Ultrafast Dissociation Dynamics of 2-Ethylpyrrole

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Abstract

To explore the effects of ring substitution on dissociation dynamics, the primary photochemistry of 2-ethylpyrrole has been explored using ultrafast ion imaging techniques. Photoexcitation to the $S_1$ state, a $\pi\sigma^*$ state, in the range of 238 to 265 nm results in cleavage of the N–H bond with an H-atom appearance lifetime of \textit{ca}. 70 fs. The insensitivity of this lifetime to photon energy, combined with a small kinetic isotope effect, suggests that tunneling does not play a major role in N–H bond cleavage. Total kinetic energy release spectra reveal modest vibrational excitation in the radical counter-fragment, increasing with photon energy. At wavelengths $\leq$ 248 nm a second, low kinetic energy H-atom loss mechanism becomes available with an appearance lifetime of approximately 1.5 ps and possibly due to the population of higher lying $^1\pi\pi^*$ states.
I. Introduction

The photochemistry and photophysics of biopolymers is of fundamental interest to chemists and biologists seeking to understand the photostability of life’s essential molecules. In an effort to understand the photochemistry of these complicated systems,\(^1\) the dynamics of the underlying subunits are investigated\(^2\) with increasing molecular complexity. This “bottom-up” approach allows molecular structure-function-property relationships to be systematically explored (see, for example, Refs. 5-7). Recently, the photochemistry of aromatic heterocycles (\textit{e.g.} phenol, pyrrole) that form the principal building blocks of diverse biological polymers has attracted the interest of spectroscopists.\(^2,8\) Of particular interest are the \(\sigma^*\leftarrow\pi\) electronic transitions present in these heterocycles.\(^4\) Photoexcitation to these states may result in several photoproducts (see, for example, Ref. 9) including the prompt loss of hydrogen atoms,\(^4\) a dissociation mechanism of potential relevance in biochemistry\(^10\) and crucial to understanding the ubiquitous presence of these photolabile biomolecules.

As the basic subunit of diverse biomolecules such as tryptophan or heme,\(^11-12\) the photodissociation of the aromatic heterocycle pyrrole (\(\text{c-C}_4\text{H}_5\text{N}\)) from the S\(_1\) \((\,\pi\sigma^*)\) state has been extensively studied with a majority of studies focusing on the rapid N–H bond fission.\(^13-16\) Utilizing a variety of time resolved techniques, several groups have investigated the ultrafast excited state dynamics \textit{via} time resolved ion yield (TR-IY) of the pyrrole cation,\(^17-19\) photoelectron spectroscopy,\(^20-21\) or H-atom elimination from pyrrole\(^17,22\) with some of the most recent work exploring the excited state dynamics of pyrrole dimers.\(^23-24\) The electronic structure and dissociation dynamics have also been extensively modeled theoretically with the most recent work focusing on the choice of initial conditions\(^25\) and the role of tunneling\(^26-28\) during H-atom loss. From these efforts, it is clear that the S\(_1\) state of pyrrole has a \(\sim0.2\) eV barrier along the N–H stretch coordinate, followed by a repulsive potential leading to the production of photoproducts (predominantly) in the electronic ground state. After photoexcitation to the S\(_1\) state below the barrier, the H-atom appearance lifetime is approximately 130 fs; the same excitation in deuterated pyrrole yields a kinetic isotope effect (KIE) of 11.\(^22\) When the photon energy places excited state population above the barrier, the H-atom
appearance lifetime decreases to ~50 fs with a KIE of 3. Both theory and experiment have concluded that this dramatic decrease in both H-atom appearance lifetime and KIE demonstrate the importance of tunneling dynamics during pyrrole photodissociation.22,26

In order to move towards larger biological systems, the effects of ring substitution on the photochemistry of the N–H bond in pyrrole must be explored. As demonstrated with phenol, another prototypical biological chromophore, ring substitution can have a substantial effect on a molecule’s primary photochemistry and photophysics (see, for example, Refs. 29-30), including the dynamics of H-atom loss. Recently, a combination of experimental and theoretical investigations by Ashfold and co-workers explored the effects of pyrrole-ring functionalization upon energy partitioning (i.e. internal vs. kinetic) during N–H bond fission in 2,5-dimethylpyrrole (2,5-DMP),31 2,4-dimethylpyrrole (2,4-DMP),32 and 2-ethylpyrrole (2-EP).32 Using high energy resolution H Rydberg atom photofragment translational spectroscopy (HRA-PTS), the group showed that the addition of alkyl groups to the ring lowered the N–H bond dissociation energy relative to bare pyrrole. Supported by calculations, the observed total kinetic energy release (TKER) spectra also revealed substituent-dependent vibrational excitation in the radical photoproducts due to Franck-Condon and molecular symmetry considerations.32

