Schwentner groups continues, both in the direction of control of electronic states in photochemistry, and towards understanding the role of different electronic states in photo induced processes.

This project is supported by the DFG in the framework

KINETICS AND MECHANISMS OF ICE AND HYDRATE NANOPARTICLE INTERCONVERSIONS

J. Paul Devlin*, Carmi Yinnon** and Victoria Buch**

Department of Chemistry, Oklahoma State University (devlin@okstate.edu)
and Fritz Haber Institute for Molecular Dynamics, The Hebrew University***

After a brief description of the interaction of strong adsorbates with ice-particle surfaces[1, 2, 3], attention will be focused on the kinetics and mechanisms by which ice and acid hydrates take-up/release strong acids such as HCl and HBr in the process of conversion of particles to new hydrate phases, $n\text{H}_2\text{O}:\text{HX}$. It will be shown that the rate of acid uptake, whether by ice or acid hydrate particles, is often controlled by the diffusion rate thru the “spherical” crust of the hydrate product that encases the initial phase. Such diffusion provides acid to the reaction zone at the interface of the old and new phases. By contrast the reverse reaction, that leads from a lower to a higher hydrate phase, may be controlled by the rate of lost of acid from the particle surface, in which case the rate depends only on the temperature and particle surface area. The FTIR spectra, for the complete inter-conversion of particles, yield values for diffusion coefficients within amorphous and crystalline hydrates, E_a values for diffusion, and acid-desorption energies for hydrate surfaces. The results will be analyzed in terms of the shrinking-core model of particle reactions and viewed in the light of a new Monte Carlo simulation of the nucleation and inter-conversion of phases, with dynamics proceeding via activated atom-vacancy exchanges on a 3-D checkerboard lattice [4].

References:

- [1] N. Uras, V. Buch and J. P. Devlin, J. Phys. Chem., 104, 9203 (2000).
- [2] J. P. Devlin, N. Uras, J. Sadlej and V. Buch, Nature, 417, 269 (2002).
- [3] V. Buch, J. Sadlej, N. Aytemiz and J. P. Devlin, J. Phys. Chem. 106, 9374 (2002).
- [4] C. A. Yinnon, V. Buch and J. P. Devlin, J. Chem. Phys. 120, in press (2004).

Detection of methyl radicals in low-temperature reactions of astrophysical interest

Yu. A. Dmitriev, R. A. Zhitnikov

A.F. Ioffe Physico-Technical Institute, St. Petersburg, Russia.

e-mail: dmitriev.mares@pop.ioffe.rssi.ru

Methane (CH₄) and ethane (C₂H₆) have been found in comets and in atmospheres of several solar planets. The observation of saturated hydrocarbons either frozen on grains or as gases provides strong evidence that the reactions on dust grains play an important role in the interstellar chemical evolution. High (> 0.5) C₂H₆/CH₄ ratio in comets has been found and a mechanism was proposed of CH₄ conversion into C₂H₆ through the production of C₂H₆ in icy grain mantles in the clouds of origin either by photolysis of CH₄-rich ice [1] or by hydrogen addition reaction to C₂H₂ condensed from the gas phase [2]. In the present report, other pathways of the formation of C₂H₆ molecules trapped in the solid CH₄ matrix through the gas-grain processes are discussed. Using EPR technique, we studied low-temperature reactions in the solid CH₄ of the products of gaseous discharge in CH₄.

In our experiments, two methane gas flows, one passing gas discharge zone (channel A) and the other passing through a separate inlet tube to avoid the gas discharge (channel B), are supplied onto the substrate at 1.2 – 4.2 K. In our first set of experiments no gas flow was fed through channel B, and, in turn, the gas flux from channel A was set at minimum so as to make it possible for the discharge to be operated. The substrate temperature was 4.2 K. The EPR records showed only the spectrum of CH₃ radicals and no spectra of C₂H₅ and H-atoms. In the next set of experiments, two flows were simultaneously incident onto the substrate at the same substrate temperature of 4.2 K: one with the gas discharge products from channel A, with a flux matching that of the previous experiments, and the other of pure CH₄, an order of magnitude greater, from channel B. The EPR records changed significantly. We found out the sum of two overlapping spectra: for CH₃ and C₂H₅ radicals. The appearance of a C₂H₅ spectrum in the second set of experiments was matched by the spectrum of hydrogen atoms. In the third set of experiments, with condensation at a substrate temperature lower than 4.2 K, the EPR spectrum shows the lines of the C₂H₅ radical even at the minimum CH₄ flow through channel A that can be set in the experimental conditions, and with no gas flow through channel B. These lines were more intense, the lower the substrate temperature. In the fourth set of experiments we found that even at substrate temperature of 4.2 K and a flow through the channel A only, the C₂H₅ spectrum may be obtained by merely increasing the flow through channel A. In all cases in which the EPR spectrum of C₂H₅ radicals showed up it was accompanied by the EPR spectrum of matrix isolated hydrogen atoms. With computer simulation we estimated the maximum ratio for the C₂H₅ and CH₃ contents more than 7:3. To explain the results, it is argued in the report that methane molecules, C₂H₆, are formed in the matrix through low-temperature reactions with subsequent hydrogen abstraction reaction, $C_2H_6 + H \rightarrow C_2H_5 + H_2$, to produce C₂H₅ radicals in CH₄-ice.

[1] K. Hiraoka, K. Yamamoto, Y. Kihara, T. Takayama, and T. Sato, *ApJ*, **514**, 524 (1999).

[2] S. A. Sandford, M. P. Bernstein, L. J. Allamandola, J. S. Jillette, and R. N. Zare, *ApJ*, **538**, 691 (2000).

INFRARED SPECTRA AND AB INITIO CALCULATIONS OF NO:CH₃Cl IN SOLID NEON AND SOLID ARGON

Nadia DOZOVA, Lahouari KRIM, Esmail ALIKHANI and Nelly LACOME.

*L.A.D.I.R. U.M.R. 7075 CNRS - Université Pierre et Marie Curie, Boîte 49,
4 Place Jussieu, 75252 Paris, Cedex 05, France
email : dozova@spmol.jussieu.fr*

Abstract

The infrared spectra of NO + CH₃Cl isolated in solid neon and solid argon at low temperature have been investigated. The NO + CH₃Cl system is remarkable due to its propensity to form (NO)₂, NO:CH₃Cl, (NO)₂:CH₃Cl and (CH₃Cl)₂, and IR spectroscopy reveals a variety of phenomena far from being fully understood. We will focus here on the NO:CH₃Cl species.

Low concentration studies (0.01 % - 0.5%) and subsequent annealing leads to the formation of 1:1 NO:CH₃Cl van der Waals complex. All vibrational modes of this complex have been detected.

Ab initio calculations of the geometrical, electronic and vibrational properties of the complex will be also presented and compared to experimental values. The bonding and reaction mechanisms will be discussed.

FAST ELECTRON IRRADIATION OF ORGANIC MOLECULES IN A XENON MATRIX: FORMATION OF NOVEL-TYPE SPECIES

Vladimir Feldman^{1,2,3}, Fedor Sukhov¹, Aleksei Orlov², Irina Tyulpina¹, Elizaveta Logacheva² and Daniil Tyurin³

¹Karpov Institute of Physical Chemistry, 10 Vorontsovo Pole Sr., Moscow 105064 Russia

²Institute of Synthetic Polymeric Materials of RAS, 70 Profsoyuznaya Str., Moscow 117393 Russia

³Department of Chemistry, Moscow State University, 199992, Moscow, Russia

e-mail: feldman@cc.nifhi.ac.ru; feldman@rad.chem.msu.ru

The discovery of rare gas hydrides (HRgY) [1] has stimulated extensive investigations aiming at cryochemical synthesis of these unusual molecules [2]. A common way of their preparation includes dissociation of a suitable precursor HY by UV laser [1, 2] or fast electrons [3] followed by annealing resulting in thermal mobilization of the trapped hydrogen atoms and formation of HRgY molecules. Up to recently, these studies were restricted to inorganic species. However, in 2002, Lundell et al. predicted a number of organoxenon hydrides (Y is an electronegative organic radical [4]), and in 2003 experimental finding of the first molecule of this kind (HXeCCH) was reported simultaneously by two groups [5, 6].

In this contribution we present detailed results of our work on acetylene and benzene and preliminary findings on some other alkynes and benzene derivatives. Our approach is based on the combination of EPR and FTIR spectroscopy as applied to the processes induced by fast electron irradiation in solid xenon doped by organic molecules. In the case of acetylene, EPR data obtained at low doses clearly show that irradiation results in dissociation of HCCH to H and CCH in nearly balanced amounts. Meanwhile, at higher doses dissociation of CCH radical yields C₂-Xe and H. Annealing at 40–45 K leads to reactions of mobilized H atoms yielding HXeCCH, HXeH and C₂H₃ radical. The former species is characterized by prominent absorption at 1486 cm⁻¹. Annealing of the samples irradiated to high doses results in additional absorption at 1478 cm⁻¹, which was assigned to HXeCC radical [5]. In order to characterize the EPR spectrum of this novel radical, we have applied relativistic DFT calculations and experimental studies in isotope enriched matrices (¹²⁹Xe and ¹³⁶Xe).

In the case of benzene, the yield of consumption of the parent molecules was found to be much lower. Nevertheless, the main reaction channel is unambiguously identified as dissociation of the C—H bonds to yield phenyl radicals and H atoms, as shown by both EPR and IR data. Annealing results in H atom loss; however, in contrast to acetylene, the principal channel is addition to benzene yielding C₆H₇ radicals. We failed to observe new absorptions, which could be definitely assigned to HXeC₆H₅ predicted by Lundell et al. [4]. One possible reason is that the new molecule may be not enough stable to be observed in our experiments.

The prospects of obtaining other novel organoxenon species will be discussed.

The work was supported by the Russian Foundation for Basic Research (pr. no. 03-03-32717).

1. M. Pettersson, J. Lundell, M. Räsänen, *J. Chem. Phys.*, **102**, 6423 (1995).
2. For review: M. Pettersson, J. Lundell, M. Räsänen, *Eur. J. Inorg. Chem.*, 729 (1999).
3. V.I. Feldman, F.F. Sukhov, *Chem. Phys. Lett.* **255**, 425 (1996).
4. J. Lundell, A. Cohen, B. Gerber, *J. Phys. Chem. A*, **106**, 11950 (2002).
5. L. Khriachtchev, H. Tanskanen, J. Lundell, M. Pettersson, M. Räsänen, *J. Am. Chem. Soc.*, **125**, 4696 (2003).
6. V.I. Feldman, F.F. Sukhov, A.Yu. Orlov, I.V. Tyulpina, *J. Am. Chem. Soc.*, **125**, 4698 (2003).

ORGANIC RADICAL CATIONS PRODUCED BY FAST ELECTRON IRRADIATION IN SOLID ARGON: EPR SPECTRA, STABILIZATION AND FRAGMENTATION

Vladimir Feldman^{1,2,3}, Fedor Sukhov¹, Aleksei Orlov² and Irina. Tyulpina¹

¹Karpov Institute of Physical Chemistry, 10 Vorontsovo Pole Sr., Moscow 105064 Russia

²Institute of Synthetic Polymeric Materials of RAS, 70 Profsoyuznaya Str., Moscow 117393 Russia

³Department of Chemistry, Moscow State University, 199992, Moscow, Russia

e-mail: feldman@cc.nifhi.ac.ru; feldman@rad.chem.msu.ru

The up-to-date knowledge on the EPR spectra, structure and properties of organic radical cations relies mainly on the data obtained by the so-called “freon matrix technique” [1], which is actually a compromise approach rather than true matrix isolation. Only several small organic radical cations were characterized by EPR spectroscopy in solid neon [2]. Recently, we have made extensive efforts to obtain the characteristics of larger chemically important ions in argon matrices [3, 4]. These species were generated by fast electron irradiation of deposited solid argon matrices doped with small amounts of studied compounds and electron scavengers (halocarbons). Here we present new results and overview of these studies.

The principal feature of the approach used in our work is that the radical cations are produced basically by indirect ionization (positive hole transfer), because the primary ionization occurs in matrix. This implies very important role of relaxation of radical cations, which possess relatively large excess energy (5 – 7 eV) due to high exothermicity of positive hole transfer from argon ions. Generally speaking, there are three basic cases: (i) inefficient relaxation, which brings about high yields of fragmentation and rearrangement products (e. g., isobutane, methyl tert-butyl ether, methylal, ethyl acetate); (ii) moderately efficient relaxation, which leads to comparable yields of fragmentation products and stabilized primary cations (e. g., acetaldehyde); (iii) efficient relaxation, which results in minor yields of fragmentation products (e. g., linear alkenes, acetone, tetrahydrofuran, alkyl benzenes, vinyl ethers). Although some trends appear to be obvious (e. g., higher stability of unsaturated and aromatic cations), other results reveal specific features of relaxation of the primary cations of similar chemical structure. The observed peculiarities are discussed in terms of competition between chemical reaction of “hot” species, intramolecular and intermolecular relaxation.

The work was supported by the Russian Foundation for Basic Research (project no. 03-03-32717) and INTAS (project no. 2000-0093)..

1. M.C.R. Symons, *Chem. Soc. Rev.*, **13**, 393 (1984).
2. L. B. Knight, *Acc. Chem. Res.*, **19**, 313 (1986).
3. V.I. Feldman, *Radiat. Phys. Chem.*, **55**, 565 (1999).
4. V.I. Feldman, F.F. Sukhov, A.Yu. Orlov, I.V. Tyulpina, *Phys. Chem. Chem. Phys.* **5**, 1769 (2003).

Charge Transfer States of C₂ Doped Krypton Solids

S.L. Fiedler, H. Kunttu, J. Eloranta

*Department of Chemistry, University of Jyväskylä, Surfontie 9, 40500 Jyväskylä, Finland
sfiedler@jyu.fi*

Although the intramolecular Mulliken (D!X) electronic absorptions have been observed for C₂ in the gas phase and in Ne, Ar, and Kr matrices, the intermolecular charge transfer absorptions have not been reported, to the authors' knowledge. Here we propose that an 180 - 210 nm absorption band observed in a C₂ doped Kr matrix can be attributed to this charge transfer process.

The deposition of acetylene, C₂H₂, in rare gas solids (RGS) was used as a precursor for C₂. Depletion of monomeric acetylene upon photolysis was confirmed by the attenuation of the ν_3 and $\nu_2+\nu_4+\nu_5$ stretching vibrational signals. Subsequent to dissociation, the electronic absorption of the fragment species was recorded in Ar, Kr and Xe matrices. Characteristic absorptions of Xe_nH [1], C (³P^o!³P, ³P^o!³D^o)/Ar[2], Kr[3], Xe, C₂ (D!X)/Ar[4], C₂Xe [5], were observed and compared well with literature values.

Energetic comparisons of the Mulliken absorptions were made to potentials obtained from *ab initio* calculations. The Kr_nC₂, neutral to charge transfer absorption spectrum was simulated using the *ab initio* potentials as input for a diatomics-in-molecules calculation. Details of the calculation and methodology are included in [6] and in [7] involving the charge transfer states of Kr_nCN. The experimental and theoretical charge transfer spectra of the C₂ and CN dopants were compared and the Kr_nC₂ spectrum was blue shifted from Kr_nCN by *ca.* 0.6 eV as anticipated by the difference in electronegativities of 3.27 eV and 3.86 eV respectively. Reasonable agreement of the simulated spectra to the experiment was found for both systems.

-
- [1] M. Kraas, P. Gürlér, Chem. Phys. Lett., **174**, 396 (1990)
 - [2] J. Lei, P.J. Dagdigian, J. Chem. Phys., **113**, 602 (2000)
 - [3] J. Eberlein, M. Creuzburg, Mol. Phys. **96**, 451 (1996)
 - [4] D.E. Milligan, M.E. Jacox, L. Abouf-Marguin, J. Chem. Phys., **46**, 4562 (1967)
 - [5] G. Maier, C. Lautz, Eur. J. Org. Chem., 769 (1998)
 - [6] S. Fiedler, H. Kunttu, J. Eloranta, (publication pending)
 - [7] S.L. Fiedler, K. Vaskonen, J. Ahokas, H. Kunttu, J. Eloranta, V.A. Apkarian, J. Chem. Phys., **117**, 8867 (2002)

PROTONATED AND FRAGMENT IONS OF ACETONITRILE MASS-SELECTIVE MATRIX-ISOLATION STUDY

Marcin Frankowski¹, Alice M. Smith-Gicklhorn¹, Zheng Sun¹, Alexey N. Ponomaryov
and Vladimir E. Bondybey^{1,2}

¹ Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstraße 4,
D-85748 Garching, Germany

² Department of Chemistry, University of California, Irvine, California 92697-2025, USA
emails for correspondence: v.e.bondybey@ch.tum.de; frankowski@ch.tum.de

An investigation of reactive cyano-compounds and particularly their molecular ions is of special interest for physical and chemical processes occurring in interstellar space. Listings of neutral and ionic molecular species (NRAO and DEMIRM) detected in spectral regions which span from radiofrequency to the far-infrared, reveal that nitriles and their metastable isomers prevail in this environment. However, radioastronomical observations resulted, so far, in the identification of only two molecular ions containing a nitrile group: HCNH^+ and HC_3NH^+ [1,2].

Searches for the protonated molecules are of considerable importance for ion-molecule reactions in the interstellar medium. Although the protonated acetonitrile, CH_3CNH^+ , has not been unambiguously identified in space, it is thought to be formed from CH_3^+ and HCN, and in turn, to be involved in formation of the acetonitrile molecule, CH_3CN . Unfortunately, the data on its IR spectroscopy are still incomplete and limited to the N–H stretching vibration [3]. The same concerns the acetonitrile cation. Quite recently, intensive studies have been carried out on the $\text{C}_2\text{H}_2\text{N}$ family of cations and radicals [4], however no infrared spectra of $\text{C}_2\text{H}_2\text{N}^+$ have been reported to date.

As demonstrated here, our FT-IR Ne-matrix study supported by DFT/B3LYP computations, partially fills this gap. The matrix-isolation technique employing mass-selective deposition of ions is a valuable tool in the spectroscopic characterization of such elusive species [5,6]. In the current work, the compounds are generated upon electron impact ionization of acetonitrile CH_3CN , and its deuterated CD_3CN analogue. In spite of the fact that the spectra recorded after mass-selective deposition allow only for tentative assignment of the parent cation, $\text{CH}(\text{D})_3\text{CN}^+$, acetonitrile turned out to be a suitable precursor for other molecular ions with apparently greater IR activity. The experiments resulted in the spectral characterization of protonated acetonitrile CH_3CNH^+ , as well as the identification of three cationic cyanomethyl $\text{C}_2\text{H}_2\text{N}^+$ isomers: H_2CCN^+ , H_2CNC^+ and HCCNH^+ . Although the spectral assignments for two ionic isomers, H_2CCN^+ and H_2CNC^+ , can be only tentative, experimental results give rather strong evidence for the occurrence of the linear HCCNH^+ ion.

[1] B.E. Turner, T. Amano, P.A. Feldman, *Astrophys. J.* **349**, 376 (1990).

[2] P. Botschwina, *Phys. Chem. Chem. Phys.* **5**, 3337 (2003).

[3] T. Amano, *Astrophys. J. Lett.* **330**, L137 (1988).

[4] R.P. Thorn, Jr., P.S. Monks, L.J. Stief, S.-C. Kuo, Z. Zhang, S.K. Ross, R.B. Klemm, *J. Phys. Chem. A* **102**, 846 (1998).

[5] A.M. Smith-Gicklhorn, M. Lorenz, R. Kołos and V.E. Bondybey, *J. Chem. Phys.* **115**, 7534 (2001).

