Photofragment velocity map imaging of H atom elimination in the first excited state of pyrrole

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Photofragment velocity map imaging was used to study the H atom elimination mechanism in the first excited state of pyrrole at \( \lambda = 243.1 \) nm. Two major channels were observed. The first one (76%) produces very fast H atoms and appears to be due to a rapid direct N–H bond breaking in the excited electronic state. The respective H atom kinetic energy distribution has a strong narrow peak at high energies, showing that \( \approx 72\% \) of the available energy is transferred into relative fragment translation. The observed angular recoil distribution which is described by an anisotropy parameter of \( \beta = -0.37 \pm 0.05 \) indicates that the excited optical transition is preferentially perpendicular with respect to the N–H dissociation coordinate. From the maximal kinetic energy release, the value of the N–H bond dissociation energy was found to be \( \delta D_0(\text{N–H}) = (32400 \pm 4000) \text{ cm}^{-1} \). The other channel (24%) leads to much slower H atoms with a very broad kinetic energy distribution, consistent with subsequent unimolecular decay reactions of the molecules in the ground electronic state after internal conversion. This conclusion was supported by similar experiments for N-methylpyrrole which showed only H atoms from the second channel and no fast component. The results corroborate the conclusion that the lowest electronic state of pyrrole has \( \pi\sigma^* \) anti-bonding character and is repulsive with respect to the stretching of the N–H bond.

1. Introduction

Pyrrole is an interesting six \( \pi \)-electron heterocyclic aromatic ring molecule in which one nitrogen atom donates two \( \pi \)-electrons and the four carbon atoms each supply another \( \pi \)-electron. Considerable effort has been directed towards the understanding of its electronic structure and photochemical properties owing to its role as a fundamental structural building block in many biologically important molecules and the relevance of the molecule and its derivatives in syntheses of biologically active compounds, organic polymers, pesticides, or organometallic magnetic compounds.4

Electronic spectra of pyrrole have been measured by ultraviolet (UV) and vacuum ultraviolet (VUV) absorption,2–5 electron energy loss (EEL),5 photoelectron (PE),6,7 and resonance-enhanced multi-photon ionization (REMPI)8 spectroscopies. Two intense absorption bands exist in the UV and near VUV, the first one with an intensity maximum near 210 nm, the second one near 165 nm. In addition, a very weak lower energy feature is found with a maximum around 240 nm.2,3 The observed spectra are, however, broad and unstructured; this has hampered their unambiguous analyses for a long time.

Extensive quantum chemical calculations have been performed to elucidate the excited electronic states.9–16 There is consensus that the simultaneous occurrence of many overlapping Rydberg series and excited valence states is responsible for the apparent complexities. Considerable dispute has remained, however, about how the observed features are to be assigned to these Rydberg and valence transitions.5,10,11,15

In the UV, the most recent calculations by Roos et al.15 confirm that the bulk of the intensity arises from a \( \pi\pi^* \) intra-valence transition to the \( 1^1\text{B}_2 \) state, in contrast to some preceding theoretical work that favored a Rydberg transition.9–11 The weak longer wavelength band23 at around 240 nm has been assigned to the \( 1^1\text{A}_2 (3\sigma) \) Rydberg state.12,15

On the other hand, this state was also postulated to have valence character, by comparison of the electronic states of pyrrole and N-methylpyrrole.17 Calculations by Sobolewski and Domcke showed that in the equilibrium configuration this \( \pi\pi^* \) state does indeed possess Rydberg character,13,14,16 as evident by the diffuseness of the \( \sigma^* \) orbital. However, the stretching of the NH bond leads to a Rydberg-to-valence transformation; the anti-bonding \( \pi^* \) orbital is located on the NH bond and the state becomes repulsive with respect to the NH bond stretching. The accompanying signature is a transfer of charge from the aromatic ring to the H atom of the NH group. As emphasized by Sobolewski and Domcke,16 this Rydberg-to-valence transformation has outstanding importance for the photochemistry of pyrrole, because the optically excited higher energy \( \pi\pi^* \) state(s) may be predissoociated by the repulsive and optically dark \( \pi^* \) state. The resulting short lifetimes of the optically accessed state(s) provide a rationale for the previously not well understood observation that pyrrole does not seem to fluoresce upon electronic excitation by nanosecond laser pulses, in contrast to N-methylpyrrole.17,18

