The critical points of adiabatic potentials of electron-vibrational systems

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The effect of the dimensionality of the space of vibrational coordinates and the topological features of the adiabatic potentials of electronic states on the absorption and luminescence spectra of electron-vibrational systems is examined. Analytical expressions are derived for the combined densities of states $J_{if}(\omega)$ for the one-, two-, and three-dimensional problems and all possible types of critical points relevant to these cases. Using the quasiclassical approximation, the dependence of the absorption and luminescence spectra is found to be determined by certain universal functions introduced in this paper. Finally, the combined densities of states are analyzed for the case where the vibrational frequencies in the final and initial electronic states are different and the adiabatic potential of the final electronic state is shifted.

1. INTRODUCTION

In Refs. 1–4 the theory of critical points1) for functions fixed on topological manifolds[5] was applied in analyzing the phonon and electron energy spectra of crystals. It was found that spatial periodicity is sufficient for the existence of such points. The special role of these points is related to the emergence at the points of singularities in the spectra of a number of physical quantities with the following mathematical properties:

$$J(\omega)=\int d\mathbf{x}\, g(\mathbf{x})\delta(f(\mathbf{x})-\omega)$$

$$=\sum_m \int ds\, g(\mathbf{s})\,|\mathrm{grad}_{\mathbf{x}} f(\mathbf{x})|^{-1}{}_{\mathbf{x}_m}, \qquad (1)$$

with $\mathbf{x}$ an (n-dimensional vector, $\mathbf{s}$ an $(n-1)$-dimensional hypersurface, and $\mathbf{x}_m$ the mth root of the equation $f(\mathbf{x})=0$. The singularities manifest themselves most strikingly in the density of phonon and electronic states and in what is known as the combined density of states. The latter is related to absorption, luminescence, and scattering optical spectra. A fairly detailed discussion of the theoretical and experimental results pertaining to critical points in the electron and phonon dispersion laws can be found in Refs. 6 and 7.

The present study is devoted to the problem of critical points of the adiabatic potentials of electron-variational systems. The role of adiabatic potentials of multiatomic media in various physical effects is well known.[8] They are especially important for the theory of absorption, luminescence, and Raman-scattering line shapes and the problem of electron-vibrational interaction in crystals with impurities and intrinsic defects.

Although adiabatic potentials are not periodic functions of vibrational coordinates, the presence of critical points in them is fairly obvious. Indeed, the stable existence of such multiatomic objects as molecules and solids irrevocably points to the fact that within a broad set of electronic states of these systems the nuclear subsystem possesses a stable position of equilibrium. This implies that there is at least one minimum for each adiabatic potential related to these electronic states. The possibility of structural phase transitions in multiatomic systems suggests that an adiabatic potential carries a set of minimum points and hence a set of maximum points. Obviously, there are no restrictions on the appearance of saddle points.

Studying adiabatic potentials near critical points and especially the features of optical spectra associated with such points is desirable for the following reasons:

(a) the features of the spectra of absorption, luminescence, and scattering of light can be identified and the contributions of adiabatic potentials not related to the topology can be isolated;

(b) fairly simple analytical expressions can be derived for adiabatic potentials near critical points and for optical spectra near the respective singularities;

(c) comparing the experimental data and the analytical expressions makes it possible to classify the critical points and determine some characteristic parameters of electron-vibrational systems; and finally,

(d) a fairly good approximate reconstruction of adiabatic potentials can be made from the known critical points via interpolation schemes.[3,9]

The simplest and most direct experimental way of finding the critical points of adiabatic potentials is to employ optical methods. In view of this we examine the combined density of states that allows for the electron-vibrational interaction. This quantity directly determines the absorption and luminescence line shapes. To illustrate the singularities that emerge at critical points, we restrict the discussion to a combined density of states calculated in the quasiclassical approximation.[10] For the sake of definiteness we select the optical transitions between nondegenerate electronic states of a molecule or an impurity center in a crystal. Then, allowing in the adiabatic potentials for terms to within the second order in the vibrational coordinates, we arrive at the following expression for the combined density of states:

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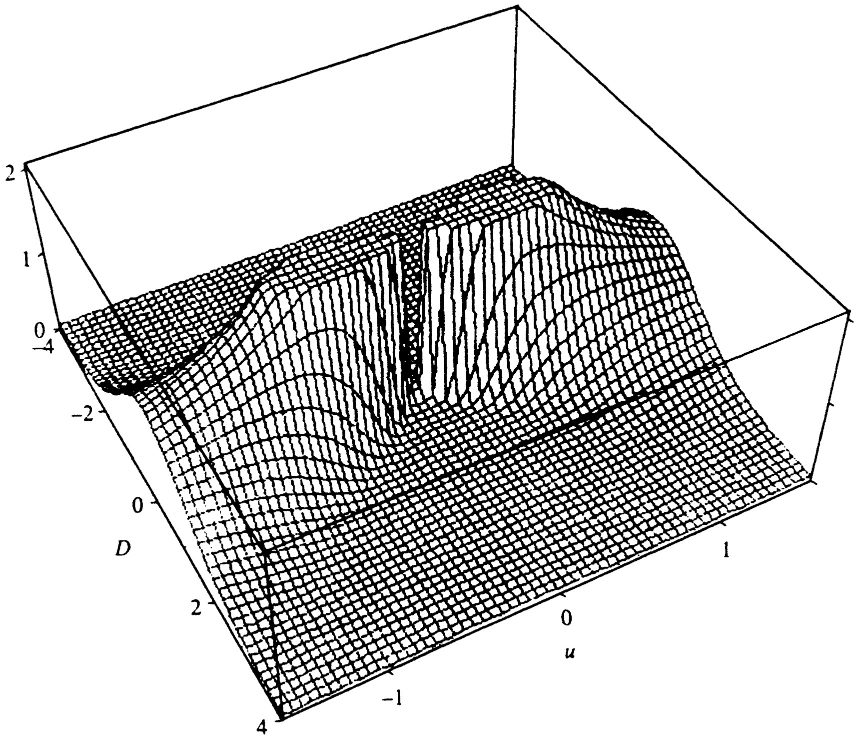

FIG. 1. The universal function $f_a(D,u)$ [Eq. (3)], which determines how the combined density of states $J_{if}(\omega)$ depends on the frequency detuning $D=\beta(\hbar\omega-E_{if})$, the parameter $u=\beta^{1/2}a$ proportional to the shift of the adiabatic potential of the final electronic state, and the temperature $\beta=k_BT$. The curvatures of the adiabatic potentials of the initial and final electronic states are assumed to coincide. The function $f_a(D,u)$ describes the case of electron-vibrational coupling with an arbitrary finite number n of vibrational modes if for u we take $(\Sigma_{m=1}^{n}u_m^2)^{1/2}$.

