Semiclassical treatment of time-dependent molecular dynamics

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LETTER TO THE EDITOR

Semiclassical treatment of time-dependent molecular dynamics

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Abstract. A semiclassical expression for the total final-state probability of one-photon-resonant two-photon excitation of a diatomic molecule by two time-delayed short laser pulses is derived. It is in good agreement with numerical results and clearly exhibits the dependence of this quantum mechanical observable on the lineshapes of both laser pulses and on the classical quantities which characterize the motion of the vibrational wavepacket generated.

Motivated by recent time-resolved studies of vibrational molecular dynamics (Gruebele and Zewail 1990, Engel *et al* 1988, Marcus 1988) we report in this letter a theoretical study of one-photon-resonant two-photon excitation of a diatomic molecule by two time-delayed short laser pulses. Such pump–probe-type experiments have recently been performed in various groups (Bowman *et al* 1989, Baumert *et al* 1990) and allow the study of the time evolution of the molecule in the excited electronic potential curve after its preparation by the first short laser pulse. With the help of semiclassical methods we consider the question of how the characteristic properties of the molecular vibrations of the excited molecule on the one hand and the lineshapes of the laser pulses on the other hand manifest themselves in the total final-state probability. In recent experiments this probability has been monitored via fluorescence or by measuring the ion yield induced by the second laser pulse. We derive a simple semiclassical expression for this physical observable which is valid for arbitrary pulse shapes and is in good agreement with numerical results.

We consider a typical pump–probe excitation scheme as shown in figure 1. A first laser pulse with electric field strength $E_1(t) = \varepsilon_1 \mathscr{E}_1(t) \, e^{-i\omega_1 t} + \mathrm{CC}$ which is centred around time

$$t_1 = \int_{-\infty}^{\infty} \mathrm{d}t \, t |\mathscr{E}_1(t)|^2 \left(\int_{-\infty}^{\infty} \mathrm{d}t |\mathscr{E}_1(t)|^2 \right)^{-1}$$

and whose pulse duration, τ_1 is determined by

$$(\tau_1)^2 = \int_{-\infty}^{\infty} \mathrm{d}t (t - t_1)^2 |\mathscr{E}_1(t)|^2 \left(\int_{-\infty}^{\infty} \mathrm{d}t |\mathscr{E}_1(t)|^2 \right)^{-1}$$

excites a diatomic molecule from some energetically low-lying bound state $|g\rangle$ with energy ε_g. If the pulse duration is so short that many vibrational states with energies ε_n are excited coherently, a vibrational wavepacket is generated. The time evolution of the localized molecular vibration may be probed by a second short laser pulse
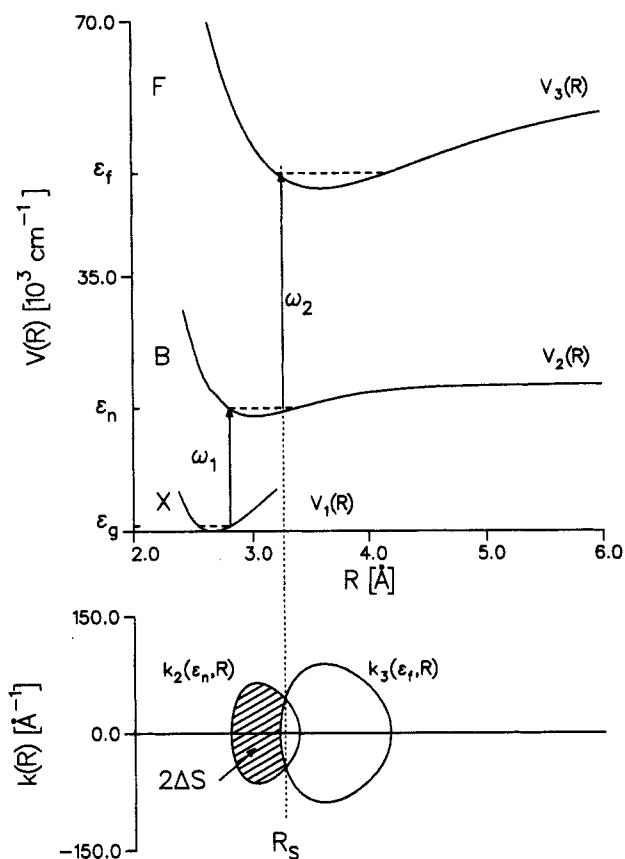
Figure 1. Molecular potential curves of the iodine molecule as a function of internuclear distance (from Engel 1990). The local momenta of intermediate and final states, $k(\varepsilon_n, R)$ and $k(\varepsilon_f, R)$, determine the transition point, R_S. The energies of the indicated vibrational states and of the transition point, R_S, correspond to the excitation process studied in figures 2 and 3.

