STAND-ALONE PROJECT

FINAL REPORT

Project number	**P26635**
Project title[1]	**Decoration of fullerenes with atoms and low-mass molecules**
Project leader	**Paul Scheier**
Project website[2]	

[1] Short title in English and German language
[2] Projects that started after January 1, 2009 are encouraged to have a website.

I. Summary for public relations work

1. Zusammenfassung für die Öffentlichkeitsarbeit

Die Oberfläche von Fullerenen und deren Cluster ist ein ideales Modell zur Untersuchung der Adsorption von Atomen und Molekülen an definierten Strukturen. Ein einzelnes Fullerene hat Ähnlichkeiten mit Nanoröhren und Graphen. Im Gegensatz zu letzteren, lassen sich Fullerene einer einzelnen Größe in höchster Reinheit (>99.99%) herstellen. Das ermöglicht massenspektrometrische Experimente, wobei die Anzahl an Adsorbate sich genau über die Masse bestimmen lässt. Der Effekt der Krümmung ist durch unterschiedlich große Fullerene steuerbar. Die Rillen zwischen zwei bzw. die Senken zwischen drei Fullerenen werden von Adsorbaten, die untereinander schwächer gebunden sind als an zur Oberfläche, bevorzugt besetzt. Im Gegensatz dazu, führt eine dominierende Bindung zwischen den Adsorbaten, zu praktisch ungestörtem Clusterwachstum auf den Fullerenoberflächen.

Kohlenstoff-, Gold-und auch Alkaliatome bilden starke chemische Bindungen mit Fullerenen was in den ersten beiden Fällen zur Erzeugung von Hanteln oder gar Ketten führt und im Fall von Alkalimetallen sogar zu Salzen. C_{60} mit Lithium wurde in vielen theoretischen Untersuchungen als hervorragender Wasserstoffspeicher vorgeschlagen. Im vorliegenden Projekt konnte dies für das System C_{60} und Cäsium auch experimentell verifiziert werden.

Die Mikrosolvatisierung von Fulleren- und Coronenionen mit Helium und Wasserstoff zeigt die Bildung von abgeschlossenen geometrischen Schalen, wobei die ersten Schale meist als fest betrachtet werden kann. Jedoch zeigen spektroskopische Untersuchungen von heliumumhüllten Fullerenionen ein teilweises Aufschmelzen der ersten Schale bei weiterer Anlagerung von Heliumatomen. Dazu werden elektronische Übergänge in C_{60}^+ angeregt, was zu einem Abdampfen der angelagerten Heliumatome führt, was massenspektrometrisch leicht nachweisbar ist. Unsere Messungen bestätigen dabei die kurz zuvor in kalten Ionenfallen bestimmten Absorptionslinien von C_{60}^+, die auch in astronomischen Spektren von diffusen interstellaren Wolken nachgewiesen wurden. Darüber hinaus konnte für eine der vier Linien eine deutliche Abweichung der Absorptionsenergie zwischen einem Heliumatom an einem fünfeckigen und einem sechseckigen Ring beobachtet werden. Dies spiegelt sich in einer deutlichen Verbreiterung der Absorptionslinien aufgrund einer statistischen Besetzung der unterschiedlichen Flächen des C_{60}^+ wieder. Diese neuartige Form der Action-Spektroskopie ist wesentlich effektiver als bisherigen Verfahren und soll daher in einem Folgeprojekt zur Suche von weiteren Trägern von diffusen interstellaren Banden eingesetzt werden.

2. Summary for public relations work

The surface of fullerenes and clusters of fullerenes represent ideal models to study the adsorption of atoms and low-mass molecules to well-defined structures. A single fullerene resembles very well carbon nanotubes or even a piece of graphene with the advantage that fullerenes can be produced with very high purity (>99.99%). This enables mass spectrometric experiments, where the number of adsorbed species can exactly by determined by simply weighing the complex. The effect of the curvature can be tuned by the size of the fullerene. Grooves between two and dimples between three fullerenes are preferential binding sites for adorbates that interact more strongly with the fullerene surface than among each other. In contrast, species with a dominant interaction among themselves, exhibit weakly perturbed cluster growth at the fullerene surface.

