Tracing dynamic self-disassociation behavior of pyrrole with novel T-shaped hydrogen bonding

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Near infrared spectroscopy (NIR) and two-dimensional correlation spectroscopy (2Dcos) were employed to study the dynamic self-disassociation behavior of hydrogen bonds in neat liquid pyrrole during heating. Two regions (7000–6430 cm\(^{-1}\) for NH-related vibrational overtones and 6200–6100 cm\(^{-1}\) for CH-related vibrational overtones and combination modes) are the focus of this paper, whose integral absorption temperature dependence exhibited a continuous convex variation. Two-dimensional correlation analysis has discerned the sequence of change of different aggregated species of pyrrole. Additionally, we carefully investigated the band shift phenomenon of N–H\(\cdot\cdot\cdot\pi\) hydrogen bonding in pyrrole dimers, and assigned this band shift as the result of the transformation of pyrrole dimers from T-shaped geometry to antiparallel geometry.

Introduction

Pyrrole, one of the most important representatives of five-membered aromatic nitrogen heterocycles, has been found to have great potential astrophysical relevance.\(^1\) Pyrrole derivatives such as chlorophyll, hemachrome, vitamin B\(_{12}\) and alkaloids are widely distributed in nature, and play an important role in maintaining life phenomena with the same central structure of porphine metal complexes.

Among all intermolecular interactions, hydrogen bonds (of both classical and newly-discovered improper, or blue-shifting, type\(^2\)–\(^6\)) are widely studied because of their relevance to molecular recognition\(^7,8\) and organic synthesis,\(^9\) as well as biochemically important phenomena (e.g. base-base interactions in DNA,\(^10\)) packing of aromatic molecules within molecular crystals\(^11\) or the tertiary structure of proteins\(^12\)). Due to the electron-deficiency of nitrogen, pyrrole is inclined to self-aggregate into clusters of various sizes through so-called “\(\pi\)-type hydrogen bonding”\(^13\)(“\(\pi\)-facial hydrogen bonding”,\(^14\) or “T-shaped hydrogen bonding”\(^13,15\) in some articles), which is a kind of intermediate hydrogen bond between classical hydrogen bonds (such as N–H\(\cdot\cdot\cdot\)O or N–H\(\cdot\cdot\cdot\)N) and very weak unspecific interactions (such as C–H\(\cdot\cdot\cdot\)F).\(^16\) Apparently different from classical hydrogen bonds, a \(\pi\)-type hydrogen bond has \(\pi\)-electron clouds serving as H-bonding proton acceptors, and, in the case of pyrrole, N–H as proton donors.\(^13\) Fig. 1 shows the structure of the T-shaped N–H\(\cdot\cdot\cdot\pi\) hydrogen bond of pyrrole dimers, which has been confirmed by experimental methods\(^13,17\) and theoretical approaches.\(^13,14\) Interestingly, unlike benzene dimers, which have nearly isoenergetic parallel displaced and T-shaped conformers,\(^2,18,19\) the pyrrole dimers adopt a single stable T-shaped conformation. A fairly small interplane angle of 55.4° has been obtained according to the microwave data.\(^20\) This suggests that the pyrrole dimers adopt a compromise geometry, which may arise from the competition between parallel dipole-dipole and \(\pi\)-stacking preferences and the more orthogonal hydrogen bond preference.\(^16\)

As a prototype of an important chemical family, pyrrole was frequently the object of vibrational spectroscopic studies,\(^21\) especially infrared spectroscopy. There are many researches focused on the spectra assignment of pyrrole in the gas phase ranging from fundamental frequency to high order overtones and combination modes.\(^22–26\) High resolution Fourier transform infra-red (FT-IR) was performed to get subtle vibrational information of pyrrole.\(^27,28\) Algebraic approaches were also employed to study CH/NH stretching levels and their possible anharmonic resonance mechanisms.\(^29\) Available studies were mainly concentrated on pyrrole dimers, and various methods have been employed to study the self-association behavior as well as the structure of pyrrole dimers. For example, L. Pejov \textit{et al.} studied pyrrole\(^13\) and indole (with the same N–H\(\cdot\cdot\cdot\pi\) H-bonding)\(^15,30\) self-association behavior in their dilute

