Inner shell electron energy loss spectroscopy of some heterocyclic molecules

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Received October 18, 1985
This paper is dedicated to Professor Arthur N. Bourns


The carbon K-shell spectra of gaseous furan, pyrrole, tetrahydrofuran, pyrrolidine, tetrahydroprpyran, and piperidine have been recorded by electron energy loss spectroscopy (ISEELS) under electric dipole scattering conditions (2.5 keV impact, small angle). The spectra are dominated by transitions to unoccupied valence states of π and σ symmetry. Features attributed to transitions to π*(CH2) levels are consistently observed below the ionization threshold in the spectra of the saturated species. The positions of continuum features are generally in agreement with a previously documented correlation with bond lengths. Additional weak continuum features are observed in the smaller saturated heterocyclic species which are ascribed to delocalized σ* states.


Faisant appel à la spectroscopie par perte d’énergie électronique (ISEELS) dans des conditions de diffusion des dipôles électriques (impact de 2.5 keV, petit angle), on a déterminé les spectres de la couche K du carbone du furanne, du pyrrole, du tétraéthylfuranne, de la pyrrolidine, du tétraéthylpyrpyrate et de la pipéridine à l’état gazeux. Les spectres sont dominés par des transitions vers des états de valence non-occupés de symétrie π ou σ. Dans les spectres des espèces saturées, on observe d’une façon systématique que les caractéristiques attribuables aux transitions vers les niveaux π*(CH2) apparaissent à des niveaux inférieurs à ceux du seuil d’ionisation. Les caractéristiques continues apparaissent généralement à des positions qui sont en accord avec les relations qui ont été observées antérieurement avec les longueurs des liaisons. Dans les espèces hétérocycliques saturées plus petites, on a observé des caractéristiques additionnelles continues faibles que l’on attribue à des états σ* délocalisés.

[Traduit par la revue]

Introduction

Over the last few years K-shell excitation studies by Inner Shell Electron Energy Loss (ISEELS) spectroscopy have proven to be particularly useful in examining the unoccupied energy levels of molecules containing the second row elements C, N, O, and F (1). The features present in the K-shell spectra of free molecules can be classified as transitions either to Rydberg orbitals or to unoccupied molecular orbitals of σ* or π* character. In contrast to valence shell excitation spectroscopy the latter dominate when the highly localized K-shell electrons are excited. An intriguing development in K-shell excitation is the evidence recently presented for an empirical relationship between bond length and σ shape resonance position (2, 3). According to this simple picture the K-shell spectrum of a molecule containing 2 or more second row atoms will exhibit a σ shape resonance associated with each bond. The position of this resonance relative to the core ionization potential (IP) can be related to the bond length through a correlation among all bonds of the same class defined by a parameter Z, the sum of the atomic numbers of the two bonded atoms. The correlation was developed from the spectra of diatomic and “pseudo-diatomic” molecules (e.g. C2H2, C2H4, HCN, H2CO etc.). A general goal of our research is to test the utility of the empirical relationship in larger molecules, both for bond length determination and spectral interpretation.

Recently studies have been reported on K-shell excitation in gas phase non-cyclic aliphatic hydrocarbons (2-4), cyclic aliphatics (5), and cyclic aromatics (6). In order to provide further understanding of inner shell excitation in different environments we have carried out an investigation of some saturated and unsaturated heterocyclic hydrocarbons, in particular furan (C4H4O), pyrrole (C4H5NH), tetrahydrofuran (C4H8O or THF), pyrrolidine (C5H11N), tetrahydroprpyran (C8H12O or THF), and piperidine (C5H12N). Heterocyclic molecules such as these are important in many organic and biochemical reactions. Furan and pyrrole in particular, have been the topics of extensive study (7). The ISEELS spectra of all of these molecules are compared to their cyclic hydrocarbon analogs (5) to explore the effect of the heteroatom on the electronic structure of the ring. The continuum features are interpreted in comparison with the results predicted from the previously documented correlation between the position of σ shape resonances and bond lengths (3).

Experimental

The experimental apparatus and techniques used to acquire the ISEELS spectra have been described in detail elsewhere (2, 5). Briefly, the spectra are produced by inelastic scattering of energetic electrons by gases at ca. 10^-4 Torr (10^-2 Pa). The spectrometer is operated with scattering angles of 1-2° and a final electron energy (2) of 2.5 keV. The spectral resolution is limited to 0.7 eV, largely determined by the thermal spread of electron energies in the monochromatized incident electron beam. The gases used were obtained from the vapours of high purity liquid samples, which, except for the THF and THP, were obtained commercially and used without further purification. THF was vacuum distilled to remove impurities (probably peroxides) detected in spectra recorded prior to distillation. A distilled THP sample was also studied to check for possible peroxide contamination. No changes were observed between the spectra of the distilled and undistilled THP samples. Air and volatile impurities in the liquids were removed by a series of freeze-pump-thaw cycles. The absolute energy scales were determined by calibrating the spectra relative to the C 1s → π* transition in CO (277.40(2) eV (8)), C2H4 (284.7(1) eV (4)) or CO2 (290.7(1) eV (9)); the N 1s → π* transition in N2 (401.10(2) eV (8)); or the O 1s → π* transition in CO (534.21(9) eV (8)). The calibrated gas was chosen for minimum overlap between the calibrated feature and the sharpest feature in the heterocyclic spectrum. In all cases the spectrum of a mixture of the two gases was recorded with each gas being let into the collision region through a separate leak valve to ensure a constant composition mixture. This approach is desirable since the spectrometer energy scale shifts slightly with changes in sample gas pressure or composition because of changes in the work function of the electron emitting surface and of surface potentials throughout the spectrometer.

