

Excitation of squeezed vibrational wave packets associated with Franck–Condon transitions in molecules

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A squeezed wave packet of vibrational states can form during the electronic excitation of a molecule by an ultrashort coherent light pulse. The pulse length must be small in comparison with the vibration period, and the spectral width small in comparison with the width of the absorption band. In this case the squeezing occurs in a system with a linear electronic-vibrational interaction. It stems from the small change in the phases of nonequilibrium vibrations which are excited during the application of the pulse. The time-dependent Wigner function of the nonequilibrium vibrational state is calculated. The mechanism for the spreading of the wave packet is discussed. The time evolution of the wave packet which arises modulates the spectral characteristics of optical processes associated with subsequent electron transitions from the excited state. The squeezing effect is manifested in this case as pulsations in the linewidth. A decrease in the fluctuations of the spatial coordinate corresponds to narrowing of the lines to a width smaller than the equilibrium value.

1. INTRODUCTION

In molecules, different nuclear potentials correspond to different electronic states. In the course of optical electron transitions, molecular vibrations are accordingly excited. If monochromatic light is absorbed, one vibrational level is excited in a transition from the ground state according to energy conservation. The electronic excitation of molecules by ultrashort (femtosecond-range) laser pulses,^{1–8} with a length τ shorter than the period of molecular vibrations ($\tau \ll \omega_0^{-1}$), has recently attracted much interest. Since the spectrum of such a pulse definitely overlaps several vibrational levels, the molecule is put in an unsteady vibrational state by the electron transition. This state represents a wave packet: a coherent superposition of vibrational eigenstates. In the limit of instantaneous excitation by a very short pulse, one can assume that the transition occurs with fixed nuclei and that the wave packet which arises is simply the initial vibrational wave function of the molecule, referred to the system of nuclear potentials of the excited electronic state.

Our purpose in the present study was to learn how the properties of a wave packet of vibrational states of a molecule formed as the result of an electronic transition are related to the characteristics of the actual laser pulse, i.e., to the shape of its envelope and to the nature of its phase modulation. Topics of this sort are of particular interest in the strong-coupling case, which is typical of many complex molecules and of impurity centers in crystals, in which cases the widths of electronic-vibrational absorption bands are more than an order of magnitude greater than the typical vibration frequencies.^{9,10} For electronic-vibrational systems with strong coupling, the pulse spectrum may partially overlap the absorption band, while the condition $\tau \ll \omega_0^{-1}$ holds quite accurately. We restrict the present paper to results on the excitation of a molecule by a Gaussian pulse with a spectrum determined by its envelope (we will not discuss the modulation of the pulse phase¹) and to results on a Franck–Condon

transition resulting exclusively from a spatial shift of harmonic nuclear potentials. It follows from the results that, when the spectral width of the pulse is smaller than the width of the absorption band but much larger than the frequency of molecular vibrations, the vibrational ground state of the molecule transforms into a squeezed state in the course of the excitation.^{12,13} If there is only a single vibrational mode, this result means that the quantum uncertainty in the vibrational coordinate immediately after the electronic transition is smaller than that in the ground state. The limiting case of an instantaneous excitation which sends the molecule into a coherent vibrational state^{14–16} is realized if the pulse spectrum spans the entire absorption band. The physical mechanism underlying this new squeezing effect is a small change in the phases of the nonequilibrium vibrations excited during the pulse.

A squeezing of molecular vibrations due to a change in frequency associated with an instantaneous Franck–Condon transition has already been discussed in the literature.^{17–21} That squeezing mechanism differs from the one which we will be discussing here in a fundamental way. In the first place, it is of a geometric nature and occurs simply because the wave function of the ground state of a simple harmonic oscillator, when examined with respect to a potential curve with an altered vibrational frequency, looks like a squeezed state. Second, it does not lead to a genuine reduction of the quantum uncertainty in the vibrational coordinate in comparison with the smaller of the uncertainties in the vibrational ground states of the potentials involved.

The squeezing effect of the present paper can be observed by virtue of its spectral manifestations in femtosecond laser experiments of the pump–(probe signal) type. We will show below that the time evolution of a packet of molecular vibrational states which arises as a result of pulsed pumping modulates the spectral characteristics of the probing processes associated with subsequent electronic transi-

tions from the excited electronic state. The motion of the packet as a whole leads to oscillations of the Stokes parameter, and the squeezing effect is manifested as pulsations in the linewidth. A decrease in the coordinate uncertainty corresponds to a narrowing of the line to a width smaller than its equilibrium value. In the limiting case of instantaneous pumping, the line-squeezing effect disappears, and the pattern of temporal oscillations in the spectrum agrees with that found previously.^{22,23}

2. THE MODEL

We consider a system specified by the Hamiltonian

$$H = H_0 + H_1(t), \quad (1)$$

$$H_0 = \sum_i \varepsilon_i a_i^\dagger a_i + \sum_{i,\lambda} \hbar \omega_\lambda C_{i\lambda} (b_\lambda^\dagger + b_\lambda) a_i^\dagger a_i + \sum_\lambda \hbar \omega_\lambda b_\lambda^\dagger b_\lambda. \quad (2)$$

