

Manifestation of Fermi resonance in optical spectra of dynamical pseudo-Jahn-Teller effect

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Abstract. Shape of optical spectrum of vibronic transition in one-dimensional model taking into account dynamical pseudo-Jahn-Teller effect was studied. Numerical calculations at large values of interaction parameter revealed periodic character of the envelope. This was interpreted as manifestation of Fermi resonance.

1. Introduction

Let's consider a vibronic system with non-degenerate ground state and two nearby excited states, where excited states interact through low-symmetry vibrations. In harmonic and linear approximations in respect to interaction the vibrational movement of such system in ground state and excited state is described by the following Hamiltonians, respectively:

$$\begin{aligned} H_g &= E_g + H_L \\ H_e &= E_e + H_L + H_{eL} \end{aligned} \quad (1)$$

where E_g and E_e are average energies of electrons in these states, and

$$\begin{aligned} H_L &= \sum_s \frac{\hbar\omega_s}{2} \left(-\frac{\partial^2}{\partial \xi_s^2} + \xi_s^2 \right), \\ H_{eL} &= \begin{pmatrix} + & - \\ \Gamma & V \\ V & -\Gamma \end{pmatrix}, \\ V &= \sum_s \hbar\omega_s k_s \xi_s. \end{aligned} \quad (2)$$

Shape of the optical spectrum corresponding to vibronic transitions from ground state to excited electronic states is determined by the function

$$I(E) = \langle g | M^+ | a \rangle F_{ab}(E - E_e + E_g) \langle b | M | g \rangle \quad (3)$$

where

$$F(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau e^{iE\tau} \left\langle e^{i(H_L + H_{eL})\tau} e^{iH_L\tau} \right\rangle. \quad (4)$$

Here M is operator of interaction of optical electrons with light, and brackets $\langle \rangle$ denote statistical averaging over vibrational states of H_L .



Due to averaging odd powers of ξ vanish, so in our diabatic representation [1] the density distribution function $F(E)$ is diagonal:

$$F(E) = \begin{pmatrix} F_+(E) & 0 \\ 0 & F_-(E) \end{pmatrix}. \quad (5)$$

Consequently,

$$I(E) = |\langle +|M|g \rangle|^2 F_+(E) + |\langle -|M|g \rangle|^2 F_-(E). \quad (6)$$

Calculating $F(E)$ according to the equation (4) we meet difficulties well-known in theory of dynamical Jahn-Teller effect which do not permit to find explicit expression. Therefore we have to use various approximations. However, moments of $F_{\pm}(E)$ are calculated exactly. First 7 of them are:

$$\begin{aligned} \mu_0 &= 1, \\ \mu_1 &= \pm\Gamma, \\ \mu_2 &= S_2 + \Gamma^2, \\ \mu_3 &= S_3 \pm \Gamma S_2 \pm \Gamma^3, \\ \mu_4 &= S_4 + 3S_2^2 + 2\Gamma^2 S_2 + \Gamma^4, \\ \mu_5 &= S_5 + 10S_3 S_2 \pm \Gamma(3S_2^2 - S_4) + 2\Gamma^2 S_3 \pm 2\Gamma^3 S_2 \pm \Gamma^5, \\ \mu_6 &= S_6 + 15S_4 S_2 + 10S_3^2 + 15S_2^3 \pm 2\Gamma(4S_3 S_2 - S_5) + \\ &+ 3\Gamma^2(3S_2^2 + S_4) S_3 + 3\Gamma^4 S_2 + \Gamma^6. \end{aligned} \quad (7)$$

Here

$$\begin{aligned} S_n &= \int_{-\infty}^{\infty} dE E^n \varphi(E), \\ \varphi(E) &= \sum_s \frac{k_s^2}{2} [(\bar{n}_s + 1) \delta(E - \hbar\omega_s) + \bar{n}_s \delta(E + \hbar\omega_s)], \\ \bar{n}_s &= e^{-\hbar\omega_s/k_B T} / \sum_s e^{-\hbar\omega_s/k_B T}. \end{aligned} \quad (8)$$

