

Spectroscopy of amorphous substances with molecular structure

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Usp. Fiz. Nauk **160**, 263–298 (February 1990)

Spectroscopy of organic molecular glasses and cold-deposited films is reviewed. The emphasis is on demonstration of the capabilities of such spectroscopy in tackling the fundamental problems in the physics of the amorphous state. It is shown that in discussing the structural properties a considerable amount of information—which can be used to identify the amorphous state, follow its thermal and time relaxation, and establish the participation of conformational transformations of molecules in these processes—can be obtained by diffraction-spectral methods combining diffraction measurements with simultaneous recording of Raman light-scattering spectra. A detailed analysis is made of the possibility of investigating the density of vibrational states by inelastic neutron scattering and Raman scattering of light. The results obtained by electron spectroscopy are discussed in the specific case of the spectra of cold-deposited-films. Much attention is given to the method of selective laser spectroscopy. A hierarchy of universal properties of a molecular amorphous substance is proposed and it is shown that spectroscopy is the main method for investigating the majority of them.

1. INTRODUCTION

Many low-molecular organic compounds—normal and cyclic hydrocarbons, monatomic and polyatomic alcohols, simple and complex esters, including amines, aromatic compounds, acroleins, succinates, maleates, etc.—form amorphous substances when supercooled. The available data indicate that number of such compounds amounts to $\approx 4\%$ of the total number known at present. Already this number is several hundreds, much greater than the number of inorganic compounds that can become amorphous.

Organic amorphous substances, which (by analogy with such concepts as a nematic, a smectic, a cholesteric, etc.) can be conveniently called *molecular amorphics*, have been the object of intensive research in the “organic glass” form already at the beginning of the present century. These investigations have been concerned mainly with thermodynamic properties (for a review see Ref. 1). Already then the nature of vitrification and the relationship between the glass-transition temperature and other thermodynamic properties, on the one hand, and the properties of the molecules of the glass-forming substances, on the other, have been considered. This has been followed by a period of loss of interest in these solids and by a second upsurge of interest in the late sixties.

The explosive growth of interest in the physics of amorphous substances, due to widening horizons of modern materials science, has increased greatly the rate of research of their fundamental properties. Although the attention has been concentrated on inorganic substances, studies of molecular amorphics have in many cases provided more detailed and deeper understanding of the fundamental properties of this new type of solid.

This has been due to the following reasons. Amorphization of inorganic compounds raises the fundamental problem of the short-range order, whereas in molecular amorphics the main structure element is a molecule and it is not destroyed by the amorphization process.

Molecular amorphics are easy to prepare, they can be made in large volumes, high vacuum is frequently unnecessary, and some other stringent conditions do not have to be

obeyed; this makes it much easier to carry out not only a single (e.g., thermodynamic) investigation, but to develop an extensive program of research.

In view of the specific nature of molecular objects, the main method for their investigation is spectroscopy. This highly-developed approach provides successful means for the investigation of molecular amorphics employing the huge arsenal of data accumulated by the spectroscopy of molecules and molecular crystals.

The purpose of the present review is to demonstrate the capabilities of spectroscopy in tackling the main problems in the physics of the amorphous state. The review is organized as follows. A detailed description of a molecular amorphous as an investigation object is given in Sec. 2 together with its definition, methods of preparation, and main thermodynamic characteristics. The foundations of the physics of the amorphous state, which is the structure of a molecular amorphous is considered in Sec. 3 and the spectroscopic approach to finding this structure is discussed. Relaxation of the structure and the ability to investigate it by spectroscopic methods are considered in Sec. 4. Spectroscopy of vibrational and electronic states of molecular amorphics are the subjects of Secs. 5 and 6, respectively. Selective laser spectroscopy of amorphics is discussed in Sec. 7 and the Conclusions deal with the hierarchy of universal properties of a molecular amorphous, confirming that spectroscopy is the main method for the investigation of the majority of amorphics.

2. MOLECULAR AMORPHIC AS AN OBJECT OF INVESTIGATIONS

2.1. Brief definition

An amorphous substance or an amorphous is a solid which is alternative to a crystal differing from the latter by the absence of the translational periodicity and characterized by a shear viscosity of at least $10^{14.6}$ P (Refs. 2 and 3). An enormous number of substances is dealt with in the physics of the amorphous state under the name of glasses. This term applies to amorphics prepared by rapid quenching of melts. However, from the beginning of investigations of glasses (mainly organic) right to the present, a glass is un-

derstood to be an amorphous exhibiting a glass transition¹⁾ and described by a characteristic known as the glass-transition temperature.³ We shall use this definition of a glass.

The absence of the translational periodicity in an amorphous does not result in a random distribution of atoms: fixed lengths and directions of the valence bonds, valence angles, and atomic and ionic radii determine the short-range order. In the case of inorganic amorphics it is usual to speak of associates and clusters,⁵ intermetallic "molecules" or molecular configurations,⁶ polyhedra (for example, quartz tetrahedra, boron icosahedra,⁷ etc.), and regular complexes.⁸ However, the problem of the true short-range ordered structure in these substances is still largely a matter of controversy. In the case of organic amorphics the *main short-range structure unit is the molecule*.

The packing of neighboring molecules is responsible for the *average order*. It is the packing that is responsible for the type of disorder occurring in a solid. Figure 1 shows four types of disorder resulting in the absence of the translational symmetry. An amorphous substance is a solid with a topological disorder.

2.2. Preparation of molecular amorphics

There are about ten different methods of making amorphics. The chief of these are thermal evaporation (deposition of films on a cold substrate), sputtering, dissociation in a glow discharge, chemical deposition in a gas, freezing of a melt, etc. The two main methods used in the case of organic amorphics are freezing of a melt and deposition of a molecular vapor on a cooled substrate. The first method yields glasses and the second—thin films.

2.2.1. Molecular glasses

Formation of an organic glass requires melt cooling rates of the order of one or more kelvin per second. This is easily achieved by immersing a glass or a metallic container containing a melt in liquid nitrogen. Samples prepared in this way are in the form of transparent "fruit drops" of dimensions limited only by the container. A typical phase diagram, in the form of the temperature dependence of the specific heat C_v , is shown in Fig. 2a. It is clear from this figure how the glass-transition temperature T_g is defined. Measurements of T_g are made by thermal differential analysis (TDA) and a typical curve obtained by this method is shown in Fig. 2b.

Extensive literature is available on thermodynamic investigations of organic glasses (for reviews see Refs. 1 and 9–13, where the bibliographies are given). It has been established that the main characteristics are governed by the molecular structure. An analysis of the experimental data led

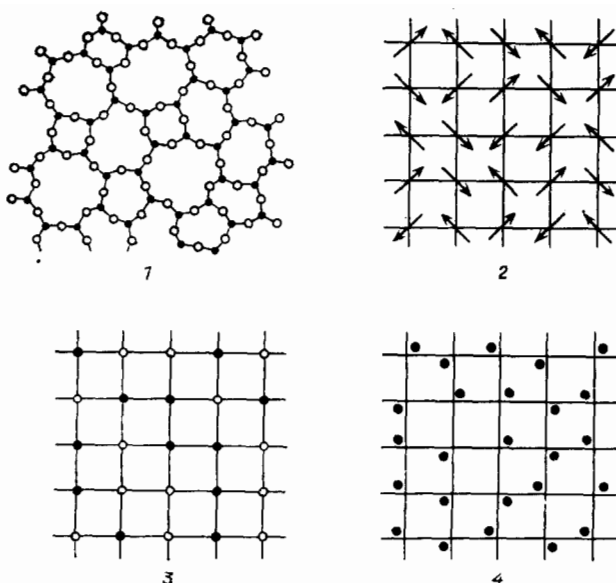


FIG. 1. Types of disorder: 1) topological disorder (absence of long-range order); 2) spin disorder in a regular lattice; 3) disorder of substitution in a regular lattice (mixed crystals); 4) vibrational disorder around equilibrium positions in a regular lattice.³

S. V. Nemilov to propose the following empirical expressions for the calculation of the glass-transition temperature and other quantities (such as the frozen configurational entropy) in the form

$$T_g = \sum_i n_i \Delta T_{gi} = n_{CH_x} \Delta T_{CH_x} + n_{OH} \Delta T_{OH} + \dots, \quad (2.1)$$

where n_i is the number of characteristic fragments in a molecule (for example, CH, CH₂, CH₃, OH, and other groups) and ΔT_{gi} represents the partial contributions made by these fragments to the glass-transition temperature.¹

2.2.2. Thin films

Condensed hydrocarbons, such as naphthalene, anthracene, etc. do not become amorphous as a result of cooling of the melt²⁾ (Ref. 14). Amorphics of this type can be prepared by deposition of a heated molecular vapor on a cooled substrate.^{14–18} The cooling rate is then 10⁹ K/s (Ref. 3).

The usual method used in the preparation of films involves deposition in vacuum when the residual pressure is 10^{−6} Torr, producing films 0.1–0.3 μm thick on a cold substrate (kept at 20 K or higher temperatures) at a rate of 0.5–100 Å/s (usually restricted to 50–100 Å/s). Another less universal method is dimerization or oligomerization of a monomer crystal (derivatives of coumarin, cyclopentanol, etc.) as a result of irradiation, which is accompanied by

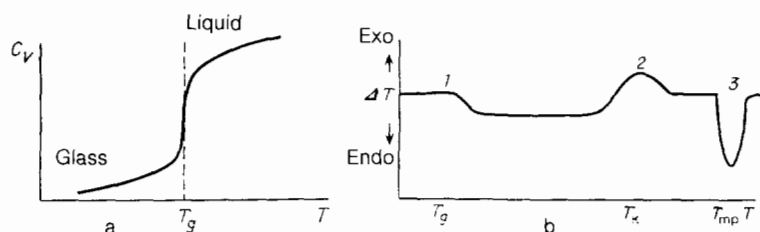


FIG. 2. Manifestation of vitrification (glass-forming transition) in thermodynamic measurements: a) schematic illustration of the change in the specific heat at constant volume C_v during cooling in the region of the glass-transition temperature; b) schematic differential thermal analysis (DTA) curve showing the glass-forming transition (1), crystallization (2), and melting (3).³

amorphization of a substance (see Ref. 8 and the bibliography given there).

3. STRUCTURE AND SPECTROSCOPY

Knowledge of the structural distribution of atoms in a solid is essential for a detailed understanding of its physical and chemical properties; this applies equally to amorphous substances and to crystals. Therefore, the bulk of experimental investigations of the amorphous state in organic materials has been concerned with their structure (for a monograph see Ref. 3). Many research programs have relied on the fact that few atoms participate in the short-range order and this has provided the basis for introducing the density functions, and the normal and reduced radial distribution functions, to describe the structural properties of an amorphous. The multiatomic nature of the short-range order in organic glasses immediately makes the structural task difficult and subject to all those complications that are encountered in structural investigations of polyatomic molecular crystals and proteins. Therefore, there have been only a few structural investigations of amorphics.²⁰⁻²⁴ These investigations do not provide detailed interpretation of the structure at the atomic level.

In addition to the quantitative problem of finding the detailed structure, the current research is concerned also with such qualitative structural problems as identification of the amorphous structure and its evolution (influence on the structure of the thermal history of a sample, subsequent annealing at different temperatures and for various durations, rate of evaporation of a film and its thickness, etc.). The establishment of a detailed structure is still a matter for structural analysis, but the problems of identification of the structure and its evolution may be tackled by spectroscopy, as demonstrated by recent diffraction-spectral investigations of some glasses.

For historical reasons investigations of molecular glasses (which have been the subject of thermodynamic investigations for several decades) and of molecular films

(which have started to attract interest only in the late sixties and early seventies) have reached recently a stage of potential structural investigations. These two types of amorphics have been tackled by two different but complementary research programs. In the case of glasses this program involves moving away from thermodynamics to structural investigations and then to vibrational spectroscopy. In the case of amorphous films there is a shift from electronic properties (localization of the states of carriers and excitons^{14,15}) to structural studies.

3.1. Diffraction-spectral investigations of glasses

In the last decade the study of rapidly frozen liquid crystals has stood out from other work on organic glasses. Major progress made in the case of these materials has been mainly due to diffraction-spectral investigations.^{26,27} This method involves simultaneous neutron-diffraction and spectroscopic investigations of a glass using Raman scattering of light (RSL). Such investigations have been carried out on two model systems of nematic liquid crystals: n-4-methoxybenzylidene-4-butylaniline (MBBA) and n-4-ethoxybenzylidene-4-butylaniline (EBBA). The structure of the MBBA molecule is shown as an inset in Fig. 13.

Figure 3 gives the angular distributions of the diffraction intensity obtained for rapidly frozen MBBA and EBBA liquid crystals, together with diffraction by stable crystalline modifications of these compounds obtained by slow cooling of liquid crystal phases (cooling rates 0.7 K/s or less). Rapid freezing of liquid crystals causes them to solidify in C_0 (MBBA) and C_1 (EBBA) phases; slow cooling produces stable crystalline modifications C_5 and C_6 in the former case and C_4 in the latter.

It is clear from Fig. 3 that the distributions of the intensities of diffraction by liquid crystals and C_0 phases of MBBA are largely similar, so that we can draw the qualitative conclusion that the C_0 phase is in a typical amorphous state. However, in the case of EBBA this is no longer true. The behavior of the C_1 phase differs considerably both from

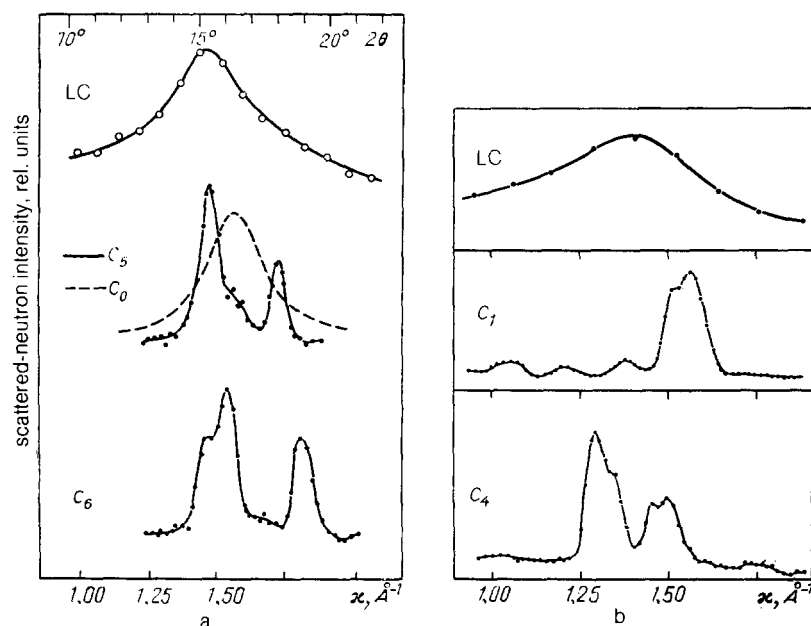


FIG. 3. Intensity distributions in neutron diffractograms of solid phases of: a) MBBA (Ref. 28); b) EBBA (Ref. 29). Diffraction by the solid phases was investigated at $T = 80$ K, that by liquid crystals (LC) at $T = 296$ K for MBBA and 320 K for EBBA. Here, C_5 , C_6 , and C_4 are stable crystalline modifications of solid MBBA and EBBA, respectively; $x = (4\pi/\lambda)\sin(\delta/2)$, where λ is the neutron wavelength and θ is the diffraction angle.

the initial phase of this liquid crystal and from the C_0 phase of MBBA. On this basis it is concluded in Ref. 29 that rapid cooling of EBBA fails to produce the amorphous state.

