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Caveats in the interpretation of time-resolved photoionization measurements: A photoelectron imaging study of pyrrole

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Abstract

We report time-resolved photoelectron imaging studies of gas-phase pyrrole over the 267-240 nm excitation region, recorded in conjunction with a 300 nm probe. Of specific interest is the lowest-lying (3s/πσ*) state, which exhibits very weak oscillator strength but is thought to be excited directly at wavelengths ≤254 nm. We conclude, however, that the only significant contribution to our photoelectron data at all wavelengths investigated is from non-resonant ionization. Our findings do not rule out (3s/πσ*) state excitation (as appears to be confirmed by supporting time-resolved ion-yield measurements), but do potentially highlight important caveats regarding the use and interpretation of photoreactant ionization measurements to interrogate dynamical processes in systems exhibiting significant topological differences between the potential energy surfaces of the neutral and cation states.

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1. INTRODUCTION

The excited state gas-phase photophysics of small heteroaromatic molecules has attracted considerable experimental and theoretical attention in recent years.\textsuperscript{1, 2} Much of this work has been motivated by the fact that such systems provide useful starting models for the chromophore sites found in a wide range of larger biological systems, with salient examples including the DNA bases and the melanin pigments. Of particular interest are the rapid and highly-efficient non-radiative relaxation pathways these systems exhibit, which have been implicated in playing a critical role in their inherent photostability following irradiation with ultraviolet (UV) light. Building on ideas first proposed by Domcke and co-workers\textsuperscript{3, 4} a common theme in many investigations is the role played by low-lying singlet states of mixed Rydberg/valence composition. Such states typically possess predominantly 3s orbital character in the vertical Franck-Condon region and become increasingly $\sigma^*$ valence in nature as O-H or N-H bonds are extended. Although often only weakly excited through direct UV absorption, these mixed Rydberg/valence states potentially act as a vital “dynamical bridge” for non-adiabatic transfer of population from an initially prepared optically bright state (often of $\pi\pi^*$ character) back to the $S_0$ ground state, where (in biological systems) excess vibrational energy may then be harmlessly dissipated into the surroundings. Mixed Rydberg/valence states are, however, also potentially dissociative along O-H or N-H stretching coordinates and studying this specific pathway – particularly in gas-phase experiments – has proved to be a useful way of determining important dynamical information.

One example of a model system in which the gas-phase UV relaxation dynamics have been extensively studied is pyrrole - a subunit of the porphyrin macrocycle that occurs frequently in Nature. The structure of pyrrole is shown schematically in Fig. 1 along with its UV absorption spectrum. Central to the work outlined here is the very weak feature extending across the 250-220 nm region. This arises as a consequence of direct absorption to a state of...
mixed Rydberg/valence character that may be labelled \( S_1(3s/\pi\sigma^*) \), with the much stronger feature appearing below 220 nm being due to excitation to the higher-lying \( S_2(\pi\pi^*) \) state. Building on initial photofragment translational spectroscopy studies by Blank et al., Ashfold and co-workers conducted a detailed wavelength-dependent investigation of H atom photofragment kinetic energy release in pyrrole over the 254-193.3 nm region using the Rydberg tagging time-of-flight technique. This work reported an onset threshold of 254 nm for the production of high kinetic energy H atom photoproducts resulting from direct (although weak) excitation to the \( S_1(3s/\pi\sigma^*) \) state. Low kinetic energy H atoms were also observed, attributable to statistical dissociation of the vibrationally hot ground state following internal conversion from \( S_1(3s/\pi\sigma^*) \) at highly extended N-H bond distances. At increased excitation energies, decay of population within the \( S_2(\pi\pi^*) \) state was also inferred to proceed via the same two fragmentation pathways after initial internal conversion to \( S_1(3s/\pi\sigma^*) \).

Similar conclusions were also reported in several studies employing \((2+1)\) resonance enhanced multiphoton ionization of H atoms in conjunction with velocity-map imaging. One of these, a femtosecond pump-probe study by Stavros and co-workers, also revealed significant differences in exponential time constants describing the appearance of H atom photofragments originating from \( S_1(3s/\pi\sigma^*) \) state dissociation following 250 nm \((126 \pm 28 \text{ fs})\) and 238 nm \((46 \pm 22 \text{ fs})\) excitation. Assisted by additional experiments on deuterated pyrrole-\( d_1 \), this was ascribed to tunnelling effects at 250 nm resulting from a small barrier along the \( S_1(3s/\pi\sigma^*) \) N-H stretching coordinate – the presence of which has also been confirmed by several theoretical investigations, as summarized in the recent work of Sapunar et al.. The 250 nm data were in partial agreement with earlier pump-probe time-of-flight measurements reported by Radloff and co-workers, who observed a similar H atom elimination timescale of 110 ± 80 fs but also a second, longer process described by a time constant of 1.1 ± 0.5 ps.
This was suggested to be a consequence of N–H dissociation from the vibrationally hot $S_0$ state following $S_1(3s/\pi\sigma^*)$ internal conversion.

