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From the History of Physics

ALEKSANDR NIKOLAEVICH TERENIN

(1896–1967)

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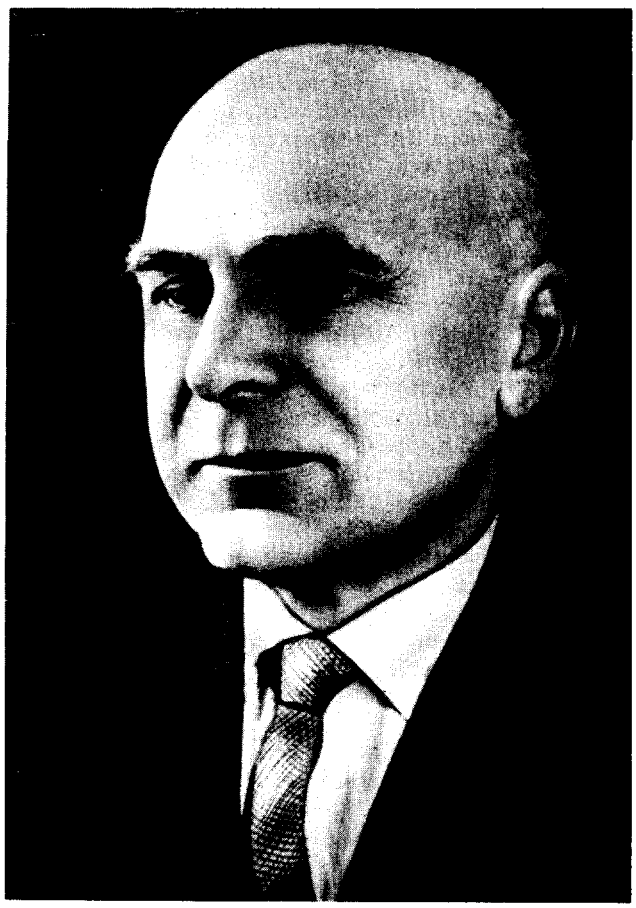
AMONG our contemporaries it is difficult to find a man for whom science was to such a degree the sole purpose and the only meaning of life as for A. N. Terenin. Having the rare combination of talent and capacity for work, he was in full sense a great toiler of science.

Terenin was born on 6 May 1896, in Kaluga. In 1907 he entered the secondary science school. It was there that this interest in science was aroused. He was a member of the physics circle, and became acquainted with K. É. Tsiolkovskiĭ. This famous fellow townsman attracted the youth's attention to problems of rocket motion, but could not convert Terenin into his faith.

In 1914, after finishing the secondary school, Terenin moved to Petrograd and entered the Psychoneurological Institute. (Later, in 1943, he wrote that he was interested in the variety of human intellect and in the possibility of working with people. He even wanted to be a play producer, but ultimately was attracted by molecules, understanding that these can be manipulated in a more brilliant manner than actors.) Soon Terenin took part in a students' strike. In 1915, his study was interrupted: he was mobilized into the army, passed through chemical-technical training courses, and was assigned to the laboratory of the military administration, where he performed his first work—spectral and photometric investigations of captured optical devices. During his whole life the spectral and luminescence research remained his main occupation.

In 1916, Terenin started auditioning in the physics and mathematics department of the Petrograd University, in 1918 he enrolled, and in 1919 he was among the best students selected by D. S. Rozhdestvenskiĭ for the just-created optical institute and assigned to the duty of "laboratory assistant in the machine shops," which entitled him to food rations, which were so important at that time, but with the obligation of rapidly and successfully continuing his studies. This group included also Academician V. A. Fock, Corresponding Members of the Academy S. É. Frish, and E. F. Gross, and many other known physicists and optics specialists.

