

# Determination of electron-phonon coupling from structured optical spectra of impurity centers

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Recent developments in the theory of impurity centers are reviewed. Particular attention is devoted to the way this theory can be exploited in the quantitative analysis of structured optical spectra through the use of formulas relating the absorption band shape to the shape of the fluorescence band. Analysis of departures from mirror-image relation between these two spectra can be used to deduce the parameters of the electron-phonon coupling from the shape of the structured bands. Topics discussed include zero-phonon lines, the dependence of their shape and position on temperature, departures from mirror-image relation for both phonon wings and the vibronic absorption and fluorescence spectra, the energy gap between the absorption and fluorescence spectra of certain molecules, and the nature of excimer emission in solids.

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## 1. INTRODUCTION

The spectroscopy of impurity centers<sup>1)</sup> has undergone considerable development in the course of the last decade. There has been considerable progress both in the depth and scope of these investigations. On the one hand, an enormous number of new chemical compounds which was previously outside the range of interest of spectroscopy has been studied. This expansion in research in this field was stimulated by searches for new materials for use in dye lasers, by the application of spectroscopic methods to biochemical and chemical

problems, and by a number of other factors. On the other hand, the attention of researchers has been increasingly drawn to quantitative questions, such as, for example, the structure of impurity molecules, the shape of the optical spectrum of impurity centers, the temperature dependence of bands and the consequences thereof, the probability of radiationless transitions, and so on. There is no doubt that quantitative answers to such questions are most simply obtained in the case of structured optical spectra. Whereas optical line spectra were previously encountered mainly in the study of paramagnetic ions in crystalline matrices, the onset of extensive utilization of normal paraffins (Shpol'skii matrices) as solvents has led to the study of line spectra of many complicated organic molecules as well.

<sup>1)</sup>In this article the term impurity center stands for an isolated ion, atom or molecule surrounded by a solid (crystalline or glassy) or a liquid solvent.

The spectral bands of impurity centers can serve as a valuable source of information on intra- and intermolecular interactions, the structure of impurity centers and changes they undergo during phototransitions, the ways in which the energy of an absorbed photon is transformed into vibrational energy, and so on. However, the information that the spectral bands undoubtedly contain is often difficult, and occasionally impossible, to extract without detailed theoretical analysis. Unfortunately, the possibilities of existing theories have not as yet been adequately exploited. Interpretations of experimental data are frequently founded on naive and occasionally erroneous theoretical discussions. All this indicates that the modern theory of the impurity center is largely unfamiliar to many experimentalists. A review of the most recent achievements of this theory may, therefore, be useful at this stage.

Considerable progress has been achieved in the course of the last 5-7 years in the quantitative theory of the shape of bands due to impurity centers. The theory is now capable of establishing a quantitative relationship between conjugate absorption and luminescence spectra with different intensity distributions (both structured and structure-free).<sup>2)</sup> The theory establishes a relationship between this conjugate property and the parameters of the electron-phonon coupling. The basic results of this theory that have not so far been presented in existing reviews<sup>1-6</sup> and monographs,<sup>7-11</sup> and the practical applications of these results in the analysis of particular experimental data, form the main body of the present review.

## 2. REASONS FOR THE BROADENING OPTICAL SPECTRA. THE ELECTRON-PHONON COUPLING

It is no exaggeration to say that the structure of an optical spectrum is one of its most important characteristics. The greater the structure of the spectrum, the easier it is to investigate such important questions as the influence of particular groups of atoms on physical, chemical, and biological properties of impurity molecules; the paths of photochemical reactions and the redistribution of photon energy among different degrees of freedom of the molecule; the identification of individual molecules at different stages of photochemical or biochemical processes, and so on. However, the very extensive experimental material now available indicates that many complicated organic molecules that are of interest to chemists, biochemists, and biologists do not have a structured optical spectrum. Why is this so? There are two possible reasons for the broadening of the bands.

### A. Inhomogeneous broadening

This broadening is due to the fact that the spectrum recorded in a particular experiment is the resultant of the spectra of an enormous number of impurity centers. Since the electronic excitation energy of an im-

impurity molecule depends on the local conditions in which the molecule is found, and these conditions (especially in glassy and liquid solvents) are not the same at different points in the specimen, the frequency of the radiation emitted or absorbed by impurity centers occupies a definite frequency interval. The magnitude of this inhomogeneous broadening may reach several hundred  $\text{cm}^{-1}$ . It is practically independent of temperature, and can be reduced by suitable choice of solvent (normal paraffins are very effective in this respect) or by monochromatic excitation.<sup>12, 13</sup> It is important to emphasize that monochromatic excitation can substantially reduce the width of the luminescence band if the optical band of each impurity center has sufficient structure.

### B. Homogeneous broadening

This is due to the electron-phonon coupling.<sup>3)</sup> It is precisely this interaction that transforms an optical line of each impurity center into a band. In this review, we shall be concerned with the band shape due to an individual impurity center, i.e., we will discuss homogeneous broadening.

The shape of an optical band can be calculated from the formula ( $\hbar = 1$ )

$$P(\omega) = 2\pi \sum_{a,b} w(a) | \langle b | H_{\text{int}} | a \rangle |^2 \delta(\omega - E_b + E_a), \quad (2.1)$$

Here  $H_{\text{int}}$  is the operator representing the interaction between light and electrons in the impurity center, and  $w(a)$  is the expectation of the initial state  $|a\rangle$  with energy  $E_a$ . The eigenfunctions  $|a\rangle, |b\rangle$  and the corresponding energies  $E_a, E_b$  of the impurity center are conveniently calculated in the Born approach.<sup>14, 15</sup> According to this approach, the total electron-phonon coupling can be divided into two parts: the nonadiabatic and the adiabatic. By taking these two parts of the interaction into account, it is possible to explain *any* transformation in the impurity center that accompanies absorption or emission of light. Unfortunately, this point is often lost in a welter of confused terminology such as "electronic regrouping," "change of conformation," and so on.

The nonadiabatic part of the interaction is responsible for radiationless transformations of electronic excitation into vibrational energy and the Jahn-Teller effect in impurity centers of high symmetry. It also influences the shape of the bands due to impurity centers of low symmetry. However, whilst the nonadiabatic part of the interaction is fundamentally important in the explanation of radiationless transitions, because such transitions vanish in the absence of the nonadiabatic part, the influence of this part of the interaction on the shape of absorption bands and, especially, the shape of luminescence bands due to centers with low symmetry, can frequently be neglected. The shape of the optical bands due to such centers can therefore be analyzed by including only the adiabatic part of the electron-phonon coupling, i.e., the adia-

<sup>2)</sup> Conjugate spectra are defined as the absorption and luminescence spectra corresponding to transitions between ground and first excited electronic states.

<sup>3)</sup> In liquid solutions or vapors, the broadening of optical lines of molecules may be due to dissociation, ionization, and so on (see footnote 15).

batic approximation can be employed.

It is well known that, in the adiabatic approximation, the wave function of an impurity center can be written in the form of the product

$$|a\rangle = \Psi^g(\mathbf{r}, \mathbf{R}) \Phi_g^e(\mathbf{R}) \quad (g=0, e) \quad (2.2)$$

of the electronic wave function  $\Psi^g$  and the vibrational wave function  $\Phi_g^e$ . The electronic function of the  $g$ -th electronic state depends parametrically on the vibrational coordinates  $\mathbf{R}$ , so that the matrix element of the operator describing the interaction with radiation

$$M(\mathbf{R}) = \int_{-\infty}^{\infty} d\mathbf{r} \Psi^0(\mathbf{r}, \mathbf{R}) H_{int} \Psi^e(\mathbf{r}, \mathbf{R}), \quad (2.3)$$

evaluated with the aid of these functions, will also depend on  $\mathbf{R}$ . The incomplete separation of the electronic and nuclear variables  $\mathbf{r}$  and  $\mathbf{R}$  in the adiabatic function  $|a\rangle$  shows that these degrees of freedom are coupled. This is sometimes referred to as the Herzberg-Teller coupling (the HT coupling). The vibrational functions  $\Phi_0^0$  and  $\Phi_e^e$  of the unexcited and excited impurity-containing crystal in the harmonic approximation are the eigenfunctions of the following Hamiltonians, respectively:

$$H^0(\mathbf{R}) = \hat{T}(\mathbf{R}) + \mathbf{R} \frac{\hat{U}^0}{2} \mathbf{R}, \quad (2.4)$$

$$H^e(\mathbf{R} + \mathbf{a}) = \hat{T}(\mathbf{R}) (\mathbf{R} + \mathbf{a}) \frac{\hat{U}^e}{2} (\mathbf{R} + \mathbf{a}); \quad (2.5)$$

where  $\hat{T}(\mathbf{R})$  is the nuclear kinetic-energy operator and the second terms on the right-hand sides of these formulas are the multidimensional Franck-Condon surfaces in the space of the variables  $\mathbf{R}$ . The shift of the minima of the surface under electronic excitation of an impurity center is described by the multidimensional vector  $\mathbf{a}$  and the change in the shape of the surface is described by the matrix  $\hat{W} = \hat{U}^e - \hat{U}^0$ .<sup>4)</sup> These two parameters determine the Franck-Condon (FC) coupling. In the harmonic approximation, the complete adiabatic interaction can be written symbolically in the following form:

$$\mathbf{a} \neq 0, \quad \hat{W} \neq 0, \quad M(\mathbf{R}) \neq \text{const.} \quad (2.6)$$

The parameters  $\mathbf{a}$ ,  $\hat{W}$  and the derivatives of  $M$  with respect to  $\mathbf{R}$  determine the intensity distribution in the conjugate absorption and fluorescence bands. These parameters have a different effect on completely and partially symmetric vibrations, respectively. This problem is discussed in greater detail in Sec. 6.

The theory that was available 5-7 years ago was capable of providing only a qualitative answer to the question as to which effects are due to the parameter  $\hat{W}$  and the derivatives of  $M$  with respect to  $\mathbf{R}$ , because the influence of these parameters on the intensity distribution was treated by the theory under serious restrictions and incompletely. This was connected with mathematical difficulties that have now been overcome, and the influence of the parameters  $\mathbf{a}$ ,  $\hat{W}$  and of the derivatives of  $M$  with respect to  $\mathbf{R}$  on the shape of the optical bands can now be examined without restrictions.

<sup>4)</sup>The phrase, "change of conformation," which is often found in chemical and biochemical literature, can be identified with the case  $\mathbf{a} \neq 0$  and  $\hat{W} \neq 0$ .

This has led to the development of a theory that provides a quantitative relationship between the intensity distribution in conjugate absorption and fluorescence bands in the absence of a mirror-image relation between them.

It is important to recall that the relationship between the shape of the conjugate absorption bands,  $I^0(\omega) = P^0(\omega)/\omega$ , the fluorescence bands,  $I^e(\omega) = \text{const} \times P^e(\omega)/\omega^3$ , where  $P^g(\omega)$  is the energy emitted or absorbed per unit time ( $g=0, e$ ), was discussed in the early literature. Thus, Blokhintsev<sup>16</sup> and Pekar<sup>1</sup> showed that the intensity distributions in conjugate spectra satisfied the mirror-image relation with respect to the energy  $\epsilon$  of the zero-phonon transition, i.e.,

$$I^0(\omega) = I^e(2\epsilon - \omega), \quad (2.7)$$

if  $\hat{W} = 0$  and  $M(\mathbf{R}) = \text{const}$ . This is the mathematical expression of the mirror-image relation of Levshin.<sup>17</sup> Stepanov<sup>18</sup> used only the assumption that the thermalization of vibrational energy was faster than that of electronic energy, and employed (2.1) to show that

$$I^e(\omega) = e^{(\epsilon - \omega)/kT} I^0(\omega), \quad (2.8)$$

which relates the Stokes part of the absorption band to the anti-Stokes part of the fluorescence band. The effect of the dependence of  $M$  on  $\mathbf{R}$  on the integrated intensity of conjugate bands has frequently been investigated in the literature,<sup>19-21</sup> and the effect of  $W$  on the half-width of bands was studied by Kristofel' *et al.*<sup>22</sup> Both the difference between the integrated intensities and the half-widths of the conjugate bands were established. However, these workers did not calculate the intensities of mutually conjugate phototransitions, i.e., phototransitions whose frequencies have mirror symmetry with respect to the frequency of the zero-phonon transition (such calculations are summarized in Secs. 3 and 6). Nevertheless, the results obtained by these workers enable us to conclude that mutually conjugate transitions have different intensities. This means that the radiative lifetime of an electronically excited impurity center cannot be determined from the integrated extinction coefficient if the intensity distributions conjugate bands do not exhibit mirror symmetry.<sup>23</sup>

