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Ab initio quantum dynamical study of the multi-state nonadiabatic photodissociation of pyrrole

S. Faraji,¹ M. Vazdar,² V. Sivaranjana Reddy,¹ M. Eckert-Maksic,² H. Lischka,^{3,4}
and H. Köppel^{1,a)}

¹Theoretical Chemistry, Institute of Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany

²Rudjer Boskovic Institute, Bijenicka c. 54, 10 000 Zagreb, Croatia

³Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, USA

⁴Institute for Theoretical Chemistry, University of Vienna, Waehringerstrasse 17, A-1090 Vienna, Austria

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There has been a substantial amount of theoretical investigations on the photodynamics of pyrrole, often relying on surface hopping techniques or, if fully quantal, confining the study to the lowest two or three singlet states. In this study we extend *ab initio* based quantum dynamical investigations to cover simultaneously the lowest five singlet states, two $\pi - \sigma^*$ and two $\pi - \pi^*$ excited states. The underlying potential energy surfaces are obtained from large-scale MRCI *ab initio* computations. These are used to extract linear and quadratic vibronic coupling constants employing the corresponding coupling models. For the N-H stretching mode Q_{24} an anharmonic treatment is necessary and also adopted. The results reveal a sub-picosecond internal conversion from the S_4 ($\pi - \pi^*$) state, corresponding to the strongly dipole-allowed transition, to the S_1 and S_2 ($\pi - \sigma^*$) states and, hence, to the ground state of pyrrole. The significance of the various vibrational modes and coupling terms is assessed. Results are also presented for the dissociation probabilities on the three lowest electronic states. © 2011 American Institute of Physics. [doi:10.1063/1.3651536]

I. INTRODUCTION

Small heteroaromatic molecules such as pyrrole, phenol, furan and others are often considered as important models for larger biomolecules such as aromatic amino acids or DNA bases. While they share essential features with these larger systems, they are small enough to allow for rather accurate and detailed quantal and dynamical investigations. Pyrrole represents a particularly prominent example^{1–12} which has been studied over many years with an increasing degree of sophistication. It features a complicated UV absorption spectrum and a rich photochemistry which is still not properly understood in all its details.^{11–14} We mention recent femtosecond pump-probe spectroscopic investigations which have revealed N–H dissociation with the appearance of fast and slow H atoms, and characteristic time constants of 0.1 ps and 1 ps, respectively.¹¹ Larger fragments such as HCN, C₃H₄ etc. are also found^{8,13,15} and their dependence on the excitation wavelength has been established. From the theoretical side pyrrole has been intensely studied with *ab initio* techniques^{2,4,5,16} and been used as a benchmark case for testing new methods for excited-state computations.⁷ Concerning the biological relevance of its photochemistry, Sobolewski, Domcke and coworkers were the first to point out the importance of the $\pi - \sigma^*$ states, and the concomitant conical intersection¹⁷ (CoIn) with the ground state, for potential N–H photodissociation and photostability through efficient internal conversion to the ground state.^{6,9,18–20} This was taken to be a

paradigm also for other related systems and treated in subsequent work. These radiationless processes are considered to be also the cause for the absence of fluorescence in these species. Later the theoretical analysis of the photodynamics has been extended to cover also ring opening and ring puckering as possible competing mechanisms.^{10,21,22} We refer to Refs. 9, 21, and 22 and references therein for a more complete coverage of the vast amount of literature on the system.

It is the purpose of the present paper to extend the available quantal treatments of the pyrrole photodynamics by including five low-energy singlet states in the theoretical analysis. Such a rather large electronic function space has been considered to date only for classical trajectory (surface hopping) calculations,^{21,22} while in quantum dynamics studies usually the two lowest excited states (that is, 2–3 electronic states in total) have been considered.^{9,20,23} The higher excited states seem most important for higher photon energies (exceeding 6–6.5 eV) because in this energy range the strongly dipole-allowed $\pi - \pi^*$ states appear which carry most of the oscillator strength. Therefore the dynamics following photoexcitation will be dominated by these transitions, and the question arises how this will influence the photoreaction and, ultimately, the fate of the photoproducts.

The theoretical approach used in this work consists of the well-established linear vibronic coupling (LVC) scheme augmented by *all* quadratic terms diagonal in the vibrational modes (also called QVC scheme). For the N–H stretching mode (Q_{24} in our nomenclature) a general anharmonic treatment is needed and adopted. Large-scale MRCI calculations are performed to determine the pertinent potential energy surfaces (PES) and coupling elements. A whole set of

^{a)} Author to whom correspondence should be addressed. Electronic mail: Horst.Koeppel@pci.uni-heidelberg.de.

TABLE I. Comparison of the present results with previous Rydberg and valence state calculations reported in the literature. f refers to the oscillator strengths (F means dipole forbidden).

		S_0	S_1	S_2	S_3	S_4
Serrano <i>et al.</i> ^a	Symmetry	A_1	A_2	B_1	B_2	A_1
		S_0	$\pi\sigma^*(3s)$	$\pi\sigma^*(3p_y)$	$\pi\sigma^*(3p_x)$	Valence
	$E_{vert}(\text{CASSCF})$		5.08	5.72	5.95	7.22
	f		F	0.0239	0.0399	0.0195
Palmer <i>et al.</i> ^b	Symmetry	A_1	A_2	B_2	A_1	B_2
		S_0	$\pi\sigma^*(3s)$	$\pi\sigma^*(3p_x)$	$\pi\pi^*$	$\pi\pi^*$
	$E_{vert}(\text{MRD-CI})$		4.806	5.912	6.672	6.769
	f				0.000	0.071
Christiansen <i>et al.</i> ^c	Symmetry	A_1	A_2	B_1	B_2	A_1
		S_0	$\pi\sigma^*$	$\pi\sigma^*$	$\pi\pi^*$	$\pi\pi^*$
	$E_{vert}(\text{CCSD})$		5.17	5.88	6.01	6.55
	f		F	0.0245	0.0617	0.0007
Roos <i>et al.</i> ^d	Symmetry	A_1	A_2	A_1	B_2	B_1
		S_0	$\pi\sigma^*(3s)$	$\pi\pi^*$	$\pi\pi^*$	$\pi\sigma^*(3p_y)$
	$E_{vert}(\text{CASPT2})$		5.22	5.82	5.87	5.87
	f		F	0.036	0.209	0.026
Vallet <i>et al.</i> ^e	Symmetry	A_1	A_2	B_1	B_2	A_1
		S_0	$\pi\sigma^*$	$\pi\sigma^*$	$\pi\pi^*$	$\pi\pi^*$
	$E_{vert}(\text{CASSCF})$		4.45	5.3		
Barbatti <i>et al.</i> ^f	Symmetry	A_1	A_2	B_1	B_2	A_1
		S_0	$\pi\sigma^*$	$\pi\sigma^*$	$\pi - 3P_x$	$\pi\pi^*$
	$E_{vert}(\text{MRCI+Q})$		5.09	5.86	5.94	6.39
Present work	Symmetry	A_1	A_2	B_1	A_1	B_2
		S_0	$\pi\sigma^*$	$\pi\sigma^*$	$\pi\pi^*$	$\pi\pi^*$
	$E_{vert}(\text{MRCI+Q})$		5.33	6.12	6.55	6.75
	f		F	5.8×10^{-4}	0.005	0.212
Experiment			5.08 ^g	6.22 ^g		5.9 ^g
			5.22 ^c			6.2-6.4 ^c

