Accurate ro-vibrational rest frequencies of DC$_4$H at infrared and millimetre wavelengths*

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ABSTRACT

Context. Diacetylene, C$_4$H$_2$, has been identified in several astronomical environments through its infrared spectrum. In contrast, monodeuterated diacetylene (DC$_4$H) has not been detected in space so far owing to the low isotopic abundance of deuterated species but also to the rather poor laboratory spectroscopic characterisation of this molecule.

Aims. The aim of this work is to provide accurate spectroscopic parameters for DC$_4$H to achieve reliable predictions for both its spectra at millimetre and infrared wavelengths.

Methods. We studied the rotational spectrum of DC$_4$H in the range 85–615 GHz by millimetre-wave spectroscopy and the infrared spectrum below 1000 cm$^{-1}$ by high-resolution, Fourier-transform spectroscopy. Several pure rotational transitions were recorded in the ground state and in excited vibrational bending states. The three fundamental bands $v_1$, $v_2$, and $v_3$ have been identified and assigned in the infrared spectrum.

Results. The rotational transitions were analysed together with the infrared data in a global fit that produces very accurate ro-vibrational parameters. The observed frequencies and wavenumbers are reported to provide precise guidance for astronomical searches.

Key words. ISM: molecules – line: identification – molecular data – molecular processes – infrared: ISM

1. Introduction

Many polyatomic molecules discovered in space are carbon chains with an acetylenic structure, i.e., featuring alternating single and triple C–C bonds. The simplest members of the family, acetylene (C$_2$H$_2$) and diacetylene (C$_4$H$_2$), play a major role in the synthesis of complex interstellar molecules: ion–neutral or neutral–neutral reactions between these moieties and C$^+$ or CN lead to the production of larger hydrocarbons (C$_n$H$_m$) or cyanopolyynes (HC$_2$CN) (Cherchneff & Glassgold 1993). Chain polymerisation then culminates in the formation of complex aliphatic and possibly aromatic structures that compose the solid carbon-based materials present in the interstellar medium (ISM, Frenklach & Feigelson 1989; Allamandola et al. 1989; Kwok 2009).

Despite their astrophysical relevance, C$_2$H$_2$ and C$_4$H$_2$ remain rather elusive for detection in the ISM due to the lack of electric permanent dipole moment and thus of pure rotational spectrum. As a result, they have only been observed in the infrared (IR). The main isotopic species of acetylene have been observed with high abundances in both cold (<100 K) and warm (100–1000 K) gas (e.g., Lacy et al. 1989; Evans et al. 1991; Carr et al. 1995; Lahuys & van Dishoeck 2000; Farrah et al. 2007; Sonnentrucker et al. 2007). Diacetylene has been observed in the proto-planetary nebulae CRL 618 and CRL 2688 (Cernicharo et al. 2001), and also outside our galaxy in a similar object embedded in the Large Magellanic Cloud (SMP LMC 11, Bernard-Salas et al. 2006). However, the high N(C$_2$H$_2$)/N(C$_4$H$_2$) column density ratio (~2) derived in CRL 618 (Cernicharo et al. 2001) suggests that substantial abundances of diacetylene may be present in the warm gas of many carbon-rich environments. C$_2$H$_2$ is also a well known constituent of the stratosphere of the giant planets and their moons (e.g., de Graauw et al. 1997; Fouchet et al. 2005; Coustenis et al. 2007). Very recently, the $^{13}$C isotopologue of diacetylene has been observed in Titan’s spectra (Jolly et al. 2010). There, it acts as a UV shield and is thought to play a major role in the photochemical reactions originating the organic aerosols (tholines) present in the atmospheres of these solar system bodies (Waite et al. 2007).

Although the cosmic deuterium-to-hydrogen ratio is a few times $10^{-5}$, isotopic fractionation mechanisms in the ISM are able to produce large D-enrichment in many molecules, and deuterated isotopologues are indeed observed with relative abundances up to a few percent or more of their parent species (Herbst 2003).

In the gas phase, the deuterium fractionation is generally driven by exothermic ion–neutral reactions in low-temperature environments (e.g., Roberts & Millar 2000). However, experimental and theoretical investigations have shown that D-enrichments in complex hydrogen-deficient organic molecules can be achieved via a barrierless and exoergic neutral–neutral reaction involving the dicarbon radical C$_2$ in its
\(a^3\Pi_u\) electronic excited state (Guo et al. 2006). This process is enhanced at high temperatures and could sustain the production of deuterated carbon chains in the warm gas, for example, close to the photosphere of evolved carbon-rich stars.