[6] A.M. Smith-Gicklhorn, M. Frankowski and V.E. Bondybey, *Phys. Chem. Chem. Phys.* **4**, 1425 (2002).

WAVEPACKET DYNAMICS IN CONDENSED PHASE: Cl₂ IN Ar

Mizuho Fushitani, Matias Bargheer, Markus Gühr, and Nikolaus Schwentner

*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee, 14195 Berlin, Germany
e-mail: mizuho.fushitani@physik.fu-berlin.de*

We report the vibrational and electronic coherence of Cl₂ molecules embedded in thin Ar crystals by using the fs pump-probe technique. A tunable pulse ($\Delta t=50$ fs) generated by NOPA was used as a pump pulse which creates a wavepacket(WP) of Cl₂ on the inner limb of the electronic excited state of B. The subsequent dynamics of the WP was monitored so that the WP was further excited by a probe pulse($\Delta t=80$ fs) to ion pair manifold states and the fluorescence from the states was recorded as a function of the time delay between the pump and probe pulses. Figure 1 shows WP dynamics of Cl₂ in solid Ar under the condition of pump/probe=490/285nm. We observed two different oscillations with 300fs and 500fs periods. The faster period appearing in the first two oscillations is assigned to the molecular vibration of Cl₂ whereas the slower one is due to a zone boundary phonon of solid Ar which can modulate a LIF signal of doped molecules coherently.[1]

We have also carried out phase locked pulse pair (PLPP) experiments where the electronic coherence of molecules can be investigated.[2] The first pulse creates coherence on molecules and the second one interferes with the same molecules constructively or destructively depending on relative phases between the PLPP, as long as the molecules keep the phase information. We applied the PLPP to the system of Cl₂ in solid Ar and monitored LIF fluorescence(A' $\rightarrow$ X and/or D $\rightarrow$ A) signals. Figure 2 shows a fluorescence interferogram after the excitation of a PLPP centered at 515nm. The first vibrational recurrence is observed around 260fs. The result indicates that the electronic coherence is preserved more than a vibrational period even in the solid where many body electronic interactions take place.

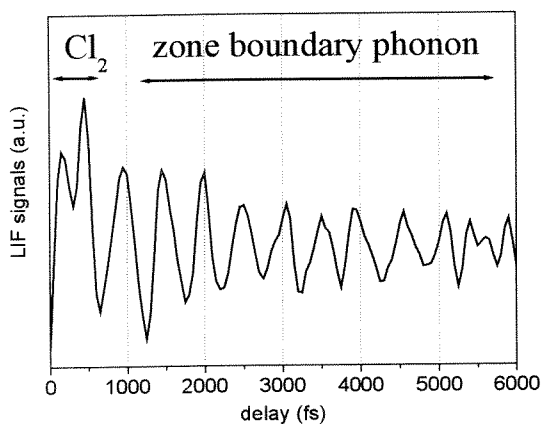


Fig. 1. Pump probe spectrum of Cl₂ in solid Ar. The oscillation with a 300fs period is due to the molecular vibration of Cl₂ while the 500fs modulation is driven by the zone boundary phonon of solid Ar.

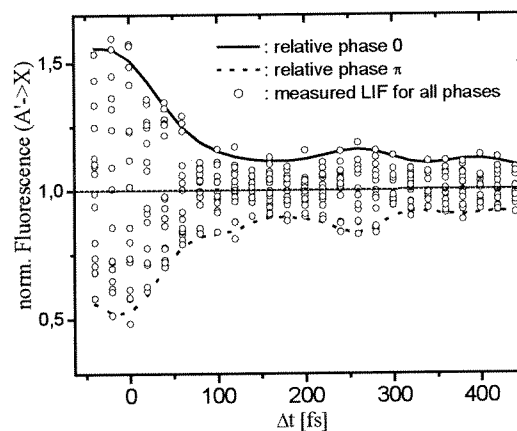


Fig. 2. Fluorescence interferogram of Cl₂ in solid Ar with 16 different phase values for each time delay(open circle). The solid(dotted) line shows LIF signals obtained by using the PLPP with relative phase 0(π). The vibrational recurrence appears at 260 fs.

- [1] M. Gühr, M. Bargheer and N. Schwentner, *Phys. Rev. Lett.*, **91**, 085504 (2003).
[2] N. F. Scherer, *et al.*, *J. Chem. Phys.*, **95**, 1487 (1991).

X-ray studies of $p\text{H}_2\text{-nD}_2$ solid solutions

Galtsov N.N., Prokhvatilov A.I., Strzhemechny M.A.

Verkin Institute for Low Temperature Physics and Engineering, 47 Lenin ave., 61103 Kharkov, Ukraine
e-mail: galtsov@ilt.kharkov.ua

The possibility of hydrogen solid isotopic mixtures separation have being discussed for more than fifty years. According to early theoretical predictions of J. Prigogine [1], W.J. Mullin and H.K. Sarin [2] $\text{H}_2\text{-D}_2$ solid mixtures inclined to separation only at temperatures under 4 K. Meanwhile, V.S. Kogan, B.G. Lazarev and R.F. Bulatova on joint x-ray and thermographic analysis observed phase separation in this system at $T < 16$ K. Still further numerous attempts to confirm this result were unsuccessful and till now solid hydrogen isotopic mixtures were considered to stay homogeneous up to 0.6 K [4] contrary to helium quantum isotopic solutions. In [5] was made a suggestion that high content of molecules with $J=1$ in solutions should facilitate $\text{H}_2\text{-D}_2$ mixtures separation. Indeed, a wide temperature-concentration region of existence of two hexagonal phases based on hydrogen and deuterium was found at x-ray investigation of fine-grained $n\text{H}_2\text{-nD}_2$ alloys [6]. Therefore, it was interesting to investigate mixtures with smaller that in $n\text{H}_2\text{-nD}_2$ content of $J=1$ molecules. For that purpose we chose $p\text{H}_2\text{-nD}_2$ system in which rotational subsystem is formed by about only 33% of $p\text{D}_2$ molecules.

In this report the results of x-ray studies of $p\text{H}_2\text{-nD}_2$ solid solutions obtained by deposition of gas mixtures with appropriate composition straight to solid phase is shown. The ranges of investigation were 5 to 95 % $n\text{D}_2$ in composition and temperature from 5 K to the respective melting points. As a results we no observed a phase separation of the investigated solid solutions $p\text{H}_2\text{-nD}_2$. We suggest some explanations for the striking difference between the results of different studies carried out to search for phase separation in solid mixtures of deuterium and hydrogen on samples prepared by different methods.

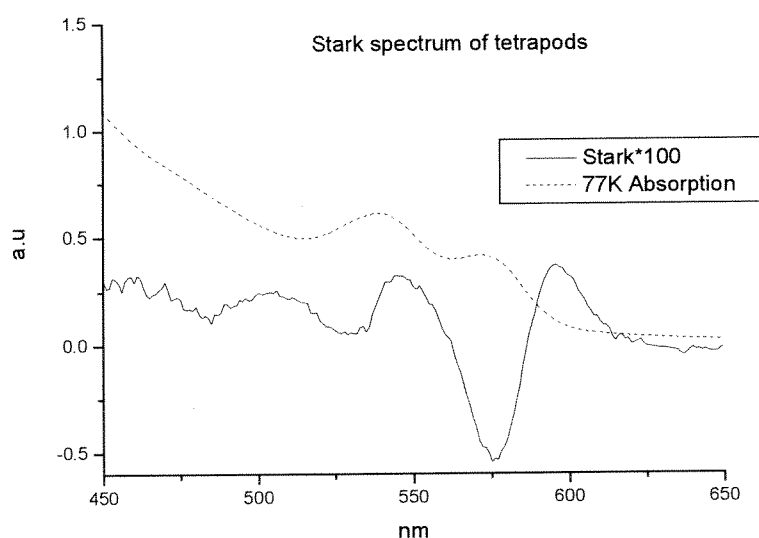
1. J. Prigogine, R. Bingen, and A. Belamans, *Physica* **20**, 633 (19554).
2. W.J. Mullin and H.K. Sarin, *Phys. Lett.* **29**, 49 (1962).
3. V.S. Kogan, B.G. Lazarev, and P.F. Bulatova, *Zh. Eksp. Teor. Fiz.* **34**, 238 (1958).
4. B.I. Verkin and A.F. Prikhot'ko (eds.), *Cryocrystals*, Kiev: Naukova Dumka (1983) 528p.
5. A.I. Prokhvatilov, *Fiz. Nizk. Temp.* **16**, 1256 (1990).
6. M.A. Strzhemechny, A.I. Prokhvatilov, G.N. Shcherbakov, and N.N. Galtsov, *J. Low Temp. Phys.* **115**, 109 (1999).

Nature of electronic states in CdSe nanocrystals studied by Stark spectroscopy

G.Giraud, M.Mohamed, L.Heinen, M.Chergui and F. Van Mourik

Laboratoire de Spectroscopie Ultrarapide (LSU) Institut des Sciences et Ingénierie Chimiques (ISIC),
Faculté des Sciences de Base, BSP Ecole Polytechnique Fédérale de Lausanne (EPFL)
Ch-1015 Lausanne-Dorigny, Switzerland. Corresponding author: Frank.vanMourik@epfl.ch

The electronic structure of nanocrystals varies according to their size and shape. [1] Among others, they can be produced as dots, rods or tetrapods. Tetrapods is a fascinating system to study because it has a tetrahedron at its centre of Zinc blende structure joint by four rods of Wurtzite structure at $(11\bar{1}), (1\bar{1}\bar{1}), (\bar{1}1\bar{1}), (\bar{1}\bar{1}1)$ surfaces. The optical and electronic structures are completely different from those of rods and dots of same diameter. The lowest electronic state is preferentially localized in the central tetrahedron of the tetrapods. This is mainly because the electron is confined in the ZB region and the hole in the WZ region as a result of WZ-ZB band alignment. To observe the different character in the electronic states of CdSe nanocrystals we performed absorption Stark spectroscopy. Previous experiments performed on CdSe nanocrystallites [2] show that the absorption stark signal is dominated by polarisation effect. In the case of tetrapods (see figure below), the Stark spectrum was observed to be dominated by the second derivative component of the lowest energy absorption band (575 nm), which indicates that this transition has significant charge transfer character (~ 20 D difference-dipole moment). The results help us to make assignments of the spectroscopic nature of the lowest three transitions observed in tetrapods.



1. Li, J.B. and L.W. Wang, Nano Letters, 2003. **3**(10): p. 1357-1363.
2. Sacra, A., et al., Journal of Chemical Physics, 1995. **103**(13): p. 5236-5245.

Probing Molecular Metal Contacts by Scattering of Surface State Electrons

Leo Gross*, Francesca Moresco*⁺, Micol Alemani*, André Gourdon §, Christian Joachim §,
and Karl-Heinz Rieder*

* *Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany,*
§ *CEMES-CNRS, 29 rue J. Marvig, P.O. Box 4347, F-31055 Toulouse Cedex, France*

A crucial problem in molecular electronics is the observation and control of the electronic contact of the molecule with its metal electrodes [1]. The contact quality relies on the precise interaction between the molecule end groups and the surface of each electrode. Here, we report on the reproducible planar contact and de-contact of a molecular wire to the edge of a Cu (111) mono-atomic step taken as a model system for the edge of an atomically well-defined electrode. The molecule holding the wire group in a planar conformation is manipulated with a low temperature scanning tunneling microscope (LT-STM). The molecule surface (electrode) interaction is probed by 2D surface state electrons, which are scattered by the adsorbates, exhibiting characteristic standing wave patterns. Comparison of STM measurements with model calculations reveal the position of the dominant scattering centers within the molecule [2]. The interaction of the terminal part of the wire with the 2D surface states of the Cu (111) surfaces notably modifies the electron standing wave patterns at the step edge [3].

- [1] C. Joachim, J. K. Gimzewski, and A. Aviram, *Nature (London)* **408**, 541 (2000).
- [2] L. Gross, F. Moresco, L. Savio, A. Gourdon, C. Joachim, and K.-H. Rieder, *Phys. Rev. Lett.*, in press (2004).
- [3] F. Moresco, L. Gross, M. Alemani, K.-H. Rieder, H. Tang, A. Gourdon, and C. Joachim, *Phys. Rev. Lett.* **91**, 036601 (2003).

⁺ Corresponding author, e-mail address: francesca.moresco@physik.fu-berlin.de

Generation of Coherent Zone Boundary Phonons by Impulsive Excitation of Molecules

M. Gühr and N. Schwentner

*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany
Markus.Guehr@physik.fu-berlin.de*

We observe coherent phonons in ultrafast pump-probe spectra on the system I_2 in solid Kr [1] and in very new spectra of $Br_2:Ar$.

A first ultrashort laser pulse (pump pulse) creates a molecular vibrational wave packet on the excited covalent states (B or A) of the halogen molecule (see fig. 1 a). A second ultrashort pulse (probe pulse) interrogates the wave packet motion on the covalent state via a transition to a charge transfer state (E or β in fig.1a). We record the laser-induced fluorescence (LIF) of the charge transfer states as a function of the delay between pump and probe pulse.

The pump-probe spectra show the dynamics of intramolecular vibrational wave packets in the first 2 ps ($Br_2:Ar$ in fig. 1b) to 4 ps ($I_2:Ar$ in fig. 1c and d). After the decay of the initial intramolecular wave packet oscillations (relaxation, dispersion and dephasing), a new dynamics with a frequency of 2 THz ($Br_2:Ar$) or 1.5 THz ($I_2:Kr$) period appears. The frequency is in resonance with the Zone Boundary Phonon (ZBP) in Ar or Kr respectively. The ZBP modulation happens to be phase stable with respect to the pump pulse upon excitation of different electronic states of the molecule (compare fig. 1c and d by dashed line) and different excitation energy in the anharmonic well of the electronic state (not shown here). It shows up independent of the molecular oscillation period and the phase stability indicates that it cannot be a host mode driven by the molecular vibration. The excitation of the host dynamics is impulsive during the pump process at $t = 0$ fs. The pump pulse transfers the molecule from its electronic ground state X to a covalent state like B or A. Thereby the electronic cloud blows up resulting in a new equilibrium position of the neighbouring host atoms. The host atoms start to oscillate around their new equilibrium and phonons are excited.

After excitation, the wave packet relaxes below the probe window after a few ps and spreads over a large internuclear distance. The ZBP stay in the vicinity of the molecule, because of their vanishing group velocity. The ZBP modulate the host density in the vicinity of the chromophore. Due to this periodic density modulation, the solvation energy of the molecular charge transfer states oscillates up and down with the phonon frequency (vertical arrows fig. 1a). The probe window shift left- and rightwards (out of and into the relaxed population) to keep the resonance (horizontal arrows in fig. 1a). This results in probing less and more population.

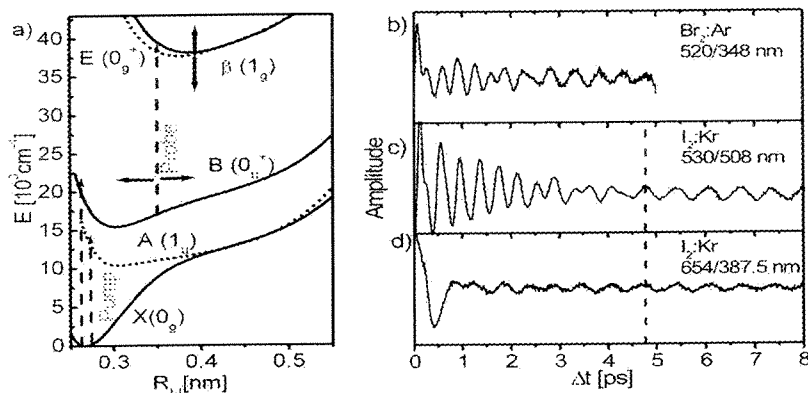


Fig. 1a: Pump-probe scheme for $I_2:Kr$. b-d: Pump-probe spectra for $Br_2:Ar$ and $I_2:Kr$.

Laser-induced recombination of self-trapped holes with electrons in preirradiated solid Ar.

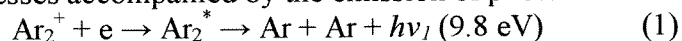
G.B. Gumenchuk, M.A. Bludov, A.G. Belov.

*Verkin Institute for Low Temperature Physics & Engineering of the National Academy of Sciences of Ukraine, 47 Lenin Ave.,
Kharkov 61103, Ukraine,
E-mail : Galina.Gumenchuk@ch.tum.de*

The results on study of photon-stimulated recombination reactions in preirradiated solid Ar are presented. Spatially separated stable charge centers – trapped electrons and self-trapped holes as well as guest ions were generated in Ar cryocrystals by low energy electron beam. A combination of the cathodoluminescence and laser-induced fluorescence methods was used to probe recombination reactions. All the measurements were performed at temperatures lower than the threshold temperature (9 K) for thermally stimulated luminescence and exoelectron emission [1] to prevent thermally stimulated release of electrons from their traps and exclude all the thermally assisted processes. After irradiation we tuned the monochromator to the wavelength of the M-band of solid Ar to register the spectrally resolved intrinsic recombination luminescence from the samples as a function of the exposure time to the laser beam. The similar procedure was used to detect recombination emission of the guest species. A standard He-Ne laser was used.

We observed an initial sharp rise in the VUV recombination luminescence intensity switching the laser on followed by a much slower decay as the traps were emptying. Photon-stimulated vacuum ultraviolet (VUV) intrinsic recombination luminescence from preirradiated solid Ar was detected for the first time. We demonstrated that the laser light of 1.96 eV energy releasing electrons from their traps gave rise to the well-known emission M-band at 9.8 eV. Additional data on photon-stimulated recombination reactions of positively charged guest ions with electrons were obtained.

Electrons released into the conduction band from their traps by visible light have two possibilities for further relaxation. They can escape the sample yielding exoelectron emission as found in [2]. Another relaxation channel is recombination reactions of the electrons with positively charged centers in the matrix. In pure Ar film the role of such kind of centers play self-trapped holes (STHs) of dimer configuration Ar_2^+ . These recombination processes accompanied by the emission of photons are described by the reactions:



The spectrally-resolved recombination luminescence detected by the reactions (1) and (2) provided a direct proof that in preirradiated Ar cryocrystals relaxation photon-stimulated processes include radiative recombination of STHs and guest ions with electrons. The data obtained demonstrate an important part of radiative processes in the relaxation of preirradiated solids.

References:

- [1] E.V. Savchenko, O.N. Grigorashchenko, A.N. Ogurtsov, V.V. Rudenkov, G.B. Gumenchuk, M. Lorenz, A. Lammers, and V.E. Bondybey, *J. Low Temp. Phys.* **122**, 379 (2001).
- [2] E.V. Savchenko, O.N. Grigorashchenko, G.B. Gumenchuk, A.G. Belov, E.M. Yurtaeva, M. Frankowski, A.M. Smith-Gicklhorn, and V.E. Bondybey, *Surface Science*, **528**, 266 (2003).

