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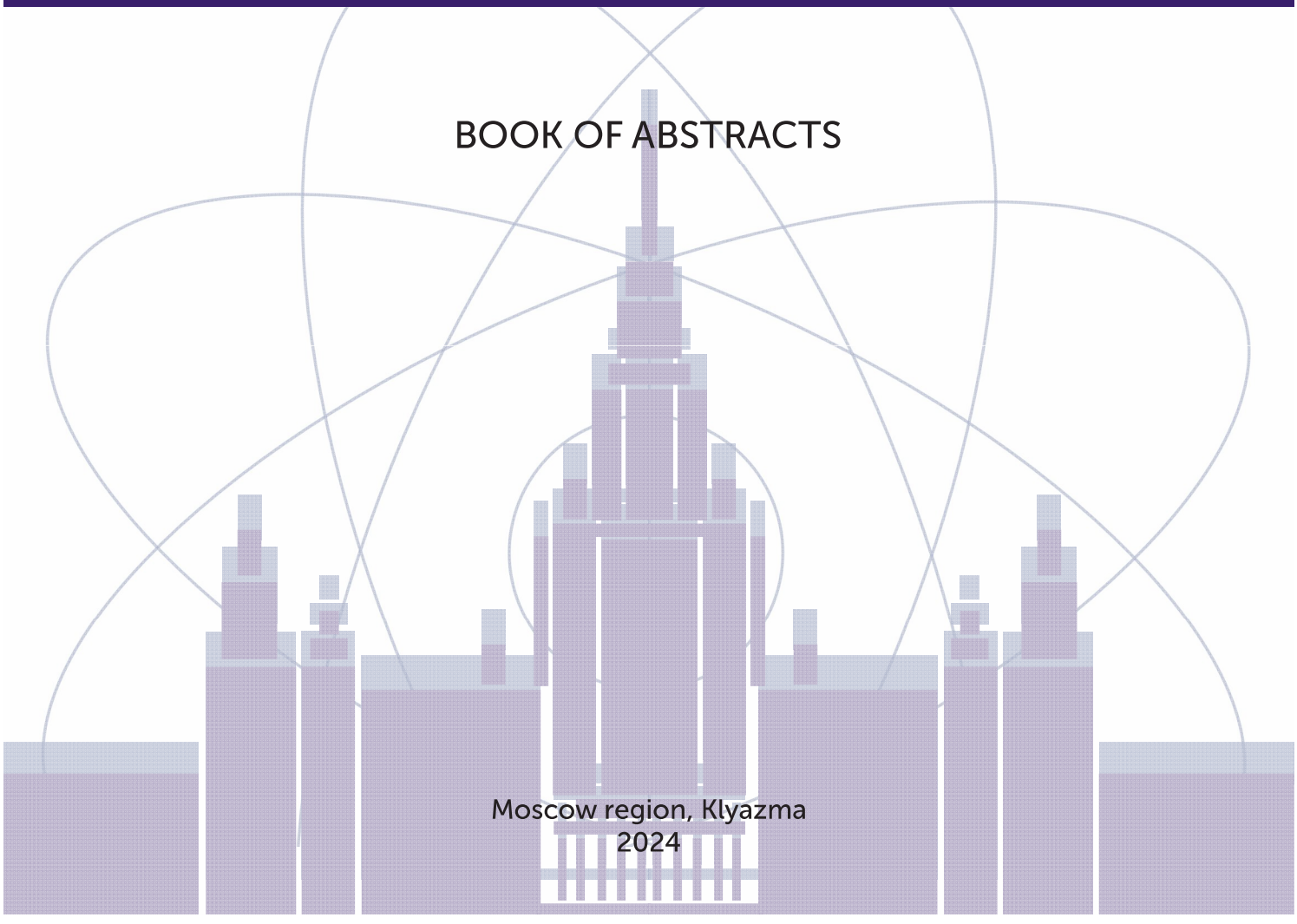
CHALLENGES 2024

INTERNATIONAL SCHOOL AND CONFERENCE "CURRENT CHALLENGES IN CHEMICAL PHYSICS AND THEORETICAL CHEMISTRY"



BOOK OF ABSTRACTS

Moscow region, Klyazma
2024

CHALLENGES 2024

INTERNATIONAL SCHOOL AND CONFERENCE "CURRENT CHALLENGES IN CHEMICAL PHYSICS AND THEORETICAL CHEMISTRY"

Book of abstracts

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М34 **Материалы Международной школы-конференции по современным проблемам химической физики и теоретической химии «CHALLENGES 2024».** — М.: Издательство "Перо", 2024. — 120 с.

