An alternative laser driven photodissociation mechanism of pyrrole via $^1\pi\sigma^*/S_0$ conical intersection

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A first principles quantum dynamics study of N–H photodissociation of pyrrole on the $S_0 - ^1\pi\sigma^* (^1A_2)$ coupled electronic states is carried out with the aid of an optimally designed UV-laser pulse. A new photodissociation path, as compared to the conventional barrier crossing on the $^1\pi\sigma^*$ state, opens up upon electronic transitions under the influence of pump-dump laser pulses, which efficiently populate both the dissociation channels. The interplay of electronic transitions due both to vibronic coupling and the laser pulse is observed in the control mechanism and discussed in detail. The proposed control mechanism seems to be robust, and not discussed in the literature so far, and is expected to trigger future experiments on the $^1\pi\sigma^*$ photochemistry of molecules of chemical and biological importance. The design of the optimal pulses and their application to enhance the overall dissociation probability is carried out within the framework of optimal control theory. The quantum dynamics of the system in the presence of pulse is treated by solving the time-dependent Schrödinger equation in the semi-classical dipole approximation. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4984775>]

I. INTRODUCTION

Pyrrole is one of the important chromophores of many biologically active organic molecules. Therefore, the photo-physics¹ and photochemistry^{2–17} of pyrrole are of fundamental interest to understand the ultrafast excited state dynamics. In this regard, studies related to its photodissociation dynamics from both experimental and theoretical fronts have received considerable attention. The photodissociation (more specifically N–H dissociation) dynamics of pyrrole is proven to be mediated predominantly via its optically dark repulsive $^1\pi\sigma^* (^1A_2)$ electronic excited state. The latter undergoes symmetry allowed crossings with excited optically bright $^1\pi\pi^*$ states as well as the electronic ground S_0 state.³ In addition, there exists a second excited $^1\pi\sigma^*$ state of 1B_1 symmetry. This state crosses both the $^1\pi\sigma^* (^1A_2)$ and S_0 states at high energies. It was demonstrated that only a minor ($\lesssim 6\%$) population transfer occurs to the second $^1\pi\sigma^*$ state when the dynamics is initiated on the first $^1\pi\sigma^*$ state.¹⁰ The participation of the $^1\pi\sigma^* (^1A_2)$ state of pyrrole in the photo-induced dynamics is evidenced by the formation of H atoms in the experiments carried out with 250 nm, 238 nm, 243.1 nm, and 242–217 nm UV-radiations.^{2,4,12,16} It was concluded from a large kinetic isotope effect that quantum tunneling plays the primary role in the photodissociation dynamics at 250 nm excitation.¹¹ The photodissociation dynamics of the initially prepared $^1\pi\sigma^* (^1A_2)$ state and the role of the vibrationally hot initial state on the branching ratio of dissociation product was theoretically examined in the recent past.⁷ It was

found that the vibrationally hot initial state opens up both $^1\pi\sigma^*$ and S_0 dissociation channels by allowing the wave packet (WP) to cross over the barrier present in the vicinity of the Franck-Condon (FC) region on the $^1\pi\sigma^*$ state [cf. Fig. 1(a)].

The photodynamics of pyrrole under field free conditions as mentioned above has been studied using a two-state two-mode model.⁷ A vibronic coupling scheme was developed to model $^1\pi\sigma^* (^1A_2)/S_0$ conical intersection (CI) with high level *ab initio* electronic structure calculations. Diabatic electronic states and electronic coupling potentials were analytically represented with the aid of *ab initio* electronic structure data. Two main coordinates designated as r (tuning coordinate, the distance of the H atom attached to N from the center-of-mass of the rest of the pyrrole ring) and Q_{11} (coupling coordinate, the normal coordinate of screwing deformation of H atoms) were considered to develop an electronic diabatic Hamiltonian.⁷ It is noteworthy that these two coordinates capture most of the essential photodynamical features of this molecule as proven in a previous study.⁸