Deuterated hydrocarbons are also important proxies for the D/H isotopic composition of planetary atmospheres, which in turn provide important information on the evolutionary models of the solar nebula (Coustenis et al. 2007, 2010). Mono-deuterated acetylene (DC\(_2\)H) has been recently detected in Titan by Cassini/CIRS yielding a D/H ratio that is significantly higher than those measured in methane (Coustenis et al. 2008). Diacetylene produces one of the strongest emission features of Titan below 1000 cm\(^{-1}\) (\(v_6\), \(v_7\), and \(v_9\) fundamental bands). Furthermore, we investigated the extension of the pure rotational spectra of the ground and of the singly excited bending states \(v_6 = 1, v_7 = 1\), and \(v_9 = 1\) to the sub millimetre (submm) region, covering the 85–615 GHz frequency interval and reaching a J quantum number as high as 74.

In this paper we present the results of a comprehensive new laboratory investigation of the ro-vibrational spectrum of DC\(_4\)H. Following what we have done in our previous papers on HC\(_4\)H (Bizzocchi et al. 2010, 2011), our main effort aims to provide state-of-the-art spectroscopic data on DC\(_4\)H to the astronomical community. These data are very useful for infrared and/or millimetre studies. The spectral analyses yielded the very accurate values of the spectroscopic constants needed to predict precise millimetre and IR rest frequencies for all the band and vibrational states investigated.

2. Experimental

The sample of DC\(_4\)H employed in this work was produced by the method described by Armitage et al. (1951), i.e. by reaction of 1,4-dichloro-2-butyne (Aldrich) with sodium hydroxide dissolved in a nearly equimolar mixture of H\(_2\)O and D\(_2\)O. The rotational spectra of DC\(_4\)H in the ground state and in the excited bending states have been recorded in selected frequency regions between 85 and 615 GHz, using the mm-wave spectrometer employed to record the \(v_8 - v_6\) difference band for the symmetric isotopologues HC\(_4\)H and DC\(_4\)D (Bizzocchi et al. 2010). Briefly, the radiation sources were phase-locked Gunn oscillators (75–115 GHz range) equipped with various frequency multipliers, and the absorption cell was a 3 m long glass tube sealed by PTFE windows. Signal detection was performed using a liquid-helium-cooled InSb detector. Source frequency modulation was applied, and the signal was demodulated at 2\(f_r\), thus obtaining the second derivative of the actual spectrum profile. About 150 rotational transition frequencies of DC\(_4\)H have been measured, with experimental uncertainties of \(\sim 30\) kHz. All the measurements were performed at room temperature, at a static pressure of \(\sim 1.5\) Pa.

The infrared spectra were recorded with a Bomem DA3.002 Fourier-transform spectrometer equipped with a Globar source, a KBr beamsplitter, and a liquid nitrogen-cooled HgCdTe detector. The attained resolution was either 0.004 or 0.006 cm\(^{-1}\). Several spectra were recorded at pressures between 40 and 800 kPa. We mostly used a 0.18 m long absorption cell, but also a multipass White-type cell with an effective pathlength of 10 m was employed. Several hundred scans, up to 860, were co-added in order to improve the signal to noise ratio of the spectra. Rotational transitions of H\(_2\)O (Toth 1991) and CO\(_2\) (Horneman 2007) were used for calibration. The average precision of our measurements was estimated to be around 0.0004 cm\(^{-1}\).

3. Observed spectra and analysis

3.1. Millimetre-wave spectra

Previous recordings of a few rotational transitions (\(v \leq 80\) GHz) for various low-lying vibrational states of DC\(_4\)H had

\[ J = 4, 8, 11, \ldots, 250 \]

\[ J = 4, 8, 11, \ldots, 250 \]
been already reported (Etoh et al. 1981; Tanaka et al. 1988; Matsumura et al. 2006). In the present work we have extended the measurements for the ground state and singly excited bending states \( v_6 = 1 \), \( v_8 = 1 \), and \( v_9 = 1 \) into the submm region, by observing \( ca. \) 150 pure rotational transitions with \( J \) ranging from 10 to 74. The assignment of the new lines was guided by the literature spectroscopic data, making use of the basic rotational energy level expression for linear polyatomic molecules, including the \( l \)-type doubling contribution where appropriate (e.g., see Eq. (5.25) in Gordy & Cook 1984). An example of the observed spectra showing ground and \( v_6 = 1 \) state transitions is given in Fig. 1. Due to the vibrationally enhanced dipole moment, the excited-state line is \( ca. \) 2.5 times more intense than the ground state line, despite the less favourable population factor.

