Report for Project NKFIH PD 134976 (2020–2023)

Background

Molecular transformations triggered by irradiation of light are key processes for various disciplines ranging from biology through chemistry to physics. One of the numerous fascinating properties of transition-metal (TM)-based functional molecules is their capability to exploit the opportunities offered by photoactivation, which can lead to the development of cutting-edge applications such as molecular data storage, photocatalysis, solar energy conversion, etc. Fundamental understanding of photoinduced molecular transformations, such as electronic transitions (internal conversion and intersystem crossing) and structural dynamics, is pivotal for designing advanced functional molecules, paving the way for new technologies. Since the elementary processes following photoexcitation involve electronic states with lifetimes ranging from femtoseconds to nanoseconds, emerging ultrafast experimental techniques are required to capture the key intermediate and metastable species. Pump-probe experiments applying ultrashort excitation and probe pulses are powerful methods for studying the dynamics of relaxation pathways, and this has received a large impetus from the advent of novel X-ray free electron lasers (XFELs). However, the recorded data can be extremely complex and difficult to interpret, even for the simplest and smallest molecules. Theory is thus of utmost importance for contrasting and complementing experiments, and even for designing new ones. In the present project, we investigated in detail the mechanism of photoinduced transformations in TM-based functional molecules using excited-state simulations. We focused on two families of photofunctional complexes: i) photoswitchable TM complexes, which are very appealing from the point of view of molecular data storage, as they are small (< 1 nm) and have the ability to undergo light-induced ultrafast transitions between their low (LS) and high-spin (HS) states, and ii) light-harvesting TM complexes that can exploit absorption of visible light in photocatalysis and solar energy energy conversion via their metal-to-ligand charge transfer (MLCT) states.

Obtained Results

During the initial period (first year) of the project, most of the research focused on theoretical investigations of the $[Fe(NCH)_6]^{2+}$ complex [P1,P2]. $[Fe(NCH)_6]^{2+}$ is a model for light-induced spin-state photoswitching in $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-propyltetrazole), which is, in fact, the first complex on which the photoswitching mechanism was investigated. It is important to note that the dynamics of $[Fe(NCH)_6]^{2+}$ represents a simplified scenario when compared to more complicated cases, such as those of Fe(II) polypyridines, as solely metal-centered (MC) states are involved (in cases of $Fe(ptz)_6](BF_4)_2$ and $[Fe(NCH)_6]^{2+}$, MLCT states do not play a role due to their higher energy). The simulation of singlet-triplet-quintet dynamics poses immense challenges, from an electronic structure point of view, and has so far been out of reach. Namely, although potential energy surfaces (PESs) are readily available using density functional theory (DFT) and time-dependent DFT (TD-DFT), calculation of triplet-quintet spin-orbit couplings (SOCs) require the utilization of higher-level multiconfigurational approaches such as multiconfigurational second-order perturbation theory (CASPT2). However, CASPT2 can be computationally rather expensive and is burdened by the often-problematic selection of the active space. We tackled this problem by employing the $[Fe(NCH)_6]^{2+}$ model complex, for which PESs along the most important modes could be calculated by CASPT2 [P1]. We used a synergistic method for the description of nuclear dynamics, which is based on the selection of dominant modes for quantum dynamics (QD) by full-dimensional trajectory surface hopping (TSH); thus, we performed 3D singlet-triplet-quintet QD/CASPT2 simulations with the modes determined by full-dimensional TSH carried out on on-the-fly DFT/TD-DFT singlet-triplet PESs. With this methodology, we have performed the first *ab initio* simulation of singlet-triplet-quintet dynamics for low-spin (LS) → high-spin (HS) photoswitching. Crucially, the simulations capture all important aspects of the excited-state mechanism revealed by time-resolved experiments [1,2] and reveal fine mechanistic details (see Figure 1).