Here H_0 is the simplest Hamiltonian in the theory of electronic-vibrational transitions which describes the shift of the average values of the normal coordinates of the set of simple harmonic oscillators associated with a change in electronic state. The operators a_i in (2) are electron operators, b_λ are phonon operators, ε_i are electron energy levels, ω_λ is the frequency of a phonon of mode λ , and $C_{i\lambda}$ is the dimensionless electron-phonon interaction constant. The multimode model is being used here because it is typical of the strong-coupling case. The Hamiltonian $H_1(t)$ determines transitions between levels. We assume that a classical external electromagnetic field is responsible for the transitions. We take the interaction with this field into account in the resonance approximation:

$$H_1(t) = \sum_{i>j} [\mu_{ij}^-(t) a_i^\dagger a_j + \mu_{ij}^+(t) a_j^\dagger a_i], \quad (3)$$

where

$$\begin{aligned} \mu_{ij}^-(t) &= \mu_{ij}^- e_k(t) \exp(-i\Omega_k t), \quad \mu_{ij}^- = \mathbf{d}_{ij} \mathbf{E}_{0k}^*/2, \\ \mu_{ij}^+(t) &= \mu_{ij}^+(t)^*, \\ e_k(t) &= \pi^{-1/2} \exp[-u_k^2(t-t_k)^2/2], \end{aligned} \quad (4)$$

and \mathbf{d}_{ij} is the dipole matrix element of the electronic transition. We assume that \mathbf{d}_{ij} does not depend on the phonon variables. In (3) and (4) we have allowed for the circumstance that a resonant interaction with Gaussian momenta with various amplitudes \mathbf{E}_k , average frequencies Ω_k , lengths u_k^{-1} , and repetition times t_k corresponds to transitions between different pairs of levels. Using the unitary transformation

$$S = \exp\left[\sum_\lambda C_{i\lambda} a_i^\dagger a_i (b_\lambda - b_\lambda^\dagger)\right]$$

in the Hamiltonian (1), we go over to the convenient new representation

$S^\dagger H S$

$$= \sum_i \varepsilon_i a_i^\dagger a_i + \sum_\lambda \hbar \omega_\lambda b_\lambda^\dagger b_\lambda + \sum_{i>j} [\mu_{ij}^-(t) D_{ij} a_i^\dagger a_j + \text{H.a.}],$$

where

$$\begin{aligned} \tilde{\varepsilon}_i &= \varepsilon_i + \sum_\lambda C_{i\lambda}^2 \hbar \omega_\lambda, \\ D_{ij} &= \exp\left[\sum_\lambda \kappa_{ij\lambda} (b_\lambda^\dagger - b_\lambda)\right], \\ \kappa_{ij\lambda} &= C_{i\lambda} - C_{j\lambda}. \end{aligned} \quad (5)$$

This unitary transformation of Hamiltonian (1) eliminates the electron-phonon interaction from the zeroth part of the Hamiltonian, H_0 , and moves it to H_1 in such a way that the vertex representing the interaction with the electromagnetic field which corresponds to a transition from level j to level i is additionally multiplied by the shift operator (5).

3. EQUILIBRIUM ABSORPTION SPECTRUM FOR A SHORT LIGHT PULSE

As an auxiliary problem we will calculate the equilibrium absorption spectrum which arises as the result of an electronic-vibrational transition caused by a short light pulse. We assume that at the initial time $t = -\infty$ the molecule is in electronic state $|i\rangle$, and its vibrations are described by an equilibrium density matrix ρ_0 . At the time $t = 0$, a light pulse in resonance with the transition $i \rightarrow j$ is applied to the molecule. The population of level j at time t calculated in second-order perturbation theory is then given by the expression

$$\begin{aligned} f_j(t) &= |\mu_{ij}|^2 \pi^{-1/2} \hbar^{-2} \int_{-\infty}^t dt_1 \int_{-\infty}^t dt_2 \exp\left[i\delta(t_1 - t_2)\right. \\ &\quad \left. - \frac{u^2}{2}(t_1^2 + t_2^2)\right] \text{Sp}[D_{ji}(t_1) \rho_0 D_{ij}(t_2)], \end{aligned} \quad (6)$$

where $\delta = \tilde{\varepsilon}_j/\hbar - \tilde{\varepsilon}_i/\hbar - \Omega$. The averaging in (6) is carried out exactly, and the expression found as a result is well known.²⁴ The result of the averaging of the more complex expressions which include the product of an arbitrary number of shift operators D is given in Ref. 25, among other places. Carrying out the averaging in (6), we switch to the new integration variables $\tau = (t_1 + t_2)/2$, $\eta = t_1 - t_2$ for convenience. As a result, (6) becomes

$$\begin{aligned} f_j(t) &= |\mu_{ij}|^2 \pi^{-1/2} \hbar^{-2} \int_{-\infty}^t d\tau \int_{-2(t-\tau)}^{2(t-\tau)} d\eta \\ &\quad \times \exp\left[-u^2 \tau^2 - \frac{u^2}{4} \eta^2 + i\delta \eta + g(\eta)\right], \end{aligned} \quad (7)$$

where

$$g(\eta) = \sum_\lambda \kappa_{ij\lambda}^2 [(n_\lambda + 1) e^{i\omega_\lambda \eta} + n_\lambda e^{-i\omega_\lambda \eta} - 2n_\lambda - 1], \quad (8)$$

and n_λ are the equilibrium occupation numbers of the phonon modes. To evaluate the integral in (7), we expand the function (8) in η and retain small terms up to second order:

$$\begin{aligned} g(\eta) &= iA \eta - 1/2 B^2 \eta^2, \quad A = \sum_\lambda \kappa_{ij\lambda}^2 \omega_\lambda, \\ B^2 &= \sum_\lambda \kappa_{ij\lambda}^2 \omega_\lambda^2 (2n_\lambda + 1). \end{aligned} \quad (9)$$

As a result we find

$$\begin{aligned} f_j(t) &= \hbar^{-2} |\mu_{ij}|^2 F(t) u^{-1} w_{i \rightarrow j}(\Omega), \\ w_{i \rightarrow j}(\Omega) &= \left(\frac{2\pi}{B^2 + u^2/2}\right)^{1/2} \exp\left[-\frac{(\delta + A)^2}{2B^2 + u^2}\right]. \end{aligned} \quad (10)$$

In (10), $w_{i \rightarrow j}(\Omega)$ is the spectrum for the absorption of the light pulse, and $F(t)$ is the preexponential factor which arises from incorporating the limit of the integration range in the integral (7). The factor $F(t)$ is normalized by the condition $F(\infty) = 1$; it approaches unity even for $t \gtrsim u^{-1}$. The explicit expression for $F(t)$ is unimportant for the problems of this paper, so we will omit it.

