most important rock-forming minerals, arable lands, deciduous forests in various phases of vegetation, etc. The dispersion drops off rapidly, so that it is possible to limit the expansion to 3-5 terms. Joint analysis of the results indicated that the spectral sensitivity functions are quite smooth and change sign, requiring piecewise realization by zones 60-100 mm wide. The shapes and positions of the zones are different in different ensembles. Broad zones correspond to high dispersions. Similar ensembles of objects give similar basic functions for different landscapes. The various ensembles contain functions of typical form that characterize the factorial dependence.

Recognizing the statistical nature of the selection, we made a joint evaluation of the results to satisfy various problems represented by different initial ensembles. A surveying-system variant with piecewise realization by multizone photography was used on the Soyuz 12 and Soyuz 13 spacecraft. A posteriori optimization by the method of principal components for combinations of photographing zones yields a result that is comparable with respect to the positions and sign changes of the zones. Different optimum zone combinations correspond to different landscapes on the photographs, but similar landscapes produce a stable combination of zones. Inadequate correction for the real atmosphere, the differences between the a priori and a posteriori ensembles, and the possibilities of technical realization make it impossible to require full identity of the results. Photometric evaluation made it possible to establish double the brightness dispersion in the synthesized image.

The problem of optimizing the parameters for optical systems for study of the earth requires broad investigation of the optical characteristics of natural objects and selection of sound criteria. Work in this area will result in the development of controllable surveying systems with strongly condensed information.

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**R. I. Personov.** The Sharp Narrowing of Spectral Bands of Organic Molecules Under Laser Excitation.
1. It is known that the electron-vibrational spectra of polyatomic organic molecules in solutions are generally diffuse, consisting of one or more broad bands (with widths in the hundreds of cm^{-1}). The question as to why these spectra are diffuse is of fundamental theoretical and applied importance. It is important to understand whether the diffuseness of the spectrum is due to broadening of intramolecular levels or to interaction with the environment. Do the broad bands have unresolved internal structure? Is there some method by which this structure could be resolved?

In 1952, Shpol'skiĭ, Il'ina, and Klimova[1] observed that, when placed in solvents of a certain type (in crystallized short-chain n-paraffins) at low temperatures, many organic compounds produce luminescence and absorption spectra that consist not of diffuse bands, but of large numbers of narrow lines (a few cm^{-1} in width). The narrow lines in the Shpol'skiĭ quasiline spectra correspond to vibronic transitions in impurity mole-

cules in which the vibrational state of the n-paraffinic matrix does not change[2]. These phononless lines (PLL) are accompanied by broad phonon wings (PW) and can be regarded as optical analogs of Mössbauer resonant γ lines (as is done in the case of other mixed organic and inorganic crystals[3]).

However, the possibility of obtaining quasiline spectra in specifically chosen n-paraffin matrices does not resolve the general problem of the origin of the diffuse spectra in arbitrary solvents, in which the bands usually remain diffuse all the way down to helium temperatures. The present paper is concerned with the results of experimental studies of this problem (conducted during the past few years at the USSR Academy of Sciences Institute of Spectroscopy's Laboratory of Electron Spectra). They are based on the observed phenomenon in which fine structure appears in the fluorescence spectra of complex molecules in frozen solutions under monochromatic laser excitation[4a].

2. It was established in [4] for various aromatic hydrocarbons, porphyrines, and dyes that on transition from ordinary methods of luminescence excitation (mercury and xenon lamps) to excitation by narrow (~ 0.1 cm^{-1}) gas-laser lines in the region of the 0-0 transition (and the lowest vibron transitions) and at sufficiently low temperatures, the emission spectrum undergoes an abrupt transformation: instead of a few diffuse bands it consists of a large number of narrow lines. The narrowest lines are a few tenths of a cm^{-1} in width. As an example, the figure shows segments of the fluorescence spectra of solutions of four substances (the first three in ethanol, the fourth in paraffin oil) under excitation by broadband sources (dashed) and under laser excitation (solid lines) at $4.2°K$[4b,c;5]. The effect in which the fine structure of the spectrum appears under laser excitation is observed in a very wide variety of solvents (crystalline and vitreous, polar and nonpolar). Analysis indicates that the narrow PLL correspond to electronic vibrational transitions in the molecules of the dissolved
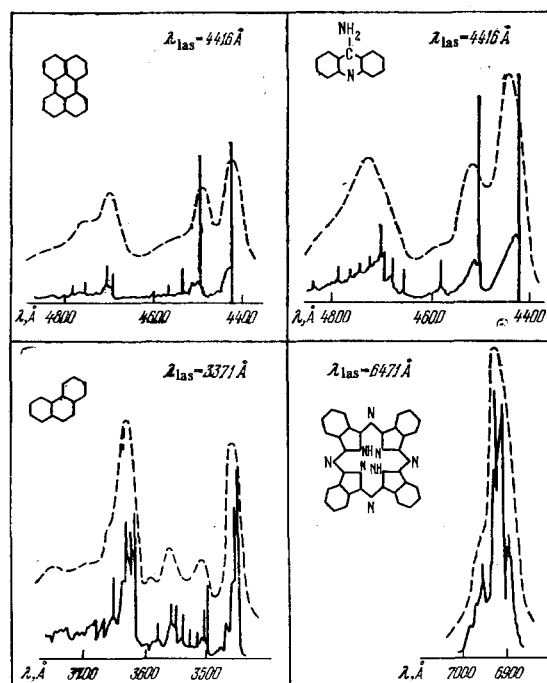
substance, and that the shapes of the PW that accompany them are basically specific for the particular solvent.

