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Obituary

Science—This is my religion Biographical Memoir of Academician Alexander Terenin (1896–1967)☆

A. Terenin was born on 6 May 1896 in Kaluga in a family of a well-to-do merchant. The parents took great care of the education of their children who, before they attended school, learned at home to read and write and also music (Alexander played not bad piano). Great attention was paid to study foreign languages; from their early years the children were taught French and English. Alexander, the youngest of six brothers and sisters, later at school also learned German and then Latin. The boy was fond of music, reading, arts and the natural sciences and humanities. Science attracted him greatly, already at 1912, the 16-years-old youth wrote in his diary as an epigraph: "*Science—this is my Religion*!" After graduating from school in 1914 he moved to St. Petersburg (then Petrograd) to enter the Psychoneurological Institute (which later became a part of Petrograd University).

On being drafted to the military service, he had to pass chemical–technical courses and was ordered to attend the laboratory of Military Department, where he carried out his first spectroscopic work, studying the German luminous paint, which they deposited onto the foresight of guns. While being on military service *Terenin* attended the lectures at the Physico-Mathematical Faculty of Petrograd University (1915) as an external student, and after demobilisation from the army he became the student of the physical branch of the Faculty in 1918. At the beginning of 1919 Professor *D. Rozhdestvensky*, the first director of the just-organized State Optical Institute, selected the 20 best students–physicists to complete the staff of laboratory assistants of the Institute. Besides *Terenin* the group included *V. Fock*, *E. Gross*, *S. Frish* and several other future brilliant scientists, whose names are now well known among the specialists (suffice it to mention the method of Hartree–Fock). Despite modest meals, important for students during the civil war, this position provided them the conditions for fruitful self-dependent scientific work, which soon gave the first results.

As a topic of diploma work, proposed by *D. Rozhdestvensky*, *Terenin* had to study the spectrum of mercury in the near IR region, which was not available for photographic registration. Having demonstrated a remarkable ingenuity, for spectrum registration the student decided to use the known Hershel effect—the disappearance of image on the photographic plate under near IR illumination. The main results of this work, carried out at the University, "*The normal orbit of the electron in the atom of mercury*" were soon published in "Nature" [1], while the method of photography in IR light was described separately [2].

In 1922 *Terenin* graduated from the University and was offered a permanent position as a scientific researcher. At the same time he carried out his work in the State Optical Institute. This parallel activity, both in the University and in the Institute, continued since then for the rest of his life. From 1920 to 1925 he carried out a cycle of researches of the energy states of metal atoms from their luminescence spectra. In a very short time he managed not only to determine, with a high accuracy for that time, the positions of energy terms of a great deal of different atoms, and he found a new phenomenon of excitation by sequential absorption of two quanta by one atom. As an important result of this period a discovery of a hyperfine structure of lines in the spectra of mercury and sodium [3], carried out in collabora-

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☆ The International Symposium on Molecular Photonics, dedicated to the 110th anniversary of Alexander Nikolaevich Terenin, was held from 28 June 2006 to 3 July 2006 in St. Petersburg, Russia. A. Terenin was well known for his works on photophysics and photochemistry of organic molecules, spectroscopic studies of adsorption and catalysis, photostimulated processes in heterogeneous systems.

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tion with *L. Dobretsov* and *E. Gross,* should be mentioned. For many years this structure remained the main source of information about the magnetic and mechanical angular moments of nuclei. After these works, the name of *Terenin* became well known among the specialists.