^aReference 1.^bReference 2.^cReference 5.^dReference 4.^eReference 9.^fReference 10.^gReference 65.

low-energy conical intersections is established which interconnects all PES of the $S_0 - S_4$ electronic states (if the mode Q_{24} is excluded, all excited, i.e., $S_1 - S_4$ states are strongly coupled). The quantum dynamical simulations rely on the wavepacket propagation method, utilizing the powerful multiconfiguration time-dependent Hartree (MCTDH) scheme. They reveal a sub-picosecond internal conversion process from the (strongly) dipole-allowed S_4 and S_3 states to the (nearly) dipole-forbidden S_2 and S_1 excited states and provide a rationale for earlier quantum investigations where these states are taken to be the initial electronic states from the outset. Including the coupling of these states with the S_0 ground state sheds new light on the issues of N–H photodissociation and photostability of pyrrole.

This paper is organized as follows. In Sec. II we detail the conceptual and computational aspects, regarding the electronic structure and dynamical calculations. Section III is devoted to present and discuss the results for the various PES and coupling terms as well as for the nuclear (wavepacket) motion; a distinction is made regarding the different treatments (i.e., harmonic vs. anharmonic) of the

N–H stretching mode ν_{24} . Finally, Sec. IV summarizes and concludes.

II. THEORETICAL AND COMPUTATIONAL FRAMEWORK

A. The Hamiltonian

In the present work, we are dealing with five singlet electronic states of pyrrole (the ground state and the four lowest valence-excited singlet states), which play a central role in the photoinduced dynamics.^{2,4-7,9,20,21} The latter states lie in the energy range from 5–7 eV above the electronic ground state. The symmetry assignments of these singlet states (in the C_{2v} molecular point group), and their energies at the ground state equilibrium geometry are given in Table I, to be discussed further below.

The 24 vibrational modes of pyrrole consist of 17 planar and 7 out-of-plane modes which belong to the following symmetry species:

$$\Gamma_{vib} = 9A_1 + 3A_2 + 4B_1 + 8B_2. \quad (1)$$

1. The multi-mode vibronic coupling approach

The conceptual framework adopted in the present study is the well-established multi-mode vibronic coupling (MMVC) approach.^{17,24,25} It relies on the use of a diabatic electronic basis (see, for example, Ref. 26) in which the interaction between different electronic states arises from the potential, rather than the nuclear kinetic energy (at least to a sufficiently good approximation). The potential energy matrix is decomposed into the potential energy $V_0(\mathbf{Q})$ of the initial electronic state, taken to be harmonic, plus an interaction term $\mathbf{W}(\mathbf{Q})$, and the latter is expanded in a Taylor series in the ground state dimensionless normal coordinates Q_i . Adopting also the harmonic form of the ground state nuclear kinetic energy T_N we have

$$H = (T_N + V_0(\mathbf{Q}))\mathbf{1} + \mathbf{W}(\mathbf{Q}), \quad (2)$$

$$T_N = -\frac{1}{2} \sum_i \hbar \omega_i \frac{\partial^2}{\partial Q_i^2}, \quad (3)$$

$$V_0 = \frac{1}{2} \sum_i \hbar \omega_i Q_i^2, \quad (4)$$

where the matrix elements of $\mathbf{W}(\mathbf{Q})$ are written as

$$W_{\alpha\alpha}(\mathbf{Q}) = E_\alpha + \sum_i \kappa_i^\alpha Q_i + \sum_{ij} g_{ij}^{(\alpha)} Q_i Q_j + \cdots \quad (5)$$

and

$$W_{\alpha\beta}(\mathbf{Q}) = \sum_i \lambda_i^{(\alpha\beta)} Q_i + \cdots \quad (\alpha \neq \beta). \quad (6)$$

The quantity $\mathbf{1}$ in Eq. (2) denotes the 5×5 unit matrix (for five electronic states under consideration). The energies E_α which appear in the diagonal elements $W_{\alpha\alpha}$ have the meaning of vertical excitation energies, referring to the center of the Franck-Condon (FC) zone, $\mathbf{Q} = \mathbf{0}$ (boldface denotes the vector of all coordinates). Because we take the diabatic and adiabatic basis states to coincide at this geometry, the E_α have no counterpart in the off-diagonal elements of Eq. (6). The quantities $\kappa_i^{(\alpha)}$ and $\lambda_i^{(\alpha\beta)}$ are referred to as first-order *intrastate* and *interstate* electron-vibrational coupling constants, respectively. The second-order intrastate coupling constants $g_{ii}^{(\alpha)}$ account for frequency changes upon the electronic transition, while the $g_{ij}^{(\alpha)}$ (for $i \neq j$) are responsible for the so-called Duschinsky rotation²⁷ of the normal modes in

the excited state. Explicit expressions for these quantities read as follows:

$$\kappa_i^{(\alpha)} = \frac{\partial \Delta V_\alpha(\mathbf{Q})}{\partial Q_i} \big|_{\mathbf{Q}=\mathbf{0}}, \quad (7)$$

$$g_{ii}^{(\alpha)} = \frac{\partial^2 \Delta V_\alpha(\mathbf{Q})}{2 \partial Q_i^2} \big|_{\mathbf{Q}=\mathbf{0}}, \quad (8)$$

$$\lambda_i^{(\alpha\beta)} = \sqrt{\frac{1}{8} \frac{\partial^2 (V_\alpha - V_\beta)^2}{\partial Q_i^2}} \big|_{\mathbf{Q}=\mathbf{0}}. \quad (9)$$

Here, V_α and V_β are the adiabatic potential energy surfaces and $\Delta V_\alpha = V_\alpha - V_0$. Truncating the series after the first-order terms defines the *linear vibronic coupling* model (LVC), while including second-order terms leads to the – as a shorthand notation – *quadratic vibronic coupling* model (QVC), and so forth.

