

# Vibrations of pyrrole, *N*-substituted pyrroles, and their cations

Alexander R. Davies, David J. Kemp, and Timothy G. Wright<sup>a</sup>

School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK

## Abstract

The vibrations of pyrrole, *N*-deuteropyrrole, *N*-fluoropyrrole, *N*-aminopyrrole and *N*-methylpyrrole are studied. The evolution of the vibrational wavenumbers of pyrrole is examined, as the mass of the nitrogen-bonded hydrogen atom is artificially increased. It is found that some vibrations are very sensitive to the mass of the substituent bonded to the nitrogen, and this can be viewed as vibrations mixing as that mass increases; however, these mixings stabilize by the time a mass of 14  $m_u$  is reached. A consistent numbering scheme for the ring-localized vibrations of *N*-substituted pyrroles is then put forward. A discussion of the vibrations of the cations of pyrrole and *N*-substituted pyrroles is then presented. Calculated vibrational wavenumbers are compared to experimental ones for pyrrole, *N*-deuteropyrrole and *N*-methylpyrrole, as well as the pyrrole cation.

**Key words:** pyrrole, *N*-substituted pyrroles, vibrations, cation

<sup>a</sup> Timothy G. Wright,

Professor of Physical and Theoretical Chemistry,

School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD (UK)

Phone: +44 115 8467076

FAX: +44 115 9513562

Email: Tim.Wright@nottingham.ac.uk

## 1. Introduction

Pyrroles are key building blocks of many biomolecules and medicines,<sup>1,2</sup> and can also be used in the formation of molecular wires.<sup>3</sup> There are various *N*-substituted pyrroles, but here we focus on *N*-deuteropyrrole (NDP), *N*-aminopyrrole (NAP), *N*-methypyrrole (NMP), and *N*-fluoropyrrole (NFP), in our analysis of the vibrations.

A compilation of the vibrational wavenumbers of ground state pyrrole (Pyr) from liquid/solution studies has been given by Scott.<sup>4</sup> More precise information on ground state vibrations would be obtained from dispersed fluorescence (DF) studies; however, these are hampered by the rapid dissociation of the excited electronic states of pyrrole following photoexcitation.<sup>5</sup> Further, we examine Pyr<sup>+</sup> and compare with the results of one-photon zero-electron-kinetic-energy (ZEKE) spectra of Pyr.<sup>6</sup> Although infrared spectroscopy has been used to study complexes of Pyr<sup>+</sup>, these have focused on the N-H stretching region.<sup>7</sup> Vibrational wavenumbers have been reported for the ground state of NDP,<sup>4</sup> but we are unaware of any values for the cation.

There has been little work on NAP to date, with the calculated geometry and harmonic vibrational wavenumbers published, albeit at a low level of theory.<sup>8</sup>

There have been several early studies on the vibrations of NMP, with many of the values being tabulated from these by Scott,<sup>4</sup> alongside a force field model. Further work on IR spectroscopy of NMP absorbed on oxide surfaces has also been published.<sup>9</sup> Some data relevant to the vibrations of NMP<sup>+</sup> are available via the observation of Rydberg states in absorption and resonance-enhanced multiphoton ionization (REMPI) spectra;<sup>10,11,12,13,14,15,16</sup> DF spectra from the first excited state have also been reported.<sup>13</sup> We have been examining the vibrations of NMP in its ground and first excited neutral states and ground state cation, as part of a combined laser-induced fluorescence and ZEKE study,<sup>15,17</sup> for which the present work is preparatory. As such, we refrain from a detailed examination of the vibrations of NMP and NMP<sup>+</sup> herein, restricting ourselves to reporting the calculated wavenumber values for each vibrational mode. In forthcoming work,<sup>17</sup> we shall comment on the DF spectra of Biswas et al.,<sup>13</sup> and the proposed assignments of the first excited neutral state vibrations,<sup>13,16</sup> as well as reported vibrational wavenumbers and assignments for vibration of the cation.

We also find that there has been very little work on NFP, with its geometry having been reported using low-level *ab initio*<sup>18</sup> and semi-empirical<sup>19</sup> calculations.

## 2. Computational details

All geometry optimization and harmonic vibrational frequency calculations were undertaken using Gaussian 16.<sup>20</sup> We employ (U)B3LYP/aug-cc-pVTZ calculations, with the unrestricted version being used for the cations. Geometries are optimized, and vibrational wavenumbers calculated, at the respective minima; the harmonic vibrational wavenumbers are scaled by a factor of 0.97,<sup>21</sup> which we have also used successfully in previous studies on substituted benzenes. We have based our methodology on that we employed when putting forward a consistent labelling scheme for the vibrations of the ring-based vibrations of the monosubstituted benzenes,<sup>22</sup> and for each of the three isomeric classes of disubstituted benzenes.<sup>23,24,25</sup> Such schemes allow comparison of vibrational activity across molecules from the same isomeric class. Here, we wish to examine the evolution of the vibrations of pyrrole as the nitrogen-bonded hydrogen atom is changed to different substituents. We do this by initially performing “artificial isotope” calculations whereby the mass of the nitrogen-bonded hydrogen atom is increased through 1 to 19  $m_u$ , to observe how the mass of the substituent affects these vibrations without introducing any changes as a result of electronic effects associated with explicitly changing the substituent. The variations in the vibrational wavenumbers can then be tracked as a function of this mass. The values obtained with that approach can then be compared to the actual calculated values for NDP, NAP, NFP and NMP. We then repeat the calculations for the cations.

## 3. Results and Discussion

### 3.1. Optimized geometries: neutral molecules.

All structures were optimized, with the resultant geometries shown in Figure 1, with a complete set of values for the geometric parameters given in the Supplementary Material.

For pyrrole, excellent agreement is obtained between the present calculated geometry [Figure 1(a)] and the structure determined from microwave studies on various isotopologues;<sup>26</sup> good agreement is also seen with the B3LYP-D3/aug-cc-pVTZ calculated structure reported in Ref. 7.

For NAP, agreement is reasonable between the present geometry [Figure 1(c)] and the calculated one presented in Ref. 18; it is also consistent with that discussed in an X-ray and NMR study.<sup>19</sup> Very good agreement is seen with the results of B3LYP/6-31+G\*\* calculations.<sup>8</sup> It is notable that the hydrogens of the NH<sub>2</sub> group lie perpendicular to the plane of the pyrrolyl ring, in contrast to aniline, where the NH<sub>2</sub> group is rotated by 90° relative to NAP. A suggested rationale<sup>18</sup> for the NAP geometry was that

this is a balance between the repulsion of the nitrogen lone pairs, and the energy gained by delocalization of the -NH<sub>2</sub> lone pair into the ring  $\pi$  system. It thus appears that, for aniline, there is more to be gained from the delocalization, while for NAP the repulsion remains the larger term and hence the amino group rotates, so that the lone pairs on the nitrogen atoms are orthogonal. We note that the -NH<sub>2</sub> group in NAP is tilted slightly off-vertical, to the left as viewed in Figure 1(c) – see Supplementary Material.

For NMP, good agreement is seen between the present structure [Figure 1(d)] and that deduced in microwave studies;<sup>27</sup> in particular, the ground state geometry has a staggered conformation of the methyl group, which agrees with other work.<sup>14,15</sup> Biswas et al.<sup>13</sup> have reported the results of MP2 and B3LYP calculations on NMP, using D95++ and 6-311G\*\* basis sets; the latter basis set gave the better agreement with the results obtained herein, with fairly similar results obtained with both levels of theory. Good agreement is also seen with the B3LYP/6-31+G\*\* results of Ref. 8.

To our knowledge, there have been no experimental determinations of the geometry of NFP, but very good agreement between the present geometry [Figure 1(b)] and that obtained with B3LYP/6-31+G\*\* calculations<sup>8</sup> is evident, although no vibrational wavenumbers were reported.

### 3.2. Vibrations: neutrals

Calculated vibrational wavenumbers for Pyr and NDP are presented in Table 1, and compared to experimental values, taken from Scott,<sup>4</sup> where available. In that work, the reported wavenumbers are separated into symmetry classes, which have been used here to assign to a particular mode. The numbering here follows the Mulliken<sup>28</sup>/Herzberg<sup>29</sup> scheme, and the vibrational modes of pyrrole are shown in Figure 2; these also agree with the modes reported in Ref. 4, obtained from a force field model. Generally, very good agreement is found, noting that the experimental data was obtained in liquids/solutions, and so are expected to be shifted from gas-phase values. Overall though, as has been shown with our previous work,<sup>22,23,24,25</sup> the modest level of theory employed here performs surprisingly well.

In Table 2 and Table 3, we show the calculated vibrational wavenumbers for NAP, NFP and NMP, where the numbering will be discussed later in this subsection.

Vibrational wavenumbers have previously been calculated for NAP using a small basis set, where the ring-localized and NH<sub>2</sub>-localized vibrations were listed together in C<sub>s</sub> symmetry classes;<sup>18</sup> no scaling was performed, but if a scaling factor of 0.9 is applied,<sup>21</sup> many of the values are in close agreement with those presented herein (Table 2 and Table 3). An IR spectroscopic study in CCl<sub>4</sub> solutions<sup>30</sup>

reported symmetric and asymmetric stretch values for the NH<sub>2</sub>-localized vibrations, obtaining values of 3300 cm<sup>-1</sup> and 3371 cm<sup>-1</sup>, respectively; the present calculated values (Table 3), 3368 cm<sup>-1</sup> and 3444 cm<sup>-1</sup>, suggest that the experimental values have undergone a solvatochromatic shift.

