The role of dissociation channels of excited electronic states in quantum optimal control of ozone isomerization: a three-state dynamical model

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ABSTRACT

The prospect of performing the open $\rightarrow$ cyclic ozone isomerization has attracted much research attention. Here we explore this consideration theoretically by performing quantum optimal control calculations to demonstrate the important role that excited-state dissociation channels could play in the isomerization transformation. In the calculations we use a three-state, one-dimensional dynamical model constructed from the lowest five $^1A'$ potential energy curves obtained with high-level *ab initio* calculations. Besides the laser field-dipole couplings between all three states, this model also includes the diabatic coupling between the two excited states at an avoided crossing leading to competing dissociation channels that can further hinder the isomerization process. The present three-state optimal control simulations examine two possible control pathways previously considered in a two-state model, and reveal that only one of the pathways is viable, achieving a robust $\sim 95\%$ yield to the cyclic target in the three-state model. This work represents a step towards an ultimate model for the open $\rightarrow$ cyclic ozone transformation capable of giving adequate guidance about the necessary experimental control field resources as well as an estimate of the ro-vibronic spectral character of cyclic ozone as a basis for an appropriate probe of its formation.

Keywords:

Quantum control

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1. Introduction

Recent progress in the laser technology bolsters the prospect that quantum control using tailored ultrashort pulse lasers [1-3] may be able to achieve some elusive dynamical objectives that are inaccessible or very difficult to obtain utilizing traditional chemical methods. In considering this challenge a general goal is to drive the system to a specified target with high efficiency while often in the presence of undesired competing channels. Ozone (O_3) isomerization from the ground-state open isomer to the quasi-stable cyclic (or ring) counterpart is one such outstanding challenge, and this objective has attracted much research over many years. From a quantum control perspective the example serves as a good test case because the isomerization competes with molecular dissociation into the oxygen molecule and atom, which is energetically more favorable. As steps along the exploration of meeting this objective, we recently carried out quantum optimal control calculations for ozone isomerization using simplified electronic (a) single-state [4,5] and (b) two-state [6] models with one-dimensional (1D) dynamics. It was found that the isomerization with the two-state model can be controlled more easily than that with the single-state model, indicating that the first excited-state potential energy curve (PEC) helps to avoid the unwanted leakage into the competing dissociation channel. This result suggests that the controlled isomerization may be achieved by exploiting selected excited-state PECs that are *not* easily accessible to the competitive processes.

In this paper we further examine the ozone isomerization mechanism suggested above by building a more general multi-excited states model constructed from the five lowest A' PECs. The net result is the addition of a third electronic state in the model, corresponding to a newly added PEC, V_{33}^d , which was not considered in the previous single-state [4,5] and two-state [6] models. As shown in Fig. 1a, the three-state model contains two avoided crossings (ACs): AC1 and AC2. AC1 was considered in our previous two-state model [6] including only V_{11}^d and V_{22}^d , whereas AC2 manifests itself as an intersection of V_{33}^d with the outer barrier of the secondary shallow well on the diabatic PEC V_{22}^d . The horizontal axis labeled by s denotes the arc length of the intrinsic reaction coordinate (IRC) [7] in the unit of $\text{amu}^{1/2} \text{ bohr}$, but in what follows it will be just written as a.u. for brevity. The present study goes beyond the previous work [5,6] by

exploring the challenge of meeting the control objective even in the presence of multiple competing channels. The three-state ozone isomerization control model examined here may be considered as the preliminary of a laboratory study utilizing properly prescribed band-limited control fields with low and high frequency cutoffs.