Unfortunately it is practically impossible to restore the form of $F(E)$ from its first moments. This becomes evident when we calculate $F(E)$ in semi-classical approximation that holds for strong vibronic interaction:

$$\begin{aligned} F^0(E) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau e^{iE\tau} \langle e^{-iH_{el}\tau} \rangle = \frac{1}{\pi} \text{Im} \left\langle \frac{1}{E - i0 - V} \right\rangle = \\ &= \frac{1}{\sqrt{2\pi S_2}} e^{-\frac{E^2 - \Gamma^2}{2S_2}} \begin{pmatrix} \sqrt{\frac{E + \Gamma}{E - \Gamma}} & 0 \\ 0 & \sqrt{\frac{E + \Gamma}{E - \Gamma}} \end{pmatrix}. \end{aligned} \quad (9)$$

Equation (9) implies that both polarizations of the semi-classical spectrum have a gap in the range $E \in [\Gamma, -\Gamma]$ and a singular point of type $(E \mp \Gamma)^{-1/2}$ at one of its boundaries.

We also note that at $\Gamma = 0$ the problem is equivalent to the one of singlet-singlet transition: equation (4) turns into well-known Lax equation:

$$F_0(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau e^{iE\tau} e^{\tilde{\varphi}(\tau) - \tilde{\varphi}(0)}, \quad (10)$$

where

$$\tilde{\varphi}(\tau) = \int_{-\infty}^{\infty} dE e^{-iE\tau} \varphi(E), \quad (11)$$

and the semi-classical spectrum is given by Gaussian:

$$F_0^0(E) = \frac{1}{\sqrt{2\pi S_2}} e^{-\frac{E^2}{2S_2}} \quad (12)$$

2. Interaction with one vibration

Now we return to quantum-mechanical calculations. Let's find $F(E)$ in case of interaction with only one vibration. In this case the calculation is much simpler and quantum effects are more clearly manifested. The problem is to find solutions for the following vibrational equation for excited electronic states:

$$(H_L + H_{eL}) \begin{pmatrix} |v+\rangle \\ |v-\rangle \end{pmatrix} = E_v \begin{pmatrix} |v+\rangle \\ |v-\rangle \end{pmatrix}. \quad (13)$$

Here

$$H_L = \frac{\hbar\omega}{2} \left(-\frac{d^2}{d\xi^2} + \xi^2 \right), \quad (14)$$

$$H_E = \hbar\omega \begin{pmatrix} G & k\xi \\ k\xi & -G \end{pmatrix}.$$

In the basis of eigenstates of vibrational Hamiltonian H_L the equation (13) splits into two equations with tridiagonal matrices:

$$\begin{pmatrix} G & \sqrt{D} & 0 & 0 & \dots \\ \sqrt{D} & 1-G & \sqrt{2D} & 0 & \dots \\ 0 & \sqrt{2D} & 2+G & \sqrt{3D} & \dots \\ & & \sqrt{3D} & 3-G & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} c_{0v}^+ \\ c_{1v}^- \\ c_{2v}^+ \\ c_{3v}^- \\ \dots \end{pmatrix} = \nu \begin{pmatrix} c_{0v}^+ \\ c_{1v}^- \\ c_{2v}^+ \\ c_{3v}^- \\ \dots \end{pmatrix}, \quad (15)$$

$$\begin{pmatrix} -G & \sqrt{D} & 0 & 0 & \dots \\ \sqrt{D} & 1+G & \sqrt{2D} & 0 & \dots \\ 0 & \sqrt{2D} & 2-G & \sqrt{3D} & \dots \\ & & \sqrt{3D} & 3+G & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} c_{0v}^- \\ c_{1v}^+ \\ c_{2v}^- \\ c_{3v}^+ \\ \dots \end{pmatrix} = \nu \begin{pmatrix} c_{0v}^- \\ c_{1v}^+ \\ c_{2v}^- \\ c_{3v}^+ \\ \dots \end{pmatrix},$$