We have been unable to locate any experimental or calculated vibrational wavenumber values for NFP, but present our calculated values in Table 2.

Calculated values for the vibrational wavenumbers of NMP have been reported by Biswas et al.<sup>13</sup> at the B3LYP/6-311G\*\* level of theory; these were unscaled and, despite the fact that the methyl group breaks the C<sub>2v</sub> symmetry, both the methyl- and ring-localized vibrations were collected together in C<sub>2v</sub> symmetry classes. These agree with the values obtained here (Table 2 and Table 3), provided a similar scaling factor similar is employed. Vibrational wavenumbers for the ground state neutral molecule have also been reported by Kanamaru,<sup>31</sup> at the MP2/6-31G\*\* level (unscaled), separated into both point group and molecular symmetry group classes; good agreement is seen with the present values. The available experimental values have been collated by Scott,<sup>4</sup> with very similar values having been obtained for some vibrations by Dines et al.<sup>9</sup> in a surface IR study – see Table 2. In Ref. 4, the vibrations were separated into *a'* and *a''* symmetry classes, but no specific assignments were made; in Ref. 9, a very brief description of each mode was given. In Table 2, we have associated each wavenumber with the best match to the calculated value, taking into account symmetry. Overall, good agreement is obtained between the present calculated values and the majority of the reported experimental ones. One exception is that for  $\nu_{20}$  for NDP; we suggest that this assignment is incorrect, with a possible reassignment to the first overtone of  $P_{11}$ .

Of note is that there are three *a*<sub>1</sub> symmetry vibrations with wavenumbers > 3000 cm<sup>-1</sup> for Pyr, but only two such for NDP, NAP, NMP and NFP, and as discussed below, this is because the N-X stretch vibration decreases sharply in wavenumber as the mass of substituent X increases; other vibrations will also be seen to be highly mass dependent.

In earlier work, we have put forward a consistent labelling scheme for monosubstituted benzenes.<sup>22</sup> The ideas underpinning this are that when substituents are added, both the wavenumber and vibrational motion can alter as a result of both mass and electron density changes, but also extra vibrations are present when the substituent is larger than a single atom. The former means that labelling schemes based upon the vibrational motions in the unsubstituted species, such as the Wilson labels<sup>32</sup> for benzene, can be highly misleading when applied to the substituted species; the latter means that labels based upon a wavenumber ordering of the vibrations, such as the Mulliken<sup>28</sup>/Herzberg<sup>29</sup> scheme, will lead to different numbers for the same vibrational motion.

Varsányi<sup>33</sup> attempted to bring order to the labels in substituted benzenes, but we have shown that those still contain significant labelling inconsistencies between similar molecules.<sup>22,23,24,25</sup> As such, in the present work, using a similar approach to Ref. 22, we put forward labels that will prove useful both in labelling the vibrations of *N*-substituted pyrroles, but we also will show how the vibrations of the parent pyrrole molecule are related to these. The scheme is based on the twenty-four ring-based vibrations, with those that are largely localised on the substituent being deemed to be separate from these: essentially, we are treating the substituent as a point mass. We calculate the vibrations as the mass of the nitrogen-bonded substituent changes. It has previously been found that, for ground state neutral substituted benzenes, there is relatively little mixing of the substituent-localized and ring-based vibrations, and similarly that electronic effects are usually small.<sup>22,23,24,25</sup>

In Figure 3(a) we show the variations in the calculated vibrational wavenumbers of pyrrole, where the mass of the nitrogen-bonded hydrogen is artificially increased from 1 to 19  $m_u$ . We also show expanded views of the 1-3  $m_u$  region in Figure 3(b) for the  $a_1$  and  $b_2$  vibrations that are particularly mass dependent; we highlight that all of the  $a_2$  symmetry vibrations are only weakly mass dependent – see Figure 3(a). On the left-hand side of each plot, the vibrations are those of <sup>1</sup>H-Pyr, while on moving across to the right-hand side, we expect these vibrations to resemble closely those of the *N*-substituted pyrroles. The plots show behaviour that is reminiscent of interactions and avoided crossings that one would see in potential energy curves of diatomic molecules. We interpret such behaviour as vibrations becoming mixed versions of each other, with the mixing particularly marked close to an “avoided crossing” region; these then evolve further, in some cases closely resembling their original forms, but with altered energy ordering (see Refs. 22 and 23 for further similar discussion and commentary); others largely lose their original identity and become significant mixtures of the original pyrrole modes. The mixing of the modes is indicated via a Duschinsky matrix in Figure 4 where the <sup>15</sup>H-Pyr modes are expressed in terms of the <sup>1</sup>H-Pyr modes; this, and other such matrices were created with the FC-LabII program.<sup>34</sup> The Duschinsky matrix in Figure 4 indicates that the vibrations of <sup>15</sup>H-Pyr are very different to those of <sup>1</sup>H-Pyr; however, from Figure 3, it is clear that, in all but one case, the curves do not undergo any further avoided crossings after 3  $m_u$ , and all become largely parallel at masses greater than 14  $m_u$ . In our earlier work,<sup>22,23,24,25</sup> we used similar observations to propose consistent labelling schemes based on monofluoro- or difluoro-substituted benzenes, such that the labels were good representations of the ring motions, whatever the substituents. Some of the largest changes occurred in the low mass region, and the same behaviour is seen here; this region represents the largest relative changes in mass, so this is not unexpected – see Figure 3(b). We thus propose a set of labels for the vibrations of *N*-substituted pyrroles that we expect to be valid for all commonly-occurring nitrogen-bonded substituents, except for commonly-occurring isotopes of hydrogen; we

denote these vibrations,  $P_i$ , with the index,  $i$ , being determined by the Mulliken<sup>28</sup>/Herzberg<sup>29</sup> numbering for ground state neutral NFP. The calculated vibrational motions for NFP and the  $P_i$  labels are shown in Figure 5.

In Table 2 we have given both the vibrational wavenumbers calculated for <sup>19</sup>H-Pyr and those calculated for NFP, and similarly for NAP and <sup>14</sup>H-Pyr, and NMP and <sup>15</sup>H-Pyr. The agreement between the two sets is generally very good, showing that the majority of the wavenumber variations result from the mass change; this is emphasised by the ratios presented, which show values close to 1.00. There are a few exceptions, which suggests that these modes are sensitive to electronic effects caused by the substitutions; these could include hyperconjugation and inductive effects. These effects, however, are not sufficient to cause any ambiguities in the assignment of the modes.

### 3.3. Optimized geometries: cations

Very little information is available on the cations. cursory information is available in the one-photon ZEKE spectrum of pyrrole on the approximate change in geometry,<sup>6</sup> with a more-detailed structure for Pyr<sup>+</sup> being available at the B3LYP-D3/aug-cc-pVTZ level in Ref. 7; the present structure, Figure 1(a), is in excellent agreement with that.

We have been unable to find any information on the geometry of NAP<sup>+</sup>, although its first and second vertical ionization energies have been measured as 8.36 eV and 9.03 eV, respectively.<sup>35</sup> We find that the amino group in the cation is planar, in contrast to the pyramidal structure in the neutral [Figure 1(c)], which is reminiscent of the planar ← pyramidal geometry changes that occurs for ammonia<sup>36</sup> and aniline;<sup>37</sup> although, as noted above, the NH<sub>2</sub> group in the neutral NAP is rotated 90° compared to neutral aniline. Our rationale for the planar geometry of NAP<sup>+</sup> is that the positive charge, mainly localized in the pyrrolyl ring  $\pi$  system, makes it more favourable for the -NH<sub>2</sub> lone pair to become involved in the  $\pi$  system, causing partial double-bond character in the N-N bond; this is confirmed by the significant shortening of this bond [Figure 1(c)] upon ionization. This also forces both N atoms to have a hybridization close to sp<sup>2</sup>, and so producing a planar geometry.

For NMP<sup>+</sup>, there is a change in conformation of the methyl group upon ionization, with there being a staggered geometry in the ground state neutral, while the cation has an eclipsed geometry – see Figure 1(b). This is in agreement with the results of recent ZEKE and two-dimensional laser-induced fluorescence (2D-LIF) spectroscopy from our group.<sup>15,17</sup>

We are unaware of any calculated or experimental information on the structure of NFP<sup>+</sup>.

### 3.4. Vibrations: cations

In Figure 6, we show plots similar to those in Figure 3, but now for the cation, where we are varying the mass of the nitrogen-bonded hydrogen atom of Pyr<sup>+</sup> artificially from 1 to 19  $m_u$ . In general terms, very similar behaviour is observed for the cation and the neutral, although there are some differences, owing to the different force fields in these species. Importantly, however, the main conclusion holds: namely, that the vibrations have settled down in form to higher mass and hence the ring-localized motions will be very similar for different substituents, excluding for commonly-occurring hydrogen isotopes. In Figure 7(a), we show Duschinsky matrices that express the <sup>1</sup>H-Pyr<sup>+</sup> vibrations in terms of the <sup>1</sup>H-Pyr ones, using the standard Mulliken<sup>28</sup>/Herzberg<sup>29</sup> labelling scheme for each of these. It can be seen that there is significant mixing of the vibrations between these two states, so much so that many of the cation vibrations cannot be straightforwardly identified with a single ground state vibration. This is true both from the Duschinsky mixing matrix, but also upon examining animations of the modes of the vibration. As such, for pyrrole, and NDP, we conclude that the ground state neutral and cation vibrations must be labelled separately.