The experiments described above all reveal that, although very weak, direct absorption to (and subsequent dissociation from) the $S_1(3s/\pi\sigma^*)$ state of pyrrole is clearly and unambiguously observable via the detection of photoproducts. In contrast, however, complimentary studies monitoring the temporal evolution of photoreactants (i.e. population dynamics within the initially excited pyrrole system) have proved to be much less conclusive in this regard. Time-resolved ion-yield and photoelectron imaging measurements by Longarte and co-workers ultimately concluded that no significant evidence of resonant ionization via the $S_1(3s/\pi\sigma^*)$ state was observed across the 260-225 nm region.\textsuperscript{13, 14} In contrast, a more recent photoelectron study conducted by Stolow and co-workers using a magnetic bottle spectrometer\textsuperscript{15} reported $S_1(3s/\pi\sigma^*)$ lifetimes of $12 \pm 10$ fs and $19 \pm 10$ fs following excitation at 242 nm and 236 nm, respectively (values somewhat shorter than the corresponding H atom appearance times quoted earlier). These authors did, however, suggest that their data gave no unequivocal evidence for the direct excitation of the $S_1(3s/\pi\sigma^*)$ state and advised that detailed studies of the photoelectron angular distribution associated with the ionization process may provide further, more definitive insight. Finally, a very recent photoelectron imaging study by Fielding and co-workers, focussing primarily on the pyrrole dimer, has also reported $S_1(3s/\pi\sigma^*)$ state lifetimes for the monomer species of 39, 49 and 22 fs (all with $\pm 10$ fs uncertainty) following excitation at 249.5, 245 and 240 nm, respectively.\textsuperscript{16} As with the work reported by Stolow and co-workers, these values do not appear to be fully reconciled with the corresponding H atom appearance times.

Motivated by the discrepancies outlined above, as well as our more general and ongoing desire to investigate the role of mixed Rydberg/valence states in the non-adiabatic
relaxation dynamics of model biological chromophores, we report a time-resolved photoelectron imaging (TRPEI) study of gas-phase pyrrole utilizing pump wavelengths of 267, 258, 250 and 240 nm and a 300 nm probe. Our primary conclusion – in agreement with that of Longarte and co-workers – is that no strong indication of dynamical features due to the population of the $S_1(3s/\pi\sigma^*)$ state are observed at all excitation wavelengths investigated. This finding is clearly suggested initially by the overall similarity of all data sets obtained (both above and below the aforementioned 254 nm threshold for the production of H atom photoproducts), but is further reinforced when one begins to consider more subtle aspects of the data – especially when comparisons are drawn with similar molecular systems where ionization signatures from states of mixed Rydberg/valence character have been conclusively identified. This is particularly apparent for the photoelectron angular distributions, which although reported previously for pyrrole in the 260-225 nm excitation region, have not until now been analysed in detail. More generally, our findings highlight several important caveats when interpreting data from time-resolved experiments employing ionization of photoreactants to interrogate excited state dynamical processes. These are particularly relevant to situations where the excited states exhibit weak absorption cross-sections and lifetimes comparable to the limiting temporal experimental resolution.

II. EXPERIMENTAL

A comprehensive description of our experimental TRPEI setup has been reported previously. Briefly, pump and probe laser pulses were derived from the fundamental 800 nm output of a 1 kHz regeneratively amplified Ti:Sapphire laser system (Spectra-Physics, Spitfire Pro/Empower) seeded by a Ti:Sapphire oscillator (Spectra Physics, Tsunami/Millennia Pro). The pump was provided by the third harmonic of this output (267 nm), or (for 258, 250 and 240 nm) generated in a two-stage non-linear mixing scheme using the signal output of an optical parametric amplifier (Spectra Physics OPA-800C) in conjunction with a separate
portion of the 800 nm fundamental. The probe (300 nm) was obtained by twice frequency doubling the signal output from a second OPA (Light Conversion, TOPAS Prime-U). Thin β-barium borate crystals were used as the non-linear medium. A PC-controlled linear translation stage enabled precise control of the temporal delay between the pump (~0.5 μJ/pulse) and probe (~2.0 μJ/pulse), which were then combined using a thin dichroic mirror and focussed into the spectrometer through a 2.0 mm thick CaF<sub>2</sub> window using a concave UV-enhanced aluminium mirror (f = 50 cm).

A helium carrier (0.25 bar) introduced pyrrole (Sigma-Aldrich, 99%) into the source chamber of the photoelectron spectrometer via an external sample reservoir and a 1 kHz pulsed valve (Ø=150 μm). The molecular beam produced then passed into the main interaction chamber through a skimmer (Ø=1.0 mm) and perpendicularly intersected the (co-propagating) pump and probe laser pulses in a region of space between the repeller and extractor of a magnetically shielded electrostatic lens set-up optimised for velocity-map imaging. Two-dimensional image data of the photoelectrons produced from the resulting ionization of pyrrole were then recorded using a 40 mm dual micro-channel plate/P47 phosphor screen in conjunction with a CCD camera (640 × 480 pixels), positioned at the end of a flight tube. Ion time-of-flight data, recorded before commencing photoelectron acquisition, confirmed no significant cluster formation in the molecular beam. TRPEI data collection repeatedly sampled pump-probe delays of -400 fs to +400 fs in 25 fs steps and also included measurement of time-invariant pump-alone and probe-alone signals at each delay position (for subsequent background subtraction). Pump-probe cross-correlations of 130 ± 10 fs (267-250 nm) and 150 ± 10 fs (240 nm) were obtained directly inside the spectrometer from non-resonant, two-colour (1 + 1′) multiphoton ionization of butadiene following systematic adjustment of single-pass prism compressors incorporated into the pump
and probe beam paths. Energy calibration data was provided by three-photon, non-resonant 267 nm ionization of xenon.