The question therefore arises to what extent the results of an analysis of the external form of the distribution curves of the diffraction intensity are final and whether there is perhaps a more convincing method for *identification of the amorphous state*.

The answer to this problem is positive because the information can be provided by diffraction-spectral investigations. Such investigations of solid phases of MBBA have established a high sensitivity of the low-frequency RSL (Raman) spectra to the phase state of a solid which led to a considerable modification of the spectrum as a result of slight (judging by the diffractogram) changes in the phase state. This sensitivity is a consequence of selection of vibrations in the spectrum in accordance with the quasimomentum. Since the amorphous state is characterized by the absence of translational symmetry, the quasimomentum is no longer a quantum number describing vibrational excitations. Interaction with light no longer satisfies the selection rule for one-phonon transitions $\mathbf{q} = \mathbf{Q} \approx 0$ and a one-phonon RSL spectrum of an amorphous is governed entirely by the density of the phonon states, in contrast to the spectrum of the $\mathbf{q} = 0$ modes of a crystal. The density of the vibrational states in molecular solids is a continuous function of the frequency³⁰ at low frequencies from zero to 15–200 cm^{-1} . Consequently, instead of the characteristic narrow-band RSL spectrum of a molecular crystal, the spectrum of an amorphous recorded in the same range should be in the form of a continuous distribution of the intensity as a function of the frequency.

Figure 4 shows the RSL spectra of the C_0 and C_4 phases of MBBA and EBBA, respectively. Clearly, the RSL spectra of these two phases are of the wide-band type, have little structure, and in contrast to diffraction are largely identical. The two spectra differ drastically from the spectrum shown in the inset and typical of crystals of both compounds. In the case of the C_1 phase of EBBA the vibrational states are inco-

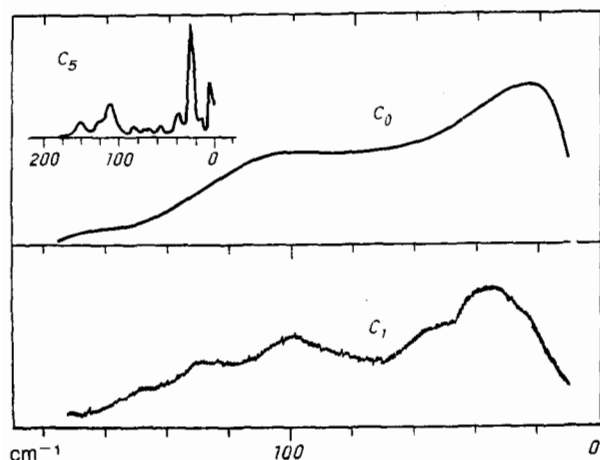


FIG. 4. Low-frequency Raman spectra of rapidly frozen phases C_0 of MBBA and C_1 of EBBA; $T = 80$ K (Ref. 29). The inset shows the Raman spectrum of the stable crystalline modification C_5 of MBBA; $T = 80$ K (Ref. 28).

herent and cannot be described by the quasimomentum, indicating the absence of translational symmetry. On the basis of the spectral evidence, we may conclude that both phases are amorphous. The question why the nematic MBBA becomes an "amorphous nematic" or a "nematic amorphous" as a result of freezing, whereas EBBA acquires more structure as a result of amorphization (possibly forming an "amorphous smectic" or a "smectic amorphous") is clearly related to the difference between the configurational entropies of these substances in the region of the glass-transition temperature (for reviews see Refs. 1 and 9). The same difference accounts for the familiar increase in the viscosity near the glass-transition temperature and in the temperature itself in the case of EBBA as compared with MBBA.

The considerable width of the peak of the diffraction pattern of the C_0 phase indicates that the dimensions of the translational ordering region are small. The position of the maximum corresponds to the dominant average distance between the atoms. Therefore, the average order of the structure of the amorphous phase of MBBA corresponds to such stacking of molecules in which the average interatomic distance is 4.28 Å and this type of order is retained over a distance of 40 Å. In the case of the C_1 phase of EBBA the average order is formed in an analogous way: the dominant interatomic spacing is 4.5 Å, but the size of the long-range order increases to 100 Å.

The main characteristic distances are clearly minimal for this type of molecule ensuring their dense packing, controlled by the short-range atom-atom potentials of the intermolecular interaction.³¹

3.2. Electron-microscopic investigations of aromatic compound films

Electron microscopic investigations of pentacene and tetracene films^{19,23} are so far the only structural investigations of film amorphics. The results are particularly valuable because they have been obtained by *in situ* investigations.

Figure 5 shows the electron diffractograms of pentacene films (of thickness ~ 2000 Å) freshly evaporated on substrates held at different temperatures.

Figure 6 shows the dependence of the diffraction intensity on the parameter $\kappa = (4\pi/\lambda) \sin(\theta/2)$ (λ is the electron wavelength and θ is the diffraction angle), similar to the parameter κ in Fig. 3.

This figure manifests clearly the gradual crystallization of a film on increase in the substrate temperature. It is worth noting the two-hump nature of the intensity distribution curves obtained for films deposited on substrates kept at low temperatures when the positions of the maxima (in the series of the plotted curves) corresponded to distances of 3.1 and 4.6 Å. The positions of these two maxima are practically independent of the substrate temperature and when a structure appears in the diffraction pattern at higher temperatures, they approach the positions of the principal 110 and 211 reflections of a crystal due to the existence of two translationally inequivalent molecules in one unit cell of the crystal. On this basis it has been concluded that amorphous acenes retain pair packing of the nearest molecules, typical of the crystal modification¹⁹ and due to the short-range nature of the atom-atom potential of the interaction between the molecules.³¹ Therefore, as in molecular glasses, the average order in cold-deposited films was governed by the short-

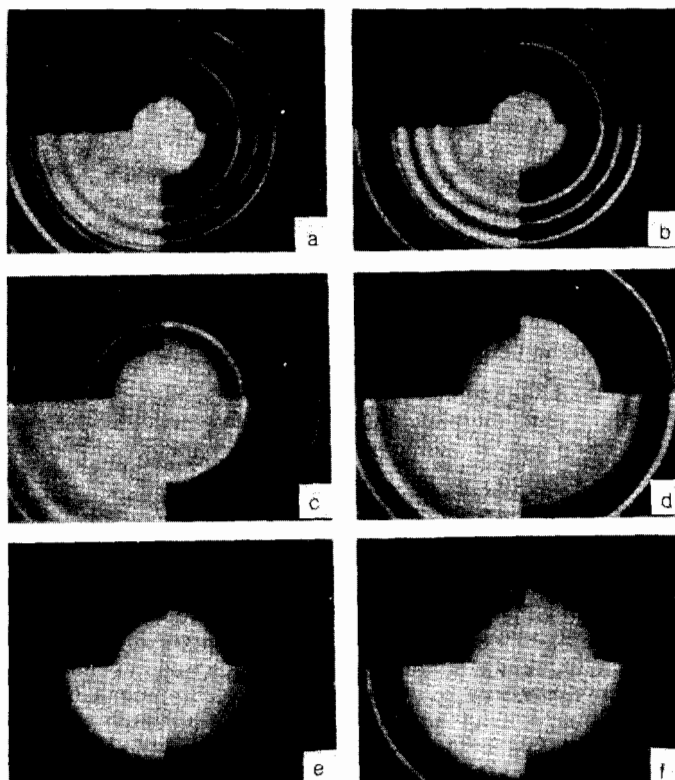


FIG. 5. Electron diffractograms obtained *in situ* for pentacene films (of thickness 2000 Å) deposited on substrates at the following temperatures (K): a) 300; b) 250; c) 200; d) 150; e) 80; f) 28. Each diffractogram is divided into four segments representing different durations of exposure in the process of photography.¹⁹ The vacuum in the chamber containing a sample was 10^{-6} Torr.

range intermolecular interaction potential, resulting in pair packing of molecules.

The half-width of the diffraction peaks indicates that the coherence length of such packing is 4–5 lattice constants in the (a, b) plane. Hence, it was concluded that the structure of amorphous films was as follows: the spatial distribution of the ensemble of molecules was *on the average* close to that expected in a fully relaxed crystalline phase, but the coordinates of the individual molecules were subject to random fluctuations.

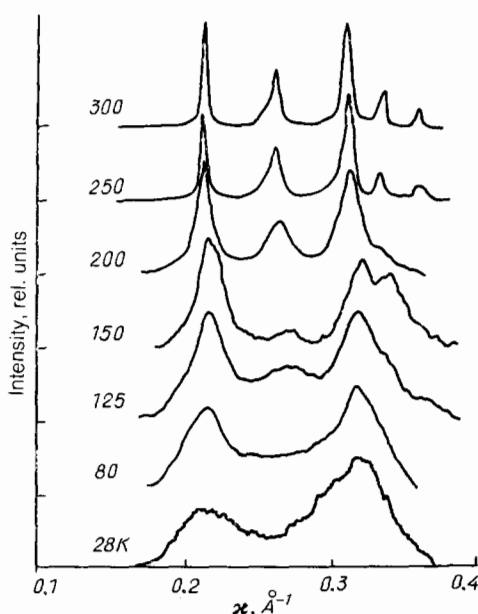


FIG. 6. Diffraction intensities for a pentacene film *in situ*. The substrate temperatures during deposition are indicated along each curve.¹⁹

However, this typically crystalline packing representing the average order of the amorphous film could be used to argue that films of this kind are not amorphous. The decisive argument in support of the identification of the state of a low-temperature film as amorphous can be provided by the results of investigations carried out using RSL, which are well known in the case of crystalline acenes.

3.3. Spectroscopy as a method for investigating the structure of amorphics

Undoubtedly, the traditional methods for structure analysis such as electron, neutron, and x-ray diffraction will always retain their leading position in determination of the quantitative structure characteristics of amorphics, such as the preferred interatomic spacing, the coherence length of the average order, the radial distribution function, etc. However, such qualitative characteristics of the amorphous state as its identification and evolution (Sec. 4) can be determined more reliably and much more simply if we use experimental spectroscopic methods of the kind employed in recording low-frequency Raman spectra.

One should mention here also the possibility of using luminescence in tackling these topics. If the lowest electronic state of crystalline forms of the substances of interest to us are characterized by wide excitonic energy bands (this is true, for example, of the condensed acene group), then the low-temperature luminescence spectra should have a phonon wing representing a pure electronic transition^{32,33} which has its own characteristic narrow-band structure because of the thermal selection of the exciton states in accordance with their quasimomentum near the bottom of the energy band. If these states remain the lowest excited states in an amorphous, the structure of the phonon wing changes in the same way as in the case of low-frequency Raman spectra (Fig. 4) since the quasimomentum of an exciton then ceases

to be a good quantum number because of the loss of the spatial periodicity. A complicating factor in the use of the characteristics of the exciton-phonon wing for the identification of an amorphous is, however, formation of a large number of structural defects in the course of amorphization with levels located below those of intrinsic electron excitations.

4. RELAXATION OF THE STRUCTURE OF AMORPHICS

4.1. Alpha and beta relaxation

Formation of a glass is accompanied by an unlimited increase in the relaxation time and this is manifested by anomalous slowing down of the processes of establishment of an equilibrium in the region of vitrification of a liquid.⁴ This effect has been discovered in a study of quantitative characteristics of the Rayleigh scattering in glassy quartz³⁴ and inelastic incoherent neutron scattering in amorphous polybutadiene.³⁵ However, the macrorelaxation and microrelaxation processes continue even after the formation of a solid phase because the solid amorphous state is not in equilibrium with respect to a supercooled liquid at the same temperature. An example of macroscopic relaxation is a change in the dimensions of a sample (such as the well-known shortening of amorphous metal ribbons, etc.). Microscopic relaxation processes alter some of the fundamental properties of an amorphous as a solid. They are related to such a universal property of an amorphous as the *intrinsic (or internal) mobility*.³ In the case of molecular glasses these processes have been investigated in detail by Johari *et al.* (see Refs. 36–42 and the bibliography given there) using the method of dielectric losses. It has been established that, irrespective of the nature of the molecules forming a glass (a polymer or a low-molecular compound, an ionic salt, silicon or quartz) and irrespective of whether the glass is isotropic or anisotropic,⁴⁰ the main characteristic which is the loss-angle tangent $\tan \delta$ ($\delta = \epsilon_2/\epsilon_1$, where ϵ_2 and ϵ_1 are the imaginary and real parts of the permittivity) has a universal temperature dependence. A typical form of this dependence is shown in Fig. 7. It is clear from this figure that throughout the investi-

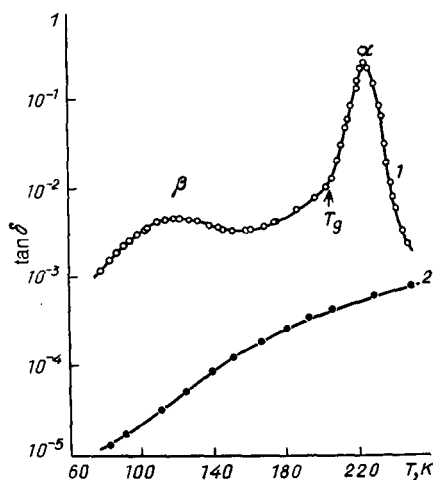


FIG. 7. Temperature dependences of the tangent of the dielectric-loss angle of a nematic glass (1) and a crystalline sample of OH-MBBA at 1 kHz (Ref. 39). Here, T_g is the glass-transition temperature.

gated temperature range the dielectric losses in a glass are one or two orders of magnitude higher than the losses in a crystal and that they exhibit a characteristic two-hump structure. These two humps represent two types of relaxation called the α and β relaxation processes which occur at high and low temperatures, respectively.

Relaxation is due to molecular motion and the occurrence of two types of relaxation indicates that there are two types of regions with different nature of dynamic ordering of the molecules. It follows from the above analysis of the widths of the neutron diffraction peaks of amorphous MBBA and EBBA, and also from other data,⁴³ that the dimensions of these regions can be from 10 to 100 Å. Therefore, the structure of a glass at the level of groups consisting of few molecules is inhomogeneous.

