SOVIET PHYSICS JETP VOLUME 28, NUMBER 6 JUNE, 1969

OPTICAL BANDS IN ELECTRON-VIBRATIONAL SYSTEMS WITH ELECTRON DEGENERACY

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Submitted June 5, 1968

Zh. Eksp. Teor. Fiz. 55, 2252–2261 (December, 1968)

Optical transitions between degenerate Γ_1 and Γ_2 terms of electron-vibrational systems are considered. Mixing of electron states by electron-phonon interaction within each degenerate term is taken into account exactly without the use of the adiabatic approximation. The calculation is carried out by the Kubo formula using the Feynman operator calculus. It is shown that the spectral curve is a superposition of bands with a common phononless line, the maximal number of bands being equal to the number of irreducible representations in the direct product $\Gamma_1 \times \Gamma_2$. The anomalous temperature dependence of intensity of the phononless line is noted and it is mentioned that a new characteristic type of adsorption may exist in systems with a degenerate ground electron term. Systems with a O_h symmetry are considered in detail.

THE adiabatic theory of optical transitions in vibronic systems, formulated by Pekar[1], Krivoglaz[2], Huang and Rhys[3], and Lax[4] (see the review of Perlin[5]) explained both the very fact of appearance of broad optical bands, and a number of subtle details of the spectrum. The theory based on the adiabatic approximation is limited to cases in which there is no degeneracy (quasidegeneracy). However, in real systems (impurity centers, molecules, etc.) the electronic levels are as a rule degenerate. This circumstance leads to the complicated problem of the dynamic Jahn-Teller effect and to the impossibility of separating the electronic and nuclear motions[6,7], so that the very concept of the potential surface becomes meaningless in most of the important cases. Consequently, there is still no theory of optical transitions between degenerate levels, in contrast with the consistent theory available in the absence of degeneracy. The recently undertaken few attempts[8-12] to take into account the complicated form of the adiabatic potential of degenerate terms for the investigation of optical transitions still leaves the theory within the framework of the adiabatic approximation, and therefore are not fully consistent.

In some particular cases, when the adiabatic potential is a multivalley surface with minima that are sufficiently deep compared with the energy of the zero-point oscillations of the nuclei, the adiabatic approximation describes sufficiently well the lowest vibronic states (static Jahn-Teller effect). The main difficulty in the theory of optical transitions in which degenerate levels take part lies in the fact that this approximation is utterly unsatisfactory for the description of vibrational states that are strongly excited as a result of an optical transition. Attempts at refining the adiabatic solutions for excited vibrational states with the aid of perturbation theory lead to practically unsurmountable difficulties, owing to the multiple degeneracy of the indicated states. Therefore, as will be shown below, the results of[9,10], obtained under the assumption of the static character of the Jahn-Teller effect, have a limited region of applicability. Serious objections are raised by the use of the adiabatic approximation[11,12] for cases in which the Jahn-Teller effect is essentially dynamic (the minima of the adiabatic potential lie along a ring).

Considerable progress was made by Perlin[13], who investigated the optical spectrum due to the transition from a nondegenerate term into a degenerate one. The complicated problem of finding the energy levels and the wave functions of the vibronic system with degeneracy is not solved in the cited paper, and the observable quantity (the light absorption coefficient) is calculated directly with the aid of the Kubo formula[14] without using the adiabatic approximation for the degenerate term.

In the present paper we investigate the general case of transitions between two degenerate terms.

1. GENERAL FORMULA FOR SPECTRAL DISTRIBUTION

The coefficient $K(\Omega)$ of absorption of light by a system with Hamiltonian $\hat{H}$ is given, accurate to factors that depend little on the frequency Ω, by[13,14]:

$$K(\Omega) = (1 - e^{-\hbar\Omega/kT}) \int_{-\infty}^{\infty} e^{-i\Omega t} J(t)\, dt, \tag{1}$$

where the generating function is $J(t) = \langle\langle d^+ d(t) \rangle\rangle$, and the symbol $\langle\langle \ldots \rangle\rangle$ denotes quantum-mechanical and statistical averaging; d is an operator acting in the electronic subsystem and causing the optical transition

$$d(t) = \exp(i\hat{H}t/\hbar)\, d \exp(-i\hat{H}t/\hbar).$$

It is convenient to represent the generating function in the form

$$J(t) = \frac{\mathrm{Sp}\{e^{-i\alpha\hat{H}/\hbar} d^+ e^{it\hat{H}/\hbar} d\}}{\mathrm{Sp}\{e^{-\hat{H}/kT}\}}, \quad \alpha = t - \frac{i\hbar}{kT}. \tag{2}$$