Since pertinent aspects of the vibronic coupling scheme have been amply discussed in the literature, we refer to these publications for more details.^{17,24,25} Here we only emphasize the importance of symmetry selection rules which impose restrictions on the modes which appear in the various summations of Eqs. (5) and (6). These are relevant, in particular, for the linear coupling terms, for which they read

$$\Gamma_\alpha \otimes \Gamma_i \otimes \Gamma_\beta \supset \Gamma_A. \quad (10)$$

Explicitly, a given vibrational mode with symmetry Γ_i can couple electronic states with symmetries Γ_α and Γ_β in first order only if the direct product on the left-hand side of Eq. (10) comprises the totally symmetric irreducible representation Γ_A of the point group in question. The generalization to the second-order terms should be apparent, though it is less restrictive.

2. Anharmonic treatment of N–H stretching mode

In view of the importance of N–H photodissociation in UV excited pyrrole, the MMVC model PES cannot be expected to even qualitatively describe the N–H stretching potential curves. This corresponds to the normal coordinate Q_{24} in our nomenclature, and for this mode proper (dissociative) PECs are to be used. The resulting 5×5 Hamiltonian matrix is written as follows:

$$\mathbf{H} = (T_N + V_0) \mathbf{1} + \mathbf{W}, \quad (11)$$

$$\mathbf{W} = \begin{pmatrix} W_0 & \lambda_{4/7}^{(0,1)} Q_{4/7} & \lambda_6^{(0,2)} Q_6 & 0 & 0 \\ \lambda_{4/7}^{(0,1)} Q_{4/7} & W_1 & \lambda_{8,14,17}^{(1,2)} Q_{8,14,17} & \lambda_{4/7}^{(1,3)} Q_{4/7} & 0 \\ \lambda_6^{(0,2)} Q_6 & \lambda_{8,14,17}^{(1,2)} Q_{8,14,17} & W_2 & \lambda_3^{(2,3)} Q_3 & \lambda_{4/7}^{(2,4)} Q_{4/7} \\ 0 & \lambda_{4/7}^{(1,3)} Q_{4/7} & \lambda_3^{(2,3)} Q_3 & W_3 & \lambda_{8,14,17}^{(3,4)} Q_{8,14,17} \\ 0 & 0 & \lambda_{4/7}^{(2,4)} Q_{4/7} & \lambda_{8,14,17}^{(3,4)} Q_{8,14,17} & W_4 \end{pmatrix}$$

with

$$W_0 = V_0(Q_{24}), \quad (12)$$

$$W_1 = V_1(Q_{24}) + \kappa^{(1)}\mathbf{Q} + \mathbf{g}^{(1)}\mathbf{Q}^2, \quad (13)$$

$$W_2 = V_2(Q_{24}) + \kappa^{(2)}\mathbf{Q} + \mathbf{g}^{(2)}\mathbf{Q}^2, \quad (14)$$

$$W_3 = V_3(Q_{24}) + \kappa^{(3)}\mathbf{Q} + \mathbf{g}^{(3)}\mathbf{Q}^2, \quad (15)$$

$$W_4 = V_4(Q_{24}) + \kappa^{(4)}\mathbf{Q} + \mathbf{g}^{(4)}\mathbf{Q}^2, \quad (16)$$

and

$$\kappa_{\Gamma_i}^{(\alpha)}\mathbf{Q} = \sum_{i \in A_1} \kappa_i^{(\alpha)} Q_i, \quad \mathbf{g}^{(\alpha)}\mathbf{Q}^2 = \sum_{i \in *} g_{ii}^{(\alpha)} Q_i^2, \quad \alpha = 1, 2, 3, 4. \quad (17)$$

The anharmonic PECs $V_\alpha(Q_{24})$ appearing in the diagonal elements are specified below, and the harmonic part of mode 24 is to be dropped in the earlier Eqs. (4) and (5). The off-diagonal elements of the Hamiltonian, Eq. (11) all follow from the selection rule (10) and the symmetries of the electronic states and vibrational modes given in Tables I and II below. The coupling modes of A_2 symmetry, ν_4 and ν_7 have been combined into an effective mode with frequency and coupling constant given in the last row of Table II. The summation in the first part of Eq. (17) is over all totally symmetric modes, that in the second part comprises all modes (for restrictions see the specification of the * below).

The dissociative PECs for mode Q_{24} are constructed as suitable linear combinations of Morse potentials plus Lorentzian and Gaussian type functions to account for corresponding features already documented in the literature.^{9,10} We parametrize them as follows:

$$V(Q_{24}) = D_0(1 - \exp(-a(Q_{24} - Q_0)))^2 + E_0. \quad (18)$$

For the S_1 and S_2 states the functions to be added are cast in the following form:

$$\Delta V_L(Q_{24}) = \frac{d}{1 + (Q_{24} - e)^2/f}, \quad (19)$$

$$\Delta V_G(Q_{24}) = d \exp(-e(Q_{24} - f)^2). \quad (20)$$

To reveal the influence of anharmonicity of mode 24 on the internal conversion processes in pyrrole, companion calculations have also been performed where it is suppressed, i.e., the pure MMVC approach is applied to all vibrational modes.

B. Electronic structure calculations

In order to reliably determine the various system parameters entering the Hamiltonian, Eqs. (4), (5), and (6), multiref-

TABLE II. Vibrational frequencies and linear coupling constants of pyrrole, all quantities in eV.

		Freq.	$A_1(S_0)$	$A_2(\pi\sigma^*)$	$B_1(\pi\sigma^*)$	$A_1(\pi\pi^*)$	$B_2(\pi\pi^*)$
A_1	ν_9^*	0.1143	0.0000	0.0692	-0.0884	-0.0452	0.0616
	ν_{10}	0.1298	0.0000	0.0016	-0.0998	-0.0154	0.1160
	ν_{12}^*	0.1389	0.0000	0.1720	-0.0595	-0.0256	0.0683
	ν_{13}^*	0.1495	0.0000	0.0156	0.0710	0.2282	0.1301
	ν_{16}	0.1826	0.0000	-0.1668	0.0628	-0.1011	-0.2035
	ν_{18}^*	0.1929	0.0000	0.1358	-0.0021	0.1488	0.1034
	ν_{21}	0.4060	0.0000	0.0119	-0.0103	-0.0257	-0.0107
	ν_{23}	0.4140	0.0000	-0.0015	0.0105	0.0714	0.0353
	ν_{24}^*	0.4885	0.0000	0.1726	0.2057	-0.0067	-0.0326
			$S_0 - S_4$	$S_1 - S_2$	$S_3 - S_4$		
B_2	ν_8^*	0.1128	0.1484	0.0986		0.0343	
	ν_{11}	0.1351	0.0036	0.0594		0.0173	
	ν_{14}^*	0.1498	0.1990	0.1654		0.0835	
	ν_{15}	0.1666	0.3110	0.0933		0.0501	
	ν_{17}^*	0.1897	0.5658	0.1903		0.0668	
	ν_{19}	0.2022	0.3719	0.1084		0.0199	
	ν_{20}	0.3926	0.1237	0.0301		0.0249	
	ν_{22}	0.4110	0.0872	0.0394		0.0144	
			$S_0 - S_2$	$S_2 - S_3$	$S_1 - S_4$		
	ν_1	0.0549	0.0000	0.0948		0.2685	
B_1	ν_3^*	0.0805	0.0000	0.0376		0.1038	
	ν_5	0.0917	0.0000	0.0183		0.0883	
	ν_6^a	0.1028	0.0630	0.0107		0.1119	
			$S_0 - S_1$	$S_1 - S_3$	$S_2 - S_4$		
A_2	ν_2	0.0782	0.0000	0.0376		0.0144	
	ν_4	0.0838	0.2345	0.0900		0.0494	
	ν_7	0.1051	0.1299	0.0720		0.0400	
	$\nu_{4/7}^*$	0.0895	0.0701 ^b	0.0812		0.0425	

