MENSHOVA EVGENIYA PETROVNA

The influence of the plasmon effect on intersystem crossings in molecular environments

ABSTRACT

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Relevance of the topic. In modern molecular photonics and photochemistry, special attention is paid to the control of spin-forbidden processes, primarily intersystem crossing (ISC), which determines the efficiency of triplet state formation. These processes underlie the generation of singlet oxygen, phosphorescence, and delayed fluorescence (DF), making them key for the development of functional materials for photodynamic therapy, sensitizers, and optoelectronic devices.

ISC is a nonradiative process between electronic states of different spin multiplicity, the efficiency of which is determined by the magnitude of spin–orbit coupling (SOC) and the energy gap $\Delta E(S_1–T_1)$. Control of this process is one of the important challenges of molecular photonics.

Such systems are of particular relevance due to the need to develop photosensitizers operating in the near-infrared (NIR) region corresponding to the "optical transparency window" of biological tissues. In this spectral range, the maximum penetration depth of radiation is achieved, which is critically important for photodynamic therapy and biomedical applications. However, the decrease in the energy of excited states in the NIR region leads to a reduction of $\Delta E(S_1–T_1)$ and an enhancement of competing nonradiative processes, which limits the efficiency of ISC and the generation of reactive oxygen species in conventional organic dyes.

Polymethine dyes, in particular pyrilcarbocyanines (PyrC), which exhibit strong absorption in the red and near-infrared regions of the spectrum, are of special interest. The sequential substitution of the heteroatom in the series O → S → Se leads to significant changes in the electronic structure, accompanied by a bathochromic shift of the spectra and a sharp increase in SOC. The heavy atom effect in Se-containing derivatives results in a substantial increase in the probability of intersystem transitions and the formation of long-lived triplet states, creating prerequisites for efficient singlet oxygen generation.

An additional important aspect is the influence of the condensed medium (e.g., polyvinyl butyral) on the photophysical properties of dyes. In a solid matrix, intermolecular interactions are enhanced, conformational mobility is restricted, and vibronic relaxation mechanisms are altered, significantly affecting ISC efficiency, delayed fluorescence, and triplet state quenching processes. In the presence of metallic nanostructures (NSs), these effects become more complex due to the competition between plasmonic enhancement and nonradiative quenching at the metal surface.

Despite the active development of plasmon-enhanced photochemistry, the mechanisms of the influence of localized plasmon fields on intersystem transitions remain insufficiently studied. In particular, there is no systematic understanding of how the nature of the heteroatom, the energy gap $\Delta E(S_1–T_1)$, the magnitude of SOC, and the morphology of metallic nanostructures affect the efficiency of triplet state generation and singlet oxygen production.

Thus, the study of the influence of the plasmon effect on phosphorescence, delayed fluorescence, and singlet oxygen generation by organic dyes immobilized in a polymer matrix and interacting with island silver films is an actual scientific problem. Solving this problem will make it possible to establish fundamental закономерности of spin-forbidden processes in complex hybrid systems and to create a scientific basis for the development of new efficient NIR photosensitizers with controlled photophysical properties.

The obtained results can be used for developing scientific foundations for optical devices, highly efficient luminescent light sources, nanosensors, functional elements of molecular electronics, photovoltaic devices, and in biophysics.

The aim of the dissertation is to study the influence of the plasmon effect on intersystem transitions in organic dye molecules, as well as on singlet oxygen generation.

To achieve this goal, the following **tasks** were addressed:

– investigation of the influence of the plasmon effect on intersystem transitions in organic dyes absorbing in the visible and near-infrared spectral regions, whose structure is modified by various heteroatoms;

– quantum-chemical study of the influence of PyrC dye structure on spin–orbit coupling;

– investigation of the influence of the plasmon effect on the photosensitization of molecular oxygen by organic molecules.

Objects of study: xanthene dyes, cationic symmetric PyrC, polymer films doped with organic dyes, plasmonic Ag and Au nanoparticles (NPs) obtained by laser ablation, and planar structures of silver (SIF) and gold (GIF) island films.