The Hamiltonian of the vibronic system is written in the form

$$\hat{H} = \hat{H}_0 + \hat{H}', \quad \hat{H}_0 = \hat{H}_e(\mathbf{r}) + \hat{H}_p(q), \quad \hat{H}' = \sum_{\varkappa} v_{\varkappa}(\mathbf{r}) q_{\varkappa}, \tag{3}$$

where $\hat{H}_e(\mathbf{r})$ is the Hamiltonian of the electrons and $\hat{H}_p(q)$ is the vibrational Hamiltonian of the lattice in the harmonic approximation. The operator of the electron-phonon interaction $\hat{H}'$ is chosen in the approximation that is linear in the normal coordinate q_K of the lattice.

For subsequent transformations we shall use the formula

$$T_c \exp\left\{\int_{z_2}^{z_1}[\alpha_1(z)V_{1z}+\alpha_2(z)V_{2z}]\,dz\right\}=\exp\left\{V_1\int_0^{z_1}\alpha_1(z)\,dz\right\}$$

$$\times T_c\exp\left\{\int_{z_2}^{z_1}\exp\left[-V_{1z}\int_0^{z}\alpha_1(x)\,dx\right]V_{2z}\exp\left[V_{1z}\int_0^{z}\alpha_1(x)\,dx\right]\alpha_2(z)\,dz\right\}$$

$$\times\exp\left\{V_1\int_{z_2}^{0}\alpha_1(z)\,dz\right\}, \tag{4}$$

which is the generalization of the formulas presented in[15,16]. Here z_1 and z_2 are complex numbers, the integration is carried out along an arbitrary contour c drawn in the complex plane from z_1 to z_2. The symbol T_c denotes ordering of the operators along this contour with respect to the index z, so that the points of the contour lying closer to z_2 are assumed to be earlier; $\alpha(z)$ are numerical functions.

Introducing independent ordering for the electronic operators (symbol s) and the phonon operators (f), we have

$$\exp(-i\alpha\hat{H}/\hbar)=\exp(-i\alpha\hat{H}_0/\hbar)U(\alpha),$$

$$\exp(it\hat{H}/\hbar)=\overline{U}(t)\exp(it\hat{H}_0/\hbar), \tag{5}$$

where U is the operator of evolution in the interaction representation

$$U(\alpha)=T_{c_1}{}^{sf}\exp\left\{-\frac{i}{\hbar\alpha}\sum_{\varkappa}\int_0^{\alpha}v_\varkappa(s)\,ds\int_0^{\alpha}q_\varkappa(f)\,df\right\},$$

$$\overline{U}(t)=T_{c_2}{}^{sf}\exp\left\{\frac{i}{\hbar t}\sum_{\varkappa}\int_0^{\alpha}v_\varkappa(s)\,ds\int_t^{0}q_\varkappa(f)\,df\right\}. \tag{6}$$

In terms of this notation, formula (2) becomes

$$J(t)=\frac{\langle\!\langle\exp[-it\hat{H}_e(\mathbf{r})/\hbar]\,U(\alpha)\,d^+\overline{U}(t)\exp[it\hat{H}_e(\mathbf{r})/\hbar]\,d\rangle\!\rangle_0}{\langle\!\langle U(-i\hbar/kT)\rangle\!\rangle_0}, \tag{7}$$

$\langle\!\langle\ldots\rangle\!\rangle$ denotes averaging with $\exp[-\hat{H}_0/kT]$. In the derivation of (7) we took into account the fact that the electronic and phonon operators commute.

The traces entering in formula (7) will be calculated by using the system of the eigenfunctions of the Hamiltonian $\hat{H}_0$ as a basis. Let $\hat{H}_0$ have degenerate electronic levels g and p (in the general case, each of them can be slightly split). We investigate the optical spectrum due to transitions between these levels. We use in the calculation the approximations assumed in[13], namely, we neglect small terms of order:
1) $\exp[-\hbar\Omega_{pg}/kT]$ ($\hbar\Omega_{pg}=E_p-E_g$, when E_p and E_g are the energies of the electronic states p and g) and 2) $|\langle g|v_K|p\rangle/\hbar\Omega_{pg}$. The first approximation makes it possible to confine ourselves in the calculation of the trace to the diagonal matrix elements on the electronic functions $|g\rangle$ of the initial state, and the second allows us to disregard the "mixing" of different multiplets by the vibronic interaction $\hat{H}'$; this mixing is of no significance in our problem.