(centred around time t_2 with pulse duration τ_2 and field strength $E_2(t) = \varepsilon_2 \mathscr{E}_2(t) \, e^{-i\omega_2 t} +$ cc) which induces transitions to final states $|f\rangle$ with energies ε_f after a time delay $t_2 - t_1$. In lowest order perturbation theory in the laser fields the probability of finding the molecule in a particular final state $|f\rangle$ after the excitation process $(t > t_2 + \tau_2)$ is given by (Alber *et al* 1986)

$$P_{g \to f} = |\langle f|\psi\rangle|^2_{t \to \infty}$$

$$= \left| \sum_n \langle f|\boldsymbol{\mu} \cdot \boldsymbol{\varepsilon}_2|n\rangle \tilde{\mathscr{E}}_2(\varepsilon_n + \omega_2 - \varepsilon_f) \, e^{-i\varepsilon_n(t_2 - t_1)} \langle n|\boldsymbol{\mu} \cdot \boldsymbol{\varepsilon}_1|g\rangle \tilde{\mathscr{E}}_1(\varepsilon_g + \omega_1 - \varepsilon_n) \right|^2$$

$$(1)$$

where $\tilde{\mathscr{E}}_i(\Delta) = \int_{-\infty}^{\infty} dt \, e^{-i\Delta(t - t_i)} \mathscr{E}_i(t)$ $(i = 1, 2)$ are the Fourier transforms of the laser pulses and $\boldsymbol{\mu}$ is the molecular dipole operator. We use Hartree atomic units. The total fluorescence from the excited final states, for example, which has been measured in recent experiments (Bowman *et al* 1889) is proportional to the total excitation probability, $P = \Sigma_f P_{g \to f}$.

In the Born-Oppenheimer approximation the molecular states may be described as products of an electronic state (which is a function of all electronic coordinates and the angular coordinates of the nuclei) and a vibrational state which characterizes the internuclear vibration within the corresponding electronic potential curve. Assuming that the electronic parts of the molecular dipole matrix elements of equation (1) are independent of the internuclear distance we find $\langle f|\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}_2|n\rangle = C\langle v_f|v_n\rangle$ and $\langle n|\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}_1|g\rangle = D\langle v_n|v_g\rangle$. Here $\langle v_f|v_n\rangle$ and $\langle v_n|v_g\rangle$ are the Franck-Condon overlap integrals between the vibrational states $|v_f\rangle$, $|v_n\rangle$ and $|v_g\rangle$ (with quantum numbers n_f, n and n_g) and the constants C and D characterize the electronic contribution to the corresponding molecular transitions. If the classical actions associated with two vibrational states, for example $|v_f\rangle$ and $|v_n\rangle$, are large, the corresponding Franck-Condon overlap integral may be evaluated semiclassically. In the primitive semiclassical approximation it is given by (Child 1980)

$$\langle v_f|v_n\rangle = \left(\frac{\mathrm{d}\varepsilon_f}{\mathrm{d}n_f}\right)^{1/2}\left(\frac{\mathrm{d}\varepsilon_n}{\mathrm{d}n}\right)^{1/2}(m/\pi)[k(R)]^{-1}\left(\frac{2\pi}{|\Delta S''(R)|}\right)^{1/2}\sin[\Delta S(R)+\pi/4]|_{R=R_S}.$$

$$(2)$$

In this equation $\Delta S(R)$ is the difference between the classical actions,

$$\Delta S(R) = \left|\int_{R_<^f}^{R}k_3(\varepsilon_f, r)\,\mathrm{d}r - \int_{R_<^n}^{R}k_2(\varepsilon_n, r)\,\mathrm{d}r\right|$$