Results and discussion

Knowledge of the core ionization threshold (IP) aids spectral analysis both through identification of Rydberg states through term values (10) and alignment of corresponding features in
different core edge spectra. In addition the correlation between shape resonance position and bond length (3) uses the IP as a reference level. Where available (11), gas phase ionization potentials measured by X-ray photoelectron spectroscopy (XPS) have been used for the carbon and heteroatom 1s IP's. However, XPS data was not available for the C 1s and O 1s IP's of THF and tetrahydrofuran (THF) and the C 1s IP's of pyrrolidine and piperidine. For these molecules the IP's were estimated from literature values of similar molecules. For THF and THP the IP's were estimated from the gas phase XPS IP's of furan, dimethyl ether, and ethanol. The 1s IP's of the carbon nearest the oxygen in these molecules are 291.6, 292.3, and 292.5 eV, respectively (11), while the more distant carbons of furan and ethanol have IP's of 290.4 and 291.1 eV. The values of THF should be similar to these and thus the C 1s IP's for the two distinguishable C 1s environments in THF and THP are estimated to be 292.0 and 290.8 eV. (Note that all carbons more than one position away from the heteroatom are expected to have IP's within 0.5 eV of each other and are essentially indistinguishable in unmonochromated XPS and in ISEEELS with the present resolution. For this reason in all of the molecules studied carbons more than one position away from the heteroatom are labelled C1 while those adjacent to the heteroatom are labelled C2.) The O 1s IP of furan is 540.0 eV while that of both dimethyl ether and ethanol is 538.6 eV (11). The O 1s IP of THF is estimated to be 539.0(5) eV, closer to the value for the non-aromatic species. The gas phase C 1s IP's were also unavailable for both pyrrolidine and piperidine. The C 1s IP's of CH₃NH₂ and (CH₃)₂, are 291.6 and 291.3 eV while that of pyrrole is 290.8 eV. The C2 IP of pyrrolidine and piperidine is expected to be similar to these and is given a value of 291.0 eV. The effect of the nitrogen is expected to disturb the ring less than the oxygen in THF so the C1 IP is estimated to be 290.3 eV, close to that for cyclic hydrocarbons. In all cases the deviation between the estimated and actual IP's is expected to be less than 0.5 eV.

1.1. Carbon K-shell spectrum of furan

Furan, an aromatic five-membered ring with C₂ᵥ symmetry, is isoelectronic with the cyclopentadienyl anion. Since the carbon K-shell spectrum of the cyclopentadienyl anion has not been studied yet a direct comparison between furan and its closest hydrocarbon analog is not possible. However, comparisons to benzene or pyridine are appropriate. The carbon K-shell electron energy loss spectrum of furan is shown in Fig. 1 while the energies and assignments of the features in the spectra are listed in Table 1.

The first four features in the carbon K-shell electron energy loss spectrum of furan are attributed to 1s → π⁺(2a₂) and C1 1s → π⁺(2a₂) transitions. These assignments are consistent with the similarity of the 1–2 and 3–4 separations. The average separation (0.83(5) eV) is an ISEEELS measure of the difference in the IP's of the two distinguishable carbon environments. This estimate is significantly lower than the measured C1–C2 splitting reported by two independent XPS measurements (15, 16). We have re-examined the published XPS spectra (16) and measure a separation of 1.0 ± 0.2 eV, somewhat lower than the reported values and in better agreement with our results. If there is a smaller C1–C2 separation in excitation (ISEEELS) rather than ionization (XPS), the electron in the π⁺(C=C) level is having a different influence on the (C1⁻¹, π⁺) state than on the (C2⁻¹, π⁺) state. Previously the carbon 1s core level separation in the monohalobenzenes was found to be essentially the same whether measured directly by XPS or indirectly by ISEEELS in terms of the separation of transitions from the different core levels to the same π⁺ level (17).