^aReplacing mode ν_3 in some calculations (see text).

^bAdopted from Ref. 9.

erence configuration interaction (MRCI) and complete active space self-consistent field (CASSCF) calculations have been performed. The CAS space comprised six π electrons in five orbitals (two π orbitals, two π^* orbitals and one Rydberg 3s orbital). This space will be conventionally designated as CAS(6,5) in the text. State averaging was performed over five singlet states with equal weights (ground state, two valence $\pi - \pi^*$ states and two Rydberg π -3s states), which will be denoted as SA-5. MRCI calculations were carried out based on the orbitals computed by the SA-5-CASSCF(6,5) wave function. The reference configurations for the MRCI were constructed within the CAS(4,4) and additional auxiliary Rydberg orbital by allowing single and double excitations from the two π orbitals into the two π^* orbitals. Only single excitations were allowed into the auxiliary Rydberg 3s orbital. The final configuration space was constructed by allowing all single and double excitations from the reference configurations into the virtual orbital space (MR-CISD). All core electrons and the lowest four additional orbitals were frozen in the MRCI calculations and the interacting space restriction²⁸ was applied. The basis set was composed of aug'-cc-pVDZ type²⁹ on the nitrogen and carbon atoms (the prime indicates that d-aug functions were removed). On the hydrogen atom connected to nitrogen, the cc-pVDZ basis set was used, whereas for the remaining hydrogen atoms the

cc'-pVDZ basis set was employed (the prime signifies that p-functions were deleted). This hybrid basis set will be denoted as BS. All energy calculations and geometry optimizations were performed by using analytical gradient and non-adiabatic coupling procedures described in References.³⁰⁻³⁴ For vertical excitation energy calculations, the Davidson correction (+Q)^{31,35,36} was used in order to describe higher order excitation effects. All CASSCF and MR-CISD+Q calculations were performed with the COLUMBUS (Refs. 37–39) program package. The atomic orbital (AO) integrals and AO gradient integrals have been calculated with program modules taken from DALTON.⁴⁰

Within this framework, first a geometry optimization is carried out, followed by a frequency calculation. This gives the S_0 structural parameters, the harmonic vibrational frequencies entering Eqs. (3) and (4) as well as the (dimensionless, see above) normal coordinates Q_i for all the vibrational modes of pyrrole. The optimized S_0 structural parameters are given in Table S1 (supplementary material⁴¹). Our computed ground state equilibrium geometry agrees well with available experimental data⁴² as well as high level density functional theory (DFT) calculations,⁴³ the typical (maximum) deviation from experiment being 0.005 Å (0.014 Å) for the bond lengths and 0.2° (0.4°) for the bond angles. The frequencies are collected in Table II, to be discussed below.

Given normal coordinate displacements Q_i from the *ab initio* calculations, the various first and second-order coupling constants entering Eqs. (5) and (6) are obtained formally through the relations (7), (8), and (9). In practice it is sometimes advantageous to use a suitable set of typically 5–7 displacements for a given mode, and compare the LVC (or LVC + QVC) model predictions with the *ab initio* results for the individual displacements. This allows one to deduce information on the quality of the coupling model adopted. The coupling constants are then determined by a least-squares fit of the model PES to the results of the *ab initio* computation. Generally the MMVC model is found to work satisfactorily well, as is deduced from a by-eye inspection of the fitted PECs in comparison to the *ab initio* data points (see, for example, Fig. S1⁴¹). An exception is given by the N–H stretching mode Q_{24} . Here the N–H dissociation, being a key feature of the nonadiabatic photodynamics of pyrrole, can apparently not be captured by the MMVC model PES. The model is still of use for describing the intramolecular relaxation preceding the photodissociation, and corresponding results will be reported below. Nevertheless, they will be complemented by computations where anharmonic, dissociative PECs for mode Q_{24} are employed as already indicated above and further detailed below.

C. Quantum dynamical calculations

The dynamical calculations performed in this work rely on fully quantal, time-dependent methods, namely wavepacket propagation techniques. For the applications of the MMVC scheme the multiconfiguration time-dependent Hartree (MCTDH) method is a highly powerful, nearly ideally suited tool to integrate the time-dependent Schrödinger

equation, and is therefore used in this work. The MCTDH method^{44–49} uses a time development of the wavefunction expanded in a basis of sets of variationally optimized time-dependent functions called single-particle functions (SPFs). The MCTDH equations of motion are obtained from the Dirac-Frenkel variational principle. By virtue of this optimization the length of this expansion can be much smaller than in standard integration schemes (so-called MCTDH contraction effect). The efficiency is even enhanced by two important additional features: each of the coordinates used in the integration scheme can comprise several physical coordinates Q_i . Furthermore, for vibronically coupled systems the wave function is written as a sum of several wavefunctions – one for each electronic state

$$\Psi(t) = \sum_{\alpha}^{n_s} \Psi_{\alpha}(t) |\alpha\rangle \quad (21)$$

(here n_s is the number of electronic states). The SPFs may then be optimized separately for each electronic state, and therefore fewer coefficients are needed in the wavefunction expansion. Both choices are employed in this work and, in combination, lead to an MCTDH contraction effect of about 6 orders of magnitude in typical applications.

We emphasize that the form, Eqs. (5) and (6), of the MMVC Hamiltonian represents a sum of low-order products of the Q_i which is exactly the form that makes the application of the MCTDH algorithm efficient.

