High resolution FTIR investigation of $^{12}$C$_2$H$_2$ in the FIR spectral range using synchrotron radiation

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**Abstract**

FIR spectra of C$_2$H$_2$ have been recorded at 0.00096 cm$^{-1}$ spectral resolution using the Canadian Light Source synchrotron facility. The analysis allowed us to assign 731 new vibration–rotation lines from 48 bands in $^{12}$C$_2$H$_2$, 38 of which are reported for the first time. Two additional bands are assigned to $^{13}$CH$^{12}$CH. The measured line positions and calculated spectra can be made available to help in the remote sensing of acetylene in the terahertz spectral range.

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1. Introduction

Despite the absence of a permanent electric dipole moment, normal acetylene ($^{12}$C$_2$H$_2$) absorbs in the FIR spectral range. The molecule indeed has two low-lying bending vibrational states, $v_4$ (trans, $\pi_u$) and $v_5$ ($e$, $\pi_u$), and the $v_5$–$v_4$ band has origin near 117.5 cm$^{-1}$. This band and the accompanying hot bands are therefore of direct relevance to space and airborne missions working in the terahertz band and the accompanying hot bands are therefore of direct relevance to space and airborne missions working in the terahertz band.

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investigations in the ground electronic state. This model, not further detailed here, takes into account the complete set of 17 830 vibration–rotation experimental transition wavenumbers published to date in the literature, that are accessing states up to 8900 cm$^{-1}$. The data base summarized in [9,10] includes the information in the FIR range published in an earlier study [5], as well as recently [3,4]. A set of global constants resulted from the simultaneous fit of all lines at full instrumental accuracy (typically 1 part in 10$^7$) [10]. As a result, spectral line positions and intensities can be reliably predicted in various energy ranges, including the one presently investigated.

Using this procedure, only slight offsets were noticed for the highest observed $J$-lines and for some of the weakest bands. The analysis of the new FIR spectra was thus straightforward. The assignments in known bands were extended and 38 new bands, counting $e$ and $f$ levels separately, were identified, as summarized in Table 1. The new bands actually involve states that were all previously characterized in the literature through IR hot bands, as identified in [9,10]. The 1085 newly measured line positions in the FIR range, including the 731 new ones are now all inserted in the Brussels (ULB) acetylene data base. The final analysis was performed using parameters determined from the complete data base, thus including the new FIR lines.

In Table 1, bands are listed according to their decreasing relative intensity, which is indicated in the last column. The relative intensities run over a factor close to 3000. Additional $J$-values could be assigned in the 10 bands previously reported in the literature, corresponding to the strongest ones in the spectrum. A total of 38 new, weaker bands were assigned and fitted within measurement accuracy using the global model and the same procedure as explained in the literature [10]. The resulting set of global parameters, which was not dramatically modified, is not further detailed in this brief report. Fig. 1 shows a portion of the spectrum, away from the band centre. The simulation in this figure arises from the global model already referred to [10] and was performed using a single vibrational transition dipole moment for all bands, $|\mu| = 0.051$ D [4]. All lines in Fig. 1 with transmittance lower/higher than 0.8 arise from lower states with two/three bending quanta excitation. We actually calculated all bands expected in the range using the global model and checked for the consistency of the assignments from the computed relative intensities. Fig. 2 shows the calculated relative intensity of all expected $R$-branches with the observed lines indicated using a dot. For the sake of clarity, line intensities from para acetylene were multiplied by a factor of 3. For the same reason, bands were not identified on the figure. The number $m$ ($=J+1$ for $R(J)$-lines) is used. The minimum intensity limit, corresponding to the noise threshold at about 0.3 on the intensity scale of Fig. 2, appears to be very consistent for all bands, whether strong or weak. We are thus confident that the analysis is complete and that even weaker bands including those with 4 quanta excitation cannot be observed under the present experimental conditions. A general view of the FIR absorption bands is presented in Fig. 3.

### Table 1

Summary of the spectral information resulting from the analysis of the FIR spectra of $^{12}$CH$_2$ and $^{13}$CH=CH. The number of assigned lines ($N$), the minimum ($J_{min}$) and maximum ($J_{max}$) $J$-values and the standard deviation ($\sigma$) are provided for each band. For those previously reported in literature, the maximum published value of $J$ is also indicated ($J_{lit}$). The predicted relative intensity of the strongest $R(J)$ line is also listed for each band (Irel).

