Final report
Project SNN 118012
Correlated electrons in confined molecular systems

Participants:

From the second year, Gyöngyi Pergerné Klupp left the project because she took a position outside Hungary, and Áron Pekker obtained a project of his own that was incompatible with his participation. We added Hajnalka Tóháti, Gergely Németh and Dániel Datz, who were later joined by Ana Cristina Cadena.

Work plan:

With the above change in personnel, the emphasis thus shifted from alkali doping to other encapsulation methods. Gyöngyi Klupp, who was the main expert in doping, left the research group and then science altogether, and the colleagues in Durham University, England (another source of alkali fullerides) also relocated and changed the course of their research. Due to the pandemic situation from 2020 on, international exchange was also hindered. Therefore, while keeping the general topic of the project, we concentrated on new molecular containers, transformations of molecular to extended systems, and local spectroscopic and microscopic methods. Except for the doping experiments, we performed most of the preparation, more than what was planned on the optical studies and some of the magnetic characterization.

We present the results organized by topic (nanocontainers, correlated systems and other possible encapsulants, encapsulated molecules and their reactions) and give the list of publications in the end, in order to be able to refer to them in the text. In case of unpublished work (including unpublished conference posters and theses) we present the results in a more detailed form.

Nanocontainers

We studied two types of nanocontainers, nanotubes and metal-organic frameworks (MOFs). We worked with high-quality nanotubes from commercial sources, where the overall structure was generally well known. We concentrated on nanoscale studies performed with our near-field infrared microscope (s-SNOM: scattering-type scanning near-field optical microscopy) that works with nm spatial resolution. We determined the defect structure on individual boron nitride nanotubes, based on the phonon lines around 1400 cm^{-1}. Spectral information could be extracted through a methodology development to tune the QCL laser in the range 1320 - 1450 cm^{-1} [A-1, C-1].

Based on near-field infrared microscopy and spectroscopy, we developed a method to distinguish individual metallic and semiconducting nanotubes based on the contrast difference with the substrate in the optical phase. Spectroscopic investigation of metallic and semiconducting tubes, respectively, showed that the phase of the scattered light followed the imaginary part of the dielectric function: Drude behavior for the metallic tubes and a nearly constant lower value for the semiconducting ones [A-2, C-2, C-3].

We detected plasmonic excitations in carbon nanotubes deposited on silicon dioxide and hexagonal boron nitride. The plasmons are strongly coupled to the phonon polaritons of the substrates and create extreme electric field confinement in the nanotubes, that can be observed as periodic fluctuations in the phase of the near-field scattering. This paper is in the second round of reviewing in Nano Letters, after favorable reviewer opinions [A-3].
We prepared another container structure, a chiral metal-organic framework, WIG-5 and characterized it by structural and spectroscopic methods. Such chiral frameworks are still rare and show a considerable potential towards stereoselective synthesis [A-4].

Correlated systems and other possible encapsulants

We summarized the pressure-dependent properties (both physical and chemical pressure) of alkali fullerides in two conference contributions [C-4, C-5], but could not pursue this topic further because of the unavailability of samples. However, we investigated the superconductor K_3C_{60} below the transition temperature by microwave absorption as a function of magnetic field. Proof-of-concept experiments on various air-sensitive materials showed that the method can be applied to both encapsulated fullerides and alkali-doped carbon nanotubes without damaging the samples [A-5]. For fine powdered samples of both K_3C_{60} and MgB_2, the microwave loss below the superconducting transition temperature increases significantly on the application of small magnetic fields, in contrast to single crystals. The effect was explained by vortex motion and was compared with calculations based on the Coffey-Clem theory. These results can be applied when evaluating measurements on encapsulated fullerides [A-6]. By the same method, the semiconductor-to-metal transition of carbon nanotube upon alkali doping could also be followed [A-5].