### 3. PHONON WINGS AS A SOURCE OF INFORMATION ON THE ELECTRON-PHONON COUPLING

The optical electrons of an impurity center interact with both intramolecular and intermolecular vibrations (phonons). The electron-phonon coupling is a special case of the interaction mentioned in the last subsection and is responsible for phototransitions with the creation and annihilation of phonons which, in turn, are responsible for band broadening. An optical band can, in general, be represented by the sum of two terms

$$I(\omega) = J(\omega) + \Phi(\omega), \quad (3.1)$$

where  $J(\omega)$  has the form of a sharp peak describing the zero-phonon line (ZPL) and the function  $\Phi(\omega)$  describes the phonon wing (PW) accompanying the ZPL. Depending on the ratio of the integrated intensities in the ZPL and PW, i.e., the ratio of  $J$  to  $\Phi$ , each of the optical bands can be assigned to one of the three types illustrated in Fig. 1. For brevity, we shall refer to the bands shown in Figs. 1a-c as  $a$ ,  $b$ , and  $c$  bands, re-

spectively. The measured ratio

$$\alpha = \frac{J}{J + \Phi} \quad (3.2)$$

determines the probability of zero-phonon transitions.<sup>5)</sup> In the theory of scattering of neutrons and x rays by crystals, a similar ratio determines the probability of elastic scattering and is called the Debye-Waller factor. It will be useful to retain this phrase for optical ZPL, i.e., for the quantity  $\alpha$ . The latter quantity depends on all the parameters characterizing the adiabatic and nonadiabatic interactions, and therefore serves as a rough measure of the strength of the electron-phonon coupling. The stronger the coupling, the smaller is the parameter  $\alpha$ . However, not all parameters have the same effect on  $\alpha$ . For example, a change in the matrix  $\hat{W}$  has very little effect on  $\alpha$  but, on the other hand, this parameter completely defines the temperature broadening of the ZPL. The quantity  $\alpha$  and the rate of temperature broadening may therefore be uncorrelated. In most cases,  $\alpha$  is a good measure of the shift  $a$  of the position of equilibrium of oscillators characterizing vibrations of the solvent.<sup>6)</sup>

An increase in temperature is accompanied by three effects, namely: (1) a reduction in the integrated intensity of the ZPL, (2) a broadening of the PW, and (3) a broadening and shift of the ZPL. The first two effects increase with decreasing value of  $\alpha$  at zero temperature and are, therefore, most appreciable in  $b$  and  $c$  bands. Conversely, the third effect is most important in spectra with  $\alpha \approx 1$ . This is illustrated in Fig. 2.

A real optical spectrum consisting of vibronic and vibronic-phonon transitions may be a superposition of different types of band. Moreover, the  $b$  bands may transform into the  $c$  bands as the temperature increase (see Fig. 3) and the spectrum loses its structure. Experimental evidence nevertheless suggests that real spectra are dominated by bands of a particular type. For example, paramagnetic ions in crystals, and many

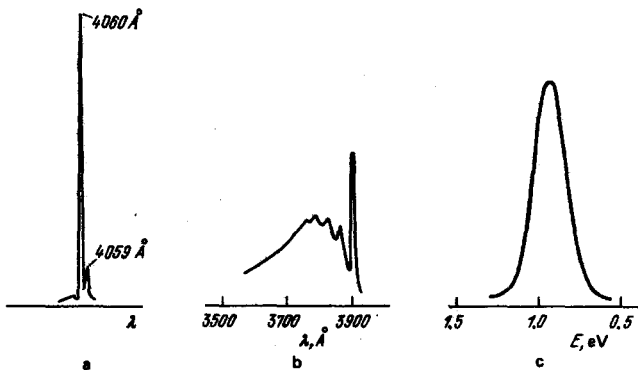


FIG. 1. Three types of optical bands corresponding to different strengths of electron-phonon coupling: (a) luminescence line of 1,12-benzperylene in  $n$ -hexane<sup>25</sup> at 4.2 K; (b) absorption band of the  $R_2$  center in LiF at 4.2 K; (c) luminescence band of the  $F$  center in KBr<sup>24</sup> at 20 K.

<sup>5)</sup>In type  $c$  bands, this ratio is small and, as a rule, cannot be measured because ZPL cannot be separated from PW.

<sup>6)</sup>In bands with forbidden  $0-0$  transitions, the ratio  $\alpha$  depends on the HT coupling. In bands with allowed  $0-0$  transitions, but weak electron-phonon coupling, i.e., when  $\alpha \approx 1$ , the parameter  $\alpha$  may also depend preferentially on the HT coupling.

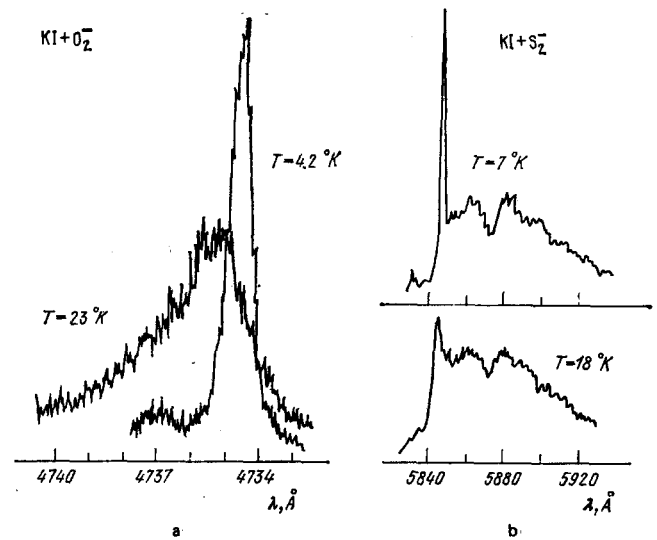


FIG. 2. Temperature dependence of type  $a$  and  $b$  bands:<sup>27</sup> (a) broadening and shift of the zero-phonon line; (b) fall in integrated intensity of the zero-phonon line.

organic molecules in  $n$ -paraffins, are mainly represented by  $a$  bands. The  $b$  bands have been observed both in organic and alkali halide matrices.<sup>25-36</sup> The  $c$  bands have, so far, been reliably identified only in alkali halide matrices. We may therefore suppose that structure-free bands due to organic dyes are vibronic-phonon transitions blended with strong PW. The  $c$  bands will be called *multiphonon bands*, whereas the  $a$  and  $b$  bands will be referred to as *structured bands*. When optical bands are examined, two problems arise right at the outset, namely: (1) which coupling (Franck-Condon or Herzberg-Teller) is responsible for the broadening and (2) what information can be obtained by studying the band shape? The answer to the first question is different for multiphonon and structured bands, and we shall therefore consider them separately.

### A. Multiphonon bands

These bands were investigated in the 1950's by Pekar, Huan, and Rhys, and by Davydov, Kubo, and Toyozaki

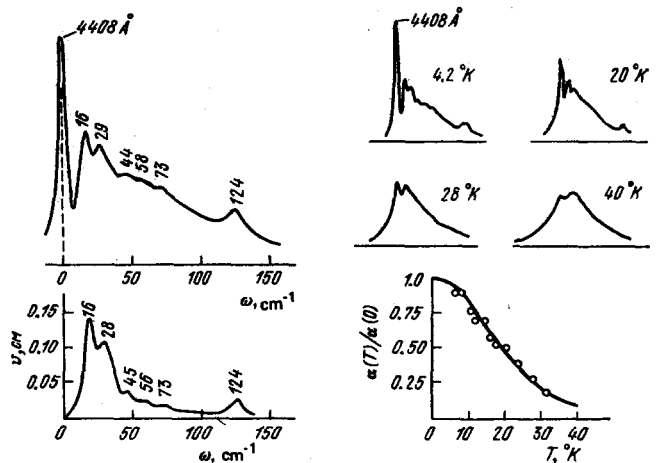


FIG. 3. Fluorescence band of perylene and  $n$ -heptane at 4.2 K (top left) and its temperature variation (top right).<sup>25</sup> The function  $v(\omega)$  is "extracted" from the band with the aid of (3.17). The temperature reduction in integrated intensity of the zero-phonon line was calculated with this particular function  $v(\omega)$ .

wa.<sup>1,37-40</sup> They showed that multiphonon bands appeared if electronic excitation of an impurity center produced a shift  $a$  in the equilibrium positions of the solvent molecules that was greater by a factor of 10–20 than the amplitude of the zero-point vibrations of the solvent crystal. In this case, the zero-phonon transitions are practically absent and the shape of the absorption PW near the maximum is approximately Gaussian:<sup>7)</sup>

$$\Phi(\omega) \approx (4\pi B(T))^{-1/2} \exp \left[ -\frac{(\omega - \epsilon - A)^2}{4B(T)} \right], \quad (3.3)$$

where the constants  $A$  and  $B$  can be expressed in terms of the phonon function  $f(\nu, T)$  (sometimes also called the Stokes loss function<sup>7)</sup>, as follows:

$$A = \int_{-\infty}^{\infty} d\nu \nu f(\nu, T), \quad (3.4)$$

$$B = \int_{-\infty}^{\infty} d\nu \frac{\nu^2}{2} f(\nu, T). \quad (3.5)$$

The particular feature of the multiphonon bands is that they have no structure. The presence of even broad structure or turning points on the band profile would undoubtedly indicate that the band under consideration is the sum of several multiphonon bands because the broadening would then be largely inhomogeneous. The half-width

$$\Delta_{\Gamma}(T) = 4 \sqrt{B(T) \ln 2} \quad (3.6)$$

of a multiphonon band must be several times greater than the Debye frequency  $\nu_D$  of the solvent, i.e., it must be not less than 200–300  $\text{cm}^{-1}$  in the case of organic impurity crystals. The formulas given by (3.3)–(3.6) and subsequent formulas given by (3.7)–(3.11) were obtained by Pekar<sup>1</sup> in the 1950's on the assumption that the Franck-Condon potential surfaces retained their shape under electronic excitation of the impurity center ( $\hat{W}=0$ ) and the Condon approximation was valid [ $M(R)=\text{const}$ ], i.e., only part of the adiabatic interaction was included. In this approximation, the conjugate absorption and fluorescence bands exhibit mirror symmetry relative to the energy of the zero-phonon transition, and the phonon function depends simply on temperature:

$$f(\nu, T) = (n(\nu) + 1) \nu(\nu) + n(-\nu) \nu(-\nu), \quad (3.7)$$

where

$$\nu(\nu) = \sum_{\kappa} \left( \frac{a_{\kappa}}{2} \right)^2 \delta(\nu - \nu_{\kappa}) = \frac{3N}{2} \xi^2(\nu) \rho(\nu), \quad (3.8)$$

$a_{\kappa}/\sqrt{2}$  is the shift of the position of equilibrium of the  $\kappa$ -th normal oscillator, referred to the amplitude of its zero-point vibrations,  $N$  is the number of molecules in the crystal,  $\xi^2(\nu)$  is a function of the electron-phonon coupling,  $n(\nu) = (e^{\nu/kT} - 1)^{-1}$ , and  $\rho(\nu)$  is the density of phonon states of the solvent containing the impurity. The single-phonon function  $\nu(\nu)$  is related to the probability  $\Phi_1(\nu)$  of the phototransition with the creation of one phonon by the simple expression:

$$\Phi_1(\nu) = (n(\nu) + 1) \nu(\nu) \exp \left[ -\int_0^{\infty} d\omega \nu(\omega) (2n(\omega) + 1) \right]. \quad (3.9)$$

If we substitute (3.7) in (3.4) and (3.5), we find that the

<sup>7)</sup>The long-wave edge of the absorption bands well away from the maximum is described by the Urbach formula.<sup>41,42</sup>

Stokes shift  $2A$  is independent of temperature because

$$A = \int_0^{\infty} d\nu \nu \nu(\nu). \quad (3.10)$$

For  $kT \gg \nu_D$ , the band half-width  $\Delta_{\Gamma}(T)$  is related to the temperature and Stokes shift, as follows:

$$\Delta_{\Gamma}^2(T) = 16B(T) \ln 2 \approx \Delta_{\Gamma}^2(0) + kTA \ln 2. \quad (3.11)$$

The question is—how will (3.3)–(3.11) change when  $\hat{W} \neq 0$  and  $M(R) \neq \text{const}$ ? The answer to this question could not be provided by the theory until relatively recently, although the influence of  $\hat{W}$  and  $M(R)$  on the optical band shape was examined by a number of workers.<sup>39,43-45</sup> More recently, this question was investigated by Osad'ko.<sup>46-48</sup> These investigations have shown that (3.3)–(3.5) retain their form, but (3.7)–(3.11) are modified. These changes are particularly well defined in structured optical bands and are therefore considered below.

## B. Structured bands

In a structured band, the PW consists of phototransitions with the creation of a small number of phonons (between one and three). Such PW can be generated by either the FC or HT coupling or both. It is usually assumed that the dependence of the electronic matrix element  $M$  on the intermolecular vibrational coordinates  $R$  is significant only when one considers PW in bands with forbidden pure electronic transitions. It will be shown below that the HT coupling may also play an important role in bands corresponding to allowed electronic transitions. There are, in fact, three qualitative criteria enabling us to identify which of the two interactions (FC or HT) is responsible for the PW. Firstly, if the PW is generated by the FC coupling, intensity must be transferred from the ZPL to the PW as the temperature increases.<sup>8)</sup> This transfer is shown in Fig. 3. The rate of energy transfer increases with increasing PW intensity at zero temperature. The following quantitative estimate is now available<sup>25,32</sup>: if the Debye-Waller factor at  $T=4$  °K is roughly 0.2–0.3, the ZPL will almost completely “drown” in the PW even at 40 °K. Secondly and conversely, if the PW is generated by the HT coupling, the integrated ZPL intensity is practically independent of temperature.<sup>47</sup> Thirdly, if both FC and HT are operating, the Debye-Waller factor will be different for the conjugate absorption and fluorescence bands.<sup>47</sup> The explicit form of the functions  $J(\omega)$  and  $\Phi(\omega)$  describing ZPL and PW in (3.1) depends on the particular form of the electron-phonon coupling. Three topical special cases are examined below.