Here $G = \Gamma/\hbar\omega$ and $D = k^2/2 = S_2/(\hbar\omega)^2$ are dimensionless parameters of splitting and vibronic interaction, and ν is quantum number of eigenstate of $H_L + H_{eL}$:

$$E_\nu = \hbar\omega \left(\nu + \frac{1}{2} \right). \quad (16)$$

Depending on whether ν is the eigenvalue of the first or of the second equation, the eigenvector is expressed as

$$\begin{pmatrix} |\nu+\rangle \\ |\nu-\rangle \end{pmatrix} = \begin{pmatrix} c_{0\nu}^+ |0\rangle + c_{2\nu}^+ |2\rangle + c_{4\nu}^+ |4\rangle + \dots \\ c_{1\nu}^- |1\rangle + c_{3\nu}^- |3\rangle + c_{5\nu}^- |5\rangle + \dots \end{pmatrix}, \quad (17)$$

or

$$\begin{pmatrix} |\nu+\rangle \\ |\nu-\rangle \end{pmatrix} = \begin{pmatrix} c_{1\nu}^+ |1\rangle + c_{3\nu}^+ |3\rangle + c_{5\nu}^+ |5\rangle + \dots \\ c_{0\nu}^- |0\rangle + c_{2\nu}^- |2\rangle + c_{4\nu}^- |4\rangle + \dots \end{pmatrix}, \quad (18)$$

where $|0\rangle, |1\rangle, |2\rangle, \dots$ are eigenvectors of the Hamiltonian H_L :

$$\begin{aligned} H_L |n\rangle &= E_n |n\rangle \\ E_n &= \hbar\omega \left(n + \frac{1}{2} \right), \\ n &= 0, 1, 2, \dots \end{aligned} \quad (19)$$

From (15) it is evident that stationary states of the Hamiltonian $H_L + H_{eL}$ are divided into two classes. Consequently, there exists an operator with two eigenvalues, which commutes with the Hamiltonian. In the coordinate representation, its effect can be determined by the following expression:

$$P \begin{pmatrix} \psi_+(\xi) \\ \psi_-(\xi) \end{pmatrix} = \begin{pmatrix} \psi_+(-\xi) \\ -\psi_-(-\xi) \end{pmatrix}. \quad (20)$$

The eigenvalues of this operator are 1 and -1, and the eigenvectors are vectors, in which one of the components is even and the other odd function of ξ :

$$\begin{aligned} P \begin{pmatrix} g(\xi) \\ u(\xi) \end{pmatrix} &= \begin{pmatrix} g(\xi) \\ u(\xi) \end{pmatrix}, \\ P \begin{pmatrix} u(\xi) \\ g(\xi) \end{pmatrix} &= - \begin{pmatrix} u(\xi) \\ g(\xi) \end{pmatrix}, \end{aligned} \quad (21)$$

where $g(-\xi) = g(\xi)$ and $u(-\xi) = -u(\xi)$.

Due to tridiagonality of energy matrices in (15) the amount of computations and necessary storage are not excessive, allowing computations at large values of D and G , i.e. in the range of transition to semi-classical spectrum. Further economy of storage and computation time appears at $T=0$, then transition occurs only from the vibrational ground state. In this case

$$F_{\pm}(E) = \sum_{\nu} |\langle \nu \pm | 0 \rangle|^2 \delta(E - E_{\nu} + E_0), \quad (22)$$

and we may compute only one component of eigenvectors $c_{0\nu}^{\pm} = \langle \nu \pm | 0 \rangle$.

As a result, the required computer resources remain within reasonable limits while taking into account several thousands of vibrational states of the Hamiltonian H_L , which in turn allows working with the values of D and G up to several hundred.