To rigorously analyze the conditions for the applicability of (10), we should incorporate the following terms of the expansion in (9). However, since the expansion is carried out near the origin, it is sufficient to require

$$|\omega_\lambda \eta_0| \ll 1, \quad (11)$$

where η_0 is a saddle point.²⁶ From (7) and (9) we find

$$\eta_0 = \frac{i(\delta + A)}{(B^2 + u^2/2)}. \quad (12)$$

In (12) we can assume $|\delta + A| \sim (2B^2 + u^2)^{1/2}$. The inequality (11) then becomes the strong-coupling condition:

$$1/2(2B^2 + u^2)^{1/2} \gg \omega_\lambda. \quad (13)$$

Analysis shows that under the strong-coupling condition the Gaussian region in which (10) holds extends substantially beyond the half-width of the absorption band. Everywhere below we assume that the average frequency of the exciting pulse is in the Gaussian region of the absorption band.

4. WIGNER FUNCTION OF NONEQUILIBRIUM MOLECULAR VIBRATIONS

As a result of the electron transition caused by the short light pulse, nonequilibrium molecular vibrations are excited. In the Schrödinger picture, the unnormalized density matrix of the nonequilibrium phonons is

$$R(t) = \int_{-\infty}^t d\tau \int_{-2(t-\tau)}^{2(t-\tau)} d\xi \exp\left(-u^2\tau^2 - \frac{u^2}{4}\xi^2 + i\delta\xi\right) \times D_{ji}(-t+\tau+\xi/2)\rho_0 D_{ij}(-t+\tau-\xi/2). \quad (14)$$

To analyze the properties of the state described by the density matrix (14), we introduce the operators \hat{Q} and \hat{P} :

$$\begin{aligned} \hat{Q} &= N^{-1} \sum_\lambda \kappa_{ji\lambda} \omega_\lambda (b_\lambda^+ + b_\lambda), \\ \hat{P} &= N^{-1} \sum_\lambda \kappa_{ji\lambda} \omega_\lambda i (b_\lambda^+ - b_\lambda), \\ N^2 &= 2 \sum_\lambda \kappa_{ji\lambda}^2 \omega_\lambda^2, \quad [\hat{Q}, \hat{P}] = i. \end{aligned} \quad (15)$$

These operators signify the collective dimensionless coordinate shift of the oscillators in the course of the $i \rightarrow j$ electronic transition and the momentum associated with it by the canonical commutation relation. We use the density matrix (14) to construct a Wigner distribution function for these quantities:

$$W(p, q) = \int \frac{d\nu}{2\pi} \int \frac{d\mu}{2\pi} \exp(-i\mu p - i\nu q) \chi(\mu, \nu), \quad (16)$$

where $\chi(\mu, \nu)$ is the generating functional (characteristic function), given by

$$\chi(\mu, \nu) = \text{Sp}[\exp(i\mu\hat{P} + i\nu\hat{Q})R(t)] / \text{Sp}[R(t)]. \quad (17)$$

The averaging in the numerator in (17) is carried out exact-

ly. As a result we find the following expression for this characteristic function:

$$\begin{aligned} \chi(\mu, \nu) &= \text{Sp}[R(t)]^{-1} \int_{-\infty}^t d\tau \int_{-2(t-\tau)}^{2(t-\tau)} d\xi \exp\left[-u^2\tau^2 - \frac{u^2}{4}\xi^2 \right. \\ &\quad \left. + i\delta\xi + g(\xi) - \frac{B^2}{2N^2}(\mu^2 + \nu^2) + i\frac{\mu}{N}P(\tau, \xi, t) + i\frac{\nu}{N}Q(\tau, \xi, t)\right], \end{aligned} \quad (18)$$

where

$$P(\tau, \xi, t) = 2 \sum_\lambda \kappa_{ji\lambda}^2 \omega_\lambda \sin \omega_\lambda(t-\tau) [(n_\lambda + 1)e^{i\omega_\lambda \xi/2} - n_\lambda e^{-i\omega_\lambda \xi/2}], \quad (19)$$

$$Q(\tau, \xi, t) = -2 \sum_\lambda \kappa_{ji\lambda}^2 \omega_\lambda \cos \omega_\lambda(t-\tau) [(n_\lambda + 1)e^{i\omega_\lambda \xi/2} - n_\lambda e^{-i\omega_\lambda \xi/2}].$$

Substituting (18) into (16), and integrating over ν and μ , we find

$$\begin{aligned} W(p, q) &= \frac{N^2}{2\pi B^2 \text{Sp}[R(t)]} \int_{-\infty}^t d\tau \int_{-2(t-\tau)}^{2(t-\tau)} d\xi \exp\left[-u^2\tau^2 - \frac{u^2}{4}\xi^2 \right. \\ &\quad \left. + i\delta\xi + g(\xi) - \frac{N^2}{2B^2}(p - N^{-1}P)^2 - \frac{N^2}{2B^2}(q - N^{-1}Q)^2\right]. \end{aligned} \quad (20)$$

