Robust control of photoassociation of slow O+H collision

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Abstract

We show that robust laser pulses can be obtained by a sampling-based method to achieve a desired photoassociation probability when uncertainties in potential curves and laser amplitudes are considered. Optimal control simulations are performed using a time-dependent wave packet method based on a single electronic state. We use a small number of samples to construct a robust field and test the performance of this field using additional samples. Excellent outcomes are obtained based on the proposed method for different uncertainties. The robust control field achieves higher average photoassociation probabilities over the tested samples, in comparison with the probabilities achieved by the optimal field designed without using the sampling-based method. The sampling-based method may also be promising in the robust control of other molecular control goals.

Keywords: Photoassociation, Collision, Robust Control, Optimal Control

1. Introduction

Quantum control is concerned with the active manipulation of physical and chemical processes on an atomic and molecular scale, aiming to design external fields to achieve efficient transfer between states of quantum systems. Optimal

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control theory (OCT) is regarded as a practical way of identifying control fields capable of driving atoms or molecules to desired states in simulations [1, 2, 3]. Many monotonic algorithms [4, 5, 6, 7, 8, 9, 10, 11] have been utilized in quantum OCT applications, including population and coherence control of three-level Λ -systems [12], phase control of a vibrational state qubit [13], photofragmentation dynamics [14], photoassociation [15], stabilization of ultracold molecules [16, 17], conversion of atoms into a molecular Bose-Einstein condensate [18], control of isomerization [19, 20, 21] and control of charge transfer [22, 23]. Most existing results considering quantum OCT applications assume that there are no uncertainties in the system dynamics. However, for most realistic quantum systems the yield of the target state can be significantly reduced due to unavoidable uncertainties such as control noise or environmental disturbances. It is desirable to design robust fields for these systems.

Robust control for quantum systems has been viewed as a key issue in developing practical quantum technologies [24]. Several methods have been proposed for the robust control for quantum systems, such as H^∞ control for linear quantum stochastic systems [25], sliding mode control for two-level quantum systems [26, 27, 28] and risk-sensitive control for sampled-data feedback systems [29]. Several results have also been presented which focus on the robust control of simplified systems with one or several model parameters [30, 31, 32]. This paper aims to investigate the robust control of molecular dynamics for the photoassociation of O+H as an example by employing the sampling-based method [31, 33, 34]. In this method, several samples are obtained according to the uncertainties of the molecular parameters and a generalized system is constructed by using these collective samples. Then, an OCT algorithm will be implemented to obtain a robust field achieving good performance.

Photoassociation has captured the attention of researchers due to its fundamental importance in the laser control of chemical reactions [35] and its wide application in forming ultracold molecules [36, 37, 38, 39, 40]. The basic case consists of two colliding atoms interacting with an applied field to create a molecule [41, 42]. The present work considers photoassociation in the presence

of infrared radiation to produce the heteronuclear OH diatomic molecules directly in the electronic ground state with a single electronic state involved [15]. This process is driven by a laser interacting with the colliding atoms via the permanent dipole moment associated with the collision. Optimal laser control of molecular photoassociation along with vibrational levels has been investigated previously using the Morse potential as the interatomic potential [15]. In this work, we use this model to examine the feasibility of employing an optimally shaped laser pulse to collisionally associate O and H to the ground vibrational state as well as considering uncertainties in the depth of the Morse potential and the laser amplitude. This scheme is realized by using multiple samples in the optimal control simulations. For the OCT calculation, we adopt the recently developed fast-kick-off algorithm [11] based on the two-point boundary-value quantum control paradigm (TBQCP) method [9, 10, 11]. Moreover, we impose a constraint on the control algorithm to ensure that the area of the optimal laser field converges to zero, and it can be readily generated physically [43].

The remainder of the paper is organized as follows. In Section 2, we present a theoretical model for the sampling-based method associated with uncertainties for the control of the photoassociation of OH in the presence of a laser field. The TBQCP optimal control algorithm is presented in Section 3. Detailed numerical results are presented in Section 4 and conclusions are drawn in Section 5. Atomic units (a.u.) are used throughout the paper.

