Physical Chemistry

The influence of ultrashort excitations on the vibrational dynamics in a diatomic molecule

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The problem of vibrational wave packet dynamics in the system of two electronic states of a diatomic molecule, where the states are coupled by infinitely short light pulses, is solved. The electronic states were modeled by shifted harmonic oscillators with different frequencies. Exact expressions for the probability densities of the wave packets in the ground and excited states were derived. The spatial, spectral, and temporal characteristics of the wave packets, namely, the range of motion, spatial width, mean energy, spectral width (the mean number of vibrational states in a wave packet), and the autocorrelation function, were calculated as functions of the molecular parameters (the frequency ratio and the distance between the potential minima) and of the delay time between the light pulses. The possibility of controlling the mean energy and spectral width of the wave packets in the ground electronic state by varying the delay time is considered. It was shown that "squeezed" wave packets can be prepared in the ground electronic state if the upper electronic state is shallow.

Key words: wave packet, ground electronic state, diatomic molecule, harmonic oscillator, Green's function, "squeezed" state, quantum dynamics, femtochemistry.

Advances in femtosecond laser spectroscopy have stimulated the emergence of a new frontier area of scientific exploration between physics and chemistry, which studies selective cleavage and formation of chemical bonds under the action of ultrashort laser pulses in the real time scale.[1-3] Advanced methods for investigation of the intramolecular dynamics employ multi-pulse sequences. Typically, the pump pulse interacting with a molecule transfers it to the non-stationary state, thus creating a wave packet (a coherent superposition of vibrational states). Temporal evolution of the wave packet can be monitored by the probe light pulses, which cause the experimentally observed light emission or photoionization current.

In most femtochemical studies carried out in the last decade, wave packets were prepared in the excited electronic states which are of prime interest for femtochemistry. However, chemical reactions can also proceed in the ground electronic state, especially in systems with several vibrational degrees of freedom. A wave packet in the ground state can be prepared using a multi-pulse "pump—dump" technique *via* an intermediate excited electronic state.[4,5] In this case, the wave packet dynamics reflects the properties of both the ground

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state in which it moves and the excited state involved in the wave packet formation. Such experiments have been carried out for a number of diatomic molecules. For instance, ground-state wave packets were prepared in the K_2 molecule using stimulated Raman scattering[4] and in the I_2 molecule by coherent anti-Stokes Raman scattering.[6,7] The wave packet dynamics was monitored by probe pulses, which had led to ionization of the molecule[4] or to polarization of the emitted light.[6,7] In all experiments, information on the dynamics was extracted from the dependences of the signal intensities on the delay time between the pump and probe pulses.

The spectral and spatial width of a wave packet, as well as specific features of its long-time evolution, are determined by a number of factors including molecular constants and parameters of the pump and probe pulses. In this work, we will consider the dynamics of a wave packet created in the ground electronic state of a diatomic molecule using a sequence of two infinitely short pulses ("white light" pulses). Despite an apparent exotic nature, this approximation is of both theoretical and practical significance, since it allows the intramolecular dynamics to be analyzed without taking into account the spectral composition of the light pulses.[8]

The aim of this work is (i) to analyze the spatial, spectral, and temporal characteristics of wave packets in the ground and intermediate excited electronic states of a diatomic molecule and (ii) to study the dependences of these parameters on the molecular constants and the delay time between the pulses. Electronic terms of the molecule are described using a model of two shifted harmonic oscillators. Neglecting the anharmonicity of the terms implies that we consider only short-time intramolecular dynamics (time intervals are of the order of several vibrational periods), so that the effects of phase dispersion are insignificant. Preliminary results for the case of oscillators with equal frequencies have been reported earlier.[9] In this work, a general case of oscillators with different frequencies is considered in detail.

Model

The model used in this work is very simple. It considers transitions between two electronic states, namely, the ground state and an excited state. Each of them is described by the harmonic oscillator potential (Fig. 1). The frequencies of the lower and upper oscillators are equal to 1 and ω, respectively. The distance between the potential minima is R and the origin is at the potential minimum of the ground state. Therefore, the potentials for the ground (U_g) and excited (U_e) states are given by the expressions

$$U_g(x) = 0.5x^2, \qquad U_e(x) = 0.5\omega^2(x - R)^2 + T_e$$

(T_e is the electronic excitation energy).

The electronic states are coupled by infinitely short light pulses. Initially, the molecule is assumed to be in the nth vibrational level of the ground electronic state. The first pulse transfers the molecule to the excited electronic state and creates there a vibrational wave packet. The second pulse, sent some delay time, τ, after the first pulse, causes stimulated emission from the excited state and the formation of a wave packet in the ground electronic state.

