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## 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  $S_0 - \pi \sigma^*({}^1A_2)$  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 photophysics<sup>1</sup> and photochemistry<sup>2-17</sup> 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  ${}^{1}\pi\sigma^{*}$  ( ${}^{1}A_{2}$ ) 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.<sup>3</sup> In addition, there exists a second excited  ${}^{1}\pi\sigma^{*}$  state of  ${}^{1}B_{1}$  symmetry. This state crosses both the  ${}^{1}\pi\sigma^{*}$  ( ${}^{1}A_{2}$ ) and  $S_{0}$  states at high energies. It was demonstrated that only a minor ( $\leq 6\%$ ) population transfer occurs to the second  ${}^{1}\pi\sigma^{*}$  state when the dynamics is initiated on the first  ${}^{1}\pi\sigma^{*}$  state.<sup>10</sup> The participation of the  ${}^{1}\pi\sigma^{*}$  ( ${}^{1}A_{2}$ ) 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.<sup>2,4,12,16</sup> It was concluded from a large kinetic isotope effect that quantum tunneling plays the primary role in the photodissociation dynamics at 250 nm excitation.<sup>11</sup> The photodissociation dynamics of the initially prepared  ${}^{1}\pi\sigma^{*}$  ( ${}^{1}A_{2}$ ) state and the role of the vibrationally hot initial state on the branching ratio of dissociation product was theoretically examined in the recent past.<sup>7</sup> 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.<sup>7</sup> A vibronic coupling scheme was developed to model  ${}^{1}\pi\sigma^{*}$  ( ${}^{1}A_{2}$ )/S<sub>0</sub> 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.<sup>7</sup> It is noteworthy that these two coordinates capture most of the essential photodynamical features of this molecule as proven in a previous study.<sup>8</sup>

In the field free case, a vibrationally excited packet was found to dissociate into both the product asymptotes, yielding a branching ratio.<sup>7</sup> However, when the WP corresponding to the ground vibrational level of the  $S_0$  state is launched on the  ${}^{1}\pi\sigma^{*}$  ( ${}^{1}A_2$ ) 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  ${}^{1}\pi\sigma^{*}$  ( ${}^{1}A_2$ ) state. In this situation, the upper adiabatic dissociation channel was found to remain essentially closed.<sup>7,11</sup> A direct transition from the  $S_0$  state to the  ${}^{1}\pi\sigma^{*}$  ( ${}^{1}A_2$ ) state of pyrrole is understandably

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