

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

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ABSTRACT

FIR spectra of C_2H_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 $^{12}\text{C}_2\text{H}_2$, 38 of which are reported for the first time. Two additional bands are assigned to $^{13}\text{CH}^{12}\text{CH}$. 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 ($^{12}\text{C}_2\text{H}_2$) absorbs in the FIR spectral range. The molecule indeed has two low-lying bending vibrational states, ν_4 (*trans*, π_g) and ν_5 (*cis*, π_u), and the ν_5 – ν_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 range such as HERSCHEL [1] and SOFIA [2], respectively. These missions have prompted several laboratory investigations in the low [3] and high [4] energy side of ν_5 – ν_4 band. The interpretation of the spectra relied on line positions and intensities available in the literature [5–7]. The most recent results reported only a few lines in the FIR range [3,4], and since the earlier FTIR data were recorded at the time using conventional absorption sources [5], it was tempting to use synchrotron radiation sources to extend the spectral information. The recent investigation by Jacquemart et al. [4] already relied on such an absorption source at SOLEIL but, as previously mentioned, only reported a few lines, the focus being on intensity measurements. We used synchrotron radiation at the Canadian Light Source (CLS) to further investigate the FIR absorption spectrum of acetylene, $^{12}\text{C}_2\text{H}_2$ at high spectral resolution. This publication focuses on line positions and relative intensity of observed bands.

2. Experiments

For this study four absorption spectra have been recorded at an apodized resolution of 0.00096 cm^{-1} in the 64 – 246 cm^{-1}

spectral range using the Bruker IFS 125 Fourier transform spectrometer located at the far-infrared beamline, Canadian Light Source, Saskatoon, Canada. All the spectra were recorded using a multipass coolable absorption cell with a 2 m base length. The cell was equipped with wedged Mylar windows. The radiation generated by the synchrotron source was detected using a Si bolometer running at 80 kHz scanning speed. The diameter of the iris was 2 mm. A 5 kHz electronic filter was used in the experiments. The sample of 99.96% purity was supplied by the Cambridge Isotope Laboratories and was used without further purification. Lines from $^{12}\text{CH}^{13}\text{CH}$ were nevertheless observed, as further detailed in the next section. Four spectra were successively recorded with the following pressure/pathlength conditions: 507 mTorr/40 m (I); 750 mTorr/56 m (II); 3 Torr/72 m (III); 750 mTorr/72 m (IV). The gas pressures were measured using a 0–1 Torr capacitance gauge (Baratron) for spectra (I), (II), and (IV). A 0–10 Torr Baratron gauge was used to monitor the pressure of spectrum (III). A T-type thermocouple mounted inside the cell was used to monitor the gas sample temperature, which was about 298 K for the four spectra. The calibration of the wavenumber scale of each spectrum was performed relative to previous acetylene measurements reported in the literature [4,5]. The acetylene lines were measured on the spectrum on which they presented the optimal intensity and signal to noise ratio. Most of the new assignments were performed on spectrum III.

3. Analysis

Over the past few years, a global vibration–rotation model of acetylene ($^{12}\text{C}_2\text{H}_2$), based on the block diagonalization of the vibration Hamiltonian into polyads [8], emerged from a series of

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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