where the local momenta are given by $k_i(\varepsilon, R) = [2m|\varepsilon - V_i(R)|]^{1/2}$ $(i = 2, 3)$ and m is the reduced mass. The left turning points of the potentials $V_2(R)$ and $V_3(R)$ are denoted $R_<^n$ and $R_<^f$. The quantity R_S is the internuclear distance at which the molecular transition takes place according to the Franck-Condon principle and is determined by the condition $k_3(\varepsilon_f, R_S) = k_2(\varepsilon_n, R_S) \equiv k(R_S)$. Equation (2) gives an adequate description of the Franck-Condon overlap integrals as long as the transition point, R_S, is well separated from the classical turning points of the corresponding electronic potentials. With the help of uniform approximations equation (2) can be generalized to cases where the transition point is located close to a turning point (Bieniek 1977, Child 1980). However, for simplicity we restrict ourselves here to cases where equation (2) is valid. Furthermore, in the following we assume that the transition from the initial state, $|g\rangle$, to the intermediate states, $|n\rangle$, is localized close to the left turning point of the electronic potential $V_2(R)$ so that the corresponding Franck-Condon overlap integral is given by

$$\langle v_n|v_g\rangle = \langle \varepsilon_n|v_g\rangle(\mathrm{d}\varepsilon_n/\mathrm{d}n)^{1/2} \tag{3}$$

with $\langle \varepsilon_n|v_g\rangle$ being approximately energy-independent.

If the pulse durations are so short that many vibrational states are excited coherently, it is more convenient to transform equation (1) with the help of the Poisson summation formula into (Alber *et al* 1986)

$$P_{g\to f} = \left|\int_{-\infty}^{\infty}\mathrm{d}\varepsilon_n\left(\frac{\mathrm{d}n}{\mathrm{d}\varepsilon_n}\right)\langle f|\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}_2|n\rangle\tilde{\mathscr{E}}_2(\varepsilon_n+\omega_2-\varepsilon_f)\,\mathrm{e}^{-\mathrm{i}\varepsilon_n(t_2-t_1)}\right.$$

$$\times\langle n|\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}_1|g\rangle\tilde{\mathscr{E}}_1(\varepsilon_g+\omega_1-\varepsilon_n) + \sum_{M=1}^{\infty}\int_{-\infty}^{\varepsilon_I}\mathrm{d}\varepsilon_n\left(\frac{\mathrm{d}n}{\mathrm{d}\varepsilon_n}\right)\langle f|\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}_2|n\rangle$$

$$\left.\times\tilde{\mathscr{E}}_2(\varepsilon_n+\omega_2-\varepsilon_f)\,\mathrm{e}^{-\mathrm{i}\varepsilon_n(t_2-t_1)}\,\mathrm{e}^{\mathrm{i}2\pi Mn(\varepsilon)}\langle n|\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}_1|g\rangle\tilde{\mathscr{E}}_1(\varepsilon_g+\omega_1-\varepsilon_n)\right|^2 \tag{4}$$

with ε_1 denoting the dissociation energy of potential $V_2(R)$. In this case the integrands of equation (4) are rapidly oscillating functions of energy and approximations may be found easily. For example, in the limiting case of negligible dispersion of the vibrational molecular wavepacket generated we may linearize the exponents of the integrand or in the opposite limit of strong dispersion we may apply the stationary phase approximation. In both cases the contributions to equation (4) are large whenever the time delay between both laser pulses, $t_2 - t_1$, corresponds to a time where the generated vibrational wavepacket is close to the transition point, R_S. The integer M in equation (4) counts the number of vibrations of the excited molecule in the potential curve $V_2(R)$. As long as the vibrational wavepacket has not spread out over the whole classically accessible range, contributions to $P_{g \to f}$ which correspond to different numbers of vibrations M are separated in time, so that only one term of the sum of equation (4) contributes significantly for a given time delay, $t_2 - t_1$, between pump and probe pulse.

For the evaluation of the total transition probability, $P = \Sigma_f P_{g \to f}$, equation (4) has to be summed over all final states. With the help of equations (2) and (3) this summation can be simplified considerably in cases where dispersion of the wavepacket is sufficiently weak that the exponents in equation (4) may be expanded up to second order with respect to energy. Approximating the sum over all final states by an integral we find, for cases where the transition point R_S lies well within the classically allowed region,

$$
P = \left| 2\pi CD \left(\frac{\mathrm{d}\varepsilon_n}{\mathrm{d}n} \right)^{-1/2} \langle \bar{n} | \boldsymbol{\mu} \cdot \boldsymbol{\varepsilon}_1 | g \rangle \right|^2 \frac{m^2}{k^2(R_S)|\Delta S''(R_S)|}
$$

