Time-dependent quantum wave-packet description of the \(1\pi\sigma^*\) photochemistry of pyrrole

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The photoinduced hydrogen elimination reaction in pyrrole via the conical intersection of the \(^1\text{B}_1 (1\pi\sigma^*)\) excited state with the electronic ground state has been investigated by time-dependent quantum wave-packet dynamics. A two-dimensional model potential-energy surface has been constructed as a function of the NH stretching and the hydrogen out-of-plane bending mode, employing multi-reference \textit{ab initio} electronic-structure methods. The branching ratio of the reactive flux at the conical intersection has been investigated in dependence on the initial vibrational state of the molecule. The results suggest that laser control of the photodissociation of pyrrole via mode-specific vibrational excitation should be possible.

1 Introduction

As the building blocks of many biologically relevant compounds such as porphyrines and chlorophylls, pyrrole and its derivatives play a prominent role in the synthesis of biologically active compounds, pesticides and organic polymers. The photophysics of pyrrole is therefore a topic of fundamental interest. The experimental UV absorption spectrum of pyrrole exhibits a broad intense band centred around 6 eV.\(^1\) Interestingly, these strongly absorbing states have a very low quantum yield of fluorescence. This indicates the existence of very fast nonradiative processes which efficiently quench the fluorescence.\(^2\)

The photophysics of pyrrole involves essentially the four lowest excited singlet states, which are \(^1\text{A}_2 (\pi\sigma^*), ^1\text{B}_2 (\pi\pi^*), ^1\text{B}_1 (\pi\sigma^*)\) and \(^1\text{A}_1 (\pi\pi^*)\) in order of increasing energy.\(^3\) The second and the fourth excited singlet state, which correspond to valence excitations from \(\pi\) to \(\pi^*\) orbitals, are strongly UV absorbing states, which explains the presence of the intense band around 6 eV in the absorption spectrum. The first and the third excited singlet state correspond to excitations from the valence \(\pi\) orbitals of pyrrole to the Rydberg-like 3s orbital. These electronic transitions possess very small oscillator strengths.\(^4\) As discussed by Sobolewski and Domcke,\(^5,6\) the 3s Rydberg orbital of pyrrole has a significant anti-bonding character with respect to the NH bond (\(\sigma^*\) character). Upon stretching of the NH bond, the \(1\pi\sigma^*\) potential-energy functions intersect the potential functions of the valence excited states, resulting in conical intersections along the reaction path for hydrogen abstraction. Due to the presence of these conical intersections between the bright valence states and the dark \(1\pi\sigma^*\) states, the population of the bright states is transferred to the dark states on a very

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short time scale of ≈20 fs. This has been confirmed recently by Köppel et al.\textsuperscript{7} for pyrrole and related five-membered heterocycles.

The \( ^1\pi\sigma^\ast \) states of pyrrole also cross the \( S_0 \) ground state, inducing two conical intersections (\( ^1\text{A}_2\text{-S}_0 \) and \( ^1\text{B}_1\text{-S}_0 \)) along the NH dissociation path, which may provide the mechanism of internal conversion to the ground state.\textsuperscript{5,6} Blank et al.\textsuperscript{8} and Wei et al.\textsuperscript{9} have investigated the photodissociation of pyrrole by photofragment translational spectroscopy. They observed two characteristically distinct kinetic-energy distributions of H atoms. They assigned the slow H atoms with a broad velocity distribution to the unimolecular decay process in the electronic ground state after internal conversion. They interpreted the fast H atoms as arising from fast direct N–H bond breaking in excited electronic states, in particular the lowest \( ^1\pi\sigma^\ast \) excited state.\textsuperscript{9}