In the field free case, a vibrationally excited packet was found to dissociate into both the product asymptotes, yielding a branching ratio.⁷ However, when the WP corresponding to the ground vibrational level of the S_0 state is launched on the $^1\pi\sigma^* (^1A_2)$ state, no branching ratio was found. In this case, the dynamics was found to be slow and dissociation was reported to occur via tunneling of the WP through the barrier of height, ~ 0.40 eV, on the $^1\pi\sigma^* (^1A_2)$ state. In this situation, the upper adiabatic dissociation channel was found to remain essentially closed.^{7,11} A direct transition from the S_0 state to the $^1\pi\sigma^* (^1A_2)$ state of pyrrole is understandably

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FIG. 1. (a) The diabatic potential energies of S_0 and 1A_2 ($\pi\sigma^*$) states of pyrrole along r (defined in the text). The location of CI and the analysis line of the dissociative WP flux are shown by an encircled cross mark and a dashed line, respectively. (b) The $|0,0\rangle$ initial WP used in the calculations is plotted in the $(r-Q_{11})$ plane.

optically forbidden in the first order. However, recent experiments carried out with 250 and 238 nm radiations directly probed the $^1\pi\sigma^*$ state and the interplay between barrier tunneling and barrier crossing dynamics was discussed.¹¹ Theoretically, the $^1\pi\sigma^*$ mixes with the optically allowed states and therefore the transition is justified and verified experimentally. The transition dipole moment (TDM) in the present work is assumed to have a certain arbitrary value so that a pulse of moderately high intensity and sufficiently longer duration can, in fact, induce transition in the dipole forbidden situation. Also, in the recent past, multi-state and multi-mode dynamics of pyrrole has been extensively studied in field free conditions.^{10,15}

In this effort we devised an alternative mechanistic route to control the dissociation dynamics by constructing an optimally controlled laser pulse (of ~ 2.2 ps time duration). The latter transfers the WP back and forth between the S_0 and $^1\pi\sigma^*$ states after its initial excitation to the $^1\pi\sigma^*$ state. In doing so, the pulse makes use of electronic transitions due to nonadiabatic effects of CI in a cooperative manner. The pulse is optimized subsequently leading to an optimal shape of the pulse to achieve the desired goal. Such an optimal pulse is shown to efficiently control the product branching ratio. Although the previous quantum control studies on photodissociation exist in this regard, their focus is limited to

controlling the dynamics associated with excited surfaces with no barriers.¹⁸ Here we explicitly consider controlling the photochemistry of the $^1\pi\sigma^*$ (1A_2) state that solely arises out of its repulsive character after the barrier. Thus our control studies may be useful in the case of excited state proton transfer/abstraction with barriers, which is often the case in large molecules.

In the following we present a control mechanism by designing optimal laser pulse(s) which efficiently transforms the slow tunneling dynamics into fast dynamics and monitors the passage of the WP through CI and gives rise to a branching ratio of photoproducts. The well known optimal control theory (OCT)^{19,20} combined with vibronic coupling theory and time-dependent wave packet propagation (TDWP) method is utilized to accomplish the task.

II. THEORY

A. Quantum dynamics and OCT

In this study, we employ the 2×2 diabatic electronic Hamiltonian (*vide supra*) including a laser-molecule interaction term (in the dipole approximation) in the off-diagonal diabatic $S_0/^1\pi\sigma^*$ (1A_2) electronic coupling. The nuclear dynamics on coupled states is studied by solving the time-dependent Schrödinger equation (TDSE),

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} |\psi_e\rangle \\ |\psi_g\rangle \end{pmatrix} = \begin{pmatrix} \hat{H}_e & \hat{V}_{ge} \\ \hat{V}_{ge}^* & \hat{H}_g \end{pmatrix} \begin{pmatrix} |\psi_e\rangle \\ |\psi_g\rangle \end{pmatrix}. \quad (1)$$

In the above equation, the suffixes e and g refer to the $^1\pi\sigma^*$ and S_0 electronic states of pyrrole, and $|\psi_e\rangle$ and $|\psi_g\rangle$, respectively, are the corresponding state vectors. The operator $\hat{H}_{g/e}$ reads

$$\hat{H}_{g/e} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} - \frac{1}{2} \omega_{11} \frac{\partial^2}{\partial Q_{11}^2} + \hat{V}_{g/e} \quad (2)$$