According to Johari *et al.*, these two types of ordered regions are as follows: I) regions with a relatively loose structure where the molecular rotation is unhindered (they are known as "mobility islands") and the motion in general is hindered by potential barriers much lower than the barrier associated with the glass transition; II) regions with close packing. If we make these assumptions, we can regard a glass as an assembly of polyhedra which are the main structural units (regions of type II) linked by intermediate regions which are loosely packed. In this model the β relaxation process originates from the fact that the rotation of molecules in regions with the loose structure is hindered so that the rotation is through small angles for short periods. The α relaxation process (which is the main mechanism) consists of rotation of molecules by larger angles in polyhedra for a longer time.

Other ideas on the inhomogeneity of the structure of glasses were developed by S.V. Nemilov.⁴⁴ According to him these type I and II regions exhibit ordering typical of a metastable liquid and of a crystal, respectively. However, ordering of the second type does not result in the formation of crystalline aggregates with all the thermodynamic properties of an equilibrium crystalline phase. In particular, the ordered regions have no phase boundaries. These two concepts of the relationship between the two types of relaxation with the two types of ordering have been used extensively in the modern approach not only to amorphous materials,⁴⁵ but also to plastic crystals.⁴⁶ Moreover, Grest and Cohen⁴⁷ suggested that the existence of such a universal property of amorphics as two-level systems (Sec. 5.4) is due to quasiliquid molecular clusters.

The existence of dielectric losses in glasses and the universality of their behavior are the most important observations supporting the description of glasses by the Goldstein model.⁴⁸ According to the Goldstein model, a liquid system consisting of N particles has an $(3N + 1)$ -dimensional potential energy surface with many minima of different depths. This multidimensional space is occupied gradually as the system evolves in time. At low temperatures the system is limited to a few deepest minima. The transitions between them require an activation energy and are temperature-dependent. The Goldstein model predicts the existence of "mobility islands" where local modifications are possible (between adjacent deep minima), but long-range motion is impossible. The model accounts for the existence of the β relaxation process at temperatures below the glass-transition point T_g and explains the evolution of the structure of

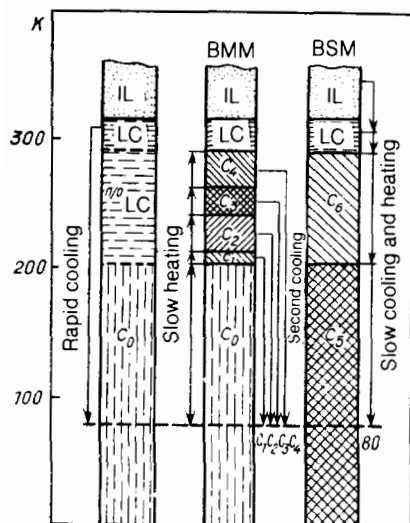


FIG. 8. Polymorphic phases of solid MBBA (Ref. 49). Here, IL is an isotropic liquid, LC is a liquid crystal, BMM is a branch of metastable modifications, and BSM is a branch of stable modifications.

amorphics during their heating above T_g as a consequence of the α relaxation process.

4.2. Multimode polymorphism

Undoubtedly, such a universal property of amorphics as the *multiplet nature of polymorphic modifications*, manifested by isothermal *multiplier* nature of polymorphic modifications, of a substance which forms a glass is related specifically to the high-temperature α relaxation.⁴⁹ Figure 8 shows schematically the polymorphic phases of solid MBBA for which this effect has been investigated in detail first and which illustrates its basic features. A refined scheme can be found in Ref. 50.

An isotropic liquid (IL) exists at temperatures $T \geq 317$ K, but at $T = 317$ K it transforms into a liquid crystal (LC). If the cooling rate is in excess of 1 K/s, a liquid crystal becomes glassy (at the glass-transition temperature $T_g \approx 205$ K) forming the main amorphous phase C_0 . This amorphous phase is stable during heating up to 205 K and then it undergoes a number of irreversible phase transitions in accordance with the chain $C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow C_4$. The last solid phase C_4 melts at 286 K and becomes a liquid crystal. It should be pointed out that the temperature range where these phase transitions occur corresponds to the range where the α relaxation process is observed in glassy MBBA.

A set of phases obtained in this way represents a branch of metastable modifications (BMM). These modifications are characterized by the fact that they transform from one to another only as a result of heating. Cooling of any of them does not induce the reverse structural transition, so that—for example at $T = 80$ K (as shown in Fig. 8)—depending on the previous thermal history of a sample, one can observe any phase belonging to the branch of metastable modifications (from C_0 to C_4) and this is the multimode polymorphism.

Slow cooling of MBBA in the liquid crystal form causes crystallization of the phase C_6 which is transformed reversibly to a low-temperature crystalline phase C_5 at $T \approx 205$ K. The set of these phases forms the branch of stable modifications (BSM). Therefore, depending on the rate of freezing of MBBA, it is possible to observe two branches of phase states:

the branch of metastable modifications (phases C_0 , C_1 , C_2 , C_3 , and C_4) and the branch of stable modifications (phases C_5 and C_6). Similar behavior is exhibited also by solid EBBA (Ref. 29).

4.3. Diffraction-spectroscopic analysis of polymorphic phases

The phenomenon of multimode polymorphism hinders identification of polymorphic phases and excludes temperature as the main indicator. Identification becomes more reliable only if we use a combined diffraction-spectroscopic method with typical results shown in Fig. 9.

Figure 9a shows a series of the diffraction intensity distribution curves for phases of the branch of metastable modifications of MBBA, whereas Fig. 9b gives the corresponding low-frequency Raman spectra. A comparison of the diffractograms fails to identify changes (qualitative and quantitative) in the structure of solid MBBA undergoing a series of transitions from the phase C_0 to the phase C_4 , whereas the corresponding fragments of the Raman spectra show clearly the gradual formation of the coherence of vibrations of solid MBBA, i.e., the appearance of the long-range translational symmetry producing gradually a structured Raman spectrum. For example, the diffraction patterns of the phases C_1 and C_4 are practically indistinguishable, but the Raman spectra indicate that the phase C_1 (and the phase C_2) is a *mesophase of the amorphous state*, whereas the phases C_3 and C_4 are already crystalline. This is an example of how spectroscopy has been used to establish for the first time the existence of mesophases in the solid state (which are similar to mesophases observed in the case of liquid crystals). By analogy with liquid crystals it has been suggested that the C_0 , C_1 ,

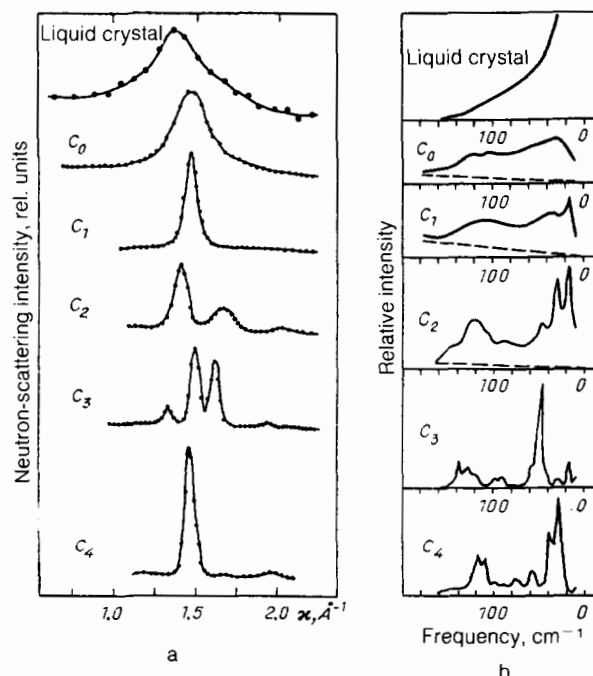


FIG. 9. Intensity distributions in the neutron diffractograms (a) and in the Raman spectra (b) of solid phases of MBBA (Ref. 38) at $T = 80$ K; in the case of the liquid crystal phase the temperature was $T = 296$ K.

and C_2 amorphous structures should be called nematic and smectic (A and C) amorphics.

Low-angle neutron scattering has been used to confirm this interpretation of the branch of metastable modifications.^{50,51} Figure 10 shows neutron scattering patterns of fully deuterated MBBA (D_{20}). An analysis of these patterns confirms that the C_0 phase has the nematic structure, whereas the structure of the C_1 phase is of the smectic A type and that of the C_2 phase has the tilted smectic structure, and the C_4 phase is crystalline.

Similar diffraction-spectroscopic investigations of the solid phases of EBBA have shown that the branch of stable modifications consists of two crystalline phases C_3 and C_4 , whereas the branch of metastable modifications consists of the phases C_1 and C_2 (Ref. 29). The phase C_2 is only slightly disordered. Therefore, the range of solid mesophases of EBBA is limited to the phase C_1 and partly the phase C_2 . It is worth drawing once again the attention to the absence of a nematic amorphous phase, although original liquid crystals are only nematic in both cases. Clearly, the tendency of EBBA to form a smectic phase in the liquid crystal region is frustrated by thermodynamic factors and such a phase appears after vitrification of EBBA due to the conformational

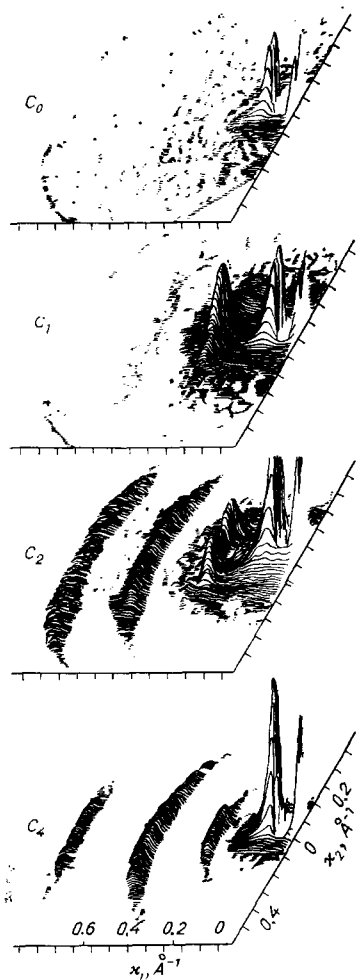


FIG. 10. Low-angle neutron scattering patterns of the MBBA modification D_{20} (Ref. 50). The vectors x_1 and x_2 give the direction of the magnetic field and of the vertical, respectively.

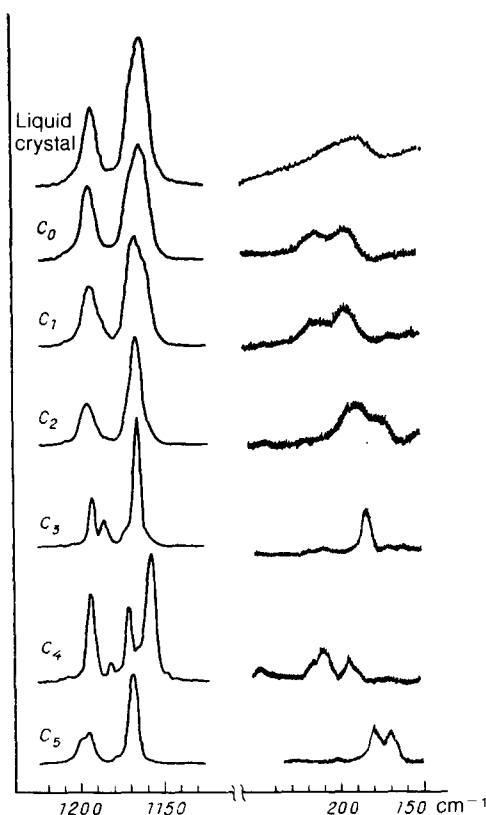


FIG. 11. Raman spectra of solid phases of MBBA (Ref. 27) recorded at $T = 80$ K; the spectrum of the liquid crystal phase was obtained at $T = 296$ K.

mobility of molecules. This mobility affects also the dependence of the low-frequency Raman spectrum of the C_1 phase on the rate of cooling of a liquid crystal (Ref. 29). The diffraction patterns remain undistinguishable.

Studies of relaxational phase transitions described above have failed to resolve the question of the participation of conformational changes in the molecule itself in these transitions. Figure 11 shows fragments of the Raman spectra obtained for solid MBBA phases in two regions²⁷ representing internal molecular vibrations. It is clear from this figure that the Raman spectra change greatly as a result of phase transitions, indicating changes in the molecular structure (short-range order). This is true also of the spectra of EBBA (Ref. 29). An analysis of the profiles of the bands representing the relevant vibrations can be used to determine these conformational changes. In this way the method of vibrational spectroscopy provides a convenient and effective method for characterization of solid phases and for studies of their relaxational evolution and associated conformational changes in the molecule.

4.4. Structural relaxation in cold-deposited films

Relaxation in amorphous films has not yet been investigated specifically, but its manifestation can be seen in the electron diffraction data mentioned earlier. Figure 12 demonstrates the influence of the rates of deposition, of the substrate temperature, and of the annealing duration on the distribution of the intensity of diffraction by tetracene films.¹⁹ It is clear from this figure that, as expected, the influence of the deposition rate is greater at higher substrate tempera-

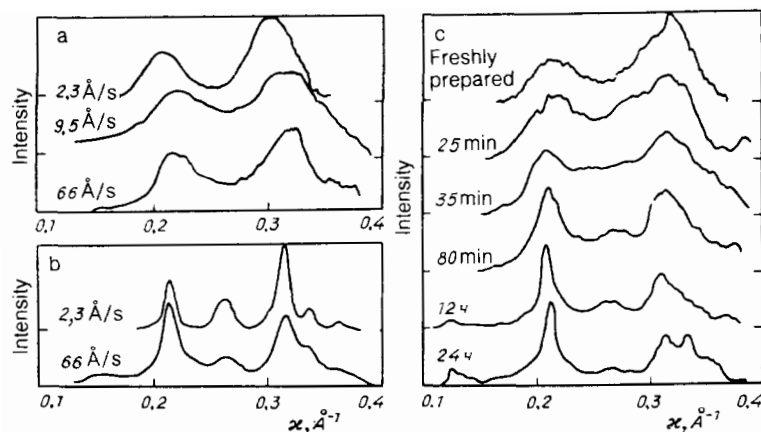


FIG. 12. Intensity distributions in the diffractograms obtained for tetracene films.¹⁹ a) Influence of the rate of deposition on a substrate kept at 80 K. b) Same as in Fig. 12a, but for films deposited on a substrate kept at 175 K. c) Influence of the duration of annealing in the case of films deposited on a substrate kept at 28 K; annealing temperature 150 K (25 min), 250 K (35 min), and 296 K for curves representing longer annealing.

tures. Annealing of an initially cold-deposited film also has a significant effect. The duration of annealing mentioned in the caption of Fig. 12 is the time interval between preparation of a film and recording of a diffractogram. The annealing temperature is that at which the diffractograms were recorded. The time after which the diffractogram ceased to vary was longer than the film heating time. This was evidence of the occurrence of relaxation processes in the film.