![Fig. 1](Image)
solutions by FT-IR and near infra-red (NIR) spectroscopy, accompanied by different levels of quantum chemical calculations to determine the parameters of the T-shaped structure. Studies of N–H···π hydrogen bond by other methods were also carried out before, such as double resonance and pure-base calorimetric. Besides these, nonlinear-infrared responses of N–H mode in pyrrole monomer and dimer were studied to examine its vibrational relaxation process. However, no research regarding pyrrole self-aggregates of more than two units was reported before until Gomez-Zavaglia and Fausto measured the FT-IR spectra of the pyrrole monomer and low-order aggregates (up to four units) in a low temperature (9 K) Ar matrix with an extensive DFT study. Their work revealed that pyrrole could form more stable cyclic H-bonding clusters with a significant cooperativity effect. Thereafter, M. Färni et al. studied the photolysis and fragmentation dynamics of size-selected pyrrole clusters produced in supersonic expansions by means of both experimental and theoretical methods. Furthermore, Matsumoto and Honma made a detailed assignment of N–H stretching vibration produced in supersonic expansions by means of both experimental and theoretical methods. However, to the best of our knowledge, no investigation on pyrrole self-disassociation in its neat liquid phase has ever been performed, especially the dynamic self-disassociation behavior under temperature perturbation. Species and interactions in neat liquid pyrrole are numerous and much more complicated to study than in its dilute conditions (e.g., solutions, inert gas matrices, etc.). In our present study, we applied NIR spectroscopy and two-dimensional correlation spectroscopy (2Dcos) to study the dynamic self-disassociation behavior of neat liquid pyrrole during heating.

Compared to mid-IR spectroscopy, NIR spectroscopy has advantages to study the hydrogen bonds and molecular interactions of self-associated molecules, such as filtration of interference spectral information (C–C, C–N, etc.), good separation of monomeric and polymeric species, easy operation to obtain proper absorption and, especially, an opposite effect on the comparable intensity between weakly associated species and strongly associated ones—that is, vibrations due to weaker hydrogen bonds have stronger overtones and weaker fundamentals. Thus, NIR spectroscopy is an established method to examine the complicated weak interactions in neat liquid pyrrole. Two-dimensional correlation spectroscopy (2Dcos) is a mathematical tool whose basic principles were first proposed in 1986 by Noda. Up to now this technique has been widely used to study spectral changes of different chemical species induced by external perturbation (e.g. temperature, time, pressure, concentration, electromagnetics, etc.). By spreading spectral signals along a second dimension, 2Dcos could sort out complex or overlapped spectral features and give an enhanced spectral resolution. Due to the different response of different species to external perturbation, additional information about inter- or intramolecular interactions or conformation changes can be extracted which cannot be obtained directly from conventional one-dimensional spectroscopy. Of particular note, 2Dcos can also discern the specific order of molecular motions under a certain physical variable.

In this paper, we firstly introduce 2Dcos into the investigation of pyrrole self-disassociation, and the combination of NIR and 2Dcos enables us to study the complicated interactions in neat liquid pyrrole and trace the dynamic variations associated with its self-disassociation behavior with increasing temperature.

Experimental

Conventional FT-NIR

The pyrrole sample used in the FT-NIR study was obtained from Aldrich and was used without further purification. The FT-NIR measurements were performed on a Bruker IFS 88 spectrometer with a spectral resolution of 4 cm–1 and 256 scans were accumulated to obtain an acceptable signal-to-noise ratio. The spectra were recorded in a variable temperature cell between 25 and 115 °C at intervals of 5 °C with an accuracy of 0.1 °C.