Yang et al.<sup>6</sup> have recorded a one-photon ZEKE spectrum of Pyr and assigned a significant number of the fundamental vibrations of Pyr<sup>+</sup>, which are shown alongside the present calculated values in Table 4. Interestingly, as well as the expected totally-symmetric vibrations being active in the spectrum, a number of formally symmetry-forbidden bands were also observed, although mechanisms exist to explain this.<sup>38</sup> The agreement between the experimental values and those calculated here and in Ref. 6 (if scaled similarly), using the same DFT method and similar basis sets, supports the assignments offered, in terms of Mulliken<sup>28</sup>/Herzberg<sup>29</sup> labels, but with the caveat that many of the cation vibrations will be significantly altered from those of the neutral molecule. The calculated value of the N-H stretch vibration in gas-phase Pyr<sup>+</sup> was 3459 cm<sup>-1</sup> in Ref. 7, which is in good agreement with the present calculated value (3489 cm<sup>-1</sup>) – Table 4.

In Table 5 we present the calculated values for the ring-localized vibrations of *N*-substituted pyrrole cations, and compare those calculated by artificially changing the nitrogen-bonded hydrogen atom in Pyr<sup>+</sup>. (The substituent vibrational wavenumbers for NAP, NMP and their cations, are given in Table 3.) Although many of the vibrations compare well between the two approaches, there are some notable differences, indicating more significant perturbations to the electronic structure; this is particularly true for NAP<sup>+</sup>, where we have noted that there is a significant change in geometry (pyramidal → planar) upon ionization. We highlight that amongst the  $a_1$  vibrations, except for NAP<sup>+</sup>,  $P_6$  and  $P_7$  have switched wavenumber order upon ionization, while for the  $b_2$  symmetry vibrations,  $P_{20}$  and  $P_{21}$  have changed order for all species – these points have been confirmed by careful examination of the



motions. These comments are borne out by the Duschinsky matrices presented in Figure 7(b) and Figure 7(c) that, despite showing some mixing, are largely dominated by the diagonal elements. It is also the case that that  $P_{20}$  and  $P_{23}$  in  $\text{NAP}^+$  have become heavily mixed so that the ring and hydrogen motions do not completely correspond to the anticipated motion (Figure 5); as such, it was difficult to assign a  $P_i$  label based on the forms of the vibration alone and use has also been made of the wavenumber order. (Technical difficulties meant that it has not been possible to create the Duschinsky matrix for  $\text{NAP}/\text{NAP}^+$ .) Also, there is significant mixing between  $P_9$  and  $P_{23}$  in  $N$ -methylpyrrole [see Figure 7(b)], suggesting that the interaction with the methyl group is enough to cause the true point group symmetry,  $C_s$ , to be experienced, even though the torsional barrier is  $\sim 10 \text{ cm}^{-1}$  in the cation.<sup>15</sup> The geometry can be seen to deviate from  $C_{2v}$  [Figure 1(b)], and  $a_1$  and  $b_2$  symmetries in  $C_{2v}$  both become  $a'$  in  $C_s$  symmetry. Although assigning a  $P_i$  label was still possible upon visualization of the vibrational mode.

#### 4. Further remarks and conclusions

In the above we have presented a complete set of geometries and vibrational wavenumbers for Pyr, NAP, NMP and NFP, together with those for their cations. We have shown that there is a strong mass dependence for some of the vibrations as the mass of the nitrogen-bonded substituent increases. This can be viewed as mixing of the pyrrole modes, and this means that many of the vibrations of the substituted pyrroles are very different to those of pyrrole itself; this is the case for both the neutral and cation species. The implication is that one cannot use the same labels for the vibrations of pyrroles and substituted pyrroles, in a similar way to that demonstrated in the corresponding case of benzenes.<sup>22,23,24,25</sup> However, for substituents with masses  $> 14 m_u$  (i.e. most commonly-occurring substituents), the forms of the vibrations are very similar – see Figure 3 – making it meaningful to label these with the same number. Indeed, even though the Duschinsky matrix might sometimes indicate a fair amount of mixing, for almost all vibrations it is relatively straightforward to identify the motion that corresponds to that in NFP from a visualization, and so to associate a  $P_i$  label with it.

Remarkably, many of the vibrational wavenumbers calculated from the pyrrole force field, while artificially increasing the mass of the nitrogen-bonded hydrogen atom, are in very good agreement with the “explicitly calculated” values, showing that electronic effects are generally small, particularly in the neutral molecules; indeed any deviations can be used as a signature that such vibrations are sensitive to substituent-induced electronic density changes. Further, although there was significantly more mixing of the modes upon ionization, it was still possible to use the  $P_i$  labels for the cation vibrations in almost all cases. For pyrrole itself, however, the modes changed substantially upon ionization, such that it is not straightforward to use the same labels for the neutral and cation.

We emphasise that the  $P_i$  labels are only expected to be applicable to the nitrogen-substituted species since, in our work on disubstituted benzenes, the vibrational motions change significantly between the *ortho*, *meta* and *para* cases.<sup>22,23,24,25</sup> This means that comparing vibrational activity upon excitation or ionization can be less than straightforward for different isomers,<sup>39</sup> but is a useful framework for assigning the spectra, and identifying phenomena such as Duschinsky mixing. Therefore, we expect the  $P_i$  labels will be useful in assigning the spectra of other *N*-substituted pyrroles, including alkyl pyrroles (other than NMP), *N*-borylpyrrole, *N*-phosphinylpyrroles, and alkali metal pyrrolides.

As indicated in the above, we shall soon publish our work on the vibrations of NMP in the ground and first excited neutral states, as well as the ground state cation,<sup>17</sup> following on from our work on the NMP torsions in the same three electronic states.<sup>15</sup>

### **Acknowledgements**

The EPSRC and the University of Nottingham are thanked for studentships to D.J.K. and A.R.D. We are grateful for access to the High-Performance Computing (HPC) resource at the University of Nottingham.

### **Data Availability Statement**

There are no additional data available for this work.

### **Supplementary Material**

Tables containing full sets of values for the geometric parameters of pyrrole, *N*-deuteropyrrole, *N*-aminopyrrole and *N*-methylpyrrole and their cations are provided.

**Table 1: Calculated and experimental vibrational wavenumbers (cm<sup>-1</sup>) for pyrrole, and *N*-deuteropyrrole in C<sub>2v</sub> symmetry.**

Symmetry	Mulliken <sup>a</sup>	Pyrrole		<i>N</i> -deuteropyrrole	
		Calculated <sup>b</sup>	Experiment <sup>c</sup>	Calculated <sup>b</sup>	Experiment <sup>c</sup>
<i>a</i> <sub>1</sub>	1	3561	3531	3166	3145 <sup>d</sup>
	2	3166	3145 <sup>d</sup>	3146	3131 <sup>d</sup>
	3	3146	3129 <sup>d</sup>	2622	2607
	4	1454	1467	1449	1460
	5	1372	1382	1372	1388
	6	1137	1144	1129	1139
	7	1057	1074	1056	1071
	8	1002	1016	998	1011
	9	875	881	863	869 <sup>d</sup>
<i>a</i> <sub>2</sub>	10	867	869	867	869 <sup>d</sup>
	11	682	710	682	708
	12	612	618	612	618
<i>b</i> <sub>1</sub>	13	826	826	823	824
	14	715	721	713	718
	15	623	601	599	
	16	483	474	375	
<i>b</i> <sub>2</sub>	17	3160	3145 <sup>d</sup>	3160	3145 <sup>d</sup>
	18	3135	3129 <sup>d</sup>	3135	3131 <sup>d</sup>
	19	1527	1530	1507	
	20	1400	1422	1337	1410 <sup>e</sup>
	21	1276	1287	1256	1210
	22	1121	1134	1061	
	23	1035	1048	898	909
	24	855	865	819	827

<sup>a</sup> Mulliken<sup>28</sup>/Herzberg<sup>29</sup> labels.

<sup>b</sup> This work – B3LYP/aug-cc-pVTZ, scaled by 0.97.

<sup>c</sup> Taken from the compilation in Ref. 4. (Note that an alternate axis system is used in Ref. 4 such that *b*<sub>1</sub> is *b*<sub>2</sub> in the present work and vice versa.)

<sup>d</sup> These values were not assigned uniquely in Ref. 4, and so each appears twice in a column.

<sup>e</sup> This assignment looks to be incorrect; in the text we have suggested a reassignment to the first overtone of *P*<sub>11</sub>.

