Temperature-Controlled Transient Absorption Spectroscopy and Its Applications

PhD Thesis Booklet

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1. Introduction and Objectives

In recent years, the practical use of quantum mechanics has opened new directions in materials science and photonics. We expanded our ability to monitor complex photophysical and photochemical processes in semiconductors and molecular systems across timescales ranging from microseconds to femtoseconds. The technique that allows for such ultrafast temporal resolution is known as transient absorption spectroscopy (TAS), which provides valuable insights into recombination mechanisms, trapping processes, and the formation of quasi-particles, such as trions. In a typical TAS experiment, a short pump pulse excites the sample, generating various excited states, while a delayed probe pulse monitors their relaxation. The 2023 Nobel Prize in Chemistry highlighted this shift by recognizing breakthroughs in quantum dots (QDs), now used in displays, bioimaging, photovoltaics, and quantum technologies. Although charge carrier dynamics of CdSe QDs is a thoroughly studied topic, there are still several unanswered questions even in the case of this prototypical semiconductor. Temperature is an often-neglected parameter in TA studies, however studies at elevated temperatures can reveal mechanistic information on ultrafast processes. The effect of external dopants on the creation of energy levels and their interaction with different recombination processes is still not fully understood. This is particularly interesting because these processes can extend the lifetime of hot carriers, which is a key requirement for hot-carrier-based devices.

TAS is effective for studying ultrafast dynamics in colloidal QDs but applying it to solid-state systems requires some adjustments. Transition-metal-dichalcogenide (TMDC) thin films have become highly relevant, with tunable properties and light–matter interaction that enable applications in photodetectors, LEDs, catalysis, and next-generation electronics. The combination of TMDC monolayers with organic semiconductor films, such as pentacene, yields heterojunctions with unique excitonic and charge separation properties. By modifying the TAS setup to transient reflection spectroscopy (TRS), we can study how exciton lifetimes and recombination pathways change at these interfaces. This can help us understand the exciton behavior in MoS_2/pentacene and WSe_2/pentacene structures and can provide insights into carrier dynamics at the junctions.

Studies mainly focused on the visible and infrared range, but the terahertz (THz) region is now also accessible due to recent technological developments. The integration of a THz probe into the TAS setup extends the spectral range, which can allow us to study the carrier dynamics at longer wavelengths. THz spectroscopy is sensitive to carrier scattering and phonon interactions. Optimizing the beam dispersion is crucial for effective THz detection, which can provide a valuable tool to observe carrier relaxation.

During my research, I aimed to find answers to the following questions and solve the following scientific/development problems:

- *Is it possible to develop a measurement setup that allows temperature control while performing TAS experiments at high temperatures?*
- *What role does temperature play in the charge carrier dynamics of CdSe/ZnS QDs? How will the recombination pathways be affected at high temperatures?*
- *What is the impact of Ga-alloying on the excited-state lifetime of CdSe/ZnS QDs?*
- *Can the TAS setup be modified to perform TRS measurements? Can this technique be used to investigate the impact of a pentacene film on the decay kinetics of A and B excitons in transition-metal-dichalcogenide/pentacene thin films?*
- *How can preliminary findings related to the effects of fundamental beam dispersion on THz radiation generation be used to develop a new THz probe path in the TAS setup?*

As a first step, I aimed to extend the capabilities of the TAS setup at ELI ALPS by incorporating temperature control to investigate the temperature-dependent charge carrier dynamics in CdSe-based QDs. The developed system enabled TAS measurements across the 30–130 °C temperature range, using liquid samples to probe the effects of temperature changes on charge carrier behavior. Initial measurements in

CdSe/ZnS QDs showed that temperature had a negligible effect on excited-state lifetime but strongly influenced carrier recombination, which suggests trion formation. Then, I explored the impact of Ga incorporation into the structure of CdSe/ZnS QDs, which further promotes the formation of trions and induces a Coulomb blockade in the relaxation dynamics, effectively prolonging the hot-carrier lifetime. In the next phase, I modified the detection geometry of the TAS setup to enable transient reflection measurements. This technique was employed to study the exciton dynamics in TMDC/pentacene thin films deposited on gold substrates. Specifically, in MoS_2/pentacene and WSe_2/pentacene heterojunctions, the presence of the pentacene film was found to have a moderate influence on the decay kinetics of A and B excitons. Furthermore, I set a more distant goal to develop a THz probe path in the TAS setup, building on previous work, where I investigated the effects of fundamental beam dispersion on terahertz radiation generation.