We also turned our attention to biological systems, exploring ultrasmall silicon carbide nanocrystals as potential bioimaging application materials. Silicon carbide can form special nanoparticles that show luminescence and are therefore potential precursors for hybrid materials with nanotubes. The first step in the investigation is the determination of optical spectra as a function of size in the nanometer range. Surface termination of the nanocrystals was determined from attenuated total reflectance infrared spectra, and absorption and photoluminescence spectroscopy was applied to investigate the optical properties in detail, both static and time-dependent, complemented by single-particle spectra. Comparing our experimental results to first-principles simulations, we concluded that quantum confinement occurs between 5.8 nm and 13 nm particle size. Below this limit, the system exhibits molecular-like behavior with dominant contribution from surface states [A-7]. By a new electroless etching method, hexagonal SiC nanoparticles as small as 1nm were prepared. These particles can be possibly filled into carbon nanotubes with typical diameters in the range 1-2 nm [A-8].

Opening to other inorganic compounds, we participated in two studies on silver salts that can be possible precursors of finely dispersed silver, $AgMnO_2$ [A-9] and $[Ag(NH_3)_2]_2SO_4$ [A-10]. We followed their redox reactions with structural and spectroscopic methods.

Encapsulated molecules and their reactions

We used carbon nanotubes as "nanoreactors", by performing chemical reactions inside the tubes. Nickel acetylacetonate was encapsulated in carbon nanotubes and annealed to obtain nickel clusters that were characterized by transmission electron microscopy and scanning probe methods. Scattering near-field optical microscopy at infrared frequencies detected nickel clusters inside individual carbon nanotubes with a spatial resolution of a few nanometers. We estimate that the size of the detected clusters is a few hundred nickel atoms and we find this quite an achievement considering that the wavelength of the illuminating light is around 10 micrometers. The sensitivity of the method was compared to magnetic force microscopy where we found the signal to be below detectable level. We also presented an analytical model for the scattering process that showed remarkable agreement with the experimental results [A-11, C-6].

We explored boron nitride nanotubes filled with C_{60} fullerene molecules. We found that coupling to the phonon-polariton of the BN sheets increases the light scattering from the encapsulated molecules, so less than 200 molecules can be detected inside the BN nanotubes based on their vibrational structure. Near-field mapping was also used to follow the photopolymerization reaction of C_{60} inside the nanotubes and identify dimers and trimers as reaction products [A-12]. The role of the collective excitations of both graphene- and boron nitride-based materials was studied further both experimentally and theoretically [C-8, C-9, C-10]. The long-term goal is to develop new tip-based single-molecule detection methods.

A special filling method, nanoextraction from supercritical carbon dioxide, was used for carbon nanotubes and sexithiophene. The advantage of this method is the low reaction temperature that prevents side reactions of the guest molecules. We compared the products with those of conventional high-temperature sublimation filling using Raman spectroscopy. We found that the two hybrid materials were different, but upon annealing the low-temperature encapsulated sample above 300 °C, the spectrum of the guest molecules became similar to the high-temperature filled one. Specific Raman lines indicated an increase in conjugation length, typical for thiophene polymerization. This way, we proved that thermal polymerization happens in this system as well. However, contrary to earlier findings on polycyclic hydrocarbons, we did not detect graphene nanoribbon formation [A-13, C-11]. Graphene nanoribbons could be prepared from coronene and trichlorobenzene. These materials are presently investigated by transmission electron microscopy and tip-enhanced Raman spectroscopy in international collaboration, and preliminary results are promising. We also published a review article on encapsulation of organic molecules in single-walled carbon nanotubes [A-14].

Possible exploitation

Although the project is centered on basic research, some elements can be considered as basis for later applications, especially the encapsulation of functional materials into the frameworks. These include luminescence, superconductivity, magnetism and chemical flexibility. Single-molecule detection is a possible scientific application, but it can also have relevance in hazardous material analysis or other cases of identifying trace amounts of various substances.

List of publications resulting from the project:

Articles in international journals:

A-1. D. Datz, G. Németh, H.M. Tóháti, Á. Pekker, K. Kamarás: **High-resolution nanospectroscopy of boron nitride nanotubes**
Phys. Status Solidi B **254,** 1700277-1-4 (2017)

A-2. G. Németh, Á. Pekker, D. Datz, H.M. Tóháti, K. Otsuka, T. Inoue, S. Maruyama, K. Kamarás: **Nanoscale characterization of individual horizontally aligned single-walled carbon nanotubes**
Phys. Status Solidi B **254,** 1700433-1-4 (2017)