The generating function J(t) assumes the form

$$J(t)=\left\{\sum_{g,g'}\sum_{p,p'}\langle g'|d^+|p\rangle\langle p'|d|g\rangle\exp\left(i\Omega_{pg}t-\frac{E_g}{kT}\right)\right.$$

$$\left.\times\langle\!\langle g|U(\alpha)|g'\rangle\langle p|\overline{U}(t)|p'\rangle\!\rangle\right\}\left\{\exp\left(-\frac{E_g}{kT}\right)\left\langle\!\!\left\langle g\left|U\left(-\frac{i\hbar}{kT}\right)\right|g'\right\rangle\!\!\right\rangle\right\}^{-1} \tag{8}$$

($\langle\ldots\rangle$ denotes phonon averaging). To calculate the phonon mean value it is convenient to represent the product of the matrix elements in (8) in the form of a double integral over the electronic coordinates, corresponding in the matrix representation to replacing the product of the matrix elements by the matrix element of the direct product of the matrices:

$$\langle\!\langle g|U(\alpha)|g'\rangle\langle p|\overline{U}(t)|p'\rangle\!\rangle=\langle g,p|\langle U(\alpha)\overline{U}(t)\rangle|g',p'\rangle, \tag{9}$$

where the variables α and t in the right side of (9) now indicate also that the matrix elements of $U(\alpha)$ and $\overline{U}(t)$ are taken on the functions of the multiplets g and p respectively.

We introduce the phonon creation and annihilation operators:

$$q_\varkappa=\frac{1}{\sqrt{2}}(Q_\varkappa+Q_\varkappa{}^+),\quad Q_\varkappa(f)=Q_\varkappa e^{i\omega_\varkappa f},\quad Q_\varkappa{}^+(f)=Q_\varkappa{}^+e^{-i\omega_\varkappa f}.$$

Separating the phonon operators in (9) with the aid of (4), and carrying out the phonon averaging[5,15], we obtain

$$\langle U(\alpha)\overline{U}(t)\rangle=T^{s}_{c_1c_2}\exp\left\{\sum_{\varkappa}\left[A_\varkappa^2(\alpha)\int_0^{\alpha}dx\int_0^{x}dy\,\varphi_\varkappa(y-x)\right.\right.$$

$$\left.\left.+A_\varkappa^2(t)\int_0^{t}dx\int_0^{x}dy\,\varphi_\varkappa(x-y)-A_\varkappa(\alpha)A_\varkappa(t)\int_0^{\alpha}dx\int_0^{t}dy\,\varphi_\varkappa(y-x)\right]\right\}, \tag{10}$$

$$A_\varkappa(\alpha)=-\frac{i}{\sqrt{2}\alpha\hbar}\int_0^{\alpha}v_\varkappa(s)\,ds,\quad A_\varkappa(t)=\frac{i}{\sqrt{2}t\hbar}\int_t^{0}v_\varkappa(s)\,ds, \tag{11}$$

$$\varphi_\varkappa(x)=(\bar{n}_\varkappa+1)e^{i\omega_\varkappa x}+\bar{n}_\varkappa e^{-i\omega_\varkappa x},$$
$$\bar{n}_\varkappa=[\exp(\hbar\omega_\varkappa/kT)-1]^{-1}. \tag{12}$$

We perform analogous transformations in the denominator of (8), thereby arriving to the following general expression for the generating function of the optical transition

$$J(t)=\left\{\sum_{g,g'}\sum_{p,p'}\langle g'p'|\mathbf{D}|p,g\rangle\exp\left(i\Omega_{pg}t-\frac{E_g}{kT}\right)\right.$$

$$\times\left\langle g,p\left|T^{s}_{c_1c_2}\exp\sum_{\varkappa}\left([A_\varkappa^2(t)-A_\varkappa^2(\alpha)]\frac{it}{\omega_\varkappa}-\frac{1}{\omega_\varkappa}[A_\varkappa(\alpha)-A_\varkappa(t)]^2\tilde{\varphi}_\varkappa(t)\right.\right.\right.$$

$$\left.\left.\left.-A_\varkappa^2(\alpha)\frac{\hbar}{\omega_\varkappa k}\right)\right|g',p\right\rangle\right\}\left\{\sum_{g}\exp\left(\frac{E_g}{kT}\right)\right.$$

$$\left.\times\left\langle g\left|T_{c_3}{}^{s}\exp\left[-\sum_{\varkappa}A_\varkappa^2\left(-\frac{i\hbar}{kT}\right)\frac{\hbar}{\omega_\varkappa kT}\right]\right|g\right\rangle\right\}^{-1},$$

$$\tilde{\varphi}_\varkappa=\varphi_\varkappa(t)-\operatorname{cth}\frac{\beta_\varkappa}{2},\quad\beta_\varkappa=\frac{\hbar\omega_\varkappa}{kT}, \tag{13}$$

where $A_K(-i\hbar/kT)$ has the same meaning as $A_K(\alpha)$. The matrix $D=d^+\times d$ is the direct product of the matrices of the electronic operators of the optical transition (for example, the dipole moment).