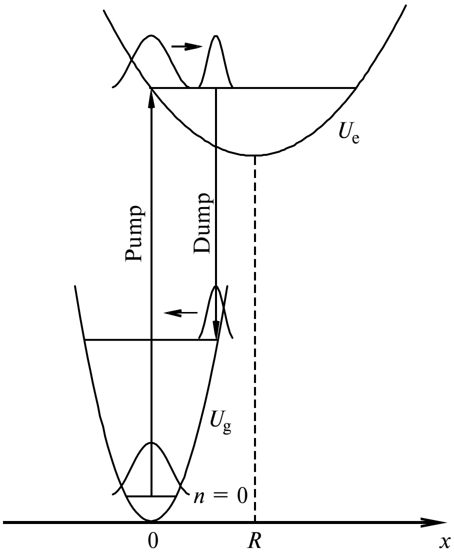

Fig. 1. Model of two shifted harmonic oscillators with different frequencies.

Such a simple model makes it possible to analyze the wave packet dynamics without taking into account the shape of light pulses, vibrational anharmonicity, and the dependence of the electronic transition moment on the internuclear distance. The model contains three main parameters, *viz.*, the ratio of vibrational frequencies (ω), the distance between potential minima (R), and the delay time between the pulses (τ). The first two parameters are molecular constants, while the third parameter characterizes the experimental conditions.

Wave packet dynamics in the excited electronic state

Wave-packet evolution in the excited state is described in the first-order perturbation theory by the wave function

$$\Psi_e(x,t) = \iint G_e(x,t;x',t')\, V(t')\varphi_n(x')\exp(-i\varepsilon_n t')\, dx'dt',$$

where $\varphi_n(x')$ and ε_n are the wave function and energy of the initial vibrational state, respectively; $V(t')$ is the operator of the interaction between the molecule and the electromagnetic field of the light pulse; and $G_e(x,t;x',t')$ is the time-dependent Green's function for the excited electronic state. Hereafter, $\hbar = \mu = 1$ ($\hbar$ is the Planck constant and μ is the reduced mass of the molecule). If the pulse duration is negligibly small compared to the vibration period of atomic nuclei, the function $V(t')$ can be replaced by the delta function, that is, $V(t') = \delta(t')$, and the expression for $\Psi_e(x,t)$ takes the form

$$\Psi_e(x,t) = \int G_e(x,t;x',0)\, \varphi_n(x')\mathrm{d}x'. \quad (1)$$

In this approximation we ignore the dependence of the electronic transition moment on the spatial coordinates.

Substituting the ground-state wave function of the harmonic oscillator and Green's function of an excited electronic state[10] into Eq. (1) and using the method of generating functions, one can obtain a general closed-form expression for the wave packet excited from the nth vibrational level. Hereafter, we will consider only the case $n = 0$. The probability density of the wave packet excited from the zeroth vibrational level of the ground electronic state is described by a Gaussian function:

$$|\Psi_e(x,t)|^2 = \frac{1}{[\pi\sigma(t)]^{1/2}} \cdot \exp\left\{-\frac{[x - R(1-\cos(\omega t))]^2}{\sigma(t)}\right\} \quad (2)$$

with its center at point $x = R(1 - \cos \omega t)$ and the width

$$\sigma(t) = \cos^2(\omega t) + \sin^2(\omega t)/\omega^2. \quad (3)$$

The wave packet oscillates periodically with the frequency of the excited state, ω. The range of motion of the wave packet center is frequency independent and equals $2R$ and during one period the wave packet can move up to $\pm R$ with respect to the equilibrium position of the upper oscillator. Generally, the width of the wave packet, $\sigma(t)$, depends on time and varies between 1 and $1/\omega^2$. The energy of the wave packet in the excited state is:

$$E = 0.25(\omega^2 + 1) + 0.5\omega^2R^2 = 0.25(\omega^2 + 1) + U_e(0). \quad (4)$$

The spectral composition of the wave packet is characterized by the mean number of vibrational states, which can be estimated from the contributions of individual states. The statistical weight of the nth vibrational state is defined as the square modulus of the overlap between the wave packet (Eq. (2)) and the wave function of the nth state:

$$f_n = |\langle\Psi_e(x,t)|\Psi_n(x)\rangle|^2.$$

The mean, or effective, number of vibrational states in the wave packet (n_{eff}) can be calculated using the statistical weights of the states, f_n [11]:

$$n_{\mathrm{eff}} = 1\Big/\sum_{n=0}^{\infty} f_n^2,$$

or, which is equivalent, using the generating function for the statistical weights. If the generating function is defined as a power series:

$$\Phi(z) = \sum_{n=0}^{\infty} f_n z^n,$$

the effective number of vibrational states in the wave packet is given by the integral:

$$n_{\mathrm{eff}} = 2\pi\Big/\left(\int_0^{2\pi} |\Phi(e^{-\mathrm{i}t})|^2 \mathrm{d}t\right). \quad (5)$$

For the wave packet in the excited electronic state the statistical weights of vibrational states can be defined by the method of generating functions:

$$f_n = \frac{1}{2^n n!} \cdot \frac{2\sqrt{\omega}}{\omega+1}\left(\frac{1-\omega}{1+\omega}\right)^n \cdot H_n^2\left(\frac{R\sqrt{\omega}}{\sqrt{1-\omega^2}}\right)\exp\left(-\frac{\omega R^2}{\omega+1}\right), \quad (6)$$

where H_n are the Hermite polynomials. If $\omega = 1$, the statistical weights are[9]:

$$f_n = \exp(-R^2/2)\frac{(R^2/2)^n}{n!},$$

and the effective number of states in the wave packet depends on the distance R between the potential minima as follows:

$$n_{\mathrm{eff}} = \exp(R^2)/I_0(R^2), \quad (7)$$

where I_0 is the modified Bessel function of the zeroth order.