In calculating the Wigner function from (19) and (20), we are interested in times $t > u$. We assume that the conditions stated in the preceding section of this paper hold. Using expansion (9) for the function $g(\xi)$, we divide by $\text{Sp}[R(t)]$ in (20):

$$\begin{aligned} W(p, q) &= \frac{N^2 u (2B^2 + u^2)^{1/2}}{(2\pi B)^2} \int d\tau \int d\xi \exp\left[-u^2\tau^2 \right. \\ &\quad \left. - \frac{1}{2}\left(B^2 + \frac{u^2}{2}\right)(\xi - \eta_0)^2 - \frac{N^2}{2B^2}(p - N^{-1}P)^2 - \frac{N^2}{2B^2}(q - N^{-1}Q)^2\right], \end{aligned} \quad (21)$$

where η_0 is given by (12). We evaluate the integral in (21) in the Gaussian approximation. For this purpose we use the functions P and Q in series form:

$$\begin{aligned} P(\tau, \xi, t) &= P_0(t) + i\xi P_1(t) + \tau P_2(t), \\ Q(\tau, \xi, t) &= Q_0(t) + i\xi Q_1(t) + \tau Q_2(t), \end{aligned} \quad (22)$$

where

$$\begin{aligned} Q_0(t) &= -2 \sum_\lambda \kappa_{ji\lambda}^2 \omega_\lambda \cos \omega_\lambda t, \\ Q_1(t) &= -\sum_\lambda \kappa_{ji\lambda}^2 \omega_\lambda^2 (2n_\lambda + 1) \cos \omega_\lambda t, \\ Q_2(t) &= -2 \sum_\lambda \kappa_{ji\lambda}^2 \omega_\lambda^2 \sin \omega_\lambda t. \end{aligned} \quad (23)$$

The coefficients $P_i(t)$ are found from the corresponding coefficients $Q_i(t)$ by adding $\pi/2$ to the arguments of the trigonometric functions in the latter. We introduce

$$p_0 = N^{-1} \left(P_0 - \frac{(\delta + A)P_1}{B^2 + u^2/2} \right), \quad q_0 = N^{-1} \left(Q_0 - \frac{(\delta + A)Q_1}{B^2 + u^2/2} \right),$$

$$p_1 = \frac{P_1}{(B^2 + u^2/2)^{1/2}}, \quad q_1 = \frac{Q_1}{(B^2 + u^2/2)^{1/2}},$$

$$p_2 = \frac{P_2}{2^{1/2}u}, \quad q_2 = \frac{Q_2}{2^{1/2}u},$$

$$a_{11} = B^2 + q_2^2 - q_1^2, \quad a_{22} = B^2 + p_2^2 - p_1^2,$$

$$a_{12} = p_1 q_1 - p_2 q_2.$$

As a result we find the following expression for the Wigner function:

$$W(p, q) = \frac{N^2}{2\pi} [a_{11}a_{22} - a_{12}^2]^{-1/2} \times \exp \left\{ -\frac{N^2 [(p-p_0)^2 a_{11} + 2(p-p_0)(q-q_0)a_{12} + (q-q_0)^2 a_{22}]}{2(a_{11}a_{22} - a_{12}^2)} \right\}. \quad (24)$$

Expression (24) can also be written in a form in which the quadratic form in the argument of the exponential function is referred to principal axes:

$$W(p, q) = \frac{N^2}{2\pi} (\lambda_+ \lambda_-)^{-1/2} \exp \left(-\frac{N^2 \bar{p}^2}{2\lambda_-} - \frac{N^2 \bar{q}^2}{2\lambda_+} \right), \quad (25)$$

where

$$\lambda_{\pm} = \frac{a_{11} + a_{22}}{2} \pm \left[\frac{(a_{11} - a_{22})^2}{4} + a_{12}^2 \right]^{1/2},$$

$$\bar{p} = (p - p_0) \cos \varphi + (q - q_0) \sin \varphi,$$

$$\bar{q} = (q - q_0) \cos \varphi - (p - p_0) \sin \varphi,$$

$$\varphi = \frac{1}{2} \arctg \frac{2a_{12}}{a_{11} - a_{22}}.$$

Expressions (24) and (25) are typical of a Wigner function which describes the superposition of a coherent squeezed signal and a thermal noise. The only difference between expression (24), (25) and the corresponding Wigner function for a single vibrational mode is that the coefficients in (23) have an anharmonic time dependence. A characteristic function $\chi(\mu, \nu)$ equivalent in physical content to Wigner function (24) was derived in Refs. 27 and 28.

All the coefficients in (24) and (25) are functions of the time. At $t = 0$, i.e., immediately after the excitation, the coefficient a_{12} vanishes, and the system of oscillators is in a squeezed state with reduced fluctuations of the collective coordinate Q :

$$\Delta Q = \frac{1}{N} \left(\frac{B^2 u^2}{2B^2 + u^2} \right)^{1/2}. \quad (26)$$

Strong squeezing is achieved in the case $B \gg u$. The condition $u \gg \omega_\lambda$ must hold simultaneously (more on this below). The squeezing effect can thus occur only in the case of strong electronic-vibrational coupling. The limiting value of the measure of dispersion of the collective coordinate is

$$\Delta Q = u/2^{1/2}N.$$

In the opposite case $u \gg B$, there is no squeezing:

$$\Delta P = \Delta Q = B/2^{1/2}N. \quad (27)$$

The nonequilibrium phonon state with different values of ΔP and ΔQ which is found from (14) in the limit $u \rightarrow \infty$ corresponds to a unitary transformation of the original density matrix ρ_0 :

$$R(t) = D_{ji}(-t) \rho_0 D_{ij}(-t). \quad (28)$$

We have used this expression previously, in Ref. 22.