Soon *Terenin* started a systematic research of photoprocesses in rarefied vapours of salts and simple molecules. In particular he discovered the photodissociation of NaI molecules accompanied by radiation from the sodium atoms. Using mass-spectroscopy *Terenin and B. Popov* [4] first succeeded to observe the photodissociation of tallium halide to give ion pairs of metal cations and halide anions. In 1927, during his business trip to Germany and Holland, *Terenin* with *P. Pringsheim* investigated the fluorescence spectra of mercury molecules [5]. It is noteworthy that these studies were carried out during the period of the creation of quantum mechanics and of modern notions about molecular structure. The latter were needed for the interpretation of the new experimental results and, on the other hand, the new experimental data stimulated further development of the theory. These studies were summarized in the monograph "*Photochemistry of the vapours of salts*" [6]. As a recognition of his scientific merits *Terenin*, was elected in 1932 as a Corresponding Member, and in 1939 as a full Member of the Academy of Sciences of the USSR.

In 1936–1941 the scope of interests of *Terenin* expanded onto the luminescence of complex organic compounds in the gaseous and condensed states. During World War II with his collaborators he participated in activities demanded for military defence, developing ways of production of the light-stable masking covers. These applied studies were accompanied by attempts to generalise the experimental material on the photophysics and photochemistry of complex molecules, which finally resulted in the discovery of triplet nature of the metastable state of organic molecules, which accounts for their phosphorescence [7]. It was already established that the spectrum of phosphorescence is shifted towards longer wavelengths with respect to the maximum of the immediate process of fluorescence under UV irradiation, and this was explained by the existence of certain long-lived metastable state; however, the nature of the latter was still unclear. Some authors supposed that the excited molecules undergo transformation into another isomeric state, but the isomerism itself could not account for the great lifetime of the excitation, which could be naturally explained by the prohibition of radiative transfer from a triplet state. A year later *G.N. Lewis* and *M. Kasha* came independently to the same conclusion. This turned out to be a very stimulating concept and soon plenty of works appeared where these notions were used and brought about new results. Among those we should mention the studies of phosphorescence of frozen binary solutions of aromatic molecules by *Terenin* and *V. Ermolaev*, resulted in the discovery of the phenomenon of triplet–triplet transfer of the electronic excitation energy from one molecule to another by the mechanism of exchange–resonance interaction [8]. The conceptions developed at that period were soon presented in the monograph by *Terenin* "*Photochemistry of dyes and allied organic compounds*" [9], which for many years became a handbook for the specialists in spectroscopy and photochemistry.

Finally, as the uttermost point of the tendency of gradual complicating of the objects of his laboratory researches, *Terenin* faced the problem of photosynthesis in natural biosystems. As a first step, he began studies of elementary photoprocesses in biologically important molecules, such as chlorophyll and its analogues, simulating discrete stages of the photosynthesis reaction. In the Institute of Biochemistry of the USSR Academy of Sciences *Terenin* organized the Laboratory of Photobiochemistry, where the main reaction of chlorophyll – reversible photoreduction – was established by *A. Krasnovskii* in 1947. Later *Terenin* with *V. Evstigneev* [10] studied the redox reactions of chlorophyll by the method of electrochemical photopotential. For the works on photochemistry of chlorophyll *Terenin* and *A. Krasnovskii* were awarded A. Bakh Prize in 1950.

By the method of electron spin resonance *Terenin* and *V. Kholmogorov* detected ion–radical products in the aggregates of chlorophyll, formed as a result of electron phototransfer in chlorophyll–water–quinone systems and in studying the primary processes of photochemical reactions of organic molecules in solutions the two-quantum character of certain reactions was established [11]. The possibility of such photoreactions, in which triplet molecules of aromatic compounds act as intermediate products and transformaters of light quanta, was grounded earlier by *Terenin*. Now many other two-quantum reactions are known, studies of which formed a new branch of science—nonlinear photochemistry.