Despite the fact that an infinitely short light pulse has an infinite spectral width, the number of states in the wave packet is finite. This is due to two reasons responsible for the spectral composition of the wave packet, namely, the spectral composition of the light pulse and the Franck—Condon factors, which describe the probabilities of electronic-vibrational transitions.[12] The Franck—Condon factors corresponding to the classically forbidden electronic-vibrational transitions are exponentially small; therefore, these transitions are not involved in the formation of the vibrational wave packet.

With increasing R, the number of states (7) asymptotically tends to a linear function of R

$$n_{\mathrm{eff}} \xrightarrow{R\to\infty} \sqrt{2\pi}R. \quad (8)$$

In the general case ($\omega \neq 1$), a closed-form expression for n_{eff} can be obtained only if R is small or if $\omega \sim 1$, *i.e.*, if the wave packet is composed of the lowest vibrational states. If the n values in formula (6) are small, the Hermite polynomial can be replaced by the highest degree of the argument, that is, $H_n(x) \approx (2x)^n$. Then, the number of states in the wave packet equals

$$n_{\mathrm{eff}} = \frac{1}{\sum_{n=0}^{\infty} f_n^2} = \frac{(\omega+1)^2}{4\omega} \cdot \frac{\exp[2\omega R^2/(\omega+1)]}{I_0[4\omega R^2/(\omega+1)^2]}.$$

The mean energy and the effective number of states in the wave packet can be readily assessed using the classical quasi-energy representation of electronic-vibrational transitions.[8] Figure 2 schematically represents the ground-state electronic term and quasi-terms of the excited state obtained by vertical shift of the potential by the energy of the Franck—Condon transition from the right and left turning points in the ground-state electronic term. Transitions to the vibrational states of the electronic term of the excited state with the energies ε_v lying between ε_1 and ε_2, where $\varepsilon_1 = U_e(1)$ and

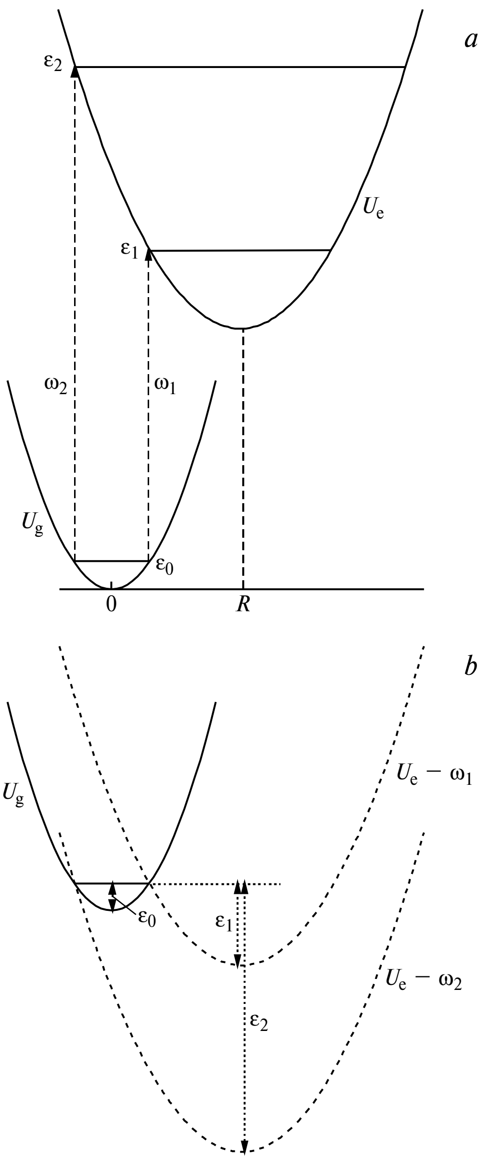

Fig. 2. Franck—Condon transitions between electronic terms of the ground (U_g) and excited (U_e) electronic states in conventional (*a*) and quasi-energy representations (*b*); ω_1 and ω_2 are the frequencies of the Franck—Condon transitions from the right and left turning points of the electronic term of the ground state, respectively; ε_1 and ε_2 are the minimum and maximum energy of vibrational states to which transition is classically allowed. Dotted lines denote the quasi-terms of the excited state, which are shifted relative to U_e by ω_1 and ω_2, respectively.