Numerical calculations were carried out on a computer M 4030 using the QL-method with shift [2]. The number of elementary rotations appeared to be slightly below N^2 , where N is the order of the matrix, and time to perform one rotation - about 2 ms. Therefore, in an hour we can calculate the spectrum, taking into account around thousand vibrational states of H_L .

3. Computed spectra

In the literature already exist results of numerical solution of the equation (13) for small D and G [1]. So we stopped at the large values of D and G , examining the way of reaching the semi-classical limit. It is well known that the envelope of the line spectrum corresponding to the vibronic transition to non-degenerate electronic state (the case of $\Gamma=0$ in our model), even when taking into account only one vibration, already at $D = 5$ is well described by the semi-classical expression (Gaussian curve). But as can be seen from figures 1 and 2, in this model, despite the high value of D , the calculated spectrum is clearly different from the semi-classical spectrum. In the region $E < -\Gamma$ semi-classical approximation works quite well. However, in the region $E > \Gamma$ clear fluctuations of the intensities of the absorption lines are noticeable. Nature of mentioned fluctuations may be well understood in terms of adiabatic potentials, if we take into account mixing of vibrational states of close energies that belong to different electronic states, i.e. Fermi resonance. Indeed, in adiabatic representation that diagonalizes H_{eL} :

$$H'_{eL} = OH'_{eL}O^T = \hbar\omega\sqrt{G^2 + k^2\xi^2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad (23)$$

where

$$O = \begin{pmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{pmatrix}, \quad (24)$$

$$\varphi = \frac{1}{2} \arctan \frac{k\xi}{G}.$$

The Hamiltonian H_L consists of two parts - kinetic and potential:

$$H_L = T + U = \frac{\hbar\omega}{2} \left\{ -\frac{d^2}{d\xi^2} \right\} + \frac{\hbar\omega}{2} \xi^2. \quad (25)$$

The latter does not change with the transition to the adiabatic representation, and the first takes the form

$$T' = OTO^T = \frac{\hbar\omega}{2} \left\{ -\frac{d^2}{d\xi^2} + \left(\frac{d}{d\xi} \frac{d\varphi}{d\xi} + \frac{d\varphi}{d\xi} \frac{d}{d\xi} \right) \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} + \left(\frac{d\varphi}{d\xi} \right)^2 \right\}, \quad (26)$$

where $\frac{d\varphi}{d\xi} = \frac{kG}{2(G^2 + k^2\xi^2)}$.

To summarize, in adiabatic representation the vibrational Hamiltonian of excited electronic states can be represented as the sum of three parts - the kinetic, potential, and mixing:

$$H'_L + H'_{eL} = T' + U' + H'_{eL} = T + W + K. \quad (27)$$

Here

$$T = \hbar\omega \left\{ -\frac{1}{2} \frac{d^2}{d\xi^2} \right\},$$

$$W = \hbar\omega \left\{ \frac{1}{2} \xi^2 + \sqrt{(G^2 + k^2\xi^2)} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \frac{k^2G^2}{8(G^2 + k^2\xi^2)^2} \right\}, \quad (28)$$

$$K = \hbar\omega \left\{ \left[\frac{d}{d\xi} \frac{kG}{2(G^2 + k^2\xi^2)} + \frac{kG}{2(G^2 + k^2\xi^2)} \frac{d}{d\xi} \right] \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right\}.$$

Usually when calculating the adiabatic potentials the third member of W is neglected. Also kinetic and mixing parts of the Hamiltonian are omitted. All this corresponds to semi-classical approximation.