Being aware of the important role of electron transfer processes in photoreactions of complex organic molecules, *Terenin* started systematic studies of photoconductivity of organic dyes. In a series of works carried out with *E. Putseiko*, *A. Vartanyan* and *V. Myl'nikov* [12], the semi-conducting properties of dyes and polymers were established for the first time. In the work by *Terenin* and *I. Akimov* [13] the phenomenon of spectral sensitisation of internal photoeffect in semiconductors was discovered and investigated in detail. Under the supervision of *Terenin* studies of the work functions of electrons emitted on irradiation of organic molecules were initiated. First measurements were carried out in 1960 by *F. Vilesov et al.* who studied photoemission from dye films, and then from dyes adsorbed on semiconductors [14]. Photoionization of the same molecules in the gas phase revealed the discrete character of the energy spectrum of photoelectrons [15]. This finding, registered as a discovery in the USSR, led to the creation of the method of photoelectron spectroscopy. The importance of it was appreciated much later, when the X-ray electron spectroscopy, developed by *K. Seigbahn,* was nominated for the Nobel prize, but by that time all the three authors of the first publication were no longer alive. The energy analysis of electrons emitted on the photoionization of molecules was completed by mass analysis of the produced ions [16]. Methodological innovations in photoelectron spectroscopy and photoionization mass spectrometry resulted in a creation of new industrial instruments, successfully applied in several chemical laboratories.

In 1932 *Terenin* organized, in the Physical Institute of the University, the Laboratory of Optics of Surface Phenomena, which in 1957 became the Laboratory of Photosynthesis, and since 1960 was known as the Laboratory of Photocatalysis.

Later on it was transformed into the Department of Biomolecular and Photon Physics, which then constituted the main part of the present Department of Photonics. His interest in the optical studies of surfaces was based on the idea that molecules in the adsorbed state undergo a perturbation, which changes the position of electronic levels in such a way that they become activated for photochemical transformations under illumination by less energetic quanta, which are normally not absorbed by free molecules. Optical methods had to provide new information about the state of molecules in the adsorbed layer, the degrees of their distortions, energy transformation processes and chemical reactions on the surfaces.

Spectral changes on adsorption were followed first in visible region, but pretty soon *Terenin* came to the conclusion that vibrational spectra should be more sensitive to perturbations, and an attempt was made by him and *K. Kasparov* [17] to apply IR spectroscopy to the studies of ammonia adsorption on pure or Fe-containing silica. The preliminary results of this work demonstrated the potentials of this method for the studies of surface species. This was about 15 years before the beginning of analogous studies by *R. Eischens* in the USA. Despite the break in these studies caused by the war and the death of *K. Kasparov* in the battlefield on the approach to Leningrad, the work was continued, and already in 1948 a thesis was defended by *N. Yaroslavsky*, where a great deal of experimental results was obtained by IR spectroscopy, in particular the bands of surface OH groups of thick porous glass samples were observed in the overtone region, as well as their perturbation by adsorbed molecules [18]. Professor *N. Sheppard* (UK) recollects: "*I had the great pleasure of meeting Academician Terenin when I was working in Cambridge in about 1960 and I took him into Trinity College for lunch. I had recently started on the study of adsorbed molecules and had just learnt of his earlier wartime published work in the overtone region. He told me of his earlier attempt to get a spectrum from ammonia on an iron catalyst. We had an excellent conversation and he spoke perfect idiomatic English.*"

Nowadays, when the total number of papers dealing with IR spectra of surface species, exceeds 20,000, it is not easy to realize how little was known about the subject. At that time commercial IR spectrometers were not yet available, and the work was done on the unique self-constructed instruments. This ability to make himself almost everything needed to obtain results, was the style of *Terenin*. When some of his colleagues visited him at home, they noticed several water-colours on the wall and enquired about their authorship. Having got to know that it was their host himself, the guests were much surprised, but the author explained: "*physicist-experimenter should know how to do everything himself*".