**Table 2: Calculated and experimental wavenumbers (cm<sup>-1</sup>) for the ring-localized vibrations of *N*-aminopyrrole, *N*-methylpyrrole, *N*-fluoropyrrole, and the corresponding <sup>x</sup>H-Pyr in C<sub>2v</sub> symmetry.**

Symmetry	<i>P<sub>i</sub></i>	NAP		NMP			NFP	
		<sup>14</sup> H-Pyr <sup>a</sup>	Calculated <sup>b</sup>	<sup>15</sup> H-Pyr <sup>a</sup>	Calculated <sup>b</sup>	Experiment <sup>c</sup>	<sup>19</sup> H-Pyr <sup>a</sup>	Calculated <sup>b</sup>
<i>a</i> <sub>1</sub>	1	3166 (0.997)	3174	3166 (1.00)	3160	3130 <sup>d</sup> (3126)	3166 (0.993)	3187
	2	3146 (1.00)	3146	3146 (1.00)	3141	3103 <sup>d</sup> (3101)	3146 (0.997)	3155
	3	1573 (1.07)	1470	1566 (1.05)	1492	1504 (1509)	1548 (1.07)	1446
	4	1374 (0.999)	1377	1374 (1.00)	1375	1416 (1419)	1373 (1.00)	1367
	5	1362 (1.06)	1282	1358 (1.06)	1278	1286 (1288)	1343 (1.07)	1254
	6	1080 (1.01)	1066	1079 (1.00)	1075	1088 (1091)	1076 (1.03)	1048
	7	1048 (1.01)	1042	1048 (1.00)	1045	1058 (1055)	1047 (1.01)	1033
	8	969 (1.01)	957	968 (1.01)	956	966	964 (1.02)	948
	9	680 (1.03)	658	668 (1.02)	652	662	627 (0.992)	632
<i>a</i> <sub>2</sub>	10	867 (1.00)	865	867 (1.00)	863	858	867 (1.01)	858
	11	682 (1.02)	667	682 (1.01)	675	688	682 (1.08)	629
	12	612 (0.994)	616	612 (1.00)	610		612 (1.01)	608
<i>b</i> <sub>1</sub>	13	821 (1.00)	818	821 (1.01)	814	815	821 (1.03)	796
	14	712 (1.00)	712	712 (1.00)	712	720	712 (1.05)	681
	15	590 (1.01)	587	590 (0.978)	603	601	590 (1.12)	527
	16	207 (1.10)	188	204 (1.10)	186	186	196 (1.39)	141
<i>b</i> <sub>2</sub>	17	3160 (1.00)	3158	3160 (1.00)	3152	3130 <sup>d</sup> (3126)	3160 (0.992)	3184
	18	3135 (1.00)	3134	3135 (1.00)	3132	3103 <sup>d</sup> (3101)	3135 (0.997)	3143
	19	1503 (0.999)	1504	1503 (0.999)	1505	1547	1503 (1.01)	1493
	20	1321 (0.990)	1334	1321 (0.979)	1350		1321 (0.962)	1373
	21	1245 (1.00)	1242	1245 (0.987)	1262	1232	1245 (1.00)	1239
	22	1055 (1.00)	1052	1055 (0.983)	1073	1043	1055 (1.01)	1046
	23	865 (1.01)	855	865 (1.00)	864	868	865 (1.02)	845
	24	422 (1.07)	394	415 (1.20)	347	354	391 (1.01)	388

<sup>a</sup> This work. These are obtained using the B3LYP/aug-cc-pVTZ force constants for Pyr and calculating the vibrational wavenumbers with the mass of the nitrogen-bonded hydrogen atom changed to the indicated mass, in  $m_u$ ; the vibrational wavenumbers were then scaled by 0.97. The values in parentheses are the ratio of the <sup>x</sup>H-Pyr value to that calculated for the actual molecule.

<sup>b</sup> This work – B3LYP/aug-cc-pVTZ, scaled by 0.97.

<sup>c</sup> Taken from the compilation in Ref. 4, with the values in parenthesis being from a surface IR study.<sup>9</sup>

<sup>d</sup> This value was not assigned uniquely in Ref. 4.

**Table 3: Calculated wavenumbers (cm<sup>-1</sup>) for the substituent-localized vibrations<sup>a</sup>**

Mode <sup>a</sup>	Description <sup>b</sup>	Neutral		Cation
		Calculated <sup>c</sup>	Experiment	Calculated <sup>c</sup>
<i>N</i> -aminopyrrole				
Am <sub>1</sub>	asym str	3444	3371 <sup>d</sup>	3560
Am <sub>2</sub>	sym str	3368	3300 <sup>d</sup>	3422
Am <sub>3</sub>	bend	1635		1600
Am <sub>4</sub>	rock	1284		1212
Am <sub>5</sub>	inversion	882		197
Am <sub>6</sub>	torsion	253		355
<i>N</i> -methylpyrrole				
Me <sub>1</sub>	asym CH <sub>2</sub> str	3026	2942 <sup>e,f</sup>	3051
Me <sub>2</sub>	sym CH <sub>2</sub> str	2996	2942 <sup>e,f</sup>	3071
Me <sub>3</sub>	sym CH <sub>3</sub> str	2935	2819 <sup>f</sup>	2976
Me <sub>4</sub>	asym. bend	1467	(1464) <sup>f</sup>	1442
Me <sub>5</sub>	sym bend	1447	1382 <sup>e,f</sup>	1463
Me <sub>6</sub>	umbrella	1409	1382 <sup>e,f</sup>	1408
Me <sub>7</sub>	sym rock <sup>g</sup>	1111	(1120) <sup>e</sup>	1117
Me <sub>8</sub>	asym rock <sup>g</sup>	1029	(1127) <sup>e</sup>	993
Me <sub>9</sub>	torsion	69		28

<sup>a</sup> The amine (Am) and methyl (Me) modes, numbered in decreasing wavenumber order in the neutral state, with cation vibrations given the same label for the corresponding motion. These motions are very distinct, and it is clear that the vibrational ordering changes upon ionization.

<sup>b</sup> Approximate description of the main motion.

<sup>c</sup> This work – B3LYP/aug-cc-pVTZ for the neutrals and UB3LYP/aug-cc-pVTZ for the cations, each scaled by 0.97.

<sup>d</sup> IR studies in CCl<sub>4</sub> solution.<sup>30</sup>

<sup>e</sup> Taken from the compilation in Ref. 4. Values in parentheses were estimated using a force field model derived from the available experimental data. This is our best attempt at associating the presented wavenumbers with these methyl-localized vibrations.

<sup>f</sup> This value was not assigned uniquely in Ref. 4.

<sup>g</sup> Of the two methyl rocks the higher wavenumber one (sym) is rocking towards and away from the ring in the cation, maintaining C<sub>s</sub> symmetry, while the lower wavenumber one (asym) is rocking either side of the reflection plane.

**Table 4: Calculated and experimental vibrational wavenumbers (cm<sup>-1</sup>) for pyrrole<sup>+</sup> and *N*-deuteropyrrole<sup>+</sup> in C<sub>2v</sub> symmetry.**

Symmetry	Mulliken <sup>a</sup>	Pyr <sup>+</sup>			NDP <sup>+</sup>
		Calculated		Experiment	Calculated
		YLM <sup>b</sup>	Present <sup>c</sup>	YLM <sup>b</sup>	Present <sup>c</sup>
<i>a</i> <sub>1</sub>	1	3602	3489		3168
	2	3271	3168		3149
	3	3253	3149		2574
	4	1549	1504	1508	1500
	5	1459	1415	1418	1409
	6	1177	1142	1150	1138
	7	1100	1066	1078	1062
	8	1075	1043	1060	1041
	9	897	869	874	856
<i>a</i> <sub>2</sub>	10	974	948	943	948
	11	858	836	838	836
	12	509	496	495	496
<i>b</i> <sub>1</sub>	13	904	884	895	880
	14	750	729	728	729
	15	670	653	679	498
<i>b</i> <sub>2</sub>	16	486	476		466
	17	3259	3156		3156
	18	3247	3143		3143
	19	1496	1450	1480	1374
	20	1336	1299	1353	1273
	21	1286	1247		1160
	22	1025	994	1003	968
	23	997	968	979	838
	24	735	713	715	713

<sup>a</sup> Mulliken<sup>28</sup>/Herzberg<sup>29</sup> labels.

<sup>b</sup> From a one-photon ZEKE spectroscopic study.<sup>6</sup>

<sup>c</sup> This work – UB3LYP/aug-cc-pVTZ, scaled by 0.97.

**Table 5: Calculated and experimental wavenumbers (cm<sup>-1</sup>) for the ring-localized vibrations of *N*-aminopyrrole<sup>+</sup>, *N*-methylpyrrole<sup>+</sup> and *N*-fluoropyrrole<sup>+</sup> and the corresponding <sup>x</sup>H-Pyr<sup>+</sup> in C<sub>2v</sub> symmetry.**

Symmetry	<i>P<sub>i</sub></i>	<sup>14</sup> H-Pyr <sup>+</sup> a	NAP <sup>+</sup> b	<sup>15</sup> H-Pyr <sup>+</sup> a	NMP <sup>+</sup> b	<sup>19</sup> H-Pyr <sup>+</sup> a	NFP <sup>+</sup> b
<i>a</i> <sub>1</sub>	1	3168 (0.997)	3176	3168 (1.00)	3167	3168 (1.00)	3165
	2	3149 (0.997)	3159	3149 (1.00)	3144	3149 (1.00)	3148
	3	1599 (1.07)	1494	1594 (1.04)	1527	1580 (1.05)	1508
	4	1467 (1.10)	1334	1466 (1.01)	1456	1463 (1.02)	1435
	5	1305 (0.912)	1431	1300 (1.07)	1218	1285 (1.04)	1239
	6	1050 (0.960)	1094	1050 (0.998)	1052	1050 (1.03)	1018
	7	1117 (1.13)	989	1116 (1.01)	1107	1114 (1.01)	1104
	8	995 (1.10)	906	993 (1.03)	968	987 (1.02)	970
	9	672 (0.984)	683	660 (1.08)	609 <sup>d</sup>	619 (0.964)	642
<i>a</i> <sub>2</sub>	10	948 (1.05)	906	948 (1.01)	942	948 (1.01)	939
	11	836 (1.24)	676	836 (1.00)	833	836 (1.03)	809
	12	496 (0.917)	541	496 (1.00)	495	496 (0.992)	500
<i>b</i> <sub>1</sub>	13	878 (1.02)	865	878 (1.01)	868	878 (1.03)	854
	14	729 (1.01)	723	729 (1.01)	721	729 (1.05)	697
	15	479 (0.813)	589	479 (0.978)	490	479 (1.13)	425
	16	261 (1.09)	240	258 (1.20)	215	247 (1.20)	206
<i>b</i> <sub>2</sub>	17	3156 (0.995)	3171	3156 (1.00)	3155	3156 (1.00)	3154
	18	3143 (0.997)	3154	3143 (1.00)	3138	3143 (1.00)	3143
	19	1361 (0.877)	1551	1361 (0.995)	1368	1361 (0.997)	1365
	20	1112 (0.869)	957 <sup>c</sup>	1112 (0.942)	1180	1111 (1.03)	1081
	21	1270 (1.33)	1280	1270 (0.995)	1275	1270 (1.01)	1252
	22	968 (0.902)	1073	968 (1.01)	955	968 (1.03)	938
	23	713 (1.26)	567 <sup>c</sup>	713 (1.10)	646 <sup>d</sup>	713 (1.39)	514
	24	428 (1.14)	374	421 (1.24)	340	397 (1.01)	392



<sup>a</sup> This work. These are obtained using the force constants for Pyr<sup>+</sup> calculated using UB3LYP/aug-cc-pVTZ and calculating the vibrational wavenumbers with the mass of the nitrogen-bonded hydrogen atom changed to the indicated mass, in  $m_u$ , scaled by 0.97. The values in parentheses are the ratio of the <sup>x</sup>H-Pyr<sup>+</sup> value to that calculated for the actual molecule.

