



Quantum optimal control of the isotope-selective rovibrational excitation of diatomic molecules



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ABSTRACT

We carry out optimal control theory calculations for isotope-selective pure rotational and vibrational-rotational excitations of diatomic molecules. The fifty-fifty mixture of diatomic isotopologues, ${}^7\text{Li}^{37}\text{Cl}$ and ${}^7\text{Li}^{35}\text{Cl}$, is considered and the molecules are irradiated with a control pulse. In the wave packet propagation we employ the method quantum mechanically rigorous for the two-dimensional system including both the radial and angular motions. We investigate quantum controls of the isotope-selective pure rotational excitation for two total times 1280000 and 2560000 a.u. (31.0 and 61.9 ps) and the vibrational-rotational excitation for three total times, 640000, 1280000, and 2560000 a.u. (15.5, 31.0, and 61.9 ps). The initial state is set to the situation that both the isotopologues are in the ground vibrational and rotational levels, $\nu = 0$ and $J = 0$. The target state for pure rotational excitation is set to ${}^7\text{Li}^{37}\text{Cl}$ ($\nu = 0, J = 1$) and ${}^7\text{Li}^{35}\text{Cl}$ ($\nu = 0, J = 0$); that for vibrational-rotational excitation is set to ${}^7\text{Li}^{37}\text{Cl}$ ($\nu = 1, J = 1$) and ${}^7\text{Li}^{35}\text{Cl}$ ($\nu = 0, J = 0$). The obtained final yields are quite high and those for the longest total time are calculated to be nearly 1.0. When total time is 1280000 a.u., the final yields for the pure rotational excitation are slightly smaller than those for the vibrational-rotational excitation. This is because the isotope shift (difference in transition energy between the two isotopologues) for the pure rotational transition between low-lying levels is much smaller than that for the vibrational-rotational transition. We thus theoretically succeed in controlling the isotope-selective excitations of diatomic molecules using the method including both radial and angular motions quantum mechanically.

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1. Introduction

Quantum control has been expected to bring a breakthrough not only in basic science but also in applied research leading to novel industrial technology. Thus a great number of studies has been devoted to quantum control for more than two decades [1–4]. One of the most important applications of quantum control is the discrimination of a mixture of physically or chemically similar species, where different species are driven into different target states at the same time with a single laser pulse. Rabitz and co-workers [5–7] presented the formulation called optimal dynamic discrimination (ODD), which is a theoretical tool to predict a control laser pulse to enable such discrimination of a mixture of similar quantum systems. It is noteworthy that some experimental demonstrations of ODD have been reported, such as the

isotope-selective ionization of diatomic molecules [8,9] and the discrimination of competitive product channels for large biomolecules [10,11].

We [12–15] have studied, using optimal control theory (OCT) [16–18], the quantum optimal control of isotope-selective vibrational excitations of a diatomic alkali halide. As a result of the numerical simulations, ODD for a mixture was successfully demonstrated; it was verified that the obtained optimal field drives the system wave packets of different initial states into different final states. In those studies molecular rotational motion was frozen and only the radial (vibrational) motion was considered.

On the other hand, we [19–22] are also interested in isotope-selective rotational excitations of diatomic alkali halides using an optical frequency comb. This is because in the current laser shaping technology the design of the frequency comb for rotational excitations of heavy diatomic molecules is more realistic than that of the laser pulse for vibrational excitations. Very recently, we [23] have proposed a method of the isotope-selective rovibrational excitation for a gas-phase mixture of diatomic alkali halides at a

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finite temperature using a laser pulse consisting of a frequency comb for rotational excitations and a subsequent bunch of pulse for vibrational excitations; it is expected that the frequency comb tuned to the rotational transition energies of one isotopologue changes the rotational-state distributions and magnifies the difference in vibrational transition energies between the isotopologues, thus enabling the isotope-selective vibrational excitation even with the single frequency pulse. The numerical simulation has shown that the proposed scheme works well for the isotope-selective rovibrational excitation for a gas-phase mixture of the diatomic ${}^7\text{Li}^{37}\text{Cl}$ and ${}^7\text{Li}^{35}\text{Cl}$ molecules at 70 K.

In the present study we perform OCT simulations to obtain optimal electric fields that enable the isotope-selective rovibrational excitation for the isotopologues: ${}^7\text{Li}^{37}\text{Cl}$ and ${}^7\text{Li}^{35}\text{Cl}$. In the wavepacket calculations both the radial (vibrational) and angular (rotational) motions are treated quantum mechanically; this is more challenging than our previous studies [12–15] mentioned above, where only the radial motion was considered. The ultimate goal might be the control of a mixed ensemble of molecules thermally distributed up to high quantum levels according to the temperature of the ensemble. We focus here, however, on the simplest cases of the isotope-selective excitations and examine the following two excitations: (i) pure rotational excitation; (ii) vibrational-rotational excitation. In the two cases the initial state is set to the condition that both ${}^7\text{Li}^{37}\text{Cl}$ and ${}^7\text{Li}^{35}\text{Cl}$ are in the ground vibrational and rotational levels, $v=0$ and $J=0$. The target states in these cases are set as follows: (i) ${}^7\text{Li}^{37}\text{Cl}$ ($v=0, J=1$), ${}^7\text{Li}^{35}\text{Cl}$ ($v=0, J=0$); (ii) ${}^7\text{Li}^{37}\text{Cl}$ ($v=1, J=1$), ${}^7\text{Li}^{35}\text{Cl}$ ($v=0, J=0$).