where $\mu = \frac{m_H m_p}{m_H + m_p}$ is the reduced mass along r (m_H and m_p denote the masses of hydrogen and the rest of the pyrrole ring, respectively) and $\omega_{11} = 664 \text{ cm}^{-1}$ is the frequency of the coupling vibrational mode Q_{11} . The operator $\hat{V}_{ge} = \hat{\mu}_{ge} \cdot \epsilon(t) + \hat{V}_{dc}$, represents the interaction of the matter and radiation field (first term on the RHS of $\hat{V}_{ge}$) and the diabatic coupling between states (second term on the RHS of $\hat{V}_{ge}$) through Q_{11} . We note that the TDM is treated as a constant in the present application in accordance with the applicability of Condon approximation in a diabatic electronic basis. Moreover, the TDM value is taken as the equilibrium dipole moment value of pyrrole (~ 1 a.u.) and is kept fixed throughout r as there exists non-vanishing TDM both in the FC region and dissociation limit. The TDSE [Eq. (1)] is solved within a semi-classical dipole approximation^{21,22} on a two dimensional grid with $3.0 \leq r \leq 15.07$ a.u. and $-15.0 \leq Q_{11} \leq 15.0$ (in dimensionless units). Numerically, the Fourier transformation method is used to evaluate the action of kinetic energy operators of the Hamiltonian on the wavefunction, and the time propagation is carried out by a second order split-operator method^{23,24} adopted to coupled electronic states.^{25,26} The propagation is carried out for a total time of ~ 2169 fs. The initial wavefunction, the vibrational eigenstate of the S_0 state, is calculated by the Fourier Grid Hamiltonian method.^{27,28} Hereafter, the

vibrational eigenstates of the S_0 state of pyrrole are designated as $|n_r, n_{Q_{11}}\rangle$, indicating the number of nodes along r and Q_{11} coordinates.

In the mathematical framework of OCT, a field dependent functional is constructed and optimized to test the performance of the laser pulse in achieving the desired objective. For the dissociation process, the objective is given in terms of maximizing the time-integrated outgoing flux of the WP across an asymptotic surface at $r = r_d$, by designing an optimal field subject to the constraints on the fluence of the field and system dynamics.

After the initial excitation of a $|n_r, n_{Q_{11}}\rangle$ wavefunction of the S_0 state to the $^1\pi\sigma^*$ state, the cost functional for the N–H dissociation process is defined by

$$J[\epsilon(t)] = \int_0^T \frac{\hbar}{\mu} \text{Im} \left[\Psi^*(r, t) \frac{\partial}{\partial r} \Psi(r, t) \right]_{r=r_d} dt - \alpha_0 \int_0^T [\epsilon(t)]^2 dt. \quad (3)$$

The first term in the RHS of the above equation is the total dissociation probability (the time integrated flux of the WP reaching the dissociation asymptotes), which serves as an objective in J . The dissociative flux is calculated along an analysis line at the asymptotes at $r_d = 11.976$ a.u., as shown in Fig. 1(a). Afterwards a sine type of damping function²⁹ is activated at $r = 13.5$ a.u., to absorb the WP in order to prevent its reflection and wraparounds at the grid boundaries. The second term in the RHS [in Eq. (3)] is the penalty constraint to lower the fluence of the pulse with an electric field component $\epsilon(t)$ to avoid the undesirable physical processes (e.g., ionization) caused by high field strengths. The quantity α_0 is a penalty factor. The aim is to optimize (maximize) this field-dependent functional $J[\epsilon(t)]$ using genetic algorithm (GA, in particular micro-GA) based optimization methods,^{30–33} to arrive at the desired goal to validate the dissociation mechanism proposed.

We note that throughout the text we follow the nomenclature suggested in Fig. 1(a) for the electronic states and dissociation limits. In this figure, the curves with same color coding represents diabatic and the curves with different color coding represent adiabatic electronic states. Therefore, the lower (S_0) curve (black) connected with the red one beyond CI represents the ground (lower) adiabatic state and the upper ($^1\pi\sigma^*$) curve (red) connected with the black one beyond the CI represents the excited (upper) adiabatic state. Therefore in this definition the black and red curves beyond the CI represent the upper and lower adiabatic dissociation channels.