$$J_{if}(\omega)=A\int_{-\infty}^{+\infty}\cdots\int\left(\prod_{n=1}^{m}\sqrt{\frac{\beta}{\pi}}dQ_n\,e^{-\beta Q_n^2}\right)\times\delta\left(\hbar\omega-E_{if}-\sum_{n=1}^{m}(a_n+w_nQ_n)Q_n\right),\qquad(2)$$

where i and f label the initial and final electronic states, Q_n is the vibrational coordinate of the nth mode, $\beta=(k_BT)^{-1}$, with k_B Boltzmann's constant and T the absolute temperature, E_{if} is the energy gap between the final and initial states, a_n is a constant describing the shift of the adiabatic potential of the final electronic state in the Q_n-direction with respect to the minimum of the ground-state adiabatic potential, w_n is a constant proportional to the difference of the vibrational frequencies of the nth mode in the final and initial electronic states,[2)] and A is a constant proportional to the square of the absolute value of the dipole moment of the optical transition.

The quantity described by the argument of the delta function in (2) is, to within the photon energy, the difference of the adiabatic potentials of the initial and final states and is represented by an m-dimensional surface in the vibrational-coordinate space. Obviously, it possesses three types of points: ordinary, elliptic, and hyperbolic. Only points of the last two types can be critical. For these all the coefficients a_n are zeros. It is well known that elliptic points correspond to maxima and minima and hyperbolic to saddle points. Saddle points break down into types whose number is determined by the dimensionality of states and the number of negative (positive) coefficients w_n.

2. THE ONE-DIMENSIONAL PROBLEM

Let us consider the combined density of states $J_{if}(\omega)$ for the case where in the final electronic state of a molecule or an intrinsic or impurity defect of a crystal there is interaction with a single vibrational mode Q.

(a) Let the frequencies of vibrations in the initial and final electronic states coincide. Then $J_{if}(\omega)$ is the product of βA by a universal function $f_a(D,u)$:

$$J_{if}(\omega)=\beta A f_a(D,u)=\frac{\beta A\sqrt{\pi}}{|u|}\exp\left(-\frac{D^2}{u^2}\right),\qquad(3)$$

where $D=\beta(\hbar\omega-E_{if})$ is the dimensionless detuning of the frequency of light from the point of electron resonance, and $u=\beta^{1/2}a$ a dimensionless constant describing the shift of the adiabatic potential of the final electronic state. A characteristic feature of the situation under discussion is the absence of low- and high-frequency thresholds in the spectral dependence of $J_{if}(\omega)$. Equation (3) shows that the combined density of states at a fixed and finite u attains its maximum value at $D=0$, in the limit $u\rightarrow 0$ the universal function $f_a(D,u)$ behaves like a delta function, and for a fixed and finite D the function $J_{if}(\omega)$ has a maximum at $u=\pm 2^{1/2}D$. To illustrate the qualitative dependence on the detuning parameter D, the shift u in the adiabatic potential, and the inverse temperature $\beta=1/k_BT$, Fig. 1 shows a plot of $f_a(D,u)$.

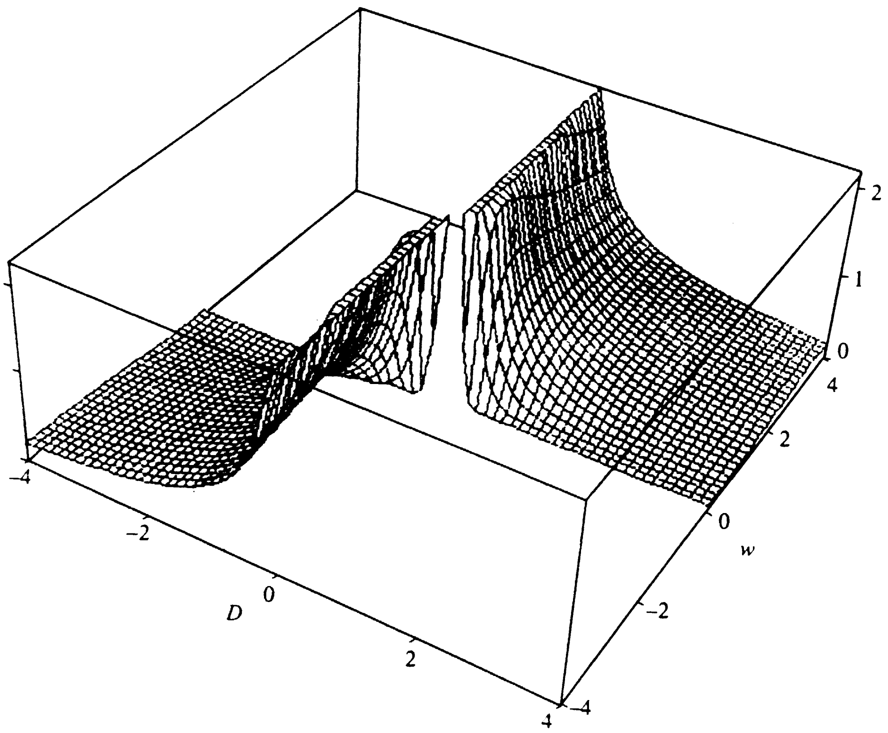

FIG. 2. The universal function $f_a(D,w)$ [Eq. (4)], which determines how the combined density of states $J_{if}(\omega)$ for the one-dimensional problem depends on the frequency detuning $D=\beta(\hbar\omega-E_{if})$, the parameter w proportional to the difference of the vibrational frequencies in the final and initial electronic states, and the temperature $\beta=1/k_BT$. The shift of the adiabatic potential in the final electronic state is assumed to be nil ($u=0$). The section of the graph with $D\geqslant 0$ and $w\geqslant 0$ belongs to a critical point of the minimum type and with $D\leqslant 0$ and $w\leqslant 0$ to a critical point of the maximum type.