2D correlation spectroscopy

NIR spectra collected in the temperature range 25–115 °C with a 5 °C interval were used to perform 2D correlation analysis. For all calculations, the spectrum recorded at room temperature (25 °C) was used as the reference spectrum. 2D correlation analysis was carried out using the software 2D Shige ver. 1.3 (© Shigeaki Morita, Kwansei-Gakuin University, Japan, 2004–2005), and was further plotted into the contour maps by the Origin program ver. 8.0. In the contour maps, red colors are defined as the positive intensities, while green colors as the negative ones.

Results and discussion

A Conventional NIR spectroscopy analysis

Spectra variations occurring in the heating of the sample are presented in Fig. 2. Only a 10 °C interval is shown here for clarity. Two spectral features can be identified according to their temperature sensitivities. The region 7000–6430 cm–1 with a strong intensity response to temperature perturbation can be assigned to the NH-related vibrational overtones associated with the pyrrole hydrogen bond, which would be emphatically analyzed. The region 6430–5600 cm–1, with a weak intensity response to temperature perturbation, was mainly contributed from the CH-related vibrational overtones and combination modes, which was too complicated to assign explicitly. In this paper, we picked out a representative region 6200–6100 cm–1 to perform later analyses.

To get an exact assignment of NH-related vibrational overtones, we searched for a standard spectrum of neat liquid pyrrole measured in its mid-IR region from the Aldrich condensed phase sample library (Library Index 83). The spectrum in the region 3550–3300 cm–1 related to N–H stretching vibrations and its corresponding second order derivative curve have been presented in Fig. 3. As we know, most of hydrogen bonding bands are broad, which is...
characteristic of all but the weakest hydrogen bond systems. An acceptable explanation is the existence of a variety of associated species in solution—dimers, trimers, tetramers...—both linear and cyclic. The spectrum of N–H stretching vibrations of pyrrole in Fig. 3 is also broad, representing the existence of various self-aggregated species in its neat liquid phase. But, surprisingly, the corresponding 2nd derivative curve shows mainly three bands, which gives us some light to distinguish the NH-related overtone bands. According to the results of infrared cavity ringdown spectroscopy of jet-cooled pyrrole clusters, these three bands at 3534, 3440 and 3402 cm$^{-1}$ can be assigned to the NH stretching vibrations of pyrrole monomers, dimers (N–H⋯π) and cyclic polymers (liquid-like), respectively. Combining this with spectral data in pyrrole/C$_1$/C$_1$/C$_1$ mers, dimers (N–H⋯π) can be assigned to the NH stretching vibrations of pyrrole mono- mers, dimers (N–H⋯π) and cyclic polymers (liquid-like), respectively. Combining this with spectral data in pyrrole dilute solutions, we deduced the final spectra assignments of NH-related overtones of neat liquid pyrrole, which have been presented in Table 1. Therein, the band at 6528 cm$^{-1}$ was assigned to cyclic polymers due to their lower absorption compared to dimers in the overtone region. For the CH-related vibrational overtones and combination modes in the region 6430–5600 cm$^{-1}$, several sharp peaks can be observed, and the band at 6136 cm$^{-1}$ mainly comes from the vibrational overtone and combination mode of C–H (β) stretching vibration ($\nu_5$). For the convenience of discussion, detailed band assignments based on later differential spectra and 2Dcos have also been presented in Table 1, and the corresponding NH/CH stretching fundamental modes are shown in Fig. 4.

Examining the tendency of spectral variations with increasing temperature, we find that the spectral intensity at 6759 cm$^{-1}$ increased with a distinct blue shift of the band position as the direction of arrows showed in Fig. 2. The spectral intensity at 6528 cm$^{-1}$ and that of the main bands in the CH-related vibrational region all decreased without observable band shifts. It is noted that the variations in the NH-related region were more intense than those in the CH-related region, indicating the significant influence of increasing temperature on the hydrogen bonding of pyrrole.