A-3. G. Németh, K. Otsuka, D. Datz, Á. Pekker, S. Maruyama, F. Borondics, K. Kamarás: **Direct visualization of ultrastrong coupling between Luttinger-liquid plasmons and phonon polaritons**
Nano Lett., under 2nd review

A-4. D. Földes, É. Kováts, G. Bortel, K. Kamarás, S. Pekker: **Preparation and characterization of a new chiral metal-organic framework with spiranes**
J. Mol. Struct., in press, DOI: 10.1016/j.molstruc.2022.132538

A-5. B.G. Márkus, G. Csősz, O. Sági, B. Gyüre-Garami, V. Lloret, S. Wild, G. Abellán, N.M. Nemes, G. Klupp, K. Kamarás, A. Hirsch, F. Hauke, F. Simon: **Electronic properties of air sensitive nanomaterials probed with microwave impedance measurements**
Phys. Status Solidi B **255,** 1800250-1-7 (2018)

A-6. G. Csősz, B.G. Márkus, A. Jánossy, N.M. Nemes, F. Murányi, G. Klupp, K. Kamarás, V.G. Kogan, S.L. Bud'ko, P.C. Canfield, F. Simon: **Giant microwave absorption in fine powders of superconductors**
Sci. Rep. **8,** 11480-1-9 (2018)

A-7. D. Beke, A. Fučiková, T.Z. Jánosi, G. Károlyházi, B. Somogyi, S. Lenk, O. Krafcsik, Zs. Czigány, J. Erostyák, K. Kamarás, J. Valenta, A. Gali: **Direct observation of transition from solid-state to molecular-like optical properties in ultrasmall silicon carbide nanoparticles**
J. Phys. Chem. C **122,** 26713-26721 (2018)

A-8. Gy. Károlyházy, D. Beke, D. Zalka, S. Lenk, O. Krafcsik, K. Kamarás, A.Gali: **Novel method for electroless etching of 6H-SiC**
Nanomaterials **10,** 538-1-8 (2020)

A-9. L. Fogaça, É. Kováts, G. Németh, K. Kamarás, K. Béres, P. Németh, V. Petrusevski, L. Bereczki, B. Holló, I. Sajó, Sz. Klébert, A. Farkas, I.Szilágyi, L.Kótai: **A solid-phase quasi-intramolecular redox reaction of $[Ag(NH_3)_2]MnO_4$: an easy way to prepare pure $AgMnO_2$**
Inorg. Chem. **60,** 3749--3760 (2021)

A-10. L. Bereczki, L.A. Fogaça, Zs. Dürvanger, V. Harmat, K. Kamarás, G. Németh, B.B. Holló, V.M. Petrusevski, E. Bódis, A. Farkas, I.M. Szilágyi, L. Kótai: **Dynamic disorder in the high-temperature polymorph of bis[diamminesilver(I)] sulfate - reasons and consequences of simultaneous ammonia release from two different polymorphs**
J. Coord. Chem. **74,** 2144--2162 (2021)

A-11. G. Németh, D. Datz, Á. Pekker, T. Saito, O. Domanov, H. Shiozawa, S. Lenk, B. Pécz, P. Koppa, K. Kamarás: **Near-field optical investigation of Ni clusters inside single-walled carbon nanotubes on the nanometer scale**
RSC Advances **9,** 34120-34124 (2019)

A-12. D. Datz, G. Németh, K.E. Walker, G.A. Rance, Á. Pekker, A.N. Khlobystov, K. Kamarás: **Polaritonic enhancement of near-field scattering of small molecules encapsulated in boron nitride nanotubes: Chemical reactions in confined spaces**
ACS Appl. Nano Mater. **4,** 4335--4339 (2021)

A-13. A. Cadena, B. Botka, E. Székely, K. Kamarás: **Encapsulation of sexithiophene molecules in single-walled carbon nanotubes using supercritical CO_2 at low temperature**
Phys. Stat. Sol. (b) **257,** 2000314-1-5 (2020)

A-14. A. Cadena, B. Botka, K. Kamarás: **Organic molecules encapsulated in single-walled carbon nanotubes**
Oxford Open Mat. Sci. **1,** itab009 (2021)

Conference presentations:

