Nonradiative transitions in molecules with excited squeezed vibrational states

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Nonradiative (nonthermal) transitions in electronic–vibrational systems involving squeezed vibrational states are considered. The nonradiative transition rate is calculated for different methods of preparing squeezed states (using an ultrashort laser pulse or by inducing parametric resonance). The highest transition rate occurs at times when the width of the wave packet of the squeezed state is at its peak value. In the case of a nonradiative nonthermal transition involving squeezed states the Arrhenius decay, which contains the dispersion of thermal vibrations, is shown to contain the dispersion of a super-Poisson distribution, which leads to an exponential increase in the nonradiative transition rate. Possible applications of this phenomenon are discussed. © *1996 American Institute of Physics.* [S1063-7761(96)00610-5]

1. INTRODUCTION

In recent years there has been an upsurge of interest in squeezed ($sq \equiv s$) vibrational states of oscillators in molecules and local centers of crystals (see, e.g., Refs. 1–3). The possibility of preparing such squeezed states by either applying ultrashort laser pulses or parametrically driving the oscillator[4] makes them fascinating objects for theoretical and experimental studies primarily because of the new relationship between the parameters of the squeezed vibrational states (in comparison to squeezed light) and, naturally, for new applications. Suffice it to note that the rates of optical and *nonradiative* transitions of electrons in molecules and condensed media determine the entire set of electron kinetic characteristics.

This paper discusses nonradiative transitions taking place in electronic–vibrational systems, which in contrast to optical transitions make significant use of deviations from the Franck–Condon principle.

As is known, above-barrier nonradiative transitions are determined by thermal fluctuations of the amplitude of oscillator vibrations, which leads to the Arrhenius law (the transition rate W is proportional to $\exp\{-\Delta/k_0T\}$, where Δ is the activation energy, and $k_0T \equiv D_T^2$ is the dispersion of the thermal vibrations). At low temperatures the probability of such fluctuations is low and one must allow for tunneling decay. For squeezed vibrational states the super-Poisson nature of the oscillator amplitude distribution (for high squeezing ratios) increases the dispersion D_s^2 of the vibration amplitude, so that $D_s^2 > D_t^2$. One indication of this fundamental result is the possibility of an (exponentially) sharp increase in the probability of (nonthermal) nonradiative transitions, which may experimentally manifest itself in anomalous luminescence quenching, a sharp increase in chemical reaction rates, including enzyme catalysis rates, and other phenomena directly related to rates of nonradiative processes.

In the Appendix we will see how an exact quantum calculation of the multiphoton transition rate $W_{if}^{(s)}$ with squeezed vibration vacuum can be reduced to the form

$$W_{if}^{(s)} = \int |\psi_i^{(s)}(Q,t_0)|^2 W_{if}^{\text{class}}(Q)\,dQ, \tag{I}$$

where i and f are the initial and final electron states, Q is the amplitude of the vibrational coordinate, $|\psi_i^{(s)}(Q,t_0)|^2$ is the probability density of the distribution of the vibrational amplitudes of the initial squeezed state at time t_0 [see Eq. (2) below], and $W_{if}^{\text{class}}(Q)$ is the probability of a nonradiative transition per unit time (the transition rate) when the electron interacts with a classical vibration of a given amplitude Q.

The calculations of nonradiative transition rates can be done separately for different ways of preparing the squeezed vibrational states, by ultrashort pulses or parametrically.

2. NONRADIATIVE DECAY OF SQUEEZED ELECTRON–VIBRATIONAL STATES EXCITED BY ULTRASHORT LIGHT PULSES

Squeezed states excited by ultrashort pulses realize a new class of states in molecules and solids.[1–3] Of greatest interest here are electronic–vibrational systems with so-called hot luminescence[5] associated with the 2→1 transition (see Fig. 1), which would indicate that the decay of excited vibrational states is slow. Electronic–vibrational (“vibronic”) squeezed states in molecules make it possible to observe the almost classical motion of nuclei on time scales t shorter than the decay times t_d of these states. New optical, photoelectron, and chemical properties of such states manifest themselves on such time scales. Below we calculate the rate of the nonradiative decay of a squeezed state for the electronic–vibrational system (a molecule or a local center in a crystal) depicted in Fig. 1.