Fig. 5(a) and (b) shows the temperature dependence of the integral absorption for the region 7000–6430 cm$^{-1}$ and 6200–6140 cm$^{-1}$, respectively. A tangent line was made at the low temperature section as the reference line. It is noted that the integral absorption for the region 7000–6430 cm$^{-1}$ shows a convex increase with increasing temperature, while that for the region 6200–6140 cm$^{-1}$ shows a convex decrease—that is, all the points in the high temperature section are under the reference line. This indicates that no obvious transition occurred during the heating process, whereas at least two species exhibited a different temperature response. The reduction of the increasing rate for the integral absorption in the region 7000–6430 cm$^{-1}$ suggests that the changing of hydrogen bonds slowed down at high temperature.

The temperature dependence of the band shift at 6759 cm$^{-1}$ corresponding to $2\nu$ (N–H⋯π) is presented in Fig. 6. The band at 6759 cm$^{-1}$ appeared to show a continuous shift to 6794 cm$^{-1}$, and no obvious transition occurred either.

However, the identification of different species and the corresponding assignments we can obtain from conventional NIR spectroscopy are still limited. To make the mechanism of spectral intensity variations and the band shift phenomenon clear, additional differential spectra and 2D correlation analyses are needed.

B Differential spectra analysis

Fig. 7 shows us the differential spectra in the 7000–5600 cm$^{-1}$ region between 25 and 115 °C. We chose the spectrum recorded at room temperature (25 °C) as the reference spectrum. From the differential spectra, we can find five main variation bands at 6836, 6663, 6528, 6156 and 6103 cm$^{-1}$. Of these, the band at 6103 cm$^{-1}$ is not discussed in this paper. The corresponding assignments have been presented in Table 1. It should be noticed that the differential spectra cannot reflect the details of band shifts. Thus, the intensity variations at some bands may result from overlapped intensity variations of two or more neighboring bands. Here, we can only make a
tentative assignment of the band at 6836 cm\(^{-1}\) to the stretching overtone of free N–H, either from the monomer or dimer. The bands at 6663 and 6528 cm\(^{-1}\) can be assigned to the stretching overtones of hydrogen bonded N–H (N–H\(\cdots\)π) from the liquid-like and solid-like phase of cyclic polymers, respectively.

With increasing temperature, the intensity of the band at 6836 cm\(^{-1}\) increased, while the intensities of the bands at 6663 and 6528 cm\(^{-1}\) decreased. It is understandable that in the heating process, larger cyclic polymers continued to disaggregate into smaller dimers and monomers.

### C 2DNIR correlation analysis

For more detailed analysis, 2D correlation spectroscopy was employed. In 2D correlation analysis, two kinds of correlation maps—synchronous and asynchronous spectra—can be obtained. Synchronous spectra represent the simultaneous or coincidental changes of spectral intensities measured at two given wavenumbers, \(\nu_1\) and \(\nu_2\). This spectrum is symmetric with respect to the diagonal line. Correlation peaks at the diagonal position (\(\nu_1 = \nu_2\), called autopeaks) correspond to the linear evolution of a certain species along the induced perturbation.\(^{47}\)

The intensities of autopeaks reflect the sensitivity of corresponding species. Asynchronous spectra represent sequential or unsynchronized changes of spectral intensities measured at two given wavenumbers, \(\nu_1\) and \(\nu_2\). This spectrum is asymmetric with respect to the diagonal line. An asynchronous correlation peak can develop only if the intensities of two dynamic spectral intensities vary out of phase with each other. Asynchronous spectra can significantly enhance spectral resolution. On the other hand, the signs of

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**Table 1** Spectral assignments derived from conventional NIR, differential spectra, 2D synchronous and asynchronous, respectively\(^{15,16,21,23,27,29,33,36,37}\)