In this paper, we describe our first attempts towards an \textit{ab initio} based quantum wave-packet description of the photoinduced hydrogen elimination and internal conversion dynamics of pyrrole \textit{via} the \( ^1\pi\sigma^\ast \) states. Multi-reference electronic-structure methods have been employed to identify the photochemically relevant molecular degrees of freedom, in particular the coupling modes\textsuperscript{10} of the \( ^1\pi\sigma^\ast\text{-S}_0 \) conical intersections. In the present work, we focus on the \( ^1\text{B}_1(\pi\sigma^\ast) \) state. Although this state is higher in energy than the \( ^1\text{A}_2(\pi\sigma^\ast) \) state, its photochemical dynamics is more interesting owing to its similarity with the photochemistry of the lowest \( ^1\pi\sigma^\ast \) state of biologically even more relevant molecules, such as indole, tryptophan and adenine. In the latter systems, the out-of-plane angle of the hydrogen atom of the azine group has been identified as the relevant coupling mode of the \( ^1\pi\sigma^\ast\text{-S}_0 \) conical intersection,\textsuperscript{5,6,11} like in the \( ^1\text{B}_1\text{-S}_0 \) conical intersection in pyrrole (the coupling mode of the \( ^1\text{A}_2(\pi\sigma^\ast)\text{-S}_0 \) intersection of pyrrole, on the other hand, corresponds to a screwing of the five-membered ring). We have constructed an accurate two-dimensional (NH stretch coordinate, NH out-of-plane angle) \textit{ab initio} potential-energy surface of the \( ^1\text{B}_1(\pi\sigma^\ast) \) and \( ^1\text{A}_1(\text{S}_0) \) states of pyrrole. The essential features of the ultrafast nonadiabatic dynamics at the conical intersection are explored, using standard methods of time-dependent quantum wave-packet propagation.

2 Theoretical framework

2.1 Reduced-dimensionality model

We treat the wave-packet dynamics of pyrrole in a two-dimensional space which is spanned by the NH-stretching coordinate (which tunes the energy gap between the ground and \( ^1\pi\sigma^\ast \) states), and the out-of-plane bending motion of the hydrogen atom of the azine group (which couples the two states). The other internal coordinates are kept frozen at their ground-state equilibrium values. Some of these modes may play a role as energy-accepting modes in the internal-conversion process. It should be kept in mind that these effects are not included in the present dynamics simulations.

The Hamiltonian of the system is written in a diabatic electronic basis as

\[
\mathcal{H} = \mathcal{H}^N + \mathcal{H}^{el}
\]

\[
\mathcal{H} = T^N \left( \begin{array}{cc}
0 & 1 \\
1 & 0
\end{array} \right) + \left( \begin{array}{cc}
V_{11} & V_{12} \\
V_{21} & V_{22}
\end{array} \right),
\]

where \( \mathcal{H}^N \) and \( \mathcal{H}^{el} \) represent the nuclear and the electronic part of the Hamiltonian operator, respectively. \( T^N \) is the nuclear kinetic-energy operator. \( V_{11} \) and \( V_{22} \) are the potential energies of the diabatic \( S_0 \) and \( ^1\pi\sigma^\ast \) states, respectively. The diabatic coupling element \( V_{12} = V_{21} \) describes the coupling between the two states. It vanishes for planar geometries (\( C_3 \)) by symmetry.

The system is considered as an effective three-body system, composed of hydrogen, nitrogen and M, the centre of mass of the rest of the rigid pyrrole ring. The nuclear geometry is described in terms of Jacobi coordinates (see Fig. 1a). \( r_{MN} \) is the distance between M and the nitrogen atom. This distance is kept fixed in the dynamics calculation. \( r \) is the distance between the active hydrogen and the centre of mass of the M–N unit, and \( \gamma \) is the angle between \( r_{MN} \) and \( r \). In this set of coordinates, the kinetic operator takes the following form

\[
T^N = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2I} \frac{\partial^2}{\partial \gamma^2},
\]
with
\[
\begin{align*}
\mu &= \frac{m_H (m_M + m_N)}{m_H + m_M + m_N}, \\
\mu_{MN} &= \frac{m_M m_N}{m_M + m_N}, \\
\mu_M &= \frac{m_C + m_H}{m_M + m_H}, \\
I &= \frac{1}{\mu r^2} + \frac{1}{\mu_{MN} r_{MN}^2}.
\end{align*}
\] (2.4)

The quantities \(m_H\), \(m_N\), and \(m_M\) denote the masses of hydrogen, nitrogen, and the four C–H pairs, respectively, and \(I\) is the moment of inertia of the total system.

### 2.2 Ab initio calculation of the adiabatic potential-energy surfaces

The \(1B_1(1\pi\sigma^*)\) state has a 3s Rydberg character at the equilibrium geometry, but rapidly acquires H (1s) character when hydrogen atom dissociates.\(^5,6\) This change of character is reflected by a small barrier (\(\approx 0.26\) eV) in the \(1\pi\sigma^*\) potential-energy function close to the equilibrium geometry (\(r_{NH} \approx 1.25\) Å). In order to account for the diffuseness of the \(\sigma^*\) orbital, it is necessary to use rather extended basis sets on each atom, and in particular on the N–H end. All atoms are described by the augmented correlation-consistent polarised valence quadruple zeta (aug-cc-pVDZ)\(^12\) basis. One diffuse s function and one set of diffuse p functions were added to the nitrogen, and two diffuse s functions and two sets of diffuse p functions were added to the active hydrogen. Their exponents were derived in an even-tempered manner from the most diffuse s and p functions present in the aug-cc-pVDZ basis by dividing the exponents successively by a factor of 3.0.