As the temperature rises, the intensity of the PLL decreases and the fine spectral structure vanishes. In the case of the examples in the figure, the PLL vanish almost completely when the specimens are heated to 40-50°K.

Analysis of the experimental results leads to the following scheme for formation of the broad spectral bands. At sufficiently low temperatures, each impurity molecule has both a strong narrow PLL in the region of the 0-0 transition (and any vibronic transition) and an accompanying comparatively broad PW (in emission on the longwave side of the PLL and in absorption on the shortwave side). Differences in local conditions for different impurity molecules scatter the positions of the respective PLL and PW (inhomogeneous broadening). Here the width of the PLL is small, while that of the PW is comparable with the maximum of this scatter. As a result, PLL belonging to different centers overlap to a lesser degree than the PW. On combination of the optical bands of many centers, therefore, the resultant peak intensity of the PLL increases much more slowly than the resultant peak intensity of the strongly overlapped PW. Although the PLL intensity at the maximum may substantially exceed the intensity at the PW maximum for each individual impurity center, combination of many optical bands of this kind results in a broad structureless band. Generally, this band may include several closely spaced vibronic transitions. Excitation of fluorescence by the laser line involves chiefly those centers whose PLL wavelengths coincide with the laser wavelength. It is therefore these impurity centers that fluoresce most strongly, and the spectrum acquires the fine structure.

3. The fluorescence spectrum is sharpest on excitation in the region of the 0-0 transition[5]. If the frequency of the exciting line is increased substantially, the spectrum becomes diffuse. This is because the high vibronic levels are considerably broader than the purely electronic levels, so that laser excitation involves a larger number of centers and the inhomogeneous broadening is suppressed to a lesser degree.

Under monochromatic excitation in the region of not too high vibronic transitions (when the spectrum is still a line spectrum), the detailed structure of the spectrum depends strongly on λ_{las}. This is because of the presence of a number of vibrational frequencies of the impurity molecules in the excited state, the difference between which is smaller than the inhomogeneous broadening. If this structure is analyzed, the fluorescence spectrum can be used to determine the vibrational frequencies of the molecule not only in the ground, but also in the excited electronic state[5].

4. The studies under discussion showed experimentally that it is possible to bring out the fine structure even in diffuse absorption spectra on the basis of excitation-spectrum measurements for narrow intervals of a fluorescence band[4b,6].

5. An effect in which impurity centers are "burned out" under laser irradiation was observed in the course of the laser-excitation experiments. This reversible process results in the appearance of narrow (less than 1 cm^{-1} wide) stable "slits" in the broadband absorption spectra[7a]. It is of one-photon nature and may be re-lated to "reorientation" of impurity molecules in the matrix as a result of an electronic transition[7b].

6. Thus, these studies indicate that the diffuse bands in the spectra of frozen solutions have latent structure. At low temperatures, they incorporate strong PLL and their accompanying PW, but inhomogeneous broadening "blurs" the picture. Generally, each diffuse band covers several vibron transitions. The fine structure of the spectrum can be developed by selective monochromatic excitation in the appropriate region of the absorption spectrum.

Further systematic research will be needed to determine how general the established relationships are. Even now, however, it can be stated that they hold for molecules of various classes and in various types of crystalline and vitreous solvents. (We note that some of the results discussed above have already been confirmed by experiments in other laboratories[8].) In our view, the appearance of fine spectral structure under selective excitation opens up new possibilities for study of intermolecular interactions in solutions (in particular, the impurity-matrix electron-phonon interaction and the characteristics of the phonon spectra of different kind of matrices), for study of the spectroscopic manifestations of intramolecular electronic and vibrational relaxations (for example, through the line widths, which, under suitable laser excitation, are already determined to a substantial degree by these processes), for detailed quantitative analysis of the basic luminescence behavior of complex molecules, etc.

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