The uncertainty relation at $t = 0$ is

$$\Delta P(0) \Delta Q(0) = \left[\frac{B^2 (u^2 B^2 + N^4/2)^2}{N^4 (2B^2 + u^2)} \right]^{1/2}. \quad (29)$$

At absolute zero we have $N^2 = 2B^2$, and the square root in (29) has the value $1/2$. This result means that if the initial state of the oscillators is the ground state then their excited state with respect to the collective variables which we have introduced is a minimal Gaussian packet. The uncertainty relation takes a particularly graphic form when all the vibrational modes have the same frequency ω_0 . In this case, the uncertainty relation, understood as $(\lambda_+ \lambda_-)^{1/2}$, holds at all times t :

$$\Delta P \Delta Q = \frac{1}{2} \left[\frac{2\kappa^2 \omega_0^2 + u^2 (2n+1)}{2\kappa^2 \omega_0^2 + u^2 / (2n+1)} \right]^{1/2} \leq \frac{1}{2} (2n+1).$$

The packet of nonequilibrium molecular vibrations which appears at $t = 0$ spreads out as it evolves. Formally, this spreading stems from the collective nature of the variables under consideration. It occurs because the various vibrational modes with different frequencies lose their phase coherence. Mathematically, this dephasing is manifested by the vanishing of the coefficients in (23) as $t \rightarrow \infty$. In this limit, the Wigner function (24) tends toward its equilibrium form, with equal values of the measures of dispersion of the momentum and coordinate fluctuations in (27). We wish to stress that the spreading of the packet due to the dephasing of the modes by no means always automatically ensures a transition to an equilibrium state. For example, it does not do so in the case in which there is a change in vibration frequency as well as a shift of the equilibrium nuclear positions in the course of the Franck-Condon transition.

The analysis of the conditions for the applicability of expression (24) is based on the following inequalities (as in the preceding section of this paper):

$$|\xi_0 \omega_\lambda| \ll 1, \quad |\tau_0 \omega_\lambda| \ll 1, \quad (30)$$

where ξ_0 and τ_0 are saddle points for the integral (21). For simplicity we restrict the analysis of inequalities (30) to the initial time $t = 0$. We then find from (21) and (22)

$$\xi_0 = \eta_0 - i2N(q - q_0)/u^2,$$

$$\tau_0 = N p_2(0) p / 2^{1/2} u [B^2 + p_2^2(0)].$$

Using expression (24) for the Wigner function, we find the estimates

$$|q - q_0| \sim N^{-1} (2a_{11})^{1/2} = \frac{u}{N} \left(\frac{2B^2}{2B^2 + u^2} \right)^{1/2},$$

$$|p| \sim N^{-1} (2a_{22})^{1/2} = N^{-1} [2(B^2 + p_2^2(0))]^{1/2}.$$

As a result, the inequalities (30) become

$$|\xi_0 \omega_\lambda| \leq |\omega_\lambda \eta_0| + 2 \frac{\omega_\lambda}{u} \left[\frac{2B^2}{2B^2 + u^2} \right]^{1/2} \ll 1,$$

$$|\tau_0 \omega_\lambda| \sim \frac{\omega_\lambda}{u} p_2(0) [B^2 + p_2^2(0)]^{-1/2} \ll 1.$$

Consequently, expression (24) holds at $u \gg \omega_\lambda$.

To conclude this section of the paper we note that the squeezing effect arises in this case because of small changes in the phases and a quantum interference of the nonequilibrium

um molecular vibrations which are excited during the pulse. That such interference is possible is a specific feature of the excitation of vibrations in the course of a Franck–Condon transition. In another example (one which also involves a coordinate shift)—that of the excitation of a charged harmonic oscillator as the result of the imposition of a uniform electric field—squeezing does not occur, regardless of the time dependence of the field.²⁹ We continue our discussion of the squeezing mechanism in the Appendix to this paper, where we derive an expression for the wave function of the molecule after it has interacted with the short light pulse.

5. TWO-STAGE EXCITATION OF A MOLECULE BY ULTRASHORT LIGHT PULSES

We turn now to the problem of two successive electronic-vibrational transitions induced in a complex molecule by ultrashort light pulses. In studying the interaction of a molecule with short light pulses we should evidently calculate the probability for a transition to the final state over a time greater than the time delay between the pulses. Physically, this time is limited by the radiative lifetimes of the excited states of the molecule. We will assume below that the radiative lifetimes are much longer than all the other time scales of the problem, including the time delay T . We assume that the molecule is initially (at $t = -\infty$) in the electronic state i and that its vibrations are described by the equilibrium density matrix. At the time $t = 0$, the first pulse is applied to the molecule. This pulse is in resonance with the electronic transition $i \rightarrow j$. At $t = T$, a second pulse, in resonance with the transition $j \rightarrow k$, is applied. The population of level k of the molecule at a time $t \gg T$ is then given by

$$f_k = \pi^{-1} \hbar^{-4} |\mu_{jk}|^2 |\mu_{ij}|^2 \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{+\infty} dt_3 \int_{-\infty}^{t_3} dt_4 \times \exp \left[-\frac{u_2^2}{2} (t_1 - T)^2 - \frac{u_1^2}{2} t_2^2 - \frac{u_1^2}{2} t_3^2 - \frac{u_2^2}{2} (t_4 - T)^2 + i\delta_2 (t_1 - t_2) + i\delta_1 (t_2 - t_3) \right] \text{Sp} [D_{kj}(t_1) D_{ji}(t_2) \rho_0 D_{ij}(t_3) D_{jk}(t_4)]. \quad (31)$$