Continuing the work of Karsili et al.,32 another study used time resolved velocity map imaging (TR-VMI) to probe H-atom loss from 2,4-DMP.33 In contrast to the H-atom appearance lifetimes from pyrrole dissociation,22 the lifetime from 2,4-DMP dissociation (ca. 120 fs) was insensitive to photon energy. A modest KIE, also in contrast to pyrrole, revealed that tunneling apparently plays a minor role in H-atom loss from 2,4-DMP. These results support the interpretation that the one-dimensional N–H bond stretch coordinate is insufficient to describe H-atom loss from 2,4-DMP. Rather, the methyl groups open up reaction coordinates “around” the barrier resulting in an effectively barrierless dissociation. Recent work on the time resolved photoelectron spectroscopy of 2,5-DMP also concluded that photoexcited population likely does not encounter a barrier as it leaves the S1 vertical Franck-Condon (vFC) region.34
In the present work, we expand upon previous investigations\textsuperscript{32-33} by examining the time resolved dissociation dynamics of H-atom loss from the S\textsubscript{1} state of 2-ethylpyrrole (2-EP, see Fig. 1 for structure and UV absorption spectrum). Though 2-EP is a structural isomer of 2,4-DMP, we find a further shortening of the H-atom appearance lifetime that is again insensitive to photon energy. Our results will be discussed with regards to structural and possible excited state potential energy surface (PES) differences.

![UV Absorption Spectrum](image)

**FIG. 1:** Vapor phase ultraviolet absorption spectra of 2-EP (solid line) and 2,4-DMP (dashed line, Ref. 33). The lines indicate the wavelength range investigated in the present study. Inset: Top and side views of 2-EP in the S\textsubscript{0} equilibrium geometry (based on calculations in Ref. 32).

## II. Methods

Experiments were performed using a time resolved velocity map imaging (TR-VMI) apparatus previously described in detail.\textsuperscript{33,35-36} 2-EP (Fischer Scientific, 98\%) was filtered through neutral alumina to remove contaminants prior to use; the purity was confirmed by \textsuperscript{1}H NMR. A molecular beam of 2-EP was produced by flowing approximately 3 bar of He over a reservoir of sample (refreshed daily) heated to \~35°C. The resulting gas mixture was then expanded into vacuum by an Even-Lavie pulsed solenoid valve\textsuperscript{37} operating at 125 Hz. The beam passes through a 2 mm skimmer that serves to separate the source and interaction chambers. In the interaction chamber, the beam is intersected by two, temporally delayed femtosecond ultraviolet (UV) laser pulses (see below) that initiate photochemistry (the “pump”) and ionize (the “probe”) the resulting photoproducts. Ions are accelerated down a time-of-flight tube by a set of ion optics based upon the design of Eppink and Parker.\textsuperscript{38} The accelerated ions impact upon an imaging stack, consisting of pair of microchannel plates
coupled to a phosphor screen (Photek, VID-240), and the resulting images are recorded by a CCD camera (Basler, A-312f) interfaced with a computer. Temporal gating of the detector electronics allow for the exclusive detection of H⁺ (or D⁺) ions.

To produce the pump and probe light, 800 nm laser pulses of ~40 fs duration are produced by a commercial Ti:sapphire oscillator and regenerative amplifier system (Spectra-Physics Tsunami and Spitfire XP) operating at 1 kHz. This fundamental beam is split and used to pump two tunable UV optical parametric amplifiers (Light Conversion, TOPAS-C) producing the two UV pulses. The pump pulse was tuned over the wavelength range of \( \lambda_{\text{pump}} = 238 \) nm (42 020 cm\(^{-1}\), the shortest TOPAS wavelength) to 265 nm (37 740 cm\(^{-1}\), the approximate onset of \( S_1 \leftarrow S_0 \) absorption in 2-EP), indicated as lines in Fig. 1. The probe pulse is centered at \( \lambda_{\text{probe}} = 243 \) nm (41 150 cm\(^{-1}\)) to provide 2 + 1 resonance enhanced multiphoton ionization (REMPI) of H-atom photofragments via the two-photon allowed 2s \( \leftarrow \) 1s transition (82 259.158 cm\(^{-1}\)). The pump pulse is temporally delayed with respect to the probe pulse (\( \Delta t \)) by a hollow corner gold retroreflector mounted on a motorized delay stage, resulting in a maximum temporal delay of \( \Delta t = 1.2 \) ns. The laser beams are focused to intersect the molecular beam within the ion optics, with the electric fields of both laser pulses parallel to the plane of the imaging stack. The design and electric potentials of the ion optics and detector projects the three-dimensional photofragment velocity distribution onto the two-dimensional imaging detector, resulting in a velocity map image (VMI).\(^{38} \)