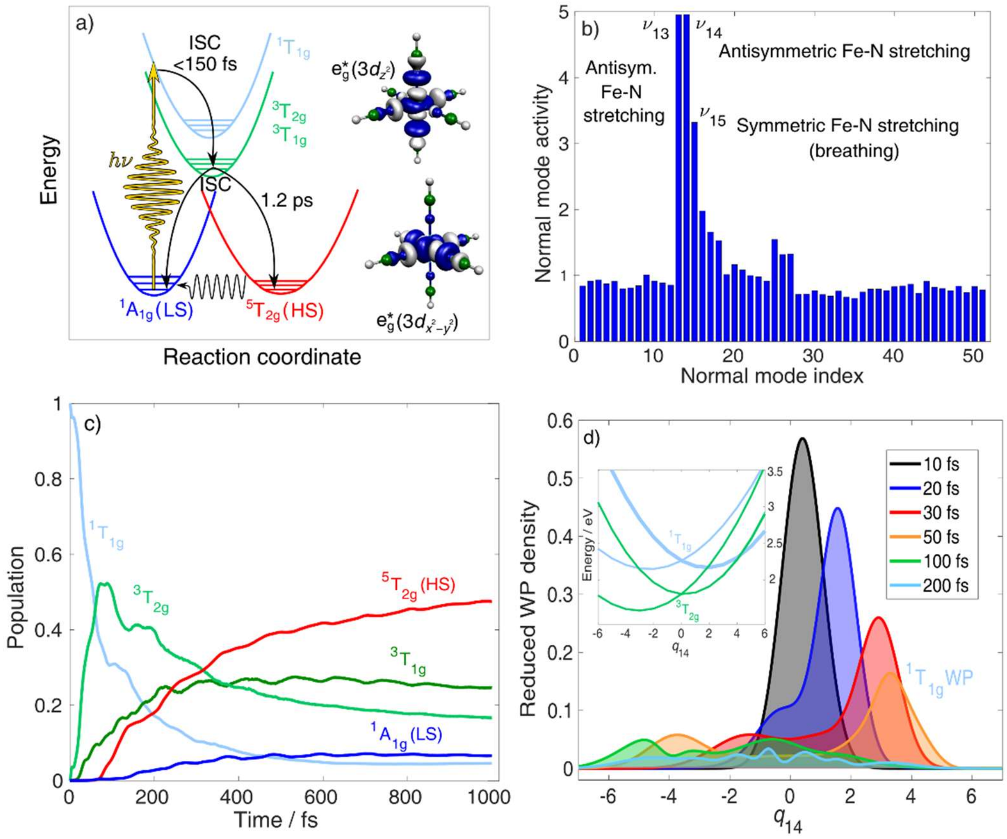


Figure 1. Summary of the synergistic spin-vibronic simulations on the octahedral model $[Fe(NCH)_6]^{2+}$ for LS → HS photoswitching [P1]. (a) Schematic mechanistic picture with the antibonding e_g^* orbitals illustrating the metal-center character of the excited states. (b) Mode selection by full-dimensional TSH (TD-DFT). (c) Population dynamics by 3D QD (CASPT2). (d) QD (CASPT2) along the antisymmetric Fe-N stretching normal mode coordinate q_{14}, illustrating singlet → triplet ISC and wavepacket spreading.

Subsequently, we continued our studies on the $[Fe(NCH)_6]^{2+}$ complex by developing a new efficient methodology [P2] aimed to allow simulation of singlet-triplet-quintet dynamics for more complicated cases (e.g., higher density of states, inclusion of MLCT states). Our computational approach has two main components: i) hybrid electronic structure description based on the combination of DFT/TD-DFT PESs and CASPT2 SOCs, and ii) application of a linear vibronic coupling (LVC) model, which is based on the harmonic oscillator approximation, diabatic states, and nonadiabatic coupling approximated to depend linearly on normal mode coordinates. This LVC methodology has, in fact, a dual role as a) its diabatic basis ensures compatibility with the scheme using CASPT2 SOCs that are taken to be independent of the nuclear geometry, and b) it offers high efficiency, as quantum chemistry calculations only need to be performed prior to dynamics simulations, the approach thus having a computational bottleneck of a single CASPT2 calculation (for each spatial/spin symmetry). The dynamics simulated for $[Fe(NCH)_6]^{2+}$ by this method in conjunction with our synergistic approach show good agreement with the above-described CASPT2 simulations [P1] and related experimental data [1,2] (see Figure 2 below). Furthermore, we exploited the capability of the methodology to analyze the location of intersystem crossings and vibrational dynamics. The approximation of constant SOCs (i.e., independent of the nuclear geometry) was also verified, whose validity has central importance for the combination of TD-DFT PESs and CASPT2 SOCs.