As a reference for the definition of internal coordinate displacements, the ground-state equilibrium geometry has been determined at the Møller–Plesset (MP2) level of theory using the Gaussian 98 ab initio package.\(^13\) The ab initio calculations of the ground and excited state potential-energy surfaces have been performed at the CASSCF level using the MOLPRO package.\(^14\) The active space involves three \(\pi\) orbitals \((1b_1 - 2b_1, 1a_2)\), two \(\pi^*\) orbitals \((3b_1, 2a_2)\), and one \(\sigma^*\) \((10a_1)\) orbital. It turned out to be necessary to include three occupied orbitals of \(\sigma\) character \((8a_1 - 9a_1, 6b_2)\), and three additional virtual orbitals of \(\sigma^*\) character \((11a_1 - 12a_1, 7b_2)\) to obtain smooth potential-energy surfaces in the region of the barrier of the \(1\pi\sigma^*\) surface. This active space corresponds to a distribution of 12 electrons in 12 orbitals.

The N–H distance has been varied between 1.9 \(a_0\) and 9.0 \(a_0\), with a high density of points (steps of 0.1 \(a_0\)) in the region of the barrier of the \(1\pi\sigma^*\) state and near the conical intersection. The out-of-plane bending angle has been varied from 0° to 70°, in steps of 5°.

### 2.3 Analytical representation of the diabatic potential functions

We wish to construct an analytical diabatic potential model which should be as simple as possible and at the same time should reproduce the ab initio potential-energy data within an accuracy of 0.1
eV or better. For the description of the potential-energy surfaces, the intermolecular distance $r_{\text{NH}}$ between nitrogen and hydrogen and the out-of-plane bond angle $\theta$ of the hydrogen atom are the most natural coordinates (see Fig. 1b). We construct the potential-energy surfaces in these coordinates, while the wave-packet propagation is performed in the Jacobi coordinates.

Details of the choice of the analytical expansions and the fitting procedure are described in a forthcoming publication. The $S_0$ diabatic potential function is approximated as

$$V_{11} = D_1^1 [1 - \exp(-a_1(r_{\text{NH}} - r_1))]^2 + \frac{1}{2} k_1(r_{\text{NH}}) \theta^2,$$

(2.5)

with

$$k_1(r) = (p_1 + p_2 r)(1 - f_1(r)) + p_3 \exp\left(-\frac{(r - d_1)}{z_1}\right)f_1(r),$$

(2.6)

$$f_1(r) = \frac{1}{2} \left[1 + \tanh\left(\frac{r - d_2}{\beta_1}\right)\right].$$

(2.7)

The $^1\pi\sigma^*$ diabatic potential function is modelled as

$$V_{22}(r_{\text{NH}}) = \frac{1}{2} \left( V_{22}^{\text{in}}(r_{\text{NH}}) + V_{22}^{\text{out}}(r_{\text{NH}}) \right) - \frac{1}{2} \sqrt{\left( V_{22}^{\text{in}}(r_{\text{NH}}) - V_{22}^{\text{out}}(r_{\text{NH}}) \right)^2 + 4 \lambda_{22}^2} + \frac{1}{2} k_2(r_{\text{NH}}) \theta^2,$$

(2.8)

with

$$V_{22}^{\text{in}}(r) = E_0^2 + D_2^{2\text{in}} [1 - \exp(-a_2(r - r_2))]^2,$$

(2.9)

$$V_{22}^{\text{out}}(r) = D_2^0 + a_3 \exp\left(-\frac{(r - r_3)}{z_2}\right),$$

(2.10)

and

$$k_2(r) = \frac{1}{2} (q_1 + q_2 r) - \frac{1}{2} \sqrt{(q_3 + q_2 r)^2 + 4 q_4^2}.$$

(2.11)

$k_2(r)$ is set to zero when $r$ is larger than 2.55 $a_0$.