Specifically, using optimal control theory (OCT) [8-10], we will investigate the dynamics of the two control pathways, 1 and 2, schematically indicated by the red and blue arrows, respectively, in Fig. 1b. Pathway 1 (in red) contains two steps [cf. Fig. 2(b) in Ref. 6]: the wave packet starting from the open isomer (the ground vibrational state of V_{11}^d) is first excited electronically into the secondary well (at $s = 9.5$ a.u.) and then driven down the slope of the PEC, passing through AC1 to form the cyclic isomer (the ground vibrational state of V_{22}^d). Pathway 2 (in blue) contains three steps: the initial ground-state open isomer wave packet is first excited to high-lying vibrational levels just below the dissociation asymptote of PEC V_{11}^d , then makes a transition to vibrational levels above AC1 in the main well of PEC V_{22}^d , and is finally driven across AC1 to reach the ground vibrational state of V_{22}^d . These two pathways were considered in the previous two-state model, with the corresponding control field low/high cutoff frequencies $\omega_l = 0.0001$ a.u. and $\omega_h = 0.3$ a.u. for pathway 1 and $\omega_l = 0.0001$ a.u. and $\omega_h = 0.1$ a.u. for pathway 2 [6]. Our purpose here is to further investigate the efficacies of each pathway, which may be hindered by processes involving the third PEC, V_{33}^d . This new study will show that (a) pathway 1 is a viable control route despite the additional dissociation channel of the third state V_{33}^d and (b) pathway 2 is unlikely to be attainable due to a large transition dipole moment between V_{11}^d and V_{33}^d along with the shallow well of V_{33}^d causing a large Franck-Condon factor between the vibrational levels of V_{11}^d and V_{33}^d . This circumstance may be qualitatively understood as follows. First, AC2 is slightly lower in energy than the barrier on V_{22}^d at around $s = 8.5$ a.u., which could open up another competing dissociation channel linked to pathway 1 if the wave packet passes through AC2 adiabatically. Second, the electronic excitation to V_{33}^d from V_{11}^d and possibly from V_{22}^d can occur through dipole coupling, as shown by the vertical dotted green lines in Fig. 1b, followed by diabatic transition through AC2 and eventual dissociation. Note that the

location of all the transitions indicated in Fig. 1 may occur over windows of some extent. Thus, the presence of V_{33}^d introduces the challenge of suppressing the dissociation of the wave packet exploiting this excited potential. Third, the transition dipole moment μ_{13}^d between V_{11}^d and V_{33}^d has significant values when $s > 9$ a.u., as shown in Fig. 2, and V_{33}^d has a shallow well around $s = 11$ a.u., leading to a large Franck-Condon factor between the vibrational levels of V_{11}^d and V_{33}^d . In any application there usually exist many ACs between various excited-state PECs, and this work, focused on the physically interesting case of ozone isomerization, is also demonstrative of managing the ensuing dynamics when competing channels with the desired product arise due to multiple accessible ACs.

The ozone open $\rightarrow$ cyclic isomerization is of basic scientific importance because it would reflect a new isomeric form of oxygen. As far as we know, gas-phase cyclic ozone has yet to be detected, and the only experimental evidence of the cyclic form is from transmission electron diffraction data of the molecule adsorbed on the MgO (111) surface [11]. It was revealed in a recent theoretical study [12] that the ozone cyclic $\rightarrow$ open isomerization transition is faster than previously believed due to strong tunneling, which suggests that fast spectral probes may be needed to detect it in the gas phase, or perhaps that the cyclic form may need to be stabilized as a complex with other species (e.g., as in Ref. [11]). In this regard, a computational density functional study [13] considered the possibility of trapping the cyclic form in transition metal complexes.

Finally, we remark that the OCT design studies of complex systems likely best serve as a guide to estimate the necessary experimental laser resources (e.g., for ozone isomerization). In this regard a full elaborate ro-vibronic model in quantitative detail is not feasible, even in the “simple” case of ozone. Beyond the present study a natural next step for improving the ozone isomerization design would be the inclusion of rotational (angular) effects, possibly within the sudden approximation, along with an assessment of the effect of going to 2D dynamical model. A final step of modelling should include suitable estimates of the ro-vibronic spectral signatures of cyclic ozone [14-16] to guide fast probes of its detection as a feedback signal for attempting optimal control experiments via adaptive feedback control (AFC) [17,18].

