Intramolecular dynamics of pyrrole

Thesis submitted in fulfillment of the requirements for the degree of "Master of Science"

By: Michael Epshtein

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Abstract

The photophysical properties of deoxyribonucleic acid (DNA) and proteins and their key constituents, with respect to ultraviolet (UV) irradiation, are affecting life and therefore of considerable interest. It was anticipated that by studying pyrrole, considered as a simplified model of the building blocks of these important biomolecules, an understanding regarding the processes that these molecules undergo through their interaction with photons will be obtained. In this work the photodissociation of vibrationally excited pyrrole is studied for the first time, in attempt to reveal details on the intramolecular vibrational redistribution (IVR) and on the role played by vibrational excitation in inducing UV electronic excitation and unimolecular transformations.

Room temperature and jet-cooled laser-based spectroscopies facilitated monitoring vibrational spectra and H fragments released in UV photodissociation of vibrationally pre-excited pyrrole. Vibrational excitation in the regions of N-H ($\nu_1$) and C-H ($\nu_2$) fundamental stretches was achieved by stimulated Raman scattering (SRS), and around the first, second and third overtone of the N-H stretch by direct near infrared excitation (NIR). Comparison of the action spectra, reflecting the H photofragments yield vs. the vibrational excitation laser wavelength, to photoacoustic Raman (PAR) spectra allowed assessing the effect of different skeletal motions on pyrrole photodissociation. For an initially excited eigenstate, primarily consisting of two quanta of ring deformation ($2\nu_{19}$), enhanced reactivity was found relative to that of an almost isoenergetic state with one quantum of symmetric C-H stretch, providing evidence for mode-specificity in a molecule with twenty four vibrational degrees of freedom. The PAR spectra also allowed obtaining information about the hot bands in the N-H and C-H stretch fundamentals vicinity. The identification of these bands and the retrieved parameters added new data to the extensive set of already known vibrational constants of pyrrole and assisted in describing the IVR process.

As for the N-H overtones, contrary to “isolated” states excited with two and three N-H stretch quanta, the one with four quanta shows strong accidental resonances with two other states involving three quanta of N-H stretch with one quantum of C-H stretch, namely $(3\nu_1+\nu_2)$ and $(3\nu_1+\nu_3)$. The inhomogeneously reduced features in the action
spectra enabled getting insight into the intramolecular interactions and the factors controlling energy flow in pyrrole. This study is an initial step in elucidating the intramolecular dynamics of vibrationally excited pyrrole on the ground and electronic potential energy surfaces.
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1. INTRODUCTION

The nucleobases and aromatic amino acids represent some of the most important building blocks of deoxyribonucleic acid (DNA) and proteins, respectively. Therefore, studying their photoexcitation and photophysics is extremely important.\textsuperscript{1,2,3} In most cases, even the building blocks are quite complicated and therefore only their constituents, which are simplified models can be investigated. One important candidate is pyrrole (C₄H₄NH), which is an aromatic five-membered ring containing a nitrogen atom (see Fig. 1.1). In particular, by studying the dissociation of vibrationally excited pyrrole, an understanding regarding the influence of reagent vibrations on the dissociation pathways and dynamics is expected to be obtained.

Recalling that vibrational excitation of molecules in their ground electronic state plays an essential role in many processes and can affect the reactivity of molecular systems, it would be beneficial to study the vibrationally mediated photodissociation (VMP)\textsuperscript{4,5,6} of pyrrole. This kind of studies may assist in finding the role played by vibrational excitation during the photoexcitation and/or the subsequent fragmentation processes. Moreover, these studies can shed light on the process of intramolecular vibrational energy redistribution (IVR),\textsuperscript{7,8,9} in which vibrational energy, initially localized in a specific mode, is redistributed among other vibrational modes of the molecule.

Here, a short description of the fundamental aspects of IVR and an overview of previous works on pyrrole will be given

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{pyrrole_structure.png}
\caption{Equilibrium geometrical structure of pyrrole. The molecular plane is defined by the a- and b-axes and the c-axis is perpendicular to the molecular plane.}
\end{figure}
1.1 Scientific background

A fruitful approach for obtaining a deeper understanding on IVR is that of studying vibrational spectroscopy of fundamentals and overtones of hydride oscillators. The vibrational spectra can be interpreted within normal mode (NM) or local mode (LM) model basis functions, provided that the necessary coupling matrix elements are included in the Hamiltonians.\textsuperscript{10} Therefore, much effort is devoted to find the important couplings in molecular systems to obtain a good correspondence between the predicted and experimental band positions and for reaching a reasonable assignment of the observed multiplet structure and their widths.

One approach for describing the vibrations in polyatomic molecules is that of the NM model,\textsuperscript{11} treating vibrations as infinitesimal displacements of the nuclei in a harmonic potential, a picture naturally including couplings among bonds in a molecule. The energies of the vibrational levels for a polyatomic molecule can be calculated from the well-known expression:\textsuperscript{12}

\[
G(v_1, v_2, \ldots) = \sum_i \omega_i \left( v_i + \frac{d_i}{2} \right) + \sum_{i < j} x_{ij} \left( v_i + \frac{d_i}{2} \right) \left( v_j + \frac{d_j}{2} \right) + \ldots, \tag{1.1}
\]

where \( \omega_i \) is the harmonic vibration wavenumber for the normal mode \( i \), \( d_i \) is the corresponding degeneracy, and \( x_{ij} \) are anharmonic constants.

When considering molecules excited to highly vibrationally excited levels using light, one must take into account that the optically active state often corresponds to a simple vibrational motion close to a zero order state, i.e., a zero order bright state (ZOBS), \( |s\rangle \), shown schematically in Fig. 1.2. In its vicinity there are other states that have no allowed optical transitions from the ground state, namely, zero order dark states (ZODS), \( |l\rangle \). Both types of states are eigenstates of the zeroth order Hamiltonian, neglecting anharmonic coupling terms. When the full molecular Hamiltonian that includes these coupling terms is considered, the resulting eigenstates can be expressed as linear combinations of the ZOBS and ZODS, \( |j\rangle = C_j^s |s\rangle + \sum_l C_j^l |l\rangle \). As a result of the coupling between ZO states, several eigenstates \( |j\rangle \) can have some component of \( |s\rangle \), and
each of these states will appear in the spectrum with an intensity proportional to their brightness, \( |C_s|^2 \).

Fig. 1.2 - Schematic representation of the optical vibrational excitation of a molecule at zero order of perturbation theory (left hand side), the molecular eigenstates are those of a conveniently simplified Hamiltonian \( H_0 \) (e.g., including only harmonic terms in the potential), and only one of these states is optically active (‘bright’). This bright state is interacting with optically inactive ‘dark’ states and is coupled to them by the initially neglected anharmonic terms. Once these terms are included in the full Hamiltonian (right hand side) the resulting eigenstates, being mixtures of the zeroth-order states, are obtained, where each one can have some bright state character, indicated by a thicker (blue) line. In the spectrum, obtained by scanning the frequency of the excitation laser, each eigenstate appears with an intensity proportional to its brightness. Taken from Ref. 8.

In addition to strong low order Fermi resonances, or other anharmonic couplings, the spectrum of highly vibrationally excited molecules, where high density of bath states occurs, may show clumps resulting from weak high order resonances. Therefore, if the spectrum is measured with sufficient resolution, instead of a single ro-vibrational transition, a set of transitions is observed. The minimal resolution allowing to resolve the lines of an “IVR multiplet” should be \( 1/(\text{number of vibrational bath states per unit energy}) \). If the experimental resolution is larger than this limit (for example, due to the laser spectral width), the IVR multiplet will not be resolved and will appear as a single homogeneously broadened rovibrational line (as shown in Fig. 1.3) with the width given by the Fermi golden rule.\(^{13}\)
\[ \Gamma = 2\pi \langle V^2 \rangle \rho, \]  

(1.2)

where \( \Gamma \) is the linewidth, \( \rho \) is the bath state density and \( \langle V^2 \rangle \) is the root-mean-squared interaction matrix element of the bright state or quasi eigenstate with the bath states. In fact, this width is the rate of the single-exponential decay of the population in the ZOBS (in time domain experiments).

![Diagram of optical excitation](image)

**Fig. 1.3** - Schematic representation of the optical excitation of a molecule to high-energy vibrational states.

As in Fig. 1.2, at order zero of perturbation theory, one bright state is embedded in a region of dark states and anharmonic couplings mix them into new states. Unlike in the previous example, these are not strictly eigenstates, since they are further coupled with the bath state and, hence, have a finite decay rate. In the measured frequency domain spectrum, each of these ‘resonance states’ appears with intensity proportional to the brightness and at the spectral resolution of our system with a width, \( \Gamma \), proportional to its decay rate. The interaction with the bath states does not affect the spectral position of the quasi eigenstates, but the eigenstates appear in the spectrum with width. Taken from Ref. 8.

The information about IVR in a frequency-domain spectrum can be reduced to a so-called “mechanistic” model,\(^7\) where one finds an effective Hamiltonian model describing the splitting and relative intensities of the ZOBS. This model is expressed in terms of a set of ZO basis states, energies and coupling terms, corresponding respectively to diagonal and off-diagonal matrix elements of the Hamiltonian. The parameters defining this model are obtained by a least-squares fit that minimizes differences between observed and calculated energies and relative intensities. Alternatively, some of these parameters may be obtained from *ab initio* potentials or by transfer from similar molecules.
By using the Hamiltonian obtained from frequency-domain spectra, it is possible to extract the temporal behavior of the ZO states. Particularly, the vibrational Hamiltonian allows us to follow the temporal evolution of the density matrix given as a function of time by:\textsuperscript{14}

\[ P(t) = U(t)P(t = 0)U^\dagger(t), \]  

\begin{equation}
\text{(1.3)}
\end{equation}

where

\[ U(t) = e^{-i\hbar/\hbar}, \]  

\begin{equation}
\text{(1.4)}
\end{equation}

and the \( P_i(t) \) diagonal element is the probability for finding the system at time \( t \) in the \( i \)-th zero-order basis state and \( P(t = 0) \) is a matrix of zeros, except of particular diagonal elements given their respective probabilities (populations) at \( t = 0 \) (for the case of a single ZOBS this probability is equal to one).

In order to investigate the IVR it is vital to correctly identify various spectral bands, related to fundamentals, overtones, combinations and hot bands. The latter appear at positions shifted relative to the principal band, due to the cross-anharmonicity term (see appendix A.1). Their relative intensity depends on the energy of the low lying level and the temperature of the system, which leads to its population, according to Boltzmann distribution.\textsuperscript{15}

The focus of this research was on pyrrole molecules possessing twenty four fundamental modes.\textsuperscript{16} The spectral regions of interest were those of the two highest fundamental modes, N-H \((v_1)\) and C-H \((v_2)\) stretches, and the N-H stretch overtones \((2v_1, 3v_1, 4v_1)\), where the density of states is much higher. In the fundamental regions two measurement methods were used: photoacoustic stimulated Raman spectroscopy (PARS)\textsuperscript{17,18} and VMP, where the vibrational excitation was induced by stimulated Raman scattering (SRS). As for the overtones regions, direct near infrared (NIR) excitation was used and the measurements were performed by photoacoustic (PA) spectroscopy and VMP.
1.2 Overview of previous works

The spectroscopy of pyrrole has been studied for decades and yet there are missing pieces in the puzzle. The first IR data on pyrrole seem to have been reported by Colblenz in 1905 in the liquid phase,\(^{19}\) while its first Raman spectrum was reported 25 years later.\(^{20}\) In 1942 Lord and Miller made the first significant vibrational analysis of the IR and Raman spectra of liquid pyrrole and its symmetrical deuterated derivatives.\(^{21}\) In the gas phase, extensive infrared and Raman investigations of pyrrole with theoretical predictions were reported.\(^{22,23,24,25,26,27}\)

In the early '90s, some studies focused on the N-H and C-H fundamentals and overtones and the close lying hot bands, using direct IR excitation.\(^{15,28,29}\) Multiple transitions were observed in the region of the third N-H stretch overtone, considered to be a result of vibrational coupling to other vibrational modes, while for the fundamental and other overtones single bands were found.\(^{28,29}\) Additionally, in these regions the \(n\nu_1+\nu_16-\nu_16\) hot band series were observed, attributed to transitions originating from the 474 cm\(^{-1}\) N-H wag fundamental. The non-diagonal anharmonicity constant for \(\nu_16\) was deduced to be \(-25\) cm\(^{-1}\).\(^{15,28}\) Several C-H stretch overtones for pyrrole were also observed, however, no assignment for the multiple peak structure was suggested.

In 1993, Klots\(^{30}\) determined the 24 fundamental vibrational frequencies of pyrrole by measuring the IR and Raman spectra of pyrrole in the gas and liquid phases. Of particular importance is the measured Raman vapor spectrum, which allowed identifying the C-H stretch (\(\nu_2\)) and observation of only two hot bands in its vicinity, due to the relatively poor spectral resolution (2 cm\(^{-1}\) bandpass with a 0.5 cm\(^{-1}\) step size of the spectrometer). Yet, these hot bands were not identified.

Later, the N-H, C-H fundamental and overtones stretch regions were investigated by Fourier transform IR (FTIR) spectroscopy at high spectral (0.005 cm\(^{-1}\)) resolution\(^{31,32,33}\) and quantum mechanical calculations.\(^{34}\) These measurements allowed determining the rotational constants of the fundamental N-H stretch. Hot bands in the vicinity of the N-H and C-H stretch fundamentals, expected to originate from the additional low frequency modes, around 600 and 700 cm\(^{-1}\), could not be resolved. As mentioned above, even if the picture is considered to be apparently understood, there is
still missing information about the hot bands series related to N-H and C-H stretches and there is still very little known about the IVR process in this molecule, issues that will be addressed in this work.