III. RESULTS

Our experimental results for the case of 267 nm excitation in pyrrole are summarized in Fig. 2. Essentially identical results were also obtained for the other three pump wavelengths studied. The upper left panel shows a representative photoelectron image (obtained at zero pump-probe delay) that has been subjected to a rapid matrix inversion, as described in detail elsewhere.\textsuperscript{17} Of particular note are the clearly visible intensity maxima present in the outer rings at angles close to 45° (and $\pi/2$ multiples thereof) – a key feature also seen in the TRPEI data of Longarte and co-workers\textsuperscript{14} that we will return to consider in more detail later. From a series of such matrix-inverted images recorded over a range of pump-probe delays, time-dependent photoelectron spectra may be obtained, as presented in the lower right panel of Fig. 2. The observed temporal signatures are extremely rapid, being effectively described by a Gaussian shape - as is more clearly illustrated by the integrated time trace shown in the lower left panel. Finally, the upper right panel of Fig. 2 shows the photoelectron spectrum obtained upon integrating over the time window around zero pump-probe delay. Two strong peaks are seen in the binding energy region between 8.2-8.4 eV with a small shoulder on one of these extending to slightly higher binding energies. The position of the peak centred at 8.22-8.24 eV is in good agreement with the previously reported D$_0$ ($\pi^1$) ionization energy of 8.21 eV.\textsuperscript{19, 20} The weak feature at ~8.7 eV may be attributed to D$_1$ ($\pi^1$) ionization.\textsuperscript{15} At all excitation wavelengths studied, the photoelectron spectra are extremely similar (as illustrated in Fig. 3), and are also in good accord with those obtained in similar time-resolved measurements that have been reported previously.\textsuperscript{14-16} As will be expanded upon shortly, it is also interesting to note the striking similarity between these spectra and the low-energy region of the He (I) ground state photoelectron spectrum.\textsuperscript{21-24}
In addition to the energy-resolved data that may be obtained from our TRPEI measurements (described above), the angular anisotropy information present in the images may be analysed in detail using the appropriate expression for $(1 + 1')$ ionization with parallel linear polarizations: \(^{25,26}\)

\[
I(E, \Delta t, \theta) = \frac{S(E, \Delta t)}{4\pi} \left[1 + \beta_2(E, \Delta t) P_2(\cos \theta) + \beta_4(E, \Delta t) P_4(\cos \theta)\right] \tag{1}
\]

Here $S(E, \Delta t)$ is the time-dependent photoelectron energy distribution acquired at each pump-probe delay time $\Delta t$, the $P_n(\cos \theta)$ terms are the $n^{th}$-order Legendre polynomials and $\beta_2$ and $\beta_4$ are the well-known anisotropy parameters. The angle $\theta = 180^\circ$ is defined by a vertical line running fully through the image shown in Fig. 2 via the centre point. Fits to our image data using Eq. 1 reveal that (within statistical uncertainty) both $\beta_2$ and $\beta_4$ are essentially invariant in both the time and energy domains at all pump wavelengths investigated. This is illustrated for the case of 267 nm excitation by the overlay plots in the upper right and lower left panels of Fig. 2. On this basis, we may therefore average the angular data over a wide range of time and energy bins to obtain good statistics within the polar photoelectron angular distribution (PAD) plots presented in Fig. 4. At all four excitation wavelengths investigated the PADs are very similar, peaking at $45^\circ$ (and $\pi/2$ multiples thereof). This similarity is also reflected in the $\beta_2$ and $\beta_4$ parameters obtained from a fit to this data using a time- and energy-integrated form of Eq. 1. In all cases the $\beta_4$ values are relatively large and negative, with values spanning -0.33 to -0.41. At 240 nm, the $\beta_2$ value (-0.09) deviates somewhat from those seen at 267-250 nm (0.41-0.25), although we may attribute this to an artefact introduced by imperfect background subtraction of the (much greater) scattered light signal incident on the MCP detector in this instance. This is an unavoidable issue as the excitation wavelength is shortened since the quantum efficiency for scatter-induced electron production at the MCP
increases by approximately an order of magnitude on moving from 250 nm to 240 nm and, additionally, the cross-section for Rayleigh scattering from optical elements such as the spectrometer windows scales as $1/\lambda^4$. This scattered light signal is not uniformly distributed over the imaging detector, being much more prominent along the direction of laser propagation (which corresponds to the horizontal direction in the image data shown in Fig. 2). As such, this specific directionality will act to reduce the overall $\beta_2$ value obtained, as is observed. Overall, therefore, the TRPEI data obtained at all excitation wavelengths are extremely similar in terms of (i) the photoelectron spectra, (ii) the temporal evolution of the pump-probe signals (being Gaussian in all instances) and (iii) the shape of the PADs. The significance of these findings will be explored further in the following section.