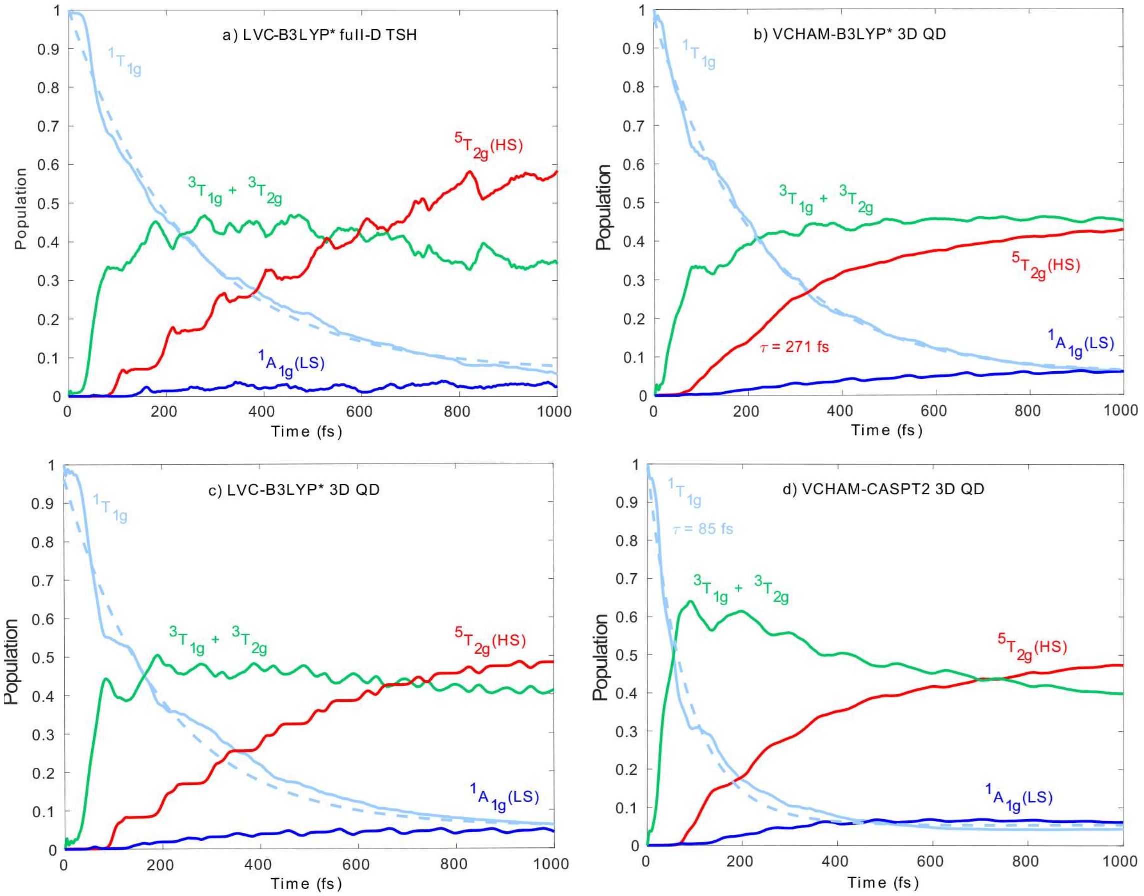


Figure 2. Simulated excited-state population dynamics of the $[Fe(NCH)_6]^{2+}$ complex [P2] ("LVC" and "VCHAM" denotes different diabatization techniques).