Time resolved ion yield (TR-IY) studies were also performed on select ions. Here, a digital oscilloscope (LeCroy LT372 Waverunner) monitors the current impacting the phosphor screen as a function of ion time-of-flight (TOF) since the interaction of the laser and molecular beams. For consistency with the imaging experiments, the electric fields of both lasers were parallel to the plane of the imaging stack. TR-IY transients were produced by integrating ion counts at specific \( m/z \) values—or, for the H⁺ transients, integrating regions of the TKER spectrum—as a function of \( \Delta t \). Characterization of the instrument response function (IRF) at temporal overlap of the pump and probe pulses (\( \Delta t = 0 \)) was performed via TR-IY of Xe⁺. The resulting transient, an example of which is
shown in the Supporting Information (SI), was fit to a Gaussian distribution with a full width at half maximum of ~100 fs, yielding a maximum temporal resolution of ca. 30 fs.

Deuterated 2-EP (\(d_1\)-EP) was produced by stirring freshly filtered 2-EP with \(d_4\)-methanol for approximately 48 hours under anhydrous, inert atmosphere. The solvent was then removed by fractional distillation under vacuum (0.5 mbar, 25°C – 45°C temperature gradient) while the product was collected over ice (ca. 4°C) and stored under inert atmosphere prior to use. H/D exchange was inferred by the reduction of \(^1\)H NMR signal at the hydride position, indicating the formation of a N–D bond. The TOF mass spectrum showed approximately equal amounts of the 2-EP and \(d_1\)-EP parent molecular ions.

One color, 243 nm “probe alone” images were subtracted from each pump-probe image; negligible \(H^+\) signal was produced by the pump laser. Experiments performed with an off-resonance probe (e.g. 245 nm) produced negligible \(H^+\) signal. Pump laser power studies were conducted at several wavelengths. In all cases, the recorded signal showed a linear dependence on pump laser power, consistent with one photon photoexcitation. To explore the signal dependence upon molecular beam characteristics, \(H^+\) transients were also taken at the shortest pump wavelengths using 4 bar of Ar to back the pulsed valve. In addition to the time resolved studies, the static UV absorption spectrum of vapor-phase 2-EP, shown in Fig. 1, was acquired using a Cary 60 UV/Vis Spectrophotometer by placing a drop of room temperature 2-EP into an empty quartz cuvette.

III. Results and Analysis

From the VMI, the original three-dimensional photofragment velocity distribution was reconstructed and integrated using the polar onion peeling (POP) method,\(^{39}\) resulting in the one-dimensional photofragment velocity and angular distributions. After calibrating to the known dissociation energetics of \(HBr\) at 200 nm,\(^{40}\) the velocity distribution may be transformed into a one-dimensional total kinetic energy release (TKER) spectrum. By conservation of energy, TKER spectra yield information about a two-body dissociation event through the following relationship:

\[
\text{TKER} + E_{\text{int}} = \frac{hc}{\lambda_{\text{pump}}} - D_0 + E_0 \quad (1)
\]
where TKER is the total kinetic energy of the system, \( E_{\text{int}} \) is the total internal energy of the photofragments (which, for H-atom loss, may be assumed to be exclusively in the molecular co-fragment), \( h\nu/\lambda_{\text{pump}} \) is the pump photon energy, \( D_0 \) is the asymptotic bond dissociation energy, and \( E_0 \) is the internal energy of the 2-EP molecule prior to photoexcitation. During POP deconvolution, the reconstructed photofragment angular distributions are fit to the known functional form and may be characterized by an anisotropy parameter \( \beta \). For a single photon initiated photodissociation event, the anisotropy parameter provides a measure of the alignment between the transition dipole moment and dissociation vector, taking the limiting values of \(-1\) or \(2\) corresponding to perpendicular or parallel transitions respectively; a value of \( \beta = 0 \) corresponds to an isotropic angular distribution.

