

Dependence of the molecular iodine B-state predissociation induced by a femtosecond laser pulse on pulse phase modulation

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Abstract. The processes of pumping and laser-induced predissociation of B-states of the I₂ molecule under the action of femtosecond laser pulses are considered theoretically. An analytical formula is derived, which describes the dependence of the predissociation on such parameters of femtosecond pulses as spectral chirp, spectral width and delay time between pulses. The formula is used to calculate numerically the dependence of the predissociation yield on the parameters of the phase modulation of the pump pulse and coupling pulse.

Keywords: femtosecond pulses, control of chemical reactions.

1. Introduction

The feasibility of controlling chemical reactions attracts attention of theorists and experimenters. Now, the most promising method of controlling chemical processes is the use of ultrashort laser pulses. Previously, use was made of laser pulses with a duration of tens of picoseconds, and now almost all experiments are performed using femtosecond laser pulses. Zewail Ahmed [1] was awarded the Nobel Prize for successes of science in this direction.

The most important feature of femtosecond pulses is their large spectral width. Rather short femtosecond pulses have a spectral width that is sufficient to excite simultaneously several vibrational states of molecules. Such simultaneously excited vibrational states are called a coherent vibrational wave packet. If the chemical reaction involves a coherent packet rather than a vibrational state, then by varying the amplitude and phase characteristics of the laser pulse, it is possible to affect significantly the efficiency of the reaction [2].

In this paper, we consider predissociation of the B-state of the I₂ molecule, induced by a femtosecond laser pulse. The B-state is preliminary populated by another femtosecond pulse, and thus the vibrational wave packet is excited in this state. We also study the dependence of the B-state predissociation intensity on the parameters of the amplitude and phase modulation of femtosecond pump and probe pulses and on the time delay between the pump pulse and coupling pulse.

In experiments with femtosecond pulses, use is commonly made of the Gaussian form of the phase modulation:

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Received 23 August 2011; revision received 19 October 2011
Kvantovaya Elektronika 41 (12) 1104–1108 (2011)
Translated by I.A. Ulitkin

$$E(t) = E_0 \exp\left(-\frac{t^2}{\tau^2}\right) \cos\left(\omega_0 t + \frac{\gamma t^2}{2} + \delta\right). \quad (1)$$

In this case, the spectral chirp β and spectral width $\Delta\omega$ are determined, as is well known [3], from the relations

$$\beta = \frac{4\gamma\tau^4}{4 + \gamma^2\tau^4}, \quad \Delta\omega = \frac{\sqrt{4 + \gamma^2\tau^4}}{\tau}. \quad (2)$$

In the experiments the spectral chirp is usually varied at a fixed spectral width. In this control method, the pulse duration increases, because variation in the spectral chirp leads to relative phase delays of harmonics in the packet.

In the present study we used the parameters of the potential curves given in [4]. To approximate the terms of the X and B states, we used the Morse potential, and to approximate the term of the a state – a modified Morse potential (Tables 1, 2 and Fig. 1). It should be noted that many theoretical and experimental papers are devoted to the definition of terms of the iodine molecule, and the results obtained by different authors may vary. A detailed discussion of this issue can be found elsewhere [5].

Table 1. Parameters of the potential, $U = D\{1 - \exp[\alpha(r - r_e)]\}^2 + T$, used in this paper.

State	D/cm^{-1}	$\alpha/\text{\AA}^{-1}$	$r_e/\text{\AA}$	T/cm^{-1}
X	12440	1.875	2.656	0
B	5169	1.696	3.025	15771

Note: r_e is the equilibrium distance; r is the internuclear distance.

Table 2. Parameters of the potential, $U = D_1 \exp[-2\alpha_1(r - r_{e1})] - 2D_2 \times \exp[-\alpha_2(r - r_{e2})] + T$, used in this paper.