**IV. DISCUSSION**

Although the exact position of the $S_1(3s/\pi\sigma^*)$ state origin in pyrrole has not been definitively determined, at 267 nm we are exciting ~0.25 eV below the 254 nm onset threshold for direct H-atom dissociation established by Ashfold and co-workers. Any small barrier present along the N-H stretching coordinate within the $S_1(3s/\pi\sigma^*)$ state (which, neglecting any tunnelling effects, could potentially prevent H-atom elimination) is also predicted to be lower than this ~0.25 eV energy gap. We may therefore be confident that our data obtained using a 267 nm pump (in conjunction with a 300 nm probe) should display spectral signatures arising entirely from non-resonant (1+1') ionization. This is clearly reflected by (i) the fact that the transient pump-probe signals obtained exhibit zero lifetime (i.e. they are of Gaussian form with a width equivalent to the independently determined instrument response function – see Fig. 2); and (ii) the photoelectron spectrum (again, see Fig. 2) exhibits a very strong resemblance to the ground state He (I) spectrum reported previously. Given these observations, the similarity of the 267 nm excitation data with
that obtained at 258, 250 and 240 nm (as illustrated, for example, in the photoelectron spectra presented in Fig. 3) then strongly suggests that non-resonant ionization is also the main contribution in all of these cases as well. This is further reinforced by the PAD plots shown in Fig. 4, which are, once again, extremely similar at all excitation wavelengths investigated. Turning the analysis of the ionization process around, moreover, the evidence for a dominant non-resonant contribution becomes even more compelling when one begins to consider what spectral signatures might reasonably expected if resonant (1+1) ionization via the S₁(3s/πσ*) state was a significant factor. This is considered in more detail below.

A. Observed Lifetime

As highlighted in the Introduction, H atom photoproduct appearance times of 110-126 fs and 46 fs have been previously attributed to direct dissociation on the S₁(3s/πσ*) potential energy surface following excitation at 250 nm and 238 nm, respectively.¹⁰,¹² In principle, this should also be reflected in our time-resolved transient data obtained at comparable excitation wavelengths, as the S₁(3s/πσ*) state should therefore exhibit some inherent (non-zero) lifetime. Although very short, such lifetimes should be resolvable in our TRPEI data (especially at 250 nm) given our instrument response function of 130-150 fs.²⁸ One caveat here, however, is the effective “detection window” along the dissociative S₁(3s/πσ*) reaction coordinate. As illustrated in the work of Longarte and co-workers,¹³ the potential energy surfaces of the S₁(3s/πσ*) state and the D₀ (π⁻¹) state of the pyrrole cation exhibit markedly different topology at extended N-H bond distances, with the former exhibiting a very shallow gradient while the latter remains strongly bound. As such, the 300 nm probe used in our current experiments may provide insufficient energy to efficiently project the vibrational wavepacket evolving on the S₁(3s/πσ*) surface into the continuum at large N-H distances. This Franck-Condon factor effect potentially serves to artificially shorten the excited state
lifetimes observed in a photoreactant measurement such as TRPEI, possibly to the point where the transient signal appears effectively Gaussian. We will return to consider this issue again, but we note that our 250 nm excitation data – obtained with a single-photon 300 nm (4.13 eV) probe – yields the same (zero) lifetime as reported by Longarte and co-workers using either a 3 × 800 nm or 1 × 267 nm (4.65 eV) ionization scheme at very similar excitation wavelengths.13, 14 We do, however, also highlight that Fielding and co-workers do quote a very short, but non-zero transient lifetime of 39 ± 10 fs for their 249.5/300nm pump/probe TRPEI data.16 Based on the previously reported $D_0 (\pi^{-1})$ ionization energy of 8.21 eV,19, 20 our present measurement projects up to 0.88 eV into the ionization continuum, whereas the Longarte studies projected considerably deeper – up to 1.30 eV. Given this difference of 0.42 eV, and the aforementioned 110-126 fs H atom appearance lifetime at 250 nm, it is perhaps surprising that no difference in observable lifetime is seen in the two photoreactant ionization measurements – even if neither is able to fully sample the necessary detection window to yield a value equivalent to the H atom photoproduct result. This therefore suggests that non-resonant ionization is the dominant contribution to the overall TRPEI signals we observe.

A second factor to consider briefly, that may also contribute to artificially shortening the excited state lifetimes observed in photoreactant ionization measurements, is that of evolution of the electronic ionization cross-section, arising as a consequence of changes in nuclear geometry. Within a simple adiabatic picture, this may be viewed as acting in combination with the Franck-Condon effect described above and is potentially very significant for states of mixed Rydberg/valence character. Our previous calculations on aniline,29 indole30 and piperidine31 have demonstrated that the change in 3s/\(\pi\sigma^*\) (or 3s/n\(\sigma^*\)) electronic character is extremely rapid and dramatic as N-H bonds are extended. Moreover,
although perhaps more speculatively, we have also argued that this evolution should serve to reduce the electronic ionization cross-section at increased N-H separation.  

