



# CPLT/2016

CHEMISTRY AND PHYSICS AT LOW TEMPERATURES 2016

## **Book of Abstracts**

3-8 July 2016  
Biarritz, France





## Preface

It is a pleasure to welcome you to France to participate in CPLT 2016.

CPLT is the result of the merging of two long-running conference series: “The Physics and Chemistry of Matrix Isolated Species” (PCMIS), which started in 1973, and the “International Conference on Low Temperature Chemistry” (ICLTC), which started in 1994. Only one PCMIS edition has previously been organised in France: at Fontevraud, in 1985. It is therefore a great pleasure to welcome you to France once again for CPLT 2016, the third “Chemistry and Physics at Low Temperatures” conference, following on from the successful meetings CPLT 2013 in Jyväskylä, Finland and CPLT 2014 in Suzdal, Russia.

CPLT is an interdisciplinary conference, gathering together scientists from many different fields of chemistry and physics. In the 2016 edition, along with our traditional topics, we have tried to introduce new aspects and people to the community, for example in the fields of gas phase studies, astrochemical ices, and clathrates. There will be 11 invited lectures, 16 invited talks, and 34 contributed talks in the following sessions:

Quantum Hosts and Cryogenic Matrices  
Spectroscopy and Dynamics at Low Temperature  
Chemical Reactions, Intermediates, and Unstable Species  
Astrophysical, Astrochemical, and Atmospheric Science  
Biological Systems  
Materials, Cryocrystals, and Clathrates  
New Techniques and Applications

Around 60 posters will be presented, 23 of them by young researchers who will compete for the best poster award. There will be also free time to allow discussions and to enjoy the conference venue.

We gratefully acknowledge the financial support received from the Universities of Bordeaux, Paris-Sud and Aix-Marseille, from our laboratories and institutes (ISM, ISMO, PIIM), from French research institutions and organisations (CNRS, PCMI, CPPS, LabEx TF, Fédération de Chimie de Marseille), from the French Society of Chemistry (SCF, Physical Chemistry Division), and from the French Society of Physics (SFP). We also thank the French Society of Vacuum (SFV) and the companies Bruker Optics France, Eurisotop, Midisciences, Acal-bfi, and Amplitude for their sponsorship.

In total, you are more than 100 participants from 16 countries. We hope that all of you will enjoy the science, the good company, and the beautiful city of Biarritz.

Biarritz, July 2016

Joëlle Mascetti, Claudine Crépin-Gilbert, Stéphane Coussan

## **Committees**

### **International Scientific Committee**

Mika Pettersson (Finland)  
Wolfram Sander (Germany)  
Joelle Mascetti (France)  
Nigel Young (UK)  
David Anderson (USA)  
Tatyana Shabatina (Russia)  
Claudine Crepin-Gilbert (France)  
Wolfgang Jäger (Canada)  
Andrey Vilesov (USA)  
Robert McMahon (USA)  
György Tarczay (Hungary)  
Tomonari Wakabayashi (Japan)  
Leonid Khriachtchev (Finland)  
Sebastian Riedel (Germany)  
Vladimir Feldman (Russia)

### **CPLT 2016 Organising Committee**

Joëlle Mascetti, Audrey Moudens, Jennifer Noble, Vicky Marcassoli (ISM, Université de Bordeaux)  
Claudine Crépin-Gilbert, Wutharath Chin (ISMO, Université Paris-Sud)  
Stéphane Coussan (PIIM, Aix-Marseille Université)

### **Chair**

Dr Joëlle Mascetti  
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### **Vice-chairs**

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Dr Stéphane Coussan, PIIM, Aix-Marseille Université, France  
Email : [stephane.coussan@univ-amu.fr](mailto:stephane.coussan@univ-amu.fr)



## Conference Events

**Welcome party on Sunday, July 3<sup>rd</sup>:** from 7.00 pm to 9.00 pm

**Lectures and Talks:** all speakers are courteously reminded to respect the duration of their talks: 30+5 minutes for invited lectures and 15+5 minutes for invited and contributed talks. A PC computer will be available in the conference room. If possible, please prepare your talk as a pdf file and give it to one of the organisers the day before your session.

**Poster sessions on Monday-Tuesday from 8.30 to 10.30 pm:** Session 1 (Monday 4<sup>th</sup>) for odd numbered posters from 1 to 55 and Session 2 (Tuesday 5<sup>th</sup>) for even numbered posters from 2 to 56. Posters must be installed in the conference room on Monday morning and will be removed on Friday morning.

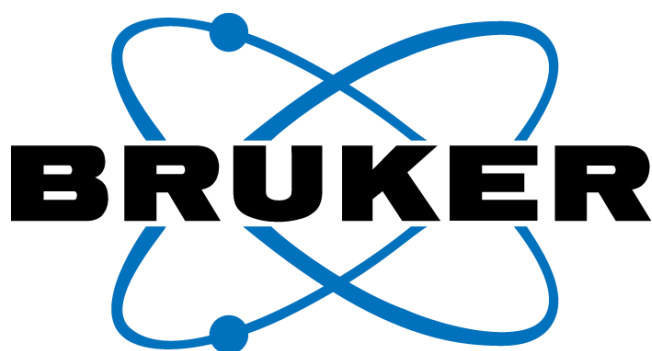
**Excursion on Wednesday 6<sup>th</sup>:** if you have not already done so, please confirm your participation on the CPLT website by Monday 4<sup>th</sup> at the latest.

**Conference dinner on Wednesday 6<sup>th</sup>:** it will be in a typical Basque restaurant called “Axafila Baïta”. Formal dress is not required.

**Pimentel prize and best poster prize:** will be announced on Thursday 7<sup>th</sup>, at the evening session.

**CPLT scientific committee:** election of new members of the committee will be held on Thursday, 7<sup>th</sup> at the evening session.

**Information on Biarritz and surroundings** (sightseeing, museums, beaches, sport activities, etc) is provided in your check-in package and can be found at the reception desk of the Domaine de Françon.





Fort d'une expérience de 25 ans, Euriso-top synthétise et commercialise la plus large gamme de composés marqués par des isotopes stables ( D, 13C, 15N, 18O ). C'est ainsi que depuis sa création en plein cœur du CEA de Saclay, que l'entreprise Euriso-top s'est imposée comme le leader européen en solvants deutérés et en molécules marquées, en proposant plus de 15.000 références produits, couvrant de multiples domaines de la recherche. Durant toutes ces années, Euriso-Top n'a eu de cesse de fournir les meilleurs solvants deutérés du marché et d'améliorer ses techniques de production pour répondre aux exigences liées aux évolutions des matériels de spectrométrie de résonnance magnétique nucléaire. Elle confirme ainsi sa vocation d'être, pour toute la communauté scientifique, le partenaire privilégié de leurs recherches.



MIDISCIENCES est spécialisée dans la maintenance, la réalisation et la commercialisation d'équipements liés aux techniques du vide. Du pompage industriel à l'Ultravide, nous proposons les composants, consommables et services rattachés à cette technologie. A ce titre MIDISCIENCES se positionne en tant qu'antenne régionale S.A.V de 3 constructeurs de renommée mondiale : EDWARDS, MIL'S, KNF. Nous assurons également la commercialisation et les réparations toutes marques, pièces détachées, documentations techniques. Nos moyens illustrent un éventail de compétence optimale :

- Installations sur site
- Interventions préventive et curative sur site ou en atelier
- Atelier de maintenance, stock de pièces et consommables
- Groupes de pompage
- Matériels de prêt ou de location pour dépannage
- DéTECTEURS de fuites hélium/ Catharomètres
- Manométrie toutes gammes de pression
- Banc d'étalonnage
- Etuve sous vide
- Compresseurs
- Soudure ARC-TIG
- Ingénierie, Applications, Conception de dispositif, Réalisations spéciales.

# PROGRAMME

## ***Sunday 3<sup>rd</sup> July***

15.00 – 19.00 **Arrivals and Registration**

19.00 – 21.00 **Welcome Reception and Buffet**

20.30 **Opening Session, Joëlle Mascetti (Bordeaux, France)**

**André Tramer dedicace, Chair : Claudine Crépin (Orsay, France)**

20.40 – 21.15 **Anne Zehnacker (Orsay, France) (IL-1)**

*Chirality effects in the structure of  $\alpha$ - and  $\beta$ -peptides: conformer-specific jet-cooled spectroscopy and vibrational circular dichroism studies*

21.15 – 21.50 **Majed Chergui (Lausanne, Suisse) (IL-2)**

*Probing the Ultrafast dynamics of molecular systems from the IR to the X-ray range*

## ***Monday 4<sup>th</sup> July***

### **Session : Quantum Hosts and Cryogenic Matrices**

**Chair: Robert Hinde (Knoxville, TN, USA)**

9.00 – 9.35 **Takamasa Momose (Vancouver, Canada) (IL-3)**

*Amino Acids in Solid Parahydrogen*

9.35 – 9.55 **Andrey Vilesov (Los Angeles, USA) (IT-1)**

*X-ray coherent diffractive imaging of quantum vortices in superfluid helium droplets*

9.55 – 10.15 **Masashi Tsuge (Hsinchu, Taiwan) (IT-2)**

*Infrared spectra of protonated species isolated in para-hydrogen matrices*

10.15 – 10.35 **David Anderson (Laramie, Wyoming, USA) (IT-3)**

*Reactivity of Hydrogen Atoms in Solid Parahydrogen: The  $H + N_2O$  Reaction*

10.35 – 11.00 - **Coffee break**

**Chair: Wolfgang Jäger (Edmonton, Canada)**

11.00 – 11.20 **Aude Simon (Toulouse, France) (IT-4)**

*Modeling molecular clusters/complexes in a rare gas environment using a quantum-classical scheme*

11.20 – 11.40 **Ephriem Mengesha (Saclay, France) (CT-1)**

*Infrared spectroscopy of acetylene-rare gas complexes in He-nanodroplets*

11.40 – 12.00 **Kim Hyeon-Deuk (Kyoto, Japan) (CT-2)**

*Distinct Structural and Dynamical Difference between Supercooled and Normal Liquids of Hydrogen Molecules*

12.00 – 12.20 **Klaus Van Haeften (Leicester, UK) (CT-3)**

*Frequency and time-domain spectroscopy of molecules in small helium clusters and bulk helium*

12.20 – 12.40 **Petr Moroshkin (Saitama, Japan) (CT-4)**

*Spectroscopy of  $Ba^+He$  excimer: first observation of bound-bound transitions between electronically excited states*

13.00 – 14.00 - **Lunch**

14.00 – 16.30 - **Free Time**

**Session : New Technologies and Applications**

**Chair: Nigel Young (Hull, UK)**

16.30 – 17.05 **Daniel Comparat (Paris, France) (IL-4)**

*Review of Cold Molecules: towards a universal decelerator for polar molecules*

17.05 – 17.25 **Claude Dedonder-Lardeux (Marseille, France) (IT-5)**

*Cold Ions, spectroscopy and mass spectrometry*

17.25 – 17.45 **Brianna Heazlewood (Oxford, UK) (CT-5)**

*Characterising Cold Ion-Molecule Reactions in Coulomb Crystals*

17.45 – 18.00 – **Coffee Break**

18.00 – 18.20 **Ara Apkarian (Irvine, USA) (IT-6)**

*Orientation dependent chirality and handedness of a nano-diatom*

18.20 – 18.40 **Florian Zischka (Munich, Germany) (CT-6)**

*A new Approach to NMR-Matrix-Isolation Spectroscopy*

18.40 – 19.00 **Baptiste Joalland (Rennes, France) (CT-7)**

*A New Laboratory Approach to Determine Low-Temperature Branching Ratios : Chirped-Pulse in Uniform Flow*

19.30 – 20.30 - **Diner**

20.30 – 22.30 **Poster Session 1 (Odd numbers from 1 to 55)**

***Tuesday 5<sup>th</sup> July***

**Session : Spectroscopy and Dynamics at Low Temperature**

**Chair: Wutharath Chin (Orsay, France)**

9.00 – 9.35 **Martin Suhm (Göttingen, Germany) (IL-5)**

*Low-Temperature Intermolecular Balances in the Gas Phase*

9.35 – 9.55 **Sonia Melandri (Bologna, Italy) (IT-7)**

*Conformational preferences of flexible molecules and molecular complexes studied by free-jet rotational spectroscopy: the importance of non-covalent interactions*

9.55 – 10.15 **Alejandro Gutiérrez-Quintanilla (La Habana, Cuba) (CT-8)**

*Dynamics and photodynamics of acetylacetone analogs in cryogenic matrices*

10.15 – 10.35 **Magdalena Saldyka (Wroclaw, Poland) (CT-9)**

*Isomerization and photodecomposition of acetohydroxamic acid in argon matrices. FTIR and theoretical studies*

10.35 – 11.00 - *Coffee break*

**Chair: Stéphane Coussan (Marseille, France)**

11.00 – 11.20 **John McCaffrey (Maynooth, Ireland) (IT-8)**

*2D-EE spectroscopy of heavier alkaline earth metals atoms Ba, Sr and Ca in rare gas matrices – CCSD(T) calculations and atomic site occupancies*

11.20 – 11.40 **Benoit Gervais (Caen, France) (IT-9)**

*Spectroscopy of alkali atoms in Ar matrix*

11.40 – 12.00 **Tomonari Wakabayashi (Osaka, Japan) (CT-10)**

*Matrix Isolation Spectroscopy of Bismuth Atoms and Molecules*

12.00 – 12.20 **Justinas Ceponkus (Vilnius, Lithuania) (CT-11)**

*Study of Water – Acetylacetone complexes by the means of matrix isolation infrared spectroscopy*

12.20 – 12.40 **Benoit Tremblay (Paris, France) (CT-12)**

*A solid neon study of the CO<sub>2</sub>-H<sub>2</sub>O and OCS-H<sub>2</sub>O van der Waals complexes from far to near-infrared region*

13.00 – 14.00 - *Lunch*

14.00 – 16.30 - *Free Time (Committee meeting at 14.00)*

### **Session : Astrophysical, Astrochemical and Atmospheric Studies (1)**

**Chair: Audrey Moudens (Cergy-Pontoise, France)**

16.30 – 17.05 **Robert Kolos (Warsaw, Poland) (IL-6)**

*Unsaturated carbon-nitrogen chain molecules in cryogenic matrices*

17.05 – 17.25 **John Maier (Basel, Switzerland) (IT-10)**

*Electronic Spectrum of C60+ in Gas-Phase at 6 K: Identification of First Diffuse Interstellar Bands*

17.25 – 17.45 **Ludovic Biennier (Rennes, France) (IT-11)**

*Cold chemistry and physics with supersonic uniform flows*

17.45 – 18.00 – *Coffee Break*

18.00 – 18.20 **Urszula Szczepaniak (Warsaw, Poland) (CT-13)**

*Vibrational and electronic spectroscopy of CH<sub>3</sub>C<sub>5</sub>N (methylcyanodiacetylene)*

18.20 – 18.40 **Jennifer Noble (Bordeaux, France) (CT-14)**

*Photochemistry of water: PAH complexes and ice mixtures: the role of molecular orientation in reactivity*

18.40 – 19.00 **Salma Bejaoui (Moffett Field, CA, USA) (CT-15)**

*Laser Induced Emission Spectroscopy of Cold and Isolated Neutral PAHs and PANH: Implications for the red rectangle emission*

19.30 – 20.30 - *Diner*

20.30 – 22.30 - **Poster Session 2 (Even numbers from 2 to 56)**

## **Wednesday 6<sup>th</sup> July**

### **Session : Astrophysical, Astrochemical and Atmospheric Studies (2)**

**Chair: Jennifer Noble (Bordeaux, France)**

9.00 – 9.35 **Ruth Signorell (Zurich, Switzerland) (IL-7)**

*Spectroscopy, a toolbox for structural information on aerosol particles*

9.35 – 9.55 **Yeni Tobon (Lille, France) (CT-16)**

*Matrix photochemistry of organic sulfur-containing species with atmospheric interest*

9.55 – 10.15 **Sergey Ryazantsev (Moscow, Russia) (CT-17)**

*Matrix-isolation studies of HOCO radicals produced by X-rays or VUV-radiation*

10.15 – 10.35 **Xavier Michaut (Paris, France) (IT-12)**

*Nuclear spin conversion of water isolated in argon matrix: Isotopic and concentration effects*

10.35 – 11.00 - *Coffee break*

**Chair: Vladimir Feldman (Moscow, Russia)**

11.00 – 11.20 **Lahouari Krim (Paris, France) (IT-13)**

*The chemistry of ground state nitrogen atoms N(<sup>4</sup>S) on cold interstellar grains: Heat-induced reaction processes vs energetic cosmic rays implications*



11.20 – 11.40 **Basile Augé (Caen, France) (CT-18)**

*Swift heavy ion irradiation on frozen nitrogen/methane ices: toward understanding formation of ultracarbonaceous Antarctic micrometeorites*

11.40 – 12.00 **Fabrice Duvernay (Marseille, France) (CT-19)**

*Low Temperature Chemistry in Cometary Ice Analogues*

12.00 – 12.20 **André Canosa (Rennes, France) (CT-20)**

*Gas Phase Reaction Kinetics of Complex Organic Molecules Investigated by the CRESU Technique between 22 and 64 K*

12.20 – 12.40 **Riccardo Spezia (Evry, France) (CT-12)**

*Ion-molecule reaction dynamics simulations to model the formation of organic molecules in the interstellar medium : from formamide to glycine*

13.00 – 14.00 - **Lunch**

14.00 – 19.30 - **Excursion**

19.30 – 22.30 – **Gala diner**

## **Thursday 7<sup>th</sup> July**

### **Session : Biological Systems**

**Chair: György Tarczay (Budapest, Hungary)**

9.00 – 9.35 **Yunjie Xu (Edmonton, Canada) (IL-8)**

*Matrix Isolation-VIBRATIONAL CIRCULAR DICHROISM Spectroscopy of Chiral Molecular Clusters*

9.35 – 10.10 **Michel Mons (Orsay, France) (IL-9)**

*Local structures in a protein chain: Interplay between main-chain and side-chain H-Bonding patterns as revealed by gas phase laser*

10.10 – 10.30 **Satchin Soorkia (Paris, France) (CT-22)**

*Gas phase experiments on oxygen-binding hemoproteins*

10.30 – 10.50 **Kaoru Yamazaki (Sapporo, Japan) (CT-23)**

*Intersystem crossing pathway of protonated phenylalanine/serine dimers*

10.50 – 11.10 - **Coffee break**

### **Session : Chemical Reactions, Intermediates and Unstable Species (1)**

**Chair: Tigran Kurtikyan (Yerevan, Armenia)**

11.10 – 11.45 **Helen Joly (Sudbury, Canada) (IL-10)**

*Novel Organometallic Radicals Characterized by Matrix Isolation Electron Paramagnetic Resonance Spectroscopy*

11.45 – 12.05 **Igor Reva (Coimbra, Portugal) (IT-14)**

*Photochemistry of Matrix-Isolated Isoxazoles*

12.05 – 12.25 **Joel Mieres-Pérez (Bochum, Germany) (CT-24)**

*Nitrenes in Reactive Matrices – from Parahydrogen to Solid Oxygen*

12.25 – 12.45 **Maria-Natalia Esteves-Lopez (Marseille, France) (CT-25)**

*UV Photochemistry of Pyridine-Water Complex: Evidence of Water Dissociation*

13.00 – 14.00 - **Lunch**

14.00 – 16.30 - **Free Time**

**Session : Chemical Reactions, Intermediates and Unstable Species (2)**

**Chair: John McCaffrey (Maynooth, Ireland)**

16.30 – 16.50 **Sebastian Riedel (Berlin, Germany) (CT-26)**

*Fluorine-Rich Fluorides: New Insights into the Chemistry of Polyfluoride Anions*

16.50 – 17.10 **György Tarczay (Budapest, Hungary) (CT-27)**

*Formation of novel Si-bearing molecules in low-temperature SiH<sub>4</sub> matrices under electron irradiation conditions*

17.10 – 17.30 **Bing-Ming Cheng (Hsinchu, Taiwan) (CT-28)**

*Photolysis of Diborane (B<sub>2</sub>H<sub>6</sub>) Dispersed in Solid Ne at 3 K with Far-ultraviolet Light*

17.30 – 17.50 **Xuefeng Wang (Tongji, China) (CT-29)**

*Silicon Tetrahydroborate and Silylidene Dihydroborate: Matrix Infrared Spectra and DFT Calculations*

17.50 – 18.05 – **Break**

**Session: Astrophysical, astrochemical and atmospheric studies (3)**

**Chair: Tomonari Wakabayashi (Osaka, Japan)**

18.05 – 18.25 **Vladimir Feldman (Moscow, Russia) (CT-30)**

*Matrix isolation studies on the radiation-induced transformations of small molecules of astrochemical interest and their complexes*

18.25 – 18.45 **Rudy Delaunay (Caen, France) (CT-31)**

*Ion-induced reactivity in cold clusters of Polycyclic Aromatic Hydrocarbon molecules*

18.45 – 19.05 **Jean-Claude Guillemin (Rennes, France) (CT-32)**

*Gas-Phase and Solid-Phase Chemistry. From the Laboratory to the Interstellar Medium*

19.30 – 20.30 - *Diner*

20.30 – 22.30 – **Pimentel Prize, Poster Prize & Committee election**

## ***Friday 8<sup>th</sup> July***

### **Session : Materials, Cryocrystals and Clathrates**

***Chair: André Canosa (Rennes, France)***

9.00 – 9.35 **Steven Sibener (Chicago, USA) (IL-11)**

*Energetic Gas-Surface Encounters at Ice Interfaces*

9.35 – 9.55 **Tatyana Shabatina (Moscow, Russia) (IT-15)**

*Cryosynthesis of hybrid nanomaterials*

9.55 – 10.15 **Arnaud Desmedt (Bordeaux, France) (IT-16)**

*Transport and selectivity properties of clathrate hydrates*

10.15 – 10.35 **Sylvain Picaud (Besançon, France) (CT-33)**

*Monte Carlo Simulations of Gas Trapping in Clathrate Hydrates at Low Temperatures*

10.35 – 11.00 **Mika Petterson (Jyväskylä, Finland) (CT-34)**

*Ultrafast dynamics of thiolate-protected gold nanoclusters - Molecules or metals?*

10.55 – 11.15 - ***Coffee break***

11.15 – 12.15 **Committee election results – Presentation of CPLT 2018 and Closing session**

13.00 – 14.00 - ***Lunch***

14.00 **Departures**

# **LECTURES AND TALKS**

**IL : Invited Lecture**

**IT : Invited Talk**

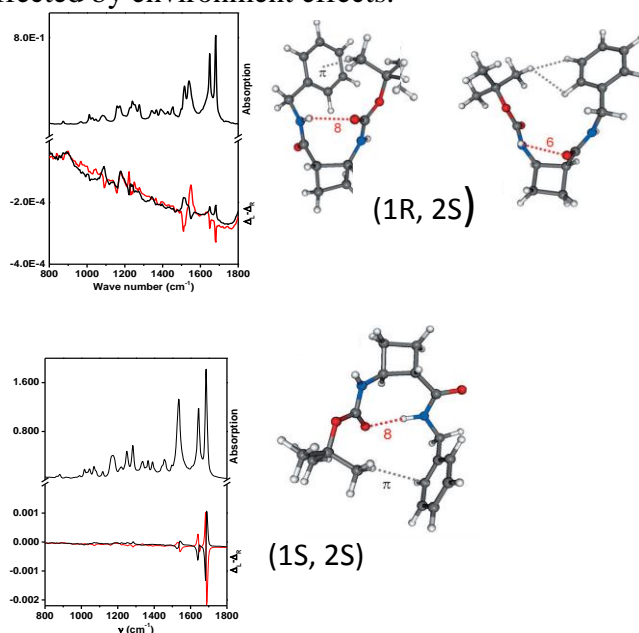
**CT : Contributed Talk**

# CHIRALITY EFFECTS IN THE STRUCTURE OF $\alpha$ - AND $\beta$ -PEPTIDES: CONFORMER-SPECIFIC JET-COOLED SPECTROSCOPY AND VIBRATIONAL CIRCULAR DICHROISM STUDIES

A.F. Perez-Mellor,<sup>a)</sup> I. Alata,<sup>a)</sup> V. Lepère,<sup>a)</sup> K. Le Barbu-Debus,<sup>a)</sup> M. Alauddin,<sup>b)</sup> E. Gloaguen,<sup>b)</sup> V. Brenner,<sup>b)</sup> B Tardivel,<sup>b)</sup> M Mons,<sup>b)</sup> V. Declerck,<sup>c)</sup> D. J. Aitken<sup>c)</sup> A. Zehnacker<sup>a)</sup>

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The importance of chirality in shaping molecular structure and interactions has prompted numerous structural studies. Among them, laser spectroscopy experiments in isolated conditions have brought structural information on chiral molecules and complexes.<sup>1,2</sup> Vibrational Circular Dichroism (VCD) is exquisitely sensitive to conformation or solvent effects and provides therefore an additional powerful tool to get structural information on chiral species at the molecular level.<sup>3</sup> It has been applied to many systems, including molecules isolated in cryogenic matrices.<sup>4</sup> We present here a study of flexible biomolecules, including natural  $\alpha$ -dipeptides as well as tailor-made  $\beta$ -peptide building blocks, with chiral centres of identical or opposite chirality. The experiments rest on conformer-specific laser spectroscopy in jet-cooled conditions, at low temperature, and VCD in the condensed phase, at room temperature, and are interpreted by means of DFT calculations. We will discuss how the structural data obtained from jet-cooled experiments<sup>5</sup> can be used to interpret the VCD spectra and how the structures are affected by environment effects.



*Condensed –phase Vibrational Circular Dichroism spectrum of 2-aminocyclobutanecarboxylic acid derivatives and structures determined by IR-UV double-resonance spectroscopy in jet-cooled conditions*

## References :

- [1] Zehnacker A., International Reviews in Physical Chemistry 33, 151 (2014)
- [2] Zehnacker A. & Suhm M. A., Angewandte Chemie-International Edition 47, 6970, (2008)
- [3] Keiderling T. A., Current Opinion in Chemical Biology 6, 682, (2002)
- [4] Tarczay G., Magyarfalvi G. & Vass E., Angewandte Chemie-International Edition 45, 1775, (2006)
- [5] Alauddin M., Gloaguen E., Brenner V., Tardivel B., Mons M., Zehnacker-Rentien A., Declerck V. & Aitken D. J., Chem. Eur. J 21, (2015)

## **PROBING THE ULTRAFAST DYNAMICS OF MOLECULAR SYSTEMS FROM THE IR TO THE X-RAY RANGE**

**M. Chergui**

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The advent of femtosecond (fs) laser technology some twenty five years ago opened a whole new era in Science because of its ability to probe in “real-time” nuclear motion in molecules, crystals, liquids and proteins. A full picture of the photoinduced physical and (bio)chemical dynamics requires interrogating different observables of the system under study. I will present different results obtained using tools as diverse as ultrafast visible spectroscopies (absorption and fluorescence), ultrafast X-ray spectroscopies, 2-dimensional Ultraviolet spectroscopy, and visible pump/infrared probe tools to probe the dynamics of molecular systems. I will also discuss future perspectives that are arising from the ultrafast methods developments in recent years.

## AMINO ACIDS IN SOLID PARAHYDROGEN

**Takamasa Momose**

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The existence of amino acids in interstellar space has been discussed for many years, but it is still under debate. The effect of UV radiation on amino acids may be one of the keys for the search of interstellar amino acids, since strong UV radiation in interstellar space may change the chemical form of these amino acids. In this experiment, conformational compositions of a couple of amino acids and the effect of UV photolysis were investigated via matrix-isolation FTIR spectroscopy and quantum chemical calculations. Solid parahydrogen was used as the matrix. In comparison with amino acids isolated in Ar matrices, it was found that more conformers were detected in as-deposited sample in parahydrogen than in Ar. Furthermore, more enhanced correlation between conformational ratio and sublimation temperature was found for some amino acids isolated in parahydrogen. UV photolysis of amino acids in parahydrogen resulted in not only its conformational changes, but also photodissociation into a CO<sub>2</sub> molecule and fragments. On the other hand, the linewidths of infrared transitions are significantly broader in parahydrogen than in Ar, in general. Advantages and disadvantages for using parahydrogen matrices for the host of matrix isolation spectroscopy of amino acids will be discussed.



# X-RAY COHERENT DIFFRACTIVE IMAGING OF QUANTUM VORTICES IN SUPERFLUID HELIUM DROPLETS

**A.F. Vilesov**

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Single-shot femtosecond X-ray coherent diffractive imaging has been used to study vorticity in single, isolated, superfluid  $^4\text{He}$  droplets ( $D=200\text{-}2000\text{ nm}$ ,  $T = 0.4\text{ K}$ ). [1] As indicated by large centrifugal deformations, the droplets' angular velocities span a range from vanishing to those close to the disintegration limit. For visualization, Xe atoms were added to the droplets where they gather in cores of the vortices forming nm-thin filaments. The formation of lattices containing hundreds of quantum vortices inside the droplets is confirmed by observing characteristic Bragg patterns from the trapped Xe clusters. In order to obtain images of single vortices from the diffraction images phase retrieval algorithm technique was developed, which relies on the interference of unknown scattering from the filaments with known scattering from the droplet itself. This noise robust, fast converging algorithm can be used to determine the absolute complex density of the scattering objects encapsulated in nanodroplets. [2] Excessive doping by Xe changes equilibrium arrangement of vortices in the droplet and leads to stabilization of widely spaced configurations. Evidence for non-stationary vortex dynamics comes from observations of asymmetric formations of vortices in some droplets. This collaborative work was performed at Linac Coherent Light Source, the free electron laser within SLAC National Accelerator Laboratory. [1]

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# INFRARED SPECTRA OF PROTONATED SPECIES ISOLATED IN PARA-HYDROGEN MATRICES

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We have recently developed a new method to investigate the infrared (IR) spectra of protonated species by using electron bombardment during deposition of a *para*-hydrogen (*p*-H<sub>2</sub>) matrix.[1] The bombardment of *p*-H<sub>2</sub> with electrons produces H<sub>3</sub><sup>+</sup> and H via H<sub>2</sub> + e<sup>-</sup> → H<sub>2</sub><sup>+</sup> + 2e<sup>-</sup> and H<sub>2</sub><sup>+</sup> + H<sub>2</sub> → H<sub>3</sub><sup>+</sup> + H reactions. Proton transfer from H<sub>3</sub><sup>+</sup> to embedded molecules produces protonated species trapped in a *p*-H<sub>2</sub> matrix. This method has been applied to produce protonated polycyclic aromatic hydrocarbons (designated H<sup>+</sup>PAH) as well as proton bound rare-gas dimers [RgHRg']<sup>+</sup> (Rg, Rg' = Xe or Kr), among which a asymmetric protonated rare-gas dimer XeHKr<sup>+</sup> was characterized for the first time.[2] The protonated species are thought to exist in interstellar media because of abundant proton sources such as H<sub>3</sub><sup>+</sup>. Of particular interest is H<sup>+</sup>PAH, which might contribute to the so-called interstellar unidentified infrared (UIR) emission bands. Our previous work on protonated pyrene and coronene [3,4] indicates that, as the size of aromatic ring increases, the spectral shifts of IR bands point the correct direction toward the positions of the UIR bands. When we extended the work to protonated ovalene (7-C<sub>32</sub>H<sub>15</sub><sup>+</sup>), we found a close resemblance between the laboratory IR spectrum and the UIR emission bands,[5] indicating that H<sup>+</sup>PAH can contribute to the UIR emission and protonated ovalene might be an important member of the interstellar PAH inventory.

We also applied this method to smaller molecules such as carbonyl sulfide (OCS), which is known to exist in interstellar media, including its protonated form. The OCS molecule has two possible protonation sites, leading to HOCS<sup>+</sup> and HSCO<sup>+</sup> isomers. Both HOCS<sup>+</sup> and HSCO<sup>+</sup> have been observed with microwave spectroscopy,[6] but only the OH stretching mode of HOCS<sup>+</sup> has been identified with gas-phase IR spectroscopy.[7] We identified three IR absorption lines of HOCS<sup>+</sup> and two of HSCO<sup>+</sup> isolated in *p*-H<sub>2</sub>. Assignments were achieved according to expected chemistry and comparison between experimental spectra (in *p*-H<sub>2</sub>, *n*-H<sub>2</sub>, and *n*-D<sub>2</sub>) and theoretical predictions. We found a significant matrix shift for the OH stretching mode of HOCS<sup>+</sup>: 2945.5 cm<sup>-1</sup> in *p*-H<sub>2</sub> and 3435.16 cm<sup>-1</sup> in gas-phase. This shift is due to proton sharing between HOCS<sup>+</sup> and the *p*-H<sub>2</sub> host. The corresponding shift for HSCO<sup>+</sup> is much smaller than that for HOCS<sup>+</sup>; possible explanations will be presented. If time permits, we will also present the experimental results on protonated CS<sub>2</sub>, N<sub>2</sub>O, and other species.

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# REACTIVITY OF HYDROGEN ATOMS IN SOLID PARAHYDROGEN: THE H + N<sub>2</sub>O REACTION

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Our group utilizes para-hydrogen (pH<sub>2</sub>) matrix isolation spectroscopy to study a variety of phenomena related to the in situ photochemistry of dopant species. In 2013 we published a short communication [1] on the 193 nm in situ photolysis of N<sub>2</sub>O in solid pH<sub>2</sub> over the temperature range between 1.6 and 4.3 K. In this work we showed that hydrogen atoms (H atoms) produced as byproducts of the in situ photochemistry continue to react with unphotolyzed N<sub>2</sub>O for hours after the photolysis laser is stopped. We attributed these slow reactions to mobile H atoms that can diffuse through the pH<sub>2</sub> solid even at the lowest temperatures studied. What originally puzzled us, however, was the H atom reactions only occur at temperatures below ca. 2.4 K, not at higher temperatures. In the communication [1], we speculated this strange temperature behavior was caused by a kinetic mechanism that involves a weakly bound pre-reactive complex of the reagents (H---N<sub>2</sub>O). At low temperature the pre-reactive complex cannot dissociate and thus once formed can only lead to reaction, while at higher temperatures the pre-reactive complex can dissociate back to isolated reactants and this effectively competes with the tunneling reaction. Since this time we have performed a number of new experiments and analysis on this reaction. We now believe the strange temperature dependence to the reaction is related to changes in the N<sub>2</sub>O solvation environment that can turn on and off access of the H atom to N<sub>2</sub>O. Thus, what we are measuring is not related to an increase in the reaction rate constant at low temperature, but rather changes in the N<sub>2</sub>O solvation environment that either permit reaction or shield the N<sub>2</sub>O from the incoming H atom. Earlier investigations of the high resolution infrared spectroscopy of N<sub>2</sub>O trapped in solid pH<sub>2</sub> first showed that the N<sub>2</sub>O spectrum changes drastically over the 1.8 to 4.9 K temperature range [2]. There appear to be two major solvation environments around the N<sub>2</sub>O and the population of these different “matrix sites” depends on temperature. This interpretation of the data implies the N<sub>2</sub>O solvation site populated at high temperature is not conducive to reaction with an H atom. We are currently trying to model the structures of these two solvation sites and will present our most recent findings at the meeting. If correct this interpretation of the data suggests that H atom reactions in solid pH<sub>2</sub> can be highly selective and that intermolecular forces can steer the chemistry into different pathways. We perform these studies in collaboration with the Professor Hinde’s group at the University of Tennessee who are experts in the many-body quantum mechanics of chemical species trapped in pH<sub>2</sub> quantum matrices.

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# MODELING MOLECULAR CLUSTERS/COMPLEXES IN A RARE GAS ENVIRONMENT USING A QUANTUM-CLASSICAL SCHEME

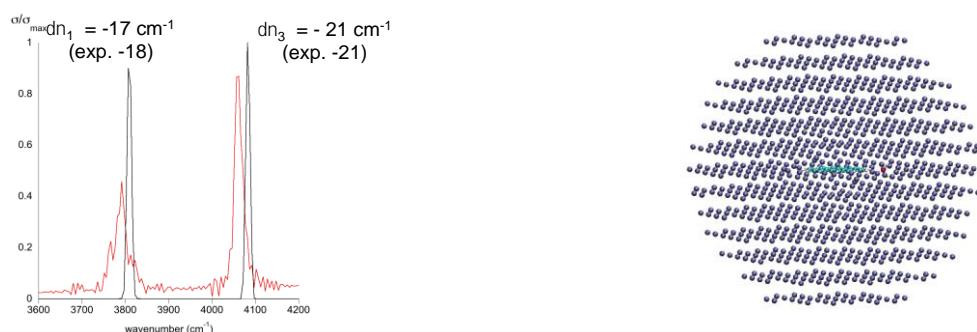
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A new hybrid quantum-classical scheme has been developed to describe the interactions between a molecular cluster/complex and a rare gas environment. In this scheme, the quantum description of the electronic structure of the active system is based on a tight-binding approximation of the density functional theory, with self-consistency regarding the charges (SCC-DFTB [1]). The rare gas environment is described *via* a classical atom-atom potential (Force Field or FF). The interactions between the active system and the atoms of the cryogenic environment are represented by local anisotropic matricial electron-atom operators, as well as by polarisation and dispersion contributions. The applications involve hydrocarbons, water clusters and hydrocarbon/water complexes in interaction with argon clusters or matrices. Structural and energetic data are obtained *via* either local or global geometry optimizations. Molecular dynamics studies in the ground-state enable the determination of finite temperature infrared (IR) spectra.

The SCC-DFTB/FF model was benchmarked on small systems ( $C_6H_6$ ,  $H_2O$ ) in interaction with argon atoms and clusters [2,3]. Enabling to treat various electronic situations, it allows in particular to determine the evolution of the ionization potentials of the active system as a function of the inert cluster size. The model has then been applied to the water molecule (see Figure 1 Left) and water nano-clusters ( $H_2O$ )<sub>n</sub> (n=2-6) embedded in argon matrices, represented by finite size crystal pieces of the face centered cubic lattice. Further investigations are currently carried out on polycyclic aromatic hydrocarbons (PAHs) and PAH- $H_2O$  complexes embedded in argon matrices (see Figure 1 Right). Structural and energetic data, as well as finite-temperature IR spectra, are discussed in the light of experimental data or other theoretical results available in the literature.

All developments and applications have been achieved within the deMonNano code [4], in the context of an ANR collaborative project (ANR PARCS no 13-BS08-0005) involving the experimental group of J. Mascetti (Institute of Molecular Sciences, Bordeaux I University).



**Figure 1: IR spectra at 10 K of (H<sub>2</sub>O)/Ar<sub>428</sub> (left) vs H<sub>2</sub>O ; (C<sub>24</sub>H<sub>12</sub>)(H<sub>2</sub>O)/Ar<sub>950</sub> optimized geometry (right)**

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# INFRARED SPECTROSCOPY OF ACETYLENE-RARE GAS COMPLEXES IN HE-NANODROPLETE

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Superfluid He nanodroplet provides an ideal environment for high resolution spectroscopic studies of species from a well-defined quantum state as it combines the advantages of supersonic free-jet (isolation and minimum environmental perturbation) and matrix (very low temperature, 0.38 K) spectroscopies. He nanodroplet is a fragile cluster with He-Cluster binding energy of 5 cm<sup>-1</sup>. Such characteristics are exploited for a long time by the Helium nanodroplet isolation (HENDI) technique to provide direct infrared absorption spectra of a wide range of molecules [1, 2]. The present work reports such measurements for documenting the high resolution rovibrational spectroscopy of Acetylene and Acetylene-rare gas complexes (C<sub>2</sub>H<sub>2</sub>; C<sub>2</sub>H<sub>2</sub>-Ne, Ar, Kr and Xe) in the  $\nu_3$  region of the asymmetric C-H stretch (Figure 1). This spectral region is interesting because a Fermi resonance exists between  $\nu_3$  and  $\nu_2+\nu_4+\nu_5$  modes which splits the  $\nu_3$  modes in a dyad. Only the absorption spectrum of pure acetylene hosted in helium droplets was reported in the literature [3]. Although the spectroscopy of acetylene-rare gas complexes is available in supersonic jet experiments for some rare gases (Ne, Ar), it was not reported in He droplets [4, 5]. This work addresses several points, in particular whether the Fermi resonance is affected by the presence of the rare gas and whether the equivalence between the two H-atoms of C<sub>2</sub>H<sub>2</sub> remains preserved after complexation.