In addition to the ro-vibrational spectroscopy, pyrrole figured as a model in numerous studies related to its UV absorption spectrum,\textsuperscript{35,36,37,38,39} and photoinduced dynamics.\textsuperscript{40,41,42,43,44,45,46} From theoretical calculations it was revealed that $^{1}\pi\pi^{*}$ states [$^{1}B_{2}(\pi\pi^{*})$ and $^{1}A_{1}(\pi\pi^{*})$] are responsible for the near-UV absorption. Furthermore, the calculations revealed that there are two additional lower excited singlet states of $^{1}\pi\sigma^{*}$ [$^{1}A_{2}(\pi\sigma^{*})$ and $^{1}B_{1}(\pi\sigma^{*})$] character, which were suggested to be optically-dark excited states.\textsuperscript{38,39,45} The dynamical aspects of pyrrole photophysics, following near UV excitation have also been studied, leading to the finding that most of the photofragments resulting from $\sim$ 243.1 nm photodissociation of pyrrole yield H + pyrrolyl radical.\textsuperscript{47} Nevertheless, it has to be emphasized that no experiments, providing information on the influence of the vibrational excitation on the photodissociation of pyrrole, were performed and it is anticipated that the current work will shed some light on this issue as well.
2. MEASUREMENT METHODS

This work is based on two main measurement methods: PA and VMP spectroscopies, where the former allows measurement of ro-vibrational spectra, while the latter monitoring of hydrogen (H) action spectra, reflecting the yield of the released H atoms as a function of vibrational excitation. Comparison of the H action spectrum to the ro-vibrational spectra will allow to figure out whether pre-vibrational excitation impacts the photodissociation of pyrrole.

2.1 Vibrational mediated photodissociation (VMP)

The VMP process consists of three main stages: excitation of the vibrational level by SRS or direct NIR excitation, promotion of the vibrationally excited molecule to an upper electronic state and finally its dissociation, and detection of the photofragments by resonantly enhanced multiphoton ionization (REMPI).4

![Diagram of VMP process](image)

Fig. 2.1 - Schematics of vibrationally mediated photodissociation followed by (2 + 1) resonantly enhanced multi-photon ionization, (a) direct ro-vibrational excitation and (b) ro-vibrational excitation via SRS.
2.1.1 Vibrational excitation

**Direct excitation:** A single photon of energy equal to the transition energy from the ground state to the required ro-vibrational state is used for vibrational excitation. Due to Born–Oppenheimer approximation\textsuperscript{48} the total wave function can be factorized, and the probability for vibrational excitation is:

\[ P_v \propto \left| \langle n| \vec{\mu} | g \rangle \right|^2 , \tag{2.1} \]

where, \( g \) is ground vibrational state of the ground electronic state, \( n \) is a vibrationally excited state and \( \vec{\mu} \) is a dipole moment vector.

\( \vec{\mu} \) varies with \( x \), where \( x \) is the displacement of the internuclear distance from equilibrium. This variation can be expressed as a Taylor series expansion:\textsuperscript{48}

\[ \vec{\mu} = \vec{\mu}_e + \left( \frac{d\vec{\mu}}{dx} \right)_e x + \frac{1}{2} \left( \frac{d^2\vec{\mu}}{dx^2} \right)_e x^2 + \frac{1}{6} \left( \frac{d^3\vec{\mu}}{dx^3} \right)_e x^3 + \ldots , \tag{2.2} \]

where the linear term refers to the transition of a harmonic oscillator, allowing vibrational quantum number changes of only \( \Delta v = \pm 1 \). The effect of higher terms is known as electrical anharmonicity, allowing transitions with \( |\Delta v| > 1 \) and in fact overtone transitions.\textsuperscript{48} As \( \Delta v \) becomes larger, the transition intensities decrease about an order of magnitude with an addition of each vibrational quantum number.\textsuperscript{7}

**Stimulated Raman scattering (SRS):** This excitation\textsuperscript{49,50} is induced by two photons, one at a pump frequency, \( \omega_p \) and one at a Stokes frequency, \( \omega_S \) which are mixed to excite a specific ro-vibrational level. The mixing occurs for all frequencies, but is greatly enhanced if the frequency difference \( \omega_p - \omega_S \) matches a Raman-active vibrational resonance. The probability for SRS vibrational excitation is:

\[ P_v \propto \left| \langle n| \vec{\alpha} | g \rangle \right|^2 , \tag{2.3} \]

where \( \vec{\alpha} \) is the polarizability tensor that can be expressed as a Taylor series expansion.
\[ \tilde{\alpha} = \tilde{\alpha}_0 + \left( \frac{d\tilde{\alpha}}{dx} \right)_0 x + \frac{1}{2} \left( \frac{d^2\tilde{\alpha}}{dx^2} \right)_0 x^2 + \frac{1}{6} \left( \frac{d^3\tilde{\alpha}}{dx^3} \right)_0 x^3 + \ldots. \] 

(2.4)

As for direct vibrational excitation, SRS has the same vibrational selection rules.\(^{48}\)

### 2.1.2 Photodissociation

The photodissociation of the vibrationally excited molecules was performed by a single ~ 243.1 nm photon. Pre-excitation of the overtone or fundamental vibrations leads to enhanced absorption of the UV photon, particularly when the Franc-Condor (FC) factors are favorable, and thus the photodissociation is more effective. The photodissociation probability \( P \) is given by:

\[ P \propto P_e \left| \langle e' | \vec{\mu} | e \rangle \right|^2 \left| \langle n' | n \rangle \right|^2, \]  

(2.5)

where \( e' \) is an electronically excited state and \( n' \) designates a vibrational state of \( e' \). Eq. 2.5, describes the probability in case of photodissociation of vibrationally excited molecules, where the first term is the probability for vibrational excitation, the second for electronic excitation, depending on \( \vec{\mu} \), the electric dipole moment operator and the third term is the overlap between the vibrational states, namely the FC term.

The reason for choosing ~ 243.1 nm photons was to fit the wavelength to the corresponding two photon REMPI transition, employed for detecting the emerging H photofragments.

### 2.1.3 Resonantly enhanced multiphoton ionization

Multiphoton ionization (MPI)\(^{51}\) is a process in which \( m \) photons, carrying total energy of, \( mh\nu \) higher than the ionization threshold, are absorbed by an atom/molecule. The process can be viewed as series of transitions via virtual states, and generally has very low cross-section. But whenever one of the transitions occurs through a resonant level, the intensity of the transition is greatly enhanced. If such a resonance occurs the
process is assigned as \((n + 1)\) REMPI, where \(n\) is the number of photon needed to reach the resonant state, \(1\) to ionize this state and \(n + 1 = m\). The probability for such a transition between an initial state \(i\) and final state \(e\) is given by:\(^5\)

\[
S_{\mu} = \sum_{k} \frac{\langle i | \mu | k \rangle \langle k | \mu | e \rangle}{E_i - E_k - \hbar \nu},
\]  

(2.6)

where \(\mu\) is the transition dipole moment and \(k\) counts all energy states between \(i\) and \(e\). Scanning the laser frequency over the region of the desired transition and measuring the ion current reflects the number density of the probed atom/molecules and their state distribution. As the resonance enhances only one specific atomic/molecular transition, REMPI is a selective ionization method. The combination of REMPI with time-of-flight mass spectrometry (TOFMS) (see below) provides a sensitive mass selective detection method. In this research \((2 + 1)\) REMPI was utilized for monitoring H photofragments via the \(2s^2S \leftarrow 1s^2S\) two photon transition, at 243.135 nm.

### 2.2 Photoacoustic spectroscopy (PA)

The PA effect is the process of acoustic wave generation as a consequence of photons absorption in a sample. The physical principles of PA spectroscopy are quite simple. Absorption of light by a sample excites part of the molecules from the ground state into higher energy levels.\(^\text{18}\) The excited molecules collide with other molecules in the gas and as a result of these collisions, the vibrational energy of these excited molecules is converted into translational kinetic energy, causing localized increase of temperature and thus of pressure in the light path and therefore generation of an acoustic wave in the sample.

By using the equation of state:

\[
P V = (\gamma - 1) U,
\]  

(2.7)

where \(P\) is the pressure, \(\gamma\) the ratio of the heat capacity \(C_p/C_v\), \(U\) translational internal energy and \(V\) the volume of the cell.
Assuming that all excited molecules relax through nonradiative channels, the pressures change by:

\[ \Delta P = (\gamma - 1)\Delta U / V = (\gamma - 1)\Delta N(\hbar \omega) / V, \]  

(2.8)

where, \( \Delta N \) is the number of excited molecules (the vibrational excitation takes place in the region of depth of focus volume where the light intensity is much higher than in the other regions of the laser beam) and \( \hbar \omega \) is the transition energy. By monitoring the pressure wave, propagating away from the source, by a tiny microphone in the cell one can record the intensity of the generated acoustic wave as a function of the photon energy.
3. **EXPERIMENTAL SYSTEM**

The experimental system used in this work consists of two main subsystems with a variety of optical and electronics devices. One, consists a TOFMS and the second a PA cell, allowing measurement of jet-cooled action spectra and PA spectra, respectively.

3.1 **The time-of-flight mass spectrometer**

The interaction of the lasers with a skinned supersonic molecular beam of the sample, in particular, the VMP process that leads to H photofragments, their ionization by REMPI and their acceleration to the detector are performed in a home-built Wiley-McLaren TOFMS. The basic principle of the TOFMS is acceleration of ions by an electric field from one end, where they are formed, to the detector which is located at the other end. The fields provide the ions with speeds, depending on their masses and charges, and therefore the TOFMS assures mass-specific detection.

The photoions are formed within the extraction region, accelerated in the second region and drifted in the field free region towards the detector as shown in the schematic of our TOFMS in Fig. 3.1.

![Fig. 3.1 - The TOFMS geometry.](image-url)
The parameters defining the TOFMS characteristics are as follows: $E_s$ and $E_d$ are the electric fields in the extraction and the acceleration regions, respectively, $s$ is the flight length from the ion formation position to the exit of the extraction field, $d$ and $D$ are the lengths of the acceleration and drift regions, respectively. The TOF as a function of ion mass can be calculated from the kinetic energy gained by the ions in the electrical fields. Assuming initial condition of zero velocity and formation of all ions at the same point ($s_0$), the total kinetic energy, $U$, gained by the ions is:

$$U = q s_0 E_s + q d E_d,$$  \hspace{1cm} (3.1)

which is independent of ion mass $m$ [amu], but depends on the ion charge, $q$. The TOF, $T$, is then given by:  \hspace{1cm} (3.2)

$$T = t_s + t_a + t_D = \gamma \sqrt{\frac{m}{2U}} \left[ 2\sqrt{k_0 s_0} + \frac{2\sqrt{k}}{k + 1} d + D \right],$$

where $\gamma = 1.02$ is a constant of proportionality and $k_0$ is the ratio between the total potential and that of the acceleration region, given by:

$$k_0 = \frac{s_0 E_s + d E_d}{s_0 E_s}.$$  \hspace{1cm} (3.3)

Two factors limit the TOFMS resolution: the initial space distribution and the initial kinetic energy distribution of the formed ions. Space resolution can be increased dramatically by space focusing, which depends on the fact that an ion initially close to the acceleration region acquires less energy and therefore eventually is overtaken by ions which have larger initial $s$ values. The focusing condition is given by:  \hspace{1cm} (3.4)

$$D = 2 s_0 \sqrt{k_0} \left[ 1 - \frac{1}{k_0 + \sqrt{k_0 s_0}} \frac{d}{s_0} \right],$$

and is the same for all ions and independent of the total energy of the system. The maximum time spread introduced by initial velocities is the difference in the flight time
between a pair of identical ions formed at the same position with the same initial speed, but with oppositely directed velocities. The double field system brings the ions to their maximum energy in about 5% of the flight time. Thus, the disturbing effect of the initial kinetic energy is usually small because it is a small percentage, on the average, of the energy determining the ion velocity at each point.

In addition to the extraction and acceleration electric fields, our TOFMS consists of two pairs of deflection plates and an Einzel lens within the drift region, which help increasing the signal by minimizing ions fly out. The detector used in the TOFMS is a microchannel plate (MCP, El-Mul), the output signal of the detector was fed into a digital oscilloscope (Lecroy, 9374) and a boxcar integrator (Stanford Research Systems, SR 280). This ion signal is then passed to a PC via an A/D converter (Keithley, DASH 16) and accumulated for further analysis.

3.1.1 Molecular beam

The TOFMS chamber was pumped by two turbo molecular pumps, one at each side (Alcatel, ATP 400, ATP 150) generating total pumping power of ~ 600 liter/min, to a background pressure of \( P \sim 1 \times 10^{-7} \) Torr, when the valve releasing the sample is closed. Following opening of the pulsed valve (Knowles Electronics, BT-9-21759) for ~ 180 \( \mu \text{s} \) at a rate of 5 Hz, pressures of \( P \sim 2 \times 10^{-6} \) Torr were obtained and used as typical working pressure.

The gas sample was prepared as a mixture, where the liquid pyrrole (Aldrich, 98% purity) was used without further purification and its vapors \( (P \sim 6.5 \text{ Torr}) \) were seeded in argon at a total pressure of 760 Torr at room temperature, expanded through a 0.8 mm orifice of a pulsed valve and skimmed ~ 2 cm downstream the nozzle exit. The molecular beam traveled another ~ 3 cm from the skimmer exit to the reaction chamber center, where it was crossed by the lasers. The time for opening the valve was controlled by the delay generator and the valve was opened ~ 700 \( \mu \text{s} \) before the arrival of the laser beams. An efficient adiabatic cooling of the molecular jet was achieved.

During the process, the thermal energy of the molecules in the source is partly transferred into expansion energy. The thermal energy comprises translational,
vibrational and rotational temperatures. As will be shown later the system enables reaching rotational temperatures of $\sim 10$ K, under the above mentioned conditions. This leads to decrease of the population in the high rotational states, resulting in reduced inhomogeneous structure and congestion in the spectra.

The use of dilute mixtures of pyrrole ($0.05\%$) with argon as carrier gas enhanced the cooling thanks to collisions between the two species. A good approximations for high-speed flow for an isentropic expanding gas, is that of an ideal gas, neglecting viscous and heat conduction effects. In these conditions the cooling can be described by: \cite{53}

$$\frac{p}{p_0} = \frac{T}{T_0}^{-\frac{\gamma}{\gamma-1}},$$

where $p_0$ and $T_0$ are the stagnation pressure and temperature, respectively, and $\gamma = C_p / C_v$ is a property of the fluid species. Because the collisions between the two species, the $\gamma$ of the mixture is a weighted average of its ingredients. Since for Ar $\gamma = 5/3$, the $\gamma$ of the mixture is close to that value.

### 3.2 Optical setup

Through this work different types of measurements and setups were used. In the fundamental N-H and C-H stretch regions the action spectra were measured by preparing the vibrational eigenstates of pyrrole via SRS, followed by UV promotion of the energized molecules to the upper potential energy surface (PES) and subsequent H photofragment detection, in a TOFMS. This experiment requires interaction of three laser beams, pump, Stokes and UV with the supersonic molecular beam of the sample in the TOFMS (Fig. 3.2). In the N-H stretch overtone spectral regions, interaction of two laser beams with the supersonic molecular beam is required (Fig. 3.2).