Given the time-dependent wavepacket (21) various time-dependent and time-independent quantities can be computed directly or indirectly. Two quantities easily extracted from $\Psi(t)$ are the electronic populations, $P_{\alpha}(t)$, and reduced densities $\rho_{\alpha}(Q_i, t)$ for the electronic state α :

$$P_{\alpha}(t) = \langle \Psi_{\alpha}(t) | \Psi_{\alpha}(t) \rangle, \quad (22)$$

$$\rho_{\alpha}(Q_i, t) = \int \Psi_{\alpha}^*(t) \Psi_{\alpha}(t) \prod_{l \neq i} dQ_l. \quad (23)$$

From the definition of the Hamiltonian (2), the populations refer to *diabatic* electronic states. Adiabatic populations have also been obtained, for two-state⁵⁰ and three-state situations,⁵¹ but are not considered in the present work.

The form of the anharmonic potentials for Q_{24} leads to N–H photodissociation in the $S_0 - S_2$ electronic states. To avoid the need for asymptotically large grids due to the large N–H distances occurring, we add a complex absorbing potential (CAP) V_c to the real potentials of Eqs. (18), (19), and (20). The CAP takes the form^{52–54}

$$V_c = -i\eta(Q_{24} - Q_c)^3 \theta(Q_{24} - Q_c). \quad (24)$$

With suitably chosen parameters the CAP absorbs that part of the wave-packet which enters the asymptotic regime where dissociation occurs and the interaction between the departing particle (here the hydrogen atom) and the residual fragment (the pyrrolyl radical) vanishes.^{52–54} Through the Heaviside step function it is “activated” beyond a threshold (i.e., sufficiently large) value Q_c of Q_{24} and extends until

the grid edge, specified below. The strength parameter η and threshold Q_c are to be chosen so as to minimize reflections from and transmission through the CAP.⁵⁴ Typically a second-order or third-order power is chosen for the functional dependence on the coordinate,⁴⁶ as done also here.

For describing the N–H photodissociation, especially the branching ratios between the various channels (see below), the reactive flux into the asymptotic regions of large N–H distances is to be determined. Often a dividing surface is introduced and the reactive flux determined as time-integral over the nuclear momentum orthogonal to this surface (see, for example, Refs. 55–57). An alternative is provided by exploiting the CAP introduced above. It has been shown that the time-accumulated flux can also be determined from the expectation value of the CAP.⁵⁸ By distinguishing between the CAPs in separate channels and analyzing the flux accordingly, also branching ratios can be obtained in a straightforward fashion (see, for example, Sec. 8.6 of Ref. 46). This procedure is followed in the present work. It is implemented in the Heidelberg MCTDH program package⁴⁹ which has been utilized for all dynamical calculations.

III. RESULTS AND DISCUSSION

All the results presented below rely on the vertical excitation energies of Table I (present work), where they are also compared with available literature data. In case of the lowest excited state S_1 , vertical energies are in a good accord with the exception of the value obtained by Vallet⁹ which is ca 0.7 eV lower than the present computational result. The same situation is found for the second lowest excited state S_2 where the value obtained by Vallet is ca. 0.8 eV lower than the current result.⁹ In the case of the valence $\pi - \pi^*$ excited states, the results are also quite similar, with the exception of the CASPT2 results obtained by Roos *et al.*,⁴ which are lower by ca. 1 eV than the MRCI results. However, it is known that the CASPT2 computational method might underestimate this transition energy as compared to other computational approaches such as MRCI,² EOM-CCSD,⁷ CC3,⁵ and TDDFT.⁵⁹ There is also good agreement of the present results with experimental data for the two $\pi - \sigma^*$ states, while our energies for the two $\pi - \pi^*$ states may be too high.

A. Potential energy surfaces and conical intersections within the MMVC scheme

In Tables II and S2 (Ref. 41), we present the results for the linear and quadratic MRCI+Q coupling constants for all vibrational modes of pyrrole in the $S_0 - S_4$ electronic states. The data have been obtained at the MRCI as well as MRCI+Q level, but for brevity only the MRCI+Q data are given. Among the linear coupling constants for non-totally symmetric modes those have been omitted which couple states with high-energy crossing seams (see below); the latter renders the interaction between these states insignificant so that the couplings are suppressed. The quadratic coupling constants comprise *all* terms that are diagonal in the vibrational modes (i.e., only the Duschinsky effect is neglected here). This extends earlier applications of the MMVC coupling scheme to multi-

FIG. 1. Representative cut through the PES of the $S_1 - S_4$ states of pyrrole. The effective coordinate connects the center of the Franck-Condon zone to the minimum of the intersections seam between the S_1 and S_2 states.

state systems, where (diagonal) quadratic coupling terms have been included usually for totally symmetric modes only. Altogether, 177 coupling constants are collected in the tables. Given that the same analysis has also been performed at the MRCI level, more than 350 coupling constants have been computed.

The sets of coupling constants and the Hamiltonian, Eqs. (2), (5), and (6) define the high dimensional potential energy surfaces of the lowest five electronic states of pyrrole. A representative cut through the $S_1 - S_4$ potential energy surfaces is presented in Fig. 1. The curves represent the potential energies along a straight line from the origin $\mathbf{Q} = \mathbf{0}$ to the minimum energy of intersection between the S_1 and S_2 electronic states within C_{2v} symmetry. All quadratic coupling constants are included in the analysis (as outlined in the appendix of Ref. 60). The value of the effective (totally symmetric) coordinate Q_{eff} denotes the distance from the origin $\mathbf{Q} = \mathbf{0}$ (center of FC zone) along this line. Figure 1 shows a whole set of interstate curve crossings which interconnect *all four* lowest excited states. These all represent a point on a seam of conical intersections and are expected to give rise to a rich vibronic dynamics which will be explored in Secs. III B–III D. These wavepacket dynamical calculations will indeed demonstrate that all four excited states are strongly coupled and the electronic population exchange between them takes place on a femtosecond time scale.

The curve crossings other than the $S_1 - S_2$ crossing do not occur at their minimal energy in the figure since the same “cut” (effective coordinate) is used in the drawing for all electronic states. The information of Fig. 1 is therefore complemented by Table III, which contains a more systematic compilation of the minimum energy data for all excited electronic states within the QVC scheme. The diagonal entries refer to the diabatic minima of the various potential energy surfaces, and the off-diagonal values are minima of the corresponding intersection seams. The diabatic minima can be determined within C_{2v} symmetry, that is, considering only totally symmetric modes. Contrary to the figure, the seam minima are all optimized separately, again utilizing expressions given in the

TABLE III. Seam minima of pyrrole for all modes (MRCI+Q data, all values in eV).

	S_1	S_2	S_3	S_4
S_1	5.05	6.00	6.71	8.59
S_2		5.95	6.29	6.48
S_3			6.28	6.48
S_4				6.48

appendix of Ref. 60. The table gives evidence that there are low-energy conical intersections between the PES of all excited states except for the S_1 and S_4 states of pyrrole. Therefore the corresponding couplings will be suppressed in the subsequent dynamical treatment (see lower right 4×4 coupling block of the Hamiltonian Eq. (11) for an explicit representation). The seam minima between the S_0 ground state and the various excited states turn out to be all high in energy within the MMVC scheme. The actual numbers are so large (well above 10 eV) that they are insignificant and suppressed in the table.