2. System Model

Figure 1 presents a schematic of the photoassociation $O+H \rightarrow OH$ in the electronic state. The arrow (purple) pointing to the left refers to the incoming wave packet representing two free atoms. We aim to find a robust control field driving the photoassociation efficiently even when uncertainties exist in the system. The robust control field is obtained by a sampling-based design approach, [31, 33] where samples obtained by discretizing the uncertain parameters are

Figure 1: The photoassociation scenario for an O+H system.

used to design the field. In this paper, we discretize the uncertain parameters into N samples, where N is a finite integer, and we use $j \in [1, \dots, N]$ to identify the index of the samples. The dynamics can be expressed in terms of a one-dimensional nuclear wave packet whose evolution is governed by the time-dependent equation

$$i\hbar \frac{\partial}{\partial t} \psi(R, t) = \hat{H} \psi(R, t), \quad (1)$$

where the angular momentum is not considered. Here, R denotes the internuclear distance between oxygen and hydrogen, $\hat{H} = \text{Diag}[\hat{H}_1, \dots, \hat{H}_N]$ denotes the Hamiltonian of N samples with $\hat{H}_j$ the Hamiltonian of the j th sample, and $\psi(R, t) = [\psi_1(R, t), \dots, \psi_N(R, t)]^T$ with $\psi_j(R, t)$ as the nuclear wave packet of the j th sample. The Hamiltonian matrix of each sample is given by

$$\hat{H}_j = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + \hat{V}_j(R) - \mu_j(R) \epsilon(t), j = 1, \dots, N, \quad (2)$$

where m is the reduced mass of the OH system, $\epsilon(t)$ is the time-dependent laser pulse which is assumed to be linearly polarized along the molecular axis, and $\hat{V}_j(R)$ and $\mu_j(R)$ are the potential energy and permanent dipole moment of the j th sample, respectively. In this paper, we consider uncertainties in the potential curve and uncertainties in the laser amplitude. It is worth mentioning that our approach, in principle, can also be applied to the case of three-dimensional nuclear wave packet dynamics, with much more expensive computational resource.

2.1. Robust control with uncertainties in the potential curve

The goal of this scheme is to find a robust field to obtain a desired photoassociation yield when uncertainties are present in the potential curves. The potential energy $\hat{V}_j(R)$ is chosen to be a Morse function, and we consider absolute uncertainties in the well depth $D_e \in [D_e^0 - \Delta, D_e^0 + \Delta]$ with a reference well depth $D_e^0 = 43763 \text{ cm}^{-1}$ and a maximum uncertainty Δ . This uncertainty may be caused by imprecise experimental measurement or theoretical calculation. Therefore, the potential curve for each sample is

$$\hat{V}_j(R) = \frac{D_e^j}{D_e^0} \hat{V}_0(R), j = 1, \dots, N, \quad (3)$$

where $D_e^j = D_e^0 - \Delta + 2(j-1)\Delta/(N-1)$ for $N > 2$ and $D_e^j = D_e^0$ for $N = 1$. The reference potential is

$$\hat{V}_0(R) = D_e^0 [e^{-2\beta(R-R_e)} - 2e^{-\beta(R-R_e)}], \quad (4)$$

where R_e is the equilibrium position, and β is a parameter which determines the potential range. Here we only take into account the uncertainties of the potential curves. Thus, the dipole moment of each sample $\mu_j(R) = \mu(R)$ for $j = 1, \dots, N$. We let

$$\mu(R) = qR_e^{-R/R_d}, \quad (5)$$

where q denotes the effective charge, and R_d denotes the range of the dipole interaction.

2.2. Robust control with uncertainties in the laser amplitude

In the second control scheme, we only consider uncertainties in the laser amplitude, which may be caused when the laser is generated. Here, we aim to obtain a reference optimal field $\epsilon(t)$ so that $\zeta\epsilon(t)$ will achieve a desired photoassociation yield. Here $\zeta \in [1.0 - \delta, 1.0 + \delta]$ is a parameter which determines the size of the uncertainty in the laser amplitude with $0 < \delta < 1$. The Hamiltonian for each sample can be written as

$$\hat{H}_j = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + \hat{V}_0(R) - \zeta_j \mu(R) \epsilon(t), j = 1, \dots, N, \quad (6)$$

95 where for $N > 1$,

$$\zeta_j = 1 - \delta + 2(j-1)\delta/(N-1), j = 1, \dots, N, \quad (7)$$

and $N = 1$ for $\zeta_1 = 1$.

