Multilevel effect on ultrafast isotope-selective vibrational excitations: Quantum optimal control study

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ABSTRACT

We demonstrate, using optimal control theory, that perfect isotope-selective molecular vibrational excitations on the ground-state potential curve in multilevel systems can be completed in much shorter time scales than those in two-level systems. We consider a gaseous isotopic mixture of cesium iodide (^{133}CsI and ^{135}CsI) and, using two-level and multilevel systems, try to obtain electric fields that drive different isotopes into different vibrational levels. As a result, we find that in multilevel systems isotope-selective excitation processes can be controlled much faster, which we call multilevel effect. It is likely that this effect makes use of the large isotope shifts of higher vibrational levels than the lowest two.

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1. Introduction

Conventional laser isotope separations have relied only on the laser frequency, utilizing narrow bandwidth lasers to selectively excite one specific isotopic species [1]. A different idea [2,3] has been proposed, based on the phenomena of wave-packet revivals. Averbukh et al. [2] first studied the isotope separation technique based on the revival phenomena taking the ^{79}Br$_2$/^{81}Br$_2$ mixture as a test case and demonstrated experimentally that substantial control over the isotope ratio can be achieved. In this scheme the molecular wave packets of different isotopes are spatially separated and localized in the course of their field-free temporal evolution. Moreover, Leibscher and Averbukh [3] theoretically investigated isotope separation for the same molecular system and predicted that two main separation scenarios are possible; one is the same as found in their previous study [2], based on the wave-packet spatial localization, and the other makes use of quantum interference between the wave packets produced on the same excited potential surface by a sequence of laser pulses. For the former case, since revivals are seen in the field-free wave-packet motion, control with the phenomena usually takes quite a long time. A year later, Verlet et al. [4] proposed a new isotope separation scheme using phase-locked pairs of optical pulses and presented a wave-packet simulation for the same molecular system. This method does not require a spatial localization of the

wave packet and allows for a complete isotope separation in much shorter time scales. As they pointed out, the basic principle underlying their approach is the same as one in the second scenario of Leibscher and Averbukh [3], i.e., quantum interference; they demonstrated, however, that more complete control can be achieved by exactly adjusting the phase difference between the two pulses.

Although these isotope separation schemes [2–4] presented a groundbreaking idea, they have a limitation that the molecular system needs to have an appropriate bound excited-state potential energy curve (PEC) that can lead to the spatial wave-packet localization through the revival phenomena [2,3] or bring π phase difference between the two isotopic wave packets after a few vibrational periods [4]. In this paper, we investigate a new separation scheme including vibrational excitations only on the ground-state PEC; since this might be simpler and less experimentally demanding, a wider range of applications is expected. To our knowledge, the first study of optimal control of vibrational state-selective dynamics on the ground-state PEC was carried out by Manz and co-workers [5,6]; they demonstrated that a high selectivity into the target state can be achieved by optimally shaped pulses. In the present work their idea [5,6] is further developed into the optimal control of isotope separation.

To accentuate the critical role of highly excited vibrational levels involved in the isotope-selective dynamics, both two-level and multilevel systems are investigated here. We focus on how much the pulse duration can be shortened while maintaining the perfect transition probability of isotope-selective vibrational excitations. Fast control has tangible advantage that it can avoid detrimental

relaxation processes such as collision and reaction, leading to the availability of high gas pressure for high throughput. Currently, we do not consider practical realization of the control laser pulse; rather, we here aim to reveal the fundamental importance of highly excited vibrational levels utilized in the ultrafast controlled process. Note that the work presented here is actually an extension of the study of Ohtsuki and Fujimura [7], but we show its effectiveness for a realistic diatomic molecular PEC.

2. Methods of calculation

We have employed optimal control theory (OCT) [8–10] to look for an optimal field that maximizes the transition probability into the target state and minimizes the laser fluence at the same time. In order to find an optimal field that completes isotope-selective transitions, the target state should be set different for different isotopes. We therefore consider the following objective functional J given in the density-matrix formalism [7,11] and try to find an optimal field that maximizes the functional J at the end of total time T:

$$J = \sum_A p_A \langle\langle W_A | \rho_A(T) \rangle\rangle - \alpha^{-1} \int_0^T \varepsilon(t)^2 dt + i \sum_A p_A$$
$$\times \int_0^T dt \langle\langle \Theta_A(t) | \left(i \frac{\partial}{\partial t} - L_A^t \right) | \rho_A(t) \rangle\rangle, \tag{1}$$

with subscript A denoting isotope A. The objective functional J contains three terms: (a) the sum of transition probabilities into the target density operator $|W_A\rangle\rangle$ at T, where $p_A = 1/N$ with N being the number of the isotopic kinds included in the mixture; (b) a penalty for the fluence of the electric field $\varepsilon(t)$ with $\alpha > 0$; (c) a dynamical constraint, with the aid of the Lagrange-multiplier density operator $|\Theta_A(t)\rangle\rangle$, specifying that the time evolution of the density operator $|\rho_A(t)\rangle\rangle$ is governed by the Liouville equation. The Liouvillian L_A^t is defined as $L_A^t = L_A - M\varepsilon(t)$, where L_A is the field-free Liouvillian and M is the commutator for the dipole moment μ. Varying the objective functional, the following coupled nonlinear equations for $|\rho_A\rangle\rangle$, $|\Theta_A\rangle\rangle$, and $\varepsilon(t)$ are obtained:

$$i \frac{\partial}{\partial t} |\rho_A(t)\rangle\rangle = (L_A - M\varepsilon(t))|\rho_A(t)\rangle\rangle, \qquad |\rho_A(0)\rangle\rangle = |\rho_{A_0}\rangle\rangle \tag{2a}$$

$$i \frac{\partial}{\partial t} |\Theta_A(t)\rangle\rangle = (L_A - M\varepsilon(t))|\Theta_A(t)\rangle\rangle, \qquad |\Theta_A(T)\rangle\rangle = |W_A\rangle\rangle \tag{2b}$$

$$\varepsilon(t) = -\alpha \sum_A p_A \text{Im}\langle\langle \Theta_A(t) | \mu | \rho_A(t) \rangle\rangle, \tag{2c}$$

with Im denoting the imaginary part. Starting with an initial guess for an optimal field $\varepsilon(t)$, these coupled equations are integrated iteratively until J reaches a convergence. The final $\varepsilon(t)$ obtained at the end of iteration is what we are seeking.