In a similar way, the coordinates at the energetic minima of the various crossing seams can be calculated⁶⁰) and are presented in Table S3.⁴¹ It is seen from the table that the high-energy $S_1 - S_4$ crossing indeed involves large displacements of the normal coordinates from the origin. The other displacements are moderate only ($Q_i = 0 \sim 2$) but go into different directions in normal coordinate space.

B. Dynamics within the MMVC scheme

We now address the quantum dynamical problem arising from photoexcitation from the S_0 ground state into the higher-energy singlet states, especially the strongly dipole-allowed S_4 state (see Table I). As indicated above, we first address the pure internal-conversion problem (ignoring the photoreaction) and employ the pure MMVC scheme for all modes (treating the PECs for mode 24 as harmonic, in order to also explore the importance of their anharmonicity on the internal conversion). The full dynamical problem defined by Tables II and S2 (Ref. 41) comprises 24 vibrational modes and excess energies of 6–7 eV. This is virtually impossible to solve even with the MCTDH formalism, not only by virtue of the rather large number of modes, but also the high excess energies involved. Fortunately, some of the vibrational modes turn out to be less important, as is evidenced by Table IV. Here some of the modes have been dropped when computing the minima of the various seams of conical intersections (see table caption). The various entries of the table reproduce the full calculation, i.e., retaining all modes, of Table III rather well. The modes included are characterized by an asterisk in Tables II and S2 (Ref. 41) and should thus represent a faithful

TABLE IV. Seam minima of pyrrole for all modes except ν_{10} , ν_{16} , ν_{21} , and ν_{23} (MRCI+Q data, all values in eV).

	S_1	S_2	S_3	S_4
S_1	5.11	6.19	6.75	9.77
S_2		6.00	6.34	6.73
S_3			6.32	6.70
S_4				6.63

FIG. 2. Time-dependent electronic populations within the MMVC scheme for the coupled $S_1 - S_4$ states of pyrrole, following a vertical excitation to the S_4 state. The upper (lower) panel displays the result obtained with (without) the quadratic couplings for the non-totally symmetric modes.

ful reduced-dimensionality description of the internal conversion processes in photoexcited pyrrole. Similarly, some of the non-totally symmetry modes can be dropped because of small coupling constants. This amounts to retaining three B_2 modes, one B_1 mode and one effective A_2 mode ($\nu_{4/7}$), as also indicated by asterisks in the tables. We are thus dealing with ten nonseparable vibrational modes which still represents a formidable numerical problem, but can be dealt with by means of the MCTDH wavepacket propagation scheme. The numbers of so-called primitive basis functions and time-dependent single-particle functions (SPFs) used in a typical propagation are collected below for the anharmonic treatment of mode 24. Also in the present case of the pure MMVC modelling, typically about 3 million SPFs are included in the propagation which is to be compared to about 10^{12} primitive basis function needed. The reduction in basis set size is thus about 10^6 (so-called MCTDH contraction effect) which renders the calculation numerically feasible.

The initial wave packet is defined by a vertical (FC-type) transition to the S_4 state, i.e., amounts to the ground vibrational level of S_0 (or, equivalently, V_0) lifted up vertically to the highest PES of the Hamiltonian (2). Following the procedures indicated above we arrive at the time-dependent (diabatic) electronic populations as presented in Fig. 2.

FIG. 3. Anharmonic potential energy curves for the $S_0 - S_4$ states of pyrrole along the N-H stretching mode normal coordinate Q_{24} . The open symbols represent the *ab initio* data points, the full lines the results of the analytic curves, fitted as described in the text.

The figure gives clear evidence of the ultrafast nonadiabatic dynamics on several intersecting PES of photoexcited pyrrole. The population of the initially excited B_2 state is seen to “decay” on a time-scale of around 20 fs, which is a typical stretching mode (high frequency) period of pyrrole. As found often for CoIn’s of multidimensional PES, the transition is virtually complete after a single encounter of the CoIn.^{17,50} Here the same phenomenon is confirmed also for multi-state situations such as in pyrrole. The electronic population is transferred first to the next lower electronic state, the $S_3(A_1)$ state of pyrrole. From there it undergoes a similar, though somewhat slower, two-step transition to the $S_1(A_2)$ state, while the intermediate $S_2(B_1)$ state remains populated rather weakly.

The two panels in the figure differ by the inclusion (or suppression) of the quadratic coupling constants for the non-totally symmetric modes. Since they are normally not considered in such multi-state computations, it seems useful to present such a comparison. It is worthwhile to note that they even reinforce the stepwise ultrafast population transfer (internal conversion processes) in electronically excited pyrrole.

Analogous results have been obtained for initial excitation to the $S_3(A_1)$ state of pyrrole. This represents the lower of the two $\pi - \pi^*$ excitations which has a much smaller oscillator strength than the higher one, but is still the second most intense in the energy range considered, see Table I. The results are not shown here for the sake of brevity, but given in Fig. S2.⁴¹ They indicate that the electronic population transfer is system-specific and not so much dependent on the initial preparation of the wave-packet. A number of further companion calculations have also been performed where a few vibrational modes have been replaced by others, not included in the calculations for Fig. 2, e.g., ν_8 by ν_{10} and ν_3 by ν_6 . The effect on the electronic populations is quite moderate, which we take as indication that the current choice of vibrational modes

is a reliable one. The results of these further calculations are also not shown here for the sake of brevity.

Although not the first in the literature, these findings are considered benchmark results for multi-state nonadiabatic quantum dynamics, at least for closed-shell molecules. They complement the few available comparable results and extend them, as stated above, by the more systematic treatment of the quadratic coupling terms. For the specific case of pyrrole, they provide an efficient mechanism for populating the nearly or rigorously (in C_{2v} symmetry) dipole-forbidden S_1 and S_2 excited states. These are often assumed from the outset to be the initial states in wave-packet dynamical investigations. The present results provide a rationale for such an assumption.

C. Anharmonic treatment of mode 24

In order to be able to treat also the N-H photodissociation of pyrrole, an anharmonic treatment of mode 24 is required. We emphasize that the full MMVC PES are anharmonic whenever coupling modes are displaced. However, for displacements along a totally symmetric mode alone, such as ν_{24} , they are harmonic which is apparently inappropriate to describe the photochemical transformation. An adequate parametrization is achieved utilizing expressions (18), (19), (20), and the parameters are determined by a least-squares fit of these analytical expressions to the *ab initio* computed energies. This leads to the numerical values collected in Table VI, and to the PECs presented in Fig. 3. For the PECs of the S_0 , S_3 and S_4 states the simple Morse expression works well, whereas for the S_1 (S_2) state PECs the Lorentzian (Gaussian) function is to be added according to Eq. (19) (Eq. (20)). (This is found to provide a distinctly better representation of the N-H stretching potentials than the opposite choice.)