The corresponding adiabatic potentials in the electron states 1, 2, and 3 interacting with the Q-vibration have the form

$$J_{1,2} = \varepsilon_{1,2} + \frac{m}{2}\omega_{1,2}^2 Q^2,$$

$$J_3 = \varepsilon_3 + \frac{m}{2}\omega_3^2 Q^2 + VQ.$$

Here m is the oscillator mass, and V is the electronic–vibrational coupling constant in the electron state 3, which

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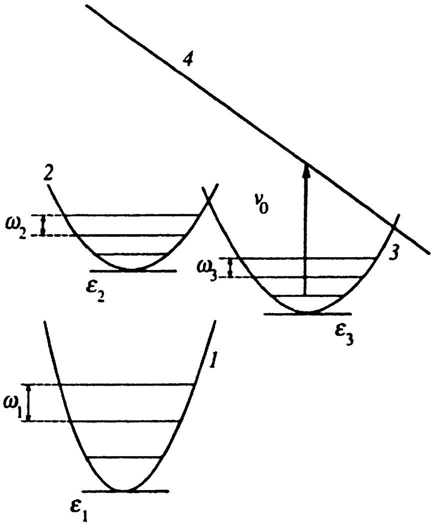


FIG. 1. Curves *1*, *2*, and *3* represent the adiabatic potentials for the corresponding electron states of the electronic–vibrational system ($\omega_1 \neq \omega_2$ and $\omega_2 = \omega_3$), and curve *4* represents the repulsive term; ε_1, ε_2, and ε_3 are energies of the minima of the adiabatic potentials for the electron states 1, 2, and 3.

determines the horizontal displacement of the parabola 3 in relation to the parabola 2.

A short light pulse of frequency Ω and field strength $\mathbf{F}_0 f(t)\sin\Omega t$, where $f(t)$ is the pulse envelope, excites a vibrational state in the upper oscillator 2 (dipole optical transitions $1 \rightarrow 2$ are assumed allowed). (Graham[7] was the first to note the preparation of squeezed states resulting from a sudden change in the oscillator frequency.)

The wave function of the upper oscillator 2 can be found by solving the following equation:

$$\psi(Q;t) = \frac{(\mathbf{d}_{12}\cdot\mathbf{F}_0)}{\hbar}\int dQ' \int dt' G(Q;t;Q;t')e^{i\Omega t} \times f(t')\psi(Q';t'). \qquad (1)$$

Here $G(Q;t;Q';t')$ is the Green's function of the harmonic oscillator.[8] Let us consider a pulse

$$f(t) = \frac{T_0}{\tau}e^{-t^2/\tau^2},$$

where τ is the pulse length and T_0 is the normalization constant, with $\tau^{-1} \gg \omega_2$. In what follows in order to simplify the calculations we assume[9] $\tau \rightarrow 0$ and $f(t) = T_0\delta(t)$, where $\delta(t)$ is the delta function. This assumption does not alter the transition pattern qualitatively but it enables us to evaluate the integral with respect to t' in (1) immediately.

For fairly low temperatures the function $\psi(Q';0)$ coincides with the wave function of the ground state of the lower oscillator 1 ($k_0 T \ll \hbar\omega_1$, where T is the temperature). Integration with respect to Q in (1) then yields

$$|\psi_2(Q;t)|^2 = \frac{N^2}{\sqrt{\pi}\sigma(t)}e^{-Q^2/\sigma^2(t)}, \qquad (2)$$

$$N^2 = \left(\frac{d_{12}F_0T_0}{\hbar}\right)^2 \cos^2\theta, \quad \theta = (\widehat{\mathbf{d}_{12},\mathbf{F}_0}),$$
$$\sigma^2(t) = \sigma_0^2\left(\eta^2\cos^2\omega_2 t + \frac{1}{\eta^2}\sin^2\omega_2 t\right), \qquad (3)$$
$$\sigma_0^2 = \frac{\hbar}{m\omega_2}, \quad \eta^2 = \frac{\omega_2}{\omega_1}.$$