Thus, in 1919 Terenin became a "laboratory assistant in the machine shop," and soon received his first scientific project, viz., to investigate the spectrum of mercury vapor in the vicinity of 1 μ. The earlier attempts to solve this problem, using sensitization of photographic plates by means of dyes, were not successful. Terenin found a solution. He recalled the



Herschel effect and registered the mercury radiation not by the darkening of the photographic plate, but by the destruction of the latent image. This was one of the first spectroscopic investigations performed at the Optical Institute. It was called "The Normal Orbit of the Electron in the Mercury Atom" and corrected MacLennan's erroneous results. All his life, starting with this investigation, Terenin was a brilliant experimenter, finding the most accurate and economical means of solving each problem.

After being graduated from the university in 1922, Terenin performed a cycle of brilliant investigations on the spectroscopy of atoms. Foregoing the then-employed low-selectivity procedures for exciting by electron impact and absorption spectra, he used and developed further the method of optical excitation of atoms. In these investigations, Terenin studied first the level schemes

From a paper delivered at a session devoted to the memory of A. N. Terenin in Leningrad, 11 May 1967.

of many atoms and investigated the stepwise excitation processes—successive absorption of two quanta by a single atom.

An essentially new result in this cycle of investigation was the discovery by Terenin, together with L. N. Dobretsov and E. F. Gross, of the hyperfine structure of the atomic line (using Na and Hg atoms as examples). This work was performed at the same time in Germany by Schuler. For many years (until newer methods were developed), the study of the hyperfine structure of spectra served as the means of investigating the magnetic and mechanical moment of nuclei.

In spite of significant progress in the then most advanced branch of physics, Terenin apparently was not satisfied by the investigation of the structure of atoms as static systems. He was interested, and remained interested during all his life, in the processes of active interaction between light and matter. From atoms Terenin moved on to molecules, and later to complexes and biological systems, but subsequently he dealt mainly not with the structure of these objects, nor even with their kinetics, but with the dynamics of their transformation under the influence of light.

In 1927, while stationed in Germany and Holland, Terenin together with P. Pringsheim investigated the fluorescence spectra of mercury molecules.

From 1925 to 1932, Terenin performed a cycle of investigations on the photochemistry of salt vapors, which gained him world fame. In this case he organized already an entire program. He chose an optimal object for investigation, since halide salts of many metals can be easily evaporated, and the strengths of their molecules vary in a wide range. Instead of low-selectivity absorption spectra, he investigated the spectra of the fluorescence observed by him in the products of photochemical decomposition of molecules; this method had unusual sensitivity and selectivity. He traced many details of the decay of diatomic and polyatomic salt molecules, he determined the energies of their dissociation, he observed experimentally the "internal recombination"—the formation in a single elementary act of relatively simple molecules following the photochemical decay of more complicated ones—and, finally, he investigated many characteristic features of the interaction between excited atoms and other particles. These investigations were summarized in the now out-of-print book "Photochemistry of Salt Vapors," published in 1934.

In 1932—1936, with the aid of investigations of photodissociation by means of the glow of the decay products, Terenin studied more complicated molecules (H_2O, CH_3OH, C_2H_5OH, NH_3, and others) exposed vacuum-ultraviolet radiation. Among his co-workers and students participating in all these investigations were I. M. Frank (now an academician), N. A. Prilezhaeva, G. G. Neuĭmin, and others.

It must be emphasized that this entire series of investigations of photochemistry of salt vapors was carried out against the background of the very initial development of modern concepts concerning the structure of molecules, during the time of establishment of quantum mechanics. Now, 30 years later, it is difficult and almost impossible to appreciate fully the significance of this cycle of investigations by Terenin to the development of the science of molecules. These investigations gained world fame. They are being continued here and abroad and have recently acquired new significance in connection with the problem of the development of molecular lasers.

Terenin's scientific merits were recognized and he was chosen in 1932 to be a Corresponding Member of the USSR Academy of Sciences.