Carbon, gold and alkali atoms, however, form strong chemical bonds with fullerenes, leading in the former two cases to the formation of dumbbells and even chains and in the case of alkali metals to salts. High potential for hydrogen storage has been predicted for complexes of C_{60} with lithium based on theoretical calculations. In the present project we could verify this experimentally for the system C_{60} and cesium.

Micro-solvation of fullerene and coronene ions with helium and hydrogen clearly exhibit geometrical shell closures where the high binding energy to the first layer often results in a solid film where the solvent atoms/molecules occupy geometrically strongly confined positions. However, optical spectroscopy of helium decorated fullerene ions indicate a partial melting of the solid layer upon occupation with additional He atoms. Laser excitation of electronic transitions of C_{60}^+ leads to the evaporation of up to several 100 adsorbed He atoms which can He atoms which can easily be observed mass spectrometrically. Our measurements confirm absorption lines of C_{60}^+ that were recently determined via photodissociation of He-tagged fullerene ions in cryogenic ion traps. In this previous study these very same lines were also observed in astronomical spectra from diffuse interstellar clouds. For one of these lines we observed a clear difference for He attached to pentagonal or hexagonal faces. This leads to a pronounced line broadening due to statistical occupation of the two types of faces of the fullerene surface. This new kind of action-spectroscopy is way more efficient and provides deeper insight into the micro-solvation and matrix shifts of the first solvent layer than previous methods. Thus we plan to utilize this advantage in a follow-up project for the search of additional carriers of the 600 known diffuse interstellar bands.

II. Brief project report

1. Report on research work

1.1 Information on the development of the research project

Decoration of fullerenes, predominantly $C_{60,}$ as well as coronene and adamantane with atoms and molecules was investigated, as proposed. Shell closures of the first layer of physisorbed species were observed for positively and negatively charged complexes. Besides mass spectrometry we started to investigate ad-layers of He attached to charged model surfaces, such as fullerenes, also via laser spectroscopy. Most of the proposed goals and several unexpected results could be achieved.

The results obtained during this project have been leading to 37 papers, published in peer reviewed journals, including Phys. Rev. Lett., Nature Communication, Angew. Chem. Int. Ed. and J. Phys. Chem. Lett. Currently six additional publications haven been submitted for publication and three of them have been already accepted. The results of this project were also presented at about 30 international conferences where 24 invited talks were given by researchers involved in this project, incl. the project leader.

1.2 Most important results and brief description of their significance (main points)

The corrugated surface of fullerenes as well as PAHs, such as coronene and corannulene represent interesting model surfaces for the physisorption and chemical binding of atoms and molecules. For adsorbates that interact more strongly with the surface than with each other, we observe preferential occupation of the center positions of the hexagonal and pentagonal faces. The van der Waals radius and the curvature of the surface strongly affect the number of species that fit into the first layer. For CO_2 we observed a pronounced difference in the occupation of the first layer for cations and anions. This could be attributed to the quadrupole moment, i.e., the positively charged carbon atom of CO_2 seeks the shortest distance to a negatively charged surface and covers the highest possible area of the surface, whereas in case of a positively charged surface, one of the oxygen atoms is closest to the surface, resulting in a higher number of CO_2 molecules in the first layer [1].

Besides the decoration of single carbonaceous molecules, i.e., fullerene or PAH, we also studied the decoration of clusters of these species with atoms or low-mass molecules. In the case of fullerenes, species that interact more weakly among each other than with the fullerene surface preferentially occupy dimple positions or grooves formed by three or two fullerenes, respectively [2-3]. For the binary systems of fullerenes and alkali atoms M (M=Na and Cs), we observe salt formation of the form $(M^+)_6C_{60}^{6-}$. Clusters with an excess of metal atoms exhibit pronounced odd-even oscillation of the ion yield due to spin pairing [4]. In the case of coronene

clusters, decorated with hydrogen molecules, we were able to confirm the theoretically predicted slipped-parallel stacking from the number of strongly bound hydrogen molecules [5].