2. Model description

In the present study we construct a three-state model by adding a third electronic PEC to a prior two-state potential model [6]. The two-state model was previously constructed using the ab initio data calculated along the IRC determined on the potential energy surface obtained by Siebert *et al* [14]. The newly added diabatic PEC V_{33}^d is constructed from adiabatic PECs V_{33}^a ($s < 10.0$ a.u.), V_{22}^a ($10.0 < s < 11.4$ a.u.), and V_{33}^a (11.4 a.u. $< s$), thus giving rise to AC2 at $s = 10.0$ a.u. in Fig. 1a. The diabaticization procedure around AC2 at $s = 10.0$ a.u. is the same as the one employed in our previous study [6]. We find that the energy difference ΔE_x between V_{22}^a and V_{33}^a at $s_x = 10.0$ a.u. is 2.16×10^{-3} a.u. and the diabatic coupling may be calculated from

$$V_{23}^d(s) = \frac{\Delta E_x}{2} \exp(-\delta(s - s_x)^2), \quad (1)$$

where δ is determined such that

$$V_{23}^d(s_x \pm 0.1) = AV_{23}^d(s_x) \quad (2)$$

is satisfied with coupling amplitude $A = 10^{-2}$. Figure 1a shows the constructed three-state 1D potential model. The lower two insets display the diabatic couplings V_{12}^d and V_{23}^d , showing that the peak of V_{23}^d is a bit higher than that of V_{12}^d . The upper right inset gives a close-up of PECs V_{22}^d and V_{33}^d near AC2 around $s = 10$ a.u.; as shown in the figure, AC2 is energetically lower by about 0.006 a.u. than the immediate left barrier on the PEC V_{22}^d , suggesting that wave-packet dissociation can take place during the controlled isomerization not only due to the electronic excitation to V_{33}^d from V_{11}^d and V_{22}^d , but also due to the adiabatic transition through AC2. As mentioned earlier, for pathway 1 these processes can open up other competing routes due to the role of PEC V_{33}^d . We employ the optimal fields for pathways 1 and 2 previously obtained based on the two-state model [6] as the initial guesses for the present three-state OCT calculations.

The dipole moments (DMs) and transition dipole moments (TDMs) in the diabatic representation along the IRC are obtained from those in the adiabatic representation using

diabatic coupling V_{23}^d in the same manner as described in Ref [6]. Figure 2 presents the z components of the constructed diabatic DM and TDM matrix elements, where the z axis is placed along the bisector of the apex angle of the open isomer of ozone. In the figure μ_{13}^d , μ_{23}^d , and μ_{33}^d are newly added beyond the previous two-state DM model. As shown, TDMs μ_{13}^d and μ_{23}^d have substantial values around $s = 10$ a.u., implying that electronic excitations to V_{33}^d from V_{11}^d and/or V_{22}^d through dipole coupling may affect the controlled dynamics.

3. Optimal control theory and wave packet propagation

In the present study we aim to find a control field that maximizes the transition probability of reaching the cyclic target state while simultaneously minimizing the laser pulse fluence. To this end we use OCT to provide an efficient means to find such an electric field; the electric field $\varepsilon(t)$ is determined so as to maximize the following objective functional:

$$J = \left| \langle \psi_f | \psi(T) \rangle \right|^2 - \alpha_0 \int_0^T dt \varepsilon(t)^2 - 2 \operatorname{Re} \left[\langle \psi(T) | \psi_f \rangle \int_0^T dt \left\langle \chi(t) \left| \frac{\partial}{\partial t} + i(H_0 + \mu \varepsilon(t)) \right| \psi(t) \right\rangle \right]. \quad (3)$$

The first term is the transition probability to be maximized, where $|\psi(t)\rangle$ is the system state propagated from time $t = 0$ to T and $|\psi_f\rangle$ is the target state. The second term is the laser fluence to be minimized, where $\alpha_0 > 0$. The third term is the dynamical constraint, where $\chi(t)$ is the Lagrange multiplier, Re denotes real part, and H_0 is the field-free Hamiltonian. The coupled equations obtained from the optimization condition $\delta J = 0$ with respect to $\psi(t)$, $\chi(t)$, and $\varepsilon(t)$ are numerically solved iteratively using the conjugate gradient method. Detailed descriptions of the OCT calculation procedure are given elsewhere [4-6].

