Theory of Molecular Excitons. By A. S. DAVYDOV. Translated from the First Russian Edition by MICHAEL KASHA, Professor of Chemistry, Florida State University, and MAX OPPEN-HEIMER, JR., Professor of Russian, State University of Iowa. McGraw-Hill Book Co., Inc., 330 West 42nd St., New York 36, N. Y. 1962. ix + 174 pp. 15.5 × 23.5 cm. Price, $7.95.

About 12 years have elapsed since the appearance of the first Russian edition of Davydov's "Theory of Light Absorption in Molecular Crystals." Virtually all of the existing relevant experimental work in this field has been carried out during these years, so it is no less than remarkable that this new English translation emerges as an authoritative and valuable contribution to such a rapidly expanding branch of chemical physics.

After an introduction which describes the early Russian contributions to crystal spectroscopy, the author deals first with the classical and quantum mechanical theories of acoustic and optical vibrations in periodic lattices (Chapter I). The influence of intermolecular interactions on the infrared and Raman spec ra of crystals is treated in Chapter II. The complete rigid lattice theory of electronic spectra in molecular crystals is presented in Chapter III along with applications of group theory to determine selection rules for Raman and infrared spectra of crystals. This chapter is an elaboration of Davydov's classic (1948) paper on the splitting of nondegenerate states in monoclinic crystals. Naphthalene, phenanthrene, benzene, calcite, and the aragonite crystal are each given a detailed discussion. The equations governing the energy states of molecular crystals are derived generally in Chapter IV which differs from Chapter III by the inclusion of lattice vibrations into the theory. This chapter also includes a discussion of multiquantum transitions, a derivation of the Schroedinger equation determining the motion of molecules in a crystal lattice containing one electronically excited molecule, and the enunciation of conditions governing the production of free and localized excitons. In Chapter V some special solutions of the general equations are obtained. It is shown that the earlier results (Chapter III) are reproduced in the limiting (rigid lattice) case. The solutions of the equations (Chapter IV) for small displacements are obtained in Chapter VI, and used to calculate the absorption coefficient of a crystal and the influence of temperature on band shape and intensity. In Chapter VII conditions for the production of localized excitons are examined, and the relative energies and band shapes of localized and free exciton absorption spectra are emphasized. Excitations to states for which the electronic wave vector is nonzero are discussed quantitatively. A phenomenological account of fluorescence and its radiationless quenching by lattice vibrations is presented in Chapter VII. In Chapter VIII, theory is compared with experiment. The following systems are discussed: Raman spectra of HCl, CS_2, and benzene; infrared spectra of ethylene and methane; electronic absorption (and often emission) spectra of crystals and vapors of benzene, naphthalene, anthracene, tetracene, phenanthrene, bromobenzene, and iodobenzene. In the last chapter, exciton theory is applied to the calculation of the energy states of polyphenyls, and a detailed calculation—including electron exchange—is given for biphenyl.

In the present light the book suffers two defects neither of which could have been said to exist when the Russian edition first appeared. Firstly, formal group theoretical methods are only touched on briefly. The readers attention should be drawn to the fact that much of the theory in Chapters III (pp. 13, 14), V (pp. 20, 23, 24), and X (39), can be developed much more succinctly using a formal factor group analysis. Secondly, the comparison of the theory with experiment is very much outdated. The assignments for naphthalene (IX, p. 37) are incomplete, and the "loca ized excitions" in the naphthalene crystal (p. 133) are an impurity artifact. The anthracene crystal absorption spectrum (p. 134) contains a b-polarized impurity band which is attributed to free excitons. The phenanthrene crystal is analyzed in terms of .our rather than two molecules in the unit cell. The whole of Chapter IX should be read with an eye on more recent experimental work.

Especially useful is the translators' effort to overcome these deficiencies by means of a bibliography of 40 key papers (1949–1961) on subsequent experimental and theoretical advances in crystal spectroscopy, and a complete bibliography of Davydov's later work.

The translators have chosen to alter the title to include the term *molecular exciton* which they feel, "... stresses the principal theme of the book—the resonance interaction of excited states of weakly coupled molecular systems." Since this is a translation of a book written in 1949, there are certain aspects of molecular exciton theory which are notably absent. For example, not mentioned in the book are: second quantization methods, which Davydov himself used later in this regard; the theory of dispersion in molecular crystals—again, tackled by Davydov later; second-order crystal field effects; and the problem of defects in molecular lattices. However, these omissions do not detract from the value of this book as an important treatise on one aspect of molecular theory.

Regardless of the few minor deficiencies that time has added, Davydov's book remains a classic in molecular crystal theory. English speaking theoretical and solid state physicists, chemists, and graduate students will be grateful to Professors Kasha and Oppenheimer for their efforts in making this important work more accessible.

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High Polymers. Volume XVII. Configurational Statistics of Polymer Chains. By M. V. VOLKENSTEIN, Institute of Macromolecular Chemistry, Leningrad, U.S.S.R. Translated from the Russian Edition of 1959 by SERGE N. TIMASHEFF and M. J. TIMASHEFF. Interscience Publishers, John Wiley and Sons, 605 Third Ave., New York 16, N. Y. 1963. x + 562 pp. 15.5 × 23.5 cm. Price, $20.00.

When one of the pioneers and continuing leaders in an active field of research is persuaded to take the time and trouble to set down a more or less detailed and connected account of its status, the result is likely to be a monograph of superior quality. Such phenomena have occasionally been observed in polymer science, and the appearance of the present volume belongs among them.

In the infancy and youth of the physical chemistry of long-chain molecules, it was learned how to treat the great multiplicity of chain configurations (now often preferably called "conformations") by the statistics of random flight, already well developed in the theory of Brownian motion. Comparisons of such calculations with experimental measurements on polymers then yielded model parameters such as the length and the optical constants of a statistical chain element (Kuhn and Grün) or the persistence length of the chain (Kratky and Porod), but these parameters bore no immediate or obvious relation to the actual molecular structures involved. If we reckon the birth of polymer statistics to have occurred in the early 1930's, with Kuhn, Mayer, Mark, and Guth as parents or sponsors, we may say that the field has now come of age; the random-flight gaussian chain still has many valid uses, but it is no longer an acceptable end result. Internal rotation in small molecules is now much better understood: we have numerical values for many barrier heights, we have data for many rotational-isomeric equilibria, and we even appear to approach quantum-mechanical insight for the ethane problem. Thus, the basic equipment is at hand for beginning to construct a true molecular theory of chain configurations. A number of workers have been engaged on this job in the last few years, in Leningrad and elsewhere. This book describes in detail the results of their efforts through 1959, but there is a brief author's preface to this translated version which points out the significant developments through most of 1962.

The chapter headings are as follows: 1. Introduction, 2. Internal Rotation in Small Molecules, 3. Rotational Isomerism, 4. Configurational Statistics of Model Chains, 5. Properties of Crystalline Polymers and Stereochemistry of Polymer Chains, 6. Configurational Statistics of Real Chains, 7. Optical Anisotropy of Polymer Chains, 8. Stretching of Polymer Chains and of the Network. Literature references are collected at the end of each chapter. There is a good subject index, but the author index which is found in the Russian original has unfortunately not been retained. There is a justifiably strong foreword by P. J. Flory.

Most of the above chapter titles are self-explanatory. The model chains discussed in Chapter 4 include the freely-jointed chain, the chain with fixed valence angles and free internal rotations, and the chain with fixed valence angles and hindered but independent internal rotations. Chains with interactions between internal rotations and with excluded volume effects are