The relative intensities of features 1 to 4 in furan provide strong support for our assignments since the 3b₁ orbital has greater density on the C1 and O atoms while the 2a₂ orbital has roughly equal density on the C1 and C2 atoms (18). This matches the experimental observations of greatly differing intensities of the transitions from C1 and C2 to the 3b₁ (#1 and #2) but very similar intensities to the 2a₂ level (#3 and #4). The possibility that features 3 and 4 are 3p Rydberg transitions
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Table 1. Energies, term values, and proposed assignments for features observed in the K-shell spectra of furan

<table>
<thead>
<tr>
<th>Feature</th>
<th>Energy (±0.1 eV)</th>
<th>Term value (eV)</th>
<th>Assignment*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₁</td>
<td>C₂</td>
</tr>
<tr>
<td>1</td>
<td>285.6</td>
<td>4.8</td>
<td>5.1</td>
</tr>
<tr>
<td>2</td>
<td>286.5</td>
<td>1.9</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>289.3</td>
<td>290.4</td>
<td>5.1</td>
</tr>
<tr>
<td>C₁ IP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂ IP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>291.4</td>
<td>-0.4</td>
<td>σ*(C=O)</td>
</tr>
<tr>
<td>6</td>
<td>297.0</td>
<td>-6.0</td>
<td>σ*(C=C)</td>
</tr>
</tbody>
</table>

(a) Carbon 1s

(b) Oxygen 1s

*Transitions occur from the indicated core level to the final orbital listed.

This feature is located 4.3(1) eV below the C 1s → π* transition in CO₂ (290.7 eV) (9). The average of two XPS determinations (15, 16).

Determined relative to the average C 1s IP.

This feature is located 1.1(1) eV above the O 1s → π* transition in CO (534.21(9) eV) (8).

was also considered but the indicated assignments are preferred because of the relative intensity evidence and also because the transitions to the second π* level in benzene and pyridine (6) have appreciable intensity and similar term values to those of features 3 and 4 in the carbon K-shell spectrum of furan. The presence of these features at similar intensity in the spectrum of condensed furan would confirm our assignment.

The two remaining features (5 and 6) present an interesting dilemma. They are assigned to C 1s → σ* transitions or σ shape resonances which should correlate with bond lengths according to the empirical analysis of σ shape resonances by Sette et al. (15).

Furan contains two different carbon–carbon bond lengths (136.1 and 143.1 pm) and one carbon–oxygen bond length (136.2 pm) (19). Thus the bond length correlation predicts three resonances in the carbon K-shell spectrum of furan around 10.6, 6.8, and 2.5 eV above the IP, corresponding to the three different bond lengths. However, only two continuum resonances are observed and they are located 0.4 and 6.0 eV above the average C 1s IP, not in the positions predicted by the simple correlation. The aromatic character of furan suggests that its resonances should be treated in a manner similar to those of benzene and pyridine (6). Further discussion of the continuum resonances (features 5 and 6) is given in section 7 in comparison to analogous features in the spectra of the other heterocyclic molecules studied.

1.2. Oxygen K-shell spectrum of furan

The oxygen K-shell electron energy loss spectrum of furan is shown in the lower panel of Fig. 1 while the energies and assignments of the observed features are listed in Table 1. Four features can be distinguished in the oxygen K-shell spectrum of furan. The first feature is assigned to the O 1s(a₁) → π*(3b₁) transition. This feature is appreciably narrower than the corresponding C 1s → π*(3b₁) features (1 and 2) in the upper panel of Fig. 1. It is clearly a single transition. In general excitations from different core levels in a molecule occur to the same set of valence antibonding orbitals with the intensities determined by dipole selection rules and overlap considerations. In oxygen 1s excitation the symmetry of furan remains C₂ᵥ and only the O 1s → π*(3b₁) transition is allowed by dipole selection rules. Thus only one O 1s → π* feature is expected. The shoulder (♯2) on the low energy side of feature 3 is assigned to a 3p Rydberg transition based on its term value of 2.4 eV (10). It is possible that this feature is the O 1s → π*(2a₂) transition observed either because of vibronic coupling or a quadrupole transition due to the finite momentum transfer under our experimental conditions. The X-ray photoabsorption spectrum of gaseous or solid furan would clarify the origin of this feature. Peaks 3 and 4 are analogous to features 5 and 6 in the carbon K-shell spectrum and are also assigned to σ shape resonances. Within the simple bond length correlation (3) only a single resonance associated with the C–O bond is expected while transitions to σ* states associated with carbon–carbon bonds should not be observed. The presence of an additional σ resonance in the oxygen K-shell spectrum suggests that there are interacting σ* levels in furan which produce delocalized σ* states similar to those in benzene and pyridine (6).