B. Photoelectron Spectra

Previous TRPEI studies of several aromatic and aliphatic amine species have revealed distinct spectral signatures are associated with the ionization of mixed (3s) Rydberg/valence states. Specifically, these take the form of a single, narrow photoelectron peak superimposed on top of a weak and much broader background. The narrow feature arises as a consequence of ionization within the vertical Franck-Condon region, where the 3s Rydberg component of the mixed character state is dominant, leading to a strong propensity for diagonal ionization (i.e. those for which $\Delta \nu = 0$, where $\nu$ is a generalised, non-mode-specific quantum number). The broader background is attributed to ionization at more extended N-H bond distances, where increased $\sigma^*$ valence character results in a lifting of the diagonal ionization propensity. As noted earlier, the photoelectron spectra of pyrrole seen at all excitation wavelengths investigated show the same overall zero-lifetime behaviour. It is possible, however, that weak spectral features reflecting longer-time dynamics associated with the $S_1(3s/\pi\sigma^*)$ state may, in some instances, be obscured by the energy-integrated analysis considered up to now. The differential nature of the TRPEI approach may therefore be exploited to see if any specific region of the photoelectron spectrum contains more subtle ionization signatures that may be attributed directly to $S_1(3s/\pi\sigma^*)$ excitation. In order to investigate this further, a Levenberg-Marquardt global fitting routine was used to model the time-dependence of the 2D photoelectron data $S(E, \Delta t)$ obtained following 250 nm excitation using two exponentially decaying functions. Each function was convoluted with the experimentally determined Gaussian cross-correlation $g(\Delta t)$ and set to originate from zero pump-probe delay, $\Delta t = 0$. 


This approach yields decay associated spectra (DAS) for each individual exponential function which plot the relative amplitudes $A_i$ returned by the fit vs photoelectron kinetic energy $E$. The fit was performed twice, firstly with both exponential time constants $\tau_1$ and $\tau_2$ allowed to float freely and then with $\tau_2$ constrained to a fixed value of 120 fs (close to the 250 nm H atom appearance times reported previously$^{10, 12}$). The outcomes of both procedures are shown in Fig. 5. In each case, the fit returns a $\tau_1$ lifetime that is effectively zero (i.e. a Gaussian response) with a DAS that is essentially identical to the photoelectron spectra seen in Fig. 3. This is not an unsurprising result given the overall temporal nature of our data. The key aim here, however, is to determine if the additional $\tau_2$ DAS yields weak features in any spectral region that might reasonably be expected for resonant ionization via a state of mixed Rydberg/valence character (i.e. a single, narrow peak superimposed on top of a weak and much broader background – as discussed earlier). Such features may potentially be obscured by much larger non-resonant signals in any energy-integrated analysis of the transient data. It is clear from Fig. 5, however, that in both the free and 120 fs constrained fits there is no apparent evidence of this signature, with the very small and unstructured amplitude seen in the $\tau_2$ DAS simply smoothing out any minor statistical noise present in the raw data. Repeating this two-exponential fit analysis for the 240 nm data (with $\tau_2$ now either free or fixed to 40 fs) produced very similar results. Once again, this finding appears to suggest that no evidence of resonant ionization from the $S_1(3s/\pi\sigma^*)$ state of pyrrole is apparent in our data. We note, however, that any ionization signature from the $S_1(3s/\pi\sigma^*)$ state may potentially still be unresolvable in this more differential analysis if dramatic reductions in the effective observable lifetime are present due to a limited detection window along the N-H stretching
coordinate (discussed in Section IV. A) - i.e. the characteristic Rydberg ionization signature anticipated is still “hidden” in the \( \tau_1 \) (Gaussian) DAS which also contains sizeable contributions from competing non-resonant processes.

