High Resolution IR-Spectra of Furane and Thiophene

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The spectra of the out-of-plane fundamental band of furane (C_4H_4O) centered at 744 cm^{-1} and of thiophene (C_4H_4S) at 712 cm^{-1} were measured in Doppler-limited resolution with a diode-laser spectrometer at Köln and with a high-resolution Fourier transform spectrometer at the University of Gießen. An interactive Loomis-Wood program was applied to identify the *c*-type transitions of furane and thiophene. The molecular parameters were determined from the observed line positions and the available microwave data by least-squares-fits using Watson's *A*-reduced Hamiltonian. Some relations among parameters appearing in different formulations of the Hamiltonian are represented explicitly in connection with the derivation of the unreduced constants. The unreduced constants were derived for both molecules using the planarity relations. We determined the inertial defects to be ≈ 0.05 amuÅ^2 in the ground state and ≈ -0.2 amuÅ^2 in the excited state for both furane and thiophene.

Key words: FTIR, Infrared spectra, Furane, Thiophene, Inertial defect.

I. Introduction

Furane (C_4H_4O) and thiophene (C_4H_4S) are both nine atomic planar ring molecules belonging to the symmetry group C_{2v}. Microwave data and low-resolution IR data of both molecules have been published [1–14]. Those earlier papers reported the rotational and centrifugal constants of the ground state, the molecular structure, and gave a vibrational analysis of band origins and the force field. In the present study the rotation-vibration bands of furane and thiophene were measured in Doppler-limited resolution (≈ 0.002 cm^{-1}) for the first time, which allowed a detailed analysis of the ground and excited vibrational states. The high-resolution Fourier transform spectrometer at Giessen and the Cologne diode-laser spectrometer were utilized for this purpose. In the previous papers [1, 2] the ν_{13} out-of-plane fundamental bands of both molecules are labeled as ν_{19}; here we follow Mulliken's recommendation for notation [15]. The out-of-plane vibrations belong to A_2 and B_1 symmetry species of C_{2v}, and the modes are numbered according to descending order of frequency in each symmetry block.

An interactive Loomis-Wood program was applied to identify the *c*-type transitions of furane from 715 cm^{-1} to 767 cm^{-1}. For thiophene we have assigned lines from 685 cm^{-1} to 725 cm^{-1}. We analyzed the observed transition frequencies by applying Watson's *A*-reduced Hamiltonian. The unreduced rotational and quartic centrifugal constants were derived for both molecules by using the planarity conditions for the centrifugal distortion constants; the detailed method is presented in section III. In the fitting procedure we used the Watson Hamiltonian in cyclindrical form because of the ease of separating the matrix elements. In a second step we transformed the derived constants back into the commonly used cartesian parameters. The determined planarity defects in the centrifugal distortion are very small for both molecules. The inertial defects in the ν_{13} excited state were found to be very large and negative, which is predicted for these planar ring molecules [16].

II. Experimental Procedures

Two Fourier transform spectrometers and one diode-laser spectrometer were employed in this work.

In a first step all fundamentals were recorded with our Cologne Bruker IFS-48 Fourier transform spectrometer with low resolution (0.5 cm^{-1}) in the frequency range from 400 cm^{-1} to 4000 cm^{-1}. Figures 1 and 2 reproduce a section of these spectra displaying the ν_{13} band.

The high-resolution spectra were measured with a Bruker IFS-120-HR Fourier transform infrared spectrometer at the University of Giessen [17], employing a 3 m sample cell with CsI windows. The H_2O spec-

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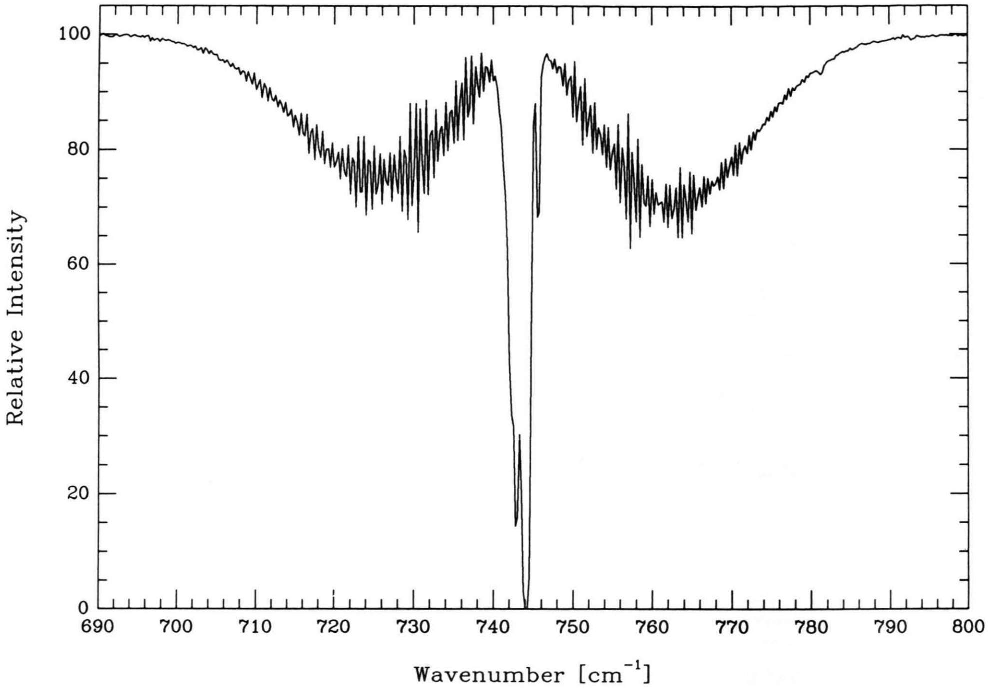

Fig. 1. The low resolution spectrum of the ν_{13} band of furane recorded with a Bruker IFS-48 Fourier transform spectrometer.