Another optical setup was required for the PARS and PA experiments including the PA cell\cite{17} (Fig. 3.3) and the interaction of the pump and Stokes beams for excitation in
the fundamental region, and only the NIR laser beam for excitation of the N-H stretch overtone regions.

Fig. 3.2 - Schematic diagram of the experiment setup used for VMP. A) Temporal synchronization of the system, where the black color pulse shows the molecular beam pulse, the red one the laser beams for vibrational excitations, and the cyan the UV photodissociating beam. B) View from above: time of flight mass spectrometer (TOFMS), microchannel plate (MCP) - ions detector, pulsed voltage (PV), power supply to the MCP (PS₁), power supply to the TOFMS components (PS₂), delay generator (DG₁) controlling the synchronization of the lasers and the second delay generator (green lines), delay generator (DG₂) controlling the synchronization of the pulsed valve and all the electronics devices (orange lines), optical parameter oscillator (OPO), second harmonic generator (SHG), third harmonic generator (THG), personal computer (PC) beam splitter (BS), dichroic mirror (DM) and C) TOFMS, view from the front.
3.2.1 VMP using stimulated Raman scattering (SRS)

In this experiment the molecular beam was intersected by three laser beams: $\omega_p$, and $\omega_S$ for SRS, inducing the vibrational excitation, and UV for promotion of the molecules to the excited electronic state and for subsequent H photofragment ionization. The tunable $\omega_p$ and $\omega_S$ beams for SRS were obtained from the signal and idler of an optical parametric oscillator (OPO) (Continuum, Sunlite EX) pumped by the third harmonic of a seeded neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Continuum, Powerlite 8010). The spatially and temporally overlapping SRS beams of parallel polarization were focused onto the interaction region of the TOFMS by a 25 cm focal length planoconvex lens. The pump and Stokes energies in the interaction region were about 18 and 15 mJ per pulse, 0.08 and 0.12 cm$^{-1}$ bandwidth respectively and ~ 5 ns duration.

The counter propagating UV beam at 243.135 nm with energy of 120 $\mu$J/pulse, ~ 6 ns duration and ~ 0.2 cm$^{-1}$ bandwidth was obtained from the doubled output of a tunable dye laser (Lambda Physik, FL 3002/ Scanmate) pumped by the third harmonic of another Nd:YAG (Big Sky, Brilliant B) laser. The UV beam was brought to a common focus with the counter propagating $\omega_p$ and $\omega_S$ beams by a 30 cm focal length planoconvex lens. The SRS beams preceded the UV beam by 10 or 50 ns where the
delays between SRS lasers and UV photons were controlled by a home built delay
generator that operated them externally. Another delay generator (Standford Research
Systems, DG535), triggered by the former, controlled the pulsed valve, boxcar,
oscilloscope and the personal computer.

3.2.2 VMP following direct vibrational excitation

In this experiment the molecular beam was intersected by two laser beams, NIR
for vibrational excitation, and UV for promotion of the molecules to the excited
electronic state and for subsequent H photofragment detection in the TOFMS, as
mentioned before.

The NIR beam for excitation of the first N–H stretch overtone was generated in an
auto-tracker by difference frequency mixing in a lithium niobate (LiNbiO₃) crystal. For
that, the output of a pulsed dye laser (Continuum ND6000), pumped by the second
harmonic of a Nd:YAG (Continuum PL8000) laser was mixed with the residual of the
Nd:YAG fundamental. The higher overtones were excited by the idler of an OPO
pumped by the third harmonic output of a seeded Nd:YAG laser. The NIR laser beams
with typical pulse energies of about 0.5, 10, and 18 mJ in the regions of the first, second
and third N-H stretches, respectively, were focused in the interaction region by a 25 cm
focal length lens. The linewidths were 0.12 cm⁻¹, and the full temporal width at half
maximum of all beams was ~ 5 ns. A similar counter propagating UV beam, as
mentioned above, was used, preceeding the NIR beam by 15 ns.

3.2.3 Photoacoustic spectroscopy using SRS and direct vibrational excitation

The laser beams for SRS and direct vibrational excitation (as already described in
the VMP process) were focused by a 20 cm focal length planoconvex lens into a 13 cm
long PA cell, ~ 3 mm away from the microphone. The PA cell was filled with pyrrole
vapor, ~ 6.5 Torr pressure. The acoustic signal produced by the vibrational excitation
was fed into a filtered (1000-3000 Hz) preamplifier (Stanford Research System, SR 560)
and then into a second channel of a boxcar integrator. Special care was taken to preclude
saturation. For this purpose the PAR spectrum at room temperature was measured three times with different filters (transmittance of 80, 50, and 50 + 80 %) that reduced the intensity of the pump and Stokes beams, allowing to conclude that there is no optical saturation.

Table 3.1 - Characteristics of the scanned regions and related lasers that were used in this work.

<table>
<thead>
<tr>
<th>Scanned region wavenumber (cm(^{-1}))</th>
<th>Excitation region</th>
<th>Beam energy mJ/pulse</th>
<th>Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>3065 – 3155</td>
<td>C-H fundamental</td>
<td>Signal: 15</td>
<td>OPO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Idler: 18</td>
<td></td>
</tr>
<tr>
<td>3480 – 3573</td>
<td>N-H fundamental</td>
<td>Signal: 15</td>
<td>OPO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Idler: 18</td>
<td></td>
</tr>
<tr>
<td>6850 – 6965</td>
<td>N-H first overtone</td>
<td>0.5</td>
<td>Dye+tracker</td>
</tr>
<tr>
<td>10700 – 10230</td>
<td>N-H second overtone</td>
<td>10</td>
<td>OPO (idler)</td>
</tr>
<tr>
<td>13155 – 13380</td>
<td>N-H third overtone</td>
<td>18</td>
<td>OPO (idler)</td>
</tr>
<tr>
<td>41135.3</td>
<td>Dissociation, (2+1) REMPI</td>
<td>0.12</td>
<td>Dye (UV)</td>
</tr>
</tbody>
</table>
4. RESULTS AND DISCUSSION

4.1 The N-H and C-H stretch fundamental region

The fundamental N-H ($v_1$) and C-H ($v_2$) stretch regions of pyrrole was investigated with emphasis on two issues: vibrational analysis and influence of different initially vibrationally excited state on photodissociation.

4.1.1 Vibrational analysis

Figures 4.1 and 4.2 show portions of the PAR spectra of pyrrole vapor in the $v_1$ and $v_2$ stretch fundamental regions, at temperatures of 21 and 65 °C, displayed as red and green traces, respectively. Immediately seen is that the spectra are characterized by several $Q$-branches, with $v_1$ and $v_2$ being the dominant ones in the respective regions. Moreover, the features corresponding to $v_1$, $v_2$, $2v_1$, and a combination band (cb) are of the same intensity at both temperatures, while the other bands, attributed to hot bands, grow in intensity at the higher temperature. The increase in PAR signal intensities of these bands is due to grow in population in the low lying vibrational states of the hot band transitions. This implies that the $v_1$ and $v_2$ dominant bands are accompanied by a set of hot bands (marked as $hb$) in the spectra.

The origins of the different observed bands were obtained by simulating the spectra. The simulation was performed using our computer code (Appendix B) on the MATLAB application, calculating the positions of the rotational states and considering that the $\Delta J = 0$ and $\Delta \tau = 0$, where $\tau = K_a - K_c$ is a "pseudo" quantum number, labeling the different states of the same $J$, for which the values are in the $-J \leq \tau \leq J$ range. Also, the Raman cross sections for all the lines in the bands were assumed to be equal and the rotational populations in the lower vibrational levels were calculated according to Boltzmann distribution. This allowed simulating the $Q$-branch intensities as a function of energy, while keeping the ground state molecular constants and those for $v_1$. 

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**Fig. 4.1** - Measured photoacoustic Raman spectra of pyrrole in the N-H ($v_1$) stretch fundamental region at 21 (red) and 65 °C (green). The red (a) and green (b) traces in the inset show expanded portions of the measured spectra at the corresponding temperatures and their simulation (blue), which is a sum of the five contributing $Q$-branches (cyan) marked by $v_1$ and $hb1$ to $hb4$.

**Fig. 4.2** - Measured photoacoustic Raman spectra of pyrrole in the C-H ($v_2$) stretch fundamental region at 21 (red) and 65 °C (green). The red (a) and green (b) traces in the inset show expanded portions of the measured spectra at the corresponding temperatures and their simulation (blue), which is a sum of the six contributing $Q$-branches (cyan) marked by $v_2$ and $hb1$ to $hb5$. 
constrained and fitting those of \( \nu_2 \) (the parameters for this band are not available in the literature) and the linewidth. As can be seen from the insets of Figs. 4.1 and 4.2, when these parameters and a Gaussian of 0.18 cm\(^{-1}\) FWHM (found from the fitting and mainly accounting for the laser linewidths) were used, a very good agreement between the calculated spectra of the \( \nu_1 \) band (cyan) and the measured ones, at the two different temperatures, was obtained. It is interesting to note that when another set of parameters was adopted for \( \nu_1 \),\(^{29}\) which only slightly differed from those of Herman and co-workers,\(^{32}\) the agreement between the calculated and measured spectra of the band was much poorer. This means that the simulation is very sensitive and a good measure of the specific parameters describing the band.

As for the \( \nu_2 \) band, the following parameters were retrieved from the simulation: \( \nu_0 = 3149.86 \) (after performing the calibration, described in Appendix C), \( A = 0.3047 \), \( B = 0.2995 \) and \( C = 0.1510(1) \) cm\(^{-1}\). This band origin is somewhat different from the value of 3148.87 cm\(^{-1}\)\(^{33}\) retrieved from the vibrational analysis of combinations, as can be seen in the inset of Fig. C.1, but matches very well the value of 3149.8 cm\(^{-1}\) obtained from Raman spectroscopy. At this point, it is important to note that the traces of the calculated \( Q \)-branches (blue) in the inset of Fig. 4.2 fit very well the measured ones at the two temperatures.

<table>
<thead>
<tr>
<th>Level</th>
<th>( \nu_0 )</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS(^a)</td>
<td>0</td>
<td>0.30456</td>
<td>0.30025</td>
<td>0.15117</td>
<td>56</td>
</tr>
<tr>
<td>( \nu_1 )</td>
<td>3530.81</td>
<td>0.30430</td>
<td>0.29990</td>
<td>0.15106</td>
<td>32</td>
</tr>
<tr>
<td>( \nu_1 )</td>
<td>3530.50</td>
<td>0.30453</td>
<td>0.29967</td>
<td>0.15114</td>
<td>29</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>3149.86</td>
<td>0.3047</td>
<td>0.2995</td>
<td>0.1510</td>
<td>this exp.</td>
</tr>
</tbody>
</table>

\( ^a \) GS – ground state.

The hot bands were included in the PAR spectra simulations by inserting bands, similar to the main ones, in the corresponding N-H and C-H regions with corresponding lower weights. As can be seen there is good correspondence between the sum of the five and six contributing bands (blue traces in the insets of Figs. 4.1 and 4.2) and the
measured PAR spectra of the N-H and C-H stretch regions, respectively. This approach allows us retrieving the band origins and the non-diagonal anharmonicities for the hot bands, existing in the N-H and C-H stretch regions, and they are listed in Tables 4.2 and 4.3, respectively.

It would be very beneficial to be able to assign these bands. Indeed, by considering the strength of some of these bands and referring to the results of the quantum calculations, some of these bands could be assigned. Therefore, quantum calculations were performed with the GAUSSIAN 09 package, at the B3LYP/6-311++G(d,p) and MP2/cc-pVTZ levels, for calculating the frequencies and anharmonicities of the vibrational levels.

Comparison of the hot band to the main bands, appearing in Figs. 4.1 and 4.2, shows that the \( \text{hb}4 \) and \( \text{hb}1 \) exhibit the highest intensities relative to \( \nu_1 \) and \( \nu_2 \), respectively, reflecting the higher population in the lower state of the transitions. Recalling that \( \nu_{16} \) is positioned at the lowest energy (474.61 cm\(^{-1}\)) it is deduced that these bands can be assigned to \( \nu_1 + \nu_{16} - \nu_{16} \) and \( \nu_2 + \nu_{16} - \nu_{16} \). The assignment of the former band is in line with previous results, obtained from the study of N-H stretch fundamental and overtones, while the second hot band is identified here for the first time.

For the other features, the calculation of the relative intensities between the main and hot bands did not reveal conclusive results. This is reasonable considering that they are related to states with close energies (only hot bands that are related to the 5 lowest vibrational states around 620 and 720 cm\(^{-1}\) are observed) making it difficult to discriminate between them according to changes in their population and therefore intensities. In principle, higher vibrational states could lead to hot bands, but in pyrrole they should be populated with less than 3% and therefore their intensity, relative to the main bands \( \nu_1 \) and \( \nu_2 \) should be very low, and as can be seen from the PARS spectra, unobservable at our conditions.

Hence, the assignment was done by comparing the spectroscopically retrieved values to the calculated ones. This seems suitable, considering that as can be seen from Appendix D Table D.1, the calculated anharmonic frequencies match very well the experimental ones. Thus by comparing the experimental anharmonicities to the
calculated nondiagonal anharmonicities, the tentative assignment listed in Tables 4.2 and 4.3 is proposed.

As can be clearly seen, a very good correspondence between the experimental and calculated nondiagonal anharmonicities is found for the bands in the N-H stretch region. Moreover, the extent of agreement between the experimental values and those calculated at the B3LYP/6-311++G(d,p) level is even higher, leading to exact match for the \( x_{1,15} \) and \( x_{1,16} \). Of particular note is the slightly positive calculated non-diagonal anharmonicity for \( x_{1,12} \), which implies that if a band corresponding to it would appear, it had to overlap the main \( \nu_1 \) band. This might offer an explanation for the appearance of only four hot bands in the N-H stretch vicinity.