In the present work we focus on quantum control of the isotope-selective vibrational excitations of the cesium iodide molecule (CsI). A mixture of the two isotopic species ^{133}CsI and ^{135}CsI is considered and the initial state is set to be the condition that both the isotopic species are in the vibrational ground level ($v = 0$) and the target state is that ^{133}CsI is in the $v = 0$ level while ^{135}CsI in the vibrational first-excited level ($v = 1$). We used the PEC and dipole moment for the electronic ground state (X0$^+$) of CsI, which we have calculated recently at a high level of quantum-chemical theory [12]. The vibrational eigenstates and energies for the X0$^+$ PECs for ^{133}CsI and ^{135}CsI were calculated using the Fourier grid Hamiltonian method [13] with 1024 evenly spaced grid points on the internuclear distance from 3.7795 to 35.0 bohr. Using the obtained vibrational eigenstates as the basis functions, Eqs. (2)–(4) were translated into the matrix forms and numerically integrated with the Runge-Kutta method. To improve the convergence behavior we employed the conjugate-gradient method with

the Polak–Ribiere–Polyak search algorithm [14]. In this work the molecular rotation is neglected and its orientation is fixed to be parallel to the field polarization. Including rotational effects might be an important issue, but here we focus only on vibrational excitations with simple model systems to obtain good insights into the mechanism of isotope-selective excitation.

Six sets of total time T (i.e., the pulse duration in time) and the number of basis functions N_{basis} were considered in the present OCT calculations and they are summarized in Table 1. First, we have investigated the simplest two-level ($N_{\text{basis}} = 2$) systems (case (i)) for the following three total times: $T = 3,680,000$ au ($\sim$89 ps) (case (i-a)); $T = 1,840,000$ au ($\sim$44.5 ps) (case (i-b)); $T = 920,000$ au ($\sim$22.2 ps) (case (i-c)). Next, in order to reveal the effect of including more than two levels on the total time T required for perfect isotope-selective vibrational excitations, we have increased N_{basis} up to 12 and studied the cases for the following two total times: $T = 460,000$ au ($\sim$11.1 ps) (case (ii-a)); $T = 230,000$ au ($\sim$5.6 ps) (case (ii-b)). Note that according to the harmonic constant of CsI, $\sim$120 cm^{-1} [15], the total time $T = 5.6$ ps is the time it takes for the CsI molecule to oscillate about 20 times around the equilibrium internuclear distance.

3. Results and discussion

First, we present the results of OCT calculations for the two-level ($N_{\text{basis}} = 2$) systems. The optimal field for case (i-a) (not shown), where $T = 3,680,000$ au, gives the final transition probabilities (i.e., yield) of 1.000 for both ^{133}CsI and ^{135}CsI (Table 1). It was found that the spectrum of the optimal field is composed only of the $v = 1 \leftarrow 0$ transition frequency for ^{135}CsI (5.5149×10^{-4} hartree). This indicates that the control mechanism presented in case (i-a) is exactly what is working in the 'conventional' laser isotope separation, where the laser frequency is the exclusive basis for separation, and that the mechanism is governed by the Rabi oscillations; the optimal field corresponds to the π pulse for ^{135}CsI and the 2π pulse for ^{133}CsI. Next, let us see what happens if the total time T is reduced to half. Fig. 1 displays the results for case (i-b) ($T = 1,840,000$ au). The optimal field (Fig 1(a)) exhibits a double-pulse feature and its spectrum (Fig. 1(b)) has frequency components of $\sim$0.00055 hartree, corresponding to the $v = 1 \leftarrow 0$ transition. The spectrum is broader than that for case (i-a), however, and has a node at the transition frequency for ^{133}CsI. Temporal evolutions of the populations of the $v = 0$ and 1 levels (Figs. 1(c) and 1(d)) show that a perfect transition is achieved at the end of the pulse (Table 1). From the double-pulse feature of the optimal field it is suggested that the control mechanism for case (i-b) is governed by quantum interference between the wave packets created by the double pulse. Then what happens if T is further reduced to half? It was found that the optimal field for case (i-c) ($T = 920,000$ au) does not cause perfect transition (figures are not shown); the final populations of the ^{133}CsI $v = 0$ and ^{135}CsI $v = 1$ levels are 0.8958 and 0.8974, respectively (Table 1), which are substantially smaller than 1.

In a two-level system, the wave packet created through the coherent superposition of the two vibrational eigenstates oscillates in the PEC with the frequency corresponding to the $v = 1 \leftarrow 0$ transition energy. Mass difference between the isotopic species makes difference in the transition energy, which leads to difference in the phase of the wave-packet oscillation. In the present isotopic molecular systems the phase difference is very small only for one oscillation, but it grows substantial after numerous oscillations. It might be reasonable to think that when the phase difference between the wave packets created by the first pulse becomes π, perfect excitation for one isotope and cancellation for the other due to quantum interference is possible by the second pulse. This