<sup>b</sup> This work – UB3LYP/aug-cc-pVTZ, scaled by 0.97.

<sup>c</sup> Modes  $P_{20}$  and  $P_{23}$  become very mixed in NAP<sup>+</sup>, and have been assigned here on the basis of wavenumber.

<sup>d</sup> Although assignable, there is a significant amount of mixing between  $P_9$  and  $P_{23}$  in NMP<sup>+</sup> – see Figure 7 and text for more details.

## Figure Captions

**Figure 1:** Optimized geometries of the neutral (left) and cation (right) geometries of: (a) Pyr; (b) NFP; (c) NAP; and (d) NMP. Selected bond lengths are given here; a more complete set of geometric parameters is given as Supplementary Material.

**Figure 2:** Vibrational mode diagrams for pyrrole. The numbering follows the Mulliken<sup>28</sup>/Herzberg<sup>29</sup> labelling scheme. Nitrogen atoms are blue, carbon atoms are dark grey, and hydrogen atoms are white. The sizes of the arrow and +/- signs are approximate indications of the magnitudes of the atomic displacements. The calculated wavenumbers can be found in Table 1.

**Figure 3:** Mass correlation diagram for the neutral molecules,  $^1\text{H-Pyr} \rightarrow ^{19}\text{H-Pyr}$ . (a) Complete plots for  $^x\text{H-Pyr}$ ,  $x = 1-19 m_u$ , showing the variation of the vibrational wavenumbers for each  $C_{2v}$  symmetry class. (b) Expanded views of the  $^x\text{H-Pyr}$  ( $x = 1-3 m_u$ ) vibrational wavenumber variation for selected vibrations. The colours are merely a guide to the eye.

**Figure 4:** Duschinsky matrix showing how the  $^1\text{H-Py}$  and  $^{15}\text{H-Py}$  vibrations can be expressed as mixtures of each other.

**Figure 5:** Vibrational mode diagrams for *N*-fluoropyrrole. The numbering follows the Mulliken<sup>28</sup>/Herzberg<sup>29</sup> labelling scheme, which is then designated the  $P_i$  labelling scheme for *N*-substituted pyrroles herein, with the label remaining fixed for the same atomic motions. The  $C_{2v}$  symmetries of each mode are given. Nitrogen atoms are blue, fluorine atoms are yellow-green, carbon atoms are dark grey, and hydrogen atoms are white. The lengths of the arrows and the sizes of the +/- signs are approximate indications of the magnitudes of the atomic displacements. The calculated wavenumbers can be found in Table 2.

**Figure 6:** Mass correlation diagram for the cations,  $^1\text{H-Pyr}^+ \rightarrow ^{19}\text{H-Pyr}^+$ . (a) Complete plots for  $^x\text{H-Pyr}^+$ ,  $x = 1-19 m_u$ , showing the variation of the vibrational wavenumbers for each  $C_{2v}$  symmetry class. (b) Expanded views of the  $^x\text{H-Pyr}^+$  ( $x = 1-4 m_u$ ) vibrational wavenumber variation for selected vibrations. The colours are merely a guide to the eye. Note that  $P_6$  and  $P_7$ , and  $P_{20}$  and  $P_{21}$  have switched order in the cation, from that in the neutral.

Figure 7: Duschinsky matrices showing how the neutral and cation vibrations can be expressed as mixtures of each other: (a) for  $^1\text{H}$ -pyrrole/ $^1\text{H}$ -pyrrole $^+$ ; (b) for *N*-methylpyrrole/*N*-methylpyrrole $^+$ ; and (c) *N*-fluoropyrrole/*N*-fluoropyrrole $^+$ . For (a), separate Mulliken<sup>28</sup>/Herzberg<sup>29</sup> labels have been used for the neutral and cation vibrations, while for (b) and (c) the cation vibrations have been labelled with the  $P_i$  labels of the neutral; however, there is significant mixing, and we have generally used the label that indicates the greatest contribution – see text.

Figure 1

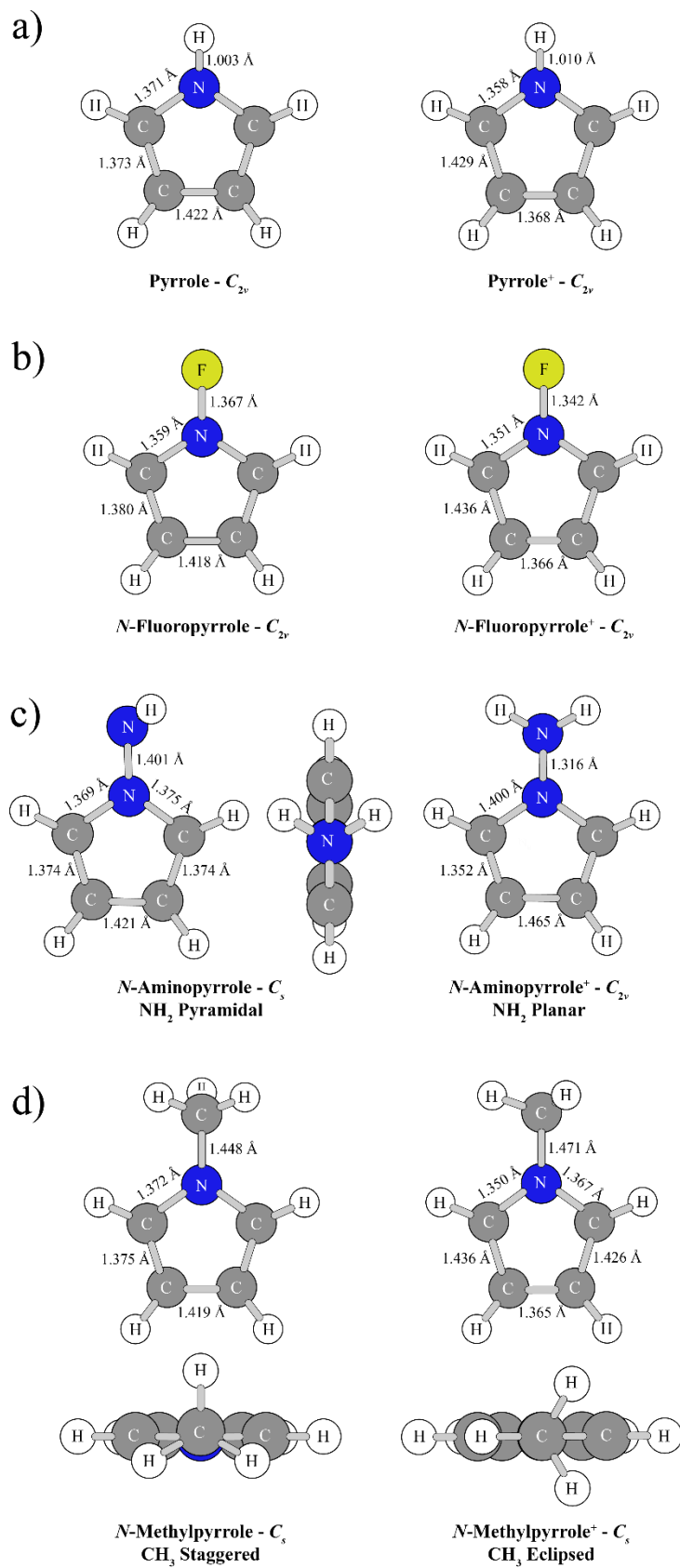
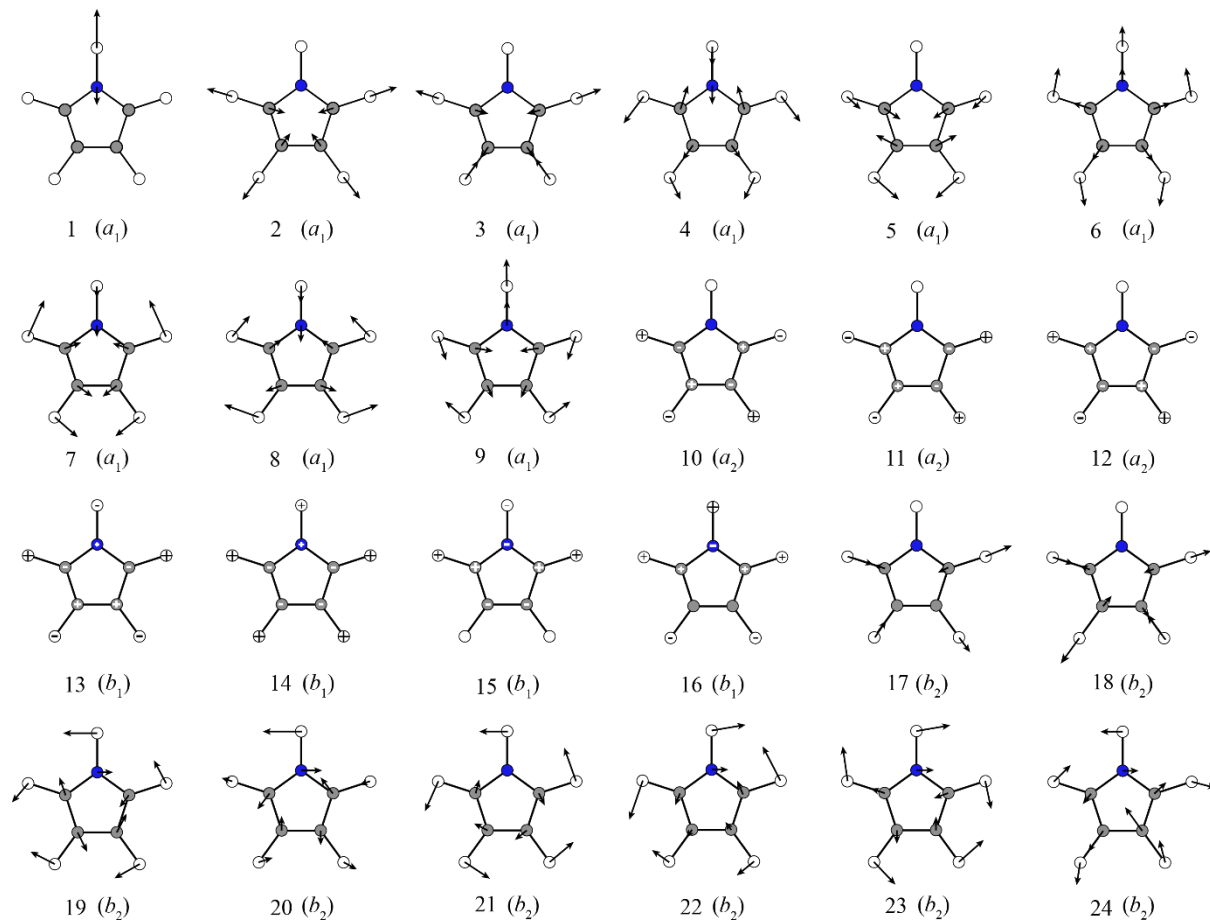