### 1. Basic model

Suppose  $a \neq 0$  and the other interaction parameters are all zero. Although this so-called basic model has frequently been discussed, one of its aspects has not been considered in the review literature. This is that, within the framework of this model, one can calculate

<sup>8)</sup>This result is already implied in the formulas given by Krivoglaz and Pekar<sup>43</sup> and Davydov.<sup>38</sup> However, it attracted its due attention only after the discovery of the Mössbauer effect.<sup>50-52</sup>

theoretically the temperature reduction in the ZPL intensity by using only the experimental PW shape function at zero temperature. If one then compares the reduction in the integrated ZPL intensity calculated in this way with experimental data, one can determine whether the FC interaction is responsible for the PW. This procedure was first used by Personov *et al.*<sup>25</sup> and is summarized below.

Within the framework of the basic model, the functions  $J(\omega)$  and  $\Phi(\omega)$  are given by

$$J(\omega) = M^2 e^{-f(T)} \delta(\omega), \quad (3.12)$$

$$f(T) = \int_{-\infty}^{\infty} dv f(v, T) = \int_0^{\infty} dv v(v) \coth \frac{v}{2kT}, \quad (3.13)$$

$$\begin{aligned} \Phi^g(\omega) = & \sum_{m=1}^{\infty} \frac{1}{m!} \int_{-\infty}^{\infty} dv_1 \dots \int_{-\infty}^{\infty} dv_m f(v_1, T) \dots f(v_m, T) \\ & \times J(\omega \mp v_1 \mp \dots \mp v_m) \end{aligned} \quad (3.14)$$

$(g=0, e),$

where  $f(v, T)$  and  $v(v)$  are given by (3.7) and (3.8). It is readily seen that

$$\Phi^o(\omega) = \Phi^e(-\omega), \quad (3.15)$$

i.e., the conjugate PW exhibits mirror symmetry relative to  $\omega=0$ , which is taken as the energy of the zero-phonon transition. Mirror symmetry of the conjugate PW is the main indication that a change in  $\hat{W}$  is, in fact, so small that it can be neglected. The  $m$ -th term in (3.14) can be interpreted as the probability of the  $m$ -phonon phototransition. Integrating the  $m$ -th term in (3.14) with respect to  $\omega$ , we obtain the well-known expression

$$\Phi_m = M^2 e^{-f(T)} \frac{f(T)^m}{m!}. \quad (3.16)$$

The multiphonon transition probability increases with increasing  $f(T)$ , as shown in Fig. 4. The PW is, therefore, of the multiphonon type for  $f > 5 - 10$ , and (3.14) is then close to the approximate formula (3.3). If, on the other hand,  $f \approx 1 - 3$ , which occurs in the case of  $b$  bands, only the first few terms are important in (3.14) and all the others are very small. The function  $v(\omega)$  can then be "extracted" from  $\Phi(\omega)$  measured at  $T=0$  by solving the equation<sup>53, 54</sup>

$$\begin{aligned} v(\omega) = & J^{-1} \left[ \Phi(\omega) \right. \\ & \left. - \frac{1}{\omega} \int_0^{\omega} dv v(v) v \Phi(\omega - v) \right]. \end{aligned} \quad (3.17)$$

If the integrated ZPL intensity  $J$  is much greater than the PW intensity, i.e.,  $\alpha \geq 0.8$ , then (3.17) shows that

$$v(\omega) \sim J^{-1} \Phi(\omega). \quad (3.18)$$

However, this approximation cannot be used if  $\alpha \approx 0.6 - 0.2$ , and one must then perform a numerical solution of (3.17). This has been done by a number of authors.<sup>25, 32, 33, 36, 60</sup> Equation (3.17) is not linear in  $v(v)$  because  $J$  is also a function of this. It is therefore usual to proceed as follows. Before the numerical solution of (3.17) is performed, the value of  $J$  determined from the experimental curve  $J(\omega)$  is substituted into this equation on the same scale on which the function  $\Phi(\omega)$  is constructed. The result of the solution of (3.17) is very dependent on the precision with which  $J$  is measured. The importance of this precision increases with

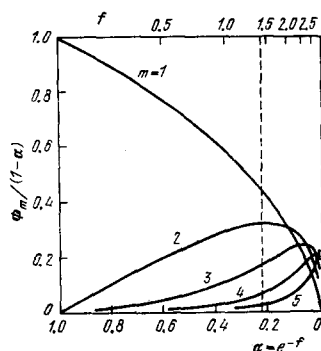


FIG. 4. Relative contribution of  $m$ -phonon phototransitions to the integrated intensity of the phonon wing for different values of the Debye-Waller factor<sup>32</sup>  $\alpha$ . Broken line shows the value of  $\alpha$  for the band shown in the top-left corner of Fig. 3.

decreasing  $J$ . In practice, therefore, Eq. (3.17) can only be used for  $\alpha \geq 0.2$ .

The connection between the temperature reduction in the integrated ZPL intensity and the PW intensity at zero temperature, expressed by (3.12) and (3.13), and by (3.17), will be different if the HT coupling is not very weak. Experimental verification of this connection is, therefore, also an indication that the HT interaction is relatively unimportant in the experimentally investigated bands. This has been shown by the authors of Refs. 25 and 32. Figure 3 shows  $v(v)$  "extracted" from the PW and the temperature reduction in the integrated ZPL intensity calculated with the aid of this function from (3.12) and (3.13). The agreement between the calculated and the measured reduction suggests that PW under investigation is of Franck-Condon origin.

## 2. The complete Franck-Condon coupling

Suppose that  $a \neq 0$  and  $\hat{W} = 0$ , i.e., the FC coupling is completely taken into account and the HT coupling is neglected. Since the matrix  $\hat{W}$  is different in the electronically excited and unexcited crystals, the normal coordinates of the vibrations are also different. This leads to the following mathematical problem: there is no coordinate system in which the multidimensional Franck-Condon overlap integral for the oscillator wave function can be split into products of one-dimensional integrals. All published calculations<sup>22, 43-45, 55-59</sup> of the effect of  $\hat{W}$  on band shape are therefore subject to serious restrictions.<sup>9)</sup> Many practical questions cannot, therefore, be answered by the theory in a way that would satisfy experimenters. It is only quite recently that many of the questions connected with the role of  $\hat{W}$  have been answered.<sup>48</sup> A summary of this work is given below.

In this case, the zero-phonon line is described by a Lorentzian function  $J(\omega)$ . The position of its maximum and its half-width are functions of temperature. This is examined in detail in Secs. 4 and 5. The function  $\Phi^e(\omega)$  for the phonon wing is described by (3.14) with  $f(v, T)$  defined by (3.7), and (3.8) replaced by the new functions  $f^e(v, T)$ . Since different normal coordinates

<sup>9)</sup>The only exception is the paper by Kubo and Toyazawa,<sup>40</sup> but practical applications of their results appear to encounter difficulties that cannot be overcome.

correspond to the excited and unexcited states, the functions  $f^0(\nu, T)$  and  $f^e(\nu, T)$  are different. The phonon wings in conjugate absorption and luminescence bands are therefore found to have different shapes. However, the integrated intensity of conjugate phonon wings is the same. Lack of mirror symmetry of this kind (the shapes are not mirror-symmetric) is the main reason for the importance of the term  $\hat{W}$  in these bands. The other feature associated with  $\hat{W}$  is that the functions  $f^e(\nu, 0)$  are not the zero-phonon functions, i.e., their nonzero values are not confined to the one-phonon interval, as in case A. They are, in fact, sums of one-, two-, three-, and so on, phonon functions. However, many-phonon functions can be neglected on the one-phonon frequency interval since, for realistic values of  $\hat{W}$ , they are much smaller than the one-phonon function  $v_1^e(\nu)$  in this interval.<sup>48</sup> Hence,

$$f^e(\nu, 0) \equiv f^e(\nu) \approx v_1^e(\nu). \quad (3.19)$$

The functions  $f^e(\nu)$  can be found from (3.17) by substituting into it the measured functions  $\Phi^e(\omega)$ , the shape of the phonon wing, and the integrated zero-phonon line intensity.

Since the perturbation introduced by the impurity into the solvent is very localized, the matrix  $\hat{W} = \hat{U}^e - \hat{U}^0$  can have only a few elements that are appreciably different from zero. So far, it has always been assumed in papers concerned with numerical results that the matrix  $\hat{W}$  has only the one element  $W$ .<sup>10)</sup> This assumption was used to establish a quantitative connection<sup>48</sup> between the functions  $f^0(\nu)$  and  $f^e(\nu)$ . By assuming that the density of phonon states was close to the Debye density, we succeeded<sup>48</sup> in calculating the shape of the one-phonon and two-phonon functions. Figure 5 shows the calculated one-phonon functions derived from the exact formula given in our previous paper.<sup>48</sup> It is clear that there is no mirror symmetry and that the departure from this symmetry progressively increases with increasing value of the parameter  $b = W/\nu_D^2$ , where  $\nu_D$  is the frequency at the limit of the phonon spectrum. According to Fig. 5,  $b = -0.2$  or  $0.2$  corresponds to quasi-local and local vibration in the absorption spectrum, respectively. This vibration can be present only in an electronically excited impurity center. It is absent from the luminescence spectrum. This new effect has not, so far, been examined experimentally.

There is considerable practical interest in establishing a simple analytic connection between the one-phonon functions  $v_1^0(\nu)$  and  $v_1^e(\nu)$  which, for  $|b| < 0.2$ , are practically identical with the functions  $f^0(\nu)$  and  $f^e(\nu)$  "extracted" from the phonon wings with the aid of (3.17). These one-phonon functions  $v_1^e(\nu)$  after they have been multiplied by the Debye-Waller factor determine the probability of absorption and emission with the creation of one phonon. For practical purposes, we may try the simple expression<sup>48</sup>

<sup>10)</sup>This approximation does not, of course, signify that we are considering the interaction between impurity-center electrons and only one vibrational mode. This model will satisfactorily describe several realistic physical situations involving phonons.

$$v_1^0(x) = \frac{r_1^0(x)}{[1 - \beta\Omega(x)]^2 + |\beta r_1^0(x)|^2}, \quad (3.20)$$

where

$$\Omega(x) = \int_0^1 \frac{dy}{\pi} \frac{2r_1^0(y)}{x^2 - y^2}; \quad (3.21)$$

$x, y = \nu/\nu_D$ ,  $\nu_D$  is the limit frequency in the one-phonon region,  $\beta = W/a^2\nu_D^3$ , and  $2a$  is the change in the equilibrium separation between the pair of molecules whose elastic constant has changed by  $W$ . The validity of (3.20) improves with decreasing  $W$ . However, even for  $|b| \approx 0.2$ , when the departure from mirror symmetry is well defined, the approximate formula given by (3.20) does satisfactorily reproduce the actual departure. This follows from Fig. 5, where the broken curve represents the functions  $v_1^0(x)$  and  $v_1^e(x)$ , associated with (3.20).

The influence of  $W$  on the Debye-Waller factor is quite slight. Realistic values of  $W$  can change this factor by 10–15% as compared with the  $W = 0$  case.<sup>48</sup> Thus, the first effect of a change in the strength matrix during excitation of an impurity center is the appearance of a difference between the shape of conjugate phonon wings. If we use (3.20) and the formula

$$\int_0^1 dx v_1^0(x) \approx a^2\nu_D, \quad (3.22)$$

together with experimental data on departures from mirror symmetry, we can determine the magnitude and sign of the parameter  $W$ . The influence of  $W$  on the absolute values of the phonon-wing and zero-phonon line intensities is quite small.