Since the system wave packet propagates on three diabatic PECs, the Schrödinger equation can be written in matrix form:

$$i \frac{\partial}{\partial t} \Psi = \mathbf{H} \Psi, \quad (4)$$

where

$$\Psi = \begin{pmatrix} \psi_1(t) \\ \psi_2(t) \\ \psi_3(t) \end{pmatrix} \quad (5)$$

with $\psi_1(t)$, $\psi_2(t)$ and $\psi_3(t)$ being the projections of the system wave packet on the diabatic PECs V_{11}^d , V_{22}^d , and V_{33}^d , respectively. The Hamiltonian matrix becomes

$$\begin{aligned} \mathbf{H} &= \mathbf{T} + \mathbf{V} \\ &= \begin{pmatrix} T_1 & 0 & 0 \\ 0 & T_2 & 0 \\ 0 & 0 & T_3 \end{pmatrix} + \begin{pmatrix} V_{11} & V_{12} & V_{13} \\ V_{21} & V_{22} & V_{23} \\ V_{31} & V_{32} & V_{33} \end{pmatrix} \\ &= \begin{pmatrix} T_1 & 0 & 0 \\ 0 & T_2 & 0 \\ 0 & 0 & T_3 \end{pmatrix} + \begin{pmatrix} V_{11}^d - \mu_{11}^d \mathcal{E}(t) & V_{12}^d - \mu_{12}^d \mathcal{E}(t) & -\mu_{13}^d \mathcal{E}(t) \\ V_{21}^d - \mu_{21}^d \mathcal{E}(t) & V_{22}^d - \mu_{22}^d \mathcal{E}(t) & V_{23}^d - \mu_{23}^d \mathcal{E}(t) \\ -\mu_{31}^d \mathcal{E}(t) & V_{32}^d - \mu_{32}^d \mathcal{E}(t) & V_{33}^d - \mu_{33}^d \mathcal{E}(t) \end{pmatrix}, \end{aligned} \quad (6)$$

where T_1 , T_2 , and T_3 are the kinetic-energy (KE) operators for nuclear motion on V_{11}^d , V_{22}^d , and V_{33}^d , respectively. The KE operator is expressed in terms of the IRC as specified in Ref. [6]. The off-diagonal elements of the potential-energy (PE) matrix $\mathbf{V}$ are responsible for the transitions between two diabatic PECs due to diabatic couplings V_{12}^d and V_{23}^d along with the TDMs μ_{12}^d , μ_{13}^d , and μ_{23}^d . The diabatic coupling $V_{13}^d = 0$ between PECs V_{11}^d and V_{33}^d , which are far apart from each other, as shown in Fig. 1a. Equation (4) is numerically solved using the split-operator method [19,20]:

$$\Psi(t + \Delta t) = \exp(-i\mathbf{V}\Delta t/2) \exp(-i\mathbf{T}\Delta t) \exp(-i\mathbf{V}\Delta t/2) \Psi(t) + O(\Delta t^3). \quad (7)$$

The action of the PE operator on the wave packet is performed in coordinate space. Since the PE matrix $\mathbf{V}$ is nondiagonal, the exponential of the PE matrix is diagonalized at every time step of the wave-packet propagation. The action of the kinetic-energy operator on the wave packet is performed in momentum space by transforming from coordinate space with the fast-Fourier-transform (FFT) algorithm, and then the wave packet is finally transformed back into the coordinate space with the inverse FFT algorithm.

The initial condition for the Schrödinger equation is the vibrational ground state of the PEC V_{11}^d , i.e., $\Psi_0 = (\phi_1^1, 0, 0)^T$ and the target state is the vibrational ground state of

the PEC V_{22}^d , i.e., $\psi_f = (0, \phi_1^2, 0)^T$ with ϕ_i^j being the i -th eigenfunction for the PEC V_{jj}^d . The eigenvalues and eigenfunctions for V_{11}^d , V_{22}^d , and V_{33}^d are calculated using the Fourier grid Hamiltonian method [21] with 512 evenly spaced grid points on the IRC from $s = -2.0$ to 16.7 a.u. In the calculations, the molecular rotational motion is frozen and the bisector of the apex angle of the open isomer is placed parallel to the field polarization direction. The total propagation time T (i.e., the pulse length) is set to 80000 a.u. (1.936 ps), and the number of time steps is 8192 ($= 2^{13}$). In the wave packet propagation a damping function [22] is introduced over the last 10 grid points to eliminate the unwanted reflection of the wave function at the grid edge.