Theoretical details are described in Sec. II. The results of calculation are presented in Sec. III and conclusions are given in Sec. IV. In the present paper we use atomic units unless otherwise noted.

2. Theoretical details

2.1. OCT for isotope-selective excitation

OCT provides an efficient tool to find an electric field $\varepsilon(t)$ that causes the transition between predetermined initial and target states with a high probability. In the present study a gas-phase mixture of isotopologues is considered and the objective functional J to be maximized is given as

$$J = \sum_A p_A \langle \psi_A(T) | O_A | \psi_A(0) \rangle - \alpha \int_0^T dt \varepsilon(t)^2 - 2 \sum_A p_A \text{Re} \left[\int_0^T dt \left\langle \chi_A(t) \left| \frac{\partial}{\partial t} + i(H_0^A - \mu \varepsilon(t)) \right| \psi_A(t) \right\rangle \right]. \quad (1)$$

The first term is the transition probability to be maximized and is referred to as final yield, where p_A is the population of isotopologue A, $\psi_A(t)$ is the wave packet of isotopologue A propagated from time $t=0$ to T , and O_A is the target operator of isotopologue A. The second term is the laser fluence to be minimized, where α is a penalty factor. In order to obtain the optimal fields that start and end with the zero amplitude, a time dependence is introduced in α :

$$\alpha = \alpha(t) = \frac{\alpha_0}{s(t)} \quad (2)$$

where α_0 is a positive constant and $s(t)$ is a shape function having a form

$$s(t) = \sin^2 \left(\frac{\pi t}{T} \right). \quad (3)$$

The third term is the dynamical constraint, where $\chi_A(t)$ is the Lagrange multiplier of isotopologue A, Re denotes the real part of

a complex number, H_0^A is the field-free Hamiltonian of isotopologue A, and μ is the dipole moment. In the present OCT calculations we consider the 1:1 mixture of ${}^7\text{Li}^{37}\text{Cl}$ (A) and ${}^7\text{Li}^{35}\text{Cl}$ (B) i.e., $p_A = p_B = 0.5$.

Varying the objective functional J with respect to $\psi_A(t)$, $\chi_A(t)$, and $\varepsilon(t)$, we obtain the following three coupled equations for each isotopologue:

$$i \frac{\partial \psi_A(t)}{\partial t} = (H_0^A - \mu \varepsilon(t)) \psi_A(t), \quad \psi_A(0) = \psi_{A,0} \quad (4a)$$

$$i \frac{\partial \chi_A(t)}{\partial t} = (H_0^A - \mu \varepsilon(t)) \chi_A(t), \quad \chi_A(T) = O_A \psi_A(T) \quad (4b)$$

$$\varepsilon(t) = -\frac{s(t)}{\alpha_0} \sum_A p_A \text{Im} \langle \chi_A(t) | \mu | \psi_A(t) \rangle, \quad (4c)$$

with Im in Eq. (4c) denoting the imaginary part. These equations are iteratively solved until the value of J is converged using the monotonically convergent algorithm [24], i.e., the optimization of J is achieved by iteratively solving the following equations at the k -th step:

$$i \frac{\partial \psi_A^k(t)}{\partial t} = (H_0^A - \mu \varepsilon^k(t)) \psi_A^k(t), \quad \psi_A^k(0) = \psi_{A,0} \quad (5a)$$

$$\varepsilon^k(t) = (1 - \delta) \tilde{\varepsilon}^{k-1}(t) - \frac{\delta s(t)}{\alpha_0} \sum_A p_A \text{Im} \langle \chi_A^{k-1}(t) | \mu | \psi_A^k(t) \rangle \quad (5b)$$

$$i \frac{\partial \chi_A^k(t)}{\partial t} = (H_0^A - \mu \tilde{\varepsilon}^k(t)) \chi_A^k(t), \quad \chi_A^k(T) = O_A \psi_A^k(T) \quad (5c)$$

$$\tilde{\varepsilon}^k(t) = (1 - \eta) \varepsilon^k(t) - \frac{\eta s(t)}{\alpha_0} \sum_A p_A \text{Im} \langle \chi_A^k(t) | \mu | \psi_A^k(t) \rangle. \quad (5d)$$

2.2. Wave packet propagation

The time-dependent Schrödinger equation for the wave packet $\psi(t)$ of nucleus, in the Born-Oppenheimer framework, is given by

$$i \frac{\partial}{\partial t} \psi(t) = H \psi, \quad (6)$$

where the total Hamiltonian H is the sum of the field-free and the light-molecule interaction parts:

$$H = H_0 + H_I. \quad (7)$$

The field-free Hamiltonian H_0 is composed of the kinetic energy operators for the radial distance R , the polar angle θ , and the azimuth angle ϕ , and of the potential energy operator $V(R)$:

$$H_0 = T_R + T_\theta + T_\phi + V(R). \quad (8)$$

In a previous work [25] potential energy curves for the LiCl molecule were calculated using high-level ab initio methods and here the calculated ground $X^1\Sigma^+$ state potential energy is employed for $V(R)$. The kinetic energy operators are given by

$$T_R = -\frac{1}{2mR^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) \quad (9)$$

$$T_\theta = -\frac{1}{2mR^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \quad (10)$$

$$T_\phi = -\frac{1}{2mR^2} \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}, \quad (11)$$

where m is the reduced mass. The field-molecule interaction term H_I is given by

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