Markov approximation for Green's functions of molecular subsystems in the condensed phase

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A general relation is found in the Markov approximation for the retarded Green's function of a subsystem interacting with a reservoir in thermodynamic equilibrium; we use it to describe spectra of anharmonically coupled high-frequency valence and resonant deformation vibrations of molecular subsystems in the condensed phase. The theory takes into account the degeneracy of the libration resonant modes which are characteristic for molecular complexes with hydrogen bonds and the presence of thermally activated reorientations of surface groups of atoms. We develop a perturbation theory for the Pauli equation and use it to calculate second-order corrections to the rate at which subsystems leave a given group of states. The results obtained agree with the observed spectra of actual molecular subsystems.

1. INTRODUCTION

Practically any experimental study of an arbitrary system reduces to measuring the response of some physical characteristic A of the system to a probing external action corresponding in the general case to some other characteristic B. The required response is then described by a retarded Green's function (GF) which is convenient for the calculations and which contains sufficiently complete information about the states of the system:

$$\begin{gathered} G(t)=-i\theta(t)\langle[\hat{A}(t),\hat{B}(0)]\rangle, \\ \hat{A}(t)=\exp\left(\frac{i}{\hbar}\hat{H}t\right)\hat{A}\exp\left(-\frac{i}{\hbar}\hat{H}t\right), \\ \langle\ldots\rangle=\mathrm{Sp}(\hat{\rho}\ldots),\qquad \hat{\rho}=\exp(-\hat{H}/T)/\mathrm{Sp}[\exp(-\hat{H}/T)], \end{gathered} \tag{1}$$

where $\hat{A}$ and $\hat{B}$ are the operators of the physical quantities A and B and $\hat{\rho}$ is the equilibrium statistical operator of the system determined by its Hamiltonian $\hat{H}$ and the absolute temperature T (in energy units). In many cases one is interested in the properties of a subsystem with a Hamiltonian $\hat{H}_S$ which is coupled with the remaining large part (reservoir) of the total system, described by the Hamiltonian $\hat{H}_R$, through an interaction $\hat{V}$. We have then

$$\hat{H}=\hat{H}_S+\hat{H}_R+\hat{V}, \tag{2}$$

and the operators $\hat{A}$ and $\hat{B}$ occur only in the Hamiltonian $\hat{H}_S$. This fact by itself does not lead to any simplification of Eq. (1) since the operator $\hat{V}$ containing the variables of the subsystem and of the reservoir does not commute with $\hat{H}_S$ or $\hat{H}_R$.

On the other hand, there exist well developed methods for calculating states of subsystems using the Markov approximation for the reduced density matrix (statistical operator) of the subsystem $\hat{\rho}_S = \mathrm{Tr}\,\hat{\rho}$ (Tr indicates the trace over the variables of the reservoir).[2] The average value of a physical quantity $A(t)$ now will be determined by the trace of the product of operators of the subsystem only:

$$A(t)=\mathrm{Sp}(\hat{\rho}_S(t)\hat{A}), \tag{3}$$

and the response to an external action described by a time-dependent operator $\hat{H}_B(t)$ will be included in the operator $\hat{\rho}_S(t)$ satisfying the equation

$$\begin{gathered} \frac{\partial}{\partial t}\hat{\rho}_S(t)+\frac{i}{\hbar}[\hat{H}_S+\langle\hat{V}\rangle_R+\hat{H}_B(t),\hat{\rho}_S(t)] \\ =-\frac{1}{\hbar^2}\int_{-\infty}^{0}d\tau\,\mathrm{Tr}\left[\Delta\hat{V},\left[\exp\left[\frac{i}{\hbar}(\hat{H}_S+\hat{H}_R)\tau\right]\right.\right. \\ \left.\left.\times\Delta\hat{V}\exp\left[-\frac{i}{\hbar}(\hat{H}_S+\hat{H}_R)\tau\right],\hat{\rho}_S(t)\hat{\rho}_R\right]\right], \\ \Delta\hat{V}=\hat{V}-\langle\hat{V}\rangle_R,\qquad \langle\hat{V}\rangle_R=\mathrm{Tr}(\hat{\rho}_R\hat{V}), \end{gathered} \tag{4}$$

where $\hat{\rho}_R$ is the equilibrium reservoir operator (the expression with a nonvanishing operator $\langle\hat{V}\rangle_R$ is derived in detail in Ref. 3).

In the present paper we obtain a Markov approximation for the GF (1) which is expressed in terms of the GF of the differential Eq. (4). The latter turns out to be extraordinarily convenient for analyzing the spectral characteristics of molecular subsystems in the condensed phase and enables us to study relaxation processes in systems with a finite number of states of a given kind. We discuss in detail the range of applications of the proposed approach.

At the present time there are a number of experimental examples of a strong temperature dependence of the line shape of high-frequency local oscillations of different molecular subsystems in the condensed phase. Among them we have the valence vibrations of the OH groups on a silica surface,[4] CO groups absorbed on the (111) surface of Pt (Ref. 5) and of Ni,[6] hydrogen on the (100) surface of Si,[7] and also molecular complexes with a hydrogen bond[8,9] (see also the surveys in Refs. 10 and 11). The frequencies ω_r of these oscillations are much higher than the Debye frequency ω_D so that the observed temperature dependences are explained by dephasing of the local oscillation by low-frequency random reorientations of the molecules[11,12] or low-frequency torsional deformation oscillations.[10,13–15] In the first case this coupling appears due to orientational factors in the correlator of the dipole moments and in the second case through the occurrence in the Hamiltonian of an anharmonic coupling of the modes considered (exchange dephasing model[16,17]). The low-frequency molecular modes in that case interact resonantly with the phonons of the reservoir of the condensed phase.

The use of the Markov approximation in the framework

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of the exchange dephasing model made it possible in Refs. 18 and 19 to obtain analytical expressions for the spectral line shape of the valence oscillations. However, comparison with experimental data showed that for a quantitative description of the observed dependences one must overestimate by an order of magnitude the value of the coefficient of the anharmonic coupling between the valence and the torsional oscillations.[13] Since this coefficient is the only anharmonic parameter of the exchange model its overestimated value indicates the need to include other sources of anharmonicity in the systems discussed.

The torsional oscillations are strongly anharmonic; they are characterized by well defined values of the energy barriers ΔU separating equivalent (with a rotation angle $\varphi = 2\pi$) or nonequivalent (with $\varphi = 2\pi/l$, $l = 2,3,\ldots$) equilibrium orientations of the molecules in the condensed phase. One can talk about torsional oscillations only for sufficiently low values of the energy $\varepsilon < \Delta U$, whereas for $\varepsilon \gtrsim \Delta U$ stochastic reorientation processes dominate which lead to a broadening of the spectral lines by the magnitude of the average reorientation frequency.[20] The simplest way to take into account the anharmonicity of the torsional oscillations thus consists in considering a limited number of orientational states (with $\varepsilon < \Delta U$), which leads to the observed Arrhenius-type temperature dependence of the line width in the factor $\exp(-\Delta U/T)$. The pre-exponential factor depends on the relations between the parameters of the problem which were established in the classical considerations of Ref. 21.

