News

AWARD OF VAVILOV GOLD MEDAL

M. A. ÉL'YASHEVICH, G. P. GURINOVICH, and K. N. SOLOV'EV

Usp. Fiz. Nauk 75, 389-390 (October, 1961)

THE presidium of the U.S.S.R. Academy of Sciences has awarded the 1961 Vavilov gold medal to Professor Éduard Vladimirovich Shpol'skii, Doctor of Physico-Mathematical Sciences, for his work on luminescence line spectra in frozen solutions.

The occurrence of line spectra in frozen solution was first observed in 1952 by É. V. Shpol'skii jointly with L. A. Klimova and A. A. Il'ina in research on fluorescence. It was shown that cooling of solutions of multi-nuclear condensed hydrocarbons in normal paraffins leads to an extraordinary narrowing of the lines in the fluorescence and phospherescence spectra, which become just as thin as the lines of vapors and gases in gas-discharge tubes (under favorable conditions the widths of the spectral lines do not exceed 2–3 cm^{-1}). In many cases regularly interrelated line groups ("multiplets") were observed, due to the peculiarities in the penetration of the multiatomic molecule into the crystal cell of the frozen solvent. Somewhat later É. V. Shpol'skii showed that similar effects are observed in absorption spectra.

These phenomena recently became widely known and called the "Shpol'skii effect."

An important factor in the Shpol'skii effect is that normal paraffins turn into a microcrystalline mass on freezing. The saturation of normal paraffins leads to the absence of various chemical interactions with the dissolved molecules, and their transparency, which extends to the vacuum ultraviolet, prevents energy exchange between the absorbing molecules and the solvent, as well as between the molecules that have somehow penetrated into the crystalline mass of the solvent. The penetrating molecules, fixed in definite positions and not interacting with each other, form an "oriented gas," as it were. The sharp spectra obtained by the Shpol'skii method, are therefore highly individualized features of many organic molecules and are highly sensitive to changes in their structures. Previously the same compounds yielded not line spectra, but broad bands without structure, even at very low temperatures (to 4°K).

An analysis made by Shpol'skii and his students showed that the frequency differences that occur in fluorescence line spectra yield the frequency of the normal oscillations of the molecule in the ground state. Accordingly, the frequency differences in absorption spectra yield the normal frequencies for the excited state.

It must be especially noted that in the case of symmetrical molecules (pyrene, perylene, coronene and others) the Shpol'skii spectra display oscillations that are forbidden in the infrared spectra and allowed in Raman spectra. This is most important, since measurements of Raman spectra are difficult, particularly in strongly absorbing and fluorescent substances.

The unique "multiplet" structure observed in the Shpol'skii spectra is closely connected with the properties that the solvent exhibits as a fine-crystal medium. This structure can serve as a reliable source of information on methods of penetration of the investigated molecules into the crystalline solvent. The high sensitivity of the Shpol'skii spectra to the influence of intramolecular and intermolecular force fields makes it possible to exhibit fine effects caused by the interaction between molecules.

The spectra obtained by the Shpol'skii method are highly individualized and exhibit distinctions not only between compounds of different structure, but between substances having the same composition but consisting of molecules of different structures i.e., different isomers. This opens up wide prospects for using the Shpol'skii effect not only for qualitative but also for quantitative analysis.

The work by Éduard Vladimorovich Shpol'skii has merited its wide recognition and will undoubtedly take place among the most valuable possessions of Soviet spectroscopic science. Research on the luminescence and absorption line spectra in frozen solutions is advancing on a wide front both in the Soviet Union and abroad, and continuously gains new applications.

Translated by J. G. Adashko