In this publication, we report on first results of a photofragment velocity map imaging investigation of the production of H atoms from pyrrole in the lowest excited electronic state at \( \lambda = 243.1 \) nm designed to collect experimental evidence regarding the postulated photochemical mechanisms. In the “one-color” experiments described in this paper, the same laser was used for the photodissociation of the pyrrole parent molecule and the detection of the H atoms by (2 + 1) REMPI spectroscopy. The results are interpreted by contrasting them with complementary measurements under similar conditions for N-methylpyrrole and with the help of the theoretical work by Domcke and co-workers.13,14,16 In addition, they are compared with an earlier investigation by photofragment translational spectroscopy (PTS).19

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The emerging picture for the photodynamics of pyrrole may be of substantial interest for our understanding of the photochemistry of the biologically important nucleic acid bases.16

2. Experimental section

The photofragment velocity map imaging apparatus built in our laboratory will be described in some detail in another publication.20 The set-up resembles the basic design of Eppink and Parker.21

A gas mixture containing ≈0.1% of pyrrole in He carrier gas was prepared by bubbling the inert gas at 1 bar pressure through the liquid sample stored in a glass reservoir at −20°C. The gases expanded into a differentially pumped stainless steel vacuum chamber through a solenoid actuated pulsed valve (General Valve #9) operated with a 350 μs pulse−1 opening time at 10 Hz repetition rate. A molecular beam entered the final vacuum chamber through a 1.5 mm diameter deuterated conical skimmer (Beam Dynamics). Based on previous experience under similar expansion conditions, the rotational temperature of the pyrrole in the cold beam is expected to be in the range of Trot ≈(20 ± 10) K.

The photolysis/probe laser beam at λ = 243.1 nm intersected the molecular beam at right angle halfway between the repeller and extractor electrodes of a Wiley-McLaren electrostatic imaging assembly. A liquid nitrogen cryo-pump surrounding the arrangement minimized the residual hydrocarbon background. The H atoms from the photodissociation of the pyrrole were detected by (2 + 1) REMPI with a microchannel plate (MCP) coupled to a phosphorescence screen. Images were recorded with a CCD camera (640 × 480 pixels, LaVision) and accumulated over 20 000–100 000 laser shots using single ion counting. Imaging measurements were made under velocity resolution and discriminate against noise. 22 Mass selectivity and centroiding to improve the detection sensitivity and spatial resolution follows by integrating over the angular directions of the reconstructed 3D recoil distribution of the H atoms. The full 3D distribution follows by rotating the figure about its symmetry axis. The vertical “line” in (b) is an artifact of the Abel inversion due to the noise in the experimental 2D image.

Fig. 1 (a) Experimental H atom photofragment velocity map image from the λ = 243.1 nm photolysis of pyrrole. The laser polarization is along the vertical axis in the plane of the figure. (b) 2D slice through the reconstructed 3D recoil distribution of the H atoms. The full 3D distribution follows by rotating the figure about its symmetry axis.

and applying the linear momentum conservation law is given in Fig. 2.

The experimental P(E,T) distribution clearly shows the existence of at least two qualitatively distinctive reaction channels, reflected in Figs. 1a and b by the sharp outer ring and the broad weaker inner feature. The observations were consequently modeled by assuming two superimposed distributions. Both could be unfolded by nonlinear least squares fitting to the experimental data as shown in Fig. 2.

The sharp outer ring which reflects the production of very fast, highly non-statistical H atoms is referred to in the following as channel (A). As it may be seen from Fig. 2, its contribution to the overall P(E,T) curve can be nicely described by a sharply peaked Gaussian, with the peak at Epeak = 6410 cm−1 and a width of ΔE = 1680 cm−1 (FWHM). The distribution (A) extends to a maximum kinetic energy release of Epeak = 8750 ± 250 cm−1. From the areas under the curves, the yield is about 76%, i.e., channel (A) is the major one.

The underlying broad distribution in Fig. 2 was conveniently fitted by a simple polynomial. This channel (B) gives slower H atoms, with a more statistically looking distribution.

From the area, it accounts for ≈24% of the observed H atoms in the experimental observation time window (≈10 ns). The respective distribution peaks at Epeak ≈4300 cm−1. On the other hand, it also shows a rather long tail, extending to ET > 10 000 cm−1. Given the carefully checked purity of the pyrrole and N-methylpyrrole (Aldrich, 98%) were used after repeated fractionated distillation until the liquid was clear. The purities were carefully checked by recording FTIR and NMR spectra.