We then exploited our developed methodology to simulate the ultrafast LS (singlet) → HS (quintet) photoswitching dynamics in the $[Fe(terpy)_2]^{2+}$ complex [P3] (terpy = 2,2':6',2"-terpyridine), which is the base molecule of our research group. It is important to stress that $[Fe(terpy)_2]^{2+}$ represents significantly higher level of complexity, compared to $[Fe(NCH)_6]^{2+}$, especially in terms of the density of electronic states, nuclear dimensionality, and the inclusion of MLCT states in addition to MC states. $[Fe(terpy)_2]^{2+}$ is a member of the family of Fe(II) polypyridine complexes, whose dynamics have been extensively studied and debated in the past decade [3–5] with two proposed mechanisms, a sequential ^{3}MLCT → ^{3}MC → ^{5}MC and a direct ^{3}MLCT → ^{5}MC. We used the hybrid DFT-TD-DFT/CASPT2/LVC methodology in conjunction with TSH to gain access to the entire singlet-triplet-quintet dynamics in full dimension. Importantly, our results offer decision to a decade-long debate on the mechanism of spin-state photoswitching in Fe(II) polypyridines. We propose a branching mechanism, in which the quintet HS state is populated on a sub-ps timescale via two sequential ^{3}MLCT → ^{3}MC → ^{5}MC pathways involving the ^{3}MC components $^3T_{1g}$ and $^3T_{2g}$ (see Figure 3). We find that the alternative direct ^{3}MLCT → ^{5}MC relaxation channel could only be operative in the absence of ^{3}MC states. Crucially, the results are in agreement with the available time-resolved experimental data on Fe(II) polypyridines, and fully describe the photorelaxation dynamics. We note that this work is the first published theory paper addressing the simulation of singlet-triplet-quintet dynamics of a Fe(II) polypryridine complex. Recently, two computational studies on the dynamics of the $[Fe(bipy)_3]^{2+}$ polypryridine complex (bipy = 2,2'-bipyridine) were reported, while one of them also using full-dimensional TSH [6], the other one employing 9D QD [7]. Importantly, there is consistency in these three works in terms of the dominance of the sequential pathway over the direct one. However, while our full-dimensional TSH reproduces all key aspects of the experimental population dynamics including the non-exponential quintet population rise and coherent oscillations, this is not the case for the drastically reduced-dimensionality (9D) QD simulation; here the quintet population rise is rather kinetic (exponential) and conversion into the quintet HS state is incomplete, i.e., nearly half of the excited-state population is stuck in triplet states at 500 fs. We observed an even more pronounced difference in the excited-state dynamics simulated by full-dimensional TSH [P4] and reduced-dimensionality (4D) QD [8] for the Fe(II)-N-heterocyclic carbene (NHC) complex $[Fe(bmip)_2]^{2+}$ (bmip = 2,6-bis(3-methyl-imidazole-1-ylidine)-pyridine), as discussed below.

