Simulation of the photodetachment spectrum of the pyrrolide anion
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This paper is dedicated to Professor Lorenz S. Cederbaum on the occasion of his 60th birthday.

Abstract

The photodetachment spectrum of the pyrrolide anion, C4H4N−, has been measured recently [A.J. Gianola, T. Ichino, R.L. Hoenigman, S. Kato, V.M. Bierbaum, W.C. Lineberger, J. Phys. Chem. A 108 (2004), 10326]. The band associated with the 12A2 ground state of the pyrrolyl radical, C4H3N, can be identified in the spectrum by its resolved vibrational progression. In contrast, the second band, belonging to the 12B1 first excited state of pyrrolyl, is very weak, broad, and unresolved, which suggests the presence of strong vibronic interaction effects. We have performed a theoretical study of the spectrum in the framework of the linear vibronic coupling model, using ab initio calculated parameters. It is shown that a 12B1→12A2 conical intersection is responsible for the unresolved part of the spectrum. The potential-energy surfaces of the 12A2 and 12B1 states of pyrrolyl as a function of the a1 and b2 ground state normal coordinates of pyrrolide have been computed with the MRCI/aug-cc-pVDZ method. Only the b2 modes can couple the involved electronic states in first order. Five totally symmetric modes (a1 symmetry) and four modes of b2 symmetry have been identified as the vibronically most active tuning and coupling vibrations, respectively. Model Hamiltonians for the description of the dynamics in the coupled vibronic manifold of the 12A2 and 12B1 states, including different subsets of these nine modes, have been constructed. The simulated spectra predict a 12A2 band with sharp peaks and a very diffuse 12B1 band stretching from 2.6 to 3.3 eV with a maximum close to 3.0 eV. The calculated spectra are in good agreement with experiment. Reasons for the unexpectedly low intensity of the 12B1 band such as an extremely short lifetime of 12B1 vibronic levels or very different photodetachment cross sections for the 12A2 and 12B1 states are discussed.

Keywords: Pyrrolide anion; Pyrrolyl radical; Vibronic coupling; Conical intersection; Photodetachment spectroscopy

1. Introduction

In recent years, the photochemical processes occurring in aromatic amino acids and nucleic bases have been of great interest because they are the most important building blocks of living beings [1–3]. In particular, pyrrole, C4H5N, and its derivatives have emerged as interesting prototype molecules for the exploration of photodetachment excited-state dynamics both from the point of view of experimental observations and theoretical calculations.

In many previous studies it has been clarified that UV absorption of these systems is followed by nonadiabatic transitions between excited electronic states and the electronic ground state that lead to ultrafast internal conversion. This mechanism can possibly explain an important property, the so called “photostability”, of the building blocks, which protects the living matter from dangerous photoreactions [1–3]. For pyrrole, it also has been found that the detachment of fast hydrogen atoms can be a result of the photoinduced dynamical processes, which lead to hydrogen and pyrrolyl radical, C4H4N [4–6]. Although there have been extensive investigations concerning the photoinduced dissociation of pyrrole [4–11], there is still quite limited information about its dissociation product, the pyrrolyl radical. Undoubtedly, knowledge of the prop-
erties of the pyrrolyl radical will provide us with a more complete picture of the photoinduced dynamics of pyrrole, but until now it is difficult to detect this radical directly in spectroscopic experiments.

In fact, the electronic structure of the pyrrolyl radical is a very interesting topic. The pyrrolyl radical can be considered as a prototypical system for the improvement of the understanding of the basic properties of aromatic heterocyclic radicals. It may be possible to extrapolate some of the results for this simple system to more complex radicals of biological relevance.

It is worthwhile to note that the pyrrolyl radical is iso-electronic with the furan radical cation. A detailed analysis of the vibronic coupling of the $1^2A_2$ and $1^2B_1$ electronic states of the latter species has been given by Trofimov et al. [12].

Recently, the 363.8 nm (3.408 eV) photodetachment spectrum of the pyrrole anion, $C_2H_4N^-$, has been measured [13]. This photodetachment spectrum provides direct information on the electronic structure of the pyrrolyl radical. The experimental spectrum displays remarkable differences between the transitions from the $1^1A_1$ ground state of the pyrrole anion to the $1^2A_2$ ground state and to the $1^2B_1$ first excited state of the pyrrolyl radical, respectively. The $1^2A_2$ band shows a partly resolved vibrational structure, which indicates that the $1^2A_2$ state is a bound state. The $1^2B_1$ band, on the other hand, could not be clearly identified in the experimental photodetachment spectrum [13]. The questions arising from this observation will be addressed in the present work.

Previous ab initio calculations have already confirmed that the potential-energy (PE) surfaces of these two states will cross each other to form a conical intersection in the vicinity of the Franck–Condon (FC) region [13]. The studies have qualitatively indicated that the strong vibronic coupling may lead to an ultrafast nonadiabatic transition from the $1^2B_1$ to $1^2A_2$ state and drastically shorten the lifetime of the $1^2B_1$ state, rendering the $1^2B_1$ spectrum structureless. These findings provide us with a starting point for the investigation of the electronic structure of the pyrrolyl radical.

The goal of the present paper is a quantitative simulation of the photodetachment spectrum of the pyrrole anion in order to improve the understanding of the different structure of these two bands. Multireference electronic structure calculations are performed to identify the relevant vibrational modes associated with this conical intersection. The electron-vibration coupling parameters are derived by a least-squares fitting procedure. The basic features of the $1^2A_2$ and $1^2B_1$ bands will be analyzed by the calculation of vibronic spectra within a time-independent framework.

2. Theoretical framework

2.1. Photodetachment

Photodetachment is the detachment of an electron from an anion by electromagnetic radiation. Our intention is to investigate the photodetachment from the pyrrolide anion, i.e., the photoelectric effect for $C_4H_4N^-$ ($\hbar = 1$ throughout):

$$C_4H_4N^- + h\nu \rightarrow C_4H_4N + e^- + E_k.$$  \hspace{1cm} (2.1)

$h\nu$ denotes the photon energy and $E_k$ the kinetic energy of the photoelectron $e^-$. The energy conservation law yields the electron binding energy $E = h\nu - E_k$. The threshold for photodetachment is the electron affinity $EA$, i.e., the difference of the ground state energy of the pyrrolyl radical, $C_4H_4N$, and the ground state energy of $C_4H_4N^-$. Thus the total energy range is

$$EA \leq E \leq h\nu.$$  \hspace{1cm} (2.2)

For $\nu = 3.408$ eV (corresponding to the wavelength $\lambda_0 = 363.8$ nm of the exciting laser used in the experiment [13]), detachment from the $1^1A_1$ ground state of pyrrole can lead to the $1^2A_2$ ground state and the $1^2B_1$ first excited state of pyrrolyl. Detachment leading to the $1^2A_1$ second excited state is not possible with this photon energy.

2.2. Hamiltonian

The vibronic coupling physics is treated in the diabatic electronic basis \{\phi_n(r, Q)\}_n=1,2 since this greatly simplifies the numerical calculations compared to a treatment in the adiabatic picture. Here $r$ denotes collectively the electronic coordinates and $Q$ the set of vibrational normal coordinates. $\phi_1$ corresponds to the $1^2A_2$ ground state and $\phi_2$ to the $1^2B_1$ first excited state of the pyrrolyl radical. Expanding \langle \phi_1(Q)|\hat{H}_{el}(Q)|\phi_2(Q)\rangle - \nu_0(Q)\delta_{mn} (\hat{H}_{el} being the electronic Hamiltonian) about $Q = 0$ up to first order leads to the approximate two-state multimode matrix Hamiltonian of linear vibronic coupling theory [14]:

$$\hat{H} = (\tilde{T}_N + \nu_0(Q))I_{12} + \left( \sum_n \kappa_n^{(1)}Q_n \sum_i \lambda_i Q_i - \sum_n \kappa_n^{(2)}Q_n \right),$$  \hspace{1cm} (2.3)

where

$$\tilde{T}_N = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial Q_i^2} - \frac{1}{2} \sum_c \frac{\partial^2}{\partial Q^2}$$  \hspace{1cm} (2.4)

is the nuclear kinetic energy operator and

$$\nu_0(Q) = \frac{1}{2} \sum_i \omega_i Q_i^2 + \frac{1}{2} \sum_c \omega_c Q_c^2$$  \hspace{1cm} (2.5)

the nuclear ground state potential of the pyrrole anion in the harmonic approximation. $Q_i$ denotes the dimensionless normal coordinate and $\omega_i$ the harmonic frequency of the $i$th vibrational mode. $\nu_0$ are the vertical detachment energies, $\kappa_n^{(n)}$ the first order intrastate and $\lambda_i$ the first order $1^2B_1$-$1^2A_2$ interstate electron-vibronic coupling constants. Due to symmetry considerations (see Section 2.3), the sums run only over either a set of coupling modes or a set of tuning modes, indicated by “$c$” and “$i$”, respectively. Coupling modes $v_c$ are those modes that couple
the two electronic states $1^2A_2$ and $1^2B_1$. Tuning modes $v_i$ are those that modulate the energy gap between the two states [14].