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Сборник включает в себя программу и аннотации докладов, представленных на Международной школе-конференции по современным проблемам химической физики и теоретической химии «CHALLENGES 2024» (пос. Поведники, Московская область, 1-5 июля 2024 г.). Тематика школы-конференции охватывает следующие направления фундаментальных исследований:

- Современные методы квантовой химии;
- Высокопроизводительные вычисления и алгоритмы машинного обучения;
- Молекулярная спектроскопия и физика планетных атмосфер;
- Радиационные аспекты моделирования климата и дистанционного зондирования; природных и антропогенных процессов;
- Фотофизика и фотохимия молекул при линейном и нелинейном возбуждении.

Сборник представляет интерес для специалистов в области физики и квантовой химии.

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General Information

Challenges 2024

The international school & conference on current challenges in chemical physics and theoretical chemistry Challenges 2024 aims at bringing together quantum chemists and physicists across various multidisciplinary fields of science. The conference themes span from the development of modern electronic structure theory methods to their application in classical and quantum molecular dynamics simulations, astrophysics, linear and nonlinear molecular spectroscopy. Key lectures on application of machine learning techniques in high-tech production and on innovation technologies for high-performance computing will be delivered by industrial representatives. To complement a more traditional program, which will include plenary and invited talks as well as poster sessions, round-table discussions on hot topics will be organized. This event will be an excellent opportunity to engage in new collaborations with scientific groups across Russia and abroad, as well as with industrial partners.

Summer school

The summer school on modern electronic structure theory methods and high-performance computing will be held within the conference. The participants of the school will be granted certificates of advanced training from the MSU School of Advanced Engineering Studies.

Themes

- Quantum Theory
- Computational and Theoretical Chemistry
- Machine Learning and High-Performance Computing
- Molecular Spectroscopy and Physics of Planetary Atmospheres
- Radiative Aspects of Climate Modeling and Remote Sensing
- Photoinduced Processes in Molecules

Round-table discussions

- Classical and quantum dynamics in molecular spectroscopy
- Modern Software for Modeling Electronic Structure and Properties of Molecular Systems
- Science and industry collaboration
- Photoinduced nonadiabatic molecular dynamics

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- Joint Stock Company RT-Techpriemka, Moscow
- Department of Chemistry, Lomonosov Moscow State University, Moscow
- Institute of Quantum Physics, Irkutsk
- Petersburg Nuclear Physics Institute, Gatchina
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Uniqueness of spin $^1/_2$

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This lecture discusses the historical background of spin experiments and associated hypotheses. The unexpected appearance of spin $^1/_2$ in the context of a relativistic electron wave equation is analyzed. We question the direction of spin and investigate the theorem on the largest projection of spin $^1/_2$. We then cover the theory of generalized angular momentum, specifically, the case of orbital momentum and spin $^1/_2$.

Effect of quantum entanglement on two-photon absorption probabilities in fluorescent proteins

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Quantum entanglement in a system of two particles is a specific correlation manifested in the fact that they, in some sense, behave like a single quantum object. For instance, the absorption rate of entangled photon pairs linearly depends on the flux density, whereas in classical two-photon absorption experiments this dependence is quadratic. This allows spectroscopic measurements to be carried out at significantly lower excitation light intensities than in classical experiments. Although the effect of a significant enhancement of two-photon absorption in the case of entangled photons compared to classical two-photon absorption has been repeatedly observed in experimental studies, the magnitude of this enhancement remains to be the subject of active debate.

Here we perform a theoretical study of the use of correlated and uncorrelated photon pairs in the two-photon $S_0 \rightarrow S_1$ absorption by the EGFP protein and its modification EGFP T203I.