Formula (13) contains no phonon operators and makes it possible to investigate the spectral curve of the optical transition between two groups of pseudodegenerate (degenerate) levels. Further calculations call for determining in explicit form the electronic matrix elements, for which purpose it is necessary to carry out T-ordering of the electronic operators. The latter is possible if one knows the time dependence of the electronic operators $v_K(s)$ in the interaction representation.

We emphasize once more that in the calculation of the spectral function we did not use the adiabatic approximation—the "mixing" of the states by the electron-phonon interaction within each multiplet was taken into account exactly.

2. TRANSITIONS BETWEEN DEGENERATE LEVELS

Let g and p be the degenerate states, whose wave functions will now be denoted by $|\Gamma_1\gamma_1\rangle$ and $|\Gamma_2\gamma_2\rangle$ (γ_1 and γ_2 number the rows of the representations Γ_1 and Γ_2). In the case of exact degeneracy of the levels g and p, formula (13) can be greatly simplified. We note, first, that the electronic T-ordering becomes formal. Indeed, the operators $v_K(s)$ which enter in A_K do not depend on the time, since the matrix H_e, made up of functions of the degenerate term, is proportional to the unit matrix and therefore commutes with all the v_K. Then

$$A_\varkappa(\alpha)=A_\varkappa(t)=A_\varkappa\left(-\frac{i\hbar}{kT}\right)=-\frac{i}{\sqrt{2}\hbar}\cdot v_\varkappa(\mathbf{r}).$$

We denote the representations in accordance with which the operators v_K are transformed by Γ_γ.[1)] We note immediately that matrix

$$\mathrm{v}_{\Gamma\gamma}{}^{\Gamma_i}=\|\langle\Gamma_i\gamma_i'|v_{\Gamma\gamma}|\Gamma_i\gamma_i''\rangle\|\neq 0,$$

if $[\Gamma_i^2]\in\Gamma$, where $[\Gamma_i^2]$ is the symmetrized square of the representation Γ_i. It is also easy to see, using the Wigner-Eckart theorem, that the sum in the form $\sum\limits_\gamma \mathrm{v}_{\Gamma}{}^2$ is a scalar on the group, i.e., the matrices can be represented in the form

$$\left\|\left\langle\Gamma_i\gamma_i'\left|f\left(\sum_\gamma v_{\Gamma\gamma}{}^2\right)\right|\Gamma_i\gamma_i''\right\rangle\right\|=f\left[\frac{1}{n(\Gamma_i)}C^2(\Gamma_i\Gamma)\right]\times 1, \quad (14)$$

where f is an arbitrary function, admitting of expansion in a power series, 1 is a unit matrix of rank $n(\Gamma_i)$ ($n(\Gamma_i)$ is the dimensionality of the representation Γ_i), and $C(\Gamma_i\Gamma)$ is the reduced matrix element[17]. We obtain the following expression for the generating function:

$$J_{\Gamma_1\Gamma_2}(t)=\frac{1}{n(\Gamma_1)}\exp\left\{i\Omega_{21}t+\sum_\Gamma\frac{it}{2\hbar^2\omega_\Gamma}\left[\frac{C^2(\Gamma_1\Gamma)}{n(\Gamma_1)}-\frac{C^2(\Gamma_2\Gamma)}{n(\Gamma_2)}\right]+\sum_\Gamma\frac{1}{2}\left[\frac{C^2(\Gamma_1\Gamma)}{n(\Gamma_1)}+\frac{C^2(\Gamma_2\Gamma)}{n(\Gamma_2)}\right](\hbar\omega_\Gamma)^{-2}\tilde{\varphi}_\Gamma(t)\right\}$$
$$\times\sum_{\gamma_1',\gamma_2'}\langle\Gamma_1\gamma_1'\Gamma_2\gamma_2'|\mathbf{W}\mathbf{D}|\Gamma_2\gamma_2'\Gamma_1\gamma_1'\rangle, \quad (15)$$

where the matrix W is given by

$$\mathbf{W}=\exp\left\{-\sum_{\Gamma\gamma}\frac{\mathrm{v}_{\Gamma\gamma}{}^{\Gamma_1}\times\mathrm{v}_{\Gamma\gamma}{}^{\Gamma_2}}{\hbar^2\omega_\Gamma{}^2}\tilde{\varphi}_\Gamma(t)\right\}. \quad (16)$$

In formula (16)

$$\sum_\gamma \mathrm{v}_{\Gamma\gamma}{}^{\Gamma_1}\times\mathrm{v}_{\Gamma\gamma}{}^{\Gamma_2}\equiv\mathbf{V}_{\Gamma_1\Gamma_2}^{\Gamma}$$

represents the sum of direct (Kronecker) products of the matrices $\mathrm{v}_{\Gamma_\gamma}^{\Gamma_i}$ and is consequently a matrix of rank $n(\Gamma_1)n(\Gamma_2)$.