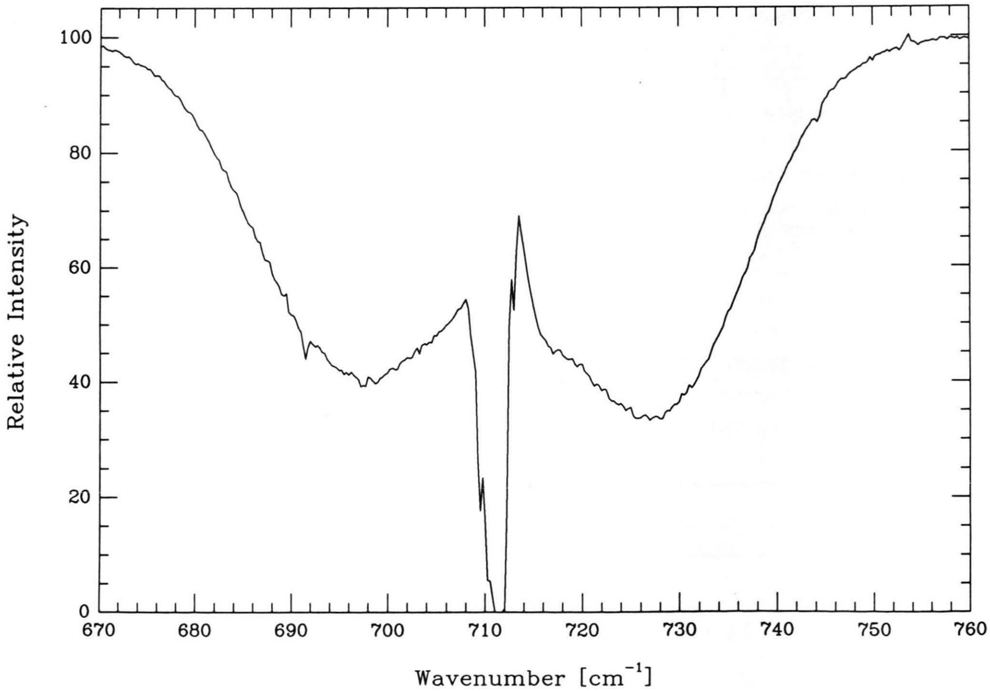

Fig. 2. The low resolution spectrum of the ν_{13} band of thiophene recorded with a Bruker IFS-48 Fourier transform spectrometer.

trum used for wavenumber calibration was measured at the same time as an impurity. The line positions of water in the frequency range have been recalibrated by measuring the OCS lines [18]. The spectrum of furane was recorded between 400 cm^{-1} and 950 cm^{-1} with a resolution of 0.0019 cm^{-1} at a pressure of 0.032 mbar with 350 scans altogether. In this case a KBr beam splitter was employed. The spectrum of thiophene was recorded with 300 scans between 390 cm^{-1} and 725 cm^{-1} at 0.148 mbar and a resolution of 0.0022 cm^{-1}. The frequency range of this measurement was limited by the transmission characteristics of the Mylar beam splitter. Thus the recorded data were usable only up to 725 cm^{-1}.

In addition, some parts of the ν_{13} band of both molecules were measured with Doppler-limited resolution with our tunable diode-laser spectrometer at Köln. The principles of measurement and calibration have been published in [19–22].

III. Spectra and Assignments

The ν_{13} band of both furane and thiophene is an out-of-plane vibration (symmetry B_1) in which the heavy atoms of the ring displace vertically to the molecular plane. This moment involves a variation of the dipole moment in this direction. Consequently this vibration exhibits *c*-type transitions.

As furane is a near oblate top ($I_A = 53.51$, $I_B = 54.67$, $I_C = 108.23$ amuÅ^2, asymmetry parameter $\varkappa = 0.916$), the variation of the dipole moment due to the ν_{13} vibration is parallel to the figure axes. Thus the spectrum of the ν_{13} band is similar to the parallel band of an oblate top; the selection rules are therefore $\Delta K_a = \pm 1$ and $\Delta K_c = 0$. The spectrum exhibits almost equally spaced groups of lines with common *J*-quantum number that are typical of parallel bands of symmetric top molecules. We identified about 3500 *c*-type transitions of furane from $P_{pq}(46_{33,13})$ at 715 cm^{-1} to $R_{rq}(41_{23,18})$ at 770 cm^{-1} in the notation $\Delta J_{\Delta K_a, \Delta K_c}(J_{K_a,K_c})$. Figures 3 and 4 show two groups of lines displaying some identified transitions.

The above selection rules are also good for the ν_{13} band of thiophene, a strongly asymmetric top molecule ($I_A = 62.86$, $I_B = 93.30$, $I_C = 156.23$ amuÅ^2, asymmetry parameter $\varkappa = -0.092$). As the spectrum of this molecule is quite complex, an interactive Loomis-Wood program was used for assigning lines. The standard Loomis-Wood program was extended to use the calculated transition frequencies based on an asymmetric top Hamiltonian as reference frequencies. It was extremely powerful to identify the lines of such a strongly asymmetric-top molecule. Figure 5