$$
\times \sum_{M=0}^{\infty} \left\{ \int_{-\infty}^{\infty} \mathrm{d}\tau |\tilde{\mathscr{E}}_2(\tau)|^2 |\mathscr{E}_1^{(M+)}(\tau - MT_{\bar{\varepsilon}} - T_2)|^2 \right.
$$

$$
\left. + \int_{-\infty}^{\infty} \mathrm{d}\tau |\tilde{\mathscr{E}}_2(\tau)|^2 |\mathscr{E}_1^{(M-)}(\tau - MT_{\bar{\varepsilon}} + T_2)|^2 \right\} \tag{5}
$$

with the 'effective' laser pulses

$$
\mathscr{E}_1^{(M\pm)}(t) = (1/2\pi) \int_{-\infty}^{\infty} \mathrm{d}\Delta \, \mathrm{e}^{\mathrm{i}\Delta(t-t_1)} \tilde{\mathscr{E}}_1(\Delta) \, \mathrm{e}^{\mathrm{i}(MT' \pm T_2')\Delta^2/2}
$$

and

$$
\tilde{\mathscr{E}}_2(t) = (1/2\pi) \int_{-\infty}^{\infty} \mathrm{d}\Delta \, \mathrm{e}^{\mathrm{i}\Delta(t-t_2)} \tilde{\mathscr{E}}_2(\Delta) \exp\left[\tfrac{1}{2}\mathrm{i} \left(\frac{m^2}{k^2(R_S)|\Delta S''|} \right) \Delta^2 \right].
$$

In the derivation of equation (5) we have assumed that the intermediate excited states are well below the dissociation threshold, ε_1, and have neglected all quantum mechanical interferences between contributions associated with different returns of the wavepacket to the transition point R_S. All quantities in equation (5) have to be evaluated at energies $\varepsilon_f = \bar{\varepsilon}_f = \bar{\varepsilon}_n + \omega_2$ and $\varepsilon_n = \bar{\varepsilon}_n = \varepsilon_g + \omega_1$. The mean classical orbit time is given by $T_{\bar{\varepsilon}} = 2\pi \, \mathrm{d}n/\mathrm{d}\varepsilon_n$ and (the modulus of) $T_2 = \mathrm{d}\,\Delta S(R_S)/\mathrm{d}\varepsilon$ is the time the classical vibrating molecule takes to evolve from the initial excitation point (here the left turning point of potential $V_2(R)$) to the transition point R_S. The quantities $T' = \mathrm{d}T/\mathrm{d}\varepsilon$ and $T_2' = \partial T_2/\partial \varepsilon|_{R_S = \mathrm{const.}}$ characterize the dispersion of the excited vibrational wavepacket. In particular, T' also determines the revival time, $T_{\mathrm{Rev}} = T_{\bar{\varepsilon}}^3/(2\pi T') \gg T_{\bar{\varepsilon}}$, which sets the timescale for the scenario of fractional revivals (Averbukh and Perelman 1989). According to the Franck-Condon principle

$[\pi m^2/(k^2|\Delta S''|)]^{1/2}$ may be interpreted as the transition time for a transition from the intermediate to the final states.

In the limit of negligible dispersion (which corresponds to a linearization approximation of the exponents of the integrand in equation (4)) the time dependence of the total final-state probability, P, reduces to the convolution of the laser intensities $|\mathscr{E}_1(t)|^2$ and $|\mathscr{E}_2(t)|^2$ at time differences $MT_{\bar\varepsilon} \pm T_2$ ($M = 0, 1, \ldots$). According to equation (5), effects of weak dispersion of the wavepacket are characterized by the 'effective' laser pulses $\mathscr{E}_1^{(M\pm)}(t)$ and $\bar{\mathscr{E}}_2(t)$. They are centred around times

$$t_1^{(M\pm)} = t_1 - (MT' \pm T'_2) \int_{-\infty}^{\infty} dt |\mathscr{E}_1(t)|^2 \varphi_1(t)'/I_1$$

and

$$\bar{t}_2 = t_2 - \left(\frac{m^2}{k^2(R_S)|\Delta S''|}\right) \int_{-\infty}^{\infty} dt |\mathscr{E}_2(t)|^2 \varphi_2(t)'/I_2$$

and their effective pulse durations, $\tau^{(M\pm)}$ and $\bar\tau$, are determined by