### 3.2. Infrared spectra

No high-resolution investigation of the IR spectra of DC₄H below 1000 cm\(^{-1}\) has ever been reported. We observed about 760 ro-vibrational transitions for the \( v_6 \), \( v_7 \), and \( v_8 \) fundamental bands. The infrared spectra were recorded at different pressures in order to have very accurate measurements even for the high-\( J \) transitions. The \( J \) values of the observed transitions are 1–117 for \( v_6 \), 1–81 for \( v_7 \), and 3–100 for \( v_8 \). Besides the \( v_6 \), \( v_7 \), and \( v_8 \) fundamental bands, several hot bands have been identified and analysed and will be the subject of a future paper. Initially, the transition wavenumbers of each band were fitted separately, in order to check the correctness of the assignments and to extend the data set. The data were analysed using the basic ro-vibrational energy level expression of a linear molecule (Fusina et al. 2011) with centrifugal distortion corrections up to the sextic term. Since all these bands involve bending modes, the \( l \)-type doubling energy contributions were included in the model. A portion of the recorded spectrum showing the \( v_6 \) fundamental and the associated hot band system is illustrated in Fig. 2.

### 3.3. Spectral analysis

Eventually, all mm-wave and infrared data were fitted simultaneously in a single least-squares procedure. A comprehensive summary of the relevant ro-vibrational theory, including the expression of the Hamiltonian matrix elements used in the present analysis is reported in Appendix A. A proper weighting factor (\( \sigma_i = 1/\sigma_i^2 \)) was assigned to each data point, in order to take the different measurement precisions of the various data sets into account. The following \( \sigma_i \) values were used for the literature data: 1 kHz for the hyperfine-free, ground-state transition frequencies derived from the FTMW study of Matsumura et al. (2006); 20 kHz for the mm-wave lines of ground, \( v_8 = 1 \), and \( v_9 = 1 \) states (Tanaka et al. 1988); 50 kHz for the \( v_6 = 1 \) rotational frequencies reported by Etoh et al. (1981). For the data collected in the present investigation, we assumed a \( \sigma_i = 20 \) or 40 kHz for the lines below or above 420 GHz, respectively. Finally, \( \sigma_i = 5 \times 10^{-4} \) cm\(^{-1}\) was adopted for the present IR measurements.

The fit of the transitions of the \( v_6 = 1 \) bending state showed anomalous residuals. Considering that the \( v_9 = 3 \) state is only 3 cm\(^{-1}\) apart, we postulated a quartic anharmonic resonance between these two states, which has been explicitly considered in our analysis. Generally speaking, to determine the interaction term (\( W_{6999} \), see Eq. (A.3) in Appendix A), it is necessary to include experimental transitions involving both interacting states. Since we did not observe any transition belonging to \( v_9 = 3 \), we chose to fix its rotational parameters in the following
Fig. 2. Portion of the infrared spectrum of DC₄H showing the ν₆ band, centred at ν₀ = 626.9609 cm⁻¹. The hot band ν₀ + ν₉ − ν₉ is also visible at ν₀ = 625.9136 cm⁻¹. Experimental conditions: pressure 67 Pa, absorption path length 0.18 m, resolution 0.004 cm⁻¹, 200 scans.

Table 1. Band origins and vibrational state constants for the unperturbed vibrational bands of DC₄H.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Ground state This work</th>
<th>Ground state (Tanaka et al. 1988)</th>
<th>ν₇ = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₀</td>
<td>/ cm⁻¹</td>
<td>471.401399(64)</td>
<td>4084.4546(18)</td>
<td>4090.6191(19)</td>
</tr>
<tr>
<td>B₉</td>
<td>/ MHz</td>
<td>4084.453438(68)</td>
<td>4084.4546(18)</td>
<td>4090.6191(19)</td>
</tr>
<tr>
<td>D₉</td>
<td>/ kHz</td>
<td>0.394107(29)</td>
<td>0.402(12)</td>
<td>0.40229(36)</td>
</tr>
<tr>
<td>H₀</td>
<td>/ mHz</td>
<td>0.0280(36)</td>
<td>0.0280</td>
<td>0.0280²</td>
</tr>
<tr>
<td>qᵣν</td>
<td>/ MHz</td>
<td>3.0402(22)</td>
<td>-3.56(54)</td>
<td></td>
</tr>
<tr>
<td>qᵣJ</td>
<td>/ Hz</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes. The numbers in parentheses are 1σ uncertainties expressed in units of the last quoted digit. (²) Fixed.

way: B₉ and D₉ were linearly extrapolated from the corresponding values of the ground and ν₀ = 1 state, while the values of ν₀ = 1 state were adopted for the other constants. Since the rotational transitions in ν₀ = 1 are also included in the global fit, the parameters of ν₀ = 3 were derived through an iterative procedure. The ℓ-doubling constants qᵣ and qᵣJ were held fixed to the values determined for ν₀ = 1. The energy separation between the two states, ΔE = Eν₀=3,ℓ=1 − Eν₀=1, was also adjusted iteratively.

