Luminescence

By Grace Marmor Spruch

The following report on the 1963 International Conference on Luminescence, held in Poland last September, is by Grace M. Spruch, a research physicist associated with New York University. She is currently working in England.

The first international conference on luminescence ever to be held took place in Poland in 1936. This was pointed out at the opening of the 1963 International Conference on Luminescence last September 25 in Torun, Poland, by Alexandre Jablonski, president of the Organizing Committee, and the man after whom the diagram used by every worker in the field of luminescence is named. As for the appropriateness of Torun for an international scientific congress—Torun is the birthplace of Copernicus. The meeting was held in the Nicholas Copernicus University.

More than two hundred scientists from Canada, Czechoslovakia, France, Germany, Great Britain, Hungary, Italy, Japan, the Netherlands, Poland, Sweden, Switzerland, the US, and the USSR attended the conference. The conference committee took care of the participants from the instant they arrived in the country. Planes and trains arriving in Warsaw were met by committee members, and participants were directed to hotels or transportation to Torun.

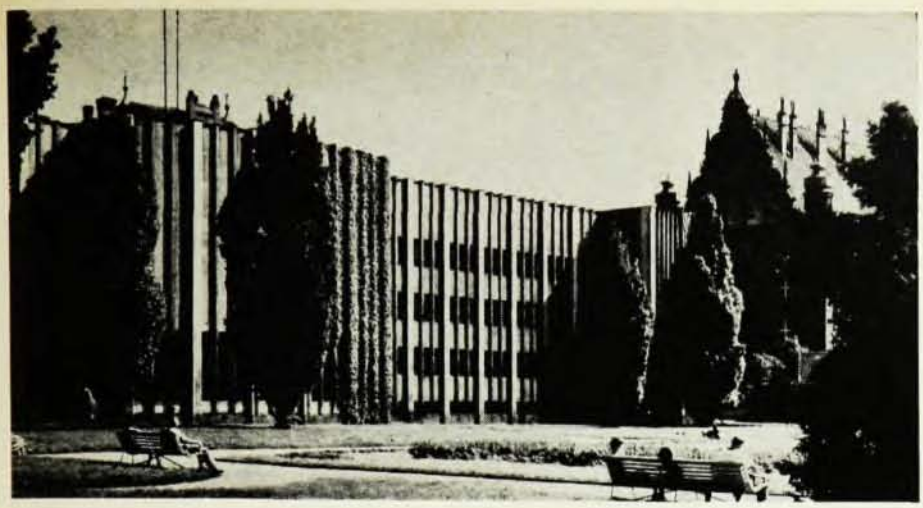
A. Kastler (Paris) and A. Jablonski (Torun and Warsaw), president of the Organizing Committee for the Conference.

Most of the talks were given in English, but German, French, and Russian were also spoken, and one talk was given in two languages. The Soviet speakers gave their papers in Russian. One of the Russians, wanting his talk to be understood by as many people as possible, first recited a sentence in Russian, and then repeated the same sentence in English.

The scientific part of the conference began with an invited paper by G. Herzberg of the Canadian National Research Council, entitled "Electronic Transitions of Simple Polyatomic Molecules". Professor Herzberg showed how the structure of molecules may be deduced from their rotational and vibrational spectra, the energy levels being related to the symmetry of the molecules. For example, a molecule consisting of three collinear atoms in the ground state might have as an excited state the center atom vibrating in a line perpendicular to the line connecting the outer two. The spectrum would show this oscillation.

Each morning and afternoon session was opened by an hour-long invited paper, after which two sessions of ten-minute papers were run concurrently, one session on organics and the other on inorganics. The first of the inorganic sessions was devoted entirely to cadmium sulfide, and such topics as trap depths, the centers responsible for the green luminescence, and the temperature dependence of the luminescence were discussed.

Opening the afternoon session, A. Kastler of the Ecole Normale Supérieure in Paris spoke on some recent results obtained by the techniques of



A view of the campus of the Nicholas Copernicus University in Torun, Poland, where the International Conference on Luminescence was held.

optical pumping. The first part of the talk was based on the thesis of Cagnac, who achieved nuclear orientation in the ground state of the odd mercury isotopes by optically pumping with circularly polarized light from a source containing ^{204}Hg, which excited only one of the four Zeeman components. He then studied the longitudinal relaxation time. Professor Kastler went on to discuss the quantum-mechanical theory of the optical pumping of an atom developed by Barrat and Cohen-Tannoudji, which predicts (1) broadening of the magnetic resonance line proportional to the light intensity, due to the shortening of the lifetime of the ground-state Zeeman levels by light absorption, and (2) displacement of the Zeeman levels of the ground state caused by irradiation, resulting in a change of the magnetic-resonance frequency (he called it the "lamp shift"). He then described the experiments of Cohen-Tannoudji, who applied Dehmelt's cross-beam technique to ^{199}Hg to confirm the theoretical predictions.

The session on organics which followed dealt with decay times and fluorescent yields, while the subject of the inorganic session was the luminescence of the alkali halides.