4. Results and discussion

We carry out the OCT calculations for pathways 1 and 2 in Fig. 1b as five distinct cases with different combinations of the three couplings, V_{23}^d , μ_{13}^d , and μ_{23}^d , as defined in the first column in Table 1 in order to reveal which one of the dipole and diabatic couplings most affect the dynamics around AC2. In the table $\circ$ and $\square$ mean, respectively, that the *ab initio* coupling is either used as it is or it is set to zero, in the OCT calculation. Specifically, Case 1 contains all three existing couplings V_{23}^d , μ_{13}^d , and μ_{23}^d ; Case 2 contains two couplings μ_{13}^d and μ_{23}^d ; Case 3 only allows for one coupling V_{23}^d ; Case 4 contains two couplings V_{23}^d and μ_{23}^d ; finally, Case 5 contains two couplings V_{23}^d and μ_{13}^d . The fully coupled Case 1 aims to show the actual optimal control efficiency for the three-state model, while the four partially coupled cases, Case 2 - Case 5, are chosen to further examine the effects of different couplings terms. There are eight ($= 2^3$) on-and-off combinations of the three couplings, but the cases of zero V_{23}^d are not investigated except for Case 2 because the effect of V_{23}^d is found to be small, as will be numerically demonstrated below, and they give almost the same results as Cases 1, 3-5.

As stated earlier, the simulations for pathways 1 and 2 shown in Fig 1b are, respectively, implemented using frequency windows with low/high cutoffs given by (1) $\omega_l = 0.0001$ and $\omega_h = 0.3$ a.u. for pathway 1 and (2) $\omega_l = 0.0001$ and $\omega_h = 0.1$ a.u. for

pathway 2. The larger frequency window with $\omega_l = 0.0001$ and $\omega_h = 0.3$ a.u. overwhelmingly favors pathway 1 dynamically, because the secondary well of V_{22}^d is directly accessible from the initial state through the electronic transition between V_{11}^d and V_{22}^d due to a large Franck-Condon factor between the associated bound-state wave functions. The narrower frequency window with a smaller high cutoff frequency $\omega_h = 0.1$ a.u. aims to turn off pathway 1 by making the secondary well of V_{22}^d dynamically inaccessible from the initial state.

4.1. Pathway 1 – low/high cutoff frequencies $\omega_l = 0.0001$ a.u. and $\omega_h = 0.3$ a.u.

4.1.a. Case 1

In this case no change is made in V_{23}^d , μ_{13}^d , and μ_{23}^d , as listed in Table 1. Figure 3 shows (a) the optimized field, (b) its power spectrum, and (c) the Husimi plot obtained in the OCT calculation for Case 1 for pathway 1. As shown in Fig. 3a, the optimized field between $t = 0$ and 20000 a.u. is highly oscillatory corresponding to a dominant frequency component associated with the $1 \rightarrow 2$ electronic excitation from the PEC V_{11}^d to the PEC V_{22}^d ; this frequency component appears around $\omega = 0.15$ a.u. in the power spectrum (Fig. 3b) and it operates from $t = 0$ to $t = 20000$ a.u. in the Husimi plot (Fig. 3c). The optimized field between $t = 20000$ and 50000 a.u. is still highly oscillatory, suggesting that the $1 \rightarrow 2$ electronic excitation is still playing a role. In the Husimi plot much weaker frequency components corresponding to the $1 \rightarrow 2$ electronic excitation are seen around $\omega = 0.15$ a.u. between $t = 20000$ and 50000 a.u. These weaker frequency components can be seen around the sharp, tall peak at $\omega = 0.15$ a.u. in the power spectrum. Between $t = 20000$ and 50000 a.u. the field amplitudes are slightly larger than those between $t = 0$ and 20000 a.u. The wave packet excited to the secondary well of the PEC V_{22}^d must be quickly driven to the left, going up the potential slope and surmounting the barrier at $s = 8.5$ a.u. before it can exit from the right on the PEC V_{33}^d ; the quick leftward motion is generated by the interaction of the molecule, via DM μ_{22}^d with a strong driving field corresponding to

sharp peaks seen between $t = 20000$ and 50000 a.u. in Fig. 3a. When $t > 50000$ a.u., the optimized field is not so highly oscillatory as that in the earlier stage, indicating that the field is composed of low frequency components that are seen in both the power spectrum and the Husimi plot. The low frequency components correspond to the fundamental and some overtones of the vibrational transition in the primary well of the PEC V_{22}^d , i.e., during the second half of the pulse the wave packet climbs down the vibrational ladder through AC1 at $s = 5.8$ a.u., finally reaching the target in the ground vibrational level of the PEC V_{22}^d . As summarized in Table 1, the optimal field for Case 1 for pathway 1 gives the final yield of 0.950 with the maximum amplitude and fluence being 0.249 and 161.2 a.u., respectively.