$$(\tau^{(M\pm)})^2 = \left[\int_{-\infty}^{\infty} dt |\mathscr{E}_1(t)|^2 [t - t_1 - \varphi_1(t)'(MT' \pm T'_2)]^2 + (MT' \pm T'_2)^2 \right.$$

$$\left. \times \int_{-\infty}^{\infty} dt(|\mathscr{E}_1(t)|')^2 - (MT' \pm T'_2)^2 \left(\int_{-\infty}^{\infty} dt |\mathscr{E}_1(t)|^2 \varphi_1(t)'\right)^2 I_1^{-1} \right] I_1^{-1}$$

and

$$\bar\tau^2 = \left\{ \int_{-\infty}^{\infty} dt |\mathscr{E}_2(t)|^2 \left[t - t_2 - \varphi_2(t)' \left(\frac{m^2}{k(R_S)^2|\Delta S''|}\right) \right]^2 + \left(\frac{m^2}{k(R_S)^2|\Delta S''|}\right)^2 \right.$$

$$\left. \times \int_{-\infty}^{\infty} dt(|\mathscr{E}_2(t)|')^2 - \left(\frac{m^2}{k^2(R_S)|\Delta S''|}\right)^2 \left(\int_{-\infty}^{\infty} dt |\mathscr{E}_2(t)|^2 \varphi_2(t)'\right)^2 I_2^{-1} \right\} I_2^{-1}.$$

$$(6)$$

The quantities $I_{1,2}$ are defined by $I_{1,2} = \int_{-\infty}^{\infty} dt |\mathscr{E}_{1,2}(t)|^2$ and the phases, $\varphi_{1,2}(t)$, are given by $\mathscr{E}_i(t) = |\mathscr{E}_i(t)| e^{i\varphi_i(t)}$ ($i = 1, 2$) with $\varphi_i(t)' = [(d/dt) \varphi_i](t)$. Considered as functions of the time delay between both laser pulses, $t_2 - t_1$, the convolutions of equation (5) are large whenever the relation $\bar{t}_2 - t_1^{(M\pm)} = MT_{\bar\varepsilon} \pm T_2$ is fulfilled. The widths of these peaks, $\sigma^{(M\pm)}$, are determined by