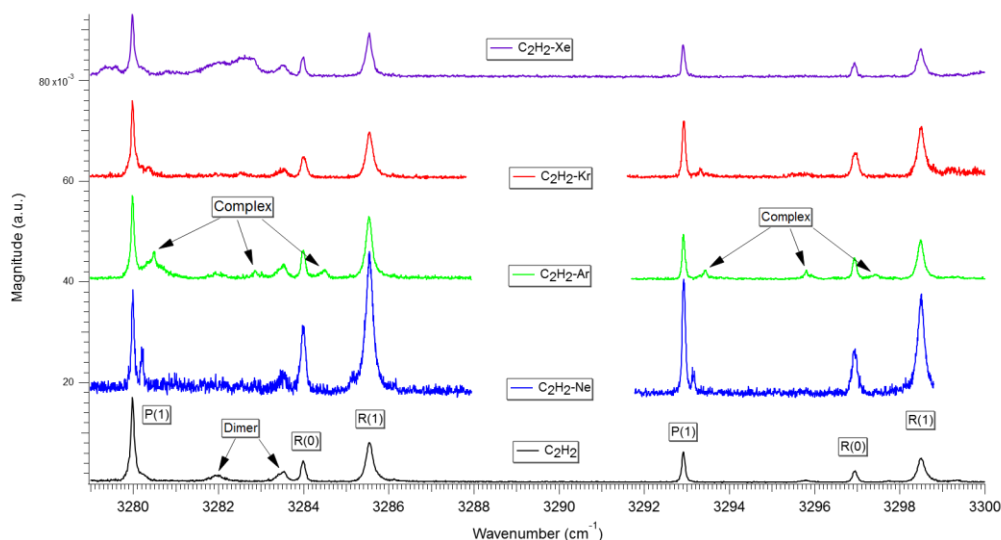


Figure 1 : Infrared absorption spectrum of acetylene and acetylene-rare gas complexes (as labeled in the figure). The spectra on the left and right side of the figure correspond to the lower and upper components of the dyad due to the Fermi resonance. (conditions:  $T_0 = 10.8$  K,  $P_0 = 8$  bars, nozzle diameter,  $D = 5$   $\mu$ m)

## References :

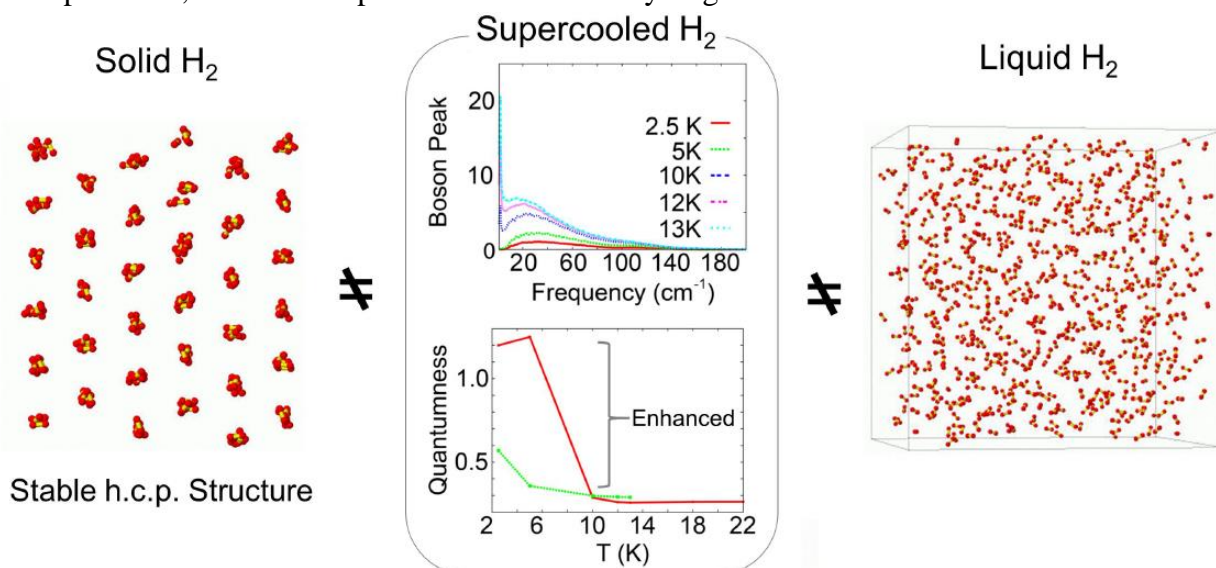
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# DISTINCT STRUCTURAL AND DYNAMICAL DIFFERENCE BETWEEN SUPERCOOLED AND NORMAL LIQUIDS OF HYDROGEN MOLECULES

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Nuclear quantum effects of hydrogen nuclei such as zero-point energy and nuclear delocalization significantly influence dynamical and structural properties of condensed H<sub>2</sub> systems as reflected in the broad radial distributions and rapid diffusions even at low temperatures. We will report the first computational study on real-time dynamics of vapor-pressure H<sub>2</sub> molecular liquids, solids, and supercooled liquids exhibiting strong nuclear quantum effects which have been hardly accessible by use of previous computational and theoretical methods like density functional theory and semiquantum molecular dynamics simulations with path integrals.[1-5] For example, in vapor-pressure H<sub>2</sub> solids, the hexagonal close-packed lattice structures and the stable lattice phonon modes with the reasonable frequency were successfully reproduced by the current method. The discrete jumps of the librational frequency, average H-H bond length as well as the H-H vibration frequency at the liquid-solid phase transition were computationally found and physically rationalized in comparison with liquid and high-pressure solid H<sub>2</sub> systems.[2] Further, we recently realized supercooled hydrogen liquids which have not been stably observed in low-temperature experiments, and demonstrated that the hydrogen supercooled liquid is not a simply cooled liquid but rather exhibits intrinsic structural and dynamical properties including a precursor of tunneling and superfluidity of hydrogens which neither normal hydrogen liquid nor solid possesses.[1] All of the insights and information we obtained will provide a milestone for planning low-temperature experiments of metastable hydrogen systems like glassy and superfluid states and for identifying and characterizing various unknown hydrogen phases at low temperatures, which will open a new avenue of hydrogen material research.



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# FREQUENCY AND TIME-DOMAIN SPECTROSCOPY OF MOLECULES IN SMALL HELIUM CLUSTERS AND BULK HELIUM

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Spectroscopy of molecules in helium clusters and droplets has attracted great interest. Detailed insight such as the interaction with a superfluid at the nanometre scale has been gained from the availability of rotationally resolved spectral line data for a wide range of molecules [1]. However, our understanding of molecule-helium interaction remains incomplete, for example, the physical origin of the observed line broadening and line shapes.

In this presentation I will report on a novel experimental methodology to resolve these issues. We have excited a beam of small C<sub>2</sub>H<sub>2</sub>-He<sub>n</sub> clusters non-resonantly with intense femtosecond laser radiation and probed the state of alignment of the C<sub>2</sub>H<sub>2</sub> molecules as a function of time. Using this technique, called impulsive alignment, it is possible to generate rotational wavepackets and probe their propagation in the time domain. A Fourier-transform of the time-spectrum yielded the *pure* complete rotational spectrum of C<sub>2</sub>H<sub>2</sub>-He in excellent agreement with theory [2].

In another experiment bulk helium was electronically excited using a corona discharge and the fluorescence spectrum was measured as a function of temperature and pressure. Intense fluorescence in the visible region showed the rotationally resolved  $d^3\Sigma^{+,u} \rightarrow b^3\Pi_g$  transition of He<sub>2</sub><sup>\*</sup>. With increasing pressure, the rotational lines merged into single features. The observed pressure dependence of linewidths, shapes and lineshifts established that within liquid helium excimers are either solvated, and cold, or ‘boiling’ within rotationally hot gas pockets. Lineshift coefficients revealed distinct regions that we attribute to phases of coexistence and separation of excimer-helium mixtures [3].

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# SPECTROSCOPY OF $\text{Ba}^+\text{He}$ EXCIMER: FIRST OBSERVATION OF BOUND-BOUND TRANSITIONS BETWEEN ELECTRONICALLY EXCITED STATES

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We present an experimental and theoretical study of the emission and absorption spectra of the  $\text{Ba}^+$  ions and  $\text{Ba}^+\text{He}$  excimer quasimolecules in a cryogenic Ba - He plasma. We observe several new spectral features in the emission spectrum which we assign to the electronic transitions between the bound states of the excimer correlating to the  $6\ ^2\text{P}_{3/2}$  and  $5\ ^2\text{D}_{3/2,5/2}$  states of  $\text{Ba}^+$ . The resulting  $\text{Ba}^+(5^2\text{D}_j)\text{He}$  is a metastable electronically excited complex with electronic orbital angular momentum  $L=2$ , thus expanding the range of known metal-helium quasimolecules. This system might be suitable for high-resolution spectroscopic studies and for the search for new polyatomic exciplex structures.

Spectroscopy of metal-helium excimers and exciplexes in a cryogenic He environment is an important and well-established topic at the intersection of atomic physics and chemistry at low temperatures. Usually, a quasimolecule is formed when a metal atom is excited to a P state and one or several He atoms approach it along the nodal line or the nodal plane of the valence electron orbital. In that configuration, the Pauli repulsion between the valence electron of the metal atom and closed electronic shells of He atoms plays no role and a bound state can be formed due to the attractive van der Waals interaction. The most characteristic feature of these complexes is their strong bound-free transitions towards the unbound electronic ground state that are spectrally very broad and strongly red-shifted with respect to the corresponding transitions of the free metal atoms. A quasimolecule formed by an electronically excited  $\text{Ba}^+(6\ ^2\text{P}_{3/2})$  ion and a ground-state He atom belongs to the class of metal-He excimers [1]. In addition,  $\text{Ba}^+$  ion possesses two low-lying electronic states:  $5\ ^2\text{D}_{3/2}$ ,  $5\ ^2\text{D}_{5/2}$  which are also able to bind He atoms.

Our assignment of the newly discovered bands is based on a theoretical model that uses *ab initio*  $\text{Ba}^+ - \text{He}$  pair interaction potentials from [2] with the spin-orbit coupling introduced by a standard method. We obtain eigenenergies and wavefunctions of the relevant vibronic states and compute Franck-Condon factors for all possible transitions between them. In total, there are four partially overlapping bands originating from the  $^2\Pi_{3/2}$  ( $6\ ^2\text{P}_{3/2}$ ) state and terminating at  $^2\Pi_{3/2}$  ( $5\ ^2\text{D}_{5/2}$ ),  $^2\Delta_{5/2}$  ( $5\ ^2\text{D}_{5/2}$ ),  $^2\Pi_{1/2}$  ( $5\ ^2\text{D}_{3/2}$ ), and  $^2\Sigma_{1/2}$  ( $5\ ^2\text{D}_{3/2}$ ) states. Our results demonstrate that there exists a large number of excimer states correlating to the  $5\ ^2\text{D}_{3/2,5/2}$  states of  $\text{Ba}^+$  that can be populated via the higher-lying  $6\ ^2\text{P}_{3/2}$  state. The new states are metastable since the corresponding electronic transitions towards the ground state are forbidden in a free ion. The observed bound-bound transitions are spectrally rather narrow, that opens a possibility to study excimer vibrations and rotations spectroscopically. The experiment is now in preparation to study the same transitions in superfluid He environment, where the formation of polyatomic exciplexes can be expected, in analogy with alkali metal-helium exciplexes [3]. Since the structure of those complexes is mainly determined by the shape of the electron density distribution of the metal atom [3], the electronic states with  $L=2$  are expected to give rise to a new family of complexes that are different from all known  $L=1$  exciplexes.

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# REVIEW OF COLD MOLECULES: TOWARDS A UNIVERSAL DECELERATOR FOR POLAR MOLECULES

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Cooling and trapping molecules at ultracold temperatures ( $<1$  mK) has been one of the most challenging tasks in experimental quantum physics for the last decade. A breakthrough in this field would give access to new quantum chemistry, studies of collective effects, metrology of fundamental constants, etc [1]. Unfortunately, the successful laser cooling technique is rarely helpful in this context. Therefore, direct cooling of molecules is generally based on supersonic expansion, cryogenic, or velocity filtering. But, these methods suffer from the fact that they produce cold sample of molecules moving at velocities of some hundred meters per second. Thus the problem to be solved has become: how to stop molecules in the laboratory frame? Many experiments use electromagnetic decelerators acting on the electric or magnetic permanent molecular dipole moment. We shall review here most of the used techniques and experiments performed with a focus on cold chemistry, on spectroscopy and on dynamics at low temperature [1].

However the existing methods have many drawbacks, such as high losses, cumbersome apparatus, ... We suggest a new approach consisting in electrically charging cooled neutral molecules, decelerating the resulting anions over short distances, and finally removing the extra electron by photo-detachment [2-3]. If such a demonstration is successful, it will open the way to produce any (even if very heavy) polar molecules at rest. At middle term perspective, we consider some “applications” such as creation of cold ion sources.

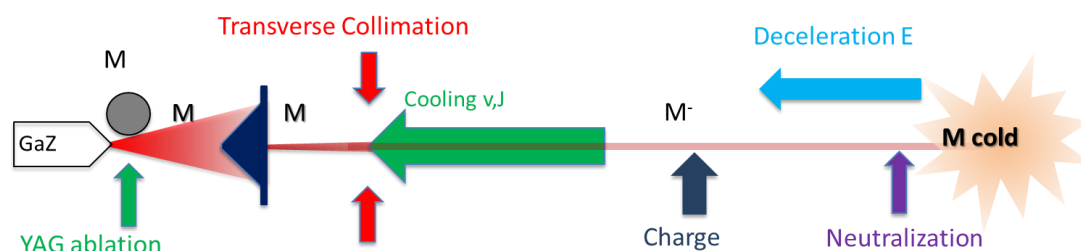


Figure : Schematic representation of the proposed apparatus: after collimation and ro-vibrational cooling [2] an incoming beam of cold molecules crosses a beam of Rydberg electron and are transformed into anions. The anions can be decelerated and possibly neutralized producing cold molecules at rest.

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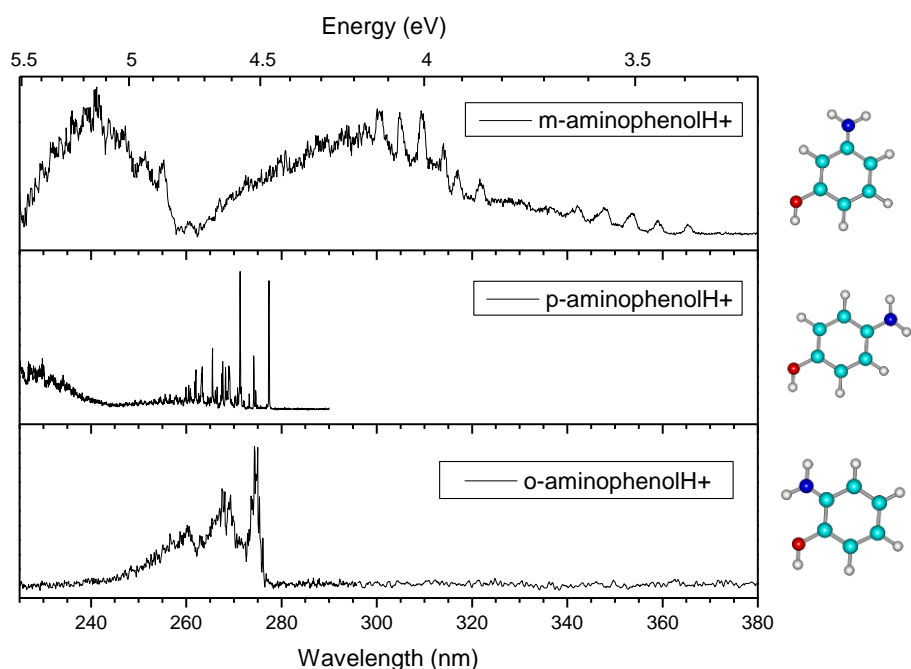
# COLD IONS, SPECTROSCOPY AND MASS SPECTROMETRY

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Mass spectrometry is a standard tool in analytical chemistry, which often uses ions issued from electrospray or MALDI sources, i.e. protonated species. In this case, the protonation site may not be so easy to determine. The best determination of the most stable protonation site in aromatic molecules relies nowadays on IR spectroscopy coupled to ab initio calculations. It appears that these methods are not necessarily unambiguous and cannot always be safely employed. We present a demonstration showing that electronic spectroscopy of cold ions complemented with ab initio calculations gives clear results on the protonation site<sup>1</sup>.

The cold ions UV spectroscopy can go one step further. In Tandem mass spectrometry (MS/MS or MS<sup>2</sup>) the identification of the ions is obtained by their fragmentation, followed by the fragmentation of their daughter ions. A similar method can be achieved adding the power of the optical spectroscopy of cold ion: UV spectroscopy of the cold parent ion, cooling of the fragment and UV spectroscopy of the cold daughter ion<sup>2</sup>. This adds two more dimensions (UV parent/UV fragment) in the ion analysis process.



photofragmentation spectra of cold protonated aminophenols

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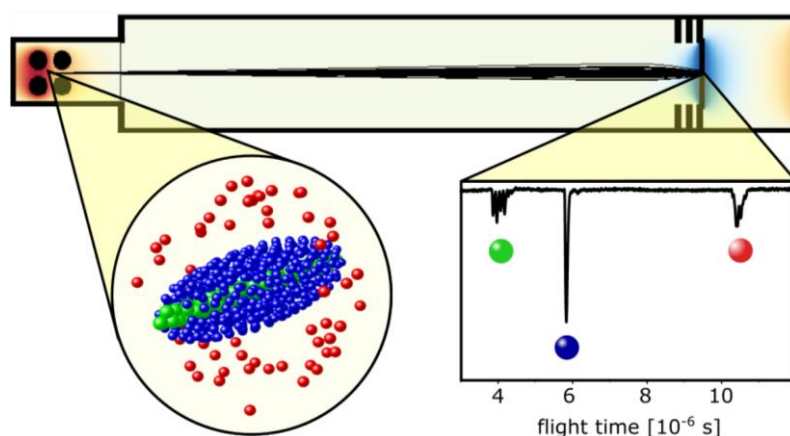
# CHARACTERISING COLD ION-MOLECULE REACTIONS IN COULOMB CRYSTALS

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Reactive collisions between Coulomb-crystallised ions held within a linear Paul ion trap and neutral molecules are observed, with the examination of a proof-of-principle charge exchange reaction between  $\text{Xe}^+$  and ammonia. A new mass-sensitive detection method is introduced, with the ejection of all ions onto an external detector at a selected time. This time-of-flight mass spectrometry (ToF-MS) approach removes ambiguity about the identities of dark ions: both the masses and relative numbers of all trapped species at the point of ejection can be ascertained directly from the ToF spectrum (see figure 1). A comparison is made with digital ejection ToF-MS and other mass-sensitive detection methodologies for ensembles of Coulomb-crystallised ions [1-2]. Combining the new ToF-MS detection capabilities with real-time imaging of the Coulomb crystal enables one to examine both the kinetics and the dynamics of ion-molecule reactions. Experimental results and detailed simulations indicate excellent detection efficiency, and the approach is broadly applicable to all ion-molecule reactions examined within an ion trap.



**Figure 1.** Experimental ToF traces are recorded following the ejection of multi-component Coulomb crystals from a linear Paul ion trap, where they pass through a flight tube and onto an external MCP detector [1]. The simulated crystal contains  $\text{Xe}^+$  ions (red),  $\text{Ca}^+$  ions (blue) and ammonia ions (green), with the peaks assigned to each of these species indicated on the experimental ToF trace.

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- [2] B. R. Heazlewood & T. P. Softley, *Annu. Rev. Phys. Chem.* **66**, 475 (2015)

# ORIENTATION DEPENDENT CHIRALITY AND HANDEDNESS OF A NANO-DIATOMIC

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Although chirality and handedness are known to play fundamental roles in chemistry, biology, physics, and life on earth, their rigorous quantification remains a challenge of current interest. Since Lord Kelvin's definition of structural chirality as broken mirror symmetry [1], there have been significant refinements and generalizations of the notion. It is understood that achiral objects may generate chiral response; that the handedness of the response may dependent on orientation or direction of observation; and chirality is connected, such that one may pass from left-handed to right-handed without ever going through an achiral state [2]. These manifestations are realized in Raman scattering measurements on isolated gold nanosphere dimers, which can be regarded as the nanoscale analog of a diatomic molecule. The seemingly achiral dimer shows dramatic circular dichroism that depends on the orientation of the dimer in the laboratory frame. In-plane rotation of the dimer by  $\pi/2$ , generates a continuous reversal in handedness, from R:L = 3:1 to R:L = 1:3 (R/L = right/left circularly polarized incident light). The phenomenon can be rigorously understood to arise from the collinear excitation of electric and magnetic dipole along the long axis of the dimer, and the recognition that the polar and axial vector nature of these excitations generates opposite parity and time-reversal symmetry. Among the fascinating implications are: a) giant magnetic fields can be generated in non-magnetic materials when  $2\pi\langle r \rangle/\lambda \sim 1$ , b) surface plasmons sustain the familiar angular momentum states,  $\Sigma$ ,  $\Pi$ ,  $\Delta$ , of diatomics, c) the hidden broken symmetry of the dimer arises from the potato-like chirality of nanospheres which splits the Kramers degeneracy of angular momentum states, d) connectedness of handedness and chirality is directly demonstrated in light scattering, and equated to measurement by a superposition of right and left circular polarizers (a laboratory in superposition), e) a quantum superposition of electric, magnetic and quadrupolar states of comparable magnitude generates local electromagnetic fields that are inaccessible classically, f) inelastic electronic Raman scattering allows the spectroscopy of plasmons on nanostructures as artificial molecules.

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# A NEW APPROACH TO NMR-MATRIX-ISOLATION SPECTROSCOPY

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Matrix-isolation is well known to be used in combination with UV, vibrational or ESR spectroscopy.<sup>[1]</sup> NMR spectroscopy on the contrary has rarely been applied for classical matrix-isolation studies in the past, due to the need of a very specific equipment.<sup>[2]</sup> Building a device capable of the condensation of a matrix-layer inside an NMR apparatus is a very difficult task. The use of magnetic metals, for example, is beyond discussion and last but not least installing a rotating cold tip, which is inevitable in order to spin the sample during the measurement, inside a shim coil is not a reasonable idea.

In the current work we start an entirely different approach. Instead of a matrix preparation inside the apparatus we produce our matrices in a dedicated matrix apparatus and transfer them under inert gas atmosphere into a conventional MAS NMR spectrometer. Adamantane has been used as a host for several species, including gases like Me<sub>3</sub>PF<sub>2</sub> and particularly reactive species, like white phosphorous (Fig. 1). With this technique several NMR experiments, including 2D and temperature dependent experiments can be applied to the matrix-samples.

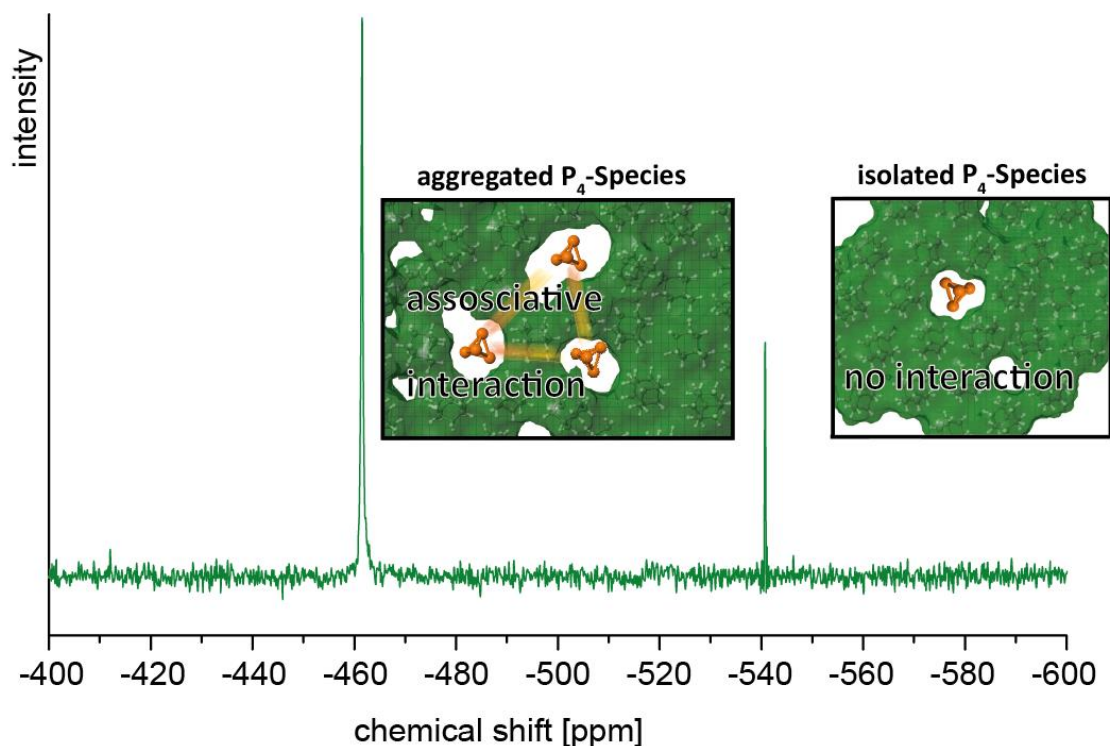


Fig. 1: NMR-Matrix-Isolation spectrum of white phosphorous.

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# A NEW LABORATORY APPROACH TO DETERMINE LOW-TEMPERATURE BRANCHING RATIOS : CHIRPED-PULSE IN UNIFORM FLOW

**Baptiste Joalland<sup>1,2</sup>, Chamara Abeysekara<sup>1</sup>, Lindsay N. Zack<sup>1</sup>, Nuwandi M. Ariyasingha<sup>1</sup>, Ian R. Sims<sup>2</sup>, Robert W. Field<sup>3</sup>, Arthur G. Suits<sup>1</sup>**

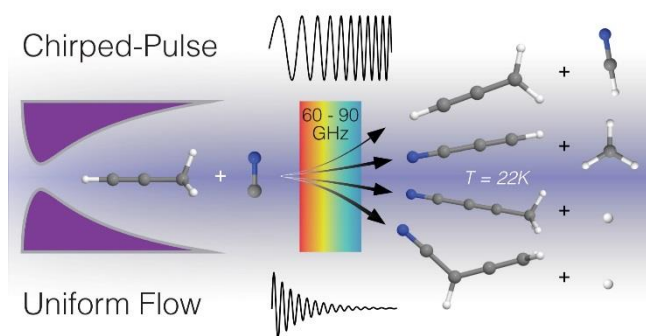
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The interplay between fundamental laboratory investigations, theoretical advances, and chemical modeling has led to tremendous progress in advancing the understanding of the complex gas-phase chemistry in the outer space. Measured or calculated reaction rates are incorporated into models to identify the key pathways that control reaction outcomes. However, experimental studies often report the rate of reactant disappearance, with product identity and branching largely unknown. This limitation arises from considerable

experimental challenges inherent to the quantitative detection of the full range of products of a given reaction, in particular for large polyatomic systems. To address these issues, we have developed a new approach incorporating chirped-pulse microwave spectroscopy [1] in low-temperature uniform supersonic flows (Chirped-Pulse in Uniform Flow, C-PUF [2,3]). This technique provides clear quantifiable spectroscopic signatures for polyatomic products in bimolecular or unimolecular reactions for virtually any species with a modest dipole moment. I will first illustrate the performance of this experimental set-up, and then discuss a number of challenges related to the collisional environment of the flow. A detailed study on the CN + C<sub>3</sub>H<sub>4</sub> reaction using the C-PUF technique at nearly 20 K will be presented, for which line intensities in the [60-90] GHz range have been used [4]. Overall, this work opens the door for applications up to the THz domain that can provide new spectroscopic data of unidentified species while providing kinetics and dynamics informations on their formation/destruction pathways.



*C-PUF can probe quantitatively all the products of multichannel reactions providing that these products exhibit permanent dipolar moments, as illustrated for the CN + C<sub>3</sub>H<sub>4</sub> reaction at 22K.*

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# LOW-TEMPERATURE INTERMOLECULAR BALANCES IN THE GAS PHASE

**Martin A. Suhm**

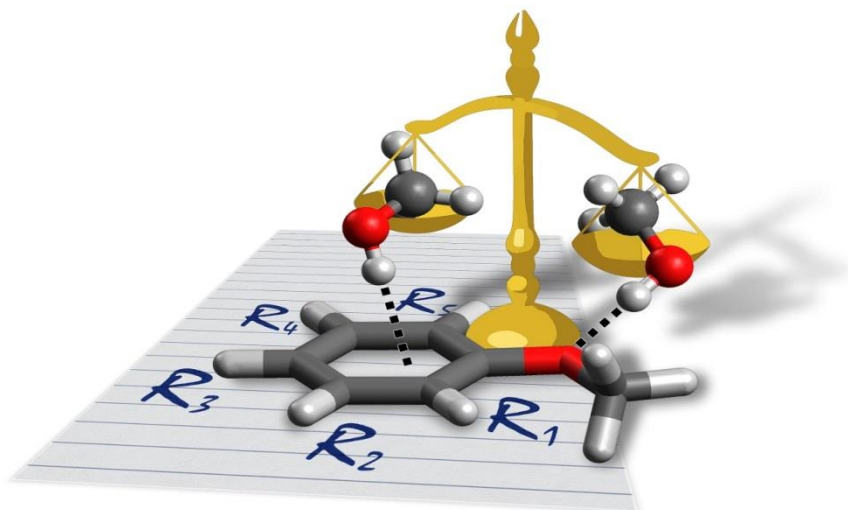
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The accurate experimental determination of intermolecular binding energies between organic molecules remains a major challenge. This is an important challenge, because theoretical models for biochemical docking preferences need to be tested for small prototype systems, if they are to be trusted in their predictions without relying on fortuitous error compensation. Cold molecular complexes allow for a focus on enthalpic rather than entropic aspects. If the molecules offer various binding sites with sufficiently different spectroscopic signature, the relative abundance of isomeric complexes at low temperature can provide an energy ranking of docking preferences. If the interconversion barriers between binding sites are low, supersonic jet cooling can achieve conformational temperatures well below 100 K. If the molecules are tuned by chemical substitution to invert their docking preference, one can thus hope for a rather sharp switch in docking conformation, with an energy resolution on the order of 1 kJ/mol.

We recently found that anisole fulfills all these requirements with respect to the docking of a protic solvent molecule like methanol to its ether oxygen or its polarizable  $\pi$  system [1]. By aromatic ring substitution, we were able to tune the docking preference from almost exclusively oxygen (in the parent compound) to mostly  $\pi$  (in heavily alkylated anisoles). The transition is so sharp that different quantum chemical methods and protocols can be rigorously tested with respect to their ability to reproduce the conformational switch [2]. This new kind of intermolecular balance experiment using FTIR spectroscopy will be described and extended to other O/ $\pi$  competition situations in the gas phase. The concept is reminiscent of room temperature solution phase intramolecular balance experiments based on NMR spectroscopy [3], which are closer to equilibrium but less accessible to accurate modeling.

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# CONFORMATIONAL PREFERENCES OF FLEXIBLE MOLECULES AND MOLECULAR COMPLEXES STUDIED BY FREE-JET ROTATIONAL SPECTROSCOPY: THE IMPORTANCE OF NON-COVALENT INTERACTIONS

Camilla Calabrese, Assimo Maris, Annalisa Vigorito, Walther Caminati and Sonia Melandri

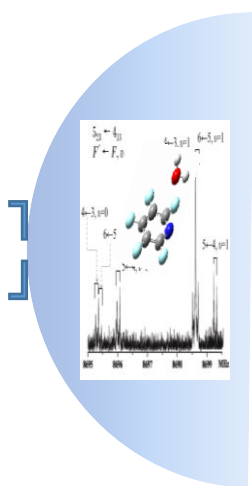
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Complex conformational surfaces originate from the flexibility of molecular systems due to the presence of multiple torsional degrees of freedom and different kinds of non bonding interactions occurring within the molecule or with the surroundings. The high number of low energy conformations and the presence of large amplitude motions taking place through shallow potential energy surfaces, represent a challenge for spectroscopic and computational methods.

Accurate data on the structures and conformations of complex organic molecules, biomolecules and molecular complexes can be obtained by rotational spectroscopy performed in the cold isolated conditions of a free jet expansion and these properties can be directly compared to the outcome of quantum mechanical calculations obtained in the same isolated conditions.

A few chosen examples of flexible organic molecules, bioactive molecules (drugs and their halogen substituted analogs), astrophysical targets and molecular complexes formed in supersonic expansions and characterized by rotational spectroscopy will be discussed.

It will be shown how non-covalent interactions compete to shape the conformational space of the molecules and the geometry of the complexes and how these interactions can be drastically changed through substitution (in particular halogen substitution) or complexation with solvent molecules. These effects can influence the flexibility (*e.g.* locking some particular conformation) or change the nature of the interactions (such as in the perfluorination effect).



# DYNAMICS AND PHOTODYNAMICS OF ACETYLACETONE ANALOGS IN CRYOGENIC MATRICES

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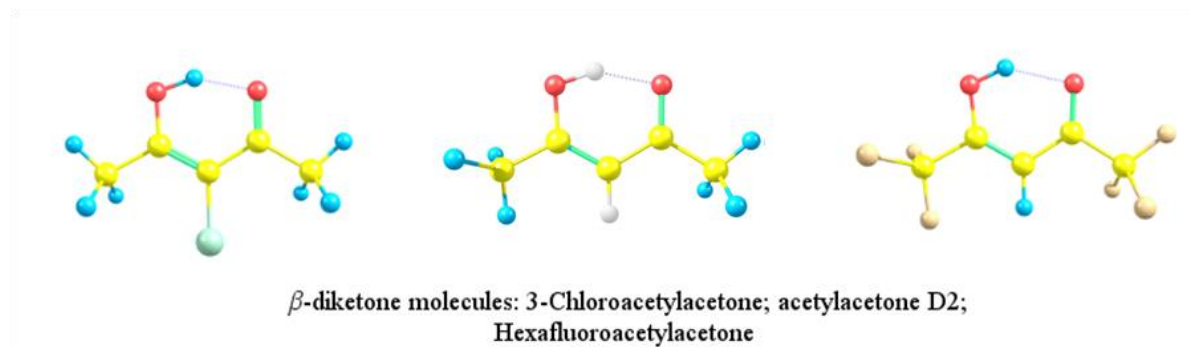
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Intramolecular hydrogen transfer and photo-isomerization are two of the main physico-chemical processes that often define the behavior of molecules of biological interest. In the present work we choose the  $\beta$ -diketone family as a model system (Figure) to study the influence of the isotopic substitution or the electronic structure on these two processes, using vibrational and electronic spectroscopies in Neon, Nitrogen and *para*-Hydrogen matrices.

Acetylacetone, the simplest member of this family was previously studied by our group<sup>1,2</sup>. We will present the extension of this research which includes different analogs of this molecule where either the isotopic composition or the electronic structure changes. In the first case, double deuterated acetylacetone was used to determine the role of the hydrogen atom of the hydroxyl group in the isomer production after UV excitation. A big influence of tunnel effect in the final isomer composition of the system was found. Isomer interconversion after IR laser excitation on the first OD stretching harmonic is also discussed.

In the second case, we focus our attention in the study of structural but not electronic analogs of the original molecule, e.g.: hexafluoroacetylacetone and 3-chloro-acetylacetone. In these systems, different kinds of isomers were stabilized after electronic excitation compared to acetylacetone. Experimental results were supported with quantum chemical calculations.



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# ISOMERIZATION AND PHOTODECOMPOSITION OF ACETOHYDROXAMIC ACID IN ARGON MATRICES. FTIR AND THEORETICAL STUDIES

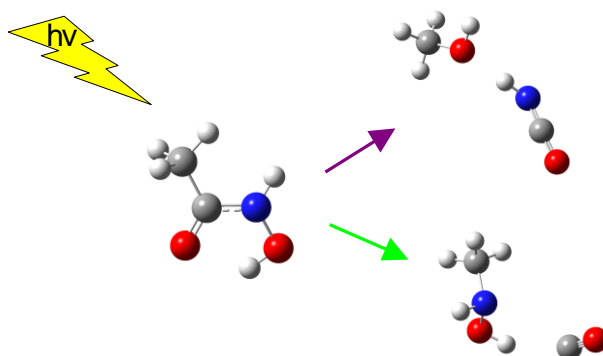
**Magdalena Saldyka**

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Hydroxamic acids (RCONHOH) exhibit a wide spectrum of biological activities [1] that stimulated progress in the chemistry of this class of compounds. They are known to be involved in iron transport phenomena, and are active as antibiotics, antitumor and antifungal agents, and specific enzyme inhibitors.[2] Extensive work has been carried out on the formation of hydroxamic acids, their reactions and structure in the ground state. However, the photochemical properties of hydroxamic acids are still not well recognized. The knowledge of the excited-state behaviour of hydroxamic acids is very important as many of these compounds, on exposure to sunlight, may be transformed to intermediates and photoproducts that are more toxic than parent compounds. According to the literature, photoirradiation of this class of compounds may lead to the initial photolytic scission of the N-O bond or to the acylaminoxyl radical generation.[3]

The literature reports on the structural properties of acetohydroxamic acid (AHA) inform that the stability of different conformers of AHA is strongly dependent on the environment. The studies on the tautomeric and structural properties of acetohydroxamic acid showed that AHA trapped from the gas phase into solid argon exists in the matrix predominantly as the 1Z keto isomer with intramolecular hydrogen bond. The 1E keto form is also present in equilibrium with the 1Z keto one, however its population is low with respect to the 1Z keto isomer.[4]

The importance of the AHA molecule for pharmaceutical applications triggers questions about the influence of UV-VIS irradiation on the structure and photochemical properties of AHA. The performed irradiation of acetohydroxamic acid isolated in argon matrices with full output of a Xe arc lamp leads to  $\text{HNCO} + \text{CH}_3\text{OH}$  and  $\text{CH}_3\text{NHOH} + \text{CO}$  product species which suggests the photodissociation channels proceeding through the scission of the N-O and C-N bonds. The identification of the products is confirmed by deuterium isotopic substitution and by the MP2/aug-cc-pVTZ calculations of the structure and infrared spectra of the identified systems.



The UV-VIS irradiation of the acetohydroxamic acid molecule isolated in solid argon leads to the formation of the  $\text{HNCO-CH}_3\text{OH}$  and  $\text{CH}_3\text{NHOH-CO}$  complexes.