<table>
<thead>
<tr>
<th>Wavenumber/cm(^{-1})</th>
<th>Assignments</th>
<th>Wavenumber/cm(^{-1})</th>
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<th>Wavenumber/cm(^{-1})</th>
<th>Assignments</th>
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<tbody>
<tr>
<td>Conventional NIR</td>
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<td>Differential spectra &amp; 2D synchronous</td>
<td></td>
<td>2D asynchronous</td>
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<tr>
<td>6794 (2\nu_2) (free N–H) (dimer)</td>
<td>6836 (2\nu_1) (free N–H)</td>
<td>6856 (2\nu_1) (free N–H) (monomer)</td>
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<tr>
<td>6759 (2\nu_3) (N–H(\cdots)π) (dimer)</td>
<td>6663 (2\nu_1) (N–H(\cdots)π) (liquid-like)</td>
<td>6794 (2\nu_2) (free N–H) (dimer)</td>
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<tr>
<td>6528 (2\nu_5) (N–H(\cdots)π) (cyclic polymers) (solid-like)</td>
<td>6528 (2\nu_1) (N–H(\cdots)π) (cyclic polymers) (solid-like)</td>
<td>6769 (2\nu_3) (N–H(\cdots)π) (dimer)</td>
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<tr>
<td>6156 (\nu_8 + \nu_7, 2\nu_6, 2\nu_8) (C–H)</td>
<td>6156 (\nu_8 + \nu_7, 2\nu_6, 2\nu_8) (C–H)</td>
<td>6624 (2\nu_1) (N–H(\cdots)π) (cyclic polymers) (liquid-like)</td>
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<td>6514 (2\nu_5) (N–H(\cdots)π) (cyclic polymers) (solid-like)</td>
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<td>6510 (2\nu_5) (N–H(\cdots)π) (cyclic polymers) (solid-like)</td>
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<td>6514 (2\nu_5) (N–H(\cdots)π) (cyclic polymers) (solid-like)</td>
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<td>6510 (2\nu_5) (N–H(\cdots)π) (cyclic polymers) (solid-like)</td>
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**Fig. 4** Schematic representation of NH/CH stretching fundamental modes of pyrrole in the regions 7000–6430 cm\(^{-1}\) and 6200–6100 cm\(^{-1}\).

The vibrational modes are plotted with reference to ref. 13, 29 and 33 and atomic displacements are only approximately reproduced.

**Fig. 5** The variation of the integral absorption as a function of temperature for the region 7000–6430 cm\(^{-1}\) (a) and the region 6200–6140 cm\(^{-1}\) (b), respectively. The dashed line is a reference line made from the tangent line at the low temperature section.
asynchronous peaks provide very useful information about the temporal sequence of events taking place during the studied process. The judging rule was summarized as Noda’s rule—that is, if the cross-peaks \((n_1, n_2, \text{ and assume } n_1 \leq n_2)\) in synchronous and asynchronous spectra have the same sign, the change at \(n_1\) may occur prior to that of \(n_2\), and vice versa.

Fig. 8(a) and (b) show us the synchronous and asynchronous spectra of pyrrole, respectively for the regions 7000–6430 cm\(^{-1}\) and 6200–6100 cm\(^{-1}\) in the temperature range 25–115 °C.

According to the synchronous spectra of the NH-related region 7000–6430 cm\(^{-1}\) in Fig. 8(a), three autopeaks with different correlation intensities can be found. It indicates that the band at 6836 cm\(^{-1}\) corresponding to \(2\nu (\text{free N–H})\) had the strongest response to temperature perturbation, then the band at 6663 cm\(^{-1}\) corresponding to \(2\nu (\text{N–H} \cdots \pi)\) (cyclic polymer) (liquid-like) took second place, and the correlation intensity of the band at 6528 cm\(^{-1}\) corresponding to \(2\nu (\text{N–H} \cdots \pi)\) (cyclic polymer) (solid-like) was too weak to be observed along the diagonal line. For the CH-related region, 6200–6100 cm\(^{-1}\), a relatively strong autopeak at 6156 cm\(^{-1}\) can be observed.

It is noted that the bands at 6663, 6528 and 6156 cm\(^{-1}\) all have positive cross-peaks, which indicates that their spectral intensities had a similar response to temperature perturbation—that is, all decreased with increasing temperature relative to the raw spectra. On the other hand, the bands at 6836 cm\(^{-1}\) have negative cross-peaks with the other three bands, indicating an increasing intensity with the increasing temperature. This was consistent with the observations derived from conventional NIR and differential spectra.