### a) TKER Spectra

Example TKER spectra of H-atom loss from 2-EP are shown in Fig. 2. Additional spectra at other pump wavelengths may be found in the SI; details of all TKER spectra may be found in Table 1. In the limit of internally cold molecules (i.e. \( E_{\text{int}} = E_0 = 0 \)) the maximum available kinetic energy, \( \text{TKER}_{\text{max}} \), is calculated using a N–H bond dissociation energy of \( 31650 \text{ cm}^{-1} \) (Ref. 32) and is indicated on each spectrum as an arrow. The TKER spectra show a clear shift in peak intensity from \( \text{TKER}_{\text{max}} \) at the longest pump wavelength to \( \sim 2000 \text{ cm}^{-1} \) below \( \text{TKER}_{\text{max}} \) as the pump wavelength is decreased to \( 248 \text{ nm} \), resulting in a nearly constant \( 6000–7000 \text{ cm}^{-1} \) high KE feature. While the spectra in Fig. 2 lack vibrational structure, the peak positions and qualitative shapes are in excellent agreement with the previously reported HRA-PTS spectra.\(^32\) For \( \lambda_{\text{pump}} > 248 \text{ nm} \) (examples shown in Fig. 2 a and b), there is no apparent difference between TKER spectra acquired at \( \Delta t = 1 \text{ ps} \) or \( \geq 100 \text{ ps} \), suggesting that N–H bond fission is complete within the first picosecond. The measured photofragment angular distributions yield an anisotropy parameter of \(-0.6 \leq \beta \leq -0.4 \) for all pump wavelengths investigated, again in agreement with the HRA-PTS result of \( \beta \approx -0.6 \).\(^32\) The constant anisotropy parameter of 2-EP is in contrast with H-atom loss from 2,4-DMP, which showed an increasing value of \( \beta \) towards 0 as the pump photon energy was increased.\(^33\)

In addition to a high KE feature at \( \sim 7000 \text{ cm}^{-1} \), at \( \lambda_{\text{pump}} \lesssim 248 \text{ nm} \) a second TKER feature appears centered at approximately \( 4000 \text{ cm}^{-1} \) (see Fig. 2 c and d). Absent at a time delay of
Δt = 200 fs, this low KE feature remains unchanged for time delays Δt ≥ 10 ps. At Δt = 200 fs, the TKER peak position and anisotropy parameter of β ≈ −0.5 are consistent with the values determined at all other pump wavelengths, suggesting that the high KE feature is due to the same dissociation mechanism as occurs at longer pump wavelengths. For Δt ≥ 10 ps, the value of β at low KE appears to be slightly positive (as shown in Figs. 2 e and S2), resulting in an average β ≈ 0 across the entire TKER spectrum.

**FIG. 2:** Example TKER spectra for pump wavelengths a) 262 nm, b) 252 nm, c) 245 nm and d) 238 nm at several time delays (Δt, indicated in the figure). The arrows indicate TKER_{max} using the results of Karsili et al.\(^{32}\) e) Anisotropy parameter β as a function of TKER for the indicated time delays at 238 nm. Inset: Subtracted (left) and deconvoluted (right) VMI image recorded at 262 nm. The arrow indicates the electric field vector of the laser pulses.

**b) H-atom Appearance Lifetimes**

To measure the H-atom appearance lifetimes, TKER spectra were recorded at numerous time delays Δt. The entire TKER feature, approximately 3000–9000 cm\(^{-1}\) depending on the pump
wavelength, was then integrated as a function of time delay to produce H⁺ transients, as shown in the examples in Fig. 3 (additional H⁺ transients may be found in the SI). To extract the appearance lifetimes, these transient data were fit with a kinetic model assuming exponential rises in H⁺ signal in forward (Δt > 0) and reverse (Δt < 0) time, as well as an exponential decay near Δt = 0, convoluted with a Gaussian IRF; further descriptions and details of the kinetic model may be found in the SI and Refs. 17, 22, and 33. For all transients, the precise location of Δt = 0 (t₀, see SI for details) was determined using either the integrated, multiphoton H⁺ signal (TKER > 15,000 cm⁻¹) or the TR-IY of Xe⁺.

FIG. 3: Integrated TKER signal intensity as a function of time delay following photoexcitation at a) 262 nm and b) 238 nm. Data are shown as black points; excluded data (due to additional reverse dynamics) are shown in red. Fits to the data are shown as solid lines with “breaks” to account for the excluded data. At 262 nm, individual components and associated time constants of the fit are shown as blue (forward time), red (reverse time), and green (multiphoton dynamics near Δt = 0); see SI for further details. The time axis has been corrected to place Δt = 0 at t₀. The gray, dashed line marks the change from a linear to logarithmic time axis.
Results from the H⁺ transients are summarized in Table 1; reported errors are the standard error from the fit. For pump wavelengths longer than 245 nm, the entire TKER spectra show an average H-atom appearance lifetime of ca. 70 fs regardless of pump photon energy. For λ_{pump} ≤ 245 nm, integration of the high KE portion of the TKER spectra (∼7000–10 000 cm⁻¹) as a function of time delay results in similar H-atom appearance lifetimes. H⁺ transients from λ_{pump} ≤ 245 nm have an additional temporal component due to the low KE TKER feature. At these short wavelengths, fits to the total transients—with fixed short time behavior from the high KE fits—return an average low KE appearance lifetime of approximately 1.5 ps. While the TKER spectrum acquired at λ_{pump} = 248 nm and Δt > 1 ps shows a slight intensity increase at low KE (see Fig. S1), attempts to fit the 248 nm H⁺ transient including a second appearance lifetime were inconclusive. At 238 nm—shown in Fig. 3 b—additional “reverse” (i.e. probe initiated) dynamics appear in the H⁺ transient and, as such, data near Δt = 0 were excluded from the fit.

c) **Deuterated 2-EP Results**

![FIG. 4: a) TKER spectrum and b) D⁺ transient from the photodissociation of d₁-EP at λ_{pump} = 257 nm.](image)

For the transient, data are shown as open circles and the total kinetic fit is shown in black. Individual components and associated time constants of the fit are shown as blue (forward time) and red (reverse time). The gray, dashed line marks the change from a linear to logarithmic time axis. The time axis has not been corrected with t₀⁻.