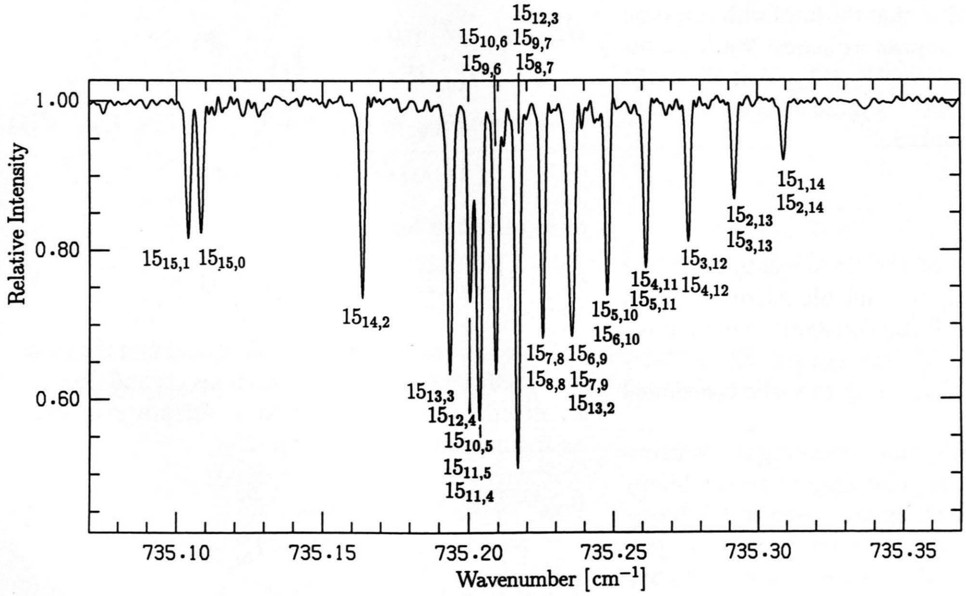

Fig. 3. A part of the high resolution FTIR spectrum of furane measured in Giessen. A typical "parallel" band structure of $P(15)$ transitions can be seen. The assignments are given by indicating the lower state quantum numbers, $J_{K_a K_c}$.

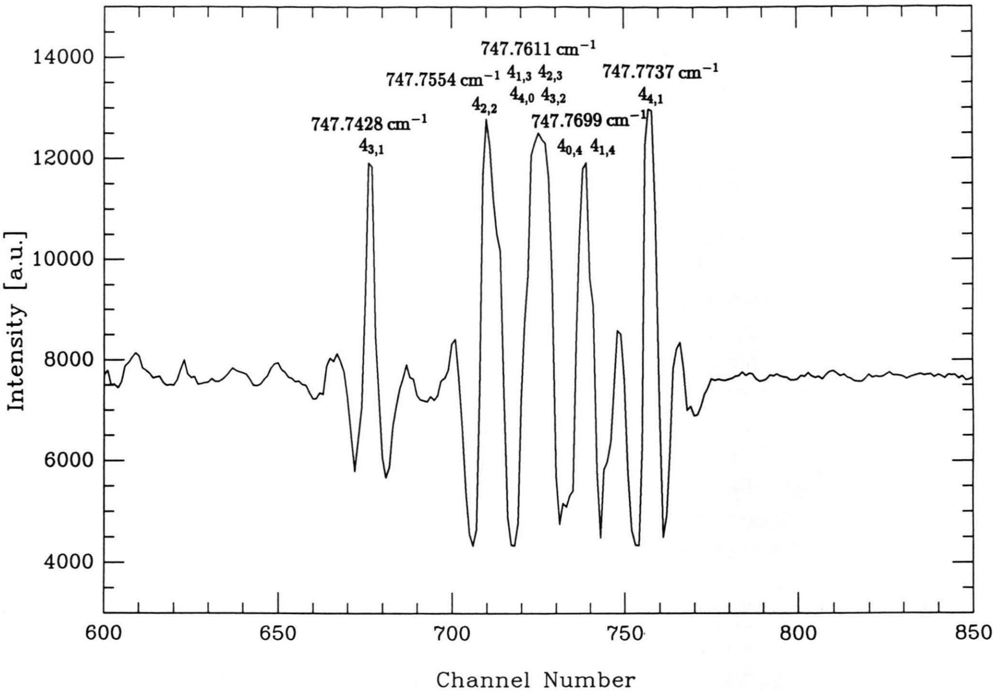

Fig. 4. The $R(4)$ transitions of furane recorded with the diode-laser spectrometer in Köln.

shows a section of a Loomis-Wood plot of the thiophene spectrum. Here we used the convention of the perpendicular band of a prolate top, i.e. the reference frequencies are selected so that the lines with common K_a quantum number appear as series. We have assigned about 2200 lines from $P_{pq}(52_{45,7})$ at 685 cm^{-1} to $R_{rq}(29_{17,13})$ at 725 cm^{-1}. Figure 6 shows a section of the spectrum of thiophene.

IV. Analysis

From the positions of the lines identified in the present work and from the available microwave data the rotational and centrifugal constants of both molecules were determined by least-squares fits to Watson's A-reduced Hamiltonian up to sextic centrifugal terms.

There are different ways for presenting the Watson-type Hamiltonian. In the following we review briefly those formulations which appear often in the literature. Some relations among the parameters are presented explicitly, especially those involved in the planarity conditions and unreduced constants, which we have used in the present study.

In general the unreduced Hamiltonian of an asymmetric top molecule can be written in cylindrical tensor form [23],

$$\begin{aligned} H_{\text{cyl}} = {} & B_{200}\hat{J}^2 + B_{020}\hat{J}_z^2 \\ & + T_{400}\hat{J}^4 + T_{220}\hat{J}^2\hat{J}_z^2 + T_{040}\hat{J}_z^4 \\ & + \tfrac{1}{2}[B_{002} + T_{202}\hat{J}^2 + T_{022}\hat{J}_z^2, \hat{J}_+^2 + \hat{J}_-^2]_+ \\ & + \tfrac{1}{2}[T_{004}, \hat{J}_+^4 + \hat{J}_-^4]_+ + \dots, \end{aligned} \tag{1}$$

or in cartesian form [23, 24],

$$H_{\text{cart}} = \sum_{\alpha} B_\alpha \hat{J}_\alpha^2 + \sum_{\alpha\beta} T_{\alpha\beta}\hat{J}_\alpha^2\hat{J}_\beta^2 + \dots . \tag{2}$$

The relations between the cylindrical and the cartesian coefficients of the Hamiltonians (1) and (2) of an asymmetric top molecule up to the 4th power of angular momentum were given in [23]:

$$\begin{aligned} B_{200} &= \tfrac{1}{2}(B_x + B_y) - 4\,T_{004} \\ &= \tfrac{1}{2}(B_x + B_y) - \tfrac{1}{4}(T_{xx} - T_{yy} - 2T_{xy}), \\ B_{020} &= B_z - B_{200} + 6\,T_{004} \\ &= \tfrac{1}{2}(2B_z - B_x - B_y) + \tfrac{5}{8}(T_{xx} + T_{yy} - 2\,T_{xy}), \end{aligned}$$

