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Non-adiabatic effects in near-adiabatic mixed-field orientation and alignment

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ABSTRACT

We present a theoretical study of the impact of a pair of moderate electric fields tilted an angle with respect to one another on a molecule. As a prototype, we consider a molecule with large rotational constant (with corresponding small rotational period) and moderate dipole moment. Within rigid-rotor approximation, the time-dependent Schrodinger equation is solved using fourth-order Runge–Kutta method. We have analysed that lower rotational states are significantly influenced by variation in pulse durations, the tilt angle between the fields and also on the electric field strengths. We also suggest a control scheme of how the rotational dynamics, orientation and alignment of a molecule can be enhanced by a combination of near-adiabatic pulses in comparision to non-adiabatic or adiabatic pulses.

1. Introduction

Laser-induced molecular orientation and alignment has become quite important tool in molecular physics over past decade. The techniques reading orientation and alignment of a molecule plays an immense role in controlling processes like photoabsorption [1,2], high-harmonic generation [3,4], multiphoton ionization [5,6], photodissociation [7], chemical reaction dynamics [8–10], attosecond science [11], femtosecond pulse generation [12,13], photoelectron angular distribution [14] and molecular imaging [15]. The study of rotational dynamics alongwith orientation and alignment of a free rigid rotor, both theoretically and experimentally, under different situations has been the topic of great interest.

The rotational dynamics of a molecule can be studied under adiabatic and non-adiabatic conditions depending upon whether the pulse duration is comparable or much smaller than the rotational period ($\tau_{rot} = \frac{h}{2B}$) of the molecule. Thus, the AREX (adiabatic rotational excitation) and NAREX (non-adiabatic rotational excitation) occur. These excitations provide a promising and versatile tool to probe and control the molecule in an external field. The corresponding molecular orientation and alignment under adiabatic and non-adiabatic conditions offer conditions for different applications. Alignment implies molecular axis parallel to the field polarisation vector, whereas an orientation refers to the axis of aligned molecule points to a particular direction with a polar angle θ between the molecular axis and the polarisation direction of the laser field [16]. Both molecular orientation and alignment are obtained in adiabatic conditions when the external fields exist. On the otherhand, the same can be accomplished even under non-adiabatic conditions after the laser pulse is over. The adiabatic and non-adiabatic orientation have recently been achieved using long rising pulse (300 ps) and very short falling time (30 fs) which makes for adiabatic to non-adiabatic transformation [17]. Due to realization of quantum computers using rotational qubits of polar molecules [18], large efforts have been devoted to developing methods that enable control over the alignment or orientation of molecules. The field-free molecular orientation by femtosecond two-color laser fields [19] and THz laser pulses [20] has also been realized. The concept of planar alignment has been reported by Sugny et al. [21]. The study of control of molecular orientation by half-cycle pulses has also been studied quite thoroughly [22].

The study of energy levels, orientation and alignment in mixed-field(electric and magnetic field) has been studied extensively for hydroxyl free radical (OH) [23,24]. The experimental and theoretical investigation of mixed-field orientation of Carbonyl Sulphide (OCS) molecule has been studied recently [25]. The theoretical study of mixed-field orientation due to combination of electrostatic field combined with nonresonant linearly polarised laser pulses on the rotational dynamics of linear polar molecules has been studied by Omiste et al. [26,27]. The classical and quantum mechanics of a diatomic molecule KCl in titled fields has also been

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studied and analysed [28]. The mixed-field orientation of an asymmetric-rotor and having permanent dipole moment has been investigated theoretically and experimentally [29]. The dynamics of orientation of a adsorbed molecule in presence of static electric and laser field has also been analysed [30].

A lot of literature is available in mixed-field(electric and laser field) leading to orientation and alignment under non-adiabatic conditions. Also, imposing adiabatic pulses leaves the molecule to its original position after the pulse is over. The near-adiabatic rotational excitation(a midway between non-adiabatic and adiabatic rotational excitation) due to mixed-field having moderate electric field strengths, giving orientation and alignment is the topic of our interest. In the present text, we have considered rotational excitation due to a combination of electric fields which are tilted with respect to one another and suggest a scheme to control the orientation and alignment of a molecule by proper combination of non-adiabatic, near-adiabatic and adiabatic pulses.

The paper is organised as follows: In Section 2 we describe the Hamiltonian of mixed-field of the present system. The results are analysed in Section 3 which are followed by the conclusions in Section 4.

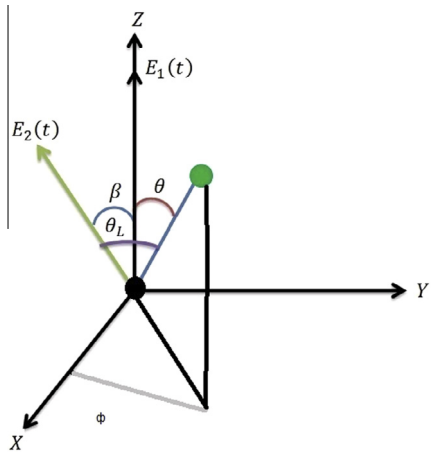

Fig. 1. The laboratory fixed coordinates (x, y, z), schematic fields configurations and molecule with different angles.