The absorption probabilities of correlated and uncorrelated photon pairs are calculated using the sum-over-states formalism. We consider two-photon resonant absorption of a degenerate photon pair. Excitation energies and transition moments are calculated using the XMCQDPT2-based QM/MM approach. The convergence of a series of the *N*-level models with increasing number of states *N* is shown to be very fast for the $S_0 \rightarrow S_1$ transition in EGFP and EGFP T203I. When considering the $0 \rightarrow 0 \rightarrow f$ and $0 \rightarrow f \rightarrow f$ permanent dipole pathways (PDP) by restricting the summation to the initial and final states only, we obtain the following approximate relation for the entangled two-photon absorption (ETPA) probability δ_e:

$$\delta_e = \delta_c(1 - \cos(\Omega_f T_e/2))^2 + \delta_+ \sin^2(\Omega_f T_e/2)$$

where δ_c is the classical TPA probability, δ_+ is the non-classical contribution due to the entanglement of the two photons absorbed, Ω_f is the $S_0 \rightarrow S_1$ energy gap, and T_e is the entanglement time.

We show that under nonlinear two-photon excitation of the $S_0 \rightarrow S_1$ transition in EGFP and EFGP T203I, the PDP channels dominate for the absoprtion of both the correlated and uncorrelated photons. The ETPA enhancement is determined by the value of the non-classical contribution δ_+, which primarily depends on the sum of the permanent dipole moments of the final and initial states, while the classical probability δ_c is determined by the difference of these dipole moments. The ETPA probability as a function of entanglement time rapidly oscillates on the femtosecond timescale. It changes from zero to the values significantly exceeding the classical one, and its average value is 2 orders of magnitude higher than δ_c. Remarkably, the T203I modification of EGFP enhances the ETPA probability, whereas it diminishes the classical one. This can be rationalized by analysing the derived equation for δ_e and considering the internal protein field and its influence on the permanent dipole moments of the EGFP chromophore in the initial and final states.

Funding The work is supported by the Russian Science Foundation grant no. 22-13-00126.

Impact of intramolecular hydrogen bonding on the photophysics of the modified GFP chromophore anion

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Green Fluorescent Proteins (GFP) are indispensable tools in molecular and cellular biology due to their high fluorescence quantum yields. However, fluorescence is lost at room temperature when the GFP chromophore is taken out of the native protein environment due to much faster internal conversion, which proceeds on a picosecond timescale through a conical intersection between the excited and ground electronic states [1]. The intramolecular rotation about the single and double bonds in the bridge moiety of the chromophore is known to be responsible for promoting internal conversion. The addition of a hydroxyl group to the ortho-position of the phenolic ring of the chromophore inhibits twisting across these bonds due to the formation of an intramolecular hydrogen bond, resulting in the increase of the fluorescence quantum yield. By using time-resolved action absorption spectroscopy of cryogenically cooled molecular ions combined with high-level ab initio calculations, we provide direct evidence for the influence of hydrogen bonding on the photoresponse of the modified deprotonated GFP chromophore — opDHBDI$^-$.

By using the XMCQDPT2/SA(2)-CASSCF(14,13)/(aug)-cc-pVDZ level of theory, we calculate the potential that hinders internal rotation about the single and double bonds of the chromophore in the ground and first excited singlet states. The excited-state potential for rotation about the single bond exhibits multiple minima with twisted geometries of the chromophore due to the presence of the intramolecular hydrogen bond. Vertical transitions from the planar minima of the s-*cis* and s-*trans* conformers in S_0 correspond to the population of the transition states in S_1, and the twisting about the single bond becomes highly active upon the $S_0 \rightarrow S_1$ transition in opDHBDI$^-$. The torsional levels and the corresponding wavefunctions are calculated using these highly anharmonic periodic potentials in S_1 and S_0. The photoabsorption spectrum is then calculated using the linear coupling model in the harmonic approximation for all modes except the torsional mode treated explicitly. The simulated $S_0 \rightarrow S_1$ absorption profile is used to interpret the vibrationally-resolved action-absorption spectrum obtained experimentally at cryogenic temperatures. We show that the most intense transition is significantly blue shifted from the band origin and corresponds to the vertical transition of the s-*cis* rotomer, whereas the weak band origin can be attributed to the transitions of the higher-energy s-*trans* rotomer. The located lowest-energy conical intersection between the S_1 and S_0 states lies 0.3 eV above the minimum in S_1, unlike that in the non-modified chromophore. We discuss the impact of the higher-lying conical intersection on the excited-state decay channels of the modified chromophore, as well as on its excited-state lifetimes, which are found to be strongly dependent on excitation wavelength across the $S_0 \rightarrow S_1$ absorption band.