2.3. Symmetry

Eqs. (2.3)-(2.5) already contain the results of symmetry selection rules. $|\Phi_1\rangle = |1^2A_2\rangle$ and $|\Phi_2\rangle = |1^2B_1\rangle$ are two (non-degenerate) electronic states of different symmetry and the electronic Hamiltonian $\hat{H}_e$ is totally symmetric. Therefore, the zeroth order off-diagonal contributions in the Taylor expansion (2.3) vanish.

The ground state of the pyrrolide anion as well as the $1^2A_2$ and $1^2B_1$ states of pyrrolyl possess $C_2$ symmetry. $C_4H_4N$ has 21 internal degrees of freedom, which correspond to eight $a_1$, three $a_2$, three $b_1$, and seven $b_2$ vibrational modes (see also Table 2). Only the seven normal coordinates $Q_i (c = 12, \ldots, 18)$ transforming according to the $b_2$ irreducible representation of the $C_2$ point group are able to couple the $1^2A_2$ state with the $1^2B_1$ state in first order, since

$$\Gamma_1 \times \Gamma_{Q_2} \times \Gamma_2 = A_2 \times A_2 \times B_2 \times \Gamma_{Q_2} \supset A_1 \Rightarrow \Gamma_{Q_2} = b_2,$$

so that the linear $1^2B_1-1^2A_2$ interstate vibronic coupling constants [14]

$$\gamma_i^{(nm)} = \left. \frac{\partial}{\partial Q_i} \langle \Phi_n | \hat{H}_n | \Phi_m \rangle \right|_0 \equiv \left\{ \begin{array}{ll} \lambda_c & \text{if } \Gamma_{Q_2} = b_2 \\ 0 & \text{otherwise} \end{array} \right. $$

(2.7)

$$\left( \lambda^{(12)}_c \equiv \gamma^{(12)}_c = \lambda_c \right)$$

can take values different from zero. Similarly, the linear intrastate vibronic coupling coefficients [14]

$$\kappa_i^{(n)} = \left. \langle \Phi_n | \frac{\partial \hat{H}_n}{\partial Q_i} | \Phi_n \rangle \right|_0 \equiv \left\{ \begin{array}{ll} \kappa_c^{(n)} & \text{if } \Gamma_{Q_2} = a_1 \\ 0 & \text{otherwise} \end{array} \right. $$

(2.8)

can be nonzero only for the eight coordinates $Q_i (c = 12, \ldots, 8)$ of $a_1$ symmetry. In first order, only these 15 in-plane distortions have the potential to couple to the $1^1A_1 \rightarrow 1^1A_2$ and $1^1A_1 \rightarrow 1^1B_1$ photodetachment processes. In this approximation, the three $a_2$ and the three $b_1$ modes are not involved at all. Apart from symmetry, we will be able to neglect some more modes after an analysis of parameters. This reduces the computational effort considerably.

2.4. Spectrum

Our goal is a quantitative simulation of the photodetachment spectrum of $C_4H_4N^-$. The calculation of the spectrum means to determine the intensity of the photoelectron lines and their energetic position, i.e., the eigenenergies of the Hamiltonian (2.3). These energies and intensities refer to $C_4H_4N$. The energy range of the spectrum is the interval (2.2). According to Fermi’s golden rule, the photodetachment line spectrum reads [15]

$$I_{\text{vdw}}(E_k) \propto \sum_f \left| \langle \Psi_0^f | \hat{H}_\text{int} | \Psi_f^{f-1}; k \rangle \right|^2 \delta[(\omega_0 - E_k) - (E_f - E_0)]$$

(2.9)

as a function of the kinetic energy $E_k = \frac{p^2}{2m_e}$ of the ejected electron of $m_e$. $\hat{H}_\text{int}$ describes the interaction of the molecule with the radiation field, $|\Psi_0^f\rangle \equiv |\Psi_0\rangle$ is the vibronic $\mathcal{N}$-electron ground state of the pyrrolide anion with energy $E_0$, and $|\Psi_f^{f-1}\rangle \equiv |\Psi_f\rangle$ are the final vibronic $(\mathcal{N} - 1)$-electron states of the pyrrolyl radical with energies $E_f$. We choose $E_0$ to be the zero of the energy scale: $E_0 = 0$. Expression (2.9) shows that the calculation of the photodetachment spectrum proceeds in analogy to an absorption spectrum. In the present study, all spectra are plotted as a function of binding energy $E = \omega_0 - E_k$.

The eigenenergies of the approximate two-state matrix Hamilton operator $\hat{H} (2.3)$ are obtained by a numerically exact solution of the time-independent vibronic Schrödinger equation:

$$\left( \hat{H} - E_f |1_2\rangle \langle 1_2 | \right) |\Psi_f\rangle = 0.$$  

(2.10)

The vibronic states $|nv\rangle = |\Phi_n\rangle |\nu\rangle$ ($n = 1, 2$) with

$$|\nu\rangle = \left\{ \{v_i\}, \{v_c\} \right\} = \left( \prod_{c} (|v_c\rangle) \right) \left( \prod_{i} (|v_i\rangle) \right) (v_i = 0, 1, 2, \ldots)$$

(2.11)

represent a complete direct-product basis of diabatic electronic states $|\Phi_n\rangle$ and eigenfunctions $|\nu_i\rangle$ of one-dimensional harmonic oscillators. We expand $|\Psi_f\rangle$ in terms of this basis [16],

$$|\Psi_f\rangle = \sum_{n=1,2} \sum_{\nu} C_{\nu n}^{f} |\Phi_n\rangle |\nu\rangle$$

(2.12)

with expansion coefficients $C_{\nu n}^{f} = \langle nv | \Psi_f \rangle$. Insertion of the expansion (2.12) into Eq. (2.10) yields the vibronic matrix eigenvalue problem

$$\left( \hat{H} - E_f |1_\infty\rangle \langle 1_\infty | \right) C' = 0.$$  

(2.13)

The infinite supermatrix $\hat{H}$ is defined as $\hat{H} = \left\{ \langle nv | \hat{H} | mu \rangle \right\}$ ($n, m = 1, 2$; $v_i, u_i = 0, 1, 2, \ldots$). Its elements are [14]

$$\langle nv | \hat{H} | mu \rangle = \left( E_n + \sum_c v_c \omega_c + \sum_e v_e \omega_e \right) \delta_{mn}$$

$$+ \sum_f k^{(e)}_{v,n} \prod_{c \neq e} \delta_{v_c u_c} $$

(2.14)

$$\langle nv | \hat{H} | mu \rangle = \sum_c \lambda_c f_{v,n} \prod_{c \neq c'} \delta_{v_c u_c} \quad (n \neq m).$$

(2.15)

Off-diagonal contributions only originate from each single normal mode matrix element

$$f_{v,n} = \langle v_i | Q_i | u_i \rangle = \sqrt{\frac{|u_i + \frac{1}{2}|}{2} \delta_{v_i u_i + 1} + \frac{|u_i|}{2} \delta_{v_i u_i - 1}}.$$  

(2.16)

$\hat{H}$ decouples into two submatrices $\hat{H}_1$ and $\hat{H}_2$, corresponding to vibronic levels of $A_2$ and $B_1$ symmetry, respectively. The expansion (2.12) is truncated by defining a finite num-
ber \( N_i \) of harmonic oscillator basis states for each degree of freedom through \( \nu_i = 0, 1, 2, \ldots, N_i - 1 \). Consequently, the eigenvalue problem (2.13) leads to two separate, finite eigenvalue problems

\[
(H_{n,d} - E_{n(1)}^{(d)} | 1_d) \mathbf{C}_d^f = 0 \quad (n = 1, 2)
\]

(2.17)

for the truncated submatrices \( H_{n,d} \) of dimension \( d = \prod_i N_{i} = \left( \prod_i N_{i} \right) \left( \prod_i N_{e} \right) \).

The Hamiltonian submatrices \( H_{n,d} \) are sparse. Therefore, the Lanczos algorithm [17] is ideally suited for their diagonalization (see Refs. [18,19] for details).

In practice, one makes an initial guess as to the numbers \( N_{e} \) and \( N_{f} \) proportional to the corresponding Poisson parameters [14]

\[
P_e = \frac{1}{2} \left( \frac{\lambda_e}{\omega_e} \right)^2
\]

(2.19)

and

\[
P_f = \frac{1}{2} \left( \frac{\lambda_f}{\omega_f} \right)^2,
\]

(2.20)

respectively, and subsequently varies these numbers to investigate convergence. Another important quantity is the relative absolute difference

\[
q_i = \frac{|\kappa_i^{(1)} - \kappa_i^{(2)}|}{\omega_i}
\]

(2.21)

which represents a measure of the tuning ability of \( \nu_i \) [14]. The modulation of the \( 1^2B_1 - 1^2A_2 \) energy gap is particularly relevant if the wave packet is initially prepared in electronic state \( 1^2B_1 \), which has a higher vertical detachment energy than \( 1^2A_2 \), because the interplay of tuning and interstate coupling modes controls the \( 1^2B_1 \rightarrow 1^2A_2 \) relaxation dynamics. A large value of \( |\kappa_i^{(1)}| \) can in fact induce significant activation of \( \nu_i \) upon electronic excitation into the \( 1^2B_1 \) state even if the Poisson parameter of this state is relatively small.