As for the C-H fundamental stretch region the picture is even more complicated. In this region there are two C-H antisymmetric stretches (\( \nu_{17}, \nu_{18} \)) and two C-H symmetric stretches (\( \nu_3, \nu_2 \)), as identified in previous works.\(^{30,31,33,34}\) The first two modes are of \( B_2 \) symmetry and therefore have no \( Q \)-branch, due to the Raman selection rules. The second two modes are of \( A_1 \) symmetry and thus have a prominent \( Q \)-branch. The \( \nu_2 \) band is indeed well seen in the spectrum due to a sharp \( Q \)-branch. However, the \( \nu_3 \) band has very low Raman cross section and therefore hardly seen in Fig. 4.2 (it can be seen much better in a saturated PARS spectrum, which is shown in Appendix C, Fig. C.2). These effects and the fact that the spread of the hot bands is lower, make the assignment even more challenging. While for \( x_{1,11} \) and \( x_{1,14} \) a very good agreement is obtained between the measured and calculated values, the match between the others is less good. According to the observed trend of increase in the anharmonicities for \( hb2 \) and \( hb3 \), they are assigned to \( \nu_2 + \nu_{12} - \nu_{12} \) and \( \nu_2 + \nu_{15} - \nu_{15} \), however, because of the small difference between the two, switching between their assignment cannot be ruled out. The assignment in this case could be also influenced somewhat by the interaction of the \( \nu_2 \) and \( 2\nu_{19} \) states (see below).
Table 4.2 - The main and hot bands observed in the range of the N-H stretch fundamental and their non-diagonal anharmonicity constants, $x_{ij}$, compared to the $x_{ij}$ values derived from calculations at the B3LYP/6-311++G(d,p) and MP2/cc-pVTZ levels and assigned accordingly.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Experiment $v_0$(cm$^{-1}$)</th>
<th>Experiment $x_{ij}$(cm$^{-1}$)</th>
<th>B3LYP/6-311++G(d,p) $x_{ij}$(cm$^{-1}$)</th>
<th>MP2/cc-pVTZ $x_{ij}$(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>$v_1$</td>
<td>3530.81</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$v_1$+$v_1$-$v_1$</td>
<td>-</td>
<td>-</td>
<td>+0.18</td>
</tr>
<tr>
<td>$hb1$</td>
<td>$v_1$+$v_1$-$v_1$</td>
<td>3530.00</td>
<td>-0.81</td>
<td>-0.97</td>
</tr>
<tr>
<td>$hb2$</td>
<td>$v_1$+$v_1$-$v_1$</td>
<td>3529.20</td>
<td>-1.61</td>
<td>-1.27</td>
</tr>
<tr>
<td>$hb3$</td>
<td>$v_1$+$v_1$-$v_1$</td>
<td>3528.75</td>
<td>-2.06</td>
<td>-2.07</td>
</tr>
<tr>
<td>$hb4$</td>
<td>$v_1$+$v_1$-$v_1$</td>
<td>3505.80</td>
<td>-25.01</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-21.34</td>
</tr>
</tbody>
</table>

Table 4.3 - The main and hot bands observed in the range of the C-H stretch fundamental and their non-diagonal anharmonicity constants, $x_{ij}$, compared to the $x_{ij}$ values derived from calculations at the B3LYP/6-311++G(d,p) and MP2/cc-pVTZ levels and assigned accordingly.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Experiment $v_0$(cm$^{-1}$)</th>
<th>Experiment $x_{ij}$(cm$^{-1}$)</th>
<th>B3LYP/6-311++G(d,p) $x_{ij}$(cm$^{-1}$)</th>
<th>MP2/cc-pVTZ $x_{ij}$(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_2$</td>
<td>$v_2$</td>
<td>3149.86</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$hb1$</td>
<td>$v_2$+$v_1$-$v_1$</td>
<td>3148.77</td>
<td>-1.09</td>
<td>-1.39</td>
</tr>
<tr>
<td>$hb2$</td>
<td>$v_2$+$v_1$-$v_1$</td>
<td>3148.42</td>
<td>-1.44</td>
<td>-0.77</td>
</tr>
<tr>
<td>$hb3$</td>
<td>$v_2$+$v_1$-$v_1$</td>
<td>3147.63</td>
<td>-2.23</td>
<td>-0.97</td>
</tr>
<tr>
<td>$hb4$</td>
<td>$v_2$+$v_1$-$v_1$</td>
<td>3146.09</td>
<td>-3.77</td>
<td>-4.03</td>
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<tr>
<td>$hb5$</td>
<td>$v_2$+$v_1$-$v_1$</td>
<td>3143.09</td>
<td>-6.77</td>
<td>-6.95</td>
</tr>
</tbody>
</table>

4.1.2 Interactions in the C-H stretch region

As mentioned above and seen from the PARS spectrum, shown in Fig. 4.2, in addition to the main and accompanying hot bands in the C-H stretch region, a feature corresponding to the deformation overtone ($2v_{19}$) is also observed. It is interesting to note that the intensity ratio between $v_2$ and $2v_{19}$, obtained from the measured spectra, is ~13 (same for both temperatures). This contradicts the results of the quantum mechanical
calculations, which showed that the calculated Raman activity of ν_{19} was almost three orders of magnitude lower than that of the symmetric C-H stretch, ν_{2} (about 0.3 vs. 228 Å^4/amu). Moreover, it is needless to say that the intensity of the 2ν_{19} overtone should be even lower. Therefore, this mismatch between the calculated and measured intensity ratios of ν_{2} and 2ν_{19} seems to be a result of some other mechanism. In particular, it is reasonable to assume that 2ν_{19} borrows some intensity from ν_{2}, which is of the same symmetry, A_{1}, by Fermi resonance, leading to its observed intensity in the spectrum, Fig. 4.2. The resonance should be only between these two states, since for the ν_{3} fundamental symmetric stretch, which is of the same symmetry, the Raman activity is much lower than that of ν_{2} and therefore it is hardly observed in the measured spectrum, Fig. 4.2 (seen in the saturated spectrum Appendix C, Fig. C.2). This low intensity hints that ν_{3} is not coupled to ν_{2} and even if it would be coupled somewhat to 2ν_{19}, the coupling term should be very small. As for the other candidates, they are not expected to be involved in the resonance, due to symmetry disagreement with the ν_{2} and 2ν_{19} states (A_{1} symmetry). This argument holds for the antisymmetric C-H stretches, ν_{17} and ν_{18}, of B_{2} symmetry, barely appearing in this spectral region (shown in the saturated PARS spectrum, Appendix C, Fig. C.2 and Ref. 33). and the upper vibrational energy levels of the hot band transitions, (see the derivation of symmetry in Appendix A). As for the upper vibrational energy levels of the hot bands, they are also situated at higher energies (474 – 720 cm^{-1}) and because this energy mismatch they should not be coupled to ν_{2}.

Therefore, we can assume that the observed frequencies and the relative intensities of the perturbed bands in the PAR spectrum are a result of a two-level interaction. This allows retrieving the energies of the ZO states and the anharmonic interaction matrix element, W, according to the derivation given in Appendix E.1 and E.2. The retrieved values for the unperturbed energies of ν_{2} and 2ν_{19}, and for W were 3144 ± 1 and 3079 ± 2, and 19 ± 1 cm^{-1}, respectively. This large ZO energy separation of 65 cm^{-1} results in a relatively weak interaction between the ν_{2} bright state and the 2ν_{19} dark state, leading the eigenstates to keep their character, so that each of them consists mainly (93 %, based on the square of the eigenvectors coefficients, reflecting the measured intensity ratio) of ν_{2} and of 2ν_{19}. 

Furthermore, preservation of the character is assisted by the low density of states in the considered energy window. The total vibrational states as calculated via the Stein-Rabinovitch extension of the Beyer-Swinehart algorithm is about three states/cm$^{-1}$, while that of states of $A_1$ symmetry should be even lower. Clearly, this small density of states is insufficient to induce statistical energy flow out of the prepared states, conserving their character to a large extent.

The spectral shift of the perturbed $\nu_2$ ($\sim 5$ cm$^{-1}$), due to the Fermi resonance with the $2\nu_{19}$ state, may raise some questions about the assignment of the hot bands (Sect. 4.1.1) related to $\nu_2$. This is due to the fact that the assignment was based on the comparison of the measured anharmonicities of the hot bands and the predicted $x_{ij}$ values obtained by anharmonic calculations, without taking the Fermi resonance into account. However, considering that almost the same Fermi resonances should occur between the upper energy levels of the hot bands related to the main $\nu_2$ band and those related to $2\nu_{19}$, the anharmonic interaction matrix element, $W$, between the unperturbed upper hot bands energy levels ($\nu_2 + \nu_j + x_{2,j}$ and $2\nu_{19} + \nu_j + 2x_{19,j}$) should be the same. Therefore, the difference between the band origins of $\nu_2$ and $2\nu_{19}$ should differ from that of the corresponding upper energy levels of the hot bands only by a small factor of $x_{2,j} - 2x_{19,j}$, which is anticipated to barely affect the energy levels shift. This implies that the influence of the Fermi resonance on the hot bands should be almost similar to that on the main band (see Appendix E.3) and therefore should not affect the assignment.

4.1.3 Mode-specific photodissociation of pyrrole

The observation that the $\nu_2$ and $2\nu_{19}$ states preserve extensively their initial character might have implications on the photodissociation outcome. Therefore, it was anticipated that by measuring the PAR and H action spectra and comparing them, some insight could be obtained. Fig. 4.3 exhibits PAR (a) and H action (b) spectra in the region of the N-H and C-H stretch fundamentals of pyrrole. The action spectrum shows the H atom yields due to $\sim 243.1$ nm photolysis of vibrationless ground state (background) and vibrationally excited molecules (peaks). The action spectrum was monitored at a delay of 10 ns between the SRS and UV beams (a similar spectrum was
obtained even at a delay of 50 ns). The features in the jet-cooled action spectrum are very narrow and even sharper than in the PAR spectrum. This narrowing of the bands in the former is due to the rotational cooling, occurring during the beam expansion (rotational temperature of ~ 10 K).

![Diagram](image)

Fig. 4.3 - Vibrational excitation spectra in the region of the fundamental N-H and C-H symmetric stretches of pyrrole: (a) PAR spectrum, (b) H action spectrum obtained by 243.135 nm dissociation of jet-cooled molecules at a delay of 10 ns between the SRS and UV beams. The intensity scale of each panel is different.

The intensity pattern in the action spectrum differs from that in the PAR spectrum, where in the former the hot band disappeared and even more fascinating is the intense feature, corresponding to the deformation overtone (2ν19). The vanishing of the low intensity bands could be a result of its masking by the background noise. Because of the different intensity pattern in the action spectrum from that in the PAR spectrum, special care was taken to preclude saturation as mentioned in Sect. 3.2.3.

The differences in the intensity patterns in the PAR and action spectra might be a result of their various origins, reflecting the SRS excitation efficiency and the H
photofragments yield in the VMP (sharp lines) process, respectively. One reason that could be foreseen to account for the present experimental results is that the enhanced reactivity of the \( \nu_2 + \nu_{14} - \nu_{14} \) and even more so of the \( 2\nu_{19} \) mode in the action spectra might be a consequence of the UV excitation of the intermediate states prepared during the vibrational excitation. By determining the ratio between the peak heights corresponding to similar features in the action and PAR spectra, the enhancement factors could be revealed. By setting the enhancement factor for \( \nu_2 \) to 1 and normalizing those of the other states to it, values of 1, 5 and 13 for the \( \nu_1, \nu_2 + \nu_{14} - \nu_{14} \) and \( 2\nu_{19} \) states, respectively, were obtained. This state specificity for \( \nu_2 + \nu_{14} - \nu_{14} \) and especially for \( 2\nu_{19} \) may indicate that these modes are barely coupled to the bath states, surviving IVR. This observation agrees well with the results of the two level deperturbation model, which accounted for the Fermi resonance (Sect. 4.1.2). As shown above, the \( \nu_2 \) bright state and the \( 2\nu_{19} \) dark state, consists mainly (93 %) of the corresponding character and preserve it, promoting excitation to the \( S_1 \) state and consequently H photofragmentation more effectively. This is supported also by our finding that the action spectrum monitored at a delay of 50 ns between the SRS and UV beam resembles that monitored at 10 ns delay, implying that even at a very long time following the vibrational excitation the character of the prepared vibrational states is preserved. Therefore, it is reasonable to assume that each such state experiences its own vibrationally dependent FC factor and therefore its own enhancement in the UV step of the VMP process.

A conceivable alternative interpretation of the observed mode-specificity would involve the different dynamics in pyrrole photodissociation as a result of intermediate vibrational excitation, however, in view of the details of the process, this seems unlikely. In particular, even at the highest combined energies (N-H symmetric stretch excitation + 243.135 nm) used in our experiment, 5.54 eV, the \( \pi\pi^* \) state (see Fig. 4.4) that is responsible for the strong UV absorptions in pyrrole cannot be accessed.\(^{59,60,40,61}\) Therefore, the excitation occurs to the weak absorbing \( S_I \) electronic state, \( \pi\sigma^* \left(^1A_2\right) \), via an electric dipole forbidden transition. This state corresponds to a 3s Rydberg orbital, which upon stretching of the N-H bond leads to a Rydberg-to-valence transformation and thus to a \( \sigma^* \) anti-bonding bond, responsible for the dominant fragmentation pathway, involving N–H dissociation. The \( \pi\sigma^* \) potential correlates with ground state products and
exhibits a conical intersection with the ground electronic state, $S_0$, at a very large N–H bond distance, implying that internal conversion to $S_0$ should not be favored. Moreover, since none of the pre-excited vibrational states is of $A_2$ symmetry, the vibrational excitation is not expected to aid the internal conversion to the $S_0$ ground state, and it is likely that as in photodissociation of molecules promoted from the vibrationless ground state the photodissociation occurs adiabatically. Therefore, it seems that the difference in outcomes of photodissociation when vibrations of different character are excited occurs by the combined effects of restricted IVR and different FC factors, leading to yield enhancements and thus to state-specificity.

Fig. 4.4 - Potential energy of the five lowest singlet electronic states, $S_0$, $^1A_2(\pi\sigma^*)$, $^1B_1(\pi\sigma^*)$, $^1B_2(\pi\pi^*)$, and $^1A_1(\pi\pi^*)$ of pyrrole as functions of $r_{\text{N–H}}$, adapted from Ref. 45.
4.2 N-H stretch overtones

The first, second and third N-H stretch overtones regions of pyrrole were investigated in attempt to obtain insight about the IVR process in regions that are characterized by higher number of bath states.