**C. Photoelectron Angular Distributions**

As highlighted in recent examples of our previous TRPEI work on various systems exhibiting excited states of mixed (3s) Rydberg/valeence character, ionization from such states within the vertical Franck-Condon region appears to produce a distinct angular distribution.\(^{29, 31-34}\) At a first (i.e., atomic-like) level of approximation, single photon ionization of a 3s orbital (which is the dominant state character in the vertical Franck-Condon region) should give rise to photoelectron partial waves of exclusively \( p \) character, peaking along the laser polarization axis (i.e. vertical with respect to the image presented in Fig. 2.). Additionally, since an orbital of \( s \) character can possess no inherent alignment, no significant \( \beta_4 \) component to the overall PAD anisotropy should be present. Finally, given the expected strong propensity for diagonal ionization from the 3s Rydberg component (see Section IV. B), this characteristic anisotropy should be localized as a relatively sharp ring feature within the overall photoelectron images. These signatures are not observed for any of the excitation wavelengths investigated in the present experiments on pyrrole. Although such features would perhaps not be expected at 267 nm and 258 nm (where we believe the \( S_1(3s/\pi\sigma^*) \) state is not energetically accessible), the lack of any significant change in the appearance of the PADs at 250 nm and 240 nm (see Fig. 4) adds further weight to the suggestion that non-resonant ionization is the overwhelmingly dominant contribution to the data in all cases. The use of the PAD data to arrive at this conclusion comes with three important caveats, however; (i) the atomic-like picture of (3s) Rydberg-state ionization is only an initial approximation and additional photoelectron partial wave contributions to the overall PAD can clearly arise though higher-\( l \) contributions to the excited state wavefunction and/or scattering off the non-
spherical molecular ion core during the ionization event. We note though that this does not seem to be a significant factor for mixed 3s/valence states in similar species we have previously investigated, where the observed PADs do peak strongly along the laser polarization direction.\textsuperscript{29, 31-34} We also highlight that the 3s Rydberg component of the S\textsubscript{1}(3s/$\pi\sigma^*$) state of pyrrole is relatively “pure” at the vertical Franck-Condon geometry, being highly localized on the N atom;\textsuperscript{35} (ii) photoionization is assumed to proceed directly and not via an auto-ionizing resonance in the continuum (leading to a PAD with a different shape to that which might otherwise be expected). Given the overall qualitative similarity between the PADs we obtain for pyrrole (using a 300 nm probe) and those reported by Longarte and co-workers (using a 267 nm probe) at equivalent pump wavelengths,\textsuperscript{14} we assume this is not an issue for the data under consideration here; (iii) ionization at more extended N-H bond distances (where $\sigma^*$ valence character is more pronounced) will not produce such distinctive PAD signatures, as the state is no longer described predominantly by a single, well-defined 3s basis orbital. In regard to this final point, the PAD information may, however, also provide a valuable counterpoint to the pyrrole lifetime and photoelectron spectra data discussed in the previous sections. There it was argued that the possibility of a limited detection window along the N-H stretching coordinate potentially obscures the presence of ionization signatures that could be unambiguously attributed to the S\textsubscript{1}(3s/$\pi\sigma^*$) state. In the PADs, however, such a limited window (if present) would be advantageous as only the very distinctive ionization signature from the 3s component of the S\textsubscript{1} state (and not the $\sigma^*$ component) may manifest in the PAD – improving the chances of unambiguous identification. As with the photoelectron spectra discussed in Section IV B, we therefore consider a more differential, energy-dependent analysis of the PAD data at 250 nm, investigating variation of $\beta_2$ and $\beta_4$ as a function of photoelectron binding energy. The aim here is to look for any subtle changes in
the anisotropy parameters over a small energy region that may indicate ionization from the 
S₁(3s/πσ*) state – most specifically this might be expected to be a suppression of the β₄ term 
due to 3s Rydberg ionization (as expanded upon previously). This information is presented in 
the overlay plots in the lower panel of Fig. 5. It is immediately clear that no significant 
variation in either β₂ or β₄ appears to be visible and, moreover, the appearance of the data is 
very similar to the equivalent data already presented in Fig. 2 for the 267 nm pump case 
(where population of the S₁(3s/πσ*) state is not expected to occur). Once again, this lends 
strong support to the suggestion that non-resonant ionization is the dominant contribution to 
the TRPEI data in all instances.

**D. Projecting Deeper into the Ionization Continuum**

Given the evidence presented in Sections IV A-C, the case for our data exhibiting 
overwhelmingly non-resonant ionization of pyrrole at all pump wavelengths studied appears 
strongly supported. This picture is, however, still not fully reconciled with the H atom 
photoprodut appearance lifetimes of pyrrole. As stated previously, these lifetimes have been 
reported as 110-126 fs and 46 fs following excitation at 250 nm and 238 nm, respectively.¹⁰, ¹² 
Even though direct absorption to the S₁(3s/πσ*) is known to be extremely weak, it is perhaps 
surprising that no evidence of any resonant ionization (in competition with non-resonant 
processes) is observed at all in our present measurements and supporting differential analysis. 
This suggests that, even in the vertical Franck-Condon region, the ionization of the S₁(3s/πσ*) 
state is extremely inefficient relative to the non-resonant alternative. A number of factors 
may, in principle, be responsible for this including (i) the potential role of any molecular 
alignment effects in the S₁(3s/πσ*) state resulting from the resonant excitation step; (ii) a very 
small (electronic) ionization cross-section of the S₁(3s/πσ*) state when compared to that of the 
ground state and (iii) very poor Franck-Condon factors for S₁(3s/πσ*) ionization relative
to those for non-resonant ionization. In regard to point (i) we note that, given the predominantly 3s Rydberg character of the $S_1$ state (at least in the vertical Franck-Condon region), alignment effects would seem to be an unlikely issue and, furthermore, we also point out that time-resolved ion-yield measurements of Longarte and co-workers, exciting pyrrole across the 260-225 nm region, employed a magic angle pump-probe polarization geometry and did not report any dynamics comparable to that of the H atom appearance lifetime. Concerning point (ii) we highlight that we have previously used correlations between photoionization cross sections and the isotropic polarizability volume $<\alpha>$ as a useful heuristic tool in assisting the interpretation of TRPEI data. Although a somewhat speculative approach, this does suggest (in conjunction with supporting experimental evidence) that the cross-section for Rydberg state ionization may well be considerably larger than for the ground state — at least at relatively low electron energies, such as those under consideration here. An additional factor to briefly consider here is the possibility of a phenomenon such as a low-energy Cooper minimum supressing the ionization of the $S_1(3s/\pi\sigma^*)$ state. Such an effect would, however, be expected to be highly energy dependent and we highlight once again that our data (using a 300 nm probe) and that of Longarte and co-workers (using a 3 × 800 nm or 1 × 267 nm probe) yields the same lack of resonant signals at very similar pump wavelengths. Furthermore, the interference-based nature of this type of effect is perhaps unlikely to be significant for predominantly s-type ionization within the vertical Franck-Condon region (which, at least within a simple atomic-like picture, yields only p partial waves upon ionization). This then leaves the Franck-Condon overlap issue raised in point (iii), which is further suggested as a possible factor contributing to the lack of observable resonant $S_1(3s/\pi\sigma^*)$ state ionization upon considering our one-colour pump-alone data. These are recorded simultaneously while performing two-colour pump-probe measurements and, although obviously revealing no temporal information, may still be
exploited as a source of additional information. Specifically, these data provide an effective
time-zero ionization picture that projects much deeper into the continuum than the two-colour
experiment, sampling a greater Franck-Condon envelope. In Fig. 6 we present the one-colour
photoelectron spectra and PADs associated with 250 and 240 nm excitation. Although not
shown in the figure, the equivalent data obtained at 267 and 258 nm are essentially identical
to the 250 nm case. The overall shape of the spectra appear very similar to those presented in
Fig. 3 for the corresponding two-colour measurements using a 300 nm probe. Additionally,
the one-colour 250 nm PAD is extremely similar in appearance to its two-colour counterpart
presented in Fig. 4, adding further weight to our previous argument that an auto-ionizing
resonance in the continuum is unlikely to be contributing to the observed angular
distributions. The PAD associated with one-colour 240 nm ionization, on the other hand, is
strikingly different to the two-colour case, peaking much more strongly along the direction of
laser polarization. As argued in the preceding section, such behaviour is consistent with what
might be expected if 3s Rydberg ionization is now making a contribution to the overall PAD.
Although other factors may also be responsible for this change (as highlighted earlier) this
observation does potentially hint that (1+1) ionization of pyrrole at 240 nm (a total photon
energy of 10.33 eV projecting up to 2.12 eV into the continuum) could now be yielding more
effective ionization of the \( S_1(3s/\pi\sigma^*) \) state relative to the competing non-resonant alternative.
Conducting a more differential analysis of the PAD data does not, however, offer any
additional insights in this regard, with neither \( \beta_2 \) nor \( \beta_4 \) exhibiting any obvious variation with
binding energy (within statistical uncertainty).