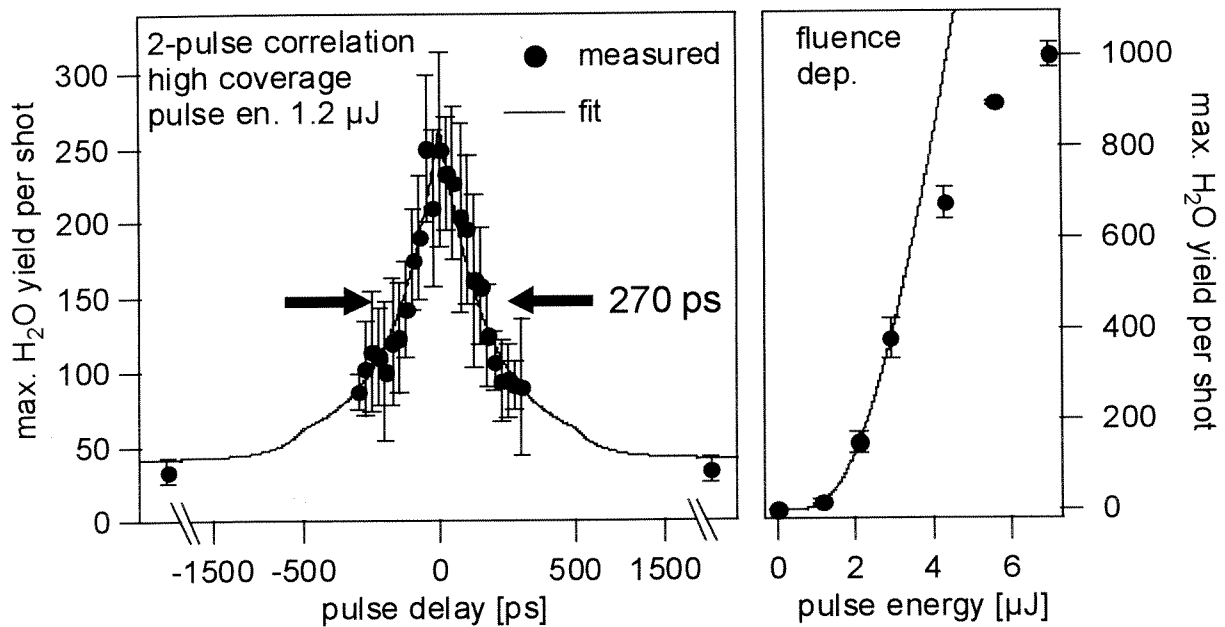
LASER INDUCED WATER DESORPTION FROM SILVER NANOPARTICLES

A. Hotzel, S. Kwiet, D. Starr*, A. Grujic, M. Wolf

Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

* Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin, Germany
arthur.hotzel@physik.fu-berlin.de

H₂O desorption from silver nanoparticles induced by femtosecond laser pulses was studied in order to investigate the influence of the surface field enhancement due to plasmon resonances on the one hand, and energy confinement on the other hand, on direct and substrate mediated photoreaction pathways [1]. The large width of the two-pulse correlation trace of the desorption yield (~ 300 ps) shows that the water desorption is a purely thermal process, mediated by coupling to the nanoparticle phonon bath. This result was found both in the multilayer and the sub-bilayer coverage regime. The H₂O desorption signal can in turn be used as an absolute measurement of the transient nanoparticle lattice temperature upon excitation with moderately strong laser pulses. The resulting cooling time constant of (450 ± 150) ps agrees well with recent time-resolved X-ray diffraction measurements [2] that showed a strong dependence of the cooling dynamics on particle size and coupling to the dielectric environment.



[1] S. Kwiet et al., submitted to *Appl. Phys. B* (2004).

[2] A. Plech et al., *Europhys. Lett.* **61**, 762 (2003).

Vibrational Coherence and fractional Revivals in Br₂:Ar

M. Gühr, H. Ibrahim and N. Schwentner

*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany
Heide.Ibrahim@physik.fu-berlin.de*

We perform ultrafast pump-probe spectroscopy in solid Ar crystals. The solid line in fig. 1a) shows a typical pump-probe spectrum of a vibrational wave packet in the B state. The modulation contrast is decaying for two reasons:

- The molecule is interacting with the matrix leading to vibrational decoherence.
- The B potential is anharmonic, thus the high energy components of the wave packet travel faster than those at lower energies, causing a wave-packet dispersion.

This Dispersion can be overcome in a distinct time intervall by exciting with a negatively chirped pulse as can be seen in the dashed line in fig. 1a). The remaining background at 1.2 ps (the point of focussing) indicates the decoherence only. By a systematic variation of the chirp parameter one deduces a vibrational decoherence time of 3 ps.

Furthermore, we used the phenomenon of fractional revivals [1] to test the coherence of a distinct number of vibrational eigenstates. When observing a 1/6 revival (induced by 1/3 of the oscillation period in the pump-probe spectrum) at least four vibrational levels have to be coupled coherently. However, employing the parameters of Br₂, it would appear at 3.5 ps, outside the vibrational coherence range of Br₂ (3 ps).

Therefore we use positively chirped pulses to shift the appearance of the 1/6 revival to about 1.2 ps (see fig. 1b)). The experiment can be fully explored by quantum simulations.

Further on, we will present pulse-sequence schemes that allow us a selective excitation of wave packets consisting of zero-phonon lines or phonon sidebands only. These pulse sequences will be obtained by using a liquid crystal modulator for influencing phase and amplitude of the pulses.

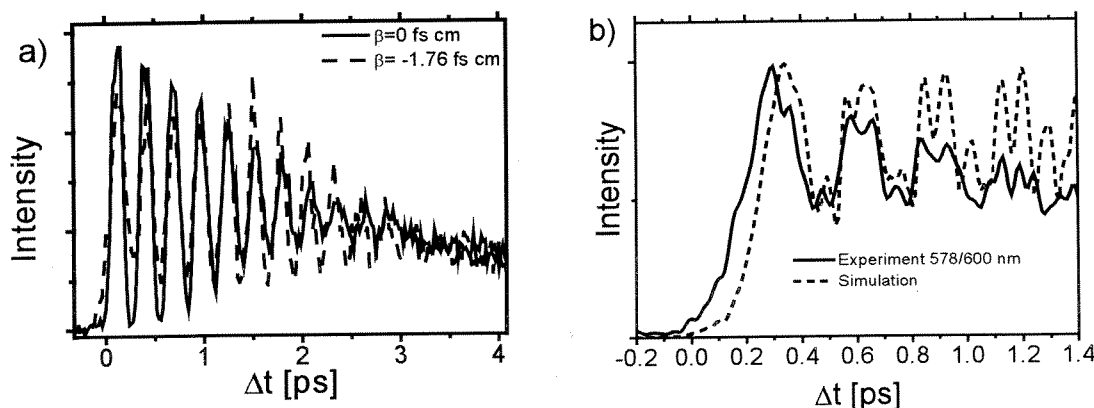


Fig. 1 a) Solid line: unchirped excitation, dashed line: a negatively chirped pump pulse shifts the focus of the wave packet to larger delay times. The dephasing background remains. b) Experiment and Simulation for a 1/6 revival. The typical structure appears at 1.2 ps.

- [1] Averbukh IS, Vrakking MJJ, Villeneuve DM, Stolow A, Phys. Rev. Lett. 77, 3518-3521 (1996) and references therein

Microwave spectroscopy of molecules in bulk liquid Helium

Masazumi Ishiguro and Yasuyuki Aratono

Advanced Science Research Center, Japan Atomic Energy Research Institute,

Tokai, Ibaraki, 319-1195, Japan

e-mail: ishiguro@popsvr.tokai.jaeri.go.jp

We have developed a microwave spectrometer aimed for the observation of pure rotational transition and tunnel splitting of molecules trapped in low temperature condensed media such as solid *para*-hydrogen, bulk liquid and solid helium. The opto-thermal detection with superconductor thin-film sensor (STS) makes it possible to obtain sufficient sensitivity to detect the signal of very low concentration species in low temperature matrixes. We applied this technique for the observation of tunnel splitting of NH₃ molecule in bulk liquid helium.

The spectra were recorded in the 8 ~ 36 GHz region at 1.4 K. Several strong lines were observed in the region of 18 ~ 25 GHz. The observed frequency of the strongest line was 22.196 GHz. Supposing this line is due to the splitting of (*J*, *K*) = (1, 1) level, which may be regarded as the strongest microwave transitions of NH₃ at 1.4 K, the tunnel splitting in liquid He becomes 93.7% of that of gas phase (23.694 GHz) [4].

It is known that the rotational structures accompanying tunnel splitting for NH₃ molecule is observable even in the solid matrixes such as Ne, Ar, Kr, Xe, and N₂ from the infrared spectroscopic studies [1]. For example, the tunnel splitting of ν_2 vibrationally excited state in solid Ne is determined to be 27 cm⁻¹ [2], and it is 76% of that for gas phase, 35.688 cm⁻¹ [3]. In liquid He, whose interaction with doped molecules is extremely weak, the change of tunnel splitting from that of gas phase is estimated to be much smaller than any other matrixes. The observed frequency of the strongest line, 22.196 GHz, supports the hypothesis that this line is due to the tunnel splitting of NH₃ in bulk liquid helium. The confirmation for the assignment using ¹⁵NH₃ isotopic species and the observation of pressure and temperature dependence for the spectra are underway.

[1] L. Abouaf-Marguin *et al.*, *J. Mol. Spectrosc.* **67**, 34 (1977)

[2] L. Abouaf-Marguin *et al.*, *Chem. Phys. Lett.* **15**, 445 (1972)

[3] S. Urban *et al.*, *Can. J. Phys.* **62**, 1775 (1984)

[4] R. L. Poynter *et al.*, *Astro Phys. J. Suppl. Series* **29**, 87 (1975)

PHOTOCHEMISTRY OF PROPYLIC ACID AND ITS ISOMERS IN SOLID ARGON.

Esa Isoniemi, Leonid Khriachtchev, Maarit Makkonen, and Markku Räsänen

*Laboratory of Physical Chemistry
Department of Chemistry
University of Helsinki
e-mail: esa.isoniemi@helsinki.fi*

Photochemistry of propylic acid (HCCCOOH) is studied at 193 nm in solids Ar. IR absorption spectra of the *trans* and the *cis* forms of propylic acid and the photolysis products are studied both experimentally and computationally. In the UV photolysis of the *trans*-propylic acid, the products are assigned mainly as *cis*-propylic acid, and complexes of acetylene, etynol, and water with carbon dioxide, carbon monoxide, and C_3O respectively. The structures of complexes and IR absorption spectra are computed and discussed in respect to experimental findings. *Trans*-propylic acid is converted into *cis* form by reactive isomerisation induced by the rare-gas cage and by direct IR pumping. Conversion of the *cis*-propylic acid into the *trans* form by tunnelling is observed.

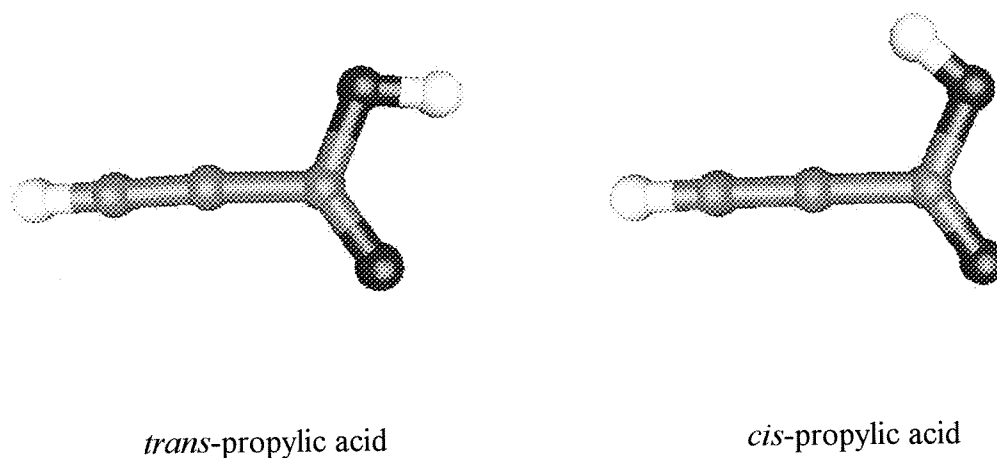


Fig. 1 Structures of *trans*-propylic acid and *cis*-propylic acid.

Electron trap-related low temperature relaxation in preirradiated Ne matrix

**I.V. Khyzhniy^{*}, E.V. Savchenko^{*}, A.G. Belov^{*}, E.M. Yurtaeva^{*}, M. Frankowski^{**},
M.K. Beyer^{**}, A.M. Smith-Gicklhorn^{**}, and V.E. Bondybey^{**}**

^{*} *Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47
Lenin Ave., Kharkov 61103, Ukraine*

^{**} *Institute of Physical and Theoretical Chemistry, TU Munich, Lichtenberg str. 4,
Garching 85747, Germany
e-mail: Khyzhniy@ilt.kharkov.ua*

Electron traps play an important role in a course of relaxation processes in irradiated solids, specifically in cryogenic matrices. Interaction of ionizing radiation with matrix changes a set of defects and produces new metastable centers – products of radiation-induced reactions involving dopants (atoms, molecules and radicals), ionic species, trapped electrons. Positively charged species incorporate intrinsic ionic species – self-trapped holes – and guests, which can be ionized in the matrix. Negatively charged centers are electrons attached to electron scavengers or trapped at some defects of structure. In view of negative electron affinity of solid Ne [1] (that means the prevailing repulsive forces between electron and surrounding atoms) only such a kind of structural defects as pores or vacancies can serve as effective traps for electrons.

At low temperatures the thermally stimulated processes are frozen and photons become crucial factor in relaxation processes. In the present study we investigated relaxation processes in the model system – solid Ne doped with N₂. This system is attractive for elucidating the role of radiative transitions in relaxation cascades because of the intense afterglow, which is caused by the formation of N atoms in metastable states upon irradiation.

The samples of Ne cryocrystals grown from the gas phase by condensation on a cooled substrate were exposed to a beam of electrons. After the irradiation we detected a long afterglow from the samples maintained at the constant low temperature. The total yield of afterglow photons was measured along with the spectrally-resolved ones. The source of these emissions is dopant atoms and molecules (or the contamination from the residual gases in the vacuum chamber). Note that before irradiation of the sample the impurities (for example N and O) are present in a molecular state. The irradiation results in dissociation of molecules into atoms. The long afterglow is caused by radiative decay of metastable states.

Simultaneously with afterglow we also detected a new effect – “afteremission” of electrons. Exoelectron emission was measured using a movable electrode under small positive potential. One can suppose that the “afteremission” is caused by the afterglow photons. These visible range photons can release electrons from the traps. Because of negative electron affinity of solid Ne there is no potential barrier to escape the surface. Note that the electrons can be released both from the deep traps and from the shallow ones due to the extremely wide conduction band in solid Ne.

[1] K.S.Song and R.T. Williams, *Self-trapped Excitons*, Springer Series in Solid State Science, vol.105 (Springer Verlag, Berlin, 1996).

[2] E.V. Savchenko, O.N. Grigorashchenko, G.B.Gumenchuk, A.N. Ogurtsov, M. Frankowski, A.M. Smith-Gicklhorn, and V.E. Bondybey, *Radiation Effects & Defects in Solids* **157**, 729 (2002).

TIME RESOLVED CARS MEASUREMENTS OF I₂ IN SOLID Kr: VIBRATIONAL STATE DEPENDENT DEPHASING TIMES BETWEEN 2.6 - 32 K

Tiina Kiviniemi*, Jukka Aumanen, Pasi Myllyperkiö and Mika Pettersson

Department of Chemistry, P.O.Box 35, FIN-40014 University of Jyväskylä, Finland

*titakivi@cc.jyu.fi

The time resolved coherent anti-Stokes Raman scattering (CARS) technique can be used to investigate molecular coherences in various phases [1]. Quite recently, femtosecond CARS was applied to study the vibrational decoherence of iodine molecule in rare gas matrices [2-4].

We have recently established a setup for femtosecond CARS measurements in rare gas matrices at the University of Jyväskylä. In this work, we have used this setup to investigate the coherence of vibrational wavepackets on the ground electronic state of I₂ in solid Kr. Dephasing times for selected vibrational states between $v=1$ and $v=16$ at five temperatures, $T = 2.6, 4.1, 10, 20,$ and 32 K, were measured. The results on both the vibrational state dependence and temperature dependence of the dephasing times will be presented and discussed.

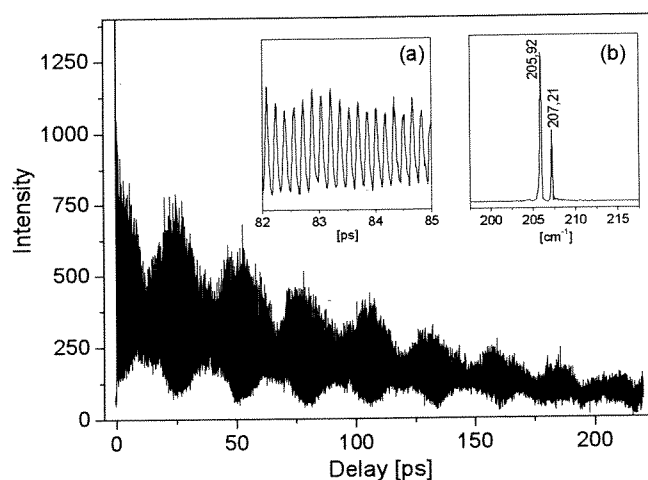


Figure 1. Time resolved CARS spectrum for a I₂/Kr 1:2600 matrix, recorded at $T = 4.1$ K. (a) An expanded view of the signal showing the oscillations, (b) Fourier transform of the signal, identifying the wavepacket as a superposition of vibrational states $v = 2, 3,$ and 4 .

References:

- [1] See, for example, B.I. Grimberg, V.V. Lozovoy, M. Dantus, and S. Mukamel, *J.Phys.Chem.A*, **106**, 697 (2002) and references therein.
- [2] M. Karavitis, R. Zadoyan, and V.A. Apkarian, *J.Chem.Phys.* **114**, 4131 (2001).
- [3] M. Karavitis, D. Segale, Z. Bihary, M. Pettersson, and V.A. Apkarian, *Low.Temp.Phys.* **29**, 814 (2003).
- [4] M. Karavitis and V.A. Apkarian, *J.Chem.Phys.* **120**, 292 (2004).

HEAT TRANSFER IN THE NONIDEAL CRYSTAL AND IMPURITY PARAHYDROGEN

O. A. Korolyuk¹⁾, A. I. Krivchikov¹⁾, B. Ya. Gorodilov¹⁾, P. Stachowiak²⁾, A. Jezowski²⁾.

¹⁾*B. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine,
47, Lenin Ave., 61103, Kharkov, Ukraine*

²⁾*W. Trzebiatowski Institute for Low Temperature Physics and Structure Research of the Polish Academy of
Sciences, P. O. Box 937, 50-950 Wroclaw, Poland
e-mail: korolyuk@ilt.kharkov.ua*

The heat transfer studies are reported, that were made on parahydrogen crystals with different (point and linear) structural defects. The thermal conductivity of pure parahydrogen and weak parahydrogen-CH₄ impurity (5-570 ppm) solutions was measured. The CH₄ molecule in the hydrogen matrix can be considered either as a heavy point defect or as a weakly hindered quantum rotor. While investigating the CH₄ effect on the thermal conductivity of hydrogen, we expected a deflection in the temperature dependence of the thermal conductivity caused by the strong resonance scattering of the phonons by the rotational excitations of the methane molecule [1]. The upper limit of the methane-parahydrogen solubility was estimated from the thermal conductivity data.

The effect of linear defects was investigated through measuring the thermal conductivity of parahydrogen-orthodeuterium (0-20%) solutions. Defects were generated by heat shocks. It is shown that the after-shock behavior of the thermal resistance is dependent on the D₂ concentration in the solution. In an impurity-free para-H₂ crystal, thermal deformation generates individual dislocations. In solutions with ortho-D₂ concentrations above 0.1% this leads to an increase in the density of the low-angle boundaries. It is shown that the density of dislocations forming low-angle boundaries is proportional to the concentration of orthodeuterium molecules.