The problems discussed here are closely connected with the problem of calculating the rate at which a particle leaves a potential well, which determine the speeds at which chemical reactions proceed. The most consistent description of low-temperature chemical reactions taking tunnelling and dissipation processes into account was given in Ref. 22. We shall be interested only in the thermally activated contribution which dominates for many systems at not too low temperatures.

We list the main results established in the present paper. The general expression obtained in Sec. 2 for the GF in the Markov approximation is made specific for the cases of resonant oscillations and for local high-frequency oscillations which are anharmonically coupled with the phonons of the reservoir through several low-temperature exchange modes (Sec. 3). Since the GF of resonant oscillations caused by the anharmonic coupling of a given mode with the quasi-continuous spectrum of the reservoir modes can be represented in an exact analytical form its comparison with the results of the Markov approximation enables us to judge the domain of applicability of the latter and to justify a number of simplifications which are used in the exchange model when one considers local low-frequency oscillations. In contrast to the results of Refs. 18 and 19 we take into account in Sec. 3 several noninteracting exchange modes. When they are degenerate the expressions for the line shape simplify and give a simple formula describing a strong one-sided temperature broadening of the spectral bands of the molecular complexes with a hydrogen bond in the condensed phase.

We show in Sec. 4 that the problem of determining the line shape of a molecular valence oscillation which is anharmonically coupled with resonant deformation oscillations, described by a subbarrier transition in the potential of a hindered rotation, reduces to the solution of the Pauli equation with perturbed transition rates. The latter are the sum of two contributions arising due to the anharmonic coupling with the deformation mode and transitions from the subbarrier into superbarrier states.

A perturbation theory for the Pauli equation is developed in Sec. 5. The results of this section are equations for the position of the maximum and the spectral line width which take into account a finite number of subbarrier deformation states and therefore simultaneously describe not only exchange dephasing, but also thermally activated reorientation broadening mechanisms. The second order of perturbation theory made it possible to generalize and make more precise the well known expressions for the rate of thermally activated departure of a particle from a potential well for the classical[21] and low-temperature[23] limits and also for the case of a single subbarrier level.[12] In Sec. 6 we discuss how these relations apply to actual experimental systems and the prospects for using the approach developed here to solve other problems.

2. MARKOV APPROXIMATION FOR THE GREEN'S FUNCTIONS

We find the linear response of a subsystem in contact with a reservoir to an external perturbation corresponding to some variable $\hat{B}$ of the subsystem and depending on the time through a function $F(t)$, so that the corresponding perturbation operator can be written in the form

$$\hat{H}_B(t) = -\hat{B}F(t). \tag{5}$$

We substitute (5) into Eq. (4) and we shall look for a solution of the latter in the form

$$\hat{\rho}_S(t) = \hat{\rho}_0 + \delta\hat{\rho}(t),$$

where $\hat{\rho}_0$ is the equilibrium statistical operator of the subsystem. The matrix elements of the linear response $\delta\hat{\rho}(t)$ in the basis of the eigenstates of the Hamiltonian $\hat{H}_S$ ($\delta\rho_{qq'}(t) = \langle q|\delta\hat{\rho}(t)|q'\rangle$, $\hat{H}_S|q\rangle = \varepsilon_q|q\rangle$) to the perturbation $\hat{H}_B(t)$ will satisfy the following equation:

$$\frac{\partial}{\partial t}\delta\rho_{qq'}(t) + \sum_{\tilde{q}\tilde{q}'}\delta\rho_{\tilde{q}\tilde{q}'}(t)\,(i\Omega_{\tilde{q}\tilde{q}'qq'} + \Gamma_{\tilde{q}\tilde{q}'qq'}) = \frac{i}{\hbar}B_{qq'}(\rho_{q'} - \rho_q)\,F(t). \tag{6}$$

Here ρ_q is the diagonal matrix element of the equilibrium statistical operator $\hat{\rho}_0$ of the subsystem and the matrices Ω and Γ with four indices are given as follows (see, e.g., Ref. 3 where these quantities are obtained taking into account a nonvanishing operator $\langle\hat{V}\rangle_R$ and nonvanishing frequency shifts arising from principal-value integrals which are usually neglected in other sources):

$$\begin{aligned}\Omega_{\tilde{q}\tilde{q}'qq'} &= \Omega_{qq'}\delta_{\tilde{q}q}\delta_{\tilde{q}'q'} - \frac{1}{\hbar}\left(\langle\hat{V}\rangle_{\tilde{q}'q'}\delta_{\tilde{q}q} - \langle\hat{V}\rangle_{q\tilde{q}}\delta_{\tilde{q}'q'}\right)\\ &- \frac{1}{2\pi\hbar^2}\int_{-\infty}^{\infty}d\omega\left\{\sum_r\left[\frac{F_{qrr\tilde{q}}(\omega)}{\Omega_{r\tilde{q}} + \omega}\delta_{\tilde{q}'q'} + \frac{F_{\tilde{q}rrq'}(\omega)}{\Omega_{\tilde{q}'r} - \omega}\delta_{\tilde{q}q}\right]\right.\\ &\left.- \frac{F_{\tilde{q}'q'q\tilde{q}}(\omega)}{\Omega_{q\tilde{q}} + \omega} - \frac{F_{\tilde{q}'q'q\tilde{q}}(\omega)}{\Omega_{\tilde{q}'q'} - \omega}\right\},\\ \Gamma_{\tilde{q}\tilde{q}'qq'} &= \frac{1}{2\hbar^2}\left\{\sum_r\left[F_{qrr\tilde{q}}(\Omega_{\tilde{q}r})\,\delta_{\tilde{q}'q'} + F_{\tilde{q}'rrq'}(\Omega_{q'r})\,\delta_{\tilde{q}q}\right]\right.\\ &\left.- F_{\tilde{q}'q'q\tilde{q}}(\Omega_{\tilde{q}q}) - F_{\tilde{q}'q'q\tilde{q}}(\Omega_{\tilde{q}'q'})\right\},\end{aligned} \tag{7}$$

$$F_{\tilde{q}\tilde{q}'qq'}(\omega)=\int_{-\infty}^{\infty} d\tau e^{i\omega\tau}\langle\Delta\hat{V}_{\tilde{q}\tilde{q}'}(\tau)\,\Delta\hat{V}_{qq'}\rangle_R,$$

$$\Delta\hat{V}_{qq'}(\tau)=\exp\left(\frac{i}{\hbar}\hat{H}_R\tau\right)\Delta\hat{V}_{qq'}\exp\left(-\frac{i}{\hbar}\hat{H}_R\tau\right),$$

$$\Omega_{qq'}=\frac{1}{\hbar}(\varepsilon_q-\varepsilon_{q'}).$$

We introduce the GF, with four indices, of the left-hand side of Eq. (6):

$$\frac{\partial}{\partial t}g_{qq'\tilde{q}\tilde{q}'}(t)+\sum_{q_1q_2}g_{q_1q_2\tilde{q}\tilde{q}'}(t)\,(i\Omega_{q_1q_2qq'}+\Gamma_{q_1q_2qq'})=-\delta(t)\,\delta_{\tilde{q}q}\delta_{q'\tilde{q}'},\tag{8}$$

in terms of which one can easily express the linear response $\delta\rho_{qq'}(t)$:

$$\delta\rho_{qq'}(t)=-\frac{i}{\hbar}\sum_{\tilde{q}\tilde{q}'}\int_{-\infty}^{\infty}dt'g_{qq'\tilde{q}\tilde{q}'}(t-t')\,B_{\tilde{q}\tilde{q}'}(\rho_{\tilde{q}'}-\rho_{\tilde{q}})\,F(t').\tag{9}$$