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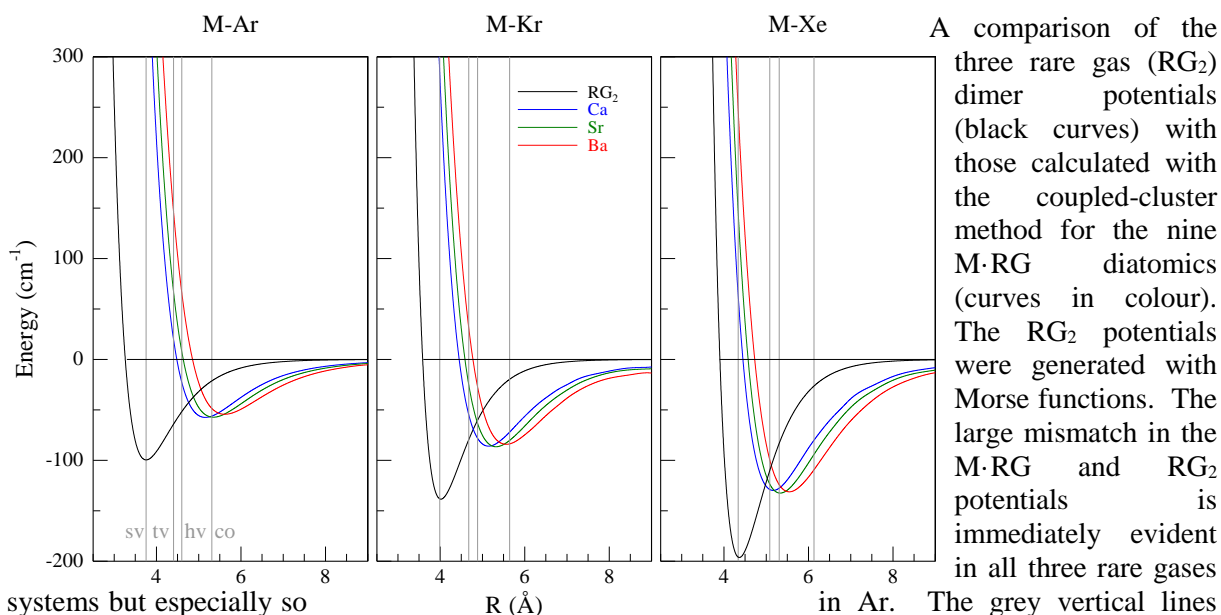
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## 2D-EE SPECTROSCOPY OF HEAVIER ALKALINE EARTH METALS ATOMS Ba, Sr AND Ca IN RARE GAS MATRICES – CCSD(T) CALCULATIONS AND ATOMIC SITE OCCUPANCIES

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A two dimensional excitation-emission (2D-EE) spectroscopic investigation of Sr/RG and Ba/RG solids (RG = Ar, Kr and Xe) has revealed [1] the presence of these heavy alkaline earth atoms in unusual sites in the solid rare gases. Sr, identified as an impurity in the barium metal used, provided the initial impetus to examine the lighter alkaline earth atom in addition to barium and calcium. An overview of the UV/Vis absorption and luminescence, recorded for well-isolated barium and strontium atoms, is presented in this study. Both of these metal atoms exhibit complex absorption profiles even after extensive annealing, behaviour that arises from their occupancy in multiple sites of isolation. 2D-EE luminescence plots are used to identify the sample conditions required to extract all the site-specific emission features. Selected excitation scans reveal exotic band-profiles indicative of the occupancy of some atoms in cylindrical sites. Contrary to a recent report [2], no evidence is found for the existence of barium cations [3] in any of the RG solids. To advance the discussion of the possible sites occupied in the three M/RG matrix systems, the ground state potential energy curves were computed for the M·RG diatomics at the coupled-cluster level of theory and are compared in the figure below.



systems but especially so in Ar. The grey vertical lines show the sizes of the cubic sites in the solid rare gases considered to accommodate a spherical guest atom. The energies of the M·RG interactions at these sites have been extracted and will be discussed. It is only in the case of Ca-Xe that a possibility exists for single vacancy (SV) site occupancy, which has a very slight (64 cm<sup>-1</sup>) repulsive interaction. For all the other M/RG systems multi-vacancy (TV, HV and CO) sites would be expected to occur.

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# SPECTROSCOPY OF ALKALI ATOMS IN Ar MATRIX

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Since the pioneering work of Andrews and Pimentel [1] numerous authors have investigated the absorption and luminescence of alkali atoms embedded in rare gas matrix [2-5]. The alkali atoms represent perhaps one of the most efficient probes of the host-guest interaction. They are indeed big atoms leading to an intense dipole absorption in the visible range favorable to experimentation. Moreover, the electronic structure of whole system is simple and it can be represented as a single electron on top of closed-shell atomic cores. We take advantage of this simplicity to develop an accurate model based on core-polarization pseudopotentials [6-8].

We present here a theoretical investigation of the spectroscopic properties of alkali atoms (Li, Na, and K) embedded in Ar matrix or deposited at the surface of Ar clusters. We determine the gas-to-matrix shifts associated to various bulk trapping sites. The remarkable agreement between our calculated results and the experimental spectra recorded by several authors allows us to establish a clear assignment of the observed spectra, which are made of contributions from crystalline sites on the one hand, and of grain boundary sites on the other hand. Our study reveals remarkably large Stokes shifts, up to  $9000\text{ cm}^{-1}$ , which could be observed experimentally to definitely identify the trapping sites. Our simulation is also successful to interpret recent photoexcitation experiments for K atoms trapped at the surface of large Ar clusters [9].

We have recently included in our model the spin-orbit coupling. For alkali atoms deposited at the surface of Ar and Ne clusters, the fine structure state population resulting from photoexcitation induced desorption is strongly sensitive to the relative strength of the spin-orbit coupling with respect to the binding energy of the alkali with the rare gas. Our simulation shows that a large amount of  $J=1/2$  population can be produced, which is consistent with a recent experimental observation for Na atoms deposited on He clusters [10].

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# MATRIX ISOLATION SPECTROSCOPY OF BISMUTH ATOMS AND MOLECULES

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Bismuth atoms and molecules have unique properties stemming from the atomic configuration of  $6p^3$  for showing large spin-orbit coupling in such a heavy element [1,2]. The mixing of different spin states results in relatively slow emission of photons from low-lying excited electronic states. We have investigated matrix-isolated bismuth atoms and molecules in solid neon matrices by laser-induced fluorescence (LIF) spectroscopy with selective excitation of Bi, Bi<sub>2</sub>, and Bi<sub>3</sub> [3-5].

Recent studies of the Bi/Ne system lead us to identify four low-lying excited states in the trimer, Bi<sub>3</sub>, through the observation of a series of new near-infrared (NIR) photoemission band systems in transition energies of 6600-13500 cm<sup>-1</sup>, exhibiting vibrational progression of 150 cm<sup>-1</sup> [4,5].

Bismuth dimer, Bi<sub>2</sub>, has extensively studied in its vapor phase, as is known for its strong emission lines in the A-X system with the origin band at 17720 cm<sup>-1</sup> [1]. We observed dispersed fluorescence spectra (DF) for the A-X transition in Bi<sub>2</sub> in solid Ne to obtain the ground-state vibrational frequency of 174 cm<sup>-1</sup>, reconfirming the result in the literature by Raman spectroscopy [2].

Photoexcitation of Bi atoms in solid Ne is followed by slow emission of photons from the low-lying electronic states stemming from the same  $6p^3$  configuration as that for the  $^4S_{3/2}$  ground state [3]. Figure 1 shows a typical time profile of the photoemission for the  $^2D_{5/2}$ - $^4S_{3/2}$  transition following the  $^2P_{1/2}$ - $^4S_{3/2}$  excitation. Rise and decay are apparent in the population at the upper  $^2D_{5/2}$  level.

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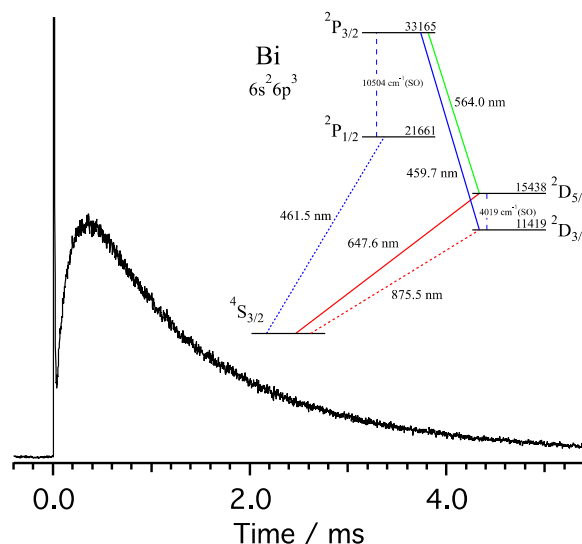


Fig. 1. Time profile of the  $^2D_{5/2}$ - $^4S_{3/2}$  emission following the  $^2P_{1/2}$ - $^4S_{3/2}$  excitation of Bi atoms in solid Ne. Rise and decay are apparent for the cascade of relaxation processes. Inset shows the level scheme for all the possible states from  $6p^3$  configuration of atomic Bi in the gas phase.



# STUDY OF WATER – ACETYLACETONE COMPLEXES BY THE MEANS OF MATRIX ISOLATION INFRARED SPECTROSCOPY

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Acetylacetone (AcAc) is a relatively simple organic compound whose structure is determined by an internal hydrogen bond. Such molecule is well suited for the model studies in order to understand properties and dynamic of internal hydrogen bond in complex systems e.g. biological molecules. One of the key questions in these studies is the influence of water molecules to the properties and dynamics of the internal hydrogen bond in the molecules. Acetylacetone has been studied extensively [1-2], but there is no comprehensive study on acetylacetone – water interactions. In this work we present study of acetylacetone – water (and their deuterated isotopologues) intermolecular complexes in different inert media.

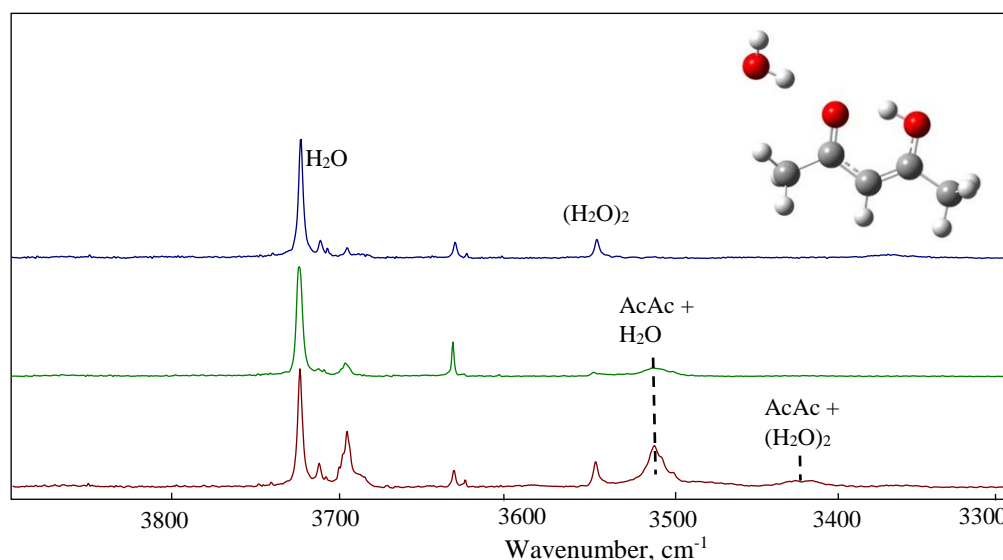


Fig 1. The most stable calculated structure of acetylacetone-water complex and experimental IR absorption spectrum in OH stretch region of pure water (top), acetylacetone water 1:1 (middle) and acetylacetone water 1:3 (bottom) isolated in nitrogen (1:500)

In the spectra of water and acetylacetone isolated in  $N_2$ , Ar, Ne, Xe matrices several additional bands are detected which cannot be assigned to the pure water or pure acetylacetone - indicating formation of acetylacetone-water complex. Of the particular interest are water molecule stretch vibrations. OH stretch band of water bound to acetylacetone molecule is observed at  $3513\text{ cm}^{-1}$  (in  $N_2$  matrix) close to the absorption of water trimer ( $3510\text{ cm}^{-1}$  [3]). This observation allows to conclude that hydrogen bond formed between water and acetylacetone is of the similar strength to the bond in the water trimer molecule. However only very small bands shifts (in all matrices) are observed for acetylacetone molecule  $C=O$ ;  $C=C$  stretch and O-H deformation vibrations manifesting that hydrogen bonded water has only minor influence to the geometry and internal hydrogen bonding of the acetylacetone molecule.

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# A SOLID NEON STUDY OF THE CO<sub>2</sub>-H<sub>2</sub>O AND OCS-H<sub>2</sub>O VAN DER WAALS COMPLEXES FROM FAR TO NEAR-INFRARED REGION

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The van der Waals complex of H<sub>2</sub>O with linear molecules (LM) has attracted some theoretical interest since it is a typical example of a weak binding complex, but a very few IR data are available in gas. For these reasons, we have studied in solid neon complexes involving OCS or CO<sub>2</sub> with water molecules. Evidence for the existence of (LM)<sub>m</sub>(H<sub>2</sub>O)<sub>n</sub> complexes have been obtained for m, n = 1-2 from the appearance of many new absorptions near the well-known monomers fundamentals [1].

Careful examination of the far infrared allows the assignment of several intermolecular modes, confirmed by the observation of combinations of intra+intermolecular transitions. All of these results significantly increase the number of one and, especially, two quanta vibrational transitions for these complexes, and anharmonic coupling constants have been derived. This shows the high sensibility of the solid neon isolation to the spectroscopy of the van der Waals complexes since two quanta transitions can't be easily observed in gas phase.

Comparison of the vibrational data will be done following the frequency shifts between the monomers and the complexes. For the water fundamentals, the shifts are relatively similar in the two complexes, but this is not the case for all the CO<sub>2</sub> and OCS ones.

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# UNSATURATED CARBON-NITROGEN CHAIN MOLECULES IN CRYOGENIC MATRICES

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An account on laboratory work concerning the spectroscopy and photochemistry of astrochemically significant cyanoacetylene-related molecules will be given. Compounds of the H-(CC)<sub>n</sub>-CN series (*n* number up to 5) were detected by radio astronomers in the interstellar gas clouds, along with cyanoacetylene isomers, and with (CC)<sub>n</sub>-CN species (*n*=1, 2; both neutral and anionic). Interesting also is the CH<sub>3</sub>-(CC)<sub>n</sub>-CN series; thus far the *n*=1 homologue has been discovered in space, accompanied by its structural isomers: propargyl and allenyl cyanides.

Cryogenic matrices offer convenient environments for uncovering spectroscopic properties of such compounds, and for the photochemical creation of novel, often unstable species of potential astrochemical significance. On one hand, the studied photo processes produced isolated molecular fragments (e.g. C<sub>3</sub>N<sup>-</sup> [1], C<sub>5</sub>N<sup>-</sup> [2]), and on the other hand, rearrangements of parent molecules were observed to occur within matrix cages, leading to isomers of the archetypical cyanoacetylene molecule [3], and to the isomers of H-(CC)<sub>2</sub>-CN [4], NC-CC-CN [5], NC-(CC)<sub>2</sub>-CN [6] or CH<sub>3</sub>-CC-CN (the most recent results from Warsaw and Marseille), identified via infrared absorption.

In addition to the above mentioned phenomena, the UV-assisted coupling of matrix-isolated unsaturated carbon-nitrogen chain precursors was found to take place, yielding larger molecules. Such a process, first demonstrated in the Marseille laboratory with the appearance of cyanodiacetylene bands in the infrared spectrum of a Ly $\alpha$ -irradiated argon matrix doped with an acetylene/cyanoacetylene mixture [7], has consequently been observed, mostly in Orsay, for a number of other systems. This was possible due to the discovery of strong phosphorescence emitted at cryogenic conditions by H-(CC)<sub>n</sub>-CN (*n*=2-4) [8], NC-(CC)<sub>n</sub>-CN (*n*=0-4) [5,9], and CH<sub>3</sub>-(CC)<sub>n</sub>-CN (*n*=2-3).

Authors acknowledge the financial support provided by the Polish National Science Centre, project No. 2011/03/B/ST4/02763, and by the French-Polish scientific cooperation programs: *Polonium* and *PICS*.

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# ELECTRONIC SPECTRUM OF C<sub>60</sub><sup>+</sup> IN GAS-PHASE AT 6 K: IDENTIFICATION OF FIRST DIFFUSE INTERSTELLAR BANDS

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After the discovery of C<sub>60</sub> (1), the question of its relevance to the diffuse interstellar bands was raised. In 1987 H.W.Kroto wrote: "The present observations indicate that C<sub>60</sub> might survive in the general interstellar medium (probably as the ion C<sub>60</sub><sup>+</sup>) " (2).

In 1994 two diffuse interstellar bands (DIBs) at 9632 and 9577 Å were detected and proposed to be the absorption features of C<sub>60</sub><sup>+</sup> (3). This was based on the proximity of these wavelengths to the two prominent absorption bands of C<sub>60</sub><sup>+</sup> measured by us in a neon matrix in 1993 (4). Confirmation of the assignment required the gas phase spectrum of C<sub>60</sub><sup>+</sup> and has taken 20 years.

The approach which succeeded confines C<sub>60</sub><sup>+</sup> ions in a radiofrequency trap, cools them by collisions with high density helium allowing formation of the weakly bound C<sub>60</sub><sup>+</sup>–He complexes below 10 K. The photofragmentation spectrum of this mass-selected complex is then recorded using a cw laser. In order to infer the position of the absorption features of the bare C<sub>60</sub><sup>+</sup> ion, measurements on C<sub>60</sub><sup>+</sup>–He<sub>2</sub> were also made. The spectra show that the presence of a helium atom shifts the absorptions by less than 0.2 Å, much less than the accuracy of the astronomical measurements. The two absorption features in the laboratory have band maxima at 9632.7(1) and 9577.5(1) Å, exactly the DIB wavelengths, and the widths and relative intensities agree. This leads to the first definite identification of now five bands among the five hundred or so DIBs known and proves the presence of gaseous C<sub>60</sub><sup>+</sup> in the interstellar medium (5), (6). The electronic spectrum of cold C<sub>70</sub><sup>+</sup> has also been obtained by this approach. The implications for the relevance of fullerene cations in general in the interstellar medium can be discussed.

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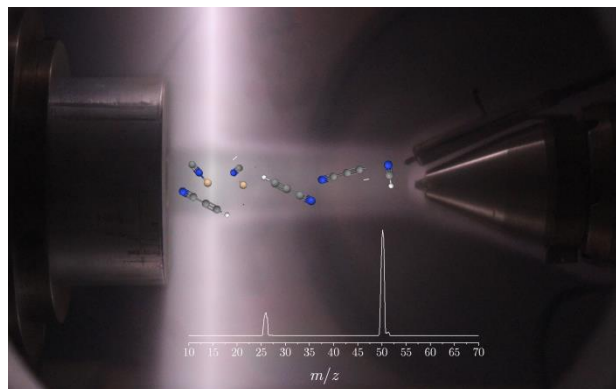
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# COLD CHEMISTRY AND PHYSICS WITH SUPERSONIC UNIFORM FLOWS

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Understanding the mechanisms of elementary reactions leading to the formation of molecules and clusters, in particular at low collision energies, is of fundamental interest and yields crucial information for modeling gaseous environments encountered in the fields of atmospheric chemistry and astrophysics. The kinetics and the products of many key reactions remain poorly known at temperatures relevant for cold environments. In the past thirty years, the development of supersonic uniform expansions greatly contributed to the experimental determination of the rate of neutral-molecule reactions at low temperatures. Many of the chemical reactions have been found extremely rapid at low temperature; hence stimulating theoretical calculations and leading to the revision of photochemical models of planetary atmospheres and dark molecular clouds.



Recently, our efforts have been extended to reactions with anions, which have been recently discovered in the interstellar medium and in the upper atmosphere of Titan. Their presence was unexpected and these discoveries strongly encouraged the search for new anions and spurred interest in the formation and destruction mechanisms of detected anions. In the laboratory, we have conducted a series of experiments using the CRESU (French acronym standing for Kinetics of Reactions in Uniform Supersonic Flows) combined with quadrupole mass spectrometry to explore the reaction of  $C_xN^-$  ( $x=1,3$ ) with cyanoacetylene  $HC_3N$  – both abundant in astrophysical environments – over the 50 – 300 K temperature range [1, 2]. Astrophysical implications of this work and perspectives will be discussed.

The CRESU can also be employed to study the mechanisms of nucleation and molecular growth. This investigation started with the condensation of Polycyclic Aromatic Hydrocarbons of interest for the formation of haze in the atmospheres of Titan and Jupiter. More recently we focused our efforts on the study of the first steps of cluster formation of water [3], and small hydrocarbons (acetylene, ethylene, ethane, propane, butane, butene). First kinetics results were obtained with a dedicated CRESU chamber combined to a time of flight mass spectrometer equipped with an electron gun. This work opens the way to the systematic exploration of the onset of nucleation of a great diversity of molecular species.

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# VIBRATIONAL AND ELECTRONIC SPECTROSCOPY OF CH<sub>3</sub>C<sub>5</sub>N (METHYLCYANODIACETYLENE)

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Methylcyanodiacetylene (2,4-hexadienenitrile, cyanopentadiyne, CH<sub>3</sub>C<sub>5</sub>N) is a known interstellar molecule [1]. However, spectroscopic studies of this compound are still very limited [2-4]. This contribution will provide insight into new data concerning vibrational (IR absorption, Raman scattering) and electronic spectroscopy of gaseous, crystalline, and cryogenic matrix-isolated methylcyanodiacetylene. Our analysis has uncovered almost all of its vibrational modes in the ground electronic state. Visible phosphorescence, observed here for the first time and resembling previously measured HC<sub>5</sub>N emissions [5], have provided information about the triplet state. The experiments were carried out in various cryogenic hosts, including Ar, Kr, Xe, N<sub>2</sub>, and *p*-H<sub>2</sub>. The two lowest singlet electronic transitions (*A-X* and *B-X*) were observed both in UV absorption and in phosphorescence excitation spectra. The analyses were supported with quantum chemical calculations.

Selected spectral features of CH<sub>3</sub>C<sub>5</sub>N, of particular interest to matrix-isolation spectroscopy, will be discussed in detail.

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This work was supported by the Polish NCN grant No. 2011/03/B/ST4/02763 and by the French-Polish grant PICS (2014-2016). U.S. acknowledges the support from Campus France (*Bourse Eiffel*) and *Scholarships for PhD students of Podlaskie Voivodeship*.

# PHOTOCHEMISTRY OF WATER: PAH COMPLEXES AND ICE MIXTURES: THE ROLE OF MOLECULAR ORIENTATION IN REACTIVITY

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Polycyclic aromatic hydrocarbons (PAHs) are believed to contribute to both the Diffuse Interstellar Bands (DIBs) and the Unidentified/Aromatic InfraRed Bands (UIR/AIBs) widely observed along interstellar lines of sight. In star forming regions, PAHs in the solid and gas phases play key roles in the chemical evolution. Several groups have shown that PAHs in water ices react, upon UV irradiation, to produce oxygenated species (e.g. Bouwman 2010, Guennoun 2011, Cook 2015).

We present the results of a recent experimental and theoretical study of the PAH:water system. FTIR and UV-visible spectroscopies have been used to investigate the photoreactivity of coronene and pyrene with water molecules at low temperatures in both argon matrices and in solid water ices. Classical molecular dynamics were used to construct an ice surface, upon which the adsorption of PAH molecules was studied. Ab-initio (DFT-B) calculations of water:PAH clusters have been used to study intermolecular interactions and the effect of the matrix on such aggregates.

We show that PAH:water systems are highly photoreactive, producing oxygenated products after short irradiation times. We will also show that the presence of a water ice is not necessary to catalyse the PAH:water reaction, but rather that small water clusters ( $n \ll 6$ ) can react with PAH molecules to form alcohols and quinones. Calculations performed on PAH:water systems involving water clusters and water ices support the conclusion that the orientation of the PAH compared to the water molecules is a key factor controlling the photo reactivity pathway. Both the matrix and water ice environments favour water reaction with the edges of PAH molecules.

First results on photo irradiation of mixed PAH:water:iron complexes will also be presented, with comparison of the IR and UV-visible bands of these organometallic systems to interstellar UIR and DIBs spectra.

This work is supported by The French National Agency for Research (ANR project PARCS n°13-BS08-0005) and the CNRS (GDR EMIE).

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# LASER INDUCED EMISSION SPECTROSCOPY OF COLD AND ISOLATED NEUTRAL PAHS AND PANH: IMPLICATIONS FOR THE RED RECTANGLE EMISSION

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Blue luminescence (BL) in the emission spectra of the red rectangle (RR) centered on the bright star HD44179 was reported by Vijh et al [1]. This observation is consistent with the broad band polarization measurements obtained by Schmidt et al [2]. Both experimental and theoretical studies support attributing BL emission to the luminescence of Polycyclic Aromatic Hydrocarbons (PAHs) excited by ultraviolet light from the star [4 and references therein]. The abundance on N to C in the interstellar medium suggests also that nitrogen substituted PAHs (PANHs) are likely abundant [3]. They exhibit similar features as PAHs and could contribute to the unidentified spectral bands. Comparing the BL to laboratory spectra obtained in a similar environment is crucial for the identification of interstellar molecules. We present in this work absorption and laser induced emission spectra of several isolated and cold PAHs and PANHs. Laser induced emission was performed first with PAHs and PANHs isolated in Argon matrix at 10 K. Then, measurements were performed with the supersonic jet techniques of the COSmIC laboratory facility at NASA Ames [4]. We focus, here, on the emission spectra (fluorescence and/or phosphorescence) of these molecules and discuss their potential contribution to the blue luminescence emission in the Red Rectangle nebula. An example of the results obtained with the Matrix Isolation Spectroscopy (MIS) technique is reported in Fig. 1.

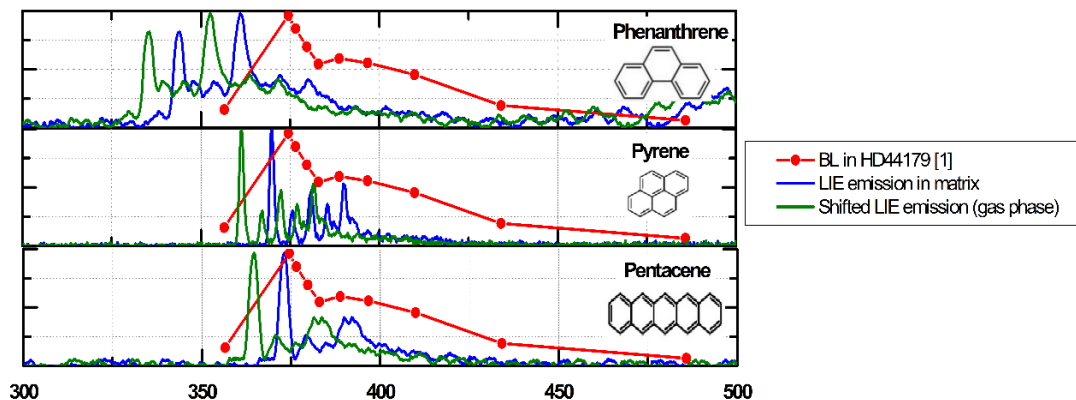


Fig.1. Laser induced emission of Phenanthrene, Pyrene and Pentacene isolated in Argon matrices at 10 K and excited with Nd:Yag-pumped dye lasers at 278.18 nm, 341 nm and 316 nm respectively. Spectra are compared to spectra of HD44179 [1]

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## **SPECTROSCOPY, A TOOLBOX FOR STRUCTURAL INFORMATION ON AEROSOL PARTICLES**

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It is well known that light interacts differently with small particles compared with bulk materials or gas phase molecules, producing spectral signatures that strongly depend on particle properties, such as size, shape, or architecture. Even nanosized aerosol particles held together by weak intermolecular interactions can exhibit such characteristic spectral signatures. This talk discusses absorption and scattering features in aerosol particle spectra from the infrared to the extreme ultraviolet spectral region, and explains their molecular origin and their use for aerosol characterization in planetary atmospheres. Various laboratory methods are discussed ranging from particle ensemble techniques to single-particle studies in optical traps. The role of small clusters as critical nuclei in the aerosol formation from the gas phase is briefly addressed.



# MATRIX PHOTOCHEMISTRY OF ORGANIC SULFUR-CONTAINING SPECIES WITH ATMOSPHERIC INTEREST

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Gaseous sulfur compounds are highly reactive and play an essential role in the formation of acid rain and the generation of atmospheric aerosols.[1,2] The sulfur-containing species evolves to different oxidation states. The most studied case is the oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> to form secondary sulfated aerosols; however, other less-studied cases could occur, for example the oxidation of H<sub>2</sub>S, R-SH or R-S-R to SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>. Gases and particles interact with solar radiation in the atmosphere leading to a variation of the atmospheric composition. In fact, many studies show that atmospheric sulfur compounds produced by marine organisms (DMS, etc.) are transformed under the influence of solar radiation to form new products or secondary aerosols.[3-5] However, the information available on the photoreactivity of organic sulfur compounds including long chain and low volatile compounds is limited. In addition, photochemical mechanisms understanding of such processes are not very well known, due to the complexity of the systems and the short lifetime of the intermediate products.

The IR matrix isolation spectroscopy is a very well suited technique for the study of photochemical mechanisms, due to the possibility of the detection of reactive intermediates, free radicals and molecular complexes. In this work, we will present the matrix isolated IR spectra of some organic sulfur containing species (e.g. CH<sub>3</sub>-OC(O)-CH<sub>2</sub>-SH, C<sub>2</sub>H<sub>5</sub>-C(O)S-CH<sub>2</sub>-CH=CH<sub>2</sub>, CH<sub>3</sub>-S-CH<sub>2</sub>-CH=CH<sub>2</sub>) as models of sulfur compound of industrial or biological origin, together with the photochemical studies using broad-band UV-visible radiation in the presence and absence of oxygen. A series of oxygen and sulfur containing compounds of atmospheric interest were formed during irradiation. In addition, sharpness of the IR absorptions, and particularly the behavior of the bands with the irradiation, allowed the assignment of the IR spectra and the proposition of reactional mechanisms. Indeed, we demonstrated that matrix isolation experiments are suitable to describe atmospheric processes.

This work was supported by funds from the "Laboratoire d'Excellence" CaPPA (LABEX ANR-11-LABX-0005-01) and ECOS-MinCyT (N°A13E05).

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# MATRIX-ISOLATION STUDIES OF HOCO RADICALS PRODUCED BY X-RAYS OR VUV-RADIATION

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Hydrocarboxyl radical (HOCO) is a key intermediate in atmospheric and combustion processes and it is probably involved in extraterrestrial prebiotic chemistry. Basic importance of this radical has stimulated extensive theoretical and experimental studies over several decades [1]. On the other hand, the application of matrix isolation to investigation of this species is rather limited. Recently we have demonstrated the formation of hydrocarboxyl radical upon X-ray irradiation of the  $\text{H}_2\text{O}\cdots\text{CO}_2$  complexes isolated in noble-gas matrices [2]. In the present work, we investigate the formation of HOCO upon irradiation of matrix-isolated formic acid (HCOOH) by X-rays and VUV light. Particular attention is drawn to the *trans*  $\rightleftharpoons$  *cis* conformational changes of HOCO.

The experiments were carried out with HCOOH/M (1/1000–2500) samples (M = noble gas or  $\text{N}_2$ ) in closed-cycle helium cryostats using FTIR spectroscopy. An X-ray tube with a tungsten anode ( $E_{\text{eff.}} \sim 20$  keV), microwave discharge lamps (Kr and Xe) and an ArF excimer laser (193 nm) were used as radiation sources. Vibrational excitation of HOCO was performed with a narrow-band optical parametric oscillator.

The experiments on X-ray radiolysis of matrix-isolated HCOOH have revealed the involvement of the  $\text{HCOOH} \rightarrow \text{HOCO} + \text{H}$  primary channel. It is the first observation of this channel of the radiation-driven decomposition of formic acid in the solid phase. The mechanism involving population of specific triplet states (inaccessible upon direct photoexcitation) was proposed for the explanation of this result [3].

HOCO also appears as a result of photolysis of HCOOH/M matrices with VUV lamps. The corresponding mechanism probably involves the formation and radiation-driven evolution of the  $\text{H}_2\text{O}\cdots\text{CO}$  intermolecular complexes. To remind, 193-nm photolysis of matrix-isolated formic acid does not lead to the formation of hydrocarboxyl radical [4].

For HOCO (with an H atom), the higher-energy *cis* conformer is found only in a nitrogen matrix. In contrast, for the deuterated species DOCO, the higher-energy *cis* conformer appears in both argon and nitrogen matrices. The *trans* and *cis* conformers of hydrocarboxyl radical can be interconverted by selective vibrational excitation as it has been demonstrated for a number of other species [5]. Similarly to carboxylic acids [5], *cis*-HOCO converts to the *trans* conformer as a result of hydrogen-atom tunneling through the torsional barrier and the kinetics of this process has been studied in detail, including isotope and matrix effects. Finally, the *trans*  $\rightleftharpoons$  *cis* transformation of hydrocarboxyl radical induced by broad-band IR radiation of the spectrometer has been investigated in a nitrogen matrix.

The obtained results may have implications for various aspects of low temperature chemistry and physics including astrochemically-relevant studies. This work was partially supported by the Russian Science Foundation (grant № 14-13-01266).

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## NUCLEAR SPIN CONVERSION OF WATER ISOLATED IN ARGON MATRIX: ISOTOPIC AND CONCENTRATION EFFECTS

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H<sub>2</sub>O and other hydrogenated molecules of astrophysical interest like H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>CO, NH<sub>3</sub>, CH<sub>3</sub>OH, or C<sub>2</sub>H<sub>4</sub> play an important role for the chemistry in the interstellar medium (ISM) and in the protosolar nebula. Because of the spin ½ of the protons, these molecules exist in different nuclear spin configurations. In case of 2 protons, they are called *para* and *ortho* isomers depending whether the total nuclear spins are  $I=0$  or  $I=1$  respectively. Due to the Pauli's exclusion principle and the properties of symmetry of the rovibrational molecular wave functions of the molecule, each species *para*, and *ortho* can be identified by its rotation-vibration spectrum. In the high temperature limit ( $>50$  K), it is known that 25% of the molecules are *para*, while 75 % are *ortho*. Below 50 K, the *ortho/para* ratio becomes strongly temperature dependent. From these ratios measured in cometary *comae* or in dark clouds, it is expected to determine the formation conditions of molecules in space, and especially the formation temperature. It is then important to know how long the *ortho* and *para* populations can be preserved in the solid state at low temperature ?

We investigated the parameters involved in the nuclear spin conversion (NSC) of water isolated in rare gas matrix at low temperatures (between 4.3 and 20 K). In this model environment, the hydrogenated molecule vibrates and rotates almost freely within the cage made of rare gas atoms. The *ortho* and *para* populations can be probed using infrared rovibrational spectroscopy. After a fast cooling from 20 K to 4.3 K, populations of the nuclear spin species do not follow the Boltzmann distribution because of a slow nuclear spin conversion. Following the time evolution of the transitions associated with the different spin isomers, characteristic times of nuclear spin conversion in various conditions of concentration and temperature were measured. Playing with the concentration of water molecules in the sample, we showed that the NSC is induced by two magnetic contributions. One is due to intermolecular spin-spin interactions and induces non exponential decay of the *ortho* populations with time for concentrated sample. The second contribution due to intramolecular interactions becomes dominant in dilute samples. We investigated temperature dependence of the NSC rates for three isotopes of water (H<sub>2</sub><sup>16</sup>O, H<sub>2</sub><sup>17</sup>O, H<sub>2</sub><sup>18</sup>O). I will present the results we obtained for these three isotopes. Especially, I will show that intramolecular contribution to NSC is strongly related to the translational-rotational energetic structure of the molecule within the cage. While the nuclear spin of <sup>17</sup>O isotope enhances dramatically the NSC, the conversion is twice faster for H<sub>2</sub><sup>18</sup>O than for H<sub>2</sub><sup>16</sup>O. Efforts are made to understand this late effect.

# THE CHEMISTRY OF GROUND STATE NITROGEN ATOMS $N(^4S)$ ON COLD INTERSTELLAR GRAINS: HEAT-INDUCED REACTION PROCESSES VS ENERGETIC COSMIC RAYS IMPLICATIONS.

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Stable hydrogen containing molecules in the interstellar medium, may be easily dissociated following irradiation by energetic cosmic rays, to form either stable or unstable chemical species. Laboratory experiments have already proved that when, for example  $NH_3$  or  $CH_3OH$  containing ices are irradiated with high energy photons or energetic particles, many chemical primary fragments are formed, due to the dissociation of C-H, N-H or O-H bonds, and the formation of these reactive species may be the first key step towards complex organic molecule evolutions in the universe. Are those hydrogen containing molecules chemically stable in dark dust clouds? What are the behaviors of those molecules involving in non-energy-induced processes? The understanding of thermal reactions between astrochemically-relevant molecules and radical species such as N, H and OH in their ground states at cryogenic temperatures is of primary importance in the astrochemical context. We experimentally show that reactions involving ground state atomic nitrogen in solid phase at very low temperature lead to the formation of highly reactive chemical fragments from stable hydrogen containing molecules via a thermal chemistry, initiated at temperatures below 10 K. These results, in addition to open a new pathway towards the increasing molecular complexity in the interstellar medium and its impact on some astrochemical modeling, they underline the problem of the low chemical stability of some species formed and destroyed in the interstellar clouds without any contribution of cosmic-ray particles or high energy photons.

# SWIFT HEAVY ION IRRADIATION ON FROZEN NITROGEN/METHANE ICES: TOWARD UNDERSTANDING FORMATION OF ULTRACARBONACEOUS ANTARCTIC MICROMETEORITES

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Micrometeorites recovered from Antarctic snow are very well preserved interplanetary dust particles. The French CONCORDIA collection of Antarctic micrometeorites (AMMs) contains primitive micrometeorites including fine-grained fluffy particles and Ultra Carbonaceous AMMs, hereafter referred as UCAMMs [1]. The UCAMMs exhibit much higher carbon content than other classes of AMMs (typically >50vol%). This carbonaceous compound is a primitive organic material (OM) characterized by an extreme D/H ratios up to 20 times the terrestrial reference (Vienna Standard Mean Ocean Water). This OM also contains minerals, including a substantial proportion of crystalline phases [2]. This OM also presents large nitrogen concentrations up to 5 times higher than observed in OM from meteorites [3]. All together the mineralogical, chemical and isotopic data obtained on UCAMMs indicate that they most probably originate from the surfaces of trans-Neptunian icy parent bodies, where the temperature stays low enough (<35 K) to retain surface N<sub>2</sub> ices together with a carbonaceous precursor. They can be processed by energetic cosmic rays over very long time scale (millions to billions of years). We irradiated a mixture of frozen N<sub>2</sub>/CH<sub>4</sub> (90:10 and 98:2), representative of the surfaces of trans-Neptunian objects, at GANIL (Caen, France) [4] with swift heavy ions (Ni<sup>11+</sup> and Ar<sup>15+</sup>) to simulate cosmic rays in the outer Solar System. The structural and chemical evolution of the ices was monitored by infrared absorption spectroscopy *in-situ* during irradiation and subsequently during annealing to room temperature. The IR spectra of the residues after annealing exhibit striking similarities with that of UCAMMs taken at SOLEIL synchrotron facility [3]. The comparison with an IR spectrum of HCN indicates an effective production of a HCN-polymer during irradiation. Ex-situ electron microprobe analysis of refractory residues was performed using the CAMPARIS facility (Paris). The measured atomic N/C ratios of about 1 comfort the formation of a poly-HCN-like residue [4].