Funding The work is supported by the Russian Science Foundation grant no. 22-13-00126. The calculations are carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University as well as the local resources (RSC Tornado) provided through the Lomonosov Moscow State University Program of Development.

References

[1] Svendsen A., Kiefer H. V., Pedersen H. B., et al., 2017, *J. Am. Chem. Soc.*, 139, 8766

Modeling kinetics of the photoinduced retinal fragmentation

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The retinal protonated Schiff base is a main component of photoactive proteins, which play a crucial role in sensory organs of organisms. The photon absorption in the protein environment leads to the isomerization of retinal, and the chromophore returns to the initial form via a series of intermediates, which are formed in the photocycle of these proteins. For the isolated molecule in the gas phase, the energy cannot, however, be released into the environment and its excess becomes redistributed among various vibrational modes in the ground electronic state following internal conversion and isomerization of retinal. This eventually results in the statistical fragmentation of the molecule in the hot ground state. The chromophore shows a remarkably selective photoresponse in the gas phase, which is triggered by a cyclization reaction with subsequent fragmentation, leading to one specific fragment ion, the truncated protonated Schiff base, and toluene [1, 2]. Such photoinduced fragmentation is used in action absorption spectroscopy, when the photophysics and fast photoinduced dynamics of the retinal protonated Schiff base is studied in the gas phase. Here, we introduce a theoretical model to describe the kinetics of the photoinduced retinal fragmentation.

We develop a methodology for calculating statistical lifetimes of isolated chromophores following their excitation by photons of different wavelengths. By using the MRMP2/CASSCF(12,12)/cc-pVDZ level of theory, we locate all intermediates and transition states along the reaction pathway for the statistical fragmentation of the retinal protonated Schiff base in the ground electronic state. The rate constants for all steps are calculated using the quasi-equilibrium theory for isolated molecules based on the numerical evaluation of densities and sums of vibrational states. The kinetic scheme is then analyzed based on the calculated rate constants. Three characteristic timescales are derived, and one of these time components can directly be compared to the experimental data obtained in the millisecond time window. The calculated (103 mcs and 146 mcs) and experimental (107 mcs and 125 mcs) lifetimes are compared at excitation wavelengths of 530 nm and 550 nm, showing excellent agreement.

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References

[1] Toker Y., Rahbek D. B., Kiefer H. V., et al., 2013, *Phys. Chem. Chem. Phys.*, 15, 19566
[2] Coughlan N. J. A., Adamson B. D., Catani K. J., et al., 2014, *J. Phys. Chem. Lett.*, 5, 3195

Role of the protein environment and structural heterogeneity in the mechanisms of photochromic reactions of microbial and animal rhodopsins

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Rhodopsins are photosensitive proteins containing the retinal protonated Schiff base (RPSB) as a chromophore group. The protein environment plays an important role in establishing high quantum yields and high rates of their primary photochemical reactions: all-*trans* $\rightarrow$ 13-*cis* and 11-*cis* $\rightarrow$ all-*trans* photoisomerization of RPSB in microbial and animal rhodopsins, respectively [1]. However, nonreactive excited states that produce no photoproducts are also observed in rhodopsins. In this work, we investigate the influence of the protein environment on the photodynamics of RPSB in the forward and reverse photoisomerization reactions and study the role of the structural heterogeneity of the protein active centers in the formation of nonreactive states in microbial and animal rhodopsins.