<table>
<thead>
<tr>
<th>$^{12}$CH$_2$</th>
<th>Lower state</th>
<th>$N$</th>
<th>$J_{min}$</th>
<th>$J_{max}$</th>
<th>$\sigma$</th>
<th>Irel</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 1 $\ell$u</td>
<td>0, 1 0/0</td>
<td>62</td>
<td>1</td>
<td>43</td>
<td>31</td>
<td>0.6</td>
</tr>
<tr>
<td>0, 1 $\ell$u</td>
<td>1, 0 0/0</td>
<td>65</td>
<td>1</td>
<td>44</td>
<td>31</td>
<td>0.5</td>
</tr>
<tr>
<td>0, 1 0/0</td>
<td>1, 0 0/0</td>
<td>54</td>
<td>2</td>
<td>39</td>
<td>25</td>
<td>0.5</td>
</tr>
<tr>
<td>1, 1 $\ell$u</td>
<td>2, 0 0/0</td>
<td>50</td>
<td>2</td>
<td>34</td>
<td>22</td>
<td>0.6</td>
</tr>
<tr>
<td>1, 1 $\ell$u</td>
<td>2, 0 0/0</td>
<td>46</td>
<td>0</td>
<td>34</td>
<td>22</td>
<td>0.4</td>
</tr>
<tr>
<td>0, 2 $\ell$u</td>
<td>1, 1 1–1</td>
<td>61</td>
<td>0</td>
<td>35</td>
<td>19</td>
<td>0.9</td>
</tr>
<tr>
<td>0, 2 $\ell$u</td>
<td>1, 1 1–1</td>
<td>49</td>
<td>3</td>
<td>37</td>
<td>21</td>
<td>0.7</td>
</tr>
</tbody>
</table>

The various bending sub-states are identified using $v_4$, $v_5$, $l_e$, $l_f$, $e$/$f$, $u$, $g$, and $l_5$ and $l_3$ the usual vibrational angular momentum quantum numbers associated to the trans-$n_2$ ($v_4$) and cis-$n_2$ ($v_5$) doubly degenerate bending vibrations.

![Fig. 1.](image-url) Transmittance spectrum of acetylene around 156 cm$^{-1}$; observed (bottom) (72 m absorption path, 3 Torr acetylene pressure, 298 K); and simulated (top) from the $^{12}$CH$_2$ global model using a single transition dipole moment $|\mu|=0.051$ D. $\bullet$: $^{13}$CH=CH, $\psi^2-v_a$, $R(14)$ lines; $\ast$: water lines.
It should be noticed that, unlike the global model, state-to-state vibration–rotation constants are unable to reproduce all assigned line and corresponding J-level wavenumbers within measurement accuracy. Rather than listing individual state constants of limited use, we decided to make the simulated spectrum resulting from the global model available on request to the ULB authors. The detailed line assignments and measurements, together with band centers can also be made available by the ULB authors.

The same assignment procedure was applied to $^{13}\text{CH}^{12}\text{CH}$, using the corresponding data base and parameters published in the literature [11], leading to identify both the e and f components of the $v_5$–$v_4$ band. Additional hot bands were predicted to be too weak to be observed under the present experimental conditions. These bands, with results also summarized in Table 1, seem to be the first FIR transitions ever reported for this isotopologue in the literature. Besides the acetylene lines, a few lines belonging to residual water vapor present in the evacuated spectrometer were identified on the spectra. Additional, weak lines are also observed on the spectra which must arise from unidentified impurities in the sample.

4. Conclusion

We have analysed four FIR spectra of $^{12}\text{C}_2\text{H}_2$ recorded at 0.00096 cm$^{-1}$ resolution using the far-infrared beamline at the Canadian Light Source. We report new spectroscopic results for 10 known and 38 new bands. In addition, two bands belonging to $^{13}\text{CH}^{12}\text{CH}$, not previously identified in the FIR spectral range, were observed in the spectra and assigned. Spectral simulations demonstrate the consistency of the analysis. We hope that this wealth of new information, including calculated cross sections that can be made available on request, will help in the detection of acetylene using remote sensing techniques in the terahertz spectral range.

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References