Effect of aligning pulse train on the orientation and alignment of a molecule in presence of orienting pulse

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ABSTRACT

Field-free molecular alignment is studied theoretically in presence of orienting laser pulse and a delayed Infrared laser (IRL) pulse train. The pulse shapes taken are sine square (sin^2) and square. The degree of alignment can be significantly enhanced by the combination of orienting pulse and IRL pulse train compared with only IRL pulse train. Special emphasis is laid on time delay between orienting and aligning pulse, the width and shape of the pulse train. By adjusting the time delay, width and intensity of coupling laser one can suppress a population of particular state while simultaneously enhancing the population of desired states.

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1. Introduction

Laser- induced molecular orientation and alignment techniques have attracted immense attention of researchers due to their ability in controlling chemical reaction dynamics [1], surface processing [2], photoabsorption [3,4], multiphoton ionization [5,6], spectral manipulation [7], high-harmonic generation [8] etc. Due to realization of quantum computers using rotational qubits of polar molecule [9], large efforts have been devoted to developing methods that enable control over the alignment or orientation of molecules. Alignment refers to confinement of molecule-fixed axes along space-fixed axes. A laser field induces an electric dipole moment in any molecule with a polarizability anisotropy, whether polar or not, and the interaction between the induced dipole and the laser field itself forces the molecule to align. In case of a linearly polarized laser field, the most polarizable axis is aligned along the polarization direction, which is sufficient to ensure strong angular confinement of the axis of the molecules and, therefore, complete alignment control of linear and symmetric top molecules occurs. Molecular alignment can be obtained either in adiabatic and non-adiabatic conditions. The first experimental demonstration of adiabatic alignment was reported by Felker et al. in 1996 [10]. When a laser pulse is much shorter than the rotational period of the molecule, the molecule cannot adiabatically adapt to the laser pulse which leaves

the system in a coherent superposition of rotational states, resulting in a time-dependent field-free alignment. This process is called either non-adiabatic alignment or impulsive alignment. A theoretical treatment of this technique has been presented by Seideman [11] in 1995, while the first experimental demonstration of impulsive alignment has been given by Rosca-Pruna et al. in 2001 [12]. The great advantage of impulsive alignment is the absence of the alignment field when the molecules are aligned. Some laser fields are usually proposed to further improve the molecular alignment, including of the laser pulse trains with the pulse separations being commensurate with the rotational period [13], the slow turn-on and rapid turn-off laser pulse [14], or the shaped laser pulses by optimal control method [15].

Since the invention of the mode-locked lasers, pulse trains have been used in the measurement of spectroscopy [16] and the generated single pulse in the train can be of attosecond duration [17] or of few-cycle oscillations [18]. In molecular systems, Warren and Zewail [19] showed that a sequence of nonresonant strong pulses could dramatically increase population inversions and multiphoton pumping. James P. Cryan et al. [20] observed experimentally a high degree of alignment in nitrogen at STP resulting from impulsive-Raman excitation with a train of eight linearly polarized laser pulses. A. Gogyan et al. [21] have reported theoretically an efficient method for population transfer to desired superposition in multilevel systems using a train of pulses combined with weak controlled lasers.

In the present work, we have investigated the rotational population and alignment of HBr molecule due to orienting pulse in combination with delayed IRL pulse train of different shaped envelopes. In the framework of rigid rotor approximation, we calculate the results for different shapes of pulses of different width of pulse train and delay between the

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orienting and aligning pulse. Further, we investigate the influence of different width of the number of pulses of the aligning pulse train on the population of the various rotational states.

The structure of this paper is organised as follows. In Section 2, the theoretical method of field-free molecular alignment is described in detail. In Section 3, molecular alignment dynamics and population are calculated and analysed. In Section 4, the conclusions are drawn.

2. Theoretical Method

The laser induced rotational excitation dynamics is studied for HBr molecule due to train of pulses of different shaped envelopes. The HBr molecule has small permanent dipole moment as compared to the traditional polar molecules (such as LiCl, KCl etc.), molecule is treated within the rigid-rotor approximation (frozen internal vibrational and electronic motion), interacting with the fields. The Hamiltonian for this model is

$$H(t) = BJ^2 + V_E(\theta, t) + V_Z(\theta, t) \tag{1}$$

where B is the rotational constant and J^2 is the squared angular momentum operator. $V_E(\theta, t)$ and $V_Z(\theta, t)$ are the interaction potential of the orienting field and IRL pulse train with the molecule respectively. Both fields are having same linear polarization directions. Here V_E, is defined as

$$V_E(\theta, t) = -\mu_0 E(t) \cos(\theta) \tag{2}$$

where θ is the angle between the molecular axis and the orienting pulse. It is precisely this angle which defines the alignment of the molecule and μ_0 is the permanent electric dipole moment along the internuclear axis. The electric field of orienting pulse is

$$E(t) = E_0 f(t) \tag{3}$$

where E_0, is the peak electric field amplitude and $f(t)$ is the pulse envelope. The two different pulse envelopes viz. sin^2 and square envelope are defined as

$$f(t) = sin^2(\pi t/t_p); \quad 0 < t < t_p \tag{4}$$

$$f(t) = 1; \quad \text{for square pulses} \tag{5}$$

where t_p is pulse duration of the sin^2 pulse and $V_Z(\theta, t)$, is the interaction due to delayed aligning pulse train