Compare 2D synchronous spectra with differential spectra, and you can find it interesting that these two methods have nearly the same results (e.g. spectral resolution, intensity variations, perturbation sensitivity, etc.). The differences are mainly at two aspects: (a) differential spectra can directly reflect the spectral intensity variations without reference to raw spectra, but 2D synchronous spectra do not; (b) 2D
synchronous spectra can additionally serve us with information about the association between two different species—that is, if two species at different wavenumbers have a cross-peak, they must have a cooperative effect upon the same perturbation with each other. Nevertheless, 2D synchronous spectra cannot reflect the details of band shifts, either. More detailed information of pyrrole self-disassociation behavior can be further extracted from 2D asynchronous spectra.

From the asynchronous spectra of pyrrole in the NH-related region 7000–6430 cm\(^{-1}\) in Fig. 8(b), we noted that all the correlation peaks were among five bands at 6856, 6794, 6769, 6624 and 6514 cm\(^{-1}\), whose assignments have been presented in Table 1 and corresponding fundamental modes in Fig. 4. Because 2D correlation analysis was carried out upon the spectra in the whole measured temperature range, the wavenumbers we read from 2D correlation spectra may not be identical to those from the reference spectrum (25 °C). However, we can still assign the band at 6769 cm\(^{-1}\) to the stretching overtone of hydrogen bonded N–H (N–H \(\cdots\) \(\pi\) in pyrrole dimers), and the bands at 6624 and 6514 cm\(^{-1}\) to the stretching overtones of liquid-like and solid-like hydrogen bonded N–H (N–H \(\cdots\) \(\pi\) in cyclic polymers), respectively. The bands at 6856 and 6794 cm\(^{-1}\) can be assigned to the stretching overtones of free-N–H in pyrrole monomers and dimers, respectively, according to the report of NIR spectra in pyrrole solutions. The lower stretching overtone of free NH in pyrrole dimers than in monomers is due to the fact that the participation of a pyrrole molecule as a hydrogen bond acceptor decreases the election density of the N–H bond. The red shift of hydrogen bonded N–H stretching overtones in pyrrole dimers from free NH in pyrrole monomer is more pronounced for the donor than that for the acceptor, and that is mainly due to a smaller intramolecular force constant in the bridging N–H.

The asynchronous spectra in the CH-related region 6200–6100 cm\(^{-1}\) exhibited two correlation peaks around 6156 cm\(^{-1}\) among three bands at 6171, 6160 and 6150 cm\(^{-1}\). According to the results of algebraic method and high resolution spectroscopy, they can be assigned to the C–H stretching overtones and combination tones \(\nu_8 + \nu_6, \nu_8 + \nu_7\) and \(2\nu_6, 2\nu_7\) (corresponding stretching fundamental modes are also shown in Fig. 4, too), respectively. The peak at 6156 cm\(^{-1}\) we observed in conventional NIR, differential spectra and synchronous spectra should be the overlapped peak of the bands at 6160 and 6150 cm\(^{-1}\). As well as enhancing spectral resolution, 2D asynchronous spectra can also discern the specific order taking place under external perturbation. To simplify Noda’s rule and make it easy to carry out, especially for chemical systems with large numbers of correlation peaks, we proposed a relatively straightforward method. We firstly listed all the signs of cross peaks in asynchronous spectra, then turned back to list the corresponding signs in synchronous spectra. We performed multiplication on the two signs of each cross-peak. The final results have been presented in Table 2. For each final sign of a cross-peak, there are two corresponding wavenumbers on the left and bottom, respectively. Because all the signs are above the diagonal line (\(\nu_1 = \nu_2\)) in accordance with our spectroscopic reading habits, the wavenumber on the bottom is affirmatively larger than the one on the left. If the sign is positive (+), the larger wavenumber or the bottom wavenumber will occur prior to the smaller wavenumber or the left wavenumber. Similarly, if the sign is negative (−), the left wavenumber will occur prior to the bottom wavenumber. If the sign is zero (or blank), we could not make an exact judgment.