In order to follow the action of the laser pulse and hence interpret the associated control mechanism, analysis of the laser driven population dynamics is carried out. In this regard, more insights can also be obtained by examining adiabatic ($P_i^a(t) = \langle \Psi(t) | \psi_i^a \rangle \langle \psi_i^a | \Psi(t) \rangle$, $i = e$ or g) and diabatic ($P_i^d(t) = \langle \Psi(t) | \psi_i^d \rangle \langle \psi_i^d | \Psi(t) \rangle$, $i = e$ or g) electronic populations. Adiabatic and diabatic electronic population probabilities are defined as expectation values of the respective projection operators constructed using ground and excited WP components.³⁴ Numerical calculation of adiabatic populations is done using adiabatic projectors constructed in a diabatic basis as suggested in Refs. 35 and 36.

B. Laser field parameterization in GA

The guess field in the GA is taken as

$$\epsilon_{ga}(t) = \epsilon \sin(\omega t) \cdot s(t), \quad (4)$$

where ϵ is the amplitude of the laser field of frequency ω . This amplitude is varied from 0 to 0.03 a.u. and the frequency is varied from 4173 cm^{-1} to 15 146 cm^{-1} (range of 0.05 a.u.) to optimize the cost functional. The envelop function, $s(t)$, ensures smooth switch on and off of the pulse at the start and end of time, respectively. It is characterized by four positive time parameters t_0 , t_1 , t_2 , and t_3 , where $t_0 < t_1 \leq t_2 < t_3$,

$$s(t) = \begin{cases} \sin^2 \left[\frac{\pi}{2} \left(\frac{t - t_0}{t_1 - t_0} \right) \right] & \text{for } t_0 \leq t \leq t_1, \\ 1 & \text{for } t_1 \leq t \leq t_2, \\ \sin^2 \left[\frac{\pi}{2} \left(\frac{t_3 - t}{t_3 - t_2} \right) \right] & \text{for } t_2 \leq t \leq t_3 = T. \end{cases} \quad (5)$$

Usually, t_0 is set to 0, and t_3 to T . The time period t_0 to t_1 is the rise time of the pulse, t_2 to t_3 is the switch off period and the intermediate section, and the envelope from t_1 to t_2 takes the value of unity giving rise to a plateau. A total time duration of 90 000 a.u. (~ 2169 fs) is considered, and a penalty factor α_0 value of 0.001 a.u. is considered here. Using the GA, different possible combinations of the amplitude (ϵ), two time parameters (t_1 and t_2), and frequency (ω) are searched. The aim is to find the best possible combination of these four parameters among all possible permutations. A combination of these four parameters that define an electric field is termed as an “individual” in the GA. In order to find the best possible solution, we consider here 10 such individuals (population size) from randomly selected parameters in the parameter space. Each parameter set then represents a chromosome (corresponding to a trial laser field) in analogy with a biological evolution process. These randomly selected individuals are then subjected to optimization in an effort to find the best solution that gives rise to a maximum value of the cost functional. This optimization is performed iteratively, as follows. In every generation, fitness of each population is measured in terms of the values of the cost functional. Subject to natural selection, a specified number of populations (electric fields) survive. The algorithm relies on the techniques of the natural selection process such as inheritance, mutation, selection, and crossover. The calculation took 23 generations for the cost functional to reach convergence using values for the GA parameters as suggested in Ref. 37.

The convergence behaviour set up by the GA with the number of generations evolved is shown in Fig. 3(b). The plot(s) shows the maximum flux (F), and the cost functional (J) values are more or less comparable and keep increasing in steps until a constant value is reached for the final generations. It can be seen that the convergence behaviour of the results presented below is very good.

III. RESULTS AND DISCUSSION

In the field free dynamics of the $|0, 0\rangle$ WP [cf. Fig. 1(b)] launched on the $^1\pi\sigma^*$ (1A_2) state, the average energy of the WP (~ 0.26 eV) is about 60% of the barrier height (~ 0.4 eV).