Co-doping of helium droplets with heliophilic C_{60} and heliophobic alkali atoms provides interesting systems to study the reactivity of two species located at different regions of large HNDs [6]. Furthermore, in combination with the third dopant hydrogen, these complexes can serve as model systems for hydrogen storage [7]. The low mass of Li together with the two isotopes make this technically most interesting alkali atom not suitable for present investigations and we used Cs instead.

The combination of a tunable laser with the high-resolution mass spectrometer and a He nanodroplet source enables efficient action spectroscopy of various ions. Several groups utilize cryogenic traps for tagging ions with He atoms [8-10]. Except for multiply-charged ions, the number of He atoms attached is limited to very few (less than 5). For C_{60}^+ we could measure electronic excitation of complexes $He_nC_{60}^+$, with $1<n<200$ [11]. Shell closures and phase transitions in the solvent layer lead to pronounced changes in the matrix shift. We observed a remarkably linear redshift of 0.07 nm for every additional He atom up to n=32, where one He atoms occupies every center of the 12 pentagonal and 20 hexagonal faces of the C_{60}^+. The first laser spectroscopy experiments were performed with a borrowed narrow-bandwidth cw-laser from the group of Roland Wester. In the meantime a new OPO laser system, tunable from 2600nm to 200nm, with a repetition rate of 1kHz was purchased by the Innsbruck Laser Core Facility and installed in the He droplet laboratory. Recently we additionally modified the instrument, rotating the ion source and the subsequent time of flight mass spectrometer by 90°. Thereby, the laser cannot interact with neutral helium droplets and the laser power as well as the wavelength are monitored throughout the measurements.

1.3 Information on the execution of the project, use of available funds and (where appropriate) any changes to the original project plan relating to the following:

The duration of the project was three years and 11 months. This is longer than the proposed length of three years. The reason are several delays in the recruitment of PhD students who could not start their theses at the expected time. The money was also spent almost as proposed, i.e., 89k€ for consumables and other costs compared to 72k€ stated in the proposal. The difference originates mainly from the maintenance of the cryo-cooler in Feb 2014 and November 2015 that was required after difficulties in reaching the required temperature. Additional costs arose, when a laser system was merged with the mass spectrometer setup. Several optical elements, such as lenses, mirrors and prisms were required and had to be bought. The rest of the money was spent on PhD students and postdoc researchers who worked for the project. No major items of equipment were purchased other than expected. The

microchannel plate detector had to be changed twice, in December 2015 and October 2017, following spectroscopy experiments with intense ion yields.

2. Personnel development – Importance of the project for the research careers of those involved (including the project leader)

Two former postdoc researchers who worked for this project submitted own proposals to the FWF that were granted (Dr. Andreas Mauracher: P 30355 and Dr. Alexander Kaiser: P 28979). Several major findings of the present project were contributing to the Habilitation of PD. Dr. Mauracher. These include the discovery and reactivity of He^{*-} and He_2^{*-} in pristine and doped helium nanodroplets. Four PhD students successfully finished their theses. Two of them are working in the R&D of MSE in Tyrol, one founded his own company and one was hired as a university assistant at the Institute for Microelectronics and Implantable Systems. For the project leader this project enabled a continuation of his research and added to a successful evaluation of his position in 2015 which was required for getting an unlimited extension of his position as a full professor. Particularly the new aspect of action spectroscopy of He tagged ions with a tunable laser is opening a complete new field of research that the project leader wants to continue in subsequent studies.

3. Effects of the project beyond the scientific field

Decoration of fullerene ions with atoms and low-mass molecules is a field of research with several possible applications, ranging from chemistry (micro solvation) material science (hydrogen storage) to astrophysics (diffuse interstellar bands) and astrochemistry (molecular synthesis on micro grains in cold and dense clouds). Particularly the possibility to measure efficiently absorption lines of cold ionic complexes is an interesting alternative to cold ion traps and provides a much deeper insight into the matrix effects due to the large number of He atoms that can be attached to these ions. Also the flexibility to form basically any complex, consisting of up to four different compounds at ultra-low temperatures and ultra-clean conditions, is unprecedented.