With this method, we can quickly draw out the specific order of the eight bands with temperature perturbation. As temperature increased, the specific order taking place in neat liquid pyrrole was as follows (→ means earlier than): 6794 cm\(^{-1}\) → 6794 cm\(^{-1}\) → 6624, 6514, 6150 cm\(^{-1}\) → 6171 cm\(^{-1}\) → 6856 cm\(^{-1}\) → 6160 cm\(^{-1}\). That is, \(2\nu_4\) (N–H \(\cdots\) \(\pi\)) (dimer) → \(2\nu_2\) (free N–H) (dimer) → \(2\nu_4\) (N–H \(\cdots\) \(\pi\)) (cyclic polymer) (liquid-like), \(2\nu_5\) (N–H \(\cdots\) \(\pi\)) (cyclic polymer) (solid-like), \(2\nu_8\) (C–H) → \(\nu_8 + \nu_6\) (C–H) → \(2\nu_1\) (free N–H) (monomer) → \(\nu_8 + \nu_7\) (C–H), \(2\nu_6\) (C–H).

We can understand this sequence with the following three aspects.

**Sequence of NH-related hydrogen bonding.** Considering NH-related vibrational overtones separately, we can examine the changes of different pyrrole self-aggregated species under temperature perturbation. It indicates that pyrrole dimers responded to the increasing temperature first, then the cyclic polymers started to disaggregate, along with the changing content (increase) of pyrrole monomers. From conventional NIR spectra and differential spectra, we noted that the band intensities at 6794 and 6769 cm\(^{-1}\), corresponding to the two N–H stretching overtones in the T-shaped pyrrole dimers, both increased continuously with increasing temperature. The increasing intensity of these two characteristic bands should be the result of the larger cyclic pyrrole polymers disaggregating into the smaller dimers. That is, with temperature increasing, pyrrole experienced this disassociation process: cyclic polymers → dimers → monomers, but the second process occurred at the lower temperature due to the lower thermal stability of pyrrole dimers than cyclic polymers. As previously reported, the higher thermal stability of cyclic polymers come from the cooperativity effect among their structural units aggregated through T-shaped N–H \(\cdots\) \(\pi\) hydrogen bonding, and this cooperativity effect will be further enhanced as the number of units increases (up to five units according to the calculated results). Since, at higher temperatures, cyclic pyrrole polymers may have completely disaggregated, there was only one species of pyrrole self-aggregates (dimers) left changing in the system, which could explain the reduction of the increasing rate for the integral absorption of the region 7000–6430 cm\(^{-1}\) in Fig. 5(a).

<table>
<thead>
<tr>
<th>Table 2</th>
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<tr>
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<tr>
<td>6769</td>
<td>+ + + + + + + + + + + + + + + +</td>
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<tr>
<td>6794</td>
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<tr>
<td>6856</td>
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| 6856 | 6794 | 6769 | 6624 | 6514 | 6171 | 6160 | 6150 |

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Sequence of CH-related stretching modes. Considering the three CH-related vibrational overtones and combination modes, we can examine the changes of C–H stretching modes under temperature perturbation. It is interesting to find that all the three bands at 6171, 6160 and 6150 cm\(^{-1}\) are associated with the same fundamental stretching mode \(\nu_{C-H}\) (\(C-H\) (\(p\))), while the symmetry of the three fundamental stretching modes exhibits an increase in the order of \(\nu_{C-H} \), \(\nu_{C-H} \), \(\nu_{C-H} \). Combining this with the sequence of changing intensity 6150 cm\(^{-1}\) \((2\nu_{C-H}) \rightarrow 6171\) cm\(^{-1}\) \((\nu_{C-H} + \nu_{C-H}) \rightarrow 6160\) cm\(^{-1}\) \((\nu_{C-H} + \nu_{C-H} + \nu_{C-H})\), we can conclude that C–H stretching vibrations experienced a changing process from asymmetric modes to symmetric modes with increasing temperature, which is in agreement with the changes of NH-related self-disassociation of pyrrole from hydrogen bonded dimers and polymers to free monomers.