3. Results

3.1 H atoms from pyrrole

Fig. 1a shows an H atom image from the photodissociation of pyrrole at λ = 243.1 nm. The observed image is the two-dimensional (2D) projection of the full three-dimensional (3D) photofragment recoil distribution. The inverse Abel transformation24 to obtain the 3D distribution was accomplished using the basis-set expansion method of Dribrinski et al.25 A cut through the 3D recoil distribution of the H atoms is displayed in Fig. 1b. The related overall center-of-mass (CM) translational energy distribution P(E,T) of the photofragments which follows by integrating over the angular directions of

Fig. 2 Overall CM translational energy distribution from the λ = 243.1 nm photolysis of pyrrole. Full line: Experimental data, dashed and dotted lines: Fits (see text). The experimental distribution has arbitrarily been scaled to a maximum value of 1.
pyrrole, impurities in the sample cannot explain the channel (B), but a weak residual signal contributing to the tail may be due to some unspecified ionization of background gases which could not be corrected for by an image subtraction with the pyrrole turned off. In addition, it cannot be excluded that the high energy tail of the fitted broad distribution includes a small contribution from two-photon induced dissociation pathways which would be expected to give very fast H atoms (channel C). In the absence of further information, it is difficult to differentiate between these minor contributions.

The attention in this paper in the following is focused mainly on channel (A). In addition to the kinetic energy release, Fig. 1 shows that the angular recoil distribution of the H atoms from channel (A) is clearly anisotropic. After integrating over the outer ring in Fig. 1b, the angular distribution could be fitted by the standard recoil anisotropy function:

\[ P(\theta) = (4\pi)^{-1}[1 + \beta P_2(\cos \theta)], \]

where \( \theta \) is the angle between the recoil velocity and laser polarization vectors, \( \beta \) is the anisotropy parameter, and \( P_2(\cos \theta) \) is the second-order Legendre polynomial. In the limiting cases of pure parallel or perpendicular transitions, \( \beta \) is known to approach the values of +2 and −1, respectively, as long as the dissociation is fast compared to the parent molecule rotation. For the H atom channel (A) in the pyrrole photodissociation at \( \lambda = 243.1 \) nm, we found a value of \( \beta = -0.37 \pm 0.05 \) which implies that the excited optical transition is preferentially perpendicular with respect to the N–H dissociation coordinate. In contrast, the broad CM translational energy contribution (channel B) is practically isotropic (\( \beta \approx 0 \)).

It will be argued below (see discussion) that the H atoms with the sharply peaked \( P(E_T) \) distribution (channel A) arise from a rapid direct N–H bond breaking in the excited electronic state of pyrrole, while the slower H atoms (channel B) may derive from more complex unimolecular dissociation processes after internal relaxation to the \( S_0 \) ground electronic state.

3.2 H atoms from N-methylpyrrole

In order to shed more light onto the H atom production mechanism and the nature of the excited electronic state(s), H atom velocity map images were also taken from the photolysis of N-methylpyrrole under the same conditions as for pyrrole. In this molecule, the H atom at the N is replaced by a CH\(_3\) group so that H atoms can arise only from C–H bond breaking.

A measured H atom image from N-methylpyrrole at \( \lambda = 243.1 \) nm is reproduced in Fig. 3a, a slice through the corresponding 3D CM recoil distribution in Fig. 3b. At the same laser fluence and with similar other experimental conditions, the signal intensity from N-methylpyrrole was significantly weaker (by about a factor of two) than for pyrrole, even though the absorption of N-methylpyrrole in a room temperature UV spectrum is about an order of magnitude stronger.

The qualitative differences between the images for pyrrole and N-methylpyrrole are striking: The N-methylpyrrole image contains no sharp outer ring, i.e., there is no “fast” H atom channel (A). Instead, we observe only the broad inner feature, corresponding to the “slow” H atom channel (B) in the pyrrole case. The results are quantitatively shown by the CM translational energy distribution for the N-methylpyrrole photodissociation in Fig. 4, obtained from the 3D recoil distribution by integrating over the angular directions. It becomes obvious that the CM translational distribution for N-methylpyrrole is similar to that of channel (B) for pyrrole, indicating related H atom formation mechanism. In particular, the peak values of the CM translational energy distributions for N-methylpyrrole and channel (B) from pyrrole are observed at about the same energies. The distribution from N-methylpyrrole also extends to rather high energies without a sharp maximum kinetic energy release threshold (\( E_{T,max} \)) as seen for channel (A) from pyrrole.