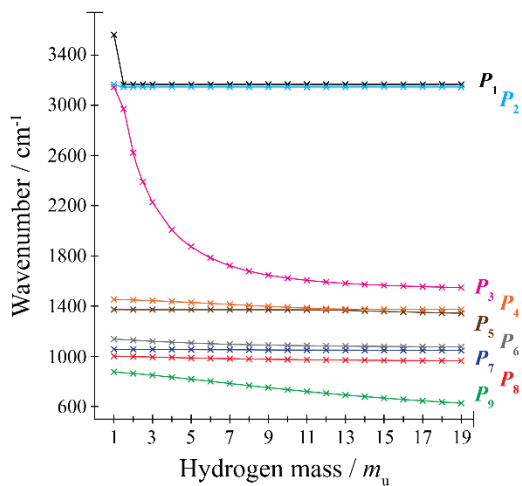
Figure 2



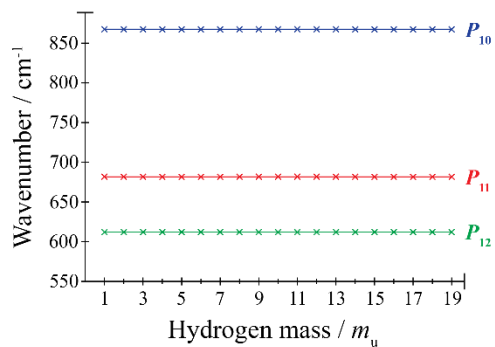
**Figure 3**

**a) Complete plots**

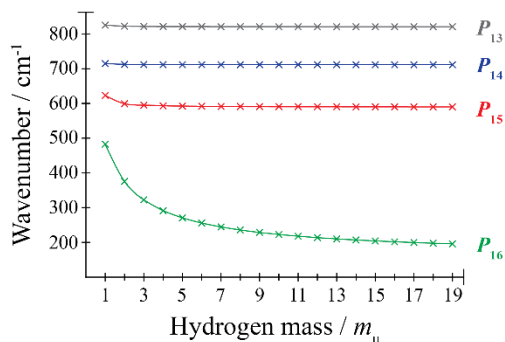
$a_1$  vibrations



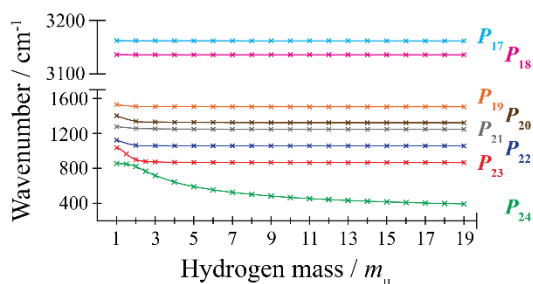
$a_2$  vibrations



$b_1$  vibrations

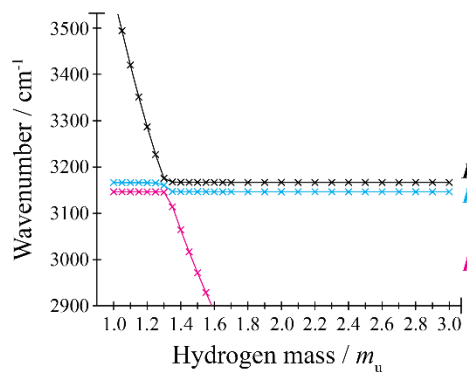


$b_2$  vibrations



**b) Expanded plots**

$a_1$  vibrations



$b_2$  vibrations

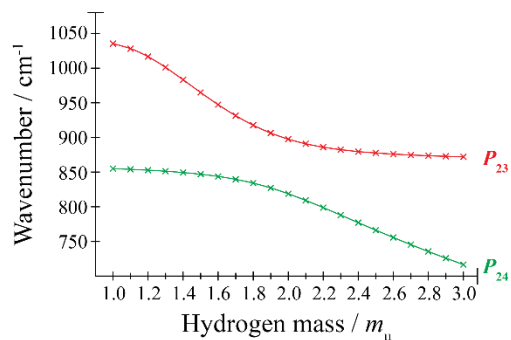


Figure 4:

