ANNOTATION

of the dissertation for the degree of Doctor of Philosophy (PhD)
8D05302–Physics

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Plasmon-enhanced photoprocesses in molecular systems

Topic relevance. Near the surface of plasmonic metal nanoparticles (NPs), molecules of organic fluorophores are exposed to reflected electromagnetic fields. Due to the strong local electric field, plasmons can significantly affect the rates of intramolecular radiative and nonradiative transitions. Due to localized plasmon resonance (LPR), the properties of electronically excited states of organic molecules change as a result of the dipole-dipole interaction of excited molecules with plasmons. These effects are useful for numerous practical applications that increase the quantum yield of radiation for energy efficient materials, such as controlled optical and laser media, luminescent sensors, optoelectronic devices, etc.

The effectiveness of the plasmon effect on absorption and fluorescence in organic fluorophores is largely determined by the geometric and spectral factors of NPs and environmental characteristics. Depending on the distance between nanoparticles and phosphor molecules, the fluorescence intensity either increases or decreases.

At the same time, much less work has been devoted to the study of the influence of plasmons of metal NPs on the processes of long-term luminescence of organic phosphors with the participation of their triplet states. Long-lived triplet states can be used in various practical applications. In particular, such sensitizer molecules are key reagents in the processes of generation of singlet oxygen $^1O_2$ for photodynamic therapy and can also be used in photovoltaic cells.

Many important photophysical and photochemical processes are based on the Förster resonance energy transfer (FRET) process, and FRET can also be used to efficiently transfer optical excitation over short distances. For example, the phenomenon of intermolecular energy transfer is the basis of FRET microscopy, and is also used to study proteins, to create biosensors, solar photocells, etc.

It is known that when a light quantum is absorbed, a phosphor molecule goes into an excited electronic state. In this case, the formation of both a singlet- and a triplet-excited molecule is possible. Despite the long lifetime, triplet molecules are considered to be “dark” and participate little in the emission process due to the spin prohibition of transitions between the T_1 and S_0 states. In addition, long-lived triplet states increase the probability of recombination processes of charge carriers. The combination of these two factors creates difficulties in the development of organic light-emitting materials and organic electronics. In this regard, a critical issue is the efficient use of triplet-excited phosphor molecules. To do this, various authors propose to use up-conversion or triplet-singlet energy transfer.

The triplet-singlet energy transfer can be used to increase the quantum efficiency of the external electroluminescence of organic light emitting diodes.

The results obtained can be used to develop scientific foundations for the production of 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 plasmonic effect of metal nanoparticles on intra- and intermolecular electronic processes in condensed molecular systems.

The objects of research are xanthene and oxazine dyes, cationic indopolycarbocyanines, plasmonic Ag and Au NPs, nanostructured films of organic luminophores, fatty acids and polymer materials obtained by the Langmuir-Blodgett technology, polymer films doped with organic dyes.

The scientific novelty consists of the following:

1. It is shown that the optimal distance at which the maximum amplification of all types of luminescence is achieved is 6-8 nm and approximately coincides with the Förster radius of the nonradiative inductive-resonance process.

2. The effect of silver NPs on the Förster energy transfer in donor-acceptor pairs with different energy transfer efficiency was studied. It is shown that plasmonic NPs affect the energy transfer rate more for a pair with a low energy transfer efficiency.

3. The influence of the plasmon effect in spin-allowed and spin-forbidden energy transfer processes in the same donor-acceptor pair of organic molecules was studied. It has been established that approximately the same increase in the efficiency of both types of energy transfer is recorded in the plasmon field of Ag NPs.

The structure and scope of the dissertation. The structure of the dissertation work is determined by the tasks set and consists of an introduction, 5 sections, a conclusion, and a bibliography. It is presented on 108 pages of typewritten text, illustrated with 49 figures, 17 tables, and contains a list of cited literature from 257 titles.

The main results include the following:

1. In the plasmonic field of metal NPs, the maximum amplification of various types of long-term luminescence from the triplet state is achieved at distances of 6–8 nm and coincides with the distance dependence for fluorescence, which is due to the mixing of singlet and triplet states due to spin-orbit coupling.

2. The plasmonic enhancement of the Förster resonant energy transfer rate is greater for a donor-acceptor pair with initial low energy transfer efficiency.

3. In the plasmon field of silver nanoparticles, approximately the same increase in the efficiency of both singlet-singlet and triplet-singlet energy transfers in the same donor–acceptor pair is observed.

Scientific and practical significance of the work:

1. The comprehensive theoretical and experimental study of the effect of plasmonic NPs on singlet- and triplet-excited molecules of organic dyes opens up the possibility of increasing the quantum yield of radiation, which is important when they are used in various practical applications, for example, in medicine, biology, electronics, sensorics, and photovoltaics.

2. Experimental data on plasmon-enhanced resonant Förster energy transfer can be used to increase the photosensitivity of solar cells in the visible region of the spectrum, to study photobiological processes associated with the collection and delivery of light energy to reaction centers, and also to create materials with desired properties, sensors, transducers and converters of light energy.

3. Data on the effect of metal NPs on triplet-singlet energy transfer can be used in optoelectronic and light-emitting devices to improve their characteristics.

Approbation of the work and publications. The main results of the work were presented and discussed at the following conferences: The 11th international scientific conference "Chaos and structures in nonlinear systems. Theory and Experiment" (Karaganda, 2019); VI International Conference dedicated to the 150th anniversary of the discovery of the Periodic Table of Chemical Elements by D.I. Mendeleev – "Supramolecular systems at the interface" (Tuapse, 2019); "IX International Conference on Photonics and Information Optics" (Moscow, 2019); I International book edition of the countries of the Commonwealth of Independent States "Best Young Scientist – 2020" (Nur-Sultan, 2020); XII International Conference "Electronic Processes in Organic and Inorganic Materials" (ICEPOM-12) (Kamianets-Podilskyi, Ukraine, 2020); 5th International Symposium on Molecular Photonics dedicated to the memory of Academician A.N. Terenin (St. Petersburg, 2021); International symposium on emerging materials and devices (Nur-Sultan, 2021); International Scientific and Practical Conference "XIV Toraighyrov Readings" (Pavlodar, 2022); International Scientific Conference "Chemical Physics of Molecules and Polyfunctional Materials" (Orenburg, 2022); XV International Scientific Conference "Physics of the Solid State" (Astana, 2022).

Publications. According to the results of the dissertation work, 15 printed works were published: 4 articles in journals included in the Web of Science Core Collection and Scopus databases (1 article in the Journal of Luminescence – Q1, IF 3.28 (2019); 2 articles in the Journal of Luminescence – Q2, IF 4.171 (2022); 1 article in the Theoretical and Experimental Chemistry – Q4, IF 0.484), 1 article included in the RSCI database, 1 article in the journal recommended by the Committee for Control in the Sphere of Science and Higher Education of the MSHE RK and 9 publications in the materials of international conferences.