Given information discussed above, we conducted exploratory time-resolved ion-yield
(TRIY) measurements using a 250 nm pump in conjunction with an intense 400 nm probe in
order to try and bridge the discrepancy between the timescales associated with the
photoreactant and photoproduct transient data. This (1+2') ionization scheme now projects up
to 2.95 eV into the continuum and will sample a much greater Franck-Condon envelope than in the TRPEI experiments described earlier. The pump and probe polarizations were set to be parallel and the transients obtained for the pyrrole parent ion are presented in Fig. 7. Clear evidence of dynamics evolving to both positive and negative pump-probe delay times is now observed. This is in addition to a Gaussian contribution to the data that may still be attributed to non-resonant ionization. Since pyrrole absorbs strongly at 200 nm (see Fig. 1), the probe-pump signal evolving in the negative time direction is likely a consequence of resonant two-photon absorption of the 400 nm pulse. The signal evolving in the positive time direction does, however, now appear to potentially provide some evidence of dynamics taking place within the $S_1(3s/\pi\sigma^*)$ state – especially given the exponential decay lifetime of $125 \pm 10$ fs extracted from a fit to the data, since this is comparable to the aforementioned H atom appearance time of 110-126 fs at the same excitation wavelength. As with many multi-photon ionization schemes, though, this assertion comes with the caveat of ionization possibly now proceeding through an additional resonant state lying at higher excitation energy (i.e. via a $(1+1'+1')$ scheme) and this being responsible for any additional dynamical signatures present in the data. Our preliminary ion-yield measurement is clearly not sufficiently differential to fully discount this possibility. Taking the Fig. 7 data in combination with other evidence presented earlier does, on the other hand, tentatively reinforce the idea that poor Franck-Condon factors for $S_1(3s/\pi\sigma^*)$ ionization (relative to those for non-resonant ionization) are the major restriction preventing its detection using probes with lower overall energy. We assume, at present, that this effect arises due to significant topological differences between the potential energy surfaces of the $S_1(3s/\pi\sigma^*)$ and $D_0$ cation states of pyrrole. This is clearly an avenue for additional future experimental TRPEI investigations exploiting both improved temporal resolution and more energetic probes.

V. CONCLUSION
Time-resolved photoelectron imaging (TRPEI) studies of gas-phase pyrrole over the 267-240 nm excitation region reveal that, in all cases, the data obtained using a 300 nm probe is most likely dominated by signals attributable to non-resonant ionization. Our findings are inconsistent with several previously reported studies interrogating H atom dissociation from the $S_1(3s/\pi\sigma^*)$ state, which although possessing very low oscillator strength, is known to be directly excited at excitation wavelengths $<$254 nm. We arrive at our conclusion by considering several separate aspects of our experimental data which, critically, are the same at all four pump wavelengths investigated – purposely chosen to sit energetically both above and below the 254 nm $S_1(3s/\pi\sigma^*)$ onset threshold. Specifically these are the Gaussian pump-probe response (that does not correlate with the H atom production lifetimes reported previously following 250 nm and 240 nm excitation), the overall appearance of the photoelectron spectra (which are strikingly similar to the He (I) ground state spectrum) and the shape of the associated photoelectron angular distributions (which do not display characteristic signatures of 3s Rydberg ionization seen previously in related systems). Additionally, supporting time-resolved ion-yield data obtained following 250 nm excitation in conjunction with a two-photon 400 nm probe yields non-Gaussian pyrrole$^+$ transients exhibiting decay constants comparable to H atom appearance times. This suggests that projecting much deeper into the ionization continuum does now reveal dynamical signatures that may be attributable to the $S_1(3s/\pi\sigma^*)$ state. Although any one piece of this evidence, taken in isolation, is not irrefutable, we argue that when all aspects are considered together, our conclusion that non-resonant ionization is the dominant contribution to the TRPEI data presented over the 267-240 nm pump region appears strongly supported. Furthermore, in considering this evidence our discussion highlights several important caveats in the more general interpretation of time-resolved experimental data obtained using photoreactant ionization to interrogate excited state dynamics – especially in situations where excited state lifetimes are very short relative to the
experimental instrument response function and absorption cross sections are very small. We hope and anticipate that this may prove to be of some interest and usefulness to others employing the similar approaches for the study of other molecular systems.