In September 2017 a new project in collaboration with another research institution and two companies was granted by the Land Tirol. This EFRE K-Regio project is based on preparatory studies obtained during the present project. Potential effects of these new studies will be of relevance for medicine and implant technology, as the primary goal is the functionalization of medically relevant surfaces with metal nanoparticles for tuning cell adhesion.

4. Other important aspects (examples)

The project leader and scientists

- Results obtained in this project were presented at several international conferences and the most prestigious contribution was a plenary lecture of the project leader at

the XXIX International Conference on Photonic, Electronic and Atomic Collisions (ICPEAC 2015) in Toledo, Spain. As a result of this presentation, we were invited by an editor of Physics Reports to write a review article for this journal which is currently in print.

- The project leader and his team organized three international conferences:
  The XIXth Symposium on Atomic, Cluster and Surface Physics, SASP 2014 that was held from February 9-14, 2014 in Obergurgl, Austria (108 participants), https://www.uibk.ac.at/sasp/sasp14/
  The 11th Conference on Quantum Fluid Clusters, QFC 2017; June 7-9 2017, Obergurgl, Austria (79 participants), https://www.uibk.ac.at/congress/qfc2017/
  The XXIst Symposium on Atomic, Cluster and Surface Physics, SASP 2018; February 11-16, 2018, Obergurgl, Austria (97 participants), https://www.uibk.ac.at/sasp/sasp18/
- Prizes/awards: the project leader received the SASP Erwin Schrödinger Gold Medal 2016 “for his outstanding experimental contributions to ion and cluster physics including in particular a wide range of systems at the nanometer scale, systems at surfaces and ion surface collisions as well as molecular systems of biological importance”.
- Coverage of results of this project by the media:
  Negatively-charged hydrogen clusters:
  - http://derstandard.at/2000055299916/Erstmals-negativ-geladene-Wasserstoffcluster-im-Labor-hergestellt
  - http://www.tt.com/panorama/wissen/12818498-91/innsbrucker-physiker-erzeugen-neue-form-von-wasserstoff.csp
  - http://www.lefigaro.fr/sciences/2017/01/17/01008-20170117ARTFIG00329-decouverte-d-une-nouvelle-forme-d-hydrogene.php
  - https://www.sciencenews.org/article/new-form-hydrogen-created

  Photodissociation of $He_mC_{60}^+$
  - http://www.tt.com/panorama/12290283-91/innsbrucker-forscher-erzeugten-erstmals-buckyballs-mit-helium-eiskruste.csp
  - http://www.chemie.de/news/160679/schneebaelle-aus-dem-labor.html
  - http://www.astronews.com/news/artikel/2016/11/1611-028.shtml
  - http://diepresse.com/home/science/5124699/Im-Weltall-nach-Fussballmolekulen-suchen
  - http://derstandard.at/2000047968695/Buckyballs-mit-Helium-Eiskruste-Kosmische-Schneebaelle-im-Labor-erzeugt

- Other aspects: The scientists involved in this project regularly contribute to activities for the public (Lange Nacht der Forschung) and education of pupils (Schülertage). During the last five years six high school pupils spent a month during their summer break in our laboratories, supported by the funding agency FFG.

5. References

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9. Campbell, E. K.; Holz, M.; Gerlich, D.; Maier, J. P., Laboratory confirmation of C_{60}^+ as the carrier of two diffuse interstellar bands. *Nature* **2015,** *523* (7560), 322.
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11. Kuhn, M.; Renzler, M.; Postler, J.; Ralser, S.; Spieler, S.; Simpson, M.; Linnartz, H.; Tielens, A. G. G. M.; Cami, J.; Mauracher, A.; Wang, Y.; Alcamí, M.; Martín, F.; Beyer, M. K.; Wester, R.; Lindinger, A.; Scheier, P., Atomically resolved phase transition of fullerene cations solvated in helium droplets. *Nature Communications* **2016,** *7*, 13550.