Equations (2) and (3) describe the temporal variations of the wave packet in the motion of the nucleus in the electron state 2. The quantity η^2 (for $\eta > 1$) characterizes the squeezing parameter r of the vibrational mode, while for $\eta < 1$ the quantity $1/\eta^2$ acts as the squeezing parameter r, with $r = (\mu + \nu)^2$, where μ and ν are the well known parameter of the Bogolyubov–Stoler transformation,[4] satisfying $|\mu|^2 - |\nu|^2 = 1$.

In the given model the decay of the squeezed state of the oscillator 2 with the wave function (2) is related to the probability $W_{23}^{(s)} = 1/\tau_d$ of a nonradiative transition from the electron state 2 to the corresponding state 3. (Naturally, there are other decay channels, say, the radiative channel, but their probabilities are considerably lower.)

The specific nature of the present problem manifests itself primarily in the initial (t_0) distribution of the vibrational states $\varphi_n(Q)$ of oscillator 2, which depends on the properties of the C_n coefficients:

$$\psi_2(Q;t_0) = \sum_n C_n\varphi_n(Q)\exp(iE_n t_0/\hbar), \qquad (4)$$

where E_n is the energy of the oscillator in state $\varphi_n(Q)$.

Nonradiative (thermal) electron transitions are associated with considerable deviation from the Franck–Condon principle. The theory of such processes is well-developed (see, e.g., Refs. 10 and 11). The main contribution to the nonradiative transition probability is provided by the region of quasicrossing (Q) of the adiabatic potentials of the initial (2) and final (3) electron states. Here the nonradiative transition rate is described by the formula

$$W_{23} = \langle W_{23}(Q)\rangle, \qquad (5)$$

where $\langle\cdots\rangle$ stands for averaging over the initial equilibrium distribution of the vibrational coordinate Q of oscillator 2, and $W_{23}(Q)$ is the nonradiative transition probability at a fixed value of the coordinate Q:

$$W_{23}(Q) = \frac{1}{\hbar^2}\,\mathrm{Re}\int_{-\infty}^{+\infty} V_{23}(Q)\exp\left(\frac{i\hat{H}_2 t_1}{\hbar}\right)V_{23}(Q) \times\exp\left(-\frac{i\hat{H}_3 t_1}{\hbar}\right)dt_1, \qquad (6)$$

with $V_{23}(Q)$ the off-diagonal electronic–vibrational interaction matrix element mixing the electron states 2 and 3, $V_{23}(Q) \approx V_{23}Q$, and $\hat{H}_{23} = \hat{T} + J_{23}(Q)$ ($\hat{T}$ is the kinetic energy operator).

If initially a squeezed vibrational state is prepared by an ultrashort pulse on the Franck–Condon transition $1 \rightarrow 2$ (i.e., a new wave function of oscillator 2 is formed), the nonthermal nonradiative transition rate $W_{23}^{(s)}$ is

$$W_{23}^{(s)}=\langle W_{23}(Q)\rangle_s, \tag{7}$$

where by $\langle\cdots\rangle_s$ we denote the operation of averaging over the initial distribution of the coordinate Q for the squeezed states of oscillator 2 at time t_0 [in full agreement with the Appendix; see also Eq. (I)].

Thus, the difference between (5) and (7) consists in the different initial distribution of the vibrational coordinate Q: for ordinary (thermal) nonradiative transitions this is the familiar Gaussian distribution, while for squeezed states it is a super-Poisson distribution. Note that the width (dispersion) of the super-Poisson distribution varies with time in such a way that the parameters of the initial distribution depend on the choice of t_0. As the wave packet characterizing the classical motion of the nucleus in the initial electron state 2 changes, the greatest contribution to the nonradiative transition probability is provided by the times t_0 at which the overlap of the nuclear wave functions $\psi_2(Q;t_0)$ and $\psi_3(Q;t_0)$ is largest. More precisely, the times are $t_0=\pi/2\omega_2$ for $\omega_1\gg\omega_2$ ($\eta\ll 1$) and $t_0=0$ for $\omega_1\ll\omega_2$ ($\eta\gg 1$) (for more details see Sec. 4).