Mention must be made of Terenin's experimental artistry. Not all can visualize at present the experimental technique which he and his co-workers used to investigate salt vapors. Home-made monochromators for the excitation of the spectra, where the entrance slit, made of slate, was inserted directly into the plasma of a high-voltage spark; a home-made spectrograph with extremely high transmission ("stump") to register weak ultraviolet fluorescence, with a housing made of oak timber; a splendid unique prism made of fluorite with a plate holder taken from an ordinary amateur 6×9 cm camera; home-made "superpowerful" 3-kw hydrogen tubes with cold electrodes; quartz vessels blown by Terenin himself and later by his co-workers, using an oxygen-hydrogen burner in the laboratory; do-it-yourself glass-blowing for all the complicated vacuum systems and the associated inventiveness dictated by expediency; formulation of the experiment in a lucid manner, with clarity of all details, with everything constructed by the experimenter's himself and aimed at a single purpose; subtle methods and an exact definition of the trend of the research. We emphasize that in Terenin's laboratory the outwardly-primitive home-made installations and instruments were always of advanced design. The first photoelectric spectrometers for ultraviolet and near-infrared produced in the Soviet Union were also constructed in his laboratory in 1939—1940.

In 1936—1941, Terenin's sphere of interest greatly expanded. Investigations of the interaction between light quanta and molecules by the fluorescence method were extended to include complex organic compounds in the gaseous state. Some summaries and the program of these investigations were contained in a paper delivered by Terenin at the Conference on Luminescence in Warsaw in 1936. Even here one could see the transition to more complicated systems—substances in the condensed state, solutions, and adsorbates.

In Terenin's main laboratory—the photochemistry laboratory—research was undertaken on the influence of the surroundings on the properties of molecules of aromatic compounds in vapors, and new paths were also blazed in the investigations of the photoelectroconductivity of dye films. Terenin's laboratory at the Physics Research Institute of the Leningrad State University had gradually been assumed the role of the laboratory for the optics of surface phenomena, and later for the optics of photocatalysis. At the high-pressure institute, in 1939, Terenin began to investigate the infrared spectra of substances at high pressures. Among the many of his students, now well known in science, were also his talented students Karp Kasparov and Vladimir Khadeev, who lost their life in the world war, as did Terenin's laboratory assistant, the outstanding experimentor Victor Ponomarev.

Terenin's accomplishments in science were recognized in 1939 by his election to full membership of the

Academy of Sciences.

The transition from the photochemistry of isolated molecules in gases and vapors to the photochemistry of matter in various condensed states (liquids, bodies of high pressures, solutions, adsorbates) was not an accident. Terenin apparently came very close to the problem of chemical utilization of solar energy, and estimated the possibility of this process and of systems in which it is realized.

His work was interrupted by the second world war. He reorganized his laboratory to help the war effort. Mention should be made here of the development of a procedure and a technology for physical coating of optical parts.

While directing his staff, Terenin did not cease to plan the resumption of the research interrupted by the war. In 1943 he advanced his hypothesis of the triplet (biradical) nature of metastable states responsible for the phosphorescence of organic substances. Taking into account the great reactivity and the lifetime of these states, it was impossible to overestimate the significance of this discovery. Without exaggerating, it can be stated that they serve as the basis of modern photochemistry. We recall that ideas similar to those advanced by Terenin were advanced independently a year later by the known American physical chemists J. N. Lewis and M. Kasha. Later, after the end of the war, Lewis, upon receiving the Soviet papers, wrote and acknowledged Terenin's priority.

Running ahead of ourselves, we note that the natural logical continuation of this work by Terenin was his discovery in 1951 together with V. L. Ermolaev, of the phenomenon of energy transfer between molecules in the triplet state. This method of energy transfer, naturally, plays a decisive role in many photochemical processes in which complex organic molecules take part.

In 1944–1946 Terenin worked on his major work "Photochemistry of Dyes," in which scattered material on the photochemistry of complex organic substances—dyes—was systematically organized as explained on the basis of the concept of chemical activity of triplet biradical and singlet states, the migration of energy of excitation, and electron transport.