By virtue of the Wigner-Eckart theorem[18], the matrix W is a scalar on the group. Performing a unitary transformation that transforms the functions $|\Gamma_1\gamma_1\Gamma_2\gamma_2\rangle$ into the basis functions of the irreducible representations $\overline{\Gamma}_i$, contained in the direct product $\Gamma_1\times\Gamma_2$, we can reduce the matrix W to a diagonal form. The calculation of the matrix elements in (15) then becomes obvious, and we arrive at the conclusion that the optical spectrum is described by a superposition of generating functions $J_{\Gamma_1\Gamma_2}^{\overline{\Gamma}_i}(t)$ of a known type:

$$J_{\Gamma_1\Gamma_2}(t)=\sum_i J_{\Gamma_1\Gamma_2}^{\overline{\Gamma}_i}(t), \quad (17)$$

where

$$J_{\Gamma_1\Gamma_2}^{\overline{\Gamma}_i}(t)=D_{\Gamma_1\Gamma_2}^{\overline{\Gamma}_i}\exp\left\{i\Omega_0 t+\frac{1}{2}\sum_\Gamma\Delta_\Gamma^{\overline{\Gamma}_i}\tilde{\varphi}_\Gamma(t)\right\}. \quad (18)$$

Here Ω_0 is the frequency of the phononless line:

$$\Omega_0=\Omega_{21}+\sum_\Gamma\frac{1}{2}(\hbar\omega_\Gamma)^{-2}\left[\frac{C^2(\Gamma_1\Gamma)}{n(\Gamma_1)}-\frac{C^2(\Gamma_2\Gamma)}{n(\Gamma_2)}\right] \quad (19)$$

$\Delta_\Gamma^{\overline{\Gamma}_i}$ is the so-called heat-release constant (the parameter of the Stokes losses):

$$\Delta_\Gamma^{\overline{\Gamma}_i}=(\hbar\omega_\Gamma)^{-2}\left[\frac{C^2(\Gamma_1\Gamma)}{n(\Gamma_1)}+\frac{C^2(\Gamma_2\Gamma)}{n(\Gamma_2)}-\frac{2}{\sqrt{n(\Gamma_1)n(\Gamma_2)}}\langle\overline{\Gamma}_i\|\mathbf{V}_{\Gamma_1\Gamma_2}^{\Gamma}\|\overline{\Gamma}_i\rangle\right], \quad (20)$$

$\langle\overline{\Gamma}_i\|\mathbf{V}_{\Gamma_1\Gamma_2}^{\Gamma}\|\overline{\Gamma}_i\rangle$ is the reduced matrix element; the $D_{\Gamma_1\Gamma_2}^{\overline{\Gamma}_i}$ determines the intensity of the spectrum,

$$D_{\Gamma_1\Gamma_2}^{\overline{\Gamma}_i}=\sum_{\overline{\gamma}_i\overline{\gamma}_i'}\langle\overline{\Gamma}_i\overline{\gamma}_i|\mathbf{D}|\overline{\Gamma}_i\overline{\gamma}_i'\rangle. \quad (21)$$

The spectral curve $K_i(\Omega)$ with a generating function of the type (18) was investigated in detail by Krivoglaz and Pekar[2]. Thus, without resorting to a concrete analysis of the spectral function, we can draw a number of general conclusions concerning the character of the optical spectrum in the presence of electronic degeneracy.

1. The spectral curve is a superposition of bands $K_i(\Omega)$. The frequencies of the phononless lines of all the bands coincide (Ω_0 does not depend on $\overline{\Gamma}_i$). Each band corresponds to its own heat-release constant $\Delta_{\Gamma_1\Gamma_2}^{\overline{\Gamma}_i}$, which determines the half-width and the position of the maximum of the band, consequently, the degeneracy of the electronic level leads in general to a splitting of the absorption band (luminescence).