$\varepsilon_2 = U_e(-1)$, are classically allowed, and it is these states of which the wave packet is composed. The classical estimate of the mean energy of the wave packet is given by the following expression:

$$E = 0.5(\varepsilon_1 + \varepsilon_2) = 0.5\omega^2(R^2 + 1) = 0.5\omega^2 + U_e(0),$$

which coincides with the exact value (*cf.* formula (4)) for $\omega = 1$. The number of states is estimated at

$$n_{\text{eff}} = (\varepsilon_2 - \varepsilon_1)/\omega = 2\omega R.$$

Comparison with the exact result (expression (8)) obtained for $\omega = 1$ shows that, qualitatively, this estimate correctly describes the dependence of the spectral width of the wave packet on the distance R between the potential minima if the frequency ratio is close to 1.

Wave packet dynamics in the ground electronic state

The second light pulse sent after a delay time τ with respect to the first pulse can cause (i) an additional excitation of the molecule from the ground state to the excited state, which can be accompanied by interference effects; (ii) the formation of a wave packet in a higher excited electronic state; and (iii) a stimulated emission from the excited state with the formation of a wave packet in the ground state. In this work, we will consider only the last-mentioned case.

The wave packet in the ground state is described in the second-order perturbation theory by the following expression:

$$\Psi_g(x,t,\tau) = \iint G_g(x,t;x',0)\, G_e(x',\tau;x'',0)\, \varphi_0(x'')\, dx'dx'' = \\ = \int G_g(x,t;x',0)\, \Psi_e(x',\tau)\, dx',$$

where the current time t starts from the second pulse. By substituting the expressions for the probability density of the wave packet in the excited state (formula (2)) and for Green's function of the ground electronic state and integrating one can obtain the probability density of a wave packet in the ground electronic state:

$$|\Psi_g(x,t,\tau)|^2 = \frac{1}{\sqrt{\pi\beta(t,\tau)}} \exp\left\{-\frac{[x - \alpha(t,\tau)]^2}{\beta(t,\tau)}\right\}. \qquad (9)$$

The wave packet described by formula (9) has a Gaussian shape and oscillates with the frequency of the ground state. The motion of the center of the wave packet is described by the function

$$\alpha(t,\tau) = R[\omega\sin(\omega\tau)\sin t - \cos(\omega\tau)\cos t + \cos t], \qquad (10)$$

and the dependence of the width of the wave packet on the current time t and delay time τ is given by the formula:

$$\beta(t,\tau) = \{\omega^2\sin^2 t + [(\omega^2 - 1)\sin(\omega\tau)\cos(\omega\tau)\sin t - \\ - \omega\sigma(\tau)\cos t]^2\}/[\omega^2\sigma(\tau)], \qquad (11)$$

where the function $\sigma(\tau)$ is given by expression (3).

The formulas (9)—(11) describe the dynamics of the wave packet created in the ground electronic state of a diatomic molecule using a sequence of two ultrashort light pulses.

The model employed contains three parameters, namely, the distance between the potential minima (R), the ratio of vibrational frequencies (ω), and the delay time between pulses (τ). The first two parameters characterize the molecular structure and, hence, are molecular constants. In contrast to this, the third parameter can be varied under the experimental conditions and is in fact a control parameter. All parameters of the wave packet in the ground state depend on the delay time. This causes some qualitative effects distinguishing the intramolecular dynamics in the ground electronic state from that in the excited state.

First of all, consider the range of motion of the center of the wave packet. In the general case ($\omega \neq 1$), at a given τ the center of the wave packet oscillates periodically with respect to the equilibrium position ($x = 0$) between the points with coordinates $\pm 2R\sin(\omega\tau/2)\sqrt{\omega^2\cos^2(\omega\tau/2)+\sin^2(\omega\tau/2)}$ corresponding to the maximum and minimum of expression (10). The range of motion, given by the expression

$$\alpha_{\max}(\tau) - \alpha_{\min}(\tau) = \\ = 4R|\sin(\omega\tau/2)|\sqrt{\omega^2\cos^2(\omega\tau/2) + \sin^2(\omega\tau/2)} \qquad (12)$$

is a periodic function of the delay time between the pulses (Fig. 3). The minimum value (0) is reached at delay times multiple to integer numbers of the vibrational periods in the excited state, $\tau = (2\pi/\omega)k$. In this case, the wave packet is just a stationary vibrational wave function. The maximum value of function (12) depends on the frequency ratio:

$$\max(\alpha_{\max}(\tau) - \alpha_{\min}(\tau)) = \begin{cases} 4R \text{ if } \omega \leq \sqrt{2} \\ 4R\omega^2 \big/ \left(2\sqrt{\omega^2 - 1}\right) \text{ if } \omega \geq \sqrt{2} \end{cases}.$$

If the upper potential is not very steep ($\omega \leq \sqrt{2}$), the maximum amplitude of vibrations is reached at delay times multiple to half-integer numbers of the vibrational periods in the excited state, $\tau = (2\pi/\omega)(k + 1/2)$. Physically, this is the most real situation, since usually the vibrational frequencies of diatomic molecules in the excited electronic state are lower than those in the ground state.

