Effect of the phase modulation of a light pulse on three-photon absorption in a system without intermediate resonance states

M.N. Krivoguz, O.M. Sarkisov, S.Ya. Umansky

Abstract. **The effect of phase modulation of a femtosecond light pulse on three-photon absorption in a diatomic system is studied. Direct three-photon transitions between the initial and final electronic states are considered. The total populations of the final electronic state are calculated for different modulation types as functions of the parameter describing modulation. It is found that the effect of modulation on the three-photon excitation probability substantially depends on the modulation regime. The results of calculations are compared with available experimental data.**

1. Introduction

The possibility of controlling chemical reactions by using femtosecond laser pulses attracts the recent attention of experimentalists and theoreticians. The discussion of different approaches to the solution of this problem can be found, for example, in papers [1, 2]. The control of chemical reactions by varying the parameters of a femtosecond laser pulse is one of the most promising approaches. The variation of the so-called chirp of a femtosecond laser pulse is used most often for this purpose (see, for example, [2]).

The channels of photochemical reactions were controlled by varying the chirp of an exciting femtosecond pulse in experiments on multiphoton ionisation of CH_2I_2 [3] and NH_3 [4]. Thus, by varying the chirp of a pump pulse, the yield of one of the products $[NH(c\,^1\Pi)]$ of five-photon photodissociation of NH_3 was increased by a factor of twelve [4].

The mechanism of chirp influence on the yield of products of multiphoton dissociation proceeding via an intermediate resonance electronic state was discussed in [5]. In this case, the dynamics of a wave packet in the intermediate resonance electronic state depends on the chirp

M.N. Krivoguz Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge. MA, 021141, office 6-234, USA; e-mail: maximian@mail.ru;
O.M. Sarkisov, S.Ya. Umansky N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, 119991 Moscow, Russia; e-mail: sarkisov@femto.chph.ras.ru, unan@center.chph.ras.ru
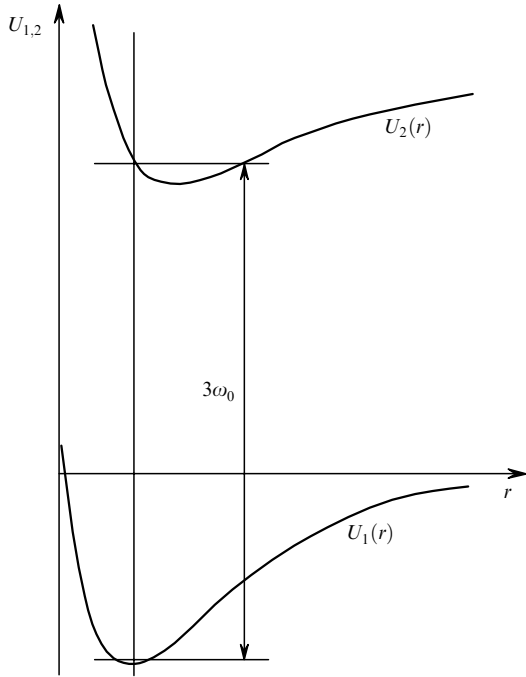
of a pump pulse. This in turn results in the dependence of the total population of the final electronic state on the chirp.

However, one can expect that phase-dependent effects can also take place when multiphoton absorption does not involve any intermediate electronic state. Such effects were observed experimentally in [6] where the fluorescence of macromolecules upon multiphoton absorption depended on the phase-modulation parameter.

The aim of this paper is to elucidate the possibility of controlling the efficiency of multiphoton absorption in a system with two electronic states by varying the phase modulation of a pump femtosecond pulse. A model problem of three-photon excitation of a diatomic molecule by a modulated femtosecond laser pulse is considered.

Everywhere atomic units ($e = \hbar = m_e = 1$) are used except indicated cases.