2. The number of bands in the spectrum coincides with the number z of the different roots of the matrix $\mathbf{V}_{\Gamma_1\Gamma_2}^{\Gamma}$. The maximum value of z is equal to the number of irreducible representations in the direct product $\Gamma_1\times\Gamma_2$.

We note that the degeneracy of the levels leads to a splitting of the spectral curve only in those cases when a non-unity vibrational representation Γ is contained simultaneously in $[\Gamma_1^2]$ and $[\Gamma_2^2]$ (interaction with a completely symmetrical oscillation does not lead to splitting). If at least one of the states is nondegenerate, then the symmetrized square of the corresponding representation contains only the unity representation, and $\Gamma_1\times\Gamma_2$ contains only one representation; therefore the optical spectrum consists of one band. This con-

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[1)] The operators $\mathrm{v}_{\Gamma\gamma}$ are transformed in accordance with the same irreducible representations as the normal coordinates $q_{\Gamma\gamma}$ of the corresponding oscillations.

clusion was first rigorously obtained by Perlin[13] for a transition from a nondegenerate to a degenerate state and, as we see here, is valid also for the inverse transition.

3. The phononless line common to all the bands is an exact superposition of the phononless lines corresponding to each band. Therefore the temperature dependence of its intensity is determined by the sum of the Debye-Waller factors with different $\Delta_{\Gamma_1\Gamma_2}^{\overline{\Gamma}_i}$. This leads to different temperature dependences of the phononless-line intensity in the presence and in the absence of degeneracy. If the heat-release parameters of at least one of the bands are small (in the presence, nevertheless, of a strong interaction with the oscillations), the theory predicts an anomalous temperature behavior of the intensity of the phononless line, which remains sufficiently intense at high temperatures.

In[7], in the adiabatic approximation and in the limiting case of a strong electron-vibrational coupling, it was concluded that a splitting takes place of the vibrational levels in systems with electron degeneracy, called "inversion" splitting in an analogy with that occurring in ammonia. In this connection the question of the possibility of inversion splitting of a phononless line was raised[20]. Our conclusion that there is no splitting of phononless lines cannot be connected with choice of the initial Hamiltonian, for in those cases when the adiabatic-potential minima corresponding to stable configurations are obtained with an operator $\hat{H}'$ that is linear in q_κ, these Hamiltonians coincide. Nor can it be connected with neglect of the "mixing" of different multiplets, which was not taken into account also in the adiabatic approach[7]. We note that this conclusion that there is no splitting of the phononless line was obtained earlier in[13] and[17] for the case of the exact degeneracy of the electronic levels of the Hamiltonian $\hat{H}_0$ (the conclusions of[17], however, pertain to the case of weak coupling, for which the aforementioned "inversion" splitting does not exist). In those papers, a splitting of the phononless lines, strongly dependent on the temperature and on the electron-phonon interaction constants, is obtained when the energy levels of the Hamiltonian $\hat{H}_0$ are split, i.e., when the electron degeneracy is lifted. We note that in ammonia, where the inversion splitting has been investigated in detail, the electronic ground state is nondegenerate even in a flat configuration[19]. It can be assumed that in the case of exact degeneracy, the splitting of the phononless lines will result from an account of the terms of higher order of q_κ in the Hamiltonian $\hat{H}'$.

The developed formalism enables us to consider also the problem of optical transitions between electronic states of a term that is degenerate in the absence of electron-phonon interaction. A calculation perfectly analogous to the derivation of (15) leads to the conclusion that a new characteristic type of absorption is possible in a vibronic system with a degenerate electronic ground-state term $|\Gamma_0\gamma_0\rangle$, not connected with transitions to other electronic states. Use is made here of approximations 1 and 2, with the aid of which formula (15) was derived, with $\hbar\Omega_{pq}$ denoting as before the distance to the next multiplet. The obtained expression for the generating function turns out to coincide with formula (15), in which it is necessary to replace p and p′ by g and g′ and to put formally $\Omega_{21} = 0$. The number of bands of the indicated absorption is determined by the number of non-identical representations in the expansion of $[\Gamma_0^2]$. The absorption is due to the complicated structure of the energy spectrum of the vibronic systems with degeneracy, and can lead to a number of singularities in the thermodynamic and magnetic properties of such systems. In the particular case when the adiabatic approximation is not valid, this absorption can be interpreted as a transition between the sheets of the adiabatic potential that are split as a result of the Jahn-Teller effect in one of the equilibrium configurations.