The ansatz for the non-adiabatic coupling term reads:

$$V_{12} = \lambda_{12}(r) \theta,$$

(2.12)

with

$$\lambda_{12}(r) = \frac{1}{2} \lambda_{\text{max}} \left[1 - \tanh\left(\frac{r - d_{12}}{\beta_2}\right)\right].$$

(2.13)

Table 1 gives the parameters appearing in eqns. (2.5)–(2.13). Note that the diabatic potential-energy functions are nonseparable in $r$ and $\theta$. The adiabatic potential-energy functions acquire an additional pronounced nonseparability through the conical intersection. The maximum deviation between the adiabatic model potential-energy and the ab initio data is 0.05 eV. The resulting diabatic and adiabatic potentials as functions of the internal coordinates $r_{\text{NH}}$ and $\theta$ are displayed in Figs. 2a and 2b, respectively.
2.4 Wave-packet propagation method

The photoinduced dynamics of pyrrole is treated in the time-dependent picture by solving the time-dependent Schrödinger equation with a wave-packet propagation method on a two-dimensional grid. The initial wave function \( \Psi(t=0) \) is given, in the Condon approximation, by the initial vibrational state in the electronic ground state. The excited-state wave function is propagated using the split-operator (SO) method. We have used the fast Fourier transform (FFT) method to evaluate the kinetic-energy part of the time propagator. To avoid problems with the finite range of the grid, we apply a damping function as defined in ref. 18. The time dependence of the adiabatic electronic populations is calculated from the expectation values of the projection operators in the respective electronic states.

We have generated the eigenfunctions of the diabatic \( S_0 \) state by using the spectral-quantisation method detailed in ref. 20. The dissociation probabilities have been calculated using as the time-cumulated flux through a dividing surface \( r = r_{\text{flux}} \), which is placed beyond the conical intersection:

\[
P^R(t) = \frac{\hbar}{\mu} \int_{r=0}^{t} \text{Im} \left( \Psi(r_{\text{flux}}, \gamma, t) \left| \frac{\partial \Psi(r_{\text{flux}}, \gamma, t')}{\partial r} \right| \right) \text{d}t'.
\] (2.14)

The energy-resolved reaction probability is defined in a similar way

\[
P^R(E) = \frac{\hbar}{\mu} \text{Im} \left( \Psi(r_{\text{flux}}, \gamma, E) \left| \frac{\partial \Psi(r_{\text{flux}}, \gamma, E)}{\partial r} \right| \right),
\] (2.15)

![Figure 2](image)

**Fig. 2** Diabatic \((V_{11}, V_{22})\) (a) and adiabatic (b) potential-energy surfaces of the \( S_0 \) and \( ^1\pi\sigma^* \) states as a function of the NH stretching coordinate \( r_{\text{NH}} \) and the H-out-of-plane coupling motion \( \theta \).
using the energy-normalised wave function $\Psi(r,\gamma,E)$, which is obtained by Fourier-transforming the time-dependent wave packet on the dividing surface:

$$
\Psi(r_{\text{flux}},\gamma,E) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(r,\gamma,t)e^{iEt/\hbar}dt|_{r=r_{\text{flux}}},
$$

(2.16)

3 Results and discussion

3.1 Vibrational eigenstates of the electronic ground state

We first report the energy spectrum of the diabatic $S_0$ state. An initial Gaussian wave packet is defined as

$$
\Psi(t = 0) = N \exp \left[ -\frac{(r-r_0)^2}{2\sigma_r^2} \right] \exp \left[ -\frac{(\gamma-\gamma_0)^2}{2\sigma_\gamma^2} \right],
$$

(3.17)

where $N$ is the normalisation constant. The parameters are chosen such that this wave packet is initially shifted ($r_0 = 4.55\ a_0$, $\gamma_0 = 0.25\ \text{rad}$) with respect to the equilibrium geometry $r_e = 4.15\ \text{au}$, $\gamma = 0$, with $\sigma_r = 0.3\ \text{au}$ and $\sigma_\gamma = 0.25\ \text{au}$ along $r$ and $\gamma$, respectively. The grid consists of $128 \times 128$ points, ranging from $3\ a_0$ to $6\ a_0$ along $r$ and $-2.0\ \text{rad}$ to $2.0\ \text{rad}$ along $\gamma$. This grid is large enough to ensure that the wave function does not reach the grid boundaries during the propagation. The total propagation time is $1.0\ \text{ps}$ with a time step $\Delta t = 0.05\ \text{fs}$. No damping function was employed in this calculation.