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REFERENCES

FIGURE CAPTIONS

Figure 1. Room-temperature UV vapour-phase absorption spectrum of pyrrole (structure inset) recorded using a commercial bench-top spectrophotometer (Shimadzu UV-2550, 0.1 nm scan interval/0.1 mm slit width). Vertical red arrows depict the various excitation wavelengths used in the present study. The detection limit shown (254 nm) is that determined by Ashfold and co-workers in Ref. 6 for the production of H atoms via direct dissociation on the S1 (3s/πσ*) potential energy surface (for more details see the main text).

Figure 2. Upper left: Abel-inverted (1 + 1’) photoelectron image obtained for pyrrole at Δt = 0 using a 267 nm pump/300 nm probe. Time-invariant pump-alone and probe-alone signals have been subtracted and the image is 4-fold symmetrised. The (linear) polarization direction of the pump and probe beams is vertical with respect to the figure. Bottom right: 2D time-dependent photoelectron spectrum of pyrrole. White dashed lines denote integration regions for data shown in the two remaining figure panels. Bottom left: Integrated transient pump-probe signal with overlays showing β2 and β4 anisotropy parameters. Top right: Integrated photoelectron spectrum, once again with β2 and β4 overlays. The data was partitioned into 0.02 eV energy bins for the initial anisotropy fits (before averaging) which were performed over the angular region 8° ≤ θ ≤ 90° to eliminate uncertainties from centre-line noise present in the Abel inverted images (see Fig. 2). Error bars denote 1σ values. For more details see main text.

Figure 3. Photoelectron spectra obtained for pyrrole following (1 + 1’) ionization using 267, 258, 250 and 240 nm probes in conjunction with a 300 nm probe. These data were obtained by integrating pump-probe transients over the small energy region close to Δt = 0 (as shown by the horizontal dashed lines in Fig. 2 for the case of 267 nm excitation).
Figure 4. Normalized polar photoelectron angular distribution (PAD) plots obtained for pyrrole following excitation over a range of pump wavelengths with subsequent ionization using 300 nm. Each angular point represents an average over a range of energy and time bins – as depicted for the case of 267 nm excitation by the area bounded by the white vertical and horizontal dashed lines shown in the lower right panel of Fig. 2. Error bars denote 1σ values. The red line is a fit to this data using a time- and energy-integrated form of Equation (1) and the β_2 and β_4 anisotropy parameters obtained from this fit are also shown. Values in parentheses denote 1σ uncertainties in the final significant figure.

Figure 5. Decay associated spectra resulting from a two-exponential fit to the time-dependent photoelectron spectrum of pyrrole obtained using a 250 nm pump in conjunction with a 300 nm probe. In the upper panel, both exponential decay constants were allowed to float in the fit, whereas in the lower panel τ_2 was constrained to a fixed value of 120 fs. For additional details see main text. The lower panel also includes overlays of the associated β_2 and β_4 anisotropy parameters, obtained using an identical approach to that employed in producing the data already presented in Fig. 2 for the case of a 267 nm pump. Error bars denote 1σ values.

Figure 6. Photoelectron spectra obtained for pyrrole following one-colour (1 + 1) ionization using 250 and 240 nm. The inset panels are the associated normalized polar photoelectron angular distribution (PAD) plots. Each angular point represents an average over the binding energy range indicated by the dashed vertical lines. Error bars denote 1σ values. The red line is a fit to this data using a time- and energy-integrated form of Equation (1) and the β_2 and β_4 anisotropy parameters obtained from this fit are also shown. Values in parentheses denote 1σ uncertainties in the final significant figure. Of particular note is the striking difference
between the 240 nm PAD and the equivalent two-colour measurement obtained using a 300 nm probe (see Fig. 4).

**Figure 7.** Time-resolved ion-yield transient obtained for the pyrrole$^+$ parent employing a 250 nm pump (~1 μJ/pulse) in conjunction with a 400 nm probe (~10 μJ/pulse) using 30 fs time steps (black circles). Also shown is a multi-exponential fit to the data (black line) with components modelling pump-probe signal decay (green line), pump-probe signal evolving to negative time delays (blue line) and Gaussian non-resonant ionization (red line). The latter has a FWHM equivalent to the independently determined cross-correlation (130 ± 10 fs). This value was obtained from pump-probe measurements conducted under the same conditions with butadiene and was also used to convolute the exponentially decaying functions used in the overall fit.
$\tau_{\text{pump-probe}} = 125 \pm 10 \text{ fs} \quad \text{for} \quad 250 + 400 \text{ nm (1+2')}