State	D_1/cm^{-1}	D_2/cm^{-1}	$\alpha_1/\text{\AA}^{-1}$	$\alpha_2/\text{\AA}^{-1}$	$r_{e1}/\text{\AA}$	$r_{e2}/\text{\AA}$	T/cm^{-1}
a _{1g} (³ Π)	281.73	63.73	1.5498	0.6853	4.0262	5.812	12440

2. Modelling of the predissociation control

Consider the process of pumping and induced predissociation. The molecule is exposed to two consecutive femtosecond laser pulses: a pump pulse and probe pulse. We assume that the laser radiation is linearly polarised. In determining the population in the ground state, we used the following assumptions [3]:

1) the electromagnetic laser field strength is small enough so that we can apply perturbation theory in the first nonvanishing order to calculate the transition amplitudes between different electronic states;

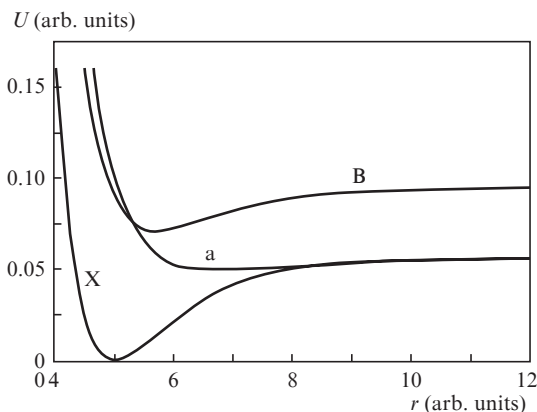


Figure 1. Potential curves used in the present paper.

2) the carrier frequencies are such that the pump radiation frequency ω_1 only provides the X \rightarrow B transition, whereas the frequency ω_2 of the probe pulse field – the B \rightarrow a transition;

3) the spectral width of pump radiation $\Delta\omega_1$ is such that only discrete energy levels of the B-state are excited;

4) the pulses do not overlap in time;

5) the interaction of vibrational and rotational degrees of freedom can be neglected;

6) the dipole moment is weakly dependent on the interatomic distance, so that we can apply the Franck–Condon approximation;

7) the initial population of the vibrational–rotational states is described by a Boltzmann distribution with a temperature of 300 K.

Taking into account these considerations, we can study the dynamics of wave packets in the molecule. Evolution of the electronic vibrational–rotational state is described by the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad (3)$$

with the Hamiltonian

$$H = H_0 + V, \quad (4)$$

where H_0 is the Hamiltonian of the unperturbed state, and the perturbation operator V describes the interaction with the laser field.

First, we consider the case where both states have only discrete levels. This case corresponds to the process of pumping. Description the predissociation process, where the transition occurs from the discrete spectrum state to the continuous spectrum state, will be obtained by a limiting process. Let the index ‘a’ represent the first electronic state, while the index ‘b’ – the second electronic state. Then the expression for the total perturbed wave function has the form

$$\Psi = \sum_i a_i(t) \exp(i\omega_i^a t) \psi_i^a + \sum_i b_i(t) \exp(i\omega_i^b t) \psi_i^b, \quad (5)$$

where the summation is over the vibrational states: $\psi_i^{a,b}$ are the i th vibrational wave functions of the electronic states a and b; $\omega_i^{a,b} = \mathcal{E}_i^{a,b}/\hbar$; $\mathcal{E}_i^{a,b}$ are the energies of the i th vibrational states of the terms a and b. Substituting (5) into the Schrödinger equation, we multiply the resulting expression by

the conjugate wave function, and using the first-order perturbation theory only, we obtain [6]

$$b_j(t) = -\frac{i}{\hbar} \int \sum_i a_i^0 \exp[i(\omega_i^a - \omega_j^b)t] V_{ij} dt, \quad (6)$$

where a_i^0 is initial value of the coefficient $a_i(t)$. In simulating the process of pumping it is necessary to find the population of individual vibrational levels. We assume that at the initial instant of time only the first vibrational level is occupied. Then

$$|b_j(t)|^2 = \frac{1}{\hbar^2} \left| \int a_1^0 \exp[i(\omega_1^a - \omega_j^b)t] V_{1j} dt \right|^2. \quad (7)$$