2.3. Robust control with two classes of uncertainties

When we consider the above two classes of uncertainties together, we may select $N = N_1 N_2$ samples by discretizing Δ and ζ into N_1 and N_2 points, 100 respectively. Hence, the Hamiltonian for each sample becomes

$$\begin{aligned} \hat{H}_j &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + \hat{V}_i(R) - \zeta_k \mu(R) \epsilon(t), \\ j &= (i-1)N_1 + k, i = 1, \dots, N_1, k = 1, \dots, N_2. \end{aligned} \quad (8)$$

We use these samples corresponding to each case by employing the control algorithm in Section 3 to obtain the robust field. The initial state of each sample for all the three cases described above is the same and taken to be a Gaussian wave packet

$$\Phi_j^i(R) = \left(\frac{2}{\pi\sigma_0}\right)^{1/4} \exp\left[-ik_0 R - \left(\frac{R-R_0}{\sigma_0}\right)^2\right], j = 1, \dots, N, \quad (9)$$

where σ_0 denotes the width, R_0 the central position, and k_0 the momentum. The collision energy E_c associated with this incoming Gaussian wave packet is

$$E_c = (k_0^2 + 1/\sigma_0^2)/2m. \quad (10)$$

The wave packets are discretized with 5120 grid points extending to 150 a_0 in order to prevent the wave packet from reflecting off the boundary. The eigenvalues and eigenvectors of the bound states for the $1s\sigma$ potential are calculated 105 using the Fourier-Grid-Hamiltonian (FGH) method [44], and we also use the same spatial discretization for the time-dependent calculations. Equation (1) is solved using the second-order split-operator method [45, 46, 47]. The time step size is chosen as 0.01 fs to ensure the accuracy of the solution.

3. Control Algorithm

Consider the photoassociation of N samples from an initial state $\Phi^i(R) = [\Phi_1^i(R), \dots, \Phi_N^i(R)]$ to be driven to a target state $\Phi^f(R) = [\Phi_1^f(R), \dots, \Phi_N^f(R)]$ at some final time $T > 0$, where $\Phi_j^f(R)$ is the target state of the j th sample. In this paper, $\Phi_j^f(R)$ is chosen as the ground vibrational state of the j th sample. We aim to find a control field to maximize the average photoassociation probability over the selected samples

$$K[T] = \frac{\sum_{j=1}^N |\langle \Phi_j^f(R) | \psi_j(T) \rangle|^2}{N}. \quad (11)$$

The control field $\epsilon(t)$ can be efficiently optimized iteratively based on a recently formulated monotonically convergent fast-kick-off TBQCP algorithm [11] with a zero-area constraint [43], and it is updated using the following recurrence relation

$$\epsilon^{[l]}(t) = \epsilon^{[l-1]}(t) + \eta S(t) [f_\mu^{[l]}(t) - \theta A_{l-1}], l = 1, 2, \dots \quad (12)$$

where $\eta > 0$ is the step size for updating the field, $\epsilon^{[l]}(t)$ is the field of the l th iteration, the index $l = 0$ corresponds to the trial field, $S(t)$ is the shape function which is chosen to be the envelope of the trial field to enforce a smooth switch on and off in the control pulse, and θA_l ensures that the area of the updated pulse converges to zero. Here $A_l = \int_0^T \epsilon^{[l]}(t) dt$ is the area of $\epsilon^{[l]}(t)$ and $\theta > 0$ (we choose $\theta = 10^{-5}$ throughout the paper). Since there is no coupling between different samples, $f_\mu^{[l]}(t)$ can be written as

$$f_\mu^{[l]}(t) = -\frac{2}{\hbar} \frac{\sum_{j=1}^N \mathcal{I} \langle \psi_j^{[l]}(t) | \chi_j^{[l-1]}(t) \rangle \langle \chi_k^{[l-1]}(t) | \mu | \psi_k^{[l]}(t) \rangle}{|\sum_{j=1}^N \langle \psi_j^{[l]}(t) | \chi_j^{[l-1]}(t) \rangle|^\alpha}, l = 1, 2, \dots, \quad (13)$$

110 where $0 \leq \alpha \leq 1$, with a faster kick-off rate at the larger value of α and the fastest one for $\alpha = 1$. Here $\chi_j^{[l-1]}(R, t)$ is the auxiliary wave function of the j th sample, which is solved by Eq. (1) in the presence of the control field $\epsilon^{[l-1]}(t)$, satisfying the terminal condition $\chi_j^{[l-1]}(R, T) = \Phi_j^f(R)$. The climbing rate depends on the control parameters η and α . We remark that in principle the
115 iteration step parameter η in Eq. (12) may assume any value, but in practice

Figure 2: (a) Windowed-Fourier transform of the laser pulse using one sample with $D_e = D_e^0$ (the colors indicate the intensity of spectrum in arbitrary units). (b) Photoassociation probabilities versus deviation from D_e^0 under the action of the optimal laser pulse in (a).

it needs to be a sufficiently small number to achieve monotonic convergence (stability) [4, 5, 6, 7, 8, 9, 10, 11]. The recurrence relation Eq. (12) will guarantee that the photoassociation probability increases from iteration to iteration.