5. SPECTROSCOPY OF VIBRATIONAL STATES OF A MOLECULAR AMORPHIC

Experimental vibrational spectroscopy of molecular amorphics has been confined so far to glasses. No studies of molecular films have yet been made. The conditions under which films are prepared and stored (vacuum container, powder structure) prevent infrared absorption measurements. However, there is no reason why Raman spectroscopy should not be used and one would expect this technique to be applied in future if only for confirmation of the amorphous state.

In the case of glasses the situation is different. The available samples are convenient for infrared and Raman spectroscopic investigations. They can be prepared in any size, scattered relatively weakly (which is good from the point of view of the infrared absorption studies), and transparent in the visible range (which is desirable in the Raman spectroscopy applications). Nevertheless, there have been few experimental studies. This is clearly due to the fact that only in the spectroscopic investigations of MBBA and EBBA the vibrational spectroscopic data have been linked closely to the fundamental properties of the amorphous state. We shall continue along this trend and consider vibrational spectroscopy techniques as a method for investigating vibrational states of amorphics and mesophases.

5.1. Vibrational spectrum

The spectrum of the vibrational states of a molecular amorphous is, like the spectrum of a molecular crystal, largely similar to the vibrational spectrum of a molecule. This is the major advantage of the organic molecular substances because the "bare" vibrational states of the main structure unit of the short-range order can be calculated sufficiently accurately by modern methods and, in particular, the form of the vibrations can be found. It immediately places vibrational spectroscopy of molecular solids at a level comparable with the corresponding spectroscopy of free molecules.

We shall now go back to the example of MBBA. The vibrational spectrum of a free molecule of this compound consists of 117 vibrations, which are split into two regions: 9–1660 cm^{-1} with 96 vibrations, and 2930–3090 cm^{-1} with 21 vibrations. The nominal density of the vibrational states is plotted in Fig. 13. The conformational softness of the molecule is manifested by a large number of low-frequency vibrations. For example, in the region up to 100 cm^{-1} there are 9 vibrations and the lowest frequency of these is only 9 cm^{-1} . It is known from the physics of phonons in molecular crystals³⁰ that the short-range atom–atom potential of the intermolecular interaction gives rise to vibrational states which are due to external degrees of freedom of a molecule describing translational and rotational motion of the molecule as a whole with frequencies between zero and 150 cm^{-1} . These vibrations are characterized by a considerable dispersion so that the density of the vibrational states is characterized by a continuous distribution (this is manifested, for example, by the spectrum of a naphthalene crystal⁵²). In the case of an overlap of the spectrum of external vibrations with the spectrum of internal molecular vibrations, the vibrational spectrum becomes much more complicated (see, for example, the spectrum of an anthracene crystal in Ref. 30). In the case

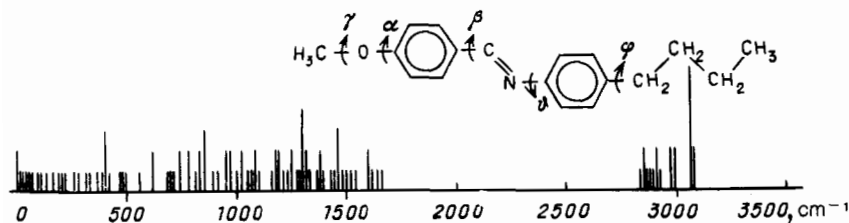


FIG. 13. Nominal density of vibrational states in the MBBA molecule. Results are given of a calculation made by V. A. Dement'ev for a molecular configuration corresponding to the angles $\alpha = \beta = \gamma = \varphi = 0$, $\nu = 40^\circ$. The inset shows the structural formula of the MBBA molecule.

of MBBA the spectrum is extremely complicated because of a large number of internal vibrations. One can no longer consider separately the external and internal degrees of freedom of this molecule. Both types of the degrees of freedom participate in each vibrational mode linking the conformation of the molecule to its motion as a whole. Therefore, this part of the vibrational spectrum is so sensitive to phase transitions. No calculations of the phonon spectra of MBBA crystals have yet been made.

5.2. Density of vibrational states. Inelastic incoherent neutron scattering spectroscopy

The most direct experimental method for investigating the density of vibrational states is inelastic incoherent neutron scattering (IINS). In the one-phonon scattering case the IINS cross section is given by

$$\sigma^{(1)}(\omega, T) = \sum_{i,j} F_i(\omega_j, \omega_0) (1 + n(\omega_j, T)) G_{ij}(\omega_j), \quad (5.1)$$

where the factor $F_i(\omega_j, \omega_0)$ contains familiar quantities describing the transfer of an energy ω_j from a neutron with an initial energy ω_0 to the excitation of vibrations in the scattering sample; $n(\omega, T)$ is the number of filled vibrational states; i is the number of an atom; $G_{ij}(\omega)$ is the density of vibrational states weighted by squares of the amplitudes of displacements of an atom i on excitation of a vibrational frequency ω_j (Ref. 53). If hydrogen is among the scattering atoms, the scattering by this element predominates because of its large IINS cross section and, therefore, for the majority of organic molecules (including MBBA) the scattering cross section $\sigma^{(1)}$ is replaced by the cross section for the scattering by the hydrogen atoms

$$\sigma^{(1)} \rightarrow \sigma_H^{(1)} = F_H(\omega, \omega_0) (1 + n(\omega, T)) G_H(\omega), \quad (5.2)$$

where $G_H(\omega)$ is the weighted (in terms of the squares of the displacements of the hydrogen atoms) density of the vibrational states

$$G_H(\omega) = \frac{M}{M_H} \sum_i \int |A_i^H|^2 \delta(\omega - \omega_i) dq. \quad (5.3)$$

In the above expression the quantities M and M_H represent the mass of the investigated molecule and of the hydrogen atom, the spectrum of the vibrations is summed over all the vibrational modes and integrated in the quasimomentum

space, and A_j^H is the amplitude of displacement of the hydrogen atom.

Many investigations of the IINS spectra of molecular crystals have shown (see, for example, Ref. 52) that at low temperatures these spectra are practically of the one-phonon nature and can be analyzed with the aid of Eq. (5.2). The quantity $G_H(\omega)$ obtained from the experimental spectrum then plays the role of the "reduced spectrum" which is a term used in an analysis of the Raman spectra of amorphics.⁵⁴

Detailed investigations have been made of IINS in molecular amorphics based on MBBA and EBBA.^{53,55,56} Figure 14 shows the experimental IINS spectra recorded at 90 K and the weighted densities of the vibrational states $G_H(\omega)$ derived in accordance with Eq. (5.2) for all the solid phases belonging to the branch of metastable modifications (Fig. 8) and for the phase C_5 belonging to the branch of stable modifications of MBBA. It is clear from Fig. 14 that phase transitions alter considerably both the IINS spectra and the densities of the vibrational states. The changes are observed in the low- and high-frequency parts of the vibrational spectrum. They are evidence of changes not only in the packing of molecules in the relevant solid phases, but also of changes in the molecular structure. Similar behavior is observed in the case of IINS spectra of EBBA.⁵⁵

A comparison of the densities $G_H(\omega)$ in the low-frequency region obtained for different phases of the branch of metastable modifications allows us to draw a number of conclusions on the nature of phase transitions in this branch. The $C_0 \rightarrow C_1$ transition causes practically no change in the density of states. However, the diffraction spectrum (Fig. 9a) shows a considerable narrowing of the peaks. Since the main features of the phonon spectrum in the low-frequency range are governed by the positions of the nearest neighbors (by the structure of the average order) these results indicate that the packing of the molecules is not affected by the phase transition in question, but the long-range order is modified, so that the nematic phase C_0 is transformed to the smectic A phase C_1 .

The subsequent transitions are accompanied by a considerable modification of the spectra of the density $G_H(\omega)$ demonstrating changes in the structure of the average order, i.e., of the molecular packing. It is clear from Fig. 14a that

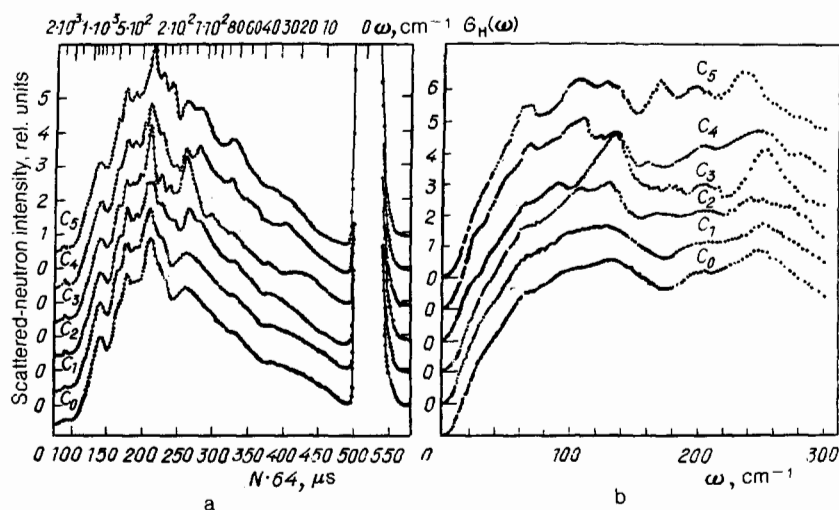


FIG. 14. Inelastic incoherent neutron scattering by solid phases (from C_0 to C_5) of MBBA at 90 K (Ref. 56): a) experimental results; b) weighted densities of the vibrational states (reduced inelastic incoherent neutron scattering spectra) $G_H(\omega)$ deduced using Eq. (5.2).

there are changes in the structure of the IINS spectrum also in the region of the hf internal molecular vibrations demonstrating that the $C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow C_4$ phase transitions are accompanied by conformational changes in the molecule (or in the structure of the short-range order).

These results allow us to understand why the density of the vibrational states in a molecular amorphous changes more in comparison with the density of a crystal than in the case of inorganic (such as Si) amorphics. Clearly, the relatively slight changes in the density of states of an inorganic amorphous are mainly due to the loss of the long-range order. This explains why in this case a transition from a crystal to an amorphous is usually represented as a continuous increase in the dimensions of a unit cell (in the limit, a cell covering the whole sample) ignoring the change in the structure of the short-range order.⁵⁴

We have to consider separately the asymptotic behavior of the densities $G_H(\omega)$ at low frequencies. In this range the frequency dependence in the spectrum of a crystal obeys the Debye law ω^2 , which means that the low-frequency part of $G_H(\omega)$ is the density of the states of acoustic phonons, which is typical of any crystal (see, for example, Ref. 54). Additional scattering is observed in the spectra of the amorphous phases C_0 and C_1 of MBBA and of the phase C_1 of EBBA (Refs. 53, 55, and 56), and this scattering increases considerably the amplitude of the density at low temperatures and it alters also the frequency dependence from ω^2 to $\omega^{1.3}$ (Fig. 15). This difference decreases at high temperatures.

Such excess IINS exhibited by an amorphous phase in the region of the Debye spectrum has been reported also for fused quartz.⁵⁷ Clearly, the phenomenon is universal as will be demonstrated clearly in a discussion of the properties of the low-frequency Raman spectra given in the next subsection.

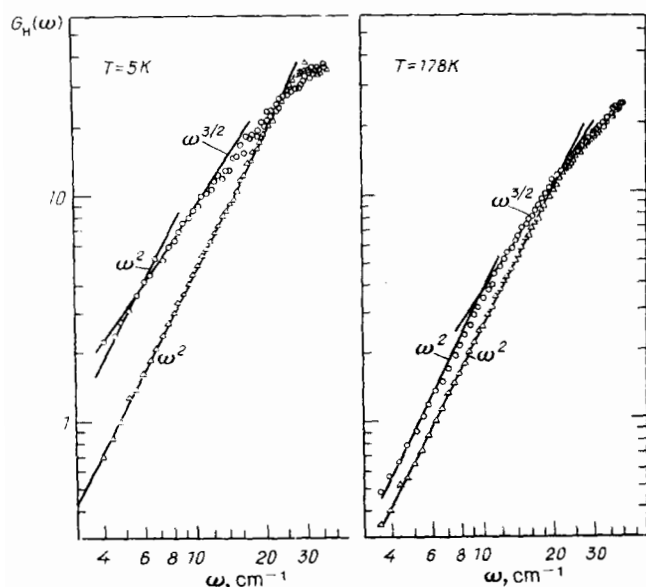


FIG. 15. Low-frequency asymptotic behavior of the density of the vibrational states of the C_0 (circles) and C_1 (triangles) phases of MBBA plotted on a logarithmic scale.⁵³

5.3. Raman spectra

5.3.1. General characterization of the optical spectra

The vibrational optical spectroscopy of polyatomic molecular solids is characterized by the circumstance that the Raman spectra are mainly of the one-phonon type. Consequently, the spectra of crystalline phases of such solids are affected greatly by the selection rule governing the quasimomentum of the phonon states: $q = Q \approx 0$. The transition to the amorphous state alters the selection rules, so that the optical field interacts with the total vibrational spectrum, i.e., the density of the vibrational states has a decisive influence on the first-order optical spectra.

In the region of the hf vibrations of molecular crystals, characterized by a narrow-band spectrum, the density of the vibrational states is highly structured (it is well approximated by a set of δ functions—see Ref. 52). In this range the vibrational spectrum is sensitive to changes in the phase state of a substance only to the degree to which changes affect the vibrational spectrum of the molecule. This is illustrated in Fig. 11. Therefore, the hf vibrational spectra are of interest from the point of view of the “molecular” approach to phase transitions because they can be used to determine the role of changes in the molecular conformation. In the case of real objects this range begins from 150 cm^{-1} .

The low-frequency part of the spectrum is more complex and, right from the very first spectroscopic investigations of amorphics, it has attracted investigators by the apparent ease of determination of the functions representing the density of the vibrational states (for a review see Ref. 54).

5.3.2. Density of states in the Raman spectra

The first-order Raman spectrum of an amorphous exhibiting harmonic vibrations can be described by^{58,59}

$$I_{ij}(\omega) = C_{ij}(\omega) g(\omega) (1 + n(\omega, T)) \omega^{-1}; \quad (5.4)$$

here, C_{ij} determines the coupling between a vibrational mode of frequency ω and the incident light in the case of a specific (ij) experimental geometry; $g(\omega)$ is the density of the vibrational states; $n(\omega, T)$ is the number of filled states. It is convenient to use the “reduced” spectrum

$$I_{ij \text{ red}} = I_{ij}(\omega) \omega (1 + n(\omega, T))^{-1} \approx C_{ij}(\omega) g(\omega) = G_{pi}(\omega). \quad (5.5)$$

The function $G_{pi}(\omega)$ then represents the density of the vibrational states weighted using the function representing the coupling between a vibrational mode and light, and in this sense it is analogous to the function G_H in Eq. (5.3).