Substituting (9) into (3) we are led to the usual way of writing down the time-dependent average value of a physical quantity $A(t)$ as the linear response to the perturbation (5):[1]

$$A(t)=\mathrm{Sp}(\hat{\rho}_0\hat{A})-\frac{1}{\hbar}\int_{-\infty}^{\infty}dt'G(t-t')F(t'),\tag{10}$$

in which the required GF (1) is determined by the following expression:

$$G(t)=i\sum_{qq'\tilde{q}\tilde{q}'}A_{q'q}g_{qq'\tilde{q}\tilde{q}'}(t)\,B_{\tilde{q}\tilde{q}'}(\rho_{\tilde{q}'}-\rho_{\tilde{q}}).\tag{11}$$

Together with Eqs. (7) and (8), Eq. (11) solves the given problem of finding the GF of a subsystem in the Markov approximation.

3. RESONANT AND HIGH-FREQUENCY LOCAL OSCILLATIONS

To begin with we consider the model of resonant oscillations which allows an exact analytical solution, which we shall compare with the result (11) of the Markov approximation. Assume that some mode with frequency ω_S (which we shall relate to the subsystem S) is harmonically coupled with the phonons of the reservoir ω_k:

$$\hat{H}_S=\hbar\omega_S(b_S^+b_S+{}^1/_2),\quad \hat{H}_R=\sum_k\hbar\omega_k(b_k^+b_k+{}^1/_2),$$
$$\hat{V}=\hbar\sum_k(\chi_kb_S^+b_k+\chi_k^*b_Sb_k^+)\tag{12}$$

(here χ_k describes interaction of the modes S and k). The contributions of (12) to the Hamiltonian (2) of the system is a quadratic form of the second quantization bose operators b_S, b_S^+, b_k, b_k^+ which can easily be diagonalized by means of a unitary transformation:

$$b_l=\sum_\nu C_{l\nu}\beta_\nu,\quad b_l^+=\sum_\nu C_{l\nu}^*\beta_\nu^+,\quad l=S,k,$$
$$\sum_k\chi_kC_{k\nu}=(\omega_\nu-\omega_S)C_{S\nu},\quad \chi_k^*C_{S\nu}=(\omega_\nu-\omega_k)C_{k\nu},\tag{13}$$

so that

$$\hat{H}=\sum_\nu\hbar\omega_\nu(\beta_\nu^+\beta_\nu+{}^1/_2).\tag{14}$$

If we choose the b_S and b_S^+ operators for the operators $\hat{A}$ and $\hat{B}$ which occur in the general definition (1) of the GF, the exact expression for the latter takes the form

$$G(t)=-i\theta(t)\sum_\nu|C_{S\nu}|^2\langle[\beta_\nu(t),\beta_\nu^+(0)]\rangle$$
$$=-i\theta(t)\sum_\nu|C_{S\nu}|^2\exp(-i\omega_\nu t).\tag{15}$$

Assuming the phonon spectrum of the reservoir to be quasicontinuous (with the frequency gaps between the levels going to zero, $\Delta\omega_\nu\to0$) and using the idea developed in Ref. 24 for describing such spectra, one can easily show that the absolute values of the squares $|C_{S\nu}|^2$ of the coefficients of the unitary transformation which we need to have a resonance form:

$$|C_{S\nu}|^2=\tilde{\eta}(\omega_\nu)\Delta\omega_\nu\{[\omega_\nu-\omega_S-\tilde{P}(\omega_\nu)]^2+\pi^2\tilde{\eta}^2(\omega_\nu)\}^{-1},\tag{16}$$

where

$$\tilde{\eta}(\omega_\nu)=\sum_k|\chi_k|^2\delta(\omega_\nu-\omega_k),\quad \tilde{P}(\omega_\nu)=\int_{-\infty}^{\infty}\frac{\tilde{\eta}(\omega)d\omega}{\omega_\nu-\omega}.\tag{17}$$

Substituting (16) into (15) and the $\Delta\omega_\nu\to0$ limit replacing the integral sum by an integral, we are led to an exact expression for the GF of the resonant oscillations:

$$G(t)=-i\theta(t)\int_{-\infty}^{\infty}\frac{\tilde{\eta}(\omega)e^{-i\omega t}d\omega}{[\omega-\omega_S-\tilde{P}(\omega)]^2+\pi^2\tilde{\eta}^2(\omega)}.\tag{18}$$

In connection with the derivation of Eq. (18) given here it is interesting to note that the Lorentz resonance form of Eq. (16), necessary to describe dissipative processes on the basis of reversible dynamic equations,[25] arises in a very natural way from the definitions formulated in Ref. 24 of the quasicontinuous spectrum of the reservoir.

We now obtain the GF of the Markov approximation, using Eqs. (7), (8), and (11). For the Hamiltonian (2), (12) of the system we have

$$\Omega_{\tilde{q}\tilde{q}'qq'}=\delta_{\tilde{q}q}\delta_{\tilde{q}'q'}(q-q')[\omega_S+\tilde{P}(\omega_S)],$$
$$\Gamma_{\tilde{q}\tilde{q}'qq'}=2\pi\tilde{\eta}(\omega_S)\{(n_S+1)[{}^1/_2(q+q')\delta_{\tilde{q}q}\delta_{\tilde{q}'q'}-(\tilde{q}\tilde{q}')^{1/2}\delta_{q,\tilde{q}-1}\delta_{q',\tilde{q}'-1}]+n_S[{}^1/_2(q+q'+2)\delta_{\tilde{q}q}\delta_{\tilde{q}'q'}-(qq')^{1/2}\delta_{q,\tilde{q}+1}\delta_{q',\tilde{q}'+1}]\},\tag{19}$$
$$n_S=[\exp(\hbar\omega_S/T)-1]^{-1}.$$

Substituting (19) into Eq. (8) and summing it over the indices q and q' we find the equation

$$\frac{\partial}{\partial t}p_{\tilde{q}}(t)+i[\omega_S+\tilde{P}(\omega_S)]\,p_{\tilde{q}}(t)+\pi\tilde{\eta}(\omega_S)\,p_{\tilde{q}}(t)=-\delta(t)\,\tilde{q}^{1/2}\tag{20}$$

for

$$p_{\tilde{q}}(t)=\sum_{q=0}^{\infty}q^{1/2}g_{q,\,q-1,\,\tilde{q},\,\tilde{q}-1}(t),\tag{21}$$

according to (11) we can express the required GF in terms of this quantity:

$$G(t)=i\sum_{\tilde q}\tilde q^{1/2}p_{\tilde q}(t)(\rho_{\tilde q-1}-\rho_{\tilde q}). \tag{22}$$

Solving Eq. (20) and subsequently summing over $\tilde q$ is elementary and gives the following result of the Markov approximation:

$$G(t)=-i\theta(t)\exp\{-i[\omega_S+\tilde P(\omega_S)]t-\pi\tilde\eta(\omega_S)t\}. \tag{23}$$

A comparison (23) with the exact Eq. (18) shows that the Markov approximation is valid for slowly changing $\tilde\eta(\omega)$ and $\tilde P(\omega)$ in the vicinity of $\omega=\omega_S$ for $\tilde\eta(\omega_S)\ll\omega_S$. The value of the integral in (18) will then be approximately determined by the pole

$$\omega\approx\omega_S+\tilde P(\omega_S)+i\pi\tilde\eta(\omega_S)$$

of the integrand, which leads to Eq. (23).