2. Experimental Methods

The experiment was performed with a high-repetition-rate (HR) laser system at ELI ALPS, delivering 6–30 fs pulses at 100 kHz with a central wavelength of 1030 nm and pulse energi2 of 1 mJ level. The setup generated the pump beam by frequency-doubling the fundamental beam in a BBO crystal, producing 515 nm pulses, while the probe beam was created by focusing the fundamental beam onto a sapphire crystal to produce a broadband white light continuum. The QPod sample holder maintained the temperature under argon flow, while the Ocean Insight FX spectrometer recorded spectra at 2000 Hz. The setup can operate between TAS and TRS modes, accommodating multiple wavelengths and achieving a temporal resolution of approximately 15–60 fs. **Figure 1** shows the basic layout of a TAS instrument. The fundamental beam (shown in the top right corner) typically has a wavelength ranging from 980 nm to 1080 nm. To observe a transient absorption change, two synchronized beams (pump and probe) interact with the sample. The incoming beam is split by a beamsplitter into two paths: the pump arm, directed to the left, and the probe arm, directed downward. The generation of the excited states (pump ON/OFF cycles) must be modulated with a mechanical chopper. A carefully chosen nonlinear crystal (BBO) in the pump beam path generates the second harmonic from the fundamental beam. Two chirp mirrors preserve the short pump pulse duration. A delay stage in the pump arm controls the time delay between the pump and probe beams.

In the current configuration, the sample holder shown is used to study liquid samples. After interacting with the sample, the pump beam is dumped. Following the downward beam path after the beamsplitter, we reach the probe beam generation unit. A lens focuses the fundamental beam on a sapphire crystal, a nonlinear optical element, which generates a broadband continuum of light in the range of 400 nm to 700 nm. This is the spectral range where we can monitor the transient absorption features of the samples. The generated white light is then directed to the sample and subsequently to the spectrometer, where the absorption changes are measured and recorded.

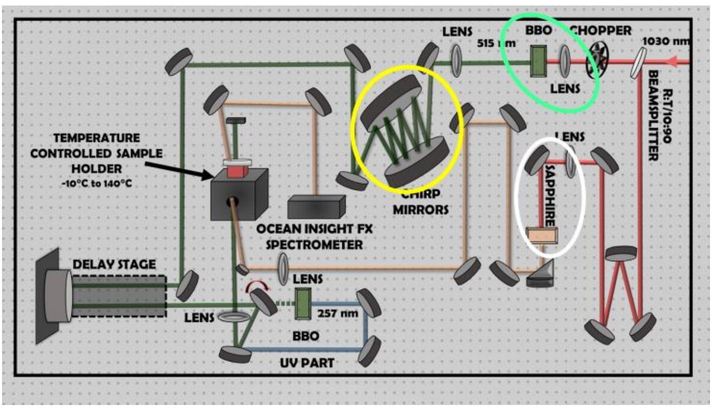

Figure 1. Schematic representation of a TAS setup. It shows the separation of the fundamental beam (red lines) into pump and probe paths with a beamsplitter, the modulation of the pump arm with a mechanical chopper to gain pump ON/OFF states, and the generation of a broadband probe continuum (white lines) using a sapphire crystal.

3. Summary of New Scientific Results

T1 I extended the capabilities of the transient absorption setup at ELI ALPS to perform temperature-controlled transient absorption measurements. The combined technique was suitable to probe the effect of temperature on the charge carrier dynamics of CdSe-based QDs. [1]

Taking advantage of ELI ALPS' high-repetition (HR-100 kHz), carrier-envelope-phase (CEP) stable laser system, I developed a temperature-controlled TAS setup optimized for ultrafast measurements with high temporal resolution, which was successfully applied to study CdSe QDs dispersions in the 30–130 °C temperature range. The system proved reliable to measure temperature-dependent changes in charge carrier dynamics without sample degradation. Initial measurements showed distinct changes in carrier populations and recombination pathways, demonstrating the applicability of the setup for observing the thermal effects on QD excitonic states.