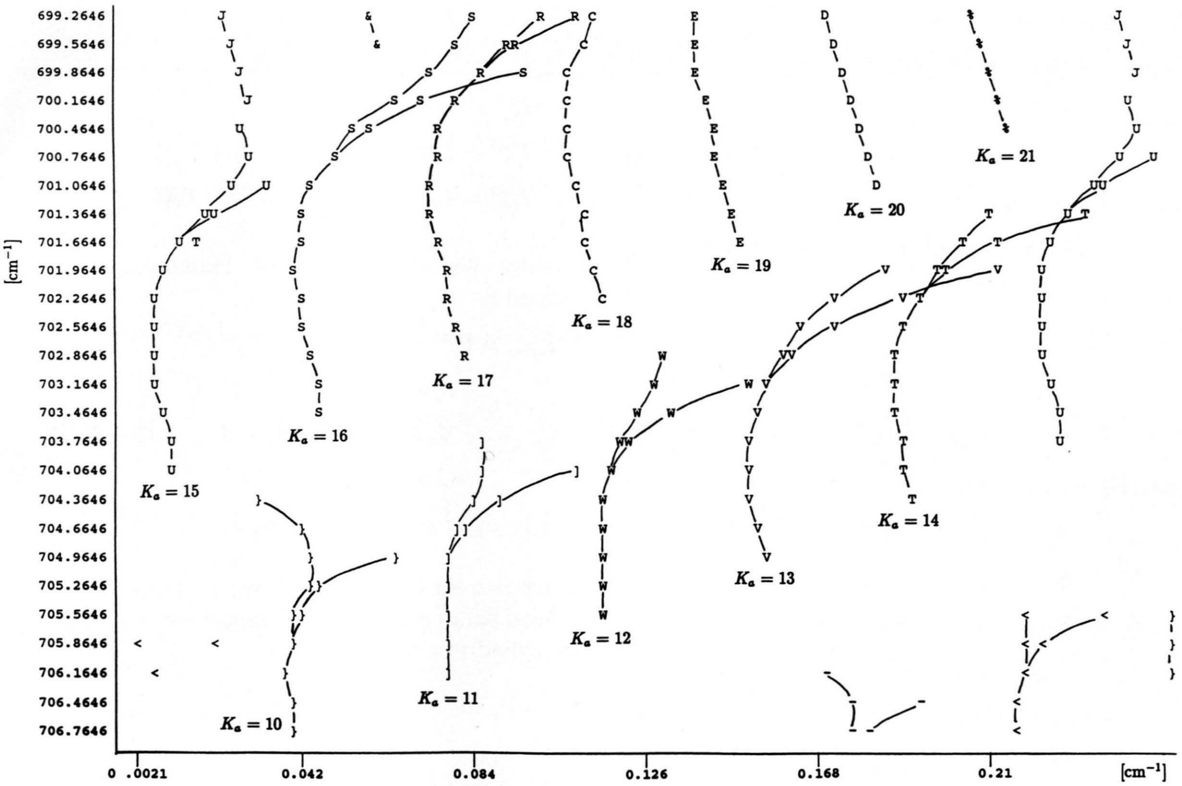

Fig. 5. Loomis-Wood diagram showing a part of the P branches of thiophene. Transitions with common K_a quantum number are marked by common letters or symbols. Lines that were not assigned are omitted in this figure.

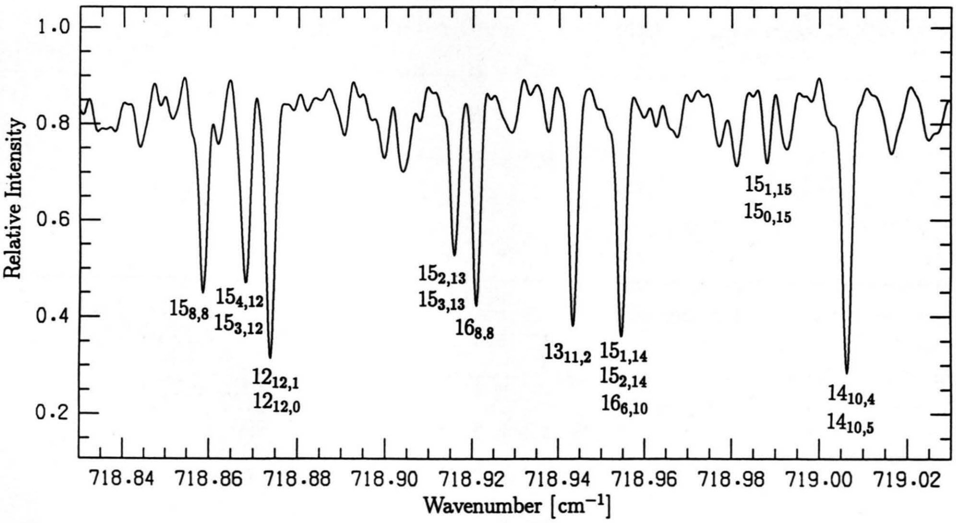

Fig. 6. A part of the thiophene spectrum recorded with the high resolution Fourier transform spectrometer in Giessen. The identified lines are R_{rq} transitions marked with the lower state $J_{K_a K_c}$.

$$\begin{aligned}
B_{002} &= \tfrac{1}{4}(B_x - B_y),\\
T_{400} &= +\tfrac{1}{8}(3\,T_{xx} + 3\,T_{yy} + 2\,T_{xy}),\\
T_{220} &= (T_{zx} + T_{yz}) - 2\,T_{400}\\
&= -\tfrac{3}{4}(T_{xx} + T_{yy}) + (T_{zx} + T_{yz} - \tfrac{1}{2}\,T_{xy}),\\
T_{040} &= T_{zz} - T_{220} - T_{400}\\
&= +\tfrac{3}{8}(T_{xx} + T_{yy} + \tfrac{8}{3}\,T_{zz}) - (T_{zx} + T_{yz} - \tfrac{1}{4}\,T_{xy}),\\
T_{202} &= \tfrac{1}{4}(T_{xx} - T_{yy}),\\
T_{022} &= \tfrac{1}{2}(T_{zx} - T_{yz}) - T_{202}\\
&= -\tfrac{1}{4}(T_{xx} - T_{yy}) + \tfrac{1}{2}(T_{zx} - T_{yz}),\\
T_{004} &= +\tfrac{1}{16}(T_{xx} + T_{yy} - 2\,T_{xy}).
\end{aligned} \tag{3}$$