2.1. Carbon K-shell spectrum of pyrrole

Pyrrole is an aromatic five-membered ring, iso-electronic with furan with the oxygen replaced by an NH group. The spectrum of pyrrole might then be expected to resemble those of furan and pyridine. The carbon K-shell electron energy loss spectrum of pyrrole and the energies and proposed assignments of the observed features are presented in Fig. 2 and Table 2 respectively. As with furan there are four possible dipole-allowed 1s → π* transitions. According to XPS (15, 16) the carbon 1s IP's are separated by 1.0 eV. Valence shell studies (20) and ab initio calculations (21) indicate that the 3b₁ and 2a₂ π* levels are separated by about 0.9 eV. The splittings of both the carbon 1s and π* levels are considerably smaller in pyrrole than in furan so the four separate transitions will not be as well resolved as in furan. The full width of the broad feature centered at 286.3 is 1.8 eV, considerably greater than the instrumental resolution (0.7 eV as measured on the C 1s → π* transition in CO or on the main beam). Close inspection of its lineshape (see inset to Fig. 2) shows a shoulder on the low energy side around 285.6 eV. Thus the low energy shoulder (♯1) is assigned to the C₁ 1s → π*(3b₁) transition and the main intensity of the peak (♯2) to the C₂ 1s → π*(3b₁) transition. As with furan the C₁ 1s → π*(3b₁) transition is weaker than the C₂ 1s → π*(3b₁), consistent with the lower density of the 3b₁ orbital on the carbons farthest from the nitrogen (18). A shoulder is not observed on feature 3, which is not unexpected at our experimental resolution from two equal intensity transitions to the π*(2a₂) level. Higher resolution spectra would be very desirable to confirm our spectral interpretation and to provide more accurate transition energies.

Peaks 4, 5, and 6 in the carbon K-shell spectrum of pyrrole are assigned to σ shape resonances similar to those in furan and pyridine. Again, as in furan, the simple relationship (3) predicts three resonances at 3.9, 7.4, and 9.6 eV above the IP in the carbon K-shell spectrum corresponding to the carbon–nitrogen (137 pm) and carbon–carbon (142, 138 pm) bond lengths (19).
Three resonances are observed at 1, 6.5, and 11 eV above the average C 1s IP. In contrast to furan the simple predictions seem to be in fair agreement with the experimental spectrum. However, the highest energy continuum feature is very broad and weak relative to the other two. While this feature may be a \( \sigma \) shape resonance, its absence in the furan spectrum suggests an alternate assignment such as a multielectron process (shake-up). The XPS satellite spectrum shows a prominent feature 7.6 eV above the main line (16) which is in reasonable agreement with the onset of feature 6 at 298 eV, about 8 eV above threshold. K-shell excitation features previously identified as shake-up onsets (22) have generally been weaker and more rapidly damped than feature 6 in pyrrole. Another possibility is a weak splitting of the \( \sigma \) shape resonances as suggested by MSX\( \alpha \) calculations for benzene (6). From the studies of benzene and pyridine (6) one expects greatest deviation from the simple correlation in delocalized aromatic molecules. Since pyrrole is more aromatic than furan (23) we have also considered the intensity weighted average interpretation for the pyrrole continuum features (see section 7).

2.2. Nitrogen K-shell spectrum of pyrrole

The nitrogen K-shell electron energy loss spectrum of pyrrole is presented in the lower panel of Fig. 2 while the energies of the features and proposed assignments are listed in Table 2. To an even greater extent than the carbon K-shell spectra, the heteroatom core spectra of pyrrole and furan are similar. As with furan, dipole selection rules identify the first feature as the N 1s(\( a_1^1 \)) \( \rightarrow \pi^*(3b_1) \) transition. A peak attributable to the N 1s \( \rightarrow \pi^*(2a_2) \) transition is not observed, as expected from its dipole-forbidden character. However, the valley between the first and second features is not baseline resolved suggesting some transition intensity which could be the dipole-forbidden \( 2a_2 \) transition. Feature 2, a shoulder on \#3, probably arises from Rydberg transitions. The two continuum features (3 and 4) are similar in appearance to those found in the oxygen K-shell spectrum of furan and are assigned correspondingly to \( \sigma \) shape resonances with the one at lower energy being closely associated with the C—N bond. The higher energy feature (\#4) could arise from shake-up. However shake-up satellites are observed only at 8.7 and 15.1 eV above the N 1s IP in pyrrole (16), neither of which correlate with the onset of feature 4 around 411 eV, about 5 eV above threshold. The presence of two resonances where only the \( \sigma^*(C—N) \) feature might be expected indicates that the \( \sigma^*(C—C) \) levels are delocalized and have some density at the nitrogen atom.

3.1. Carbon K-shell spectrum of tetrahydrofuran

The carbon K-shell electron energy loss spectrum of tetrahydrofuran (THF) is shown in Fig. 3 while the energies and proposed assignments of the observed features are listed in Table 3. Tetrahydrofuran is the oxygen heterocyclic analog of cyclopentane and thus the carbon K shell spectrum of THF might be expected to be similar to that of cyclopentane (5). While the spectra are not precisely the same, some similarities can be noted. In cyclopentane, as in cyclohexane, a sharp
feature below the IP has been assigned to transitions to a \(\pi^*(\text{CH}_2)\) level (5). This assignment was based on the observation of a corresponding feature in the C 1s spectra of both solid and chemisorbed cyclohexane recorded by partial photoelectron yield (near edge X-ray absorption fine structure, NEXAFS). A strong polarization dependence of the NEXAFS feature was observed, consistent with transitions to a state of \(\pi\) symmetry with respect to the C–H bond. Both its observation in the condensed phase spectrum and the strong polarization dependence rule out a Rydberg assignment for this feature. The existence of unoccupied \(\pi^*(\text{CH}_2)\) levels, their spatial distribution and their importance in descriptions of the electronic structure of saturated organic molecules has been noted by Jorgensen and Salem (18). Based on comparison to cyclopentane and cyclohexane features 1 and 2 in THF are also assigned to \(\pi^*(\text{CH}_2)\) states corresponding to transitions from the C1 and C2 levels, respectively.