By using molecular dynamics simulations and extended multiconfiguration quasi-degenerate perturbation theory (XMCQDPT2) [2] combined with the effective fragment potential method (EFP) [3], we calculate the S_0–S_1 vibronic band shapes of RPSB in the active centers of microbial rhodopsins KR2, ESR, and bacteriorhodopsin, as well as animal bovine rhodopsin. We show that each rhodopsin selectively excite certain vibrational modes of the RPSB polyene chain upon the S_0–S_1 transition, thus determining the different specificity and efficiency of the primary photoisomerization reaction in these proteins. Remarkably, the reverse photochromic reactions show specificity only in microbial rhodopsins, whereas the specificity of the reverse photoisomerization is lost in visual rhodopsin. The high efficiency of the direct 11-*cis* $\rightarrow$ all-*trans* photoisomerization reaction and the low probability of the reverse photoreaction might indicate evolutionary much higher tuned chromophore-protein interactions in animal rhodopsins.

We also reveal structural heterogeneity of the retinal-binding pocket in the KR2 and ESR rhodopsins, characterized by several distinct conformations of their active centers. This is thought to be related to the presence of nonreactive states in the photodynamics of these proteins.

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References

[1] Ernst O. P., Lodowski D. T., Elstner M., et al., 2014, *Chem. Rev.*, 114, 126
[2] Granovsky A. A., 2011, *J. Chem. Phys.*, 134
[3] Gordon M. S., Freitag M. A., Bandyopadhyay P., et al., 2001, *J. Phys. Chem. A*, 105, 293

Modeling photoabsorption spectra of conformationally flexible calcium indicators in solution upon one- and two-photon excitation

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Fura-2 is a ratiometric fluorescent dye, which binds to free intracellular Ca^{2+} ions and is widely used for calcium imaging in living cells. Upon complexation, the absorption maximum of Fura-2 shifts from 375 nm to 340 nm, and the ratio of the emission intensities at these wavelengths can directly be related to the amount of intracellular calcium [1]. However, continuous exposure of samples to the blue and UV light has a detrimental effect, as it causes their deterioration due to photobleaching and photodamage. Moreover, the short-wavelength light is unable to penetrate tissues deeper than 40 mm. These issues can be addressed by employing two-photon excitation, which practically assembled in two-photon scanning microscopy (2PEF) with near-infrared laser light. Here, we introduce a methodology for modeling one- and two-photon absorption spectra of conformationally flexible fluorescent dyes in solution to optimize their brightness for bioimaging applications. We also apply the new methodology for calculating spectral profiles of Fura-2 in a free state and bound to Ca^{2+} ions in aqueous solution upon one- and two-photon excitation.

Our methodology explicitly accounts for both the homogeneous and inhomogeneous spectral broadening effects. It combines MD sampling techniques with high-level quantum chemistry calculations of one- and two-photon transition parameters for multiple structures taken along the MD trajectory. The following major steps are performed: MD simulations using the NPT ensemble at 300 K, QM/MM (PBE0/(aug)-cc-pVDZ/CHARMM) geometry optimization, XMCQDPT2 [2] / EFP [3] calculations of transition parameters, simulating Franck-Condon vibronic band shapes using a linear coupling model, calculations of two-photon absorption cross-sections using a sum-over-states approach, modelling overall one- and two-photon absorption spectra.

We show that the contribution from inhomogeneous broadening is crucial for accurate modeling of both the one- and two-photon absorption profiles of conformationally flexible dyes like Fura-2 in solution. We also reveal a strong correlation between the calculated two-photon absorption cross-sections and the changes in permanent dipole moments upon the transition. Chemical modifications of Fura-2, which increase the intramolecular charge transfer character upon the transition, can therefore be used to enhance its nonlinear photophysical properties.