Therefore, the barrier crossing path and the upper adiabatic dissociation channel remain closed in this situation. Quantum tunneling is the only possible path for this WP to dissociate through the ${}^1\pi\sigma^*$ (1A_2)/ S_0 CI. Using the semiclassical Wentzel-Kramers-Brillouin (WKB) formula, a transmission probability of ~ 0.6 is estimated for a choice of the barrier width of $0.1112 a_0$. This reveals about 60% of the WP on the ${}^1\pi\sigma^*$ state can tunnel through the barrier over a longer time period. Even after tunneling, the WP does not acquire enough energy to reach the upper adiabatic dissociation limit. The dissociation probability calculated along the flux line [as shown in Fig. 1(a)] on the adiabatic asymptotes is plotted as a function of time in Fig. 2 and shown by the dashed line. It can be seen from the figure that in this situation the dissociation solely takes place on the lower adiabatic asymptote. Examination of time-dependence of diabatic and adiabatic electronic populations (cf. Fig. S1 of the [supplementary material](#)) in this situation reveals that the diabatic populations essentially do not change

in time while adiabatic populations exhibit a monotonic change in time. This implies that after an initial excitation, the WP remains on the ${}^1\pi\sigma^*$ diabatic. The ${}^1\pi\sigma^*$ diabatic asymptotically correlates to the lower adiabatic. Therefore, the population of the latter grows and that of the upper adiabatic depletes in time. The cumulative dissociation probability in conjunction with the population dynamics supports the inference that the dynamics of the $|0,0\rangle$ wavefunction is governed by the barrier tunneling followed by a passage through the ${}^1\pi\sigma^*$ / S_0 CI in the field free condition.

It is obvious from the above discussions that the barrier crossing is negligible in the dynamics of the $|0,0\rangle$ wavefunction in the absence of a laser pulse. In this situation, vibrationally excited initial WPs have been shown to enhance the barrier crossing dynamics in addition to the tunneling.⁷ The mechanism proposed in the present work relies on a control pulse which initiates a sequence of events. A part of the WP initially excited to the ${}^1\pi\sigma^*$ state is first dumped back to the S_0 state by the pulse. The latter creates a vibrationally hot WP on the S_0 state which spreads along r as well as Q_{11} and subsequently reaches the CI. The part of the WP remaining on the ${}^1\pi\sigma^*$ state simultaneously and relatively slowly tunnels through the barrier and reaches CI and interferes with the vibrationally hot S_0 WP components reaching there. The composite WP moves towards the lower adiabatic dissociation limit. Since the control pulse is active its pump component remains operational and the composite WP experiences an effective pump action of the pulse in the coordinate region beyond CI. This is because in this region, the carrier frequency ($\sim 8905 \text{ cm}^{-1}$) of the optimized pulse is near-resonant with the asymptotic energy gap ($\sim 8850\text{--}8920 \text{ cm}^{-1}$) at $r \approx 7.86 \text{ a.u.}$ The TDM has a nearly constant value of $\sim 0.1350 \text{ a.u.}$ (calculated *ab initio*) in this asymptotic region. In that way, the pumped components of the composite WP dissociate on the upper adiabatic channel and the remaining ones on the lower channel. This mechanism is further confirmed by switching off the laser-molecule interaction beyond CI. In such a situation, the dissociation probability on the upper adiabatic channel becomes minimal (~ 0.1). This shows that the optimized pulse acquires the capability of producing photoproducts through the upper dissociation channel which is closed otherwise. This simultaneous dump and pump action of the control pulse remains on during the entire course of the dynamics along with the nonadiabatic passage of the WP through CI.

An initial infrared pulse of frequency $\sim 4173 \text{ cm}^{-1}$ is guessed based on the energy difference between $|0,0\rangle$ and $|1,1\rangle$ vibrational levels. This guess pulse is then optimized. The optimal pulse [shown as an insert in Fig. 2(a)] has a maximum amplitude of 0.0216 a.u. ($\sim 14 \text{ TW/cm}^2$) with associated pulse shape parameters, t_1 and t_2 , having values of $\sim 585 \text{ fs}$ and $\sim 1506 \text{ fs}$, respectively. The optimal pulse has a carrier frequency of $\sim 8905 \text{ cm}^{-1}$ ($\sim 1200 \text{ nm}$) as obtained from the power spectrum [shown as an insert in Fig. 2(a)]. As stated above, action of this pulse on the WP on the ${}^1\pi\sigma^*$ state transfers population to the vibrationally excited levels of S_0 , which acquires nodal structure along r and also Q_{11} [cf. Figs. 2(b) and 2(c)]. Finally, a part of it reaches the dissociation asymptotes directly and a part of it is transferred back to the ${}^1\pi\sigma^*$ state by