2. Hamiltonian of a mixed-field

The electric field-induced rotational excitation dynamics is studied for molecule which is exposed to fields $E_1(t)$ and $E_2(t)$ having moderate field strengths and are at an angle β with respect to each other. The field $E_1(t)$ lies along the z-axis making an angle θ with the permanent dipole moment of the molecule whereas $E_2(t)$ is tilted at an angle β with respect to the z-axis and lies in the x–z plane (see Fig. 1). The description of the system is studied within rigid-rotor approximation, assuming that the vibrational and electronic dynamics are not affected by the fields. Thus, the Hamiltonian reads (atomic units are used throughout i.e. $\hbar = m_e = e = 1$)

$$H(t) = H_0 + H_1(\theta, t) + H_2(\theta, t) \tag{1}$$

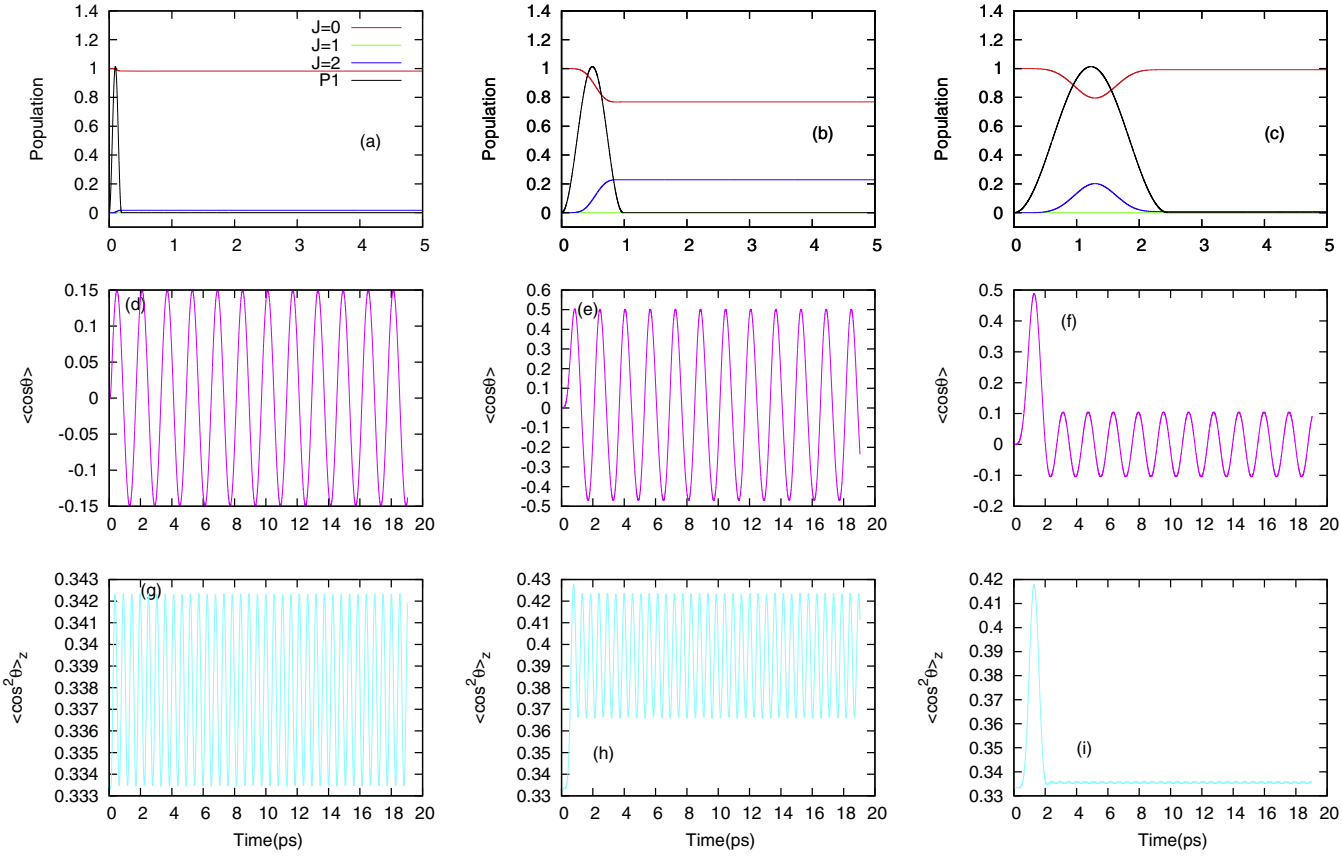

Fig. 2. Rotational population, orientation and alignment as a function of time in picoseconds for a SSQP (shown as P1) of different pulse durations. The pulse duration of pulses are 0.2 ps (panel (a)), 1.0 ps (panel (b)) and 2.5 ps (panel (c)) respectively. The field strength of the pulse is equal to 250 kV/cm (or 4.8×10^{-5} a.u) and P1 is equal to E_0(a.u.) $\times$ 20833.33. The denotation of curves is shown in Fig. 2(a).