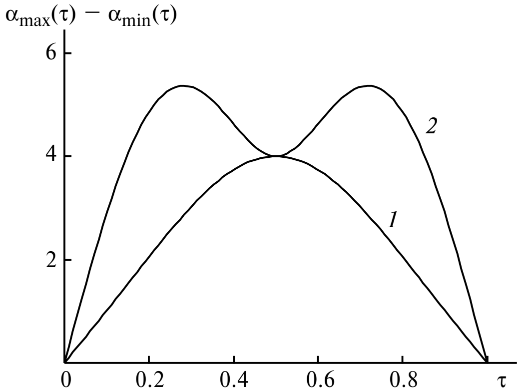

Fig. 3. The range of motion of the wave packet in the ground electronic state as a function of the delay time between the pulses: a shallow upper potential ($\omega = 0.8$) (*1*) and a steep upper potential ($\omega = \sqrt{6}$) (*2*). Time is given in units of the vibrational period in the excited electronic state ($T = 2\pi/\omega$) and the range is given in units of R.

Thus, choosing an appropriate delay time between the light pulses allows the range of motion of the wave packet in the ground state to be extended (depending on ω) by two or more times as compared to the range of motion in the excited state ($2R$).

Generally, at a given delay time τ the spatial width of the wave packet (expression (11)) periodically varies between the following values:

$$\beta_{\max,\min}(\tau) = [1/(2\omega^2)][2\omega^2 + (\omega^2 - 1)^2\sin^2(\omega\tau)] \pm \\ \pm [(\omega^2 - 1)/(2\omega^2)]\sin(\omega\tau)\sqrt{(\omega^2 + 1)^2\sin^2(\omega\tau) + 4\omega^2\cos^2(\omega\tau)}.$$

At $\sin(\omega\tau) = 0$, *i.e.*, at delay times multiple to half the vibrational period in the excited electronic state, these two values coincide and, hence, the width of the wave packet does not depend on the current time t. The largest difference between the maximum and minimum width of the wave packet (from $\beta_{\min} = \omega^2$ to $\beta_{\max} = 1/\omega^2$ for $\omega < 1$ and from $\beta_{\min} = 1/\omega^2$ to $\beta_{\max} = \omega^2$ for $\omega > 1$) is achieved if $\sin(\omega\tau) = \pm 1$, which corresponds to the action of the second pulse on the wave packet in the equilibrium position of the excited state.

Thus, if $\omega < 1$ (the case of real diatomic molecules), the maximum widths of the wave packets in the ground and excited state coincide and are equal to $1/\omega^2$, whereas the minimum width of the wave packet in the ground state is by a factor of $1/\omega^2$ smaller than that of the wave packet in the excited state. This means that one can prepare strongly localized wave packets in the ground state by choosing an allowed electronic transition to the excited state with a shallow potential ($\omega \ll 1$) and using a sequence of two pulses for creating the wave packet.

The mean energy of the wave packet is calculated as the mean value of the ground-state Hamiltonian with wave packet (9):

$$E(\tau) = 0.5 + [(\omega^2 - 1)(\omega^2 + 2R^2\omega^2 - 1)/(4\omega^2)]\sin^2(\omega\tau) + \\ + 2R^2\sin^2(\omega\tau/2). \qquad (13)$$

The dependence of E on τ has a period equal to the vibrational period in the excited state, $T = 2\pi/\omega$. The maximum mean energy ($E_{\max}$) and the type of the $E(\tau)$ dependence are determined by the ratio of the parameters of Eq. (13). If the upper potentials are both not very shallow and not very steep ($\omega \sim 1$), $E_{\max} = 0.5 + 2R^2$; this value is independent of ω and is achieved at delay times multiple to half-integer numbers of the vibrational periods in the excited state, $\tau = (n + 0.5)T$ (Fig. 4, curve *1*). If the upper potential is very steep or very shallow, the value $E = 0.5 + 2R^2$ corresponds to a local minimum (Fig. 4, curve *2*), while the $E_{\max}$ value is determined by the frequency ratio, ω.

In all cases, correct choice of the delay time τ makes it possible to prepare a wave packet in the ground state, the energy of which is much higher than that of the wave packet in the excited state (see expression (4)). A salient feature of this procedure is that the energy difference increases as the distance R between the potential minima increases.

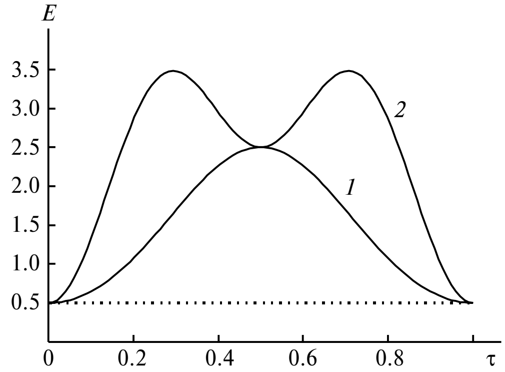

Fig. 4. Dependence of the mean energy of the wave packet in the ground electronic state on the delay time between the pulses: close frequencies of the electronic terms of the ground and excited states ($\omega = 0.8$, $R = 1$) (*1*) and a shallow upper potential ($\omega = 0.3$, $R = 1$) (*2*). The delay time is given in units of the vibrational period in the excited electronic state.