Figure 4 shows the temporal evolution of the following quantities for Case 1 for pathway 1: (a) the expectation value of the molecular field-free Hamiltonian, $\langle H_0 \rangle$; (b) the expectation value of position, $\langle s \rangle$; (c) populations $\langle \psi_1 | \psi_1 \rangle$, $\langle \psi_2 | \psi_2 \rangle$, and $\langle \psi_3 | \psi_3 \rangle$ in the diabatic states V_{11}^d , V_{22}^d , and V_{33}^d , respectively, and the norm $\langle \Psi | \Psi \rangle$ of the total wave packet. As shown in Fig. 4a, direct electronic transitions among PECs V_{11}^d , V_{22}^d , and V_{33}^d take place between $t = 0$ and 40000 a.u., characterized by high oscillations in $\langle H_0 \rangle$. Figure 4b reveals that $\langle s \rangle$ oscillates rapidly with moderate amplitude between $t = 10000$ and 40000 a.u., indicating vertical electronic transitions among the three PECs. This is followed by slow oscillations between $t = 40000$ and 70000 a.u. before finally reaching the target at $t = 80000$ a.u., showing that after $t = 40000$ a.u. a major portion of the wave packet stays in the primary well of the PEC V_{22}^d and descends the vibrational ladder of the PEC. As shown in the inset in Fig. 4c, the temporal change in $\langle \psi_3 | \psi_3 \rangle$ shows roughly two stages centered around $t = 10000$ and 40000 a.u. The first stage is mostly attributed to the electronic excitation from the PEC V_{11}^d to the PEC V_{33}^d and the second stage is caused by the electronic transition between PECs V_{22}^d and V_{33}^d taking place through the dipole coupling μ_{23}^d . It is possible, however, that the wave-packet transition from V_{22}^d to V_{33}^d through the diabatic coupling V_{23}^d at AC2 also contributes to $\langle \psi_3 | \psi_3 \rangle$. In the next subsection we present the OCT results for cases 2-5 and discuss the contributions of dipole vs. diabatic couplings around AC2.

4.1.b. Cases 2-5

The dissociation of the wave packet along pathway 1 might be caused by one or all of the following three processes: (i) transition from the PEC V_{22}^d to the PEC V_{33}^d due to the diabatic coupling V_{23}^d at AC2; (ii) electronic excitation from the PEC V_{11}^d to the PEC V_{33}^d due to the dipole coupling μ_{13}^d ; (iii) electronic excitation from the PEC V_{22}^d to the PEC V_{33}^d due to the dipole coupling μ_{23}^d . In process (i) the wave packet likely dissociates since the dissociative asymptote of the PEC V_{33}^d is about 0.015 a.u. lower in energy than the corresponding AC. Processes (ii) and (iii) are followed by diabatic passage through AC2 and some degree of leakage into the dissociative asymptote. The OCT calculations in Case 2 and Case 3 reveal the importance of process (i) and those in Case 4 and Case 5 elucidate, respectively, how much the processes (ii) and (iii) affect leakage of the wave packet.

As shown in Table 1, the OCT result in Case 2 is essentially the same as that in Case 1, suggesting that the effect of the diabatic coupling at AC2 on the control dynamics is small. The yield obtained in Case 3, 0.969, is somewhat larger than that in Case 1, indicating that dipole couplings between PECs V_{11}^d and V_{33}^d and/or between PECs V_{22}^d and V_{33}^d are important but the effect of the diabatic coupling at AC2 is small. The maximum field amplitude and fluence of the optimal field in Case 3 are slightly smaller than those in Case 1 and Case 2. The OCT calculation in Case 4 gives a slightly smaller yield than in Case 1 but the difference is not significant; this means that the electronic transition between PECs V_{11}^d and V_{33}^d due to the dipole coupling μ_{13}^d does not strongly suppress the isomerization. The OCT calculation in Case 5 also gives a yield, 0.969, close to that for the two-state model, indicating that the electronic transition due to the dipole coupling through μ_{23}^d can suppress the isomerization. The maximum field amplitudes and fluences of the optimal fields in Case 5 and Case 3 are similar, but smaller than those in the other three cases.