A set of reduced Raman spectra for solid phases of MBBA is plotted in Fig. 16 together with the experimental spectra. The reduced spectra manifest the amorphous nature of the phases C_1 and C_2 to an even greater degree than the experimental spectra. The Raman spectrum of the C_1 phase has a boson peak at 13 cm^{-1} , which is due to an increase in the correlation length of the long-range order in a glass,⁶¹ in agreement with the broadening of the region of the long-range ordering in MBBA on transition from the C_0 to the C_1 phase deduced from the IINS spectra.

The reduced Raman spectra of the C_0 and C_1 phases are compared in Fig. 16b with the spectra of the weighted density of the vibrational states $G_H(\omega)$, i.e., with the reduced

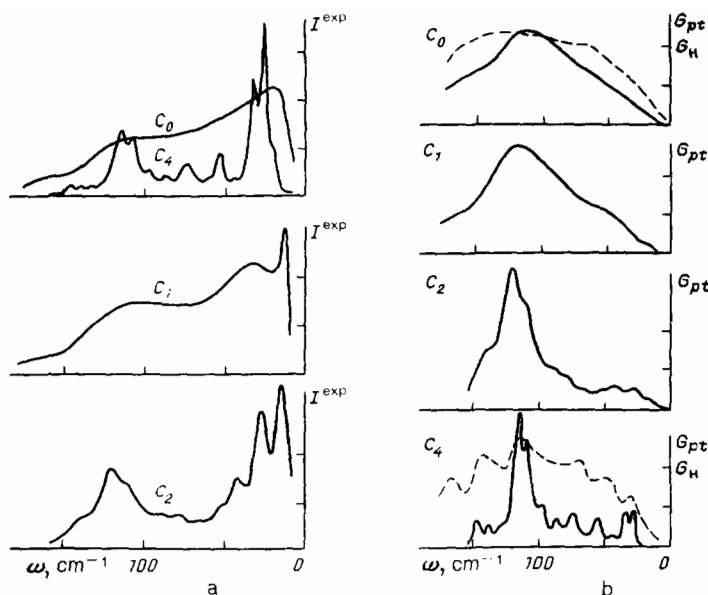


FIG. 16. Experimental (a) and reduced (b) low-frequency Raman spectra of the solid phases of MBBA (Ref. 60). $T = 80$ K. The dashed curves represent the reduced spectra of inelastic incoherent neutron scattering of the C_0 and C_4 phases at $T = 90$ K (Ref. 53).

IINS spectra. The difference between the $G_{pt}(\omega)$ and $G_H(\omega)$ spectra of the C_4 crystalline phase is clearly primarily due to selection of the modes in the $G_{pt}(\omega)$ spectrum because of the selection rule governing the quasimomentum. The difference between the $G_{pt}(\omega)$ and $G_H(\omega)$ spectra for the C_0 phase is a manifestation of the difference of the weighting factors in Eqs. (5.3) and (5.5). As demonstrated for a series of molecular crystals, the weighting factor for $G_H(\omega)$ hardly affects the similarity of this function to the density of the vibrational states $g(\omega)$. Consequently, a comparison of the $G_{pt}(\omega)$ and $G_H(\omega)$ spectra for the C_0 phase leads to the conclusion that the function $C_{ij}(\omega)$ representing the coupling between vibrations and light exhibits a strongly nonmonotonic frequency dependence.⁶⁰

Changes in the $G_{pt}(\omega)$ spectra along the series of phases C_0 , C_1 , C_2 , and C_4 reflect the changes occurring in the density of the vibrational states and in the function $C_{ij}(\omega)$. A comparison of the $G_H(\omega)$ spectra of the C_0 and C_4 phases shows that the relatively small changes in the density of the vibrational states along the series of structural transitions cannot account for the striking changes in the $G_{pt}(\omega)$ spectra. The main reason for the latter changes is the function $C_{ij}(\omega)$, which can be represented in the form^{58,59}

$$C_{ij}(\omega_s) = \sum_{k,l} B_{kl}(\omega_s) \frac{8\pi\Lambda_s^{-1}}{(q^2 - \Lambda_s^{-2})^2} p_{ik} p_{jl}; \quad (5.6)$$

where the index s labels the vibrational modes, B_{kl} contains the polarization characteristics of the modes; Λ_s is the correlation length in which the s mode can be represented by a plane wave; p_{ik} are the components of the elastooptic constants. The Lorentzian of Eq. (5.6) describes the "extended" selection rule governing the quasimomentum. In the limit $\Lambda_s \rightarrow \infty$ it reduces to $\delta(\omega)$ and governs the selection rule $q \approx 0$ for a crystal. If Λ_s is finite, the selection rules are determined by the dispersion of the quasimomenta $\Delta q \approx 1.3\Lambda_s^{-1}$. Therefore, the smaller (larger) the value of Λ_s , the greater (smaller) is the smearing of the s mode in the Raman spectrum. The value of Λ_s varies differently for different modes and this accounts for the different structure of

G_{pt} in the case of the spectra of the C_1 , C_2 , and C_4 phases.

In the limit $\omega \rightarrow 0$ we find that the Debye approximation yields $C_{ij}(\omega) \approx \omega^2$ for an amorphous.^{58,59} This means that at low frequencies we have $G_{pt}(\omega) \approx \omega^4$. However, the $G_{pt}(\omega)$ spectrum of the C_0 phase of MBBA does not obey this dependence in the frequency range $\omega < 25 \text{ cm}^{-1}$. As in the case of the IINS spectra, the amplitude of the function $G_{pt}(\omega)$ deduced from the experimental spectrum is much larger than the quantity governed by the ω^4 law. The experimental spectrum exhibits an excess scattering at low frequencies. Therefore, in the case of the IINS and the Raman scattering of light we are dealing with the universal dynamic property of an amorphous which is the quasielastic scattering. It is known that such scattering is a manifestation of the universal property of organic glasses which is a slow (reorientational) motion of structure elements in a sample. However, we have mentioned already the occurrence of internal motion. It represents reorientational modification of the structure of these soft molecules corresponding to the β relaxation processes. This problem is closely connected to the specific low-frequency states of an amorphous.

5.4. Tunnel states

The most widely used model of the tunnel states is that postulating two-level states⁶²⁻⁶⁶ introduced in order to account for the anomalous behavior of the thermal properties of amorphics at low temperatures.³⁾ These states correspond to the degrees of freedom describing the tunneling of atoms or groups of atoms from one potential well to another (relaxation processes occurring in the β relaxation region). Osad'ko and Shtvgashev⁶⁷ introduced the concept of a quantum of excitation of two level states and of a tunnelon. The energy characteristics of a tunnelon are the difference between its energies in the two states of a given system Δ and the tunneling parameter λ . The physical reason for the introduction of two-level states is the relaxational motion that results in ordering of the structure. Such ordering can be considered as a transition of an amorphous system from one

potential well of a two-level state to another. We have mentioned earlier two types of ordering of amorphics (Sec. 4.1), so that it is obvious that two-level states may be associated with liquid-type ordering, i.e., with the existence of any homogeneity in the structure of an amorphic at the level of a group of molecules. We have mentioned earlier that one of the models of a two-level state is a quasiliquid molecular cluster.⁴⁷ The inhomogeneity of a quasiliquid structure of this kind gives rise to a set of two-level states which differ in respect of the parameters Δ and λ . Since the structural parameters of the packing of molecules are known to obey the Gaussian distribution,¹⁹ it has been suggested that the parameters Δ and λ of tunnelons also have a Gaussian distribution,^{68,70} resulting in a frequency dependence of the density of the energy of the tunnel states given by

$$\rho = \rho_0 \left(\frac{E}{\hbar\omega_0} \right)^{0.3-0.5}. \quad (5.7)$$

We can thus see that introduction of two-level states can account in a natural manner for the existence of slow reorientational motion giving rise to quasielastic scattering in the IINS and Raman spectra. The nature of these states makes the quasielastic scattering of neutrons⁷¹⁻⁷⁴ and photons⁵⁸ a truly universal property of amorphics.

We shall conclude by noting that spectroscopy has played a decisive role in confirming the model of two-level states as the main description of the low-energy states of amorphics. The existence of two-level states has been postulated during the early stages of the development of the physics of the amorphous state.⁶²⁻⁶⁶ However, there are other possible explanations of the universal anomalous thermal properties. An important confirmation of the model of two-level states has been the discovery of the quasielastic scattering of neutrons and photons described above. However, undoubtedly the final recognition of two-level states has been provided by the results obtained by selective laser spectroscopy of amorphics (Sec. 7).

6. SPECTROSCOPY OF ELECTRONIC STATES

6.1. General characterization of electronic states

In this section we shall be interested in that side of studies of electronic states of amorphics which relates them to excitonic states of the corresponding molecular crystals. We shall therefore be interested primarily in films of amorphous acenes because the crystals of these compounds manifest particularly strikingly the excitonic properties.⁷⁵ Glasses are used widely in studies of electronic states as matrices containing the dissolved molecules. Laser spectroscopy of such systems will be considered in the next section.

The energy of excitonic (purely electronic) states of a molecular crystal with two molecules per electron cell is described by

$$\varepsilon(\mathbf{k}) = \varepsilon_g + D + L_{11}(\mathbf{k}) \pm L_{12}(\mathbf{k}), \quad (6.1)$$

where ε_g is the energy of excitation of a free molecule and D describes the statistical gas-crystal shift due to nonresonant interaction between an excited molecule and the surrounding unexcited molecules; $L_{11}(\mathbf{k})$ and $L_{12}(\mathbf{k})$ represent the resonant interaction between the translationally equivalent and translationally inequivalent molecules, respectively. The quantity $\Delta = 2L_{12}(0)$ is the Davydov splitting of the

excitonic absorption bands. It is important to stress that practically all the acenes obey $D \gg L_{11}, L_{12}$.

The transition from a crystal to an amorphic not only changes the selection rule $\mathbf{k} = 0$ for optical transitions, but also the values of D , $L_{11}(\mathbf{k})$, and $L_{12}(\mathbf{k})$. As pointed out earlier, amorphous films are systems with a static disorder. Consequently, the change in the intermolecular distances $\Delta r/r$ results in relative changes in $D(\sigma/D, \sigma = \Delta D)$, L_{11} and L_{12} (Ref. 14) ($l/L, l = \Delta L$).

The probability of finding a specific value of ΔD is given by the expression

$$N(\Delta D) = (2\pi\sigma^2)^{-1/2} \exp \left[-\frac{(\Delta D)^2}{2\sigma^2} \right]. \quad (6.2)$$

Similar expressions can be written down for $N(\Delta L)$.

The ratio of σ to the half-width of the excitonic energy band $B[B \approx L_{12}(9)]$ governs the degree of disorder of an amorphic. A weak structural disorder corresponds to the case $\sigma/B < 0.3$ (Ref. 76) and when the ratio in question becomes $\sigma/B > 0.3$ the system exhibits an intermediate disorder. In the case of a weak disorder the optical transitions in an amorphic are similar to those in a crystal and the latter are only slightly disturbed by the additional scattering due to the disorder. The result is the appearance of an Urbach tail in the low-frequency wing of the absorption spectrum (as found in the spectra of amorphous silicon and germanium).

If $\sigma > 0.3B$, the excitonic energy bands of a crystal change to a distribution of the local states of the Gaussian type in an amorphic (Fig. 17) and the optical transitions no longer obey the law of conservation of the quasimomentum. An inhomogeneous width of an absorption band in the optical spectrum is governed by the value of σ corresponding to the average fluctuation of a static shift in Eq. (6.1). We are speaking here only of fluctuations of the term D . Since $D \gg L_{11}, L_{12}$, the fluctuations of the resonance terms obey $l \ll \sigma$ so that they play no significant role in the absorption spectra. In this case of the intermediate degree of structural disorder the absorption band profiles are governed by the distributions $N(\varepsilon)$ and do not obey the Urbach rule in the tails of the short-wavelength wings. Amorphous films of tetracene and pentacene deposited on a cold substrate and in-

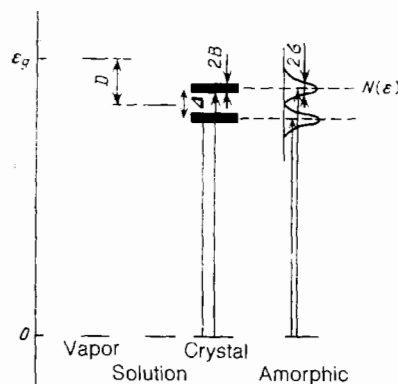


FIG. 17. Spectrum of the electronic states of molecular solids. Here, ε_g is the energy of an electron excitation of a molecule, $N(\varepsilon)$ is the density of the electronic states, D is the static shift, Δ is the Davydov splitting, $2B$ is the width of an exciton band, and 2σ is the width of an absorption band at its midamplitude.

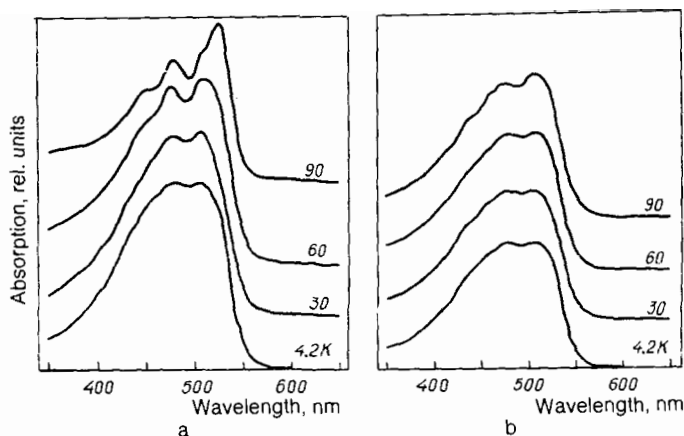


FIG. 18. Absorption spectra of cold-deposited tetracene films⁷⁶: a) freshly prepared films (deposition rate 50 Å/s, film thickness 2000 Å, residual pressure in the chamber less than 5×10^{-6} mbar; numbers represent the substrate temperature during deposition of a film; the spectra were recorded at the same temperatures); b) spectra of a film deposited on a substrate at $T = 4.2$ K, recorded during various stages of the annealing process. The numbers alongside the curves are the temperatures at which the spectra were recorded. Heating between measurements was at a rate of 0.6 K/min.

vestigated in greatest detail by absorption spectroscopy belong to the latter case.

In general, random disordering is accompanied by the diagonal and nondiagonal disorder. However, because of the inequality $l \ll \sigma$, we can regard amorphous acene films as belonging to systems with the diagonal disorder.¹⁴

6.2. Absorption spectra of cold-deposited acene films

The absorption spectra of tetracene films at wavelengths corresponding to the first electronic-transition $S_0 \rightarrow S_1$ are shown in Fig. 18. Cooling of the substrate broadens the spectra of the freshly prepared films (Fig. 18a) and shifts them to shorter wavelengths. Heating of a film deposited on a substrate kept at a temperature of 4.2 K exhibits sharpening of the spectral features right up to 90 K (Fig. 18b).