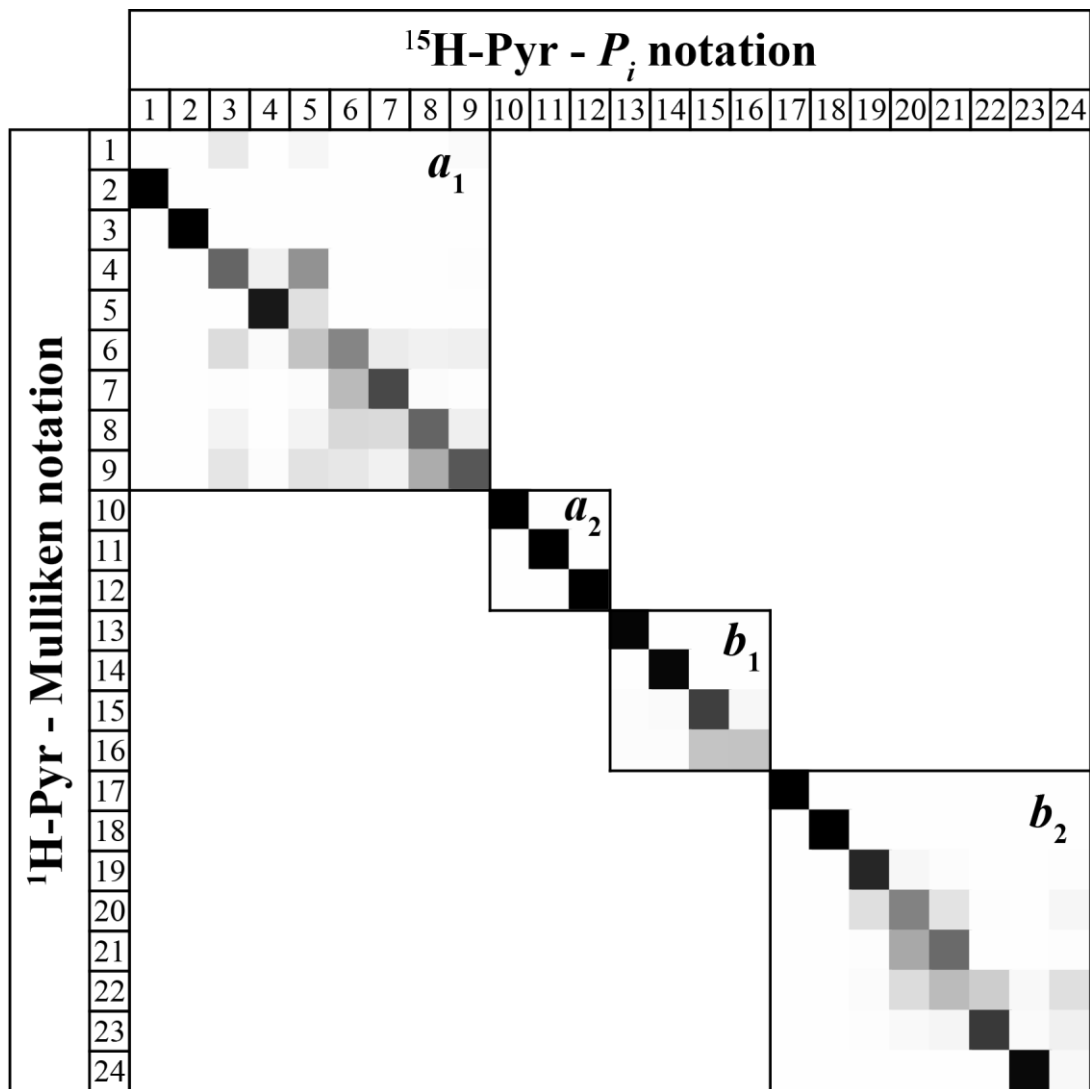
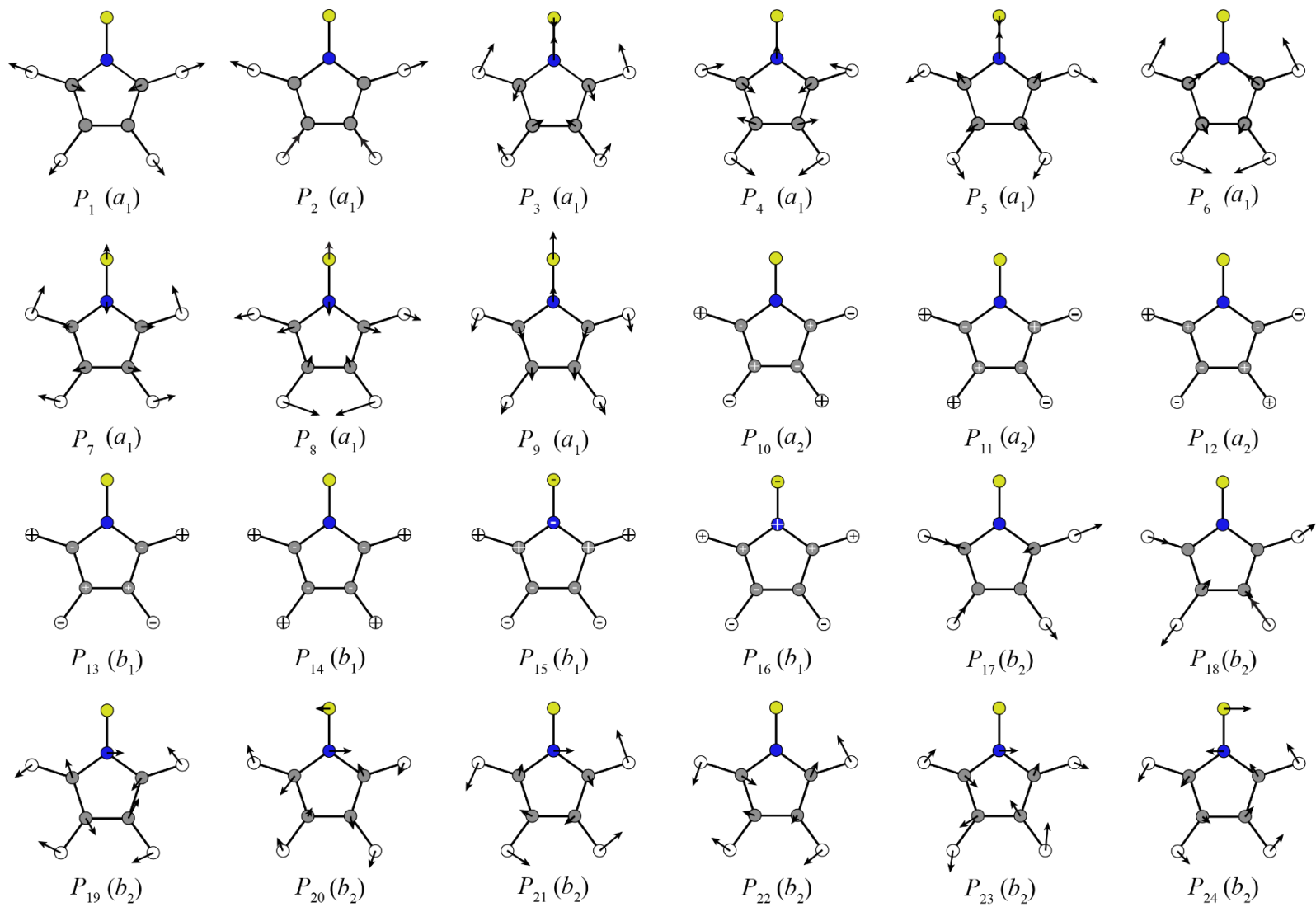


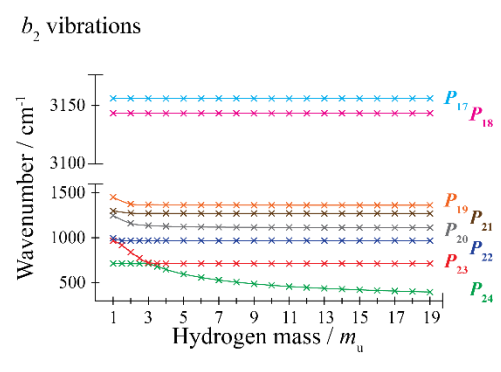
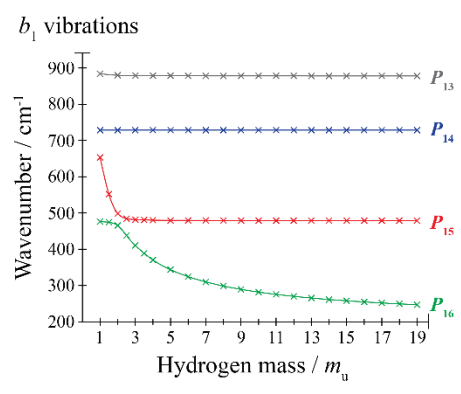
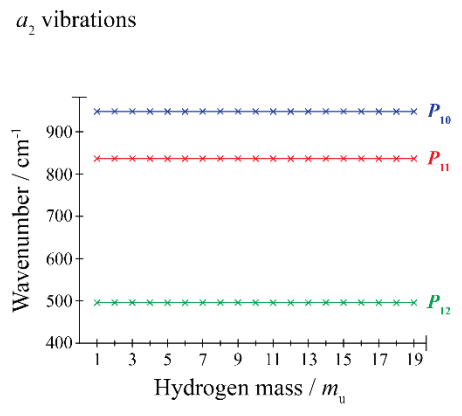
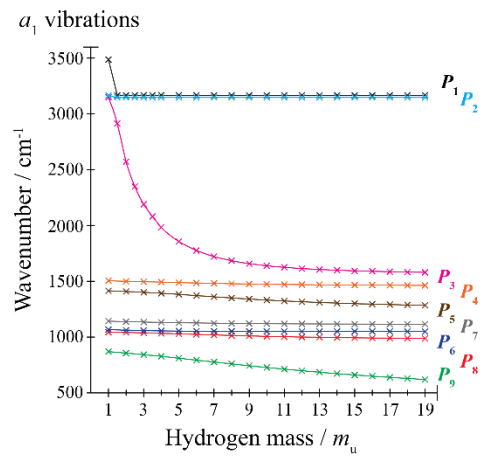
Figure 5