From the analyses given above it is found that the main cause of the wave-packet

dissociation is the process (iii), associated with electronic excitation from the PEC V_{22}^d to the PEC V_{33}^d due to the dipole coupling μ_{23}^d . The process (i), diabatic coupling V_{23}^d , and the process (ii), dipole coupling μ_{13}^d , are minor contributors to dissociation.

4.1.c. Comparison with the result using the two-state model optimal field

As given in Table 1, the optimal field for the two-state model gives, without further optimization in the three-state model, a yield of 0.234. Field optimization based on OCT results in the final yield of 0.950 for the three-state model. Despite a distinct difference in the final yields between the two optimized fields, the general form of the optimized field for the three-state model is similar to that for the two-state model, as explained below. The maximum field amplitude and fluence of the optimized field for the three-state model are 0.250 and 161.1 a.u., respectively, and those for the two-state model are 0.222 and 140.4 a.u. (Table 1). The optimized fields in the time domain (Fig. 3a and Fig. 6a in Ref. [6]) and in the frequency domain (Fig. 3b and Fig. 6b in Ref. [6]) are quite similar between the two-state and three-state models. The main difference is that the amplitudes of the field for the three-state model are a bit larger than those for the two-state model between $t = 15000$ and 50000 a.u. The similarity between the two optimized fields results in the similar temporal behaviors of the expectation values of the field-free Hamiltonian (Fig. 4a and Fig. 7a in Ref. [6]), the position (Fig. 4b and Fig. 7b in Ref. [6]), and the state populations (Fig. 4c and Fig. 7c in Ref. [6]). Furthermore, the rather good unoptimized initial yield of 0.234 in the three-state model also reflects the similarity of the underlying dynamics of the two- and three-state models. We may interpret the model comparison as reflecting convergence of the key dynamics as the model increases in detail.

4.2. Pathway 2 Case 1 – low/high cutoff frequencies $\omega_l = 0.0001$ a.u. and $\omega_h = 0.1$ a.u.

The smaller frequency window here cuts off the transition from the initial state to the secondary well of V_{22}^d , but permits the transitions to both (i) the inner part (to the left of the second well) of V_{22}^d and (ii) the asymptotic part (to the right of AC2 around $s =$

10 a.u.) of V_{33}^d .

We first calculated the target yield without any optimization for the present three-state model using a previously optimized field for pathway 2 for the two-state model. It was found that the final yield was nearly zero, as shown in Table 1. We also found that as the wave packet evolves, component ψ_3 continues to be significant for $t > 15000$ a.u., eventually leading to dissociation, and the component ψ_2 is insignificant throughout the pulse duration (not shown). Moreover, despite our best efforts, even when frequency components larger than 0.08 a.u. (i.e., below the high frequency cutoff $\omega_h = 0.1$ a.u.) were removed, we failed to obtain a field that enabled a direct transition exclusively following just pathway 2 to a high vibrational level of the primary well of V_{22}^d from the open isomer. Instead, we always find a field that starts with a transition to a vibrational level of the shallow well of V_{33}^d around $s = 11$ a.u. This is due to a large transition dipole moment μ_{13}^d between V_{11}^d and V_{33}^d at $s > 9$ a.u., as shown in Fig. 2, and due to non-negligible Franck-Condon factors between the vibrational levels of V_{11}^d and those of the shallow well of V_{33}^d . Thus, pathway 2 becomes an improbable isomerization control route in the three-state model, demonstrating the important role played by the third state V_{33}^d that brings about an additional shallow well just below the shallow well of V_{22}^d in the previous two-state model.

5. Conclusion

The previous quantum optimal control calculations for the ozone open $\rightarrow$ cyclic isomerization used both single-state [4,5] and two-state [6] 1D reaction-path models. The present study considered a more complete three-state diabatic 1D model constructed from the lowest five $^1A'$ PECs obtained with high-level *ab initio* calculations. This study further examined the effect of multiple excited states, and avoided crossings between them, for molecular isomerization control in the presence of multiple competing dissociative channels going beyond the previous models. The fully coupled three-state 1D model OCT calculations (Case 1) show that the final yield for the isomerization is ~ 0.95 . The four

partially coupled OCT calculations (Case 2 – Case 5) revealed that the main cause of the wave-packet leakage into dissociation is the coupling μ_{23}^d . The three-state model further showed that the previously considered pathway 2 in the two-state model is an unlikely route for ozone isomerization.