Quantitative information was obtained by subjecting the widest experimental spectrum of a freshly prepared film at 4.2 K (Fig. 18a) to a computer analysis of the profile. The analysis was based on the assumption that the observed absorption band is a superposition of Gaussians corresponding to two series of bands representing two components of the Davydov doublet $\bar{\nu}_0(1)$ and $\bar{\nu}_0(2)$ of a pure crystal, and their vibronic replicas represent the totally symmetric vibration at 1380 cm^{-1} . A profile analysis was made in three

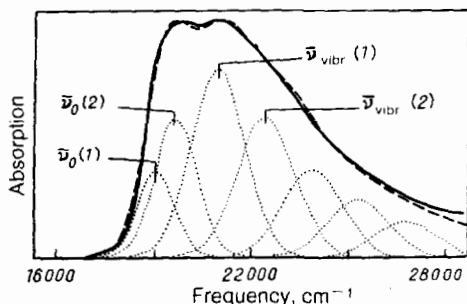


FIG. 19. profile analysis of the absorption spectrum of a freshly prepared tetracene film⁷⁶ recorded at $T = 4.2$ K. The dashed curve represents the envelope of the dotted curves. The continuous curve is the experimental spectrum. Here, $\bar{\nu}_0(1)$, $\bar{\nu}_0(2)$, $\bar{\nu}_{\text{vib}}(1)$, and $\bar{\nu}_{\text{vib}}(2)$ represent the positions of the centers of gravity of the bands of two Davydov components of the exciton absorption and of the first vibronic band.

stages. The first stage was the optimization of the widths of the absorption bands and this was followed by the optimization of the band positions on condition that the widths and intensities remained constant; the final stage was the optimization of the intensities. The results of this procedure are plotted in Fig. 19. The distance between the maxima $\bar{\nu}_0(1)$ and $\bar{\nu}_0(2)$ was found to be close to the magnitude of the Davydov splitting in a crystal ($\sim 700 \text{ cm}^{-1}$). The Gaussian widths of the bands were quantities of the same order of magnitude. Therefore, these results demonstrate that tetracene films do indeed belong to the class of systems with an intermediate structural disorder. The experimental spectrum did not have the Urbach tail in the short-wavelength wing and it was described very well by a set of Gaussian curves.

Electron microscopic investigations of the films made it possible to determine the average fluctuation in the intermolecular distance, which was used to calculate the widths of the absorption bands of the lowest components of the Davydov doublet as a function of the substrate temperature, which again agreed very well with the experimental results.⁷⁶

The main feature of the absorption spectrum was the presence of a series of band doublets corresponding to the factor group splitting by a crystal. This confirmed one of the main conclusions obtained from electron microscopy (see Sec. 3.2) that the average order in an amorphous film consists of pair packing of molecules and the relative orientation in a pair changes (relaxes!) on transition from the amorphous to the crystalline state. This is the most general property of amorphous acene films, as demonstrated by a profile analysis of the absorption spectrum of the $S_0 \rightarrow S_1$ transition in a film of pentacene.⁷⁶

6.3. Vibronic spectra

The problem of the vibronic states is closely related to the analysis of the absorption spectrum of an amorphous film. The vibronic states of a molecular crystal are classified as one-, two-, and many-particle,⁷⁵ depending on the nature of the vibronic coupling, which determines the characteristic form of the vibronic spectrum of a crystal.

In the general case of a one-phonon vibronic state (involving one internal molecular vibration), the energy spec-

trum consists of a dissociated two-particle state and a one-particle bound state if the energy of the electronic-vibrational coupling is sufficient to split off such a state. Consequently, the absorption spectrum exhibits two types of ions: wide bands due to the two-particle absorption and narrow bands due to the one-particle absorption⁷⁵; the relative intensities of these bands depend on the nature of the vibronic coupling.

The vibronic spectrum of an amorphous substance depends on the degree of the structural disorder.⁷⁷ If $\sigma/B < 0.3$, the disorder is weak and the spectrum of a crystal is practically unaffected by the transition to the amorphous state.

The narrow one-particle absorption bands become somewhat broader in the amorphous state and this is typical of weakly disordered systems (such as isotopically mixed crystals⁷⁵), whereas the two-particle bands are practically unaffected.

In the intermediate structural disorder case characterized by $\sigma/B > 0.3$ there is a change in the actual meaning of the vibronic states. The spectrum of the energies in the region of the one- and two-particle states changes to a set of local excitations and each of them has a Gaussian distribution. The greatest changes in the absorption spectrum are then exhibited by the one-particle vibronic absorption bands which become inhomogeneously broadened to a width σ . The two-particle absorption bands which already have a width $\sim B$ in the case of a crystal are broadened much less because $\sigma < B$ (Ref. 77). It therefore follows that the vibronic spectrum of an amorphous differs considerably from the spectrum of a crystal if the latter is mainly of the one-particle nature (this is true, for example, of the spectrum of benzene—see Ref. 75), but the difference is small if the spectrum of a crystal is of the two-particle nature (this applies to anthracene⁷⁷ and all higher acenes). Since the vibronic spectra of crystals of tetracene and pentacene are of the two-particle nature, we can see why the vibronic spectra of amorphous films of these compounds are broadened less compared with crystals, in contrast to the broadening of the absorption bands representing purely electronic transitions.¹⁴ The vibronic absorption bands of amorphous tetracene and pentacene films correspond to the situation in which the electronic and vibrational excitations are localized at different molecules and the distances between them are different for different pairs, but these distances also have a Gaussian distribution. A similar approach accounts for the two-phonon spectrum of HCl (Ref. 78).

6.4. Fluorescence of cold-deposited films

Luminescence spectroscopy provides means for the investigation of relaxed excited states. When higher states in the electronic spectrum are excited, then during the lifetime of an excited state the excitation relaxes along internal molecular channels to the lowest excited state and its subsequent fate is determined either by luminescence or relaxation to the states of structure defects. One of such characteristic defects in an amorphous is the state of a pair of molecules of the excimer type. The intermolecular potential of such a pair is repulsive in the ground state, so that a bound state is not formed. However, in the excited state the potential of a pair has a minimum¹⁴ and the corresponding levels are located below the electronic excitation state of mon-

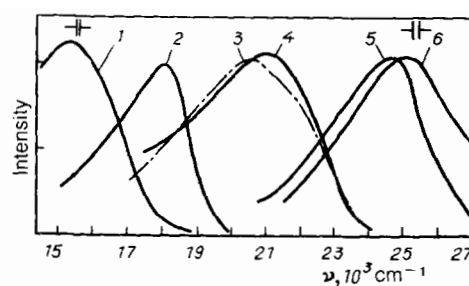


FIG. 20. Fluorescence spectra of films deposited at $T = 77$ K (Ref. 14): 1) tetracene; 2) perylene; 3) fluoranthene; 4) anthracene; 5) chrysene; 6) naphthalene.

omers of the basic substance. Consequently, the fluorescence spectra of amorphous films are of the wide-band nature and are shifted toward the red wavelengths (Fig. 20), in agreement with the excimer luminescence scheme. The amorphous state is characterized by a set of such excimer-like defects and the total concentration of the defect centers is then $\sim 1\%$. Investigations of the time-resolved luminescence of anthracene film⁷⁹ have indeed confirmed that the fluorescence spectrum represents a superposition of three bands with different lifetimes corresponding to different pair conformations differing in respect of the degree of overlap of the benzene rings and the degree to which the short molecular axes are parallel. In the case of tetracene⁸⁰ it has been found that time-resolved spectroscopy reveals a strong excimer band superimposed on the band of monomer defects. We can therefore expect such time-resolved luminescence investigations to be useful in studies of structural relaxation of films.

6.5. Triplet states and transfer of excitation

Phosphorescence of molecular amorphics has been investigated in greatest detail in the case of evaporated films of benzophenone, phenanthrene, and anthraquinone, and of glassy benzophenone.⁸¹ It has been established that the phosphorescence spectra of these amorphics depend on time (Fig. 21). After a short time ($10 < \tau < 100 \mu s$) the phospho-

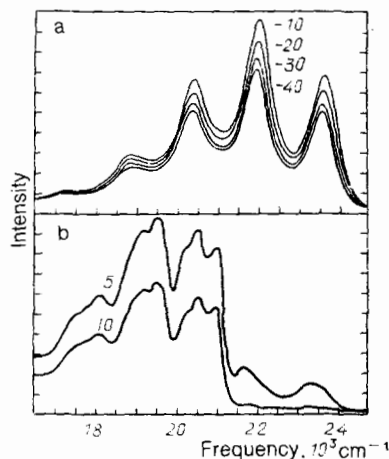


FIG. 21. Time-integrated phosphorescence of a freshly prepared amorphous benzophenone film deposited at 77 K (Ref. 81). The numbers give the delay times between pulses from an exciting nitrogen laser and the moment when a detector was switched on. a) Time in microseconds; b) time in milliseconds.

rescence spectrum represents the spectrum of isolated benzophenone molecules subjected to inhomogeneous broadening at their positions (Fig. 21a). This broadening can be shown to be due to the dispersion of the flexible angles between the phenyl rings. The center of the average band of the purely electronic transition is shifted in the red direction compared with the spectrum of a crystal because of the diffusion-controlled relaxation of the energy of the triplet excitation within a Gaussian set of the T_1 states of the amorphous. The intensity of the spectrum decreases with time and a new spectrum appears at longer wavelengths (Fig. 21b) due to the phosphorescence of structure defects.

This striking result is of intrinsic interest and, moreover, it provides means for a quantitative investigation of the transfer of excitation from "host" to "impurity" states of an amorphous on the basis of the time dependence of the ratio of the intensities in the spectra shown in Figs. 21a and 21b. An investigation of this kind demonstrated that the transfer of excitation in an amorphous can be explained quantitatively using the theory of Ref. 82 based on the effective medium approximation and applied to an asymmetric distribution of the hopping rates (a related topic was considered in Ref. 83, which was concerned with generalization of a self-consistent diagram expansion).

It has thus been shown that the transfer of a triplet excitation in organic amorphics is of dispersive (time-dependent) nature and can be explained by a stochastic model dealing with disordering of the energies of states and not with structural disordering, although physically the former is the consequence of the latter. Propagation of an excitation within an inhomogeneously broadened distribution of states represents the case of relaxation of an individual particle in a series of hierarchically related consecutive events, when usually the faster step includes a slower one.⁸¹

7. SELECTIVE LASER SPECTROSCOPY OF AMORPHICS

7.1. Nonexponential kinetics of glasses

We have considered so far the spectral properties of an amorphous as such. In this section we shall discuss spectroscopy of electronic states of an impurity center in an amorphous medium. Major progress has been made in this field during the last decade and this has been due to, on the one hand, rapid development of various methods of selective laser spectroscopy^{84,85} and, on the other, due to the circumstance that this spectroscopy has led to the development of an experimental method for investigating two-level states.

Selective laser spectroscopy involves determination of the kinetic parameters of the processes of decay of an electronic excitation of a molecule by spectroscopic or time-dependent methods. It is therefore sometimes called also optical dephasing or damping spectroscopy. Before we consider selective laser spectroscopy methods, we must summarize general characteristics of kinetic processes in glasses.

As pointed out above, a large number of different characteristics of organic amorphics can be described satisfactorily as a function of the microscopic position parameter using the Gaussian distribution function. A striking example of this situation is the above analysis of the absorption band profiles of amorphous tetracene (Sec. 5.2). It demonstrates the fact that the ground and excited electronic states are position-sensitive and have a distribution reflecting random

fluctuations of the intermolecular conformations.¹⁹ The conclusion about the kinetics of elementary electronic processes which can be drawn from this observation⁶⁸ is that the rates of these processes should be position-sensitive leading to a dispersion of the relaxation times due to the nonexponential kinetics. This should be manifested in, for example, studies of the diffusion of free charges or of electronic excitations. If we begin with a random position of an energy level of a molecule within an inhomogeneous local distribution, we find that a diffusing excitation relaxes from the energy point of view if the width of the energy distribution is $\gg kT$. The process can be regarded as a sequence of linked relaxation stages. For example, the time dependence of the diffusion of triplet states in amorphous benzophenone mentioned in Sec. 6.5 (Ref. 81) follows a law of the type $\exp[-(t/t_0)^\alpha]$, which is in agreement with an analysis of relaxation in a system undergoing hierarchically related events.^{86,87}

Random fluctuations of molecular environment in an amorphous may influence also the chemical reaction rate. Thus, it has been shown that a reversal of photochemical transformation of the spiropyran molecule to the merocyanine form in a polymer matrix⁸⁸ can be understood on the basis of a nonexponential dispersive reaction.⁸⁹ The dispersion of the reaction constants is the result of random variation of an energy barrier controlled by molecular rotation. It is found that the hypothesis of the Gaussian distribution of the activation energy provides a satisfactory basis for a quantitative description of the experimental results. A very similar procedure has been used to show that the nonexponential kinetics of the extraction of hydrogen from organic glasses⁹⁰ can also be explained in terms of random fluctuations of the critical reaction parameter, which in this case is the state to which a proton tunnels in a two-well potential.

We thus reach the conclusion that the *nonexponential kinetics* is one further universal property of organic amorphics.⁶⁸ Consequently, the relaxation processes involving two-level systems should be first-order dispersive reactions on the assumption that local relaxation is a tunnel process and the tunneling parameters Δ and λ obey a Gaussian distribution.

7.2. Relaxation processes and selective laser spectroscopy methods

Spectroscopic methods for the investigation of relaxation are based on the temperature dependence of the homogeneous width Γ_{SLS} of an electronic transition (the subscript SLS refers to selective laser spectroscopy). The need to separate narrow bands with a homogeneous width against the background of wide absorption and fluorescence bands of pure and doped amorphous systems has led to a rapid development of selective laser spectroscopy methods which began in the early seventies. The number of published papers on the subject is very large, so that we shall refer the reader only to fairly complete reviews^{84,91-95} and to some recent overview papers^{85,96-103} which are cited in the text below.

Various methods have been developed for the determination of Γ_{SLS} and among these are hole (dip) burning spectroscopy, selective excitation (fluorescence) spectroscopy, and holographic hole burning.^{85,96} All these methods result in significant narrowing of absorption or luminescence

bands, compared with the results obtained by conventional spectroscopy, since this makes it possible to eliminate the influence of a static structural disorder on the frequency of an optical transition.

Coherent or time-dependent selective laser spectroscopy methods have become popular recently^{85,96} and they include photon echo, stimulated or cumulation photon echo, time-resolved photochemical holography, and detection of hole burning on the basis of induced damping. These methods yield the damping time $\tau = 2\pi/\Gamma_{\text{SLS}}$.

For a long time it had been assumed that the values of Γ_{SLS} measured or calculated on the basis of various spectroscopic and time-resolved experiments are concerned with the same homogeneous measurement of a band by selective laser spectroscopy or a band with a homogeneous width. However, a detailed discussion is given in Ref. 96 of the circumstance that in reality each of the selective laser spectroscopy methods has its own characteristic time (for example, the measurement time in the photon echo method is 10^{-11} – 10^{-9} s, whereas in the hole burning spectroscopy it is 10^2 s, etc.). Therefore, the measured values of Γ_{SLS} and τ in the case of an amorphous characterized by a set of relaxation times represent different relaxation processes. This can in part account for the disagreement of the values of Γ_{SLS} obtained by different methods.