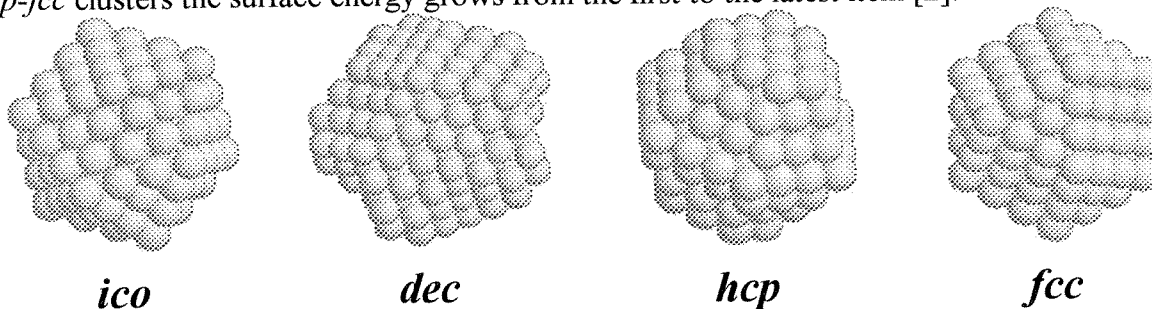
[1] V. V. Dudkin, B. Ya. Gorodilov, A. I. Krivchikov, and V. G. Manzhelii, *Low Temp. Phys.* **26**, 762 (2000).

NEON CLUSTERS IN NANOPOROUS CONFINEMENT OF AMORPHOUS CARBON FILMS

N.V. Krainyukova

*Institute for Low Temperature Physics and Engineering NASU, 47 Lenin ave., Kharkov 61103, Ukraine,
e-mail: krainyukova@ilt.kharkov.ua*

Neon clusters formed on an amorphous carbon substrate as deposited from the vapor phase were studied by means of transmission high energy electron diffraction using the liquid helium cryostat. Remarkable similarity was found earlier [1] between films of amorphous carbon grown from sublimated graphite and random Schwarzite forms. Random Schwarzite exceptionally stable forms of carbon [1] show interconnected net of channels because their constraints are negatively curved graphitic sheets and can be considered as a kind of porous materials. Electron diffractograms were analysed on the basis of assumption that there exist a cluster size distribution in samples formed on substrate and multi-shell structures such as icosahedra (*ico*), decahedra (*dec*), *fcc* and *hcp* were probed for different sizes up to ~15000 atoms. The experimental data were considered as a result of a superposition of diffracted intensities from clusters of different sizes and structures. The comparative analysis was based on the *R*-factor minimization. The total size and structure distribution function found shows the preference of multiply twinned particles (MTPs) such as icosahedra and decahedra with fivefold symmetry and a smaller amount of *fcc* and *hcp* structures. Considered growth mechanisms ('inward' from pore walls) are presumably governed by confined pore-like geometry in an amorphous carbon substrate. Preference of MTPs in growth 'inward' processes follows from the surface energy minimum requirement that drives the structures formed when crystallization starts at a cluster surface. In the sequence icosahedra-decahedra-*hcp*-*fcc* clusters the surface energy grows from the first to the latest item [2].



- [1] S. J. Townsend, T. J. Lenosky, D.A. Muller, C. S. Nickols, V. Elser, *Phys. Rev. Lett.*, **69**, 921 (1992).
- [2] N.V.Krainyukova, B.W. van de Waal, *Thin Solid Films*, **459**, 169 (2003).

Stark deceleration and cooling of large molecules

Jochen Küpper*, Kirstin Wohlfart, Hendrick L. Bethlem,
Henrik Haak and Gerard Meijer

Fritz-Haber-Institut der MPG, Faradayweg 4–6, D-14195 Berlin

The study of biomolecules in the gas-phase is an important approach towards a detailed understanding of the *building blocks* of life. Over the last years a lot of progress was made in experiments to examine the intrinsic properties of biomolecules using gas-phase spectroscopy [1].

The preparation of ultracold, isolated biomolecules allows improved studies using high-resolution spectroscopy or scattering experiments. Our group has developed the Stark deceleration technique to manipulate the external degrees of freedom of neutral, polar molecules [2]. This allows to decelerate molecules to arbitrary low velocities, inject them in storage rings, or trap them three-dimensionally, reaching temperatures of approximately 1 mK.

Here we describe how these techniques can be used to manipulate large organic molecules or biomolecules. We present first results on *Alternate Gradient* focusing of molecules in high-field seeking states and introduce a new experiment we are currently setting up for the deceleration of large molecules of biological interest.

References

- [1] Special issue "Biomolecules in the gas-phase", *Eur. Phys. J. D* **20**, 309 (2002).
- [2] H.L. Bethlem and G. Meijer, *Int. Rev. Phys. Chem.* **22**, 73 (2003).

*Email: jochen@fhi-berlin.mpg.de

Time-resolved CARS studies of vibrational coherences in the condensed phase: I₂ in solid krypton

¹Michael Karavitis, ¹Ilya Goldschleger, ¹V. Ara Apkarian, and ^{1,2}Takayuki Kumada

¹*Department of Chemistry, University of California, Irvine, CA 92697-2025*

²*Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan
e-mail: kumada@popsvr.tokai.jaeri.go.jp*

Time-resolved, electronically resonant, parametric four-wave mixing processes allow detailed preparation, manipulation, and interrogation of molecular ro-vibronic coherences. We implement this tool in the present to carry out systematic studies of vibrational dephasing of molecular iodine isolated in solid Kr. Using ultrashort laser pulses with adjustable time-bandwidth profiles, we extract ν -dependent rates of dephasing and dissipation for $\nu = 1 - 19$, as a function of temperature for $T = 6 - 45$ K.

The experiments are carried out on thin films of I₂/Kr, using three 25-100 fs laser pulses from two home-built non-collinear optical parametric amplifiers (NOPA) pumped by a 1kHz regeneratively amplified Ti:Sapphire laser. Intensities of time-resolved coherent anti-stokes Raman scattering (TR-CARS) from the sample are measured for coincident pump (P) and Stokes (S) beams, as a function of probe (P') time.

The decay rate of the coherence of the Raman packet γ depends on temperature T and vibrational quantum number ν . γ is independent of T below 10 K, but it steeply increases with T above. The ν -dependence is essentially linear for $T \rightarrow 0$, whereas it can be fit with a quadratic dependence on ν for high T . The entire data set can be well represented by the functional form:

$$\gamma(\nu) = \frac{\nu}{\tau_1} + \frac{\nu^2}{\tau_2} \exp(-\theta/T) \quad (1)$$

where $\tau_1 = 355 \pm 10$ ps, $\tau_2 = 560 \pm 70$ ps, and $\theta = 54 \pm 4$ K, to be compared with the Debye temperature of 72 K of solid Kr. For $T < 10$ K, when the high frequency phonons are not populated, the decay becomes T -independent, suggesting dissipation by the spontaneous creation of phonons. Note that to bridge the vibrational energy gap of the molecule, the dissipation must involve the simultaneous creation of four phonons. On the other hand, for $T > 10$ K, pure dephasing is activated by the thermally populated phonons. A density of states analysis for phonon projections on the molecular coordinate is used to identify the nature of the pseudo local phonons responsible for the observed dephasing. Given the relatively well known interaction potentials between guest and host, quantitative treatments of this system can be expected.

[1] M. Karavitis and V. A. Apkarian, *J. Chem. Phys.* **120**, 292 (2004).

THE CONFORMATIONAL BEHAVIOR OF SERINE: AN EXPERIMENTAL MATRIX-ISOLATION FT-IR AND THEORETICAL DFT(B3LYP)/6-31++G** STUDY

Bert Lambie, Riet Ramaekers and Guido Maes

Department of Chemistry, University of Leuven, B-3001 Leuven, Belgium
bert.lambie@chem.kuleuven.ac.be

The conformational equilibria of neutral serine are studied by experimental matrix-isolation Fourier transform infrared spectroscopy in combination with theoretical DFT(B3LYP)/6-31++G** calculations. The most detailed theoretical study of the potential energy surface of serine was accomplished by Gronert and O'Hair [1]. Their results were used as a starting point in the DFT calculations performed in this work. In addition, we calculated the infrared frequencies and intensities of the most stable conformers of serine. In order to correct for deficiencies in the calculated (harmonic) frequencies the force constants were scaled, giving a better fit to experimentally observed vibrational frequencies and infrared intensities [2]. The calculated relative energies suggest that four conformers are sufficiently stable to appear in the gas phase (Figure 1).

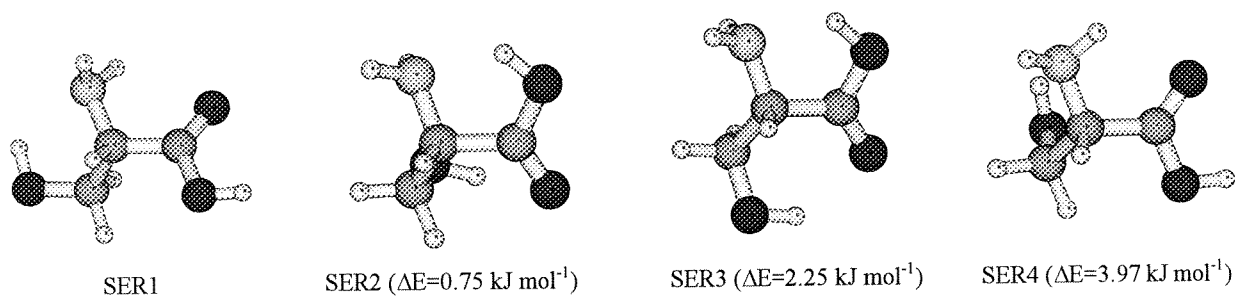


Figure 1. The four most stable conformers of serine (DFT(B3LYP)6-31++G**)

Matrix-isolation is a suitable technique to simulate the gas phase. All four conformers could be distinguished in the experimental matrix infrared spectra [3]. For the equilibria SER2/SER1 and SER3/SER1, a disagreement between the experimental rotamerization constant K_R^{exp} and the theoretical constant K_R^{th} was found. A relatively strong intramolecular H-bond in conformers SER2 and SER3 is at the origin of this discrepancy.

- [1] S. Gronert and R.A.J. O'Hair, *J. Am. Chem. Soc.*, **117**, 2071 (1995)
- [2] J. Baker, A.A. Jarzecki, P. Pulay, *J. Phys. Chem. A*, **102**, 1412 (1998)
- [3] B. Lambie, R. Ramaekers, G. Maes, *J. Phys. Chem. A*, submitted

Acknowledgements: Research financed by a Ph.D. grant of the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT-Vlaanderen).

3-Hydroxyflavone: An Example for Photochemistry in Superfluid Helium Droplets

Rudolf Lehnig, Alkwin Slenczka

*Institut für Physikalische und Theoretische Chemie, Universität Regensburg,
93040 Regensburg, Germany
rudolf.lehnig@chemie.uni-regensburg.de*

The investigation of the excited state intramolecular proton transfer (ESIPT) of 3-hydroxyflavone (3-hf) embedded in superfluid helium droplets will be presented. Upon electronic excitation 3-hf is known to undergo a tautomerization [1]. This proton transfer gives rise to emission with a Stokes shift of almost 8000 cm^{-1} . Furthermore, polar solvents are known to inhibit the proton transfer leading to emission of the normal form of 3-hf without the large Stokes shift [2]. Both, the tautomerization of the bare 3-hf and the influence of single polar solvent molecules attached to the 3-hf molecule demonstrate the advantages of the investigation of photochemical processes in superfluid helium droplets. The very low temperature of only 380 mK [3] gives rise to emission spectra of internally cold molecular compounds. While the tautomerization of the bare 3-hf molecule was observed to be unaffected by the helium environment, the influence of single water molecules is different from the observations reported for a gas phase experiment [4]. The emission spectrum of the cold tautomer in helium droplets allowed for extracting a time constant of $236 \pm 6\text{ fs}$ for the proton back transfer by the analysis of the line shapes. Our experiment features various properties of superfluid helium droplets, showing they are an ideal matrix for chemistry at low temperatures.

- [1] P.K. Sengupta and M. Kasha, *Chem. Phys. Lett.*, **68**, 382 (1979)
- [2] D. McMorro and M. Kasha, *J. Phys. Chem.*, **88**, 2235 (1984)
- [3] M. Hartmann, R.E. Miller, J.P. Toennies and A. Vilesov, *Phys. Rev. Lett.*, **75**, 1566 (1995)
- [4] A. Ito, Y. Fujiwara and M. Itoh, *J. Chem. Phys.*, **96**, 7474 (1992)

Theoretical modelling of electronic spectroscopy in superfluid ^4He

Lauri Lehtovaara*, Jussi Eloranta

Department of chemistry, University of Jyväskylä, Surfontie 9, 40500 Jyväskylä, Finland

**email: lauri@jyu.fi*

Single atoms or molecules (e.g. chromophores) inside superfluid ^4He droplets have been subject of numerous experimental studies [1]. The obtained electronic spectra show sharp zero phonon line (ZPL) accompanied by a weak phonon sideband. Whereas ZPL corresponds to pure electronic excitation of the chromophore, the sideband arises from coupling to superfluid's collective excitations. Further investigation of the sideband shows two different maxima, which are associated with the turning points (e.g. roton and maxon) in the superfluid ^4He bulk dispersion relation. In addition to the features found in the known experimental data, our earlier simulations predict that spectral features related to droplet standing wave solutions should persist at 0 K. In practice these features are lost because: a) thermal motion ($T \sim 0.4$ K) of the chromophore inside the droplet, b) concentration of thermal excitations on the droplet surface (e.g. ripplons), and c) distribution of droplet sizes in experiments [2]. However, case a) might be overcome if the droplet is small and solvation is strong.

The most reasonable way to model electronic spectroscopy in helium droplets is to describe superfluid with time dependent density functional theory (TD-DFT) [3, 4] and to treat the chromophore as a two-level system. The first order polarization can be written as

$$P^{(1)}(\omega, t) = \langle \psi^{(0)} | \mu | \psi^{(1)} \rangle + c.c. = \frac{i}{\hbar} \int_0^t e^{-\frac{i}{\hbar} \int_0^{t'} H_0(t'') dt'' - i\omega t'} dt' + c.c.$$

where $\psi^{(0)}$ is the zeroth order electronic wavefunction and H_0 is time dependent electronic Hamiltonian including chromophore - superfluid interaction. The absorption spectrum can now be obtained by Fourier transforming $P(\omega, t)$ to $P(\omega, \omega')$ and setting $\omega = \omega'$. The electronic field part can be removed from H_0 since it's just a constant offset to energy. H_0 reduces to contain only chromophore - superfluid interaction

$$E_{\text{ext}}(t) = \int \rho_{\text{He}}^{\text{excited}}(r, t) V_{\text{excited}}(r) d^3r - \int \rho_{\text{He}}^{\text{ground}}(r, t) V_{\text{ground}}(r) d^3r$$

where V_{excited} and V_{ground} are the chromophore - He pair potentials.

Earlier simulations have investigated only spherically symmetric cases [2]. In this work we study two anisotropic cases. The first case has anisotropic p -orbital shaped ground state and isotropic excited state and the second has vice versa. To distinguish the effect of the anisotropy we study these two cases also with spherically averaged potentials and compare the obtained spectra.

- [1] F. Stienkemeier and A. F. Vilesov, *J. Chem. Phys.*, **115**, 10119 (2001).
- [2] J. Eloranta, H. Ye. Seferyan, and V. A. Apkarian, Submitted to *Chem. Phys. Lett.* (2004).
- [3] F. Dalfovo, A. Lastri, L. Pricapenko, S. Stringari, and J. Treiner, *Phys. Rev. B*, **52**, 1193 (1995).
- [4] L. Lehtovaara, T. Kiljunen, and J. Eloranta, *J. Comp. Phys.*, **194**, 78 (2004).

INTERACTION OF CHARGE CENTERS WITH ORTHOMOLECULES IN PARAHYDROGEN

V.A.Lykah¹, E.S. Syrkin², T.V.Svitenko-Krasnokutskaya¹

¹⁾ NTU 'Kharkiv Polytechnic Institute', Kharkiv, 21 Frunze str., 61002, Ukraine;

Email: lykah@ilt.kharkov.ua; lykah@kpi.kharkov.ua

²⁾ Institute for Low Temperature Physics and Engineering, Ukrainian Academy of Science, 47 Lenin ave., 61102, Ukraine; E-mail: syrkin@ilt.kharkov.ua

Experiments [1] have shown dependence of conductivity of rigid hydrogen on a type of the carrier and orthomolecules concentration. The supposition about formation of a small radius polaron with different microscopic structure was expressed.

Under low temperature the fine structure of charge centres of molecules could produce different chemical dynamics. In the present work the interaction of the charge centre with a small amount (concentration) orthomolecules is considered. Hamiltonian of the system includes the energies of the lattice H_l , charge-lattice interaction H_{el} , orthomolecule H_{or} , interactions of orthomolecule-lattice H_{lor} and -charge H_{eor} . Paramolecule of hydrogen has a total spin $J=0$ and is spherical, orthomolecule has $J=1$ and is prolated; orthomolecule interaction with the first neighbors in HCP paramatrix is isotropic, and orthomolecules are oriented probably [2]. Electrostatic part of interaction charge - molecule could be written as

$$H_{eor} = V_1 - V_2 P_2(\cos \theta); \quad V_1 = -\alpha q^2 / 2\epsilon R^4; \quad V_2 = \epsilon^{-1}(\gamma q^2 / R^4 - Qq / 2R^3); \quad (1)$$

where α (γ) is isotropic (anisotropic) part of molecule polarizability, Q is its quadrupole moment, q is charge, R is distance from center of the charge to center of a molecule, θ is angle between R and axes of a molecule, ϵ is effective dielectric permeability, $P_2(x)$ is Legendre polynom. The terms $\sim R^{-4}$ are stipulated by polarizability of a molecule, the term $\sim R^{-3}$ is stipulated by interaction of a quadrupole moment of a molecule with a heterogeneity of an electric field and depends on its charge sign. The quantization of molecular rotator movement in the potential (1) is done following to perturbation theory for expansion on base of wave functions $|Jm\rangle$ of undisturbed rotator [3]. The matrix elements of a potential of interaction $\langle Jm|V|Jm\rangle = V^{JJ(m)}$ accept values $V_{ep}^{00(0)} = V_1^{00(0)}$ for $J=0$, $m=0$ (paramolecule), $V_{eor}^{11(0)} = V_1^{11(0)} - a_{10}V_2^{11(0)}$ for $J=1$, $m=0$ (orthomolecule with orientation of an axes along a direction of the field), $V_{eor}^{11(\pm 1)} = V_1^{11(\pm 1)} - a_{11}V_2^{11(\pm 1)}$ (orthomolecule is perpendicular to the field). Here factors are $a_{10} > a_{11} > 0$. For the positive charge condition $V_2 > 0$ is always satisfied, i.e. in a ground state orthomolecule oriented along an electric field and its attraction to the center is more then for adjacent paramolecules. Evaluation following [2] give a difference in energy of interaction some tens Kelvin, and exceeds elastic interactions in a lattice. For the negative charge value of V_2 is much less and changes a sign under distance increasing. It means a modification of orientation of a ground state of a molecule orthomolecule, values of these energies are comparable to energy of elastic interactions and require further analysis. The orthomolecule distribution near the charge centers for small concentration is considered.

[1] A.A.Levchenko, L.P.Mezhov-Deglin. Soviet JETP, **98**, 349 (1990).