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## LOW TEMPERATURE CHEMISTRY IN COMETARY ICE ANALOGUES

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There are convincing evidences that the formation of complex organic molecules occurred in a variety of astrophysical environments. Among them, precursors of biomolecules are of particular significance due to their exobiological implications. Hexamethylenetetramine (HMT,  $C_6H_{12}N_4$ ) and the polyoxymethylene (POM,  $-(CH_2O)_n-$ ) are of prime interest since they are supposed to be present in cometary environments. They are also ones of the main components of the organic residue formed from the warming of photolysed interstellar/cometary ice analogues. In this work, we study the warming/photolysis of water-dominated cometary ice analogues containing **formaldehyde** ( $H_2CO$ ). Based on infrared and mass spectrometry measurements, and complemented by quantum chemical calculations, we report that  $NH_2CH_2OH$ ,  $HOCH_2OH$ , and POM are formed during the warming ( $T < 50$  K) of the initial ice that also contains  $NH_3$ .<sup>(1,2)</sup> The branching ratios between the three products strongly depend on the initial  $H_2CO/NH_3$  concentration ratio. Moreover, the influence of the initial ice composition on the formation of POM oligomers ( $HO-(CH_2O)_n-H$ ,  $n < 5$ ) as well as their thermal instability between 200 and 320 K are investigated. Finally, the implications of these results with respect to cometary nucleus chemistry and their impact on POM detection by the *Rosetta* mission are discussed. In addition, the mechanism for HMT formation in interstellar or cometary ice analogues containing  $H_2CO$ ,  $NH_3$ , and  $HCOOH$  has been determined by combining laboratory experiments and DFT calculations.<sup>(3,4)</sup> We show that HMT is **thermally formed** from  $H_2CO$  and  $NH_3$  activated by  $HCOOH$ . These results strengthen the hypothesis that HMT and its intermediates should be present in comets, where they may be detected with the COSAC or COSIMA instrument of the *Rosetta* mission.<sup>(3)</sup>

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# GAS PHASE REACTION KINETICS OF COMPLEX ORGANIC MOLECULES INVESTIGATED BY THE CRESU TECHNIQUE BETWEEN 22 AND 64 K

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Complex Organic Molecules (COMs) have been found in many interstellar objects. Interestingly, for quite a long time, COMs have been observed in "lukewarm" regions such as hot cores and hot corinos. Grain surface chemistry was claimed to be the source for the synthesis of COMs during the warm-up of grains at temperatures  $> 30$  K. These were subsequently expected to desorb to the gas phase at temperatures  $> 100$  K. In contrast, only a few observations of COMs were available in the cold gas environments until recently. Investigations of the dense core B1-b [1,2] and prestellar cores [3,4] shed a new light on the mechanisms responsible for the presence of COMs in such cold regions ( $T \sim 10$  K) for which the previous mentioned formation process on grains does not hold. Gas phase reactions which were left apart at first sight were reconsidered as a possible route to the formation of COMs in cold environments.

In the present work, the reactivity of OH radicals with a series of COMs, including  $\text{HC(O)OCH}_3$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{CH}_3\text{OCH}_3$  and  $\text{CH}_3\text{C(O)CH}_3$ , was studied using the CRESU method (*Cinétique de Réaction en Ecoulement Supersonique Uniforme*, standing for *Reaction Kinetics in a Uniform Supersonic Expansion*), associated to the PLP-LIF technique (Pulsed Laser Photolysis – Laser Induced Fluorescence) [5-8] in a joint collaboration between the University of Castilla-La Mancha (Spain) and the University of Rennes 1 (France). Reactions have been studied in the temperature range 22 – 64 K and extensions up to 100 K are in progress. Although these reactions present an Arrhenius behavior at temperatures around 300 K and are not very efficient at  $\sim 200$  K, the experimental rate coefficients were found to dramatically increase at very low temperatures for all reactants. The presence of a weakly bound pre-reactive complex which lifetime increases as temperature decreases is responsible for this behavior. Reactions occur either by tunneling through products or via a three-body process which stabilizes the adduct. The last results and their potential impact on interstellar chemistry will be presented.

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# ION-MOLECULE REACTION DYNAMICS SIMULATIONS TO MODEL THE FORMATION OF ORGANIC MOLECULES IN THE INTERSTELLAR MEDIUM: FROM FORMAMIDE TO GLYCINE

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Different molecules have been observed in the interstellar medium (ISM), like glycolaldehyde,<sup>[1]</sup> urea<sup>[2]</sup> or formamide.<sup>[3]</sup> This last is the smallest molecule with a peptide bond. While they have been observed thanks to radio-astronomy, the mechanisms by which they are formed in the ISM are not clear. In particular it is not evident how cold molecules are able to pass energy barriers that were pointed out in static quantum chemistry calculations.<sup>[4,5]</sup> We used chemical dynamics to answer to this question.<sup>[6]</sup> In particular we studied the formation mechanism of formamide and glycine, for which gas phase experiments were reported by Bohme and co-workers.<sup>[7]</sup>

For formamide we have considered all the possible ion/molecule reactions between neutral and protonated forms of H<sub>2</sub>CO, NH<sub>2</sub>OH and NH<sub>3</sub> by tuning collision energies in the 0.05 – 4 eV range with low internal temperature (15 K) for initial reactants. Simulations were done using both MP2 and semi-empirical Hamiltonians giving similar results. In particular the reaction pathway for protonated formamide precursor was observed as well as other products less expected. From these results we built a possible scenario for the formation of formamide in the ISM.<sup>[8]</sup>

Finally, after a detailed benchmarking of different semi-empirical methods with respect to MP2 simulations, we have applied the same method for the formation of glycine by ion molecule reaction as suggested by experiments of the Bohme group.<sup>[7]</sup> Also in this case, we show how the formation of protonated glycine can be achieved and the underlying mechanisms understood by means of chemical dynamics simulations. The effect of internal temperature on the reactivity is here considered to discuss the use of room-temperature ion-molecule reactions (like done experimentally to synthesize protonated glycine<sup>[7]</sup>) to model reactivity in the cold ISM.

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# MATRIX ISOLATION-VIBRATIONAL CIRCULAR DICHROISM SPECTROSCOPY OF CHIRAL MOLECULAR CLUSTERS.

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Vibrational circular dichroism (VCD) spectral features contain unique information about both chirality and conformational equilibria of chiral molecules. The matrix-isolation (MI) technique offers substantial control over sample compositions and yields spectra with very narrow bandwidth. MI-VCD spectroscopy therefore has the potential to combine the advantages of both techniques into one powerful tool.<sup>1</sup> We have successfully completed a MI-VCD setup and utilized it to probe conformational equilibria and chirality transfer in a number of chiral molecular systems.<sup>2</sup> More recently, we have implemented a pulse nozzle deposition source which allows us to study low vapor solid samples and their hydrogen-bonded clusters. I will discuss self-aggregation of lactic acid and its hydrogen-bonded complexes with water studied with this setup. Chirality transfer from methyl lactate to a gaseous molecule at room temperature, NH<sub>3</sub>, was also investigated. MI-VCD experiments also provide the much needed high quality experimental VCD data for advancing the theoretical VCD treatment on combination and overtone bands. I will discuss how MI-VCD research helps to bridge our understanding of properties of isolated chiral molecules and those in solution.

*This work was funded by the University of Alberta and the Natural Sciences and Engineering Research Council (NSERC) of Canada. We also gratefully acknowledge access to the computing facilities of Compute/Calcul Canada. YX holds a Tier I Canada Research Chair in Chirality and Chirality Recognition.*

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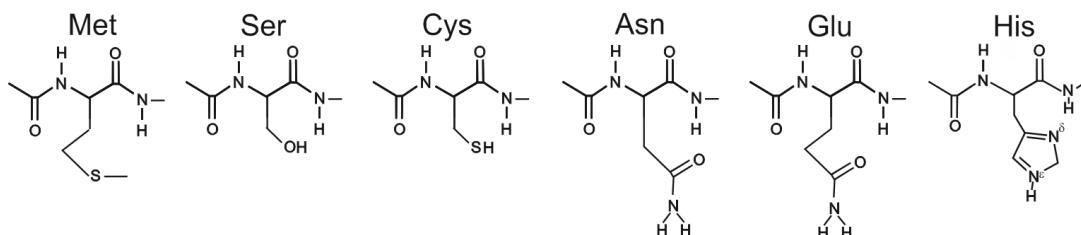
# LOCAL STRUCTURES IN A PROTEIN CHAIN: INTERPLAY BETWEEN MAIN-CHAIN AND SIDE-CHAIN H- BONDING PATTERNS AS REVEALED BY GAS PHASE LASER SPECTROSCOPY

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Investigating short models of a protein chain, composed of one or two capped residues, isolated in the gas phase, is an elegant way to document the several local intramolecular interactions that occur within a residue or with its neighbor. It enables spectroscopists to provide experimental benchmark data and to understand how the interplay between these features can control the structure and energetics of the most stable conformations and finally influence the conformational distributions [1]. Neutral species have thus been investigated for nearly a decade using the gas phase lasers spectroscopic techniques coupled with a convenient vaporizing and cooling preparation procedure, namely laser-desorption from a solid sample, coupled to a pulsed supersonic expansion [1]. In the last years, the interest has been focused on neutral residues that possess H-bond acceptor side chains (Phenylalanine [2] and Methionine[3]) or both donor and/or acceptor side chains (Serine, Cysteine [4] and more recently Asparagine, Glutamine and Histidine), with emphasis put on the theoretical descriptions of these systems.

The presentation will illustrate how the donor/acceptor capabilities of the side chain and the resulting local side-chain/main-chain interactions, do influence the conformational populations compared to reference species devoid of such features (Alanine for instance [5]). Species rich in aromatic rings (Phe, His) will document the role of NH- $\pi$  interactions in a hydrophobic environment [2]. For residues having both donor and acceptor sites, we will see how the size of the residue can control the type of H-bonding pattern, together with the strength of the interactions (only one in Ser and Cys, and two simultaneous in Asn and Glu). Finally, the conformational diversity in the fascinating case of the histidine residue (His), made possible by the simultaneous presence of donor and acceptor sites and together with the five-membered ring tautomerism, will be described.



The strength of these interactions within the constrained context of a peptide backbone will be compared to those encountered in free dimers, in the perspective of documenting frustration effects in these systems, a key concept for conformational isomerizations, peptide flexibility and biofunctionality.

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# GAS PHASE EXPERIMENTS ON OXYGEN-BINDING HEMOPROTEINS

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In textbooks, bonding of O<sub>2</sub> with ferrous heme proceeds through the simultaneous oxidation of the ferrous iron (Fe<sup>II</sup>) to ferric iron (Fe<sup>III</sup>) and the reduction of O<sub>2</sub> into O<sub>2</sub><sup>-</sup>. Despite this apparent agreement, the theoretical description of the heme Fe<sup>II</sup>-O<sub>2</sub> bond has been challenged since the first interpretation given by Pauling in 1936.<sup>[1]</sup> The change in oxidation state of the iron atom within heme (+II → +III) is of the highest relevance to O<sub>2</sub> bonding and to the nature of the [heme Fe-O<sub>2</sub>] bond. In this context, we have recently developed different strategies to study the properties of the O<sub>2</sub> binding to Heme. Particular attention will be paid to the formation and characterization of [Heme Fe<sup>III</sup>-O<sub>2</sub>]<sup>+</sup> complex cation and [Heme Fe<sup>II</sup>-O<sub>2</sub>]H<sup>+</sup> protonated complex in a temperature-controlled cold quadrupole ion trap. The bond formation enthalpies with O<sub>2</sub> have been derived from Van't Hoff plots of experimentally determined equilibrium constants for ligand binding reactions in the gas phase.<sup>[2]</sup> This is the first observation of the [Heme Fe<sup>III</sup>-O<sub>2</sub>]<sup>+</sup> cationic complex, since O<sub>2</sub> does not bind to ferric heme at normal temperature in living organisms. The bond formation enthalpy of the latter complex (790±80 cm<sup>-1</sup>) is rather strong as compared to [Heme Fe<sup>III</sup>-N<sub>2</sub>]<sup>+</sup> (190±40 cm<sup>-1</sup>), showing the formation of an incipient Fe-O bond, which is confirmed by the electronic absorption spectra of the two complexes. Surprisingly, the bond formation enthalpy is only a factor of four greater in [Heme Fe<sup>II</sup>-O<sub>2</sub>]H<sup>+</sup>. However, it has long been recognized that O<sub>2</sub> binding in heme occurs in a highly cooperative manner and is crucially modulated by a proximal histidine ligand at the Fe<sup>II</sup> center and its propensity for electron donation or withdrawal.<sup>[3]</sup> This systematic experimental study of ligand binding to ferrous and ferric heme lays the basis and provide data for a quantum chemical description of the electronic states involved in one of the most important chemical reactions in living organisms.

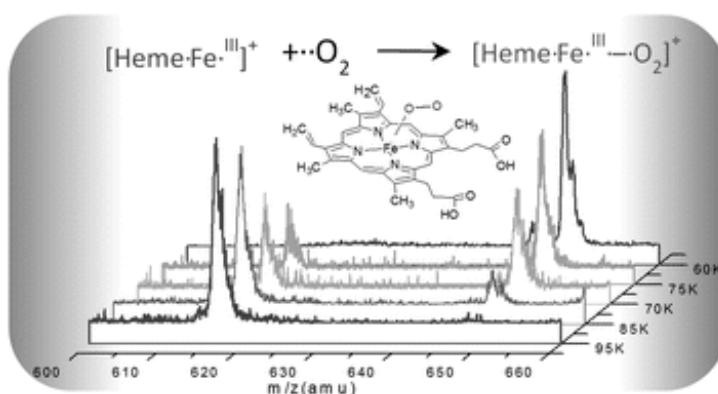


Figure 2 Mass spectra showing the appearance of the [heme Fe<sup>III</sup>-O<sub>2</sub>]<sup>+</sup> complex as a function of the temperature of the quadrupole ion trap (60-95 K).

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# INTERSYSTEM CROSSING PATHWAY OF PROTONATED PHENYLALANINE/SERINE DIMERS

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Radiation damage triggered by strong ultraviolet radiation harms our body and results in the aging of our skin [1]. To understand the mechanism of the radiation damage, it is essential to investigate the photochemical processes of proteins and amino acids. Lorentz *et al.* investigated the nonradiative relaxation pathway of the protonated phenylalanine/serine PheH<sup>+</sup>/Ser dimers by the conformer selective nanosecond (ns) ultraviolet pump infrared (IR) probe spectroscopy at the initial temperature of ~10 K. They found that a PheH<sup>+</sup>/Ser dimer with an OH- $\pi$  bond between the OH group of Ser and phenyl ring of Ser undergoes intersystem crossing (ISC) from the first-excited singlet (S<sub>1</sub>) state to the lowest triplet (T<sub>1</sub>) state with the lifetime of ~60 ns after band origin excitation [2]. They also observed OH- $\pi$  bond dissociation after the ISC to the T<sub>1</sub> state. To clarify the early stage of the ISC inducing the OH- $\pi$  bond dissociation, we quantum-chemically investigated the ISC pathways.

To determine the structure, we first systematically searched the stable conformers of PheH<sup>+</sup>/Ser by the single-component artificial force induced reaction method [3] and compared the experimental IR-dip spectra at ~10 K [4] to the simulated IR spectra at the B3LYP-D3/6-31G+(*d,p*) level of theory including anharmonic terms. The assigned structure is shown in Fig. 1a. We next searched the minimum energy seam of crossing (MESX) geometries between the S<sub>1</sub> (<sup>1</sup> $\pi$ - $\pi^*$ ) state and triplet states (T<sub>*n*</sub>/S<sub>1</sub>, *n* = 4,5) around the S<sub>1</sub> minimum shown in Fig. 1b at the TD-CAM-B3LYP/6-31G(*d*) level of theory. We found that an ISC path *via* an T<sub>5</sub>/S<sub>1</sub> (<sup>3</sup>*n*- $\pi^*$ /<sup>1</sup> $\pi$ - $\pi^*$ ) crossing shown in Fig. 1c is the dominant ISC pathway. The T<sub>5</sub>/S<sub>1</sub> crossing is located at the potential energy height of 5.41 eV from the S<sub>0</sub> minimum, which is almost the same height as the S<sub>1</sub> minimum and easily accessible even in the case of band origin excitation. The magnitude of spin-orbit coupling at the T<sub>5</sub>/S<sub>1</sub> crossing is estimated to be 0.96 cm<sup>-1</sup> at the TD-CAM-B3LYP/6-31G(*d*) level of theory, which is large enough to promote the ISC in the timescale of 10-100 ns.

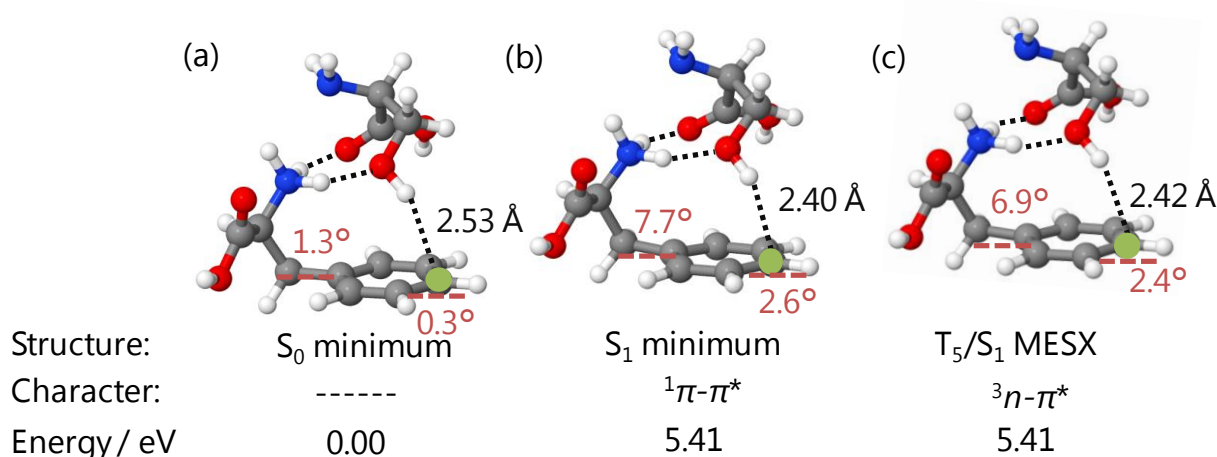


Fig. 1. Key structures for the ISC process of the PheH<sup>+</sup>/Ser dimer with an OH- $\pi$  bond.

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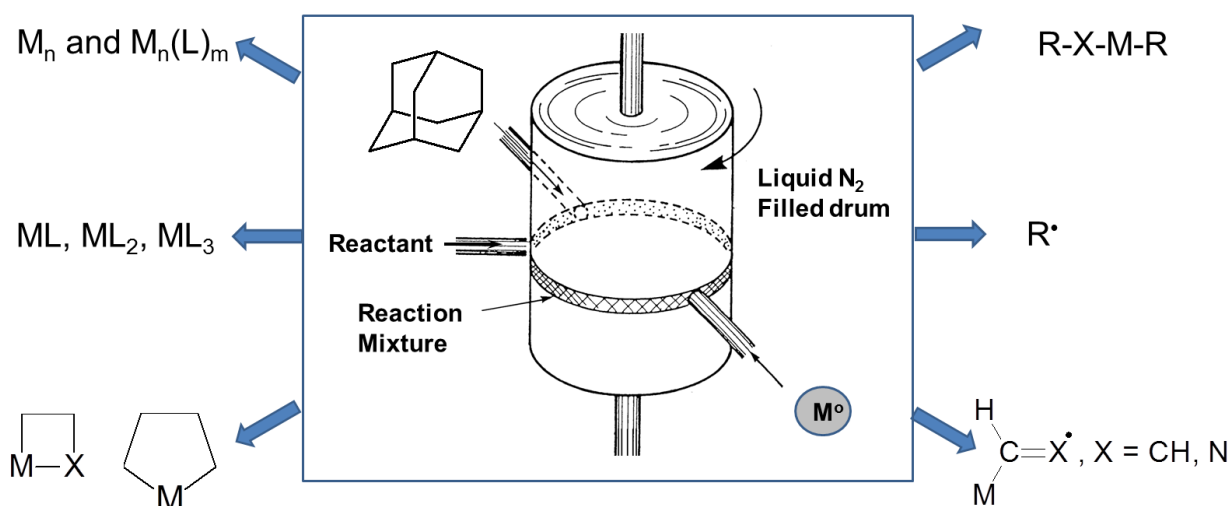
# NOVEL ORGANOMETALLIC RADICALS CHARACTERIZED BY MATRIX ISOLATION ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

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There is no question that metal centers play an important role in the catalysis of chemical reactions. An understanding of the nature of the interaction between the metal and the target substrate is necessary to further exploit metals as effective mediators of chemical transformations. Matrix isolation electron paramagnetic resonance (EPR) spectroscopy has been used to characterize the high energy intermediates prepared using a metal atom reactor known as a 'rotating cryostat'.<sup>1</sup> During a run, the stainless steel drum, housed in this specialized reactor maintained at  $< 10^{-6}$  Torr, was filled with liquid nitrogen and spun at about 2000 rpm. Metal atoms, prepared by resistively heating wire or turnings, were co-condensed with a substrate and trapped in an adamantane matrix on the surface of the cold drum. The reaction mixture was transferred to a quartz tube, under vacuum, and the paramagnetic products subjected to EPR spectroscopic analysis at temperatures ranging from 77 – 250 K.

Because metal atoms are coordinately unsaturated, they are more reactive than the same atoms found in complexes or on surfaces. The paramagnetic products found in metal atom reactions include small metal clusters,  $\sigma$ - and  $\pi$ - mono-, di- and tri-ligand complexes, organometallic vinyls and iminyls, and carbon-centered radicals. In addition, metal atoms have been found to insert into many different types of bonds producing highly reactive organometallic intermediates. Metal activation of bonds can potentially lead to alternate synthetic routes. In this presentation, particular emphasis will be placed on recent findings on the isolation and characterization of novel metallacyclic intermediates.<sup>2</sup> Finally, the importance of using density functional theory (DFT) calculations, of nuclear hyperfine interaction values, to support the EPR spectral assignments of the organometallic radicals will be demonstrated.



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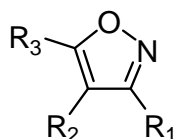
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# PHOTOCHEMISTRY OF MATRIX-ISOLATED ISOXAZOLES

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A structural feature that distinguishes isoxazoles (Scheme 1) from other heterocycles is the fact that its ring has properties of an aromatic system and, at the same time, has a weak N–O bond that plays a central role in their chemistry. Under thermal and photochemical treatment, the N–O bond cleavage is described as the first step of their transformation.



Scheme 1. General structure of isoxazole molecule.

In this communication, we shall overview the photochemistry of several isoxazole derivatives studied in the Coimbra laboratory. Narrowband tunable UV-irradiations of the matrix-isolated isoxazoles were undertaken *in situ* by means of an optical parametric oscillator.

For the parent isoxazole molecule ( $R_1=R_2=R_3=H$ ) [1], this approach allowed us to capture previously unobserved reaction intermediates: 2-formyl-2*H*-azirine, 3-formylketenimine, 3-hydroxypropenenitrile, imidoyleketene, and 3-oxopropanenitrile.

For 3,5-dimethylisoxazole ( $R_1=R_3=CH_3$ ;  $R_2=H$ ), the two primary photoproducts were captured: 2-acetyl-3-methyl-2*H*-azirine and 3-acetyl-N-methylketenimine. The methyl substitutions blocked many of the *H*-shifts reactions characteristic of the parent isoxazole and allowed observation of other reaction channels. In particular the successful capture of elusive acetyl nitrile ylide was achieved, only one of a few experimentally observed nitrile ylides [2].

The mechanisms of isoxazole ring-cleavage and isomerization reactions, including various intramolecular hydrogen-atom shifts, will be analyzed. Hereby, it will become evident that the photochemically induced reactions of isoxazoles differ from their thermally-induced rearrangements [3].

Finally, the photochemistry of 1,2-benzisoxazoles, i.e. compounds with a benzene-fused isoxazole ring structure, will be presented. Currently these studies are in progress.

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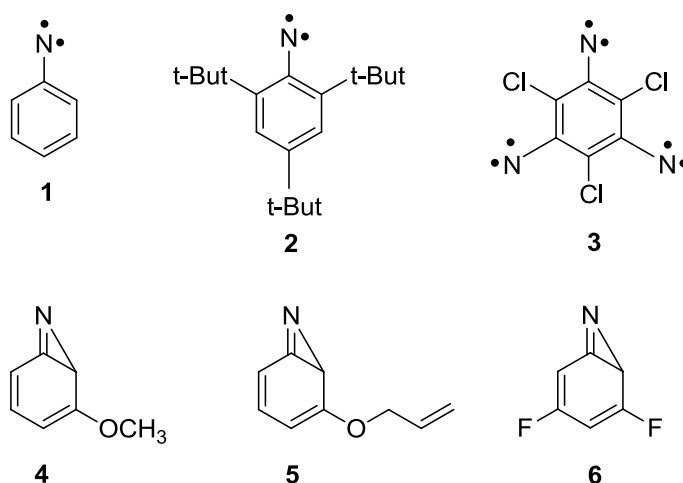
# NITRENES IN REACTIVE MATRICES – FROM PARAHYDROGEN TO SOLID OXYGEN

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Nitrenes as reactive intermediates have attracted wide interest since they are key species for practical applications such as photoaffinity labelling<sup>1</sup>, photoresists<sup>2</sup> and due to be potentially suitable to be used as building blocks for organic magnets. Our group has studied these intermediates and its reactions by means of the Matrix Isolation technique for many years<sup>3</sup>. In this work we would like to present our recent results on the behavior of nitrenes not only in conventional, non-reactive matrix hosts but also in reactive matrices like water, oxygen and *p*-hydrogen.



We studied the thermal and photochemical reactions of triplet phenylnitrene (**1**) with oxygen in O<sub>2</sub>-doped matrices and in pure oxygen<sup>4</sup>. We were able to isolate **1** in pure oxygen at 4 K. Under similar conditions, carbenes react completely in minutes. Phenylnitrene was also isolated in *p*-hydrogen at 2.8 K, where a similar photochemistry to argon was observed. Intramolecular reactions of nitrenes were studied using a tert-butyl-substituted nitrene (**2**). Photochemical insertion of the nitrene center into the CH bond of the substituent is preferable than the reaction with the matrix host even in pure hydrogen. The insertion product was as well the main product in the thermolysis of the corresponding tert-butyl-substituted azide. Water was also used as reactive host for the matrix experiments and a trinitrene with septet ground state (**3**) was isolated in pure water and oxygen matrices showing an unprecedented stability. Finally, another kind of reactive intermediates, benzazirines (2H-type), formed in the ring expansion of nitrenes, were isolated and spectroscopically characterized; only very few reports of spectroscopic characterization of this kind of intermediates have been reported. Here three new benzazirines (**4**), (**5**), (**6**) and its ring expansion to the corresponding ketenimines were studied in argon and *p*-hydrogen matrices at 3K.

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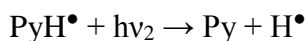
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# UV PHOTOCHEMISTRY OF PYRIDINE-WATER COMPLEX: EVIDENCE OF WATER DISSOCIATION

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A major challenge to generate green energy from sunlight would be to split water into H<sup>•</sup> and OH<sup>•</sup> radicals via photo-sensitisation using a simple organic catalyst. If the ultimate goal is to use visible radiation to split water associated with a photo-catalyst, one has to start with simple prototype systems. Recently, ab-initio calculations<sup>1</sup> predict that pyridine (Py) can act as a photo-catalyst to split water by absorption of a UV photon. In a second step, Py may be regenerated by absorption of a second photon, following the next reactions:



To test this prediction, we performed two different types of experiment. In one hand, we have followed by FTIR spectroscopy, the UV irradiation effects on the Py-H<sub>2</sub>O complex trapped in cryogenic matrices. These experiments<sup>2</sup> shown that, whatever the matrix, UV irradiation induce a proton transfer from water toward Py, leading to the PyH<sup>+</sup> photoproduct. The same results have been observed with Py-NH<sub>3</sub> complex. In the other side, the spectroscopy of PyH<sup>•</sup> has been characterized at low temperature in a supersonic expansion<sup>3</sup>. Since PyH<sup>•</sup> can be probed through one UV photon ionization, experiments with two lasers (pump-probe) have demonstrated that the UV excitation of complex Py(H<sub>2</sub>O)<sub>n</sub> clusters lead to the formation of the PyH<sup>•</sup> radical. In both cases, we can confirm the water dissociation.

We have evidenced the water splitting reaction upon UV irradiation. The last step of the process, the regeneration of the catalyst Py through photo-detachment of the hydrogen atom has to be studied. As the goal is to achieve this water photo-dissociation using sunlight, we are looking forward to test, theoretically and experimentally, bigger systems able to “store” at least two visible photons to induce water splitting.

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# FLUORINE-RICH FLUORIDES: NEW INSIGHTS INTO THE CHEMISTRY OF POLYFLUORIDE ANIONS

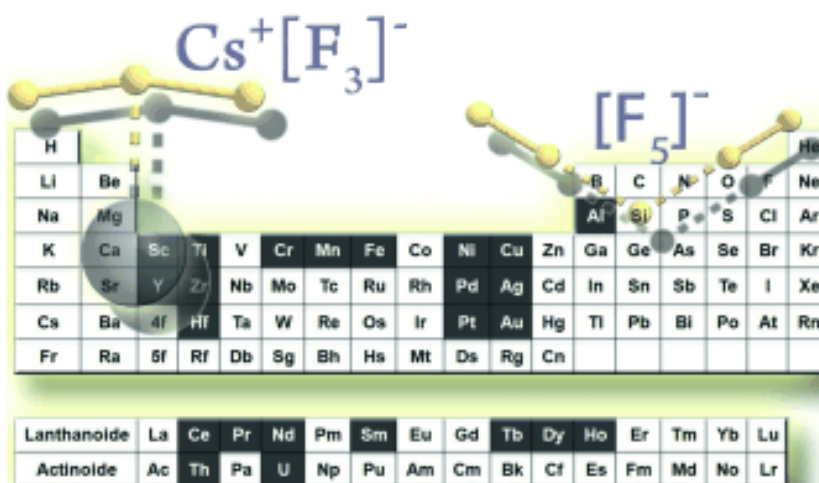
Frenio A. Redeker, Thomas Vent-Schmidt, Felix Brosi, Stefanie Kieninger, Tobias Schlöder, Carsten Müller, Helmut Beckers, Sebastian Riedel

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In the recent years several high oxidized metal based compounds have been investigated under cryogenic conditions using matrix-isolation spectroscopy. Quantum-chemical calculations confirm these experimental assignments and provide fruitful information's about the stability and properties of such cryogenic compounds.<sup>[1]</sup>

In this context the formation of free polyfluoride anions is reported.<sup>[2]</sup> Polyfluoride anions have been investigated by matrix-isolation spectroscopy and quantum-chemical methods. For the first time the higher polyfluoride anion  $[\text{F}_5]^-$  has been observed under cryogenic conditions in neon matrices.<sup>[3,4]</sup> Beyond this, new techniques have been developed to prepare ion-pair complexes such as  $\text{M}^+[\text{F}_3]^-$  in the gas-phase.

Here we present our latest research results of such aforementioned compounds.



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# FORMATION OF NOVEL SI-BEARING MOLECULES IN LOW-TEMPERATURE SiH<sub>4</sub> MATRICES UNDER ELECTRON IRRADIATION CONDITIONS

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We will present our recent results on the chemistry of low-temperature pure SiH<sub>4</sub> and binary SiH<sub>4</sub>/CO and SiH<sub>4</sub>/CO<sub>2</sub> ices under electron irradiation conditions.

The research project was carried out on the Keck machine[1,2] operated at University of Hawai'i at Manoa. The main chamber of this high-tech setup can be evacuated down to a base pressure of  $\sim 10^{-11}$  mbar. The samples, deposited onto a polished substrate, were investigated during the irradiation by UV and IR spectroscopic methods in the temperature range of 5.5 to 320 K. For the gas phase detection and analysis of the desorbed species a sensitive quadrupole mass spectrometer and a novel photoionization reflection time-of-flight mass spectrometer (PI-ReTOF-MS) with a tunable laser light source were used. The latter equipment allowed both the determination of the ionization potentials and, due to the fragment-free photoionization, the determination of molecular masses.

Besides other species, higher silanes (S<sub>n</sub>H<sub>2n+2</sub> up to  $n=19$ ), silanols, and the novel silyl ketene were identified among the reaction products. Experiments carried out on mixtures of different isotopomers shed light on the mechanism of the formation of these molecules.

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# PHOTOLYSIS OF DIBORANE(6) DISPERSED IN SOLID Ne AT 3 K WITH FAR-ULTRAVIOLET LIGHT.

**Bing-Ming Cheng,<sup>1</sup> Sheng-Lung Chou,<sup>1</sup> Jen-Iu Lo,<sup>1</sup> Yu-Chain Peng,<sup>1</sup> Meng-Yeh Lin,<sup>1</sup> Hsiao-Chi Lu,<sup>1</sup> and J. F. Ogilvie<sup>2</sup>**

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Diborane (B<sub>2</sub>H<sub>6</sub>) adopts a molecular structure containing two bridging hydrogen (B-H-B) atoms and four terminal hydrogen (B-H) atoms. The atypical B-H-B bond characterizes an electron-deficient feature of covalent chemical bonds in diborane(6), which thus became a prototype of the B-H-B bond in molecular structure. As gaseous and solid diborane(6) exhibit strong continuous absorptions in the wavelength range 105-230 nm, it is of interest to investigate the electronic transitions and photochemistry of diborane(6) in this far-ultraviolet region. After recording the ultraviolet absorption spectrum, we irradiated samples of B<sub>2</sub>H<sub>6</sub> dispersed in solid neon at 3 K with light of tunable wavelength selected from a synchrotron source. In our photochemical experiment, we could simultaneously record the UV-visible emission spectra during irradiation of samples with the far-UV light; by this means, we recorded the emissions of atoms B and H and radicals BH, BH<sub>2</sub> and BH<sub>3</sub>. After photolysis, we recorded the UV-visible and infrared absorption spectra of the samples. In the UV region, the (0,0) absorption line of transition  $A^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$  of B<sub>2</sub> was observed at 326.62 nm; the (1,0) lines of <sup>11</sup>B<sub>2</sub>, <sup>11</sup>B<sup>10</sup>B and <sup>10</sup>B<sub>2</sub> were recorded at 316.92, 316.40 and 316.66 nm, respectively. Accordingly,  $\Delta G_{1/2}$  of  $A^3\Sigma_u^-$  state for <sup>11</sup>B<sub>2</sub>, <sup>11</sup>B<sup>10</sup>B and <sup>10</sup>B<sub>2</sub> are derived to be 937.1, 963.0 and 989.0 cm<sup>-1</sup>, respectively, in solid neon. In the infrared absorption spectra, we identified photolysis products BH, BH<sub>2</sub>, BH<sub>3</sub> and HBBH. Lines in another set with common properties of growth and decay are characteristic of a carrier containing two boron atoms and at least three hydrogen atoms, which we identify as diborane(4), B<sub>2</sub>H<sub>4</sub>, according to isotopic shifts, both from <sup>10</sup>B and <sup>11</sup>B and from H and D, consistent with the results of quantum-chemical calculations of vibrational wavenumbers. These calculations indicate that this new species B<sub>2</sub>H<sub>4</sub> possesses two bridging B-H-B bonds but of orientation different from those in B<sub>2</sub>H<sub>6</sub>. Our work thus establishes a new prototype, diborane(4), for bridging B-H-B bonds in molecular structure.<sup>[1]</sup> We recorded further new infrared absorption lines, which will be discussed in the presentation.

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# SILICON TETRAHYDROBORATE AND SILYLIDENE DIHYDROBORATE: MATRIX INFRARED SPECTRA AND DFT CALCULATIONS

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Matrix isolation technique and DFT theoretical calculations were employed to study the reaction of boron atoms with silane. Based on the IR spectra and experiments with  $\text{SiD}_4$ ,  $^{10}\text{B}$  and  $^{11}\text{B}$ , together with quantum chemical calculations, the insertion product silyl boron hydride  $\text{HBSiH}_3$ , silylidene boron dihydride  $\text{H}_2\text{BSiH}_2$  formed by  $\alpha$ -H transfer and silicon tetrahydroborate  $\text{Si}(\mu\text{-H})_2\text{BH}_2$  have been identified. AIM, NBO, ELF theoretical methods are used to have an insight into the 3c-2e bond in  $\text{Si}(\mu\text{-H})_2\text{BH}_2$  molecule, and reaction mechanism is discussed.

# MATRIX ISOLATION STUDIES ON THE RADIATION-INDUCED TRANSFORMATIONS OF SMALL MOLECULES OF ASTROCHEMICAL INTEREST AND THEIR COMPLEXES

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Small molecules (typically, 3 to 6 atoms) of both natural and anthropogenic origin widely occur in Earth and planetary atmospheres as well as in planetary and interstellar ices, where they are continuously affected by solar and galactic radiation. The understanding on the mechanisms of their radiation-induced transformations in cold environment is of considerable significance for different areas, ranging from ecology and climatic aspects to extraterrestrial prebiotic evolution of matter. The matrix isolation technique was applied for characterization of intermediates resulting from the molecules of atmospheric and astrochemical importance during several decades. However, most of these studies were related to photochemistry and focused on spectroscopic aspects rather than reaction kinetics and mechanisms.

This presentation gives an overview of very recent model studies on the radiation-induced degradation and reactions of a number of small molecules presenting interest for astrochemistry and atmospheric chemistry (such as H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>2</sub>, HCN, and simple freons) carried out in our laboratory [1–4]. The matrix isolation experiments using X-ray irradiation in solid Ne, Ar, Kr and Xe matrices were performed with an original complex of closed-cycle helium cryostats based on a combination of FTIR and EPR spectroscopy. In addition to characterization of intermediates and molecular products, we have paid special attention to the studies of their dynamics and reaction kinetics at low temperatures, which is particularly relevant to the simulation of reactions in planetary and interstellar ices. According to the results, in many cases, the X-ray-induced degradation is significantly different from the photochemical processes under the action of UV/VUV light. The basic features of the high-energy reactions are (i) involvement of “hot” ionic channels; (ii) population of optically unattainable excited states (particularly, higher triplet states); (iii) predominating role of positive hole and energy transfer. It was found that the reactions of mobile radiation-induced hydrogen and oxygen atoms could play an important role in mixed systems containing different kinds of isolated molecules. We have also investigated the peculiarities of the radiation-induced transformations of “frozen” intermolecular complexes (e.g., H<sub>2</sub>O...CO<sub>2</sub>, HCN...CO<sub>2</sub>, CH<sub>3</sub>OH...H<sub>2</sub>O), which demonstrated dramatic effect of weak molecular interaction on the radiation-chemical evolution at low temperatures in certain systems [2]. The preliminary results of more complex molecules (like C<sub>2</sub>H<sub>5</sub>OH) are also presented. Finally, we discuss possible implications of our approach for astrochemistry and atmospheric chemistry and directions of future studies.

This work was supported by a grant from the Russian Science Foundation (project 14-13-01266).

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# ION-INDUCED REACTIVITY IN COLD CLUSTERS OF POLYCYCLIC AROMATIC HYDROCARBON MOLECULES

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Polycyclic Aromatic Hydrocarbon molecules (PAHs) consist of fused aromatic carbon rings, typically with hexagonal benzene-like structure. Due to their astrophysical relevance, PAHs have been widely studied in the laboratory, particularly by spectroscopic methods, in order to identify PAHs in astrophysical environments. However, the processes of formation and growth of PAH in astrophysical environment are still not fully understood [1]. In this context, ions colliding with clusters of  $C_{60}$  molecules surprisingly induce the formation of  $C_{119}$  [2].