Similar to the TKER spectra and H⁺ transients shown in Figs. 2 and 3, a TKER spectrum and D⁺ transient from the photodissociation of d₁-EP at λ_{pump} = 257 nm are shown in Fig. 4. The TKER spectrum is peaked at 5450 cm⁻¹, approximately 800 cm⁻¹ less than the peak TKER value in the corresponding H-atom spectrum (due to the differences in the zero-point energies of the vibrational
modes lost during the dissociation) and in agreement with the trends observed from the HRA-PTS study of $d_5$-pyrrole.\textsuperscript{42} Using the same kinetic model as above, the best fit to the D$^+$ transient data shown in Fig. 4 b yields a D-atom appearance lifetime of $140 \pm 20$ fs which, when compared to the average H-atom appearance lifetime, yields a KIE $= 2$. TKER spectra from $d_1$-EP at $\lambda_{\text{pump}} = 238$ nm are shown in the SI. Similar to the spectra shown in Fig. 2 d, a second, low KE feature appears at longer time delays.

d) TR-IY Transients

Example TR-IY transients for the 2-EP parent molecular ion ($m/z = 95$) at 252 and 238 nm are shown in the SI. These transients were fit with a kinetic model assuming exponential decays, in both forward and reverse time, convoluted with a Gaussian IRF function; further details of this kinetic model may also be found in the SI. At 252 nm, the 2-EP parent ion shows an increase in signal at $\Delta t = 0$, followed by an ultrafast decay with a $66 \pm 14$ fs lifetime, similar to the behavior of 2,5-DMP.\textsuperscript{34} At 238 nm, an additional decay lifetime is needed to produce a satisfactory fit, yielding $\tau_1 < 30$ fs (i.e. below the temporal resolution of the experiment) and $\tau_2 = 970 \pm 80$ fs.

Table 1: TKER spectral information and H-atom (or D-atom) appearance lifetimes for 2-EP.

<table>
<thead>
<tr>
<th>Pump Wavelength (nm)</th>
<th>TKER$_{\text{max}}$ (cm$^{-1}$)</th>
<th>Peak TKER (cm$^{-1}$)</th>
<th>Anisotropy Parameter</th>
<th>H-atom Appearance Lifetime (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>265</td>
<td>6090</td>
<td>6000</td>
<td>$-0.6$</td>
<td>$70 \pm 20$</td>
</tr>
<tr>
<td>262</td>
<td>6520</td>
<td>6600</td>
<td>$-0.5$</td>
<td>$55 \pm 13$</td>
</tr>
<tr>
<td>257</td>
<td>7260</td>
<td>6200</td>
<td>$-0.5$</td>
<td>$60 \pm 30$</td>
</tr>
<tr>
<td>252</td>
<td>8030</td>
<td>6800</td>
<td>$-0.5$</td>
<td>$70 \pm 20$</td>
</tr>
<tr>
<td>248</td>
<td>8670</td>
<td>6600</td>
<td>$-0.6$</td>
<td>$80 \pm 20$</td>
</tr>
<tr>
<td>245, high KE</td>
<td>9170</td>
<td>6600</td>
<td>$-0.5$</td>
<td>$68 \pm 10$</td>
</tr>
<tr>
<td>245, low KE</td>
<td>$-$\textsuperscript{a}</td>
<td>$\sim 4000$</td>
<td>$-$</td>
<td>$1600 \pm 600$</td>
</tr>
<tr>
<td>241, high KE</td>
<td>9844</td>
<td>6700</td>
<td>$-0.5$</td>
<td>$76 \pm 10$</td>
</tr>
<tr>
<td>241, low KE</td>
<td>$-$</td>
<td>$\sim 4000$</td>
<td>0.05</td>
<td>$1600 \pm 200$</td>
</tr>
<tr>
<td>238, high KE</td>
<td>10370</td>
<td>6900</td>
<td>$-0.4$</td>
<td>$70 \pm 20$</td>
</tr>
<tr>
<td>238, low KE</td>
<td>$-$</td>
<td>$\sim 4000$</td>
<td>0.07</td>
<td>$1520 \pm 120$</td>
</tr>
<tr>
<td>257 (D-atom)</td>
<td>$-$</td>
<td>5300</td>
<td>$-0.4$</td>
<td>$140 \pm 20$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} $-$, unknown quantity or low signal-to-noise ratio