4.2.1 Vibrational spectroscopy and analysis

Fig. 4.5 shows the room temperature PA (panel (a)) and the jet-cooled H action spectra (panel (c)) together with the respective simulated spectra ( (b) and (d)) in the first (A), second (B) and third (C) N-H stretch overtone regions of pyrrole. As mentioned above, the PA spectra represent the pure vibrational excited state of pyrrole, while the action spectra exhibit the H atom yields due to ~ 243.1 nm photolysis of vibrationless ground state and vibrationally excited molecules. The ratio of the H yield from the photolysis of vibrationally excited pyrrole to that from vibrationless ground state molecules was calculated to obtain the enhancements for the dominant features observed in the first, second and third overtone regions and was found to be 3.4(4), 2.4(3) and 1.9(1), respectively.

Considering that pyrrole is an asymmetric, quasi-oblate rotor with $A \approx B \approx 2C$, exhibiting $A$-type bands with characteristic $P$, $Q$- and $R$-branches, where the rotational transitions obey the $\Delta K_c = \pm 1$ and $\Delta K_a = 0, \pm 2$ selection rules, analysis of the spectra was performed. In the first stage, simulations of the PA (Figs. 4.5A(b), 4.5B(b) and 4.5C(b)) and action (Figs. 4.5 A(d), 4.5B(d) and 4.5C(d)) spectra were carried out by the JB95 asymmetric rotor program. These simulations were performed employing $A$-type bands, with the previously retrieved molecular constants for ground and N-H excited vibrational states of pyrrole (Table 4.4). These constants together with the H nuclei spin statistics in pyrrole of 5 and 3, accounting for the intensity alternation of the rovibrational lines starting from even and odd $K_a$ levels, respectively, were constrained to their values during the fitting procedure. The molecular constants of the main bands, in each region, were also adopted for the hot bands and in the region of $4\nu_1$ also for the bands related to
Fig. 4.5 - Vibrational overtone excitation of the first (A), second (B), and third (C) overtone of the N–H stretch region of pyrrole: (a) photoacoustic (PA) spectrum, (b) simulated PA spectrum, using the molecular constants of Table I, (c) jet-cooled action spectrum monitoring the yield of H photofragments, following 243.135 nm photodissociation of vibrationally excited molecules and (d) simulated action spectrum. The cyan solid lines in the simulated spectrum (panel C(b)) represent the three contributing A¹ type bands and the magenta line their sum. The spectrum calibration is described in Appendix F.
the states with three quanta of N-H stretch and a quantum of C-H stretches, i.e., $3\nu_1 + \nu_2$ and $3\nu_1 + \nu_3$, respectively.

Table 4.4 - Values of band origins and vibrational parameters (cm$^{-1}$) for the ground and excited N-H stretch levels of pyrrole.

<table>
<thead>
<tr>
<th>Level</th>
<th>$\nu_0$</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS$^a$</td>
<td>0</td>
<td>0.30456</td>
<td>0.30025</td>
<td>0.15117</td>
<td>56</td>
</tr>
<tr>
<td>$2\nu_1$</td>
<td>6924.63</td>
<td>0.3045</td>
<td>0.29932</td>
<td>0.1509221</td>
<td>31</td>
</tr>
<tr>
<td>$3\nu_1$</td>
<td>10184.17</td>
<td>0.3045</td>
<td>0.2985</td>
<td>0.15069</td>
<td>63</td>
</tr>
<tr>
<td>$4\nu_1^b$</td>
<td>13301</td>
<td>0.3044</td>
<td>0.2979</td>
<td>0.1506</td>
<td>29</td>
</tr>
</tbody>
</table>

$^a$ GS - ground state.

$^b$ The band origins of the additional bands appearing in the region of $4\nu_1$ band, i.e., $3\nu_1 + \nu_2$ and $3\nu_1 + \nu_3$ were found to be at 13315.4 and 13340.5 cm$^{-1}$, respectively.

In addition, the Lorentzian linewidths of the rovibrational transitions in the PA and action spectra and the rotational temperature for the latter were used as fitting parameters, leading to a 10 K rotational temperature of pyrrole in the sample and to 0.15(2), 0.20(2) and 1.0(1) cm$^{-1}$ laser deconvoluted linewidths, for the bands in the $2\nu_1$, $3\nu_1$ and $4\nu_1$ regions, respectively. These linewidths, are in fact the linewidths of particular rovibrational transitions, broadened by their interaction with the bath states (see Fig. 1.3).

In general, the spectra are characterized by prominent and low intensity features, corresponding to N-H stretch transitions, $n\nu_1$, overtones ($n$ is the overtone quantum number) and to hot bands corresponding to the $n\nu_1 + \nu_{16} - \nu_{16}$. The hot bands related to $n\nu_1 + \nu_{16} - \nu_{16}$, appear in the different energetic windows at 6873.5, 10105.2 and 13196.8 cm$^{-1}$. As for the other hot bands, that appeared in the PAR spectra of the fundamental N-H stretch region (Fig. 4.1, Table 4.2), they could not clearly be observed. This is due to their low off-diagonal anharmonicities and the fact that the main features are relatively broad. At any rate, some small features, appearing as shoulders are observed in the
action spectra (panel (c) of Fig. 4.5), and are related to the additional hot bands, but were not taken into account in the simulated ones.

While the prominent features in the first and second N-H stretch overtone regions consist of single isolated bands, the one in the third overtone region is more complicated. In particular, the PA spectrum (Fig. 4.5C(a)) shows a complex irregular broad contour with a main band at 13301 cm\(^{-1}\), together with a sudden increase in the \(R\)-branch envelop intensity, around 13315.4 and 13340.5 cm\(^{-1}\). This hints to the presence of three different features in this energetic region, which are exposed as resolved bands in the action spectrum (Fig. 4.5C(c)), providing convincing evidence for their occurrence.

An additional interesting aspect of Figs. 4.5C(a) and 4.5C(c) is that the contours of the main bands in the measured PA and H action spectra of the third N-H stretch overtone, are smooth, alluding to unresolved rotational structure in this region. This differs from the behavior encountered in the 2\(v_1\) and 3\(v_1\) overtone regions, Figs. 4.5A(a) – 4.5A(d) and Figs. 4.5B(a) – 4.5B(d), and even more so from the expanded portions of the PA and action spectra of 3\(v_1\) shown in Fig. 4.6. Immediately apparent is that the rotational structure of 3\(v_1\) is resolved and, moreover, that rotational perturbations occur in the spectra. These perturbations can be noticed from the comparison of the measured and simulated spectra, where in the former weaker \(Q\)-branch and transitions on both sides are observed. This is in fact due to the use of "effective" rotational constants in the simulation that fit best the measured spectrum. Such perturbations were already observed in the high resolution Fourier IR transform spectrum of 2\(v_1\), and in the spectrum of 3\(v_1\).
Fig. 4.6 - A portion of the spectra of the second N–H stretch overtone of pyrrole: (a) photoacoustic (PA) (blue) and simulated PA (magenta), and (b) jet-cooled action (green), following 243.135 nm photodissociation of vibrationally excited molecules and simulated action spectrum (red).

The different behavior observed in the PA and action spectra for the first and second N-H stretch overtone regions compared to that in the third N-H stretch overtone allows distinguishing between the IVR processes occurring in the different energetic windows. While in the $2\nu_1$ and $3\nu_1$ regions isolated single-bands were observed, in the $4\nu_1$ region, two additional bands, assigned to $3\nu_1 + \nu_2$ and $3\nu_1 + \nu_3$, were encountered. These bands are a result of the interaction of the $4\nu_1$ ZOBS with the ZODS in its vicinity. Therefore, an important issue is to retrieve the temporal evolution of the states in this region and to compare it to that in the lower overtones regions.

For that reason a second phase analysis was performed, where the vibrational Hamiltonian matrix of the triad interacting levels was considered. This matrix consists of diagonal elements, corresponding to the energies of the ZO states and off-diagonal elements, describing the interactions between them. By diagonalizing the matrix, the eigenvalues and eigenvectors were obtained. Their derivation was assisted by least-square fitting of the eigenvalues to the observed band origins and the square of the eigenvector coefficients to the intensities. However, since more than one solution is
possible, we preferred to use values of the energies of the ZO states that were obtained by other means, before solving the matrix.

\[
\Delta G_0 / n = \omega_1^0 n + x_{11}^0 n^2 + y_{111}^0 n^3 ,
\]

(4.1)

where \( \omega_1^0 \) is the vibrational frequency, and \( x_{11}^0 \) and \( y_{111}^0 \) are the anharmonicity parameters, as defined in Ref 32, the vibrational parameters \( \omega_1^0 = 3600.2 \), \( x_{11}^0 = 69.85 \) and \( y_{111}^0 = 0.45 \text{ cm}^{-1} \) were obtained. This fitted line also allowed extrapolation to \( n = 4 \), enabling to retrieve the value of 13312.1 cm\(^{-1} \) for the \( 4\nu_1 \) bright state energy. The bright state energy can be also calculated from the center of gravity of the observed features in the spectrum, excluding hot bands. Indeed, by taking into account the positions of the bands and their weights (13301, 13315 and 13340 cm\(^{-1} \) and 0.56, 0.25 and 0.19 for \( 4\nu_1 \), \( 3\nu_1 + \nu_2 \) and \( 3\nu_1 + \nu_3 \), respectively) a value of 13312.1 cm\(^{-1} \) was calculated, showing a very good agreement to that obtained from the Birge-Sponer plot. Based on the measured frequency of the \( 3\nu_1 \) transition (from Fig. 4.5B(a)) and \( \nu_2 \) (from the SRS

\[ \text{Fig. 4.7 - Birge-Sponer plot of the } \nu_1 \text{ bands in pyrrole.} \]
spectrum, Fig. 4.2, Table 4.3) and the known $\nu_3$ frequencies and $x_{1,2} = +0.42$ and $x_{1,3} = -0.48$ cm$^{-1}$ anharmonicities, the energies of the dark states $3\nu_1 + \nu_2$ and $3\nu_1 + \nu_3$ were found to be $\sim 13334$ and $\sim 13311$ cm$^{-1}$, respectively. Therefore, using the values of the energies of the $4\nu_1, 3\nu_1 + \nu_2$ and $3\nu_1 + \nu_3$ ZO states (bright and dark states) on the diagonal and the couplings as non-diagonal elements and numerically diagonalizing the Hamiltonian matrix (comparing to the eigenstates appearing in the spectrum of Fig. 4.5C(c)) the interaction matrix elements $W_{4\nu_1,3\nu_1+\nu_3} = 8$, $W_{4\nu_1,3\nu_1+\nu_2} = 12$ and $W_{3\nu_1+\nu_2,3\nu_1+\nu_3} = 1$ cm$^{-1}$ were retrieved (Appendix G). These values correspond to larger interaction elements between the bright and dark state than between the dark states themselves, and contradict the assumed equal values of 8 cm$^{-1}$.29

4.2.2 Time dependent intramolecular vibrational redistribution

Based on the resultant vibrational Hamiltonian, the temporal evolution of the density matrix and the temporal behavior of the states were derived, while considering the density matrix given in Eq. 1.4 and the description thereby. The population probability in the $i$th state at time $t$ is:

$$P_i(t) = P_{ii}(t)e^{-\frac{\nu_i}{\tau_i}}$$

where $\tau_i = (2\pi c\Delta \nu)^{-1}$ is the decay constant of the $i$th state, obtained via the Heisenberg uncertainty principle ($\Delta E \Delta \tau \geq \hbar$), from the homogeneous broadening of the measured spectra. The resulting temporal behavior of the states in the region of $4\nu_1$ of pyrrole, up to 20 ps, is shown in Fig. 4.8. It is clearly seen that the states exhibit quantum beats and exponential relaxation. The beats are a result of the strong coupling of the initially excited N–H stretching state to the other states, which are accidentally coupled to it, leading to a periodic return of the vibrational energy to the excited mode in the time domain.

In fact, the $4\nu_1$ region in pyrrole is characterized by prominent beating together with energy flow, via weak interactions, from the strongly interacting states to the bath
modes. This behavior differs from that observed in the first and second N–H stretch overtone regions, where strong resonances, leading to splitting were not observed, and the lifetime of the initially excited vibrational states, as estimated from the homogeneous broadening, was found to be longer. In particular, the estimated lifetimes for 2ν₁ and 3ν₁ were found to be 35 and 27 ps, respectively, compared to 5 ps for the states in the 4ν₁ region.

One possibility would be that the lifetimes could be related to the density of states in the regions of the various overtones. Nevertheless, when the total vibrational state density was calculated via the Stein-Rabinovitch extension of the Beyer-Swinehart algorithm, densities of ~ 10³, ~ 4 x 10⁴ and ~ 8 x 10⁵ (should be lower for A₁ symmetry states) in the regions of 2ν₁, 3ν₁ and 4ν₁, respectively, were found. Comparison of the lifetimes of 2ν₁, 3ν₁ and 4ν₁ shows that the first two are about the same, while that of the latter decreases by a factor of about 5 - 7. This means that the total density of states, which shows about a similar increase (more than an order of magnitude) while passing from one energetic window to the other could not be the only reason to the observed lifetimes. Therefore, it is likely that the longer lifetimes for the lower N–H stretch overtones (2ν₁ and 3ν₁) is a result of missing resonances, hindering the energy flow out of the initially vibrationally excited states to the bath states.

**Fig 4.8** - Time dependent probabilities of the states of pyrrole in the third N–H stretch overtone region, obtained from the vibrational Hamiltonian, assuming that the 4ν₁ state contains all the initial population (calculated in Appendix G).
5. SUMMARY

In this work spectroscopic measurements in the gas phase were employed for getting insight into the intramolecular dynamics in pyrrole. In particular, PAR spectra at 21 and 65 °C and jet-cooled action spectra of pyrrole in the N-H ($v_1$) and C-H ($v_2$) stretch fundamentals region were measured. Taking advantage of the relatively narrow features, exhibiting the $Q$-branches of the bands in the PAR spectra and of the intensity dependence of the bands on temperature, the close lying hot bands could be resolved, allowing origins and off-diagonal anharmonicities. The latter values were compared to the corresponding calculated non-diagonal anharmonicities and due to their good agreement, tentative assignment of the measured bands was proposed, allowing to add new data to the extensive set of already known vibrational constants of pyrrole and to shed more light on the vibrational structure of pyrrole.