In the case of predissociation, the total population

$$P_{\text{tot}} = \sum_j |b_j(t)|^2 = \frac{1}{\hbar^2} \sum_j \left| \int \sum_i a_i^0 \exp[i(\omega_i^a - \omega_j^b)t] V_{ij} dt \right|^2. \quad (8)$$

Passing from the summation over j to integration in the energies \mathcal{E} , we obtain

$$P_{\text{tot}} = \left| \sum_j b_j(t) \right|^2 = \frac{1}{\hbar^2} \int \rho(\mathcal{E}) \times \left| \int \sum_i a_i^0 \exp\left[i\left(\omega_i^a - \frac{\mathcal{E}}{\hbar}\right)t\right] V_{ij} dt \right|^2 d\mathcal{E}, \quad (9)$$

where $\rho(\mathcal{E})$ is the level density.

3. Calculation of overlap integrals

The perturbation operator V is the scalar product of the dipole moment vector of the molecule by the electric field strength vector of laser radiation. Its calculation requires several procedures: to calculate the overlap integrals of vibrational states, to take into account the rotation of the molecule and to calculate the time integral.

Because the rotation of the molecules leads only to an additional factor, we will first consider it. It is needed to represent the scalar product of spherical tensors, corresponding to the electric field strength vector \mathbf{E}_t and dipole moment vector $\boldsymbol{\mu}_e$ [7], as:

$$H'(t) = -T^1(\mathbf{E}_t) \cdot T^1(\boldsymbol{\mu}_e) = -T_0^1(\mathbf{E}_t) \cdot T_0^1(\boldsymbol{\mu}_e). \quad (10)$$

If we denote the angular part of the wave function as $|J, \Omega, M_j\rangle$, we obtain an expression for the matrix elements:

$$\begin{aligned} \langle J, \Omega, M_j | -E_0(t) T_0^1(\boldsymbol{\mu}_e) [D_{00}^{(1)}]^* | J', \Omega', M_j' \rangle \\ = -E_0(t) \mu_0 (-1)^{J-M_j} \end{aligned} \quad (11)$$

$$\times \begin{pmatrix} J & 1 & J' \\ -M_j & 0 & M_j' \end{pmatrix} (-1)^{J-\Omega} \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \sqrt{(2J+1)(2J'+1)},$$

where the matrices denote the Wigner 3-j symbols; J is the rotational number; Ω is the total angular momentum of the electrons; M_j is the projection of \mathbf{J} on the z axis; $D_{00}^{(1)}$ is the D-function [8]; q is the number of the component of the spherical tensor (10). The values of the matrix elements of the dipole moment μ_0 are known from the literature: $\mu_0 = 0.03 \text{ D}$

for the $B \rightarrow a$ transition [9] and 0.8 D for the $X \rightarrow B$ transition between ground and first excited states [10].

Let us discuss now the computation of the time integral. This part of the calculation is also common both for the process of pumping and for the process of predissociation. Time-dependent part of the perturbation has the form

$$V = \exp\left[\frac{(t-t_0)^2}{\tau^2}\right] \cos\left(\omega t + \frac{\gamma}{2}t^2\right) \\ = \exp\left[\frac{(t-t_0)^2}{\tau^2}\right] \operatorname{Re}\left\{\exp\left[i\left(\omega t + \frac{\gamma}{2}t^2\right)\right]\right\}. \quad (12)$$

Consider the inner time integral entering into expression (9):

$$\int_{-\infty}^{\infty} \exp\left[i\left(\omega_i - \frac{\mathcal{E}}{\hbar}\right)t\right] \exp\left[-\frac{t^2}{\tau^2} + i\left(\omega + \frac{\gamma}{2}t^2\right)\right] \\ \times \exp\left[i\left(\omega_i - \frac{\mathcal{E}}{\hbar}\right)t_0\right] dt, \quad (13)$$

where ω_i is the frequency corresponding to the i th vibrational level. This is a usual Gaussian integral. It can be easily evaluated and is equal to

$$\exp\left[-\frac{\tau^2(\omega_i - \mathcal{E}/\hbar + \omega)^2}{4(1 + \tau^4\gamma^2/4)} - \left(1 + i\tau^2\frac{\gamma}{2}\right)\right] \sqrt{\pi} \\ \times \frac{\exp[-i\arctan(\tau^2\gamma/2)] \exp[i(\omega_i - \mathcal{E}/\hbar)t_0]}{\sqrt{1/\tau^4 + \gamma^2/4}}. \quad (14)$$