These observations lend strong support to the conclusion that the “fast” H atoms (channel A) from pyrrole are indeed directly related to the breaking of the N–H bond.

4. Discussion

The experimentally measured kinetic energy distributions of the H atoms from the photodissociation of pyrrole shed interesting light onto the photochemistry of the molecule in connection especially with the recent theoretical work on the electronically excited state dynamics by Domecke and co-workers.

4.1 Electronic states of pyrrole and N–H bond breaking (channel A)

The consensus from the more recent theoretical investigations of pyrrole is that the optically allowed excited electronic states of the molecule in the UV spectral region have ππ* character. To the best of our knowledge, attempts to detect laser induced fluorescence of these states after nanosecond pulsed laser excitation have failed. The explanation by the theoretical calculations of Sobolewski and Domecke is that the lowest
electronically excited singlet state of pyrrole is the $\pi\sigma^*$ state.\textsuperscript{13,14} The $\pi\pi^*$ state is supposed to interact with the $\pi\sigma^*$ state through a conical intersection which may lead to a rapid radiation-less electronic transition. As mentioned above, the $\pi\sigma^*$ state is of mixed Rydberg/valence character. The $\sigma^*$ natural orbital is localized on the N–H bond and anti-bonding with respect to this bond. This localization and the anti-bonding character provides a strong driving force for a rapid detachment of the H atom in the $\pi\sigma^*$ state. Thus, the $\pi\sigma^*$ potential surface is essentially repulsive with respect to the stretching of the N–H bond.\textsuperscript{13,14}

The transition at $\lambda = 243.1$ nm excited in the present experiments has been assigned to the $\pi\pi^*$ state.\textsuperscript{2,3} The origin is predicted at about 248 nm.\textsuperscript{15} The $\pi\pi^*$ state cannot be reached at the wavelength used, but it is of interest because it may donate some of its oscillator strength to the $\pi\sigma^*$ state (see below).

Taking the pyrrole molecule in the $yz$ plane with $z$ as the $C_2\nu$ axis, the $\pi\sigma^*$ state has $1\text{A}_1\text{S}_0$ symmetry.\textsuperscript{15} On the other hand, the electronic ground state of the pyrrolyl radical which is formed by dissociation of the N–H bond has $3\text{A}_2\text{S}_0$ symmetry.\textsuperscript{27} Having $1\text{A}_1\text{S}_0$ symmetry, the ground electronic state of pyrrole ($S_0$) cannot correlate with H–pyrrolyl in $2\text{A}_2\text{S}_0$ symmetry in its lowest dissociation limit. The $1\text{A}_1\text{S}_0$ ground state of pyrrole thus correlates to a higher dissociation limit. However, the $1\text{A}_2\text{S}_1$ ($\pi\pi^*$) electronically excited state does correlate asymptotically with the ground state of pyrrolyl and H in the $1\text{S}_0$ ground state, which is the lowest dissociation limit. In a multi-dimensional picture, there arises a conical intersection between the $1\text{A}_2\text{S}_1$ ($\pi\pi^*$) and $1\text{A}_1\text{S}_0$ potential hypersurfaces which can promote an ultrafast relaxation from the $1\text{A}_2\text{S}_1$ ($\pi\pi^*$) to the ground surface.\textsuperscript{13} This transition is promoted by vibrational modes of $\text{A}_2\text{S}_0$ symmetry, which correspond to a screwing of the aromatic ring.

The theoretical calculations demonstrate that the electronic transition from $S_0$ to $1\text{A}_2\text{S}_1$ ($\pi\pi^*$) is electric dipole forbidden. On the other hand, the nearby $1\text{B}_2\text{S}_1$ ($\pi\pi^*$) state possesses a strong transition dipole direction in the molecular plane perpendicular to the N–H bond.\textsuperscript{13} The appearance of the $1\text{A}_1\text{S}_0$ ($\pi\pi^*$) state in the spectrum may thus be attributed to a vibronic coupling between the $1\text{A}_2\text{S}_1$ ($\pi\pi^*$) and $1\text{A}_1\text{S}_0$ potential hypersurfaces which can give rise to out-of-plane vibrations with $b_3\text{S}_0$ symmetry. With a predicted oscillator strength of about $17\%$ of that of the $1\text{B}_2\text{S}_1$ state, the $2\text{A}_1\text{S}_1$ ($\pi\pi^*$) state predicted at almost the same energy may also contribute to the intensity borrowing.