The final data set, purged of perturbed spectral features and spurious measurements, comprises a total of 787 transitions. The overall weighted root mean square of the fit residuals is 0.795. The parameters derived from the least-squares procedure are listed in Tables 1–3. The fitted constants are all very well determined, and the comparison with previously available data (also reported in the Tables) shows improvements up to two orders of magnitude in precision. Including the precise mm-wave data in the data set was beneficial for significantly reducing the correlations between the lower- and upper- state parameters of the analysed IR bands. Indeed, the slightly lower precision of the parameters of the ν₇ = 1 state derives from the lack of pure rotational data for that state. This is because excitation of the ν₇ vibrational mode does not enhance the dipole moment, and the lower population prevents any observation of the corresponding rotational lines.

4. Discussion and conclusions

The set of spectroscopic constants we have derived is a remarkable improvement over the previous work (Etoh et al. 1981; Tanaka et al. 1988) because it allows calculation of a very reliable set of rest frequencies for the rotational (millimetre) and ro-vibrational (IR) transitions that involve the ground-state and most of the singly excited bending states.

We collected the complete set of measured line positions, along with a comprehensive listing of predictions calculated from the spectroscopic data of Tables 1–3. The list also includes the estimated uncertainty at the 1σ level of each transition as determined statistically by the least-squares fits (Albritton et al. 1976). This table is available in its entirety in a machine-readable...
Table 2. Band origins and vibrational state constants for the unperturbed vibrational bands of DC₄H.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>( \nu_0 = 1 ) (This work)</th>
<th>( \nu_0 = 1 ) (Tanaka et al. 1988)</th>
<th>( \nu_0 = 1 ) (This work)</th>
<th>( \nu_0 = 1 ) (Tanaka et al. 1988)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_0 )</td>
<td>/ cm(^{-1})</td>
<td>498.395521(30)</td>
<td>210(^a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_0 )</td>
<td>/ MHz</td>
<td>4089.64590(17)</td>
<td>4089.6490(51)</td>
<td>4095.68839(19)</td>
<td>4095.6938(52)</td>
</tr>
<tr>
<td>( D_0 )</td>
<td>/ kHz</td>
<td>0.395035(30)</td>
<td>0.413(30)</td>
<td>0.409462(60)</td>
<td>0.433(30)</td>
</tr>
<tr>
<td>( H_0 )</td>
<td>/ mHz</td>
<td>0.02800(^b)</td>
<td>0.02800(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( q_{v} )</td>
<td>/ MHz</td>
<td>2.63072(34)</td>
<td>2.631(2)</td>
<td>5.56810(38)</td>
<td>5.568(2)</td>
</tr>
<tr>
<td>( q_{vJ} )</td>
<td>/ Hz</td>
<td>−0.74699(99)</td>
<td>−10.88(12)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes. The numbers in parentheses are 1\( \sigma \) uncertainties expressed in units of the last quoted digit. \(^a\) Low-resolution IR value from Owen et al. (1987). \(^b\) Fixed.

Table 3. Band origin and vibrational state constants for the perturbed \( \nu_0 \) band of DC₄H.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>( \nu_0 = 1 ) (This work)</th>
<th>( \nu_0 = 1 ) (Etoh et al. 1981)</th>
</tr>
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<tr>
<td>( \nu_0 )</td>
<td>/ cm(^{-1})</td>
<td>626.960886(97)</td>
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<tr>
<td>( B_0 )</td>
<td>/ MHz</td>
<td>4086.17536(79)</td>
<td>4086.2165(44)</td>
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<td>( D_0 )</td>
<td>/ kHz</td>
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<td>0.40836(36)</td>
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<tr>
<td>( H_0 )</td>
<td>/ mHz</td>
<td>0.04000(75)</td>
<td>0.02800(^b)</td>
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<tr>
<td>( q_{v} )</td>
<td>/ MHz</td>
<td>2.11692(20)</td>
<td>2.1316(28)</td>
</tr>
<tr>
<td>( q_{vJ} )</td>
<td>/ Hz</td>
<td>−0.538(44)</td>
<td>−10.88(^b)</td>
</tr>
<tr>
<td>( W_{v00} )</td>
<td>/ cm(^{-1})</td>
<td>0.10804(89)</td>
<td></td>
</tr>
<tr>
<td>( \Delta \nu )</td>
<td>/ cm(^{-1})</td>
<td>3.039114(^b)</td>
<td></td>
</tr>
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</table>

Notes. The numbers in parentheses are 1\( \sigma \) uncertainties expressed in units of the last quoted digit. \(^a\) Assumed values, see text. \( \Delta \nu = E_{\nu_0} - E_{\nu_{\nu_0}} \).

