Summary of research (PD124623 project)

I note that some points of the detailed work plan were completed only partially, and several additional research achievements were obtained, which fit into the topics of the research plan, but were not included in the original detailed work plan.

The publications and conference presentations related to the different projects are indicated at the end of each section.

(1) Laser-induced alignment and orientation

(1.1) A cross-platform software for simulating laser-induced alignment and orientation dynamics of linear-, symmetric- and asymmetric tops was developed. This is a user-friendly software to aid experimentalists, and can be used for arbitrary molecules. Currently two implementations are available, one in JAVA and one in Mathematica. The software uses the rigid-rotor approximation, takes into account the dipole and polarizability interaction with the external field, it can simulate adiabatic or diabatic (field-free) alignment and orientation, accounts for finite temperature, nuclear spin statistical weights, and allows two pulse simulations. [P13, C12]

(1.2) Based on investigations on the laser-induced rovibrational dynamics of H_2O and H_2He^+ using accurate variational techniques, a book chapter in “Progress in Ultrafast Intense Laser Science XIV” (PUILS) was published, which presents how vibrational motion and rovibrational couplings can influence the laser-induced alignment dynamics of molecules. A general theoretical framework is presented and the importance of vibration-induced structural changes and the symmetry of the excited vibrational modes is emphasized. [B3, C14, C15]

(1.3) A general program for simulating laser-induced rovibrational dynamics was developed using the Mathematica software. Based on user-defined molecular models, the software solves the time-dependent Schrödinger equation for the given system, which interacts with a user defined laser pulse. The temporal evolution of eigenstate populations and the expectation values of user-defined physical quantities can be computed and plotted by the software. The above software was used to simulate the laser driven rovibrational dynamics of H_2O with various models to describe the system. In the different models, the basis functions to describe the time-dependent dynamics and the molecular properties (dipole moment, polarizability) accounting for the molecule-laser interaction were approximated in different ways. The basis functions tested were (1) variational rovibrational eigenstates, (2) rigid rotor rotational states multiplied by variational vibrational states, (3) rigid rotor rotational states multiplied by harmonic oscillator vibrational states (4) rigid rotor rotational states with vibrations neglected. As for the molecular properties, they were determined as the expectation values evaluated with the various eigenstate models above, also varying different molecular frame embeddings in order to explore the effect of different embeddings on the expectation values. It was found that in a wide range of laser parameters, when the dynamics is dominated by rotational excitation within a single vibrational manifold (Raman-type transitions or dipole transitions “diagonal” in the vibrational subspace) the different theoretical models give fairly similar results. On the other hand, when vibrational transition amplitudes start to play a role, the situation becomes more involved. The accurate determination of the molecular parameters becomes crucial, which can be significantly different in the different models, indicating that qualitatively wrong results might be computed if care is not taken in the choices of molecular frame embedding and vibrational mode representation. Some further computations are needed before publication. [C13]

(2) Structure and photodissociation of $H_nHe_m^+$ clusters

(2.1) Variational calculations on the triatomic H_2He^+ system in order to understand the details of its rovibrational motions were carried out, serving also as a prerequisite and the first step for carrying out appropriate dynamics simulations for this system in laser fields. For H_2He^+, all its bound states, its dissociation channels, and many of its quasibound resonance states have been determined and characterized. The quasibound metastable states are expected to play an important role in certain laser-induced dynamics of H_2He^+. [P12, C8, C11]

(2.2) To facilitate their further investigation, the structure and some dynamical properties of the HHe_n^+ type systems (n=1-18) were investigated using accurate ab initio quantum chemical methods. The shell structure of the solvating He atoms were revealed and signatures of microscopic superfluidity were found. The results formed the basis of a joint project with the Stephan Schlemmer group (University of Köln), detailed below. [P9]

(2.2) The photodissociation dynamics of HHe_m^+ clusters (m=2-6) was investigated. The experimental work on the (multi)photon dissociation of these systems was carried out by the Köln group in the FELIX free-electron laser facility, while the theoretical simulations were done in Budapest. Based on our joint effort, the IR spectrum of HHe_m^+ species were obtained for the first time. [P6]

(2.3) High-resolution IR spectra of HHe_2^+ and HHe_3^+ were obtained experimentally (Köln), supported and interpreted by theoretical simulations (Budapest). For HHe_3^+ the observed broad features point to a lifetime of a few ps in the vibrationally excited state. For HHe_2^+, a fundamental linear molecule consisting of only three nuclei and four electrons, measurement of three accurate rovibrational transitions were made, pinning down its molecular parameters for the first time. [P1]

(3) Light-dressed spectroscopy

When molecules interact with laser fields, whose amplitude has a temporal evolution much slower than typical molecular timescales, the system can usually be described by so-called light-dressed states.