The spectral width of the wave packet in the ground electronic state can be assessed similarly to the case of the wave packet in the excited state. Since the general expression for the statistical weights of vibrational states is too complicated, we will consider a number of particular cases.

For equal frequencies ($\omega = 1$) the generating function for statistical weights has the form

$$\Phi(z,\tau) = \sum_{n=0}^{\infty} f_n(\tau)z^n = \exp[-R^2(1 - \cos\tau)(1 - z)],$$

and the statistical weights of vibrational states are given by the following expression:

$$f_n(\tau) = \{[R^2(1 - \cos\tau)]^n/n!\}\exp[-R^2(1 - \cos\tau)].$$

The effective number of states depends on the delay time as follows:

$$n_{\text{eff}}(\tau) = \frac{1}{\sum\limits_{n=0}^{\infty} f_n^2(\tau)} = \frac{\exp[2R^2(1 - \cos\tau)]}{I_0[2R^2(1 - \cos\tau)]}. \qquad (14)$$

This is a periodic function. Its maximum value is achieved at $\tau = \pi$, when the second light pulse acts on the wave packet in the excited state, which is at the right turning point. At large values of the argument, $R^2(1 - \cos\tau)$, the number of states asymptotically tends to

$$n_{\text{eff}}(\tau) \xrightarrow{R\to\infty} 2\sqrt{2\pi}R|\sin(\tau/2)|. \qquad (15)$$

At $\tau = \pi$, this value is twice as large as the number of states in the wave packet moving in the excited state (*cf.* expression (8)). It is noteworthy that the twofold increase in the number of vibrational states in the wave packet is due to the changes in the statistical weights of individual vibrational states rather than to changes in its spatial width, which is constant and equals 1 for $\omega = 1$. This means that there is no one-to-one correspondence between the spatial width of the wave packet and its spectral width.

In the general case ($\omega \neq 1$), the effective number of states can be numerically calculated using formula (5) and the method of generating function for the statistical weights (Fig. 5). As can be seen in Fig. 5, the type of the dependence $n_{\text{eff}}(\tau)$ is determined by the frequency ratio, ω. If $\omega < 1$, which is typical of diatomic molecules, this dependence has a double-humped shape with a local minimum at $\tau = \pi/\omega$ (see Fig. 5, *a*). If $\omega > 1$, the number of states in the wave packet moving in the ground state at $\tau = \pi/\omega$ is maximum (see Fig. 5, *b*) and does not depend on the frequency ratio. In this case, the statistical weights can be calculated using the formula

$$f_n(\pi/\omega) = [(2R^2)^n/n!]\exp(-2R^2),$$

and the number of states equals:

$$n_{\text{eff}}(\pi/\omega) = 1\Big/\sum_{n=0}^{\infty} f_n^2 = \exp(4R^2)/[I_0(4R^2)].$$

At large distances R between the potential minima, the number of states corresponding to $\tau = \pi/\omega$ asymptotically tends to

$$n_{\text{eff}}(\pi/\omega) \xrightarrow{R\to\infty} 2\sqrt{2\pi}R. \qquad (16)$$

Comparison of the spectral widths of the wave packets in the excited and ground states suggests that (i) at $\omega = 1$ the maximum spectral width of the wave packet in the ground state is twice as large as that of the wave

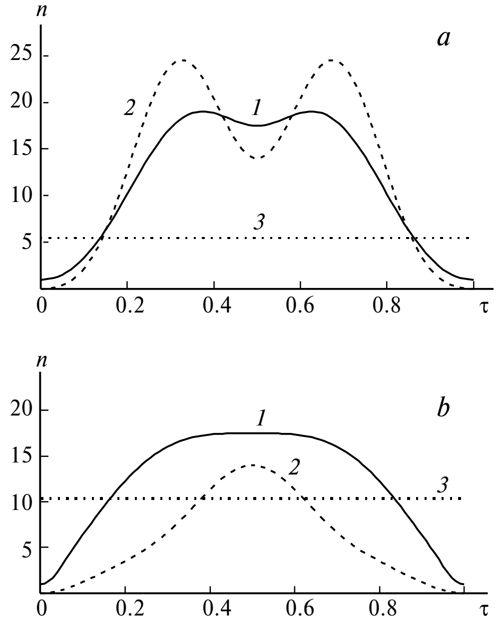

Fig. 5. Dependence of the number of states in the wave packet moving in the ground state on the delay time between the pulses: a shallow upper potential ($\omega = 0.6$, $R = 3.5$) (*a*) and a steep upper potential ($\omega = 1.2$, $R = 3.5$) (*b*). The results of exact quantum-mechanical calculations (*1*), the classical estimate by formula (18) (*2*), and the number of states in the wave packet moving in the excited state (*3*). The delay time is given in units of the vibrational period in the excited electronic state.

packet in the excited state; (ii) at $\omega < 1$ the ratio of the spectral widths in the ground and excited states is greater than two (see Fig. 5, *a*) and increases with decreasing ω; and (iii) at $\omega > 1$ this ratio is less than two (see Fig. 5, *b*) and decreases as ω increases.