It is suggested by the present experimental results that the optical transition to the excited $1\text{A}_2\text{S}_1$ ($\pi\pi^*$) electronic state at $\lambda = 243.1$ nm results in a fast direct N–H bond breaking on the repulsive excited potential energy surface. Unimolecular dissociation of the N–H bond after internal conversion to the $S_0$ ground state cannot be the main channel in view of the reported experimental data for the thermal unimolecular reaction\textsuperscript{26–30} (see below) and in view of the observed high vibrational modes of $b_1\text{S}_0$ symmetry. On the contrary, it seems favored compared to the relaxation to the ground state by momentum conservation during the fast downhill motion on the $1\text{A}_2\text{S}_1$ ($\pi\pi^*$) hypersurface along the repulsive N–H dissociation coordinate. The calculations by Sobolewski and Domcke show that the above mentioned conical intersection between the $1\text{A}_2\text{S}_1$ ($\pi\pi^*$) and $1\text{A}_1\text{S}_0$ hypersurfaces occurs at a very large N–H bond distance compared to the equilibrium value so that an internal conversion to the $S_0$ ground state is not favored. Thus, the $1\text{A}_2\text{S}_1$ ($\pi\pi^*$) excited electronic state is the most probable source of the fast H atom fragments of the observed dissociation process in channel (A), forming the sharp outer ring in the photofragment images in Fig. 1.

The experimentally observed anisotropy factor of $b = -0.37$ is consistent with a vibronic coupling mechanism between the $1\text{A}_2\text{S}_1$ and $1\text{B}_2\text{S}_1$ states (transition dipole perpendicular to the NH bond). The N–H bond breaking has to occur on a time scale shorter than the pyrrole rotational period.

### 4.2 Pyrrole dissociation in channel (B) and $N$-methylpyrrole

The slow H atoms with the broad translational energy distribution (channel B) are concluded to arise from subsequent unimolecular fragmentation processes after internal conversion of the electronically excited pyrrole molecules to the $S_0$ ground electronic state. In this case, the thermal unimolecular reactions of pyrrole should give some hints.

The thermal isomerization and decomposition of pyrrole have been studied in shock tubes.\textsuperscript{28–29} The major products were found to be HCN, methylacetylene, and acetylene, besides some other species appearing in smaller quantities. Thus, the thermal decomposition leads to a destruction of the aromatic ring. According to the measured thermal activation energy\textsuperscript{27–29} and the available \textit{ab initio} calculations,\textsuperscript{27,30–32} N–H bond fission is energetically disfavored. Instead, H atoms have been predicted to arise from secondary reactions following the ring opening, including C–H and N–H bond breaking.\textsuperscript{32} The proposed mechanism for the thermal pyrolysis of pyrrole includes 117 elementary reactions, which exceeds the scope of this discussion. One plausible source for H atoms is the dissociation of an NCHCHCH=CH$_2$ biradical, which occurs as an intermediate ring opening product, to H + cyanalyl.\textsuperscript{32} This reaction and possible additional sources from other ring opening products\textsuperscript{32} are expected to lead to H atoms with a largely isotropic spatial and broad translational energy distribution, consistent with the experimental observations for channel (B). It has to be added at this point, however, that H atom formation from these reactions may be delayed compared to channel (A). Thus, the 24% branching ratio in the observation time window for H atom formation from the pyrrole after relaxation to the electronic ground state may be only a lower limit.