The distinction between the hot and cold bands also enabled revealing the interacting states in the region of the fundamental C-H stretch ($v_2$) and building a two level model describing the Fermi resonance interaction between this state and the overtone of the ring deformation (2$v_{19}$). The deperturbation analysis showed that the characteristics of these vibrational states are preserved. To test whether this preservation of character has implications on the photodissociation outcome, the H action spectra in the same energetic region were measured. Comparison of the latter to the corresponding PAR spectrum showed that the N-H and C-H stretch fundamentals and particularly the overtone of the deformation, enhance the photodissociation, while bringing different FC factors into play, and leading to most effective enhancement upon preparation of the 2$v_{19}$ eigenstate. The different FC factors could be only because the primary characteristics of the initially excited mode is preserved, excluding the possibility of statistical behavior.

As for the first, second and third N-H stretch overtone regions in pyrrole, the measured room temperature PA and jet-cooled action spectra allowed us to open a window for watching the vibrational pattern and the dynamics of energy flow out of the initially excited vibrational states. The measurements and simulations of the PA and particularly of the action spectra allowed us to uncover the features in each region and the
homogeneous linewidths of the transitions. In the first and second overtone regions the N-H stretches were isolated and the IVR was by weak couplings to the bath states (Eq. 1.3), unlike in the fundamental region. However, in the third overtone region the energy flow was governed by strong couplings to dark states and by weak ones to the bath states. The action spectra provided enough spectral resolution for observing the relatively strong coupled $4\nu_1$, $3\nu_1 + \nu_2$ and $3\nu_1 + \nu_3$ states. By considering the vibrational Hamiltonian that was obtained for the states in the $4\nu_1$ region, and the linewidths in this manifold and in the lower overtones, we were able to reveal the intramolecular dynamics, showing that it is sensitive to the coupling structure.

This approach allowed obtaining evidence of the intramolecular dynamics in pyrrole, coming from the mode selectivity in dissociation and from the strong interactions and IVR lifetimes deduced from spectral linewidths. It is to be admitted that the molecular ultraviolet photodissociation is a very important and interesting process, and particularly, that of pre-excited vibrational states. As shown here, it provides avenues for assessing the intramolecular dynamics on the ground electronic state, but also on the excited electronic states by obtaining an understanding about the influence of initial vibrational excitation on its dissociation pathways and dynamics. This will be performed in the next stage of our research, by using the velocity map imaging,\textsuperscript{64,61} for detection of the released H fragments, while obtaining information about the photofragment velocity distribution (kinetic energy and angular distributions). A demonstration of the outcome of the photodissociation by this method would be a significant advancement in the understanding of the physics of the influence of pre-excited vibrational states on dissociation pathways and dynamics in pyrrole.
6. SCIENTIFIC PUBLICATION RESULTING FROM THIS WORK

1) "Mode-specific Photodissociation of Vibrationally Excited Pyrrole"

2) "Vibrational Dynamics of Pyrrole via Frequency-Domain Spectroscopy"
   Selected for the January 15, 2012 issue of Virtual Journal of Biological Physics Research published by the American Physical Society and the American Institute of Physics, an edited compilation of links to articles from participating publishers, covering a focused area of frontier research. http://www.vjbio.org

3) "Revealing the Hot Bands in the Regions of the N-H and C-H Stretch Fundamentals of Pyrrole"
APPENDIX

A. Hot and cold bands symmetry and spectral range

The hot bands in the spectra, Figs. 4.1 and 4.2 appear at energies close to those of the main bands. The band origins observed in the spectra are in fact related to the transition energies from the lower vibrational to the upper vibrational states of the hot band. Consequently, the energy of the upper levels differs from that of the observed bands. To discuss this issue, it is convenient to use vibrational term values, \( G_{(n)} \) instead of energy levels, since they invariably have dimensions of wavenumber, so that \( G_{(n)} = E_n / \hbar c \). An additional issue of importance is the symmetry of the upper vibrational state in a particular Raman transition and the type of the band that is observed in the measured spectrum. These two points will be discussed here briefly:

1) Energy

The energy of the upper vibrational level of a hot band \((n\nu_2 + \nu_j - \nu_j)\) is:

\[
G_{(n\nu_2+\nu_j)} = n\nu_i + \nu_j + n\nu_{i,j},
\]

where, the lower vibrational energy level of the hot band is \( \nu_j \) and the off diagonal anharmonicity is \( \nu_{i,j} \). The energy corresponding to the hot band transition is given by:

\[
G_{(m\nu_2+\nu_j)} - G_{(\nu_j)} = n\nu_j + n\nu_{i,j}.
\]  

(A.2)

This energy depends not only on the vibrational term values of the upper and lower vibrational levels, but also on the anharmonicity, as shown in Fig. A.1.
2) Symmetry

Pyrrole belongs to the $C_{2v}$ symmetry point group. Each of the 24 pyrrole fundamental modes is represented by one of the four symmetry species: $A_1$, $A_2$, $B_1$ or $B_2$, related to the symmetry operations: $E$, $C_2(a)$, $\sigma_v(ab)$ and $\sigma_v(ac)$, and given in Table A.1.

Table A.1 - Character table of the $C_{2v}$ symmetry point group, taken from Refs. 33, 48.

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_2(a)$</th>
<th>$\sigma_v(ab)$</th>
<th>$\sigma_v(ac)$</th>
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</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

In this work it was very important to consider the symmetry issue, particularly in the C-H fundamental stretch region for investigating IVR. This region was measured by variants of Raman spectroscopy and therefore, the pyrrole symmetric ($A_1$) vibrational transitions are expected to exhibit sharp central $Q$-branches, and the non-symmetric vibrations ($A_2$,
B₁ and B₂) central minima. The Raman vibrational transition intensity is proportional to $|\tilde{R}|^2$, where:

$$\tilde{R} = \int \psi_s \tilde{\alpha} \psi_g d\tau,$$

implying that $\tilde{R} = 0$ for a forbidden transition and $\tilde{R} \neq 0$ for an allowed transition. The requirement that the integral of Eq. A.3 should be non-zero can be satisfied if the integrand is totally symmetric:

$$\Gamma(\psi_s) \times \Gamma(\tilde{\alpha}) \times \Gamma(\psi_g) = A₁.$$

By testing this condition for the different types of bands encountered in the spectra, one can obtain the symmetry species of the upper vibrational levels and of the transition. For the cold bands, when the lower vibrational state is the ground state ($\psi_g$) of A₁ symmetry, it is required that $\Gamma(\tilde{\alpha}) = \Gamma(\psi_s)$ for an allowed transition, meaning that the band type is represented by the symmetry of the upper vibrational level. As for the hot bands:

$$\Gamma(\psi_i + \psi_j) \times \Gamma(\tilde{\alpha}) \times \Gamma(\psi_j) = \Gamma(\psi_i) \times \Gamma(\psi_j) \times \Gamma(\tilde{\alpha}) \times \Gamma(\psi_j) = \Gamma(\psi_i) \times \Gamma(\psi_j) = A₁,$$

where $\psi_s = \psi_i + \psi_j$, it is required that $\Gamma(\tilde{\alpha}) = \Gamma(\psi_i)$ for an allowed transition, meaning that the type of the hot band appearing in the spectrum should be similar to that of the main band, namely of the same symmetry, as can be seen in the measured spectrum (Figs. 4.1, 4.2). Nevertheless, the symmetry of the upper vibrational level of the hot band, corresponds to that of the involved states, implying that it is equal to:

$$\Gamma(\psi_i + \psi_j) = \Gamma(\psi_i) \times \Gamma(\psi_j).$$

Therefore, in the C-H stretch region the symmetry of the upper levels of the observed hot bands (A₂, B₁) differ from that of the main band ($\nu_2$ is of A₁ symmetry). This analysis is needed for IVR understanding. In principle, IVR can take place between the vibrational upper levels, however, if their symmetry differs, the energy flow between these states is
forbidden. This can be shown by considering that the coupling term between two vibrational upper states is:

\[ W_{ij} = \int \psi_i \hat{H} \psi_j d\tau. \]  

(A.7)

The symmetry requirement for the integral of Eq. A.7 to be non zero is:

\[ \Gamma(\psi_i) \times \Gamma(H) \times \Gamma(\psi_j) = \Gamma(\psi_i) \times \Gamma(\psi_j) = A_1, \]  

(A.8)

if \[ \Gamma(\psi_i) \neq \Gamma(\psi_j) \rightarrow \Gamma(\psi_i) \times \Gamma(\psi_j) \neq A_1. \]
B. Asymmetric rotor

Ro-vibrational transitions involve the changing of the vibrational quantum number, \( v \), together with the angular momentum quantum numbers, \( J \), \( K_a \) and \( K_b \). In an asymmetric rotor the three moments of inertia along the molecular axes differ, namely, \( I_a < I_b < I_c \). The molecular rotational constants are defined by:

\[
A = \frac{\hbar}{8\pi^2 c I_a}; \quad B = \frac{\hbar}{8\pi^2 c I_b}; \quad C = \frac{\hbar}{8\pi^2 c I_c},
\]

where \( A > B > C \), \( \hbar \) is the Planck constant and \( c \) is the speed of light in vacuum.

The general Hamiltonian is written as:

\[
H_r = AJ_a^2 + BJ_b^2 + CJ_c^2,
\]

This can be rewritten as:

\[
H_r = \alpha J^2 + \beta J_c^2 + \gamma (J^{+2} + J^{-2}),
\]

where \( \alpha = \frac{1}{2}(A + B) \), \( \beta = C - \frac{1}{2}(A + B) \), \( \gamma = \frac{1}{4}(A - B) \), \( J^+ = J_a + iJ_b \), \( J^- = J_a - iJ_b \).

The matrix elements of the Hamiltonian are obtained from:

\[
\langle JK | J^2 | JK \rangle = J(J + 1),
\]

\[
\langle JK | J_c^2 | JK \rangle = K^2,
\]

\[
\langle JK' | J^+ J^+ | JK \rangle = \sqrt{(J - K)(J + K + 1)(J - K - 1)(J + K + 2)} \delta_{K' - 2, K},
\]

\[
\langle JK' | J^- J^- | JK \rangle = \sqrt{(J + K)(J - K + 1)(J + K - 1)(J - K + 2)} \delta_{K' + 2, K},
\]

Due to the last two expressions the Hamiltonian is not diagonal.

As mentioned in Sect. 4.1.1 the rotational eigenvalues of the vibrational ground state and vibrational upper state were calculated by the following Matlab code, that
diagonalizes the Hamiltonian matrix from Eq. B.2. The different transitions and their positions were obtained by subtracting the rotational eigenvalues of the vibrational ground state from those of the upper state. The intensity of these transitions is related to the Boltzmann ratio and therefore, depends on the temperature (which is a parameter in the code). The rotational constants of the vibrationally excited state for N-H stretch (ν₁) were taken from Ref. 32 (Table 4.1), while for the C-H symmetric stretch (ν₂) were found by the fitting.

Matlab code for fitting the calculated Q-branches to the measured ones in asymmetric top molecules

```matlab
clearall;
lsql=300;
load ramanfile.dat; % loading y(signal) axis of measurement spectrum
load xaxis.dat; % loading x(wavenumber) axis of measurement spectrum
A1=0.30456; Bl=0.30025; Cl=0.15117; % setting rotational constants in the ground state
T=290; % measurement temperature
Jmax=80; % number of rotational transitions without degeneration
for dv=0.18:0.01:0.18; % setting/finding line width
    for origin=3530.81:0.005:3530.81 % setting/finding band origin
        for Au=0.3043:0.0005:0.3043 % setting/finding rotational constant in upper vibrational level
            for Bu=0.2999:0.0005:0.2999 % setting/finding rotational constant in upper vibrational level
                for Cu=0.15106:0.0005:0.15106 % setting/finding rotational constant in upper vibrational level
                    t=1;s1=0;clear P;
                    El=zeros(Jmax+1,Jmax+1,Jmax+1);Eu=El;
                    % resetting the undiagonal energy matrix
                    for J=1:Jmax % calculating the matrix of energy eigenvalues
                        M1=zeros(2*J+1);Mu=zeros(2*J+1);K=-J:J;
                        % Ml undiagonal energy matrix of vibrational ground states,
                        Mu undiagonal energy matrix of excited vibrational states
```
MainDiagonalOfMl=0.5*(Bl+Cl)*J*(J+1)+0.5*(2*Al-Bl-Cl)*K.^2;
% calculates the main diagonal of Ml
DiagonalUpperOfMl=0.25*(Bl-Cl).*sqrt((J*(J+1)-K.*(K-1)).*(J*(J+1)-(K-1)).*(K-2));%Calculates the +2 diagonal of Ml
DiagonalLowerOfMl=0.25*(Bl-Cl.*sqrt((J*(J+1)-K.*(K+1)).*(J*(J+1)-(K+1)).*(K+2)));%Calculates the -2 diagonal of Ml

MainDiagonalOfMu=0.5*(Bu+Cu)*J*(J+1)+0.5*(2*Au-Bu-Cu)*K.^2;
%calculates the main diagonal of Mu
DiagonalUpperOfMu=0.25*(Bu-Cu).*sqrt((J*(J+1)-K.*(K-1)).*(J*(J+1)-(K-1)).*(K-2));%Calculates the +2 diagonal of Ml
DiagonalLowerOfMu=0.25*(Bu-Cu).*sqrt((J*(J+1)-K.*(K+1)).*(J*(J+1)-(K+1)).*(K+2)));%Calculates the -2 diagonal of Ml

Ml=diag(MainDiagonalOfMl,0)+diag(DiagonalUpperOfMl,2)
+diag(DiagonalLowerOfMl,-2);
Mu=diag(MainDiagonalOfMu,0)+diag(DiagonalUpperOfMu,2)
+diag(DiagonalLowerOfMu,-2);

Tl=eig (Ml); Tl=sort(Tl);
% finds eigenvalues of Ml and sorts them in ascending order
Tu=eig (Mu); Tu=sort(Tu); % finds eigenvalues of Mu and sorts them in ascending order

for i=1:2*J+1
    P(i)=origin+Tu(i,1)-Tl(i,1); % number of transition from band origin
    Nl(i)=(2*J+1)*exp(-Tl(i,1)/(0.694*T));
    % intensity calculation of transition by boltsman
    t=t+1;
end
P1=P';I1=Nl';

%******************************************graph******************************************
i=0;D=size(P1);
D1=D(1,1); % number of rotational transitions
M=size(xaxis);% number of measurement points

for x=1:M
    i=i+1;
    Int=0;
    % code for plotting graph
for k=1:D1
    Int=Int+I1(k,1)*exp(-2*(xaxis(x)-P1(k,1))^2/(dv)^2);
    % convolute the rotational transitions with Gaussian for each measurement point
End
Amp(i)=Int;
end
Amp1=Amp';
Amp1=Amp1/max(Amp1);
%plot(Ax,Amp1)
L=size(ramanfile);
L1=L(1,1);
lsq=0;
for j=1:L1-1
    lsq=lsq+(ramanfile(j)-Amp1(j))^2; % least squares of measured and calculated spectra.
end
if lsq<lsq1
    lsq=lsq
    origin % setting for N-H stretch (v1), output for C-H stretch (v2)
    Au % setting for N-H stretch (v1), output for C-H stretch (v2)
    Bu % setting for N-H stretch (v1), output for C-H stretch (v2)
    Cu % setting for N-H stretch (v1), output for C-H stretch (v2)
    Dv % output for N-H stretch (v1) & C-H stretch (v2)
    end
end
end
dlmwrite('Amp1.dat',Amp1, 't')% calculated spectrum
C. Calibration of the spectra in the C-H fundamental region

The spectra were calibrated according to the band origin positions of $\nu_1$, $\nu_1 + \nu_{16}$ - $\nu_{16}$ and $2\nu_{19}$ features that were well observed in the measured spectrum and are given in Ref. 33 and match those given in Ref. 30. It is interesting to note that two hot bands $\nu_2 + \nu_{14}$ - $\nu_{14}$, $\nu_2 + \nu_{11}$ - $\nu_{11}$ and the C-H stretch ($\nu_3$) band that were observed in the measured spectrum (Fig. 4.2 and Fig. C.2) and also observed in Refs. 30 and 33, respectively. These bands were added to the calibration line, and fit very well (marked by the circle in Fig. C.1).