(b) If the difference of the adiabatic potentials of the initial and final electronic states at the origin of coordinates ($Q=0$) has a critical point ($a=0$ and w finite),[3)] in the one-dimensional case it can be either a minimum or a maximum. Irrespective of the type of critical point, the analytical expression for the combined density of states $J_{if}(\omega)$ has the following form:

$$J_{if}(\omega)=\beta A f_b(D,w)$$
$$=\frac{\beta A\pi^{-1/2}}{(wD)^{-1/2}}\exp\{-D/w\}. \tag{4}$$

In contrast to the previous case the spectral dependence of $J_{if}(\omega)$ has a threshold nature and possesses a branch point of order 2 of the $1/D^{-1/2}$ type. This singularity is similar to those in the density of electronic and phonon states of crystals. The spectral threshold of $J_{if}(\omega)$ coincides with the point of electron resonance, $D=0$. If the critical point is a minimum (w positive), $J_{if}(\omega)$ has a low-frequency threshold $D\geqslant 0$. Such a possibility is realized in the case where the adiabatic potential in the final electronic state possesses a minimum and the curvature of this potential is greater than in the initial state. If the critical point is a maximum (w negative), $J_{if}(\omega)$ has a high-frequency threshold $D\leqslant 0$. This is possible when the adiabatic potential of the final electronic state possesses a maximum or minimum with a curvature less than in the initial state.The graph of the universal function $f_b(D,w)$ for the first and second cases (w positive and w negative) is depicted in Fig. 2. Note that for a fixed detuning $D\neq 0$ the combined density of states attains its peak value at $w=2D$.

If in addition to a shift in the adiabatic potential the vibrational frequencies in the initial and final states are distinct (a and w finite), the expression for the combined density of states $J_{if}(\omega)$ acquires the following form:

$$J_{if}(\omega)=\beta A f_c(D,u,w)=\beta A\pi^{-1/2}\frac{\exp\{-(u^2/4w^2+Z_1/w)\}\cosh\{(u/w)(u^2/4w^2+Z_1/w)^{1/2}\}}{(wZ_1)^{1/2}}, \tag{5}$$

where $z_1=D+u^2(4w)^{-1}$ is the frequency detuning renormalized by the electron-vibrational interaction. This formula for $J_{ij}(\omega)$ is the most general and corresponds in the one-dimensional case to the shift of the critical points of the argument of the delta function in (2) from the origin of coordinates $Q=0$ to the position $Q=Q_0=\pm a(2w)^{-1}$. The spectral dependence of $J_{ij}(\omega)$ is of a threshold nature and possesses a branch point of order 2. In contrast to case (b), the spectral threshold occurs at a photon energy of $\hbar\omega=E_{if}-u^2/4w$. For a critical point of

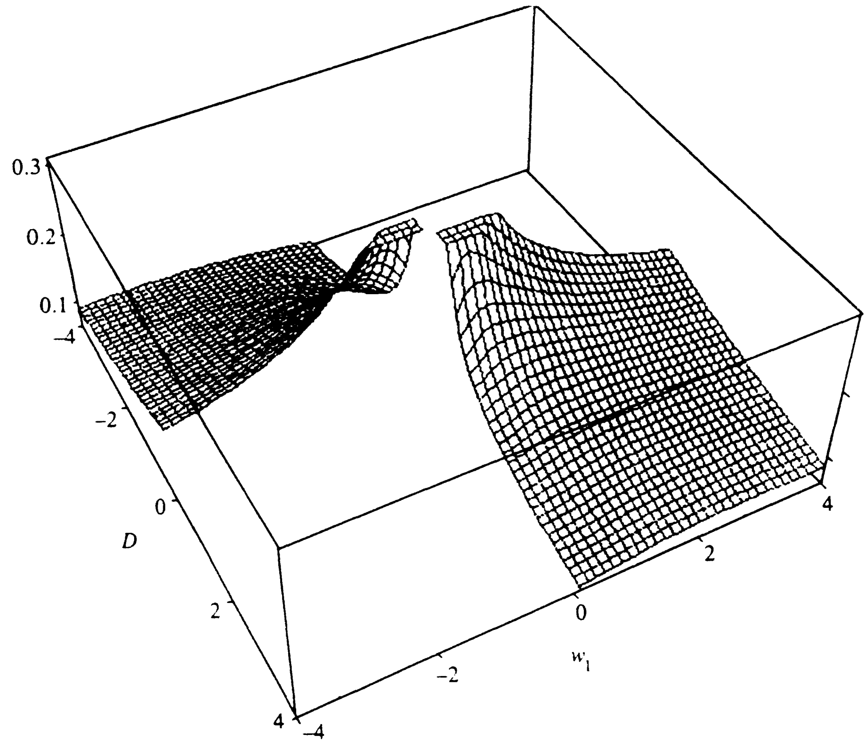

FIG. 3. The universal function $f_b(D,w_1,w_2)$ [Eq. (6)], which determines how the combined density of states $J_{if}(\omega)$ for the two-dimensional problem depends on the frequency detuning $D=\beta(\hbar\omega-E_{if})$, the parameters w_1 and w_2 proportional to the difference of the vibrational frequencies in the final and initial electronic states, and the temperature $\beta=1/k_BT$. It is assumed that w_2 and there is no shift of the adiabatic potential in the final electronic state ($u_1=u_2=0$). The section of the graph with $D\geqslant 0$ and $w\geqslant 0$ belongs to a critical point of the minimum type and with $D\leqslant 0$ and $w\leqslant 0$ to a critical point of the maximum type.

the minimum type (w positive) this yields a shift toward the long-wave part of the spectrum, and for a critical point of the maximum type (w negative) a shift toward the short-wave part.

3. THE TWO-DIMENSIONAL PROBLEM

Let us examine the combined density of states $J_{if}(\omega)$ in the case where in the final electronic state of a molecule or impurity ion there is an interaction with two vibrational modes, Q_1 and Q_2.

(a) If the vibrational frequencies in the initial and final electronic states coincide ($w_1=w_2=0$), the function $J_{ij}(\omega)$ is described by Eq. (3) with $u=(u_1^2+u_2^2)^{1/2}$. In Fig. 1 the respective universal function $f_a(D,u_1,u_2)$ is plotted as a function of the frequency detuning D, the parameter u, and the temperature $\beta=1/k_BT$.

(b) If the difference of the adiabatic potentials of the final and initial electronic states at thecoordinate origin ($Q_1=Q_2=0$) has a critical point ($a_1=a_2=0$, and w_1 and w_2 finite), the point can be a minimum (w_1 and w_2 positive) or a maximum (w_1 and w_2 negative) or a saddle point (w_1w_2 negative).

In the case of critical points of the minimum or maximum type, the combined density of states $J_{if}(\omega)$ has the same analytical form and can be expressed in terms of the modified Bessel function $I_n(x)$ (see Ref. 11) as follows:

$$J_{ij}(\omega)=\beta A f_b(D,w_1,w_2)$$

$$=\frac{\beta A}{(w_1w_2)^{1/2}}\exp(-D\tau_+)I_0(D\tau_-), \qquad (6)$$

with $\tau'_\pm=0.5(1/w_2\pm 1/w_1)$. Here for both w_1 and w_2 positive $J_{if}(\omega)$ has a low-frequency threshold $D\geqslant 0$ and for both w_1 and w_2 negative a high-frequency threshold $D\leqslant 0$. The universal function $f_b(D,w_1,w_2)$ is plotted in Fig. 3 for $w_2=1$. As Eq. (6) shows, such a choice of parameter w_2 makes it possible to illustrate qualitatively the dependence of $J_{if}(\omega)$ on the detuning D and the differences of the vibrational frequencies of the final and initial electronic states, w_n, in all essentially different ranges of arguments of $f_b(D,w_1,w_2)$.