120 4. Results and Discussions

In the calculations, the parameters of the potential curve and dipole moment are taken from Ref. [15], and we choose $R_0 = 13.4$ a.u., $\sigma_0 = 5.12$ a.u. and $E_c = 0.025$ eV (201.7 cm $^{-1}$) for the initial scattering state. The target state is chosen as the lowest vibrational state associated with each sample potential. The calculations are performed over the time interval $[-900, 900]$ fs. The initial trial field $\epsilon^{[0]}(t)$ is chosen to have a cosine square envelope shape with chirped frequency

$$\epsilon^{[0]}(t) = \epsilon_0^{[0]} \cos^2[\pi(t - t_0)/\tau] \cos[\omega_0(t - t_0) + \gamma(t - t_0)^2], \quad (14)$$

where $\epsilon_0^{[0]} = 265.0$ MV/cm ($\approx 5.15 \times 10^{-2}$ a.u.) is the peak amplitude, $\tau = 1770$ fs is the duration of the pulse, $\omega_0 = 2543$ cm $^{-1}$ ($\approx 1.16 \times 10^{-2}$ a.u.) is the carrier frequency, $t_0 = 0$ fs denotes the time corresponding to the peak amplitude, and $\gamma = 2.71 \times 10^{-7}$ a.u. is the chirp rate. The specific values we choose for ω_0 and γ can make the temporal laser frequency cover the transition frequency 423 cm $^{-1}$ between the initial scattering state and $v = 20$ at earlier time, and gradually cover the increasing eigenenergy differences of two neighboring vibrational levels from higher to lower levels, and eventually transfer the population to the lowest vibrational state.

First, we calculate the optimal laser pulses using only one sample ($D_e = D_e^0$). The step size η of the optimal control algorithm is set as 11.0. In order to demonstrate the optimal field in both the time and frequency domains, we introduce a windowed-fourier transform [48, 49]

$$W(\omega, t) = \left| \int_{-\infty}^{\infty} d\tau_w H(\tau_w - t, T_w) E(\tau) e^{i\omega\tau_w} \right|^2, \quad (15)$$

where t and ω denote the time and frequency, respectively, and the Blackman window function $H(\tau_w - t, T_w)$ is

$$H(\tau_w, T_w) = \begin{cases} 0.42 + 0.50 \cos(\frac{2\pi}{T_w} \tau_w) + 0.08 \cos(\frac{4\pi}{T_w} \tau_w), & |\tau_w| \leq T_w/2 \\ 0, & |\tau_w| \geq T_w/2 \end{cases} \quad (16)$$

with $T_w = 1800$ fs being the temporal resolution. Figure 2 (a) demonstrates the windowed-fourier transform $W(\omega, t)$ of the optimal laser pulse, achieving a photoassociation probability of 0.995 after 1426 iterations. The strongest two peaks appear at $\omega \approx 4700$ cm $^{-1}$ and 5800 cm $^{-1}$ at early time, and a chirp attribute is also apparent. The spectra lower than 4000 cm $^{-1}$ of both two laser pulses cover all the energy differences between two neighboring vibrational levels. We use the laser pulse in Fig. 2(a) to test 200 samples obtained by uniformly sampling with the maximum uncertainty $\Delta = 100$ cm $^{-1}$. The photoassociation probabilities versus deviation $\delta_{D_e} = D_e - D_e^0$ from D_e^0 are shown in Fig. 2(b) by the black solid line. The photoassociation probability goes down to 0.830 at $\delta_{D_e} = -100$ cm $^{-1}$ and 0.850 at $\delta_{D_e} = 100$ cm $^{-1}$, showing the necessity of considering its

robustness. We use this pulse as the trial pulse in the following calculations.