The energy eigenvalues of the 15 lowest vibrational states and their assignments in terms of quantum numbers are given in Table 2. The fundamental of the coupling mode is $850\ \text{cm}^{-1}$ when the stretching mode is not excited. It decreases to $834\ \text{cm}^{-1}$ for $v = 1$ of the stretching mode. The fundamental of the stretching mode is $3602\ \text{cm}^{-1}$. The experimental values (see ref. 21 and references therein) of the fundamentals of the NH-stretching and out-of-plane bending are $3531\ \text{cm}^{-1}$ and $475\ \text{cm}^{-1}$, respectively. While our diabatic surface reproduces the stretching fundamental with good accuracy, the calculated bending fundamental is significantly too large. This effect reflects the strong coupling of the $1B_1(\pi\sigma^*)$ and $S_0$ states via the out-of-plane bending mode: the repulsion of the surfaces upon bending flattens the adiabatic $S_0$ surface.

3.2 Wave-packet dynamics at the $1\pi\sigma^*$$-S_0$ conical intersection

The main focus of the present work is on the investigation of the effect of mode-specific vibrational excitation on the dynamics near the conical intersection. We have employed the same grid along $\gamma$ and the same grid spacing along $r$ as for the generation of the vibrational eigenstates of the $S_0$ state. The grid along $r$ has been extended up to $27.17\ a_0$, with a total number of $1024$ grid points. The absorbing function was placed at $26.5\ a_0$. The wave function is propagated for $300\ \text{fs}$ with a time step $\Delta t = 0.05\ \text{fs}$. The total propagation time is long enough to ensure that the probabilities of the

<table>
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<th>$E_n$/cm$^{-1}$</th>
<th>$(n_r,n_\gamma)$</th>
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<td>6738</td>
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Table 2  Eigenvalues ($E_n$) and assignments ($n_r, n_\gamma$) of the pseudospectral peaks of the diabatic ground state
different channels are converged. The probabilities are monitored by the calculation of the time-cumulated flux and energy-resolved flux on the $S_0$ and $1\pi\sigma^*$ states before the conical intersection ($r = 5 \alpha_0$) and at the dissociation limits ($r = 9 \alpha_0$).

We use the 15 lowest eigenfunctions discussed in the previous section as initial wave functions, placing them vertically in the $1\pi\sigma^*$ diabatic state. For all initial conditions, we observe similar features in the evolution of the excited-state wave function. In all cases, we note very fast, but weak oscillations (Rabi-type oscillations) in the diabatic population of the $1\pi\sigma^*$ and $S_0$ states, see Fig. 3, which result from the non-zero coupling of these two states in the Franck–Condon region. Due to the existence of a barrier in the $1\pi\sigma^*$ potential-energy surface, there are two ways for the wave packet to escape the potential well in which it is placed by vertical excitation. The high-energy part of the wave packet overcomes the barrier and reaches the conical intersection directly within about 10 fs. The low-energy part escapes the potential well by tunnelling, which happens on a longer time scale. These two processes can be distinguished via the profile of the population dynamics and the time-cumulated flux, see Figs. 3 and 4.

When the wave packet reaches the region of the conical intersection, it splits into two parts. One part follows a diabatic path and moves towards the lower adiabatic dissociation limit, as illustrated by the flux calculated on the lower dissociation channel, see Fig. 4. The other part is transferred to upper adiabatic surface, see Fig. 3. It dissociates directly to the higher adiabatic limit without being trapped in the upper adiabatic cone (see Fig. 4). The reason is that the initial mean energy of the wave packet is higher than both dissociation limits. Therefore, the wave packet passes the conical intersection region only once, as revealed by the monotonous population dynamics in the adiabatic picture. The probability of internal conversion, that is, return of the system to the electronic ground state without dissociation, is close to zero in the present model. This finding does not reflect the real situation for two reasons. First, we have neglected the coupling of the highly excited $B_2(\pi\pi^*)$ state with the lower-lying $1A_2(\pi\sigma^*)$ and $1B_2(\pi\pi^*)$ excited states. Second, we have neglected intramolecular vibrational relaxation (IVR) effects, arising from the anharmonic coupling of the photochemically active with the many inactive vibrational degrees of freedom. Extensions of the model are required to account for these effects.