The formulated restrictions on the functions $\tilde P(\omega)$ and $\tilde\eta(\omega)$ are important for an understanding of a number of approximations which have been made in the exchange dephasing model[16,17] when finding the spectral line shape for a high-frequency local oscillation.[18,19] The Hamiltonian of this model with a high-frequency mode ω_a and a single low-frequency exchange mode ω_S is given by Eq. (2) in which $\hat H_R$ and $\hat V$ are given by Eqs. (12) while $\hat H_S$ has the following form:

$$\hat H_S=\hbar\omega_a(a^+a+{}^1/_2)+\hbar\omega_S(b^+b+{}^1/_2)+\hbar\gamma a^+ab^+b, \tag{24}$$

where a and a^+ are the second quantization operators of the mode a. The high-frequency mode is coupled through the anharmonicity coefficient γ with the resonant oscillations having frequency ω_S [or, more strictly, having the renormalized frequency $\omega_S+\tilde P(\omega_S)$]. The required GF of the high-frequency mode is in the Markov approximation obtained from the general Eq. (11) for $\hat A=a$, $\hat B=a^+$ and the GF $g_{qq'\tilde q\tilde q'}$ with $q=\{n_a,n_b\}$ $(a^+a|n_a\rangle=n_a|n_a\rangle$, $b^+b|n_b\rangle=n_b|n_b\rangle)$:

$$G(t)=i\sum_{n_bn_b'}g_{n_bn_b'}(t)\rho_{n_b'},\qquad g_{n_bn_b'}(t)=g_{1n_b,\,0n_b,\,1n_b',\,0n_b'}(t). \tag{25}$$

In this formula we have used the inequality $\hbar\omega_a\gg T$, thanks to which it is sufficient to consider states with $n_a=0$ and 1, and also to put $\rho_{1n_b}=0$ (the quantity ρ_{0n_b} is denoted by ρ_{n_b}). Equation (8) for $g_{n_bn_b'}(t)$ contains the matrix element with four indices $\Gamma_{\tilde q\tilde q'qq'}$ of the collision integral, which has the structure of the corresponding expression in (19) with $q=q'=n_b$, $\tilde q=\tilde q'=n_b'$, and with the difference that due to the last term in (24) the quantities $\tilde\eta(\omega_S)$ and n_S depend on the frequency ω_S to within a term proportional to γ. Since we have assumed the function $\tilde\eta(\omega)$ to be slowly changing in the vicinity of the point $\omega=\omega_S$, for $\gamma\ll\omega_S$ we can neglect this difference.

In the Markov approximation for $\tilde\eta(\omega_S)$ and $\gamma\ll\omega_S$ the GF $g_{n_bn_b'}(t)$ will therefore satisfy the equation

$$\frac{\partial}{\partial t}g_{n_bn_b'}(t)+\{i(\omega_a+\gamma n_b)+[n_b+(n_b+1)\xi]w_0\}g_{n_bn_b'}(t)$$
$$-(n_b+1)w_0g_{n_b+1,\,n_b'}(t)-n_b\xi w_0g_{n_b-1,\,n_b'}(t)=-\delta(t)\delta_{n_bn_b'}, \tag{26}$$
$$w_0=2\pi\tilde\eta(\omega_S)/(1-\xi),\quad \xi=\exp(-\hbar\omega_S/T).$$

The structure of the left-hand side of Eq. (26) is the same as the homogeneous equation of Ref. 17 for the matrix elements $\rho_{0n_b,1n_b}$ of the reduced density matrix of the subsystem considered. A numerical solution of that equation was given in Ref. 13. Exact analytical expressions for the spectral line shape of a high-frequency local oscillation were obtained in terms of this model by generating-function[18] and temperature-GF[19] methods. Using the approach of Ref. 18 one can easily obtain an analytical expression for the GF (25) in the case of several low-frequency exchange modes ω_j $(j=1,2,\ldots,l)$ which do not interact with one another either directly or through the reservoir:

$$G(t)=-i\theta(t)\exp(-i\omega_at)\prod_{j=1}^{l}\frac{(1-\tilde\xi_j)\exp(-i\lambda_jt)}{1-\tilde\xi_j\exp(-i\nu_jt)}. \tag{27}$$

Here we have

$$\tilde\xi=\left(\frac{1-\mu}{1-\xi\mu}\right)^2\xi,\quad \lambda=-\frac{i\xi\eta}{1-\xi}(1-\mu),\quad \nu=-\frac{i\eta(1-\xi\mu^2)}{(1-\xi)\mu},$$
$$\mu=\frac{1-\xi}{2\xi}\left[\frac{1+\xi}{1-\xi}+i\frac{\gamma}{\eta}-\left(1+2i\frac{1+\xi}{1-\xi}\frac{\gamma}{\eta}-\frac{\gamma^2}{\eta^2}\right)^{1/2}\right], \tag{28}$$
$$\eta=2\pi\tilde\eta(\omega_S)$$

and to simplify the notation we have omitted the index j of the quantities ξ, γ, η, μ, $\tilde\xi$, λ, and ν.

One can simplify Eq. (27) in the case, important in practice, of l degenerate exchange modes which is realized, for instance, for molecular complexes with hydrogen bonds. For the high-frequency mode ω_a one can use the valence or deformation oscillation of a hydrogen atom which is anharmonically coupled with four $(l=4)$ degenerate libration modes, the low frequencies of which are caused by the relatively weak interactions of the hydrogen bond of two molecular fragments (Fig. 1). The spectral function of the high-frequency oscillation near ω_a for the l degenerate exchange modes, after we have expanded the denominator in (27) in a series and integrated over the time, takes the form

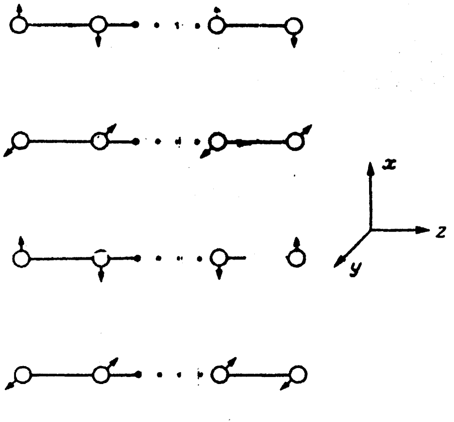

FIG. 1. Low-frequency modes of librational oscillations of a molecular complex with a hydrogen bond.