These results are confirmed by the classical estimate of the mean energy and the number of states in the wave packet moving in the ground state (Fig. 6). When the second pulse at time τ acts on the wave packet in the excited state (expression (2)), the center of the wave packet is at the point $r(\tau) = R[1 - \cos(\omega\tau)]$ and its spatial width is $\sigma(\tau) = \cos^2(\omega\tau) + (1/\omega^2)\sin^2(\omega\tau)$. This means that the wave packet is spread between the points $r_{1,2} = r(\tau) \pm \sigma(\tau)$. Transitions to vibrational states of the ground electronic state are classically allowed if the vibrational energies ε_v lie between ε_1 and ε_2, where $\varepsilon_1 = \min[U_g(r_1), U_g(r_2)]$ and $\varepsilon_2 = \max[U_g(r_1), U_g(r_2)]$, and it is these vibrational states of which the wave packet in the ground electronic state is composed. The mean energy of the wave packet equals

$$E = 0.5(\varepsilon_1 + \varepsilon_2) = 0.5(r^2 + \sigma^2) =$$
$$= 0.5R^2[1 - \cos(\omega\tau)]^2 + 0.5[\cos^2(\omega\tau) + (1/\omega^2)\sin^2(\omega\tau)]^2. \quad (17)$$

For equal frequencies ($\omega = 1$), this result coincides with the exact value given by formula (13). If the frequencies of the excited and ground states are close ($\omega \sim 1$), the first term in expression (17) is dominant and the dependence $E(\tau)$ is identical to that shown in Fig. 4 (curve *1*), while the maximum energy ($E_{\max} = 0.5 + 2R^2$) is achieved at half the vibrational period in the excited state ($\cos(\omega\tau) = -1$), which is in complete agreement with the results of quantum-mechanical calculations.

If the upper potential is sufficiently shallow ($\omega \ll 1$), the second term in expression (17) is dominant and the dependence $E(\tau)$ passes through two maxima (see Fig. 4, curve *2*).

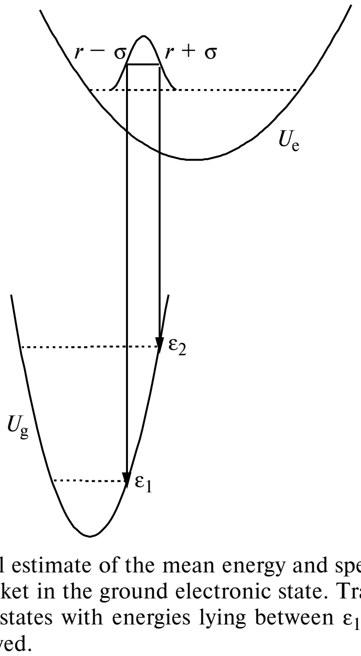

Fig. 6. Classical estimate of the mean energy and spectral width of the wave packet in the ground electronic state. Transitions to the vibrational states with energies lying between ε_1 and ε_2 are classically allowed.

The difference between the classical energies gives an estimate of the number of states in the wave packet moving in the ground state:

$$n_{\text{eff}}(\tau) = \varepsilon_2 - \varepsilon_1 = 2r(\tau)\sigma(\tau) =$$
$$= 2R[1 - \cos(\omega\tau)][\cos^2(\omega\tau) + (1/\omega^2)\sin^2(\omega\tau)]. \quad (18)$$

As for the mean energy, the dependence of the number of states in the wave packet on the delay time can pass through one or two maxima, which depends on the frequency ratio ω (see Fig. 5).

If the upper potential is steep ($\omega > 1$), the maximum number of states in the wave packet is achieved at half the vibrational period in the excited state (see Fig. 5, *b*), does not depend on the frequency ratio, and equals $4R$, which is confirmed by the exact result obtained from quantum-mechanical calculations (see expression (16)). If the upper potential is shallow, the same number of states in the wave packet ($4R$) is also achieved at $\tau = \pi/\omega$; however, it corresponds now to a local minimum (see Fig. 5, *a*). The maximum number of states is inversely proportional to the square of the frequency ratio and is much greater than the spectral width of the wave packet in the excited state, which is proportional to ω.