$$V_z(\theta, t) = -1/4[E_1(t)]^2 (\Delta\alpha \cos^2(\theta) + \alpha_\perp) \tag{6}$$

where $E_1(t) = E_{01} f(t)$, E_{01} is the amplitude of delayed aligning pulse, $\Delta\alpha = \alpha_\parallel - \alpha_\perp$, is the difference between the parallel ($\parallel$) and perpendicular ($\perp$) components of polarizability tensor of molecule. In order to ensure the observed rotational excitation is induced by non-adiabatic rotational excitation (NAREX) process, a quantum dynamical calculation is performed to calculate the population by solving the time dependent Schrödinger equation (TDSE) [22]

$$\iota \frac{\partial \psi}{\partial t}(\theta, \phi; t) = H(t)\psi(\theta, \phi; t) \tag{7}$$

We have solved Eq. (7) using fourth-order Runge-Kutta method [23–26] with the initial condition taken as molecule being in the ground rotational $J = M = 0$ state at $t = 0$ state. The measure of orientation is taken as the expectation value of $\cos(\theta)$,

$$\langle cos^2\theta \rangle(t) = \int_0^{2\pi} \int_0^{\pi} cos\theta(t)|\psi(\theta, \phi; t)|^2 sin\theta d\theta d\phi \tag{8}$$

The orientation parameter $\langle cos\theta \rangle(t)$ varies within the interval $[-1,1]$ and the perfect orientation is signified by the extremum value of $\langle cos\theta \rangle(t)$.

Similarly, to measure alignment, one can find the expectation value of $cos^2\theta$,

$$\langle cos^2\theta \rangle(t) = \int_0^{2\pi} \int_0^{\pi} cos^2\theta(t)|\psi(\theta, \phi; t)|^2 sin\theta d\theta d\phi \tag{9}$$

The alignment parameter $\langle cos^2\theta \rangle$ (t) ϵ[0,1] and for perfect alignment $\langle cos^2\theta \rangle$(t) = 1. The analysis was made under the assumption that the unperturbed molecule resides initially in a specific eigenstate of the field-free system.

3. Results and Discussions

In the present paper, we have studied variation of non-adiabatic rotational excitation (NAREX), orientation and maximum value of alignment of HBr molecule exposed initially by orienting pulse and then kicked by delayed IRL pulse train of different shaped envelopes i.e. sin^2 and square. Square and ramped pulses have been utilized to achieve orientation and alignment of molecules [27–32]. It is possible to obtain the square laser pulse by tailoring the ultrashort laser pulse in frequency domain [33]. Although the shape of the pulse has little influence on the physics behind the process, yet it is quite effective in changing the rotational state and alignment of the molecule. A pulse shape plays a significant role in controlling population in various rotational states, because in square pulse, we have sharp cut down, that leads to larger coupling to higher rotational quantum numbers as compared to sin^2 pulse. Hence square pulse is better to promote population in higher rotational states. Falling edge of sin^2 pulse decreases smoothly and supports population transfer to lower rotational states.

We performed simulations using HBr molecule. HBr is a polar molecule with moderate permanent dipole moment $\mu_o = 0.828D$ and rotational constant $B = 8.3482$ cm^{-1}. Dynamics presented here is shown with pulse train of five subpulses. The pulse duration of each pulse is varying from 0.1 ps to 0.3 ps and the frequency of the pulse is taken to be 2400 cm^{-1}. The rotational constant of HBr shows that the rotational period of the molecule is approximately 2.0 ps [34]. The electric field amplitude (E_0) of orienting pulse and intensity (I) of aligning pulse are 1500 KV/cm and 3.35×10^{13} W/cm^2 respectively. An orienting pulse, applied initially to the molecule helps in population transfer between states with opposite parity ($\Delta J = \pm 1$) and thus decelerates the rotation of molecular dipoles having acute angle w.r.t orientation direction and accelerates dipole having obtuse angles. When delayed IRL pulse is applied to such a system, all the molecules gain nearly the same rotational velocity and further increase in value of alignment takes place. When aligning a molecule, there will be some maximum intensity above which undesirable non-linear effects will occur [35]. For example, at the ionization saturation intensity most molecules will ionize. A pulse train divides the total energy over many pulses and therefore avoids ionization but conserves the subpulse duration [36]. Therefore, dividing energy between multiple pulses while preserving the shortest subpulse duration is an effective way to increase the alignment of molecule. The pulse repetition period is large enough so that the wings vanish before the next pulse arrives, and consecutive pulses do not overlap. Moreover, this method represents an effective way to achieve coherent distributions centred on very high lying J states.

Fig. 1 represents the variation of transition probability in rotational states and alignment as a function of time in picoseconds. Here orienting pulse is of sin^2 shape having orienting pulse width (OPW) of 0.2 ps and at a delay of 1.9 ps molecule is kicked by aligning IRL pulse train of five pulses of sin^2 shape. Width of the pulses in IRL pulse train is varied from 0.1 ps to 0.3 ps in panels (a) to (c) respectively and their corresponding alignment is shown in panels (d) to (f). The effect of pulse train width (PTW) is clearly shown in the figure. It is found