Despite experimental difficulties, already at that time IR spectroscopy was applied to the study of photoprocesses on the surfaces of ZnO and TiO_2 by *V. Filimonov* [19]. These studies, developed later by *A. Alexeev S. Gerasimov and K. Bulanin* [20], become now topical and much needed for ecology in order to understand the role of heterogeneous photoprocesses in the balance of polluted atmospheres and in ozone layer protection. The sensitivity of IR spectra was not always sufficient to detect the formation of ionic or radical species arising under UV illumination of adsorbed aromatic molecules, or as a result of protonation on strong proton-donating sites. Appearance of such species was observed on silica–alumina, titania, magnesia and some other oxides using diffuse reflection and electron spin resonance spectroscopy by *A. Sidorov*, *E. Kotov*, *V. Barachevskii*, *V. Kholmogorov* [21]. Another manifestation of photoprocesses in the adsorbed layer is the desorption of molecules under irradiation. In this way the photodecomposition of adsorbed ammonia was first detected in the early work with *K. Kasparov* [22]. Later on, in the works by *Yu. Solonitsyn*, *L. Basov* and *A. Lisachenko* manometric studies of the kinetics of photoprocesses were completed by mass-spectroscopic analysis of the desorbed gases. Further developments of photochemistry and spectroscopy of adsorbed polyatomic molecules have been carried out by *G. Lyalin and S. Litke.*

To understand the way molecules interact with surface sites, spectral manifestations of H-bonding or coordination sites have to be known, and in a series of works IR spectra of such model systems were investigated [23]. These enabled the later characterization of the strengths of surface hydroxyls or coordinately unsaturated metal ions (Lewis acid sites) by frequency shifts observed on adsorption [24], and finally to find the correspondence between spectra of hydroxyl cover of metal oxides and those of bulk or of gas molecules as studied in the works by *V. Filimonov and A. Tsyganenko* [25].

In characterizing *Terenin's* published researches, British spectroscopist Prof. E.J. Bowen, the chairman of the International Photobiology Congress in Oxford (1964), said: '*Few of his papers had ended with inconclusive results. He possessed the supreme faculty of being able to ask the right question in the design of his experiments and has been constantly awarded by significant conclusions*'. All his works have been new and original. His "Introduction to spectroscopy" (1933) [26] was one of the first books where the last achievements of quantum mechanics were presented, and for a long time it was the best textbook on the subject for both students and specialists. He paved new ways and never stopped to develop details of his discoveries. And today his inexhaustible energy amazes. *Terenin*, when finishing work on his last book was already ill, but corrected the manuscript on a special reading-desk attached to his hospital bed. This book – "*Photonics of molecules of dyes and related organic compounds'* [27] – became the essence of his brilliant scientific career, provided a program for his many disciples and followers.

The great scientific merits of *Terenin* were recognised both in the USSR and abroad. In 1945 the Stalin Prize was awarded to him; in 1954 the S. Vavilov Gold Medal of the USSR Academy of Sciences; in 1959 the Ciamician Gold Medal of the University of Bologna, in 1964 the Finzen Gold Medal. He was awarded many medals by the Soviet Government, and the Title of a Hero of Socialist Labour. In 1958 *Terenin* was elected an Honorary Fellow of Physico-Chemical Society of France and the Chemical Society of London in the UK.

The scientific heritage of *Terenin* is huge. Many of his works have been added to the golden fund of world science, and they live on as a part of the basic set of knowledge used by modern scientists active in photochemical research. He gave lectures to schoolchildren to awaken in them an interest in scientific researches. He initiated the organization of special classes at school No. 38 who 2 days a week during last three school years have had their industrial practice not at a factory, as was typical of urban children of that time, but in the Institute of Physics. Many of them later chose the physical faculty of St. Petersburg University to continue their education, and even if not, practice in the Institute gave a lot of technical or practical skills to young people. They have had the experience of photography, soldering, glass blowing, electrical measurements and plenty of practical knowledge of the type of how to make a device for a certain purpose and where to find the necessary materials and instruments. He did not spare his time for the young investigators. He controlled their work in the laboratory, asking about the purpose and methods used, aiming at understanding, – as far as possible – the sense of what they are doing. Every pupil had to have a journal for everyday notes and the results of measurements. Not everyone who had such a practice stayed working in science, but the sparks of interest in the nature around us remain for the all the life of his numerous disciples.

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