The third feature in the C 1s spectrum of THF is a \(\sigma\) shape resonance associated with the carbon–carbon and carbon–oxygen bonds. All of the carbon–carbon bond lengths in THF are very similar (19) and therefore only one \(\sigma(C–C)\) resonance is expected at 1.1 eV above the IP. In addition the bond length correlation predicts a \(\sigma\) shape resonance for the C–O bond at 0.6 eV above the IP which should be roughly 40% as intense as the \(\sigma(C–C)\) feature. Close examination of feature 3 in Fig. 3 reveals indications of two maxima (at 290.7 and 291.2 eV) at the top of this broad peak. The 0.5 eV separation of these maxima is in good agreement with the predicted separation of the \(\sigma(C–O)\) and \(\sigma(C–C)\) resonances. Feature 3 is significantly broader than the \(\sigma(C–O)\) resonance in the O 1s spectrum (feature 2 in the lower panel of Fig. 3). The increased width of this feature in the C 1s spectrum is likely associated with the overlap of the lower energy \(\sigma(C–O)\) resonance with two \(\pi^*(C–C)\) features at higher energy separated by the 1.2 eV spacing of the two C 1s levels. According to the simple correlation (3) feature 4 is too high in energy to correlate directly with any of the bond lengths in THF. A continuum feature similar to peak 4 in THF was also observed in cyclopentane (5) and was assigned to transitions to a second \(\pi^*\) state, possibly arising from the overlap of in-ring orbitals. A similar assignment is proposed for feature 4 in THF (see section 7 for further discussion).

### 3.2. Oxygen K-shell spectrum of tetrahydrofuran

The oxygen K-shell electron energy loss spectrum for THF is shown in the lower panel of Fig. 3 while the energies and proposed assignments of the observed features are listed in Table 3. The oxygen K-shell spectrum is quite similar to the carbon K-shell spectrum, indicating that the unoccupied levels are substantially delocalized. A weak peak, observed at 531 eV, is attributed to residual peroxide since a much more intense peak was observed at exactly the same energy in the undistilled sample. The first THF feature, which appears only as a shoulder, is assigned to transitions to the \(\pi^*(\text{CH}_2)\) level as in the carbon K-shell spectrum. This indicates that these levels are not localized on the carbon atoms but can be reached by a 1s excitation from any atom provided it is dipole-allowed. The second feature is assigned to a \(\sigma\) shape resonance associated with the C–O bond. The final feature in the oxygen K-shell
spectrum is a transition to a second $\sigma$ shape resonance analogous to feature 4 in the carbon K-shell spectrum.

4.1. Carbon K-shell spectrum of pyrrolidine

Pyrrolidine, $C_5H_7N$, is the nitrogen heterocyclic analog of cyclopentane. Since nitrogen is not as electronegative as oxygen, the perturbation of the ring electronic structure is expected to be less and the carbon K-shell spectrum of pyrrolidine, shown in Fig. 4, should be somewhat less that of cyclopentane more closely than does that of THF. The energies and assignments of spectral features are listed in Table 4. There are four identifiable features in the spectrum. The first and second features occur at an energy and intensity similar to the features assigned to the C 1s $\rightarrow \pi^*(CH_2)$ transitions in cyclopentane and THF (see Fig. 7). The two C 1s $\rightarrow \pi^*(CH_2)$ transitions in pyrrolidine are closely spaced because of the small separation of the C$_1$ and C$_2$ carbon 1s levels. The separation of features 1 and 2 (0.7(1) eV) is in good agreement with that of the two C 1s IP’s estimated from the IP’s of similar molecules. The $\pi^*(CH_2)$ transitions in pyrrolidine are less distinct than those in THF because of the separation of the two C 1s levels is considerably smaller.

The major feature (\#3) is assigned to the $\sigma$ shape resonance associated with the carbon–carbon bond. There should also be a resonance associated with the carbon–nitrogen bond. However, the $\sigma(C-N)$ transition does not appear as a distinct feature because of overlap with the $\sigma(C-C)$ resonance. Feature 4 is assigned to a second $\sigma$ transition, possibly associated with an in-ring $\sigma^*$ state, similar to those seen in cyclopentane and THF. These features are discussed in more detail in section 7.