Let the time-independent part of the perturbation have the form $\mu_i(\mathcal{E}) = \mu_i^{\text{vib}}(\mathcal{E})$, where $\mu_i^{\text{vib}}(\mathcal{E})$ is the overlap integral of the i th wave function of the discrete spectrum and of the wave function of a continuous spectrum, corresponding to the energy \mathcal{E} . The expression for the transition probability can be simplified by using the previously introduced spectral chirp and spectral width. Then, the final expression for the population of the state a can be written as

$$P_{\text{tot}} = \frac{\mu_0^2 \pi |\bar{E}|^2}{\hbar^2} \frac{\tau}{\Delta\omega} \int_{E_{\text{min}}}^{\infty} \rho(\mathcal{E}) \left| \sum_{i=i_{\text{min}}}^{i_{\text{max}}} a_i^0 \mu_i^{\text{vib}}(\mathcal{E}) \right. \\ \times \exp\left[-\frac{(\omega_i - \mathcal{E}/\hbar + \omega)^2}{\Delta\omega^2}\right] \cos\left[\left(\omega_i - \frac{\mathcal{E}}{\hbar}\right)t_0 \right. \\ \left. \left. - \left(\omega_i - \frac{\mathcal{E}}{\hbar} + \omega\right)^2 \frac{\beta}{8}\right] \right|^2 d\mathcal{E}. \quad (15)$$

Consider now the problem of calculating the overlap integrals of vibrational wave functions. For the process of pumping, the integral is calculated using the explicit expressions for the vibrational wave functions. For the process of predissociation, $\mu_i^{\text{vib}}(\mathcal{E})$ is the overlap integral of the i th vibrational wave function of the attracting state with a nuclear function of the repulsive state with energy \mathcal{E} . Using the semiclassical approximation, we obtain [8]

$$\mu(\mathcal{E}) = \frac{2}{\sqrt{v|F_1 - F_2|}} \cos\left(\frac{S_0}{\hbar} + \frac{\pi}{4}\right). \quad (16)$$

Here, at the point of intersection of the terms (the internuclear distance $r = r_0$), the velocities of the relative radial motion of nuclei are $v_1 = v_2 = v$;

$$F_{1,2} = \left. \frac{dU_{1,2}(r)}{dr} \right|_{r=r_0}$$

are the forces at the point of intersection of the terms; $U_{1,2}(r)$ are the potentials of the corresponding terms. An explicit expression for S_0 is given by

$$S_0 = \int_{a_1}^{r_0} \sqrt{2m[\mathcal{E} - U_1(r)]} dr \\ - \int_{a_2}^{r_0} \sqrt{2m[\mathcal{E} - U_2(r)]} dr, \quad r = r_0, \quad (17)$$

where m is the mass of the atom; a_1, a_2 are the turning points. We assume that the population of rotational levels is distributed according to Boltzmann's law:

$$\rho_B(J, i) = \frac{(2J+1) \exp[-\mathcal{E}(i, J)/(k_B T)]}{Q_{\text{vib}} Q_{\text{rot}}}. \quad (18)$$

Here Q_{vib} and Q_{rot} are vibrational and rotational state sums. Putting it all together and going over from integration in energies to integration in wave numbers k , we obtain the resulting expression for the predissociation probability in the form

$$P_{\text{tot}} = \frac{\mu_0^2 \pi |\bar{E}|^2}{\hbar^2} \frac{\tau}{\Delta\omega} \int_{k_{\text{min}}}^{\infty} \left| \sum_{J_1, J_2} \sum_{M_{J_1}=-J_1}^{J_1} \sum_{M_{J_2}=-J_2}^{J_2} \sum_{i=i_{\text{min}}}^{i_{\text{max}}} \frac{\rho_B(J, i)}{2J_1+1} \right. \\ \times a_i^0 \mu_i^{\text{vib}}(k, J_1, M_{J_1}, J_2, M_{J_2}) \Xi(k, \omega_i, \Delta\omega, \tau_0, \omega, \beta) \left. \right|^2 dk, \\ k^2 = 2m\mathcal{E}/\hbar^2, \quad (19)$$