In order to shed light on the influence of mode-selective vibrational excitation on the branching ratio of two dissociation channels, we discuss the flux at the dissociation limits for different initial states. If we put one quantum of energy into the tuning mode, initial vibrational state $(0,0)$, the wave packet reaches the conical intersection earlier than in the $(0,0)$ case and the population transfer occurs on a short time scale, see Fig. 3c. It is noteworthy that the branching ratio does not depend on excitations along the tuning mode (see Fig. 5a). The branching of the reactive flux at the conical intersection depends, on the other hand, strongly on the excitation level of the coupling mode, as shown by Figs. 5(b) and 5(c). For the $(0,0)$ initial wave function, most of the wave packet (75%) dissociates to the lower adiabatic limit, while 25% of the flux arrives at the upper adiabatic limit. When exciting the coupling mode by one quantum, the flux splits almost equally between the two channels. If we put more energy into the coupling mode, the wave packet dissociates primarily to the higher adiabatic limit. The branching ratio saturates at 25%/75% for $n_r = 4$. Similar observations can be made for the series $(1, n_r)$, $n_r = 0, 4$; see Fig. 5(c). In summary, we conclude that excitations along the coupling mode have a strong impact on the behaviour of the wave packet at the conical intersection. This fact can be used to tune the branching ratio between the two dissociation limits.

In these time-dependent wave-packet calculations for a two-mode model of a $1\pi\sigma^*$–$S_0$ conical intersection, we have pointed out that upon excitation of the coupling mode, a significant amount of the population remains in the upper diabatic state and dissociates rapidly. This observation reflects the fact that the excess energy cannot be absorbed by other degrees of freedom. It has been found that inclusion of additional modes generally induces a vibrational damping of the modes actively involved in the photodynamics. $^{22}$ This results in a lowering of the long-time limit of the population of the upper adiabatic state due to vibrational relaxation in the lower adiabatic potential-energy surface. For our present model, this would imply a reduction of the population of the higher dissociation channel and an increased probability for internal conversion. However, the calculation of the minimal-energy reaction path shows that other degrees of freedom are not strongly coupled with the NH-stretch coordinate and remain close to their values at the ground-state equilibrium geometry of pyrrole. As a consequence, our findings that excitations of the...
Fig. 3 Population probabilities of the diabatic $^1\pi\sigma^*$ state and ground state (full lines). The population probabilities of the upper adiabatic $S_1$ and lower adiabatic $S_0$ states are shown by the lines with crosses and circles, respectively, for the initial conditions (0,0) (a), (0,1) (b) and (1,0) (c). The insets display the diabatic population of the $^1\pi\sigma^*$ state for the first 20 fs.
coupling mode influence the branching ratio between the two dissociative channels is expected to be qualitatively correct.

We have studied in this work, for simplicity, a two-state model, neglecting other low-lying excited states. Due to the presence of multiple conical intersections between the bright $^1\pi\pi^*$ states and the two dark $^1\pi\sigma^*$ states in the Franck–Condon region, the optically prepared wave packet may have a complicated shape once it arrives in one of the $^1\pi\sigma^*$ states by internal conversion from the $^1\pi\pi^*$ states. By using different initial conditions in our simulations, we wanted to understand

Fig. 4 Time-cumulated flux measured on the upper $S_1$ (lines with crosses) and lower $S_0$ (lines with circles) adiabatic dissociation limits, for initial conditions (0,0) (a), (0,1) (b) and (1,0) (c).
the evolution of different components of this possibly complex wave packet. The investigation of the wave-packet dynamics at the lower $^1\text{A}_2(\pi\sigma^*)$-$\text{S}_0$ conical intersection is in progress.

4 Conclusions

As a first step towards a first-principles mechanistic understanding of the $^1\pi\sigma^*$-driven photochemistry of aromatic biomolecules, we have investigated the quantum wave-packet dynamics of a two-dimensional model of the $^1\text{B}_1(\pi\sigma^*)$ excited state of pyrrole and its conical intersection with the electronic ground state. The photochemically reactive NH stretching mode and the vibronically active hydrogen out-of-plane bending model have been taken into account. We have investigated, in particular, the dependence of the branching ratio of the two hydrogen dissociation channels (corresponding to the $^2\pi$ and $^2\sigma$ pyrrolyl radicals) on the initial vibrational state. A considerable dependence of the branching ratio on the level of excitation of the bending mode has been found. This finding indicates that a control of the photodissociation dynamics of pyrrole via mode-specific IR excitation, as has recently been demonstrated for ammonia,$^{23}$ should also be possible for pyrrole.

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