Table 1

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

Upper state	Lower state	N	J_{\min}	J_{\max} (Lit.)	$\sigma \times 10^4$ (cm^{-1})	Irel
$^{12}\text{C}_2\text{H}_2$						
0 1, 0 1fu	1 0, 1 0fg	62	1	43 (31)	0.6	1000.00
0 1, 0 1eu	1 0, 1 0eg	65	1	44 (31)	0.5	993.58
0 1, 0 1fu	1 0, 1 0eg	15	1	15 (11)	0.5	180.40
0 1, 0 1eu	1 0, 1 0fg	13	1	13 (10)	0.5	97.90
1 1, 1 1fu	2 0, 2 0fg	54	2	39 (25)	0.5	95.04
1 1, 1 1eu	2 0, 2 0eg	50	2	34 (22)	0.6	85.49
1 1, 1 -1eu	2 0, 0 0eg	46	0	34 (22)	0.4	70.80
0 2, 0 0eg	1 1, 1 -1eu	61	0	35 (19)	0.9	65.97
0 2, 0 2eg	1 1, 1 1eu	49	3	37 (21)	0.7	55.80
0 2, 0 2fg	1 1, 1 1fu	54	2	38 (20)	0.8	55.56
1 1, 1 1eu	2 0, 2 0fg	12	2	14	1.0	37.77
1 1, 1 1fu	2 0, 2 0eg	13	3	15	1.0	25.52
1 1, 1 1eu	2 0, 0 0eg	41	6	36	0.9	22.81
0 2, 0 2fg	1 1, 1 1eu	10	2	14	0.8	22.28
1 1, 1 -1eu	2 0, 2 0eg	36	7	38	1.0	20.56
0 2, 0 2eg	1 1, 1 1fu	11	2	15	0.6	15.07
2 1, 2 1fu	3 0, 3 0fg	38	3	29	0.9	6.20
2 1, 2 1eu	3 0, 3 0eg	33	3	24	0.9	6.03
1 2, 1 2fg	2 1, 2 1fu	34	3	30	1.2	5.12
1 2, 1 2eg	2 1, 2 1eu	39	3	28	1.3	5.11
1 2, 1 0eg	2 1, 2 -1eu	40	3	31	0.9	4.44
1 2, 1 0fg	2 1, 2 -1fu	34	2	30	1.1	4.18
2 1, 2 1fu	3 0, 3 0eg	8	3	12	0.5	4.05
2 1, 2 -1eu	3 0, 1 0eg	24	2	22	1.2	3.84
2 1, 2 -1fu	3 0, 1 0fg	19	5	25	0.9	3.77
1 2, 1 2eg	2 1, 2 1fu	9	3	11	1.0	3.24
2 1, 2 1eu	3 0, 3 0fg	5	3	8	0.9	2.98
0 3, 0 1fu	1 2, 1 0fg	29	3	27	1.4	2.95
0 3, 0 1eu	1 2, 1 0eg	29	2	26	1.0	2.95
1 2, 1 2fg	2 1, 2 1eu	8	3	10	0.7	2.39
0 3, 0 3eu	1 2, 1 2eg	29	3	26	2.4	2.29
0 3, 0 3fu	1 2, 1 2fg	30	3	25	1.0	2.28
2 1, 2 1eu	3 0, 1 0eg	10	14	28	1.0	1.54
0 3, 0 3fu	1 2, 1 2eg	3	3	5	0.8	1.44
2 1, 0 1fu	3 0, 1 0fg	6	7	19	1.3	1.09
0 3, 0 3eu	1 2, 1 2fg	3	3	5	1.4	1.06
1 2, 1 0fg	2 1, 0 1fu	10	8	26	2.4	1.04
1 2, -1 2fg	2 1, 2 -1fu	5	12	20	1.3	0.95
2 1, 0 1eu	3 0, 1 0eg	5	6	14	0.3	0.94
2 1, 2 -1eu	3 0, 3 0eg	5	16	28	2.3	0.88
1 2, 1 0eg	2 1, 0 1eu	8	3	19	2.2	0.86
2 1, 0 1eu	3 0, 3 0eg	6	16	25	1.2	0.85
1 2, -1 2eg	2 1, 2 -1eu	4	11	19	1.8	0.82
1 2, -1 2eg	2 1, 0 1eu	4	11	21	1.7	0.78
2 1, 2 1fu	3 0, 1 0fg	5	19	27	1.0	0.70
1 2, -1 2fg	2 1, 0 1fu	3	12	16	0.7	0.70
2 1, 0 1fu	3 0, 3 0fg	7	17	29	1.7	0.58
1 2, 1 2eg	2 1, 0 1eu	1	17	17	0.1	0.31
$^{13}\text{CH}^{12}\text{CH}$						
0 1, 0 1e	1 0, 1 0e	16	7	25	1.4	22.85
0 1, 0 1f	1 0, 1 0f	17	7	24	1.3	22.80

The various bending sub-states are identified using $v_4 v_5$, $l_4 l_5 e/f u/g$, with l_4 and l_5 the usual vibrational angular momentum quantum numbers associated to the $trans-\pi_g$ (v_4) and $cis-\pi_u$ (v_5) doubly degenerate bending vibrations.