4.1. Numerical results for robust control with uncertainties in the potential curve

150 In the calculations, we stop the iterations once the increase of $K[T]$ at each iteration is no more than 10^{-5} in 100 consecutive iterations. We select $N = 11$ samples with $\Delta = 100 \text{ cm}^{-1}$ and $\eta = 1.0$ to maximize $K[T]$ in Eq. (11). We achieve $K[T] = 0.985$ after almost 50000 iterations. To have a better understanding of spectral distributions of the robust pulse, we demonstrate the

155 average populations of the vibrational levels relevant to a higher frequency distribution over the eleven samples in Fig. 3(d). Note that the uncertainties of the potential curve gives rise to the shift of the eigenvalues of the vibrational states, therefore, we use average values to match the transitions among the vibrational states. The Windowed-Fourier transform $W(\omega, t)$ of the corresponding laser

160 pulse is demonstrated in Fig. 3(a). The stronger distribution in the frequency domain is significantly shifted to a higher region, compared with that in Fig. 2 (a), and the strongest peak appears at $\omega = 9400 \text{ cm}^{-1}$ at the beginning of the pulse which corresponds to the transition between $v = 19$ and $v = 11$ with the average transition frequency 9425 cm^{-1} . Another two peaks appear in the

165 vicinity of $\omega \approx 7500 \text{ cm}^{-1}$ and 8800 cm^{-1} , which correspond to the transitions lying between $v = 19$ and $v = 12$ with the average transition frequency 7617 cm^{-1} and between $v = 18$ and $v = 11$ with the average transition frequency 8876 cm^{-1} . The relevant time-dependent populations can be seen in Fig. 3(d). It appears that there are more frequent oscillations, because the pulse duration

170 is squeezed into a smaller range. Therefore, we present the temporal population of $v = 11$ from -250 fs to -200 fs, showing the smooth population change versus time. We also demonstrate Windowed-Fourier transform of the lower frequency distribution of this pulse which covers the eigenenergy differences between all the two neighboring vibrational levels. Compared with its higher frequency

175 counterpart, it is much weaker. We calculate the photoassociation probabilities of the same 200 samples used in Fig. 2(c) to examine the robustness of the

control fields in Fig. 3(b) (represented by the black solid line). The values are distributed from 0.969 at $\delta_{D_e} \approx \mp 100 \text{ cm}^{-1}$ to 0.991 at $\delta_{D_e} \approx -10 \text{ cm}^{-1}$ with an average value of 0.986. For comparison, the photoassociation probabilities
180 versus δ_{D_e} achieved by the laser pulse in Fig. 2(b) are drawn with the red dashed line, most of which are lower than those achieved by the robust field.

4.2. Numerical results for robust control with uncertainties in the laser amplitude

We also demonstrate Windowed-Fourier transforms $W(\omega, t)$ of the robust
185 control pulses when uncertainties in the laser amplitude are taken into account by selecting $N = 11$ samples in Fig. 4(a) and (b). The optimal algorithm parameters are set at $\delta = 0.1$ and $\eta = 1.0$, and we choose the same trial field as in Fig. 2(a). Similarly, we demonstrate the average populations of the vibrational
190 levels relevant with the higher frequency distribution over the eleven samples in Fig. 4(d). For the spectrum with higher frequency components in Fig. 4(a), the strongest spectral peak is at $\omega \approx 8150 \text{ cm}^{-1}$, matching the transition between $v = 17$ and $v = 11$ with the transition frequency 8148 cm^{-1} . Another two major peaks at $\omega \approx 6700 \text{ cm}^{-1}$ and 7500 cm^{-1} which may correspond to the transition
195 between scattering state and $v = 13$ with the transition frequency 6778.6 cm^{-1} and the transition between $v = 19$ and $v = 12$ with the transition frequency 7617.9 cm^{-1} . The lower frequency component are shown in Fig. 4(b), which is also much weaker than its higher counterpart. This part of frequency spectrum covers the transitions between two neighbouring vibrational levels. Figure 4
200 (c) depicts the photoassociation probabilities of 200 samples versus ζ under the action of the trial field in Fig. 2(a) (red dashed line) and the robust fields in Fig. 4(a) and (b) (black solid line). With the trial field, the photoassociation probability goes down as ζ increases or decreases from $\zeta = 1.0$. The value drops to only 0.025 at $\zeta = 0.9$ and 0.270 at $\zeta = 1.1$ with an average value of 0.530 over
205 these 200 samples. However, when the robust control field is implemented, the average photoassociation probability goes up to 0.980. Even at the boundaries