We will, however, proceed differently: we consider $T + W$ as the unperturbed Hamiltonian, and K as a perturbation. Note that both of these operators, as well as the transformation matrix O commute with the operator P . Consequently,

$$P' = OPO^T = P, \quad (29)$$

i.e. similarly to diabatic representation in the adiabatic representation stationary states are also described by vectors with components of different parity. As the Hamiltonian $T + W$ is diagonal and K contributes only in the second order of perturbation theory, in the adiabatic representation one of the two components predominates over the other. The second component is significant only when energies of stationary states of upper and lower potentials are close.

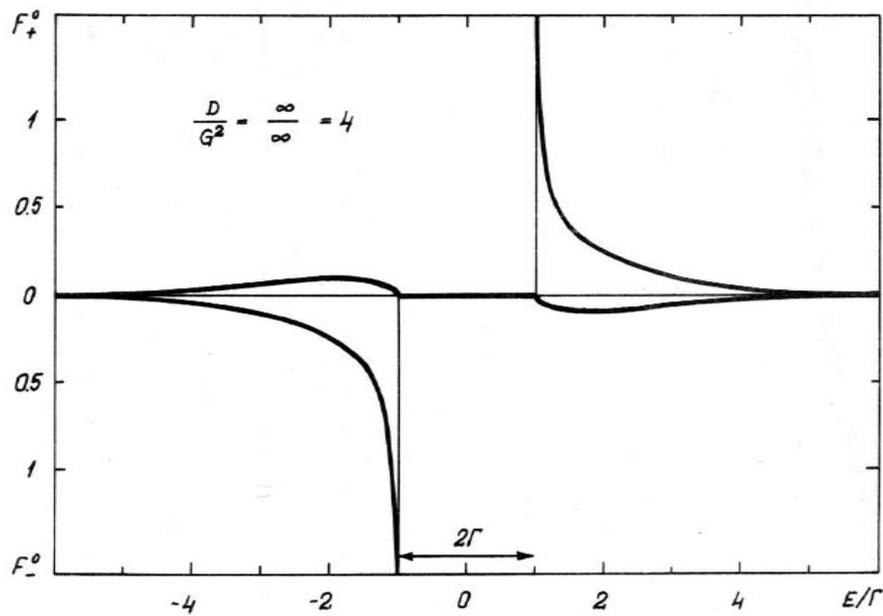


Figure 1. Shapes of functions $F_+^0(E)$ and $F_-^0(E)$ of the absorption spectrum of the two polarizations.

$S_2/\Gamma^2 = 4$, semiclassical approximation.

From the shapes of the potentials it is clear that most of the spectrum is located in two areas, respectively, adjacent to $E = -\Gamma$ from the left, and $E = \Gamma$ from the right. In the first of them, the transition occurs to high levels of the lower potential. Therefore, the spectrum there is well described by the semiclassical approximation. The only exception is a neighborhood of the upper barrier point $E \approx -\Gamma$, where it is essential to take into account the kinetic energy operator T .

In the second region $E > \Gamma$ along with levels of lower potential exist lower levels of the upper potential, into which the probability of transition from the ground vibrational state of H_L is high. The distance between these levels is several times greater than the distance between the energy levels of the lower potential that is approximately equal to $\hbar\omega/2$ (see the upper right side of figure 3). If we take into account that the transition can only occur into vibrational states that are even in respect to ξ , strong absorption lines should appear in $F_+(E)$ at frequencies close to even stationary states of the upper potential, and in $F_-(E)$ respectively, close to odd ones. Due to the mixing caused by the operator K these lines must be accompanied by satellites, corresponding to transitions into nearby states of opposite parity of the lower potential. According to Fermi resonance the intensity of these lines should increase with diminishing distance between the respective levels and the levels of the upper potential. All this is indeed observed in our calculated spectrum.

In order to obtain quantitative results in the adiabatic representation one should first solve the Schrodinger equation with the Hamiltonian $T + W$ for high vibrational levels of the lower potential, which can be practically realized only by the WKB method. Such calculations we did not perform, because in the given model they are more complex than the calculations described above and are only of auxiliary importance. Nevertheless, using the simplest version of this method, we calculated positions of the energy levels of the unperturbed Hamiltonian $T + W$ in the area of the upper potential. Results of these calculations are shown in figure 3.