The quality of the fit can be judged by inspecting Fig. 3 which shows the individual energies as discrete symbols

TABLE V. Number of basis functions for the primitive as well as the time-dependent (SPF) basis used in the MCTDH calculations for the $S_0 - S_4$ electronic states of pyrrole. For mode 24, the primitive basis refers to an FFT treatment (grid), otherwise to harmonic oscillator basis functions.

Modes	Primitive basis	SPF basis
($\nu_9, \nu_{12}, \nu_{13}$)	(19, 20, 20)	[23, 30, 35, 21, 21]
(ν_{18}, ν_{24})	(20, 128)	[23, 26, 33, 21, 21]
($\nu_8, \nu_{14}, \nu_{17}$)	(23, 20, 20)	[31, 42, 38, 30, 30]
($\nu_3, \nu_{4/7}$)	(18, 18)	[29, 35, 30, 28, 28]

along with the fitted curves (full lines). It is seen to be very satisfactory for our purposes. However, high level *ab initio* calculations of the potential energy surfaces of pyrrole¹⁰ reveal that the S_0 dissociation energy is around 5.6 eV, which is by ca. 1 eV lower than the present fitted value of 6.55 eV. The quantitative agreement with the S_0 dissociation energy is therefore not perfect and the reason behind this can be that MRCI instead of MRCI+Q values were used. In the same work, S_1 and S_2 dissociation energies were also found to be slightly below the S_0 value (around 5 eV) and qualitative agreement for the S_1 and S_2 states was obtained. A comparison with experimental results reveals that the dissociation energy of the N–H bond of pyrrole is around 32500 cm⁻¹ or 4 eV.¹³ *Ab initio* calculations with single reference methods, such as the G2 method,⁶¹ yield a value of 4.1 eV. Therefore, the present S_0 dissociation energy seems to be somewhat too high if it is compared with the MRCI+Q *ab initio* results and quite high as compared to the experimental value. Due to the facts presented above, the two data points for $Q_{24} = 6, 7$ have been omitted when fitting the PEC for the S_0 state, because the present MRCI treatment is not adapted to treat large N–H distances accurately.

To solve the dynamical problem thus defined, we again employ the MCTDH formalism, but replace the underlying HO basis functions for the harmonic mode 24 by a fast Fourier transformation (FFT) treatment with 128 equidistant grid points ranging from $Q_{24} = -4$ to $+30$. The full MCTDH basis set details are collected in Table V. The numbers confirm viz. make more precise the aforementioned contraction effect of $\sim 10^6$. To avoid artificial effects from the grid boundary we employ a CAP as described in Sec. II C. It is activated at $Q_c = 17$ (see also Fig. 3). By choosing $\eta = 3 \cdot 10^{-4}$ eV for the S_0 state and $8 \cdot 10^{-4}$ eV for the S_1 and S_2 states, it has been ensured that the summed transmission and reflection probabilities remain below $10^{-3} - 10^{-4}$ which is sufficiently small

TABLE VI. Parameters for potential energy curve for mode 24 according to Eqs. (18), (19), and (20). For the S_1 state, the quantities d, e and f refer to Eq. (19), for the S_2 state they refer to Eq. (20).

	D_0	a	Q_0	d	e	f	E_0
S_0	6.549	0.194	0.001	...	...	...	0.000
S_1	8.394	0.601	-1.812	10.537	-2.198	4.617	-3.518
S_2	0.009	0.415	4.785	0.489	0.157	2.874	5.643
S_3	7.443	0.184	0.0275	...	...	...	6.546
S_4	4.277	0.236	-0.001	...	...	...	6.748

FIG. 4. Time-dependent electronic populations (upper panel) and reactive flux (lower panel) for the coupled $S_0 - S_4$ states of pyrrole, following a vertical excitation to the S_4 state. In the lower panel the left hand scale refers to the $A_1(S_0)$ state (see the arrow), the right hand scale to the $A_2(S_1)$ and $B_1(S_2)$ states. The reactive flux for N–H dissociation occurs for the $S_0 - S_2$ states only, owing to the PECs along Q_{24} , see Fig. 3.

for our purposes. Finally, in all calculations in this section, the quadratic coupling terms (see Eq. (17)) are included for totally symmetric as well as non-totally symmetric vibrational modes.

The result of the dynamic calculation is depicted in Fig. 4. for the system being initially excited to the $S_4(B_2)$ state. The upper panel presents the relative electronic populations, that is, the populations divided by their sum (= squared norm of the time-dependent wave function). The latter quantity is displayed in the inset to the panel. It decreases from the initial value of unity due to the effect of the CAP, and can be viewed as the survival probability of the parent system (pyrrole) before dissociation takes place. The difference to unity represents the cumulative reactive flux which is decomposed in the lower panel into the three different channels corresponding to the three different PECs (those of the S_0 , S_1 and S_2 states) on which dissociation may take place. It is seen that the dissociation is not quite complete after the 200 fs propagation time considered in the calculation. It is thus slower than in the earlier study of Ref. 9 where the process was found essentially complete after ~ 100 fs. We attribute this difference to the different, higher-energy initial state in the present study.

FIG. 5. Time-dependent electronic populations (upper panel) and reactive flux (lower panel) for the coupled $S_0 - S_4$ states of pyrrole, following a vertical excitation to the S_4 state. The B_1 mode ν_3 has been replaced by ν_6 , thus allowing for $S_0 - S_2$ coupling in the calculation (see Eq. (11)). In the lower panel the left hand scale refers to the $A_1(S_0)$ state (see the arrow), the right hand scale to the $A_2(S_1)$ and $B_1(S_2)$ states. The reactive flux for N–H dissociation occurs for the $S_0 - S_2$ states only, owing to the PECs along Q_{24} , see Fig. 3.

Due to the restriction to a single B_1 mode, ν_3 (motivated by its importance for the internal conversion process according to Table II) the $S_0 - S_2(\pi - \sigma^*)$ coupling element in Eq. (11) is suppressed. The large computational effort involved in the wave packet propagation makes the additional inclusion of ν_6 very cumbersome, if not impossible. We have therefore decided to replace the B_1 mode ν_3 by ν_6 and thus include the aforementioned coupling between the second $\pi - \sigma^*$ and the S_0 state in the computation. The results are presented in Fig. 5. Compared to Fig. 4, the population of the $A_1(\pi - \pi^*)$ state increases, while that of the $B_1(\pi - \sigma^*)$ state decreases now. This is due to the smaller interaction between these states because of the interchange of the two modes (see Table II, column with $S_2 - S_3$ coupling constants). Therefore less population is transferred from the prior populated, higher energy (S_3) state to the lower one. Also, the reactive flux into the S_0 state increases considerably, as becomes apparent when comparing the lower panels. This seems plausible, since an additional coupling to the S_0 state exists when including mode ν_6 . On the other hand, the electronic popula-

tions are hardly affected, see the upper panels of both figures. The additional coupling specifically affects the reactive flux, which may be due to the higher energy of the $S_0 - B_1(\pi - \sigma^*)$ CoIn compared to that of the $S_0 - A_2(\pi - \sigma^*)$ CoIn in Fig. 3.

Finally, in Fig. 6 we present snapshots of the nuclear density along the N–H stretching coordinate Q_{24} . They are obtained by including the coupling mode ν_6 as in Fig. 5. The colour code adopted for the densities is the same as for the electronic populations in the previous figures. In line with those, the density for the $S_3(A_1)$ state (pink lines) exceeds that for the $S_4(B_2)$ state (light blue lines) already for 18 fs. The former dominates in the panels, except for $t = 72$ fs (see Fig. 5). Here the $A_2(\pi - \sigma^*)$ state has maximum population, which is caused by the long “tails” (for large positive values of Q_{24}) in the densities which develop in the two $\pi - \sigma^*$ states starting at around 36 fs. This is apparently due to the dissociative PECs of these states and, for $t = 72$ fs, becomes visible also for the S_0 ground state. It is noteworthy that the S_0 nuclear densities have nonvanishing contributions also for small values of Q_{24} , corresponding to the bound region near the minimum of the S_0 PEC. This was not observed in earlier wave-packet calculations with fewer vibrational modes and electronic states.⁹ It seems intriguing in view of the appearance of slow H atoms in pyrrole photodissociation, to be further discussed below.

D. Comparison with experiment

The present, extensive quantum-dynamical computations allow for some useful, direct and indirect, conclusions about the many experimental findings,^{11–13,15,62–64} especially concerning the time scale and energy dependence of the photodissociation process.

The H atoms appearing as a consequence of the photodissociation of pyrrole are well known to consist of a slow and a fast component. The latter is associated with a time constant of ~ 100 fs, the former with ~ 1 ps.¹¹ The fast component is generally accepted to involve dissociation on the $\pi - \sigma^*$ states. The reactive flux we calculate for these two states (see Figs. (4) and (5)) indeed increases on a time scale of 100 fs and involves excess energies of 1–1.5 eV. This agrees nicely with experiment, and thus provides a microscopic picture for these observations (earlier similar results were based on surface hopping calculations and electronic populations only). The longer time scale (~ 1 ps) for the slow H atoms cannot be captured by the present (rather short) propagation times.

The branching ratio between slow and fast H atoms has been shown to increase with the energy of the primary excitation.¹² We can “mimic” this dependence by comparing results with the initial wave packet being located in the S_3 or S_4 state (both states differ by 0.2 eV excitation energy according to Table I; the additional results for the electronic populations and reactive fluxes are given in Figs. S3 and S4 (Ref. 41)). Furthermore we note that our dissociation energies of the lowest three states are somewhat high, by 0.2–0.5 eV (see also the discussion in Sec. III C above). We have slightly adjusted them, by decreasing the value of D_0 (to 6.0 eV, see

FIG. 6. Time-dependent wavepacket snapshots corresponding to the electronic populations presented in Fig. 5. Also the colour code adopted for the calculation is the same as in the earlier Figs. 4 and 5.

Table VI) and shifting down in energy the PECs of the two $\pi - \sigma^*$ states (by 0.2–0.3 eV). In combination with the two different initial states (S_3 and S_4) this gives rise to four different excess energies, which can moreover be compared between the calculations including ν_3 or ν_6 . The result of such a comparison is compiled in Fig. 7.

The figure shows indeed a substantial increase of the ratio for S_0 to $\pi - \sigma^*$ photodissociation (or equivalently: slow to fast H atoms) as a function of the excess energy (here relative to the S_0 asymptote). This reflects the trend observed experimentally,¹² but the absolute numbers are considerably too small. Often the occurrence of slow H atoms is attributed

to IVR processes (in combination with internal conversion) preceding photodissociation. This is not reflected in our calculations despite the rather large number of vibrational modes included. Possibly there are specific coupling mechanisms not included in our Hamiltonian framework, such as ring-puckering conical intersections,^{10,21} which are responsible for this phenomenon. These would be especially relevant also for N-methylpyrrole where the fast photoproducts are largely suppressed.^{13,63}

IV. SUMMARY AND CONCLUDING REMARKS

In this work we have performed an extensive *ab initio* MRCI as well as quantum wave-packet study of the multi-state and multi-mode nonadiabatic photodissociation in pyrrole. Five intersecting, strongly coupled PESs have been included in the analysis which extends earlier quantum dynamical investigations to higher energies and allows to include the (strongly) dipole-allowed $\pi - \pi^*$ transitions in a unified form in the analysis. Two lines of approach have been followed. In the first one, the pure MMVC treatment, the underlying *diabatic* PES are taken to be harmonic. This amounts to four strongly interacting states, the $S_1 - S_4$ singlet excited states. Benchmark calculations have been reported which provide a microscopic mechanism of populating the reactive S_1 and S_2 excited states of pyrrole. Ten nonseparable vibrational modes were included in the quantum dynamical treatment, which becomes possible by means of the MCTDH wave-packet propagation method. Secondly, this approach has been augmented by an anharmonic description of the two $(\pi\sigma^*)$ - S_0 PECs along the N–H stretching coordinate Q_{24} . This accounts for the low-energy conical intersections

FIG. 7. Estimated $S_0:(A_2(\pi\sigma^*)+B_1(\pi\sigma^*))$ branching ratios for pyrrole photodissociation as a function of S_0 excess energies; comparison of calculations with either ν_3 or ν_6 included.

between the $A_2(\pi\sigma^*)$ - S_0 and $B_1(\pi\sigma^*)$ - S_0 PESs and increases the strongly coupled electronic manifold from four to five singlet states. They have all been treated quantum dynamically in a unified way, and the description of the nonadiabatic N–H photodissociation thus been included in addition to the ultrafast internal conversion processes in pyrrole. In combination, these two aspects render the present study novel, with a wide range of applications also for other systems.

The dependence of the key dynamical features on the system parameters has been elucidated by a number of companion calculations with different modes and/or coupling constants retained. The experimental time constant for the production of fast H atoms (100 fs) has been well reproduced. To deduce quantitative information on the branching ratio of fast vs. slow H atoms requires the inclusion of further coupling mechanisms such as (presumably) the ring-puckering conical intersections. This, as well as the treatment of other photochemical reaction channels, is to be pursued in future work.

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