2. Description of the model

Consider a diatomic molecule with two electronic states $|1\rangle$ and $|2\rangle$. We assume that both potential curves $U_1(r)$ and $U_2(r)$ (r is the internuclear distance) corresponding to these states are attractive. The rotation of the molecule is neglected. The corresponding time-dependent discrete vibronic states are denoted as $|1, n_1\rangle$ and $|2, n_2\rangle$, where n_1 and n_2 are the vibronic quantum numbers. We also assume that the photoinduced $|1, n_1\rangle \rightarrow |2, n_2\rangle$ transitions are allowed dipole transitions.

The molecule interacts with a femtosecond laser pulse. The time dependence of the electric field strength E of such a pulse is commonly written in the form

$$E(t) = E_0(t) \cos[\omega_0 t + \eta(t)]. \tag{1}$$

Here, $E_0(t)$ is the pulse envelope; ω_0 is the carrier frequency; and the function $\eta(t)$ describes phase modulation.

It is assumed that the frequencies of most probable transitions between the two electronic potential curves $U_1(r)$ and $U_2(r)$ are close to $3\omega_0$ (Fig. 1). Therefore, the $|2, n_2\rangle$; states can be populated due to the three-photon absorption transition from the $|1, n_1\rangle$ states induced by the femtosecond pulse.

The electric field strength $E(t)$ can be written in the complex form

$$E(t) = A(t) \exp(-i\omega_0 t) + B(t) \exp(i\omega_0 t), \tag{2}$$

where $A(t)$ and $B(t)$ are the complex amplitudes. The absorption of a photon is determined by the first term in (2)

Figure 1. Model of two electronic states.

(see, fore example, [5]), while the second term can be neglected because it provides the rapid oscillation of the integrand in the expression for the transition amplitude.

The electric field strength in a femtosecond laser pulse is usually $10^5 - 10^6$ V cm^{-1}, which is much lower than the strength of intramolecular electric fields. Therefore, the problem under study can be solved within the framework of the nonstationary perturbation theory, in which a perturbation is the interaction of electric field (1) with the dipole moment D of the molecule:

$$\hat{V}(t) = -E(t)D. \tag{3}$$

We will seek the wave function of the system in the external electric field $E(t)$ in the form

$$\Psi(t) = \sum_{n_1} a_{n_1}(t)|1, n_1\rangle + \sum_{n_2} b_{n_2}(t)|2, n_2\rangle. \tag{4}$$

The coefficients a_{n_1} and b_{n_2} should satisfy the initial conditions

$$a_{n_1}|_{t\to-\infty} = \delta_{n_1 0}, \quad b_{n_2}|_{t\to-\infty} = 0. \tag{5}$$

The amplitude $A_{n_2'}^{(3)}$ of the three-photon transition to the final $|2, n_2\rangle$ state is determined by the expression

$$A_{n_2'}^{(3)}(\infty) = i \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{t_3} dt_2 \int_{-\infty}^{t_2} dt_1 \tag{6}$$

$$\times \sum_{n_1}\sum_{n_2} \langle 2, n_2'|\hat{V}(t_3)|1, n_1\rangle\langle 1, n_1|\hat{V}(t_2)|2, n_2\rangle\langle 2, n_2|\hat{V}(t_1)|1, 0\rangle.$$

The expression for the matrix elements $\hat{V}(t)$ in (6) in the Condon approximation has the form

$$\langle 1, n_1|\hat{V}(t)|2, n_2\rangle = \langle 2, n_2|\hat{V}(t)|1, n_1\rangle^*$$

$$= -\langle 1, n_1|D|2, n_2\rangle E(t) = -S_{n_1 n_2} D_{12} E(t)$$

$$\times \exp(-i\Delta E_{21}^e t + i\varepsilon_{n_1} t - i\varepsilon_{n_2} t). \tag{7}$$

Here, D_{12} is the electronic matrix element of the dipole moment; $S_{n_1 n_2}$ is the overlap integral for the vibrational wave functions in the states $|1, n_1\rangle$ and $|2, n_2\rangle$; ε_{n_1} and ε_{n_2} are the energies of vibrational levels in the $|1\rangle$ and $|2\rangle$ electronic states; and ΔE_{21}^e is the difference of the minima of potential curves of the $|2\rangle$ and $|1\rangle$ electronic states. The overlap integrals $S_{n_1 n_2}$ were calculated numerically by using the uniform quasi-classical approximation for the nuclear wave functions of a discrete spectrum (see, for example, [7, 8]). The model potential curves of the $|1\rangle$ and $|2\rangle$ electronic states were used, which approximately coincided with the attractive potential curves of the I_2 molecule.