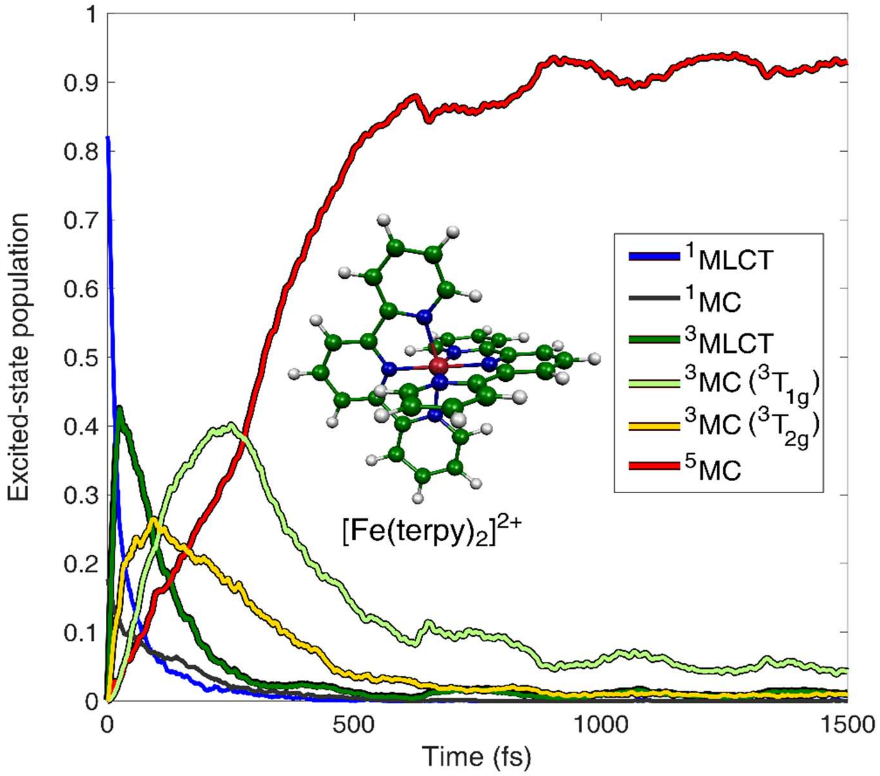
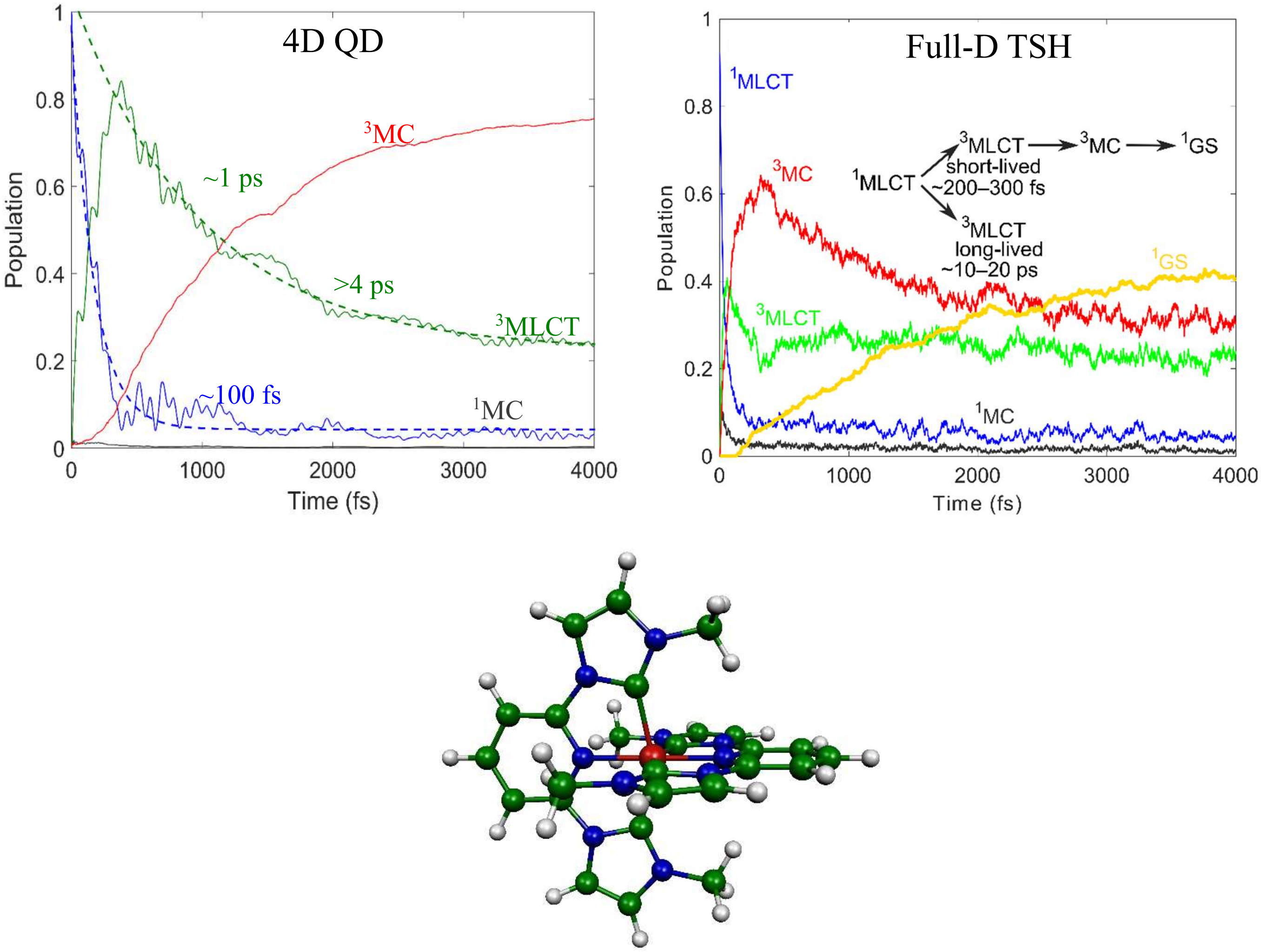


Figure 3. Molecular structure and simulated excited-state dynamics of the $[Fe(terpy)_2]^{2+}$ complex [P3].