FIG. 2. (a) Dissociation probability as a function of time. The dashed line represents the dissociation to the lower adiabatic asymptote in the absence of the field. The dissociation to the lower and upper adiabats in the presence of the field is shown by dot-dashed and solid lines, respectively. The optimized laser pulse in the time domain is shown as an insert at the upper left corner and its frequency domain structure is shown as an insert at the lower right corner. [(b)–(e)] Snapshot of the WP components evolving on the diabatic S_0 state [(b) and (c)] and diabatic $\pi\sigma^*$ state [(d) and (e)] at different times during the field driven dynamics (see the text for details).

the pump component of the control pulse which remains on throughout the dynamics.

It can be seen from Figs. 2(d) and 2(e) that the WP component on the $^1\pi\sigma^*$ state also acquires the nodal structure beyond the barrier at $r \approx 5.1$ a.u. This originates from WP components that arrive back to the $^1\pi\sigma^*$ state because of the pump action of the control pulse. These components possess enough energy to dissociate into both the asymptotes. The pump action appears to be more effective after the WP crosses the CI as explicitly confirmed by switching off the laser-molecule interactions at different regions of the coordinate space. The upper dissociation channel appears to be minor when this interaction is switched off beyond $r \approx 6.2$ a.u.

In order to understand the WP dynamics portrayed in Figs. 2(b)–2(e) better, we examined one-dimensional cuts (not shown here for brevity) of the WP probability density along the coupling coordinate Q_{11} . It is observed that in the absence of the pulse the transferred WP on the S_0 diabatic state acquires a nearly symmetrical node at $Q_{11} = 0$. The diabatic coupling is an odd function of Q_{11} , and since the WP can return only via CI such a node appears in this situation. This is a clear signature of the well known geometric phase effect.¹⁴ In the presence of the pulse, the situation becomes quite irregular, and the dumped WP on the S_0 diabat often develops non-symmetrical nodal structure away from $Q_{11} = 0$ because of laser-molecule interaction and interference effects as can be seen from Figs. 2(b) and 2(c). In the absence of the pulse, the $|0,0\rangle$ WP transferred to the $^1\pi\sigma^*$ diabat on the other hand does not acquire any node. This is because the WP component evolving on the $^1\pi\sigma^*$ diabat retains the overall vibronic symmetry. In the presence of the pulse, non-symmetrical nodal structure often appears [cf. Figs. 2(d) and 2(e)] because of interference with the WP components due to pump action of the pulse as stated above.

In contrast to the field free case, the laser driven dynamics yields dissociation products on both the adiabatic asymptotes. The dissociation probabilities calculated on the lower and upper adiabatic asymptotes are shown as dot-dashed and solid lines, respectively, in Fig. 2(a). It can be seen that in this situation predominant dissociation takes place via the upper adiabatic asymptote. Quantitatively, it is much different from the dissociation achieved by a vibrationally excited $(1,1)$ packet that reaches the upper adiabatic asymptote through the barrier crossing mechanism in the field free case.⁷ In Fig. 3(a), the corresponding population dynamics driven by the optimal pulse is shown. It can be seen that the population of both the diabatic states changes in time. As time progresses, both the diabatic $^1\pi\sigma^*$ and adiabatic upper state populations [A and C in Fig. 3(a), respectively] decrease and those of the diabatic S_0 and adiabatic lower state [B and D in Fig. 3(a), respectively] increase. The maximum population transfer between the two electronic states occurs within ~ 1.0 ps. And by this time the dissociation probabilities of both the channels attain a peak value as can be seen from Fig. 2(a). At longer times, the dissociation probabilities saturate at 60% and 40% on the upper and lower adiabatic asymptotes, respectively. This shows that almost entire population is driven to dissociation at the end of the pulse duration. It is worthwhile to point out that intramolecular vibrational relaxation (IVR) turns out to be

FIG. 3. Population dynamics and convergence behaviour: (a) time dependence of adiabatic and diabatic electronic populations in the field driven photodissociation dynamics of pyrrole. The line types are given in the legend and discussed in the text, (b) convergence behaviour of the cost functional (J) and total flux (F) with the number of generations shown by the dashed and solid lines, respectively.

insignificant ($\leq 1.2\%$) in this case as confirmed by minimal overlap of the time evolved WP with the eigenvectors of the low-lying vibrational levels of the S_0 state at the end of the pulse duration.