Let us calculate $W_{23}(Q)$ in the classical limit. In (6) we must make the following substitutions:

$$\exp\left(\frac{i\hat{H}_2t}{\hbar}\right)\exp\left(-\frac{i\hat{H}_3t}{\hbar}\right)$$

$$\rightarrow\exp\left\{\frac{i}{\hbar}\int_{\bar{t}}^{t}(H_2(t')-H_3(t'))dt'\right\},$$

$$\exp\left(\frac{i\hat{H}_2t}{\hbar}\right)Q\exp\left(-\frac{i\hat{H}_2t}{\hbar}\right)\rightarrow Q\cos(\omega_2t+\varphi).$$

Here φ is the phase, and $\bar{t}$ is an arbitrary point. We obtain

$$W_{23}^{\mathrm{class}}(Q)=\frac{V_{23}^2Q^2}{\hbar^2}\,\mathrm{Re}\int_{-\infty}^{+\infty}dt_1$$

$$\times\exp\left\{\frac{i}{\hbar}(\varepsilon_2-\varepsilon_3)(t_1-\bar{t})\right\}\cos(\omega_2t_1+\varphi)$$

$$\times\exp\left\{i\frac{VQ}{\hbar\omega_2}[\sin(\omega_2t_1+\varphi)-\sin(\omega_2\bar{t}+\varphi)]\right\}. \tag{8}$$

If the initial distribution over the vibrational states were of the Poisson type, the calculation of W_{23}^{coh} would reduce to averaging (8) over the energy distribution in the initial coherent state (see the Appendix).

In the case of squeezed vacuum states we have

$$W_{23}^{(s)}=\frac{\overline{N^2}}{\sqrt{\pi}}\frac{2}{\sigma(t_0)}\int_0^{\infty}\exp\left(-\frac{Q^2}{\sigma^2(t_0)}\right)W_{23}^{\mathrm{class}}(Q)dQ. \tag{9}$$

Here $\overline{N^2}$ stands for the average of N^2 over the angle θ [see Eq. (2)].

The integrals in (8) and (9) can be calculated directly and, ultimately the integrals are reduced to hypergeometric series.[12] In the limit of small values of the parameter

$$\rho=\frac{V\sigma(t_0)}{|\varepsilon_2-\varepsilon_3|}\ll 1$$

we find, reasoning along the lines of Refs. 13 and 14,

$$W_{23}^{(s)}\approx(2p_0-1)!!W_{23}^{\mathrm{coh}} \tag{10}$$

(p_0 is the number of phonons generated in the transition). In the most interesting case $\rho\sim 1$, the hypergeometric series cannot be approximated, while the integral in (8) can be estimated by the saddle-point method. At the saddle point t^* we can take the pre-exponential factor outside the integral sign:

$$|\cos(\omega_2t^*+\varphi)|\approx\left|\frac{\varepsilon_2-\varepsilon_3}{VQ}\right|. \tag{11}$$

Now we can evaluate the integrals in (8) and (9). We employ the expansion

$$\exp[ix\sin(\omega t+\varphi)]=\sum_{n=-\infty}^{+\infty}J_n(x)\exp[in(\omega t+\varphi)],$$

where $J_n(x)$ is the Bessel function of a real argument. In the limit $\bar{t}\rightarrow-\infty$, only the "diagonal" ($n=m$) structures remain in such expansions, i.e., the phase φ is not involved in the calculation. The answer is ($\rho\sim 1$)

$$W_{23}^{(s)}=\overline{N^2}\Omega_0\sum_n e^{-z}I_n(z)\delta\left(\frac{|\varepsilon_2-\varepsilon_3|}{\hbar\omega_2}-n\right),$$