T2 I performed temperature-dependent TAS measurements on CdSe/ZnS QD dispersions, and found that temperature increase had a negligible effect on the lifetime, however it significantly affected the fraction of charge carriers participating in the different recombination channels. [1]

In CdSe/ZnS QD dispersions, temperature increase did not significantly alter the excited-state lifetime, suggesting that the primary recombination pathways are stable in the observed temperature range, with typical lifetimes of t_1 ~5 ps and t_2 ~250 ps. However, TAS measurements revealed notable changes in the distribution of charge carriers, indicating that temperature affects the balance between radiative and nonradiative processes. This redistribution of carriers may result from changes in trap states or quasi-particle (trion) formation.

T3 I revealed, that the amount of Ga in the structure of CdSe/ZnS QDs had a significant effect on the excited-state lifetime. The incorporated Ga promotes the formation of trions and induces a Coulomb blockade in the relaxation dynamics of the samples, which prolongs the hot-carrier lifetime. [1]

Ga incorporation in CdSe/ZnS QDs with 2.5%, 7.5%, and 15% nominal concentrations influenced charge carrier dynamics and promoted trion formation and induced Coulomb blockade effects (added charges increase electrostatic potential, restricting further carrier movement), resulting in prolonged hot-carrier lifetimes. Steady-state UV-Vis and photoluminescence measurements showed that Ga-alloyed QDs have slower kinetic decay compared to undoped samples. In the case of CdSe/ZnS, the fast and slow components of the decay were $t_1 \approx 0.4$ ps and $t_2 \approx 2$ ps, for CdSe:7.5% Ga/ZnS these values increased to $t_1 \approx 12$ ps and $t_2 \approx 25$ ps. This indicates the impact of Ga on relaxation dynamics. Temperature-dependent TAS showed that although the overall lifetimes stayed the same, along each recombination path of the charge carriers, temperature influenced the amplitudes of the decay components differently: A_1 decreased from 0.24 to 0.14%, while A_2 increased from 0.25 to 0.53%, suggesting more trion-related processes in the doped samples.

T4 I extended the capabilities of the transient absorption setup at ELI ALPS by altering its detection geometry, enabling transient reflection measurements. I used the developed technique to investigate exciton dynamics in various transition-metal-dichalcogenide/pentacene thin film samples on gold substrates. [2]

Altering the detection geometry to implement TRS enables the investigation of exciton dynamics at TMDC/organic semiconductor interfaces. While in liquid samples the probe light passes through the sample, in thin films, the reflected probe light must be effectively collected. This requires sufficient optical density and sample area. The MoS_2 and WSe_2 monolayers were deposited on a gold substrate and covered with a 20 nm thick pentacene layer. TRS measurements successfully revealed a 21 ± 3 ps decay component in MoS_2/pentacene heterojunctions associated with hole transfer. This discrepancy highlights the importance of substrate material and molecular orientation in determining exciton dissociation dynamics.

T5 I demonstrated that in the case of MoS_2-pentacene and WSe_2-pentacene heterojunctions the presence of the pentacene film had an impact on the decay kinetics of A and B excitons. [2]

The presence of pentacene in MoS_2 and WSe_2 heterojunctions accelerated the exciton decay kinetics, as evidenced by multiexponential decay fitting. In MoS_2/pentacene, the A exciton decay was characterized by a 21 ps component linked to hole transfer, while in WSe_2/pentacene, the B exciton signal required an additional fast, 7 ps component in connection with the hole transfer, extending the slower decay component to 705 ps.