By using (6) and (7) and retaining only the first term in (2), we obtain the following expression for $A_{n_2'}^{(3)}$:

$$A_{n_2'}^{(3)} = -D_{12}^3 i \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{t_3} dt_2 \int_{-\infty}^{t_2} dt_1$$

$$\times \sum_{n_1}\sum_{n_2} S_{n_1 n_2'} S_{n_1 n_2} S_{n_2 n_1 = 0}\{A(t_3)\exp[i(\Delta_{2n_2' 1n_1} + 2\omega_0)t_3]\}$$

$$\times\{A(t_2)\exp[-i(\Delta_{2n_2 1n_1} + 4\omega_0)t_2]\}$$

$$\times\{A(t_1)\exp[i(\Delta_{2n_2 1n_1=0} + 2\omega_0)t_1]\}. \tag{8}$$

Here,

$$\Delta_{2n_2(n_2') 1n_1} = \Delta E_{21}^e + \varepsilon_{n_2(n_2')} - \varepsilon_{n_1} - 3\omega_0 \tag{9}$$

is the resonance detuning.

The complex amplitude $A(t)$ of the electric field changes slowly during the pulse compared to the oscillating term $\exp(i2\omega_0 t)$. For $p \gg 1$ and $f(-\infty) = 0$,

$$\int_{-\infty}^{x} f(y)\exp(-ipy)dy = \frac{i}{p} f(x)\exp(-ipx)$$

$$-\frac{i}{p}\int_{-\infty}^{x} f'(y)\exp(-ipy)dy \approx \frac{i}{p} f(x)\exp(-ipx), \tag{10}$$

so that a simple expression for $A_{n_2'}^{(3)}$ follows from (8):

$$A_{n_2'}^{(3)} = -iD_{12}^3 \sum_{n_1}\sum_{n_2} S_{n_1 n_2'} S_{n_1 n_2} S_{n_2 n_1 = 0}$$

$$\times \frac{1}{2\omega_0 + \Delta_{2n_2 1n_1=0}} \frac{1}{2\omega_0 - \Delta_{2n_2 1n_1=0} + \Delta_{2n_2 1n_1}}$$

$$\times \int_{-\infty}^{\infty} A^3(t_3)\exp(i\Delta_{2n_2' 1n_1=0} t_3)dt_3. \tag{11}$$

The total population P_2 of the final attractive $|2\rangle$ electronic

state is equal to the sum of populations of vibrational states:

$$P_2 = \sum_{n'_2} \left| A_{n'_2}^{(3)} \right|^2. \tag{12}$$

3. Phase modulation regimes

The simplest type of femtosecond pulses used in photochemistry is Gaussian pulses with quadratic modulation, for which the complex amplitude [see (2)] has the form

$$A(t) = A_0 \exp\left(-\frac{t^2}{\tau^2}\right) \exp[-i\eta(t)], \quad \eta(t) = \frac{\gamma t^2}{2}. \tag{13}$$

Here, τ is the pulse duration and γ the time chirp.