$N$-methylpyrrole lacks the N–H dissociation channel. The methyl group implies a weak perturbation of the electronic structure and symmetry compared to pyrrole. The electronic spectrum is slightly red-shifted, and the absorption at $\lambda = 243.1$ nm is substantially stronger. According to McDiarmid and co-workers, the 243.1 nm radiation excites the $N$-methylpyrrole molecule to its lowest excited electronic state which is thought to be the $1\text{A}_2\text{S}_1$ (3s) Rydberg state.\textsuperscript{17} The spectra observed in absorption, by (2 + 1) REMPI spectroscopy, and by laser induced fluorescence excitation (in contrast to pyrrole) show a structured band system around 240 nm involving $b_3\text{S}_0$ vibrational modes.\textsuperscript{17} As for pyrrole, the forbidden transition should be enabled with perpendicular character by vibronic coupling. The experimental translational energy distribution for $N$-methylpyrrole is similar to that of channel (B) of pyrrole which indicates that the H atoms may be formed by similar mechanisms. The differences between H atom images from pyrrole and $N$-methylpyrrole demonstrate the different valence/Rydberg characters of the lowest electronic states of the molecules\textsuperscript{13,14,17} and show that the fast H atom detachment by N–H bond breaking in the excited state of pyrrole is the fluorescence quenching channel. As for channel (B) from pyrrole (see above), the observed H atoms from $N$-methylpyrrole may arise via several pathways, including different unimolecular decomposition reactions of the vibrationally hot molecules formed by an internal conversion to the $S_0$ ground state.

### 4.3 N–H bond dissociation energy of pyrrole

Accepting the conclusion that the fast H atoms in the pyrrole photolysis (channel A) arise from the direct N–H dissociation, we may determine the value of the N–H bond dissociation energy $D_E$(N–H) from the observed maximal kinetic energy release ($E_{\text{kin}}^\text{max}$). The maximal fragment translational energy
is assumed to correspond to internally cold products. Under this condition, the value of \( D_b(N-H) \) follows from the energy balance

\[
E_{th}(243.1 \text{ nm}) = D_b(N-H) + E_{T}^{\text{max}} - E_{int},
\]

where \( E_{th} \) is the internal energy of the initial pyrrole molecules, which may be assumed to be negligible in the cold molecular beam expansion. The experimental result of \( E_{T}^{\text{max}} = 8750 \text{ cm}^{-1} \) leads to a value of

\[
D_b(N-H) = (32400 \pm 4000) \text{ cm}^{-1}.
\]

This result is slightly lower than a recent \( ab \text{ initio} \) value (33180 cm\(^{-1}\)).\(^{27}\) The error limits of our value stem from the velocity measurements for the light H atoms, the uncertainties induced by the long tail in the distribution in Fig. 2 from channel (B), and the uncertainties in the fitting of the \( P(E_t) \) distributions of the channels.

### 4.4 Comparison with previous work

The photodissociation of pyrrole in the first excited electronic state has previously been studied at \( \lambda = 248 \text{ nm} \) by PTS.\(^{19}\) The formation of H atoms and the corresponding pyrrolyl radicals were detected. Our velocity map imaging results are compared with the PTS results in Table 1. As seen, the value of \( E_{T}^{\text{peak}} \) for the "fast" H elimination channel is about 460 cm\(^{-1}\) larger in our measurements. Within the experimental uncertainties, this reflects the difference of the photon energies at 243 nm and 248 nm (\( \Delta E \approx \text{800 cm}^{-1} \)). The difference between the two values for the N–H bond energy is larger (1600 cm\(^{-1}\)), as the \( E_{T}^{\text{peak}} \) value determined by PTS was higher than that from the velocity map imaging results. This larger difference compared to the good agreement between the \( E_{T}^{\text{peak}} \) values is due to the substantial uncertainty in the determination of \( E_{T}^{\text{peak}} \) in the PTS work.

The yields of the different H atom formation channels should be compared only with considerable caution. The H atom yield from the excited state N–H dissociation in our measurement (76%) is significantly higher than that measured by PTS (47%), while the yield from the ground state after internal conversion is lower in our measurements (24%) than in the PTS work (42%). The PTS study also showed some evidence for a C–H bond breaking in the excited state (11%), but the signal-to-noise ratio was rather poor. The differences might be due to the different detection times after the photolysis. In our measurements, the H atoms were ionized in the same photolysis laser pulse (\( \Delta t = 10 \text{ ns} \)), while in the PTS experiments the fragments were ionized using electron bombardment at much longer time delays. However, as already noted above, the unimolecular decay reactions occurring after the electronic relaxation to \( S_0 \) should be much slower than the fast direct N–H dissociation in the excited state. This would lead to different apparent branching ratios. The advantage of the short detection time scale in our work is that the fast N–H dissociation in the excited state (channel \( A \)), which is the process of main interest, appears to be nicely isolated.