T6 I studied how fundamental beam dispersion affects THz generation, finding that controlling GDD and phase mismatch can optimize THz intensity. This is a key step for the future development of the TAS-THz probing setup. [3]

I studied the impact of group delay dispersion (GDD) and phase mismatch on THz generation from two-color laser-induced air plasma. We demonstrated that optimal THz yield can be achieved by precisely controlling these parameters. The key findings showed that the THz intensity changed with the BBO crystal's position and that GDD significantly affected both the shape and strength of the THz pulses. This allows that optimal THz yield can be achieved by precisely controlling these parameters. These insights are very important for the effective generation of THz radiation in the TAS setup at ELI ALPS, because the tunability of THz radiation is valuable for probing ultrafast carrier dynamics.

4. List of Publications

Publications related to the scientific topic of the dissertation:

[1] K. Sárosi, C. Tuinenga, G. F. Samu, K. Mogyorósi, J. Dudás, B. Tóth, P. Jójárt, B. Gilicze, I. Seres, Zs. Bengery, Cs. Janáky, V. Chikán
Temperature Dependent Carrier Dynamics in Ga-Alloyed CdSe/ZnS Core–Shell Quantum Dots
The Journal of Physical Chemistry C 128 (9), 3815–3823 (2024).
DOI: 10.1021/acs.jpcc.3c04689
IF_{2023}: 3.3

[2] P. A. Markeev, E. Najafidehaghani, G. F. Samu, **K. Sárosi,** S. B. Kalkan, Z. Gan, A. George, V. Reisner, K. Mogyorósi, V. Chikán, B. Nickel, A. Turchanin, M. P. de Jong
Exciton Dynamics in MoS_2–Pentacene and WSe_2–Pentacene Heterojunctions
ACS Nano 16 (10), 16668–16676 (2022).
DOI: 10.1021/acsnano.2c06156
IF_{2023}:15.8

[3] R. Flender, **K. Sárosi**, E. Petrács, A. Börzsönyi, V. Chikán
Control of THz field waveform emitted from air plasma by chirping two-color laser pulses
Optics Communications 436, 222–226 (2019).
DOI: 10.1016/j.optcom.2018.12.064
IF_{2020}: 2.31

∑IF = 21.41

Further publications:

R. Flender, **K. Sárosi,** A. Börzsönyi, V. Chikan
The impact of dispersion of ultrashort light pulses on the THz radiation formation from asymmetric air plasmas
Proceedings of SPIE 10228, 102281B (2017).
DOI: 10.1117/12.2265663
IF_{2018}: 0.61

R. Flender, **K. Sárosi,** E. Petrács, A. Börzsönyi, V. Chikan
Controlling terahertz spectrum in asymmetric air plasmas: The role of GDD and phase
Proceedings of SPIE 10684, 1068428 (2018).
DOI: 10.1117/12.2307411
IF_{2019}: 0.49

K. Mogyorósi, **K. Sárosi**, I. Seres, P. Jójárt, M. Füle, V. Chikan
Formation of CN Radical from Nitrogen and Carbon Condensation and from Photodissociation in Femtosecond Laser-Induced Plasmas: Time-Resolved FT-UV–Vis Spectroscopic Study of the Violet Emission of CN Radical
Journal of Physical Chemistry A 124 (14), 2755–2767 (2020).
DOI: 10.1021/acs.jpca.0c00361
IF_{2021}: 2.94

K. Mogyorósi, **K. Sárosi,** V. Chikan
Direct Production of CH ($A^2\Delta$) Radical from Intense Femtosecond Near-IR Laser Pulses
Journal of Physical Chemistry A 124 (40), 8112–8119 (2020).
DOI: 10.1021/acs.jpca.0c05206
IF_{2021}: 2.94

X. Chen, **K. Sárosi**, B. Tóth, B. Gilicze, Zs. Bengery, K. Mogyorósi, Cs. Janáky, G. F. Samu
Electrochemical Modulation of Hole Extraction in NiO/Perovskite Bilayers
Advanced Materials Interfaces (2025).
DOI: 10.1002/admi.202500159
IF_{2025}: 4.3