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References

[1] Wiederschain G. Y., 2011, *Biochemistry*, 76, 1276
[2] Granovsky A. A., 2011, *J. Chem. Phys.*, 134, 214113
[3] Gordon M. S., Freitag M. A., Bandyopadhyay P., et al., 2001, *J. Phys. Chem. A*, 105, 293

Branching in internal conversion of the methylene iminium cation

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The interaction of molecules with light is essential for many natural processes and vital functions of living organisms. For example, 11-*cis* retinal in the form of a protonated Schiff base is a key element of rhodopsin, which is a protein that plays an important role in human vision. The photoinduced isomerization of 11-*cis* retinal, leading to the formation of its all-*trans* form, causes structural changes in the rhodopsin protein. These changes trigger the generation of a nerve impulse. The isomerization process is one of the fastest natural processes, with nuclear rearrangements occurring within hundreds of femtoseconds. However, the mechanism behind this reaction has not yet been fully understood due to the difficulty in studying it using high-precision quantum chemistry methods, which require a significant amount of time for calculations. In order to investigate the mechanism of photochemical isomerization, a small molecular model of the methylene iminium cation has been chosen. This work aims at studying the relaxation mechanisms of the electronically excited methylene iminium cation using second-order extended multiconfiguration quasi-degenerate perturbation theory (XMCQDPT2).

By using the XMCQDPT2/SA(3)-CASSCF(12,12)/aug-cc-pVDZ level of theory, we have studied the potential energy surfaces of the methylene iminium cation in the S_0, S_1, and S_2 states. The S_2 state is found to be of a $\pi\pi^*$ character, while S_1 corresponds to the $\sigma\pi^*$ excited state, and the corresponding $S_0 \rightarrow S_1$ transition happens to be optically dark at the equilibrium geometry of the molecule in the ground electronic state. Therefore, the photoinduced dynamics of the molecule starts in the S_2 state. Stationary points and three conical intersections between different states are identified, and topographies of the potential energy surfaces around the conical intersections are analyzed. We show that the main relaxation pathway is associated with the passage of the excited molecule through two conical intersections, resulting in its barrierless isomerization. This finding is consistent with the internal conversion mechanism of the methylene iminium cation as described in the literature.

We also reveal another relaxation pathway through two conical intersections, S_2/S_1 and S_1/S_0; however, the second conical intersection is of a different nature compared to that of the main relaxation pathway. Unlike the S_1 state of the main branch, which acquires the $\pi\pi^*$ character after the passage of the first S_2/S_1 conical intersection, it remains its $\sigma\pi^*$ origin along the minor pathway. This minor channel in the relaxation mechanism of the methylene iminium cation has not been reported so far. The minor branch may lead to the re-population of the initial ground state or to the photoinduced fragmentation of the molecule through the loss of H_2. The branching ratio of the two channels and its impact on the photoinduced dynamics of the methylene iminium cation are discussed.

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Non-adiabatic excited-state dynamics simulations based on highly accurate quantum chemistry and neural network interatomic potentials

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The interaction of light with biological molecules is central to the vital activity of living organisms. These processes are remarkably efficient and occur on a timescale down to sub-picoseconds. In the understanding of the photoinduced dynamics, theoretical studies play an essential role because they provide many useful physical insights, for instance, excited-state reaction pathways, impact of protein environments, and detailed molecular motion in the dynamics. However, a proper selection of electronic structure methods is essential for accurate modeling. Systems with quasi-degeneracy require multi-reference approaches, accounting for both static and dynamic electron correlation. The on-the-fly excited-state dynamics is generally very expensive due to high computational costs, particularly when a high-level electronic structure method is used. Great efforts are currently being made to construct excited-state potential energy surfaces by using machine learning approaches and to use them for speeding up dynamics simulations.

Here, we aim at developing a comprehesive computational protocol to explore general nonadiabatic dynamics in complex molecular systems by combining on-the-fly trajectory-surface hopping mixed quantum-classical dynamics with multiconfiguration quasi-degenerate perturbation theory (XMCQDPT2) [1]. To speed up the nonadiabatic dynamics simulations, we use an E(3)-equivariant neural network approach [2] for learning interatomic potentials from the XMCQDPT2 and underlying CASSCF calculations. The developed methodology is extensively tested on the photoinduced dynamics of the methylene iminium cation, $CH_2NH_2^+$ — a small model molecule featuring a single double bond of the retinal protonated Schiff base important in vision. The results are obtained using potentials, which are based on the XMCQDPT2/SA(3)-CASSCF(12,12)/aug-cc-pVDZ and SA(3)-CASSCF(12,12)/aug-cc-pVDZ methods. Three electronic states are monitored during the photoinduced dynamics simulations — optically bright S_2, dark S_1, and ground S_0. The probability of hopping events between different electronic states are estimated based on the overlap of electronic wave functions at two successive points along the trajectory propagation. The time step for propagation is set to 0.2 fs, and each trajectory out of the total of 100 is simulated up to 500 fs. Initial conditions are generated according to the Wigner distribution for ground-state normal modes at 300 K. Population dynamics, key molecular motions, excited-state lifetimes, and branching in the nonadiabatic dynamics of $CH_2NH_2^+$, occurring through three conical intersections and involving photoisomerization and photoinduced fragmentation, are analyzed and discussed.