The intensity of the line at the position \( E_f \) is proportional to \( |\langle \Psi_0 | H_{\text{int}} | \Psi_f \rangle|^2 \), cf. Eq. (2.9). The ground state \( |\Psi_0 \rangle \) of the pyrrolide anion is to a good approximation a Born–Oppenheimer product:

\[
|\Psi_0 \rangle = |\Phi_0 \rangle |0\rangle,
\]

(2.22)

where \( |\Phi_0 \rangle \) and \( |0\rangle \) denote the electronic and the vibrational ground states, respectively. The final vibronic states \( |\Psi_f \rangle \) of the radical, on the other hand, are given by Eq. (2.12). \( H_{\text{int}} \) is treated in the dipole approximation. Applying the Condon approximation in the diabatic basis

\[
\tau_n(Q) = \langle \Phi_0 | H_{\text{int}} | \Phi_n \rangle \approx \tau_n = \text{const.}
\]

(2.23)

the transition matrix element from Eq. (2.9) becomes

\[
\langle 0 | \langle \Phi_0 | H_{\text{int}} | \Psi_f \rangle \rangle \propto \sum_{n=1,2} \sum_{v} \langle 0 | \tau_n | v \rangle C_{nv}^f = \tau_1 C_{10}^f + \tau_2 C_{20}^f.
\]

(2.24)

In the Condon approximation for photodetachment from the ground state, only the first component \( C_{10}^f \) of the eigenvectors of the submatrices \( H_n \) \((n = 1, 2)\) determines the intensity of the \( f \)th line. Obviously, this drastically reduces the numerical effort. In all computations of the present study, \( \tau_1 = \tau_2 \) is assumed for the photoelectron transitions.

The intensity of the \( f \)th line of the spectrum (2.9) for excitation of a final vibronic state \( |\Psi_f \rangle \) of pyrrolide from the ground state \( |\Psi_0 \rangle \) of pyrrolyl is proportional to the partial-channel cross section \( \sigma_{f,q}(E_k) \) for photodetachment of an electron from orbital \( \Phi_q \). \( \sigma_{f,q}(E_k) \) can be evaluated according to [20]

\[
\sigma_{f,q}(E_k) \propto |\tau_{k,q}|^2 |\xi_{f,q}|^2.
\]

(2.25)

The factor \( |\xi_{k,q}|^2 \) is referred to as orbital detachment cross section, \( |\xi_{f,q}|^2 \) as spectroscopic factor (or pole strength). The corresponding matrix elements are \( \tau_{k,q} = \langle k | H_{\text{int}} | \Phi_q \rangle \), where \( |k\rangle \) is the one-electron scattering function, and \( \xi_{f,q} = \langle \Psi_f \xi \rangle \langle \Psi_0 \rangle \), where \( \xi \) is the annihilation operator. The \( \sigma_{f,q}(E_k) \) factors associated with the diabatic \( \alpha_2(\pi) \) and \( b_1(\pi) \) orbitals are taken to be independent of the nuclear geometry (Condon approximation).

The electronic part of the spectroscopic factors has been determined at the MRCI level, as described in Ref. [21]. The result for both the \( 1^2A_2 \) and \( 1^2B_1 \) state is similar: \( |(1^2A_2 | \Phi_q | 1^2A_1) |^2 \approx 0.6 \approx |(1^2B_1 | \Phi_q | 1^2A_1) |^2 \). The \( |\tau_{k,q}|^2 \) factors are more difficult to calculate and have not been determined in the present study.

The finite experimental resolution and the collective effect of neglected modes as well as degrees of freedom not considered here (e.g., rotation) are taken into account by a phenomenological line broadening. For this purpose, the line spectrum (2.9) is convoluted with a Lorentzian of an appropriate full width at half maximum (FWHM) to obtain the envelope of the spectrum.

3. Electronic structure methods

This study concentrates on the electronic ground state \( 1^1A_1 \) of the pyrrolyl anion as well as the ground \( 1^2A_2 \) and the first excited \( 1^2B_1 \) electronic state of the pyrrolyl radical. Previous studies indicate that the \( 1^1A_1 \) wave function of pyrrolyl is not very diffuse and can be described by a basis set of DZP quality, supplemented by diffuse functions [13,22]. The \( 1^2A_2 \) and \( 1^2B_1 \) states of pyrrolyl are formed by detachment of an electron from the two highest occupied molecular orbitals of \( \alpha_2 \) and \( b_1 \) symmetry, respectively, of the pyrrolyl anion and can be expected to be more compact than the anion ground state. In Ref. [13], these states have been treated with an augmented DZP level basis set. Throughout the present study, we have employed the aug-cc-pVDZ basis set [23] to adequately represent the three states of interest.
Since photodetachment will take place at the equilibrium geometry of the pyrrolide ground state, this nuclear configuration defines the reference structure for the calculation of the PE functions. The search for the minimum of the $^1A_1$ state of pyrrole and the determination of the normal modes have been carried out at the MP2 level with the GAUSSIAN03 program [24].

We have calculated the PE functions of these three electronic states in the FC region along different relevant normal-mode displacements. The procedure for the construction of normal-mode displacements has been described in detail in Ref. [25]. After calculating the reference geometry and the force field of the pyrroline anion, we obtained the transformation matrix $B$ between the dimensionless normal coordinates $Q$ and Cartesian coordinates. It is also possible to express the internal symmetry coordinates $s$ as a linear combination of Cartesian coordinates via a matrix $C$. Further, a linear relation between internal symmetry coordinates $s$ and dimensionless normal coordinates $Q$ is established via a matrix $L = BC^{-1}$. In other words, for finite displacements from the reference configuration, the coordinates $Q$ can be considered to be linear combinations of the symmetry coordinates $s$. Subsequently, a Cartesian geometry corresponding to a given displacement $Q = (Q_1, Q_2, \ldots, Q_{21})$ is constructed by explicitly considering the changes of internal bond length and bond angle variables in the transformation through an iterative scheme.

The calculations of the $^1A_1$ pyrroline ground state as well as of the $^1B_2$ and $^1B_1$ wave functions of pyrroline have been performed with the CASSCF [26,27] and internally contracted MRCI electronic structure methods [28–30]. In the CASSCF calculations, the five valence $\pi$ and $\pi^*$ orbitals have been selected as active orbitals, with six and five active electrons for the pyrroline and pyrrole system, respectively. Since the numbers of CASSCF configuration state functions (CSFs) are quite small for this active space, all CSFs have been included in the reference space for the MRCI calculations.

Making the displacements along the $a_i$ modes, the system remains in $C_{2i}$ symmetry. Thus all states have been optimized individually. The CASSCF (internally contracted MRCI) expansion length is 28 (623964) for the ground state of the pyrroline anion, as well as 36 (799405) and 36 (801388) for the $^1A_2$ and $^1B_1$ states of pyrroline, respectively.

If the molecular frame is distorted along normal coordinates transforming according to the $b_2$ irreducible representation, the symmetry is reduced from $C_2$, to $C_{\infty}$, and the $^1A_2$ and $^1B_1$ states of pyrroline are correlated with the $^2A''$ and $^2A''$ states in the $C_i$ point group or vice versa. The ground state and the first excited state can therefore interact in the $C_i$ point group and both wave functions should be included with equal weights in the CASSCF functional to ensure a balanced description. A CASSCF (internally contracted MRCI) expansion length of 50 (1246820) is obtained for the $^1A'$ state of pyrroline and of 75 (2586845) for the two wave functions of $^2A''$ symmetry.

It is well known that the MRCI method is not a size-consistent method. Because the anion and the radical possess a different number of electrons, it is difficult to obtain a balanced correlation energy for the anion and the radical. The energy for the photodetachment of an electron from the $a_2$ orbital of pyrroline at the reference structure to form the $^1A_2$ state of pyrrolyl has therefore been estimated by the CCSD method [31].

To get direct information about the $^1A_2$ ground state of the pyrrolyl radical, we have optimized its geometry and performed a frequency calculation with density functional theory (DFT) using the B3LYP functional [32,33] and the 6-311G(d,p) basis set. In the case of pyrrolyl, a part of the $^1A_1-^1A_2$ degeneracy subspace can be reached by a relatively small displacement from the reference geometry along the normal coordinate $Q_4$ (see Section 5.2). This conical intersection point will be denoted as CI($Q_4$) in the following. To characterize this conical intersection, we also have performed ab initio calculations of the PE surfaces along the coupling modes near the crossing point.

4. Determination of vibronic coupling constants

The dynamics of the pyrrolyl system will be treated in terms of the ground state normal coordinates of the pyrroline anion. Therefore, information about the dependence of the energy of the electronic states on these coordinates in the vicinity of the reference geometry is required for the calculation of the vibronic coupling constants.