Here we have set $t = \infty$, in view of the discussion above. The quantities δ_1 and δ_2 in (31) are the detunings for the first and second transitions, respectively. We change variables in (31). We set $t_1 - t_2 = \xi$, $t_1 + t_2 = 2\tau$, $t_2 - t_3 = \eta$, $t_2 + t_3 = 2\tau + 2\sigma - 2T$. As a result we find an integrand in (31) in which only the exponential function depends on the variable t , by virtue of the properties of the trace. The integration over τ can then be carried out immediately. After an averaging, expression (31) becomes

$$f_k = \pi^{-1} \hbar^{-4} w(u_1 u_2)^{-1} |\mu_{ij}|^2 |\mu_{jk}|^2 \int_{-\infty}^T d\sigma \int_{-\infty}^{+\infty} d\xi \int_{\xi-2T+2\sigma}^{\xi+2T-2\sigma} d\eta \times \exp \left[-w^2 \sigma^2 - \frac{u_1^2}{4} \eta^2 - \frac{u_2^2}{4} \xi^2 + i\delta_2 \xi + i\delta_1 \eta + g_1(\eta) + g_2(\xi) + g_{12}(\eta, \xi, \sigma; T) \right], \quad (32)$$

where $w^2 = u_1^2 u_2^2 / (u_1^2 + u_2^2)$, the functions g_1 and g_2 are given by (8), in which we use the coefficients $\kappa_{ij\lambda}$ and $\kappa_{jk\lambda}$, which correspond to the first and second transitions; and the function g_{12} describes the coupling of the transitions:

$$g_{12}(\eta, \xi, \sigma; T) = \sum_{\lambda} \kappa_{kj\lambda} \kappa_{ij\lambda} \{ (n_{\lambda} + 1) [\exp(i\omega_{\lambda}(\xi/2 + \eta/2 + T - \sigma)) + \exp(i\omega_{\lambda}(\xi/2 + \eta/2 - T + \sigma)) - \exp(-i\omega_{\lambda}(\xi/2 - \eta/2 - T + \sigma)) - \exp(-i\omega_{\lambda}(\xi/2 - \eta/2 + T - \sigma))] + n_{\lambda} [\dots]^* \}. \quad (33)$$

The notation $[\dots]^*$ in (33) means the complex conjugate of the factor which follows $n_{\lambda} + 1$. To evaluate the integral in (32), we expand the functions g_1 , g_2 , and g_{12} in series in $\omega_{\lambda} \eta$, $\omega_{\lambda} \xi$, and $\omega_{\lambda} \sigma$, and we retain terms up to second order inclusively:

$$g_{12}(\xi, \eta, \sigma; T) = iA_{12}(T) \xi - B_{12}^2(T) \xi \eta + iC_{12}^2(T) \xi \sigma, \quad (34)$$

$$A_{12}(T) = 2 \sum_{\lambda} \kappa_{kj\lambda} \kappa_{ij\lambda} \omega_{\lambda} \cos \omega_{\lambda} T,$$

$$B_{12}^2(T) = \sum_{\lambda} \kappa_{kj\lambda} \kappa_{ij\lambda} \omega_{\lambda}^2 (2n_{\lambda} + 1) \cos \omega_{\lambda} T, \quad (35)$$

$$C_{12}^2(T) = 2 \sum_{\lambda} \kappa_{kj\lambda} \kappa_{ij\lambda} \omega_{\lambda}^2 \sin \omega_{\lambda} T.$$

As a result we find the following expression for the integral in (32):

$$f_k = \hbar^{-4} |\mu_{ij}|^2 |\mu_{jk}|^2 (u_1 u_2)^{-1} w_{i \rightarrow j} F(T) w_{j \rightarrow k}(T), \quad (36)$$

$$w_{j \rightarrow k}(T) = \left(\frac{2\pi}{\bar{B}^2(T)} \right)^{1/2} \exp \left[-\frac{(\delta_2 + \bar{A}_2(T))^2}{2\bar{B}^2(T)} \right],$$

where $w_{i \rightarrow j}$ is given by (10), and $w_{j \rightarrow k}(T)$ is the nonequilibrium spectrum for the absorption of the second light pulse. In (36) we have introduced

$$\bar{A}_2(T) = A_2 + A_{12}(T) - \frac{(\delta_1 + A_1) B_{12}^2(T)}{B_1^2 + u_1^2/2}, \quad (37)$$

$$\bar{B}^2(T) = B_2^2 + \frac{u_2^2}{2} - \frac{B_{12}^4(T)}{B_1^2 + u_1^2/2} + \frac{C_{12}^4(T)}{2w^2}, \quad (38)$$

where the coefficients A_i and B_i^2 are given by (9) for the first and second transitions, respectively.

Let us analyze the consequences of expressions (36)–(38). We first consider the limiting case in which the initial excitation of the molecule is by a broad-band pulse. In other words, we assume that the spectral width of the first pulse is much greater than the width of the absorption band for the $i \rightarrow j$ transition. We also assume $u_1 \gg u_2$. Then we can formally take the limit $u_1 \rightarrow \infty$ in the expression for $w_{j \rightarrow k}(T)$. As a result we find

$$w_{j \rightarrow k}(T) |_{u_1 \rightarrow \infty} = \left(\frac{2\pi}{B_2^2 + u_2^2/2 + C_{12}^4(T)/2u_2^2} \right)^{1/2} \times \exp \left[-\frac{(\delta_2 + A_2 + A_{12}(T))^2}{2(B_2^2 + u_2^2/2 + C_{12}^4(T)/2u_2^2)} \right]. \quad (39)$$

In this case the nonequilibrium spectrum is described by a Gaussian curve with a time-dependent Stokes parameter. There is also a temporal modulation of the width of the distribution. Expression (39) was derived in the approximation

which corresponds to an instantaneous transfer of the equilibrium initial vibrational density matrix to the system of potentials of the electronic state of the molecule which is excited. An instantaneous transfer of this sort is described in the model at hand by a unitary transformation of the density matrix in accordance with (28).