### 3. Combined effect of Franck-Condon and Herzberg-Teller coupling

Suppose  $a \neq 0$  and  $M(R) \neq \text{const}$ , and let us assume that the change in the shape of the Franck-Condon potential surfaces can be neglected. The departure from mirror symmetry that arises in this case is different from that discussed in subsection 2 because the Debye-Waller factor is different for the conjugate absorption and

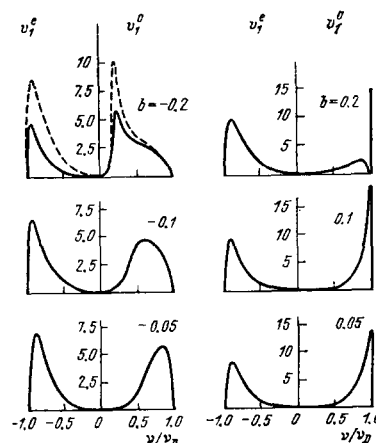


FIG. 5. Violation of mirror symmetry of one-phonon functions due to the change in the force matrix  $U$  during a phototransition. Solid curves are calculated from the exact formulas given in our previous paper;<sup>48</sup> broken curves are calculated from the approximate formulas in the same paper. The two are related through Eq. (3.20) ( $b = W/\nu_D^2, a^2\nu_D = 1$ ).

fluorescent bands, i.e., the areas under the conjugate phonon wings are different (this is the departure from mirror symmetry in area, Fig. 6). This is the most reliable indication of the fact that the phonon wing is due to both types of coupling. When the HT coupling is present, the multiphonon phototransition is no longer expressed in terms of the convolution of identical phonon functions as in subsections 1 and 2, above. Equation (3.17), founded precisely on this property of multiphonon transitions, is therefore no longer valid. However, if the HT coupling is weak enough, so that the parameter characterizing its magnitude is much greater than its square, we may suppose that (3.17) is approximately valid. It then involves the quantity

$$J = \sqrt{J^0 J^e}, \quad (3.23)$$

where  $J^0$  and  $J^e$  are the integrated intensities of the zero-phonon absorption and fluorescence bands, measured on the scale on which the integrated intensities of zero-phonon plus phonon-wing absorption and fluorescence bands are equal to unity. The functions "extracted" from the phonon wing can be approximately described by the following expressions (positive and negative signs refer to  $f^0$  and  $f^e$ , respectively):

$$f^{\pm}(\nu) \approx v^{\pm}(\nu) = \sum_{\kappa} \left( \frac{\alpha_{\kappa}}{2} \pm \alpha_{\kappa} \right)^2 \delta(\nu - \nu_{\kappa}), \quad (3.24)$$

where

$$\alpha_{\kappa} = \left( \frac{\partial M(R)}{\partial R_{\kappa}} \frac{1}{M(R)} \right)_{-a/2} \quad (3.25)$$

is the parameter characterizing the influence of the HT coupling on the  $\kappa$ th vibrational mode, and  $a_{\kappa}$  is the shift in the equilibrium position of this oscillator. If we suppose that the electronic matrix element depends only on those coordinates  $R$  for which there is a shift in the equilibrium positions during the electronic excitation of the impurity center, then

$$\alpha_{\kappa} \approx \eta \frac{a_{\kappa}}{2}. \quad (3.26)$$

In this approximation, the one-phonon functions  $v^{\pm}(\nu)$  and their integrated values  $v^{\pm} = -\ln J^{\pm}$  are given by

$$v^{\pm}(\nu) = (1 \pm \eta)^2 \frac{3N}{2} \xi^2(\nu) \rho(\nu) = (1 \pm \eta)^2 v(\nu), \quad (3.27)$$

$$2\eta \approx \frac{v^0 - v^e}{v^0 + v^e}, \quad (3.28)$$

$$v \approx \frac{v^0 + v^e}{2}. \quad (3.29)$$

The last formula enables us to find the strength of the

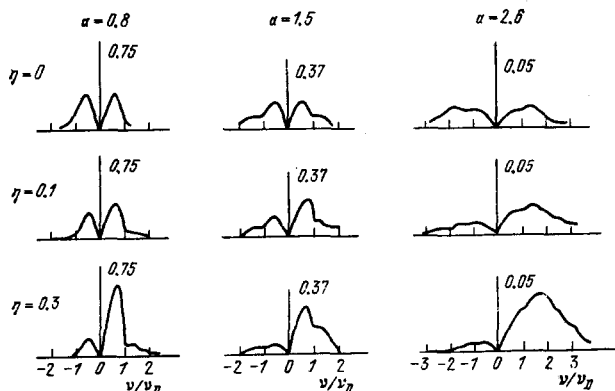


FIG. 6. Violation of mirror symmetry of conjugate optical bands at zero temperature due to the combined effect of FS and HT coupling<sup>47</sup> ( $\alpha = \sqrt{2}v$ ).

FC coupling, whereas (3.28) yields the relative strength of the HT and the FC coupling. The temperature reduction in the integrated intensity of the zero-phonon line in this case can also be obtained from (3.12) and (3.13), except that the function  $v(\nu)$  in the latter expression must be replaced by the average of  $v^0(\nu)$  and  $v^e(\nu)$ . Figure 6 shows the shapes of the absorption and fluorescence bands at  $T=0$ , calculated<sup>47</sup> with the aid of (3.12)–(3.14) and (3.27) for different values of  $v$  and  $\eta$ . It is clear that even a small departure from the Condon approximation ( $\eta=0.1$ ) leads to an appreciable departure from mirror symmetry. The degree of this departure does not depend on the absolute strength of the HT coupling but on the relative strength of the HT and the FC coupling.

In conclusion of our discussion of the use of phonon wings in studies of the electron-phonon coupling, we note that there have been no quantitative experimental studies of structurally conjugate absorption and fluorescence bands. However, the theory given in this subsection shows that it is precisely the study of conjugate phonon wings that can be a source of important and fundamentally new information.

#### 4. TEMPERATURE BROADENING AND THE SHIFT OF ZERO-PHONON LINES

The electron-phonon coupling generates not only the phonon wings but also the temperature broadening and the shift of the zero-phonon lines. Appreciable temperature broadening of the optical zero-phonon lines is the main property that distinguishes them from the Mössbauer  $\gamma$ -lines. Attempts to relate the half-width of the zero-phonon lines corresponding to the first singlet-singlet or singlet-triplet transition to the lifetime  $\tau$  of the excited electronic state with the aid of the formula

$$\gamma = \frac{\hbar}{\tau} \quad (4.1)$$

lead to a contradiction because the observed half-width exceeds the half-width associated with the lifetime given by (4.1) by two or three orders of magnitude.<sup>11</sup> This contradiction, and the fact that the half-width of vibronic zero-phonon lines is practically the same as the half-width of the pure electronic zero-phonon line,<sup>62</sup> lead to the conclusion that the radiative and radiationless transitions are of secondary importance in the broadening of such zero-phonon lines. Various mechanisms have been proposed for the observed half-width of optical zero-phonon lines.<sup>63–66</sup> However, none of them has so far received convincing experimental confirmation. Moreover, some of these mechanisms (the fluctuation mechanism<sup>63, 64</sup> and the anharmonic mechanism<sup>66</sup>) have raised some theoretical objections.<sup>67, 78</sup> In this review, therefore, we shall confine our attention to the mechanism proposed by Silsbee.<sup>65</sup> This temperature broadening mechanism, sometimes referred to as the Raman or the modulation mechanism, will be referred to in this paper as the adiabatic mechanism in

<sup>11</sup>We note the paper by Korotaev *et al.*,<sup>64</sup> in which it is shown that the  $T-T$  absorption bands of certain complex molecules have the Lorentz shape and half-widths approximately equal to 300–400  $\text{cm}^{-1}$ .



order to emphasize the fact that it can produce the zero-phonon line broadening in the adiabatic approximation.<sup>12)</sup> There is little doubt as to the validity of this mechanism.

In 1962, Silsbee showed<sup>65</sup> that the second moment of the optical line depends on temperature if the change in  $W$  of the force matrix of the crystal during electronic excitation of an impurity center is different from zero. Later, McCumber and Sturge<sup>69</sup> and Krivoglaz<sup>66</sup> used a perturbation theory in  $W$  to derive a formula for the temperature dependence of the half-width  $\gamma(T)$  and shift  $\delta(T)$  of the zero-phonon line. In the course of the subsequent years, the problem of broadening, shift, and shape of the zero-phonon line was examined without the use of perturbation theory in  $W$ , and the following formula was derived for the temperature broadening and shift of the zero-phonon line of Lorentz shape<sup>70, 47</sup>:

$$\frac{\gamma(T)}{2} + i\delta(T) = i\delta(0) + \int_0^{\infty} \frac{d\nu}{2\pi} \ln \left( 1 + \frac{i2Wn(\nu)\Gamma(\nu)}{1 - W\Omega(\nu) - iW\Gamma(\nu)} \right). \quad (4.2)$$

It was assumed in the derivation of this formula that the matrix  $\hat{W}$  had only one nonzero element (see footnote 10). The function  $\Gamma(\nu)$  can be approximately expressed<sup>48</sup> in terms of the one-phonon function  $\nu_1^e(\nu)$  as follows:

$$\Gamma(\nu) = \frac{\nu_1^e(\nu)}{a^2\nu_D\nu}, \quad (4.3)$$

and the function  $\Omega(\nu)$  is given by (3.21). Recently, the present author and S. A. Zhdanov obtained a generalization of (4.2) to the case where  $\hat{W}$  is a matrix of arbitrary rank:

$$\frac{\gamma(T)}{2} + i\delta(T) = i\delta(0) + \int_0^{\infty} \frac{d\nu}{2\pi} \ln \left\{ \text{Det} \left( \hat{I} + \frac{i2n(\nu)\hat{W}\hat{\Gamma}(\nu)}{\hat{I} - \hat{W}\hat{\Omega}(\nu) + i\hat{W}\hat{\Gamma}(\nu)} \right) \right\}. \quad (4.4)$$

It is important to note that all numerical calculations of the temperature broadening and shift have so far been based on the assumption that  $\hat{W}$  is a matrix of rank 1. We have therefore confined our attention to this case in the present review. Numerical calculations based on (4.2) and an examination of this expression are given in the literature.<sup>71-73</sup> Figure 7 shows some of the numerical results. The most important conclusion of this analysis and of the analysis given in Ref. 47 are summarized below.

#### A. Shape of the zero-phonon line and dependence of the shape on $W$ only

If the only assumption we make is that the function  $\Gamma(\nu)$  in (4.2) is bounded, we can show that the zero-phonon line of an isolated impurity center should have the Lorentz shape.<sup>13)</sup> The half-widths  $\gamma(T)$  and shift  $\delta(T)$  of the line position as functions of temperature are given by (4.2) and (4.4). The shift  $a$  in the positions of equilibrium of the oscillators, and also the HT coupling

<sup>12)</sup>Nonadiabatic broadening mechanisms have frequently been discussed in the literature. References can be found in a book by Perlin and Tsukerblat.<sup>9</sup>

<sup>13)</sup>The half-width of the zero-phonon line can be associated with a lifetime but there is no simple physical interpretation that can be given to this lifetime.

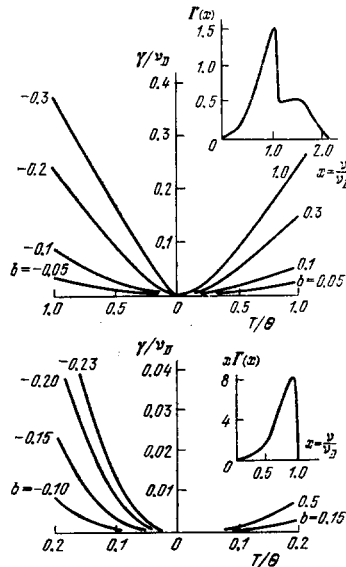


FIG. 7. Temperature broadening of the zero-phonon line, calculated from Eq. (4.2). The function  $\Gamma(x)$  is shown on the right in each case. The upper  $\Gamma(x)$  is area-normalized to unity and the lower is normalized so that  $\int_0^{\infty} dx x\Gamma(x) = \pi$ . The numbers against the  $\gamma(T)$  curves are the corresponding values of the parameter  $b = W/\nu_D^2\theta = k\nu_D$ .

which plays a dominant role in the appearance of the phonon wings, do not affect the temperature broadening or the shift of the zero-phonon line. This means that the appearance of the phonon wings and the temperature broadening and shift of the zero-phonon lines are due to different terms in the electron-phonon coupling.<sup>47</sup>

#### B. Connection between zero-phonon lines in conjugate absorption and fluorescence bands

This is not a trivial question because the optical zero-phonon line is not due to a phototransition without a change in the state of the phonon subsystem (as in the case of the Mössbauer  $\gamma$ -line). Theoretical analysis shows that the half-width and shift of the zero-phonon lines in conjugate absorption and luminescence bands are given by expressions that are superficially different.<sup>47</sup> However, it can be shown<sup>47</sup> that they do, in fact, give the same numerical results, i.e., the zero-phonon lines in conjugate bands exhibit resonance behavior at any temperature and are broadened in the same way, with

$$\gamma(0) = 0. \quad (4.5)$$

#### C. Connection between equation (4.2) and approximate expressions

The perturbation theory in  $W$  is valid if

$$W\Gamma_m \ll 1, \quad (4.6)$$

where  $\Gamma_m$  is the maximum value of the weighted density of phonon states  $\Gamma(\nu)$ . In the first nonvanishing approximation in  $W$ , the expression given by (4.2) leads to the following formulas for weak temperature broadening and shift<sup>66, 69</sup>:

$$\begin{cases} \delta(T) = W \int_0^{\infty} \frac{d\nu}{\pi} \Gamma(\nu) n(\nu), \\ \gamma(T) = 2W^2 \int_0^{\infty} \frac{d\nu}{\pi} \Gamma^2(\nu) n(\nu) (n(\nu) + 1). \end{cases} \quad (4.7)$$

If we use the Debye approximation for the phonon spectrum in these formulas and substitute  $\Gamma(\nu/\nu_D) = 3\pi(\nu/\nu_D)^3$ , where  $\nu_D$  is the Debye frequency, we obtain

$$\begin{cases} \delta(T) = \nu_D \cdot 3b \left(\frac{T}{\Theta}\right)^4 \int_0^{\Theta/T} \frac{x^3 dx}{e^x - 1}, \\ \gamma(T) = \nu_D \cdot 18\pi b^2 \left(\frac{T}{\Theta}\right)^7 \int_0^{\Theta/T} \frac{x^6 e^x dx}{(e^x - 1)^2}, \end{cases} \quad (4.8)$$

where  $\Theta$  is the Debye temperature and  $b = W/\nu_D^2$  is a dimensionless parameter. These expressions are very frequently used in the analysis of experimental data. They involve the two parameters  $b$  and  $\Theta$ .