The laser driven dynamics is much faster as compared to the field free case. An analysis of the average energy of the WP on the S_0 and $^1\pi\sigma^*$ states in the presence of pulse reveals that the packet on both the states has components with sufficient energy to reach the dissociation limit during the entire course of dynamics. The average energies of these packets are shown in Fig. 4(a). The sudden drop in the energy of the S_0 diabatic WP is due to the removal of high energy components of the WP by the damping function activated at the grid boundaries. As can be seen, it causes rise of dissociation probability between 1 and 1.25 ps [cf. Fig. 2(a)]. The time-frequency analysis of the laser pulse using the Husimi distribution³⁸ is shown in Fig. 4(b). As can be seen from the latter figure, the maximum contribution to the transition comes from the pulse in the frequency range of ~ 8850 – 8950 cm^{-1} between ~ 500 and 1600 fs. This is on par with the population dynamics [cf. Fig. 3(a)] and the associated dissociation probabilities [cf. Fig. 2(a)].

FIG. 4. Average energy of diabatic packets and the Husimi plot of the optimal field: (a) average energy of the WP evolving on the S_0 (black line) and $\pi\sigma^*$ (red line) diabatic states as a function of time, (b) the Husimi plot of the time-frequency characteristics of the optimally controlled laser pulse.

Calculations are also carried out keeping the initial guess value of the frequency (i.e., $\sim 4173 \text{ cm}^{-1}$) fixed during optimization while varying the amplitude and time parameters.

FIG. 5. Results of calculations by varying the frequency: (a)–(d) are the optimal field, frequency spectrum, time-integrated flux, and diabatic-adiabatic population dynamics, respectively.

The results of these fixed frequency calculations are presented as a [supplementary material](#) in Fig. S2. A comparative study of these results with the frequency optimized results reveals that, in the latter case, the dissociation probability of the upper channel is enhanced [cf. Fig. 2(a) versus Fig. S2(d) of the [supplementary material](#)]. The underlying reason is attributed to the less effective electronic population transfer between the two diabatic states [cf. Fig. S2(e) of the [supplementary material](#)] by the pulse in action and its relatively less energy, in the fixed frequency case as compared to the frequency optimized case.

Checks are also exercised by taking frequencies of the initial guess pulse close to the optimal result (i.e., either side of 8905 cm^{-1} with -100 cm^{-1} and $+300 \text{ cm}^{-1}$) and performing fixed frequency calculations. This confirms that the control is robust; that is, small variations in the optimal field parameters do not change the fidelity significantly. As can be seen from Fig. 5(a), a relatively complex pulse (or rather a train of pulses) with variations in the amplitude profile yields a quantitatively somewhat different net dissociation probability (~ 0.8) [cf. Fig. 5(c)] compared to frequency optimized results (~ 1.0). However, the overall mechanism remains unaltered. It can also be seen from the frequency structure [cf. Fig. 5(b)] of this moderately complicated time-dependent field that the contributions to transitions between the two electronic states can come from three carrier frequencies depending upon their relative intensity, to effectively yield photoproducts. This is unlike the case of frequency optimized results where a single carrier frequency of the time-dependent field [cf. Fig. 2(a)] is involved during the control dynamics. Therefore, the alternative control mechanism to photodissociation of pyrrole can be brought about not only by optimal pulses which have seemingly simple shape but also by moderately complicated optimal pulses. Hence the power of optimization lies in finding a special combination of amplitude, frequency, and pulse shape parameters (t_1 and t_2) for a given initial guess, to achieve a successful control.