[2] Yu.A.Freiman, V.G.Manzhelii. *Physics of Cryocrystals*. Woodbury, NY, USA (1996).

[3] S.Flugge, *Practical quantum mechanics*, Springer (1971).

Phase Separation and Homogenization of ^3He - ^4He Solid Mixtures

V. Grigor'ev, V. Maidanov, A. Penzev, A. Polev, S. Rubets, E. Rudavskii, A. Rybalko,
E. Syrnikov

B. Verkin Institute for Low Temperature Physics and Engineering, Kharkov, Ukraine
E-mail: maidanov@ilt.kharkov.ua

Comprehensive experimental results on phase separation and homogenization of ^3He - ^4He solid mixtures are described. A new method developed for obtaining high-quality crystals by cycling the temperature of a solid mixture within the separation region makes it possible to obtain reproducible values of time constants for growth and dissolution of the new phase.

The comparison of kinetics of the separation and homogenization processes in solid ^3He - ^4He mixtures was carried out with using the precise barometry. Three types of samples were investigated – dilute mixtures of ^3He in ^4He , dilute mixtures of ^4He in ^3He and concentrated ^3He - ^4He mixtures. The rate of the initial step of homogenization is found to exceed the separation rate in more than 500 times. Such situation occurs for all samples under consideration and doesn't depend on the initial mixture concentration. According to the present-day view of kinetic processes in quantum crystals the impurity atoms in the concentrated mixtures should be localized. Observation of the appreciate separation rate in the concentrated mixtures indicates that new unknown mechanism of the mass transport occurs under such conditions. The fast homogenization is considered as an evidence of nondiffusional character of the process.

The study was supported by the State Foundation of Ukraine for Basic research (Project 02.07/00391).

Isotope control of K₂- and NaK-Dimers

Franziska Vetter, Andrea Merli, Albrecht Lindinger, Mateusz Plewicki,
Cosmin Lupulescu, Stefan Weber, and Ludger Wöste

*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin,
franziska.vetter@physik.fu-berlin.de, andrea.merli@physik.fu-berlin.de*

We report on selective ionization of different isotopes in an ionization process. This method is demonstrated for potassium ($^{39,39}\text{K}_2$, $^{39,41}\text{K}_2$) and mixed alkaline ($^{23}\text{Na}^{39}\text{K}$, $^{23}\text{Na}^{41}\text{K}$) dimers by applying evolution strategies in a closed feedback loop.

The dimers are prepared in an adiabatic coexpansion of alkaline vapor and argon carrier gas through a nozzle into the vacuum. We focus the laser beam (Ti:sapphire oscillator) onto the cluster beam and produce the photoions. The experiments are carried out in the low power regime. Independent and simultaneous phase and amplitude modulation is possible with the pulse shaper consisting of two liquid crystal modulator masks (CRI) placed in the Fourier plane of a zero dispersion compressor. The implemented closed loop experiment combines ion detection with a programmable pulse shaper that is driven by a self-learning optimization algorithm based on evolution strategies [1].

For the potassium dimer the regular ratio of one isotope over the other is 6.9 in the molecular beam. We achieved a surprisingly high enhancement of one isotope versus the other and vice versa with a total factor of 140 by applying simultaneous phase and amplitude modulation. The measured spectra for minimization and maximization show several distinct sharp peaks that can be associated with the vibrational levels of the two transitions $A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ and $(2)^1\Pi_g \leftarrow A^1\Sigma_u^+$ of the $^{39,41}\text{K}_2$ and the $^{39,39}\text{K}_2$ isotope, respectively [2]. Also we compare the acquired pulse shapes for combined phase and amplitude with pure amplitude modulation. From their spectra we are able to extract information about their optimally chosen differing ionization paths via the involved vibrational states. The selection in the second excitation step is less effective for pure amplitude modulation because of the missing time evolution. Furthermore, we compare the temporal shape of the optimal pulse forms for phase and amplitude with pure phase optimization. Here we saw a comparably low factor between minimization and maximization that indicate that the temporal shape is less efficient.

The experiment with NaK dimers shows a difference to the K₂ experiment because of the different mechanism of minimization and maximization of the isotope ratio. Thereto, the different isotopes ($^{23}\text{Na}^{39}\text{K}$, $^{23}\text{Na}^{41}\text{K}$) utilizes vibrational levels of differing electronic states. For the minimization process the ionization takes places with following transitions $A(2)^1\Sigma^+ \leftarrow X(1)^1\Sigma^+$, $B(3)^1\Pi \leftarrow A(2)^1\Sigma^+$. Whereas, the ionization path for the maximization use the $A(6)^1\Sigma^+$ state instead of the $B(3)^1\Pi$.

These experiments show the selectivity of the genetic algorithm and demonstrates the potential of the presented method since it is not restricted to a single transition.

[1] S. Vajda, Andreas Bartelt, Eva-Cristina Kaposta, Thomas Leisner, Cosmin Lupulescu, Shinichirou Minemoto, Porfirio Rosendo-Francisco, Ludger Wöste, *Chem. Phys.* **267**, 231 (2001)

[2] A. Lindinger, Cosmin Lupulescu, Mateusz Plewicki, Franziska Vetter, Andrea Merli, and Ludger Wöste, *PRL* **93**, 033001-1 (2004)

Nuclear spin relaxation of methane in solid parahydrogen.

Yuki Miyamoto, Mizuho Fushitani, Daisuke Ando, and Takamasa Momose

Department of Chemistry, Graduate School of Science, Kyoto University, JAPAN

yu-ki@kuchem.kyoto-u.ac.jp

Because of the weakness of nuclear magnetic interactions, relaxation between different nuclear spin states is very slow in the gas phase. On the contrary, the relaxation in condensed phase sometimes becomes quite fast.[1] However, the mechanism of the fast relaxation in condensed phases has not been well understood yet. Here, we present our recent work on the nuclear spin relaxation process of methane in solid parahydrogen.

Methane molecules trapped in solid parahydrogen rotate almost freely. As shown in Figure 1 and 2, infrared absorptions of CH₄ and CD₄ clearly show rotational branches. Transitions labeled as R(1), Q(1), P(1) are those from the $J=1, I=1$ state, while the transition labeled as R(0) is that from the $J=0, I=2$ state. After several hours, the R(1), Q(1), and P(1) transitions disappeared and the R(0) transition became intense. The change can be attributed to the nuclear spin relaxation from $I=1$ to $I=2$. [2] By analyzing the temporal change in intensity, the rates of nuclear spin relaxation were obtained. Details of the analysis will be presented.

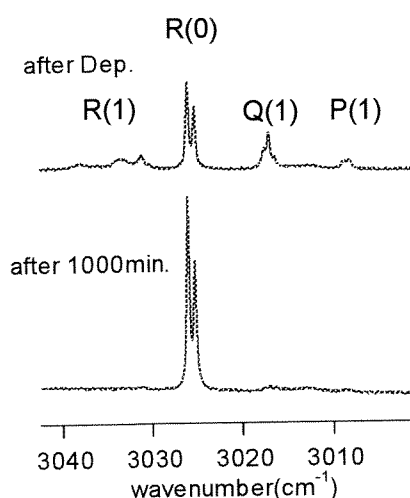


Figure 1. FTIR spectrum of ν_3 band of CH₄

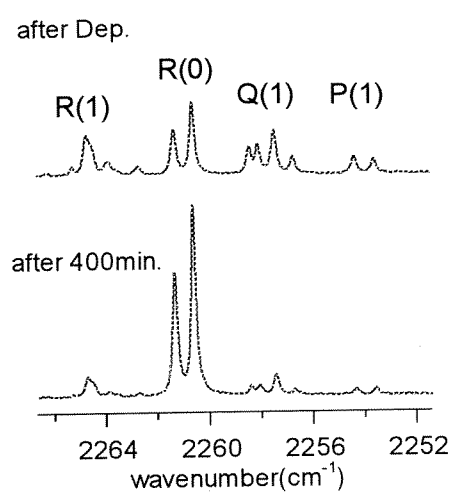


Figure 2. FTIR spectrum of ν_3 band of CD₄

[1] K. P. Wong, J. D. Noble, M. Bloom, and S. Alexander, *J. Mag. Reson.* **1** 55 (1969)

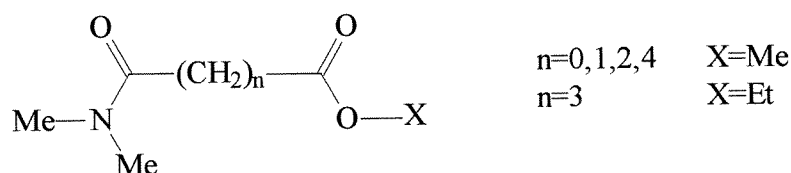
[2] M. Miki and T. Momose, *Low Temp. Phys.* **92** 661 (2000)

STRUCTURE AND PHOTOCHEMICAL TRANSFORMATIONS OF AMIDOESTER RADICAL CATIONS WITH METHYLENE "BRIDGE" IN LOW-TEMPERATURE FREON MATRIXES

Kirill Nuzhdin, Vladimir Feldman, Mikhail Melnikov

*Department of Chemistry, Moscow State University, 199992, Moscow, Russia
e-mail: kirill.nuzhdin@rad.chem.msu.ru*

Bifunctional radical cations provide an interesting model for investigation of long-range interactions and electron transfer in the radiation chemistry of complex organic systems and macromolecules. In this work we report the results of the matrix EPR study of structure and properties of a series of amidoester radical cations with methylene "bridge" of variable length:



The radical cations were produced by X-ray irradiation of frozen Freon solutions of amidoesters at 77 K. As expected, these species revealed high spin population on amide group, which corresponds to binomial septet with the proton hyperfine couplings of approximately 3,1 mT in the EPR spectra. Thermal reactions of all the radical cations under consideration were found to yield neutral radicals with radical site centered on carbon atom of amide fragment (binomial triplet, 1,9 mT). This result implies that only amide moiety is involved in thermal transformations occurring at 110 – 120 K.

In contrast with this observation, the photochemical reactions of the isolated radical cations occurring under the action of light with $\lambda = 380$ nm show significant dependence of the methylene "bridge" length. In particular, formation of neutral radicals with radical site centered on a carbon atom of methylene "bridge" was found for the species with $n = 2$ to 4. Detailed investigations using a combination of EPR and optical spectroscopy were carried out for amidoester with $n = 3$. In this case, photolysis yields the radical, which is characterized by doublet (4 mT) of triplets (2,2 mT). Such an EPR spectrum was attributed to the species resulting from intramolecular H atom transfer from α -position, which is determined by favourable transition state geometry. Reaction mechanisms and possible role of electron transfer from ester group in photochemical reactions are discussed.

This study was supported by INTAS (project no. 2000-0093).

Matrix Isolation and Ab Initio Study of the H₂O₂···SO₂ complex

Susanna Pehkonen^a, Jan Lundell^a, Leonid Khriachtchev^a, Mika Pettersson^b and Markku Räsänen^a

^a *Department of Chemistry, University of Helsinki, P.O.Box 55 (A.I.Virtasen aukio 1), FIN-00014 University of Helsinki, Finland*

^b *Department of Chemistry, University of Jyväskylä, Finland*

Complexation and photochemical reactions of hydrogen peroxide and sulfur dioxide have been studied in various low-temperature rare gas matrices. Complexes between H₂O₂ and SO₂ are characterized using Fourier transform infrared spectroscopy and ab initio calculations. In solid Ar, the H₂O₂···SO₂ complex absorptions are found at wavenumbers of 3572.8, 3518.7, 3511.2, 3504.3, 1340.3, 1280.2 and 1149.9 cm⁻¹. Computationally, a cyclic complex, where both S···O and OH···O interactions contribute to the overall complexation, is a stable configuration. The OH···O interaction is characterized as a hydrogen-bonded complex based on the downward vibrational shift and enhanced vibrational intensity. In Kr and Xe matrices, the bonded OH stretching frequencies deviate from the values in Ar, and it is proposed that the matrix material influences the structure of the H₂O₂···SO₂ complex. UV photolysis of the H₂O₂···SO₂ complex produces mainly a complex between sulfur trioxide and water via in-cage reaction in all studied matrices. In solid Kr, photolysis of the H₂O···SO₃ complex at 193 nm partially recovers the H₂O₂···SO₂ complex.

E-mail: susanna.pehkonen@helsinki.fi

EMISSION SPECTROSCOPY OF ATOMIC (H, HE, N, O) AND DIATOMIC (H₂, HE₂, N₂, O₂, NO) IMPURITIES INJECTED INTO SUPERFLUID HELIUM*.

Jussi Ahokas ^a, Jussi Eloranta ^a, Henrik Kunttu ^a, Evgeny A. Popov ^{a,b}

^a Department of Chemistry, University of Jyväskylä, Finland

^b Institute of Energy Problems of Chemical Physics, Chernogolovka, Russia

* Supported by Academy of Finland. e-mail: eap@epr.chem.jyu.fi.

Upon prolonged injection of impurity doped helium gas jet onto bulk superfluid helium (HeII), an impurity-helium solid (IHS) is formed [1]. IHS solid was found to consist of porous network of coalesced impurity-helium clusters. Its thermal properties resemble extremely porous aerogels, which are filled with liquid helium [2]. The exact formation mechanism of IHS is not yet properly understood on the molecular scales. Especially, cluster formation in the gas jet and in the gas-liquid contact region ("crater") has only been studying since the year 2002 [3].

Recently, we have monitored emissions from atomic N ($^2D - ^4S$) transition (α -group, "green afterglow"), as well as the Vegard-Kaplan band, N₂ ($A \ ^3\Sigma_u^+ - X \ ^1\Sigma_g^+$), of molecular nitrogen [3]. Here we present our new data on N ($^2P - ^2D$), O ($^1S - ^1D$), N₂ ($C \ ^3\Pi - B \ ^3\Pi_g$), and O₂ ($C \ ^3\Delta_u - X \ ^3\Sigma_g^-$) emission spectra, as well as the β -, γ -, δ - bands of NO. We observed matrix shifts of atomic transitions of N ($^2P - ^2D$), O ($^1S - ^1D$) as well as molecular oxygen O₂ ($C \ ^3\Delta_u - X \ ^3\Sigma_g^-$) Herzberg bands. These observations support our conclusion on extensive clustering in a gas jet prior to its penetration into bulk HeII [3].

Experiments with a discharged helium gas jet have shown that it is possible to generate intrinsic excitations in HeII. Surprisingly, number of highly excited atomic and diatomic states were emitting in the bulk HeII. Moreover, intensities of some transitions were greatly enhanced at the surface as well in the bulk HeII as compared to the gas jet. Metastable triplet He atoms and molecules concentrate on the liquid surface because they do not have sufficient kinetic energy to penetrate into the liquid. In the high concentration region the triplet-triplet annihilation reactions produce ionic helium species via the Penning ionization scheme [4]. Electron-ion recombination populates highly excited atomic and diatomic excimers in the "crater" and bulk HeII. Quenching of the helium emissions by N₂, O₂, and H₂ impurities was also studied. When clusters of N/N₂ impurity were suspended in HeII, bright green phosphorescence (522nm) on atomic N ($^2D - ^4S$) transition was excited in the bulk HeII few seconds after He discharged gas jet impinged the surface of HeII. In the case of N₂ and O₂ impurities emissions originated from both allowed and forbidden atomic and molecular transitions. Hydrogen has no atomic metastables and the molecular triplet ($e \ ^3\Sigma_u^+$) state has only limited metastability. In presence of H₂ we have observed strong atomic Balmer H α ($^2S - ^2P$, $^2P - ^2D$) and weak molecular H₂ ($e \ ^3\Sigma_u^+ - a \ ^3\Sigma_g^+$) emission.

- [1] E. B. Gordon, L. P. Mezhev-Deglin, and O. F. Pugachev, JETP Lett. **19**, 63 (1974).
- [2] E. A. Popov, A. A. Pelmenov, E. B. Gordon, J. Low. Temp. Phys. **119**, 367 (2000).
- [3] E. A. Popov, J. Ahokas, J. Eloranta, H. Kunttu, Low Temp. Phys., **29**, 510 (2003).
- [4] N. Schwentner, E. E. Koch, J. Jortner, Electronic excitations in condensed rare gases, Springer, Berlin, 1985.

CORRELATION BETWEEN THE THERMAL PRESSURE AND ISOCHORIC THERMAL CONDUCTIVITY OF SOLIDS CO₂ AND NH₃

O. I. Pursky¹ and V. A. Konstantinov²

¹Technological State University of Cherkassy, 18006, Ukraine
E-mail: pursky_o@ukr.net

²Institute for Low Temperature Physics & Engineering NASU, 61103, Ukraine
E-mail: konstantinov@ilt.kharkov.ua

At temperatures close to or above the Debye temperature ($T \geq \Theta_D$) the lattice thermal conductivity of dielectric crystals is determined solely by phonon scattering and it is expected to obey the $\lambda \propto 1/T$ law. To compare correctly experimental results with theory it is necessary to perform experiments at constant density to exclude effect of thermal expansion. The experimental studies of isochoric thermal conductivity of molecular crystals have revealed however the considerable deviations from this dependence [1].

Deviation of isochoric thermal conductivity from dependence of $1/T$ is associated with the presence of orientation motion of molecules at lattice sites[2]. But it is necessary mention that weak dependence than $1/T$ is observed in solidified inert gases which is characterized by the absence of orientational motion. Some molecular crystals, that consists of strongly asymmetric molecules and in which orientation order is maintained during the whole range of the solid phase existence, also have deviations from the $1/T$ law[2]. These results point out it's impossible to explain the reasons of deflection of isochoric thermal conductivity from classic dependence of $1/T$ only by influencing of phonon-rotational interaction.

The results of researches pressure dependence of thermal conductivity[3,4] are specified on its dependence on pressure. At the isochoric experiment in the explored crystals there is growth of thermal pressure[1] which on the value comparably with pressure at direct researches of pressure dependence of thermal conductivity[3,4].

A model is suggested to describe the behaviour of isochoric thermal conductivity of molecular crystals in the orientationally ordered phases, which assumed that the heat transfer is determined by phonon-phonon interactions and additional influencing of thermal pressure. Using the model suggested the thermal conductivity of solid CO₂ and NH₃ is discussed. Temperature dependences of thermal pressure and isochoric thermal conductivity are obtained for samples of different molar volumes. The isothermal pressure dependence of thermal conductivity of solids CO₂ and NH₃ are calculated. Behavior of isochoric thermal conductivity of solids CO₂ and NH₃ is explained by phonon-phonon scattering and influencing thermal pressure.

References:

- [1] V.G. Manzhelii, and V.A. Konstantinov, in "Die Kunst of Phonons" ed. By T. Paszkiewicz and K. Rapsewicz, Plenum Press, New York (1994).
- [2] O.I. Pursky, N.N. Zholonko, and V.A. Konstantinov, Low Temp. Phys. **29**, 771 (2003).
- [3] R.G. Ross, P. Andersson, Mol. Phys. **36**, 39 (1978)
- [4] R.G. Ross, P. Andersson and G. Backstrom, Mol. Phys. **38**, 377 (1979).

Corresponding author: Oleg Pursky, Pursky_O@ukr.net

Elementary stages of relaxation processes in ion-containing cryomatrices as probed by activation spectroscopy.