**Figure 6**

**a) Complete plots**



**b) Expanded plots**

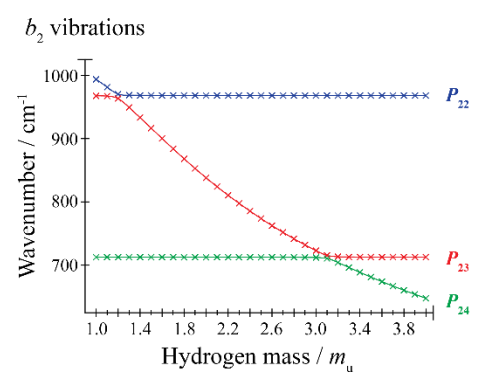
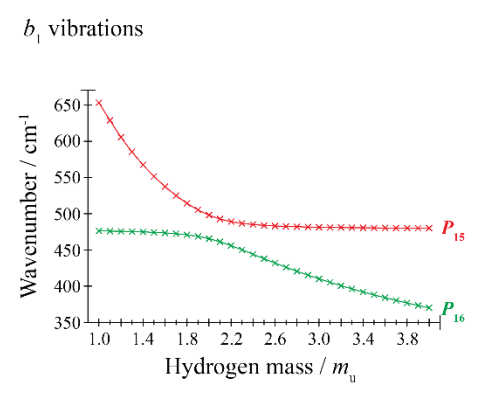
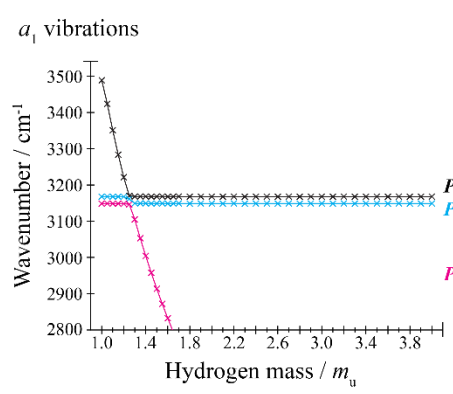
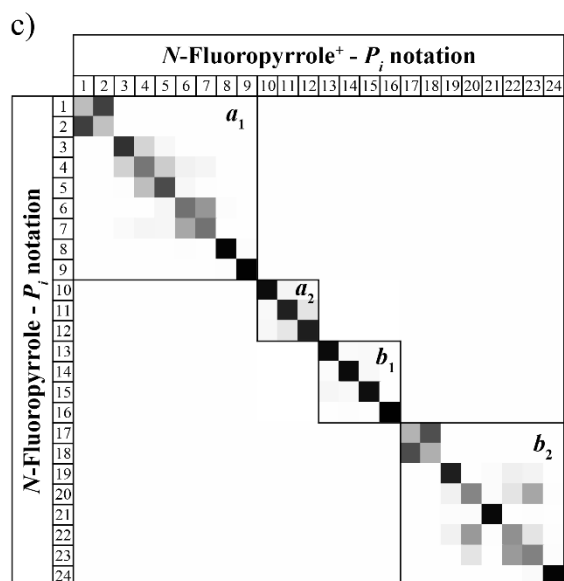
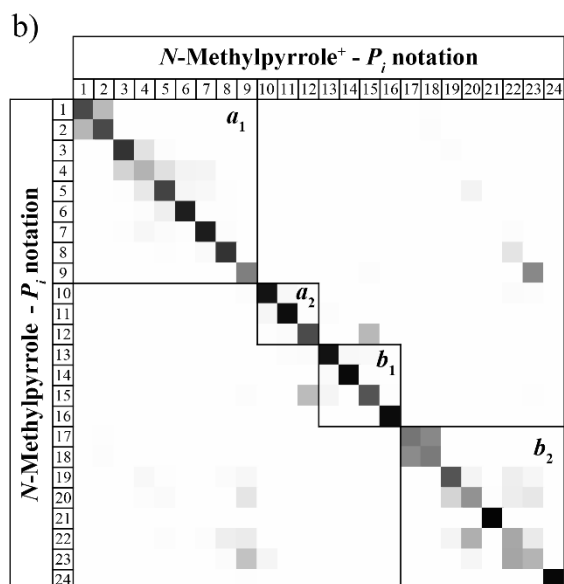
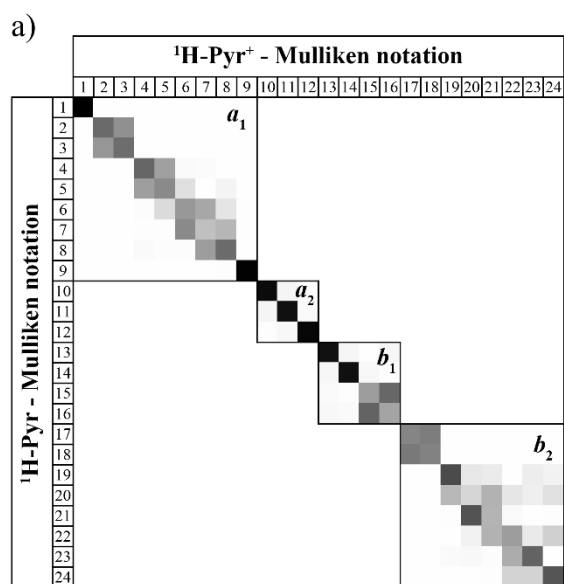


Figure 7



## References

---

- <sup>1</sup> V. Bhardwaj, D. Gumber, V. Abbot, S. Dhiman, and P. Sharma, *RSC Adv.* **5**, 15233 (2015).
- <sup>2</sup> S. Chavda, K. Mulder, T. Brown, H. Makay, B. Babu, L. Westrate, A. Ferguson, S. Lin, K. Kiakos, J. P. Ramos, M. Munde, W. D. Wilson, J. A. Hartley and M. Lee, *Med. Chem.* **6**, 150 (2010)
- <sup>3</sup> Y. Fu, X. Cheng, J. Zhao, T. Kong, C. Chi and X. Zhang, *Polymer J.* **44**, 1048 (2012).
- <sup>4</sup> D. W. Scott, *J. Molec. Spectrosc.* **37**, 77 (1971).
- <sup>5</sup> G. Wu, S. P. Neville, O. Schalk, T. Sekikawa, M. N. R. Ashfold, G. A. Worth and A. Stolow, *J. Chem. Phys.* **142**, 074302 (2015).
- <sup>6</sup> J. Yang, J. Li, and Y. Mo, *J. Chem. Phys.* **125**, 174313 (2006).
- <sup>7</sup> M. Schütz, Y. Matsumoto, A. Bouchet, M. Öztürk, and O. Dopfer, *Phys. Chem. Chem. Phys.* **19**, 3970 (2017).
- <sup>8</sup> K. Zborowski, I. Alkora and J. Elguero, *Struct. Chem.* **18**, 797 (2007).
- <sup>9</sup> T. J. Dines, L. D. Macgregor, and C. H. Rochester, *J. Coll. Interf. Sci.* **245**, 221 (2002).
- <sup>10</sup> G. Milazzo, *Gazz. Chim. Ital.* **74**, 152 (1944).
- <sup>11</sup> R. McDiarmid and X. Xing, *J. Chem. Phys.* **105**, 867 (1996).
- <sup>12</sup> C. D. Cooper, A. D. Williamson, J. C. Miller, and R. N. Compton, *J. Chem. Phys.* **73**, 1527 (1980).
- <sup>13</sup> N. Biswas, S. Wategaonkar, and J. G. Philis, *Chem. Phys.* **293**, 99 (2003).
- <sup>14</sup> J. G. Philis, *Chem. Phys. Lett.* **353**, 84 (2002).
- <sup>15</sup> A. R. Davies, D. J. Kemp, and T. G. Wright, *Chem. Phys. Lett.* (accepted, in press).
- <sup>16</sup> K. C. Woo and S. K. Kim, *Phys. Chem. Chem. Phys.* **21**, 14387 (2019).
- <sup>17</sup> A. R. Davies, D. J. Kemp, and T. G. Wright, work in progress.
- <sup>18</sup> N. V. Riggs and L. Radom, *Aust. J. Chem.* **241**, 397 (1988). Although not stated explicitly in this work, these appear to be Hartree-Fock (HF) theory calculations.
- <sup>19</sup> M. de al Concepción Foces-Foces, F. Hernández Cano, R. M. Claramunt, D. Sanz, J. Catalán, F. Abero, A. Fruchier, and J. Elguero, *J. Chem. Soc. Perkin Trans. 2* 237 (1990).
- <sup>20</sup> Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd,

- 
- E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- <sup>21</sup> P. Sinha, S. E. Boesch, C. Gu, R. A. Wheeler, and A. K. Wilson, *J. Phys. Chem. A* **108**, 9213 (2004).
- <sup>22</sup> A. M. Gardner and T. G. Wright, *J. Chem. Phys.* **135**, 114305 (2011).
- <sup>23</sup> A. Andrejeva, A. M. Gardner, W. D. Tuttle and T. G. Wright, *J. Molec. Spectrosc.*, **321**, 28 (2016).
- <sup>24</sup> W. D. Tuttle, A. M. Gardner, A. Andrejeva, D. J. Kemp, J. C. A. Wakefield and T. G. Wright, *J. Molec. Spectrosc.* **344**, 46 (2018).
- <sup>25</sup> D. J. Kemp, W. D. Tuttle, F. M. S. Jones, A. M. Gardner, A. Andrejeva, J. C. A. Wakefield and T. G. Wright, *J. Molec. Spectrosc.* **346**, 46 (2018).
- <sup>26</sup> L. Nygaard, J. T. Nielsen, J. Kirchheiner, G. Maltesen, J. Rastrup-Andersen, and G. Ole Sørensen, *J. Molec. Struct.* **3**, 491 (1969).
- <sup>27</sup> W. Arnold, H. Dreizler, and H. D. Rudolph, *Z. Naturforsch.* **23a**, 301 (1968).
- <sup>28</sup> R. S. Mulliken, *J. Chem. Phys.* **23**, 1997 (1955).
- <sup>29</sup> G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, Krieger, Malabar, 1991.
- <sup>30</sup> L. K. Dyllal, *Spectrochim. Acta. A*, **44**, 283 (1988).
- <sup>31</sup> N. Kanamaru, *J. Molec. Struct. (Theochem)* **686**, 15 (2004).
- <sup>32</sup> E. B. Wilson, Jr, *Phys. Rev.* **45**, 706, (1934).
- <sup>33</sup> G. Varsányi, *Assignments of the Vibrational Spectra of Seven Hundred Benzene Derivatives*, Wiley, New York, 1974.
- <sup>34</sup> I. Pugliesi and K. Müller-Dethlefs, *J. Phys. Chem. A*, **110**, 4657 (2006), a free download of the software can be found at <http://www.fclab2.net>
- <sup>35</sup> W. Flitsch, H. Peeters, W. Schulten, and P. Radelmacher, *Tetrahedron*, **34**, 2301 (1978).
- <sup>36</sup> G. Reiser, W. Habenicht, and K. Müller-Dethlefs, *J. Chem. Phys.* **98**, 8462 (1993).
- <sup>37</sup> X. Song, M. Yang, E. R. Davidson, and J. P. Reilly, *J. Chem. Phys.* **99**, 3224 (1993).
- <sup>38</sup> D. J. Kemp, A. M. Gardner, W. D. Tuttle, J. Midgley, K. L. Reid and T. G. Wright *J. Chem. Phys.* **149** 094301 (2018).
- <sup>39</sup> A. R. Davies, D. J. Kemp, and T. G. Wright, *AIP Advances*. (In press) DOI: 10.1063/5.0032146.