$$z=\frac{1}{2}\rho^2\left(\frac{\varepsilon_2-\varepsilon_3}{\hbar\omega_2}\right)^2, \tag{12}$$

$$\Omega_0=\frac{2\sqrt{\pi}V_{23}^2}{\omega_2\hbar^2}\frac{|\varepsilon_2-\varepsilon_3|\sigma(t_0)}{V}, \tag{13}$$

where $I_n(z)$ is the modified Bessel function. Allowing for decay in the electronic–vibrational state 3 with a dimensionless constant $\gamma=\gamma_3/\omega_2$ leads to a replacement of the delta function by a Lorentzian. For $z>n$ we use the well-known expansion for the modified Bessel function. Then

$$W_{23}^{(s)}\approx\frac{\overline{N^2}\Omega_0}{\sqrt{2\pi}(p_0^2+z^2)^{1/4}}\exp\left\{\sqrt{p_0^2+z^2}-p_0\,\mathrm{arsinh}\,\frac{p_0}{z}\right\}$$

$$\times\frac{\gamma}{(|\varepsilon_2-\varepsilon_3|/\hbar\omega_2-p_0)^2+\gamma^2}, \tag{14}$$

with $p_0=[|\varepsilon_2-\varepsilon_3|/\hbar\omega_2]$, where $[a_0]$ is the integral part of the number a_0.

The above formula implies (for $\eta>1$ and $\omega_1>\omega_2$) that the nonradiative transition probability satisfies

$$W_{23}^{(s)}\propto\exp\left\{-\frac{1}{\rho^2}\right\}=\exp\left\{-\frac{|\varepsilon_2-\varepsilon_3|^2\eta^2}{V^2\sigma_0^2}\right\},$$

and as the squeezing parameter $1/\eta^2$ increases the probability $W_{23}^{(s)}$ grows exponentially.

3. NONRADIATIVE TRANSITIONS IN MOLECULES INVOLVING PARAMETRICALLY EXCITED SQUEEZED STATES

An important class of squeezed states is represented by states excited parametrically. Parametric resonance in the quantum case leads to an oscillator wave function that has the form of the wave function of the squeezed state.[4] The squeezing ratio of such a state builds up exponentially with the passage of time according to the law $\exp\{\frac{1}{4}\alpha_0\omega_2 t\}$, where α_0 is the dimensionless coupling constant of two vibrations interacting parametrically.

The wave-function probability density $|\psi(Q;t_0)|^2$ at times $t_0=\pi k/\omega_2$ $(k=0,1,2,3,\dots)$ when the dispersion is maximal $[d^2(t_0)\equiv d^2_{\max}]$ is

$$|\psi(Q;t_0)|^2=\frac{1}{\sqrt{\pi}d(t_0)}\exp\left\{-\frac{[Q-Q_0(t_0)]^2}{d^2(t_0)}\right\},$$
$$Q_0(t_0)=\left(\frac{2\hbar}{m\omega_2}\right)^{1/2}\alpha_0\exp\left(\frac{\alpha_0\omega_2 t_0}{4}\right)\cos\omega_2 t_0, \tag{15}$$
$$d^2(t_0)=\frac{\hbar}{m\omega_2}\exp\left(\frac{\alpha_0\omega_2 t_0}{2}\right),$$

where m is the oscillator mass.

In the limit $\alpha_0\ll 1$ we can easily verify that the term with $Q_0(t_0)$ can be dropped from (15) $[Q_0(t_0)\ll d(t_0)]$. In this case for the probability of a nonradiative transition in which initially there is a squeezed state we can use the result of Sec. 2, i.e., Eq. (14), in which $\sigma^2(t_0)$ is replaced by $d^2(t_0)$;

$$W^{(s)}_{23}\approx\frac{2V^2_{23}|\varepsilon_2-\varepsilon_3|}{V^2\hbar}\exp\left\{-\frac{\Delta}{D^2_s}\right\},$$
$$\Delta=\frac{|\varepsilon_2-\varepsilon_3|^2}{2V^2}m\omega_2^2,\quad D^2_s=\frac{m\omega_2^2}{2}d^2_{\max}, \tag{16}$$