The Fourier transform of complex amplitude (13), as a function of $\Omega = \omega - \omega_0$ at frequencies ω close to ω_0 has the form

$$E(\Omega) = |E(\Omega)| \exp[i\varphi(\Omega)], \tag{14}$$

where

$$|E(\Omega)| \propto \exp\left(-\frac{\Omega^2}{\Delta\omega^2}\right); \quad \varphi(\Omega) = \frac{\beta\Omega^2}{2}; \tag{15}$$

$$\Delta\omega = \frac{(4 + \gamma^2\tau^4)^{1/2}}{\tau} \tag{16}$$

is the spectral width; and

$$\beta = \frac{4\gamma\tau^4}{4 + \gamma^2\tau^4} \tag{17}$$

is the so-called spectral chirp.

Consider several cases.

Case 1. The most natural way to study the effect of the phase modulation of a Gaussian femtosecond light pulse on the processes induced by this pulse is the variation of the time chirp γ at the fixed pulse duration τ. One can see from (16) that the spectral width of the pulse depends on the absolute value $|\gamma|$ of the chirp. The larger is $|\gamma|$, the larger is the spectral width of the pulse and smaller the square of the Fourier component of the electric field.

Figure 2 shows the dependence of the excitation probability P_2 on the spectral chirp β calculated from (11) and
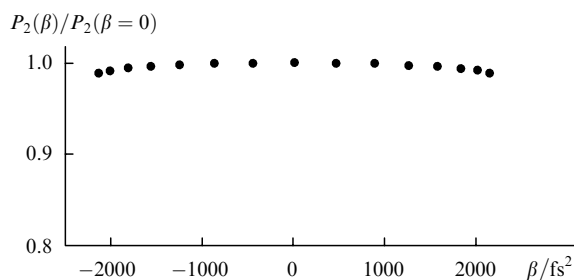
Figure 2. Dependence of the population P_2 of the final electronic state of the spectral chirp β upon phase modulation preserving the pulse duration.

(12) by varying the time chirp γ and at the fixed pulse duration τ.

Case 2. In experimental studies of the effect of phase modulation on the processes induced by a femtosecond pulse, another variant of phase modulation is used, as a rule (see, for example, [2, 4]), when the spectral chirp β is directly varied at the fixed spectral width $\Delta\omega$. It follows from (15)–(17) that in this case, the square of the Fourier component of the electric field does not change but the pulse duration increases. Figure 3 shows the dependence of P_2 on β calculated numerically for the fixed spectral width of the pulse.
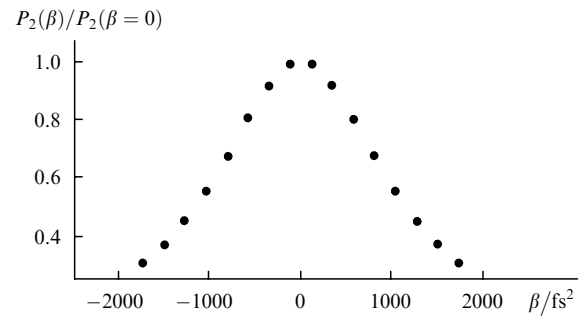
Figure 3. Dependence of the population P_2 of the final electronic state on the spectral chirp β upon phase modulation preserving the spectral width of the pulse.

A comparison of Figs 2 and 3 shows that the phase modulation of the pulse at the fixed spectral width (rather than at a constant duration of the Gaussian femtosecond pulse) substantially affects the integrated population P_2. Note that in both cases the dependence of P_2 on the spectral chirp β is symmetric with respect to $\beta = 0$. This dependence considerably differs from the dependence observed upon three-photon excitation via an intermediate resonance state [5]. In the latter case, the dependence $P_2(\beta)$ is strongly asymmetric.

Case 3. Modern methods for shaping femtosecond pulses allow one to obtain much more complicated phase modulation. In particular, the phase modulation of the excitation pulse used in experimental paper [6] was described by the expression

$$E(\Omega) = A_0 \exp\left(-\frac{\Omega^2}{\Delta\omega^2}\right) \exp[i\varphi(\Omega)], \tag{18}$$

$$\varphi(\Omega) = \alpha\cos(\xi\Omega - \delta),$$

where α is the modulation depth and ξ is the variable parameter; the phase shift δ plays here the role of the modulation parameter.