In the case of a saddle critical point (for definiteness we assume $w_1>0$ and $w_2<0$) we have

$$J_{if}(\omega)=\beta A f_{sp}(D,w_1,w_2)$$

$$=\frac{\beta A}{\pi(w_1|w_2|)^{1/2}}\exp(-D\tau'_-)K_0(|D|\tau'_+), \qquad (7)$$

where

$$\tau'_\pm=0.5(1/|w_2|\pm 1/w_1)$$

and $K_n(x)$ the modified Bessel function.[11] There is no threshold in the spectral dependence of the combined density of states, and at the point of electron resonance ($D=0$) there is a singularity of the logarithmic type. The universal function $f_{sp}(D,w_1,w_2)$ is plotted in Fig. 4 for $w_2=1$.

(c) In the most general case for the two-dimensional problem, namely, where there is a shift of the adiabatic potential of the final electronic state (a_n finite) and the curvature of the adiabatic potential differs from that of the adiabatic potential of the initial state (w_n finite), that is, the critical points are not at the origin of coordinates but

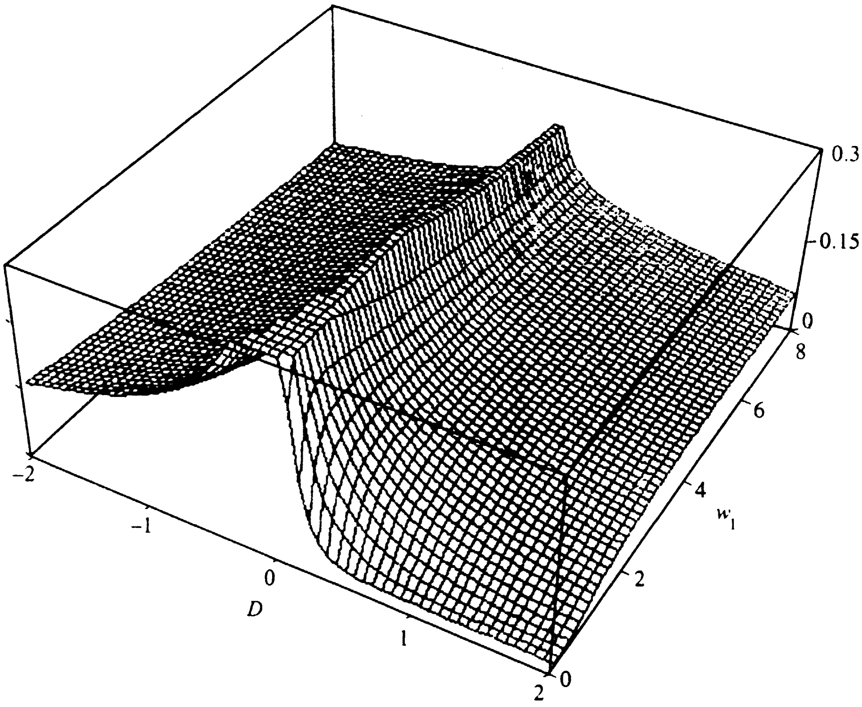

FIG. 4. The universal function $f_{sp}(D,w_1,w_2)$ [Eq. (7)], which determines, in the presence of a saddle point, how the combined density of states $J_{if}(\omega)$ for the two-dimensional problem depends on the frequency detuning $D=\beta(\hbar\omega-E_{if})$, the parameters w_1 and w_2 proportional to the difference of the vibrational frequencies in the final and initial electronic states, and the temperature $\beta=1/k_BT$. It is assumed that $|w_2|=1$ and there is no shift of the adiabatic potential in the final electronic state ($u_1=u_2=0$).

are shifted to the position $Q_{0n}=\pm a_n/2w_n$, the analytical expression for the combined density of states $J_{if}(\omega)$ becomes noticeably more complicated. For instance, for a critical point of the minimum type (w_1 and w_2 positive) and for an arbitrary ratio[4)] of w_1 to w_2 the function $J_{if}(\omega)$ is given by the following formula:

$$J_{if}(\omega)=\beta A f_c(D,u_1,u_2,w_1,w_2)$$

$$=\frac{\beta A\exp(-\lambda_2-Z_2\tau_+)}{(w_1w_2)^{1/2}}$$

$$\times\sum_{n=-\infty}^{\infty}\cos(2n\arcsin^{-1}t)I_n(Z_2\tau_-)I_{2n}(Z_2^{1/2}\xi), \tag{8}$$

where

$$\lambda_n=0.25\sum_{j=1}^{n}\left(\frac{u_j}{w_j}\right)^2,\quad z_n=D+0.25\sum_{j=1}^{n}\frac{u_j^2}{w_j},$$

$$t=\frac{u_2}{w_2^{3/2}\xi},\quad \xi=\left(\frac{u_1^2}{w_1^3}+\frac{u_2^2}{w_2^3}\right)^{1/2}. \tag{9}$$