The parameters $\kappa_i^{(n)}$ can be conveniently determined as the excited-state energy gradients of the $^1A_2$ and $^1B_1$ states at the pyrroline ground state equilibrium configuration, cf. Eq. (2.8). In addition to this direct evaluation we also alternatively calculated the $\kappa_i^{(n)}$ for both electronic states by least-squares fitting of the excitation energy functions defined by the electronic model Hamiltonian to the ab initio results.

One option to determine $\lambda_c$ is using a least-squares fitting procedure [34] near the equilibrium configuration. The quality of the fit depends critically not only on the accuracy of the curvature of the PE functions, but in addition on the precision of the $^1B_1-^1A_2$ energy difference $\Delta = E_2 - E_1$. With a finite value of $\Delta$, the fitting procedure can also result in multiple solutions for the parameters. The different parameter sets have in common that they yield good descriptions of the adiabatic PE surfaces of the two coupled states, but may correspond to different diabatic PE matrices that may represent different physical scenarios with respect to the strength of interstate and intrastate coupling (cf. Ref. [35] for an analysis of this issue). One possibility to avoid this problem is to eliminate $\Delta$ in the fitting procedure [36]. In the system at hand, the intersection is located in the vicinity of the ground state equilibrium geometry. Thus, it is reasonable to determine $\lambda_c$ near the conical intersection and assume that $\lambda_c$ is not a function of $Q_c$, cf. Ref. [14].
5. Results of electronic structure calculations

5.1. Electronic ground state of pyrrolide and pyrrolyl: equilibrium geometries, normal frequencies, and detachment energies

The geometry optimization of the $1^2A_1$ state of pyrrolide yields the nuclear configuration given in Table 1. This structure, which will be referred to as the reference geometry in the following, is in good agreement with previous results [13]. A comparison of our optimized structure of the radical using the 6-311G(d,p) basis set with the previous results at the B3LYP/6-311++G(d,p) level of theory shows that the choice of the basis set has a noticeable influence on the obtained geometries. Significant deviations can be noted in particular for the distance of different C-C bonds (see Table 1). The double and single bonds are found to be longer and shorter, respectively, with the additional diffuse basis functions.

Harmonic frequencies of the ground state of the pyrrolide anion, $\omega_{1,A_1}$ and of the pyrrolyl radical, $\omega_{1,R_1}$, obtained at the MP2/aug-cc-pVDZ and B3LYP/6-311G(d,p) level of theory, respectively, are given in Table 2. According to Herzberg [37], we number the 21 normal modes in the sequence of the symmetry groups $a_1$, $a_2$, $b_2$, $b_1$, ordered by decreasing pyrrolyl frequency within each group. The $i$th mode $v_i$ denotes both the pyrrolide and the pyrrolyl modes of same type. We have examined the normal modes and established the correlations between the individual normal-mode motions in these two systems. The frequency ordering of some modes interchange. For example, the normal-mode motions in these two systems. The frequency ordering of some modes interchange. For example, the normal-mode motions in these two systems. The frequency ordering of some modes interchange. For example, the normal-mode motions in these two systems. The frequency ordering of some modes interchange. For example, the normal-mode motions in these two systems.

The 11 detachment energies $\epsilon_{A_1}$ of pyrrolide have been calculated within the MP2/aug-cc-pVDZ and B3LYP/6-311G(d,p) level $\epsilon_{A_1}$ of pyrrolide have been calculated within the MP2/aug-cc-pVDZ and B3LYP/6-311G(d,p) level of theory, as well as the corresponding Poisson parameters $g_{A_1}$, Eq. (2.21). It can be seen that the Poisson parameters for the high-frequency CH stretching modes $v_1$ and $v_2$ are $p_{A_1}(< 0.01$ for both $A_1$ and $B_1$ symmetries, so that the vibronic activity of these vibrations is negligible. The six modes $v_3$, $v_4$, $v_5$, $v_6$, $v_7$, $v_8$

<table>
<thead>
<tr>
<th>Mode</th>
<th>Symmetry</th>
<th>$\omega_{A_1} (cm^{-1})$</th>
<th>$\omega_{R_1} (cm^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>$a_1$</td>
<td>3222.2</td>
<td>3245.7</td>
</tr>
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<td>$a_1$</td>
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<td>3198.0</td>
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<tr>
<td>$v_3$</td>
<td>$a_1$</td>
<td>1442.8</td>
<td>1434.2</td>
</tr>
<tr>
<td>$v_4$</td>
<td>$a_1$</td>
<td>1422.0</td>
<td>1560.7</td>
</tr>
<tr>
<td>$v_5$</td>
<td>$a_1$</td>
<td>1149.5</td>
<td>1204.3</td>
</tr>
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<td>$v_6$</td>
<td>$a_1$</td>
<td>1097.5</td>
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<tr>
<td>$v_7$</td>
<td>$a_1$</td>
<td>1012.5</td>
<td>1091.4</td>
</tr>
<tr>
<td>$v_8$</td>
<td>$a_1$</td>
<td>852.4</td>
<td>883.1</td>
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<td>$v_9$</td>
<td>$a_2$</td>
<td>739.7</td>
<td>913.1</td>
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<td>$v_{10}$</td>
<td>$a_2$</td>
<td>672.6</td>
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</tr>
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<td>$v_{11}$</td>
<td>$a_2$</td>
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<td>$v_{12}$</td>
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</tr>
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<td>$v_{16}$</td>
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<td>$v_{17}$</td>
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<td>$v_{18}$</td>
<td>$b_2$</td>
<td>867.7</td>
<td>655.6</td>
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<td>$v_{20}$</td>
<td>$b_1$</td>
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<td>714.6</td>
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<td>$v_{21}$</td>
<td>$b_1$</td>
<td>640.8</td>
<td>544.3</td>
</tr>
</tbody>
</table>

The linear intrastate coupling constants $k^{(n)}$, Eq. (2.8), for the eight totally symmetric normal modes $v_i$ ($i = 1, \ldots, 8$) of pyrrolide have been calculated within the $C_{2v}$ point group for the $1^2A_2$ and $1^2B_1$ states of pyrrolyl. Both direct numerical differentiation and two-parameter least-squares fit methods yield nearly identical values for the $k^{(n)}$ coefficients. Table 3 contains the $k^{(n)}$ values, the anionic ground state frequencies $\omega_{A_1}$, as well as the corresponding Poisson parameters $p_{A_1}$, Eq. (2.20), and the tuning activity parameters $q_{A_1}$, Eq. (2.21).
A. Motzke et al. / Chemical Physics 329 (2006) 50–64

Table 3
The intrastate vibronic coupling constants $\kappa^{(i)}$ in eV, the ground state frequencies $\omega_{A,\kappa}$ of the pyrrolide anion (pyrrolyl radical) in eV, the dimensionless Poisson parameters $p_{A,\kappa} = \frac{1}{2}\left[|\kappa^{(1)}|/\omega_{A,\kappa}^2\right]$, and the dimensionless parameters $q_{\kappa} = |\kappa^{(1)} - \kappa^{(2)}|/\omega_{A,\kappa}$.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\kappa^{(1)}$ (eV)</th>
<th>$\kappa^{(2)}$ (eV)</th>
<th>$\omega_{A,\kappa}$ (eV)</th>
<th>$p_{A,\kappa}^{(1)}$</th>
<th>$p_{A,\kappa}^{(2)}$</th>
<th>$q_{\kappa}$</th>
<th>$\omega_{R,\kappa}$ (eV)</th>
<th>$p_{R,\kappa}^{(1)}$</th>
<th>$p_{R,\kappa}^{(2)}$</th>
<th>$q_{R,\kappa}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>0.0350</td>
<td>0.0454</td>
<td>0.3995</td>
<td>0.004</td>
<td>0.006</td>
<td>0.2002</td>
<td>0.0350</td>
<td>0.0454</td>
<td>0.3995</td>
<td>0.004</td>
</tr>
<tr>
<td>$v_2$</td>
<td>0.0715</td>
<td>0.0223</td>
<td>0.3947</td>
<td>0.001</td>
<td>0.002</td>
<td>0.1012</td>
<td>0.0102</td>
<td>0.1056</td>
<td>0.1778</td>
<td>0.0184</td>
</tr>
<tr>
<td>$v_3$</td>
<td>0.1080</td>
<td>0.0809</td>
<td>0.1789</td>
<td>0.182</td>
<td>0.246</td>
<td>2.102</td>
<td>0.1080</td>
<td>0.0809</td>
<td>0.1789</td>
<td>0.182</td>
</tr>
<tr>
<td>$v_4$</td>
<td>0.2002</td>
<td>0.1703</td>
<td>0.1763</td>
<td>0.645</td>
<td>0.249</td>
<td>0.968</td>
<td>0.2002</td>
<td>0.1703</td>
<td>0.1763</td>
<td>0.645</td>
</tr>
<tr>
<td>$v_5$</td>
<td>0.0374</td>
<td>0.1005</td>
<td>0.1425</td>
<td>0.035</td>
<td>0.122</td>
<td>1.182</td>
<td>0.0374</td>
<td>0.1005</td>
<td>0.1425</td>
<td>0.035</td>
</tr>
<tr>
<td>$v_6$</td>
<td>0.0937</td>
<td>0.0672</td>
<td>0.1361</td>
<td>0.237</td>
<td>0.117</td>
<td>1.016</td>
<td>0.0937</td>
<td>0.0672</td>
<td>0.1361</td>
<td>0.237</td>
</tr>
<tr>
<td>$v_7$</td>
<td>0.0666</td>
<td>0.0609</td>
<td>0.1255</td>
<td>0.141</td>
<td>0.311</td>
<td>1.325</td>
<td>0.0666</td>
<td>0.0609</td>
<td>0.1255</td>
<td>0.141</td>
</tr>
<tr>
<td>$v_8$</td>
<td>-0.0568</td>
<td>0.0833</td>
<td>0.1057</td>
<td>0.144</td>
<td>0.311</td>
<td>1.325</td>
<td>-0.0568</td>
<td>0.0833</td>
<td>0.1057</td>
<td>0.144</td>
</tr>
</tbody>
</table>