Fig. C.1 - Calibration by linear fit, according to the band origin positions of $\nu_1$, $\nu_1 + \nu_{16}$ - $\nu_{16}$ and $2\nu_{19}$ features (full circle) observed in the measured spectrum (OPO wavenumber) in the present work (given in Table C.1) and the band origins, corresponding to these features, taken from Ref. 33.
Table C.1 - Band origin positions that were used in Fig. C.1. Full black circles refer to bands that were used for calibration, circles refer to bands appearing on the calibration fit and the blue circle refers to the band origin of \( \nu_2 \).

<table>
<thead>
<tr>
<th>calibrated</th>
<th>Band origins</th>
<th>uncalibrated</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3530.81</td>
<td>3530.81(^a)</td>
<td>2933.27</td>
<td>( \nu_1 )</td>
</tr>
<tr>
<td>3505.80</td>
<td>3505.80(^a)</td>
<td>2908.19</td>
<td>( \nu_1+\nu_{16}-\nu_{16} )</td>
</tr>
<tr>
<td>3149.86</td>
<td>3148.87(^b)</td>
<td>2551.31</td>
<td>( \nu_2 )</td>
</tr>
<tr>
<td>3146.03</td>
<td>3146.00(^b)</td>
<td>2547.56</td>
<td>( \nu_2+\nu_{14}-\nu_{14} )</td>
</tr>
<tr>
<td>3143.03</td>
<td>3143.00(^b)</td>
<td>2544.59</td>
<td>( \nu_2+\nu_{11}-\nu_{11} )</td>
</tr>
<tr>
<td>3127.87</td>
<td>3127.87(^a)</td>
<td>2529.29</td>
<td>( \nu_3 )</td>
</tr>
<tr>
<td>3074.07</td>
<td>3074.07(^a)</td>
<td>2475.31</td>
<td>( 2\nu_{19} )</td>
</tr>
</tbody>
</table>

\(^a\) taken from Ref. 33, \(^b\) taken from Ref. 30.

Fig. C.2 - Measured saturated PAR spectrum (at room temperature) in the C-H fundamental stretch region.
### D. Pyrrole fundamental modes

**Table D.1 -** Pyrrole vibrational normal modes and their frequencies from experiment and from calculations at the B3LYP/6-311++G(d,p) and MP2/cc-pVTZ levels.

<table>
<thead>
<tr>
<th>symmetry</th>
<th>Assignment</th>
<th>Experiment&lt;sup&gt;a&lt;/sup&gt; $\nu_0$ (cm$^{-1}$)</th>
<th>B3LYP/6-311++G(d,p) $\nu_i$ (cm$^{-1}$)</th>
<th>MP2/cc-pVTZ $\nu_i$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$\nu_1$</td>
<td>3530.81</td>
<td>3507.87</td>
<td>3532.49</td>
</tr>
<tr>
<td></td>
<td>$\nu_2$</td>
<td>3149.86&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3136.94</td>
<td>3181.87</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$</td>
<td>3127.87</td>
<td>3114.96</td>
<td>3161.77</td>
</tr>
<tr>
<td></td>
<td>$\nu_4$</td>
<td>1472.05</td>
<td>1460.23</td>
<td>1473.13</td>
</tr>
<tr>
<td></td>
<td>$\nu_5$</td>
<td>1401.08</td>
<td>1386.54</td>
<td>1403.82</td>
</tr>
<tr>
<td></td>
<td>$\nu_6$</td>
<td>1148.17</td>
<td>1148.48</td>
<td>1156.00</td>
</tr>
<tr>
<td></td>
<td>$\nu_7$</td>
<td>1074.53</td>
<td>1071.34</td>
<td>1087.81</td>
</tr>
<tr>
<td></td>
<td>$\nu_8$</td>
<td>1017.01</td>
<td>1015.11</td>
<td>1028.20</td>
</tr>
<tr>
<td></td>
<td>$\nu_9$</td>
<td>881.54</td>
<td>884.10</td>
<td>874.58</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$\nu_{10}$</td>
<td>864.1</td>
<td>864.32</td>
<td>871.77</td>
</tr>
<tr>
<td></td>
<td>$\nu_{11}$</td>
<td>692.2</td>
<td>688.23</td>
<td>678.42</td>
</tr>
<tr>
<td></td>
<td>$\nu_{12}$</td>
<td>614.01</td>
<td>615.22</td>
<td>622.82</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$\nu_{13}$</td>
<td>826.82</td>
<td>828.81</td>
<td>815.52</td>
</tr>
<tr>
<td></td>
<td>$\nu_{14}$</td>
<td>722.13</td>
<td>718.96</td>
<td>721.97</td>
</tr>
<tr>
<td></td>
<td>$\nu_{15}$</td>
<td>620.67</td>
<td>622.06</td>
<td>638.06</td>
</tr>
<tr>
<td></td>
<td>$\nu_{16}$</td>
<td>474.61</td>
<td>488.87</td>
<td>507.30</td>
</tr>
<tr>
<td></td>
<td>$\nu_{17}$</td>
<td>3143.15</td>
<td>3130.74</td>
<td>3175.57</td>
</tr>
<tr>
<td></td>
<td>$\nu_{18}$</td>
<td>3118.6</td>
<td>3104.74</td>
<td>3152.18</td>
</tr>
<tr>
<td></td>
<td>$\nu_{19}$</td>
<td>1518.55</td>
<td>1537.78</td>
<td>1523.60</td>
</tr>
<tr>
<td></td>
<td>$\nu_{20}$</td>
<td>1424.45</td>
<td>1402.19</td>
<td>1439.81</td>
</tr>
<tr>
<td></td>
<td>$\nu_{21}$</td>
<td>1288.46</td>
<td>1279.68</td>
<td>1284.31</td>
</tr>
<tr>
<td></td>
<td>$\nu_{22}$</td>
<td>1134.1</td>
<td>1130.94</td>
<td>1143.69</td>
</tr>
<tr>
<td></td>
<td>$\nu_{23}$</td>
<td>1049.05</td>
<td>1046.13</td>
<td>1047.54</td>
</tr>
<tr>
<td></td>
<td>$\nu_{24}$</td>
<td>865.6</td>
<td>868.05</td>
<td>856.84</td>
</tr>
</tbody>
</table>

<sup>a</sup> Ref. 33, <sup>b</sup> Ref. 30.
Fig. D.1 - The 24 normal modes of vibration in pyrrole from calculations of GAUSSIAN 09 package, at the B3LYP/6-311++G(d,p) level.
E. Fermi resonances and first-order perturbation

In the PARS spectrum three cold bands of $A_1$ symmetry appeared (Fig. 4.2). As mentioned above, the coupling term between $v_2$ and $v_3$ is negligible. Taking advantage of this constraint, we can assume two limiting situations: a) $v_3$ state is totally dark and therefore seen only due to coupling with $2v_{19}$ (Fig. 4.2, C.2) and b) this band appears only since it carries some Raman activity. The second option seems reasonable since fundamental stretch modes usually carry some brightness. In attempt to describe the intramolecular dynamics for the both options three and two level models have to be considered, respectively. If indeed the $v_3$ band intensity appears due to interaction with the $2v_{19}$ state, the three level model can give an error estimate for the parameters (coupling term and the energies of the ZO states) obtained by the two level model. Moreover, the two level model allows obtaining the effect of the Fermi resonance between the $v_2$ and $2v_{19}$ on the upper levels of the hot bands.

1) The two level model

As mentioned above, this model takes into account only the interaction between the $2v_{19}$ and $v_2$ states. The bands that appear in the PAR spectrum are the vibrational eigenfunctions of pyrrole.

The matrix that represents the energies of these eigenstates is:\textsuperscript{12}

\[
H = \begin{pmatrix}
E_{v_2} & 0 \\
0 & E_{2v_{19}}
\end{pmatrix}.
\] (E.1)

However, in the first order approximation (harmonic potential) the energy states are $E_{v_2}^0$ and $E_{2v_{19}}^0$ and the anharmonic interaction between them is marked by the matrix elements $W$. Therefore, the Hamiltonian that represents the first order energy levels with anharmonic interactions is:

55
\[ H^0 = \begin{pmatrix} E_{v_2}^0 & W \\ W & E_{2v_{19}}^0 \end{pmatrix}. \]  

(E.2)

The vibrational eigenstates \( \psi_{v_2}, \psi_{2v_{19}} \) can be written as superposition of the ZO states \( \psi_{v_2}^0, \psi_{2v_{19}}^0 \):

\[
\psi_{v_2} = \alpha_1 \psi_{v_2}^0 - \alpha_2 \psi_{2v_{19}}^0, \\
\psi_{2v_{19}} = \alpha_2 \psi_{v_2}^0 + \alpha_1 \psi_{2v_{19}}^0,
\]

where, \( \alpha_1^2 + \alpha_2^2 = 1 \), is the normalization.

From symmetry, the transition matrix from the first order basis states to the eigenstates base is:

\[
T = \begin{pmatrix} \alpha_1 & -\alpha_2 \\ \alpha_2 & \alpha_1 \end{pmatrix}.
\]

(E.5)

Therefore, \( T^{-1}H^0T = H \).

The solution of this equation leads to:

\[
E_{v_2} = \frac{1}{2}(E_{v_2}^0 + E_{2v_{19}}^0) + \frac{1}{2}\sqrt{4W^2 + \delta^2},
\]

(E.6)

\[
E_{2v_{19}} = \frac{1}{2}(E_{v_2}^0 + E_{2v_{19}}^0) - \frac{1}{2}\sqrt{4W^2 + \delta^2},
\]

(E.7)

\[
\alpha_1^2 = \frac{\sqrt{4W^2 + \delta^2} + \delta}{2\sqrt{4W^2 + \delta^2}},
\]

(E.8)

\[
\alpha_2^2 = \frac{\sqrt{4W^2 + \delta^2} - \delta}{2\sqrt{4W^2 + \delta^2}},
\]

(E.9)
where, $\delta = E_{v_2}^0 - E_{2v_{19}}^0$.

Because the $\psi_{2v_{19}}^0$ is a dark state, it has no impact on the intensity and the intensity ratio appearing in the spectrum is given by:

$$\frac{\alpha_1^2}{\alpha_2^2} = \frac{I_{v_3}}{I_{2v_{19}}} = I = 14.$$  \hspace{1cm} (E.10)

From Eqs. E.6, E.7, E.8 and E.9, the following parameters are found:

$$E_{v_2}^0 = \frac{I}{I+1} E_{v_2} + \frac{1}{I+1} E_{2v_{19}} = 3144.8 \text{ cm}^{-1}, \quad E_{2v_{19}}^0 = \frac{I}{I+1} E_{2v_{19}} + \frac{1}{I+1} E_{v_2} = 3079.1 \text{ cm}^{-1}$$

$$W = \frac{\sqrt{I}}{I+1} (E_{v_2} - E_{2v_{19}}) = 18.9 \text{ cm}^{-1}, \quad \alpha_1^2 = 0.93, \quad \alpha_2^2 = 0.07.$$

2) The three level model

As for the three level model, where the $v_3$ ZO state is a dark state and the related band appears in the spectrum due to coupling with the $2v_{19}$ state, the calculation were performed by a Matlab written code (see below). The code accounts for the Hamiltonian matrix of the ZO energies of the states and the coupling elements:

$$H^0 = \left( \begin{array}{ccc} E_{2v_{19}}^0 & W_{2v_{19},v_3} & W_{2v_{19},v_2} \\ W_{2v_{19},v_3} & E_{v_3}^0 & W_{v_3,v_2} \\ W_{2v_{19},v_2} & W_{v_3,v_2} & E_{v_2}^0 \end{array} \right).$$  \hspace{1cm} (E.11)

assuming that the coupling term, $W_{v_3,v_2} = 0$. Also, the vibrational eigenstates $\psi_{2v_{19}}^0$, $\psi_{v_3}^0$, $\psi_{v_2}^0$ can be written as superposition of the ZO states $\psi_{2v_{19}}^0$, $\psi_{v_3}^0$, $\psi_{v_2}^0$:

$$\psi_{2v_{19}} = \alpha_1 \psi_{2v_{19}}^0 + \alpha_2 \psi_{v_3}^0 + \alpha_3 \psi_{v_2}^0,$$  \hspace{1cm} (E.12)

$$\psi_{v_3} = \beta_1 \psi_{2v_{19}}^0 + \beta_2 \psi_{v_3}^0 + \beta_3 \psi_{v_2}^0,$$  \hspace{1cm} (E.13)
\[ \psi_{v_2} = \gamma_1 \psi_{v_2}^0 + \gamma_2 \psi_{v_3}^0 + \gamma_3 \psi_{v_3}^0, \]  
(E.14)

and the normalization condition is:

\[ \alpha_1^2 + \alpha_2^2 + \alpha_3^2 = 1, \quad \beta_1^2 + \beta_2^2 + \beta_3^2 = 1, \quad \gamma_1^2 + \gamma_2^2 + \gamma_3^2 = 1. \]  
(E.15)