III. Attachments

(lists may be as long as required)

1. Scholarly / scientific publications

Planned publications

(journals, monographs, anthologies, contributions to anthologies, proceedings, research data, etc.)

Author(s)	A. Mauracher et al.		
Title	Cold Physics and Chemistry: Collisions, Ionization and Reactions inside Helium Nanodroplets Close to Zero K.		
Sources	Physics Reports		
URL (if applicable)	10.1016/j.physrep.2018.05.001		
Peer Review	yes ☒	no ☐	
Status	in press/accepted ☒	submitted ☐	in preparation ☐

Author(s)	M. Mahmoodi-Darian et al.
Title	Doubly charged coronene clusters - much smaller than previously observed.
Sources	J. Chem. Phys.

URL (if applicable)			
Peer Review	yes ☒	no ☐	
Status	in press/accepted ☒	submitted ☐	in preparation ☐

Author(s)	M. Gatchell et al.		
Title	Protonation and the problem of magic argon clusters.		
Sources	Phys. Rev. Lett.		
URL (if applicable)			
Peer Review	yes ☒	no ☐	
Status	in press/accepted ☐	submitted ☒	in preparation ☐

Author(s)	L. Kranabetter et al.		
Title	Uptake and Accommodation of Water Clusters by Adamantane Clusters in Helium Droplets: Interplay Between Magic Number Clusters.		
Sources	Phys. Chem. Chem. Phys.		
URL (if applicable)			
Peer Review	yes ☒	no ☐	
Status	in press/accepted ☐	submitted ☒	in preparation ☐

Author(s)	S. Raggl et al.		
Title	Helium nanodroplets doped with copper and water.		
Sources	Eur. Phys. J. D		
URL (if applicable)			
Peer Review	yes ☒	no ☐	
Status	in press/accepted ☐	submitted ☒	in preparation ☐

Author(s)	M. Goulart et al.		
Title	Highly Stable $C_{60}AuC_{60}^{\pm}$ Dumbbells		
Sources	J. Phys. Chem. Lett.		
URL (if applicable)			
Peer Review	yes ☒	no ☐	
Status	in press/accepted ☒	submitted ☐	in preparation ☐

2. Most important academic awards

(Specific academic awards, honours, prizes, medals or other merits)

Name of award	n=national / i=international
SASP Erwin Schrödinger Gold Medal 2016	i

3. Information on results relevant to commercial applications

4. Publications for the general public and other publications

5. Development of collaborations

N				Nationality of collaboration partner (please use the ISO-3-letter country code)
	G			Gender **F (**female) **M** (male)
		E		Extent **E1** **low** (e.g. no joint publications, but mention in acknowledgements or similar); **E2** **medium** (collaboration e.g. with occasional joint publications, exchange of materials or similar, but no longer-term exchange of personnel); **E3** **high** (extensive collaboration with mutual hosting of group members for research stays, regular joint publications, etc.)
			D	Discipline **W** **within the discipline** (within the same scientific field) **I** **interdisciplinary** (involving two or more disciplines) **T** **transdisciplinary** (collaborations outside the sciences)

N	G	E	D	Name	Institution
DEU	M	E3	W	Sergiy Krasnokutskiy	Univ. Jena
FRA	F	E3	W	Linda Feketeova	Claude Bernard Univ. Lyon 1
NLD	M	E2	I	Harold Linnartz	University of Leiden
USA	M	E3	W	Olof Echt	Univ. of New Hampshire
IRN	F	E3	W	Masoomeh Mahmoodi Darian	Karaj Branch, Islamic Azad University

Note: General scientific contact and occasional meetings should not be considered collaborations for the purposes of this report.

6. Development of human resources in the course of the project

	In progress	Completed	Gender f	Gender m
Full professorship				
Venia thesis (*Habilitation*) / Equivalent senior scientist qualification		1		1
Postdoc		5	1	6
Ph.D. theses	1	4		5
Master's theses				
Diploma theses		1		
Bachelor's theses				