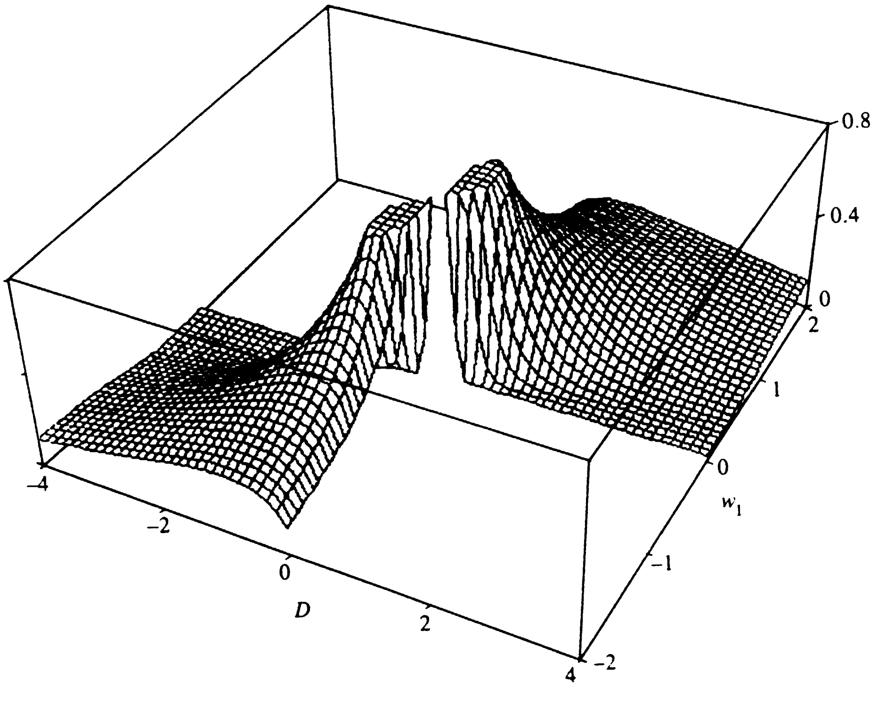

FIG. 5. The universal function $f_{sph}(D,w_1,w_2)$ [Eq. (14)], which determines how the combined density of states $J_{if}(\omega)$ for the three-dimensional problem depends on the frequency detuning $D=\beta(\hbar\omega-E_{if})$, the parameter w proportional to the difference of the vibrational frequencies in the final and initial electronic states, and the temperature $\beta=1/k_BT$. It is assumed that the difference of the adiabatic potentials is a sphere ($w_1=w_2=w_3=w$) and that there is no shift of the adiabatic potential in the final electronic state ($u_1=u_2=u_3=0$). The section of the graph with $D\geqslant0$ and $w\geqslant0$ refers to the case of a critical point of the minimum type and with $D\leqslant0$ and $w\leqslant0$ to a critical point of the maximum type.

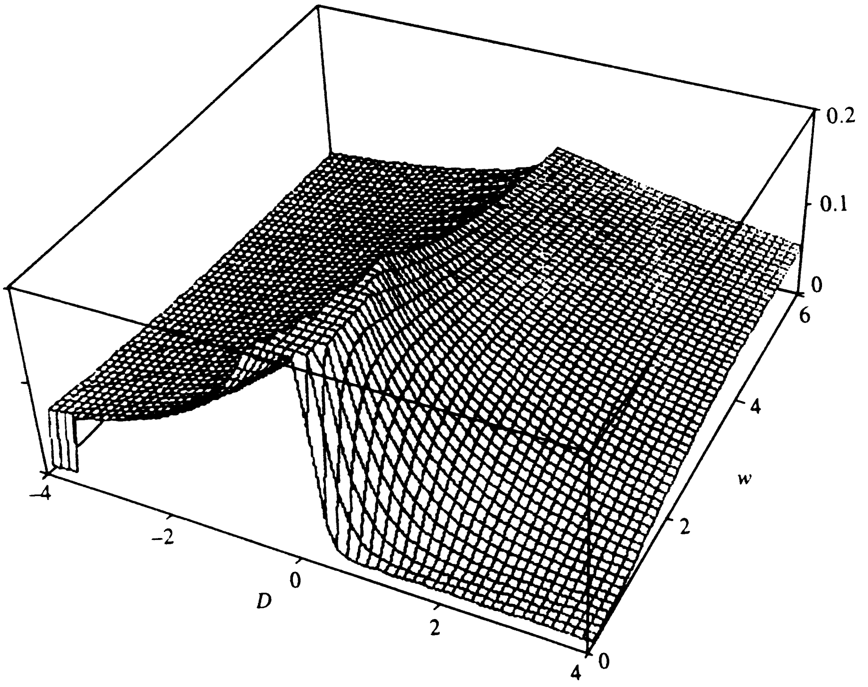

FIG. 6. The universal function $f_{sp}^{(1)} \times (D,w,w,w_3)$ [Eq. (7)], which determines, in the presence of a saddle point of the first type, the dependence of the combined density of states $J_{if}(\omega)$ for the three-dimensional problem depends on the frequency detuning $D=\beta(\hbar\omega-E_{if})$, the parameters w and w_3 proportional to the difference of the vibrational frequencies in the final and initial electronic states, and the temperature $\beta=1/k_BT$. It is assumed that $|w_2|=1$ and that there is no shift of the adiabatic potential in the final electronic state $(u_1=u_2=0)$.

The quantity z_n is the frequency detuning renormalized by the electron-vibrational interaction. As before, the combined density of states $J_{if}(\omega)$ has a low-frequency threshold. But the shift in the adiabatic potential of the final electronic state leads to a situation in which the threshold is displaced from the point of electron resonance $D=0$ to the long-wave region of the spectrum, $\hbar\omega \geqslant E_{if} - u_1^2/4w_1 - u_2^2/4w_2$. When the adiabatic-potential difference is a circle $(w_1=w_2=w)$, the analytical expression for the combined density of states $J_{if}(\omega)$ simplifies and the has form

$$J_{if}(\omega)=\beta A f_c(D,u_1,u_2,w,w) = \beta A \frac{\exp(-\lambda_2-Z_2/w) I_0(Z_2^{1/2}\zeta)}{w}. \qquad (10)$$

For a critical point of the minimum type (w_1 and w_2 negative), $J_{if}(\omega)$ is determined by the same Eqs. (8) and (10) in which $|w_n|$ must be substituted for w_n and $D'=-D$ for D.

But if the critical point is a saddle point (say, $w_1>0$ and $w_2<0$), the combined density of states can be represented only in integral form:

$$J_{if}(\omega)=\beta A f_{sp}(D,u_1,u_2,w_1,w_2) = \beta A \frac{2}{\pi(w_1|w_2|)^{1/2}} \exp\left(-\lambda_2-\frac{Z_2'}{|w_2|}\right) \times \int_{(Z')^{1/2}}^{\infty} dx \frac{\exp(-x^2\tau_+')}{(x^2-Z_2')^{1/2}} \cosh\left(\frac{u_1}{w_1^{3/2}}x\right) \times \cosh\left(\frac{u_2}{|w_2|^{3/2}}(x^2-Z_2')^{1/2}\right), \qquad (11)$$

where $z_2'=D+u_1^2/4w_1-u_2^2/4|w_2|$ is the frequency detuning renormalized by the electron-vibrational coupling. But even this form makes it possible to draw conclusions concerning the effect of the shift of the adiabatic potential of the final electronic state on the most important changes in the spectral dependence of $J_{if}(\omega)$. We see that the logarithmic singularity has remained, but now it is shifted from the point of electron resonance $D=0$ and occurs at $\hbar\omega=E_{if}-u_1^2/4w_1+u_2^2/4|w_2|$.

IV. THE THREE-DIMENSIONAL PROBLEM

Let us examine the combined density of states $J_{if}(\omega)$ for the case where in the final electronic state there is an interaction with three vibrational modes, Q_1, Q_2, and Q_3.