4.2. Nitrogen K-shell spectrum of pyrrolidine

The nitrogen K-shell spectrum of pyrrolidine is shown in the lower panel of Fig. 4 while the energies and proposed assignments of the observed features are listed in Table 4. The nitrogen K-shell spectrum shows four features and bears a strong resemblance to the carbon K-shell spectrum of pyrrolidine. The first feature is at essentially the same energy as the intense N 1s $\rightarrow \pi^*$ transition in N$_2$ and was originally suspected to arise from nitrogen impurity of air leak. However, the absence of signal in the oxygen K-shell region eliminated the air leak explanation. Extensive degassing was done to remove any N$_2$ trapped in the liquid. The intensity of feature 1 with respect to the rest of the spectrum remained constant throughout successive degassings. Thus we are convinced that this is a true spectral feature of pyrrolidine. In analogy with features 1 and 2 in the C 1s spectrum it is assigned to transitions to a decoupled $\pi^*(CH_2)$ level. The shoulder 2, on the low energy side of the third feature, is assigned to a $3p$ Rydberg transition based on its term value of 2.1 eV. The largest feature in the spectrum is the $\sigma$ shape resonance associated with the carbon–nitrogen bond. Feature 4 is assigned to a second $\sigma$ shape resonance analogous to that observed in the C 1s spectra of pyrrolidine, THF, and cyclopentane (see Fig. 7). The $\pi^*(CH_2)$ and continuum features are discussed further in section 7.

5.1. Carbon K-shell spectrum of tetrahydrofuran

The carbon K-shell spectrum of tetrahydrofuran (THF) is
presented in Fig. 5 while the energies and proposed assignments are listed in Table 5. The spectrum is similar to those of cyclohexane (5) and piperidine (section 6.1) and resembles that of THF. According to our estimates the C 1s IP's of the two distinguishable carbon environments differ by about 1.2(7) eV. Thus transitions from these two levels to a common unoccupied level should be clearly resolved with our apparatus. On this basis the first two features are assigned to C1 1s → π*(CH2) and C2 1s → π*(CH2) transitions, respectively, analogous to the assignments of the first features in the carbon K-shell spectra of both cyclohexane and piperidine. The measured separation of features 1 and 2 (1.64(1) eV) suggests that the separation of the estimated C 1s IP's of THF may be too small. The total intensity of the C 1s → π*(CH2) transitions increases as heavier heteroatoms are substituted for carbon (see Fig. 7). The explanation for this is not clear although the shift in intensity from C1 to C2 excitation in the CH2 → NH → O sequence indicates that the electron density in the π*(CH2) orbital shifts systematically towards the heteroatom end of the molecule. Further discussion of the π*(CH2) transitions is given in section 7.

The third feature is assigned to the σ(C—C) shape resonance. There is no distinguishable feature from the σ(C—O) presumably since it overlaps the σ(C—C) resonance. The predicted σ(C—C) and σ(C—O) resonance positions are 0.9 and 0.5 eV above the edge while feature 3 has a width of at least 4 eV. This is noticeably wider than the continuum resonance in the oxygen K-shell spectrum of THF (feature 2 in the lower panel of Fig. 5) because of overlapping transitions from the C1 and C2 levels to both the σ(C—C) and σ(C—O) levels. As with piperidine (section 6.1) the σ resonance region is in good accord with the expectations from the simple correlation, in contrast to the situation in the spectra of the five-membered ring heterocyclics.

5.2. Oxygen K-shell spectrum of tetrahydropyran

The oxygen K-shell spectrum of THP is shown in the lower panel of Fig. 5 while the energies and proposed assignments are listed in Table 5. A weak feature is observed around 531 eV from the O 1s → π* transition in impurity O2 or possibly peroxo contamination. The THP oxygen K-shell spectrum is dominated by one intense broad feature which is attributed to the σ shape resonance associated with the C—O bond. There is a relatively intense shoulder on the low energy side of the σ*(C—O) feature which likely arises from transitions to the σ*(CH2) level. As with the nitrogen K-shell spectrum of piperidine (section 6.2) the simple one bond, one resonance picture (3) is in good agreement with the observed spectrum.

6.1. Carbon K-shell spectrum of piperidine

The carbon K-shell electron energy loss spectrum of piperidine, C6H14O, is shown in Fig. 6 while the energies and proposed assignments of the observed features are listed in Table 6. The carbon K-shell spectrum of piperidine should and does closely resemble that of cyclohexane since the replacement of a CH2 with an NH group should have even less effect in a six- than a five-membered ring. The first and second features in the carbon K-shell spectrum of piperidine are assigned to the C1 1s → π*(CH2) and C2 1s → π*(CH2) transitions, respectively. The separation of 0.82(4) eV between these two features is an ISEELS estimate of the splitting of the C1 and C2 levels. In
contrast to the C1 — C2 separation of the \( \pi^* (C==C) \) transitions in furan and pyrrole, it is in good agreement with that of the estimated C 1s IP's.