E.V. Savchenko^{*}, O.N. Grigorashchenko^{*}, G.B. Gumenchuk^{*}, I.V. Khyzhniy^{*},
M. Frankowski^{**}, M.K. Beyer^{**}, A.M. Smith-Gicklhorn^{**}, V.E. Bondybey^{**}

^{*} Verkin Institute for Low Temperature Physics & Engineering of the National Academy of Sciences of Ukraine, 47 Lenin Ave.,
61103 Kharkov, Ukraine,

^{**} Institut für Physikalische und Theoretische Chemie, TU München, Lichtenbergstr. 4,
85747 Garching, Germany
e-mail: savchenko@ilt.kharkov.ua

Conversion and transfer of energy in ion containing cryogenic solids are of obvious chemical interest because these processes are to a large extent responsible for the stability and dynamics of ionic species particularly in cryomatrices. The relaxation processes in doped matrices involve not only charged but also neutral species generated upon irradiation. The relaxation can be initiated even at low temperatures by photon flux from an external or internal source of light as observed in [1]. Considering the thermally-induced relaxation, there are two kind of relaxation processes: (i) electronic ones involving charged species and (ii) atomic processes involving neutral species. Usually the electronic and atomic processes are studied separately and a lot of information is accumulated on thermally assisted atom mobility [2,3] and charge recombination [4,5]. Recently we found interesting interconnection between the cases (i) and (ii) [1,6]. It was shown that the thermally-induced recombination of neutral atoms accompanied by chemiluminescence stimulates electronic relaxation – release of electrons from their traps followed by charge recombination.

Here we report the extension of these studies in Ar and Ne matrices doped with molecular species. In order to distinguish fast (i) and relatively slow diffusion-controlled (ii) processes we used the isothermal decay method of current activation spectroscopy – thermally stimulated exoelectron emission (TSEE). Fast (i) processes are characterized by sharp increase in the yield of exoelectron emission current upon step-wise increase of the temperature T . The yield exponentially decreased while T was kept constant. Slow (ii) processes in contrast were viewed as wide maxima arising with some delay with respect to the temperature step. The data obtained confirmed the suggested scenario of triggering the electronic relaxation via diffusion-controlled recombination reactions of neutral species and demonstrate perspectives of current activation spectroscopy for the study of relaxation paths involving both electronic and atomic processes.

References:

- [1] E.V. Savchenko, O.N. Grigorashchenko, A.N. Ogurtsov, V.V. Rudenkov, M. Lorenz, M. Frankowski, A.M. Smith-Gicklhorn, and V.E. Bondybey, *J. Luminescence* **94-95**, 475 (2001).
- [2] V.A. Apkarian, N. Schwentner, *Chem. Rev.*, **99**, 1481 (1999).
- [3] L. Khriachtchev, M. Pettersson, S. Pehkonen, E. Isoniemi, and M. Räsänen, *J. Chem. Phys.* **111**, 1650 (1999).
- [4] A.N. Ogurtsov, E.V. Savchenko, O.N. Grigorashchenko, S.A. Gubin, I.Ya. Fugol, *Low Temp. Phys.* **22**, 922 (1996).
- [5] M. Kink, R. Kink, V. Kisand, J. Maksimov, M. Selg, *Nucl. Instrum. & Methods B* **122**, 668 (1997).
- [6] E.V. Savchenko, O.N. Grigorashchenko, G.B. Gumenchuk, A.G. Belov, E.M. Yurtaeva, M. Frankowski, A.M. Smith-Gicklhorn, and V.E. Bondybey, *Surface Science*, **528**, 266 (2003).

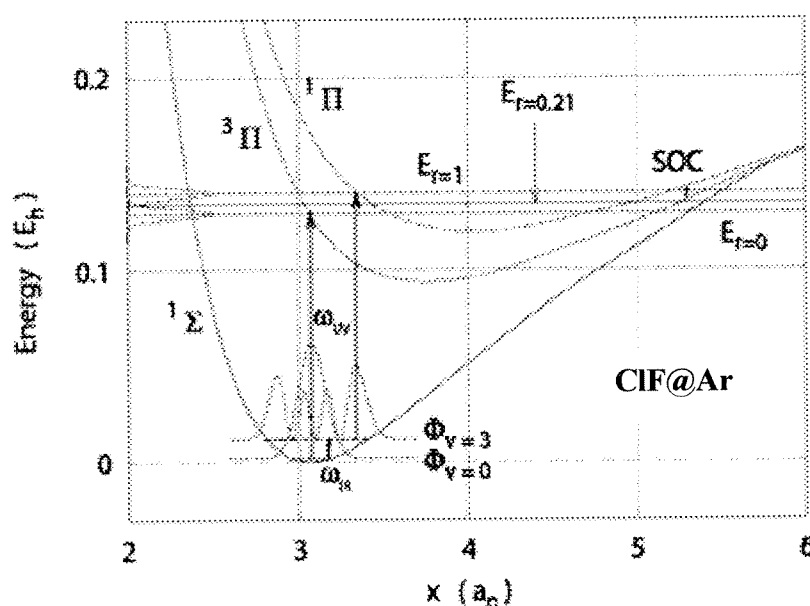
COHERENT SPIN CONTROL FOR DIHALOGENS IN ARGON

M.V. Korolkov^{a,b}, O. Kühn^a, J. Manz^a, M. Schröder^a

a) Institut für Chemie, Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustr. 3, D-14195 Berlin, Germany, korolkov@chemie.fu-berlin.de

b) B. I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Skaryna Ave. 70, 220602 Minsk, Republic of Belarus

The recent experimental and theoretical discovery of sub-picosecond spin flip induced by the photodissociation dynamics of dihalogenes in rare gas matrices, e.g., ClF in an Ar matrix [1,2], is extended to coherent spin control by laser pulses [3,4]. The mechanism consists of several steps which are illustrated schematically in the figure adapted from [3]. First, the



dihalogene is prepared in a coherent superposition of two vibrational states, typically the ground state and an excited state, with ratio r . Second, a UV laser pulse induces transitions from the initial coherent vibrational state to a coherent superposition of electronically excited singlet and triplet states. Third, the excited states evolve from the initial Franck-Condon domains to larger bond stretches (x). Here, the singlet and triplet states are near degenerate such that spin orbit

coupling (SOC) can induce sufficient coherent intersystem crossings between the singlet and triplet states. Control of the initial vibrational coherence is thus converted into coherent changes of the dominant triplet or singlet characters, with very high spatial and temporal resolutions of tens of picometers and femtoseconds, respectively. Our predictions are based on quantum simulations of the laser driven wave packet dynamics, using a model of reduced dimensionality which is supported by classical trajectory simulations [5]. The new coherent spin control may be used for control of sequel processes, e.g. cage exit supported by spin-orbit coupling [6,7].

- [1] M. Bargheer, M. Y. Niv, R. B. Gerber, N. Schwentner, *Phys. Rev. Lett.* **89**, 108301 (2002).
- [2] M. Bargheer, R. B. Gerber, M.V. Korolkov, O. Kühn, J. Manz, M. Schröder, N. Schwentner, *Phys. Chem. Chem. Phys.* **4**, 5554 (2002).
- [3] M. V. Korolkov, J. Manz, *J. Chem. Phys.* **120**, 11522 (2004).
- [4] M. V. Korolkov, O. Kühn, J. Manz, M. Schröder, to be published.
- [5] M. Schröder, PhD thesis, Freie Universität Berlin (2004).
- [6] M. V. Korolkov, J. Manz, *Chem. Phys. Lett.*, in press.
- [7] R. B. Gerber, private communication, 2004.

GAS-PHASE KINETICS AND DYNAMICS AT VERY LOW TEMPERATURES: OBTAINING DATA FOR ASTROCHEMISTRY

David Carty,^a André Canosa,^b Andrew Goddard,^a Sven Köhler,^a Sébastien D. Le Picard,^b Alejandra Pàramo,^{a,b} Ian R. Sims^{a,b} and Ian W.M. Smith^a

^aSchool of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

^bPALMS – UMR 6627 du CNRS, Equipe Astrochimie Expérimentale, Université de Rennes 1, Bat. 11c, Campus de Beaulieu, 35042 Rennes Cedex, France; Electronic mail: ian.sims@univ-rennes1.fr

Chemistry at very low temperatures – and, in particular, the study of collisional processes in the gas phase – is a fascinating area of research, both for its fundamental interest and for its application to such diverse environments as the atmospheres of Earth and other planets, and the synthesis of a wide range of molecular species within dense interstellar clouds (ISCs). In recent years we have used the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow) technique to enable studies of gas-phase reaction kinetics and energy transfer under fully thermal conditions at temperatures down to 7 K. This contribution will focus on the results of some recent studies of (1) inelastic collisions and (2) reactive collisions:

(1) *Inelastic collisions.* Infrared – vacuum ultraviolet double resonance experiments (IRVUVDR) experiments have been implemented in CRESU apparatus to measure total and state-to-state rotational energy transfer rate coefficients for CO – He collisions at temperatures down to 15 K. The results are shown to be in remarkably good agreement with those obtained in *ab initio* scattering calculations by Cecchi-Pestellini *et al.*[1] Very recently, we have also measured total removal rate coefficients for CO in specific rotational states in collision with H₂ at room temperature and plan to extend these measurement down to 6.6 K. These results are of significant astrochemical interest, concerning collisions between the two most abundant molecules in interstellar space. We have also made similar measurements for C(³P_J) in specific spin orbit states.

(2) *reactive collisions.* The reaction $O + OH \rightarrow O_2 + H$ is the principal source of interstellar O₂, and hitherto has not been studied below ca. 160 K. We use a novel VUV co-photolysis technique to produce both unstable reactants within the CRESU flow and obtain rate coefficients which are at substantial variance with those used in current astrochemical models. We will present the new technique and the results obtained to date.

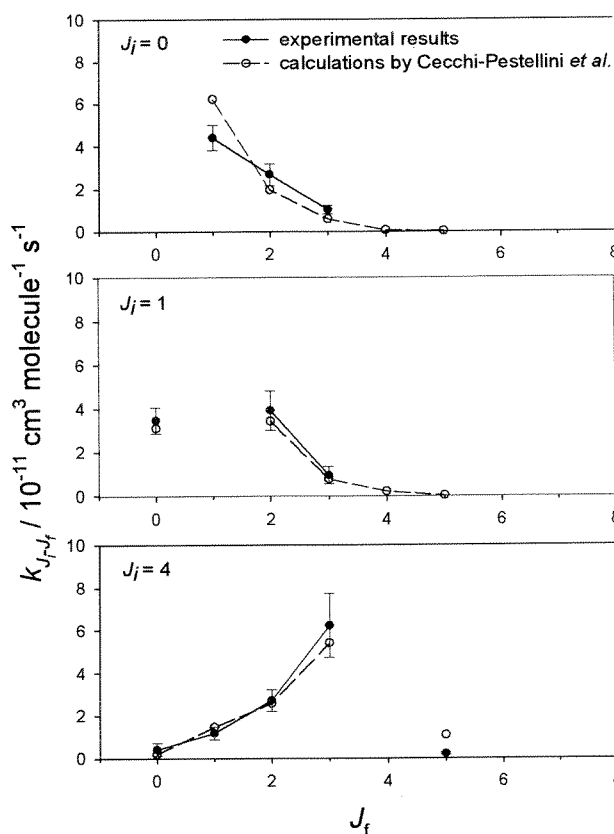


FIG. 1. Experimental state-to-state rate coefficients for rotationally inelastic collision between CO ($X^1\Sigma^+$, $v=2$, $J_i=0, 1$ and 4) and He at 15 K compared with theoretical results of Cecchi-Pestellini *et al.*

[1]C. Cecchi-Pestellini, E. Bodo, N. Balakrishnan, A. Dalgarno, *Astrophys J*, **571**, 1015 (2002).

LOW TEMPERATURE COMPLEXES OF SAMARIUM AND EUROPIUM WITH 4-PENTHYL-4'-CYANOBIPHENYL

T.I. Shabatina¹, A.V. Vlasov¹, A.Yu. Ivanov², G.G. Sheina², G.B. Sergeev¹

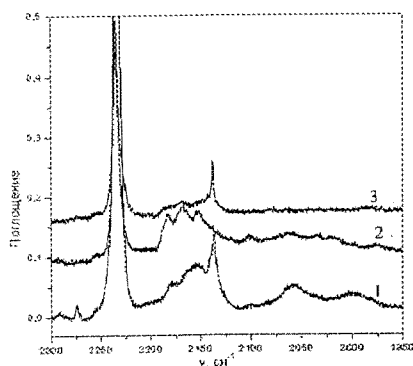
¹Department of Chemistry, Moscow State University

²B.I. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine
tsh@cryo.chem.msu.su

Metastable complexes of samarium and europium with mesogenic 4-pentyl-4'-cyanobiphenyl (5CB) were produced by low temperature co-condensation of reagents vapor in our previous works [1, 2]. It has been established the formation of the two complexes with different stoichiometric composition: metal/ligand (M/L) 1/2 (complex I) and 1/1 (complex II). In the temperature range 170-210 K complex I transforms to complex II. Thus, complex II is more stable than complex I.

Complexes of samarium with 5CB have been investigated by FTIR-spectroscopy using matrix isolation technique in argon at 6-10 K. The formation of complexes I and II in the co-condensates depends upon the ratio of the reagents and matrix component argon. At the mole ratio Sm/5CB/argon 1/33/10000 only complex I produces. Under these conditions the appearance of complex I in FTIR-spectra shows that this complex forms from atoms samarium with 5CB. At the M/L ratio 1/400÷1/5000 the both complexes have been obtained.

The structures of the complexes of europium with 5CB have been modeling at DFT level with the exchange-correlating potential B3LYP using the NWCHEM program [3]. Optimized sandwich structures include two ligand molecules and one or two atoms of Eu, placed between two benzene rings of different ligand molecules. The stabilization energy of the complexes depends on multiplicity. Maximal stabilization energy occurs for multiplicity 10 for complex I and for 15 for complex II – 10.6 and 31.3 kcal/mole correspondingly. Thus, the structure of complex II is more stable than for complex I. This fact is agreed with the experimental data obtained [1, 2].



FTIR-spectra of co-condensates Sm/5CB/Ar at the different mole ratios.

1 – 1/10/400, T=6,5 K;
2 – 1/24/5000, T=10,5 K;
3 – 1/33/10000, T=10,5 K.

Acknowledgements. This work was financially supported by RFBR grants (02-03-32469, 04-03-32748) and INTAS grant 2000-00-911.

[1] T.I. Shabatina, A.V. Vlasov, D.J. Stuffkens, E.V. Vovk, G.B. Sergeev // *Spectrochim. Acta, Part A*, 2000, **56**, 2539.

[2] T.I. Shabatina, A.V. Vlasov, G.B. Sergeev // *Mol. Cryst. Liq. Cryst.* 2001, **356**, 149.

[3] A.V. Vlasov, T.I. Shabatina, S.V. Konyukhov, A.Yu. Ermilov, A.V. Nemukhin, G.B. Sergeev // *J. Strukt. Chem. (Russ.)*, 2004, **45**, №3, 406.

Low temperature synthesis and spectroscopic (IR, UV, ESR) characterisation of paramagnetic copper atom complexes with mesogenic cyanobiphenyl ligands

A.A. Belyaev, A.A. Bogdanova, , V.A. Timoshenko, T.I. Shabatina

*Department of Chemistry, Moscow State University, 119992 Moscow, Russia,
<tsh@kinet.chem.msu.ru>*

Copper-organic mesogenic complexes are of great interest due to their possible paramagnetism and interesting spectroscopic properties. The interaction of copper atoms with mesogenic molecules 4-pentyl-4'-cyanobiphenyl (5CB) were made by low temperature co-condensation of metal and ligand vapors under molecular beam conditions.

The comprehensive IR-study revealed the appearance of the new wide band in comparison of the neat ligand film at 2122 cm^{-1} that was referred to Cu-5CB complex formation. In CN-group stretching vibrations region ($\sim 2200\text{ cm}^{-1}$) the shift at the complex band $100\text{-}200\text{ cm}^{-1}$ is similar to π -complex formation. This band is stable in temperature range $80\text{-}200\text{ K}$ and disappeared at higher temperatures due to complex degradation. In ESR-spectra of Cu 5CB co-condensates highly anisotropic multiple signal was recorded. Computer modeling of the spectra allowed us to consider this quartet signal belonged to copper atom complex with two $\text{C}\equiv\text{N}$ groups (Cu^{63} and Cu^{65} , $I=3/2$) of cyanophenyl ligands.

There was also central singlet signal which intensity rises by heating of the samples up to temperature of 200 K due to spin resonance of conducting electrons in copper nanoparticles, formed by copper complex thermal degradation.

The data obtained by UV-Vis spectroscopy confirmed the IR and ESR data. Low temperature co-condensation of copper atoms and 5CB ligand molecules led to the intensive absorbance band at 450 nm appearance, that was in accordance with the green-yellow color of co-condensate films. This band disappeared by heating of the samples up to $180\text{-}200\text{ K}$ and a new band at $520\text{-}560\text{ nm}$ simultaneously appeared, which is characteristic to copper nanosized particles.

Acknowledgements: The work was supported by RFBR grant 04-03-32748 and INTAS grant 2000-00911.

References:

1. T.I. Shabatina, G.B. Sergeev. Russian Chemical Reviews 72(7), 571-589 (2003)
2. T.I. Shabatina, V.A. Timoshenko, A.A. Belyaev, Yu.N. Morosov, G.B. Sergeev. Russ. Bull. Chem. 2002, t. 387, №2, pp 219-222
3. T.I. Shabatina, V.A. timoshenko, Yu.N. Morosov, G.B. Sergeev. Mol. Cryst. Liq. Cryst., 390, 43-47 (2003)

CRYOCHEMICAL STABILIZATION AND THERMAL EVOLUTION OF ACTIVE SILVER AND COPPER SPECIES IN ADAMANTANE MATRIX

Yu.N.Morozov¹, N.Sogoshi², V.A.Timoshenko¹, T.I.Shabatina¹G.B.Sergeev¹

1 – Moscow State University, Chemistry Department;

2 – Saitama University, Department of Chemistry, Faculty of Science.

<tsh@kinet.chem.msu.ru>

Plastic mesogens have been used as matrices for isolation of some active species of different nature. Varying of the chemical structure of matrix allowed to stabilize, for example, metal atoms, small clusters and nanoparticles at liquid nitrogen and higher temperatures up to 300 K [1]. The structural and dynamic properties of plastic mesophases are promising also for carrying out of different chemical processes of active species with different organic and inorganic substances during their thermal and photochemical activation.

We have studied the model system silver (copper) – adamantane using ESR technique. The samples were obtained by co-condensation of silver and adamantane vapors under molecular beam conditions on cooled by liquid nitrogen surfaces. Construction of ESR-cryostat allowed us to carry out monitoring of physical and chemical process in the film samples both during co-condensation and following annealing of the samples.

In all cases the stabilisation of two types of metal species took place at 80 K. There are multiple lines with g-factor close to 2,00 belonged to metal atoms stabilised in different crystallographic positions of matrix. The values of HF splitting constants are: for site 1, $A_{109} = 727,6$ G, $A_{107} = 632,4$ G; for site 2, $A_{109} = 691,6$ G, $A_{107} = 600,3$ G. Varying the components ratio from 1/200 up to 1/100 led to the increase of the integral intensity of metal atoms stabilised in site 1. Annealing of the samples in temperature range 77-150 K led to rapid decrease of the integral intensity stabilised in site 1, the concentration of the paramagnetic centers stabilised in site 2 is almost unchanged.

Further heating of the samples from 150 up to 210 K led to the decrease of concentration of metal atoms stabilised in adamantane matrix and simultaneous increase of metal nanoclusters. At 210 K we observed the solid-phase transition in adamantane matrix, that led to rapid decrease of the concentration of the both types of paramagnetic centers due to rising of matrix molecular mobility.

The results on photoinduced aggregation of metallic centers in adamantane matrix are also discussed.