The population P_2 was calculated for the same parameters of the excitation pulse described by (18) as in [6]. The results of calculations are presented in Fig. 4. The oscillating dependence $P_2(\delta)$ in Fig. 4 is similar to that observed in [6]. Note that the values of δ_{ex} at which $P_2(\delta)$ has extrema depend on the detuning from the resonance (Fig. 5). As shown in the next section, in the case of zero detuning, $\delta_{ex} = \pi/2 + \pi k$, where k is an integer.
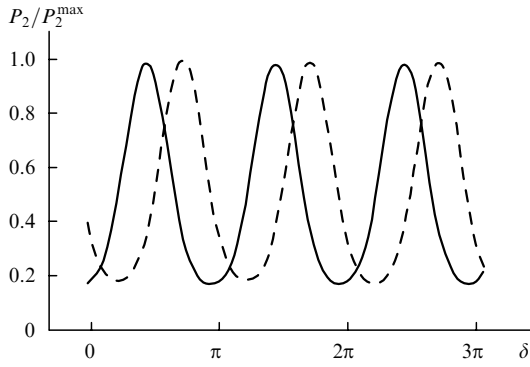
Figure 4. Dependences of the population P_2 of the final electronic state on the modulation parameter δ for detunings Δ_1 (solid curve) and Δ_2 (dashed curve) shown in Fig. 5.
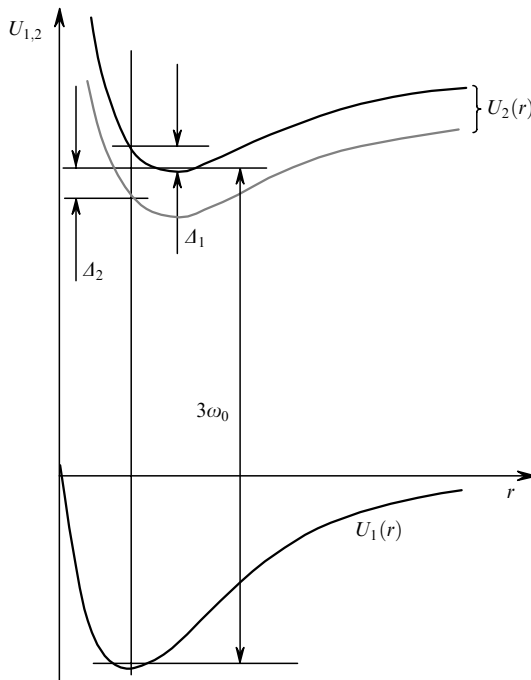

Figure 5. Model of two electronic states with different detunings from the resonance.

4. Interpretation of the phase modulation in cases 2 and 3

Our numerical calculations have demonstrated that the population P_2 of the final electronic state depends on the phase modulation of the excitation pulse. This dependence can be interpreted analytically in the following way. Consider the integral

$$I = \int_{-\infty}^{\infty} A^3(t_3) \exp(i\Delta_{2n'_2 1n_1=0}t_3)dt_3. \qquad (19)$$

This is the part of expression (11) that depends on the phase modulation. By substituting the Fourier transform $A(t_3)$ into (19), we obtain

$$I = \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{\infty} d\Omega_1 \int_{-\infty}^{\infty} d\Omega_2 \int_{-\infty}^{\infty} d\Omega_3 |E(\Omega_1)| \times$$

$$\times |E(\Omega_2)||E(\Omega_3)| \exp\{i[\varphi(\Omega_1) + \varphi(\Omega_2) + \varphi(\Omega_3)]\}$$

$$\times \exp[-i(\Omega_1 + \Omega_2 + \Omega_3)t_3] \exp(i\Delta_{2n'_2 1n_1=0}t_3), \qquad (20)$$

where $\Omega_i = \omega_i - \omega_0$ $(i = 1 - 3)$. The integration of expression (20) with respect to t_3 gives