$$(\sigma^{(M\pm)})^2 = [\tau^{(M\pm)}]^2 + \bar\tau^2.$$

In figures 2 and 3 we compare the total excitation probability calculated from equation (5) (broken curves) with numerical calculations based on the exact expression of equation (1) (full curves). Figure 2 shows the total excitation probability P for an iodine molecule (Bowman *et al* 1989, Metiu and Engel 1990) as a function of the time delay between both laser pulses, $t_2 - t_1$. As initial state we have chosen the third vibrational state of the ground-state electronic potential. In the case of a thermal distribution of initial states at room temperature this state gives the dominant contribution to transitions between potentials $V_1(R)$ and $V_2(R)$ for the laser frequency considered in figure 2. In the evaluation of the broken curve the Franck-Condon factor of the first transition, $|v_g\rangle \to |v_n\rangle$, which is localized close to the left turning point of the potential $V_2(R)$, has been calculated with the help of a uniform semiclassical approximation (Bieniek 1977, Child 1980). The peaks in figure 2 correspond to those
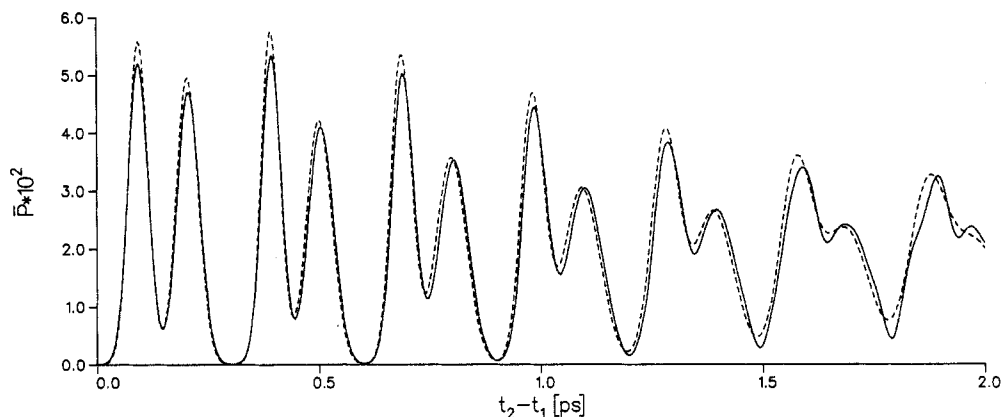
Figure 2. Total final-state probability, $\bar{P} = P/|2\pi CD\tau_1\tau_2\mathscr{E}_1(t_1)\mathscr{E}_2(t_2)|^2$, as a function of the time delay, $t_2 - t_1$, between pump and probe pulse with $T_{\tilde{e}} = 296.33$ fs and $T_2 = 92.84$ fs; numerical calculation based on equation (1) (full curve), semiclassical approximation of equation (5) (broken curve). Both laser pulses have identical Gaussian pulse shapes with $\tau_1 = \tau_2 = 15$ fs (which corresponds to a FWHM of the intensity correlation function of 50 fs), $\varphi_i(t) = 0$ ($i = 1, 2$) and wavelengths $\lambda_1 = 620$ nm, $\lambda_2 = 310$ nm.
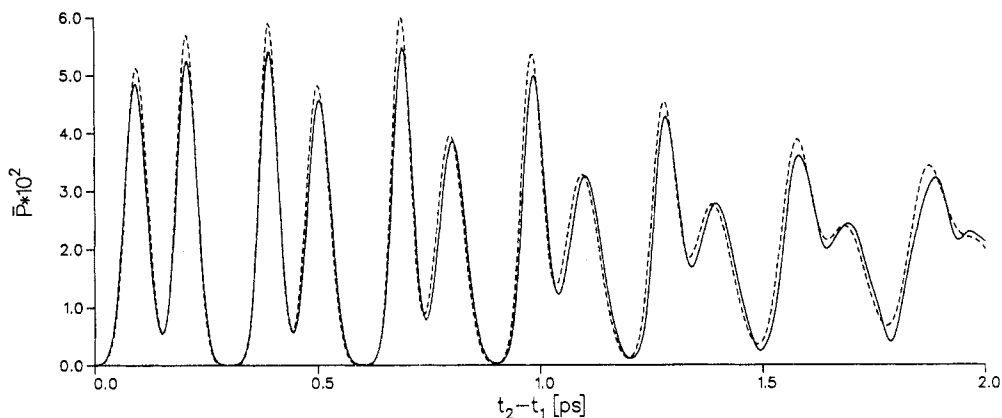

Figure 3. Same as figure 2 but with $\varphi_1(t) = \frac{1}{8}[(t - t_1)/\tau_1]^2$ and $\varphi_2(t) = 0$.

times at which the vibrational wavepacket, which has been generated close to the left turning point of potential $V_2(r)$, is close to the transition point R_S. The variation of their widths from peak to peak may be understood from equations (5) and (6) by noting that for the parameters chosen we have $T_2 > 0$, $T'_2 < 0$ and $t_1^{(M\pm)} = t_1$, $\bar{t}_2 = t_2$. In this case equations (5) and (6) imply that the first absorption peak, which corresponds to the absorption of the second laser photon before the vibrational wavepacket has reached the outer turning point of its orbit, is narrower than the second absorption peak, which corresponds to the absorption process after reflection at the outer turning point. This is a result of changes in the width of the wavepacket as it evolves under the influence of the potential $V_2(R)$. With increasing number of revolutions M, the wavepacket spreads out and the absorption peaks are broadened. However, in agree-

ment with equations (6), the peaks associated with photon absorption before and after the outer turning point of the potential, $V_2(R)$, are broadened in different ways. With increasing time delay, $t_2 - t_1$, quantum mechanical interferences between contributions associated with different absorption peaks become important. These effects have been neglected in equation (5).

Figure 3 shows the total excitation probability in a case where the phase of the first laser pulse, $\varphi_1(t)$, is slowly varying. According to equations (6) such a chirping of the laser pulse leads to additional modulations of the widths of the absorption peaks. Physically speaking, this reflects the fact that a phase modulation of the first laser pulse influences the preparation of a vibrational wavepacket, thus affecting the changes of its width as it evolves in the potential $V_2(R)$. From figure 3 we notice that the absorption peaks associated with photon absorption before and after the outer turning point are affected in different ways. Whereas we observe a narrowing of the first, third and fifth peak, which correspond to absorption before the outer turning point, the peaks associated with absorption after the turning point are all broadened. Similar effects caused by chirped laser pulses have also been found in connection with the generation of Rydberg wavepackets by short laser pulses (Alber *et al* 1986, Noordam *et al* 1990).

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