Inversely we can write

$$\begin{aligned}
B_x &= B_{200} + 2\,B_{002} + 4\,T_{004}\,,\\
B_y &= B_{200} - 2\,B_{002} + 4\,T_{004}\,,\\
B_z &= B_{200} + B_{020} - 6\,T_{004}\,,\\
T_{xx} &= T_{400} + 2\,T_{004} + 2\,T_{202}\,,\\
T_{yy} &= T_{400} + 2\,T_{004} - 2\,T_{202}\,,\\
T_{zz} &= T_{400} + T_{040} + T_{220}\,,\\
T_{xy} &= T_{400} - 6\,T_{004}\,,\\
T_{zx} &= T_{400} + \tfrac{1}{2}\,T_{220} + T_{202} + T_{022}\,,\\
T_{yz} &= T_{400} + \tfrac{1}{2}\,T_{220} - T_{202} - T_{022}\,.
\end{aligned} \tag{4}$$

Watson's *A*-reduced Hamiltonian in cartesian form is

$$\hat{H}^{(A)}_{\text{cart}} = \sum_{\alpha} B^{(A)}_{\alpha}\,\hat{J}^2_{\alpha} + \sum_{\alpha\beta} T^{(A)}_{\alpha\beta}\,\hat{J}^2_{\alpha}\,\hat{J}^2_{\beta} + \dots\,, \tag{5}$$

or in cylindrical form

$$\begin{aligned}
H^{(A)}_{\text{cyl}} = {} & B^{(A)}_{200}\,\hat{J}^2 + B^{(A)}_{020}\,\hat{J}^2_z\\
& + T^{(A)}_{400}\,\hat{J}^4 + T^{(A)}_{220}\,\hat{J}^2\,\hat{J}^2_z + T^{(A)}_{040}\,\hat{J}^4_z\\
& + \tfrac{1}{2}\,[B^{(A)}_{002} + T^{(A)}_{202}\,\hat{J}^2 + T^{(A)}_{022}\,\hat{J}^2_z\,,\,\hat{J}^2_+ + \hat{J}^2_-]_+ \dots\,.
\end{aligned} \tag{6}$$

The relations between the cyclindrical parameters and the cartesian ones in the *A*-reduction are essentially the same as (4), where we have to restrict $T^{(A)}_{004}$ to be zero, as required for the *A*-reduction:

$$\begin{aligned}
B^{(A)}_x &= B^{(A)}_{200} + 2\,B^{(A)}_{002}\,,\\
B^{(A)}_y &= B^{(A)}_{200} - 2\,B^{(A)}_{002}\,,\\
B^{(A)}_z &= B^{(A)}_{200} + B^{(A)}_{020}\,,\\
T^{(A)}_{xx} &= T_{400} + 2\,T^{(A)}_{202}\,,\\
T^{(A)}_{yy} &= T_{400} - 2\,T^{(A)}_{202}\,,\\
T^{(A)}_{zz} &= T^{(A)}_{400} + T^{(A)}_{040} + T^{(A)}_{220}\,,\\
T^{(A)}_{xy} &= T^{(A)}_{400}\,,\\
T^{(A)}_{zx} &= T^{(A)}_{400} + \tfrac{1}{2}\,T^{(A)}_{220} + T^{(A)}_{202} + T^{(A)}_{022}\,,\\
T^{(A)}_{yz} &= T^{(A)}_{400} + \tfrac{1}{2}\,T^{(A)}_{220} - T^{(A)}_{202} - T^{(A)}_{022}\,.
\end{aligned} \tag{7}$$

Usually Watson's *A*-reduced Hamiltonian is expressed as

$$\begin{aligned}
\hat{H}^{(A)}_{\text{Watson}} = {} & B^{(A)}_x\,\hat{J}^2_x + B^{(A)}_y\,\hat{J}^2_y + B^{(A)}_z\,\hat{J}^2_z\\
& - \Delta_J\,\hat{J}^4 - \Delta_{JK}\,\hat{J}^2\,\hat{J}^2_z - \Delta_K\,\hat{J}^4_z\\
& + \Phi_J\,\hat{J}^6 + \Phi_{JK}\,\hat{J}^4\,\hat{J}^2_z + \Phi_{KJ}\,\hat{J}^2\,\hat{J}^4_z + \Phi_K\,\hat{J}^6_z\\
& - (2\,\delta_J\,\hat{J}^2 - 2\,\phi_J\,\hat{J}^4)\,(\hat{J}^2_x - \hat{J}^2_y)\\
& + [-\delta_K\,\hat{J}^2_z + \phi_{JK}\,\hat{J}^2\,\hat{J}^2_z + \phi_K\,\hat{J}^4_z\,,\,\hat{J}^2_x - \hat{J}^2_y]_+ + \dots\,,
\end{aligned} \tag{8}$$

which is used in the present work. The quartic centrifugal parameters of this Hamiltonian correspond to the cylindrical parameters as

$$\begin{aligned}
\Delta_J &= -\,T^{(A)}_{400}, & \delta_J &= -\,T^{(A)}_{202},\\
\Delta_{JK} &= -\,T^{(A)}_{220}, & \delta_K &= -\,T^{(A)}_{022}\,.\\
\Delta_K &= -\,T^{(A)}_{040}\,,
\end{aligned} \tag{9}$$