Table 4. Measured and predicted line positions of DC₄H.

<table>
<thead>
<tr>
<th>( J' )</th>
<th>( \ell' )</th>
<th>( p' )</th>
<th>( \varphi' )</th>
<th>( J )</th>
<th>( l )</th>
<th>( p )</th>
<th>( v )</th>
<th>( RF_{\text{meas}} )</th>
<th>( RF_{\text{pred}} )</th>
<th>( 1\sigma )</th>
<th>Unit</th>
<th>( S_{J'\ell} )</th>
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<tbody>
<tr>
<td>27</td>
<td>0</td>
<td>e</td>
<td>0</td>
<td>26</td>
<td>0</td>
<td>e</td>
<td>0</td>
<td>220 529.4600</td>
<td>0.0033</td>
<td>MHz</td>
<td>27.000</td>
<td></td>
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<tr>
<td>28</td>
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<td>e</td>
<td>0</td>
<td>27</td>
<td>0</td>
<td>e</td>
<td>0</td>
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<tr>
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<td>0</td>
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<td>3.4 \times 10^{-3}</td>
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<td>cm(^{-1})</td>
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<td>e</td>
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<td>616.501459</td>
<td>3.4 \times 10^{-3}</td>
<td>cm(^{-1})</td>
<td>18.488</td>
<td></td>
</tr>
</tbody>
</table>

Notes. For a detailed description see Sect. 4. This table is available in its entirety at the CDS. A portion is shown here to indicate its form and content.

(1–4) \( J', \ell', p', \varphi' \). Rotational, vibrational quantum numbers, and \( e/\ell \) parity of the upper level;
(5–8) \( J, l, p, v \). Rotational, vibrational quantum numbers, and \( e/\ell \) parity of the lower level;
(9) \( RF_{\text{meas}} \). Measured line position. The numbers in parentheses are the assumed experimental uncertainties expressed in units of the last quoted digit;
(10) \( RF_{\text{pred}} \). Predicted line position evaluated from the spectroscopic constants of Tables 1–3;
(11) 1\( \sigma \). Estimated error of the prediction at 1\( \sigma \) level;
(12) unit. MHz or cm\(^{-1}\);
(13) \( S_{J'\ell} \). Line strength.

The corresponding Einstein A-coefficients for spontaneous emission can then be calculated for each \( J' \rightarrow J \) line using (Herzberg 1950)

\[
A_{J'\ell} = \frac{16\pi^3}{3\varepsilon_0c^2} \frac{\nu_{J'\ell}}{2J' + 1} S_{J'\ell} \mathcal{R}^2,
\]

where \( \nu_{J'\ell} \) is the transition frequency (units of Hz), \( S_{J'\ell} \) the line strength factor as given in Table 4, and \( \mathcal{R}^2 \) the squared transition dipole moment (units of C\(^2\) m\(^2\)). For a purely rotational transition, \( \mathcal{R}^2 = \mu^2 \), where \( \mu \) is the permanent electric dipole moment.
For a vibration-rotation transition, the squared transition dipole moment is expressed as

\[ r^2 = |R_{v'1}^0|^2 F, \]  

where \([R_{v'1}^0]\) is the rotationless vibrational transition dipole moment, and \(F\) the product of the Herman-Wallis factors which, for linear molecules, are expressed as

\[ F_{R} = [1 + A J m + A_{RP}^2 m^2]^2 \]  
\[ F_{Q} = [1 + A_{Q}^2 J(J + 1)]^2 \]

for \(P\) and \(R\) branch lines, and

where \(m = -J\) and \(m = J + 1\) for the \(P\) and \(R\) branches, respectively.

In this work we have provided important spectroscopic information about the monodeuterated isotopologue of diacetylene. A number of rotational and ro-vibrational parameters were determined from a global fit of microwave and infrared data. The list of observed transitions, together with the line strength factors, can be a useful guide for astronomical searches of this molecule.

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