(3.1) A general theoretical framework was formulated for computing (a) the light-dressed states of molecules in medium intensity laser field, and for computing (b) transitions between the light dressed states induced by a probe pulse. The nonadiabatic effects of light-induced conical intersections were revealed in the absorption and stimulated emission spectra of light-dressed molecules. [P11,P4,C9,C10]

(3.2) A more in-depth study was carried out on the light-dressed spectroscopy of molecules and numerical results were generated for the Na_2 molecule. The effects of the temperature, the dressing-light intensity and frequency and the effects of the turn-on time of the dressing field was investigated. A procedure to derive forbidden field-free transition frequencies from light-dressed spectra was also proposed. [B2,P7,C5,C7]

(3.3) As an alternative to interactions of atoms or molecules with intense laser fields, strong light−matter coupling can also be achieved, both for atoms and molecules, by their confinement in microscale cavities. The rovibronic spectrum of molecules dressed by the quantized radiation field of an optical cavity was investigated. The formation of light-induced conical intersections induced by the quantized radiation field was shown by identifying light-induced nonadiabatic effects in the spectrum. The coupling strength and the dependence of the field-dressed spectrum on the cavity mode wavelength was also investigated from the weak to the ultrastrong coupling regimes, and the formation of polariton states in the strong coupling regime was demonstrated [P10,C2,C6].

(3.4) The composite system of a molecule and an atomic ensemble, interacting with the confined mode of a microscopic cavity, was investigated. It was found that the indirect coupling between atoms and molecule, due to their interaction with the cavity radiation mode, leads to a coherent mixing of atomic and molecular states, and the general field-dressed states of the excited state manifold carry signatures of atomic, molecular, as well as photonic excitations. This is reflected in the absorption spectrum, an intensity borrowing effect could be identified in the atomic transition peak, originating from the contamination of the atomic excited state with excited molecular rovibronic states. It was also shown that by changing the cavity wavelength and the atomic transition frequency, the potential energy landscape of the polaritonic states and the corresponding spectrum could be altered significantly. This shows, that by adding a second type of entity to a quantum system confined in a microscopic cavity, the dynamics of the system and its response to light can be significantly modified and manipulated. [P3,C2]

(4) Rovibrational motion of weakly bound complexes

A new efficient and semi-automatic algorithm was developed for computing quasibound/resonance rovibrational states of polyatomic molecules. The new approach is based on using a Complex Absorbing Potential (CAP) to compute eigenvectors (basis functions) with proper boundary conditions for resonance computations. The proper basis functions are identified among the many eigenvectors of the CAP-perturbed Hamiltonian with the help of an eigenvalue clustering algorithm. Once the appropriate basis functions are at hand, the quasibound states can be expanded in a standard linear, variational way. The new algorithm was tested on the $(H_2)_2$ dimer and the $ArNO^+$ systems, and should be useful in future studies on quasibound states or the laser-induced rovibrational dynamics of weakly-bound complexes, in which the quasibound states most likely play a significant role. [P2,P8]

(5) Strong-field Fourier-Transform Spectroscopy

We derived and implemented a theoretical method for simulating the rovibrational dynamics of H_2O^+ molecules generated by ionizing the ground vibrational state of neutral H_2O. The nuclear wavepacket of neutral H_2O is projected onto the cationic potential energy surface, i.e., instantaneous ionization is assumed. The wave packet is expanded in the basis of the cationic rovibrational eigenstates, computed using variational methods. Information on such dynamics can help assign and interpret the so-called “Strong-field Fourier-Transform Spectroscopy” pump-and-probe experiments carried out by the Yamanouchi group at the University of Tokyo. In these experiments cations are generated in a superposition state by the pump pulse, and are probed by further ionization and Coulomb explosion after a given time-delay. The observed fragment signal oscillates as a function of time delay, and the Fourier transform (FT) of the signal represents transition frequencies corresponding to the cations generated by the pump pulse. In our initial theoretical model the experimental signal was reproduced by evaluating the temporal evolution of cation structural parameters and taking their FT. In the second year the model was extended to account for the molecular structure dependence of the ionization probability, i.e., the ionization probability during the probe pulse (which is directly related to the observed signal) is evaluated using the expectation value of structure-dependent ionization probability surfaces. Simulations were carried out for both H_2O^+ and D_2O^+. Agreement with experiment is very good. For finalizing the publication, some additional experiments are still needed in Tokyo, but these are delayed due to the COVID-19 pandemic. [C1,C3,C4]