The origin of the relationship between the homogeneous width of a band or the decay time, on the one hand, and relaxation processes in an amorphous on the other, can be understood if we consider a model of an impurity center.

7.3. Model of an impurity center in an amorphous

The model adopted at present is as follows (see, for example, the review given in Ref. 103 and the bibliography cited there). Optical electrons of an impurity molecule interact with tunnel two-level states of an amorphous (as shown schematically in Fig. 22a). The tunnelon-phonon interaction (i.e. the interaction of two-level states with the thermostat) is responsible for the difference between the two-level states representing the ground and excited electronic states of an impurity molecule (as shown schematically in Fig. 22b). The band widths of optical transitions accompanied by the absorption (Γ_1) and emission (resonant Γ_2 or nonresonant Γ_3) of light are described by the parameters of these interactions. The static disordering of the average order gives rise to a dependence of the energies of the levels of a

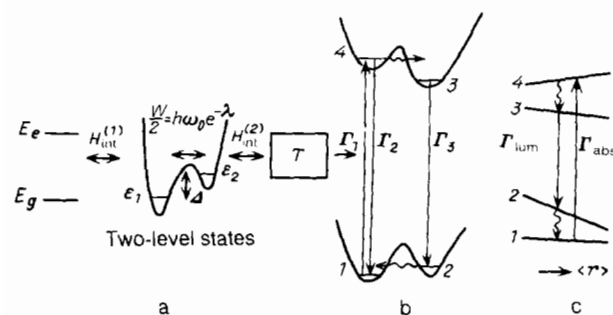


FIG. 22. Model of an impurity center in an amorphous. Here, E_g and E_e are the energies of the ground and excited states of an impurity molecule; the rest of the notation is explained in text.

two-well potential of a molecule in an amorphous system on the parameter of such disordering $\langle r \rangle$ (Fig. 22c). A slow relaxation-induced change in this parameter (β relaxation) makes an additional contribution to the band width because of a change in the frequency of an electronic transition with time, which is known as spectral diffusion.⁹⁶

In addition to relaxation processes involving low-energy two-level states, the damping of an electronic excitation may be due to the interaction of the electrons of a molecule with local or acoustic vibrations of the matrix.

The multiplet nature of the relaxation processes responsible for the width Γ_{SLS} of a band observed by selective laser spectroscopy is manifested most strikingly in the temperature dependence of the band width,⁹⁶ which can be described as follows:

$$\Gamma_{\text{SLS}} = aT^\alpha + bT^\beta + ce^{-\Delta E/kT} + dT^{\delta-1} \quad (7.1)$$

The first term in this equation describes the damping due to the tunnel relaxation processes involving two-level states or the electron-tunnelon interaction of an impurity molecule with the host matrix. It follows from the experimental results that the parameter a depends on the nature of the amorphous matrix and the parameter α lies within a narrow range defined by $1 \leq \alpha \leq 1.7$ (on the average, it is found that $\alpha = 1.3$ —see Ref. 96). The second term describes the relaxation processes due to spectral diffusion.^{85,96} As in the tunnel relaxation case, the parameter b is governed by the nature of the amorphous and the parameter β lies within the interval $0.7 \leq \beta \leq 1.3$ (on the average $\beta \approx 1$). The last two terms in Eq. (7.1) describe the damping due to the interaction of an electronic excitation of an impurity molecule with local and acoustic vibrations of the matrix, respectively. Since the energy of local vibrations is $\Delta E \geq 20 \text{ cm}^{-1}$, the interaction with local vibrations is important only at $T > 10 \text{ K}$. At low temperatures the contribution due to the interaction with the acoustic vibrations is also negligible. Therefore, at temperatures $T < 10 \text{ K}$ the main contribution to the damping of a band with a homogeneous width comes from relaxation processes described by the first two terms. Only the first process is responsible for the intrinsic homogeneous width.

Representation of the temperature dependence of the width of a homogeneous band in a form given by Eq. (7.1) makes it possible to account for two main features of SLS bands of amorphics compared with the bands of impurity centers in crystals: at low temperatures the SLS bands of amorphics are characterized by: 1) a value of Γ_{SLS} which is between one and three orders of magnitude greater than in the case of crystalline media; 2) a characteristic relatively slow temperature dependence $\Gamma_{\text{SLS}} \propto T^m$, where $0.5 \leq m \leq 1.8$. These characteristics are a direct experimental proof of the existence of the tunnel states (tunnelons) and are of universal nature.

7.4. Spectroscopic investigation of relaxation

7.4.1. Selective excitation spectroscopy

The relationship between the width of the luminescence and absorption bands deduced from the scheme in Fig. 22b is given by the expression¹⁰⁰

$$\Gamma_{\text{lum}} = \frac{|S_3 - S_2|}{|S_4 - S_1|} \Gamma_{\text{abs}}, \quad (7.2)$$

where S_i represents the slope of the dependence of the energy of the i -th level on the parameter $\langle r \rangle$. If $|S_3 - S_2| \ll |S_4 - S_1|$, then $\Gamma_{lum} \ll \Gamma_{abs}$ and a narrow luminescence band can be observed even when the excitation band is wide. This is how selective excitation of fluorescence was achieved for the first time.¹⁰⁴ However, selective excitation spectroscopy is applied relatively rarely to molecular amorphics.⁸⁵ One of the few examples of such applications to an impurity-free amorphous is the selective excitation of the phosphorescence within a wide $S_0 \rightarrow T_1$ absorption band at $T = 4.2$ K in a film of β -bromonaphthalene cold-deposited at 4.2 K. It was established that scanning of the excitation energy in the direction of approach to the phosphorescence spectrum¹⁰⁵ within an inhomogeneously broadened profile of a purely electronic transition reduced the Stokes shift between the phosphorescence and absorption. This was evidence of a gradual reduction in the ability of an electron excitation to diffuse on lowering of its energy. The observed effect has been explained using a model of stochastic hopping transfer of energy via a Gaussian density of states.

An example of the application of selective excitation spectroscopy in the case of an amorphous system with impurities is the study of the phosphorescence of coronene and 5-bromoacenaphthene in a glassy solution in 1-bromobutane.⁶⁹ Selective excitation of an impurity was followed by a study of the temperature dependence of the half-width of the zero-phonon line, which at low temperatures of 1.8–4.2 K was found to obey the $T^{1.25 \pm 0.2}$ law.

7.4.2. Hole burning spectroscopy and photon echo

Hole burning spectroscopy is the technique used most widely (for a review see Ref. 101). The photon echo spectroscopy has been recently gaining in popularity.¹⁰² Figure 23a shows a typical hole (dip) burning spectrum obtained for the impurity molecule of resorufin in glycerol glass,⁹⁶ representing the zero-phonon band of a purely electronic transition accompanied by a phonon wing. Figure 23b compares the temperature dependences of the damping times deduced from the width of the zero-phonon line of the spectrum and also found by the photon echo method. It is worth

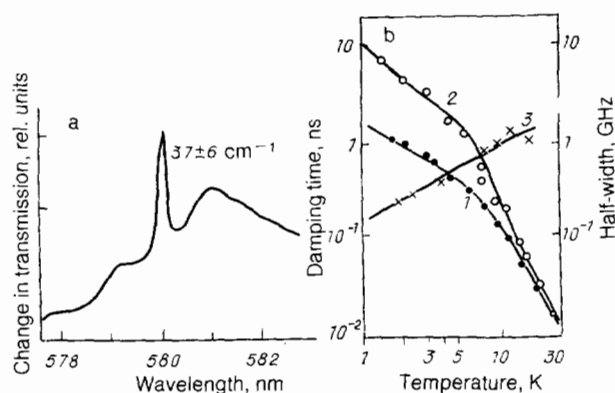


FIG. 23. Optical dephasing in a resorufin/glycerol glass⁹⁶: a) hole burning spectrum at 16.8 K (the width of the central zero-phonon band was governed by the spectrometer resolution); b) temperature dependence of the damping times deduced by hole burning spectroscopy (1) and photon echo (2) methods, and of the width of the band Γ due to spectral diffusion (3).

noting that at low temperatures the damping time deduced by hole burning spectroscopy is almost an order of magnitude less than that measured directly by the photon echo method. This is associated with the fact that, because of the long measurement time in the case of hole burning spectroscopy, it follows from Eq. (7.1) that the total measured width consists of the homogeneous width, due to the interaction with two-level states, and the width induced by spectral diffusion. On the other hand, the "fast" photon echo method can determine the damping due to just the former process. The difference between the values of Γ_{SLS} found by the methods of hole burning spectroscopy and by the photon echo technique has made it possible to determine the width of a homogeneous band which is due to spectral diffusion Γ_{scd} , the temperature dependence of which is also given in Fig. 23.

At temperatures above 10 K the results obtained by the hole burning and photon echo methods agree. This is due to the fact that the main process of damping of an electronic excitation is its interaction with a local vibration of frequency ~ 37 cm⁻¹, which agrees with the position of the maximum in the phonon wing in Fig. 23a.

Therefore, this example shows that different methods of selective laser spectroscopy can yield different values of the optical dephasing time. Therefore, the use of a set of selective laser spectroscopy methods should make it possible to determine the times of various relaxation processes. Selective laser spectroscopy provides the only direct method for the investigation of two-level states and it should be possible to develop a technique for the determination of the parameters of these states.⁶⁷

8. CONCLUSIONS

The term *universal property* has been used frequently in the text above. The very term universality clearly implies a reduction of some set, for example, the set of various chemical structures, to just one or two characteristic relationships. An impression therefore might be gained that there is some excessive degree of universality in the case of amorphics. The reason for this is that the universal properties of amorphous substances are in fact many in number, but they obey a hierarchy. An analysis of the causes and consequences makes it possible to propose a hierarchical structure shown in Fig. 24.

The prime causes of the properties of amorphics are two: statistical scatter of the microscopic position parameter $\langle r \rangle$ and the intrinsic mobility of molecules. The former is responsible for the *position-sensitive* properties such as the Gaussian distribution of *all* numerical parameters of an amorphous and for the nonexponential or dispersive kinetics of *all* the microscopic processes. The second is responsible for a batch of properties which can be regarded as relaxation. They include primarily the α and β relaxation processes, which in turn are responsible for quasielastic scattering of the particles incident on the amorphous multimode polymorphism, existence of mesophases in the solid state, and an increase in the rank of the mesophase in the course of amorphization of liquid crystals.

Naturally, these two groups of properties are of shared origin and are closely interrelated. Therefore, they are considered jointly using the concept of two-level states which in turn are responsible for the universality of the thermal prop-

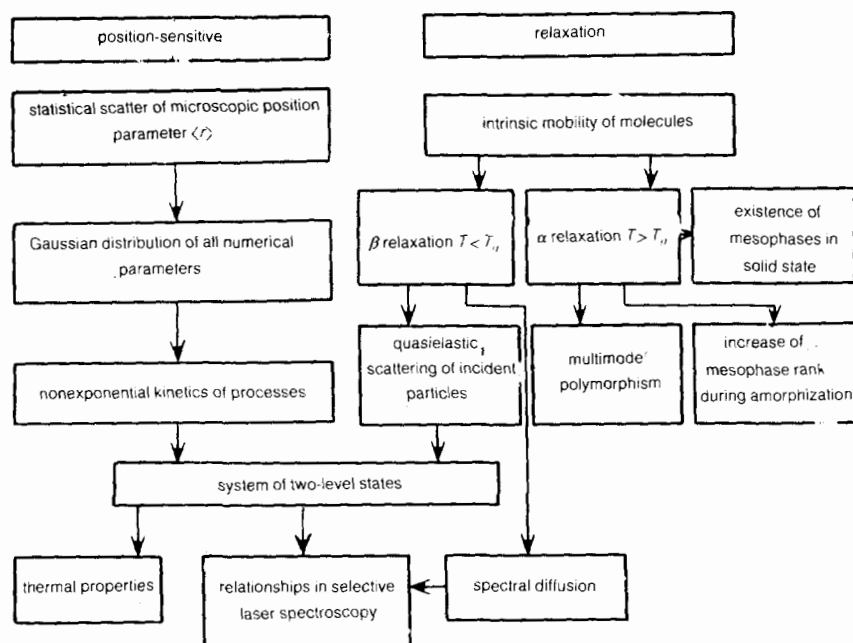


FIG. 24. Hierarchy of the universal properties of a molecular amorphous.

erties and for the relationships used in selective laser spectroscopy. Naturally, the scheme in Fig. 24 is not meant to be exhaustive, but it provides sufficient illustration of the main relationships typical of the amorphous state.

¹¹ In this review we shall not treat such topics as the nature and models of the glass transition, because this has been dealt with in detail in Ref. 4.

²¹ Among the factors favoring vitrification a considerable role is played by the conformational softness of the molecule and the existence of polymorphism in the solid phase. The molecules of acenes are conformationally rigid and the crystals composed of them are usually monomorphic.

³¹ It should be noted that the concept of two-level states used widely in the physics of amorphous materials is attributed to Anderson and Phillips^{63,64} (see, for example, Ref. 3) and is conceptually close to the Goldstein model⁴⁸ of a multidimensional surface representing the potential energy and characterized by many closely spaced minima, used to explain α and β relaxation in glasses (Sec. 4.1).

¹⁵ S. V. Nemilov, *Fiz. Khim. Stekla* **3**, 423 (1977) [Sov. J. Glass Chem. Phys. (1977)].

²⁵ N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed., Clarendon Press, Oxford (1979) [Russ. transl., Mir, M., 1982].

³⁵ S. R. Elliott, *Physics of Amorphous Materials*, Longman Press, London (1984); new edition (1988).

⁴⁵ J. Jäckle, *Rep. Prog. Phys.* **49**, 171 (1986).

⁵⁵ R. W. Cahn, *J. Phys. (Paris)* **43**, Colloq. 9, C9-55 (1982).

⁶⁵ D. Mercier and J. C. S. Levy, *Phys. Rev. B* **27**, 1292 (1983).

⁷⁵ L. S. Palatnik, A. A. Koz'ma, and A. A. Nechitaïl, *Kristallografiya* **28**, 136 (1983) [Sov. Phys. Crystallogr. **28**, 73 (1983)].

⁸⁵ N. Rivier, *Adv. Phys.* **36**, 95 (1987).

⁹⁵ S. V. Nemilov, *Fiz. Khim. Stekla* **2**, 97 (1976) [Sov. J. Glass Chem. Phys. (1976)].

¹⁰⁵ S. V. Nemilov, *Fiz. Khim. Stekla* **6**, 257 (1980) [*ibid.* (1980)].