$$S(\omega)=-\frac{1}{\pi}\operatorname{Im}G(\omega),$$

$$G(\omega)=\frac{(1-\tilde{\xi})^{l}}{(l-1)!}\sum_{n=0}^{\infty}\frac{(n+l-1)!}{n!}\,\frac{\tilde{\xi}^{n}}{\omega-\omega_a-l\lambda-n\nu}. \qquad (29)$$

For $l=1$ the expression obtained reduces to the results obtained in Refs. 18 and 19 and in the high-temperature limit ($T\gg\hbar\omega_j$) and for $\eta\ll\gamma$ gives a simple formula[11,26] for the strong single-sided temperature broadening of the spectral lines of complexes with hydrogen bonds:

$$S(\omega)=\frac{\hbar\omega_j}{(l-1)!\,|\gamma|\,T}\,\theta(z)z^{l-1}e^{-z},\quad z=\frac{\hbar\omega_i}{\gamma T}(\omega-\omega_a). \qquad (30)$$

The exact Eq. (29) takes into account the effect of the reservoir (the condensed phase) on the spectral line shape through the parameter η. Consideration of an actual microscopic model of the valence-deformation oscillations makes it possible to estimate the basic parameters γ and η of the theory and to introduce the anharmonicity of the exchange mode which is connected with the presence of a reoriented barrier of the deformation oscillations and thereby to fully exploit the advantage of the GF representation in the form (11) which allows summation over a finite number of states.

4. VALENCE-DEFORMATION OSCILLATIONS OF MOLECULAR SUBSYSTEMS WITH HYDROGEN BONDS

As a simple model which takes into account valence and deformation oscillations of molecules and which is imbedded in the condensed phase we consider a diatomic molecule with two degrees of freedom corresponding to valence (in the radial variable r) and torsional (in the angular variable φ) oscillations:

$$\begin{gathered}\hat{H}_S\equiv\hat{H}_{r\varphi}=-\frac{\hbar^2}{2m^*}\frac{\partial^2}{\partial r^2}-\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\varphi^2}+U(r,\varphi),\\ U(r,\varphi)\approx{}^1/_2m^*\omega_r^{\,2}(r-r_0)^2+U_{anh}(r)\\ +{}^1/_2\Delta U(r)(1-\cos l\varphi),\quad l=1,\,2,\,\ldots,\end{gathered} \qquad (31)$$

where m is the mass of the atom subject to angular deformations, m^* is the reduced mass of the molecule, r_0 is the equilibrium radial distance, and the approximate expression for the potential $U(r,\varphi)$ describes the valence oscillation of frequency ω_r and the hindered rotation of the molecule in the l th well potential of the surrounding atoms. A reduced Hamiltonian was used in Refs. 3 and 11 for the description of the vibrational states of surface groups of atoms with rotational degrees of freedom and can serve as a microscopic model which takes into account the basic factors that form the spectral line of the high-frequency valence oscillation of a molecule coupled with the low-frequency deformation mode.

The presence of the radial variable r in the operator of the angular kinetic energy and the radial dependence of the reorientation barrier $\Delta U(r)$ guarantees the coupling of the radial and the deformation motions. The largest contribution to the broadening of the spectral line of the valence oscillations with the high frequency $\omega_r>3\omega_D$ (ω_D is the Debye frequency) comes from the fourth-degree anharmonic coupling terms, which are proportional to $(r-r_0)^2\varphi^2$ and which take into account the self-scattering of the local oscillation interacting with the low-frequency modes.[27,28] The third-degree anharmonicity $(r-r_0)\varphi^2$ gives a contribution of comparable order of magnitude to the temperature-dependent shift of the same line (in the expression for the line shift the corresponding anharmonicity coefficients $C_{rr\varphi\varphi}$ and $C_{r\varphi\varphi}$ occur in the combination $C_{rr\varphi\varphi}-C_{r\varphi\varphi}C_{rrr}/m^*\omega_r^2$ and the first and second terms turn out to be of the same order[29]). The conclusion from Ref. 17 which has entered the literature, namely, that the contribution of $(r-r_0)^2\varphi^2$ also dominates in the line shift was based on the simplification that all anharmonicity coefficients are equal to unity. Neglecting (as in Refs. 13 to 19) the anharmonic terms which do not contribute to the spectral line broadening, after changing to the second-quantization operators of the valence oscillations we get the following representation for $\hat{H}_{r\varphi}$:

$$\begin{gathered}\hat{H}_{r\varphi}=\hbar\omega_r(a^+a+{}^1/_2)+\hat{H}_\varphi+\hbar(\omega_\varphi^{\,2}/\omega_r)\varphi^2a^+a,\\ \hat{H}_\varphi=-\frac{\hbar^2}{2mr_0^{\,2}}\frac{\partial^2}{\partial\varphi^2}+\frac{1}{2}\Delta U(r_0)\,(1-\cos l\varphi),\end{gathered} \qquad (32)$$

where $\omega_\varphi\approx l(\Delta U/2mr_0^2)^{1/2}$ is the characteristic frequency of the torsional oscillations.

In Fig. 2 we show schematically the eigenvalues $\varepsilon_{n_a\sigma}$ of the Hamiltonian $\hat{H}_{r\varphi}$ which depend on the radial, n_a, and the deformation, σ, quantum numbers. For $\varepsilon_{0\sigma}\ll\Delta U$ the levels are grouped so that the gaps between groups are approximately the same and equal to $\hbar\omega_\varphi$ whereas the tunnelling splitting which occurs for $l>1$ in each group of l levels is exponentially small in the parameter $4\Delta U/\hbar\omega_\varphi$.[3,11] Neglecting the tunnelling splitting we can assume the eigenstates $|0\sigma\rangle$ to be localized in the wells of the deformation potential so that

$$\begin{gathered}\varepsilon_{0\sigma}=\hbar\omega_\varphi(\sigma+{}^1/_2),\ \sigma=0,\,1,\,\ldots\ll N+1\sim\Delta U(r_0)/\hbar\omega_\varphi,\\ \langle 0\sigma'|\cos\varphi|0\sigma\rangle=\delta_{\sigma'\sigma},\ \langle 0\sigma'|\sin\varphi|0\sigma\rangle\\ =(\hbar/2mr_0^{\,2}\omega_\varphi)^{1/2}[\sigma^{1/2}\delta_{\sigma',\sigma-1}+(\sigma+1)^{1/2}\delta_{\sigma',\sigma+1}].\end{gathered} \qquad (33)$$

When the molecule has a single equilibrium orientation ($l=1$) the deformation potential is also characterized by a

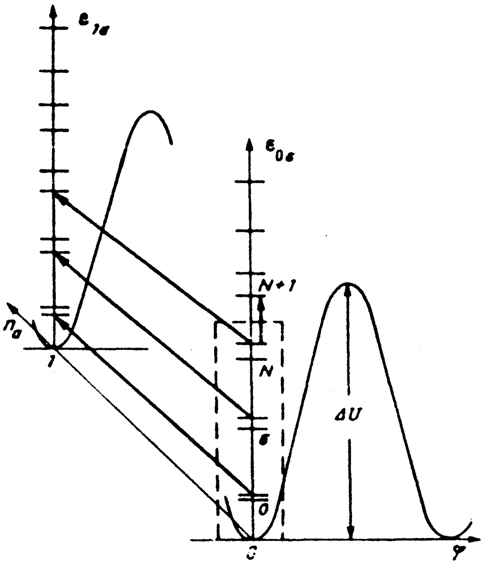

FIG. 2. Transitions guaranteeing the departure of a molecule from hindered rotation subbarrier states for $n_a=0$.