Whereas "Photochemistry of Salt Vapors" was more readily a summary of a cycle of work performed by Terenin's school, "Photochemistry of Dyes" was an exposition of the system of his ideas and views, the basis on which research planned even before the war continued to develop. Of course, the four-year interruption in 1941–1945 refined, enriched, and expanded his plans. In 1943, in his speech "Light and Chemistry" at the General Assembly of the USSR Academy of Sciences, Terenin considered the prospects of photochemistry and noted the importance of its connections with biochemistry and research on photosynthesis. In 1945, Terenin and his doctoral candidate A. A. Krasnovskiĭ (now a Corresponding Member of the USSR Academy of Sciences) organized at the Institute of Biochemistry of the USSR Academy of Sciences a photobiochemistry laboratory, which greatly enlarged the then already existing laboratory of photochemistry and photocatalysis.

In the succeeding two decades, Terenin organized a large cycle of investigations of the problem of the elementary photoprocess in a variety of systems. The end purpose of this research was to create artificial systems for effective chemical utilization of solar radiation, capable of competing with natural systems. The investigations were carried out in various directions. In his paper at the Seventh Session in Memory of Academician D. S. Rozhdestvenskiĭ, on 7 May 1953, Terenin considered the problem, indicating that the artificial system should obviously not be a replica of a natural one resulting from complex evolution, but that a study of natural systems can yield important information on ways of realizing the chemical act as a result of relatively few quanta of solar light. Various ways of chemical utilization of quantum absorption are possible, either directly in the absorbing molecule, or as a result of migration of the excitation energy or the transport of the electron released by the light towards the center of the chemical reaction. The complexity of the action of chlorophyll and the need for high physical and chemical organization of the photosynthesis system are already known. Allowance for all these circumstances called for the organization of numerous various researches, which were brilliantly realized by Terenin. As the absorption centers for the quantum energy and also of objects of the primary photochemical processes, utilizing the energy delivered to them in one form or another, he investigated the entire possible range from simple molecules to complex organic compounds, dyes, and finally to chlorophyll and its analogs in various combinations. He investigated differently organized systems of gas mixtures, solutions, adsorbed and condensed substances, and also uniquely ordered biological systems such as chloroplasts. He investigated the absorption of light, the migration and conversion of quantum energy, the photoelectric and chemical ways of realization of this energy in a great variety of combinations of these systems.

Of course, all that can be done in a single article is merely list the trends and researches developed by Terenin in the last two decades and performed by him and his closest co-workers. Some idea of the scope of these investigations, which are being carried out in a number of institutes and laboratories, can be found in the collection "Elementary Processes in Molecules," published in 1966 in honor of Terenin's 70th birthday.

The researches can be subdivided into five groups.

1. Molecular spectroscopy and energetics of molecules. Terenin resumed most recently, together with N. Ya. Dodonova, work on photodissociative single molecules. In the field of energetics of complex molecules, Terenin and V. L. Ermolaev successfully developed research on the triplet-triplet energy transport discovered by them. At the Institute of High Pressure Physics, Terenin together with Yu. A. Klyuev continued research initiated by him in 1940 on the spectra of substances at high pressures.

Investigations of the transformations of the energy of a light quantum absorbed by a complex molecule, initiated with A. N. Terenin, are being continued by the present author and his co-workers, among whom mention should be made of N. A. Borisevich, who is now greatly expanding this work at the Belorussian Academy of Sciences, and N. G. Bakhshiev. These yielded information on the intramolecular processes that lead to the formation of continuous spectra, a proposed classifica-

tion of these spectra and corresponding molecular models, information on the transfer of vibrational energy in molecular collisions, and details concerning the influence of the average internal field of the light wave in a medium on the spectra and properties of the molecule. Work on the intra- and intermolecular transformations of light energy in complex molecules are also being continued by one of the first of Terenin's co-workers, N. A. Prilezhaeva, and her students in the Siberian Physicotechnical Institute.