where Δ is the potential barrier of the reaction. We have arrived at an expression that is similar to the formula for nonradiative transition rates for equilibrium thermal vibrations, with the only difference that D^2_T is replaced by D^2_s The distinguishing feature of (16) and its difference from (14) primarily lies in the fact that for parametrically excited squeezed vibrational states, $d^2_{\max}$ and hence D^2_s exponentially increase with time.

4. DISCUSSION

We start our discussion with the case of a squeezed vibrational state prepared by an ultrashort light pulse. For $\rho\gg 1$ [see Eq. (14)]

$$W^{(s)}_{23}\approx\kappa\omega_2,\qquad \kappa=\frac{2\overline{N^2}p_0V^2_{23}}{V^2}.$$

The value of the parameter κ is determined by v^2_{23}/V^2, i.e., the ratio of the off-diagonal electronic–vibrational interaction matrix element to the diagonal element. The typical values of this ratio lie in the range 10^{-2}–10^{-3}, so that the nonradiative decay of the electronic–vibrational states of oscillator 2 "allows" the wave packet to perform a large number (of order $1/\kappa$) of oscillatory variations of its halfwidth after the initial moment at which the squeezed state was prepared.

To discover nonradiative transitions in experiments one can use the method of a second reading pulse (delayed after the initial moment of preparation of the squeezed stated by time T_1) with a frequency ν_0, a pulse that mixes the states of the oscillator 3 with those of the repulsive term 4 (see Fig. 1).[6] (Direct mixing of the states of oscillator 2 with the term 4 takes place at frequencies higher than ν_0 and may be forbidden by, say, selection rules.) States 2 and 3 are assumed to have different symmetries.

Since the Stokes constant

$$a=\left(\frac{V\sigma(T_1)}{\hbar\omega_2}\right)^2$$

depends on the delay time T_1 and this dependence is of a pulsating nature,[3] the densities of the products of the system's decay to the repulsive term are also pulsating functions of the delay time T_1 and reach their peak values at $T_1=t_0+2\pi k/\omega_2$ $(k=0,1,2,3,\dots,t_0=\pi/2\omega_2$, and $\omega_1\gg\omega_2)$.

At low temperatures, the excitation of the system by a long pulse may lead to a high quantum yield of luminescence in the $2\rightarrow 1$ transition, which is due to a low tunneling decay probability W^{tun}_{23} But when the system is excited by an ultrashort pulse, the nonradiative transition probability $W^{(s)}_{23}$ becomes high $(W^{(s)}_{23}\gg W^{\text{tun}}_{23})$ and the quantum yield luminescence on the $2\rightarrow 1$ drops sharply.

Other spectroscopic methods, for instance, resonant scattering involving oscillator 3, can also be used.

Now let us use the results of Sec. 3 to examine the case of squeezed vibrational states generated parametrically. Parametric resonance in molecules has been thoroughly studied, starting with the works of Fermi and Mandel'shtam (see Ref. 15). In the simple case of a molecule of the CO_2 type, the stiffer valence vibration x of frequency $2\omega_2$ drives the deformation vibration y of frequency ω_2 due to the anharmonic interaction of the vibrations, $H'\propto\alpha_0 xy^2$. Since the shift in levels related to a Fermi resonance is small, the dimensionless constant α_0 is usually of order 10^{-1}–10^{-2}.

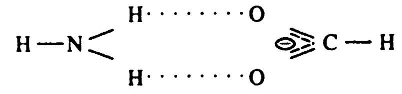
Suppose that at time $t=0$ a quantum electron state i was prepared (by optical excitation or in some other way). The decay rate of this electron state in a molecule for which there is coupling between the electron and the deformation vibration can be calculated by Eq. (16). [When the vibrations are considered in the classical setting, the emergence of a parametric resonance for small α_0 is related to the fact that in the energy of the anharmonic interaction the stiff valence vibration is assumed harmonic, so that $H'\propto\alpha_0 x_0\sin(2\omega_2 t)y^2$. Note that the amplitude x_0 is fixed by the initial condition. Here it is important that $d^2(t_0)\lesssim x^2_0$.]