The sharper the peaks in the function  $\Gamma(\nu)$ , the more difficult it is to satisfy condition (4.6). For example, if the crystal vibrations include a well-localized vibration  $\nu_i$ , then  $\Gamma(\nu) \approx \delta(\nu - \nu_i)$ . It then follows from (4.7) that  $\gamma(T) = \infty$ . This meaningless result is an illustration of the fact that the perturbation theory in  $W$  is not correct in the presence of strongly localized vibrations.<sup>14)</sup> If, however, we suppose that the vibration is not strictly localized and has a half-width  $2\gamma_i$ , i.e.,

$$\Gamma(\nu) \approx \frac{1}{\nu_i} \frac{\gamma_i}{(\nu - \nu_i)^2 + \gamma_i^2}, \quad (4.9)$$

then (4.7) leads to the formulas first established by Krivoglaz<sup>66</sup>:

$$\begin{cases} \delta(T) = \nu_i \frac{W}{\nu_i^2} n(\nu_i), \\ \gamma(T) = \nu_i \frac{W}{\nu_i^2} \frac{W}{\nu_i \gamma_i} n(\nu_i) [n(\nu_i) + 1]. \end{cases} \quad (4.10)$$

These expressions have frequently been used in the analysis of experimental data.<sup>74-76</sup> The condition for their validity is

$$\frac{W}{\nu_i \gamma_i} \ll 1, \quad (4.11)$$

which follows from (4.6).

At low enough temperatures, for which  $n(\nu) \ll 1$  for all frequencies for which  $\Gamma(\nu)$  differs appreciably from zero, we can expand the integrand in (4.2) into a series in  $n(\nu)$  and obtain the following expression for the low-temperature broadening and shift<sup>77</sup>:

$$\delta(T) - i \frac{\gamma(T)}{2} = \int_0^{\infty} \frac{d\nu}{\pi} n(\nu) \frac{W\Gamma(\nu)}{1 - W\Omega(\nu) + iW\Gamma(\nu)}. \quad (4.12)$$

This expression has also been used in the interpretation of experimental data.<sup>33, 78, 79</sup>

#### D. "Limiting" and weak broadening

The exact formula given by (4.2) has one very important property, namely, it predicts a bounded rate of temperature broadening, i.e., the rate of temperature broadening  $\Delta\gamma/\Delta T$  ceases to increase for practical purposes with increasing  $W$  for relatively small values of  $W$ . Numerical calculations show<sup>73</sup> that the maximum achievable rate of temperature broadening is  $0.3 \text{ cm}^{-1}/\text{deg}$ , i.e.,

$$\frac{\Delta\gamma}{\Delta T} \leq 0.3 \text{ cm}^{-1}/\text{deg}. \quad (4.13)$$

The formula given by (4.2) can also be used to determine the limit for the rate of temperature broadening

<sup>14)</sup> According to the more accurate formula given by (4.2), the interaction with the perfectly localized vibrations does not contribute to the ZPL half-width.<sup>73</sup>

that can be described by (4.7), (4.8), and (4.10). Comparison of the broadening calculated from the exact formula (4.2) with that obtained from the approximate formula (4.7) has shown<sup>73</sup> that, when

$$\frac{\Delta\gamma}{\Delta T} \leq 0.05 \text{ cm}^{-1}/\text{deg} \quad (4.14)$$

the approximate and exact curves may be regarded as very close to one another. The condition given by (4.14) may therefore be looked upon as the upper limit for weak temperature broadening.

The temperature shift of the zero-phonon line due to a change in  $W$  of the force matrix is less than the temperature broadening. It occurs in the direction of the red part of the spectrum, if elastic forces become weaker ( $W < 0$ ), and in the violet direction, if they become stronger ( $W > 0$ ) during the excitation of the impurity center.

### 5. EXPERIMENTAL STUDIES OF SHIFT AND BROADENING OF THE ZERO-PHONON LINE AND COMPARISON WITH THEORY

We must now consider the extent to which the theoretical treatments summarized in the last section agree with experimental results. The shape of the zero-phonon line and its broadening and shift have been the subject of many experimental investigations.<sup>28-31, 33, 62, 74-76, 80-84, 87-89</sup>

#### A. Shape of zero-phonon line

The shape of the zero-phonon line has often been studied. For example, Al'shits *et al.*<sup>80</sup> have established that the zero-phonon line of perylene in *n*-octane and 1, 12-benzperylene in *n*-hexane has the Gaussian shape at 4.2 °K, and that its half-width is very dependent on the way in which the impurity crystal has been prepared and amounts to a few  $\text{cm}^{-1}$ . The line shape gradually changes as the temperature is increased, and eventually assumes the Lorentz shape at 40 °K. At intermediate temperatures, it can be described by the Voigt curve with the Gauss parameter independent of temperature and the Lorentz parameter decreasing rapidly with increasing temperature. All this enabled these workers to assign the Gaussian component to inhomogeneous broadening and the Lorentz component to  $W$ .

Freiberg<sup>27</sup> investigated the shape of one of the vibronic zero-phonon lines of  $O_2$  in KCl crystals and showed that the zero-phonon line shape was already described by the Voigt shape at 4.2 °K with the Gauss and Lorentz parameters having comparable values and being very dependent on the method of preparation of the crystal.<sup>27</sup> On this basis, the entire half-width of the zero-phonon line (a few  $\text{cm}^{-1}$  at 4.2 °K) was assigned to inhomogeneous broadening. The Gaussian component was assigned to dislocations and the Lorentz component to point defects because these components depended on the dislocation density and the density of point defects, respectively.

These results indicate that the half-width of the zero-phonon line, which amounts to a few  $\text{cm}^{-1}$  at 4.2 °K is due to inhomogeneous broadening. It is, nevertheless,

interesting to consider the homogeneous half-width of the zero-phonon line at this temperature. The recently discovered effect of hole burning in inhomogeneous broadened lines<sup>82, 85, 86</sup> can be used to resolve this problem. It was found<sup>82</sup> that the homogeneous half-width of the 0-0 zero-phonon line of perylene in ethanol at 4.2 °K is approximately 0.3 cm<sup>-1</sup>. The same method was used to establish<sup>86</sup> that the homogeneous half-width of the 6940 Å zero-phonon line of H<sub>2</sub>-phthalocyanine in *n*-octane at 5 °K is 0.03 cm<sup>-1</sup>. Its half-width is lower by a factor of a hundred than the inhomogeneous broadening seen in the fluorescence spectrum under usual excitation with a lamp.

Thus, although the homogeneous half-width of the zero-phonon line at 4.2 °K is very much smaller than the inhomogeneous line width, it is, nevertheless, greater by one or two orders of magnitude than the radiative half-width, whose relation to the lifetime is given by (4.1). Since (4.2) predicts that  $\gamma \neq 0$  at 4.2 °K, we may suppose that this residual homogeneous half-width may be due to the adiabatic mechanism. To verify this suggestion, Voelker *et al.*<sup>76</sup> have measured the temperature dependence of the homogeneous half-width of the zero-phonon line of H<sub>2</sub>-porphin in *n*-octane in the range 1.4–4.2 °K. By approximating the experimental points with the theoretical curve for  $\gamma(T)$ , calculated from (4.10), it was found that the residual half-width at zero temperature was  $\gamma \approx 3 \times 10^{-4}$  cm<sup>-1</sup>. The relation between this and the lifetime of the electronic excitation in the H<sub>2</sub>-porphin molecule is, in fact, given by (4.1). Similar studies of the residual half-width of the zero-phonon line using its temperature dependence in the range 4.2–30 °K have been reported by Goročovski and Rebane.<sup>75</sup>

### B. Temperature broadening and shift of zero-phonon lines in conjugate absorption and fluorescence bands

There is very little published information in this field. Figure 8 shows the data reported by Personov and Solodunov,<sup>81</sup> which show that the temperature dependence of the maximum of the quasines is different in the absorption and the fluorescence spectra. This departure from resonance behavior is in conflict with the predictions of the theory. It is probably due to the fact that the zero-phonon line was not separated from the phonon background in these quasines.<sup>81</sup> A special study of the temperature dependence of the zero-phonon lines in conjugate spectra has been reported by Sheka

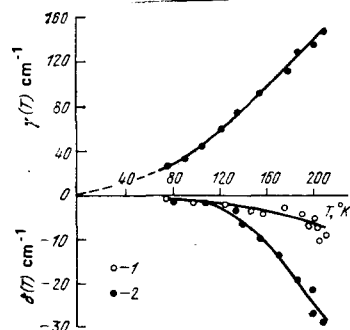


FIG. 8. Temperature broadening and shift of the 4030 Å quasilines due to 3,4-benzpyrene in *n*-octane:<sup>81</sup> 1—absorption line; 2—fluorescence line.

and Meletov.<sup>86</sup> Their measurements of the half-width and shift of the zero-phonon lines in conjugate spectra of three different impurity molecules confirm the theoretical prediction that the zero-phonon lines on conjugate spectra are identical.

### C. Method used to compare measured and calculated half-widths

The method used to compare measured and calculated half-widths must be carefully examined because it often turns out to be suspect. In the great majority of experimental papers, temperature broadening is compared with the simple formulas given by (4.8) and (4.10). These formulas contain two parameters, namely,  $W$ , which characterizes the electron-phonon coupling, and the parameter  $\Theta$  or  $\nu_i$ , which characterizes the phonon, the interaction with which is responsible for the broadening of the zero-phonon line. The choice of phonon parameters  $\Theta$  or  $\nu_i$  is often a matter of controversy, and the temperature curve  $\gamma(T)$  is very dependent on the magnitude of the parameters in the temperature range under consideration. In most cases, no restriction is imposed in these papers on the magnitude of the coupling parameter  $W$ , although a restriction on its magnitude does exist. It is defined by (4.14). Agreement between theoretical and experimental data obtained under these conditions may well turn out to be fortuitous. At the very least, it provides no foundation for the conclusion that the adiabatic mechanism of temperature broadening has been experimentally confirmed. This is illustrated by the data shown in Table I. Experimental data on the broadening of all the zero-phonon lines other than the 4518 Å line have been interpreted in terms of (4.8) or (4.10) either by the workers who obtained these data or by other workers. The penultimate column of the table shows the mean rate of temperature broadening of the zero-phonon lines which we have calculated from the corresponding experimental points. Comparison of these rates with the theoretical criteria given by (4.13) and (4.14), which follow from the formula given by (4.2) which is more accurate than (4.8) and (4.10), shows that there is even a qualitative dis-

TABLE I. Data on zero-phonon lines of organic impurity crystals whose temperature broadening has been compared with theory.

Impurity molecule	Spectrum	$\lambda$ ZPL Å	Solvent	Temperature range	$\frac{\Delta\gamma}{\Delta T}$ cm <sup>-1</sup> /deg	Reference
1,12-benzperylene	Fluor.	4060	<i>n</i> -hexane	$T > 77$ °K	0.9	81
3,4-benzpyrene	»	4030	<i>n</i> -octane	ditto	0.8	
Perylene	»	4454	<i>n</i> -hexane	»	1.2	83
1,2-benzpyrene	»	3876	»	»	0.8	
Naphthanthrone	»	4191	»	»	0.7	83
Dibenzperopyrene	»	4138	»	»	1.0	
Coronene	»	4446	»	»	0.6	88
1,12-benzperylene	Fluor.	4060	<i>n</i> -hexane	$T < 77$ °K	0.05	80
Perylene	»	4518	<i>n</i> -octane	$T < 77$ °K	0.25	
Anthracene	Conj.abs.	5567	<i>n</i> -heptane	$T < 77$ °K	0.10	31
Coronene	»	4449	»	$T < 77$ °K	0.15	
Phenylmionoase-azulene	»	5567	Terphenyl	$T < 30$ °K	0.10	84
Azulene	»	7000	Naphthalene	$T < 30$ °K	0.15	
Naphthalene	Phosph.	4698	Benzophenone	$T < 77$ °K	0.17	83
Anthracene	Conj.abs.	3925	Naphthalene	$T < 30$ °K	0.15	
H <sub>2</sub> -porphyrin	»	6123	<i>n</i> -octane	1.4 °K < $T < 4.2$ °K	10 <sup>-4</sup>	76
»	»	6135	»	1.4 °K < $T < 4.2$ °K	2 · 10 <sup>-3</sup>	
»	»	6146	»	1.4 °K < $T < 4.2$ °K	10 <sup>-3</sup>	
»	»	6149	»	1.4 °K < $T < 4.2$ °K	10 <sup>-4</sup>	
H <sub>2</sub> -tetra-4 Tert-butylphthalocyanine	»	6930	Tetradecane	$T < 30$ °K	0,02	75

crepancy between theory and experiment for  $T > 77^\circ\text{K}$ . At low temperatures ( $T < 77^\circ\text{K}$ ), there is no qualitative discrepancy, but the broadening can in no way be said to be in general agreement with the approximate formulas given by (4.8) or (4.10). The temperature broadening of the zero-phonon lines in the low-temperature region is still more rapid for many of the alkali halide crystals. Table II shows the rate of temperature broadening for several zero-phonon lines investigated by Rebane and Freiberg.<sup>27, 28, 74</sup> In practically all these cases, the criterion given by (4.13) is not satisfied.