Acknowledgements. The work was partially supported by RFBR grant 04-03-32748 and INTAS grant 2000-00-911

[1]. A.J.Buck, B.Mile, J.A.Howard, J.Am.Chem.Soc., 1983, 105, pp. 3381 – 3387.

THE ESR STUDY OF CHEMICAL INTERACTIONS IN TRIPLE SOLID SILVER - CARBON TETRACHLORIDE - MESOGENIC CYANOBIPHENYL CO-CONDENSATE SYSTEM

V.A.Timoshenko, Yu.N.Morosov, A.A.Belyaev, T.I.Shabatina, G.B.Sergeev

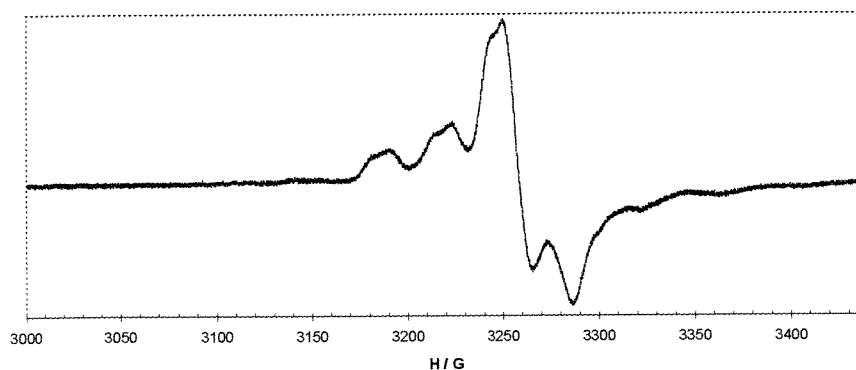
Department of chemistry. Moscow State University, 119992 Moscow, Russia, <ash@kinet.chem.msu.ru>

The possibilities of new metal-mesogenic complexes formation and there chemical reactions have been demonstrated via low temperature CVD technique using co-deposition of metal (silver), carbon tetrachloride and mesogenic 4-n-pentyl-4'-cyanobiphenyl (5CB) on the cooled surfaces.

Triple silver and carbon tetrachloride containing cyanobiphenyl film samples ($l=20-50\text{ }\mu\text{m}$) were obtained by reagents vapor co-condensation on cooled quartz surfaces under molecular beam condition. The ESR spectroscopic study of the samples were realized in situ under vacuum conditions using special cryostat [1] in temperature range 77-350 K. ESR-spectra were recorded on digital Rubin ESR-spectrometer at 3 cm band with 100 kHz high frequency modulation.

Typical ESR spectrum of solid phase triple Ag/5CB/CCl₄ co-condensate is presented at Fig.1. The ESR spectra of the samples obtained consist of four main components, the relative intensity of the components depends on the reagent ratio in triple system. The ESR-spectrum of Ag/5CB/CCl₄ co-condensate films with 5CB/CCl₄ ratio more than 100 showed at 77-150 K two doublet lines in lower and higher fields with $g = 1.9995$, $A(\text{Ag}^{109})=641\text{ G}$, $A(\text{Ag}^{107})=558\text{ G}$ due to atomic silver-cyanobiphenyl π -complexes [1]. For the samples with 5CB/CCl₄ ratio less than 100/3 the doublet lines were not found and a complex line with g -factor to 2,025 was detected due to triple Ag-5CB-CCl₄ σ -complex formation. The anisotropic central signal with g -factor close to 2.003 presented in the ESR in all cases that could be referred to silver nanocluster's spin resonance of conducting electrons. Heating of the samples led to the appearance of new signal, which could be referred to the formation of CCl₃[•]-radical due to the reactions of silver atoms, included in complexes structure, and silver clusters with chlorine derivatives.

Fig.1 ESR spectrum of Ag/CCl₄/5CB co-condensate film (1:10:100) at 77 K



Acknowledgements. The work was supported by RFBR grant 04-03-32748 and INTAS grant 2000-00911.

[1] Shabatina T.I., Timoshenko V.A., Morosov Yu.N., Sergeev G.B., *Mol.Cryst.Liq.Cryst.*, 2001, 356, 143

The comparison of conformational structures of pyrimidine nucleosides isolated in the low temperature Ar matrices.

A.Yu. Ivanov, G. Sheina

*Institute for Low Temperature Physics and Engineering,
Ukrainian Academy of Sciences, 47 Lenin Ave., 61103 Kharkov,*

Previously, for the first time, we used FTIR matrix spectroscopy for the investigation of conformational behavior of 2'-deoxy pyrimidine nucleosides: 2'-deoxyuridine and thymidine [1,2]. Now the FTIR spectra of uridine in Ar matrices were obtained in the range 4000-200 cm^{-1} . The experimental conditions were optimized to exclude the thermal decomposition. The temperatures of evaporation for uridine were about 430 K. The matrix-to-substance ratio (M/S) was fixed by using the low temperature differential quartz crystal microbalance. M/S for all substances in Ar matrices were about 800:1. The stability of conformers were estimated by the methods HF/6-31G (d,p), DFT/6-31G (d,p) and MP2/6-31G (d,p). Ab initio calculations of the infrared spectra were performed by the method DFT/6-31G (d,p) and with using correlation consistent basis sets also. The actual occupancy of conformational isomers in matrix samples was determined.

Syn-conformations with the intramolecular H-bond $\text{O5'H}\dots\text{O2}$ are common peculiarity of 2'-deoxyuridine, thymidine and uridine. Syn-conformers are stabilized by the intramolecular hydrogen bond $\text{O5'H}\dots\text{O2}$, and the dominant conformation of ribose ring is C2'-endo. It was shown that anti-conformers are dominant for these pyrimidine nucleosides. The ribose rings of main anti-conformers of 2'-deoxy pyrimidine nucleosides are in the C2'-endo conformation and the ribose rings of minor anti-conformers have the C3'-endo conformation, stabilized by intramolecular hydrogen bonds $\text{O3'H}\dots\text{O5'}$ and $\text{O5'H}\dots\text{O3'}$. Unlike these 2'-deoxy nucleosides minor anti-conformers of uridine stabilized intramolecular hydrogen bond $\text{O2'H}\dots\text{O2}$.

Acknowledgement: This investigation was supported by the Ukrainian Academy of Sciences and in part by the INTAS-INTERNATIONAL ASSOCIATION under grant No. INTAS 00 – 00911.

1. A.Yu. Ivanov, S.A. Krasnokutski, G.Sheina, Yu.P.Blagoi
Spectrochimica Acta Part A 59, 2003, 1959-1973

2.A.Yu.Ivanov, S.A.Krasnokutski, G.G.Sheina
Fizika Nizkich Temperatur, V29, №9-10, sept./oct. 2003, p.1065-1070

The peculiarities of vibrational spectra of 1-methyl-uracil--Sm complexes isolated in Ar matrices.

A.Yu. Ivanov¹, G.Sheina¹, T.Shabatina², G.Sergeev²

¹ *Institute for Low Temperature Physics and Engineering,
Ukrainian Academy of Sciences, 47 Lenin Ave., 61103 Kharkov, Ukraine*
² *Moscow State University, Russia*

For this report the FTIR spectra of 1-methyl-uracil, and 1-methyl-uracil---Sm complexes were obtained in the ranges 4000-400 cm^{-1} with KBr and CaF_2 beamsplitter and apodized resolution 0.4 cm^{-1} . For the simultaneous evaporating and trapping in the low temperature matrices thermounstable DNA fragments (1-methyl-uracil) and substances with high evaporation temperature (Sm) we placed the Knudsen cell for biomolecules in line with the evaporation cell for metals . The temperatures of evaporation for 1-methyl-uracil were about 360 K and 940K for Sm. The matrix-to-substance ratio (M/S) was fixed by using the low temperature differential quartz crystal microbalance. M/S for complexes samarium:1-methyl-uracil :Ar were about 1:1: 200.

Two new bands 1670 cm^{-1} and 1655 cm^{-1} were found in the matrix 1-methyl-uracil---Sm spectra. It should be noted that the ring bands 1650 cm^{-1} and 748 cm^{-1} were not disappeared in the spectra of complexes with Sm. It may be assumed that 1670 cm^{-1} and 1655 cm^{-1} are accordingly assigned to νC2O and νC4O of complex. The annealing of matrix samples at 28-30K has influence on the equilibrium of complexes markedly. After annealing, the intensity of bands 1670 cm^{-1} and 1655 cm^{-1} decreased (the intensity of band 1527 cm^{-1} increased). This result is correlated with the concentration measurements. Because of this, it can be assumed that atoms of Sm create complexes with a unit molecules of 1-methyl-uracil basically. The creation of sandwich-complexes in the matrices may be connected with the band 1527 cm^{-1} .

Acknowledgement: This investigation was supported by the INTAS-INTERNATIONAL ASSOCIATION under grant No. INTAS 00 – 00911.

The vibrational spectra of complexes of 1-methyl-uracil with metal chlorides

A.Yu. Ivanov, G.Sheina

*Institute for Low Temperature Physics and Engineering,
Ukrainian Academy of Sciences, 47 Lenin Ave., 61103 Kharkov, Ukraine*

The FTIR spectra of complexes of 1-methyl-uracil with sodium and copper chlorides were obtained in the ranges 4000-400 cm^{-1} with KBr and CaF_2 beamsplitter and apodized resolution 0.4 cm^{-1} . For the simultaneous evaporating and trapping in the low temperature matrices thermounstable DNA fragments (1-methyl-uracil) and substances with high evaporation temperature (metal chlorides) we placed the Knudsen cell for biomolecules in line with the evaporation cell for metals. The matrix-to-substance ratio (M/S) was fixed by using the low temperature differential quartz crystal microbalance. M/S for complexes - metal chlorides: 1-methyl-uracil : Ar were about 3:1: 200.

In the region of the stretching vibrations $\nu(\text{C}=\text{O})$, new bands 1690 cm^{-1} and 1681 cm^{-1} was found in the spectra of complexes of copper chlorides. Also in the spectra of complexes with copper chlorides the intensity of band 1650 cm^{-1} was decreased dramatically. After annealing of matrix sample this band is disappeared completely. It is good correlation between behavior of the band 1650 cm^{-1} and 748 cm^{-1} . The band 748 cm^{-1} has unambiguous assignment to the ring vibrations (νC4C5 , νC5C6 , νC6C1 according the calculation). In the earlier works the assignment of the band 1650 cm^{-1} (or 1636 cm^{-1}) to $\text{C5}=\text{C6}$ bond of pyrimidine ring was not clear. But now the band 1650 cm^{-1} can be assigned to $\text{C5}=\text{C6}$ bond of pyrimidine ring unambiguously. The nature of 1636 cm^{-1} band may be explained by Fermi resonance with $\text{C}=\text{O}$ groups. The dramatic changes of $\text{C5}=\text{C6}$ band may be a marked property of complexes with coordination bonds between copper and C5, C6.

New bands 1694 cm^{-1} and 1677 cm^{-1} was found in the spectra of complexes of sodium chlorides. But unlike complexes with copper, in the spectra of complexes of sodium chlorides the strong changes of the bands of 1-methyl-uracil 1650 cm^{-1} and 748 cm^{-1} were not registered.

Acknowledgement: This investigation was supported by the Ukrainian Academy of Sciences and in part by the INTAS-INTERNATIONAL ASSOCIATION under grant No. INTAS 00 – 00911.

LABILE ALUMINUM CHLORIDE COMPLEXES IN THE HYDROCARBON MATRICES

M.I. Shilina, R.V. Bakharev, V.V. Smirnov

Chemistry Department, Lomonosov Moscow State University
119992, Lenynsky Gory, Moscow, Russia, E-mail: mish@kinet.chem.msu.ru

Aluminium halide complexes are very important in capacity as catalysts. Establishment of detailed reaction mechanism is hindered by the difficulty of registration of active intermediates and labile complexes. Direct spectroscopic observation of catalytic species unstable in solutions becomes possible by solid state studies at low temperatures.

Using the low temperature condensation method the syntheses of aluminium chloride complexes with different promoters of catalytic activity (water, transition metal chloride, alkyl halide, nitroalkane) have been carried out in hydrocarbon matrices. Species of the various compositions were obtained; unknown earlier spectral characteristics (IR, UV/vis) and the regions of their thermal stability were revealed at 80-290K. The structures of observable labile particles are offered on the basis of the vibrational spectra and quantum-mechanical accounts with use of density functional theory. Dynamic studies of the labile complexes *in situ* by IR spectroscopy allowed observing their transformations at low temperatures.

It turned out, for example, that aluminum halide is capable to stabilize both tertiary and secondary carbenium ions. IR spectra of the received molecular complex and carbocation at interaction of aluminum chloride with 2chloro-2-methylpropane are shown in a Fig. Secondary carbenium ion at the presence of aluminum halide is stabilized by us for the first time. It is less steady than tertiary, the ranges of their stability are 130-180 K. Addition of traps molecules such as aromatic hydrocarbon results to form strong sigma complexes living down to room temperatures.

Low temperature reactions of alkane conversion were revealed on aluminum chloride catalytic complexes. Conditions of limited molecular mobility allowed to divide the processes into separate stages and to select the most advantageous direction of reaction. The intermediate stabilization by hydrocarbon matrix provided an opportunity of establishment of mechanism of alkane transformation.

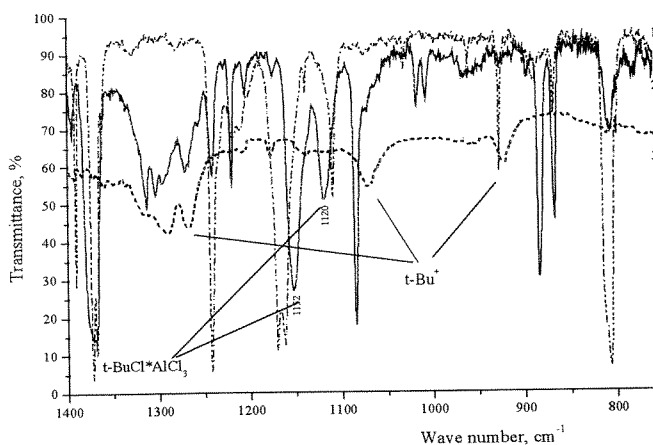


Fig.1. IR-spectra of the 2-chloro-2-methylpropane (1) and its co-condensates with aluminum chloride in n-octane matrix at 80 K: AlCl_3/RCl : 1,2 (2); 5 (3)

R.V.Bakharev acknowledges "Haldor - Topsoe" firm for the financial support.

PREDICTIONS OF NOVEL XE COMPOUNDS WITH BN

Alice M. Smith-Gicklhorn¹, Marcin Frankowski¹, Alexey N. Ponomaryow¹
and Vladimir E. Bondybey^{1,2}

¹ Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

² Department of Chemistry, University of California, Irvine, California 92697-2025, USA
emails for correspondence: v.e.bondybey@ch.tum.de; smith@ch.tum.de

The recent observation of organic Xe compounds, in particular XeC₂ [1] and HXeCCH [2-4] in rare gas matrices have stimulated us to search for the BN-isoelectronic analogs of these compounds. Here we present quantum chemical calculations using density functional theory on XeBN (XeNB), as well as Xe insertion into iminoborane to form HXeBNH and into borazine forming HXeB₃N₃H₅ [5]. In both cases, insertion into NH and BH bonds were considered and their relative stability compared. For iminoborane, double-inserted Xe was also treated and for borazine, both doubly and triply inserted.

Prospects for the experimental detection of the Xe-inserted BN compounds in the infrared are discussed together with our experimental attempts to prepare and study these species in a Xe matrix. In view of the very large infrared intensity (between 1000 and 4000 km/mol) predicted for the XeH stretch and the predicted stability of these compounds, in many cases greater than the corresponding carbon compounds, their detection should be a matter of the proper experiment.

- [1] M. Frankowski, A.M. Smith-Gicklhorn and V.E. Bondybey, *Can. J. Chem.* **82**, (2004).
- [2] J. Lundell, A. Cohen and R.B. Gerber, *J. Phys. Chem. A* **106**, 11950 (2002).
- [3] L. Khriachtchev, H. Tanskanen, J. Lundell, M. Pettersson, H. Kiljunen and M. Räsänen, *J. Am. Chem. Soc.* **125**, 4696 (2003)
- [4] V.I. Feldman, F.F. Sukhov, A. Yu. Orlov and I.V. Tyulpina, *J. Am. Chem. Soc.* **125**, 4698 (2003).
- [5] A.M. Smith-Gicklhorn, M. Frankowski and V.E. Bondybey, *Mol. Phys.* Submitted.

Structure and transitions of condensed oxygen films

A.A.Solodovnik, V.V.Danchuk, M.A.Strzemechny

*B.Verkin Institute for Low Temperature Physics and Engineering of National Academy of Sciences of Ukraine,
47 Lenin ave. Kharkov 61103, Ukraine.
solodovnik@ilt.kharkov.ua*

Solid oxygen represents the unusual combination of a magnetic material with a molecular crystal. The lowest temperature α - phase is characterized by an ordered arrangement of molecule axes and magnetic moments. The α - modification has the monoclinic structure of $C2/m$ symmetry [1-3] and the antiferromagnetic behavior. The intermediate β - phase (a rhombohedral lattice) is the result of a phase transition at $T=23.8$ K. Experimental information concerning the structure of small-size O_2 crystallites [4, 5] is not identical with bulk solids [2]. This fact can be caused by both the size factor and the peculiarities of the deposition process. The additional modifications were observed in thin oxygen films [4]. One, which is formed in the temperature range of the α - phase, was called α' . Its origin has been ascribed to a size effect, however according to [2] this modification realized in the samples containing impurities. The data on amorphous phase are not sufficient for understanding of its origin. The conflicting literature on the problem of the transformations in solid oxygen suggests a reinvestigation.

Investigations were carried out by transmission electron diffraction using a helium cryostat. Measurements were made in the temperature range between 5 K and the sublimation point. The specimens were prepared directly *in situ* by depositing the 99.99% pure gas simultaneously on an amorphous carbon and a polycrystalline Al substrates. The electron beam was very narrow to reduce the radiation effect. With this aim also we used the Faraday cylinder, which let the electron beam through only during recording. The procedure was capable of detecting short-lived states and it was important for the investigation of the growth process, phase transitions.

The influence of the quenching conditions on the crystal growth has been investigated. The new conditions for the formation of a magnetically distorted α' - phase were established. The as grown oxygen films had the short live α' structure, which transformed into α - phase or β - modification depending on the temperature range. Heating the deposits above 24 K caused a transition from low temperature phase to the intermediate modification, which was accompanied by an appearance of α' reflections on the diffraction pattern. Amorphous oxygen was observed as a result of rapid cooling or heating of samples. In following the amorphous films became crystalline. A new non-equilibrium phase of solid oxygen was observed in the samples deposited under certain conditions. A possible explanation of this fact was suggested.

- [1] C. S. Barrett, L. Meyer, J. Wasserman, *J. Chem. Phys.*, **47**, 592, 1967.
- [2] I. N. Krupskii, A. I. Prokhvatilov, Yu. A. Freiman, A. I. Erenburg, *Fiz. Nizk. Temp.*, **5**, 271, 1979.
- [3] R. A. Alikhanov, *JETP Lett.*, **5**, 430, 1967.
- [4] E. M. Horl, *Acta Cryst.*, **B25**, 2515, 1969.
- [5] D. Wallacher, P. Huber, K. Knorr, *J. Low Temp. Phys.*, **122**, 313, 2001.