IV. Discussion
For pump wavelengths longer than 245 nm, the TKER spectra, angular distributions, and spectral onset of the $S_1 \leftarrow S_0$ transition in 2-EP are all consistent with distributions and trends from the HRA-PTS study by Karsili et al.\textsuperscript{32} At the lowest photon energy studied, the TKER feature is peaked at the TKER$_{\text{max}}$ assuming N–H bond fission; higher pump photon energies merely result in increased vibrational excitation of the C$_6$H$_8$N radical co-fragment and a relatively constant peak TKER feature. The portion of the main TKER feature greater than TKER$_{\text{max}}$ is largely due to the broadband laser pulse (ca. 500 cm$^{-1}$ FWHM). While H-atom loss from the $\alpha$ carbon of the ethyl group is energetically feasible at 265 nm—assuming a similar dissociation energy to the corresponding C–H bond in ethyl benzene—\textsuperscript{43} the resulting TKER$_{\text{max}}$ would be $\sim$7900 cm$^{-1}$, well above the observed peak at 6000 cm$^{-1}$ in the experimental TKER spectrum. Finally, the appearance of similar D-atom results of the photodissociation of $d_1$-EP suggest that N–H cleavage is responsible for the observed H-atom signal. Given the above evidence, N–H bond fission to produce the 2-ethylpyrrol-1-yl radical (2-EPyl) is thus the most likely dissociation mechanism and the observed dynamics may be interpreted as such.

Fits to the H-atom transients recorded at $\lambda_{\text{pump}} > 245$ nm (and the high KE H-atoms at $\lambda_{\text{pump}} \leq 245$ nm) all return a H-atom appearance lifetime of approximately 70 fs, similar to pyrrole photodissociation above the $S_1$ barrier (50 fs),\textsuperscript{22} and consistent with ultrafast dissociation along a repulsive excited state surface. However, the measured lifetime is shorter than either 2,4-DMP\textsuperscript{33} (120 fs) or pyrrole photoexcited below the barrier (130 fs). In addition to the short appearance lifetime, the invariance of the lifetime with photon energy and the modest KIE $\approx 2$ suggest that the broadband laser pulse creates an excited state wavepacket favorably placed for rapid, barrier-free N–H bond fission, similar to the dissociation of 2,4-DMP.\textsuperscript{33} The agreement between the H-atom appearance lifetime and the 2-EP$^+$ transient decay lifetime at $\lambda_{\text{pump}} = 252$ nm suggests that, at longer wavelengths, N–H bond cleavage may be the primary decay pathway out of the vFC region. Two possible, and not exclusive, scenarios to explain this behavior become readily apparent. In the first scenario, the barrier along the N–H stretch coordinate is quite small and, given the $\sim$500 cm$^{-1}$ bandwidth of the pump laser, these experiments would thus be insensitive to said barrier. Alternatively, the reaction coordinate for H-atom loss – not exclusively the N–H stretch – may not have a significant barrier to dissociation.
Though details of the S\textsubscript{1} surface along the N–H stretch coordinate in 2-EP have not been published, the negligible barrier in the first scenario seems unlikely as the S\textsubscript{1} well depth in pyrrole \emph{increases} with alkyl substitution.\textsuperscript{22,26,32,34} Given that previous studies of 2,4-DMP\textsuperscript{33} and 2,5-DMP\textsuperscript{34} both concluded that tunneling plays a minor role in the S\textsubscript{1} state dynamics and dissociation, the latter scenario seems more likely to apply to 2-EP. Ultimately, dynamical calculations upon the 2-EP S\textsubscript{1} potential energy surface would be of significant interest to help determine the route to dissociation.

While it is tempting to attribute the shortening of the lifetime to the difference in the density of states between 2,4-DMP and 2-EP, this explanation does not address the difference in angular distribution behavior (for 2,4-DMP, $\beta$ approaches 0 with increasing photon energy\textsuperscript{33} while, for 2-EP, $\beta$ remains constant). Rather, the different behaviors of these isomers may be due to the reduction in symmetry, $C_\text{s}$ for 2,4-DMP \emph{vs.} $C_1$ for 2-EP, which will result in a greater number of dipole allowed electronic transitions in 2-EP (namely, the $\sigma^* \leftarrow \pi$ transition to the S\textsubscript{1} state). Qualitatively, the effects of molecular symmetry may be seen in Fig. 1, where the long wavelength absorption in 2-EP is approximately twice as intense (relative to the strong $\pi^* \leftarrow \pi$ transitions at shorter wavelengths) as the same feature in 2,4-DMP. In the case of the more symmetric 2,4-DMP, the increase in $\beta$ towards 0 was attributed to vibronic enhancement of the S\textsubscript{1} $\leftarrow$ S\textsubscript{0} transition with higher lying, allowed $\pi^* \leftarrow \pi$ transitions. While similar mixing may be occurring in 2-EP, the allowed transition to the S\textsubscript{1} state may reduce the relative importance of any “mixed” excitations and thus preserve the H-atom angular distribution at all wavelengths. However, further work (such as the H-atom appearance lifetime from the dissociation of 2,5-DMP) will be needed to explore the effects of molecular symmetry and ring substitution on pyrrole dissociation in greater detail.