Thus, comparison of the measured temperature broadening with calculations based on (4.2) shows a discrepancy at high temperatures in the case of organic crystals, and even at low temperatures in the case of alkali-halide crystals. This discrepancy has not previously been noted, which shows that the approximate formulas given by (4.8) and (4.10) have a high degree of approximativeness in the comparison between theory and experiment. The discrepancy also shows that the origin of the broadening of zero-phonon lines can be established with the aid of (4.2) and the ensuing (4.8) and (4.10) alone. The reason for the discrepancy is still not clear. Additional theoretical and experimental studies are clearly necessary.

#### D. Importance of the adiabatic mechanism of broadening of zero-phonon lines

This can be reliably demonstrated only by a simultaneous experimental investigation of departures from mirror symmetry of phonon wings in conjugate absorption and fluorescence bands, on the one hand, and the temperature broadening of zero-phonon lines, on the other. In fact, a change in the force matrix will produce both a departure from mirror symmetry of the phonon wings and a broadening of the zero-phonon lines. Consequently, there must be a quantitative correlation between these two effects. A qualitative connection between the departure from mirror symmetry of phonon wings and temperature broadening of zero-phonon lines was established in our previous paper.<sup>46</sup> It is expressed by the fact that (4.2) and (3.20) involve the same theoretical parameter  $\beta = W/a^2\nu_0^2$  and the function  $v_1^e(\nu)$ . If the latter function is "extracted" from the fluorescence phonon wing and if by suitably choosing the parameter  $\beta$  it is possible to achieve agreement between the function  $v_1^0(\nu)$  calculated from (3.20) and the function "extracted" from the phonon wing of the absorption band, this will undoubtedly show that the departure from mirror symmetry of conjugate phonon wings is, in fact, due to a change in the shape of the Franck-Condon

TABLE II. Rate of temperature broadening of the zero-phonon lines of certain impurity centers in alkali halide matrices.

Crystal with impurity	$\frac{\Delta\nu}{\Delta T}$ , cm <sup>-1</sup> /deg		$\gamma$ (4.2 °K), cm <sup>-1</sup>
	$T < 20^\circ\text{K}$	$T > 20^\circ\text{K}$	
KCl + O <sub>2</sub> <sup>-</sup>	0.12	0.35	3
KI + O <sub>2</sub> <sup>-</sup>	0.30	1.00	3
CsBr + O <sub>2</sub> <sup>-</sup>	0.25	0.50	2
KBr + O <sub>2</sub> <sup>-</sup>	0.50	1.00	13
KI + S <sub>2</sub> <sup>-</sup>	0.60	—	6

potential surface. The expression given by (4.2), which describes the temperature broadening of the zero-phonon lines, will not then contain free parameters and unknown functions. If the theoretical curve calculated from this formula is close to the experimental points, this will reliably indicate the presence of the adiabatic mechanism of broadening of the zero-phonon line. Unfortunately, simultaneous experimental studies of the temperature broadening and violations of mirror symmetry of the phonon wings have not as yet been performed.

#### E. Temperature shift of zero-phonon lines

The shift calculated from (4.2) does not, as a rule, agree with experimental data. This shows that there is some shift mechanism which was not taken into account in (4.2). Fitchen<sup>89</sup> has noted that the ZPL shift must depend on the thermal expansion of the crystal lattice of the solvent. In fact, it is well known that the electronic level separation in a molecule is very dependent on its interaction with the surroundings. Thermal expansion modifies the interaction with the environment and leads to a change in the electronic excitation energy and hence to change in the ZPL shift. Fitchen<sup>89</sup> has suggested that

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V - \frac{\alpha(T)}{\kappa(T)} \left(\frac{\partial E}{\partial P}\right)_T, \quad (5.1)$$

which relates the measured shift  $(\partial E/\partial T)_P$  to the shift  $(\partial E/\partial T)_V$  due to the electron/phonon coupling. The second term describes the shift due to thermal expansion in terms of the volume expansion coefficient  $\alpha(T)$ , the isothermal compressibility  $\kappa(T)$ , and the pressure shift  $(\partial E/\partial P)_T$ . The pressure shifts of some of the zero-phonon lines have been measured and it was shown that the second term in (5.1) was comparable with the first.<sup>90</sup>

#### 6. DETERMINATION OF THE VIBRONIC INTERACTION FROM STRUCTURED VIBRONIC SPECTRA

The vibronic interaction in the adiabatic approximation consists of the shift  $a$  in the positions of equilibrium of intramolecular oscillators (FC coupling) and the dependence of the electronic matrix element  $M$  on the intramolecular vibrational coordinates  $R_s$  (HT coupling). Intramolecular vibrations correspond to discrete frequencies  $\Omega_s$ , separated from one another by finite frequency intervals. The vibronic interaction cannot, therefore, broaden optical bands. It simply "stretches" the optical spectrum along the frequency scale. If we were able to include the electron-phonon coupling, we would be in a position to obtain the spectrum of the impurity center consisting of narrow vibronic zero-phonon lines corresponding to phototransitions with the creation of quanta of intramolecular vibrations.<sup>15)</sup> Weak electron-phonon coupling produces a

<sup>15)</sup>Byrne and Ross<sup>91</sup> have listed the following twelve reasons for the diffuseness of optical spectra of polyatomic molecules in the vapor phase: (1) dissociation; (2) ionization; (3) predissociation; (4) autodissociation; (5) preisomerization; (6) anharmonicity of vibrations; (7) electronic relaxation; (8) high density of vibrational levels (vibrational congestion); (9) high density of electronic levels; (10) nonuniform isotopic composition of the vapor; (11) molecular rotation; (12) vibrational sequences. The only reason for the broadening of optical lines can be the interaction between the electrons in the molecule and the continuum of states. Therefore, the first four effects should, in fact, lead to a broadening of the

low-intensity phonon wing which then accompanies each vibronic zero-phonon line (Fig. 9a). In the simplest case, where the HT coupling is absent and the vibrations are harmonic, the vibronic band consisting of the zero-phonon line and the accompanying phonon wing is an exact replica of the 0-0 band (this is the similarity rule). Departures from this rule have been examined experimentally by Rebane *et al.*<sup>95,96</sup> They explain them in terms of the anharmonism of the vibrations. We shall consider below the intensity distribution in the vibronic spectrum by ignoring the phonon wing. If, however, the experimental spectrum contains an appreciable contribution of band intensity to the phonon wing (Fig. 9b), the integrated intensity, assigned below to the vibronic zero-phonon line alone, must be interpreted as referring to the entire vibronic band, i.e., zero-phonon line plus the phonon wing.

The intensity distribution in the vibronic spectrum can be described qualitatively by a model in which the completely symmetric (CS) vibrations appear in the optical spectrum because of the shifts  $a_s^{CS}$  in the equilibrium positions of the corresponding oscillators and the non completely symmetric (NCS) vibrations because of the dependence of  $M$  on the corresponding NCS coordinates. Within the framework of this theoretical model, the distribution of intensity in conjugate vibronic absorption and fluorescence spectra should be mirror-symmetric. However, there are many examples of violations of this symmetry. One is shown in Fig. 10. It is clear that the explanation of such phenomena will require a more complicated vibronic interaction and, in particular, it will be necessary to take into account the dependence of the electronic matrix element  $M$  on the CS vibrational coordinates. The dependence of  $M$  on the CS coordinates may lead to different intensities of CS vibronic peaks in the absorption and fluorescence spectra, i.e., to the departure from mirror symmetry. This was pointed out already in 1941 by Spomer and Wollman,<sup>97</sup> but the point was subsequently forgotten. About eight years ago, Craig and Small<sup>98</sup> and, independently, Osad'ko,<sup>99</sup> again drew attention to it. The effect of this more generalized vibronic interaction on optical spectra of impurity centers has in recent years been the subject of a number of experimental and theoretical investigations.<sup>47,100,101</sup> The most important results of these studies are discussed below.

The intensity distribution  $I^a(\omega)$  in the absorption spectrum and the intensity  $I^f(\omega)$  of the conjugate lumines-

lines and the fifth through seventh should have no effect on the broadening. Undoubtedly, the eighth through twelfth effects facilitate the broadening of the real optical spectrum but the role of some of them has been overestimated. For example, Byrne and Ross quote vibrational congestion as the reason for the spreading of the optical spectrum of chlorophyll, but the most recent spectroscopic data indicate the presence of fine structure in the electronic-vibrational spectra of chlorophyll.<sup>92-94</sup> The translational or rotational motion of a molecule or its components is transformed in solid matrices into the vibrational (phonon) motion. Phonons are also associated with the continuum of states, so that electron-phonon coupling is the only possible reason for the inhomogeneous broadening of the optical lines of an impurity center.

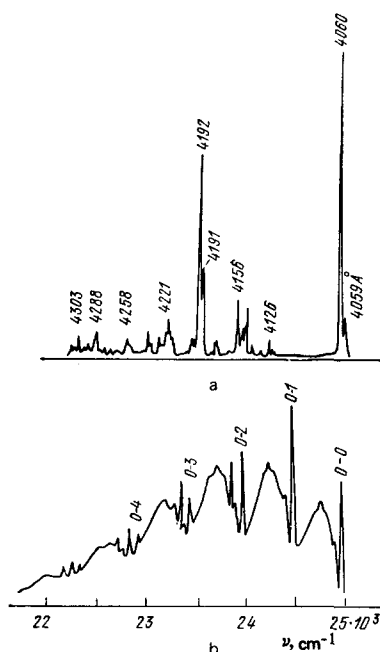


FIG. 9. Structured vibronic fluorescence spectra at 4.2 °K: (a) 1,12-benzperylene in *n*-hexane;<sup>25</sup> (b)  $PO_2$  in KCl.<sup>126</sup>

cence spectrum are given by the following general formulas<sup>47</sup>

$$I^a(\omega) = L^2(0) \delta(\omega - \varepsilon) + \sum_x \left[ \left( \frac{a_x}{2} \pm \frac{\partial}{\partial R_x} \right) L(R) \right]_{R=0}^2 \delta(\omega - \varepsilon \mp \Omega_x) + \frac{1}{2!} \sum_{x, x'} \left[ \left( \frac{a_x}{2} \pm \frac{\partial}{\partial R_x} \right) \left( \frac{a_{x'}}{2} \pm \frac{\partial}{\partial R_{x'}} \right) L(R) \right]_{R=0}^2 \delta(\omega - \varepsilon \mp \Omega_x \mp \Omega_{x'}) + \frac{1}{3!} \sum_{x, x', x''} \left[ \left( \frac{a_x}{2} \pm \frac{\partial}{\partial R_x} \right) \left( \frac{a_{x'}}{2} \pm \frac{\partial}{\partial R_{x'}} \right) \left( \frac{a_{x''}}{2} \pm \frac{\partial}{\partial R_{x''}} \right) L(R) \right]_{R=0}^2 \times \delta(\omega - \varepsilon \mp \Omega_x \mp \Omega_{x'} \mp \Omega_{x''}). \quad (6.1)$$

This formula takes into account the shift  $a_x$  in the positions of equilibrium of the normal coordinates  $R_x$ , the dependence of  $M$  on  $R_x$ , without limitation on  $a_x$ , and the form of the functional dependence of  $M$  on  $R_x$ . The upper sign in (6.1) refers to absorption and the lower to emission. The first term describes 0-0 zero-phonon lines and the subsequent terms describe, respectively, the one-, two-, and three-quantum, etc. delta-type vibronic zero-phonon lines. The integrated intensity of the vibronic zero-phonon line or, more precisely, of the entire vibronic band, is given by the square of the bracketed expression associated with the corresponding delta function. Derivatives of  $L(R)$  at the origin are the parameters characterizing the HT coupling. They are related to the derivatives of  $M(R)$  with respect to  $R_x$ ,

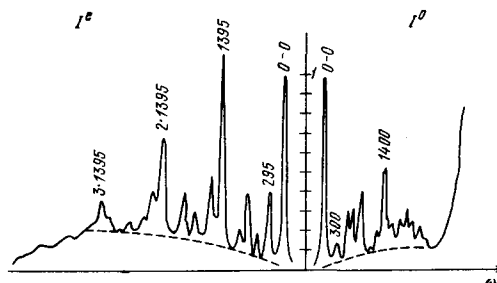


FIG. 10. Conjugate optical spectra of chrysene in *n*-heptane at 77 °K with different intensity distributions.<sup>100</sup> The 0-0 lines are the resonance lines.