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, $|\mu| = 0.051\text{ D}$ [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.

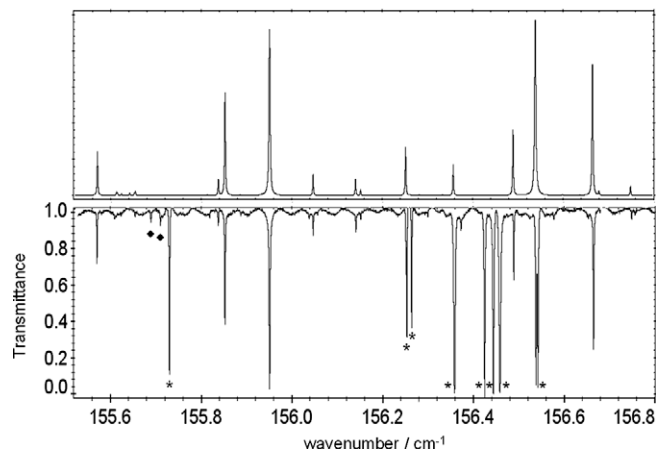


Fig. 1. Transmittance spectrum of acetylene around 156 cm^{-1} : observed (bottom) (72 m absorption path, 3 Torr acetylene pressure, 298 K); and simulated (top) from the $^{12}\text{C}_2\text{H}_2$ global model using a single transition dipole moment $|\mu| = 0.051\text{ D}$. ♦: $^{13}\text{CH}^{12}\text{CH}$, v_5-v_4 , $R(14)$ lines; *: water lines.

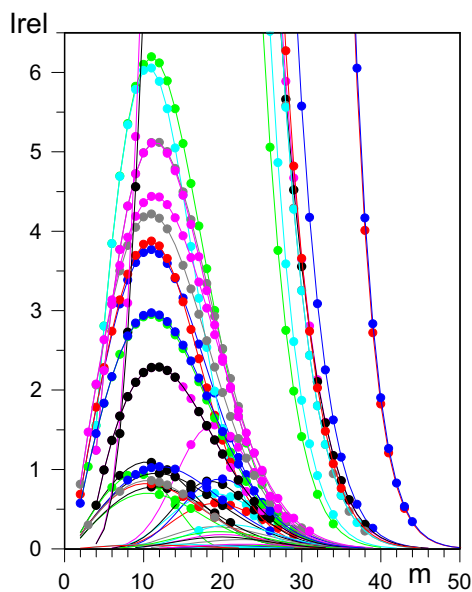


Fig. 2. Simulated relative intensities of R-branches of $^{12}\text{C}_2\text{H}_2$ in the FIR spectral region, as a function of m ($=j+1$), from the global model with a single transition dipole moment $|\mu| = 0.051$ D. Observed $R(J)$ lines are indicated using dots. Line intensities from para acetylene were multiplied by a factor 3 on the figure.

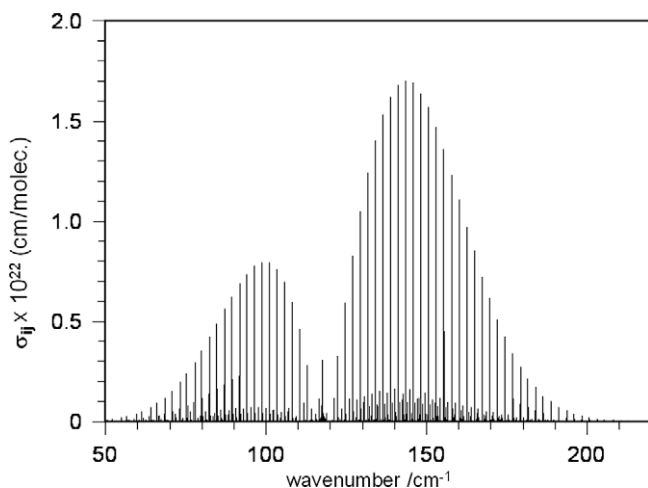


Fig. 3. FIR spectrum of $^{12}\text{C}_2\text{H}_2$ simulated from the global model with a single transition dipole moment $|\mu| = 0.051$ D.

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 $\nu_5-\nu_4$ 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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