The spatial anisotropy found in the present study differs from that observed in the PTS work (\( \beta = +0.33 \)).\(^{15}\) It is pointed out that this PTS value stems from a polarization dependent measurement of the \( m/z = 66 \text{ mass} \) signal \((C_4H_4N^+), \) not from an \( H^+ \) measurement, so that different reaction channels may contribute. An explanation is nevertheless not obvious. One possibility would be that our \( \beta \) value may be affected by a "fly-out" effect, i.e., very fast H atoms moving in a direction perpendicular to the laser beam might escape detection. However, we did observe a positive \( \beta \) value (\( \beta = +1.30 \)) in a photofragment imaging study of H atoms from HCO (A\(^-\)A\(^2\)) where the kinetic energy release is considerably larger.\(^{13}\) Thus, the fly-out should be minimal. We also note that \( P(E_t) \) and \( \beta \) were obtained in the present work in the same measurement. The differences between the \( \beta \) parameters may also be a result of the different photolysis energies in the two studies. If the electronic transition is mediated by vibronic coupling, then the recoil direction of the H atoms may depend on the specific vibronic level reached at each wavelength.

### 5. Conclusions

The electronic excitation of pyrrole to its first excited state (1\(^1\)A\(^2\)) leads to a rapid direct N–H bond dissociation, giving rise to very "fast" H atoms with a strongly peaked, narrow kinetic energy distribution. This is in agreement with the postulate that the excited state has \( \pi\pi^* \) character rather than being a simple Rydberg state. From the maximal kinetic energy release, the N–H bond dissociation energy is

\[
D_b(N-H) = (32400 \pm 4000) \text{ cm}^{-1}.
\]

A predominantly perpendicular anisotropy (\( \beta = -0.37 \)) indicates that the forbidden transition to the 1\(^1\)A\(^2\) state gets some intensity from vibronic coupling to the nearby 1\(^1\)B\(^2\) (\( \pi\pi^* \)) state. Fast N–H bond dissociation of the electronically excited molecules is concluded to be the fluorescence quenching mechanism for pyrrole.

The translational energy distributions for the "slow" H atom channels for pyrrole and for N-methylpyrrole are similar and likely due to H atom formation processes in the ground electronic state after internal conversion from the excited state.

The reported experimental results for pyrrole may be of substantial interest regarding the ongoing discussions about the photochemistry of the nucleic acid bases. In the DNA bases, a low-lying threshold for fluorescence quenching exists which must be due to very fast non-radiative processes. We note the apparent lack of fluorescence from the pyrimidine bases uracil and thymine and the sudden disappearance of fluorescence from the purine bases adenine and guanine above a high energy cut-off.\(^{33,37}\) It has been suggested that a \( \pi\pi^* - \pi\pi^* \) coupling is responsible for the fluorescence quenching but this does not explain the postulated ultrashort lifetime of the \( \pi\pi^* \) state.\(^{38}\) Rapid N–H and/or O–H predissociation processes via the \( \pi\pi^* \) states as suggested by the present experimental results for pyrrole would provide an alternative explanation.

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| Table 1 Comparison between the H atom photofragment velocity mapping imaging results (this work) and the results from photofragment translational spectroscopy (ref. 18) |
|-----------------------------------|-----------------|-----------|
|                                | This work | PTS (ref. 18) |
| \( E_{th}/(\text{cm}^{-1}) \) | 41135 | 40323 |
| \( E_{T}^{\text{peak}}/(\text{cm}^{-1}) \) | 6410 | 5950 |
| \( D_b(N-H)/(\text{cm}^{-1}) \) | 32400 | 30800 |
| Branching ratios*              |          |            |
| Excited state N-H dissociation | 76%      | 47%       |
| Ground state C–H/N–H dissociation | 24% | 42%      |
| Excited state C–H dissociation | —        | 11%       |

\[ a \] Photon energy. \[ b \] Value of \( E_{T}^{\text{peak}} \) for the “fast” H atoms (channel A). \[ c \] Value for the N–H bond dissociation energy \( D_b(N-H) \) derived from \( E_{th} \) and the measured maximum kinetic energy release \( E_{T}^{\text{max}} \). \[ d \] Note that the value for the ground state dissociation channel refers to the detection time window used (see text).
a preprint of his work prior to publication and J. Gripp for measurements of the UV absorption spectra of pyrrole and N-methylpyrrole. J. Wei would like to thank the Alexander von Humboldt-Stiftung for a fellowship supporting his work in Kiel.

References