well defined barrier ΔU which separates the equivalent minima. The subsystem Hamiltonian (24) used in the exchange dephasing model[16,17] with $\omega_a = \omega_r$, $\omega_S = \omega_\varphi$, and

$$\gamma=\frac{\hbar\omega_\varphi}{2mr_0^2\omega_r},\quad \varphi=\left(\frac{\hbar}{2mr_0^2\omega_\varphi}\right)^{1/2}(b+b^+) \tag{34}$$

correctly describes only the subbarrier deformation states (the operators b and b^+ are now defined by the standard expressions for the matrix elements of the subbarrier states only). For the operators $\hat{A}$ and $\hat{B}$ in the GF (1) when we describe the high-frequency response, taking the orientation of the molecule into account, we must put

$$\hat{A}=a\cos\varphi,\quad \hat{B}=a^+\cos\varphi. \tag{35}$$

By virtue of the properties of (33) the matrix elements $A_{q'q}$ and $B_{\bar{q}\bar{q}'}$ in (11) will be diagonal in the quantum numbers σ only for the subbarrier states, and the operator $\hat{V}$ takes the form (12) for those states.

Indeed, it is shown in Ref. 12 (see also Ref. 3) that the interaction of the reorienting molecule with the matrix of the solid (in which it is embedded due to the rigid coupling with a single of its atoms) can be written as the energy of the d'Alembert force—$m\ddot{\mathbf{u}}$ in the noninertial frame of reference of the center of mass of the molecule undergoing an acceleration $\ddot{\mathbf{u}}$ due to the vibrations of the solid: $V = m\mathbf{r}\ddot{\mathbf{u}}$. Expressing the deformation vector $\mathbf{u}$ in terms of the second quantization operators of the phonons of the reservoir and using the fact that the operators b and b^+ arise due to the presence of $\sin\varphi$ in the vector $\mathbf{r} = r_0(\cos\varphi, \sin\varphi)$, we arrive for the subbarrier states to Eq. (12) for $\hat{V}$ with

$$\chi_k=\frac{1}{2}\left(\frac{m\omega_k^3}{\rho V\omega_\varphi}\right)^{1/2}, \tag{36}$$

where ρ is the density of the medium and V the volume of the basic region. In the case of a Debye spectrum for the phonons of the reservoir, characterized by the average sound speed c or the Debye frequency ω_D and the mass M of the elementary cell, the width of the resonant deformation mode takes the form[12]

$$\eta=2\pi\sum_k|\chi_k|^2\delta(\omega_\varphi-\omega_k)=\frac{m\omega_\varphi^4}{4\pi\rho c^3}=\frac{3\pi}{2}\frac{m}{M}\left(\frac{\omega_\varphi}{\omega_D}\right)^3\omega_\varphi. \tag{37}$$

For real systems we have $m < M$, $(\omega_\varphi/\omega_D)^3 \ll 1$, $\hbar/2mr_0^2\omega_\varphi \ll 1$ and the estimates (34) and (37) satisfy the conditions η, $\gamma \ll \omega_\varphi$ formulated in Sec. 3 for the Markov approximation.

Transitions between superbarrier states ($\sigma > N$, see Fig. 2) bring in elements of the density matrix which are off-diagonal in σ and which for $\Delta U > T$ give a small contribution to the spectral function at frequencies of the order $\omega_r + (\varepsilon_{0\sigma} - \varepsilon_{0\sigma'})/\hbar$ $(\sigma \neq \sigma')$. As we are interested in the spectral function at frequencies near ω_r we can neglect this contribution.

The required expression for the GF of the high-frequency mode, taking into account the anharmonic coupling of the latter with the exchange deformation mode, which is characterized by a well defined value of the reorientation barrier ΔU, thus takes the form (25) with a restricted summation over the quantum numbers $n_b = \sigma = 0,1,\ldots,N$ of the subbarrier states. It is then expedient to rewrite Eq. (26) in the following form:

$$\frac{\partial}{\partial t}g_{\sigma\sigma'}(t)+(i\omega_r+v_\sigma)g_{\sigma\sigma'}(t)+\sum_{\sigma''=0}^{N}W_{\sigma\sigma''}g_{\sigma''\sigma'}(t)=-\delta(t)\delta_{\sigma\sigma'}, \tag{38}$$

$$v_\sigma=i\gamma\sigma+w_0(N+1)\xi\delta_{\sigma N},\quad \xi=\exp(-\hbar\omega_\varphi/T), \tag{39}$$

$$W_{\sigma\sigma'}=w_0\{[\sigma+(\sigma+1)\xi-(N+1)\xi\delta_{\sigma N}]\delta_{\sigma'\sigma}-(\sigma+1)\delta_{\sigma',\sigma+1}-\sigma\xi\delta_{\sigma',\sigma-1}\},\quad \sigma,\sigma'=0,1,\ldots,N, \tag{40}$$

which corresponds to the Pauli equation with transition rates that are perturbed relative to $W_{\sigma\sigma'}$. The perturbations v_σ determine the rate at which the molecule leaves the subbarrier states which in Fig. 2 are enclosed by the dashed lines, and they consist of two contributions: departures due to the anharmonic coupling of the valence and the torsional oscillations and those due to the strong anharmonicity of the torsional oscillations which in the present model are determined by the magnitude of the barrier ΔU. The last contribution which is proportional to $w_0(N+1)\xi$ was neglected in Ref. 13, since an equation of the type (38) with finite N was used for a numerical approximation of the $N\to\infty$ case. In the next section we consider the properties of the GF of the Pauli equation with unperturbed transition rates $W_{\sigma\sigma'}$ satisfying the principle of detailed balance, we construct a perturbation theory in the small corrections to the transition rates, and we give detailed results for a model with v_σ and $W_{\sigma\sigma'}$ of the form (39) and (40).

5. PERTURBATION THEORY FOR THE TRANSITION RATES IN THE PAULI EQUATION

We consider a subsystem characterized by states with energies ε_q and transition rates $W_{qq'}$ from a state q' into a state q, satisfying the principle of detailed balance.

$$w_{qq'}=\frac{\rho_q}{\rho_{q'}}w_{q'q},\quad \rho_q=\frac{\exp(-\varepsilon_q/T)}{\sum_q\exp(-\varepsilon_q/T)}. \tag{41}$$

We write the Pauli equation[30] for the probability $p_q(t)$ for finding the subsystem in the state q at time t in the following form, which is convenient for further transformations:

$$\frac{d}{dt}p_q(t)+\sum_{q'}W_{qq'}p_{q'}(t)=0,\quad W_{qq'}=\delta_{qq'}\sum_{q''}w_{q''q}-w_{qq'}. \tag{42}$$