The coefficients in Watson's *A*-reduced Hamiltonian (8) are related to the coefficients of the unreduced Hamiltonian (1) or (2) as follows [23]:

$$\begin{aligned}
B^{(A)}_x &= B_x - 8\,(\sigma + 1)\,T_{004}\\
&= B_x - \tfrac{1}{2}\,(\sigma + 1)\,(T_{xx} + T_{yy} - 2\,T_{xy})\,,\\
B^{(A)}_y &= B_y + 8\,(\sigma - 1)\,T_{004}\\
&= B_y + \tfrac{1}{2}\,(\sigma - 1)\,(T_{xx} + T_{yy} - 2\,T_{xy}),\\
B^{(A)}_z &= B_z + 16\,T_{004}\\
&= B_z + (T_{xx} + T_{yy} - 2 - T_{xy})\,,\\
-\Delta_J &= T_{400} + 2\,T_{004}\\
&= \tfrac{1}{2}\,(T_{xx} + T_{yy})\,,\\
-\Delta_{JK} &= T_{220} - 12\,T_{004}\\
&= T_{zx} + T_{yz} + T_{xy} - \tfrac{3}{2}\,(T_{xx} + T_{yy})\,,\\
-\Delta_K &= T_{040} + 10\,T_{004}\\
&= (T_{xx} + T_{yy} + T_{zz}) - (T_{zx} + T_{yz} + T_{xy})\,,\\
-\delta_J &= T_{202}\\
&= \tfrac{1}{4}\,(T_{xx} - T_{yy})\,,
\end{aligned} \tag{10}$$

$$\begin{aligned} -\delta_K &= T_{022} + 4\sigma\, T_{004} \\ &= \tfrac{1}{2}\left(T_{zx} - T_{yz} - \sigma\, T_{xy}\right) - \tfrac{1}{4}\left(T_{xx}(1-\sigma) - T_{yy}(1+\sigma)\right), \end{aligned}$$

where $\sigma = (2B_z - B_x - B_y)/(B_x - B_y)$ is the asymmetry parameter.

The parameters of the Hamiltonian in (8) of the ground state and the $v_{13} = 1$ state of both furane and thiophene were determined from the observed lines with the help of available microwave data by least-squares fits. They are presented in Tables 1 and 2.

The reduction independent linear combinations in terms of the coefficients of the A-reduced Hamiltonian (5) are [23]

$$\begin{aligned} B_x &= B_x^{(A)} - 2\,T_{yz}^{(A)}, \\ B_y &= B_y^{(A)} - 2\,T_{zx}^{(A)}, \\ B_z &= B_z^{(A)} - 2\,T_{xy}^{(A)}, \\ T_{xx} &= T_{xx}^{(A)}, \\ T_{yy} &= T_{yy}^{(A)}, \\ T_{zz} &= T_{zz}^{(A)}, \\ T_1 &= T_1^{(A)} = T_{xy}^{(A)} + T_{yz}^{(A)} + T_{zx}^{(A)}, \\ T_2 &= T_2^{(A)} = B_x^{(A)}\,T_{yz}^{(A)} + B_y^{(A)}\,T_{zx}^{(A)} + B_z^{(A)}\,T_{xy}^{(A)}. \end{aligned}$$

Thus the diagonal $T^{(A)}$ parameters, $T_{\alpha\alpha}^{(A)}$, are reduction independent. The off-diagonal coefficients $T_{\alpha\beta}^{(A)}$ depend on the reduction and are related to the unreduced constants $T_{\alpha\beta}$ by

$$T_{xy}^{(A)} = T_{xy} + 8\,T_{008} = \tfrac{1}{2}\,(T_{xx} + T_{yy}), \tag{11}$$

$$\begin{aligned} T_{yz}^{(A)} &= T_{yz} - 4\,(\sigma+1)\,T_{004} \\ &= T_{yz} - \tfrac{1}{4}\,(1+\sigma)\,(T_{xx} + T_{yy} - 2\,T_{xy}), \end{aligned} \tag{12}$$

$$\begin{aligned} T_{zx}^{(A)} &= T_{zx} + 4\,(\sigma-1)\,T_{004} \\ &= T_{zx} + \tfrac{1}{4}\,(\sigma-1)\,(T_{xx} + T_{yy} - 2\,T_{xy}). \end{aligned} \tag{13}$$

It is evident that there are only eight determinable constants up to the forth power of J, whereas the unreduced Hamiltonian (2) contains nine coefficients. If the unreduced constants are to be determined, an additional relation should be introduced. In case of furane or thiophene one can use the planarity conditions for this purpose. For a planar molecule, the a- and b-axis are in the molecular plane. Considerations as to the planar structure of molecules lead to the relations [23]

$$T_{ca} = \tfrac{1}{2}\,A^{(e)2}\,C^{(e)2}\left(\frac{T_{aa}}{A^{(e)4}} - \frac{T_{bb}}{B^{(e)4}} + \frac{T_{cc}}{C^{(e)2}}\right), \tag{14}$$

Table 1. Rotational and centrifugal constants for the ground state and the v_{13} state of furane *.

Constant	Ground state	$v_{13} = 1$ state	Units
$A^{(A)}$	9447.1216(85)	9427.7517(38)	MHz
$B^{(A)}$	9246.7471(82)	9231.2821(30)	MHz
$C^{(A)}$	4670.8255(84)	4672.9007(22)	MHz
Δ_J	1.751(13)	1.7276(32)	kHz
Δ_{JK}	−0.257(37)	−0.215(11)	kHz
Δ_K	1.863	1.784(12)	kHz
δ_J	0.69793(25)	0.68603(74)	kHz
δ_K	1.3157(17)	1.2478(24)	kHz
Φ_J	0.00131(67)	0.0016(14)	Hz
Φ_{JK}	−0.0053(25)	−0.0102(71)	Hz
Φ_{KJ}	−0.0039(71)	0.023(14)	Hz
Φ_K	0.0145(47)	−0.0183(96)	Hz
v_0	0.0	744.656384(11)	cm^{-1}

* Numbers in parentheses are one standard errors.

Table 2. Rotational and centrifugal constants for the ground state and the v_{13} state of thiophene *.