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References

[1] Granovsky A. A., 2011, *J. Chem. Phys.*, 134, 214113
[2] Batzner S., Musaelian A., Sun L., et al., 2022, *Nat. Commun.*, 13, 2453

Predicting emulsion type in octane-$C_{10}E_4$-water systems using dissipative particle dynamics simulation

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Hydrocarbon production in the modern world is an extremely important issue. Nowadays one of the most useful approaches for increasing the efficiency of oil recovery is the injection of chemical agents into the oil well. These agents reduce interfacial energy in the oil-water system, which increases the efficiency of oil recovery. Quite effective reagents for this goal are surfactant mixtures with alkalis. Due to the complex composition of oil, an important task is to optimize the composition of the reagents and production conditions. Experimental selection of the optimal surfactant composition is highly complicated and requires significant time. Improvement of molecular modeling tools and computer technology provides great opportunities for predicting the properties and effectiveness of surfactant mixtures used to reduce interfacial tension in the oil-water system [1]. Dissipative particle dynamics (DPD) simulation is a very useful technique for estimating properties of large molecular systems [2]. DPD it takes less computational forces than similar molecular dynamics and DFT-methods but still provides accurate results.

In DPD simulations all particles are represented as soft beads, interacting with each other by weak repulsive force. Repulsion parameters could be estimated from experimental data or using DFT.

In the present work DPD simulations in a model octane-$C_{10}E_4$-water system were used for prediction of interfacial properties and microemulsion stability in different conditions. Repulsion parameters were optimized for better accordance with experimental data. To estimate the microemulsion type we used the 'method of moments' approach, based on the calculation of the first moment of surface tension [3].

Acknowledgements The calculations are carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University as well as the local resources (RSC Tornado) provided through the Lomonosov Moscow State University Program of Development.

References

[1] Creton B., Nieto-Draghi C., Pannacci N., 2012, *Oil gas sci. technol. (En ligne)*, 67, 969
[2] Lavagnini E., Cook J. L., Warren P. B., et al., 2021, *J. Phys. Chem. B*, 125, 3942
[3] Fraaije J. G. E. M., Tandon K., Jain S., et al., 2013, *Langmuir*, 29, 2136

Round-Table C

Photoinduced Nonadiabatic Molecular Dynamics

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Nonadiabatic dynamics simulations are powerful tools for elucidating complicated photoinduced processes in molecules. Due to high computational costs, mixed quantum–classical dynamics is often used to propagate nuclear dynamics through classical trajectories, whereas electrons are treated at the quantum mechanical level. To recover nonadiabatic information various algorithms are employed. The advantage of treating the nuclei classically is the ability to simulate molecular systems in full dimensionality. The electronic properties are usually computed on-the-fly; however, the costs of such simulations are prohibitively high when accurate electronic structure theory methods are used. Moreover, the local approximation implied by the classical trajectories also fails to describe non-local quantum effects, as tunneling and quantum interference, as well as the results can be affected by decoherence errors. We suggest this round-table discussion to focus on recent advances in developing theoretical frameworks and efficient computational algorithms for simulating ultrafast photoresponse of molecular systems. We also aim at bridging the gap between the experimentalists and theoreticians to discuss various topics of mutual interest, such as ultrafast time-resolved spectroscopy.

Main topics

- Mixed quantum-classical molecular dynamics;
- Neural network potentials;
- Time-resolved spectroscopy;
- Two-dimensional vibrational-electronic spectroscopy;
- Entangled two-photon absorption spectroscopy.

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