The principle of detailed balance, valid for the quantities $W_{qq'}$, guarantees the diagonalization of the nonsymmetric matrix $W_{qq'}$ with nonnegative elements:

$$\sum_{q'}W_{qq'}C_{q'\nu}=\mu_\nu C_{q\nu}, \tag{43}$$

where the eigenvalues μ_ν are also nonnegative and the orthonormalization relations for the matrix elements $C_{q\nu}$ are defined with weights ρ_q:

$$\sum_\nu C_{q\nu}C_{q'\nu}=\rho_q\delta_{qq'},\quad \sum_q\rho_q^{-1}C_{q\nu}C_{q\nu'}=\delta_{\nu\nu'}. \tag{44}$$

If we denote the initial probabilities for state occupation at time $t = 0$ by $p_q(0)$, the solution of Eq. (42) takes the following form:

$$p_q(t)=\sum_{q'}\rho_{q'}^{-1}p_{q'}(0)\sum_\nu C_{q\nu}C_{q'\nu}\exp(-\mu_\nu t). \tag{45}$$

The quantities introduced here have a number of properties necessary for establishing thermodynamic equilibrium of the subsystem with the reservoir for $t \to \infty$. First of all we note that by virtue of the definition (42) the summation of the matrix elements $W_{qq'}$ over the first index gives zero. Therefore summation over q of both sides of Eq. (43) makes the product $\mu_\nu \Sigma_q C_{q\nu}$ vanish. As the rows C_q of the transformation are linearly independent it follows that there exists at least one eigenvalue μ_ν equal to zero. We denote the corresponding index ν by zero and we have then $\mu_0 = 0$ and $\Sigma_q C_{q\nu} = 0$ for $\nu \neq 0$. Summing the first of Eqs. (44) over q and using the fact that $\Sigma_q \rho_q = 1$ we find

$$\mu_0 = 0, \quad C_{q0} = \rho_q, \quad \sum_q C_{q\nu} = \delta_{\nu 0}. \tag{46}$$

These properties lead to the physically obvious consequences of the solution of (45):

$$\sum_q p_q(t) = \sum_q p_q(0) = 1,$$

$p_q(t) = \rho_q$ for $p_q(0) = \rho_q$, and $p_q(\infty) = \rho_q$ for arbitrary initial conditions.

The frequency Fourier component $g^{(0)}_{qq'}(\omega)$ of the GF of the unperturbed Pauli equation (42) [satisfying Eq. (42) with $-\delta(t)\delta_{qq'}$ on the right-hand side], if we take (44) into account, has a pole for $\omega = 0$:

$$g^{(0)}_{qq'}(\omega) = -i \sum_\nu \frac{C_{q\nu} C_{q'\nu} \rho_{q'}^{-1}}{\omega + i\mu_\nu} = -i \frac{\rho_q}{\omega} - \varepsilon_{qq'}(\omega). \tag{47}$$

Here $\varepsilon_{qq'}(\omega)$ is determined by the general expression for $g^{(0)}_{qq'}(\omega)$ in which we exclude from the sum over ν the term with $\mu_\nu = 0$ so that, for instance, $\varepsilon_{qq'}(0)$ is, when we take into account the weight factor ρ_q, a pseudo inverse matrix with respect to $W_{qq'}$ and satisfies the following identities:

$$\sum_{q''} W_{qq''} \varepsilon_{q''q'}(0) = \delta_{qq'} - \rho_q, \quad \sum_q \varepsilon_{qq'}(0) = 0. \tag{48}$$

We now consider perturbations of the transition rates, adding to $W_{qq'}$ the contribution $v_q \delta_{qq'}$ which is diagonal in q. The perturbed GF $g_{qq'}(\omega)$ will then be connected with the unperturbed one through the Dyson equation

$$g_{qq'}(\omega) = g^{(0)}_{qq'}(\omega) + \sum_{q''} g^{(0)}_{qq''}(\omega) v_{q''} g_{q''q'}(\omega). \tag{49}$$

To second order in v_q the required retarded GF (25) is equal to

$$G(t) = -i\theta(t)\exp(-\tilde{\Gamma} t), \quad \tilde{\Gamma} = \sum_q v_q \rho_q - \sum_{qq'} v_q \varepsilon_{qq'}(0) v_{q'} \rho_{q'} \tag{50}$$

and apart from the factor $-i\theta(t)$ determines the probability that the subsystem leaves the given group of states (e.g., the one enclosed in the box in Fig. 2). The quantity $\tilde{\Gamma}$ acquires the meaning (since v_q and $\tilde{\Gamma}$ can take on complex values) of a generalized loss rate. The spectral function corresponding to Eqs. (25) and (38) acquires a Lorentzian shape:

$$S(\omega) = -\frac{1}{\pi} \operatorname{Im} \frac{1}{\omega - \omega_r + i\tilde{\Gamma}}. \tag{51}$$

The first term in the expression (50) for $\tilde{\Gamma}$ has a simple physical meaning: it sums the perturbed loss rates from each level of the subsystem, taking into account the equilibrium probabilities for their occupation. The second term, on the other hand, already depends on the unperturbed rates for transitions between states of the subsystem and by virtue of the definition of $\varepsilon_{qq'}(0)$ is inversely proportional to them.

We evaluate the pseudo-inverse matrix $\varepsilon_{qq'}(0)$ of the transition rates (40) between $N+1$ low-energy states of a harmonic oscillator which interacts resonantly with the phonons of the reservoir. For this it is necessary to carry out the following operations: 1) write $g^{(0)}_{qq'}(\omega)$ as the ratio of the appropriate cofactor and the determinant of the matrix $i\omega\delta_{qq'} - W_{qq'}$; 2) expand this quantity in a Laurent series in ω and then the principal part of the Laurent series gives the first term of the right-hand side of Eq. (47) and the terms of zeroth degree in ω from the regular part of the Laurent series determine the required $\varepsilon_{qq'}(0)$ matrix; 3) calculate the determinants which appear and their derivatives with respect to ω for $\omega = 0$ using relatively simple recurrence relations obtained by expanding a determinant of quasi-triangular shape (like the matrix (40) for $W_{qq'}$) with respect to an arbitrary row or column. As a result we get

$$\varepsilon_{qq'}(0) = \frac{\rho_q}{\rho_{q'}} \varepsilon_{q'q}(0) = \frac{\rho_q}{w_0(1-\xi)} \left[\sum_{k=1}^{q'} \frac{\xi^{-k}-1}{k} + \sum_{k=q+1}^{N} \frac{1-\xi^{N+1-k}}{k} - \frac{1}{1-\xi^{N+1}} \sum_{k=1}^{N} \frac{(1-\xi^k)(1-\xi^{N+1-k})}{k} \right], \quad q \geqslant q', \quad \rho_q = \frac{1-\xi}{1-\xi^{N+1}} \xi^q. \tag{52}$$

Here $q, q' = 0,1,\ldots,N$ and it is understood that for $q = q' = 0$ and for $q = N$ sums with an upper limit of summation smaller than the lower one vanish. One checks easily that Eq. (52) found here satisfies the identities (48).