(a) If the vibrational frequencies in the initial and final electronic states coincide $(w_1=w_2=w_3=0)$, then, as in the previous cases of lower dimensionality, $J_{if}(\omega)$ is described by the expression (3) in which $u=(u_1^2+u_2^2+u_3^2)^{1/2}$. In Fig. 1 the respective universal function $f_a(D,u_1,u_2,u_3)$ is plotted as a function of the frequency detuning D, the parameter u, and the temperature $\beta=1/k_BT$.

(b) In the three-dimensional case considered here, the difference of the adiabatic potentials of the final and initial electronic states at the origin of coordinates $(Q_1=Q_2=Q_3=Q_4)$ can have critical points $(a_1=a_2=a_3=a_4$, and w_1, w_2, and w_3 finite) of the minimum type (w_1, w_2, and w_3 positive), the maximum type (w_1, w_2, and w_3 negative), and saddle points of the first (w_1 and w_2 positive and w_3 negative) and second (w_1 and w_2 negative and w_3 positive) types.

The combined density of states $J_{if}(\omega)$ for w_1, w_2, and w_3 positive (a minimum) is represented in the form of a series in the Kummer functions[11] $M(a;b;x)$ as follows:

$$\begin{aligned} J_{if}(\omega) &= \beta A f_b(D,w_1,w_2,w_3) \\ &= \beta AC\left(\frac{D}{w_3}\right)^{1/2} \\ &\quad\times\exp\left(-\frac{D}{w_3}\right)\sum_{m=0}^{\infty}\frac{(\nu^2-\mu^2)^m}{2^{2m}m!}I_m\left(\frac{\mu-\nu}{2}\right) \\ &\quad\times\sum_{n=0}^{m}(-1)^n\binom{n}{n}\Gamma\left[\begin{matrix}2n+1\\2n+3/2\end{matrix}\right]\left(\frac{D}{w_3}\right)^{2n}M\biggl(2n \\ &\quad+1;2n+\frac{3}{2};-0.5(\mu+\nu)\frac{D}{w_3}\biggr), \end{aligned} \tag{12}$$

where $C=(w_1w_2w_3)^{-1/2}$, $\mu=(w_3-w_1)/w_1$, $\nu=(w_3-w_2)/w_2$,

$$\binom{n}{m}=\frac{m!}{n!(m-n)!},\quad \Gamma\left[\begin{matrix}b\\a\end{matrix}\right]=\frac{\Gamma(a)}{\Gamma(b)},$$

with $\Gamma(x)$ the gamma function.[11] For w_1, w_2, and w_3 negative (a maximum) $J_{if}(\omega)$ is described by the same formula (12) but with $|w_n|$ substituted for w_n and $D'=-D$ for D. Equation (12) shows that for a critical point of the minimum type the spectral dependence of the combined density of states has a low-frequency threshold $D\geqslant 0$, and for a critical point of the maximum type it has a high-frequency threshold $D\leqslant 0$. In both cases the threshold coincides with the point of electron resonance, $D=0$. Near a threshold ($|D\ll 1|$) $J_{if}(\omega)$ exhibits a characteristic spectral dependence $J_{if}(\omega)\sim D^{1/2}$. The above expression for the combined density of states $J_{ij}(\omega)$ refers to the case where the difference of the adiabatic potentials of the initial and final electronic states is represented by an ellipsoid of arbitrary shape. All three semiaxes of this ellipsoid are different ($w_1\neq w_2\neq w_3$). But if two semiaxes coincide (say, $w_1=w_2=w\neq w_3$), that is, if we are dealing with an ellipsoid of revolution, the analytical expression for $J_{ij}(\omega)$ simplifies considerably:

$$\begin{aligned} J_{if}(\omega) &= \beta A f_{er}(D,w,w,w_3) \\ &= \beta A\frac{\exp(-D/w)}{w}|1-\alpha|^{-1/2} \\ &\quad\times\begin{cases}\operatorname{erf}\left(\left[\dfrac{1-\alpha}{\alpha}\dfrac{D}{w}\right]^{1/2}\right), & \alpha<1\\[2ex] \operatorname{erfi}\left(\left[\dfrac{\alpha-1}{\alpha}\dfrac{D}{w}\right]^{1/2}\right), & \alpha>1,\end{cases} \end{aligned} \tag{13}$$

where $\alpha=w_3w^{-1}$, and $\operatorname{erf}(x)$ and $\operatorname{erfi}(x)=i^{-1}\operatorname{erf}(ix)$ are the error functions of the real and imaginary arguments.[11] If all three semiaxes are equal ($w_1=w_2=w_3=w$), the ellipsoid transforms into a sphere. The combined density of states $J_{ij}(\omega)$ in this case can be expressed in terms of elementary functions:

$$J_{if}(\omega)=\beta A f_{sh}(D,w,w,w)=\beta A\frac{2\exp(-D/w)}{\pi^{1/2}w^{3/2}}D^{1/2}. \tag{14}$$

The universal function $f_{sh}(D,w,w,w)$ is plotted in Fig. 5. The selection of Eq. (14) to illustrate the dependence of $J_{ij}(\omega)$ on the frequency detuning D and the parameters w_n is determined by the fact that qualitatively the plot of this function coincides with the plots of the more complicated expressions (12) and (13). At the same time, the features exhibited by Fig. 5 can easily be explained by analyzing the simple formula (14).

If the difference of the adiabatic potentials of the final and initial electronic states has a saddle critical point of the first type (w_1 and w_2 positive and w_3 negative), the combined density of states $J_{if}(\omega)$ can be represented by the following series in the Kummer functions $U(a;b;x)$ (see Ref. 11):

$$\begin{aligned} J_{ij}(\omega) &= \beta A f_{sp}^{(1)}(D,w_1,w_2,w_3) \\ &= \beta AC\sum_{m=0}^{\infty}\frac{1}{2^m m!}\left(\frac{\psi-\varphi}{\psi+\varphi}\right)^m I_m\left(\frac{\varphi-\psi}{\varphi+\psi}\right)\sum_{n=0}^{m}(-1)^n\binom{n}{m}[0.5(\varphi+\psi)D]^{2n}|D|^{1/2} \\ &\quad\times\begin{cases}\exp\{D[1/|w_3|-0.5(\varphi+\psi)]\}U(0.5;2n+\tfrac{3}{2};0.5(\varphi+\psi)D) & \text{if } D\geqslant 0,\\ \exp(D/|w_3|)\Gamma[{}^{2n+1}_{0.5}]U(2n+1;2n+\tfrac{3}{2};0.5(\varphi+\psi)D) & \text{if } D\leqslant 0,\end{cases} \end{aligned} \tag{15}$$

where $C=(w_1w_2|w_3|)^{-1/2}$, $\varphi=1/w_1+1/|w_3|$, $\psi=1/w_2+1/|w_3|$.