We have studied the interaction of slow singly and multiply charged ions with cold neutral clusters of PAHs at the low-energy ion beam facility ARIBE in GANIL (Caen, France). Clusters are produced in a  $LN_2$  cooled gas aggregation source and the products of the collisions are analyzed by time-of-flight mass spectrometry. The analysis shows that, besides the fragmentation, the interaction leads to the formation of highly reactive species which promptly react with neighboring molecules before the cluster dissociates (ps timescale). Thus, we observe a rich distribution of growth products (see Figure 1) [3]. The fast creation of reactive fragments is due to ion collisions with molecule nuclei, a process specific to ion interaction with matter. Classical molecular dynamics simulations of the entire collision process, from the ion impact to the formation of new molecular species, reproduce the essential features of the measured molecular growth process. These results show that slow ion impact can initiate a growth mechanism inside of molecular clusters which could be important for the physical chemistry in planetary atmospheres such as the one of Saturn's moon Titan where keV  $O^+$  bombardment occurs.

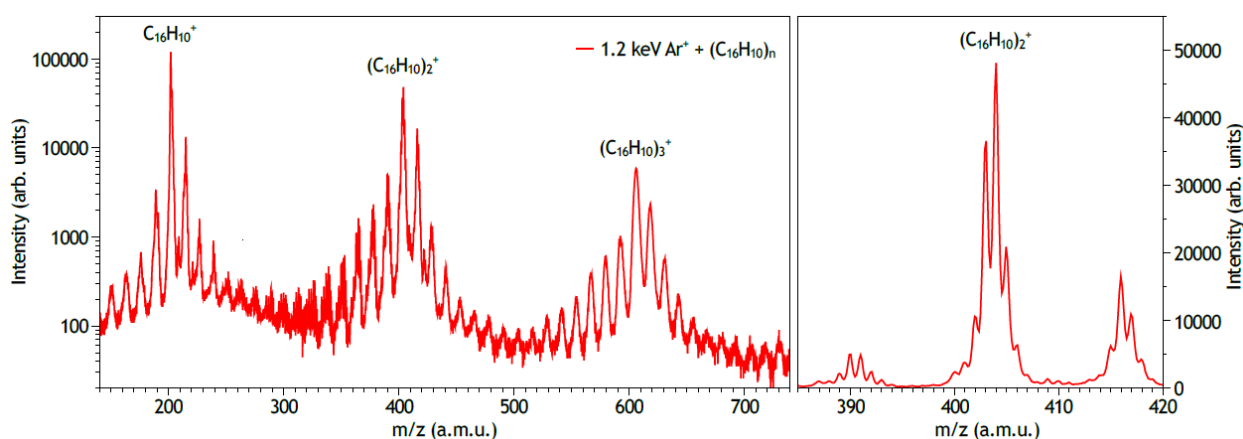


Figure 3: Left panel – Cationic mass spectrum of collisions between 1.2 keV  $Ar^+$  and pyrene ( $C_{16}H_{10}$ ) clusters. Right panel – Zoom in the pyrene dimer region.

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## GAS-PHASE AND SOLID-PHASE CHEMISTRY. FROM THE LABORATORY TO THE INTERSTELLAR MEDIUM.

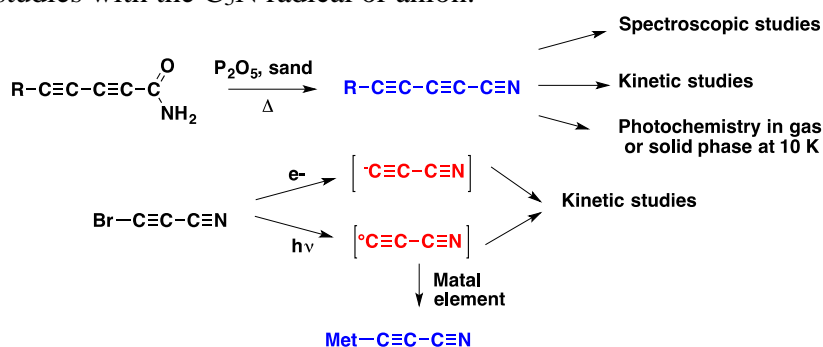
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The improvement of our understanding of the chemistry of the interstellar medium (ISM) needs the availability in lab of many compounds. Having in hand species detected in the ISM allows to clarify their chemistry or photochemistry in experimental conditions as close as possible to those of the ISM or Planetary atmospheres and thus to define new candidates. The recording of the spectra of these latter allows their identification in the ISM if they are present.

Among the compounds we studied, the cyanopolynes have a particular place. Ten years ago, we have synthesized the cyanobutadiyne ( $\text{H-C}\equiv\text{C-C}\equiv\text{C-CN}$ ) for the first time in pure form.<sup>[1]</sup> Another approach of this compound was extended to the preparation of another molecule detected in the ISM, the hexadiynenitrile ( $\text{CH}_3\text{-C}\equiv\text{C-C}\equiv\text{C-CN}$ ).<sup>[2]</sup> We have studied the photochemical formation in gas phase of these cyanopolynes and smaller homologues,<sup>[1]</sup> and photolysis of these compounds condensed onto a gold-plated metal surface cooled to 20 K or onto a sapphire window at 22 K have been developed in collaborations.<sup>[3]</sup>

Non-detected compounds of the ISM are also of interest to generate anions or radicals which have been detected or postulated in this medium. Thus, bromocyanoacetylene ( $\text{Br-C}\equiv\text{C-CN}$ ) has been used as a precursor of the corresponding anion or radical  $\text{C}_3\text{N}$  in very low temperature kinetic experiments simulating planetary atmospheres or the ISM.<sup>[4]</sup> On the other hand such compounds have also been used to generate new candidates by coupling photochemistry (to generate the radical) and laser ablation on a metal. Thus, the aluminum cyanoacetylide ( $\text{Al-C}\equiv\text{C-CN}$ ) has been synthesized as a first example. The recording of its microwave spectrum was the next step before to try to detect it in the ISM.<sup>[5]</sup> Our recent synthesis of the higher homologue,  $\text{Br-C}\equiv\text{C-C}\equiv\text{C-CN}$ ,<sup>[6]</sup> opens the way to similar kinetic or spectroscopic studies with the  $\text{C}_5\text{N}$  radical or anion.



Studies where the availability of these alkynylcyanides is a prerequisite to perform low temperature chemical or photochemical transformations followed by infrared analysis or kinetic measurements will be presented.

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# ENERGETIC GAS-SURFACE ENCOUNTERS AT ICE INTERFACES

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The interaction of energetic atomic and molecular species with ice is of fundamental importance for both terrestrial and astrophysical chemistry. Our initial efforts in ice chemistry, involving both experiment and numerical simulations, demonstrated that translational energy activates the embedding of Xe and Kr atoms in the near surface region of ice surfaces [1-3]. We have also explored the sticking of water on ice [4] as well as the sputtering of ice in the hyperthermal regime using high kinetic energy neutral atom bombardment [5]. These studies revealed a rich palette of dynamics that are dependent upon the kinetic energy and momentum of the gas-surface encounter, the size and mass of the incident specie, as well as the nature of the ice itself; differing dynamics are seen for crystalline ice in comparison to amorphous solid water. We have expanded these studies to include the energetic embedding dynamics of molecular systems, first CF<sub>4</sub> [6] and most recently CO<sub>2</sub> [7], with ice interfaces using a combination of *in situ* FTIR, scattering, and desorption measurements. CF<sub>4</sub> and CO<sub>2</sub> with high translational energies ( $\geq 3$  eV) were observed to embed in amorphous solid water. Just as with Xe and Kr, the initial adsorption rate is strongly activated by translational energy, with the embedding probabilities for both molecules being less than that for Kr and Xe. At  $E_i = 3$  eV, the embedding probability for Xe and Kr is  $\sim 5 \times 10^{-4}$ , for CF<sub>4</sub>  $\sim 5 \times 10^{-5}$ , and for CO<sub>2</sub>  $\sim 10^{-6}$ . The CO<sub>2</sub>/ice system is of particular interest because of its fundamental role in the Earth's aqueous, atmospheric, permafrost, and seabed geosciences, as well as in the interstellar and circumstellar regions. These results show that energetic ballistic embedding in ice is a general phenomenon, and represents a significant new channel by which incident species can be trapped under conditions where they would otherwise not be bound stably as surface adsorbates, with direct implications for environmental science, trace gas collection/release, and the composition of astrophysical icy bodies in space.

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# CRYOSYNTHESIS OF HYBRID NANOMATERIALS

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The use of low temperature technique (4-100 K) enlarges the possibilities of nanochemistry and opens new prospects in creation of bulk and film materials with new conducting, protecting and sensor properties. Low temperatures and matrix isolation technique have been used for stabilization of highly energetic and very active metal species as small clusters and nanoparticles [1-3]. The main scope of our work is to combine the unique properties of metal clusters and nanoparticles with organic substances, particularly polymers and liquid crystals in order to develop the new generation of sensors, catalysts and functional materials.

Cryosynthesis of different hybrid film nanosystems and nanostructured materials including metal nanoparticles has been carried out using metal and organic component molecular beams co-condensation technique under high vacuum and low temperatures. The joint and layer-by-layer condensation of metals (Ag, Mg, Cu, Pb, Sm and Eu) and different active and inert organic and inorganic compounds vapors on the cooled surfaces at 10-300 K were made [4,5].

New metal-containing materials were produced using silver and copper nanoclusters and mesogenic derivatives of alkyl- and alkoxybiphenyls. Controlled thermal treatment of co-condensate samples followed by the directed formation of metal nanoparticles from 2 up to 100 nm stabilized in liquid crystalline matrices. It was shown TEM, AFM data that thermal treatment and molecular self-organisation of mesogenic matrix control the size and morphology of nanoparticles and their aggregates formed in the system. Optical spectra of silver- and copper-biphenyl films at 300K contain plasmonic bands characteristic for metal nanoparticles at 420-440 nm and 560-600 nm. The interaction of the samples with carbon tetrachloride vapor led to the decreasing of the absorbance at plasmonic resonance band [6,7].

Polymer films containing nanosized Zn, Cd, Ag, Pb, Mg and Mn particles were obtained by joint and layer-by-layer condensation with para-xylylene monomer on cooled surface. Co-condensate samples were polymerized by heating up to 110-130 K or by light irradiation at 80 K. The hybrid poly-para-xylylene films with metal nanoparticles could be withdrawn from the reaction vessel and studied by different methods. The particle size histogram demonstrates rather narrow size distribution over the range 2-8 nm with the average size of 5,5 nm. High sensitivity for ammonia and water vapors was shown for films containing lead nanoparticles, having a response exhausted 3-4 orders of magnitude in their electrical conductivity [5].

Recently, production of structurally and size modified drug substances was realized via cryoformation of the solid phase substance obtained by low temperature condensation of their vapors on the cooled surface and using freeze drying technique. We have succeeded also to obtain new hybrid biomaterials based on antimicrobial drugs doped by silver nanoparticles with the activity higher than of the initial components

**Acknowledgements.** The work is financially supported by Russian Foundation of Basic Research.

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# TRANSPORT AND SELECTIVITY PROPERTIES OF CLATHRATE HYDRATES.

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Clathrate hydrates are nanoporous crystalline materials made of a matrix of hydrogen-bonded water molecules (forming host cages) that is stabilized by the presence of foreign guest molecules. The natural existence of large quantities of hydrocarbon hydrates in deep oceans and permafrost is certainly at the origin of numerous applications [1] in the broad areas of energy, environmental sciences and technologies (e.g. gas storage such as hydrogen [2]). In astrophysics, these systems are involved in many models describing comet and planet formation [3]. At a physical-chemistry level, their nanostructuration confers on these materials specific properties (e.g. super-protonic conductivity [4], “glass-like” thermal conductivity [5], etc...). In all these issues, the molecular selectivity and transport properties play an important role. Raman scattering, together with complementary approaches such DFT calculations or neutron scattering, brings unvaluable information due to the specific chemical sensitivity of this spectroscopic techniques. The presentation will focus on recent results ranging from the hydrogen diffusion through the water cages [6] to the high molecular selectivity of carbon monoxide into mixed clathrate hydrates [7].



Tetrahydrofuran ( $C_4H_8O$ ) in the water cavity of its clathrate hydrate.

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## MONTE CARLO SIMULATIONS OF GAS TRAPPING IN CLATHRATE HYDRATES AT LOW TEMPERATURES.

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It is actually tempting to overcome the important deficiency of clathrate equilibrium data at low temperatures by using theoretical approaches such as the van der Waals & Platteeuw method. However, this usual thermodynamic approach is most often based on simplified intermolecular potentials calibrated on equilibrium measurements performed at high temperatures. As a consequence, its ability for predicting the composition of clathrates in the outer Solar System could be questionable. In this work, we show that Monte Carlo simulations performed in the Grand Canonical ensemble (GCMC) can be used to determine theoretically the amount of gas species trapped in clathrate hydrates at low temperature in various situations as encountered in the Solar System.

First, single guest clathrate has been considered with a particular focus on the ammonia molecule which is thought to contribute to the outgassing of methane clathrate hydrates into Titan and Enceladus due to its role as a water-ice antifreeze and methane clathrate thermodynamic inhibitor. However, recent experimental results have suggested that NH<sub>3</sub> clathrate of structure I could be stable at the very low temperatures typical of these Moon's atmospheres (i.e., below 150 K [1]). GCMC simulations have thus been performed to determine the NH<sub>3</sub> occupancy in clathrate as a function of the partial gas pressure and for different temperatures. The results show that the strong hydrogen bonding between ammonia and water molecules tends to strongly destabilize the clathrate cages. As a consequence, stabilizing the ammonia clathrate in molecular simulations appears very difficult, indicating that this clathrate could be stable in very specific conditions, only.

In a second application, we have considered the multiple-guest (MG) clathrate formed from a gas mixture of CO and N<sub>2</sub> to investigate the temperature dependence of the trapping of these two species in clathrate formed on the Jupiter family comet 67P/Churyumov-Gerasimenko (67P). Thus, we have performed GCMC simulations to simulate the composition of a MG clathrate formed from a gaseous mixture of N<sub>2</sub> and CO in proportions corresponding to those expected for the protosolar nebula (87.1 % for CO and 12.9 % for N<sub>2</sub>) in the 20-100 K temperature range. The results show that, at thermodynamic conditions relevant to those of the protosolar nebula, CO has a much higher propensity than N<sub>2</sub> to be trapped in clathrates. Moreover, assuming that 67P agglomerated from clathrates, our calculations suggest that the cometary grains must have formed at temperatures ranging between ~ 31.8 and 69.9 K in the protosolar nebula to match the N<sub>2</sub>/CO ratio measured by the ROSINA mass spectrometer [2].

These two applications illustrate the efficiency of the GCMC method for studying gas trapping in clathrates at low temperature of interest for planetary sciences.

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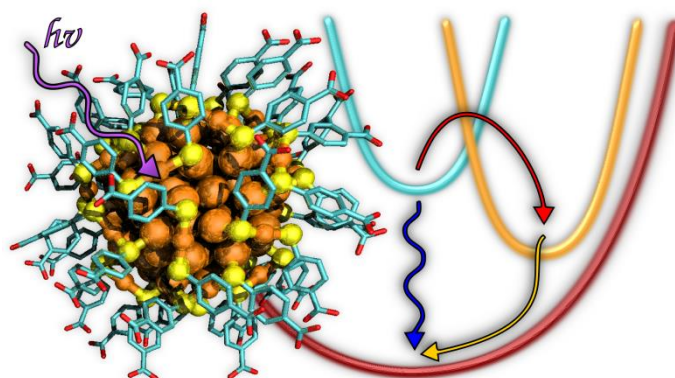
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# ULTRAFAST DYNAMICS OF THIOLATE-PROTECTED GOLD NANOCCLUSERS – MOLECULES OR METALS?

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An important fundamental question in chemistry and nanoscience concerns the behavior of systems when their size increases from atomic limit towards bulk matter. Considering metal nanoparticles, a key property in this regard is the existence or absence of a band gap or HOMO-LUMO gap. Upon closing the energy gap, properties change from molecular-like towards metallic. We have studied this general question via ultrafast photodynamical studies of well-defined ligand-protected gold nanoclusters having 102 – 144 gold atoms. Whereas bare metal clusters are highly reactive and unstable, organic ligand-shell acts as a kind of a “matrix” which makes clusters stable at room temperature and in solution phase. Energy relaxation dynamics is an excellent probe for the electronic structure since it is very sensitive to the existence of an energy gap and thus dramatic difference in dynamics is expected to occur when the gap closes. The present study shows strikingly that the transition from molecular to metallic behavior occurs between ~130 and 144 gold atom clusters. By combining experimental and theoretical work, we are able to present a complete picture of relaxation dynamics for the studied clusters, showing several timescales for relaxation from subpicosecond to longer than nanosecond. Surprisingly, our study reveals an important role of the triplet state in the molecular clusters.



**Figure 1.** Au<sub>102</sub>(pMBA)<sub>44</sub> nanocluster (pMBA = para-mercaptopbenzoic acid) and schematic presentation of its lowest electronic states.

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# POSTERS

# STEERING H-ATOM DIFFUSION THROUGH IMPURITY-DOPED SOLID PARAHYDROGEN

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Ultraviolet irradiation of solid parahydrogen (pH<sub>2</sub>) matrices doped with suitable H atom precursor molecules generates H atoms in situ through a series of photoinitiated chemical reactions. These H atoms move through the matrix via a quantum diffusion process that involves the tunneling-mediated reaction  $\text{H} + \text{H}_2 = \text{H}_2 + \text{H}$ . The mobile H atoms may react chemically with other species that are also embedded in the pH<sub>2</sub> matrix; an investigation of the kinetics of these H atom reactions provides us with information about reaction dynamics in the pH<sub>2</sub> matrix environment. Here we use quantum Monte Carlo simulations to investigate the energy landscape that mobile H atoms experience as they diffuse through an impurity-doped pH<sub>2</sub> matrix. Depending on the relative magnitudes of the long-range interactions of H–H<sub>2</sub> and H–impurity pairs, the presence of an impurity in the pH<sub>2</sub> matrix can create an effective, matrix-induced barrier to H + impurity reactions. Tunneling through this barrier could be the rate-determining step for some H atom reactions in solid pH<sub>2</sub>.

# PROBING COMPLEX NUCLEAR DYNAMICS OF PROTON TRANSFER REACTION INTERMEDIATES TRAPPED IN CRYOGENIC HYDROFLUORIC ACID SOLUTIONS

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Amorphous binary HF:H<sub>2</sub>O molecular solids allow conventional spectroscopic studies of the trapped metastable solvent configurations near the transition state in the proton transfer reactions [1,2]. The signature of a strong intermolecular vibrational coupling between the HF stretching and H<sub>2</sub>O bending modes is observed in infrared spectra of cryogenic hydrofluoric acid solutions [3]. A simple perturbation theory analysis reveals the magnitude of this coupling providing a compelling molecular-level description of the underlying mechanism [3]. Using the HF(H<sub>2</sub>O)<sub>5</sub> gas phase cluster as model, the intermolecular vibrational coupling mechanism is analyzed. We found that a strictly electrostatic description of the intermolecular interactions yields a coupling constant that is one order of magnitude too small and of the opposite sign compared to that obtained from electronic structure-based potentials [3]. These toy models reveal why simple electrostatic models are unable to describe intermolecular v-v couplings along a strong hydrogen bond, further highlighting the crucial role of n→σ\* electron transfer in proton transfer reactions [3]. Our findings demonstrate the distinctively covalent character of strong H-bonds thereby highlighting important shortcomings in the prevalent electrostatic models used to describe H-bond dynamics. They also provide much needed insight into the dynamics of dissociative adsorption for HF [4], HCl [5], and HNO<sub>3</sub> [6,7] on condensed water.

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# NON-ADIABATIC MOLECULAR DYNAMICS SIMULATION OF PHOTO-EXCITED ALKALI DIMERS AND ATOMS IN RARE GAS CLUSTERS

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When coupled to a rare gas cluster, alkali atoms, M, and cationic molecules,  $M_2^+$ , represent a class of ideal systems to probe the relaxation of a photo-excited chromophore coupled to a solvent. The electronic structure of whole system is indeed simple and it can be represented efficiently as a single electron on top of closed-shell atomic cores. As such, a model based on core-polarization pseudopotentials [1-4] allows us to obtain the energy, forces and non-adiabatic coupling that drives the relaxation of the system following photo-excitation. We investigate several aspects of the relaxation dynamics of such systems by means of non-adiabatic molecular dynamics simulation with surface hopping.

On the one hand, we explore the relaxation dynamics of photo-excited cationic dimers embedded in small clusters such like  $Li_2^+Ne_n$  or  $Na_2^+Ar_n$ . For the series of  $Li_2^+$  in  $Ne_{n=1-22}$  clusters, we show how the passage through the various conical intersections on the potential energy surface explored along the relaxation path determines the final population of the various exit channels associated to dissociative relaxation dynamics [2].

On the other hand, we investigate the relaxation of photo-excited alkali atoms (Li, Na, K and Rb) trapped at the surface of small ( $n=1-6$ ) and large ( $n=800$ ) rare gas clusters [4]. We emphasize the role of spin-orbit coupling to drive the system toward its final fine-structure state for dissociative trajectories. For Ar and Ne clusters, the variation of the relative strength of the spin-orbit coupling with respect to the binding energy of the alkali with the rare gas modifies significantly the population of the fine-structure states. For some particular choices of the alkali rare gas pair, our simulation shows that a large amount of  $J=1/2$  population can be produced. This the case for large  $NaNe_{800}$  clusters for which more than 80% of the trajectories end in the  $J=1/2$  state. Our result compares favorably with a recent experimental result for Na atom trapped at the surface of large He clusters [5].

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## ALPHA-CHLORODERIVATIVES OF MALONALDEHYDE AND ACETYLACETONE IN MATRICES.

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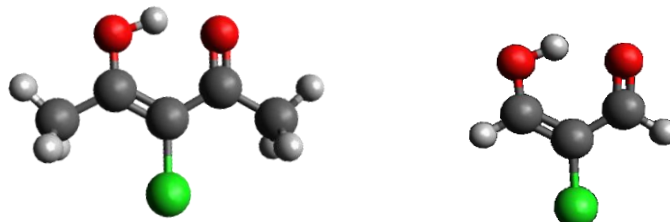
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Malonaldehyde (MA) and acetylacetone (AA) are prototypes of molecules with an internal H bond in their enol form. Both of them are quasi-cyclic in this most stable form (chelated form) but stabilization of open isomers produced by UV irradiation is possible when they are embedded in a matrix.

The substitution of the  $\alpha$  hydrogen by a chlorine atom increases the strength of the H bond in the chelated form of acetylacetone. It also changes the stability order of the different isomers because of the formation of an H bond between the chlorine and the hydrogen of the OH group in some isomers. We present experimental results obtained in Ne and pH<sub>2</sub> matrices, highlighting in one hand matrix effects, especially on vibrational bands of the chelated enols, and in the other hand the substitution effects, when comparing with our results on the non substituted molecules (MA and AA)<sup>1</sup>. Experimental results are supported by quantum chemical calculations.



*figure : Left :  $\alpha$  chloro acetylacetone, right :  $\alpha$  chloro malonaldehyde*

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# NON-ADIABATIC DYNAMICS OF ELECTRONICALLY EXCITED METAL ATOMS (M=Zn, Cd) EMBEDDED IN RARE GAS MATRICES: MOLECULAR DYNAMICS WITH QUANTUM TRANSITIONS.

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Photo-induced processes in metal atoms has been studied for some decades because of their importance for developing optoelectronic devices. Matrix Isolation stands out as one of the most useful experimental techniques to deal with it. Despite numerous theoretical and experimental studies, many questions remain unanswered most of them about metal site occupancy in rare gas matrices. A Molecular Dynamics with Quantum Transitions approach is employed in order to gain insight about the spectroscopic and structural characteristics of these systems. In this study were simulated three model site occupancy: single vacancy, tetra vacancy and hexa vacancy as is proposed according to several experimental results [1-3]. The absorption and emission spectra are in good agreement with the experimental UV Luminescence Spectroscopy results. From calculated absorption spectra the matrix composition was determined weighting each site contribution. We have also perform molecular dynamics calculations mimicking the matrix growth in order to compare this result with that obtained from the weighted absorption spectra. On the other hand, the time evolution of the system shows that upon excitation the metal atom migrates to form a planar configuration M-Rg  $n$  ( $n = 4, 5, 6$ ). Although all the excited states are accessible, fluorescence takes place from the lowest adiabatic excited state. This fact indicates that non radiative processes play a fundamental role in electronic population transference explained by couplings between these electronic states.

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# JET-COOLED HIGH RESOLUTION INFRARED SPECTROSCOPY OF SMALL VAN DER WAALS SF<sub>6</sub> CLUSTERS

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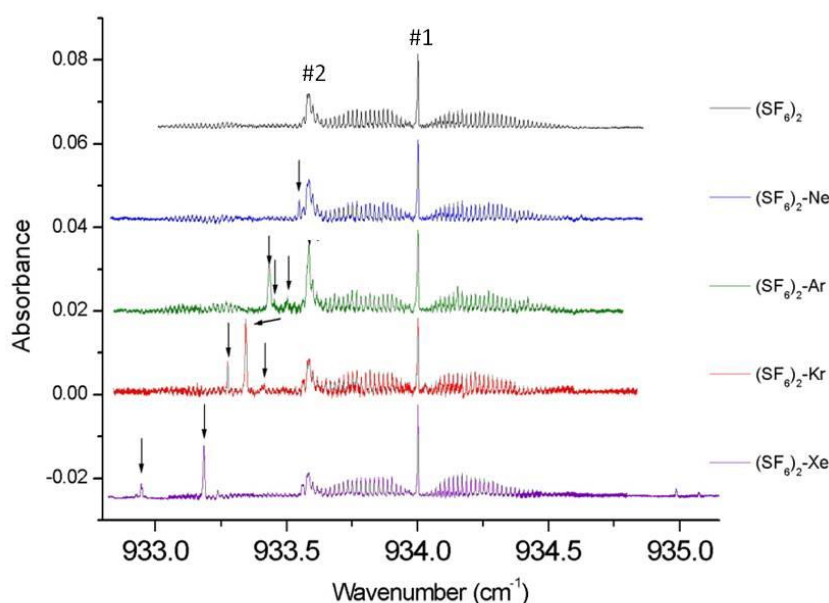
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Using a pulsed slit nozzle multipass absorption spectrometer with a tunable quantum cascade laser we investigated van der Waals clusters involving sulfur hexafluoride in the spectral range near the  $\nu_3$  stretching vibration. Different sized homo-complexes were generated in a planar supersonic expansion with typically 0.5 % SF<sub>6</sub> diluted in 6 bar He. Firstly, several rotationally resolved parallel and perpendicular bands of (SF<sub>6</sub>)<sub>2</sub>, at 934.0 and 956.1 cm<sup>-1</sup> (#1 structure) in agreement with Takami et al. [1] but also one band at 933.6 cm<sup>-1</sup> (#2 structure) never observed previously, were analyzed in light of a recent theoretical study predicting three nearly isoenergetic isomers of  $D_{2d}$ ,  $C_{2h}$  and  $C_2$  symmetry for the dimer. [2] Furthermore, some broader bands were detected around 937.7 and 964 cm<sup>-1</sup> and assigned to (SF<sub>6</sub>)<sub>3</sub> and (SF<sub>6</sub>)<sub>4</sub> clusters on the grounds of concentration effects and/or ab initio calculations. Lastly, with 0.5 % rare gas (Rg = Ne, Ar, Kr and Xe) added to the SF<sub>6</sub>/He gas mixture, a series of van der Waals hetero-trimers (SF<sub>6</sub>)<sub>2</sub>-Rg were observed, which display a remarkable linear dependence of the vibrational shift with the polarizability of the rare gas atom provided that the SF<sub>6</sub> dimer structure is #2. In the same time no transitions belonging to the binary complexes SF<sub>6</sub>-Rg were found near the  $\nu_3$  monomer band. This result suggests a complex thermodynamics within the pulsed supersonic expansion leading to the preponderance of (SF<sub>6</sub>)<sub>2</sub>-Rg clusters over SF<sub>6</sub>-Rg binary systems.

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# INFRARED SPECTRA OF SYMMETRIC MOLECULES ( $\text{SiH}_4$ , $\text{CHF}_3$ ) IN LOW TEMPERATURE MATRICES. CHANGES IN A SYMMETRY OF THE MOLECULES

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A symmetry lowering of molecules of silane  $\text{SiH}_4$  ( $T_d$  symmetry) and fluoroform  $\text{CHF}_3$  ( $C_{3v}$ ) in low temperature matrices was studied in this work. The concentration and temperature dependences of spectra and absorption band splitting in the fundamental and combinational band regions were investigated. The recording of spectra in these regions allows reliable determination of the symmetry of molecules in the matrices. The methods of spectra recording with high resolution ( $0.1 - 0.01 \text{ cm}^{-1}$ ) in low temperature matrices ( $T = 7 - 15 \text{ K}$ ) were developed. In the fundamental region of  $\text{SiH}_4$  in Ar matrix the narrow bands with width of  $0.05 \text{ cm}^{-1}$  and the splitting near  $0.1 \text{ cm}^{-1}$  were observed. The matrices were deposited onto gold-plated copper mirror. But even at double passage of radiation through the matrix the absorbance of some bands in the combination region was as small as  $D < 0.05$  in spite of 6 h deposition time.

**$\text{SiH}_4$ .** The detailed study of the absorption spectra of monoisotopic  $^{28}\text{SiH}_4$  in Ar and  $\text{N}_2$  matrices in the fundamental ( $\nu_3$  and  $\nu_4$ ) and combination ( $\nu_2+\nu_4$ ,  $\nu_1+\nu_4$ ,  $\nu_3+\nu_4$ ,  $\nu_2+\nu_3$ ,  $2\nu_3$ , and  $\nu_1+\nu_3$ ) band regions was done. The spectra of  $\text{SiH}_4$  in  $\text{N}_2$  matrices contain a triplet in the stretching region and a doublet in the bending region, while the doublets are observed in both regions in spectra of Ar matrices. The combination bands in the low-temperature matrices are split into a number of components. The analysis of frequencies and relative intensities of all the splitting components of studied bands in conjunction with local mode model predictions show that the  $\text{SiH}_4$  molecules have the  $C_{3v}$  symmetry in the  $\text{N}_2$  matrices [1], whereas in the Ar matrix they have the  $D_{2d}$  symmetry.

**$\text{CHF}_3$ .**  $\text{CHF}_3$  was studied in the fundamental region predominantly. However preliminary data on weak second order bands have also been obtained. The splitting of C-H bending and C-F stretching bands of  $E$  symmetry was observed in  $\text{N}_2$  matrix (from  $\sim 0.4 \text{ cm}^{-1}$  for the  $\nu_6$  FCF bending band to  $\sim 3 \text{ cm}^{-1}$  for the  $\nu_4$  CHF bending band). The static and Car-Parrinello molecular dynamic simulations predict the symmetry lowering from  $C_{3v}$  to  $C_s$  because interaction of fluoroform molecules with all neighbor  $\text{N}_2$  molecules. In Ar matrix no the degeneracy lifting effects were observed [2].

**Acknowledgements.** This study was supported by Russian Foundation for Basic Research, grant no. 15-03-04605. The spectra were recorded in the Center for Geo-Environmental Research and Modeling (GEOMODEL) of Research park of St. Petersburg State University.

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**INFRARED MATRIX ISOLATION STUDY OF VAN DER WAALS  
COMPLEXES  
BETWEEN CO<sub>2</sub> OR OCS WITH WATER FROM 100 TO 7000 CM<sup>-1</sup>**

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The van der Waals complexes of H<sub>2</sub>O with CO<sub>2</sub> or OCS has typical examples of a weak binding complex involving less than 3 kcal/mol. Up to now a very few experimental vibrational data are available. We have studied by FTIR the complexes involving CO<sub>2</sub> or OCS with water molecules in solid neon. Many new absorption bands close to the well known monomers fundamentals give evidence for (CO<sub>2</sub> or OCS):(H<sub>2</sub>O) complexes and the existence of different conformers will be discussed with the support of theoretical results. Concentration effects combined to detailed vibrational analysis allowed identification of transitions for the 1:1, 1:2, and 2:1 complexes, respectively. Careful examination of the far infrared spectral region allows the assignment of several intermolecular modes. Anharmonic coupling constants have been derived from observation of combinations transitions. Our results show the high sensibility of the solid neon isolation to investigate weak van der Waals hydrated complexes in a large frequency range in contrast with the gas phase experiments and this analysis gives data base to theoretical studies [1].

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# OPTICAL EMISSION SPECTROSCOPY OF MATRIX ISOLATED BISMUTH DIMER IN SOLID NEON

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Rare-gas atoms with closed-shell electronic structure had been thought to hardly form a chemical bond. Since the synthesis of a xenon-containing compound, XePtF<sub>6</sub>, in 1962 [1], chemical bonding of rare-gas atoms has been evidenced experimentally by a variety of compounds [2-5]. In most cases, counterpart of the chemical bond with rare-gas atoms is halogens. Concerning the light rare-gas element of neon, the only compound reported so far is the one with the most electronegative element of fluorine [2].

We conducted matrix isolation spectroscopy of bismuth dimer, Bi<sub>2</sub>, in solid Ne to study physical interaction or chemical bonding between Bi<sub>2</sub> and Ne. The heavy element of bismuth, <sup>209</sup>Bi, is largely polarizable, forming dimers and trimers in the gas phase as well as in the matrices [6, 7].

Optical emission spectra for the A-X transition in Bi<sub>2</sub> were recorded in solid Ne with excitation wavelengths between 540.0 nm and 565.6 nm. Each vibronic band was accompanied by a series of satellite bands unaccountable by a single vibrational progression for the stretching mode in Bi<sub>2</sub>. Figure 1 depicts an example of the satellite. Strong emission was observed upon selective excitations with an increment of 134 cm<sup>-1</sup> [8], especially at 562.0 nm, while weaker emission was discernible upon excitations at wavelengths between the strong resonances. Upon the excitation higher in energy by 38 cm<sup>-1</sup> than the resonance at 562.0 nm, the emission band for the satellite was peaking at wavelength higher in energy by 40 cm<sup>-1</sup>. The appearance of the satellite band is associated with the interaction between Bi<sub>2</sub> and Ne.

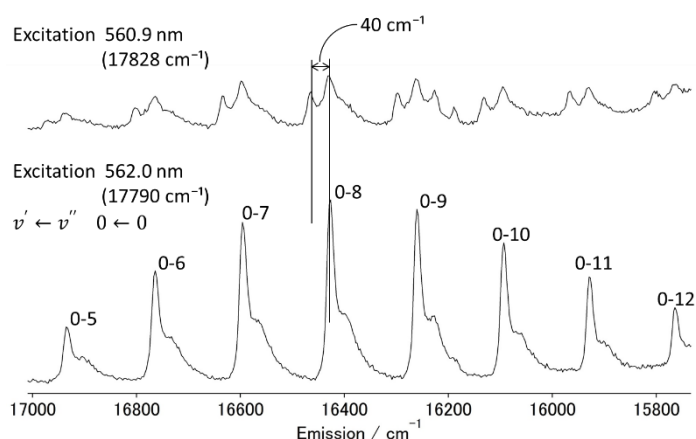


Figure 1. Selected emission spectra for the A-X system in Bi<sub>2</sub> in solid Ne, strong resonance to the 0-0 excitation at 17790 cm<sup>-1</sup> (bottom) and weak satellites upon the excitation at 17828 cm<sup>-1</sup> (top).

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# ELECTROCHEMICALLY GENERATED CATIONIC INTERMEDIATES AS STUDIED BY *IN SITU* RAMAN SPECTROSCOPY

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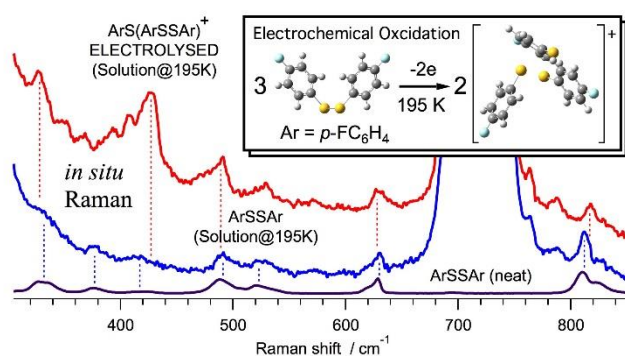
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Electrochemical reaction affords various intermediate species in the production of useful reagents in industrial chemistry. Some are neutral radical and others are cationic species. Most of these are stable only under low temperature conditions. In order to control electrochemical reactions, *in situ* monitoring of intermediate species is important. We have developed an *in situ* Raman spectroscopic detection system for the low temperature condition at -78°C and applied it to the electrochemical reaction converting disulfide, ArSSAr, into arylbis(arylthio)sulfonium ion, ArS(ArSSAr)<sup>+</sup>, where Ar depicts *para*-fluorophenyl group, *p*-FC<sub>6</sub>H<sub>4</sub> [1].

For the system working at the low temperature, invention of a vacuum-tight optical probe was crucial for avoiding the scattering of light by the accumulating frost. The 785 nm cw laser beam was conducted through the reaction cell, containing a solution of reactant molecules, ArSSAr, and electrolyte ions, Bu<sub>4</sub>N<sup>+</sup> and BF<sub>4</sub><sup>-</sup>. Scattered light was conducted through an optical fiber to a polychromator to obtain Raman spectra.

A series of Raman spectra were recorded during the electrolysis. Selected spectra are shown in Figure 1. The carrier for a group of signals showing an increasing intensity proportionally to the consumed current was identified as the sulfonium ion, ArS(ArSSAr)<sup>+</sup>. The characteristic Raman band peaking at 427 cm<sup>-1</sup> was attributed to one of the stretching vibrational modes of the S<sub>3</sub> moiety of the cation, with the aid of molecular orbital calculations. The Raman probe was advantageous for the detection of species having low-frequency vibrational modes of homo-nuclear skeletal bonding of relatively heavy elements.



**Figure 1.** Raman spectra recorded before and after electrolysis at -78°C, converting the neutral dimer, ArSSAr, into the cationic trimer, ArS(ArSSAr)<sup>+</sup> [1].

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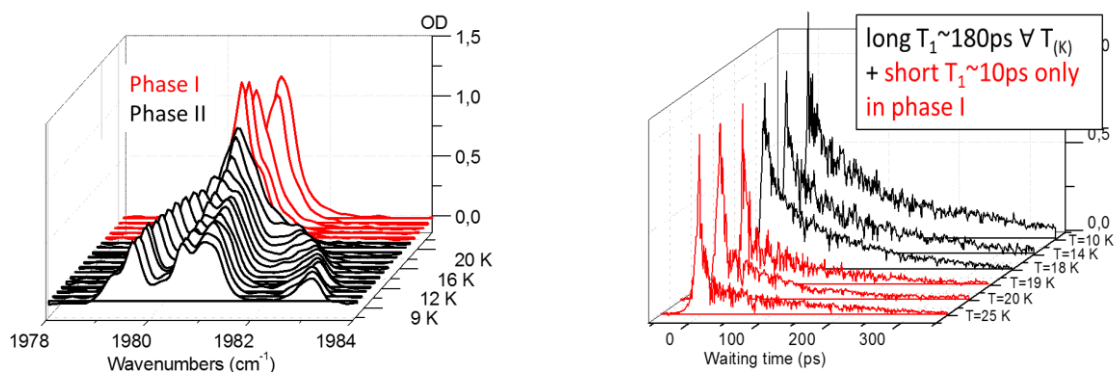
# Ultrafast vibrational dynamics of organometallics trapped in cryogenic solids probed by IR photon echo

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Vibrational dynamics provides a fine tool for probing the effects of environment on the molecular processes at the electronic ground state. Vibrational line shapes in condensed phases contain the details of the interactions of a vibrational mode with its environment. But the homogeneous line shape which contains the important microscopic dynamics is blurred by inhomogeneous broadening. This can be circumvented in the time-domain with the stimulated IR photon echo technique, where three femtosecond IR pulses successively interact with the molecule: it directly gives access to the homogeneous contribution and to dephasing processes through the measure of T<sub>2</sub> (coherent time) and it also informs on the population dynamics through T<sub>1</sub>, population relaxation time [1, 2].