From the intensity ratios, observed in the spectrum, two additional equations are obtained: \( \gamma_3^2 / \alpha_3^2 = 14 \), \( \beta_3^2 / \gamma_3^2 = 40 \), when considered that only \( \psi_{v_2}^0 \) is a bright state. These equations lead to the possibility of obtaining a single solution when numerically solving the following: \( T^{-1}H^0T = H \),

where

\[ T = \begin{pmatrix} \alpha_1 & \beta_1 & \gamma_1 \\ \alpha_2 & \beta_2 & \gamma_2 \\ \alpha_3 & \beta_3 & \gamma_3 \end{pmatrix}, \]  
(E.16)

and \( H \) is diagonal Hamiltonian of the eigenfunction

\[ H = \begin{pmatrix} E_{2v_0} & 0 & 0 \\ 0 & E_{v_3} & 0 \\ 0 & 0 & E_{v_2} \end{pmatrix}. \]  
(E.17)

**Matlab code for solving the** \( T^{-1}H^0T = H \):

```matlab
for W1=1:0.1:20 % cross anharmonicity coupling elements
    for W2=1:0.1:25 % cross anharmonicity coupling elements
        for W3=0:0.1:0 % cross anharmonicity coupling elements (W3=0)
            for E2=3115:0.1:3130 % zero order energy
                for E3=3140:0.1:3150 % zero order energy
                    for E1=3075:0.1:3085 % zero order energy
                        h=[E1 W1 W2;W1 E2 W3;W2 W3 E3];
```
\[ [T,H] = \text{eig}(h); \]

\[
\text{if } \text{abs}(H(1,1)-3074) < 0.1 \& \text{abs}(H(2,2)-3127.8) < 0.1 \& \\
\text{abs}(H(3,3)-3149.8) < 0.1 \& \\
\text{abs}((T(3,3)^2)/(T(3,2)^2))-40 < 0.1 \& \\
\text{abs}((T(3,3)^2)/(T(3,1)^2))-14 < 0.1
\]

% Terms for the eigenfunction that were seen in the experiment data and
% the intensity ratio between the bands from experiment data too

\[
T \ % \text{Transition matrix} \nonumber \\
H \ % \text{Hamiltonian in the base of eigenstates} \nonumber \\
h \ % \text{Hamiltonian in the base of zero order} \nonumber \\
\text{States } (H^0) \nonumber 
\]

end

end

end

end

end

end

end

end

end

end

\[ \text{the results from the calculation are:} \]

\[
\begin{array}{cccccccc}
0.9523 & -0.1329 & 0.2747 & 3074.0 & 0 & 0 & 3080.7 & 9.3 & 18.8 \\
-0.1685 & -0.9795 & 0.1101 & H = 0 & 3127.9 & 0 & h = 9.3 & 3126.6 & 0 \\
-0.2544 & 0.1511 & 0.9552 & 0 & 0 & 3149.8 & 18.8 & 0 & 3144.4
\end{array}
\]
3) Two level model for the upper energy levels of the hot bands

The main idea is to find out the cross anharmonicity of the eigenstates, due to the Fermi resonance between \( \nu_2 \) and \( 2\nu_{19} \), and to compare it with the cross anharmonicity of the ZO states that were calculated by Gaussian (Tables 3.2 and 3.3). The unperturbed upper energy levels of the hot bands, related to \( \nu_2 \), are: 

\[
E^0_{\nu_2+\nu_j+2\nu_{19},j} = \nu_2 + \nu_j + x_{2,j}
\]

and the off-diagonal anharmonicity is:

\[
x_{2,j} = E^0_{\nu_2+\nu_j+\nu_{19},j} - E^0_{\nu_2+\nu_j}. \tag{E.18}
\]

In this case, \( \delta \), is defined as:

\[
\delta_{\nu_2} = E^0_{\nu_2+\nu_j+\nu_{19},j} - E^0_{\nu_2+\nu_j+2\nu_{19},j} = \delta + x_{2,j} - 2x_{19,j}. \tag{E.19}
\]

Using Eq. E.6, the upper energy level related to the hot bands, affected by Fermi resonances is:

\[
E_{\nu_2+\nu_j+\nu_{19},j} = \frac{1}{2} \left( E^0_{\nu_2+\nu_j+\nu_{19},j} + E^0_{\nu_2+\nu_j+2\nu_{19},j} \right) + \frac{1}{2} \sqrt{4W^2 + \delta_{\nu_2}^2}
\]

\[
= \frac{1}{2} \left( E^0_{\nu_2} + E^0_{2\nu_{19}} \right) + \frac{1}{2} \left( x_{2,j} + 2x_{19,j} + \sqrt{4W^2 + \delta_{\nu_2}^2} \right), \tag{E.20}
\]

where \( \delta \to \delta_{\nu_2} \), \( E^0_{\nu_2} \to E^0_{\nu_2+\nu_j+\nu_{19},j} \), \( E^0_{2\nu_{19}} \to E^0_{\nu_2+\nu_j+2\nu_{19},j} \).

The shifted upper energy level of the hot bands, related to \( \nu_2 \), without taking into account off-diagonal anharmonicity is:

\[
E_{\nu_2+\nu_j} = \frac{1}{2} \left( E^0_{\nu_2} + E^0_{2\nu_{19}} \right) + \nu_j + \frac{1}{2} \sqrt{4W^2 + \delta^2}. \tag{E.21}
\]

When the off-diagonal anharmonicity is taken into account, according to Eqs. E.20 and E.21 the following is obtained:

\[
x_{2,j}^{FR} = E_{\nu_2+\nu_j+\nu_{19},j} - E_{\nu_2+\nu_j} = \frac{1}{2} \left( x_{2,j} + 2x_{19,j} + \sqrt{4W^2 + \delta_{\nu_2}^2} - \sqrt{4W^2 + \delta^2} \right). \tag{E.22}
\]
where coupling term \( W = 18.9 \text{ cm}^{-1} \) does not change, and the \( x_{19,j} \) values obtained from Gaussian calculation. The results that obtained by Eq. E.22 with experimental and calculated cross anharmonicity are presented in Table E.1.

Table E.1 - Non-diagonal anharmonicity constants, \( x_{i,j} \), for the states in the C-H stretch fundamental region. These values are compared to the \( x_{i,j} \) values derived from the calculations at the B3LYP/6-311++G(d,p) level and to the corrected non-diagonal anharmonicities, \( x_{i,j}^{FR} \) that were obtained after the Fermi resonance was taken into account.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Experiment ( x_{i,j} ) (cm(^{-1}))</th>
<th>( x_{i,j}^{FR} ) (cm(^{-1}))</th>
<th>B3LYP/6-311++G(d,p) ( x_{i,j} ) (cm(^{-1}))</th>
<th>B3LYP/6311++G(d,p) ( x_{19,j} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_2 )</td>
<td>( \nu_2 )</td>
<td>-1.09</td>
<td>-1.41</td>
<td>-1.39</td>
</tr>
<tr>
<td>( hb1 )</td>
<td>( \nu_2 + \nu_{16} - \nu_{16} )</td>
<td>-1.44</td>
<td>-0.85</td>
<td>-0.77</td>
</tr>
<tr>
<td>( hb2 )</td>
<td>( \nu_2 + \nu_{12} - \nu_{12} )</td>
<td>-2.23</td>
<td>-0.99</td>
<td>-0.97</td>
</tr>
<tr>
<td>( hb3 )</td>
<td>( \nu_2 + \nu_{15} - \nu_{15} )</td>
<td>-3.77</td>
<td>-3.92</td>
<td>-4.03</td>
</tr>
<tr>
<td>( hb4 )</td>
<td>( \nu_2 + \nu_{14} - \nu_{14} )</td>
<td>-6.77</td>
<td>-6.75</td>
<td>-6.95</td>
</tr>
<tr>
<td>( hb5 )</td>
<td>( \nu_2 + \nu_{11} - \nu_{11} )</td>
<td>-6.77</td>
<td>-6.75</td>
<td>-6.95</td>
</tr>
</tbody>
</table>
F. Calibration of the spectra of the N-H stretch overtones

The positions of the lines in the measured spectra of water in the different spectral regions were compared to the HITRAN database.\textsuperscript{66} Comparison of the HITRAN water spectra to the measured PA and action spectra of the N-H stretch overtones, allowed calibration of the latter.

Fig. F.1 - PA spectra of water vapor in the first (A), second (B) and third (C) N-H overtone regions of pyrrole. B and C spectra exhibits only the spectra of water vapor, while A also the calibrated and uncalibrated PA spectrum of the second N-H stretch overtone of pyrrole.
G. Deptonurbation analysis for the third N-H stretch overtone region and calculation of the time-dependent IVR

The bands that appear in the PA and action spectra of pyrrole correspond to the vibrational eigenstates. In the third N-H stretch overtone region, three interacting bands are observed. The Hamiltonian matrix of the ZO energy of each state and the coupling elements is:

\[
H^0 = \begin{pmatrix}
E_{4v_1}^0 & W_{4v_1,3v_1+v_2} & W_{4v_1,3v_1+v_3} \\
W_{4v_1,3v_1+v_2} & E_{3v_1+v_2}^0 & W_{3v_1+v_2,3v_1+v_3} \\
W_{4v_1,3v_1+v_3} & W_{3v_1+v_2,3v_1+v_3} & E_{3v_1+v_3}^0
\end{pmatrix}.
\]  

(G.1)

From the Birge-Sponer (Fig. 4.6) plot, the \(E_{4v_1}^0\) was found to be 13312.1 cm\(^{-1}\).

The vibrational eigenstates \(\psi_{4v_1}, \psi_{3v_1+v_2}, \psi_{3v_1+v_3}\) can be written as superposition of the zero order approximation eigenstates \(\psi_{4v_1}^0, \psi_{4v_1+v_2}^0, \psi_{4v_1+v_3}^0\) according to:

\[
\psi_{4v_1} = \alpha_1 \psi_{4v_1}^0 + \alpha_2 \psi_{4v_1+v_2}^0 + \alpha_3 \psi_{4v_1+v_3}^0, \tag{G.2}
\]

\[
\psi_{3v_1+v_2} = \beta_1 \psi_{4v_1}^0 + \beta_2 \psi_{4v_1+v_2}^0 + \beta_3 \psi_{4v_1+v_3}^0, \tag{G.3}
\]

\[
\psi_{3v_1+v_3} = \gamma_1 \psi_{4v_1}^0 + \gamma_2 \psi_{4v_1+v_3}^0 + \gamma_3 \psi_{4v_1+v_2}^0. \tag{G.4}
\]

From the ratio of intensities that appears in the spectrum we have:

\(\alpha_i^2 = 0.54, \beta_i^2 = 0.27, \gamma_i^2 = 0.19\), where we considered that only \(\psi_{4v_1}^0\) was a bright state.

The algorithm calculates the following equation: \(T^{-1}H^0T = H\) where

\[
H = \begin{pmatrix}
E_{4v_1} & 0 & 0 \\
0 & E_{3v_1+v_3} & 0 \\
0 & 0 & E_{3v_1+v_2}
\end{pmatrix}.
\]  

(G.5)
The equation $T^{-1}HT = H$ was solved by the Matlab code, using the same algorithm as in Appendix E.2, and three coupling terms were found.

In addition, to the strong resonance interactions, there are interactions with the bath states. Therefore, the three bands appear with intensity proportional to their brightness and a width $\Gamma$ proportional to the decay rate. The time dependent energy flow between the states and the bath states was calculated by the following algorithm:

**Matlab code for time evolution of the states in the third N-H stretch overtone region:**

```matlab
k=1;
P0=[1 0 0;0 0 0;0 0 0]; % Density matrix of ZOBS, 4$\nu_1$ at t=0
for t=0:0.01:20
    k=k+1;
    U=expm(-j*H0*t*1.88E+11); % Evolution Operator shown in Eq. 1.4, where 1.88*10^{11} is the energy (J) to wavenumber (cm^{-1}) constant transition as mentioned in Appendix A, (2\pi c)G_{m}=E_{m}/\hbar
    P=U*P0*conj(U); % The population probability in the i-th state at time t, Eq. 1.3
    x(k)=P(1,1)*exp(-t/5.3E-12); % ZOBS time evolution, where 5.3 is the decay constant of the state, as shown in Eq. 4.2
    y(k)=P(2,2)*exp(-t/5.3E-12); % ZODS time evolution (3$\nu_1$+$\nu_2$)
    z(k)=P(3,3)*exp(-t/5.3E-12); % ZODS time evolution (3$\nu_1$+$\nu_3$)
end
real(x')
real(y')
real(z')
```
References


28 D.L. Snavely, F.R. Blackburn, Y. Ranasinghe, V.A. Walters, and M. Gonzalez Del Riego,
57. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.;
Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al.
Gaussian 09, revision C.01; Gaussian, Inc.: Wallingford, CT, 2010. Arrange the format
58. MultiWell-2011 Software, 2011, designed and maintained by J. R. Barker with contributors N. F. Ortiz, J. M. Preses, L. L. Lohr, A. Maranzana, P. J. Stimac, T. L. Nguyen, and T. J. D. Kumar; University of


The properties of the deoxyribonucleic acid (DNA) and its proteins, as well as the components of their major UV-sensitive photoreceptor, are of great interest. We expect that by studying the molecular spectroscopy of the excited photoreceptor, we can understand the interactions with light that affect various processes in the molecule. In this work, the breakdown of the excited photoreceptor vibrational and rotational states is learned for the first time, in order to understand the flow of energy within the molecule, and the effects of vibrational and rotational excitation on electronic UV breakdown.

Spectroscopic monitoring and laser-based near infrared (NIR) spectroscopy allowed the acquisition of spectrum and vibrational and rotational components of the excited molecule. For the first overtone region of the stretching of the C-H (ν2) and N-H (ν1) vibrations, the breakdown was observed with the help of vibrational and rotational components of the excited molecule.

The results show the vibrational and rotational components of the excited molecule. For the second overtone region of the stretching of the N-H, we found that the second overtone is isolated, while the third overtone is resonant with two additional states, composed of two quanta of the stretching of the N-H and one quantum of the stretching of the C-H, respectively.

The results of this study are a step towards understanding the molecular dynamics within the excited photoreceptor on the electronic potential surface.
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נכתב: מיכאל אפשטיין

יולי 2012