In summary, the collective results of the one-, two-, and three-state 1D models show that (i) control of the isomerization can be facilitated, even in the presence of an unfavorable competing channel on the ground-state potential by exploiting the excited-state potentials, (ii) some unfavorable channels can lead to dissociation due to diabatic and/or dipole couplings between the excited-state potentials, but they are mostly avoidable with a properly designed laser pulse, as summarized in Table I, and (iii) the results for pathway 1 show a good degree of robustness to Hamiltonian variations.

The 1D model for the control of ozone isomerization is intended to capture the essence of control dynamics along the IRC-based minimum energy path of the ground-state potential surface. The nearly converged result for pathway 1 based on similar results from all the models strongly suggests that appropriate optimized fields for isomerization control likely may be found in laboratory with suitable optical resources. It is still challenging to generate pulses with the character shown in Fig. 3, including disparate low and high wavelengths. However, advancements in laser technology are moving rapidly. For example, ultrabroadband laser sources may be realized a number of ways including with chirped-pulse upconversion based on four-wave difference frequency generation (FWDG) [23]; pulse shaping of ultrashort laser broad bandwidth pulses is also getting more sophisticated using reflective micromirror arrays based on the micro-electro-mechanical-system (MEMS) technology [24]. Thus we hope that the results in this paper will further boost development of the appropriate technologies to explore control of ozone isomerization directly in the laboratory.

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Table 1
Simulation results.

Case ^a				α_0	Max. field amp./a.u.	Fluence/a.u.	Yield
V_{23}^d	μ_{13}^d	μ_{23}^d					
Pathway 1							
1:	○	○	○	0.0001	0.250	161.1	0.950
2:	×	○	○	0.0001	0.246	161.9	0.948
3:	○	×	×	0.0001	0.214	141.7	0.969
4:	○	×	○	0.0001	0.281	162.9	0.943
5:	○	○	×	0.0001	0.219	140.7	0.969
Two-state model ^b				0.0005	0.222	140.4	0.973
No opt. in Case 1 ^c					0.222	140.4	0.234
Pathway2							
Two-state model ^b				0.0001	0.774	1318.6	0.637
No opt. in Case 1 ^c					0.774	1318.6	0.004

^a○:The ab initio data for the indicated coupling is used in the OCT calculation; : The coupling is set to zero.

^bRef. [6].

^cThe result for the present three-state model obtained using the optimal field for the two-state model without further optimization.

Figure captions

Fig. 1. (a) The three-state 1D model consisting of three diabatic PECs V_{11}^d and V_{22}^d , and V_{33}^d and two diabatic couplings V_{12}^d and V_{23}^d (inset); (b) Control pathways 1 (red) and 2 (blue). The vertical dotted green lines show the electronic excitations to V_{33}^d from V_{11}^d and possibly from V_{22}^d through dipole coupling.

Fig. 2. The z components of dipole moments (DMs) and transition dipole moments (TDMs) in the diabatic representation along the IRC s . The z axis lies along the bisector of the apex angle of the open isomer of ozone.

Fig. 3. (a) The optimal field, (b) its spectrum, and (c) its Husimi plot, obtained for Case 1.

Fig. 4. Temporal evolution driven by the optimal field (Fig. 3a) obtained in Case 1: (a) the expectation value of molecular field-free Hamiltonian, $\langle H_0 \rangle$. The origin of the vertical axis corresponds to the asymptotic energy of V_{11}^d ; (b) the expectation value of position, $\langle s \rangle$; (c) the populations of the diabatic states V_{11}^d , V_{22}^d , and V_{33}^d and the norm of wave packets, $\langle \psi_1 | \psi_1 \rangle$, $\langle \psi_2 | \psi_2 \rangle$, $\langle \psi_3 | \psi_3 \rangle$, and $\langle \Psi | \Psi \rangle$.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Quantum control of cyclic ozone (O_3) formation

Graphical Abstract