We present the vibrational dynamics study of W(CO)<sub>6</sub> and Fe(CO)<sub>5</sub> organometallic complexes trapped in cryogenic solids. The CO stretching modes of the complexes are used to study the influence of the solid on the dynamics [3]. In the case of W(CO)<sub>6</sub> isolated in solid methane linear and non-linear vibrational spectroscopies enable the identification of a clear temperature behavior of the dynamics and W(CO)<sub>6</sub> turns out to be an original tool for following the phase transition of methane (~ 20K). In the case of Fe(CO)<sub>5</sub> trapped in nitrogen matrix (Figure 1), two CO modes are coherently excited and the vibrational dynamics reveals the presence of energy transfer between the two modes. These studies show that different processes occurring in the time scale of tens of picoseconds can be well separated and identified by the IR photon echo technique.



**Figure 1-** Left: Absorption spectra of W(CO)<sub>6</sub> in methane at different temperatures. Right: Temperature-evolution of T<sub>1</sub> population relaxation time as a function of T<sub>w</sub> waiting times.

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# RADIATION-CHEMISTRY OF HCN-CO<sub>2</sub>-NOBLE GAS SYSTEMS AT LOW TEMPERATURES

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Hydrogen cyanide and related species observed in interstellar medium attract attention of researchers as possible precursors for synthesis of prebiotic molecules occurring under high energy irradiation at extreme temperatures [1]. Essential features of such processes may be revealed by model matrix isolation studies [2]. Meanwhile, this method is also useful for investigation of the radiation-induced transformations of weakly interacting complexes, such as H<sub>2</sub>O-CO<sub>2</sub> [3], using double doped matrices. Such investigations may provide interesting information relevant to astrochemical ices and reveal unique spectroscopic features of the complexes formed by unstable species.

Here we report a FTIR spectroscopic study of the radiation-induced processes in solid noble gas matrices containing different concentrations of HCN (DCN) and CO<sub>2</sub>. The matrix samples were irradiated with X-rays (maximum energy 33 keV) at 6 K and then annealed carefully in the temperature range from 6 to 50 K. The IR spectra were recorded at 6 K. Absorption bands assigned to the HCN-CO<sub>2</sub> complexes of different geometry were observed in the deposited samples. The CO<sub>2</sub>-induced bands in the H-C stretch region of HCN were particularly prominent, if the deposition was carried out at higher temperatures. The identification was confirmed by the quantum-chemical calculations at the CCSD(T)/L2 level.

Irradiation results in decomposition of both HCN and CO<sub>2</sub> molecules. It is worth noting that addition of carbon dioxide makes the radiation-induced decomposition of HCN significantly less effective. The principal products of the radiolysis of triple systems are H, CN, HNC and CO. No evidence for the reactions of mobile O atoms produced from CO<sub>2</sub> with HCN molecules was found. The thermally induced reactions of H atoms were studied in a krypton matrix. These reactions result in appearance of the known absorptions of H<sub>2</sub>CN, HCNH, HCO and HKrCN). In addition, we observed some new CO<sub>2</sub>-induced absorptions, which can be tentatively assigned to the HCNH-CO<sub>2</sub> and HKrCN-CO<sub>2</sub> complexes. The quantum-chemical calculations predict three stable HKrCN-CO<sub>2</sub> complexes characterized by significant blue shift of the H—Kr stretching bands in the IR spectra. The blue shift is in qualitative agreement with the experimental observations, however, additional arguments are required for an unequivocal assignment.

This work was supported by the Russian Science Foundation (project no. 14-13-01266).

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# MECHANISM OF RADIOLYSIS OF FLUOROFORM IN SOLID NOBLE GAS MATRICES.

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Fluoroform is one of the "haloforms", a class of compounds with the formula  $\text{CHX}_3$  ( $\text{X} = \text{halogen}$ ). Due to low reactivity and low toxicity it is used as refrigerant and fire suppressant. Recently it was shown that emission of fluorofom is significantly grown during last three decades, so it makes contribution to global warming process. Furthermore, it does not readily undergo photolysis on reaching the stratosphere. Also, its reactions with other atmospheric scavengers are believed to be negligible, so its lifetime in atmosphere is estimated to be 260 years. Meanwhile, the mechanism of photolytic and radiolytic decomposition is still poorly studied and it presents both fundamental and practical interest. Matrix isolation in solid noble gases is a suitable approach to elucidate possible mechanisms of such transformations occurring in radiation environment.

In this work we report a FTIR spectroscopic study on the radiolysis and postradiation thermal reactions of  $\text{CHF}_3$  in solid Ne, Ar, Kr and Xe. The matrix deposited samples (typically,  $\text{CHF}_3/\text{Ng} = 1/1000$ ) were irradiated with X-rays at ca. 6 K. It is noteworthy that the efficiency of fluorofom decomposition decreases markedly when going from Ar to Xe. Such effect may be explained by high ionizing potential of fluorofom (13.86 eV). This implies that the degradation processes in Ar and Ne matrices mainly occur through the positive hole transfer from matrix, which may be confirmed by the formation of matrix solvated protons ( $\text{Ar}_2\text{H}^+$ ). On the other hand, in the cases of krypton and xenon, positive hole transfer is inefficient, or even impossible, and the observed degradation results from the reactions of excited states. The main products of decomposition in all matrices are  $\text{CF}_3$ ,  $:\text{CF}_2$ ,  $\text{CHF}_2$  and anionic complex  $[(\text{F}-\text{H}):\text{CF}_2]^-$ . The analysis of dose dependence in an argon matrix provides an evidence that the trifluoromethyl radical and complex anion are principal primary radiolysis products. Prolonged irradiation to high doses causes the formation of  $\text{CF}_3^+$  and  $\text{CF}_2^+$ . In contrast, in the case of Xe and Kr matrices, the amounts of all produced species are roughly comparable.

It should be noted that irradiation in all matrices gives fluorine and hydrogen atoms. The production of considerable amounts of fluorine atoms is somewhat unexpected and it is probably related to particular excited states populated under high-energy irradiation. "Hot" F atoms are mobile at 6 K and they probably yield  $\text{CF}_4$ . In addition, there is an indirect evidence for thermal reactions of F atoms, which occur at 15 K in solid argon, at 20 K in krypton and at 30 K in xenon. The relative yield of  $\text{CF}_4$  in xenon is significantly higher than that in other matrices, which is in accord with dominating role of neutral species produced from excited states in this matrix. In addition,  $\text{HKrF}$  and  $\text{HXeH}$  were found as the products of thermal reactions of H atoms occurring in krypton and xenon matrices, respectively.

Finally, we discuss possible manifestations of the formation of novel molecules of noble gas hydrides ( $\text{HKrCF}_3$  and  $\text{HXeCF}_3$ ).

This work was supported by a grant from Russian Science Foundation (project no. 14-13-01266).

# RADIATION-INDUCED TRANSFORMATIONS OF ISOLATED METHANOL MOLECULES IN SOLID NOBLE GAS MATRICES.

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The radiation-induced transformations of small molecules at low temperatures play an important role in the atmospheric, planetary and interstellar chemistry. Methanol is one of the most abundant organic molecules in the interstellar medium [1]. The radiation chemistry of liquid and glassy methanol is well studied [2], but there are virtually no works on the radiolysis of isolated methanol molecules. In order to elucidate the mechanism of the primary processes involved in the degradation of isolated methanol molecules in inert ices, we have examined the effect of X-ray irradiation on CH<sub>3</sub>OH and CD<sub>3</sub>OH in various solid noble gas matrices.

Basic features of our experimental approach for matrix isolation studies of the radiation-induced processes were described previously [3]. Gaseous mixtures of CH<sub>3</sub>OH (or deuterium substituted methanol) and noble gases (Ne, Ar, Kr, or Xe) in typical dilution 1:1000 were slowly deposited onto a KBr plate at the temperatures of 7 – 30 K, depending on the matrix used. Deposited samples were irradiated with X-rays (effective energy ca. 20 keV) at 6 K for 1 – 120 min in order to monitor the dose dependence. Irradiated samples were then annealed for 5 min at different temperatures up to 49 K (depending on the matrix). IR spectra of the samples were recorded using a Bruker TENSOR FTIR-spectrometer (cooled MCT detector, resolution of 1 cm<sup>-1</sup>, averaging by 144 scans).

The FTIR spectra of deposited samples show absorptions of isolated methanol and trace amounts of methanol-water complexes, methanol clusters, matrix-isolated water and carbon dioxide. The main products of radiolysis of isolated CH<sub>3</sub>OH are CH<sub>2</sub>OH, CO, HCO, H<sub>2</sub>CO, and Ng<sub>2</sub>H<sup>+</sup>. The relative yield of CH<sub>2</sub>OH increased markedly while going from Ne to Xe matrix. It should be noted, that CO appears in all matrices, even at low conversion degree of methanol (less than 5%), and its concentration significantly grows with increasing absorbed dose. We have seen no evidence for trapped CH<sub>3</sub>O radical in matrices, but there is an indirect sign of its involvement from the experiments with isotopically substituted methanol. Conversion degree of CD<sub>3</sub>OH after irradiation in noble gas matrices is essentially lower than that for CH<sub>3</sub>OH. The main products of radiolysis in this case are CD<sub>2</sub>OH, CD<sub>2</sub>OD, CO, D<sub>2</sub>CO, HDCO, Ng<sub>2</sub>H<sup>+</sup>. Small amount of HCO also appears, while no absorptions of DCO can be seen after radiolysis.

Experiments with electron scavenger (SF<sub>6</sub>) were carried out to elucidate the relative role of ionic and neutral excited states and possible mechanism of the radiation-induced transformations of isolated methanol is proposed.

Increasing temperature (up to 25 K in Kr and 33 K in Xe) in irradiated methanol/Ng leads to reactions of the thermally mobilized H atoms yielding CH<sub>2</sub>OH and HCO radicals. In addition, the formation of XeH<sub>2</sub> was observed in the case of xenon matrix.

In summary, we may conclude that the radiation-induced transformations of matrix isolated methanol molecules reveal diverse degradation pathways, which were not found in the radiolysis of glassy methanol. These results may be important for better understanding of the fate of methanol in astrochemically relevant ices.

This work was supported by the Russian Science Foundation (project no. 14-13-01266).

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# AZIRIDINE RADICAL CATION IN THE MATRIX OF CF<sub>3</sub>CCl<sub>3</sub> AT 77 K: CYCLIC FORM AND ITS PHOTOTRANSFORMATION

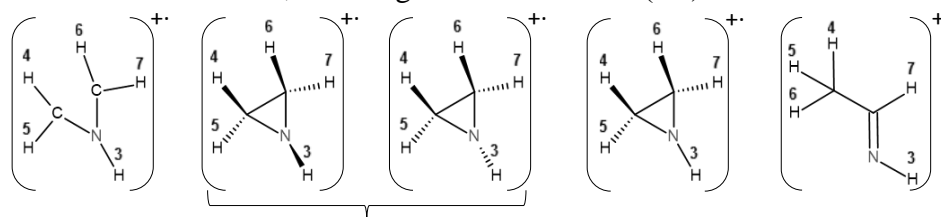
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Quantum chemical calculations demonstrate that, upon photoionization for the aziridine RC, not only the delocalized open form is stable (**I**), but the same can be said about the cyclic form (**II**), which is stable in two conformations. Meanwhile, for the transition state lying along this pathway, the  $\alpha$ -H atom is positioned within the plane of the cycle (**IIa**). While attempting to analyse a cross-section of the PES which follows the coordinate corresponding to C–N bond cleavage, intramolecular atom transfer has been observed for one of the methylene hydrogen atoms in the aziridine RC, resulting in CH<sub>3</sub>CH=NH<sup>+</sup> (**III**).



An EPR spectrum that can be represented as a superposition of an odd and an even signal has been detected in frozen aziridine/CF<sub>3</sub>CCl<sub>3</sub> solutions at 77 K. At the same time, absorption bands in the region of  $\lambda \approx 420\text{--}750$  nm arise in the optical absorption spectrum of the sample. The action of light with  $\lambda = 546$  nm results in the disappearance of a complex band. The EPR spectrum of paramagnetic species remaining in the sample upon photolysis with visible light can be suitably simulated with the following isotropic hfc constants:  $a_{\text{iso}}(4\text{H}) = 1.61$  mT,  $a_{\text{iso}}(1\text{H}) = 0.43$  mT,  $a_{\text{iso}}(^{14}\text{N}) = 0.77$  mT. The comparison of the fitting results obtained for the experimental spectra with the data in literature and with the quantum calculation results allow us to conclude that the six-line EPR spectrum should be attributed to the open form of the RC (**I**). Meanwhile, the difference EPR spectrum, obtained upon subtracting the spectrum detected in the sample after the action of light with  $\lambda = 546$  nm from the spectrum detected upon x-ray irradiation, is an odd one. Essentially, the quantum chemical computations for the cyclic RC form (**II**) can be used as a source of hfc constants that are required in order to simulate the odd EPR signal; however, this fitting appears to be rather artificial for several reasons (technical as well as fundamental). The energy barrier which characterizes the transition between the two conformations of the cyclic form of the RC is quite low, essentially denying the possibility of identifying either one of the conformations as preferable. This, combined with the notion of the  $\alpha$ -H atom residing in the plane of the cycle for the transition state, allows us to use the values of the hfc constants found in our calculations for the transition state in our fittings. The optimization of those constants led us to a reasonable representation of the spectrum with the following values:  $a_{\text{iso}}(4\text{H}) = 3.19$  mT,  $a_{\text{xx}}(1\text{H}) = -3.32$  mT,  $a_{\text{yy}}(1\text{H}) = -3.69$  mT,  $a_{\text{zz}}(1\text{H}) = -2.01$  mT,  $a_{\parallel}(^{14}\text{N}) = 7.42$  mT,  $a_{\perp}(^{14}\text{N}) = 1.70$  mT. In the EPR spectra detected upon the phototransformation of the cyclic RC form, not even trace amounts of the characteristic aziridinyl radical signal can be detected, which excludes deprotonation of the cyclic aziridine RC from the list of possible photochemical mechanisms. Therefore, we interpret the mechanism of the reaction as a result of C–C bond cleavage with subsequent formation of the aziridine RC in its open form (**I**). This work has been performed with financial support granted by the Russian Foundation for Basic Research (projects №№ 13-03-00099, 14-03-32014). Calculations have been performed using resources of the Supercomputing Center of the Lomonosov Moscow State University [1].

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# SWITCHING THE SPIN STATE OF DIPHENYLCARBENE VIA HALOGEN BONDING

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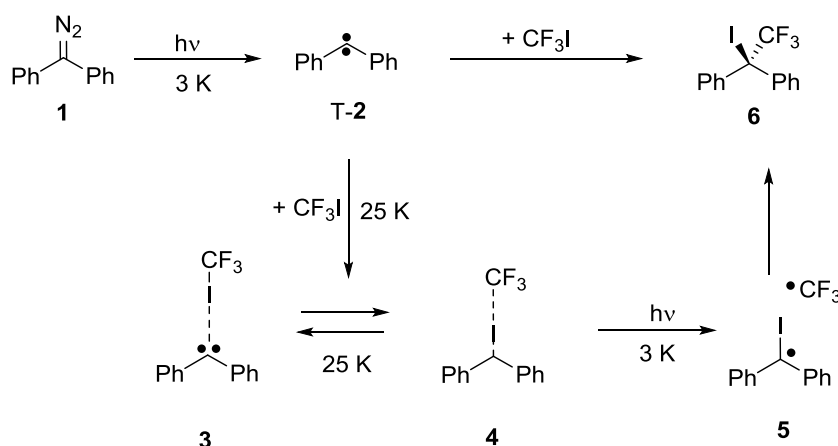
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The spin state is a fundamental property of carbenes and plays an important role in their chemical reactions. The work presented here shows that halogen bonding is a powerful principle to control the spin state of a carbene.

Diphenyldiazomethane **1** was photolysed to generate the ground state triplet diphenylcarbene T-**2** in low temperature argon matrices doped with 0.5 – 1 % of trifluoro iodomethane. Comparisons of experimental and calculated infrared spectra suggest that triplet carbene T-**2** is converted to a halogen bonded complex **3** of the highly polar singlet carbene with CF<sub>3</sub>I is formed upon warming the matrix up to 25 K. This finding is supported by UV/Vis and EPR experiments, which show the conversion of T-**2** into an EPR silent product. In addition to **3**, a second complex **4** is formed during annealing, which results from a transfer of the iodine atom to the carbene center of **2**. Moreover, it was found that both complexes **3** and **4** are formed in an equilibrium state, and by cooling from 25 K back to 3 K the equilibrium is shifted in direction of the thermodynamically preferred structure **4**. Hence, the barrier for interconversion of **3** to **4** must be low. Furthermore, it was observed that irradiation causes the conversion of **3** and **4** to the radical pair of CF<sub>3</sub> and benzhydryl iodine **5**. Besides T-**2**, **3**, **4** and radicals CF<sub>3</sub> and **5**, small amounts of another product, which signals continuously increased throughout the experiments, is observed, which is tentatively assigned to insertion product **6**.



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# PHOTOCHEMISTRY OF THIAZOLE ISOLATED IN LOW-TEMPERATURE ARGON MATRICES

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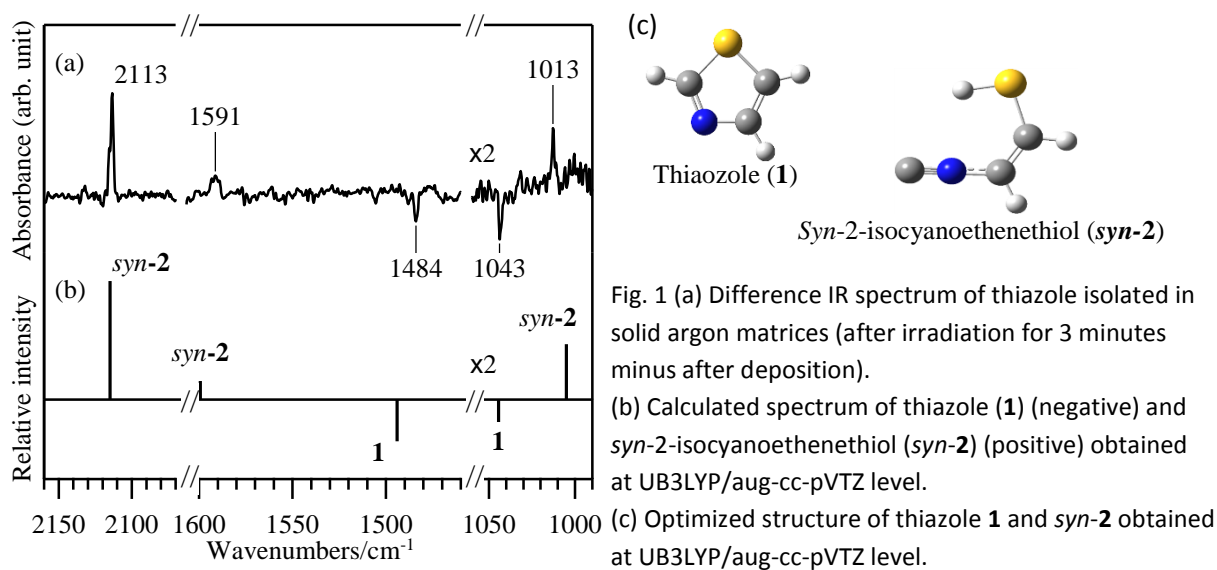
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The thiazole ring is one of the components of natural products such as thiamine (Vitamin B1). In addition, thiazole derivatives are contained in a lot of natural and synthetic products with a wide range of pharmacological activities. Thus it is important to investigate the stability and reactivity of thiazole (**1**), providing the information on the property of natural products including the thiazole ring. About the photochemistry of thiazole, it is known that thiazole produces no reaction products, while isothiazole, an isomer of thiazole, is converted to thiazole by photoirradiation in liquid phase [1, 2]. However, the photochemistry of matrix-isolated thiazole has not been reported yet. In this study, the photochemistry of thiazole isolated in solid argon matrices has been studied using infrared spectroscopy.

In the difference IR spectrum of thiazole/Ar matrices (after short-time irradiation for 3 min minus after deposition), we observed the new bands at 2113, 1591, and 1013  $\text{cm}^{-1}$  with decreasing of the thiazole bands at 1484 and 1043  $\text{cm}^{-1}$  (Fig. 1a). These observed bands do not match to the reported bands of isothiazole in gas phase [3]. By comparison between the observed spectra and calculated spectral patterns obtained by DFT calculations (Fig. 1b), we assigned these new bands to *syn*-2-isocyanoethenethiol (*syn*-2), the spectral pattern of which has not been reported, although the existence of that species is predicted by DFT calculations. The absorbance of *syn*-2 decreased upon prolonged irradiation and the other new bands appeared, leading to the conclusion that *syn*-2 is so reactive that it converts to new photoproducts even in a low-temperature argon matrix.



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# HYDROGEN AND HALOGEN BONDING INTERACTION OF N-HETEROCYCLIC CARBENE

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A matrix isolation infrared spectroscopy study and quantum chemical calculations were carried out for the direct observation of hydrogen as well as halogen bonded complexes of a N-heterocyclic carbene, the stable 1, 3-di-tert-butyl-imidazol-2-ylidene (**1**). In **1**, the carbene carbon is highly nucleophilic due to adjacent nitrogen centers. Such electron rich nucleophilic species can act as powerful Lewis base and form in our case strong hydrogen bond when interacting with water and halogen bond through a  $\sigma$ -hole of  $\text{ICF}_3$  (Figure 1). **1** was trapped in a solid Ar matrix doped with 1% trifluoroiodomethane at 3 K, after annealing of the matrix at 30 K, a formation of a halogen bonded complex between **1** and trifluoroiodomethane was observed. Irradiation of the matrix isolated halogen bonded complex with 254 nm leads to the breaking of the halogen bonded complex and formation of trifluoromethyl ( $\text{CF}_3$ ) radical. Further annealing of the irradiated matrix showed decrease in intensity of  $\text{CF}_3$  radical, accompanied by increase in bands of the halogen bonded complex. At no instance, the formation of an insertion product was observed. Similar experiments were carried out in Ar matrix doped with 1% water to study hydrogen bonding interactions. A hydrogen bonded complex between **1** and water was observed upon annealing the matrix at 30 K. However, no clear evidence for the formation of an insertion product or any rearrangement was observed. The halogen as well as hydrogen bonded complexes were calculated at RB3LYP-D3/6-311G (d, p) level of theory. According to calculations, the hydrogen bonded complex of **1** with water is more stable than the halogen bonded complex with trifluoroiodomethane, with a larger stabilization energy of  $-17 \text{ Kcal mol}^{-1}$ .

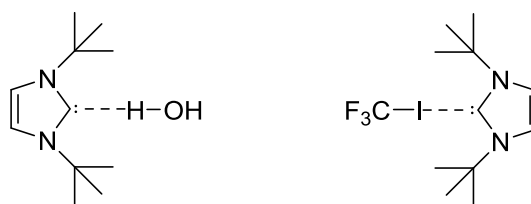


Figure 1: Hydrogen and halogen bonding interaction of 1, 3-di-tert-butyl-imidazol-2-ylidene

# REACTION OF BIS(*p*-METHOXYPHENYL)CARBENE – A BISTABLE CARBENE – WITH OXYGEN: A MATRIX ISOLATION STUDY

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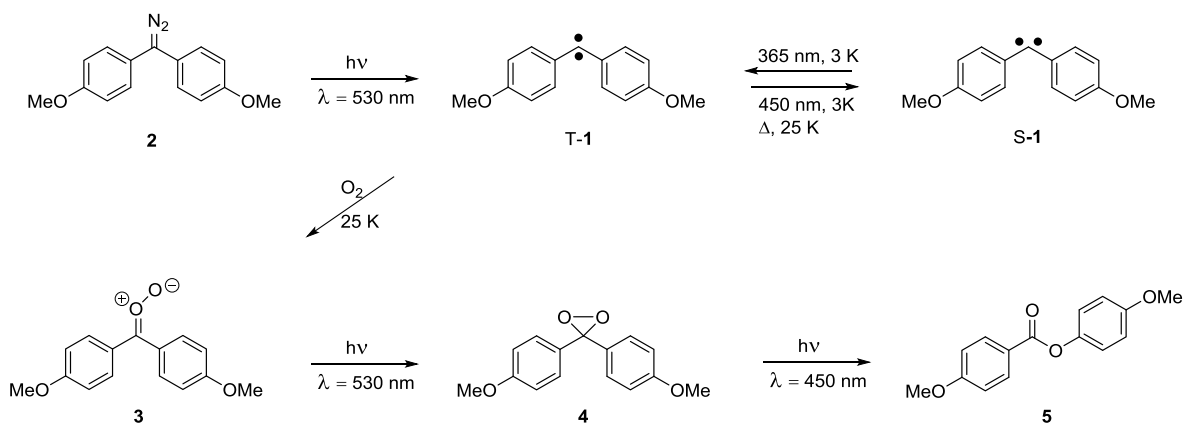
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Bis(*p*-methoxyphenyl)carbene (**1**) is the first carbene that shows the peculiar characteristic to coexist in both its lowest energy singlet and triplet states at cryogenic conditions. Recently in our group we investigated the thermal and photochemical properties of this carbene in argon matrices by IR, UV–vis, and X-band EPR spectroscopy. While UV (365 nm) irradiation of the system produces predominantly the triplet, visible (450 nm) light converts the triplet to the singlet carbene. Annealing to higher temperatures (>10 K) results in the formation of the singlet carbene.<sup>1</sup>

We extended our study showing the dependency of the singlet-triplet ratio in different matrices. After irradiation (530 nm) of the diazo precursor **2** the singlet-triplet ratio was about 50:50. Annealing to 50 K in xenon causes a singlet increase to 66:34. In neon this value was already observed at 7 K. Annealing to 25 K in argon shows a ratio of 75:25.

Furthermore, to explore the spin specificity of our system, we investigate the reaction of bis(*p*-methoxyphenyl)carbene with 1% of oxygen in an argon matrix under matrix isolation conditions. The triplet state of **1** reacts almost exclusively with oxygen giving the corresponding oxidation products, while the singlet remains substantially unreacted.



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# MATRIX ISOLATION AND SPECTROSCOPIC CHARACTERIZATION OF PENTAFLUOROPENYL RADICAL.

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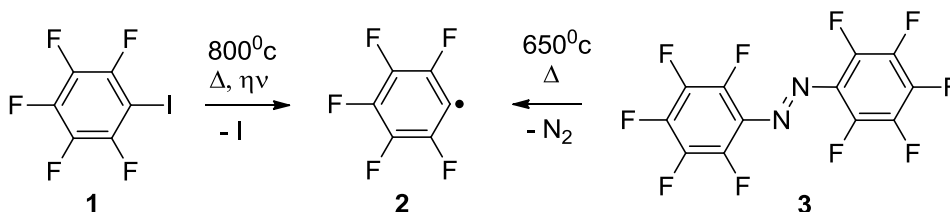
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The phenylradical is a highly reactive intermediate of key importance to organic chemistry that has been extensively studied in solution, in the gas phase, and in low temperature matrices<sup>[1]</sup>. Because of its fundamental importance, it has been subject to many spectroscopic and mechanistic studies.

Fluorination has a large influence on the electronic properties of phenyl radicals, in particular it is increasing their electrophilicity, and therefore the pentafluorophenylradical **2** is an interesting molecule to study. Trapping experiments in solution suggest that **2**, synthesized by reaction of pentafluoroaniline with pentyl nitrite in refluxing solvents, reacts as a highly electrophilic radical. The infrared laser induced decomposition of C<sub>6</sub>F<sub>5</sub>X precursors of **2** in the gas phase resulted in the complete destruction of the benzene ring and formation of C<sub>2</sub>F<sub>4</sub> as one of the key products along with radical **2**. Although the highly reactive **2** is a plausible primary intermediate in the decomposition of C<sub>6</sub>F<sub>6</sub>, there was no direct evidence for the formation of this species. Obviously, the gas phase degradation of C<sub>6</sub>F<sub>5</sub>X results in the rupture of both C-C and C-F bonds which presumably yield highly reactive small radicals such as CF and F atoms that so far escaped direct spectroscopic detection.

To shed some light in the complex thermochemistry of highly fluorinated benzene derivatives we investigated the thermal and photochemical decomposition of pentafluoroiodobenzene **1** using matrix isolation spectroscopy.



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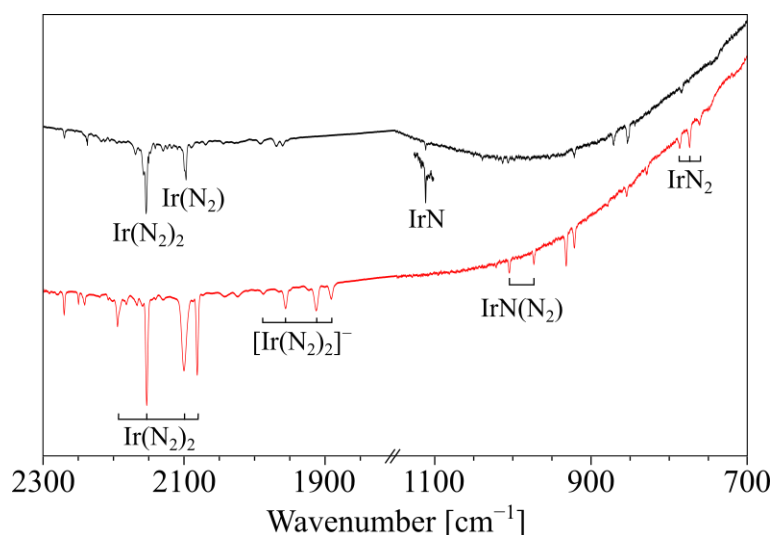
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# REACTION OF LASER-ABLATED IRIIDIUM WITH DINITROGEN: INFRARED SPECTRA OF IRIIDIUM NITRIDES AND IRIIDIUM DINITROGEN-COMPLEXES

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To date, the only known binary iridium nitrogen compound is iridium mononitride observed in a hollow cathode lamp and characterized by its vibrational wavenumber of  $1116\text{ cm}^{-1}$ .<sup>[1]</sup> We have treated laser-ablated iridium atoms with dinitrogen and isolated the products in solid neon, argon and dinitrogen. Novel binary iridium nitrogen species are identified by fourier transform infrared spectroscopy (see figure) performing matrix annealing, photolysis and nitrogen  $^{14}\text{N}_2$ : $^{15}\text{N}_2$  isotope substitution experiments. The assignments are supported by frequency calculations using density functional theory and ab initio methods. The linear dinitrogen complex  $\text{Ir}(\text{N}_2)_2$  and the dinitrogen nitrido complex  $\text{IrN}(\text{N}_2)$  are the major products. The NN stretching wavenumbers are  $2153\text{ cm}^{-1}$  and  $2243\text{ cm}^{-1}$  respectively. Additionally, weaker bands for  $\text{Ir}(\text{N}_2)$ ,  $\text{IrN}$ ,  $\text{IrN}_2$  and the anion  $[\text{Ir}(\text{N}_2)_2]^-$  are observed at  $2154\text{ cm}^{-1}$ ,  $1111\text{ cm}^{-1}$ ,  $787\text{ cm}^{-1}$  and  $1956\text{ cm}^{-1}$ , respectively.



*Infrared spectra of Iridium atoms co-condensed at 5 K with 0.5 %  $^{14}\text{N}_2$  (upper) and 0.5 %  $^{14}\text{N}_2$ : $^{15}\text{N}_2$  (lower) with neon. The spectral region of  $1150 - 700\text{ cm}^{-1}$  is seven fold magnified. Binary iridium nitrogen compounds are indicated.*

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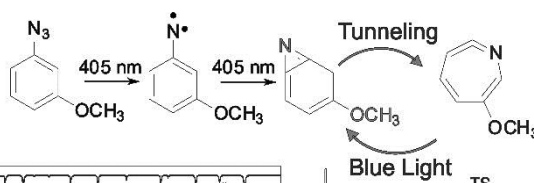
# HEAVY-ATOM TUNNELING IN THE RING EXPANSION OF 3 NEW BENZAZIRINES.

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The direct observation of benzazirines has been rare especially when they are not blocked in position 2 respect to the nitrogen center. They are thought to be intermediates in the ring expansion of nitrenes, which have been widely studied because of its properties as biochemical labeling agents and building blocks for molecular magnets<sup>1</sup>. In this work we isolated and spectroscopically observed 3 new benzazirines. Interestingly we also observed that the isomerization by ring expansion to the 7 membered ring isomer occurs even at temperatures between 3 K - 8 K despite having activation barriers of more than 4,8 kcal/mol, the process is controlled by heavy atom tunneling, and is reversible for several cycles by irradiation with blue light. The tunneling rates were experimentally determined to be in the order of  $10^{-6} \text{ s}^{-1}$  and a temperature independent behavior was observed between 3 - 30K. The discovery of these 3 new systems proves that the ring expansion of benzazirines driven by tunneling is more common that was thought, giving new insights in the reactivity of these intermediates.



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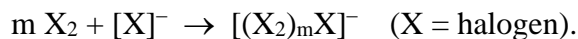
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# FREE POLYHALOGEN MONOANIONS AND MOLECULAR ALKALINE METAL TRIHALIDES IN SOLID NOBLE GAS MATRICES

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We report on spectroscopic studies of polyhalogen monoanions isolated in solid noble gas matrices at temperatures <15 K. These anions can be considered as halogen-bonded systems,<sup>[1]</sup> which might be formed according to



Examples for X = I, Br are known for long time and previously this series was extended to the lighter halogens X = Cl, F.<sup>[2]</sup> The polychloride anions  $[\text{Cl}_3]^-$  and  $[\text{Cl}_3\text{--Cl}_2]^-$  were found in extended solid state ionic structures. Ion pairs  $[\text{MX}_3]$  (M = K, Rb, Cs and X = Cl, F) as well as free  $[\text{F}_3]^-$  anions can be studied in solid noble gas matrices at low temperatures.<sup>[2]</sup>

Novel results were obtained from metal atoms and monomeric ion pairs MX (M = Li–Cs, X = F, Cl), both produced by IR-Laser ablation of the corresponding solids, and their reaction with  $\text{F}_2$  and  $\text{Cl}_2$ , respectively. The products were deposited in noble gases (Ar, Ne) at 5 K and characterized by their IR-spectra. Laser-ablated Pt atoms in the presence of  $\text{F}_2$  provided high yields of the hitherto unknown  $[\text{F}_5]^-$  anion.<sup>[3]</sup> Deposits obtained from monomeric CsX (X = Cl, F) with  $\text{Cl}_2$  and  $\text{F}_2$ , respectively, allowed for the first time comparative spectroscopic studies on isolated  $[\text{CsX}_3]$  ion pairs and free  $[\text{X}_3]^-$  anions.<sup>[4]</sup>

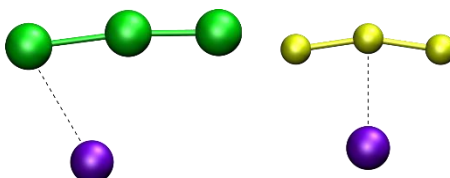


Figure 1: CCSD(T)/def2-TZVPP structures of  $\text{CsCl-Cl}_2$  (left) and  $\text{CsF}_3$  (right).

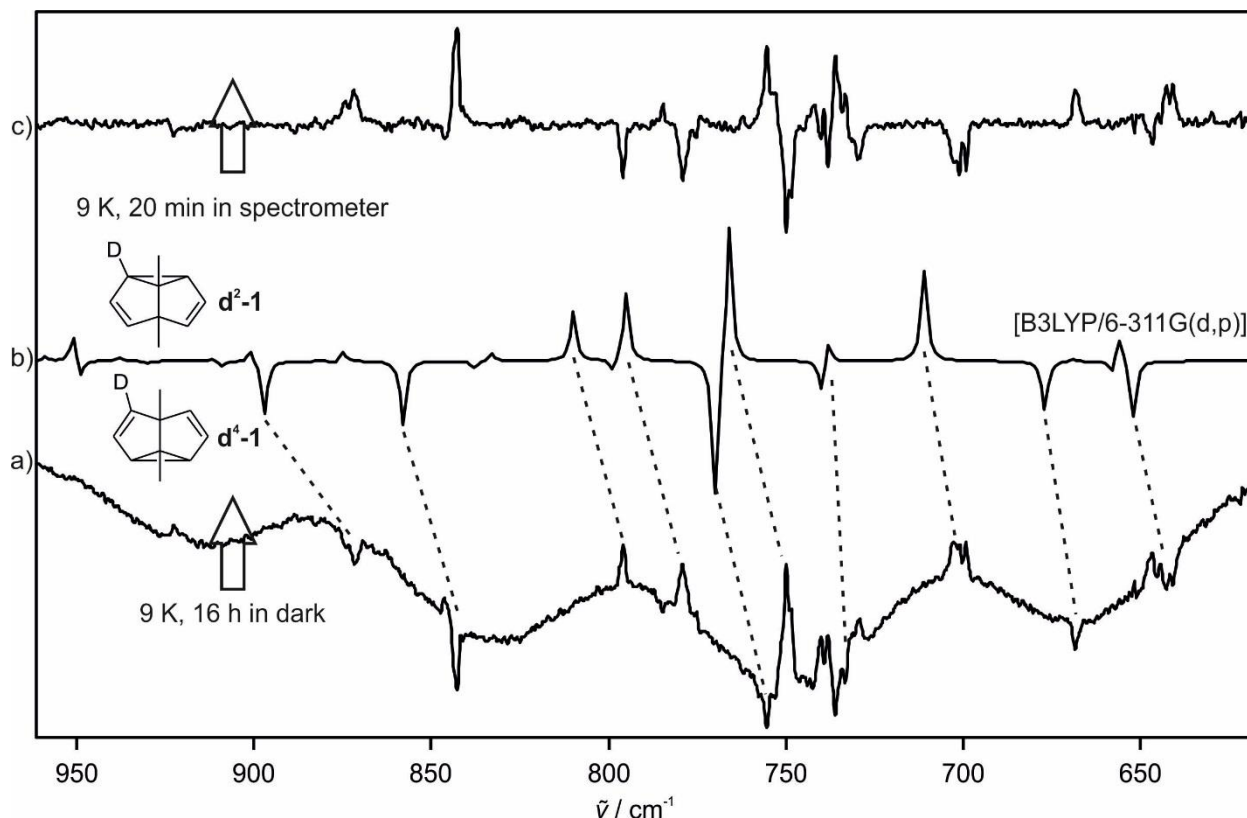
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# COPE REARRANGEMENT OF 1,5-DIMETHYLSEMIBULLVALENE-2(4)-d<sub>1</sub>: EXPERIMENTAL EVIDENCE FOR CONTRIBUTION OF HEAVY-ATOM TUNNELING

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As an experimental test of the theoretical prediction by Borden et al.<sup>[1]</sup> that heavy-atom tunneling is involved in the degenerate Cope rearrangement of semibullvalenes at cryogenic temperatures, mono-deuterated 1,5-dimethylsemibullvalene isomers **d<sup>2</sup>-1** and **d<sup>4</sup>-1** were prepared and investigated by IR spectroscopy using the matrix isolation technique.



**Figure 1.** (a) Experimental IR difference spectrum obtained after 16 h in the dark. (b) Experimental IR difference spectrum after subsequent broadband irradiation. (c) Calculated IR difference spectrum.