K. Mogyorósi, B.Tóth, **K. Sárosi**, B. Gilicze, J. Csontos, T. Somoskői, S. Tóth, P. Prasannan, L. Tóth, S. S. Taylor, N. Skoufis, L. Barron, K. Varga, C. Covington, V. Chikán.,
CH(A) Radical Formation in Coulomb Explosion from Butane Seeded Plasma Generated with Chirp-Controlled Ultrashort Laser Pulses (2025).
DOI 10.1021/acsomega.4c11074 in *ACS Omega*.
IF_{2025}: 3.7

∑∑IF = 36.39

Poster Presentations:

K. Sárosi, R. Flender, A. Börzsönyi, V. Chikán
Aszimmetrikus levegőplazmában keltett terahertzes rövidimpulzusok vizsgálata
Magyar Fizikus Vándorgyűlés, Szeged, Hungary, August 24–27, 2016
K. Sárosi, R. Flender, A. Börzsönyi, V. Chikán
The impact of dispersion of the ultrashort light pulses on the THz radiation from asymmetric air plasmas
ELI-ALPS User Workshop, Szeged, Hungary, November 10–11, 2016

R. Flender, **K. Sárosi,** A. Börzsönyi, V. Chikán
The impact of dispersion of the ultrashort light pulses on the THz radiation formation from asymmetric air plasmas
SPIE Optics + Optoelectronics, Prague, Czech Republic, April 24–27, 2017

R. Flender, **K. Sárosi**, E. Petrács, A. Börzsönyi, V. Chikán
The impact of dispersion and phase difference of ultrashort light pulses on the THz intensity generated from two-color asymmetric air plasma
LAMELIS Workshop, Szeged, Hungary, July 20, 2018

K. Sárosi, C. Tuinenga, G. F. Samu, K. Mogyorósi, J. Dudás, P. Jójárt, B. Gilicze, I. Seres, Zs. Bengery, Cs. Janáky, V. Chikán
Temperature dependent carrier dynamics of gallium alloyed CdSe/ZnS QD samples
ELISS 2024, Szeged, Hungary, September 2–6, 2024

Oral Presentations

K. Sárosi, C. Tuinenga, G. F. Samu , K. Mogyorósi, J. Dudás, P. Jójárt, B. Gilicze, I. Seres, Z. Bengery, C. Janáky, V. Chikán
Investigation of charge carrier dynamics in semiconductors with femtosecond transient absorption/reflection spectroscopy
4th User Meeting, Dolní Břežany, Czech Republic, June 26–28, 2024

Társszerzői nyilatkozat

Alulírott nyilatkozom arról, hogy **Sárosi Krisztina** "*Temperature Controlled Transient Absorption Spectroscopy and its Applications*" című doktori értekezésének T1, T2, T3, T4, T5 és T6 tézispontjaiban szereplő, az alábbi cikkekben közösen publikált eredmények elérésében a jelölt szerepe meghatározó volt. Ezeket az eredményeket korábban nem használtam tudományos fokozat megszerzésére, és ezt a jövőben sem teszem.

[T1-T3] K. Sárosi, C. Tuinenga, G. F. Samu, K. Mogyorósi, J. Dudás, B. Tóth, P. Jójárt, B. Gilicze, I. Seres, Zs. Bengery, Cs. Janáky, V. Chikán
Temperature Dependent Carrier Dynamics in Ga-Alloyed CdSe/ZnS Core–Shell Quantum Dots
The Journal of Physical Chemistry C 128 (9), 3815–3823 (2024).
DOI: 10.1021/acs.jpcc.3c04689

[T4-T5] P. A. Markeev, E. Najafidehaghani, G. F. Samu, K. Sárosi, S. B. Kalkan, Z. Gan, A. George, V. Reisner, K. Mogyorósi, V. Chikán, B. Nickel, A. Turchanin, M. P. de Jong
Exciton Dynamics in MoS_2–Pentacene and WSe_2–Pentacene Heterojunctions
ACS Nano 16 (10), 16668–16676 (2022).
DOI: 10.1021/acsnano.2c06156

[T6] R. Flender, K. Sárosi, E. Petrács, A. Börzsönyi, V. Chikán
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Optics Communications 436, 222–226 (2019).
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