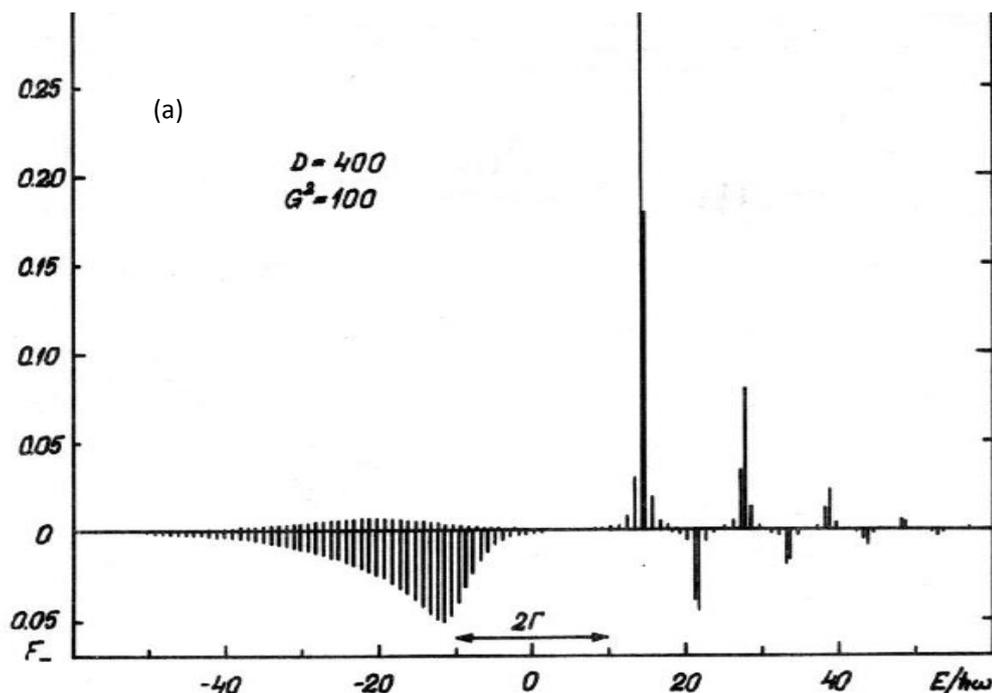
4. Optical spectra of dimers

A problem similar to that considered in this paper arises in the theory of optical spectra of dimers, but there one must also take into account the interaction with another, totally symmetric vibration. This vibration interacts equally with both excited electronic states and does not mix them. Therefore, its effect is reduced to the convolution of the density distribution function $F_{\pm}(E)$ with another density distribution function $F_0(E)$ calculated at the same D , but at $G=0$ (equation (10)). In our model (one totally symmetric vibration, $T=0$) $F_0(E)$ is given by the Poisson distribution:

$$F_0(E) = \sum_{n=0}^{\infty} \frac{D^n}{n!} \delta(E - n\hbar\nu). \quad (30)$$

Calculation and analysis of such spectra at moderate D and G was performed in the works [1]. It is easy to obtain the corresponding spectra also at the values of D and G we used, however, even without calculations it is clear that the resulting spectra are strongly smoothed. Taking into account many vibration frequencies and the finite temperature changes the spectra towards the same direction. Therefore, the conditions for observing manifestations of Fermi resonance in real spectra of dimers are not particularly favorable.

This work was first published in Russian as [3].