3. CONCRETE EXAMPLES. O_h SYMMETRY

By way of a concrete example of the application of the foregoing conclusions let us consider the case when the Hamiltonian of the impurity center or of the molecule has O_h symmetry. An investigation of other cases is analogous, and the results can be directly applied to systems whose symmetry is described by the subgroups of the group O_h. The possible degenerate states in this group are transformed in accordance with the representations E and T. Since

$$[E^2] = A_{1g} + E_g, \quad [T_1^2] = [T_2^2] = A_{1g} + E_g + T_{2g},$$

it follows that it is necessary to take into account, besides the completely symmetrical interaction, also the interaction of the electrons with oscillations of symmetry e_g (tetragonal) and t_{2g} (trigonal)[2]. Choosing the basis displacements of the nuclei and the basis functions of the representations corresponding to the considered electronic states in accordance with the work of Tanabe and Kamimura[18], we obtain the following matrix representation of the operators $v_{\Gamma\gamma}$:

$$v_{a_1}{}^{\Gamma} = \frac{1}{\sqrt{n(\Gamma)}} C(\Gamma a_1)\cdot 1, \quad v_{e1}{}^{T} = -\frac{1}{2\sqrt{3}} C(Te)\left(1 - \frac{3}{2}S_z^2 + \frac{3}{2}S_z\right),$$

$$v_{e2}{}^{T} = \frac{1}{2} C(Te)\left(-1 + \frac{3}{2}S_z^2 + \frac{1}{2}S_z\right),$$

$$v_{t_21}^{T} = \frac{1}{2\sqrt{3}} C(Tt_2)(S_x + S_xS_z + S_zS_x),$$

$$v_{t_22}^{T} = \frac{1}{\sqrt{6}} C(Tt_2)(S_x^2 - S_y^2), \quad v_{t_23}^{T} = \frac{1}{2\sqrt{3}} C(Tt_2)(S_x - S_xS_z - S_zS_x),$$

$$v_{e1}{}^{E} = -\frac{1}{2} C(Ee)\sigma_z, \quad v_{e2}{}^{E} = \frac{1}{2} C(Ee)\sigma_x, \tag{22}$$

where σ_i are Pauli matrices and S_i are the spin-operator matrices for the spin S = 1. Using the Wigner-Eckart theorem for the product of tensor operators, we obtain

$$\left\langle \overline{\Gamma}_i\overline{\gamma}_i \left| \sum_{\Gamma} V_{\Gamma_1\Gamma_2}^{\Gamma} \frac{\widetilde{\varphi}_\Gamma}{\hbar^2\omega_\Gamma^2} \right| \overline{\Gamma}_i\gamma_i \right\rangle \equiv \langle \overline{\Gamma}_i\overline{\gamma}_i \| \overline{\Gamma}_i\overline{\gamma}_i \rangle$$

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[2] For convenience we shall henceforth denote the vibrational representations by lower-case letters (c_2, e, a_1).

$$= \sum_{\Gamma,\ \gamma}\ \sum_{\gamma_1,\ \gamma_2}\ \sum_{\gamma_1',\ \gamma_2'} C(\Gamma_1\Gamma)\,C(\Gamma_2\Gamma)\,\frac{\varphi_\Gamma(t)}{\hbar^2\omega_\Gamma{}^2\sqrt{n(\Gamma_1)\,n(\Gamma_2)}}$$

$$+\cdot\langle\Gamma_1\gamma_1\,|\,\Gamma_1\gamma_1'\Gamma\gamma\rangle\langle\Gamma_2\gamma_2\,|\,\Gamma_2\gamma_2'\Gamma\gamma\rangle\cdot\langle\Gamma_1\gamma_1\Gamma_2\gamma_2\,|\,\overline{\Gamma}_i\overline{\gamma}_i\rangle\langle\overline{\Gamma}_i\overline{\gamma}_i\,|\,\Gamma_1\gamma_1\Gamma_2\gamma_2\rangle, \tag{23}$$

where $\langle\Gamma\gamma|\Gamma_1\gamma_1\Gamma_2\gamma_2\rangle$ are Clebsch-Gordan coefficients.

1. Transition $E \rightleftarrows E;\ E\times E = A_1 + A_2 + E$:

$$\langle A_1\|A_1\rangle = \sum_{\Gamma=a_1,\ e}\frac{1}{2}\frac{\tilde{\varphi}_\Gamma}{\hbar^2\omega_\Gamma{}^2}C_1(E\Gamma)C_2(E\Gamma),$$

$$\langle A_2\|A_2\rangle = \sum_{\Gamma=a_1,\ e}\frac{\tilde{\varphi}_\Gamma}{\hbar^2\omega_\Gamma{}^2}C_1(E\Gamma)C_2(E\Gamma)\left[\frac{1}{2}\delta(\Gamma a_1)-\frac{1}{2}\delta(\Gamma e)\right],$$

$$\langle E\|E\rangle = \sum_{\Gamma=a_1}\frac{\tilde{\varphi}_{a_1}}{\hbar^2\omega_\Gamma{}^2}C_1(Ea_1)C_2(Ea_1). \tag{24}$$