where

$$\Xi(k, \omega_i, \Delta\omega, \tau_0, \omega, \beta) = \exp\left\{-\frac{[\omega_i - \hbar k^2/(2m) + \omega]^2}{\Delta\omega^2}\right\} \\ \times \cos\left[\left(\omega_i - \frac{\hbar k^2}{2m}\right)\tau_0 - \left(\omega_i - \frac{\hbar k^2}{2m} + \omega\right)^2 \frac{\beta}{8}\right]; \quad (20)$$

$$\mu_i^{\text{vib}}(\mathcal{E}, J_1, M_{J_1}, J_2, M_{J_2}) = \frac{2(-1)^{2J_2 - \Omega - M_{J_2}}}{\sqrt{v|F_1 - F_2|}} \cos\left(\frac{S_0}{\hbar} + \frac{\pi}{4}\right) \\ \times \begin{pmatrix} J_2 & 1 & J_1 \\ -M_{J_2} & 0 & M_{J_1} \end{pmatrix} \begin{pmatrix} J_2 & 1 & J_1 \\ -\Omega & q & \Omega' \end{pmatrix} \sqrt{(2J_2+1)(2J_1+1)}; \quad (21)$$

τ_0 is the time delay between the pump pulse and probe pulse.

Consider the coefficient $\mu_i^{\text{vib}}(\mathcal{E}, J_1, M_{J_1}, J_2, M_{J_2})$. One can see that expression (21) involves the product of 3-j symbols, which are different from zero only if the sum of the elements of the bottom line is zero, whereas the elements of the top line satisfy the triangle rule. Therefore, we conclude that $M_{J_1} = M_{J_2}$. In addition, $J_2 = J_1 \pm 1, J_1$. Consequently, we eliminate the summation over M_{J_2} , which greatly simplifies the calculation. However, even in this case, the calculation of the probability by formula (19) is very problematic, and hence we will use reasonable physical approximations.

4. Simplifications

Note, first of all, that for small values of J (approximately 5–10), calculations can be performed on a personal computer in a reasonable time. However, at room temperatures the

states with rotational numbers 50–200 are excited. Therefore, we will use the approximation of large J . First, we neglect the dependence of the energy levels on J . This allows us to separately carry out the summation over the 3- j symbols.

Consider the relation

$$A = \sum_{J_2=J_1+1, J_1} (-1)^{2J_2-\Omega-M_{J_2}} \begin{pmatrix} J_2 & 1 & J_1 \\ -M_{J_1} & 0 & M_{J_2} \end{pmatrix} \begin{pmatrix} J_2 & 1 & J_1 \\ -1 & q & 1 \end{pmatrix} \times \sqrt{(2J_2+1)(2J_1+1)}. \quad (22)$$

The exact expression for it has the form:

$$A = -\frac{(-1)^{-1-2J_1}(1+2J_1)M_{J_1}}{J_1(1+3J_1+2J_1^2)} - (-1)^{-1+2J_1-2M_{J_1}} \times \sqrt{[1+2(-1+J_1)](1+2J_1)} \frac{\sqrt{(J_1^2-1)(J_1^2-M_{J_1}^2)}}{J_1(-1+4J_1^2)} - (-1)^{-1-2J_1} \times \frac{\sqrt{(1+2J_1)[1+2(J_1+1)]} \sqrt{J_1(2+J_1)(1+2J_1+J_1^2-M_{J_1}^2)}}{3+11J_1+12J_1^2+4J_1^3}. \quad (23)$$

Just note that in the summation over M_J from $-J$ to J the first term vanishes. In the limit of large J , expression (23) is simplified and becomes asymptotically equal to

$$\frac{\sqrt{J^2-M_J^2}}{J} \approx 1 - \frac{1}{2} \left(\frac{M_J}{J} \right)^2. \quad (24)$$