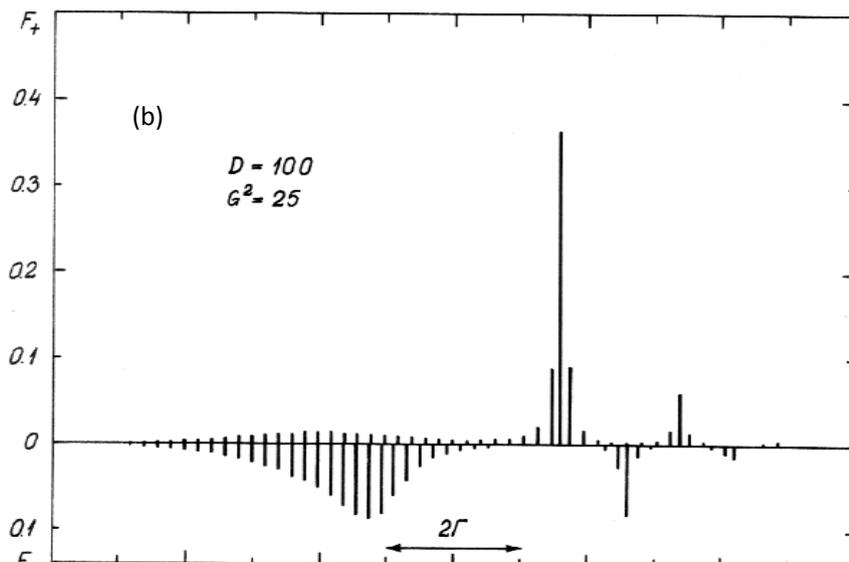


Figure 2. Shapes of functions $F_+^0(E)$ and $F_-^0(E)$ of the absorption spectrum of the two polarizations. $S_2/\Gamma^2 = 4$, quantum calculation. $S_2 = 400(\hbar\omega)^2$, $\Gamma = 10\hbar\omega$ (a); $S_2 = 100(\hbar\omega)^2$, $\Gamma = 5\hbar\omega$ (b).

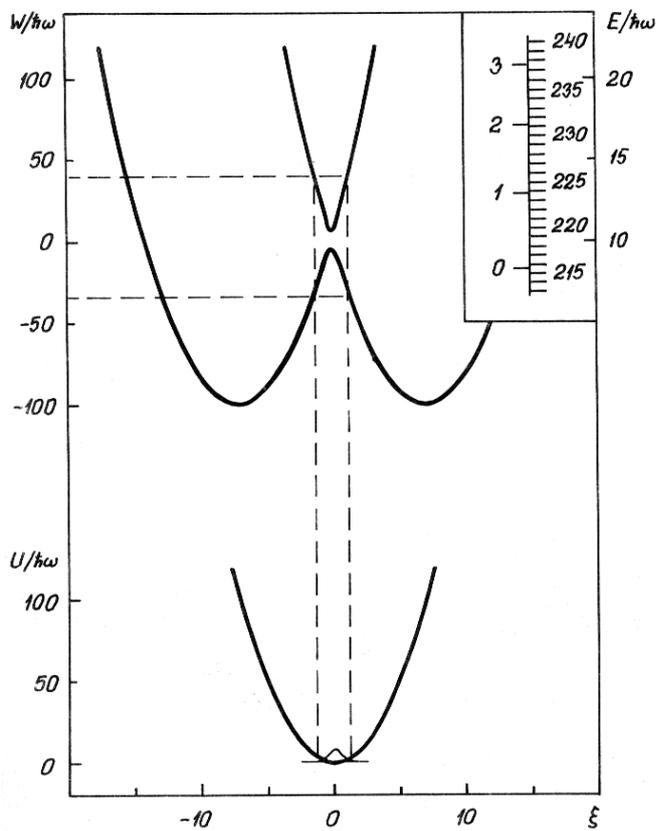


Figure 3. Adiabatic potentials in the ground (U) and excited (W) electronic states. The upper right corner shows the positions of energy levels of potentials of the excited electronic state, calculated by the WKB method.

$S_2/\Gamma^2 = 4$, $S_2 = 100(\hbar\omega)^2$, $\Gamma = 5\hbar\omega$.

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