We turn now to the case in which the spectral widths of the first and second pulses are smaller than the widths of the equilibrium absorption bands for the corresponding transitions. In this case the time evolution of the spectrum for the absorption of the second pulse acquires some interesting new features. According to (37), the Stokes parameter now depends on the central frequency of the first pulse. If this central frequency of the first pulse corresponds to the center of the absorption band, however, the time evolution of the Stokes parameter is described by the previous expression. The absolute value of those additional variations in the Stokes parameter, (37) (due to the detuning of the frequency of the first pulse from the center of the absorption band), for which the general expression (36) remains valid can be estimated by $|B_{12}^2(T)|(B_1^2 + u_1^2/2)^{-1/2}$. At values $T \ll \omega_\lambda^{-1}$, the absorption spectrum for the second pulse becomes sharply narrower. We set $T = 0$ in (38):

$$B_2^2(0) = \frac{1}{2} \frac{u_2^2 B_1^2 + u_1^2 B_2^2 + u_1^2 u_2^2 / 2}{B_1^2 + u_1^2 / 2} + \frac{B_1^2 B_2^2 - B_{12}^4(0)}{B_1^2 + u_1^2 / 2}. \quad (40)$$

By virtue of the definitions (9) and (35) of the coefficients B_1^2 , B_2^2 , and $B_{12}^2(0)$, the last fraction on the right side of (40) is not negative; it is equal to zero if $\kappa_{kj\lambda} = s\kappa_{jil}$. In other words, the shifts of the average oscillator coordinates in the course of the second electronic transition for all modes are proportional to the displacements in the course of the first transition in an identical way. In the case $\kappa_{kj\lambda} = s\kappa_{jil}$, identical collective shifts of the coordinates, (15), correspond to the first and second transitions. In this case the limiting values of the spectral width for $T = 0$ and $T = \infty$ [i.e., for a value of T for which the coefficients (35) can be assumed zero] are

$$\bar{B}_2^2(0) = \frac{1}{2} u_2^2 + s^2 \frac{B_1^2 u_1^2}{2B_1^2 + u_1^2}, \quad (41)$$

$$\bar{B}_2^2(\infty) = \frac{1}{2} u_2^2 + s^2 B_1^2$$

and we have $\bar{B}_2^2(0) \ll \bar{B}_2^2(\infty)$ if $s^2 B_1^2 \gg u_2^2/2$, $B_1^2 \gg u_1^2/2$. Expression (41) for $\bar{B}_2^2(0)$ obviously corresponds to (26). As in the preceding sections of this paper, we can easily show that the condition $\bar{B}_2^2(0) \gg \omega_\lambda^2$ —a necessary condition for the applicability of expansion (34)—imposes a lower limit on the width of the spectral distribution.

This temporal modulation of the excitation spectrum might find practical applications in photochemical reactions involving states attainable by means of two-photon transitions.³⁰ For example, if the equilibrium absorption spectrum for a transition from a photoexcited electronic state of certain molecules in solution overlapped the absorption spectrum of the solvent, the nonequilibrium spectrum could, for a certain value of the time delay, fall in the transparency region, so an efficient two-stage pulsed excitation of the molecules would become possible.

Temporal modulation is also seen in measurements of

the induced absorption spectrum for the probing pulse, which is given by

$$S = - \int_{-\infty}^{+\infty} dt E_2(t) \dot{P}_3(t) = \int_{-\infty}^{+\infty} dt \dot{E}_2^-(t) P_3^+(t) + \text{c.c.}, \quad (42)$$

where $P_3^+(t)$ is the positive-frequency part of the cubic polarization corresponding to this excitation scheme. A calculation from (42) yields an expression which differs from that in (36) in the form of the preexponential factor.

APPENDIX

We assume that at $t = -\infty$ the molecule is in electronic state $|i\rangle$ and in the vibrational ground state $|0\rangle$. After the interaction with the light pulse, the wave function of the molecule is

$$|\psi, t\rangle = |i, t\rangle |0\rangle - \frac{i\mu_{ij}^-}{\hbar u} |j, t\rangle |u, t\rangle, \quad (A1)$$

where $|i, t\rangle = \exp(-i\varepsilon_i t/\hbar)|i\rangle$, and $|u, t\rangle$ is the vibrational wave function of the molecule in the excited electronic state, given by

$$|u, t\rangle = \frac{u}{\pi^{1/4}} \int_{-\infty}^{+\infty} d\tau \exp\left(i\delta\tau - \frac{u^2}{2}\tau^2\right) D(\tau-t)|0\rangle, \quad (A2)$$

$$D(\tau-t) = \exp\{\kappa[b^+ e^{i\omega(\tau-t)} - b e^{-i\omega(\tau-t)}]\}. \quad (A3)$$