The third feature is assigned to overlapping \( \sigma (C==C) \) and \( \sigma (C==N) \) shape resonances. Interestingly a peak analogous to peak 4 in the carbon K-shell spectrum of pyrrolidine is not observed in piperidine. This feature was also less intense in cyclohexane than in cyclopentane (5). This suggests that the positions and intensities of continuum excitations depend on ring geometry as well as on the type of heteroatom and the bond lengths (see section 7).

6.2. Nitrogen K-shell spectrum of piperidine

The nitrogen K-shell electron energy loss spectrum of piperidine is shown in the lower panel of Fig. 6 while the energies and proposed assignments of the observed features are listed in Table 6. The N 1s and C 1s spectra of piperidine are very similar indicating that transitions are occurring to a common set of delocalized levels. The first feature, a sharp, well-resolved peak, is quite intense and is likely due to the N 1s \( \rightarrow \pi^* (CH_2) \) transition as in pyrrolidine. Observation of an unchanging intensity with successive degassings ruled out the possibility of impurity N\(_2\) in the sample. The presence of this transition in the heteroatom core edge spectrum of each of the saturated heterocyclic molecules is an indication that the \( \pi^* (CH_2) \) orbital is not highly localized on the carbon atoms. The second feature is the \( \sigma \) shape resonance from the carbon—nitrogen bond. There are no features beyond this peak again suggesting that the intensity of the second \( \sigma \) shape resonance which was present in the five-membered saturated rings is strongly geometry dependent. Since the feature is present at a low intensity in cyclohexane but absent in piperidine, a dependence on the heteroatom also exists.

7. Systematics of \( \pi^* \) intensities and the positions of K-shell continuum resonances

A comparison of the carbon K-shell spectra of the CH\(_2\), NH, and O five- and six-membered rings is presented in Fig. 7. There are interesting trends in the intensities of the discrete features attributed to the \( \pi^* (CH_2) \) states. The NH and O heterocyclics each have two distinguishable C 1s environments and a splitting of the \( \pi^* (CH_2) \) features is observed, as expected. Because of the 50% increase in number of C1 carbons one might expect a large increase in the C1 \( \rightarrow \pi^* (CH_2) \) transition relative to that from C2 as the ring size increases from 5 to 6. Although an increase is observed it is much smaller than expected. A more dramatic effect is observed in the comparison of the NH and O species. The C2 \( \rightarrow \pi^* (CH_2) \) feature is substantially more intense in THF or THP than it is in pyrrolidine or piperidine. This suggests that the \( \pi^* (CH_2) \) level has considerably greater density at the heteroatom end of the molecule and that the electron density shifts towards the heteroatom as the heteroatom electronegativity increases. This is also consistent with the increased intensity of the \( \pi^* (CH_2) \) features in the O K-shell spectra of THF and THP relative to those in the N K-shell spectra of pyrrolidine or piperidine (see Figs. 3—6) (although the shift to higher energy caused by the more electronegative O results in greater overlap with higher energy features in the O 1s spectra). Finally there is an obvious increase in the width of the first continuum feature through the CH\(_2\) \( \rightarrow \) NH \( \rightarrow \) O sequence in both the five- and six-membered ring series. This increased width is partially due to overlap of the \( \sigma (C==C) \) and \( \sigma (C==O) \)
resonances in the heterocyclics but it is also indicative of the occurrence of transitions to both $\sigma^*$ levels from each of the two distinguishable C 1$s$ levels which are separated by increasing amounts in the NH (0.7 eV) and O (1.2 eV) cases. This same trend of increasing widths of $\sigma$ resonances is apparent also in the series cyclopentene (5), pyrrole (Fig. 2), and furan (Fig. 1), again in good agreement with contributions of transitions from two separate C 1$s$ levels.

Turning now to the positions of continuum features, the correlation between $\delta$, the shape resonance position relative to the IP, and $R$, the bond length, gives reasonable results for the ISEELS spectra of many molecules (2, 3, 5). Among the heterocyclic molecules studied in this work, those with simple bonding generally show good agreement between predicted and experimental results. However, although there is a continuum feature in each of the saturated molecules which correlates well with bond length, an additional continuum feature is also observed, in some cases with appreciable intensity. The second continuum feature in THF and pyrrolidine is similar to that seen in cyclopentane (5) and is similarly assigned to in-ring $\sigma^*$ states. This feature appears to decrease in intensity from THF to pyrrolidine and then to cyclopentane (see Fig. 7). This is consistent with shorter C–O and C–N bonds. The more constrained geometry should increase the overlap of the in-ring $\sigma^*$ orbitals and thus the splitting of the derived states. It is interesting to note that compared to the five-membered rings, the spectra of the six-membered rings are all in much better agreement with the one bond, one resonance picture. A second continuum feature is observed weakly only in the spectrum of cyclohexane (see Fig. 7). This suggests that the overlap of $\sigma^*$ states is less in the larger rings so that delocalization and splittings are greatly reduced compared to smaller rings. Note however that the continuum resonances in the C 1$s$ spectra of the six-membered rings are significantly wider than the first continuum resonances in the corresponding five-membered ring. The increased width suggests that there may be overlap with a second resonance.