Constant	Ground state	$v_{13} = 1$ state	Units
$A^{(A)}$	8041.464(12)	8026.529(12)	MHz
$B^{(A)}$	5418.1882(32)	5412.6767(45)	MHz
$C^{(A)}$	3235.7729(37)	3236.7961(46)	MHz
Δ_J	0.795(30)	0.786(29)	kHz
Δ_{JK}	−0.31(11)	−0.34(11)	kHz
Δ_K	2.029(95)	1.984(98)	kHz
δ_J	0.271(12)	0.269(12)	kHz
δ_K	0.970(81)	0.899(80)	kHz
Φ_J	−0.0293(59)	−0.0323(63)	Hz
Φ_{JK}	0.168(28)	0.186(29)	Hz
Φ_{KJ}	−0.434(36)	−0.479(40)	Hz
v_0	0.0	712.103733(20)	cm^{-1}

* Numbers in parentheses are one standard errors.

$$T_{bc} = \tfrac{1}{2}\,B^{(e)2}\,C^{(e)2}\left(-\frac{T_{aa}}{A^{(e)4}} + \frac{T_{bb}}{B^{(e)4}} + \frac{T_{cc}}{C^{(e)4}}\right). \tag{15}$$

In addition, a single planarity condition can be expressed in terms of the reduction independent parameters [23]

$$\begin{aligned} &(A^{(e)} + B^{(e)})\,\Delta T_{cc} \\ &\quad = (A^{(e)} + B^{(e)})\,T_{cc} + C^{(e)}\,T_1 - T_2 = 0\,. \end{aligned} \tag{16}$$

From (7) and (9) the following equations can be obtained using the I^r representation (i.e. $x=b$, $y=c$ and $z=a$):

$$\begin{aligned} T_{bb}^{(A)} &= -\Delta_J - 2\,\delta_J\,, \\ T_{cc}^{(A)} &= -\Delta_J + 2\,\delta_J\,, \\ T_{aa}^{(A)} &= -\Delta_J - \Delta_{JK} - \Delta_K\,, \end{aligned}$$

$$\begin{aligned} T_{bc}^{(A)} &= -\Delta_J , \\ T_{ca}^{(A)} &= -\Delta_J - \tfrac{1}{2}\Delta_{JK} + \delta_J + \delta_K , \\ T_{ab}^{(A)} &= -\Delta_J - \tfrac{1}{2}\Delta_{JK} - \delta_J - \delta_K , \\ T_1^{(A)} &= -3\Delta_J - \Delta_{JK} , \\ T_2^{(A)} &= -(A^{(A)} + B^{(A)} + C^{(A)})\,\Delta_J - \tfrac{1}{2}(B^{(A)} + C^{(A)})\,\Delta_{JK} \\ &\quad + (B^{(A)} - C^{(A)})(\delta_J + \delta_K) . \end{aligned} \tag{17}$$

Since $T_{\alpha\alpha} = T_{\alpha\alpha}^{(A)}$, the problem in obtaining a set of unreduced constants is only to find the $T_{\alpha\beta}$. There are several independent methods for that:

(i) The first method is to use the planarity relation (15) to determine T_{bc} with the approximation $A^{(e)} \approx A^{(A)}$, $B^{(e)} \approx B^{(A)}$, $C^{(e)} \approx C^{(A)}$ and $\sigma \approx \alpha^{(A)}$. Using (11) we obtain

$$T_{004} = +\tfrac{1}{8}(T_{bc}^{(A)} - T_{bc}) .$$

The other two, T_{ab} and T_{ca}, are then determined from (12) and (13).

(ii) The second method is to determine T_{ca} from the planarity relation (14) and to obtain

$$T_{004} = \frac{T_{ca} - T_{ca}^{(A)}}{4(\sigma - 1)}$$

from (13). The remaining T_{ab} and T_{bc} are calculated from (11) and (12).

(iii) The third method: T_{ca} is determined from (14), and then using T_1 and T_2 we obtain T_{ab} and T_{bc}.

(iv) The fourth method is to calculate T_{bc} from (15) and then to use T_1 and T_2 to determine T_{ab} and T_{ca}.

Then the unreduced rotational constants can be calculated by the first three equations in (10). In order to avoid the approximation $\sigma \approx \sigma^{(A)}$ used above, an iterative method was introduced: The determined A, B, and C were used to calculate σ and $A^{(e)}$, $B^{(e)}$, and $C^{(e)}$, and then the procedure was repeated. The iteration was repeated until the constants were self-consistent.

The derivation from the planarity condition (16), can be described by the defect [23, 26]

$$\Delta T_{cc} = T_{cc} + \frac{C^{(e)} T_1 - T_2}{A^{(e)} + B^{(e)}} . \tag{18}$$

The obtained parameters are shown in Tables 3, 4, 5, and 6 together with the inertial defect

$$\Delta = I_C - I_A - I_B . \tag{19}$$

The coefficients derived using the four different methods differ only slightly and thus the averaged values are listed in Tables 3, 4, 5, and 6.

Table 3. Reduced and unreduced rotational and centrifugal constants for the ground state of furane*.

Constants	A-reduced	Unreduced	Units
A	9447.12160(42)	9447.12371(42)	MHz
B	9246.74718(41)	9246.74498(41)	MHz
C	4670.82558(42)	4670.82567(42)	MHz
T_{aa}	−3.3568(38)	−3.3568(38)	kHz
T_{bb}	−3.14677(70)	−3.14677(70)	kHz
T_{cc}	−0.35505(70)	−0.35505(70)	kHz
T_{ab}	−3.6359(14)	−3.5898(32)	kHz
T_{ca}	0.3914(14)	−0.7093(31)	kHz
T_{bc}	−1.75091(65)	−0.6964(30)	kHz
T_1	−4.9955(27)	−4.9955(53)	kHz
T_2	−29.904(16)	−29.905(43)	MHz^2
T_{400}	−1.75091(40)	−1.4873(10)	kHz
T_{220}	0.2573(22)	−1.3246(49)	kHz
T_{040}	−1.8632(44)	−0.5450(63)	kHz
T_{202}	−0.69793(25)	−0.69793(25)	kHz
T_{022}	−1.31574(10)	−0.7423(22)	kHz
T_{004}	0.0	−0.13182(37)	kHz
σ	1.08757773(26)	1.08757966(26)	
ΔT_{cc}	−0.00350(70)	−0.00350(27)	kHz
Δ	0.0487(27)	0.0487(27)	amuÅ^2

* Numbers in parentheses are one standard errors.