C-1. D. Datz, G. Németh, H.M. Tóháti, T. Gál, Ö. Sepsi, P. Koppa, Á. Pekker, K. Kamarás: **s-SNOM measurements of boron nitride nanotubes**
XXXIst International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2017), Kirchberg, Austria, March 4-11, 2017, poster

C-2. G. Németh, D. Datz, H.M. Tóháti, Á. Pekker, K. Kamarás, K. Otsuka, T. Inoue, S. Maruyama: **Nanoscale characterization of individual horizontally aligned single-walled carbon nanotubes**
XXXIst International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2017), Kirchberg, Austria, March 4-11, 2017, poster

C-3. K. Kamarás, D. Datz, G. Németh, Á. Pekker, H.M. Tóháti, A. Cernescu, K. Otsuka, T. Inoue, S. Maruyama, K.E. Walker, G.A. Rance, A.N. Khlobystov, H. Shiozawa: **Near-field infrared spectroscopy and microscopy on nanotubes**
International Conference on Low-Energy Electrodynamics in Solids, Portonovo, Italy, June 24-29, 2018, lecture

C-4. K. Kamarás, J. Horváth, G. Németh, G. Klupp, K. Prassides, F. Capitani, F. Borondics: **Pressure dependence of the infrared spectra of a molecular Jahn-Teller metal**
13th Soleil Users' Meeting, Saint-Aubin, France, Jan. 18-19, poster

C-5. K. Kamarás, J. Horváth, G. Németh, G. Klupp, P. Matus, F. Capitani, F. Borondics: **Vibrational signatures of the Jahn-Teller metal state in expanded fullerides under chemical and physical pressure**
International Conference on Diamond and Carbon Materials, Dubrovnik, Croatia, Sep. 2-6, 2018, lecture

C-6. G. Németh, D. Datz, H.M. Tóháti, Á. Pekker, K. Kamarás, T. Saito, O. Domanov, H. Shiozawa: **Investigation of Ni clusters inside single-walled carbon nanotubes on the sub-wavelength scale**
XXXIInd International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2018), Kirchberg, Austria, March 17-24, 2018, poster

C-7. D. Datz, G. Németh, Á. Pekker, K. Kamarás: **Polariton-enhanced molecular absorption in boron nitride nanotubes: experiments and numerical calculations**

International Conference on Low-Energy Electrodynamics in Solids, online, June 28 - July 8, 2021, poster

C-8. G. Németh, D. Datz, Á. Pekker, F. Borondics, K. Kamarás: **Ultrasensitive molecule detection via tip-launched graphene plasmons**
International Conference on Low-Energy Electrodynamics in Solids, online, June 28 - July 8, 2021, poster

C-9. G. Németh: **Közeli terű infravörös spektroszkópia**
Hungarian Academy of Sciences, Session "Physics of Condensed Matter", Nov. 12, 2020, lecture

C-10. K. Kamarás, Á. Pekker, D. Datz, G. Németh, H.M. Tóháti, K.E. Walker, G.A. Rance, A.N. Khlobystov: **Encapsulation of molecules into carbon and boron nitride nanotubes - a comparison**
Joint Meeting of the DPG and EPS Condensed Matter Divisions, Berlin, Germany, March 11-16, 2018, lecture

C-11. A. Cadena, E. Székely, B. Botka, K. Kamarás: **Graphene nanoribbons from sulfur-containing precursors**
XXXIVth International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2020), Kirchberg, Austria, March 7-14, 2020, poster

Student theses connected to the project:

T-1. Horváth J.: **Szénalapú nanoszerkezetek vizsgálata infravörös spektroszkópiával,** Budapest University of Technology and Economics, 2017, M. Sc. thesis

Seminars and colloquia:

[S-1] Cairo University, December 17, 2018, Katalin Kamarás
[S-2] University of Glasgow, June 5, 2018, Katalin Kamarás
[S-3] University of Tennessee, Knoxville, August 22, 2017, Katalin Kamarás
[S-4] Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, February 2021, Dániel Datz

Outreach:
Popular science lectures:

[P-1] K. Kamarás: Szerves molekulák nanoszerkezetekben, Oct. 8, 2020, ELTE „Alkímia ma"
[P-2] K. Kamarás: Tűerősített közeli terű optikai mikroszkópia. Feb. 21, 2021 ELTE „Az atomoktól a csillagokig"