The most interesting application of Eq. (16) is the corollary by which $D^2_s>\Delta$, i.e., $\exp(\alpha_0\omega_2 t_0/2)>2\Delta/\hbar\omega_2$, and the nonradiative transition probability attains its maximum value. Here the activation dependence vanishes from (16) and we have

$$W^{(s)}_{23}\approx\kappa_1\omega_2,\qquad \kappa_1=\frac{2p_0V^2_{23}}{V^2}.$$

It is this probability that must be compared with the probability of the decay of the electron state by other possible channels. The nonactivational nature of the nonradiative transition probability in the interaction with squeezed vibrations could be important for the kinetics of chemical and biological processes; for instance, it could lead to an anomalous increase in the rate of redox enzyme reactions (for the various aspects of multiphoton enzyme catalyses see Ref. 16). Here the initial moment is when the substrate and enzyme collide and form a substrate–enzyme complex. The anomalous increase of the enzyme catalysis rate occurs when the coordinate of the reaction of transformation of the substrate–enzyme complex into a free product and an enzyme coincides with the coordinate of the squeezed vibration or when then two are related indirectly. Since the conformational states of the active center of the enzyme play an important role in catalysis, the deformation of such configurations in parametric resonances may have a strong effect on the catalysis rate (the vibrations can be excited by the energy of the substrate–enzyme collision).

A simple example (a fragment of more complex chemical reactions) is the breaking of the peptide bond in the formamide molecule $H_2N{-}COH$ in the molecule's collision with the OH^- ion (see Ref. 17). The process releases 4.3 eV. The resulting complex



contains two hydrogen bonds, whose breaking forms two free molecules, NH_3 and $COOH^-$. The necessary energy is 0.78 eV. According to Ref. 18, $\omega_{CH}\approx 3000\,\mathrm{cm}^{-1}$ and $\omega_{CO}\approx 1400\,\mathrm{cm}^{-1}$. Since these vibrations are coupled by an anharmonic interaction, there can be a resonance between an overtone of the CO-vibration and the fundamental tone of the CH-vibration. The driving of the CO-vibration caused by the stored energy in the stiff vibration of the CH-bond changes the coordinate of the reaction of breaking of the hydrogen bond and ensures the rapid formation of free reaction products.

Other obvious manifestations of the increase in the nonradiative transition rates caused by parametric excitation of squeezed vibrations can also be related to a change in the quantum yield of luminescence, i.e., anomalous quenching of luminescence.

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APPENDIX

Let us calculate the mathematical expectation of the evolution operator $\hat{R}$ over the squeezed states $|\beta(t_0)\rangle_{\rm sq}$ at the initial time t_0, with the operator reduced to the antinormal form[19]

$$A\hat{R}=A\,\exp\left\{-\frac{iV}{\hbar\omega}(1-e^{-i\omega t})a\right\}\times\exp\left\{-\frac{iV}{\hbar\omega}(1-e^{+i\omega t})a^{+}\right\}\equiv\sum_{n=0}^{\infty}A_n(t)a^n(a^{+})^n, \tag{A1}$$

where a^+ and a are the photon creation and annihilation operators. The coefficients $A_n(t)$ are determined by (A1).