The second day started with a lecture by H. G. Kuhn of Oxford on a survey of methods and applications of high-resolution spectroscopy, which dealt mainly with interferometric spectroscopy. General problems of intensity and resolving power were discussed and a critical comparison was made between direct recording and photographic methods. While the photographic plate receives light of all wavelengths simultaneously, with a low quantum efficiency, the recorder receives light only from a narrow band but with high quantum efficiency. Linearity of response and large wavelength range are advantages of the recording method, but the requirement of constancy of the source is a disadvantage. Problems to which high-resolution methods have been applied were discussed, problems concerning fine and hyperfine structures and isotope shifts in atomic spectra. Dr. Kuhn also stressed the usefulness of interferometric methods for the study of line profiles and reported on some recent work on helium in which a direct measurement of radiation widths was made and resonance broadening studied.

The subject matter of the organic session which followed was energy transfer and polarization of solutions. The inorganic session was devoted solely to zinc sulfide.

G. Porter of Sheffield University spoke on some studies of the triplet state by flash photolysis methods. He pointed out that the study of luminescence is, to a large extent, the study of the radiationless processes which compete with light emission, and, for organic molecules, the key to the radiationless process is the metastable state in the Jablonski diagram, which is now known to be the lowest triplet level. In gases and liquids, where phosphorescence is normally absent, the formation and decay of triplet states can be studied by means of absorption spectra using flash photolysis. One finds that radiationless conversion by intersystem crossing from triplet to ground state, although prominent in solids and rigid solutions, rarely occurs in fluid media owing to the predominance of bimolecular processes. The quenchers principally responsible are oxygen, oxygenated compounds, and molecules with low-lying triplet levels. When these are removed, as can readily be done by going over to the gas phase, triplet-triplet collisional quenching predominates. Only when all these processes are eliminated does the triplet decay constant have a fundamental significance.

Professor Feofilov of Leningrad spoke on the luminescence of trivalent and bivalent ions of the

The Town Hall in Torun—"one of the most splendid medieval town halls in Europe"—where the conferees attended a concert.

rare earths in crystals of the fluorite type, pointing out that there is much interest in crystals activated with ions which give line spectra because of their application to lasers. He discussed the structure of the luminescence centers, the spectra, and excitation processes in synthetic monocrystals MeF_2 (Me = Ca, Sr, Ba) activated by Re^{3+} and Re^{2+}. The absorption and luminescence spectra of Re^{3+} are determined entirely by the forbidden transitions between energy terms of the $4f^k$ configuration. In the case of Re^{2+} the absorption spectrum is determined by allowed transitions to the mixed $4f^{k-1}5d$ configuration but the luminescence may correspond to allowed as well as forbidden transitions, depending upon the relative positions of terms of the $4f^k$ and $4f^{k-1}5d$ configurations. The ions Nd^{2+}, Dy^{2+}, Ho^{2+}, Er^{2+} and Tm^{2+} (formerly unknown) were found in natural fluorite crystals.

In the single session which followed, the talks were concerned mostly with electroluminescence.

The final morning of the conference was given over to two concurrent sessions of talks which did not readily fit into standard categories. In the inorganic session, K. Luchner of the Technische Hochschule in Munich described experiments which applied the Mossbauer effect to luminescence for the first time. The luminescence properties of iron in zinc sulfide (red band after firing at 600°C, killing after firing at 1000°C) were related to the state of the iron. It was found from the isomeric shift that iron is incorporated as Fe^{3+} at two different lattice sites. After firing at 600°C the iron occupies regular lattice sites, while after firing at 1000°C the iron is mostly at sites characterized by an electric field gradient, the latter determined from quadrupole splitting.

The closing session was a general discussion of problems which had been raised during the conference. J. B. Birks of the University of Manchester, who delights in stirring up controversy at luminescence conferences, engaged in a mild one with G. Oster of Brooklyn Polytechnic Institute. Professor Oster questioned the existence of eximers first proposed by Forster for pyrene and extended to other aromatic compounds by Birks. He argued that ground-state dimers can form and be fluorescent, as might be the case in a poor solvent, such as methanol, added to a benzene solution of pyrene; and the fact that the fluorescence appears in plastics would rule out a diffusion-controlled process. An intermediate stand was taken by V. Levshin of Moscow University, who argued for the existence of permanent dimers which are fluorescent, in the case of arcridine orange, to weak dimers, in the case of the fused-ring aromatic hydrocarbons.

The social evening of the conference began with a rare artistic experience, a concert given in Torun's Town Hall. Torun itself is like an old woodcut. It has some of the best preserved thirteenth to sixteenth century town houses in Poland, and the Town Hall is one of the most splendid medieval town halls in Europe. On the paneled walls of the huge Burgher Room in which the concert was held hang portraits, reminiscent of Holbein's "Erasmus", of distinguished citizens of the past; one is of Copernicus. In this old world setting the Ancient Music Ensemble of the Ignatius Paderewski Pomerania Philharmonic performed beautifully music by Gabrielli, Scarlatti, and Orlando de Lasso. It was to Professor Jablonski that we owed this perfect harmony of music and surroundings. Professor Jablonski is himself an accomplished musician. When he was a student in physics, before the invention of the government research grant, he supported his studies by playing the violin with the Warsaw opera.

I know that I speak for all the participants in expressing deep gratitude to Professors Jablonski and Swinarski, and to Dr. Frackowiak and the rest of the organizing committee, for an extremely successful and especially enjoyable conference.