Chemical Compounds Formed from Diacetylene and Noble-Gas Atoms: HKrC₄H and HXeC₄H

Hanna Tanskanen,¹ Leonid Khriachtchev,¹ Jan Lundell,¹ Harri Kiljunen,² Markku Räsänen¹

¹Department of Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, FINLAND and ²VERIFIN, P.O. Box 55, FIN-00014 University of Helsinki, FINLAND
E-mail: hanna.tanskanen@helsinki.fi

Novel organic noble-gas compounds, HNgC₄H (Ng = Kr or Xe), have been identified in matrix-isolation experiments supported by ab initio calculations.¹ These molecules are prepared in low-temperature noble-gas matrixes via UV photolysis of diacetylene and subsequent thermal mobilization of H atoms at 30 and 45 K for Kr and Xe, respectively. The HNgC₄H compounds are the largest molecules among the known noble-gas hydrides. The strongest IR absorption bands of these are the H-Ng stretching modes with the most intense components at 1290 cm⁻¹ for HKrC₄H and at 1532 cm⁻¹ for HXeC₄H. In addition, a number of weaker absorptions (C-H stretching, C-C-C bending and C-C-H bending modes) are found in the spectra in agreement with the theoretical predictions. The IR absorption spectra indicate some further stabilization of the HNgC₄H molecules as compared with the corresponding HNgC₂H species identified recently.^{2,3} The computational energetic results support this trend. We expect that the larger molecules HNgC₆H and HNgC₈H are even more stable and the HNgC_{2n}H species are good candidates for bulk organic noble-gas material.

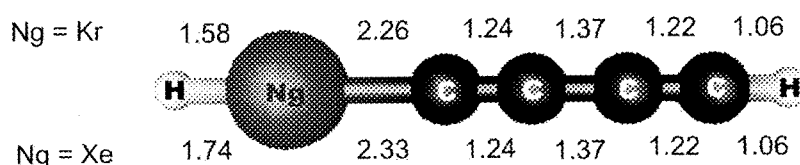


Figure 1. Equilibrium structures of the HNgC₄H molecules (Ng = Kr or Xe) at the MP2/LJ18(Xe),6-311G++(2d,2p) level. The bond lengths are in Å.

References:

- [1] H. Tanskanen, L. Khriachtchev, J. Lundell, H. Kiljunen, M. Räsänen, *J. Am. Chem. Soc.*, **125**, 16361 (2003).
- [2] L. Khriachtchev, H. Tanskanen, J. Lundell, M. Pettersson, H. Kiljunen, M. Räsänen *J. Am. Chem. Soc.*, **125**, 4696 (2003).
- [3] L. Khriachtchev, H. Tanskanen, A. Cohen, R. B. Gerber, J. Lundell, M. Pettersson, H. Kiljunen, M. Räsänen *J. Am. Chem. Soc.*, **125**, 6876 (2003).

SOLVATION OF HCl BY METHANOL AND DIMETHYL ETHER

N. Uras-Aytemiz*, O. Boylu*, J. Sadlej[§], J. P. Devlin[&], V. Buch[#]

* Department of Chemistry, Suleyman Demirel University, 32260 Isparta-Turkey (e-mail: aytemiz@fef.sdu.edu.tr)

[§] Department of Chemistry, University of Warsaw, 02-093 Warsaw, Poland

[&] Department of Chemistry, Oklahoma State University, 74078OK-USA

[#] Department of Physical Chemistry and the Fritz Haber Research Center, The Hebrew University, 91904 Jerusalem, Israel

Acid solvation in/on the solid phase is of interest both in basic and atmospheric chemistry. In our recent study [1], we proposed a picture how HX (HCl and HBr) can be solvated on/in ice nanoparticles. The aim of this study is to further examine solid-phase acid solvation on/in different solvents, namely methanol and dimethyl ether. *Ab initio* calculations and Monte Carlo simulations are carried out to investigate typical bonding configurations, and to interpret experimental spectra.

[1] J.P. Devlin, N. Uras., J. Sadlej, V. Buch, *Nature*, 417, 269-271 (2002).

Photodissociation of formaldehyde in rare gas matrixes

Kari J. Vaskonen and Henrik M. Kunttu

*Department of Chemistry, University of Jyväskylä, Finland
e-mail: kari@epr.jyu.fi*

Formaldehyde serves as an ideal prototype for studying photochemical process. In this work it has been used to extend earlier studies concerning photodissociation process of diatomic molecules in condensed matter and especially, effect of rare gas matrix for photodissociation process of polyatomic molecules. Infrared (IR) spectroscopy and electron paramagnetic resonance (EPR) are combined to study photodissociation of formaldehyde at photolysis wavelengths 308, 248, and 193 nm in rare gas matrixes. The photodissociation cross sections derived from the IR data show strong dependence on the matrix host and photolysis wavelength. Dissociation efficiency in Xe is 1-2 orders of magnitude higher than in the other matrixes. The kinetics of formation of atomic hydrogen and the final hydrogen atom concentration in the fully photolyzed sample vary significantly in different matrixes. In the 248 nm photolysis, the final number of hydrogen atoms in Kr and Ar matrixes is only 1/20 and 1/40 of the Xe matrix number, respectively. This behavior is discussed in the frame of simple kinetic model. The anomalously fast dissociation at 193 nm in Xe matrix is discussed.

FRAGMENTATION OF IONIZED NEON CLUSTERS IN SUPERFLUID HELIUM NANODROPLETS

DAVID BONHOMMEAU, ALEXANDRA VIEL AND NADINE HALBERSTADT
LPQ/IRSAMC, Uni. P. Sabatier, 118 route de Narbonne, F-31062 Toulouse, France
alexandra.viel@irsamc.ups-tlse.fr

Over the last few years, spectroscopy of molecules and clusters attached and embedded in helium clusters has become a growing and significant field of quantum matrix spectroscopy. Clusters of ^4He appear to provide an ideal, cold quantum matrix characterized by weak interactions with guest dopants.

In the case of mass spectroscopy experiments of Ne_n -doped helium droplets, the ionization step leads to fragmentation of the helium droplet as well as of the host cluster.[1]

We present recent developments in theoretical analysis of the fragmentation dynamics of Ne_n^+ embedded in helium clusters.[2] The simulation relies on the molecular dynamics with quantum transition (MDQT) method[3] to treat the inherently multi-surface nature of the dynamics. The potential energy surfaces are described in the diatomics-in-molecules (DIM) model[4] which allows the modeling of the delocalization of the charge over the neon cluster. In this mixed quantum/classical method, the electronic part is treated quantum-mechanically, while the positions of the neon atoms are propagated classically on a single adiabatic potential energy surface with hops between the surfaces allowed. The helium environment is described by an *ad hoc* model, using a friction force acting on neon atoms with velocities above the Landau critical velocity. Results of our simulation and comparison with available experimental data are presented.

References

- [1] T. Ruchti *et al.* *J. Chem. Phys.* **109**, 10679 (1998)
- [2] D. Bonhommeau, A. Viel and N. Halberstadt *J. Chem. Phys.* **120**, 11359 (2004)
- [3] J. C. Tully, *J. Chem. Phys.* **93**, 1061 (1990)
- [4] F. Y. Naumkin and D. J. Wales, *Mol. Phys.* **93**, 633 (1998).

Coherent Control Experiments Employing Pulse Cleaning and Parameterization Techniques

S. M. Weber, A. Lindinger, F. Vetter, M. Plewicky, A. Merli, and L. Wöste

*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin
weberst@physik.fu-berlin.de (corresponding author)*

We present two approaches that help simplifying the interpretation and understanding the results from optimal control experiments performed with shaped fs-laser pulses together with evolutionary algorithms. The first one will be to apply genetic pressure with different strengths on the spectral components of laser pulses with appropriate cost functions. This method enables to remove unnecessary frequencies, is able to provide an insight into the electronic transitions to particular vibrational states and even allows influencing the ionization path. Also, we can extract hints on how the Pareto-optimal front of the conflicting optimization goals: ion yield and transmission looks like in the respective function space.

The second approach is a method that enables to restrict the huge search space that usually accompanies optical control experiments that are performed with pulse shapers using liquid crystal modulators. The parameters are defined in a physical intuitive and meaningful way, for example subpulse distance, chirp, and intensity. By calculating the transfer functions necessary to obtain these pulses experimentally and combining the pulseform generation with the evolutionary algorithm it becomes possible to perform ‘controlled’ control experiments. We show that imposing limits, for example, on subpulse number, chirp, and distance can be a valuable tool to gradually investigate the molecular dynamics of the cold alkaline cluster NaK.

CO₂ NANO-PARTICLE AGGREGATION AND COALESCENCE STUDIED BY IR SPECTRA AND MOLECULAR DYNAMICS SIMULATIONS.

Carmi Yinnon^{*a}, Victoria Buch^{*}, Paul Devlin⁺

^{*}*The Fritz Haber Institute for Molecular Dynamics, Hebrew University, Jerusalem 91904, Israel*

⁺*Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078*

a) *carmiy@fh.huji.ac.il*

The IR spectra of CO₂ nano-particles whose radii are in the range of 10-100 nm were measured. These particles are nucleated from the gas phase and left to evolve at temperatures of 40 to 110 K. In a typical spectrum three major features dominate. Two features are stable, while the third low frequency TO-like band is time and temperature dependent. Depending on experimental conditions, either growth or decrease of the TO-feature can be observed with time. To explain the phenomena molecular dynamics simulations of CO₂ particle nucleation, aggregation and sintering were performed. The calculations corroborate the recent hypothesis that CO₂ primary nano-particle shape is of the cubo-octaheadral motif. We further demonstrate how aggregation accounts for the low energy feature in the IR spectrum. It is shown that upon particle sticking an amorphous neck is created. The neck may become crystalline, as a result of global rotation of the particles. The low energy feature is associated with neck crystallization. Sintering of the aggregate removes the feature. From these results a qualitative model is designed explaining the temperature and time dependence.

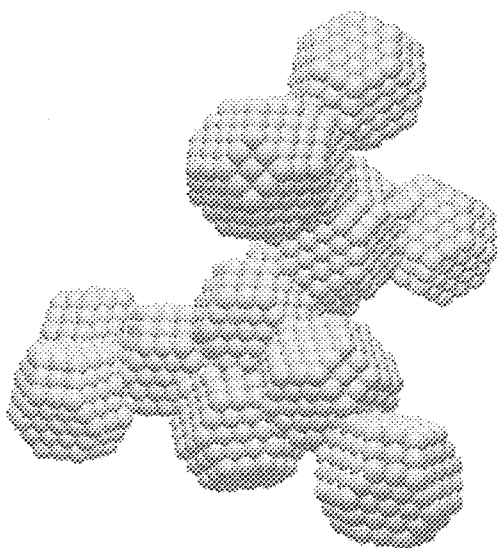


FIG 1. Aggregate of CO₂ particles, each consisting of 200 molecules.

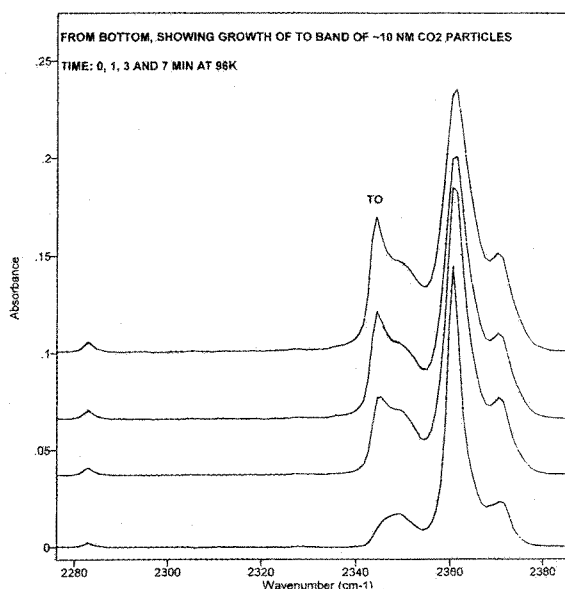


FIG 2. IR Spectra of CO₂ particles showing growth of TO-like band.

LIST OF PARTICIPANTS

Jussi Ahokas
jusahok@cc.jyu.fi

Nobuyuki Akai
rosso@hiroshima-u.ac.jp

Aleksandr V. Akimov
shura@icp.ac.ru

David T. Anderson
danderso@uwo.edu

Daisuke Ando
adaisuke@kuchem.kyoto-u.ac.jp

V. Ara Apkarian
aapkaria@uci.edu

Mykhaylo I. Bagatskiy
bagatskii@ilt.kharkov.ua

Joost M. Bakker
jmbakker@fhi-berlin.mpg.de

Ethan P. Bernard
epb22@cornell.edu

Thorsten M. Bernhardt
tbernhar@physik.fu-berlin.de

Martin K. Beyer
martin.beyer@ch.tum.de

Alexander Borowski
borowski@chemie.fu-berlin.de

Victoria Buch
viki@fh.huji.ac.il

Gerd Buntkowsky
bunt@chemie.fu-berlin.de

Majed Chergui
majed.chergui@epfl.ch

David C. Clary
david.clary@chem.ox.ac.uk

Arik Cohen
arikco@fh.huji.ac.il

David F. Coker
coker@bu.edu

Claudine Crépin
claudine.crepin-gilbert@ppm.u-psud.fr

J. Paul Devlin
devlin@okstate.edu

Yurij A. Dmitriev
dmitriev.mares@pop.ioffe.rssi.ru

Nadia Dozova
dozova@spmol.jussieu.fr

Jussi Eloranta
eloranta@jyu.fi

Dmitry G. Eshchenko
dimitry.eshchenko@psi.ch

Hagai Eshet
hagai@eshet.com

Mario E. Fajardo
mario.fajardo@eglin.af.mil

Vladimir Feldman
feldman@cc.nifhi.ac.ru

Steven L. Fiedler
sfiedler@jyu.fi

Marcin Frankowski
frankowski@ch.tum.de

Mizuho Fushitani
mizuho.fushitani@physik.fu-berlin.de

Nikolay Galtsov
galtsov@ilt.kharkov.ua

Robert Benny Gerber
benny@fh.huji.ac.il

Gerard Giraud
gerard.giraud@epfl.ch

Alejandro Gonzalez
alejandros.gonzalez@epfl.ch

Leo Gross
leo.gross@physik.fu-berlin.de

Markus Gühr
Markus.Guehr@physik.fu-berlin.de

Galina B. Gumenchuk
Galina.Gumenchuk@ch.tum.de

Arthur Hotzel
arthur.hotzel@physik.fu-berlin.de

Heide Ibrahim
Heide.Ibrahim@physik.fu-berlin.de

Masazumi Ishiguro
ishiguro@popsvr.tokai.jaeri.go.jp

Esa Isoniemi
esa.isoniemi@helsinki.fi

Mark A. Johnson
Mark.johnson@yale.edu

Leonid Khryashchev
leonid.khriachtchev@helsinki.fi

Ivan V. Khyzhniy
Khyzhniy@ilt.kharkov.ua

Toni Kiljunen
Toni.Kiljunen@physik.fu-berlin.de

Tiina Kiviniemi
titakivi@cc.jyu.fi

Karl Kleinermanns
Kleinermanns@uni-duesseldorf.de

Oksana A. Korolyuk
korolyuk@ilt.kharkov.ua

Nina V. Krainyukova
krainyukova@ilt.kharkov.ua

Oliver Kühn
ok@chemie.fu-berlin.de

Jochen Küpper
jochen@fhi-berlin.mpg.de

Takayuki Kumada
kumada@popsvr.tokai.jaeri.go.jp

Bert Lambie
bert.lambie@chem.kuleuven.ac.be

Rudolf Lehnig
rudolf.lehnig@chemie.uni-regensburg.de

Lauri Lehtovaara
lauri@jyu.fi

Antti Lignell
lignell@csc.fi

Albrecht Lindinger
lindin@physik.fu-berlin.de

Victor A. Lykah
lykah@ilt.kharkov.ua

Volodymyr Maidanov
maidanov@ilt.kharkov.ua

Jörn Manz
jmanz@chemie.fu-berlin.de

Gerard Meijer
meijer@fhi-berlin.mpg.de

Andrea Merli
andrea.merli@physik.fu-berlin.de

Leonid P. Mezhov-Deglin
mezhov@issp.ac.ru

Indu B. Mishra
imishra@juno.com

Eugenii Ya. Misochko
misochko@icp.ac.ru

Yuki Miyamoto
yu-ki@kuchem.kyoto-u.ac.jp

Takamasa Momose
momose@kuchem.kyoto-u.ac.jp

Francesca Moresco
francesca.moresco@physik.fu-berlin.de

Munetaka Nakata
necom@cc.tuat.ac.jp

Kirill Nuzhdin
kirill.nuzhdin@rad.chem.msu.ru

Nina Owschimikow
nina.owschimikow@physik.fu-berlin.de

Susanna Pehkonen
susanna.pehkonen@helsinki.fi

Paul W. Percival
percival@sfu.ca

Mika Pettersson
mijopett@cc.jyu.fi

Alexey Ponomaryov
alexey.ponomaryov@ch.tum.de

Evgeny A. Popov
eap@epr.chem.jyu.fi

Michael Pschyrembel
Michael.Pschyrembel@Leybold.com

Oleg I. Pursky
pursky_o@ukr.net

Markku Räsänen
markku.rasanen@helsinki.fi

Bertrand R. Rowe
Bertrand.rowe@univ-rennes1.fr

Elena V. Savchenko
savchenko@ilt.kharkov.ua

Richard J. Saykally
saykally@uclink4.berkeley.edu

Maike Schröder
maikesch@chemie.fu-berlin.de

Nikolaus Schwentner
nikolaus.schwentner@physik.fu-berlin.de

Gleb B. Sergeev
gbs@kinet.chem.msu.ru

Tatyana I. Shabatina
tsh@cryo.chem.msu.ru

Galina Sheina
sheina@ilt.kharkov.ua

Tadamasa Shida
shida@gen.kanagawa-it.ac.jp

Marina I. Shilina
mish@kinet.chem.msu.ru

Ian R. Sims
ian.sims@univ-rennes1.fr

Alice M. Smith-Gicklhorn
smith@ch.tum.de

Manfred Soltwisch
manfred.soltwisch@physik.fu-berlin.de

Angelina A. Solodovnik
solodovnik@ilt.kharkov.ua

Frank Stienkemeier
franks@physik.uni-bielefeld.de

Vyacheslav G. Storchak
storchak@stor.polyn.kiae.su

Mikhail A. Strzhemechny
strzhemechny@ilt.kharkov.ua

Hanna Tanskanen
hanna.tanskanen@helsinki.fi

J. Peter Toennies
jtoenni@gwdg.de

Ingeborg Twesten
ingeborg.twesten@physik.fu-berlin.de

Nevin Uras-Aytemiz
aytemiz@fef.sdu.edu.tr

Kari J. Vaskonen
kari@epr.jyu.fi

Franziska Vetter
franziska.vetter@physik.fu-berlin.de

Alexandra Viel
alexandra.viel@irsamc.ups.tlse.fr

Stefan M. Weber
weberst@physik.fu-berlin.de

Roland Wester
roland.wester@physik.uni-freiburg.de

K. Birgitta Whaley
whaley@socrates.berkeley.edu

John S. Winn
john.s.winn@dartmouth.edu

Martin Wolf
wolf@physik.fu-berlin.de

Carmi Yinnon
carmiy@fh.huji.ac.il

Sven Zoephel
szoephel@vts-createc.com

Impressum

Herausgeber: Prof. Dr. N. Schwentner, Ingeborg Twesten
Institut für Experimentalphysik, FB Physik der Freien Universität Berlin
Arnimallee 14, D-14195 Berlin
Tel. +49-30-8385 6035

Auflage 160 Stück
Stand September 2004

ISBN 3-929619-35-0
Alle Rechte vorbehalten