¹¹⁵ S. V. Nemilov, *Fiz. Khim. Stekla* **7**, 575 (1981) [*ibid.* (1981)].

¹²⁵ S. V. Nemilov, *Fiz. Khim. Stekla* **8**, 11 (1982) [*ibid.* (1982)].

¹³⁵ S. V. Nemilov, *Fiz. Khim. Stekla* **13**, 645 (1987) [*ibid.* (1987)].

¹⁴⁵ H. Bässler, *Phys. Status Solidi B* **107**, 9 (1981).

¹⁵⁵ Y. Kamura, K. Seki, and H. Inokuchi, *Chem. Phys. Lett.* **30**, 35 (1975).

¹⁶⁵ Y. Kamura, I. Shirotani, H. Inokuchi, and Y. Maruyama, *Chem. Lett.* **6**, 627 (1974).

¹⁷⁵ Y. Maruyama and N. Iwasaki, *Chem. Phys. Lett.* **24**, 26 (1974).

¹⁸⁵ W. Arden, L. M. Peter, and G. Vaubel, *J. Lumin.* **9**, 257 (1974).

¹⁹⁵ R. Eiermann, G. M. Parkinson, H. Bässler, and J. M. Thomas, *J. Phys. Chem.* **87**, 544 (1983).

²⁰⁵ I. G. Chistyakov and B. K. Vainshtein, *Kristallografiya* **8**, 570 (1963) [Sov. Phys. Crystallogr. **8**, 458 (1963)].

²¹⁵ J. E. Lydon and J. O. Kessler, *J. Phys. (Paris)* **36**, Colloq. 1, C1-153 (1975).

²²⁵ V. K. Dolganov, L. A. Novomlinskii, and I. M. Shmyt'ko, *Fiz. Tverd. Tela (Leningrad)* **24**, 2605 (1982) [Sov. Phys. Solid State **24**, 1476 (1982)].

²³⁵ R. Eiermann, G. M. Parkinson, H. Bässler, and J. M. Thomas, *J. Phys. Chem.* **86**, 313 (1982).

²⁴⁵ B. K. Vainshtein and E. A. Kosterin, Abstracts of Papers presented at Fifth Socialist-Block Conf. on Liquid Crystals, Odessa, 1983 [in Russian], Vol. 1, p. 76.

²⁵⁵ É. A. Silin'sh, *Electronic States of Molecular Crystals* [in Russian], Zinatne, Riga (1978).

²⁶⁵ V. K. Dolganov, M. Gal, N. Kroo, L. Rosta, and E. F. Sheka, *Mol. Cryst. Liq. Cryst. Lett.* **92**, 281 (1984).

²⁷⁵ V. K. Dolganov, M. Gal, N. Kroo, L. Rosta, and E. F. Sheka, *J. Mol. Struct.* **114**, 325 (1984).

²⁸⁵ N. Kroo, L. Rosta, M. Gal, V. K. Dolganov, and E. F. Sheka, Preprint No. 72, KFKI, Budapest (1985).

²⁹⁵ V. K. Dolganov, M. Gal, N. Kroo, L. Rosta, and J. Szabon, Preprint No. 95, KFKI, Budapest (1985).

³⁰⁵ T. A. Krivenko, V. A. Dement'ev, E. L. Bokhenkov, A. I. Kolesnikov, and E. F. Sheka, *Mol. Cryst. Liq. Cryst.* **104**, 207 (1984).

³¹⁵ A. I. Kitaigorodskii, *Molecular Crystals and Molecules*, Academic Press, N. Y., 1973 [Russ. original, Nauka, M. (1971)].

³²⁵ K. P. Meletov and E. F. Sheka, *Izv. Akad. Nauk SSSR Ser. Fiz.* **42**, 435 (1978) [Bull. Acad. Sci. USSR **42** (2), 174 (1978)].

³³⁵ K. P. Meletov, E. I. Rashba, and E. F. Sheka, *Izv. Akad. Nauk SSSR Ser. Fiz.* **44**, 702 (1980) [Bull. Acad. Sci. USSR **44** (4), 14 (1980)].

³⁴⁵ E. E. Gorodetskii, A. M. Evtushenkov, Yu. F. Kiyachenko, A. V. Kryukov, and S. M. Rytov, *Zh. Eksp. Teor. Fiz.* **92**, 1401 (1987) [Sov. Phys. JETP **65**, 787 (1987)].

³⁵⁵ B. Frick, D. Richter, W. Petry, and U. Buchenau, *Z. Phys. B* **70**, 73 (1988).

³⁶⁵ G. P. Johari and M. Goldstein, *J. Chem. Phys.* **53**, 2372 (1970).

³⁷⁵ G. P. Johari and M. Goldstein, *J. Chem. Phys.* **55**, 4245 (1971).

³⁸⁵ G. P. Johari, *J. Chem. Phys.* **58**, 1766 (1973).

³⁹⁵ G. P. Johari, *Philos. Mag. B* **46**, 549 (1982).

⁴⁰⁵ G. P. Johari and J. W. Goodby, *J. Chem. Phys.* **77**, 5165 (1982).

⁴¹⁵ G. P. Johari, J. W. Goodby, and G. E. Johnson, *Nature (London)* **297**, 315 (1982).

⁴²⁵ K. Pathmanathan and G. P. Johari, *J. Phys. C* **18**, 6535 (1985).

⁴³⁵ S. A. Dzyuba and Yu. D. Tsvetkov, *Zh. Strukt. Khim.* **28** (3), 15

- (1987). [J. Struct. Chem. (USSR) **28**, 343 (1987)].
- ⁴³S. V. Nemilov, Fiz. Khim. Stekla **8**, 11 (1982). [Sov. J. Glass Chem. Fiz. (1982)].
- ⁴⁴R. Parthasarathy, K. J. Rao, and C. N. R. Rao, Chem. Soc. Rev. **12**, 361 (1983).
- ⁴⁵C. Bessada, A. H. Fuchs, B. Rousseau, and H. Szwarc, J. Phys. C **21**, 731 (1988).
- ⁴⁶G. S. Grest and M. H. Cohen, Adv. Chem. Phys. **48**, 455 (1981).
- ⁴⁷M. Goldstein, J. Chem. Phys. **51**, 3728 (1969).
- ⁴⁸V. K. Dolganov, N. Kroo, L. Rosta, E. F. Sheka, and J. Szaboń, Mol. Cryst. Liq. Cryst. **127**, 187 (1985).
- ⁴⁹L. Rosta, N. Kroo, V. K. Dolganov, P. Pacher, V. G. Simkin, Gy. Török, and G. Pepy, Mol. Cryst. Liq. Cryst. **144**, 297 (1987).
- ⁵⁰G. Pepy and L. Rosta, Preprint No. 73, KFKI, Budapest (1985).
- ⁵¹A. I. Kolesnikov, V. A. Dement'ev, É. L. Bokhenkov, T. A. Krivenko, and E. F. Sheka, Fiz. Tverd. Tela (Leningrad) **25**, 2881 (1983) [Sov. Phys. Solid State **25**, 1663 (1983)].
- ⁵²A. V. Belushkin, V. K. Dolganov, I. Natkaniec, and E. F. Sheka, Fiz. Tverd. Tela (Leningrad) **27**, 3091 (1985). [Sov. Phys. Solid State **27**, 1856 (1985)].
- ⁵³M. H. Brodsky, in *Light Scattering in Solids I* (ed. by M. Cardona), Springer Verlag, Berlin, 1975, p. 205; 2nd ed., 1983, p. 205. [Topics in Applied Physics, Vol. 8]. [Russ. transl., Mir, M., 1979, p. 239].
- ⁵⁴A. V. Belushkin, V. K. Dolganov, T. Zaleski, W. Nawroci, I. Natkaniec, and E. F. Sheka, Soobshch. OIYaI, R14-84-414 (1984).
- ⁵⁵A. V. Belushkin, V. K. Dolganov, I. Natkaniec, and V. G. Simkim, Mol. Cryst. Liq. Cryst. **B 150**, 187 (1987).
- ⁵⁶U. Buchenau, N. Nucker, and A. J. Dianoux, Phys. Rev. Lett. **53**, 2316 (1984).
- ⁵⁷J. Jäckle, in *Amorphous Solids: Low Temperature Properties* (ed. by W. A. Phillips), Springer Verlag, Berlin (1981), p. 135 [Topics in Current Physics, Vol. 24].
- ⁵⁸R. Shuker and R. W. Gammon, Phys. Rev. Lett. **25**, 222 (1970).
- ⁵⁹M. Gal, V. K. Dolganov, H. Kroo, L. Rosta, and E. F. Sheka, Fiz. Tverd. Tela (Leningrad) **27**, 3084 (1985) [Sov. Phys. Solid State **27**, 1852 (1985)].
- ⁶⁰A. J. Martin and W. Brenig, Phys. Status Solidi B **64**, 163 (1974).
- ⁶¹A. C. Anderson, in *Amorphous Solids: Low Temperature Properties* (ed. by W. A. Phillips), Springer Verlag, Berlin (1981), p. 65 [Topics in Current Physics, Vol. 24].
- ⁶²P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).
- ⁶³W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).
- ⁶⁴J. Jäckle, Z. Phys. **257**, 212 (1972).
- ⁶⁵W. A. Phillips, Rep. Prog. Phys. **50**, 1657 (1987).
- ⁶⁶I. S. Osad'ko and A. A. Shtygashev, J. Lumin. **36**, 315 (1987).
- ⁶⁷R. Jankowiak, R. Richert, and H. Bässler, J. Phys. Chem. **89**, 4569 (1985).
- ⁶⁸J. Fünfschilling and I. Zschokke-Gränacher, Chem. Phys. Lett. **110**, 315 (1984).
- ⁶⁹R. Jankowiak, G. J. Small, and K. B. Athreya, J. Phys. Chem. **90**, 3896 (1986).
- ⁷⁰V. G. Karpov, M. I. Klinger, and F. N. Ignat'ev, Zh. Eksp. Teor. Fiz. **84**, 760 (1983) [Sov. Phys. JETP **57**, 439 (1983)].
- ⁷¹N. M. Plakida, S. Stamenković, and G. M. Vujčić, J. Phys. C **21**, 2609 (1988).
- ⁷²T. A. Krivenko and E. F. Sheka, Fiz. Tverd. Tela (Leningrad) **27**, 1563 (1985) [Sov. Phys. Solid State **27**, 944 (1985)].
- ⁷³S. V. Maleyev, J. Phys. C **19**, 1657 (1986).
- ⁷⁴V. L. Broude, E. I. Rashba, and E. F. Sheka, *Spectroscopy of Molecular Excitons*, Springer-Verlag, Berlin, 1985 [Russ. original Energoizdat, M., 1981].
- ⁷⁵R. Jankowiak, K. D. Rockwitz, and H. Bässler, J. Phys. Chem. **87**, 552 (1983).
- ⁷⁶J. Klafter and J. Jortner, J. Chem. Phys. **77**, 2812 (1982).
- ⁷⁷J. Chesnoy, D. Ricard, and C. Flytzanis, Chem. Phys. **42**, 337 (1979).
- ⁷⁸J. Hofmann, K. P. Seefeld, W. Hofberger, and H. Bässler, Mol. Phys. **37**, 973 (1979).
- ⁷⁹G. Peter and H. Bässler, Chem. Phys. **49**, 9 (1980).
- ⁸⁰R. Richert and H. Bässler, J. Chem. Phys. **84**, 3567 (1986).
- ⁸¹M. Grünwald, B. Pohlmann, B. Movaghar, and D. Würtz, Philos. Mag. B **49**, 341 (1984).
- ⁸²R. P. Parson and R. Kopelman, J. Chem. Phys. **82**, 3692 (1985).
- ⁸³L. A. Rebane, A. A. Gorokhovskii, and J. V. Kikas, Appl. Phys. B **29**, 235 (1982).
- ⁸⁴*Optical Linewidths in Glasses* (ed. by M. J. Weber), in J. Lumin. **36**, Nos. 4 and 5, 179-329 (1987).
- ⁸⁵R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **53**, 958 (1984).
- ⁸⁶H. J. Queisser, Phys. Rev. Lett. **54**, 233 (1985).
- ⁸⁷G. Smets, Adv. Polym. Sci. **50**, 17 (1983).
- ⁸⁸R. Richert and H. Bässler, Chem. Phys. Lett. **116**, 302 (1985).
- ⁸⁹T. Doba, K. U. Ingold, W. Siebrand, and T. A. Wildmann, Chem. Phys. Lett. **115**, 51 (1985).
- ⁹⁰R. Jankowiak, L. Shu, M. J. Kenney, and G. J. Small, J. Lumin. **36**, 293 (1987).
- ⁹¹R. I. Personov, in *Spectroscopy and Excitation Dynamics of Molecular Systems* (ed. by V. M. Agranovich and R. M. Hochstrasser), North-Holland, Amsterdam (1983), p. 515 [Modern Problems in Condensed Matter Sciences, Vol. 4].
- ⁹²G. J. Small, *ibid.*, p. 420.
- ⁹³S. K. Lyo, in *Organic Molecular Aggregates: Electronic Excitation and Interaction Processes* (Proc. Intern. Symposium on Organic Materials at Schloss Elmau, Bavaria, 1983, ed. by P. Reineker, H. Haken, and H. C. Wolf), Springer Verlag, Berlin (1983), p. 215.
- ⁹⁴J. Friedrich and D. Haarer, Angew. Chem. **96**, 96 (1986).
- ⁹⁵M. Berg, C. A. Walsh, L. R. Narasimhan, K. A. Littau, and M. D. Fayer, J. Chem. Phys. **88**, 1564 (1988).
- ⁹⁶A. A. Gorokhovskii, Izv. Akad. Nauk SSSR Ser. Fiz. **52**, 636 (1988) [Bull. Acad. Sci. USSR **52**, No. 4, 8 (1988)].
- ⁹⁷P. Reineker and K. Kassner, J. Lumin. **38**, 125 (1987).
- ⁹⁸R. M. Macfarlane and R. M. Shelby, J. Lumin. **36**, 179 (1987).
- ⁹⁹W. M. Yen and R. T. Brundage, J. Lumin. **36**, 209 (1987).
- ¹⁰⁰K. K. Rebane and A. A. Gorokhovskii, J. Lumin. **36**, 237 (1987).
- ¹⁰¹J. Hegarty, J. Lumin. **36**, 273 (1987).
- ¹⁰²R. Silbey and K. Kassner, J. Lumin. **36**, 283 (1987).
- ¹⁰³Yu. V. Denisov and V. A. Kizel', Opt. Spektrosk. **23**, 472 (1967) [Opt. Spectrosc. (USSR) **23**, 251 (1967)].
- ¹⁰⁴R. Jankowiak, B. Ries, and H. Bässler, Phys. Status Solidi B **124**, 363 (1984).
- ¹⁰⁵J. Fünfschilling and I. Zschokke-Gränacher, Chem. Phys. Lett. **110**, 315 (1984).

Translated by A. Tybulewicz