For the problem (38) to (40) to second order in the perturbation theory of (50) and (51), which is valid for $\gamma \ll \eta$ and $\xi^{N+1} \ll 1$ we can now find the half-width Γ of the spectral function and the shift $\Delta\omega$ of the maximum relative to ω_r:

$$\Gamma = \operatorname{Re} \tilde{\Gamma} = (N+1)\eta \frac{\xi^{N+1}}{1-\xi^{N+1}} A_N(\xi) + \frac{\gamma^2}{\eta} \frac{\xi}{(1-\xi)^2} B_N(\xi), \tag{53}$$

$$\Delta\omega = \operatorname{Im} \tilde{\Gamma} = \gamma \frac{\xi}{1-\xi} C_N(\xi), \tag{54}$$

where

$$\begin{gathered} A_N(\xi) = 1 - \frac{(N+1)\xi^{N+1}}{(1-\xi^{N+1})^2} f_N(\xi), \quad f_N(\xi) = \sum_{k=1}^{N} \frac{(1-\xi^k)^2}{k\xi^k}, \\ B_N(\xi) = 1 - \frac{(N+1)(1-\xi)^2 \xi^N}{1-\xi^{N+1}} \left[A_N(\xi) + \frac{\xi}{1-\xi} + D_N(\xi) \right], \\ C_N(\xi) = 1 - \frac{(N+1)(1-\xi)\xi^N}{1-\xi^{N+1}} [2A_N(\xi) - 1 + D_N(\xi)], \\ D_N(\xi) = \frac{2}{1-\xi^{N+1}} \left[N - \frac{\xi(1-\xi^N)}{1-\xi} \right]. \end{gathered} \tag{55}$$

For a single subbarrier level we have $A_0(\xi) = 1$, $B_0(\xi) = C_0(\xi) = 0$, and the half-width of the spectral function is determined solely by the reorientation rate, which is equal to the transition rate to the first excited state of the deformation oscillations:[12]

$$\Gamma=\eta n(\omega_\varphi),\quad n(\omega_\varphi)=[\exp(\hbar\omega_\varphi/T)-1]^{-1}. \tag{56}$$

For two subbarrier levels ($N=1$) Eqs. (55) are an approximation for $\xi \ll 1$ of the result of the two-level problem, valid for any values of ξ:

$$A_1(\xi)=\frac{1}{4\xi^2}(1+\xi)[1+3\xi-(1+6\xi+\xi^2)^{1/2}],$$
$$B_1(\xi)=\frac{(1-\xi)^3}{(1+6\xi+\xi^2)^{3/2}},\ C_1(\xi)=\frac{1-\xi}{2\xi}\left[1-\frac{1+\xi}{(1+6\xi+\xi^2)^{1/2}}\right]. \tag{57}$$

Finally, in the other limiting case, $N\to\infty$, the functions $B_N(\xi)$ and $C_N(\xi)$ are approximately equal to unity and Eqs. (53) and (54) reduce to the results of Ref. 13 for $\gamma \ll \eta$.

We draw attention to the fact that in first order of perturbation theory we have $A_N(\xi)=1$ and $B_N(\xi)=0$ in Eq. (53) for any N and the expression for the rate of departure of the molecule from the subbarrier states reduces to two well known special cases. The first of these corresponds to the low-temperature limit $\xi\to 0$ for which[23]

$$\eta=w_0(1-\xi)\approx w_0,\ \Gamma=(N+1)w_0\exp(-\Delta U/T).$$

The second special case corresponds to the classical limit $1-\xi\to\hbar\omega_\varphi/T\to 0$ and gives Kramers' result:[21]

$$\Gamma=w_0(\Delta U/T)\exp(-\Delta U/T),$$

in which the parameter w_0 serves as the "viscosity" coefficient. In second-order perturbation theory the coefficient $A_N(\xi)$ makes the first-order result more precise. For $N\gg 1$ and $\xi\lesssim 0.5$ we get from (55) the asymptotic expression

$$A_N(\xi)\approx 1-\xi/(1-\xi).$$

6. DISCUSSION

The main results of the present paper which can be used for describing spectra of high-frequency local oscillations of molecular subsystems in the condensed phase are contained in Eqs. (29), (30), and (53) to (55) which involve two parameters, γ and η. According to the estimates of Ref. 31 molecular complexes with hydrogen bonds are characterized by values $\gamma\approx 3\ \mathrm{cm}^{-1}$ of the anharmonic coupling coefficient and frequencies $\omega_j\approx 30\ \mathrm{cm}^{-1}$, much less than the Debye frequency ω_D, of the librational oscillations. This fact leads to the inequality $\eta\ll\gamma$ and the validity of Eq. (30), in agreement with the experimental data of Refs. 8 and 9 (a discussion of this problem is given in Refs. 11 and 26).

Estimates of the parameters γ and η for surface groups of atoms, carried out by using Eqs. (34) and (37) or similar relations in Ref. 13, show that $\gamma/\eta\sim 0.1$. If we put $\gamma/\eta=0.1$ in (53) the reorientation contribution to the broadening starts to dominate over the anharmonic contribution with the coefficient γ, starting at temperatures $T>0.5\hbar\omega_\varphi$ for $N=3$ or $T>0.9\hbar\omega_\varphi$ for $N=5$. Assuming that the values of the barriers ΔU for CO bridge groups on Ni(111) correspond to $N\lesssim 3$ and with the realistic estimates $\omega_\varphi\approx 184\ \mathrm{cm}^{-1}$, $\omega_r\approx 1900\ \mathrm{cm}^{-1}$, $\gamma\sim 1\ \mathrm{cm}^{-1}$, $\eta\approx 30\ \mathrm{cm}^{-1}$ the reorientation contribution to Eq. (53) can explain the broadening of the spectral lines of the valence CO oscillations observed in Ref. 13. Apart from the contribution (54) from the fourth-degree anharmonicity $(r-r_0)^2\varphi^2$, even the third-degree anharmonicity of the form $(r-r_0)\varphi^2$, and also other low-frequency oscillational modes of the substrate,[29] will give a comparable contribution to the shift of the maximum of the same line. Neglecting the other low-frequency modes and taking into account only a single harmonic ($N\to\infty$) mode overestimates by an order of magnitude the value of the only anharmonic parameter γ for the description of the observed spectra.[13,15,19]

The purely reorientational broadening mechanism with a single threefold quasi-degenerate subbarrier level is characteristic for the spectral line of the valence oscillations of the OH groups on a SiO_2 surface. Equation (56) describes the observed temperature dependence of the halfwidth of the line for $\omega_\varphi\approx 200\ \mathrm{cm}^{-1}$ and $\eta\approx 4\ \mathrm{cm}^{-1}$ (for this system $\gamma\approx 0.9\ \mathrm{cm}^{-1}$ holds and in (56) we have $\gamma^2/\eta\approx 0.2\ \mathrm{cm}^{-1}$, which is much less than the value of η).[3,11,12] Equations (53), (54), and (57) can be used for the system of OD groups on a SiO_2 surface as in that case one can put the number of subbarrier levels equal to two due to the doubled mass of the reorientating atom.

Note that the value of the results of the present paper is not exhausted by the application to actual systems. Equation (11) for the GF in the Markov approximation and the development of the perturbation theory for the Pauli equation which describes many physical systems satisfactorily have a rather general character. An example of the use of the proposed approaches is the problem of calculating the rates of transitions of a particle between locally coupled subsystems. The description of the spectrum of the latter considered in Ref. 32, which was carried out by means of quantum-mechanical GF, can easily be reformulated in terms of the GF of the Pauli equation.

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