2. **Photoelectronics of molecules.** The investigations of the photoconductivity of dye films initiated by Terenin and A. T. Vartanyan in 1938 are being continued in the photochemistry laboratory. In the photocatalysis laboratory, Terenin carried out in 1957 together with F. I. Vilesov a cycle of investigations on the photoionization of organic molecules in the gas phase. A. T. Vartanyan and F. I. Vilesov are successfully continuing these investigations with their co-workers. Starting in 1945, Terenin and E. K. Putseĭko employed a contactless method of recording rapid photoelectric processes. New classes of organic photosemiconductors of electronic and whole type were discovered, and spectral sensitization of inorganic semiconductors by organic molecules, including phthalocyanines, chlorophyll and its analogs, was observed. The mechanism of spectral sensitization was investigated subsequently by Terenin and I. A. Akimov. All these results are important for the understanding of the action of complex pigments in photochemical processes, and are used in electrophotography.

3. **Photochemical investigations.** These include essentially the already mentioned work on the photodissociation and photoionization of molecules, carried out by Terenin with N. Ya. Dodonova, F. I. Vilesov, and a number of co-workers, and still being continued. In addition, Terenin paid much attention to the reactions of phototransport of the proton and electron, a study of which was initiated in 1947 together with A. V. Karyakin. These investigations are continuing to this day by spectral-luminescence methods, combinations of pulse-excitation methods, high-speed spectroscopy, and electron paramagnetic resonance, developed and realized in the photochemistry laboratory. Here Terenin together with V. E. Kholmogorov discovered two-quantum reactions of photolysis of different organic compounds sensitized with aromatic amines, hydrocarbons, dyes, and pigments. Recently, Terenin and his co-workers investigated the possibility of creating effective photogalvanic systems.

4. **Spectroscopy of the adsorbed state.** As early as in 1934, Terenin started to work in the Laboratory of the Optics of Surface Phenomena on the spectroscopy of matter in the adsorbed state. In the post war years, these investigations were greatly expanded using a variety of methods of vibrational and electronic spectroscopy, as well as luminescence, particularly the quenching of the latter when acting on adsorbed molecules. Important data were obtained on the photosorption and photodesorption, on the change of the bond strength in adsorbed molecules, on their activation with light and on photoionization, and on their reactions. Taking part in these investigations were L. N. Kurbatov, E. I. Kotov, V. N. Filimonov, and others. The infrared spectra of water and other substances, adsorbed in silica gel, were investigated by N. G. Yaroslavskiĭ and A. N. Sidorov.

We note that the work of Academician of the Estonian Academy of Sciences F. D. Klement was initiated in the same laboratory, and was subsequently transferred to the Institute of Physics of the Estonian Academy of Sciences in Tartu, which became one of the world's centers of research on the luminescence of solids.

5. **Photoprocesses in pigments and photosynthesis.** In the Laboratory of Photobiochemistry organized by A. N. Terenin at the A. N. Bakh Institute of Biochemistry of the USSR Academy of Sciences, A. A. Krasnovskiĭ discovered the reaction of chlorophyll, namely the reversible photoreduction. Later, Terenin with V. B. Evstingeev organized there a large cycle of investigations of photoprocesses in chlorophyll by the method of electrochemical photopotential. Investigations of chlorophyll and pigments related to it were carried out by Terenin in his other laboratories by the methods of infrared spectroscopy, photoelectronics, pulse photolysis, and electron paramagnetic resonance. In addition, Terenin developed work on photosynthesis at the Moscow State University (F. F. Litvin) and maintained connections with the Belorussian Academy of Sciences (G. P. Gurinovich).

Terenin was one of the initiators of the organization of the Institute of Photosynthesis of the USSR Academy of Sciences, whose director is his student V. B. Evstingeev. The base for the creation of this institute was the Institute of Biochemistry, and especially the Laboratory of Photobiochemistry.