Finally, we studied how the photorelaxation pathways can be manipulated by chemical modification of the ligands: we simulated the excited-state dynamics of $[Fe(bmip)_2]^{2+}$ [P4], which can be thought as a derivative of the base molecule $[Fe(terpy)_2]^{2+}$, with the outer pyridine rings replaced by five-membered NHC rings (see Figure 4, bottom). Fe-NHC complexes got into scientific focus a decade ago with the discovery of the $[Fe(bmip)_2]^{2+}$ photosensitizer [9], which exhibited a ^{3}MLCT lifetime that is ca. 100 times larger than the one of $[Fe(bipy)_3]^{2+}$ (~9 ps vs ~100 fs); this was a very promising result for potential applications in photocatalysis and solar energy conversion. Previously, we supported the results of time-resolved optical spectroscopy experiments by 4D QD simulations (using 4 Fe-ligand stretching modes), which indeed indicated that the ^{3}MLCT states decay on a picosecond timescale (see Figure 4, top, left). More recent time-resolved X-ray spectroscopy experiments [10] have shown, however, that a significant part of the ^{3}MLCT population (~40%) is, in fact, converted into ^{3}MC in ~110 fs, while the remaining ^{3}MLCT fraction (~60%) is long lived, characterized by a lifetime of ~9 ps. Using full-dimensional TSH carried out on DFT/TD-DFT LVC potentials, we obtained a rather similar ^{3}MLCT/^{3}MC branching (see Figure 4, top, right) and explained that the early-rising ^{3}MC component is due to ligand motion triggered by the MLCT excitation (such ligand modes were not included in our previous 4D QD simulations [8], which is the reason why the early ^{3}MC component is missing, see Figure 4, top, left). Furthermore, in agreement with time-resolved experiments [9,10], we observed coherent oscillations along the Fe-ligand breathing mode, which we identified as a fingerprint for the sub-ps ^{3}MC component.



$[Fe(bmip)_2]^{2+}$

Figure 4. Top: excited-state dynamics of the $[Fe(bmip)_2]^{2+}$ complex, simulated by 4D QD (left) and full-dimensional TSH (right). Bottom: molecular structure of the $[Fe(bmip)_2]^{2+}$ complex.

We note that within the project, we started to study another type of chemical modification of the terpy core with -H → -F substitution at the 6,6” positions on the outer pyridine rings; the corresponding substituted terpy complex is named $[Fe(dfterpy)_2]^{2+}$. However, as we prioritized the above-described study on the dynamics of the $[Fe(bmip)_2]^{2+}$ complex, we could only resume our investigations on $[Fe(dfterpy)_2]^{2+}$ during the end of the project. Our calculations reproduced the experimental observation that $[Fe(dfterpy)_2]^{2+}$ exhibits thermal spin-crossover behavior [11], caused by significant reduction of the HS-LS energy gap in comparison to the parent $[Fe(terpy)_2]^{2+}$ complex. We identified a rather similar LS (singlet) → HS (quintet) photoswitching mechanism as for $[Fe(terpy)_2]^{2+}$, and have started to explore dynamics initiated from the photoexcited quintet state (which was experimentally found to lead to a 14 ps-lived MLCT state [11]).

Within the project, we participated in international collaborations resulting in several works addressing the ultrafast dynamics of various molecules, both computationally [P5–P7], and in combination with time-resolved experiments [P8–P10], as well as advancing methodologies for the simulation of ultrafast excited-state dynamics and experiments (simulation of X-ray absorption spectroscopic signals [P11] and excited-state solvation [P12]).

Scientific Output and Summary of Financial Report

The project resulted in 12 scientific papers published in prestigious peer-reviewed journals (three of them in top journals with IF > 10), three invited talks at international conferences, one contributed talk, and one poster.

All funds allocated to the project have been spent in accordance with the overall budget of 25500 kHUF. All costs are in agreement with the originally planned budget with the exception of investments for which there is a significant deviation (237 kHUF planned vs 1256 kHUF achieved). The reason for this difference is twofold: i) due to the COVID-19 pandemic, not all planned travels could be realized and thus redistribution of funds within the budget was necessary, and ii) as depreciation and technical problems occurred with the frist laptop bought at the initial period of the project, we purchased a second laptop; this and other equipment benefiting the project (e.g., an UPS for the local computational infrastructure) required to move funds into the investments section. For detailed financial data, see the separate financial report.

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