as follows:

$$\left( \frac{\partial}{\partial R_{x_1}} \dots \frac{\partial}{\partial R_{x_k}} L(R) \right)_{R=0} = e^{-a^2/8} \int_{-\infty}^{\infty} \frac{dR}{(2\pi)^{N/2}} e^{-R^2/2} \frac{\partial}{\partial R_{x_1}} \dots \frac{\partial}{\partial R_{x_k}} M \left( R - \frac{a}{2} \right). \quad (6.2)$$

From (6.2) and the fact that  $i_0 = 1$  and

$$i_k = \int_{-\infty}^{\infty} \frac{dR_{x_k}}{\sqrt{2\pi}} R_{x_k}^{2k} e^{-R_{x_k}^2/2} = 1 \cdot 3 \cdot 5 \dots (2k-1) \quad (k=1, 2, 3, \dots), \quad (6.3)$$

we can easily obtain the connection between the derivatives of  $L$  at the origin and the derivatives of  $M$  at the point  $-a/2$  lying midway between the position of equilibrium 0 and  $-a$ , which correspond to the unexcited and excited impurity centers, respectively. For example, if  $M(R) = M(0) + \sum_x (\partial M / \partial R_x) R_x$ , then

$$\begin{cases} L(0) = e^{-a^2/8} \left[ M(0) - \sum_x \left( \frac{\partial M}{\partial R_x} \right)_0 \frac{a_x}{2} \right] = e^{-a^2/8} M \left( -\frac{a}{2} \right), \\ \left( \frac{\partial L}{\partial R_x} \right)_0 = e^{-a^2/8} \left( \frac{\partial M}{\partial R_x} \right)_0 = e^{-a^2/8} \left( \frac{\partial M}{\partial R_x} \right)_{-a/2}. \end{cases} \quad (6.4)$$

The formula given by (6.1) will provide the answer to any question relating to the vibronic optical spectrum of the displacements  $a_x$  in the positions of equilibrium and the dependence of  $M$  on  $R_x$ . Practical application of (6.1) proceeds along the following lines: (1) the theoretical model is selected, i.e., a set of nonzero parameters is chosen for (6.1); (2) these parameters are then calculated by comparing the coefficients in front of the delta functions in (6.1) with measured intensities of vibronic peaks; (3) a check is made on the chosen parameters by comparing the calculated and measured intensities of the vibronic peaks used to determine the parameters. Two criteria are used in choosing the theoretical model, namely, it must provide a qualitative explanation of the leading features of the conjugate absorption and luminescence spectra and it must be the simplest possible model.

(a) If the electronic transition is allowed and the conjugate absorption and luminescence spectra are mirror-symmetric, the simplest model capable of describing this situation is:

$$a_s^{CS} \neq 0, \quad \frac{\partial L}{\partial R_n^{NCS}} \neq 0. \quad (6.5)$$

According to this model,

$$I^s(\omega) = L^2(0) I_{FC}^s(\omega) + \sum_n \left( \frac{\partial L}{\partial R_n^{NCS}} \right)^2 I_{FC}^s(\omega \mp \Omega_n^{NCS}), \quad (6.6)$$

where

$$\begin{aligned} I_{FC}^s(\omega) &= \delta(\omega - \varepsilon) + \sum_i \left( \frac{a_i^{CS}}{2} \right)^2 \delta(\omega - \varepsilon \mp \Omega_i^{CS}) \\ &+ \frac{1}{2!} \sum_{i, i'} \left( \frac{a_i^{CS}}{2} \right)^2 \left( \frac{a_{i'}^{CS}}{2} \right)^2 \delta(\omega - \varepsilon \mp \Omega_i^{CS} \mp \Omega_{i'}^{CS}) \end{aligned} \quad (6.7)$$

is the function describing the Franck-Condon intensity distribution in CS progressions. For a single progression, (6.7) gives the well-known intensity distribution

$$\frac{I_k}{I_0} = \frac{1}{k!} \left( \frac{a}{2} \right)^{2k}. \quad (6.8)$$

NCS vibrations appear as one-quantum peaks acting as "spurious origins" for different CS progressions. The intensity distribution in a CS progression is similar for 0-0 zero-phonon lines and one-quantum vibronic peaks.

(b) If the electronic transition is allowed and the mir-

ror symmetry in CS progressions developing from 0-0 zero-phonon lines is violated (see Fig. 10), the simplest theoretical model capable of explaining this situation is

$$a_s^{CS} \neq 0, \quad \frac{\partial L}{\partial R_n^{NCS}} \neq 0, \quad \frac{\partial L}{\partial R_s^{CS}} \neq 0. \quad (6.9)$$

In this case,

$$\begin{aligned} I^s(\omega) &= \sum_n \left( \frac{\partial L}{\partial R_n^{NCS}} \right)^2 I_{FC}^s(\omega \mp \Omega_n^{NCS}) \\ &+ L^2(0) \left[ \delta(\omega - \varepsilon) + \sum_i \left( \frac{a_i^{CS}}{2} \pm \alpha_i^{CS} \right)^2 \delta(\omega - \varepsilon \mp \Omega_i^{CS}) \right. \\ &+ \frac{1}{2!} \sum_{i, i'} \left( \frac{a_i^{CS}}{2} \frac{a_{i'}^{CS}}{2} \pm \frac{a_i^{CS}}{2} \alpha_{i'}^{CS} \pm \frac{a_{i'}^{CS}}{2} \alpha_i^{CS} \right)^2 \\ &\quad \left. \times \delta(\omega - \varepsilon \mp \Omega_i^{CS} \mp \Omega_{i'}^{CS}) + \dots \right], \end{aligned} \quad (6.10)$$

where

$$\alpha_s^{CS} = \left( \frac{\partial L}{\partial R_s^{CS}} \right)_0 \frac{1}{L(0)} \quad (6.11)$$

is the parameter describing the violation of mirror symmetry in CS progressions developing from the 0-0 zero-phonon line. The intensity distribution in these progressions is no longer of the Franck-Condon kind. However, similar progressions developing from one-quantum vibronic NCS peaks do have the Franck-Condon intensity distribution (this is the violation of the similarity rule).

(c) If the electronic transition is forbidden (or weak), and the mirror symmetry in CS progressions developing from one-quantum vibronic peaks is violated, the simplest theoretical model capable of describing the situation is

$$a_s^{CS} \neq 0, \quad \frac{\partial L}{\partial R_s^{CS}} \neq 0, \quad \frac{\partial L}{\partial R_n^{NCS}} \neq 0, \quad \frac{\partial^2 L}{\partial R_n^{NCS} \partial R_s^{CS}} \neq 0. \quad (6.12)$$

Within the framework of this model,

$$\begin{aligned} I^s(\omega) &= \sum_i \left( \frac{\partial L}{\partial R_i^{CS}} \right)^2 I_{FC}^s(\omega \mp \Omega_i^{CS}) + \sum_n \left( \frac{\partial L}{\partial R_n^{NCS}} \right)^2 \left[ \delta(\omega - \varepsilon \mp \Omega_n^{NCS}) \right. \\ &+ \sum_i \left( \frac{a_i^{CS}}{2} \pm \alpha_i(n) \right)^2 \delta(\omega - \varepsilon \mp \Omega_n^{NCS} \mp \Omega_i^{CS}) \\ &+ \frac{1}{2!} \sum_{i, i'} \left( \frac{a_i^{CS}}{2} \frac{a_{i'}^{CS}}{2} \pm \frac{a_i^{CS}}{2} \alpha_{i'}(n) \pm \frac{a_{i'}^{CS}}{2} \alpha_i(n) \right)^2 \\ &\quad \left. \times \delta(\omega - \varepsilon \mp \Omega_n^{NCS} \mp \Omega_i^{CS} \mp \Omega_{i'}^{CS}) + \dots \right]. \end{aligned} \quad (6.13)$$

In CS progressions developing from one-quantum CS peaks, the intensity distribution is of the Franck-Condon type and is mirror-symmetric, whereas, in cs progressions developing from one-quantum NCS peaks, the distribution is not of the Franck-Condon type and mirror symmetry is violated. The "anti-Condon" parameter is

$$\alpha_s(n) = \left( \frac{\partial^2 L(R)}{\partial R_s^{CS} \partial R_n^{NCS}} \right)_0 \left( \frac{\partial L(R)}{\partial R_n^{NCS}} \right)_0^{-1} \quad (6.14)$$

and depends not only on the subscript  $s$  of the CS vibration but also on the subscript  $n$  associated with the "spurious origin." Other possible theoretical models can be examined in a similar fashion.

It is well known that the presence of a finite HT coupling may be regarded as evidence for the fact that the first electronic excited state is influenced by the second, third, and so on state. A nonzero derivative  $\partial L / \partial R_s^{CS}$  signifies that the first excited state is appreciably affected by the higher electronic states of the same

symmetry as the first. The second excited state of organic molecules is usually found to have different symmetry compared with the first; a nonzero  $\partial L/\partial R_s^{CS}$  shows that the higher electronic states are important. This has been investigated by Bolotnikova and El'mikova.<sup>103</sup> They have analyzed the parameter

$$\beta_k = \frac{M_{0k}/M_{01}}{\epsilon_k - \epsilon_1}, \quad (6.15)$$

where  $\epsilon_k$  and  $M_{0k}$  are the energy of the  $k$ th electronic level of the impurity molecule and the electronic matrix element for the  $k-0$  transition. The magnitude of the parameter was investigated for 14 organic molecules. Since  $M_{0k}$  increases with increasing  $k$ , the coefficients  $\beta_2, \beta_3, \beta_4$  were found to be of the same order, i.e.,  $\beta_2 \approx \beta_3 \approx \beta_4 \approx \beta$ . The molecules that were investigated were divided into two groups, in accordance with the value of  $\beta$ . Molecules in the first group (anthracene, naphthalene, perylene, and anthanthrene) have  $\beta \approx 10^{-4} - 10^{-5}$  cm and their conjugate spectra are mirror-symmetric. Molecules in the second group (benzene, naphthalene, phenanthrene, pyrene, chrysene, 1, 2, -benzpyrene, 3, 4-benzpyrene, 1, 12-benzperylene) have values of  $\beta$  that are greater by an order of magnitude, and the mirror symmetry of their conjugate spectra is violated.

The formula given by (6.1) and the various special cases that follow from it have frequently been used to analyze experimental data.<sup>102-111</sup> Gradyushko *et al.*<sup>106, 109</sup> have found that all the CS vibrations appear with different intensities in the absorption and fluorescence conjugate spectra of  $H_2$ -phthalocyanine (these spectra consist mainly of one-phonon vibronic peaks), whereas all the NCS vibrations appear with the same intensity. In most papers, the vibronic interaction was investigated, nevertheless, on the basis of the intensity distribution in only one of the spectra (fluorescence or phosphorescence).<sup>102, 107, 108, 110, 111</sup> The absence of the conjugate spectrum does, of course, impede the study of these effects because it reduces the number of independent experimental data. The associated difficulties and ways of overcoming them are analyzed in the literature.<sup>107, 110, 111</sup> It has been shown that, when the vibronic spectrum contains a substantial number of overtones, it is possible to choose unambiguously a theoretical model capable of predicting the spectrum under investigation. Theoretical analysis of the intensity distribution with the aid of formulas such as (6.1) is useful in finding answers to various questions. For example, Korotaeva and Naumova<sup>110</sup> have shown that, when a heavy atom is introduced into the solvent molecule, the vibronic spin-orbit interaction in the impurity molecule is modified to a greater extent than the purely electronic spin-orbit interaction. Gastilovich *et al.*<sup>108</sup> have identified definite groups of atoms as being responsible for the vibronic interaction. Nersesova and Shtrokirkh<sup>111</sup> have not only confirmed the simultaneous effects of CS and NCS vibrations in strong vibronic peaks at 500 and 700  $\text{cm}^{-1}$  in the fluorescence spectrum of naphthalene but have also found the percentage contribution of these vibrations to the intensity of these peaks. The above work has thus demonstrated that quantitative studies of the intensity distribution in structured vibronic spectra with the aid of

(6.1) provides us with new possibilities and with solutions to many questions that have so far been in dispute.

## 7. SPECTRA OF IMPURITY CENTERS WITH SHARP ANOMALIES

In the preceding subsections, the connection between conjugate absorption and luminescence spectra was examined on the basis of two assumptions. Firstly, we ignored the nonadiabatic part of the electron-phonon coupling and, secondly, the adiabatic potential in (2.4) and (2.5) was replaced by a quadratic function of the vibrational coordinates. Many effects, for example, relatively small departures from mirror symmetry between conjugate absorption and luminescence spectra, temperature broadening of zero-phonon lines, "transfer" of intensity from the zero-phonon line to the phonon wing as the temperature increases, and so on, can be satisfactorily described, even quantitatively, within the framework of these two approximations. However, optical spectra of certain impurity centers have anomalies that are very difficult, and occasionally impossible, to explain within the framework of a theory based on the above two approximations. These anomalies include the break in the frequency scale between the long-wave edge of the absorption band and the short-wave edge of the conjugate fluorescence band (Fig. 11), the presence of structure in one of the spectra, and the lack of structure (partial or total) in the conjugate spectrum (Fig. 11b).