Now we perform an elementary summation over M_J , using the known formula for the sum of the squares of consecutive integers. Then, we obtain

$$2J+1 - \frac{(1+J)(1+2J)}{6J}. \quad (25)$$

Again using the limit of large J , we obtain an asymptotic expression for (25):

$$1 + \frac{5}{3}J. \quad (26)$$

Now all the terms in (19), depending on J , will gather in the expression

$$\frac{\rho_B(J, i)}{2J+1} \left(1 + \frac{5}{3}J\right), \quad (27)$$

which in the limit of large J transforms into

$$\frac{5}{6} \rho_B(J, i). \quad (28)$$

Thus, at high rotational numbers expression (19) is considerably simplified:

$$P_{\text{tot}} = \frac{\mu_0^2 \pi |\bar{E}|^2}{\hbar^2} \frac{\tau}{\Delta\omega} \int_{k_{\min}}^{\infty} \left| \sum_{i=i_{\min}}^{i_{\max}} \sum_j \frac{10}{6} \rho_B(J, i) a_i^0 \right. \\ \left. \times \Xi(k, \omega_i, \Delta\omega, \tau_0, \omega, \beta) \frac{\cos(S_0/\hbar + \pi/4)}{\sqrt{|v| |F_1 - F_2|}} \right|^2 dk. \quad (29)$$

In principle, we can perform the summation over J with good accuracy, assuming that the sum of the density values is close to unity with good accuracy. In this case, formula (19) is also considerably simplified:

$$P_{\text{tot}} = \frac{\mu_0^2 \pi |\bar{E}|^2}{\hbar^2} \frac{25\tau}{9\Delta\omega} \int_{k_{\min}}^{\infty} \left| \sum_{i=i_{\min}}^{i_{\max}} a_i^0 \exp \left\{ \frac{[\omega_i - \hbar k^2/(2m) + \omega]^2}{\Delta\omega^2} \right\} \right. \\ \left. \times \cos \left[\left(\omega_i - \frac{\hbar k^2}{2m} \right) \tau_0 - \left(\omega_i - \frac{\hbar k^2}{2m} + \omega \right) \frac{\beta}{8} \right] \right. \\ \left. \times \frac{\cos(S_0/\hbar + \pi/4)}{\sqrt{|v| |F_1 - F_2|}} \right|^2 dk. \quad (30)$$

There remains, however, the problem of determining the coefficients a_i^0 , whose squares represent the populations of the B state. Because in our case the B state is also pumped by a femtosecond laser, with only the first vibrational level being initially populated in the X-state, formula (30) can be used to obtain expressions for these coefficients:

$$a_i^0 = S_{0i} \frac{\mu_0 |\bar{E}|}{\hbar} \sqrt{\frac{\pi\tau}{\Delta\omega}} \exp \left[\frac{(\omega_0 - \mathcal{E}/\hbar + \omega)^2}{\Delta\omega^2} \right] \\ \times \cos \left[\left(\omega_0 - \frac{\mathcal{E}_i}{\hbar} + \omega \right) \frac{\beta}{8} \right], \quad (31)$$

where S_{0i} is the overlap integral of the first vibrational level of the X state with the i th vibrational level of the B state. It should be noted that the formulas can be used only when the pulses do not overlap in time. Otherwise, we would not have the right to conduct separate time integration for the population of each state.

5. Results and conclusions

In the calculations we used the following parameters of laser radiation:

- (i) intensity of the pump and coupling laser fields, $3 \times 10^8 \text{ V m}^{-1}$;
- (ii) pulse duration, 20 fs; spectral width, 30 fs $^{-1}$;
- (iii) pump wavelength, 500 nm, which corresponds to the absorption band;
- (iv) coupling radiation wavelength, 800 nm;
- (v) spectral chirps of the pump pulse and coupling pulse, 10 fs $^{-2}$; delay time between pulses, 5000 fs (unless otherwise stated).

These parameters correspond to the parameters of femtosecond lasers used in experiments. We studied the dependence of the predissociation intensity on the delay time and spectral chirps.