2. Transition $T \rightleftarrows E;\ T\times E = T_1 + T_2$:

$$\langle T_1\|T_1\rangle = \sum_{\Gamma=a_1,\ e}\frac{\tilde{\varphi}_\Gamma}{\hbar^2\omega_\Gamma{}^2}C(E\Gamma)C(T\Gamma)\left[\frac{1}{2\sqrt{3}}\delta(\Gamma e)+\frac{1}{\sqrt{6}}\delta(\Gamma a_1)\right],$$

$$\langle T_2\|T_2\rangle = \sum_{\Gamma=a_1,\ e}\frac{\tilde{\varphi}_\Gamma}{\hbar^2\omega_\Gamma{}^2}C(E\Gamma)C(T\Gamma)\left[-\frac{1}{2\sqrt{3}}\delta(\Gamma e)+\frac{1}{\sqrt{6}}\delta(\Gamma a_1)\right]. \tag{25}$$

3. Transition $T \rightleftarrows T;\ T\times T = A_1 + E + T_1 + T_2$:

$$\langle A_1\|A_1\rangle = \sum_{\Gamma=a_1,\ e,\ t_2}\frac{\tilde{\varphi}_\Gamma}{\hbar^2\omega_\Gamma{}^2}C_1(T\Gamma)C_2(T\Gamma)\left[\frac{1}{3}\delta(\Gamma a_1)+\frac{1}{3}\delta(\Gamma e)+\frac{1}{3}\delta(\Gamma t_2)\right],$$

$$\langle E\|E\rangle = \sum_{\Gamma=a_1,\ e,\ t_2}\frac{\tilde{\varphi}_\Gamma}{\hbar^2\omega_\Gamma{}^2}C_1(T\Gamma)C_2(T\Gamma)\left[\frac{1}{3}\delta(\Gamma a_1)+\frac{1}{3}\delta(\Gamma e)-\frac{1}{6}\delta(\Gamma t_2)\right],$$

$$\langle T_1\|T_1\rangle = \sum_{\Gamma=a_1,\ e,\ t_2}\frac{\tilde{\varphi}_\Gamma}{\hbar^2\omega_\Gamma{}^2}C_1(T\Gamma)C_2(T\Gamma)\left[\frac{1}{3}\delta(\Gamma a_1)-\frac{1}{6}\delta(\Gamma e)-\frac{1}{6}\delta(\Gamma t_2)\right],$$

$$\langle T_2\|T_2\rangle = \sum_{\Gamma=a_1,\ e,\ t_2}\frac{\tilde{\varphi}^\Gamma}{\hbar^2\omega_\Gamma{}^2}C_1(T\Gamma)C_2(T\Gamma)\left[\frac{1}{3}\delta(\Gamma a_1)-\frac{1}{6}\delta(\Gamma e)+\frac{1}{6}\delta(\Gamma t_2)\right]. \tag{26}$$

Formulas (17)–(20), with allowance for (24)–(26), make it possible to construct the spectral curve for the considered transitions. If the interaction with certain active modes is negligibly small, then the number of bands turns out to be smaller than the maximum possible (the results are summarized in the table). In those cases when the adiabatic approximation is valid for the degenerate term (the electronic equation can be diagonalized with the aid of a unitary transformation whose matrix does not depend on the vibrational coordinates), the results admit of a simple physical interpretation in the language of the Franck-Condon principle. An example is the transition T ⇄ T, when the e_g vibrations are active and lead, upon interaction with the electrons, to tetragonal minima of the adiabatic potential[9]. The Jahn-Teller effect is then static—the vibronic states in each minimum are stationary, since nonradiative transitions between the equilibrium configurations are forbidden. In this case each tetragonal minimum of the ground state (of symmetry D_{4h}) corresponds to a splitting of the non-self-consistent excited abiabatic T-state into two components ($T \rightarrow A + E$), leading to a doublet splitting of the optical bands.

Transitions	$E \rightleftarrows E$	$E \rightleftarrows T$	$T \rightleftarrows T$		
Active vibrations	e_g	e_g	e_g	t_{2g}	$t_{2g}+e_g$
Number of bands	3	2	2	3	4

The authors are grateful to Yu. E. Perlin and I. B. Bersuker for continuous interest in the work, and to V. L. Bonch-Bruevich and R. A. Suris for a discussion of the results.

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Translated by J. G. Adashko
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