Sequence between NH- and CH-related vibrations. From the sequence above, we noted that NH-related vibrations had an earlier response to increasing temperature than CH-related vibrations. It is understandable that the destruction of N–H \(\cdot \pi\) hydrogen bonding consequentially induced the electron density changes of pyrrole rings, which would further influence the CH-related vibrations. This phenomenon is in agreement with the previous experimental observations in liquid and solution phase pyrrole which showed the vibrational energy flow from the N–H to the ring through an intermolecular process.\(^{17}\)

D Explanations for band shift phenomenon of N–H \(\cdot \pi\) hydrogen bonding in pyrrole dimers

From our previous 2D correlation analysis, we obtained the specific order of the two characteristic bands for pyrrole dimers: 6769 cm\(^{-1}\) \(\rightarrow 6794\) cm\(^{-1}\). This was manifested as a band shift from 6759 cm\(^{-1}\) to 6794 cm\(^{-1}\) in conventional NIR spectra. When the temperature increased to nearly 115 °C, the end shifted wavenumber of N–H \(\cdot \pi\) hydrogen bonding had been equal to that of free N–H in pyrrole dimers (6794 cm\(^{-1}\)).

We studied this band shift phenomenon carefully, and only one changing process could explain it. That is, when temperature increased, pyrrole dimers with T-shaped geometry associated through N–H \(\cdot \pi\) hydrogen bonding continuously transformed to the ones with antiparallel geometry associated through \(\pi\)-stacking and dipole–dipole interactions. In other words, the increasing temperature is more beneficial to the latter process from 25 to 115 °C. The solid section of the arrow represents the tendency of dynamic variations among different pyrrole species with increasing temperature. The solid section of the arrow means an earlier response to temperature increasing, while the hollow one means a later response. Then the detailed changes can be described as follows: at lower temperature, pyrrole mainly self-aggregates into various sizes of clusters, including T-shaped dimers, cyclic trimers, cyclic tetramers, cyclic pentamers as well as more stable cyclic polymers. As temperature increased, the less stable dimers started to disassociate into monomers through an intermediate antiparallel geometry maintained by dipole–dipole and \(\pi\)-stacking interactions. At higher temperatures, the relatively stable larger cyclic polymers started to disaggregate into smaller dimers first, and then further into pyrrole monomers. Throughout the heating process, the content of pyrrole monomers was always increasing.

Conclusion

Near infrared spectroscopy (NIR) and 2D correlation spectroscopy (2Dclos) have been employed to study the dynamic self-disassociation behavior of neat liquid pyrrole in the heating process (25–115 °C). The direction of the central arrow represents the tendency of dynamic variations among different pyrrole species with increasing temperature. The solid section of the arrow means an earlier response to temperature increasing, while the hollow one means a later response. Then the detailed changes can be described as follows: at lower temperature, pyrrole mainly self-aggregates into various sizes of clusters, including T-shaped dimers, cyclic trimers, cyclic tetramers, cyclic pentamers as well as more stable cyclic polymers. As temperature increased, the less stable dimers started to disassociate into monomers through an intermediate antiparallel geometry maintained by dipole–dipole and \(\pi\)-stacking interactions. At higher temperatures, the relatively stable larger cyclic polymers started to disaggregate into smaller dimers first, and then further into pyrrole monomers. Throughout the heating process, the content of pyrrole monomers was always increasing.
pyrrole dimers had the first response to the increasing temperature, then more stable cyclic polymers started to disaggregate, along with the content increasing of pyrrole monomers. At the same time, CH-related vibrations experienced a changing process from asymmetric modes to symmetric modes, in conformity with the changes of NH-related self-dissociation of pyrrole from hydrogen bonded dimers and cyclic polymers to free monomers. NH-related hydrogen bonding had an earlier response to temperature increasing than CH-related vibrations.

On the other hand, we carefully investigated the band shift phenomenon of N–H → π hydrogen bonding in pyrrole dimers, and tentatively owed this band shift to the result of the transformation of pyrrole dimers from T-shaped geometry to an antiparallel geometry.

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