Conference presentations

[C1] Strong-field Fourier-transform spectra of H_2O^+ and D_2O^+ **(poster presentation)**
T. Szidarovszky, A. G. Császár, H. Kageyama, T. Ando, A. Iwasaki, K. Yamanouchi
(1st Annual Workshop and Joint WG meeting of COST Action CA18222 on Attosecond Chemistry (AttoChem), virtual event, 2020. September 9-11)

[C2] Light-dressed spectroscopy of confined molecular systems **(invited talk)**
T. Szidarovszky, G. J. Halász, Á. Vibók
(Ultrafast processes in atoms, molecules and nano systems: classical and quantum descriptions UPAMON2020, Mátrafüred, Hungary, 2020. April 19-23)
-RESCHEDULED TO LATE 2020 DUE TO COVID PANDEMIC-

[C3] Simulating the strong-field Fourier-transform spectra of H_2O^+ and D_2O^+ **(invited talk)**
T. Szidarovszky, A. G. Császár, H. Kageyama, T. Ando, A. Iwasaki, K. Yamanouchi
(Anyag- és Molekulaszerkezeti Munkabizottság ülés, Mátrafüred, Hungary, 2019. October 11-12)

[C4] Simulating the strong-field Fourier-transform spectra of H_2O^+ and D_2O^+ **(invited talk)**
T. Szidarovszky, A. G. Császár, H. Kageyama, T. Ando, A. Iwasaki, K. Yamanouchi
(International Symposium on Ultrafast Intense Laser Science, Kushiro, Japan, 2019. August 4-9)

[C5] Rovibronic spectra of light-dressed molecule **(poster presentation)**
T. Szidarovszky, G. J. Halász, A. G. Császár, L. S. Cederbaum, Á. Vibók
(International Symposium on Ultrafast Intense Laser Science, Visegrád, Hungary, 2018. October 14-19)

[C6] Rovibronic spectra of molecules dressed by quantum light **(poster presentation)**
T. Szidarovszky, G. J. Halász, A. G. Császár, L. S. Cederbaum, Á. Vibók
(International Symposium on Ultrafast Intense Laser Science, Visegrád, Hungary, 2018. October 14-19)

[C7] Rovibronic spectra of light-dressed molecules **(invited talk)**
T. Szidarovszky, G. J. Halász, A. G. Császár, L. S. Cederbaum, Á. Vibók
(16th Central European Symposium on Theoretical Chemistry, Srni, Czech Republic, 2018. September 9-12)

[C8] Computation of rovibrational resonance states **(invited talk)**
T. Szidarovszky
(Bridging Experiment and Theory in Precision Spectroscopy COST summer school, Torun, Poland, 2018. June 26-30)

[C9] Rovibronic spectra of light-dressed molecules **(poster presentation)**
T. Szidarovszky, G. J. Halász, A. G. Császár, L. S. Cederbaum, Á. Vibók
(3rd General Meeting of the CM1405 COST Action, MOLIM: Molecules in Motion, Budapest, Hungary, 2018. April 19-21)

[C10] Rovibronic spectra of light-dressed molecules **(poster presentation)**
T. Szidarovszky, G. J. Halász, A. G. Császár, L. S. Cederbaum, Á. Vibók
(3rd AMOC Meeting (Anharmonicity in Medium-Sized Molecules and Clusters), Budapest, Hungary, 2018. April 16-19)

[C11] Rovibrational resonances in H_2He^+ **(poster presentation)**
D. Papp, A. G. Császár, K. Yamanouchi, T. Szidarovszky
(3rd AMOC Meeting (Anharmonicity in Medium-Sized Molecules and Clusters), Budapest, Hungary, 2018. April 16-19)

[C12] LIMAO: a cross-platform software for simulating the laser-induced alignment and orientation dynamics of linear-, symmetric- and asymmetric tops **(poster presentation)**
T. Szidarovszky, M. Jono, A. G. Császár, K. Yamanouchi
(International Symposium on Ultrafast Intense Laser Science, Lijiang, China, 2017. October 29 - November 3)

[C13] Molecules in intense laser field II. **(invited talk)**
T. Szidarovszky
(International Symposium on Ultrafast Intense Laser Science, Lijiang, China, 2017. October 29 - November 3)