In order to further validate the dynamical control mechanism emerged above in the two states and two modes model,

we extended the model by including two more relevant coupling modes of A_2 symmetry. These modes are designated as Q_{12} and Q_{10} . Following the work of Lan *et al.*,⁸ we constructed an effective coupling mode as $Q_{\text{eff}} = \sum_c \frac{\lambda_c}{\lambda_{\text{eff}}} Q_c$. In this equation, λ_c λ_{eff} are coupling constants of the individual coupling modes and the effective coupling mode, respectively. These coupling coordinates are schematically shown in Fig. S3 of the [supplementary material](#) and the values of corresponding coupling constants and frequencies are presented in Table S1 of the [supplementary material](#). The results of these calculations are shown in Fig. 6. It can be seen from the time profile of the optimized field [shown as an insert in Fig. 6(a)], its corresponding frequency spectrum [shown as an insert in Fig. 6(a)] and the resulting dynamical outcomes, such as dissociation probabilities [cf. Fig. 6(a)] and populations [cf. Fig. 6(b)] that the mechanistic details of the dynamics

FIG. 6. Results of calculations with effective coupling mode: (a) Dissociation probability as functions of time. The dashed line represents the dissociation to the lower adiabatic asymptote in the absence of the field. The dissociation to the lower and upper adiabats in the presence of the field is shown by dot-dashed and solid lines, respectively. The optimized laser pulse in the time domain is shown as an insert at the upper left corner and its frequency domain structure is shown as an insert at the lower right corner. (b) Time dependence of adiabatic and diabatic electronic populations in the field driven photodissociation dynamics of pyrrole. Same color coding of lines as in Fig. 3(a) is used to facilitate comparison.

remain same as discussed above in the case of frequency optimized calculations involving Q_{11} only [cf. Figs. 2(a) and 3(a)]. However, in this case the action of the optimized pulse whose peak amplitude/carrier frequency (in the range ~ 0.0145 a.u./ 10220 cm^{-1}) is lower/higher than that of the latter case (~ 0.0216 a.u./ 8095 cm^{-1}) is confined to a longer time duration [~ 241 fs to ~ 1450 fs, obtained from the Husimi plot (not shown here)]. The action of the optimized pulse in that duration is clearly reflected in the population dynamics [cf. Fig. 6(b)] and flux behaviour [cf. Fig. 6(a)]. It is clear from Figs. 6(a) and 6(b) that the relative increase in the dissociation rate and population transfer rate as compared to those shown in Figs. 2(a) and 3(a) is due to the inclusion of additional coupling modes, as expected. Nevertheless, the total dissociation probability remains almost the same and an interpretation of these results follows the same line of arguments as of those shown in Figs. 2(a) and 3(a). IVR is minimal in this case also. Therefore, in this sense, the theoretical model captured most of the essential photodynamical features of the pyrrole molecule. Calculations involving inclusion of additional electronic states and vibrational modes would be worthwhile and appear to be quite challenging within an optimal control formalism. Such an exercise is currently underway in our group.

IV. SUMMARY AND CONCLUSIONS

In summary, an alternative (to a widely known barrier crossing mechanism via vibrational ladder climbing) and efficient photodissociation mechanism of pyrrole on electronically coupled S_0 - $1\pi\sigma^*$ states is established in this article. The dissociation dynamics is governed by an optimally designed control pulse(s) that acts after the initial excitation of the ground vibrational wave function of the S_0 (adiabatic) state to the $1\pi\sigma^*$ (adiabatic) state. The control pulse dumps a fraction of WP components on the $1\pi\sigma^*$ state to the S_0 state. These dumped WP components on the S_0 possess enough energy along the reaction coordinate. A fast dynamics on the S_0 state in addition to slow tunneling of remaining WP components on the $1\pi\sigma^*$ state follow thereafter. These WP components reach the $1\pi\sigma^*/S_0$ CI and dissociate into both the upper and lower adiabatic channels. The dissociation to the upper channel is mainly facilitated by the pump components of the control pulse (which remains on throughout the dynamics) after the packet crosses CI and this dissociation dominates at longer time.

An increase in the energy of the time evolved WP increases the dissociation probability of the upper channel. This is explicitly verified by utilizing control pulses with different energy. The barrier crossing path, which opens up the upper adiabatic asymptote in the field free case, is closed for the $|0,0\rangle$ packet. With the aid of an optimally controlled laser pulse, dissociation to the upper adiabatic asymptote is accomplished here through an alternative path. The optimized pulse has a smooth profile in time and is highly band-width limited. Such simple pulse shapes are experimentally realizable. We hope that this work may trigger control experiments in this direction. Multidimensional control calculation involving more electronic states and nuclear degrees of freedom is a future goal.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the results of population dynamics under field free conditions, frequency fixed calculations, normal mode definitions, and the associated numerical values.

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