$$I = \int_{-\infty}^{\infty} d\Omega_1 \int_{-\infty}^{\infty} d\Omega_2 |E(\Omega_1)||E(\Omega_2)||$$

$$\times |E(\Delta_{2n'_2 1n_1=0} - \Omega_1 - \Omega_2)| \exp\{i[\varphi(\Omega_1) + \varphi(\Omega_2)$$

$$+ \varphi(\Delta_{2n'_2 1n_1=0} - \Omega_1 - \Omega_2)]\}. \qquad (21)$$

The integral I has the maximum value when the argument of the complex exponential vanishes:

$$\varphi(\Omega_1) + \varphi(\Omega_2) + \varphi(\Delta_{2n'_2 1n_1=0} - \Omega_1 - \Omega_2) = 0. \qquad (22)$$

By comparing expression (22) with the results of numerical calculations discussed above, we obtain that if $\varphi(\Omega) = \beta\Omega^2/2$, Eqn (22) is satisfied for $\beta = 0$ irrespective of the detuning value $\Delta_{2n'_2 1n_1=0}$. Therefore, $P_2(\beta)$ has a maximum at $\beta = 0$ (see Fig. 3). If $\varphi(\Omega) = \alpha \cos(\gamma\Omega - \delta)$, then for $\Delta_{2n'_2 1n_1=0} \approx 0$, $P_2(\delta)$ has maxima at $\delta \approx \pi/2 + \pi k$.

5. Discussion

Three-photon excitation via the intermediate resonance state by chirped femtosecond Gaussian pulses was studied in [5]. In this case, the results of calculations depend substantially on the formation and evolution of a vibrational wave packet in the intermediate electronic state. It is this evolution that causes the asymmetric dependence of the results on the chirp with respect to zero.

In the case considered in the paper, an intermediate electronic state is absent, and therefore the dependence on the chirp is symmetric with respect to $\beta = 0$ (see Figs 2 and 3). In this case, the phase modulation of the pulse at a constant duration of the Gaussian pulse in fact does not affect the results of calculations (see Fig. 2). At the same time, the results drastically depend on the spectral chirp if phase modulation is performed at a constant spectral width of the pulse (see Fig. 3). This effect was called [6] multiphoton intrapulse interference. The obtained results show in fact that in the case of multiphoton excitation without intermediate resonance states, the 'pure' phase modulation caused by linear chirping does not affect the final result. Indeed, upon varying the spectral chirp at a constant spectral width of the pulse, the pulse duration changes.

In [6], the fluorescence of polyatomic molecules, including proteins was studied in solutions upon excitation by phase-modulated femtosecond pulses. The dependences of the fluorescence intensity on the modulation parameter of the laser pulse described by expression (18) were obtained. They proved to be approximately the same for different molecules and very similar to those presented in Fig. 4. This suggests that a simple model with two electronic states considered in our paper can be used for the qualitative interpretation of experimental data [6].

References

1. Zare R.N. *Science*, **279**, 1875 (1998).
2. Sarkisov O.M., Umansky S.Ya. *Usp. Khim.*, **70**, 515 (2001).
3. Pastric I., Brown E.J., Zhang Q., Dantus M. *J. Chem. Phys*, **108**, 4375 (1998).
4. Gostev F.E., Dzhailaubekov A.E., Petrukhin A.N., Titov A.A., Umansky S.Ya., Sarkisov O.M. *Khim. Fiz.*, **19** (12), 11 (2000).
5. Krivoguz M.N., Sarkisov O.M., Umansky S.Ya. *Khim. Fiz.*, **23** (2), 86 (2004).
6. Walowicz K.A., Pastirk I., Lozovoy V.V., Dantus M. *J. Phys. Chem. A*, **106**, 9369 (2002).
7. Uzer T., Child M.S. *Mol. Phys.*, **41**, 1177 (1980).
8. Bieniek R.J. *Phys. Rev. A*, **23**, 2826 (1981).