Similar to the results from 2,4-DMP dissociation,\textsuperscript{33} an additional feature appears at low KE in the TKER spectra for $\lambda_{\text{pump}} \leq 248$ nm (exemplified in Fig. 2 c and d). As can be seen in Fig. 2 e and Fig. S2 in the SI, the low KE feature has a small positive value of $\beta$, in marked contrast with the high KE value of $\beta = -0.5$ and similar to the value of $\beta \approx 0$ from the 2,4-DMP low KE H-atom angular distribution.\textsuperscript{33} Given the differences in the KE and angular distributions, and that the H-atom appearance lifetime for this low KE feature is substantially longer (1.5 ps) than the high KE feature,
an additional dissociation mechanism must be invoked for this signal. To evaluate the possible
dissociation mechanisms, we must first consider the source of these low KE H-atoms. As previously
established for 2,4-DMP, assignment of this spectral feature to clusters in the molecular beam may be
eliminated based on several factors, including: the minimal cluster signal in the observed TOF
spectrum; the low concentration, < 0.5%, of 2-EP in the molecular beam; and the insensitivity of the
low KE feature to choice of backing gas (see Methods), stagnation pressure, or other molecular beam
parameters. Additionally, as mentioned in Sec. II, the use of a fresh 2-EP sample every day minimizes
the possibility that this feature is due to a contaminating species. Karsili et al. also report a modest
increase in the low KE portion of the HRA-PTS TKER spectrum with a 246 nm pump wavelength,
further supporting the assignment of this low KE feature to the dissociation of 2-EP. The similar low
KE feature seen in the TKER from d1-EP at λpump = 238 nm (see SI) strongly indicates that the low KE
H-atoms are due to cleavage of the hydride bond in 2-EP. As a final note, attribution of the near-zero
value of β to rotational motion of 2-EP prior to dissociation is unlikely given the short H-atom
appearance lifetime of 1.5 ps.

With the assignment of these low KE H-atoms to N–H bond fission, we can conclude that the
2-EPyl radical internal energy must be greater and this dissociation mechanism must either (i)
produce electronically excited 2-EPyl radical or (ii) involve coupling to a greater number of
vibrational modes than the ultrafast dissociation from the S1 state. The overlapping TKER features
make a firm assignment of TKERmax, and thus the 2-EPyl radical internal energy, impossible. It is thus
unclear whether these low KE H-atoms are due to decay along the S1 or another higher energy
surface, possibly similar to the S2 (1πσ*) surface of 2,4-DMP. Due to the similarity of 2,4-DMP and
2-EP, the 2-EPyl radical D1 state is expected to lie approximately 7000 cm−1 above the D0 state, which would limit TKERmax for this channel to ~3000 cm−1, slightly below the peak of the observed
low KE feature. Though it cannot be entirely eliminated, possibility (i) thus seems unlikely given the observed energetics.