and $v_8$ can be identified as relevant tuning modes owing to larger Poisson parameters, as well as larger tuning activity parameters. Among them, mode $v_4$ is by far the dominant totally symmetric mode both in terms of PC activity as well as tuning effect. Mode $v_5$, in contrast, does not need to be included here, because it appears not to be an important contributor of intensity to the $1^2A^2$ band of the spectrum, cf. the corresponding Poisson parameter $p_{A,\kappa}^{(1)} = 0.035$. Thus, the five $a_1$ modes $v_3$, $v_4$, $v_6$, $v_7$, and $v_8$ are involved in the model Hamiltonians (see below). Fig. 2 provides a picture of the nuclear displacements associated with the normal modes $v_3$, $v_4$, $v_6$, $v_7$, $v_8$, $v_5$, $v_3$ and $v_4$ are primarily CC stretching modes. CH and CCC deformation are the main displacements of $v_6$, $v_7$, and $v_8$.

We have obtained the adiabatic excitation energies of the $1^2A^2$ and $2^2A^2$ states of pyrrolyl as a function of the seven normal coordinates of $b_2$ symmetry. The linear interstate coupling constants $\lambda_{\kappa}$, Eq. (2.7), have been determined near the conical intersection. Table 4 lists the $\lambda_{\kappa}$, the anionic ground state frequencies $\omega_{A,\kappa}$, and the corresponding Poisson parameters $p_{A,\kappa}$, Eq. (2.19). From the $p_{A,\kappa}$ values we conclude that $v_{14}$, $v_{15}$, $v_{16}$, and $v_{18}$ are the most important $1^2B_1-1^2A_2$ coupling modes. The $\lambda_{\kappa}$ ($c = 12, 13, 17$) constants of the three remaining $b_2$ modes are negligible. The nuclear displacements associated with $Q_{14}$, $Q_{15}$, $Q_{16}$, and $Q_{18}$ are depicted in Fig. 2.

Fig. 3 shows the ab initio potential energies of the $1^2A_2$ and $1^2B_1$ states of pyrrolyl as a function of the normal coordinates $Q_3$, $Q_4$, $Q_6$, $Q_7$, and $Q_8$ together with the harmonic model PE functions that are defined in Section 6. The curvatures of the PE functions of the pyrrolyl states and of the pyrrolyl ground state are identical (since no

Fig. 1. The C$_{2v}$ ground state equilibrium structure of the pyrrolide anion, C$_4$H$_4$N$^-$. Fig. 2. The nine normal-mode displacements (calculated for the ground state of pyrrolyl) which are most relevant for the $1^2A_2-1^2B_1$ vibronic interaction problem in pyrrolyl. $v_3$, $v_4$, $v_6$, $v_7$, and $v_8$ transform according to the totally symmetric representation of the $C_{2v}$ point group. $v_{14}$, $v_{15}$, $v_{16}$, and $v_{18}$ are of $b_2$ symmetry.
quadratic coupling terms are included in the model Hamiltonian). The good agreement of \textit{ab initio} and harmonic model functions indicates that the linear coupling model describes the \textit{ab initio} data quite well. Again, the confirmative conclusion can be drawn here that \( v_4 \) is the dominant tuning mode. Elongation of \( v_4 \) leads to a conical intersection of the \( 1^2A_2 \) and \( 1^2B_1 \) states. The two radical states intersect in the vicinity of the minimum of the upper state.

Fig. 4 illustrates the dependence of the adiabatic detachment energies of the \( 1^2A^\prime \) and \( 2^2A^\prime \) states of pyrrolyl on the four dominant interstate coupling modes near the conical intersection. Both \textit{ab initio} and model adiabatic energy functions are shown. The model functions constitute an excellent approximation to the exact energies. Obviously, it is confirmed that \( v_{14} \) and \( v_{15} \) are the two strongest coupling modes.

The shape of the \( 1^2B_1-1^2A_2 \) conical intersection CI(\( Q_4 \)) in both the adiabatic and diabatic electronic representation is illustrated in Fig. 5. This view shows the PE surfaces in a space spanned by \( Q_4 \) and \( Q_{14} \), corresponding to the most active tuning mode, \( v_4 \), and to one of the two strongest coupling modes, \( v_{14} \), respectively. The adiabatic surfaces in Fig. 5(a) clearly demonstrate that the degeneracy point is very near to the minimum of the upper surface. This means that a wave packet prepared in the \( 1^2B_1 \) state by vertical excitation will follow the energy gradients, mostly along \( Q_4 \), and move directly towards the conical intersection, where the nonadiabatic coupling induces the ultrafast population transfer from the \( 1^2B_1 \) to the \( 1^2A_2 \) state. After this nonadiabatic transition, a strong gradient along \( Q_4 \) in the \( 1^2A_2 \) state will drive the nuclear motion towards the equilibrium region of the electronic ground state of the pyrrolyl radical. This mechanism leads to a very efficient internal conversion. Fig. 5(b) shows the two intersecting diagonal elements of the diabatic electronic Hamiltonian. According to the labeling, each PE surface is associated with either \( A_2 \) or \( B_1 \) electronic character. The linear dependence of the diabatic coupling element on \( Q_{14} \) can be seen from Fig. 5(c).

Although the linear vibronic coupling model describes the PE functions of the pyrrolyl radical quite well, there are differences in detail in the vibrational frequencies. In particular, the ground state frequencies of the pyrrolide anion, \( \omega_{A_2} \), and of the pyrrolyl radical, \( \omega_{B_1} \), are different

### Table 4

The vibronic \( 1^2B_1-1^2A_2 \) coupling constants \( \lambda_i \) in eV, the pyrrolide anion (pyrrolyl radical) ground state frequencies \( \omega_{A_{2,c}} \) (\( \omega_{B_{1,c}} \)) in eV, and the dimensionless Poisson parameters \( p_{A_{2,c}} = \frac{1}{2} \lambda_i / \omega_{A_{2,c}} \) (\( p_{B_{1,c}} = \frac{1}{2} \lambda_i / \omega_{B_{1,c}} \)).

<table>
<thead>
<tr>
<th>Mode</th>
<th>( \lambda_i ) (eV)</th>
<th>( \omega_{A_{2,c}} ) (eV)</th>
<th>( p_{A_{2,c}} )</th>
<th>( \omega_{B_{1,c}} ) (eV)</th>
<th>( p_{B_{1,c}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_{12} )</td>
<td>0.0048</td>
<td>0.3969</td>
<td>0.000</td>
<td>0.4000</td>
<td>0.000</td>
</tr>
<tr>
<td>( v_{13} )</td>
<td>0.0031</td>
<td>0.3938</td>
<td>0.000</td>
<td>0.3960</td>
<td>0.000</td>
</tr>
<tr>
<td>( v_{14} )</td>
<td>0.1988</td>
<td>0.1796</td>
<td>0.613</td>
<td>0.1681</td>
<td>0.699</td>
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<tr>
<td>( v_{15} )</td>
<td>0.1783</td>
<td>0.1628</td>
<td>0.600</td>
<td>0.1333</td>
<td>0.894</td>
</tr>
<tr>
<td>( v_{16} )</td>
<td>0.1074</td>
<td>0.1525</td>
<td>0.248</td>
<td>0.1602</td>
<td>0.225</td>
</tr>
<tr>
<td>( v_{17} )</td>
<td>0.0390</td>
<td>0.1263</td>
<td>0.048</td>
<td>0.1158</td>
<td>0.057</td>
</tr>
<tr>
<td>( v_{18} )</td>
<td>0.0768</td>
<td>0.1076</td>
<td>0.255</td>
<td>0.0813</td>
<td>0.447</td>
</tr>
</tbody>
</table>

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Fig. 3. Potential energies of the \( 1^2A_2 \) and \( 1^2B_1 \) states of pyrrolyl as a function of the totally symmetric ground-state normal coordinates \( Q_3 \), \( Q_4 \), \( Q_6 \), \( Q_7 \), and \( Q_8 \) of the pyrrolide anion. The stars represent MRCI/aug-cc-pVDZ energies, the continuous lines the adiabatic model functions. The conical intersection point CI(\( Q_4 \)) is clearly visible along \( Q_4 \).
Thus, it may be necessary to take the frequency changes into account. In principle, a systematic approach to implement this effect involves the expansion of the Hamiltonian beyond the first order. But this procedure requires a very large computational effort. As a compromise between accuracy and cost, we have set up an ad hoc model Hamiltonian to account for the frequency changes by photodetachment. The idea of this ad hoc Hamiltonian is to simply replace the normal frequencies of the pyrrolide anion by those of the pyrrolyl radical, keeping all other parameters \( \kappa^{(n)}_t, \lambda_t, \) and \( E_0 \) unchanged. Of course, this approach is not fully consistent, because the normal coordinates differ in these two systems. Nevertheless, this ad hoc Hamiltonian provides insight into the influence of the frequency shifts on the spectra. The frequencies \( x_{R,t} \) as well as the parameters \( p_{R,t}^{(a)}, q_{R,t} \) of the \( a_1 \) modes and the frequencies \( \omega_{R,e} \) as well as the parameters \( p_{R,e} \) of the \( b_2 \) modes in this ad hoc model are included in Tables 3 and 4, respectively. These two tables support our selections of tuning and coupling modes for the calculation of spectra.

6. Photodetachment spectrum of the pyrrolide anion

In this section, we compare model calculations of the photoelectron bands corresponding to the interacting
$1^2A_2$ and $1^2B_1$ states of the pyrrolyl radical with the experimental 363.8 nm (3.408 eV) spectrum reported by Gianola et al. [13]. Essentially, the low-energy part of the spectrum belongs to the $1^2A_2$ ground state of pyrrolyl, the higher energy part to its $1^2B_1$ first excited state. The experimental spectrum is characterized by a fairly sharp, resolved vibrational progression for the ground state band of pyrrolyl, while only a completely diffuse background of low intensity is observed in the energy range of the first excited state.

Within the linear vibronic coupling model, the nuclear motion on the coupled $1^2A_2$ and $1^2B_1$ PE surfaces involving the most important modes of $a_1$ and $b_2$ symmetry is treated numerically exactly. In Section 5.2, we identified these most relevant modes due to their Poisson (and $q_i$) parameters. Simulated spectra for five combinations of tuning and coupling modes are discussed in the present study. These combinations will be referred to as sets $1 + 2$, $5 + 2$, $4 + 4$, $5 + 0$, and $0 + 4$ in the following. Set $1 + 2$ contains the dominant totally symmetric vibration $v_4$ and the two dominant $1^2B_1^{-1}1^2A_2$ coupling modes $v_{14}$ and $v_{15}$. Set $5 + 2$ comprises the five most important $a_1$ modes $v_3$, $v_4$, $v_6$, $v_7$, and $v_8$, as well as the two most active $b_2$ modes $v_{14}$ and $v_{15}$. Set $4 + 4$ includes only the four dominant tuning modes, $v_3$, $v_4$, $v_6$, and $v_8$, but in addition also the four key coupling modes, $v_{14}$, $v_{15}$, $v_{16}$, and $v_{18}$. Furthermore, calculations have been performed that solely include either tuning modes (set $5 + 0$) or coupling modes (set $0 + 4$). Table 5 defines the corresponding five model Hamiltonians according to Eqs. (2.3)–(2.5) by specifying the tuning and coupling subsets.

We thus restrict the number of modes in the model Hamiltonian to a maximum of eight to limit the computational effort. All other modes can be considered to be relatively weakly coupled to the core vibronic system. No diabatic frequency shifts are included in the model Hamiltonians, cf. Eq. (2.3). In fact, we found them to be very small (not shown here). Duschinsky effects [38], i.e., the effects of normal coordinate rotation between the pyrrolyl anion ground state and the two states of the pyrrolyl radical, have also been neglected.

The stick spectra generated by the Lanczos method are convoluted with a Lorentzian function of FWHM of 10 meV (chosen corresponding to the width of the experimental $1^2A_2$ origin peak) to simulate the spectral envelope. Converged results for the different photodetachment spectra computed for the present study (Figs. 6, 7, 8(b) and (c) and 9(b) and (c) are obtained with the basis set dimensions and the numbers of Lanczos iterations compiled in Table 6. The respective ground state frequencies of the pyrrolyl anion, $\omega_{A,i}$, listed in Table 2 have been used for the preparation of the theoretical spectra, except for the spectra shown in Fig. 9(b) and (c). For those two figures, the respective frequencies of the $1^2A_2$ state of the pyrrolyl radical, $\omega_{B,i}$, were used (Table 2). For comparison, the experimental spectrum is depicted in Fig. 8(a) as well as in Fig. 9(a).

The theoretical spectra shown in the figures have been shifted to higher energies in order to match the position $E_A = 2.145$ eV of the experimental $1^2A_2$ origin peak. The energetic shifts are included in Table 6. The maximum of the envelope is normalized to 1, the maximum of the line spectrum to 0.5. The normalization has been applied to the entire energy range of the $1^2A_2 + 1^2B_1$ spectrum. All calculations take the coupling of the two states $1^2B_1$ and $1^2A_2$ into account. Transitions of $A_2$ vibronic symmetry are drawn with a gray tone, transitions of the $B_1$ vibronic manifold are reproduced in black. In this way intensity borrowing peaks are distinguished.

### 6.1. Calculations with pyrrolyl anion frequencies

Let us first consider a reduced-dimensionality spectrum, shown in Fig. 6. Only the three (according to their Poisson and $q_{A,i}$ parameters) most relevant modes of the system, $v_4$, $v_{14}$, and $v_{15}$, have been included in the vibronic model Hamiltonian $H_{1+2}$ (cf. Tables 5 and 6). The resulting $1 + 2$ spectrum (Fig. 6) obviously can reproduce some of the features of the $1^2A_2$ band (cf. Fig. 8(a)), while the intensity distribution beyond $\approx 2.7$ eV does not agree with experiment. This property of the $1 + 2$ core model is replicated in the more sophisticated $5 + 2$ and $4 + 4$ simulations, as will be discussed below. At 2.346 eV (corresponding to a frequency of 1621 cm$^{-1}$), the fundamental of $v_4$ is identified. Another strong transition is found at 2.305 eV.
Intensity borrowing peaks from the $^1\!^2B_1$ vibronic manifold are present, the strongest one at 2.229 eV (677 cm<sup>-1</sup>). The origin peak of the $^1\!^2B_1$ band in the $1+2$ spectrum is located at 2.607 eV.

In Fig. 7, the (1$^2B_1$–1$^2A_2$ coupled) results of calculations of the $1^2A_2$ band including four selected subsets of vibrational modes are presented. Fig. 7(a) and (b) displays the theoretical spectra obtained with the vibronic model Hamiltonians $\mathbf{H}_{5,0}$ and $\mathbf{H}_{0,4}$, i.e., with truncated Hamiltonians $\mathbf{H}_{5,2}$ and $\mathbf{H}_{4,4}$, respectively (cf. Tables 5 and 6). Note that the first maximum in Fig. 7(a) is lower than 1, while the first maximum in Fig. 7(b)–(d) is equal to 1. The reason is the normalization referring to the entire $1^2A_2 + 1^2B_1$ spectrum: the intensity of the 0–0 transition of the $1^2B_1$ spectrum is even higher in the case of Fig. 7(a). Intensity borrowing exists in Fig. 7(b)–(d).

The spectrum in Fig. 7(a), including only the five most important tuning modes, is dominated by the progression in mode $v_4$. This impression is amplified by the fact that the model frequencies of $v_3$ and $v_4$ are nearly degenerate and $v_3$ is also substantially excited. Further significant transitions are found for the lower frequency modes $v_6$, $v_7$, and $v_8$. A comparison with the experimental spectrum in Fig. 8(a) suggests that the $1^2A_2$ band reflects mainly contributions by the tuning modes but also indicates large deviations between the experimental and theoretical intensity distributions.

In Fig. 7(b) gives an idea of the importance of the four most prominent coupling modes. The leading excitations in the pure coupling mode spectrum are located at 2.259 eV and 2.298 eV. The vibronic interaction with the $1^2B_1$ state implies several intensity borrowing peaks, the most intense one at 2.173 eV (226 cm<sup>-1</sup>), followed by two others at 2.342 eV and 2.376 eV. The mass shifts of the adiabatic excitation energies of the coupling mode levels relative to the diabatic frequencies of the individual modes indicate the strong influence of $1^2B_1–1^2A_2$ vibronic coupling on the $1^2A_2$ band. At first glance, one would have expected the fundamentals of $v_{14}$ and $v_{15}$ in the $1^2A_2$ band to be close in energy because of the similar values of $\omega_{A,c}$ and $\omega_{c,c}$ ($c = 14, 15$) for both modes. That this is not the case, seems to be the result of a resonance effect.

The inclusion of additional modes via model Hamiltonians $\mathbf{H}_{5,2}$ and $\mathbf{H}_{4,4}$ (cf. Tables 5 and 6) improves the description of the $1^2A_2$ band and can to some extent explain the diffuse appearance of the experimental spec-
vibronic transitions at higher excitation energies. The pure tuning mode spectrum in Fig. 7 (a) and the 5 + 2 calculation in Fig. 7 (c) differ primarily in the higher energy region: the destructive effect of the two included coupling modes \( m_{14} \) and \( m_{15} \) on the tuning mode progressions becomes obvious beyond \( \approx 2.35 \) eV. Fig. 7 (c) and (d) emphasizes the low-energy parts of the eigenvalue spectra of the full model Hamiltonians \( \hat{H}_{5+2} \) and \( \hat{H}_{4+4} \). The normal frequencies of pyrrolide have been employed for the calculations. The theoretical line spectra have been convoluted with Lorentzians of width 10 meV (FWHM). Both calculations take the interplay between tuning and coupling modes fully into account. Inspection of both figures reveals that the impact of the two low-frequency coupling modes \( m_{16} \) and \( m_{18} \) on the vibronic structure of the \( 1\text{B}_1 \) spectrum is not negligible. It leads to a greatly different intensity distribution not only in the overtone region, but also in the energy domain of the fundamentals. A striking example is the clearly resolved intensity borrowing peak at 2.215 eV in the 4 + 4 spectrum. The

Table 6
The model Hamiltonian, the number of harmonic oscillator basis functions, \( N_\nu \) for each mode \( \nu \) included, the dimension of the secular submatrices, \( d = \prod N_\nu \), cf. Eq. (2.18), and the number of Lanczos iterations, \( N_L \), used to calculate the theoretical stick spectra shown in the corresponding figures.

<table>
<thead>
<tr>
<th>Model</th>
<th>( \nu_3 )</th>
<th>( \nu_4 )</th>
<th>( \nu_5 )</th>
<th>( \nu_6 )</th>
<th>( \nu_7 )</th>
<th>( \nu_8 )</th>
<th>( \nu_{14} )</th>
<th>( \nu_{15} )</th>
<th>( \nu_{16} )</th>
<th>( \nu_{18} )</th>
<th>( d )</th>
<th>( N_L )</th>
<th>Shift (eV)</th>
<th>Figure(s)</th>
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<tbody>
<tr>
<td>( \hat{H}_{5+2} ) &amp; – &amp; 14 &amp; – &amp; – &amp; – &amp; 13 &amp; 13 &amp; – &amp; – &amp; – &amp; 2366 &amp; 2000 &amp; 0.209 &amp; Fig. 6</td>
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<td>( \hat{H}_{4+0} ) &amp; 5 &amp; 14 &amp; 6 &amp; 5 &amp; 8 &amp; – &amp; – &amp; – &amp; – &amp; – &amp; 16800 &amp; 5000 &amp; 0.265 &amp; Fig. 7(a)</td>
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<td>( \hat{H}_{4+4} ) &amp; – &amp; – &amp; – &amp; – &amp; – &amp; 13 &amp; 13 &amp; 6 &amp; 6 &amp; – &amp; 6084 &amp; 5000 &amp; 0.153 &amp; Fig. 7(b)</td>
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<td>( \hat{H}_{5+2} ) &amp; 5 &amp; 14 &amp; 6 &amp; 5 &amp; 8 &amp; 13 &amp; 13 &amp; – &amp; – &amp; – &amp; 2839200 &amp; 5000 &amp; 0.295 &amp; Figs. 7(c) and 8(b)</td>
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<td>( \hat{H}_{4+4} ) &amp; 5 &amp; 14 &amp; 6 &amp; 5 &amp; 8 &amp; 13 &amp; 13 &amp; 6 &amp; 6 &amp; – &amp; 2044240 &amp; 5000 &amp; 0.291 &amp; Figs. 7(d) and 8(c)</td>
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<td>( \hat{H}_{5+2} ) &amp; 5 &amp; 11 &amp; 6 &amp; 5 &amp; 6 &amp; 13 &amp; 17 &amp; – &amp; – &amp; – &amp; 2187900 &amp; 5000 &amp; 0.288 &amp; Fig. 9(b)</td>
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<td>( \hat{H}_{4+4} ) &amp; 5 &amp; 11 &amp; 6 &amp; – &amp; 6 &amp; 13 &amp; 17 &amp; 5 &amp; 9 &amp; 19691100 &amp; 5000 &amp; 0.288 &amp; Fig. 9(c)</td>
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In addition, the energetic shifts in eV are given.
corresponding detachment is obviously strongly enhanced by inclusion of \( \nu_{16} \) and \( \nu_{18} \) into the model Hamiltonian since no corresponding peak can be found in the \( 5 + 2 \) spectrum.

Up to \( \approx 2.5 \) eV, the \( 5 + 2 \) model is in better agreement with the experimental spectrum than the \( 4 + 4 \) Hamiltonian (cf. Fig. 8). With \( \mathbf{H}_{5,2} \) (Fig. 8(b)), the first prominent vibrationally excited transition in the experimental spectrum (Fig. 8(a)) can be explained as a combination of the fundamentals of \( \nu_6, \nu_7 \), and \( \nu_8 \). The triplet reproduces to a good approximation the structure of this asymmetric second peak, which is characterized by a shoulder on the red side. Three individual vibrational transitions of pyrrolyl have been identified from the experimental spectrum in Ref. [13], with frequencies \( 925 \pm 65 \) cm\(^{-1} \), \( 1012 \pm 25 \) cm\(^{-1} \), and \( 1464 \pm 20 \) cm\(^{-1} \). The two lower energy levels are associated with the asymmetric second peak, the highest frequency corresponds to the third peak. The \( 5 + 2 \) calculation suggests an identification of these transitions with the fundamentals of \( \nu_8, \nu_6, \) and \( \nu_4 \) of the pyrrolyl radical. This assignment implies that the level \( \nu_4 \) has not been resolved in the experimental spectrum.

Inspection of Fig. 8(c) reveals that the \( 4 + 4 \) calculation yields an intensity distribution that is consistent with the asymmetric structure of the first strong vibrational excitation in the experimental spectrum. The first intensity borrowing peak appearing at \( 2.215 \) eV (564 cm\(^{-1} \)) in the \( 4 + 4 \) spectrum cannot be distinguished in the experiment, but this transition may be hidden as a part of the red shoulder of this peak. An interesting effect is further the strong activation and quenching of the level \( \nu_5 \) by the \( 4 + 4 \) and \( 5 + 2 \) models, respectively.

The \( 5 + 2 \) and \( 4 + 4 \) models are not able, however, to correctly predict the observed intensity ratios between the second and third main transitions in the experimental spectrum. The strength of the fundamental of \( \nu_4 \) is overestimated. One possible explanation for the intensity pattern resulting from the \( 5 + 2 \) and \( 4 + 4 \) calculations may be the neglect of second and higher order couplings in both Hamiltonians.

Also, the estimate of both the \( 5 + 2 \) (Fig. 8(b)) and \( 4 + 4 \) (Fig. 8(c)) calculations of a pronounced, broad band ranging from 2.6 to 3.3 eV is in contrast to the observed photoelectron intensity in this energy range. Interesting is that this energy range is dominated by the experimental spectrum (Fig. 8(a)) can be explained as a combination of the fundamentals of \( \nu_6, \nu_7, \) and \( \nu_8 \). The triplet reproduces to a good approximation the structure of this asymmetric second peak, which is characterized by a shoulder on the red side. Three individual vibrational transitions of pyrrolyl have been identified from the experimental spectrum in Ref. [13], with frequencies \( 925 \pm 65 \) cm\(^{-1} \), \( 1012 \pm 25 \) cm\(^{-1} \), and \( 1464 \pm 20 \) cm\(^{-1} \). The two lower energy levels are associated with the asymmetric second peak, the highest frequency corresponds to the third peak. The \( 5 + 2 \) calculation suggests an identification of these transitions with the fundamentals of \( \nu_8, \nu_6, \) and \( \nu_4 \) of the pyrrolyl radical. This assignment implies that the level \( \nu_4 \) has not been resolved in the experimental spectrum.

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Also, the estimate of both the \( 5 + 2 \) (Fig. 8(b)) and \( 4 + 4 \) (Fig. 8(c)) calculations of a pronounced, broad band ranging from 2.6 to 3.3 eV is in contrast to the observed photoelectron intensity in this energy range. Interesting is that the shape of the theoretical \( 1^2B_1 \) bands in Fig. 8(b) and (c). The vertical detachment energy of the \( 1^2B_1 \) state defined for the model Hamiltonians is \( E_2 = 2.617 \) eV (Section 5.1). Since the two corresponding spectra are shifted to higher energies by 0.295 eV and 0.291 eV (cf. Table 6) to match the position of the experimental \( 1^2A_2 \) origin peak, the actual \( 1^2B_1 \) vertical energy employed for the calculations is 2.912 eV and 2.908 eV, respectively. Inspection of the \( 1^2B_1 \) band simulations reveals that by far most of the intensity is accumulated above 2.91 eV, a very unusual situation. From a time-independent point of view, this result is consistent with large overlap integrals of excited vibrational states in the adiabatic \( 1^2B_1 \) oscillator with the initial wave packet. In other words, the topology of the model PE surfaces leads to this vibrational excitation of the \( 1^2B_1 \) state upon photodetachment.

### 6.2. Calculations with pyrrolyl radical frequencies

A systematic approach to account for the different shapes of the pyrrolyl ground state and pyrrolyl ground as well as first excited state would require an expansion of the diabatic potential functions to full second or even higher order [39,40]. As discussed above, we take the frequency changes in the pyrrolyl radical in an approximate way into account. The pyrrolyl \( 1^2A_2 \) state normal frequencies (Table 2) also have been employed for the description of the \( 1^2B_1 \) state. The motivation for this model is the expectation of an improved description of the vibrational structure of the \( 1^2A_2 \) band.

In Fig. 9, the spectra computed with Hamiltonians \( \mathbf{H}_{5,2} \) (b) and \( \mathbf{H}_{4,4} \) (c) and employing pyrrolyl radical frequencies are compared to the experimental spectrum (a). As expected, an analysis of Fig. 9(b) and (c) shows that the energetic positions of the vibronic lines in the \( 1^2A_2 \) band are in good agreement with the measurement (a), better than the resulting locations by employing pyrrolyl anion frequencies (cf. Fig. 8(b) and (c)).

Both Fig. 9(b) and (c) gives the impression that the asymmetric structure of the band centered at 2.27 eV can be better reproduced using pyrrolyl frequencies. The \( 4 + 4 \) calculation yields a particularly good agreement with experiment in this energy region, which is dominated by the fundamentals of \( \nu_6, \nu_7, \) and \( \nu_8 \). A comparison of Fig. 9(b) with the pyrrolyl frequency calculation in Fig. 8(b) shows that the level \( \nu_4 \) is not as prominent in the \( 5 + 2 \) calculation with pyrrolyl frequencies (note \( \omega_{R,S} < \omega_{R,S} \)). Interestingly, no intensity borrowing peaks are present below 2.3 eV in Fig. 8(b), while one can be recognized at 2.224 eV (637 cm\(^{-1} \)) in Fig. 9(b). Both calculations performed with radical frequencies predict about the same intensity for the corresponding detachment, but the \( 4 + 4 \) calculation places the energy closer to the origin peak. No transition that could be associated with this intensity borrowing peak can be clearly discerned in the experimental spectrum, but it may be part of the origin peak or of the band at 2.27 eV. Replacing pyrrolide by pyrrolyl frequencies in the calculations does not improve the agreement with experiment regarding the prominent feature observed at 2.33 eV. The intensity of this peak is overestimated also in Fig. 9(b) and (c). The \( 5 + 2 \) calculations (Figs. 8(b) and 9(b)) attribute the band measured at 2.33 eV mainly to the fundamental of \( \nu_4 \), while the \( 4 + 4 \) results (Figs. 8(c) and 9(c)) indicate that other vibrations are contributing.

Both the \( 5 + 2 \) and \( 4 + 4 \) calculations with pyrrolyl frequencies predict two relatively similar, broad bands close to 2.5 eV, one slightly below and the other slightly above this energy. A broad band of appropriate intensity is actually present in the experimental spectrum centered at \( \approx 2.46 \) eV. A stronger band beyond 2.5 eV is, however,
absent in the measurement. Only a weak hump can be noticed at 2.52 eV that may correspond to the calculated bands in this energy region. The theoretical spectra obtained with pyrrolide frequencies (Fig. 8 (b) and (c)) also show significant intensity between 2.5 eV and 2.6 eV. This deviation between theory and measurement seems to be related to the nature of the approximation and does not appear to be very sensitive to the parameters of the model.

The calculations with pyrrolyl frequencies predict an intensity distribution for the $1^2B_1$ band that is very similar to the pyrrolide frequency results. Again, most of the photoelectrons are detected at energies beyond the vertical detachment energy and the maxima of both the $5 + 2$ and $4 + 4$ models are located close to 3.0 eV. This can be interpreted as the production of vibrationally excited levels of the pyrrolyl radical when an electron is removed from the $b_1$ orbital of the pyrrolide anion.

7. Conclusions

The ab initio calculations confirm the existence of a $1^2B_1–1^2A_2$ conical intersection along the vibrational mode $v_4$, cf. Fig. 3. The two radical states intersect in the vicinity of the potential minimum of the excited state, which causes strong vibronic coupling. Figs. 8 and 9 demonstrate that the linear vibronic coupling model qualitatively explains the experimental photodetachment spectrum, especially the broad, unstructured $1^2B_1$ band. Three normal modes are by far dominant, the tuning mode $v_4$ and the two coupling modes $v_{14}$ and $v_{15}$. In addition, the four totally symmetric modes $v_3$, $v_6$, $v_7$, and $v_8$ as well as the two coupling modes $v_{16}$ and $v_{18}$ are identified to be relevant.

The energetic positions in the simulated $1^2A_2$ band are in good agreement with the experimental ones when the radical frequencies $\omega_{A_2}$ are employed (cf. Fig. 9). In particular, the locations of the asymmetric second and the third peak are reproduced. The measured frequencies are $925 \pm 65 \text{ cm}^{-1}$ and $1012 \pm 25 \text{ cm}^{-1}$ for the second peak, and $1464 \pm 20 \text{ cm}^{-1}$ for the third peak. Test calculations allow us to assign these peaks to be mainly due to the modes $v_8$, $v_6$, and $v_4$ with fundamentals of $883 \text{ cm}^{-1}$, $1043 \text{ cm}^{-1}$, and $1561 \text{ cm}^{-1}$, respectively.

The photoelectron intensities in the $1^2A_2$ band are slightly underestimated for the asymmetric second peak and overestimated for the third peak compared to the experimental findings. Figs. 8 and 9 show that the vibronic fine structure of the $1^2A_2$ band is somewhat better reproduced by employing the radical frequencies. Throughout, the model calculations predict that intensity borrowing peaks are not playing a substantial role for the intensity distribution in the $1^2A_2$ spectrum, but the fundamentals of the dominating coupling modes $v_{14}$ and $v_{15}$ may be part of the origin band or the first excited band. However, the overtones of these two vibrations do possibly add significant intensity to the band observed at 2.33 eV which is certainly not only associated with the level $v_4$ but is more complex.

As shown by Figs. 8 and 9, the linear vibronic coupling model nicely reproduces the complete diffuseness of the $1^2B_1$ band and the long structureless tail extending beyond 3 eV binding energy. It is the consequence of the directly accessible conical intersection of the $1^2B_1$ excited state with the $1^2A_2$ ground state of the pyrrolyl radical.

Compared to experiment, the intensity of the simulated $1^2B_1$ band is too high. One possible reason for this is a relatively low energy of photoelectrons in the energy domain of the $1^2B_1$ state. The wavelength of the exciting laser is 363.8 nm, which means that photoelectrons at an excitation energy of 3.4 eV have near-zero kinetic energy. Photoelectrons of very low energy are more difficult to detect experimentally and this effect may at least partially explain the low intensities observed beyond an excitation energy of 3.0 eV.

Another important factor may be a considerable difference in the partial-channel cross sections $\sigma_{j,a}(E_k)$ for detachment from the pyrrolyl anion ground state, leading to the $1^2A_2$ and $1^2B_1$ states of pyrrolyl. The electronic part of the pole strength factors $|\xi_{s,j}|^2$ has been estimated by the MRCI method to be about equal for the $1^2A_2$ and $1^2B_1$ states (see Section 2.4). This would imply $|t_{k,h}|^2 \ll |t_{k,a}|^2$, i.e., the orbital detachment cross section for the photodetachment from the $b_1$ orbital might be much smaller than for removal of an electron from the $a_2$ orbital. An explicit evaluation of the matrix elements $t_{k,h}$ and $t_{k,a}$ would be required to obtain a reliable estimate of the effect of the partial-channel cross sections on the observed photoelectron intensities.

Let us finally compare the vibronic-coupling effects in the pyrrolyl radical and the furan radical cation. While the $2^2A_2$ electronic ground state has a vibrationally structured spectrum in both cases, the $1^2B_1$ band of the furan cation exhibits resolvable, although strongly broadened, vibronic structure. The $1^2B_1$ band of pyrrolyl is essentially structureless, as discussed above. The crucial difference between both systems is the energy gap of the $1^2A_2$ and $1^2B_1$ states, which is about 1.5 eV in the furan radical cation and about 0.5 eV in the pyrrolyl radical. Due to the smaller energy gap, the vibronic-coupling effects are considerably more pronounced in the pyrrolyl radical than in the furan cation.

Acknowledgements

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References