One can see from Figs 2–4 that there is an oscillatory dependence of the predissociation intensity on the spectral chirps and delay time between pulses. This dependence of the delay time is easy to explain. The delay time enters into formula (30) as the argument of the cosine. Thus, the predissociation intensity will be maximal when all the components of the packet will be oscillating in phase at the turning point. This fact explains the observed peaks.

The oscillatory dependence of the predissociation intensity on the spectral chirp has a similar nature. In the case of the pump pulse, as seen from equation (31), the spectral chirp controls the relative populations of vibrational states of the wave packet. Because each state has its own frequency, the change in the population causes a change in the general form of the wave packet oscillation. Although the exact frequency of the packet oscillations is not affected by the population of individual states, the exact frequency that is equal to the lowest multiple of all frequencies has no practical sense. If the population of the levels in the packet is considerably irregu-

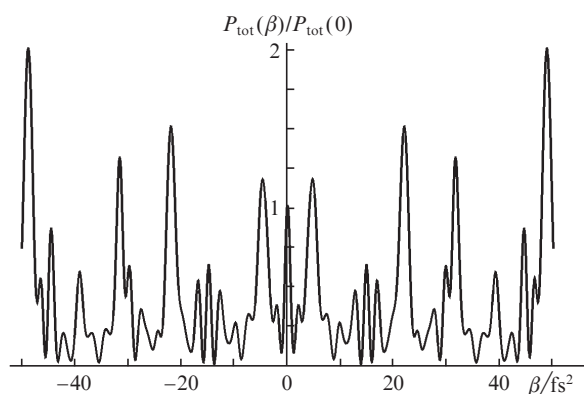


Figure 2. Dependence of the predissociation intensity on the spectral chirp of the pump pulse.

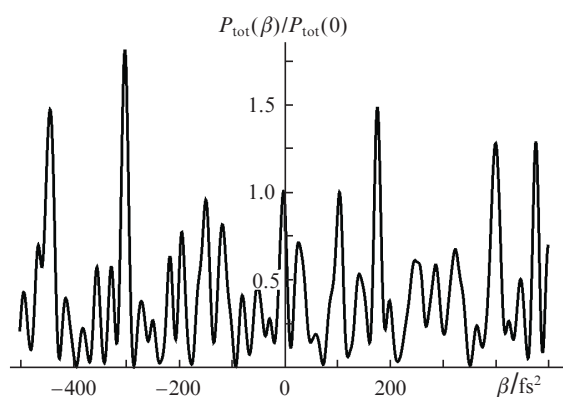


Figure 3. Dependence of the predissociation intensity on the spectral chirp of the coupling pulse.

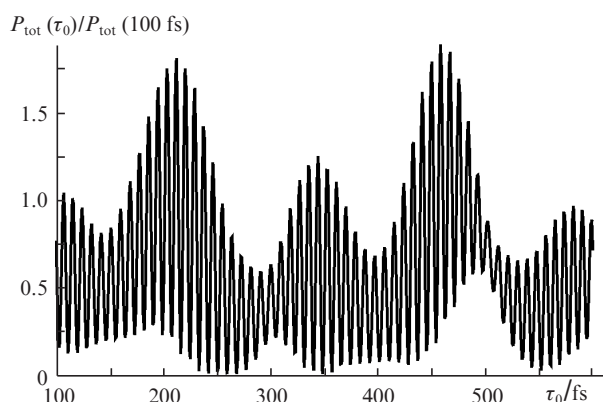


Figure 4. Dependence of the predissociation intensity on the delay time between the pulses.

lar, the oscillation frequency of the packet will be determined by the most populated levels.

The dependence of the predissociation intensity on the spectral chirp of the coupling pulse is explained in a similar way. The spectral chirp enters into (30) as the argument of the cosine and thus controls the relative contribution of individual vibrational states.

Therefore, it is possible to control predissociation by changing the time delay between the pump pulse and coupling

pulse at their fixed phase characteristics and by varying the phase characteristics of the coupling pulse. For the experimental observation of such control, use can be made of a mass spectrometer, recording the yield of atomic iodine.

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