Designing of Wave Packets by using Delayed Phase-locked Femtosecond Pulses of Different Durations

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Abstract.

Ab-initio study on the quantum interference of two vibrational wavepackets on $A^1\Sigma^+$ state of NaH molecule excited by two delayed phase-locked 4 femtosecond pulses (pump and control) has revealed that coherent control over populating selective vibrational levels or selective product state can be achieved. We have investigated here how the quantum interference of two wavepackets can be controlled to design a wavepacket which resembles one or two vibrational levels on the excited bound state leading to large overlap with these vibrational levels and hence enhancing the cross section of excitation to selected vibrational levels wiping out the population flow to other nearby levels covered by the bandwidth of the pulses. It will be shown here that the designing of interfering wavepacket can be controlled by controlling the pulse duration and carrier frequency of two delayed phase-locked ultrashort pulses.

1. Introduction

Coherent control of quantum systems has potential applications in various fields like quantum computation and information, coherent cooling, chemical reaction, etc [1]. Wavepacket interferometry is widely used in studies of quantum control. In this technique wavepackets are generated on the excited state using ultrashort pulses and the interference between the wavepackets depend on the delay and relative phase difference between the pulses. By careful choice of the time delay and the phase difference between the pulses, population on the excited state can be enhanced or diminished. In recent experiments it has been shown that quantum interference can be used to extract both amplitude and phase information stored in the wavepackets [2]. Quantum interference between wavepackets can be probed by fluorescence measurement [2-4], ionization [5, 6, 7] or photodissociation [8].
In the present study, we have theoretically investigated the role of pulse duration and the carrier frequency on the quantum interference of wavepackets in NaH molecule. Scheme for the present study is shown in figure 1. Two phase-locked and delayed Gaussian femtosecond pulses (pump and control) sequentially excite two wavepackets on the \( A^1\Sigma^+ \) state of NaH molecule. Two wavepackets are allowed to propagate freely on the excited potential energy surface and to interfere. This interfering wavepacket oscillates on the potential energy surface. Previously we have shown that quantum interference probed by photodissociation is dependent on the delay time and phase difference between the pulses [1, 8]. It was also shown that for a selective delay only even or odd vibrational levels can be populated by changing the phase difference between pulses. In this work it will be shown that further control over the population in selective vibrational levels can be achieved by controlling the pulse duration and the carrier frequency of the ultrashort pulses.

2. Theory

Time dependent Fourier grid method [9, 10] is widely used to calculate total photodissociation cross section for one-photon excitation. We have extended this method to calculate two or three-photon dissociation cross section [8, 11] and vibrational excitation and de-excitation cross section for the bound-bound transition [1, 12]. The theory for vibrational excitation in pump-control method is given below.

By the first pulse, the molecule is excited from ground vibronic state to the intermediate \( A^1\Sigma^+ \) state. Wavepacket amplitude on the excited surface [1] at time \( t=T \) and at internuclear separation \( R \) is,

\[
(i\hbar)\chi_{e1}(R, T) = \int_0^T dt_1 \exp\left[-\frac{iH_e(T - t_1)}{\hbar}\right]D_{eg}(R)\chi_g(R, 0) \exp\left[-\frac{iH_gt_1}{\hbar}\right]
\]

where \( \chi_{gv}(R, 0) \) is the eigenfunction of the vibrational level \( v \) of the ground state \( g \) at time \( t=0 \). \( H_g \) and \( H_e \) are the total Hamiltonian for the ground state \( g \) and the excited state \( e \) (bound \( A^1\Sigma^+ \) state) respectively. \( D_{ge} \) is the electronic dipole transition moment for transition from the ground state \( g \) to the state \( e \), \( T \) is the duration of the pump pulse. The ground vibrational
wavefunction $\chi_{gv}(R, 0)$ is obtained by using time-independent Fourier Grid Hamiltonian method. After a time interval $t'$ where $t' = \tau_{control} + t_\phi$ where $\tau_{control}$ is the delay between the pump and control pulses and $t_\phi = \frac{\phi}{\omega}$ is the delay corresponding to the relative phase difference $\phi$. The control pulse excites another wavepacket $\chi_2$ on the $A^1\Sigma^+$ state surface of the same form as in equation (1), with $T$ being replaced by $T'$ (duration of the second pulse). The resultant wavepacket on the $A^1\Sigma^+$ state surface at time $T + t' + T'$ is the sum of these two wavepackets [1]. It is then allowed to propagate for a long time on the $A^1\Sigma^+$ potential energy surface and the excitation cross sections to different vibrational levels are obtained by the fourier transform of the autocorrelation functions [1]. The propagated wavepackets on the excited state surface is calculated by using Chebyshev scheme [13]. Electric field at time $t_i$ is given by $\epsilon(t_i) = g(t_i) \exp[i\omega t_i]$ where $g(t_i)$ is the temporal profile of the pulse and $\omega$ is its carrier frequency. We have used Gaussian pulses. For details of calculation see [1].

3. Results and discussion

We have calculated the spectrum for excitation of NaH molecule from $v=0$ level of the ground $X^1\Sigma^+$ state to the $A^1\Sigma^+$ state by the pump and control pulses. Wavepackets on the $A^1\Sigma^+$ state formed by the pump and control pulses interfere to modify vibrational population in this state depending upon the relative phase ($\phi$) as well as the delay ($\tau_{control}$) between these two pulses. It is found that only even vibrational levels ($v=8,10,12$) are excited by two delayed ($1.5 T_{vib}$, phase difference $\phi = 3\pi/2$) 10 fs pulses (figure 2a). However by changing the temporal width of the pulses to 20 fs only $v=10$ level is excited with larger cross section (figure 3a). This enhancement of the cross section occurs due to the fact that different wavepackets (solid line curve in figures 2c and 3c) are constructed for different pulse durations leading to different overlaps of the composite wavepackets with $v=10$ level (figures 2b and 3b), although the wavepackets oscillate in phase with $v=10$ level (line with solid circle) and out of phase with $v=9$ and 11 levels (dash-dotted and dashed lines respectively) in both the cases. In
figures 2c and 3c the vibrational wave functions (for v=9,10 and 11 levels) are scaled to make these comparable in magnitude with that of wavepacket. It can be shown that the cross section depends also on the carrier frequency of the pulses.

4. Conclusions
It has been demonstrated theoretically (ab-initio) that a wavepacket can be constructed (by controlling the interference of two wavepackets excited by two delayed phase-locked ultrashort pulses) on an excited electronic state of a molecule (NaH) to resemble one or two vibrational levels of the excited state, thus leading to selectivity in vibrational excitations. This designing of wavepackets can be further controlled by changing the pulse duration and carrier frequency of pump and control pulses leading to enhancement or damping of excited populations in selective vibrational levels.

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