For a critical point of the second type (w_1 and w_2 negative and w_3 positive),

$$J_{if}(\omega)=\beta A f_{sp}^{(2)}(D,w_1,w_2,w_3). \tag{16}$$

The universal function $f_{sp}^{(2)}(D,w_1,w_2,w_3)$ can be obtained from $f_{sp}^{(1)}(D,w_1,w_2,w_3)$ [see Eq. (15)] by replacement of $|w_3|$ with w_3, w_1 with $|w_1|$, and w_2 with $|w_2|$ and by mirror reflection with respect to $D=0$, that is, by substituting $D'=-D$ for D. There is no threshold in the spectral dependence of $J_{if}(\omega)$, but the first derivative of $J_{if}(\omega)$ has a singularity, a discontinuity at the point of electron resonance, $D=0$.

Equation (15) was obtained for arbitrary absolute values of the parameters w_n. The analytical expression for the combined density of states $J_{if}(\omega)$ simplifies considerably in the case where the absolute values of the quantities w_n with the same sign are equal. For instance, for $w_1=w_2=w>0$ and $w_3<0$ (a saddle point of the first type),

$$J_{if}(\omega)=\beta A f_{sp}^{(1)}(D,w,w,w_3) =\frac{\beta A \exp(-D/w)}{[w(w^+|w_3|)]^{1/2}} \times\begin{cases} 1, & D\geqslant 0,\\ \operatorname{erfc}\left(\left[\dfrac{w+|w_3|}{|w_3|}\cdot\dfrac{|D|}{w}\right]^{1/2}\right), & D\leqslant 0, \end{cases} \tag{17}$$

where $\operatorname{erfc}(x)=1-\operatorname{erf}(x)$. A plot of the universal function $f_{sp}^{(1)}$ is given in Fig. 6. The case where all three parameters w_n are equal is of no particular interest because the expression for $J_{if}(\omega)$ does simplify.

(c) Let us consider the most general situation for the three-dimensional problem: namely, the adiabatic potential of the final electronic state is shifted in relation to the adiabatic potential of the initial state (a_1, a_2, and a_3 finite) and the potentials have different curvatures (w_1, w_2, and w_3 finite).

In the case of a critical point of the minimum type (w_1, w_2, and w_3 positive), the combined density of states can be written as

$$\begin{aligned} J_{if}(\omega)&=\beta A f_c(D,u_1,u_2,u_3,w_1,w_2,w_3)\\ &=\beta A\frac{Z_3^{1/2}}{\pi^{1/2}(w_1w_2w_3)^{1/2}}\exp(-\lambda_3-Z_3\tau_+)\\ &\quad\times\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{(-1)^{(m+n)}r^m s^n}{2^{n+m}m!n!}\sum_{k=0}^{m}\\ &\quad(-1)^k 2^{m-k}\binom{k}{m}\Big\{I_m(r)I_n(s)N[\rho,\gamma,2(n+m\\ &\quad+k)]+2\sum_{l=1}^{\infty}\cos(2l\arcsin t)I_{m+l}(r)I_{n+2l}(s)\\ &\quad\times\sum_{p=0}^{2l}(-1)^p\binom{p}{2l}N(\rho,\gamma,2(n+m+k+p))\Big\}, \end{aligned} \tag{18}$$

where

$$r=Z_3\tau_-,\quad s=Z_3^{1/2}\xi,\quad \rho=Z_3^{1/2}u_3/w_3^{3/2},$$

$$\gamma=Z_3(1/w_3-\tau_+),$$

with Z_3 the frequency detuning renormalized by the electron-vibrational interaction, the quantities t, $\tau_\pm$, ξ, and λ_3 defined by Eqs. (6) and (9), and the expression for the function $N(\rho,\gamma,2m)$ given in the Appendix. If the difference of the adiabatic potentials of the final and initial electronic states is an ellipsoid of revolution ($w_1=w_2=w$), we have

$$\begin{aligned} J_{if}(\omega)&=\beta A f_{er}(D,u_1,u_2,u_3,w,w,w_3)\\ &=\beta A\frac{Z_3^{1/2}}{\pi^{1/2}w(w_3)^{1/2}}\exp\left(-\lambda_3-\frac{Z_3}{w}\right)\\ &\quad\times\sum_{n=0}^{\infty}\frac{s^n}{2^n n!}I_n(s)N(\rho,\gamma,2n). \end{aligned} \tag{19}$$

The analytical expression for $J_{if}(\omega)$ in the case where the difference of the adiabatic potentials constitutes a sphere ($w_1=w_2=w_3=w$) is not given here. If necessary, it can easily be obtained from Eq. (19) by putting $w_3=w$.

The explicit form of the combined density of states $J_{if}(\omega)$ when there is a critical point of the minimum type (w_1, w_2, and w_3 negative) is determined from Eqs. (18) and (19) in which $|w_n|$ must be substituted for w_n and $D'=-D$ for D.

Equations (18) and (19) show that the shift of the adiabatic potential of the final electronic state does not change the threshold nature of the spectral dependence of $J_{ij}(\omega)$. However, the renormalization of the frequency detuning leads to a situation in which for Z_3 small the combined density of states is proportional to $Z_3^{1/2}$ and not to $D^{1/2}$, as it was earlier.

In the case of saddle critical points the combined density of states can be represented only in integral form. For instance, for a saddle point of the first type (w_1 and w_2 positive and w_3 negative) we have

$$\begin{aligned} J_{if}(\omega)&=\beta A f_{sp}^{-1}(D,u_1,u_2,u_3,w_1,w_2,w_3)\\ &=\beta A\frac{\exp(-\lambda_3+Z_3'/|w_3|)}{\pi^{1/2}(w_1w_2|w_3|)}\int_\eta^\infty dx\\ &\quad\times\exp\left\{-x\left(\frac{1}{|w_3|}+\tau_+\right)\right\}\cosh\left(\frac{u_3}{|w_3|^{3/2}}(x\right.\\ &\quad\left.-Z_2')^{1/2}\right)\sum_{n=-\infty}^{\infty}\cos(2n\arcsin t)\\ &\quad\times I_n(x\tau_-)I_{2n}(x^{1/2}\xi), \end{aligned} \tag{20}$$

where

$$\eta=\begin{cases}0 & \text{if } Z_3'\leqslant 0,\\ Z_3' & \text{if } Z_3'>0, \quad Z_3'=D+0.25\left(\dfrac{u_1^2}{w_1}+\dfrac{u_2^2}{w_2}-\dfrac{u_3^2}{|w_3|}\right).\end{cases}$$

A characteristic feature of the given situation is the absence of frequency thresholds and the renormalization of the frequency detuning Z_3'. There also remains the discontinuity in the first derivative of $J_{if}(\omega)$. However, $Z_3'=0$ is a singular point. An analytical expression for the combined density of states $J_{if}(\omega)$ in the presence of a saddle point of the second type (w_1 and w_2 negative and w_3 positive) can be obtained from Eq. (20) by replacing w_1 with $|w_1|$, w_2 with $|w_2|$, $|w_3|$ with w_3, and D with $D'=-D$.