Research methods: Experimental studies were carried out using absorption spectroscopy, steady-state fluorimetry, laser kinetic spectroscopy based on photon counting, and dynamic light scattering. The surface morphology of metallic NPs and their aggregates was studied by scanning electron microscopy.

Scientific novelty includes the following main results:

1. The influence of the plasmon effect on intramolecular electronic transitions in organic dye molecules modified by different heteroatoms has been studied;
2. A theoretical model has been developed that allows quantitative estimation of radiative and nonradiative transition rates in a plasmonic field;
3. For the first time, the heavy atom effect on the photonics of pyrilcarbocyanine dyes in the near-infrared region has been studied;
4. It has been established that the plasmon effect enhances the efficiency of singlet oxygen photosensitization by triplet states of dye molecules.

Main provisions submitted for defense:

1. The influence of plasmonic nanoparticles on the phosphorescence of rhodamine dyes is associated with the intensity borrowing effect for the spin-forbidden triplet–singlet transition ($T_1 \rightarrow S_0$) from allowed $S_n \rightarrow S_0$ transitions;
2. An increase in the chalcogen mass in PyrC dyes leads to an increase in the SOC matrix element $\langle S_1|H_{so}|T_1\rangle$, which enhances ISC from S_1 to T_1;
3. 3. The plasmonic effect of metal nanoparticles enhances the efficiency of singlet oxygen photosensitization.

Personal contribution of the author. The author carried out the synthesis of island silver and gold films, as well as Ag and Au NPs by laser ablation. Solutions and polymer films of organic dyes were prepared. All spectral-luminescent and kinetic measurements were performed. Computer processing of experimental data was conducted. Analysis of the results and conclusions were carried out jointly with scientific advisors.

Relation to research programs. The dissertation was carried out within the framework of the research projects “Dynamics of electronic processes in plasmonic nanostructures and their influence on molecular photonics” (2022–2024, RK No. AP14870117) and “Activation of molecular oxygen by new polymethine dyes, carbon dots, and plasmonic nanoparticles” (2024–2026, RK No. AP23490195), coordinated by the Committee of Science of the Ministry of Science and Higher Education.

Approbation and publications. The main results of the work were presented and discussed at the following international conferences: International Research and Practice Conference "Nanotechnology and Nanomaterials" (Lviv, 2022); International Scientific Conference "Chemical Physics of Molecules and Polyfunctional Materials" (Orenburg, 2022); International Conference "Fundamental and Applied Problems of Modern Physics" (Tashkent, 2023); Republican Scientific and Practical Conference dedicated to the 85th anniversary of Candidate of Technical Sciences, Methodologist, Mentor of the Generation, Professor S.D. Daribekov (Karaganda, 2025).

Publications. Based on the results of the dissertation work, 7 printed works were published: 1 article in a journal included in the Thomson Reuters and Scopus databases (1 article in Physical Chemistry Chemical Physics - Q2, IF 2.9 (2024); 2 articles in journals recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Higher Education of the Republic of Kazakhstan and 4 publications in the proceedings of international conferences.

Practical significance:

1. The developed model allows prediction of luminescence quantum yields and targeted design of dye structures with desired photophysical properties, reducing the volume of experimental work;
2. The established patterns of the influence of heavy atoms and plasmonic nanostructures enable control of intersystem transitions and enhancement of luminescence, which is important for optoelectronics and sensing technologies;
3. The achieved efficiency of singlet oxygen generation and its

enhancement in a plasmonic field provide a basis for developing NIR-active photosensitizers for photodynamic therapy and other biomedical applications.

Structure and scope of the dissertation. The structure of the dissertation is determined by the stated objectives and consists of an introduction, five sections, a conclusion, and a bibliography. It is presented on 121 typewritten pages, illustrated with 41 figures and 27 tables, and contains a bibliography of 286 references.