[C14] Többatomos molekulák térbeli irányítása lézerfénnyel **(invited talk)**
T. Szidarovszky
(Anyag- és Molekulaszerkezeti Munkabizottság ülése, Budapest, 2017. September 21-22)

[C15] Laser-induced alignment dynamics of polyatomic molecules **(invited talk)**
T. Szidarovszky, A. G. Császár, M. Jono, K. Yamanouchi
(MOLIM2017 – Molecules in Motion, Zürich, Switzerland, 2017. April 18-20)

Publications in scientific journals

[P1] Infrared signatures of HHe_2^+ and HHe_3^+
M. Töpfer, A. Jensen, K. Nagamori, H. Kohguchi, T. Szidarovszky, A. G. Császár, S. Schlemmer and O. Asvany *Phys. Chem. Chem. Phys.* 22, 22885-22888 (2020).

[P2] Rotational-vibrational resonance states
A. G. Császár, I. Simkó, T. Szidarovszky, G. C. Groenenboom, T. Karman and Ad van der Avoird *Phys. Chem. Chem. Phys.* 22, 15081 (2020).

[P3] Three-player polaritons: nonadiabatic fingerprints in an entangled atom-molecule-photon system
T. Szidarovszky, G. J. Halász and Á. Vibók *New J. Phys.* 22, 053001 (2020).

[P4] Robust field-dressed spectra of diatomics in an optical lattice
M. Pawlak, T. Szidarovszky, G. J. Halász and Á. Vibók *Phys. Chem. Chem. Phys.* 22, 3715-3723 (2020).

[P5] Excited-state populations in the multiconfiguration time-dependent Hartree-Fock method
E. Lötstedt, T. Szidarovszky, F. H. M. Faisal, T. Kato and K. Yamanouchi *J. Phys. B*, 53, 105601 (2020).

[P6] Infrared signatures of the HHe_n^+ and DHe_n^+, n = 3-6, complexes
O. Asvany, S. Schlemmer, T. Szidarovszky and A. G. Császár *J. Phys. Chem. Lett.* 10, 5325-5330 (2019).

[P7] Rovibronic spectra of molecules dressed by light fields
T. Szidarovszky, A. G. Császár, G. J. Halász and Á. Vibók *Phys. Rev. A* 100, 033414 (2019).

[P8] Toward automated variational computation of rovibrational resonances. A case study of the H_2 dimer
I. Simkó, T. Szidarovszky and A. G. Császár *J. Chem. Theory Comput.* 15, 4156-4169 (2019).

[P9] Fingerprints of microscopic superfluidity in HHe_n^+ clusters
A. G. Császár, T. Szidarovszky, O. Asvany and S. Schlemmer *Mol. Phys.* 117, 1559-1583 (2019).

[P10] Conical intersections induced by quantum light: field-dressed spectra from the weak to the ultrastrong coupling regimes
T. Szidarovszky, G. J. Halász, A. G. Császár, Lorenz S. Cederbaum and Á. Vibók *J. Phys. Chem. Lett.* 9, 6215-6223 (2018).

[P11] Direct signatures of light-induced conical intersections on the field-dressed spectrum of Na_2
T. Szidarovszky, G. J. Halász, A. G. Császár, Lorenz S. Cederbaum and Á. Vibók *J. Phys. Chem. Lett.* 9, 2739-2745 (2018).

[P12] Rovibrational resonances in H_2He^+
D. Papp, A. G. Császár, K. Yamanouchi and T. Szidarovszky, *J. Chem. Theory Comput.* 14, 1523-1533 (2018).

[P13] LIMAO: Cross-platform software for simulating laser-induced alignment and orientation dynamics of linear-, symmetric- and asymmetric tops
T. Szidarovszky, M. Jono and K. Yamanouchi, *Comput. Phys. Commun.* 228, 219-228 (2018).

Publications in books

[B1] Exact numerical methods for stationary-state-based quantum dynamics of complex polyatomic molecules
A. G. Császár, C. Fábri, T. Szidarovszky, in *Molecular Spectroscopy and Quantum Dynamics* (2021), chapter 2.

[B2] Light-dressed spectroscopy of molecules
T. Szidarovszky, A. G. Császár, G. J. Halász, Á. Vibók, in *Progress in Ultrafast Intense Laser Science* volume XV (2020), chapter 4.

[B3] Laser-induced alignment and orientation dynamics beyond the rigid-rotor approximation
T. Szidarovszky, K. Yamanouchi, in *Progress in Ultrafast Intense Laser Science* volume XIV (2019), chapter 2.