Table 4. Reduced and unreduced rotational and centrifugal constants for the ν_{13} state of furane*.

Constants	A-reduced	Unreduced	Units
A	9427.7517(19)	9427.7537(19)	MHz
B	9231.2821(15)	9231.2800(15)	MHz
C	4672.9007(11)	4672.9008(11)	MHz
T_{aa}	−3.2965(82)	−3.2965(82)	kHz
T_{bb}	−3.0997(18)	−3.0997(18)	kHz
T_{cc}	−0.3555(18)	−0.3555(18)	kHz
T_{ab}	−3.5539(34)	−3.5106(80)	kHz
T_{ca}	0.3137(34)	−0.7349(76)	kHz
T_{bc}	−1.7276(16)	−0.7223(73)	kHz
T_1	−4.9678(72)	−4.968(13)	kHz
T_2	−29.998(38)	−30.00(10)	MHz^2
T_{400}	−1.7276(10)	−1.4763(26)	kHz
T_{220}	0.2150(52)	−1.293(12)	kHz
T_{040}	−1.7840(98)	−0.527(15)	kHz
T_{202}	−0.68603(62)	−0.68603(62)	kHz
T_{022}	−1.2478(25)	−0.7018(55)	kHz
T_{004}	0.0(0)	−0.12566(92)	kHz
σ	1.08620146(11)	1.0862033(11)	
ΔT_{cc}	0.0081(18)	0.0081(68)	kHz
Δ	−0.2008(48)	−0.2008(48)	amuÅ^2

* Numbers in parentheses are one standard errors.

Table 5. Reduced and unreduced rotational and centrifugal constants for the ground state of thiophene*.

Constants	A-reduced	Unreduced	Units
A	8041.4596(58)	8041.4603(58)	MHz
B	5418.1886(17)	5418.1870(17)	MHz
C	3235.7713(19)	3235.7721(19)	MHz
T_{aa}	−2.475(53)	−2.475(53)	kHz
T_{bb}	−1.318(20)	−1.318(20)	kHz
T_{cc}	−0.164(20)	−0.164(20)	kHz
T_{ab}	−1.952(46)	−1.52(12)	kHz
T_{ca}	0.599(46)	−0.20(11)	kHz
T_{bc}	−0.741(16)	−0.379(52)	kHz
T_1	−2.094(48)	−2.09(17)	kHz
T_2	−9.03(32)	−9.03(84)	MHz^2
T_{400}	−0.711(12)	−0.650(25)	kHz
T_{220}	0.128(69)	−0.42(17)	kHz
T_{040}	−1.862(88)	−1.41(18)	kHz
T_{202}	−0.2886(72)	−0.2886(72)	kHz
T_{022}	−0.987(33)	−0.370(82)	kHz
T_{004}	0.0(0)	−0.0453(66)	kHz
σ	3.4040048(66)	3.4040097(66)	
ΔT_{cc}	0.0038(20)	0.0039(77)	kHz
Δ	0.0638(91)	0.0638(91)	amuÅ^2

* Numbers in parentheses are one standard errors.

Table 6. Reduced and unreduced rotational and centrifugal constants for the ν_{13} state of thiophene*.

Constants	A-reduced	Unreduced	Units
A	8026.5237(62)	8026.5244(62)	MHz
B	5412.6800(23)	5412.6785(23)	MHz
C	3236.7975(24)	3236.7983(24)	MHz
T_{aa}	−2.385(54)	−2.385(54)	kHz
T_{bb}	−1.308(20)	−1.308(20)	kHz
T_{cc}	−0.159(20)	−0.159(20)	kHz
T_{ab}	−1.861(45)	−1.44(12)	kHz
T_{ca}	0.551(45)	−0.21(11)	kHz
T_{bc}	−0.000734(16)	−0.387(51)	kHz
T_1	−2.043(47)	−2.04(17)	kHz
T_2	−8.93(31)	−8.93(82)	MHz^2
T_{400}	−0.734(11)	−0.647(25)	kHz
T_{220}	0.158(68)	−0.36(17)	kHz
T_{040}	−1.808(87)	−1.38(18)	kHz
T_{202}	−0.2871 (70)	−0.2871(71)	kHz
T_{022}	−0.919(33)	−0.330(81)	kHz
T_{004}	0.0(0)	−0.0433(65)	kHz
σ	3.4025595(79)	3.4025641(79)	
ΔT_{cc}	0.013(20)	0.013(76)	kHz
Δ	−0.198(10)	−0.198(10)	amuÅ^2

* Numbers in parentheses are one standard errors.

V. Discussion

In the present study we have determined the molecular parameters of furane and thiophene for the ν_{13} excited state and revised the parameters of the ground state. Gordy and Cook [16] wrote, using furane and thiophene as examples, "If one or more of the out-of-plane vibrations is low, much of the in-plane contribution can be cancelled with very small inertial defect resulting". The present results confirm this argument: We have very small positive inertial defects for both molecules for the ground state, which are consistent with those already reported. The inertial defects in the excited ν_{13} vibrational state are negative and fairly large for both molecules, as expected.

The planarity defects for the quartic centrifugal constants are found to be very small for both molecules. Thus we can safely conclude that the unreduced constants determined in this study using the planarity relations are quite reliable. The ambiguity in calculating the unreduced constants originates from the different definitions of the rotational constants and is removed mostly by the iterative procedure. The only assumption which is not theoretically correct, is the use of unreduced rotational constants in place of the equilibrium ones for the planarity conditions.

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