As predicted, **d<sup>4</sup>-1** does indeed rearrange to the thermodynamically more stable **d<sup>2</sup>-1** at cryogenic temperatures in the dark (though broadband irradiation with  $\lambda > 2000 \text{ cm}^{-1}$  causes an equilibration of the isotopomeric ratio). Since this reaction proceeds with a rate constant in the order of  $10^{-4} \text{ s}^{-1}$  despite an experimental barrier<sup>[2]</sup> of  $\Delta H^\ddagger = 4.5 \text{ kcal mol}^{-1}$  with only a shallow temperature-dependence, the results are interpreted in terms of heavy-atom tunneling.

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# MATRIX-ISOLATION TECHNIQUE COUPLED WITH RAMAN SPECTROSCOPY

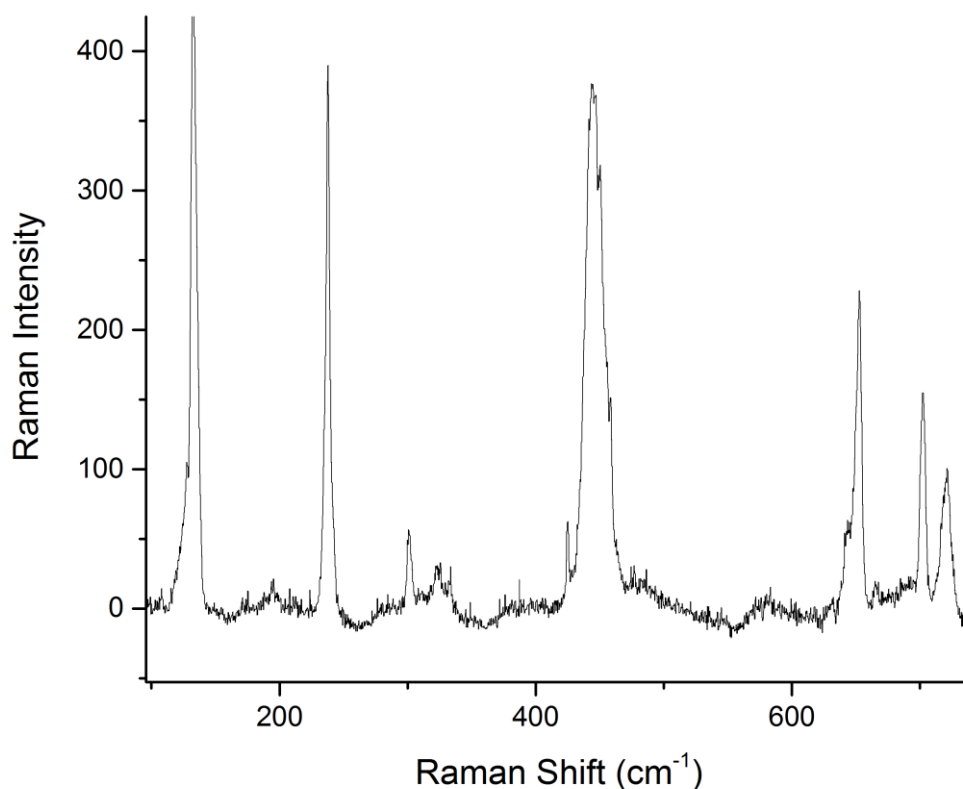
**Raphael Hahn, Helmut Beckers, Sebastian Hasenstab-Riedel.**

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Vibrational spectroscopy of matrix isolated species usually takes the form of infrared absorption spectroscopy. Nevertheless, Raman spectroscopy presents certain interesting features which make it a suitable tool to investigate the vibrational properties of molecules.

The use of Raman spectroscopy in the matrix has been pioneered by Shirk and Claasen<sup>[1]</sup>, Ozin and co-workers<sup>[2]</sup>, and Nibler and Coe<sup>[3]</sup> in 1971.

We present here a set-up for the use of Raman spectroscopy to investigate matrix isolated species, along with several applications to the study of inorganic molecules and their photochemistry.



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# UV LASER INDUCED PHOTOTRANSFORMATIONS OF 2-(1,2,4-TRIAZOLYL)BENZOIC ACID ISOLATED IN LOW TEMPERATURE MATRICES

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<sup>b</sup>*Department of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska Street, 64/13, Kyiv 01601, Ukraine*

An increasing interest is currently given to triazoles, a family of compounds with a five membered heterocyclic ring containing three nitrogen atoms. These species, especially connected to a six-membered ring, play an important role in numerous biological activities. Particularly 1,2,4-triazoles have a great value as human therapeutic agents. They show a broad spectrum of pharmacological activities like antifungal, antitumor, anti-inflammatory, antibacterial, antidepressant or antiviral.[1] On the other hand, the literature reports on triazoles refer to their significant use as interesting organic ligands in modern syntheses of materials exhibiting magnetic exchange coupling or spin-crossover phenomenon. [2] They are also very stimulating heterocycles from an academic viewpoint due to their tautomeric and conformational properties and very interesting photochemistry.[3,4]

The structure, isomerization pathways and vibrational spectra of 2-(1,2,4-triazolyl)benzoic acid (TRAC) molecule were investigated by DFT calculations and matrix isolation FTIR spectroscopy. Among twenty two minima located on PES, nine species are characterized by the presence of the N-H...O or O-H...N intramolecular hydrogen bond. A global minimum is the 2-TRAC1 isomer with the annular H atom attached to the N2 atom of the triazole ring. This structure was identified in argon and nitrogen matrices.

In situ photochemical transformations of TRAC isolated in low temperature matrices were induced by UV laser light. The UV radiation in the 330-220 nm range induced conformationally selective transformations of 2-TRAC1 form into less stable 2-TRAC2 conformer as well as the reverse reaction. Photodecarboxylation of the studied compound was also observed. Exposing TRAC/Ar and TRAC/N<sub>2</sub> matrices to the monochromatic radiation of the 325 nm wavelength led to the formation of phenyl-1,2,4-triazole and carbon dioxide.

The research was supported by the National Science Centre Project No. 2014/13/D/ST4/01741. A grant of computer time from the Wrocław Center for Networking and Supercomputing is gratefully acknowledged.

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# CONFORMATIONAL DISTORTION OF $\alpha$ -PHENYLETHYL AMINE IN CRYOGENIC MATRICES – A MATRIX ISOLATION VCD STUDY

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Vibrational Circular Dichroism (VCD) spectroscopy measures the small difference in the absorption of left- and right circularly polarized infrared light by chiral samples. Therefore, it is very sensitive to the structures, especially conformational changes, of chiral molecules. It is, however, almost always applied for the investigations of chiral molecules in solution where severe line broadening often occurs due to intermolecular interactions. This can sometimes prevent a definite determination of contributions from different conformers to the spectra. The matrix isolation (MI) technique allows measurements of infrared spectra with much higher resolution, i.e. much narrower bandwidth. Hence, the combination of the two methods, MI-VCD spectroscopy, yields a powerful tool to study the structures of and inter- and intra-molecular interactions involving chiral molecules with very high resolution.

In this study, the chiral amine  $\alpha$ -phenylethyl amine (PEA) was isolated in cryogenic matrices and investigated by VCD and infrared spectroscopy. The potential energy surface (PES) of PEA features five different conformers connected by relatively low conformational transition states. Based on the IR spectra, it could be confirmed that all conformational energy barriers are passed at the deposition temperature of 20 K, and that only the global minimum conformation of PEA is populated in both argon or nitrogen matrices. However, differences in the calculated and experimental VCD spectra indicate deviations from the minimum structure by perturbation of the phenyl ring as well as the amine orientation. The degree of perturbation is found to also depend on the choice of the host gas, which shows the subtle influence of the environment in the conformational distortion of PEA. <sup>[1]</sup>

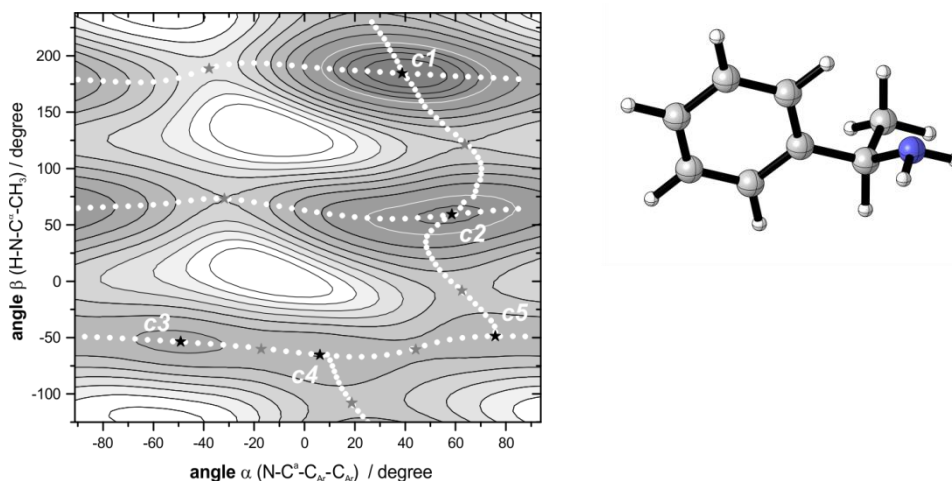


Fig. 1: Potential energy surface with stationary points (minima black, transition states gray) and molecular structure of  $\alpha$ -phenylethyl amine.

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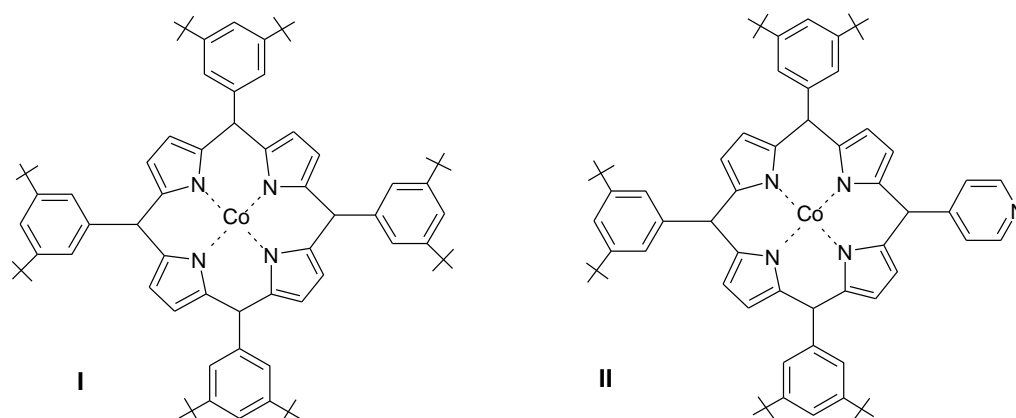
# INTERACTION OF DIATOMIC LIGANDS WITH SUBLIMED LAYERS OF CO-PORPHYRINS CONTAINING BULKY PERIPHERAL SUBSTITUENTS

**Kurtikyan T. S.,<sup>1</sup> Hovhannisyan A. A.,<sup>1</sup> Lubimtsev A. V.,<sup>2</sup> Ageeva T. A.,<sup>2</sup> Koifman O. I.<sup>2</sup>**

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The construction of microporous materials containing coordinatively unsaturated metal ions in their network is an attractive tool for tailoring materials with useful chemoresponsive properties. In this regard the cobaltous complexes of 5,10,15,20-(3',5'-di-tertbutylphenyl)porphyrin (**I**) and 5-(pyridyl-4'-yl)-10,15,20-(3',5'-di-tertbutylphenyl)-porphyrin (**II**) were synthesized and their thin films were prepared by sublimation onto a substrate inside a vacuum optical cryostat.



In contrast to the layers of Co(TPP) ([5,10,15,20-tetraphenylporphyrinato]cobalt(II)) that lose their porosity and ligand-binding ability upon storage at ambient conditions, the films of **I** conserve these properties. Obviously, the bulky tert-butyl groups of **I** prevent the close packing of molecules in the films keeping the metal ions accessible to different ligands for a long time. As a result, these films can be repeatedly used for various applications.

The self-assembly of **II** in sublimed layers leads to the formation of one-dimensional coordination oligomers, in which the pyridyl group of one molecule is coordinated with the metal ion of an adjacent molecule in the layer. The low temperature interaction of O<sub>2</sub>(<sup>18</sup>O<sub>2</sub>), CO(C<sup>18</sup>O) and their mixtures with the films of **I** and **II** were studied by FTIR and UV-vis spectroscopies. It will be shown that films of **II** reveal different binding properties in relation to these ligands. Both 5- and 6-coordinate complexes are formed with the O<sub>2</sub>-ligand, the former at the end of oligomers and the latter with one coordination site occupied by the pyridyl group of an adjacent molecule, while only the end group of oligomers binds CO, forming exclusively 5-coordinate species. As a consequence, the films of **II**, revealing different binding abilities in relation to O<sub>2</sub> and CO, can be used for practical purposes, particularly, for gas separation.

Financial support by the State Committee of Science, Republic of Armenia (Grant 15RF-055) is greatly appreciated.

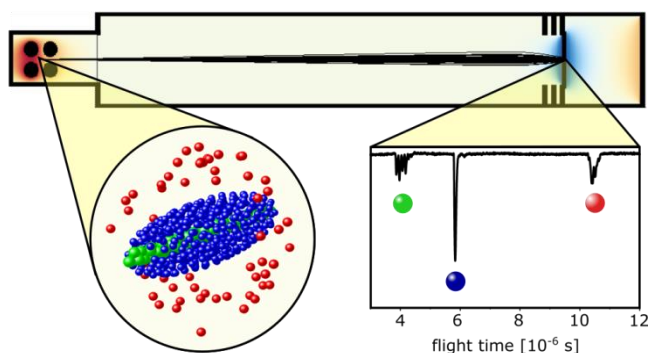
# COLD REACTIVE COLLISIONS BETWEEN NEUTRAL MOLECULES AND COLD, TRAPPED IONS

**Lorenzo S. Petralia<sup>1</sup>, Frederick J. J. Cascarini<sup>1</sup>, Katharina A. E. Meyer<sup>1</sup>,  
Chris J. Rennick<sup>1</sup>, Brianna R. Heazlewood<sup>1</sup>, Tim P. Softley<sup>1</sup>**

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We study ion-molecule reactions under cold conditions, where quantum effects become important. By controlling the properties of both the ionic and neutral reactants, we can examine state-selected reaction dynamics and kinetics as a function of collision energy [1]. Cold neutral molecules are introduced into the reaction chamber through a Stark decelerator [2]; the ionic reactants are held in a linear Paul ion trap. The ensemble of laser-cooled atomic ions within the trap undergoes a phase transition, adopting an ordered structure called a Coulomb crystal [3]. Other non-laser cooled species can be sympathetically cooled into the Coulomb crystal, enabling a range of ionic targets to be prepared.

Reactions are investigated by monitoring the change in the morphology of the crystal over time (observed via laser-induced fluorescence) and by performing time-of-flight mass spectrometry. In particular, a charge exchange reaction between sympathetically cooled  $\text{Xe}^+$  ions and deuterated isotopologues of ammonia is studied using a novel damped cosine ion trap [4].



**Fig. 1.** Pictorial view of the detection process. Coulomb crystals are formed within the ion trap and subsequently ejected towards an MCP detector in order to perform time-of-flight mass-spectrometry.

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# CRYOSYNTHESIS, STABILIZATION AND PROPERTIES OF CORE-SHELL SILVER NANOPARTICLES IN ORGANIC MATRIX AND COVERED BY AMORPHOUS CARBON

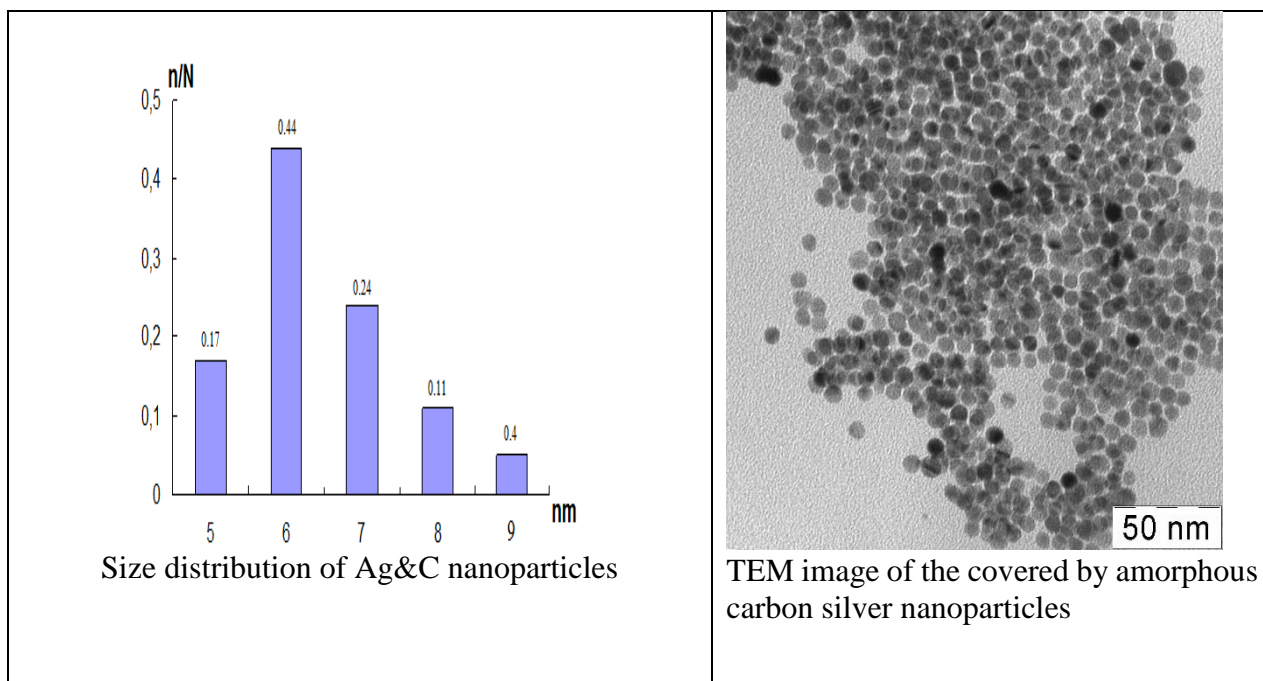
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Vyacheslav V. Zagorskii, Tatyana I. Shabatina

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Synthesis and application of hybrid metal-containing nanostructured materials are of great interest due to their unique physical and chemical, catalytic, optical properties.

Silver containing poly-para-xylylene polymer film samples have been obtained with high vacuum low temperature condensation and studied by transmission electron microscopy (TEM), electron diffraction and optical spectroscopy. The silver atoms beam condensation rate has been measured with quartz microbalance method. The obtained data show the formation and stabilization of globular silver particles randomly distributed in polymeric film. The average size of silver nanoparticles was  $(3.8 \pm 0.3)$  nm for the samples obtained at 1050°C and  $(4.6 \pm 0.3)$  nm for the samples obtained at 1100°C.

Subjecting of the silver-containing polymer film samples by vacuum pyrolysis at 650-700 °C the formation of silver nanoparticles covered by amorphous carbon shell was determined. Encapsulated in amorphous carbon silver nanoparticles have been obtained by vacuum pyrolysis of polymeric films at 650-700 °C. Metal concentration in the samples was varied from 0.1 up to 10 mol % by changing of silver evaporation temperature from 950 up to 1100°C.



The samples were studied by TEM, electron and X-ray diffraction and Raman spectroscopy. TEM image and size distribution diagram were shown at Fig.1 correspondingly. Average size of the particles is  $(6.8 \pm 1.0)$  nm for the sample obtained by silver evaporation temperature of 1100 °C.

**Acknowledgements.** The work is financially supported by Russian Scientific Foundation RSF- 16-13-10365.

## UPGRADE OF A FTIR SPECTROMETER WITH DIAMOND OPTICS.

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In order to optimize IR measurements of mass-selected ions isolated in cryogenic matrices [1], we have upgraded our Bruker IFS66vs FTIR spectrometer. A diamond beam splitter (Fig. 1) and UHV diamond viewports were installed. We also modified a detector chamber to allow measurement with 5 different detectors. This means we can now obtain FT absorption spectra from 11000 cm<sup>-1</sup> to 20cm<sup>-1</sup> with the same sample, selecting only a proper IR detector. Performance of the upgraded FTIR spectrometer was tested on various matrix isolated fullerene ions.



Fig. 1. Modified diamond beam splitter.

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## CRYOSYNTHESIS OF NEW DRUG SUBSTANCES NANOFORMS

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Evaporation and condensation at low temperatures is widely used to obtain the nanoparticles of metals and semiconductors from the atoms [1]. The instability of many organic compounds by heating practically eliminates the direct application of the method of evaporation-condensation for the preparation of organic nanoparticles. For the synthesis of such particles have been used the dry and wet grinding, supercritical fluids, laser ablation and other methods [2].

For the production of crystalline nanoparticles of drug substances have developed an original strategy of the dynamic approach. The strategy combines the joint effect of high and low temperature, gas and solid phase and allows to control the interactions of the heated initial substance with the heated inert gas carrier.

Hot stream containing molecules of original drug substances, interacted with a cold surface. The resulting temperature gradient led to supersaturation and non-equilibrium homogeneous nucleation, aggregation and nanoparticles or nanoforms formation stabilized by cold surface. Cyclicity and increasing the output of products was ensured by the continuity of the process.

The proposed technology does not use solvents and have been applied in practice with the tranquilizer phenazepam (7-bromo-5-(ortho-clorphenyl)-2,3-dihydro-1H-1,4-benzodiazepine-2-on) and steroid neuro hormone 3-beta-hydroxy-androst-5-ene-17-she (DHEA). For phenazepam discovered a new polymorphic modification [3], defined its crystal structure, the crystallite size was 50-70 nm.

For DHEA know of six different polymorphic modifications. We obtained the new seventh modification [4], established its crystal structure, the crystallite size was 100±10 nm.

Tests on animals have demonstrated that the new nanoforms have increased biopharmacological activity compared to the original pharmacopoeia drug substances. Properties of a substance change when they are in the form of nanoparticles or in the form of polymorphic modifications [2]. New polymorphic modification obtained by us in the form of nanoparticles. This circumstance did not allow us to separate the influence of the nanoparticles and polymorphic structures on animals.

This clarification is important because the simultaneous transformation of the particles size and solid structure opens the possibility of a synergistic effect on the properties of known drug substances [1-4].

The work was done under financial support of RFBR grant No 15-03-05178.

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**FULLERENE IONS IN MATRICES AND IN SPACE.****Dmitry Strelnikov, Bastian Kern, Manfred M. Kappes***Karlsruhe Institute of Technology, Institute of Physical Chemistry II,  
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Recently we obtained optical absorption spectra of  $C_{60}^{+/++/-}$ ,  $C_{70}^{+/++/-}$  in a broad range from UV to Far-IR [1,2]. It turned out that DFT calculations reproduce spectra of  $C_{60}$  ions very well, but fail in case of  $C_{70}$  ions. Comparing our IR laboratory data to the astronomical data, taken by the Spitzer space telescope, we suggest several objects, where  $C_{60}^{+}$  are probably present [3].  $C_{70}^{+/-}$  spectral features could not be found, so far, in the astronomical data.

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# CRYOCHEMICAL SYNTHESIS AND ANTIBACTERIAL ACTIVITY OF HYBRID COMPOSITIONS BASED ON AG AND CU NANOPARTICLES INCLUDED IN NANOCRYSTALS OF ANTIBIOTICS

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Wide and not always reasonable use of antibiotics and other antimicrobial agents in medicine has led to the emergence of many resistant strains of microorganisms. In our days, this problem is solved by the synthesis of new antibiotics and simultaneous use of antibiotics and metals nanoparticles. Cryochemical modification is a powerful method of reducing the size of drug substances particles, changing their form and crystal structure in order to improve their pharmaceutical properties. A possible application of this method is to obtain hybrid nanocompositions of metal particles and drugs.

Antibacterial compositions were produced by low temperature freeze drying technique of water solution containing compositions including Ag or Cu nanoparticles and dioxidine or gentamicin. TEM, electron microdiffraction, UV absorption spectroscopy, X-ray diffraction, differential thermal analysis (DTA), Fourier transformation infrared spectroscopy (FTIR) showed the presence in the compositions of Cu/Ag nanoparticles of 5-70 nm in diameter and nanoparticles of antibiotic of 60-250 nm in diameter.

New cryoformed hybrid nanosized compositions of metal particles and antibiotic demonstrates higher antibacterial activity against *Escherichia coli* 52 compared to the original drug and metal nanoparticles.

*Acknowledgements.* The work was financially supported by Russian Scientific Foundation (grant N 16-13-10365).

# THE PRODUCTION AND ISOLATION OF AZIDE RADICAL AT LOW TEMPERATURE : A KEY FOR THE NITROGEN CHEMISTRY IN THE DARK CLOUD

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In the last two decades the interstellar occurrence of  $N_2$  has been questioned and until now it is not well defined because its presence cannot be observed directly, particularly in the dark molecular clouds. The abundance of  $N_2$  affects considerably the nitrogen chemistry and so the prebiotic chemistry. Le Gal & al.[1] has used nitrogen hydrides and Maret & al. [2], Knaugh & al. [3] and Daranlot & al. [4] have used  $N_2H$  to try to estimate  $N_2$  quantities in molecular clouds but it is still considered an open problem. Azide radical  $N_3$  is not observed in the interstellar medium yet. Nevertheless, Hudson & Moore [5] suppose that a part of N may exist in the form of  $N_3$  and it could be used to follow the  $N_2$  abundance. In first place, the essential is to understand the chemistry of  $N_3$ , and more specifically its formation in the interstellar medium. Amicangelo & al. have performed a series of experiments oriented to understand if  $N_3$  is formed in gas phase or solid phase but their results are not conclusive [6]. In other previous works very energetic irradiation is used to dissociated  $HN_3$  molecules, or to produce energetic  $N(^2D)$  atoms or  $N_4$  intermediates with the aim of produced azide radical. In this present work, we are using the matrix-isolation technique in Ne and  $N_2$  carried out from 3K to 30K associated to a microwave discharge in  $N_2$  gas to form  $N(^4S)$  atoms. Similar results, as Amicangelo & al.'s results, were obtained at 10K and 20K. But the consequences of the news results of the experiments achieved between 3 and 10K show a different conclusion. We conclude that the mobility of N atoms in solid matrix of  $N_2$  or Ne is an efficient system to produce azide radical without additional energy and it is completely reasonable to hope find  $N_3$  in dust grains in the molecular clouds. Therefore the azide radical could be used in the molecular clouds to estimate the  $N_2$  abundance.

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## DESIGN AND TESTING OF TEMPERATURE TUNABLE LAVAL NOZZLES FOR ASTROCHEMICAL APPLICATIONS

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Laval nozzles are used for more than thirty years as chemical reactors in order to study the reactivity of bimolecular and three-body processes at very low temperatures [1]. They are the heart of the CRESU (*Cinétique de Réaction en Ecoulement Supersonique Uniforme*, standing for *Reaction Kinetics in a Uniform Supersonic Expansion*) technique that has been recently implemented at the University of Castilla-La Mancha (UCLM) in Ciudad Real (Spain) [2,3]. In this technique, a low temperature flow is generated by isentropic expansion of a buffer gas through the Laval nozzle thanks to a usually large pumping system. The suitably designed shape of the Laval nozzle allows to obtain supersonic flows uniform in terms of temperature, velocity and density for several tens of centimeters. The inner profile of the Laval nozzle is determined from a homemade program provided that the nature and the flow rate  $Q$  of the buffer gas, the desired temperature  $T$  and pressure  $P$  in the supersonic flow and the reservoir temperature  $T_{res}$  are fixed [4]. Therefore, usually, a large number of Laval nozzles are required to match a significant range of temperatures (typ. 15 -295 K).

In the present work, we did a series of characterizations for a couple of Laval nozzles using different buffer gases including well defined mixtures. This allowed us to find new working conditions doing an inverse calculation: for a given geometry and gas mixture, the flow rates,  $T$  and  $P$  were adjusted until the correct existing profile was found. Doing this, it has been possible to generate a series of supersonic flows in the temperature range 22 – 64 K for one nozzle and 35 – 79 K for a second nozzle using different mixtures made of helium and nitrogen. These were introduced in the CRESU apparatus either continuously or in a pulsed way using, in this latter situation, the aerodynamic chopper recently installed at UCLM [2]. The flows were characterized by the Pitot tube technique using a specifically designed probe containing a fast response pressure sensor in direct contact with the flow. A very good agreement was found between calculations and Pitot tube characterizations. The temperature and density profiles will be shown at the conference for different gas mixtures. This is clearly a significant experimental facility of great interest for the study of reaction kinetics of interstellar concern.

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# VIBRONIC STRUCTURE OF CATIONS by PHOTOABSORPTION and PHOTOELECTRON SPECTROSCOPIES in the case of COLD PAHs MONOMERS and DIMERS : A CRITICAL COMPARISON

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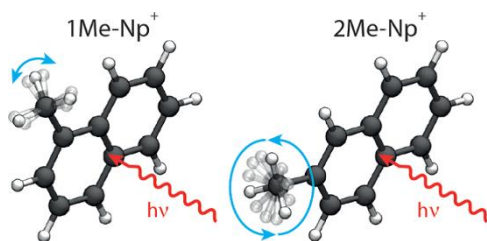
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Polycyclic aromatic (PAHs), in neutral forms as well as in cationic forms, have been put forward since about three decades in an attempt to interpret, and thus to exploit from the astrophysical point of view, the mid-infrared emission features which are almost ubiquitously observed from any molecular cloud in interstellar space, as soon as it is submitted to intense UV/VUV irradiation from surrounding stars<sup>[1]</sup>. For this reason, many laboratory studies on such species, as well as theoretical chemistry studies, have been developed giving rise to a very rich literature in physical chemistry and chemical physics journals.

Getting spectroscopic information about cations generally requires more sophisticated experimental techniques than in the case of neutrals. In addition, valuable spectroscopic information on such large molecular systems requires low-temperature techniques, like matrix isolation and/or cooling by supersonic expansion, in order to limit the spectral congestion. In recent years several studies aiming at getting information about spectral and dynamical properties of this class of species have been achieved by the teams at Orsay and Toulouse, some of them through collaboration with the team of the DESIRS beamline at the SOLEIL synchrotron. In this last case, photoelectron spectra (PES) can be recorded with an accuracy as good as 5 meV. Comparatively the capability of pulsed (nanosecond) laser spectroscopy is much better (resolution as low as 0.1 cm<sup>-1</sup>), but it is restricted to dipole-allowed vibronic transitions.

Using the information collected in some of our recent studies<sup>[2-5]</sup> - including naphthalene C<sub>10</sub>H<sub>8</sub><sup>+</sup> cation and its methylated derivatives (see Figure), coronene cation C<sub>24</sub>H<sub>12</sub><sup>+</sup> and its usual benzo(ghi)perylene impurity, as well as some of their dimers -, as well as literature data based on matrix isolation spectroscopy, the complementarity of the different approaches will be discussed.



While PES normally give access to all electronic states (which can be perturbed by vibronic couplings), optical transitions are restricted by symmetry selection rules. In the case of cationic dimers the intermolecular potential is strongly affected by the presence of charge transfer interactions.

Directions towards new advances in the understanding of the influence of vibronic structure and couplings on the processes relevant for astrochemistry will be discussed.

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# A MASS SELECTIVE RADIOFREQUENCY TRANSFER LINE FOR THE INJECTION OF MOLECULAR IONS IN A COLD UNIFORM SUPERSONIC FLOW

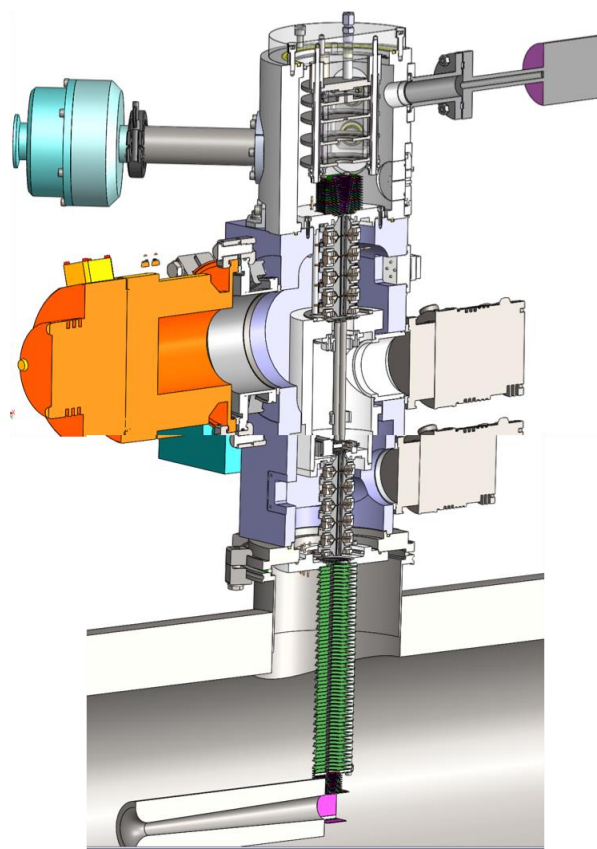
**Baptiste Joalland,<sup>1,\*</sup> Ludovic Biennier,<sup>1</sup> Sophie Carles,<sup>1</sup> Alexander Lekkas,<sup>2</sup> Dimitris Papanastasiou,<sup>2</sup> and Emmanuel Raptakis<sup>2</sup>**

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The astrochemical molecular inventory has recently been enriched with the detection of several anions ( $C_4H^-$ ,  $C_6H^-$  [1],  $C_8H^-$ ,  $CN^-$  [2],  $C_3N^-$ , and  $C_5N^-$ ). So far, the chemical pathways leading to the formation/destruction of these species have hardly been investigated. At the Physics Institute in Rennes, we explore the reactivity (reaction rates, product identities, and branching) of these species by means of uniform supersonic flows issued from specifically designed Laval nozzles, a technique that provides an ideal environment to thermalize gas-phase reactants and products at low temperature (20-30K). [3,4] In this poster, we report on the design considerations of our current instrumental developments regarding a customized, dedicated ion source that enables the injection of significant amounts of mass-selected ions into the dense isentropic core of our uniform supersonic flows. Particular attention is given to reaching the best compromise between mass-selection at low pressure and flow injection at elevated pressure made possible by ion optics simulations in realistic flow fields. Experimental data to characterize transmission efficiency as well as first results on the reactivity of key interstellar anions are also presented.



*CAD of the ionization source and radiofrequency transfer line to selectively transmit ions to the reaction chamber and inject them as close as possible to the Laval nozzle exit.*

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# NEGATIVE CATALYTIC EFFECT OF AMORPHOUS SOLID WATER ON THE SURFACE REACTION OF DIMETHYL ETHER WITH DEUTERIUM ATOMS AT 15 K

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Amorphous solid water (ASW) plays crucial roles in interstellar chemistry as a cold catalytic surface for various chemical and physical processes. Previous studies reported that the surface of ASW lowers an activation barrier of some reactions such as tunneling hydrogen addition to formaldehyde [1]. In addition, some reactions of H and D atoms with molecules such as CO were found to be enhanced on ASW at higher temperatures due to the longer residence time of the atoms on ASW [2]. So, does ASW always act as a “positive” catalyst for chemical reactions on interstellar grains? In the present poster, we will show experimental results on the “negative” catalytic effect of ASW on the quantum-tunneling hydrogen abstraction from dimethyl ether (DME: CH<sub>3</sub>OCH<sub>3</sub>) by deuterium (D) atoms at low temperatures. By forming a complex with water via a hydrogen bond, the C-H stretching band of DME shows a blue-shift as a result of the C-H bond contraction [3], which may suppress the reaction compared to that of pure solid DME with D atoms.

The experiments were performed in an apparatus which is mainly composed of an ultra-high vacuum chamber, an atomic source, and a FTIR. The base pressure of the reaction chamber is about 10<sup>-8</sup> Pa. DME-H<sub>2</sub>O complex with the thickness of ~25 monolayers (1 monolayer = 10<sup>15</sup> molecules cm<sup>-2</sup>) was produced by the vapor-deposition of the mixed gas (DME:H<sub>2</sub>O = 1:4) onto an Al substrate at 15 K. D atoms were produced by the dissociation of D<sub>2</sub> molecules in microwave-induced plasma and cooled to 100 K. The sample solid was exposed to D atoms for up to 240 min at 15 K. Progress in reaction was monitored in-situ by the FTIR. The reaction of pure solid DME (~10 monolayers) with D atoms was also investigated under the same experimental conditions for comparison.

When pure solid DME was exposed to D atoms at 15 K, the formation of deuterated DME was observed on the FTIR spectrum of the reaction product, which indicates the occurrence of hydrogen (H)-D substitution of DME. We propose the successive H-abstraction and D-addition occurred as follows: (1) CH<sub>3</sub>OCH<sub>3</sub> + D → CH<sub>2</sub>OCH<sub>3</sub> + HD, (2) CH<sub>2</sub>OCH<sub>3</sub> + D → CH<sub>2</sub>DOCH<sub>3</sub>. Since reaction (1) has a large activation barrier of ~3600 K in the gas phase [4], quantum-tunneling is required for the reaction to occur at 15 K.

When solid DME in the complex reacted with D atoms, the H-D substitution reactions also occurred under the same experimental conditions. However, the reaction was more than 20 times slower than pure solid DME + D. This would be due to the strengthening of the C-H bond, which is attributable to the formation of a complex with H<sub>2</sub>O via hydrogen bond. Although the H-D substitution is slower in the presence of ASW compared to the case of pure DME solid, this reaction could have a contribution to the D-enrichment of DME in interstellar medium (CH<sub>3</sub>OCH<sub>2</sub>D/CH<sub>3</sub>OCH<sub>3</sub> ~ 0.15 [5]).

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## USING GENETIC ALGORITHMS TO INCREASE THE DECELERATIVE ABILITY OF A SHORT ZEEMAN DECELERATOR

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Zeeman deceleration is an experimental technique in which strong inhomogeneous magnetic fields inside an array of solenoid coils are used to manipulate the velocity of a supersonic beam of paramagnetic atoms or molecules.

In a short Zeeman decelerator, the maximum time for which a pulse of current can be applied to each solenoid coil is mainly limited by the cooling efficiency of the decelerator. Standard switching sequences, which are obtained by simulating the trajectory of a synchronous particle, can be optimised using genetic algorithms to increase the number of particles decelerated to a certain velocity range.

The resulting non-intuitive switching schemes are able to decelerate more effectively, without requiring the long switching times that would be needed for standard sequences and can therefore be used to increase the amount of deceleration achievable by any particular decelerator.

Our 12-stage Zeeman decelerator can reduce the velocity of a beam of ground state  $^2S_{1/2}$  hydrogen atoms from 500 m/s to 200 m/s with standard switching sequences before the pulse duration for the last coil becomes too long to implement. We show that the same beam can be decelerated to below 100 m/s using genetic algorithm optimized sequences, corresponding to a further 20% decrease in final velocity compared to the regular scheme.

A novel detection approach allows us to experimentally probe the beam velocities and particle trajectory simulations give us insight into the deceleration mechanism.

# LOW TEMPERATURE VIBRATIONAL SPECTROSCOPY OF CANCEROUS BIOLOGICAL TISSUE

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Vibrational spectra of biological tissues suffer from being composed of the featureless broad bands. These experimental spectral bands represent a mixture of bands arising from various normal vibrations in proteins, carbohydrates, amino acids and lipids. Despite the overlapping of the bands, the spectra can be used for studies of some chemical features of the tissue. Recently we showed [1,2] that both – IR and SERS spectroscopies of extracellular fluid, which contains single cells of contacting tissue, can be used for the discrimination of normal and cancerous tissue. Unfortunately, assignment of the vibrational spectral bands is very approximate due to the overlapping. That is why any technique which allows increase intensity of the experimental vibrational bands as well as to separate the bands is beneficial. The influence of temperature on the intensity of SERS spectral bands is expected to differ from this in the case of conventional Raman and IR spectra, since the enhancement effect is very sensitive to distance between metal surface and chemical groups of the molecule under interest, and the distance can be strongly temperature dependent.