4. CONCLUSION

In Sec. 4 we established the analytical expressions for the combined density of states $J_{ij}(\omega)$ that determine the absorption and luminescence line shapes of molecules and of intrinsic and impurity defects of crystals in the case of electron- vibrational interaction with one, two, and three vibrational modes. Theoretically similar results can be obtained for physical systems of higher dimensionality. For one thing, if the curvatures of the adiabatic potentials of the initial and final electronic states coincide ($w_n=0$) and the potentials are only shifted in relation to each other (a_n finite), the combined density of states $J_{if}(\omega)$ for an arbitrary dimensionality n is described by Eq. (3) in which $u=(\Sigma_{m=1}^{n}u_m^2)^{1/2}$. However, a detailed analysis of such situations is of less interest than that of the cases discussed in this paper. There are two reasons for this. First, if the curvature of the adiabatic potential of the final electronic state differs from that of the initial state, the analytical expressions for $J_{ij}(\omega)$ become grossly complicated as the number of vibrational modes taken into account grows. Second, and this is more essential, the spectral features of the combined density of states $J_{ij}(\omega)$ become less pronounced as the dimensionality of the problem grows. Indeed, as demonstrated above, in the presence of critical points, $J_{if}(\omega)$ has a singularity of the $1/D^{-1/2}$ type in the one-dimensional case, a logarithmic singularity in the two-dimensional case, and only a discontinuity in its first derivative in the three- dimensional case. As the dimensionality grows, the spectral singularities become discontinuities in higher-order derivatives. Their discovery is aggravated by serious experimental difficulties and requires special spectroscopic methods, such as the modulation spectroscopy technique.[12]

To sum up:

(a) We have established that the form of the combined density of states $J_{if}(\omega)$ and, hence, the absorption and luminescence spectra strongly depend on the number of vibrational modes involved in the electron-vibrational coupling in the final electronic state and on the type of critical point of the difference of adiabatic potentials.

(b) We have obtained in the quasiclassical approximation the analytical expressions for the spectral dependence of the combined density of states $J_{ij}(\omega)$. The cases of electron-vibrational coupling in the finite electronic state with one, two, and three vibrational modes have been examined, as well as all possible (for such cases) types of critical points of the adiabatic-potential difference. We have demonstrated that when there are critical points of the maximum or minimum type, the spectral dependence of $J_{if}(\omega)$ is of a threshold nature. But if the critical point is of a saddle-point type, there is no threshold.

(c) We have established that the combined densities of states $J_{ij}(\omega)$ are essentially temperature- dependent. Within the adopted approximations, their nontrivial temperature dependence is determined by the universal functions f introduced in the paper. Graphical representations of the universal functions for a number of characteristic situations are given for purposes of illustration.

(d) We have analyzed the combined densities of state $J_{if}(\omega)$ for the case where the critical points of the adiabatic potential of the final electronic state are shifted in relation to those of the initial state. The most important result of this shift is found to be the renormalization of the frequency detuning from the point of electron resonance. This leads to a shift in the spectral features of $J_{ij}(\omega)$, but their shape remains unchanged. For one thing, if the difference of the adiabatic potentials possesses a critical point of the minimum type, there is a shift toward the long-wave part of spectrum, and if the critical point is of the maximum type, the shift is toward the short-wave part.

In addition to such obvious systems as molecules consisting of a moderate number of atoms, the results of this paper can be applied to intrinsic and impurity defects of crystals. Although the vibrational subsystem of a crystal is essentially multimode (phonon dispersion), it can be described in some cases by a small number of effective vibrational modes using the methods reviewed in Ref. 13. There is also a class of what is known as molecular defects, whose electron-vibrational coupling with the local vibrations generated by these very defects is predominant. These defects can usually be described in terms of quasimolecular models and, hence, the above results are applicable.

This paper discusses only orbitally nondegenerate electronic states. More interesting, however, is the study of the effect of critical points of the adiabatic potentials on the optical spectra in a situation with the Jahn–Teller effect.[14] Also, in order to be able to compare the theoretical results and the experimental data within a broad range of values of the physical parameters, the quasiclassical approximation must be dropped. Work in this direction is currently being done.

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5. APPENDIX

The function $N(\rho,\gamma,2m)$ can be expressed in terms of the error function $\mathrm{erf}(x)$ (see Ref. 11), and for $\gamma\neq 0$ assumes the form

$$N(\rho,\gamma,2m)=0.5\exp\left(\frac{\rho^2}{4\gamma}\right)\left\{\sum_{n=0}^{m}\binom{2n}{2m}\left(\frac{\rho}{2\gamma}\right)^{2(m-n)}\gamma^{-n-1/2}(2n-1)!!\left(\frac{\pi^{1/2}}{2^n}[\mathrm{erf}(g_+)+\mathrm{erf}(g_-)]\right.\right.$$

$$\left.+\sum_{k=0}^{n-1}\frac{g_+{}^{2(n-k)-1}\exp(-g_+^2)+g_-^{2(n-k)-1}\exp(-g_-^2)}{2^k(2n-2k-1)!!}\right)+\sum_{n=0}^{m-1}\binom{2n+1}{2m}$$

$$\left.\times\left(\frac{\rho}{2\gamma}\right)^{2(m-n)-1}\gamma^{-n-1}n!\sum_{k=0}^{n}\frac{g_+^{2(n-k)}\exp(-g_+^2)+g_-^{2(n-k)}\exp(-g_-^2)}{(n-k)!}\right\},$$

where $g_\pm=\gamma^{1/2}\pm\rho/2\gamma^{1/2}$. At $\gamma=0$ we have

$$N(\rho,0,2m)=\frac{2}{\rho}\sinh(\rho)+\sum_{k=1}^{2m}\frac{2m(2m-1)\dots(2m-k+1)}{\rho^m}$$

$$\times[(-1)^n\exp(\rho)-\exp(-\rho)].$$

1)By definition, a critical point is one at which the gradient of a function, $\mathrm{grad}_x\mathbf{f}(\mathbf{x})$, vanishes.

2)The directions of the principal axes of the adiabatic potentials in both states are assumed to be the same.

3)The vibrational frequencies in the initial and final electronic states are different.

4)The difference of the adiabatic potentials of the initial and final electronic states constitutes an ellipse.

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