These anomalies can occasionally be explained by "trivial" factors. For example, the break in the frequency scale between the absorption and fluorescence spectra of naphthalene single crystals was explained by Shpak<sup>113</sup> by the presence of  $\beta$ -methylnaphthalene impurity in naphthalene, which was difficult to separate out. The break between the absorption and fluorescence spectra of polyenes (Fig. 11a) has been explained in terms of the presence of a low-intensity long-wave electronic transition.<sup>114-118</sup> This long-wave transition has practically no effect on the intensity distribution in the absorption band, but determines the origin and shape of the fluorescence spectrum. Davydov and Kislukha<sup>119, 120</sup> have introduced a four-level scheme to explain the break on the frequency scale between absorption and emission spectra. They have examined the change in the length of the transtetraene molecule

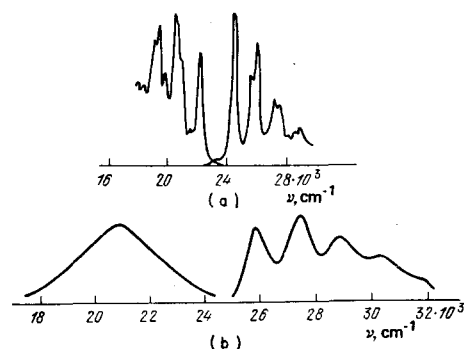


FIG. 11. Optical spectra with sharp anomalies: (a) absorption and fluorescence bands of diphenyloctatetraene in ether isopentane ethanol (5:5:2) at 77 °K;<sup>114</sup> (b) structured absorption and structureless emission of anthracene in alcohol at 77 °K.<sup>112</sup>

under electronic excitation. The four-level scheme has also been discussed by Neporent<sup>121-123</sup> and by other workers.<sup>124, 125</sup> Figure 12 shows the four-level scheme and the various associated equilibrium configurations of the spiroopyran molecule.<sup>121</sup> Optical transitions are shown by solid arrows and radiationless transitions accompanied by a change in the shape of the molecules ("electronic regrouping") are shown by wavy arrows. This scheme was put forward by Neporent<sup>121</sup> as a way of explaining at least two facts, namely, the diffuse appearance of the optical spectra of complicated molecules and the break on the frequency scale between the absorption spectrum and the fluorescence spectrum. "Nonstationary Franck-Condon states," which involve the broadened levels in the energy level scheme of Fig. 12, are introduced to explain the first fact. Neporent associates the nonstationary nature of these states with intramolecular vibronic interactions. This is difficult to accept (see footnote 15 and associated text on that page). On the other hand, there are no basic objections to the explanation of the second fact in terms of the four-level scheme, but it generates other difficulties which are difficult to resolve. Firstly, it is difficult to understand the absence of the optical transition shown by the broken arrow in Fig. 12 (for example, in Nd<sup>3+</sup> ions, whose energy level scheme is similar to the four-level scheme of Fig. 12, such transitions are, in fact, observed<sup>127</sup>). Secondly, it is not clear what is the nature of electronic level II [in organic molecules, the largest energy separation is usually between the ground (I) and first excited (II) states]. Since the explanation based on the four-level scheme generates, in our view, more difficulties than it resolves, we are forced to ask another question, namely, what would be the shape of the conjugate optical spectra if the adiabatic potential of the impurity center were to have more than one minimum in at least one of the coordinates?

Figure 13 illustrates the situation where the phototransition occurs between two electronic states, the adiabatic potential of one of which has two minima in the vibrational coordinate  $R_1$ . If the height of the barrier associated with the potential corresponding to the upper electronic state exceeds by a substantial factor the vibration frequency which is the most active one in the optical spectrum, the intensity distribution  $I^0(\omega)$  in the absorption spectrum and the intensity distribution  $I^e(\omega)$  in the fluorescence spectrum are given by<sup>128</sup>:

$$I^0(\omega) \approx M^2(\mathbf{a}) \int_{-\infty}^{\infty} dt \exp [i(\omega - \varepsilon^0)t + \int_{-\infty}^{\infty} d\nu f^0(\nu)(e^{-i\nu t} - 1)], \quad (7.1)$$

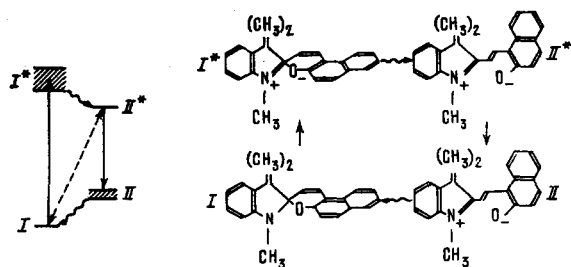


FIG. 12. Change in the conformation of the spiroopyran molecule and the four-level scheme.<sup>121</sup>

$$I^e(\omega) \approx M^2(\mathbf{b}) \int_{-\infty}^{\infty} dt \exp \left[ -i(\omega - \varepsilon^e)t + \int_{-\infty}^{\infty} d\nu f^e(\nu)(e^{-i\nu t} - 1) \right], \quad (7.2)$$

where

$$f^0(\nu) = \sum_{\kappa} a_{\kappa}^0 \delta(\nu - \nu_{\kappa}), \quad (7.3)$$

$$f^e(\nu) = \sum_{\kappa} b_{\kappa}^e \delta(\nu - \nu_{\kappa}). \quad (7.4)$$

In these expressions,  $(a_{\kappa} = (\alpha_{\kappa}^0 - \alpha_{\kappa}^e)/2)$  and  $(b_{\kappa} = (\beta_{\kappa}^e - \alpha_{\kappa}^0)/2)$  are the differences between the minima of the potential surfaces and  $\kappa$  is the normal vibration index. The expressions given by (7.1) and (7.2) can be transformed to the form given by (3.12)–(3.14). The quantities  $M^2(\mathbf{a})$  and  $M^2(\mathbf{b})$  determine the integrated intensity of the absorption and fluorescence spectra, respectively. Since the difference  $\mathbf{a} - \mathbf{b}$  can be of the order of the interatomic separation, the two intensities may be very different. The second feature is that there is a break amounting to  $\varepsilon^0 - \varepsilon^e$  between the 0-0 transitions in the absorption and fluorescence spectra. The third feature is that, since the integrated values of the phonon functions  $f^0(\nu)$  and  $f^e(\nu)$  are very different ( $f^0 \ll f^e$ ), the fluorescence spectrum is dominated by multiphonon phototransitions, whereas the absorption spectrum is dominated by the 0-0 transition and one- or two-quantum transitions. The shape of the optical spectra corresponding to the situation where  $R_1$  is the intramolecular coordinate (a) and the intermolecular coordinate (b), whilst the probability of the tunneling transition  $P_n$  is much greater than the phototransition probability  $I^0$ , is shown schematically on the right of Fig. 13. If, however,  $P_n \approx I^0$ , one should see both the long-wave luminescence spectrum and the short-wave luminescence band (broken curve in Fig. 13). If the adiabatic potentials for the first and lowest states have several minima, the electronic-vibrational transitions may generate different spectral distributions. Only two of them are considered below. They are relevant to the problem of excimer emission and the "multiplet" problem.

### A. Excimers

It has long been known that the formation of dimers is accompanied by the emission of broad-band structureless radiation, shifted away from the structured dimer absorption by several thousand  $\text{cm}^{-1}$  toward the red (Fig. 11b). This emission is often ascribed to the excimer, defined as a dimer, with a purely repulsive potential in the electronic ground state.<sup>129, 130</sup> Excimer emission is observed both in liquid and solid solutions. In the latter case, it is difficult to understand how a

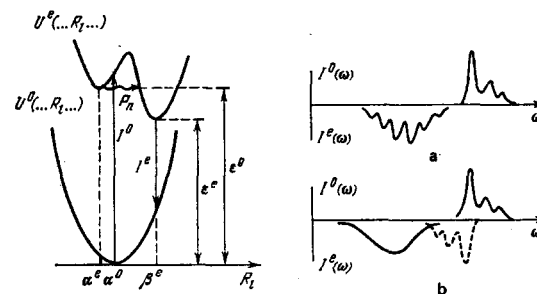


FIG. 13. Adiabatic potentials of an impurity center and schematic representation of the corresponding absorption and fluorescence bands  $I^0(\omega)$  and  $I^e(\omega)$ .  $R_1$  represents the intra- (a) and intermolecular (b) coordinates.



real adiabatic potential can fail to have a minimum in the ground state. The repulsive potential in the definition of an excimer is introduced to explain the absence of absorption by the excimer. However, the dimer must have precisely this property if its potential energy in the excited state is to depend on the separation or the angle between the molecules, as shown in Fig. 13. Therefore a new definition of an excimer has been introduced<sup>128</sup> as a dimer whose potential energy in the excited state has more than one minimum in the intermolecular coordinate (Fig. 13). The following main facts can then be easily understood: (1) the shift of the excimer emission maximum toward the red relative to the dimer absorption region; (2) the absence of structure in the excimer emission; (3) the absence of structureless absorption conjugate with respect to the excimer emission; (4) the appearance of excimer emission due to the structured dimer fluorescence which sometimes takes place with increasing temperature.<sup>131-133</sup>

### B. "Multiplets"

It is well known that optical spectra of many molecules dissolved in *n*-paraffins and certain other matrices consist of "multiplets," i.e., groups of lines that are found to repeat throughout the optical spectrum of the impurity center. Shpol'skii has examined this phenomenon<sup>124</sup> and suggested that not all the impurity centers find themselves under the same conditions in such matrices. Thus, there are several types of spatially separated impurity centers whose electronic levels are shifted relative to one another under the influence of different local environments. Both emission and absorption of light by such solid solutions will then exhibit multiplet structure. This point of view has been confirmed by other workers.<sup>29, 135, 136</sup> Selective excitation of the individual components of the multiplet has been used to simplify the multiplet structure of the fluorescence spectrum.<sup>29, 135</sup> However, it was also established<sup>137</sup> that selective excitation of one component of a multiplet might be accompanied by the excitation of another in the fluorescence spectrum. This can be explained in a general way with the aid of Fig. 14, which shows the potential energy of the impurity center as a function of the coordinate characterizing the position of the impurity molecule in solution. Under white-light excitation, the absorption and fluorescence spectra take the form shown in Fig. 14, i.e., a doublet structure appears. When one of the doublet components is excited by monochromatic light, the other component may appear in the fluorescence spectrum. A large change in the position of equilibrium of the molecule may appear spectroscopically as a transformation of the impurity center of

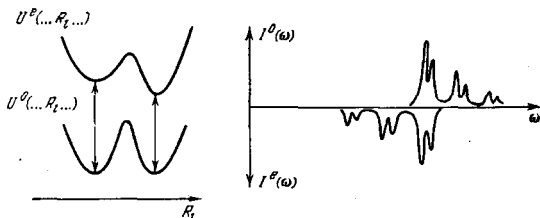


FIG. 14. Dependence of adiabatic potentials of an impurity molecule on the orientational coordinate  $R_i$  and the doublet structure of the corresponding optical spectrum.

one type into an impurity center of another type. One hopes that this can be used as a basis for an understanding of the transformation of impurity centers under the influence of laser radiation.<sup>82</sup>

## 8. CONCLUSIONS

We have reviewed the results of the theory which, whilst being microscopic, is, nevertheless, phenomenological in character because the parameters of the adiabatic potentials and phonon spectrum that are necessary for calculating the optical bands must be introduced externally into the theory. Its main disadvantage is that the band shapes cannot be calculated numerically without first specifying the magnitudes of some of the parameters. The main advantage of the theory is its generality; many of the special questions, for example, type of solvent, physical and chemical characteristics of the impurity center, particular shape of the phonon spectrum, and so on, are unimportant for this theory. To exploit this advantage to the full, the phenomenological theory must unify all effects of common origin. It is only after this unification that the set of theoretical formulas representing different points of view and depending on unknown parameters can be justifiably referred to as a *theory*. As recently as ten years ago, this plan was largely unrealizable. For example, the theory was unable to express the shape of conjugate absorption and luminescence bands in terms of the same theoretical parameters (apart from the trivial case of mirror symmetry) even though it was obvious that all the details on the conjugate bands were generated by the same electron-phonon coupling. Such a theory has, by now, been constructed and we have tried to review it here. Progress was achieved by overcoming various mathematical difficulties. This technical aspect of the subject is not reflected in our review, but the necessary information can be found in the references cited at the end. We are now in a position to conclude that the departure from mirror symmetry can serve as an important source of information on the Herzberg-Teller coupling and on the change in the shape of the potential Franck-Condon surfaces during phototransitions. Although we have devoted considerable space in this review to the way in which information on the electron-phonon coupling can be obtained by suitably analyzing the experimental data, it is not, unfortunately, always possible to demonstrate the utility of the theoretical formulas in relation to particular experimental data because, so far, very few simultaneous studies of conjugate bands have been carried out. For example, no one has yet carried out a simultaneous study of the structured phonon wings of conjugate bands and the temperature broadening of zero-phonon lines. Having solved the quantitative problem of the connection between conjugate absorption and fluorescence spectra, the theory offers new possibilities to the experimenter. One would hope that these will be fully exploited in the near future and that new information on the electron-phonon coupling will become available as a result.

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