Figure 3: (a) Windowed-Fourier transform of higher frequency distributions of the laser pulse using eleven samples corresponding to Eq. (3). (b) Windowed-Fourier transform of lower frequency distributions of the laser pulse using eleven samples corresponding to Eq. (3) (the colors indicate the intensity of the spectrum in arbitrary units in (a) and (b)). (c) Photoassociation probabilities versus the deviation from D_e^0 under the action of the robust laser pulse in (a) and (b) (black solid line), and the laser pulse in Fig. 2(b) (red dashed line), respectively. (d) The average populations of the vibrational levels relevant with the higher frequency distributions over the eleven samples.

of $\zeta = 0.9$ and 1.1 , the photoassociation probabilities reach 0.958 and 0.963 , respectively. The values of the testing points are much higher than most of those achieved by the trial field, showing an apparent advantage of a robust design.

Figure 4: (a) Windowed-Fourier transform of the laser pulse using eleven samples corresponding to Eq. (7). (b) Windowed-Fourier transform of lower frequency distributions of the laser pulse using eleven samples corresponding to Eq. (7) (the colors indicate the intensity of the spectrum in arbitrary units in (a) and (b)). (c) Photoassociation probabilities versus the uncertainties in the laser amplitude under the action of the optimal laser pulse in (a) and (b) (black solid line) and in Fig. 2(b) (red dashed line), respectively. (d) The average populations of the vibrational levels relevant with the higher frequency distributions over the eleven samples.

4.3. Numerical results for robust control with two classes of uncertainties

We start with the trail field in Fig. 2(a) and construct a robust field with the two classes of uncertainties together (Eq. (8)) using $\Delta = 50 \text{ cm}^{-1}$, $\delta = 0.05$ and $N_1 = N_2 = 5$. Figure 5(a) demonstrates the Windowed-Fourier transform

Figure 5: (a) Windowed-Fourier transform of the laser pulse using twenty five samples ($\Delta = 50 \text{ cm}^{-1}$, $\delta = 0.05$, $N_1 = N_2 = 5$). (b) Photoassociation probabilities versus the two classes of uncertainties under the action of the optimal laser pulse in (a). (c) The average populations of the vibrational levels relevant with the higher frequency distributions over the twenty five samples.

215 of this field, driving $K[T] = 0.947$, and the time-dependent populations of some relevant states are plotted in Fig. 5(c). In Fig. 5(a), the higher frequency components of this spectrum cover the transitions between the scattering state and vibrational states or between different vibrational states, whose lower counterparts are mainly responsible for the transitions between two adjacent vibra-
 220 tional states. The strongest appears at around $\omega = 8500 \text{ cm}^{-1}$ matching the transition between the scattering state and $v = 12$ with the average transition frequency 8405 cm^{-1} , and another peak at $\omega \approx 6000 \text{ cm}^{-1}$ may correspond to the transition between $v = 19$ and $v = 13$ with the average transition frequency 5990.2 cm^{-1} . In Fig. 5(b), we evenly select 2601 samples for $\Delta = 50 \text{ cm}^{-1}$
 225 and $\delta = 0.05$ to test the photoassociation probabilities. The probabilities also

decrease with the deviations increasing from $D_e = 0$ and $\zeta = 1$. The highest probability 0.975 appears at $\delta_{D_e} = 0$ and $\zeta = 1.014$, and the lowest point occurs at $\delta_{D_e} = 50 \text{ cm}^{-1}$ and $\zeta = 0.950$. The average probability is 0.958, showing enhanced robustness for smaller uncertainties.

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5. Conclusion

We presented a systematic methodology for robust control of photoassociation of slow O+H collision. Specifically, we used a sampling-based control scheme to obtain robust laser pulses to achieve a desired photoassociation probability in the presence of uncertainties in potential curves and laser amplitudes. The optimal control calculations are performed using a time-dependent wave packet method based on a single electronic state model. The control fields produced excellent outcomes for molecular systems with uncertainties. With uncertainty in the potential curve taken into account, the robust control field achieves an average photoassociation probability of 0.986 over the tested samples, in comparison with 0.954 achieved by the optimal field without considering any uncertainties. When uncertainty in the laser amplitude is considered, an average photoassociation probability of 0.980 over the tested samples is achieved by the robust control field in contrast with only 0.520 achieved by the optimal field with only one sample. When we extend our scheme to simultaneously include the two classes of uncertainties, the robustness decreases a little, but still shows the validity of sampling-based robust control. The robust control design method employed in this paper is also applicable to the control of other molecular dynamics with various distributions of uncertain parameters.

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