In the particular case of equal frequencies, expression (18) for the number of states is simplified:

$$n_{\text{eff}}(\tau) = 2R(1 - \cos\tau) = 4R\sin^2(\tau/2).$$

Comparison with the exact result obtained from quantum-mechanical calculations (see expression (15)) shows that, qualitatively, the classical estimate correctly describes the dependence of the spectral width of the wave packet on both the distance between the potential minima and the delay time between the pulses.

The autocorrelation function, $S(t,\tau)$, is an important temporal characteristic of the wave packet. The function $S(t,\tau)$ is defined[11] as the square of the overlap between the wave packet at time t and the initial wave packet:

$$S(t,\tau) = |\langle \Psi_g(x,t,\tau)|\Psi_g(x,0,\tau)\rangle|^2 = \left|\sum_n f_n(\tau)\exp(-\mathrm{i}nt)\right|^2. \quad (19)$$

This is a periodic function of the current time t with a period of 2π. Qualitative features of the autocorrelation function depend on the molecular constants. Since the range of motion of the wave packet at large R and ω values is rather wide (see Fig. 3, curve *2*), most of the time the wave packet is far from the initial position and the autocorrelation function is close to zero. Another picture is observed at low frequencies and short distances between the potential minima (Fig. 7). In this case, at any delay time the wave packet is located for some time near the initial position and the autocorrelation function can have several maxima and minima, which indicates a rather complex pattern of the motion of the wave packet.

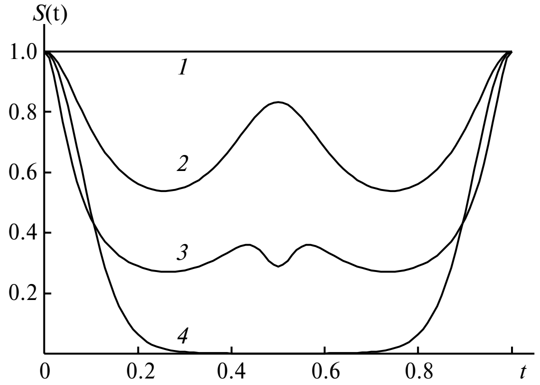

Fig. 7. Autocorrelation functions $S(t)$ of the wave packets in the ground electronic state (formula (19)); molecular constants: $\omega = 0.4$, $R = 1$, the delay time between pulses (in units of the vibrational period in the excited state) $\tau = 0$ (*1*), 0.1 (*2*), 0.2 (*3*), and 0.5 (*4*). The current time t is given in units of the vibrational periods in the ground state ($T = 2\pi$).

Thus, in this work we obtained a solution of the problem of the wave packet dynamics in the system of two shifted harmonic oscillators with different frequencies. The states of the system were assumed to be coupled by infinitely short light pulses, which made it possible to analyze the wave packet dynamics without taking into account the pulse shape effects.

We derived exact expressions for the wave functions of the wave packets in the ground and excited electronic states and calculated dynamic parameters of the wave packets, namely, the range of motion, the spatial width, mean energy, spectral width (the mean number of vibrational states in the wave packet), and the autocorrelation function.

Analysis of the expressions obtained suggests that the delay time can be used as an efficient tool for controlling the dynamics of the wave packets in the ground state. All parameters of such wave packets are periodic functions of the delay time and their periods are equal to the vibrational period in the excited state.

By varying the delay time it is possible to change the range of motion of the wave packet in the ground electronic state from 0 up to double the range of oscillations in the excited state. The spatial width of the wave packet can vary from ω^2 to $1/\omega^2$; this indicates the possibility of creating strongly "squeezed" (compared to the initial vibrational state and excited state) wave packets if the upper potential is shallow ($\omega \ll 1$).

In the case of equal frequencies ($\omega = 1$) the spectral width of the wave packet in the ground state changes periodically with delay time between 1 and $2\sqrt{2\pi}R$, the latter value being twice as large as the number of states in the wave packet moving in the excited state. The increase in the spectral width of the wave packet is due to only the increase in the amplitude of its motion rather than to a change in its spatial width. If $\omega \neq 1$ and the upper potential is shallow, both numerical quantum-mechanical calculations and the classical estimates show that the maximum spectral width of the wave packet in the ground state can be several times larger than that of the wave packet in the excited state.

Yet another important aspect of the intramolecular dynamics is related to the features of the dependence of the parameters of the wave packet in the ground state on the delay time τ. The dependences of all the wave packet parameters (except for the spatial width) on τ can pass through one or two maxima (see Figs. 3—5). In all cases, parameters of the wave packet in the ground electronic state reach their extreme values (either global maxima or local minima) at the delay time $\tau = \pi/\omega$ corresponding to the time when the second light pulse acts on the wave packet in the excited state, which is in the right turning point. The type of extremum is determined by the ratio of vibrational frequencies, ω. If $\omega < 1$ (a shallow upper potential), the dependences of the mean energy and spectral width of the wave packet on the delay time pass through two maxima. Since for most real diatomic molecules the excited electronic state is characterized by a more shallow potential than the ground state, there is a possibility of fine control of the mean energy and spectral width of the wave packet in the ground state by varying the delay time between the light pulses.

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