For simplicity we adopt a model of a molecule with a single vibrational mode. Let us analyze (A2) in the limiting cases $u \ll \omega$ and $u \gg \omega$. In the first of these cases, we expand the coherent state in eigenstates of a simple harmonic oscillator. Expression (A2) then becomes

$$|u, t\rangle = 2^{1/2} \pi^{1/4} \sum_n \exp\left[-\frac{(\delta+n\omega)^2}{2u^2}\right] \frac{\kappa^n}{(n!)^{1/2}} |n, t\rangle, \quad (A4)$$

$$|n, t\rangle = \exp(-in\omega t) |n\rangle.$$

In the limit $u \rightarrow 0$, we are left with only one term in the sum over n in (A4). For this one term we have $\delta + n\omega = 0$; i.e., the single vibrational state $|n, t\rangle$ is excited. In the state $|n, t\rangle$, the variances of the quadrature components of the annihilation operator $b = b_1 + ib_2$ are equal:

$$\Delta b_1^2 = \Delta b_2^2 = \frac{1}{4} + \frac{n}{2}. \quad (A5)$$

To analyze (A2) in the limit $u \gg \omega$, we set

$$\exp(\pm i\omega\tau) = 1 \pm i\omega\tau \quad (A6)$$

in (A3). Expansion (A6) is equivalent to expansion (22) in the text proper. As a result, putting the operator expression in the integrand in (A2) in the normally ordered form, and carrying out the integration, we find

$$|u, t\rangle = 2^{1/2} \pi^{1/4} (1 + \kappa^2 \omega^2 u^{-2})^{-1/2} \exp\left[-\frac{\Delta^2}{2(u^2 + \kappa^2 \omega^2)}\right] \times \exp\{\kappa[b^+(t) - b(t)]\} \exp\left[-\frac{\kappa\omega\Delta}{u^2 + \kappa^2 \omega^2} b^+(t) - \frac{\kappa^2 \omega^2}{2(u^2 + \kappa^2 \omega^2)} b^{+2}(t)\right] |0\rangle, \quad (A7)$$

$$\Delta = \delta + \kappa^2 \omega.$$

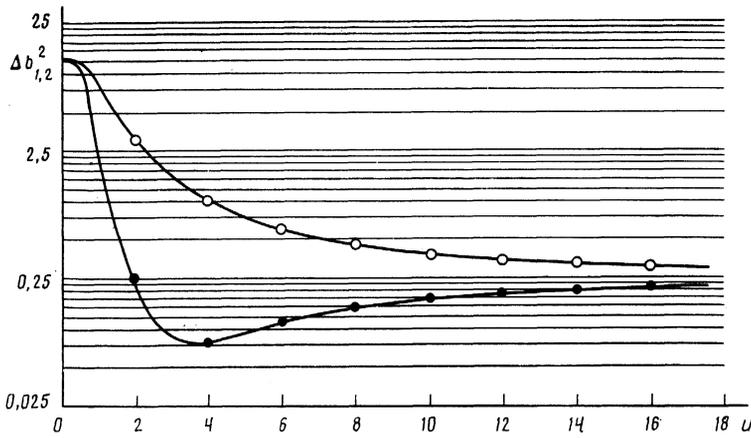


FIG. 1. The uncertainties (●) Δb_1^2 and (○) Δb_2^2 as functions of the reciprocal pulse length u (in units of the vibration frequency ω) for $\kappa = 5$ and $\Delta = 0$. In the broad region $u \geq 2\omega$ we have $\Delta b_1^2 < 0.25$, i.e., the vibrational state is squeezed. The minimum value $\Delta b_1^2 = 0.075$ is reached at $u = 3.64\omega$.

Using the operator identity

$$\begin{aligned} & \exp(-\beta b^+ - \alpha b^{+2}) \exp\left(\frac{\beta}{1+2\alpha} b\right) \\ &= \exp\left(\frac{1}{2} \frac{\beta^2}{1+2\alpha}\right) \exp\left[\frac{-\beta}{1+2\alpha} (b^+ - b)\right] \exp(-\alpha b^{+2}) \end{aligned}$$

and Hollenhorst's formula³¹

$$\exp\left[\frac{1}{2} z (b^2 - b^{+2})\right] |0\rangle = (\text{ch } z)^{-1/2} \exp(-1/2 \text{th } z b^{+2}) |0\rangle,$$

we can put expression (A7) in the form

$$\begin{aligned} |u, t\rangle &= \left[\frac{4\pi}{1+2\kappa^2\omega^2 u^2} \right]^{1/4} \exp\left(-\frac{1}{2} \frac{\Delta^2}{u^2+2\kappa^2\omega^2}\right) \\ &\times \exp\left\{ \kappa \left(1 - \frac{\omega\Delta}{u^2+2\omega^2\kappa^2}\right) [b^+(t) - b(t)] \right\} \\ &\times \exp\left\{ \frac{1}{4} \ln(1+2\kappa^2\omega^2 u^2) [b^2(t) - b^{+2}(t)] \right\} |0\rangle, \end{aligned} \quad (\text{A8})$$

which contains the product of unitary shift and squeezing operators. In the limit $u^2 \gg 2\kappa^2\omega^2$, wave function (A8) corresponds to a coherent state. At a finite value of u , the wave function in (A8) describes an ideal coherent squeezed state which minimizes the uncertainty relation. It is physically obvious that this squeezing should also occur at values of u for which the condition $\Delta b_1 \Delta b_2 > 1/4$ holds. This property of the wave function (A2) for the particular case $\kappa = 5$, $\Delta = 0$ is illustrated in Fig. 1, which shows the results of numerical calculations based on expression (A4) for values $t = \pi m/\omega$, where m is a natural number. We see that squeezing of the fluctuations b_1 below the vacuum level is achieved for $u \gtrsim 2\omega$, while an ideal squeezed state is achieved for $u \gtrsim 4\omega$. The quantities Δb_1 and Δb_2 trade places after a quarter-period of the molecular vibrations. An asymmetry $\Delta b_1 \neq \Delta b_2$ is sufficient for temporal modulation of the spectral width; i.e., modulation also occurs in the region with $\Delta b_1 \Delta b_2 > 1/4$.

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