The mathematical expectation of the operator $\hat{R}$, or $\bar{R}$, can be written as

$$\bar{R}\equiv\langle\beta(t_0)|\hat{R}|\beta(t_0)\rangle_{\rm sq}=\frac{1}{\pi}\sum_{n=0}^{\infty}A_n(t)\langle\beta(t_0)|a^n|\alpha\rangle\langle\alpha|(a^{+})^n|\beta(t_0)\rangle_{\rm sq}d^2\alpha, \tag{A2}$$

$$\bar{R}=\frac{1}{\pi}\int|\langle\alpha|\beta(t)\rangle_{\rm sq}|^2\sum_{n=0}^{\infty}A_n(t)|\alpha|^{2n}d^2\alpha. \tag{A3}$$

We can easily establish that

$$\sum_{n=0}^{\infty}A_n(t)|\alpha|^{2n}=J_0\left(\frac{4V\sigma_0}{\hbar\omega}|\alpha|\sin\frac{\omega t}{2}\right)\equiv R^{\rm coh}(\alpha). \tag{A4}$$

Here $J_0(b)$ is the Bessel function of a real argument. The expression (A3) has the meaning of the expectation value of the evolution operator calculated for coherent states. This can be verified directly by averaging (A1) with the coherent-state distribution function (see, e.g., Refs. 19 and 20).

It is well known that $R^{\rm coh}(\alpha)$ corresponds exactly to the quantity calculated for a classical vibration (if one ignores unimportant extensive corrections of order $1/L^3$, where L^3 is the volume of the main region). Thus,

$$R^{\rm coh}(\alpha)=R^{\rm class}(\alpha). \tag{A5}$$

Let us write $\langle\alpha|\beta(t_0)\rangle_{\rm sq}$ in the form

$$\langle\alpha|\beta(t_0)_{\rm sq}=\int_{-\infty}^{+\infty}dx\langle\alpha|x\rangle\langle x|\beta(t_0)\rangle_{\rm sq}=\int_{-\infty}^{+\infty}dx\varphi_\alpha(x)\psi_{\beta(t_0)}(x), \tag{A6}$$

where

$$\varphi_\alpha(x)=\exp\left(-\frac{1}{2}|\alpha|^2\right)\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}\varphi_n\left(\frac{x}{\sigma_0}\right),$$

and $\psi_{\beta(t_0)}(x)$ is defined in (2). Here $\varphi_n(x/\sigma_0)$ is the oscillator wave function.

Further calculations can be done most easily if we take into account (A4) and evaluate the integral with respect to (A2) ($|\alpha|\equiv Q/\sigma_0$ and $\delta^2\alpha\equiv QdQd\varphi/\sigma_0^2$). We also use the expansion

$$e^{z\cos\varphi}=\sum_{m=-\infty}^{\infty}I_m(z)e^{im\varphi}.$$

Here $I_m(z)$ is the modified Bessel function. The term with $m=0$ provides a nonzero contribution. Usually the most important range of parameter α is that in which the multiphoton transition probability is far from vanishing, so that $|\alpha|V\sigma_0/\hbar\omega\gtrsim 1$ holds ($r\gg 1$; see above). For $z\gg 1$ we have the following expansion for $I_0(z)$:

$$I_0(z)\approx\frac{1}{\sqrt{2\pi z}}e^z. \tag{A7}$$

Bearing in mind the above remarks, we obtain

$$\begin{aligned}\bar{R}&=\int_{-\infty}^{+\infty}|\psi_{\beta(t_0)}(Q)|^2 J_0\left(\frac{4V}{\hbar\omega}|Q|\sin\frac{\omega t}{2}\right)dQ,\\ \bar{R}&=\int_{-\infty}^{+\infty}|\psi_{\beta(t_0)}(Q)|^2 R^{\mathrm{coh}}(Q)dQ.\end{aligned}\tag{A8}$$

As is known, the mathematical expectation of the evolution operator, $\bar{R}$, determines (with exponential accuracy) the dependence of the rate of a multiphoton process of the parameters of the system. Allowing for the pre-exponential factors and Eq. (A5), we can write the expression for the nonradiative transition rate in the final form as

$$W_{if}^{(s)}=\int_{-\infty}^{+\infty}|\psi_i(Q;t_0)|^2 W_{if}^{\mathrm{class}}(Q)dQ.\tag{A9}$$

This is similar to the formula for the rate of a multiphoton transition in the interaction of a localized electron with the squeezed vacuum of the electromagnetic-field.[21,22]

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