In the two aromatic molecules, furan and pyrrole, the number and positions of the observed resonance features are not fully consistent with the simple correlation suggesting that a different interpretation may be required. In the K-shell continua of benzene, pyridine (6), and borazine (24) two resonances are observed whereas only one is expected (2, 3). Based on the correlation derived from smaller molecules the intensity-weighted average (IWA) positions of the experimentally observed resonances give much better estimates of the C–C, C–N, and B–N bond lengths than the positions of any single resonance feature (6, 24). The merits of a similar approach for the spectra of furan and pyrrole have been investigated. The intensity weighted average positions were determined by first subtracting an estimate of the smooth continuum upon which the resonances are located. The position and area of each background-subtracted peak were then measured and the IWA calculated. The relevant data for all of the molecules studied in this work are listed in Table 7 while the observed resonance positions and their intensity weighted averages are plotted against bond length in Fig. 8. For both furan and pyrrole, the intensity weighted averages of the two heteroatom continuum resonances gives better agreement with the correlation than does the position of either of the individual features. The continuum resonances in the carbon K-shell spectrum of pyrrole are well interpreted within the simple correlation. For the carbon–carbon distances in furan, if peak 5 is assigned to overlapping $\sigma(C–O)$ and $\sigma(C–C)$ and peak 6 to $\sigma(C=C)$, the IWA improves the situation relative to this one-bond one-resonance assignment although the fit is not spectacular. This may be a reflection of the lesser degree of aromaticity in pyrrole or furan with respect to benzene and pyridine. The decrease in $\pi$ delocalization appears
to be accompanied by a decrease in \( \sigma \) delocalization which results in a situation intermediate between benzene and the more localized aliphatic molecules. An alternate assignment of furan gives good agreement with the bond length correlation within the simple one bond one resonance picture. This occurs if peak 5 in the C K-shell spectrum of furan is assigned to \( \sigma(C-O) \) and peak 6 to \( \sigma(C-C) \), with no feature in the spectrum being explicitly associated with \( \sigma(C=C) \). A high energy tail on peak 6 can be discerned by comparison to the O K-shell spectrum which may be how the \( \sigma(C=C) \) intensity appears in furan. This interpretation is the one presented in Tables 1 and 7. Calculations of the continuum cross-sections in furan and pyrrole would be helpful in evaluating these alternate interpretations.

For all of the heterocyclic molecules the heteroatom core spectrum resembled the C 1s spectrum of the same molecule quite closely. This indicates that the unoccupied levels in these molecules are extensively delocalized so that, within symmetry restrictions, transitions to all antibonding orbitals occur from any site with finite intensity. In the heteroatom spectra of furan and pyrrole, the first \( \sigma \) shape resonance is more intense, relative to the higher energy resonance, than it is in the corresponding carbon 1s spectrum. This resonance is approximately where the \( \sigma(C-O) \) or \( \sigma(C-N) \) shape resonances would be expected in a localized picture. The increased intensity of this feature, relative to its counterpart in the carbon spectrum, appears to be a further reflection of the decrease in aromaticity of furan and pyrrole relative to pyridine and benzene, where the two continuum resonances are more similar in intensity (6).

Conclusions

The core excitation spectra of furan, pyrrole, tetrahydropyrrole, pyridine, tetrahydrofuran, and piperidine have been recorded by gas phase ISEELS spectroscopy and assignments have been proposed for all observed features. To our knowledge none of these spectra have been reported previously. The spectra of the saturated heterocyclic molecules are similar to those of their cyclic hydrocarbon analogs. In all cases the carbon and heteroatom K-shell spectra are generally similar indicating that transitions occur to a common set of extensively delocalized unoccupied levels. Features attributed to a \( \pi^* \) (CH\(_2\)) state were observed about 3 eV below the IP in both the carbon and heteroatom spectra of all of the saturated heterocycles studied.
The correlation of experimental σ shape resonance positions with bond lengths shows reasonable agreement with earlier results. This is further indication that the empirical approach developed by Sette et al. (3) can be useful for a wide variety of molecules. However, the complications of additional continuum features and the somewhat greater scatter in the correlation for more complex molecules appears to limit the accuracy of the structural information obtainable. The greatest accuracy is expected from shifts in resonance position in the same molecule in different environments, as in geometry changes of a surface adsorbed molecule. From the viewpoint of gas phase K-shell spectroscopy the correlation between resonance position and bond length provides a useful framework for spectral interpretation.

Acknowledgements

This research was supported by grants from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Exxon Research and Engineering Co. (New Jersey). A. P. Hitchcock acknowledges the support of an NSERC University Research Fellowship.