Only now, after examining everything done by Terenin for almost 50 years of intense labor, can we estimate the tremendous contribution that he personally made to science. All his work was new and original. He blazed new and unique trails and never stopped to develop the details of his discoveries. Some of these discoveries are so important, they they now seem as obvious as the fact that the earth is spherical or that energy is conserved.

One can only be struck by Terenin's inexhaustible energy, which was not limited to suggesting something and discussing the results, but who took very active participation in the performance of the rest of the work. But direction on the part of Terenin did not inhibit the independence of his students. He tried to get all of them into the habit of being demanding of their results. His participation was the larger, the younger the performer, and many of his co-workers received advice not only in private personal contacts, but also in the form of notes from his trips, from vacations, and even from the hospital, where Terenin would go only when seriously ill. One cannot help to recall that he completed the work on his last paper while already seriously ill, demanding that a special pulpit be attached to his hospital bed. This book "Photonics of Dyes," is, like "Photochemistry of Dyes," the net result of 20 years' work and a program for his many students and co-workers.

In giving due credit to Terenin's scientific-organizational talent, it must be emphasized that his most striking property as a scientist was still his ability to device and to organize a broad task-oriented front of scientific work and participate at the same time in the details of many of them, the most surprising feature was his abil-

ity to organize each experiment in such a way, as to obtain in substantial form the answer to each question. Terenin's experiments did not call for large amounts of measurements, error analysis, and a determination of the degree of uniqueness of the obtained result. Almost each of his experiments was a unique crucial experiment, was critical with respect to the formulated problem and gave an ambiguous answer.

Besides the tremendous scientific heritage that Terenin left us, he also left a large school of students and co-workers, capable of continuing his work. He had been Professor of the Leningrad University since 1932, and was later in charge of the Department of Molecular Biophysics.

Terenin attached great significance to publications and to exchange of scientific information. At all the conferences in the USSR and abroad he was always one of the most disciplined and active participants. The position of an authoritative listener and supreme judge was for him organically inacceptable, and with characteristic vitality he entered into discussions on any question of interest to him, and he required the same of his co-workers. During the last decade, Terenin represented distinction with Soviet science at several dozen international scientific conferences. Terenin authority among the Soviet and foreign scientists was quite high. The "title" of student or co-workers of A. N. Terenin ensured favorable relation from perfectly unknown scientists in the USSR and abroad.

Terenin was the chairman of the Scientific Council on Photosynthesis of the USSR Academy of Sciences and a member of the Commission on Spectroscopy of the USSR Academy of Sciences. He was the representative of the USSR in the International Commission on Spectroscopy at the Union of Pure and Applied Chemistry.

Terenin's great scientific services were recognized many times in USSR and abroad. In 1945 he was awarded a First Degree State Prize, and in 1954 the S. I. Vavilov Gold Medal of the USSR Academy of Sciences. He was an honorary member of the French Society of Physical Chemistry and of the British Chemical Society. In 1959, he received the gold medal of the Bologna University for work in the field of molecular spectroscopy, and in 1964 he was awarded a gold medal at the International Congress on Photobiology.

Terenin died too soon. In spite of his 70 years, he died a young man. He was in the bloom of realization of his ideas, full of new scientific plans. He was active and mobile. He was young also as a sportsman. Youth never interfered with his being a mature man and citizen. He knew how to be thoughtful and prudent in the development of his scientific work. For many years, besides feverish scientific activity, Terenin was a scientific director of the Optical Institute and in Charge of its spectroscopic division. He worried about the development of the optical industry and paid much attention to domestic instrument building. He was able to make practical use of his work, and did much for the benefit and the might of the Soviet Union.

The Soviet government greatly valued A. N. Terenin's services. He was awarded the title of Hero of Socialist Labor, he was given five Orders of Lenin, the Order of Labor Red Banner, the Order of the Red Star, and medals.

Translated by J. G. Adashko