In this work we have made an attempt to improve the assignment of the SERS spectral bands of extracellular fluid taken from normal and cancerous kidney tissue by examining the temperature evolution of the SERS bands in the 300 - 10 K temperature range. The samples were prepared by sliding the kidney tissue over a substrate - calcium fluoride optical window. For producing the SERS signal the dried fluid film was covered by silver nanoparticle colloidal solution. The temperature evolution of the spectra (see Fig.) reveals that surface enhancement factor for adenine ring Raman bands at  $725\text{ cm}^{-1}$  is more sensitive to the temperature than that for the neighboring bands of phenylalanine/cystine and glycogen. This finding helps for more accurate spectral assignment in this spectral region.

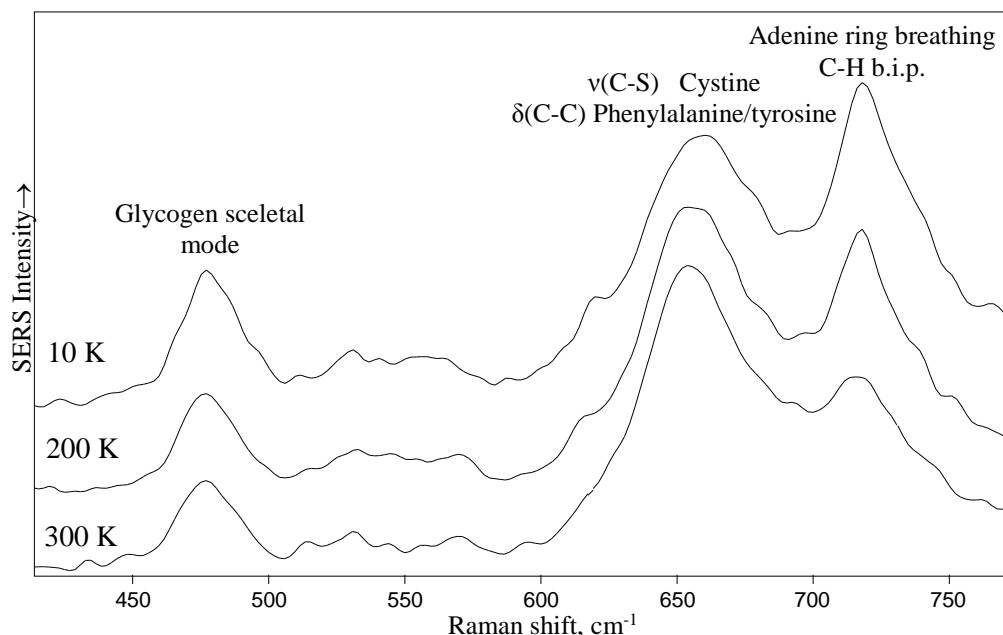


Fig. The temperature evolution of the SERS spectrum ( $400\text{-}800\text{ cm}^{-1}$ ) of extracellular fluid taken from cancerous kidney tissue. Excitation wavelength -1064 nm.

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## A PULSED CRESU EXPERIMENT FOR KINETICS AND COLLISIONAL PROCESSES STUDY DOWN TO 10K

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The study of reaction kinetics in the gas phase at very low temperatures (5-200 K) is of great interest for astrophysics, from the chemistry of planetary atmospheres to the chemistry of the interstellar medium and permits us to improve our understanding of chemical reactivity by extending the validity scope of temperature dependent models.

In this aim, the CRESU (French acronym for Reaction Kinetics in Uniform Supersonic Flow) technique, first developed by Dupeyrat and coworkers [1], has been implemented in Bordeaux since 2005 [2]. This powerful technique consists in using a Laval Nozzle, combined with a very high capacity pumping system which generates, by an isentropic expansion, a cold supersonic flow. Density, temperature and pressure of the jet are controlled by the stagnation conditions ( $P_0$ ,  $T_0$ ), the Mach number and the heat capacity of the buffer gas ( $N_2$ , He, Ar). Up to now, the Bordeaux CRESU is able to reach temperatures as low as 50 K and can create a supersonic flow, with limited Mach number ( $M < 3$ ) and hydrodynamic time ( $\sim 350 \mu s$ ). The flow is also characterized by a relatively high molecular density ( $\sim 10^{17}$  molecule. $cm^{-3}$ ).

Here we present a new pulsed CRESU apparatus, first developed in Rennes [3,4] and still under construction in Bordeaux, based on the use of a Laval nozzle combined with a perforated disc spinning at high speed and called an “aerodynamic chopper”, registered as a patent by S. B. Morales and B.R. Rowe [5]. This specific pulsed system will enable us to maintain the stagnation conditions ( $P_0$ ,  $T_0$ ) while the system moves towards a quasi steady state. In this case, the velocity of gas in the reservoir is considered to be close to zero: the reservoir will be thus very good in terms of aerodynamics. This pulsed CRESU apparatus will be able to run at lower molecular concentration ( $\sim 10^{15}$  molecule. $cm^{-3}$ ) and will need a reduced pumping capacity ( $\sim 2000 m^3.h^{-1}$ ) and much reduced gas consumption.

Our poster shows the advantages, design and restrictions of this evolution of the CRESU technique and how it is theoretically possible to obtain, with this specific pulsed supersonic flow, a very high Mach number uniform jet ( $M \gg 6$ ) enabling us to reach temperatures down to a few Kelvin.

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# CONFORMATIONAL AND PHOTOCHEMICAL PROPERTIES OF *o*-GUAIACOL AND *p*-GUAIACOL. MATRIX ISOLATION FTIR AND THEORETICAL STUDIES

**Justyna Krupa, Maria Wierzejewska, Iwona Kosendiak**

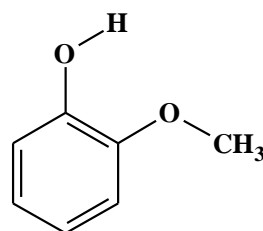
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The compounds known as plants phenols have drawn attention of scientists due to their unique properties as antioxidants and free radical scavengers. One of the biologically active plant phenols is *o*-guaiacol (*o*-methoxyphenol, oGU). This compound is used in medical and dental practices because of its analgesic, anti-inflammatory and anesthetic properties. In turn, the oGU isomer *p*-guaiacol (4-methoxyphenol, mequinol, pGU) is used in medicine as skin lightning agent due to its inhibiting ability in melanin synthesis.

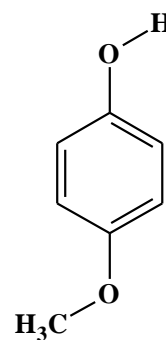
In this contribution, the molecular structure and photochemistry of *o*-guaiacol (oGU) and *p*-guaiacol (pGU) were studied in argon matrices by infrared spectroscopy and B3LYPD3/6-311++G(2d,2p) calculations.

The performed calculations revealed the presence of three conformers of oGU and two of pGU. Only the most stable structure of oGU, with the intramolecular –OH...OCH<sub>3</sub> hydrogen bond, was identified in the experimental oGU/Ar spectra. In turn, for pGU the results indicate that both conformers were present in the experiment. The performed matrix isolation studies are consistent with theoretical predictions. According to the B3LYPD3 calculations the gas phase abundance was predicted to be 49 and 51% for the two pGU conformers whereas the oGU population equals nearly 100% for the most stable structure.

The UV photolysis of the studied compounds was also carried out, with the initial O–H bond cleavage and formation of the *o*- or *p*-methoxyphenol radicals, followed by the radicals recombination to form cyclohexadienone derivatives. The latter molecules transform by ring opening into the long-chain conjugated ketenes. The photoproducted ketenes were found to undergo subsequent photo-decarbonylation.



*o*-guaiacol  
(oGU)



*p*-guaiacol  
(pGU)

## Acknowledgements

A grant of computer time from the Wrocław Center for Networking and Supercomputing is gratefully acknowledged. Project was supported by Wrocław Centre of Biotechnology, programme The Leading National Research Centre (KNOW) for years 2014-2018.

# MOLECULAR DYNAMICS SIMULATIONS OF WATER ADSORPTION AROUND SMALL ORGANIC AGGREGATES AT LOW TEMPERATURES

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Aerosols formed by carboxylic acids represent a significant fraction of the total organic matter in the atmosphere. These aerosols, which are often characterized by an intricate composition, generally have carboxyl groups and free hydroxyls on their surface that can form hydrogen bonds with water molecules. Organic aerosols are thus suspected to be effective condensation nuclei for the formation of liquid water droplets in clouds in the lower stratosphere. Similar process is also suspected to be effective for the formation of ice clouds in the upper troposphere. The importance of organic aerosols on the physico-chemistry of the atmosphere therefore requires a better understanding of their interaction with the surrounding water molecules at low temperatures, to which studies at the molecular level can contribute [1,2].

In the present work, we thus used molecular dynamics simulations to study the interaction of organic aerosols in the presence of water molecules. The aerosols considered are modeled by aggregates of small carboxylic acid molecules (containing formic, acetic, and propionic acids and also some mixing of them) placed in interaction with a variable amount of water molecules representing different relative humidity. Our results show that both the temperature and the water content have a strong influence on the behavior of the acid-water system. Different situations are thus evidenced for the acid–water aggregates (Fig. 1), corresponding either to water adsorption on large acid grains at very low temperatures (below 150 K) or to the formation of droplets consisting of mixed or demixed acid and water molecules at higher temperatures (typically above 200 K). At intermediate temperatures (between 150 and 200 K), an intricate situation is obtained, characterized by a partial deliquescence of the acid aggregates [3,4]. These results represent an additional step towards modeling of organic cloud condensation nuclei, leading to a deeper understanding of the complicated and environmentally relevant problem of heterogeneous nucleation of water.

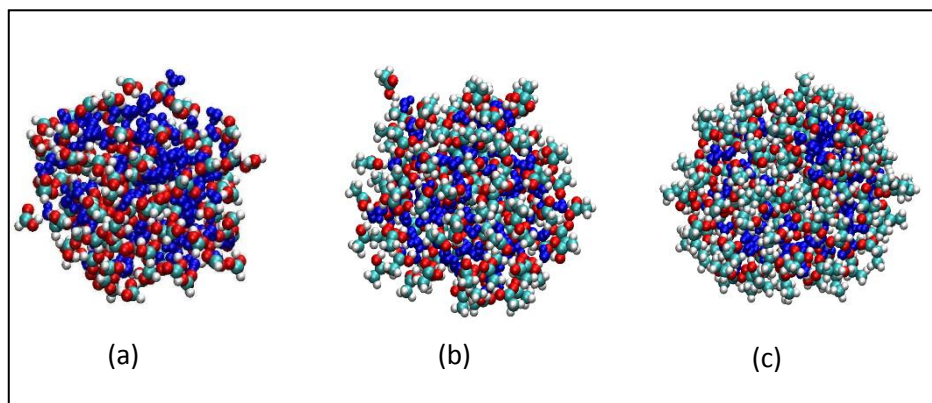


Figure 1: (a) Formic, (b) acetic and (c) propionic acid aggregates interacting with a small amount of water molecules, as modelled in the MD simulations at 200 K.

## References :

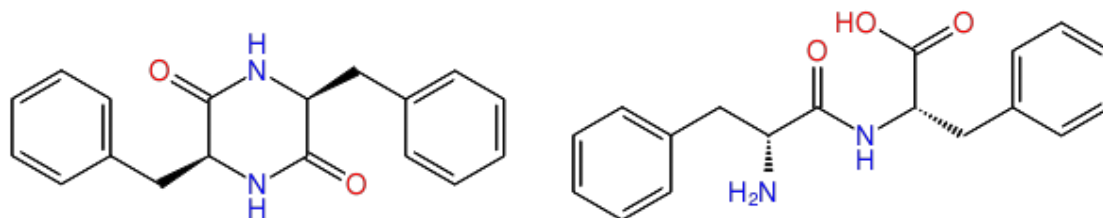
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# BI-CHROMOPHORIC CHIRAL PEPTIDES STUDIED BY CONFORMATION-SENSITIVE VIBRATIONAL SPECTROSCOPY

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Chirality and stereochemistry play a key role in organic chemistry. Most of the biological processes involve interaction between chiral molecules. Gas-phase studies of chiral molecules under neutral or ionic form have helped to understand the nature of the forces responsible for chiral recognition in an isolated pair at molecular level. The aim of this work is to study the conformational preferences of neutral and ionic Bi-chromophoric chiral peptides in the gas phase, like linear and cyclic diphenylalanine (Phe-Phe) (**Fig. a.**). Combining laser spectroscopy with supersonic expansion, R2PI and IR–UV hole burning spectra have been obtained to identify the vibrational signature of different conformers. In the cyclic Phe-Phe systems, we identified one conformer for each LD\_cyclic(Phe-Phe) and LL\_cyclic(Phe-Phe). While in linear (Phe-Phe) systems is a bit more complicated, we identified three conformers for LD\_linear(Phe-Phe) and two for LL\_linear(Phe-Phe). The experimental results have been compared with DFT calculations of the most stable conformers and their vibrational modes. Structures have been proposed by comparing the calculation results with experimental data.



**Fig a.:** System under study. *Left* – cyclic (Phe-Phe). *Right* – linear (Phe-Phe)

## UV PHOTOLYSIS OF VINYL ISOCYANIDE IN AN AR MATRIX

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Numerous groups have studied the physical and reactive properties of vinyl cyanide using diverse techniques. Recently, it was reported [1] that photolysis of vinyl cyanide ( $\text{H}_2\text{C}=\text{CHCN}$ ) in an Ar matrix using Lyman alpha radiation results in the formation of  $\text{HC}_3\text{N}$ , typical  $\text{HC}_3\text{N}$  photolysis products, and complexes including  $\text{HCCH/HCN}$  and  $\text{HCCH/HNC}$ . No isomeric  $\text{C}_3\text{H}_3\text{N}$  species was reported aside from vinyl isocyanide. Although vinyl cyanide may form  $\text{HC}_3\text{N}$  directly, no similar path was postulated for vinyl isocyanide conversion to  $\text{HCCNC}$ . In the work reported here, we explore the use of pure vinyl isocyanide ( $\text{H}_2\text{C}=\text{CHNC}$ ) as a photolysis precursor to determine whether or not such a path to  $\text{HCCNC}$  exists. If  $\text{HCCNC}$  can be produced preferentially and in reasonable concentrations, this would facilitate identification of less intense bands of this chemical or various photolysis products derived from it. Vinyl isocyanide in an Ar matrix was photolyzed using a Kr continuum microwave discharge light source (127-160 nm with maxima at 133 and 147 nm) and monitored using FTIR spectroscopy. These measurements are accompanied by quantum chemical calculations for the vinyl isocyanide potential surface. Taking into account calculated absorption intensities, lower concentrations of  $\text{HCCNC}$  are formed than  $\text{HC}_3\text{N}$  over the time scale of our experiment. Vinyl cyanide formation was also observed, but again, no other  $\text{C}_3\text{H}_3\text{N}$  isomers could be identified based on calculations. We also observed strong signals for complexes including  $\text{HCCH/HCN}$  and  $\text{HCCH/HNC}$ . This matches with the conclusions of [1] suggesting that there is no direct path for formation isocyanoacetylene ( $\text{HCCNC}$ ) starting from vinyl isocyanide, details of which will be presented in the poster.

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# GLYCOCONJUGATES AND GLYCOMIMICS IN THE GAS PHASE: CONFORMATION AND INTERACTION WITH SOLVENT MOLECULES.

Intissar Belaazi<sup>1</sup>, Pierre Çarçabal<sup>1</sup>, Maja Kandziora<sup>1</sup>, Rolando Lozada-Garcia<sup>1,2</sup>, Gerard O'Connor<sup>1</sup>, Oliver Schwardt<sup>3</sup>, Martin Smiesko<sup>4</sup>, Beatrice Wagner<sup>3</sup>.

<sup>1</sup>*Institut des Sciences Moléculaires d'Orsay, CNRS, Université Paris Sud, France.*

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## Introduction:

The conformation of sugars (and their hydrates) has been well studied in the gas phase, but little is known on glycoconjugates. They include natural molecular assemblies such as glycoproteins and also synthetic systems, such as glycolipids or glycomimics. These molecules are “engineered” for specific purposes, in particular in the perspective of better exploiting the specificity of sugars and improving the impact of glycotherapy. The influence of the modification of natural sugars on their conformational preferences and on their interaction with their environment (solvent, partner biomolecule) is a central aspect of their design.

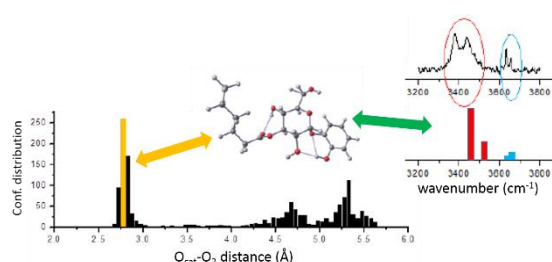
## Methods:

The experimental approach relies on the observation of the vibrational spectra of the interrogated species. Their interpretation is based on their comparison with the spectra predicted by quantum chemistry methods. Typically, only few conformers are observed and not all possible conformers can be treated by quantum chemistry methods because of the cost in computational resources. Molecular mechanics modelling allows exploring all the conformational landscapes and identify the global conformational preferences of the system. It is then possible to estimate how representative the observed conformations are, treating the molecular mechanics data with simple statistical tools.

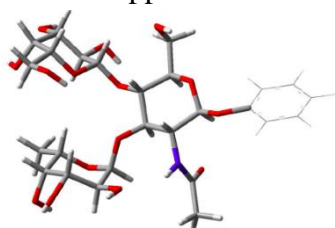
## Results:

For the first time in the gas phase, we have studied a glycolipid model and confronted its unique observed conformation to the *ca.* 1500 conformations predicted by the molecular mechanics exploration. The observed conformation reflects the major conformational preferences of the system.

The effect of modifications of the molecule (methylation) and of the interaction with a single water molecule has also been studied.



We have applied the same approach to mimics of the Lewis<sup>x</sup> antigen and their hydrated clusters.



The previously observed spectra of the isolated natural antigen have been reinterpreted to the light of “dispersion including” functionals and the influence of hydration has been made possible by the observation of its hydrated complex. These results leads to appreciations on solvent effects in such molecules and to interrogations on the (good) use of the many functionals that are now available.

# CRYOGENIC PHOTOCHEMICAL SYNTHESIS OF LONG UNSATURATED CARBON-NITROGEN CHAIN: CH<sub>3</sub>C<sub>7</sub>N

**U. Szczepaniak<sup>a,b,\*</sup>, J.-C. Guillemin<sup>c</sup>, M. Gronowski<sup>a</sup>, M. Chevalier<sup>b</sup>, R. Kołos<sup>a</sup>, Claudine Crépin<sup>b</sup>**

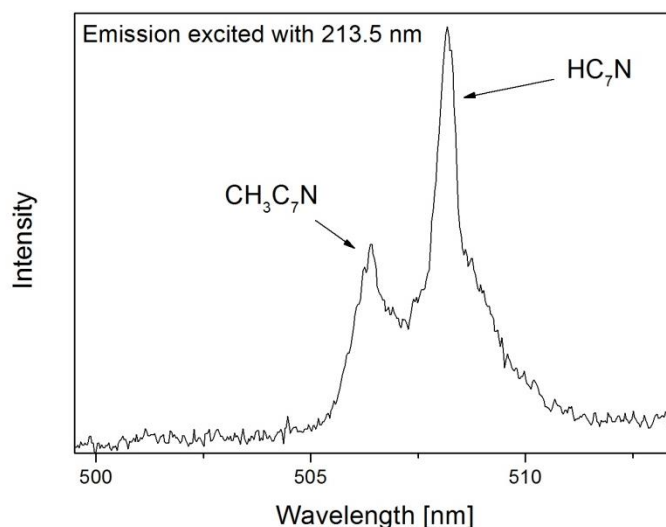
<sup>a</sup> *Institute of Physical Chemistry, Polish Academy of Sciences, POLAND;* <sup>b</sup> *Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS, Univ. Paris-Sud, Université Paris-Saclay, FRANCE;* <sup>c</sup> *Institut des Sciences Chimiques de Rennes, FRANCE;* \* [uszczeplaniak@ichf.edu.pl](mailto:uszczeplaniak@ichf.edu.pl); [urszula.szczeplaniak@u-psud.fr](mailto:urszula.szczeplaniak@u-psud.fr)

Synthesis of CH<sub>3</sub>C<sub>7</sub>N (methylcyanotriacetylene) following the UV photolysis and subsequent coupling of smaller molecules (CH<sub>3</sub>C<sub>2</sub>H and HC<sub>5</sub>N) has been observed in solid krypton:



Gas mixture containing Kr, CH<sub>3</sub>C<sub>2</sub>H, and HC<sub>5</sub>N in a ratio of 500:1:1 or 500:2:1 was deposited onto a sapphire substrate held at 30 K inside a closed-cycle helium refrigerator. The sample was irradiated with an ArF excimer laser (193 nm). Visible luminescence of products excited with an OPO laser (192-400 nm) was discovered. In particular, CH<sub>3</sub>C<sub>7</sub>N phosphorescence was identified. Spectral assignments were assisted with quantum chemical calculations of ground-state vibrational frequencies and of the singlet-triplet splitting.

Two different concentrations were used in order to differentiate between the produced CH<sub>3</sub>C<sub>7</sub>N and HC<sub>7</sub>N molecules, characterized by mutually similar phosphorescence spectra. Emission lifetimes were measured to show the common origin of observed bands.



Our former findings on the photochemical coupling of unsaturated chain molecules in rare gas solids [1-3] concerned the syntheses of H(CC)<sub>n</sub>CN-series compounds. This work demonstrates the usefulness of such an approach in synthesizing similar, yet bulkier methylated cyanopolyynes.

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## EXOTIC PROTONATED SPECIES PRODUCED BY UV-INDUCED PHOTOFRAGMENTATION : PROTONATED CINCHONIDINE

**I. Alata<sup>(1)</sup>, V. Lepere<sup>(1)</sup>, D. Scuderi<sup>(2)</sup>, K. Le Barbu-Debus<sup>(1)</sup>, A. Zehnacker-Rentien<sup>(1)</sup>.**

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A metastable protonated cinchona alkaloid was produced in the gas phase by UV-Induced photofragmentation (UVPD) of a protonated dimer in an ion trap <sup>1</sup>. The obtained protonation site is not accessible by classical protonation ways. Protonation of Cinchonidine produced by UVPD occurs on the quinoline aromatic ring (Figure 4), in contrast with protonation observed by collision-induced dissociation (CID) of the dimer or protonated monomer coming directly from ESI source <sup>2</sup>. Infrared multiphoton dissociation spectrum (IRMPD) has been obtained and compared by DFT calculations to elaborate the structure and protonation site on the molecule.

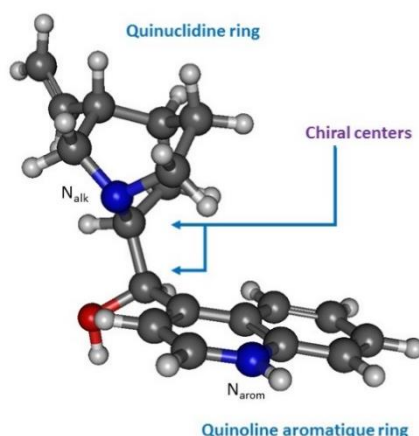


Figure 5: Protonated Cinchonidine where the protonation occurs on the aromatic ring.

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# AB INITIO CALCULATIONS OF LOW TEMPERATURE HYDROCARBON SPECTRA FOR ASTROPHYSICS: APPLICATION TO THE MODELING OF METHANE ABSORPTION IN THE TITAN ATMOSPHERE IN WIDE IR RANGE

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Knowledge of intensities of spectral transitions in various temperature ranges including very low-T conditions is essential for the modeling of optical properties of planetary atmospheres and for other astrophysical applications. The temperature dependence of spectral features is crucial, but quantified experimental information in a wide spectral range is generally missing. A significant progress has been recently achieved in first principles quantum mechanical predictions ( ab initio electronic structure + variational nuclear motion calculations) of rotationally resolved spectra for hydrocarbon molecules as methane , ethylene and their isotopic species [1-2] . We have recently reported “TheoReTS” information system (<http://theorets.univ-reims.fr>), (<http://theorets.tsu.ru>) for theoretical spectra based on variational predictions from molecular potential energy and dipole moment surfaces [3] that permits online simulation of radiative properties including low-T conditions of cold planets. In this work we apply ab initio predictions of the spectra of methane isotopologues down to T=80 K for the modeling of the transmittance in the atmosphere of Titan, Saturn’s largest satellite explored by the Cassini-Huygens space mission. A very good agreement in wide Infra-Red range from 6000 to 11000 cm<sup>-1</sup> in comparison with experimental data obtained by the Descent Imager / Spectral Radiometer (DISR) on the Huygens probe [4,5] at various altitudes will be reported.

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# THE DFT STUDY OF THE SMALL SILVER CLUSTERS LOW TEMPERATURE INTERACTIONS WITH CHOLESTEROL AND THIOCHOLESTEROL LIGANDS

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The small silver clusters  $\text{Ag}_n$  ( $n=1-3, 13$ ) and their complexes with Cholesterol (Ch) and Thiocholesterol (TCh) ligands are studied with DFT-B3LYP and second order Moeller-Plesset perturbation theory (MP2). Large complexes  $\text{Ag}_n\text{-Ch}$  and  $\text{Ag}_n\text{-TCh}$  ( $n=3, 13$ ) are calculated at DFT level of theory. The equilibrium structures and binding energies are calculated. The trends of the structures and energetics with the growth of cluster size are discussed. The metal part of the  $\text{Ag}_{13}\text{-Ch}$  and  $\text{Ag}_{13}\text{-TCh}$  complexes is the slightly distorted icosahedron with the Ag-Ag distances are about 2.8-3.0 Å. The cholesterol ligand is coordinated to a face of the silver icosahedron whereas the thiocholesterol ligand - to the edge of polyhedron (see at the Fig.1).

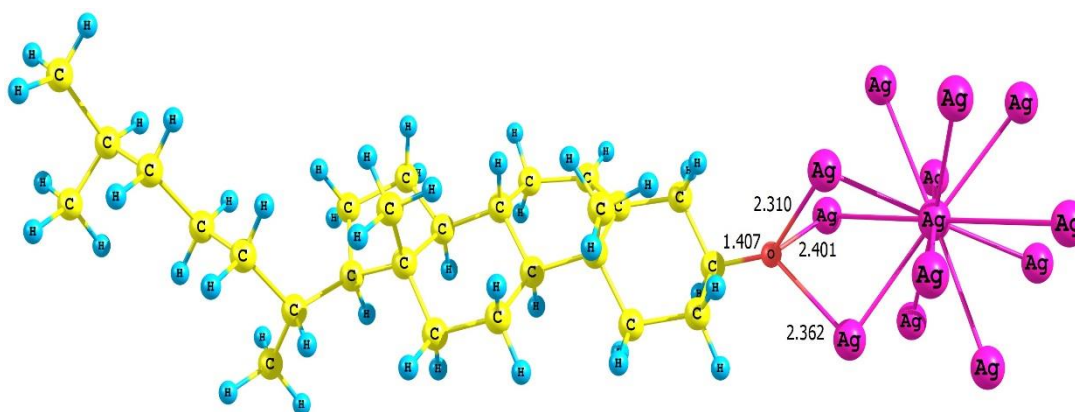


Figure.1. The DFT-B3LYP calculated structure of  $\text{Ag}_{13}\text{-Ch}$  complex.

In the case of thiocholesterol ligand the complex structure both Ag-S distances (2.537 and 2.547 Å) are almost equal.

**Acknowledgements.** The authors thank the Research Computing Center of MSU for providing computational resources.

The work is financially supported by Russian Science Foundation RSF- 16-13-10365.

# FORMATION OF COMPLEX ORGANIC MOLECULES IN THE INTERSTELLAR MEDIUM BY RADICAL CHEMISTRY

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In the interstellar medium (ISM), multiple organic molecules were observed and characterized by different spectroscopic techniques. Some of these molecules carries a large number of atoms and are called Complex Organic Molecules (COMs). COMs are of primal interest since they are part of small bodies of the ISM and are supposed to have played a role in the emergence of life on the Early Earth.

COMs are observed in multiple kind of environment such as hot cores and cometary environments. Each environment presents their own processes. These processes – VUV irradiation, hydrogen bombardments, thermal changes – are closely linked to the formation mechanisms of COMs but we still do not clearly understand such mechanisms. Our work focuses on the role of radical species in the formation of COMs under astrophysical conditions. ISM conditions are reproduced in laboratory to produce cometary ice analogues. These analogues are submitted to energetic and non-energetic processes. The changes in the chemical composition of the ice analogues are observed by spectroscopic techniques – infrared and mass spectrometries.

Radical chemistry is particular since reactive intermediates are so unstable that, in most of cases, we are not able to identify them before they react. The properties of cryogenic matrix technique, combined with quantum calculations, enable the characterization of unstable species (HCO, CH<sub>2</sub>OH...) at low temperature. We are also able to study their reactivity using the very same technique.

These intermediates lead to the formation of some of the most massive detected COMs (glycolaldehyde, ethylene glycol) or to COMs potentially detectable in a particular astrophysical environment. These results could be of use for the understanding of ROSETTA mission results or to the discovery of new COMs in the ISM.

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# IN-SITU SPECTRAL STUDY OF NITRIC OXIDE INTERACTION WITH DIOXYGEN COMPLEXES OF MN-PORPHYRINS

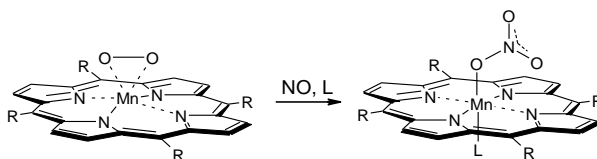
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Nitric oxide (NO) plays important regulatory functions in mammalian biology. However, its overproduction is harmful. Heme proteins are the principal agents responsible for the NO scavenging. Reaction of NO with HbO<sub>2</sub>, so called nitric oxide dioxygenation (NOD) reaction, leads to formation of nitrate anion and the ferric form of the protein, metHb. There are controversial data regarding to the mechanism of this biologically important reaction and spectral studies of NO interaction with dioxygen complexes of modeling metalloporphyrins could help to throw light on this problem.

*In-situ* FT-IR and UV-visible monitoring of the NO reaction with specially constructed thin layers of dioxygen complexes of general formula (L)M(Por)(O<sub>2</sub>) (M = Fe, Co, Por - meso-tetraphenyl- and meso-tetra-p-tolyl-porphyrinato dianions (TPP and TTP, correspondingly), L = electronodonor ligands) showed that these heme-modelling compounds were able to promote NOD-reaction. For iron derivatives the formation of the six-coordinate nitrato complexes were observed already at very low temperatures (80-100 K) without appearance of any spectrally detectable intermediate species [1]. In the case of Co-porphyrins, however, the intermediate was formed at temperature interval 80-120 K, that was assigned to the putative six-coordinate peroxynitrite complex (L)Co(Por)(<sup>1</sup>η-OONO) [2].

In contrast to the Fe and Co analogues, the Mn-porphyrins bind dioxygen in the side-on fashion. Additionally, they do not form 6-coordinate dioxygen complexes. It will be demonstrated here that the formation of Mn-porphyrin nitrato complexes Mn(Por)(η<sup>1</sup>-ONO<sub>2</sub>) takes place in this case too. However together with nitrato complexes comparable quantities of nitrito species Mn(Por)(η<sup>1</sup>-ONO) are also formed. This result conclusion was firmly confirmed by evaluating the vibrational spectra in the experiments with <sup>18</sup>O<sub>2</sub>, <sup>15</sup>NO, N<sup>18</sup>O and <sup>15</sup>N<sup>18</sup>O gases. It will be also demonstrated that in the presence of donor ligands in the layers, the 6-coordinate nitrato-complexes of Mn-porphyrins (L)Mn(Por)(η<sup>1</sup>-ONO<sub>2</sub>) (L = different electron donor



ligands) [3] are preferentially formed with only minor quantities of the nitrito species. The intermediates formed in the course of the reaction were spectrally characterized and the possible mechanism of the NOD-reaction performed by Mn-porphyrins is offered.

Financial support by the State Committee of Science, Republic of Armenia (Grant #15T-1D172) is greatly appreciated.

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# PROTONATED NAPHTHALENE MONOMER & DIMERS AS POSSIBLE INTERSTELLAR SPECIES.

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In this research, structural and bonding characteristics and vibrational and electronic spectra of protonated naphthalene (a small polycyclic aromatic hydrocarbon, PAH) monomers and dimers as possible interstellar species, are calculated using ab initio computational methods. Unprotonated ( $N$ ) and 3 isomers of the protonated naphthalene ( $[NH]^+$ ) monomer, and 6 isomers of unprotonated ( $N_2$ ) and 3 isomers of protonated naphthalene ( $[N_2H]^+$ ) dimer have been considered for this study. Relative stabilities, specific vibrational bands which may be used for identification and assignment of the bands in the unidentified infrared spectra received from space are analyzed and discussed. Structural optimizations are carried out at the B3LYP and MP2 levels of theory using 6-311++G\*\* and aug-cc-pVTZ basis sets, and the electronic spectra of molecules are calculated at CIS ( $N_{states} = 5 \text{ \& } 10, 50-50$ )/aug-cc-pVTZ. Analysis of the results obtained in this study shows that it is possible to distinguish between the unprotonated and protonated naphthalene monomers and dimers. Therefore, some vibrational and electronic bands are suggested as specific features of these species to be detected and assigned in the recorded IR and Visible/Ultraviolet spectra of different parts of the space. As shown in Figure 1, each of these species has some unique absorption peaks both in their infrared and electronic spectra which can be used to distinguish them.

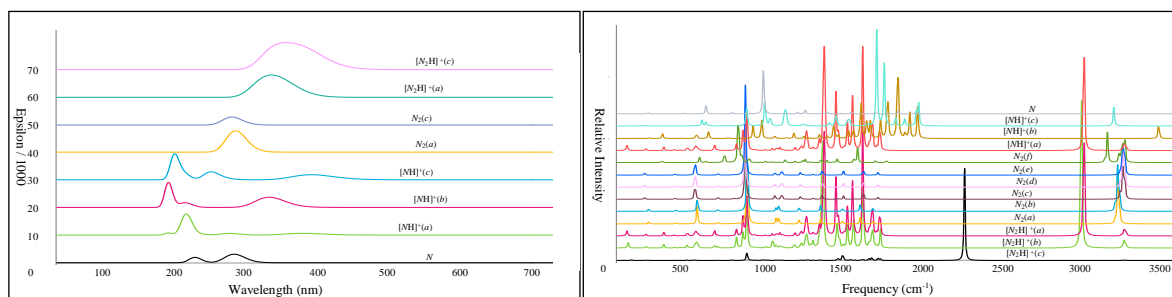


Figure 1: Electronic (left) and vibrational (right) spectra of protonated and unprotonated naphthalene monomers and dimers.

## Keywords:

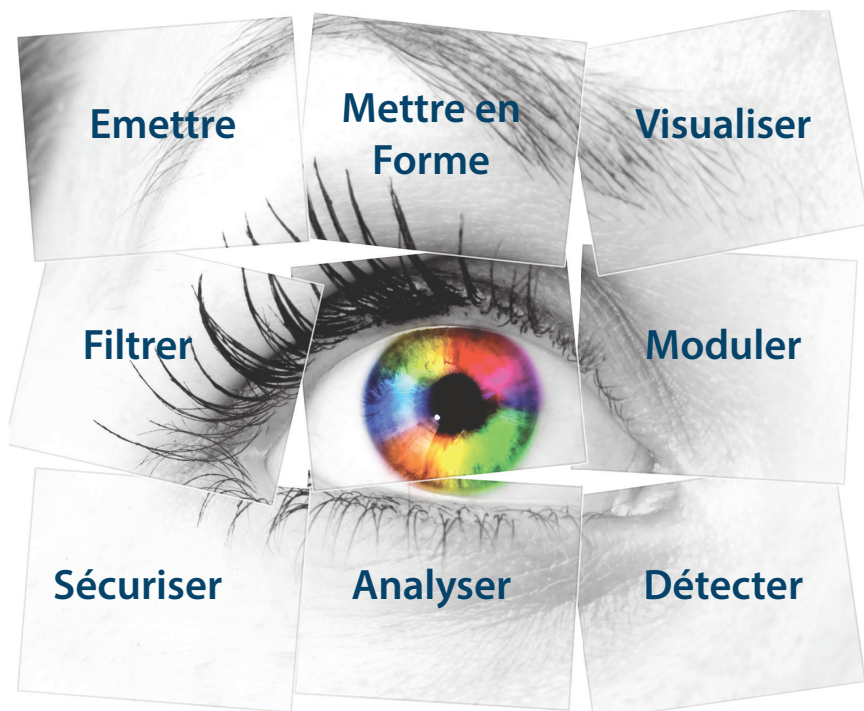
Protonated naphthalene, dimer, PAH, B3LYP, MP2, RCI, Interstellar species, IR & UV-Vis spectra.

## Acknowledgements

The calculations have been performed on the National High-Performance Computing Center – Isfahan University of Technology. The authors thank them.

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CPLT2016	Sunday, 3rd July 2016	Monday, 4th	Tuesday, 5th	Wednesday, 6th	Thursday, 7th	Friday, 8th
9.00-13.00 Morning sessions		<b>QHCM</b> T. Momose A. Vilesov M. Tsuge D. Anderson	<b>SDLT</b> M. Suhm S. Melandri A. Gutiérrez-Quintanilla M. Sařdyka	<b>AAS</b> R. Signorell Y. Tobon S. Ryazantsev X. Michaut	<b>BioS</b> Y. Xu M. Mons S. Soorkia K. Yamazaki	<b>MCC</b> S. Sibener T. Shabatina A. Desmedt S. Picaut M. Pettersson
Break 25 min		COFFEE BREAK				
		A. Simon E.T. Mengesha K. Hyeon-Deuk K. von Haefen P. Moroshkin	J. Mc Caffrey B. Gervais T. Wakabayashi J. Ceponkus B. Tremblay	L. Krim B. Augé F. Duvernay A. Canosa R. Spezia	<b>CRUIS</b> H. Joly I. Reva J. Mieres-Pérez N. Esteves-Lopez	Election results Presentation of CPLT 2018 <i>Closing session</i>
13.00-14.00	LUNCH					
14.00-16.30	Arrivals from 13.00	FREE TIME		FREE TIME		
16.30-19.00 Afternoon sessions	Registration from 15.00	<b>New Tech &amp; Appl</b> D. Comparat C. Jouvét B. Heazlewood	<b>AAS</b> R. Kolos J. Maier L. Biennier  Coffee break U. Szczepaniak J. Noble S. Bejaoui	<a href="#">EXCURSION</a>		
Break 15 min	Welcome buffet from 19.00 to 21.00	Coffee break A. Apkarian F. Zischka B. Joalland		DINER		
19.30-20.30		DINER		DINER		
20.30-22.30 Evening sessions	<i>Opening Session</i> <b>André Tramer dedace</b> A. Zehnacker M. Chergui	Poster session1 (odd numbers)	Poster session 2 (even numbers)	<a href="#">GALA DINER</a>		
				Pimentel Prize Poster prize Committee elections		







# CPLT/2016

CHEMISTRY AND PHYSICS AT LOW TEMPERATURES

Biarritz, France - 3-8 July 2016



*Domaine de Françon, Biarritz, France*



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