With situation (ii), we must address why the population of additional vibrational modes has a
distinct spectral onset and is coincident with an elongation of the dissociation lifetime. The
The appearance of the low KE feature could be related to population of higher lying electronic excited states with an absorption onset of approximately 245 nm, in reasonable agreement with the static absorption spectrum shown in Fig. 1 and consistent with the excited state dynamics of 2,5-DMP.\(^{34}\) Assuming that the dissociation produces 2-EPyl in the ground electronic state (see discussion above), the population initially excited to \(S_n\) (where \(n\) denotes one or more excited states lying above \(S_1\)) must undergo internal conversion (IC) to the \(S_1\) state followed by dissociation to produce ground electronic state 2-EPyl. Indeed, the similarity of the low KE appearance lifetime (1.5 ps) with the second decay lifetime from the 2-EP parent ion transient (~1 ps) suggests that migration out of the vFC region—\(e.g., \text{via IC}\)—may be the rate limiting step to dissociation at these wavelengths. It is important to note that other, excited state de-excitation pathways may contribute to the difference between the two lifetimes (a detail that may also explain the shortening of the 2-EP\(^+\) sub-picosecond decay lifetime as \(\lambda_{\text{pump}}\) is decreased). As with pyrrole, the shift in TKER could be due to the involvement of high energy C–H vibrational and ring-stretching modes during IC,\(^{45}\) with vibrational excitation retained in the 2-EPyl radical co-fragment after dissociation. Recent theoretical work by Shalashilin and co-workers on the dynamics of H-atom loss from pyrrole\(^{27}\) found several trajectories, involving contributions from higher lying excited states, that eject low KE H-atoms. Furthermore, H-atoms from these trajectories were ejected perpendicular to the molecular plane and, assuming the same transition dipole moment as the \(S_1 \rightarrow S_0\) transition, would thus result in \(\beta \geq 0\). While relatively few trajectories showed this behavior, the calculated photoexcitation was essentially “at threshold,” meaning that these pathways may become more important at higher excitation energies. It thus seems reasonable to conclude that the low KE H-atoms with a small, positive anisotropy parameter observed herein are due to population of higher lying electronic excited states of 2-EP. If IC is involved in the low KE dissociation mechanism, we would expect the low KE appearance lifetime to decrease with increasing photon energy. Unfortunately, this trend cannot be evaluated due to the limited number of, and uncertainty in the, reported lifetimes (see Table 1).

To close the discussion of the low KE feature, we note that while fits to the high KE transients for \(\lambda_{\text{pump}} \leq 245\) nm remain acceptable (see Fig. S4 in the SI), the quality of the total H\(^+\)
transient fits decreases with decreasing pump wavelength. This decrease in fit quality, particularly near $\Delta t = 0$ (see Fig. S7 in the SI), may be due to a breakdown of the assumption of parallel dynamics. Indeed, if population in a higher lying excited state must first decay to another state (e.g. $S_1$) prior to dissociation, then a sequential kinetic model would be a more appropriate description of these low KE H-atoms. However, a more rigorous analysis of this low KE feature is beyond the scope of the present investigation of photodissociation from the $S_1$ state of 2-EP.

Finally, as discussed in the SI, the TKER spectrum derived from the $m/z = 80$ photofragment is likely due to cleavage of the C–C bond within the ethyl group, producing a CH$_3$ radical and a benzyl radical-like C$_5$H$_6$N species (2-methylene pyrrole radical). A low average KE, along with an appearance lifetime of $\gg 1.2$ ns for the $m/z = 80$ fragment, suggests that this channel is due to dissociation on the ground electronic state after vibrational energy randomization. As a rise in the $m/z = 80$ signal is only observed at 238 nm, CH$_3$ loss is either a minor decay channel or is only accessible with higher photon energies.

V. Conclusions

We have shown that in the wavelength range of 238 to 265 nm, photoexcitation to the $S_1$ state of 2-ethylpyrrole results in ultrafast H-atom loss. TKER spectra show increasing 2-EPyl vibrational excitation with increasing pump photon energy, consistent with the previous HRA-PTS study on this system. The H$^+$ transients reveal an H-atom appearance lifetime of $\sim 70$ fs, consistent with prompt dissociation along a repulsive surface. The insensitivity of this appearance lifetime to pump photon energy and the modest KIE suggest that the H-atom loss coordinate is effectively barrierless. At the shortest wavelengths studied, a second, low KE feature appears in the TKER spectra with a lifetime of 1.5 ps; tentatively assigned to H-atom loss following population of higher lying singlet states. At the shortest wavelength studied, evidence for ground state CH$_3$ loss was also found.

Along with the previous studies of 2-EP, 2,4-DMP, and 2,5-DMP, the results from the present investigation further supports the following trend: the addition of alkyl groups to the aromatic ring provides a route “around” the excited state barrier along the N–H stretch coordinate, resulting in a net decrease in H-atom appearance lifetime. The symmetry of the molecule may play an
important role in the dissociation and additional insights may be gained by exploring the effects of different substituents on the ring. Thus, while subtle changes in the geometry of $\text{C}_6\text{H}_9\text{N}$ have an impact on the excited state dynamics (e.g. the reduction in H-atom appearance lifetime), the global photodynamics of these molecules apparently remains relatively constant as molecular complexity is increased. Importantly, this work reinforces the importance of systematic exploration of the structure-property-function triad; mapping and understanding these changes is essential for a complete “bottom-up” elucidation of the photochemistry of pyrrole-based biomolecules.

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Supporting Information

Additional TKER spectra, VMI recorded at 238 nm, details of the IRF and kinetic models, additional H$^+$ transients, $d_1$-EP TKER spectra at 238 nm, 2-EP$^+$ TR-IY transients, a detailed view of the 238 nm H$^+$ transients, and the $m/z = 80$ TR-IY transient and TKER spectrum.

References


TOC Graphic: