Vibration–rotation spectra of $^{13}$C containing acetylene: anharmonic resonances

E. Venuti $^{a,b}$, G. Di Lonardo $^a$, P. Ferracuti $^a$, L. Fusina $^a$, I.M. Mills $^b$

$^a$ Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, Viale Risorgimento 4, 40136, Bologna, Italy
$^b$ Department of Chemistry, University of Reading, Reading RG6 2AD, England

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Abstract

High resolution vibration–rotation spectra of $^{13}$C$_2$H$_2$ were recorded in a number of regions from 2000 to 5200 cm$^{-1}$ at Doppler or pressure limited resolution. In these spectral ranges cold and hot bands involving the bending-stretching combination levels have been analyzed up to high $J$ values. Anharmonic quartic resonances for the combination levels $\nu_3 + m\nu_4 + n\nu_5$, $\nu_2 + m\nu_4 + (n+2)\nu_5$ and $\nu_3 + (m-1)\nu_4 + (n+1)\nu_5$ have been studied, and the $l$-type resonances within each polyad have been explicitly taken into account in the analysis of the data. The least-squares refinement provides deperturbed values for band origins and rotational constants, obtained by fitting rotation lines only up to $J = 20$ with root mean square errors of $= 0.0003$ cm$^{-1}$. The band origins allowed us to determine a number of the anharmonicity constants $\chi^0_0$.

1. Introduction

Two important quartic anharmonic resonances characterize the low energy spectrum of $^{12}$C$_2$H$_2$ and $^{13}$C$_2$H$_2$, both involving interaction of CH stretching with CC stretching plus two quanta of H-bending excitation. The first is between the $\Sigma_u^+$ states $\nu_3$ and $\nu_2 + \nu_4 + \nu_5$, and the second is between the $\Sigma_g^+$ states $\nu_4$ and $\nu_2 + 2\nu_5$. In $^{13}$C$_2$H$_2$ the stronger resonance occurs between $\nu_4$ and $\nu_2 + 2\nu_5$, due to the near accidental degeneracy of these two states in this isotopomer. The resonance between the well separated $\Sigma_u^+ \nu_3$ and $\nu_2 + \nu_4 + \nu_5$ is weak and shows in the $^{13}$C$_2$H$_2$ spectrum as a slight shift of the vibrational energies (less than 0.5 cm$^{-1}$), barely affecting the rotational constants [1]. Its effect was previously neglected in our global analysis of the transitions involving the levels $\nu_3 + m\nu_4 + n\nu_5$ with $m + n \leq 2$, and included in an effective diagonal constant [2]. In fact, the $\nu_3$ with $\nu_2 + \nu_4 + \nu_5$ coupling is very important in $^{12}$C$_2$H$_2$ [3–11], where these $\Sigma_u^+$ levels are almost degenerate. We have explicitly included both resonances in the further analysis that we report here.

Usually, the effects of vibrational perturbations become more and more important at higher energy, due both to the increasing number of levels which can interact and to the dependence of the coupling terms on the number of excited vibrational quanta. Perturbations hardly detectable in the low energy range can become important at higher frequency because of a reduced energy gap between interacting levels, due to the different anharmonicity of the vibrations involved in the interactions. This occurs, for instance, in $^{13}$C$_2$H$_2$, where the $K_{2345}$ resonance becomes stronger when a quantum of $\nu_3$ is excited in the dyad $\nu_1 + \nu_3 + \nu_2 + \nu_4 + \nu_5$ [12].

In the present work we have extended the analysis of the anharmonic interaction in $^{13}$C$_2$H$_2$ to polyads involving bending-stretching combination levels $\nu_1 + m\nu_4 + n\nu_5$, $\nu_2 + m\nu_4 + (n+2)\nu_5$ and $\nu_3 + (m-1)\nu_4 + (n+1)\nu_5$, in
order to follow the effect of the interactions into a higher energy range. The levels of such a resonant polyad are characterized by a polyad quantum number (or pseudo-quantum number [13,14]) \( V \) defined by \( V = 5\nu_1 + 3\nu_2 + 5\nu_3 + \nu_4 + \nu_5 \).

The perturbations were investigated at Doppler or pressure limited resolution by detecting either cold band transitions from the ground state or hot bands originating from the lowest excited bending levels.

The observed energy levels were fitted by least-squares refinement to a rovibrational Hamiltonian as described further below. The fit yielded deperturbed band centres used to derive a set of deperturbed anharmonic constants, which could enable us to calculate an anharmonic force field for this molecule.

The results of the analysis show how in the diads \( \nu_1 + m\nu_5/\nu_2 + (m+2)\nu_5 \) the mixing between the interacting states increases with the energy, approaching 50% for the pair \((\nu_1 + 2\nu_5)^{0,+2}/(\nu_2 + 4\nu_5)^{0,+2}\). For the weaker resonances it is shown that, even though the energy gaps between coupled levels are quite large, the \( K_{2345} \) value of about 12.8 cm\(^{-1}\) produces shifts which cannot be neglected in a detailed analysis of the spectrum.

2. Experimental details

The spectra were recorded on a Bomem DA 3.002 at a resolution ranging from 0.006 to 0.008 cm\(^{-1}\). The sample of acetylene enriched with \(^{13}\)C was purchased from Cambridge Isotope Laboratories.

The spectra in the 3 \( \mu \)m region were recorded with a White-type cell, with pathlengths ranging from 0.18 to 5 m, by employing a Globar source and a Hg:Cd:Te or a In:Sn detector at 77 K. Pressures varying from 150 to 1330 Pa were necessary to observe weak hot bands. Pathlengths of 5 to 42 m and pressures from 130 to 3900 Pa were used in recording the spectra in the ranges 3750–4150 and 4350–4750 cm\(^{-1}\), with a resolution varying from 0.004 to 0.008 cm\(^{-1}\). A quartz-halogen lamp was used as a source.

The 3 \( \mu \)m spectral range was calibrated by using as secondary standard the accurate wavenumbers calculated for \( \nu_5 = 1 \) levels as obtained from the hot band \( \nu_1 (\Sigma_u^+) \leftarrow \nu_4 (\Pi_u) \) in the 4 \( \mu \)m region. Accurate values for the \( \nu_4 = 1 \) energy levels have been reported in our previous work on the bending states [15].

The spectra between 3750 and 4150 cm\(^{-1}\) were calibrated by using as standards both \( \text{H}_2\text{O} \) and \( \text{CO} \) wavenumbers [16]. Spectra in the higher energy region were calibrated against CO.

3. Theory

To describe the bending energy levels of a linear molecule and to deal with vibration and rotation \( l \)-type resonances [17–25] we have used a similar model to that in our previous papers [2,15]. The one significant difference in this work is that rotational \( l \)-resonance interactions between \( \Sigma \) and \( \Delta \) vibrational states, and between \( \Pi \) and \( \Phi \) states, have been absorbed into effective rotational constants for the states. Thus the Hamiltonian matrix factorizes into \( \Sigma , \Pi , \Delta \) and \( \Phi \) vibrational blocks. We also use a basis of parity eigenstates, so that the \( e \) and \( f \) blocks factorize due to symmetry. The presence of rotational \( l \)-resonance interactions then appears mainly as anomalous contributions to the effective centrifugal distortion constants \( D \).

The anharmonic resonances which characterize the spectrum of \(^{13}\)C\(_2\)H\(_2\) originate from two effective quartic potential terms of the Hamiltonian. We denote the corresponding coefficients with a capital \( K \), in contrast to the lower case \( k \) used earlier, for the reasons presented in Section 5 of this paper. The effective Hamiltonian is:

\[
\mathcal{H} = K_{1235} q_1 q_2 q_5 + q_5 \ + \ K_{2345} q_2 q_3 (q_4 + q_5 + q_4 - q_5) . \tag{1}
\]

The matrix elements arising from the application of this interaction Hamiltonian have the following expression in the signed-\( l \) basis:
\[ \langle v_1, v_2, v_3; v_4^{l_4}, v_5^{l_5}, J, k | \mathcal{H} | v_1 - 1, v_2 + 1, v_3; v_4^{l_4}, (v_5 + 2)^{l_5}, J, k \rangle \\
= \frac{1}{2} K_{1255} \sqrt{v_1(v_2 + 1)} [(v_5 + 2)^2 - l_5^2], \quad (2) \]

\[ \langle v_1, v_2, v_3; v_4^{l_4}, v_5^{l_5}, J, k | \mathcal{H} | v_1, v_2 + 1, v_3 - 1; (v_4 + 1)^{l_4+1}, (v_5 + 1)^{l_5+1}, J, k \rangle \\
= \frac{1}{2} K_{2345} \sqrt{(v_2 + 1)v_3} [(v_4 \pm l_4 + 2)(v_5 \mp l_5 + 2)] \quad (3) \]

with \( k = l_4 + l_5 \).

In this work only resonances involving the excitation of at most one quantum of each stretching mode at a time have been studied. Therefore in all the matrix elements of interest \( v_2 \leq 1, v_1 \leq 1, \) and \( v_2 = 0 \) in (2) and (3). The coupling terms in Eqs. (2) and (3) depend on the bending quantum numbers approximately as \( v_3 \) and \( (v_4 v_5)^{1/2} \) respectively. Thus, the strength of the coupling can increase with energy even over a short interval. Also, in the treatment of our data we have assumed the anharmonic constants \( K_{1255} \) and \( K_{2345} \) to have no vibrational dependence in the energy range investigated. Therefore Eqs. (2) and (3) account for all the vibrational dependence of the coupling term.

In the treatment of the perturbation between \( \nu_1 (\Sigma_u^+) \) and \( \nu_2 + 2 \nu_5 (\Sigma_u^+) \) levels [2], we have assumed the rotational dependence of the coupling term to be given by

\[ W' = \frac{1}{2} K'_{1255} \sqrt{v_1(v_2 + 1)} [(v_5 + 2)^2 - l_5^2] [J(J + 1) - k^2] \quad (4) \]

In Ref. [11] it was shown that in case of very strong coupling such as the nearly degenerate \( \nu_1 (\Sigma_u^+) \) and \( \nu_2 + \nu_4 + \nu_5 (\Sigma_u^+) \) levels in \( ^{12}\text{C}_2\text{H}_2 \), higher order \( J \)-dependent terms were required such as \( K''_{2345} [J(J + 1) - k^2]^2 \) but we have not found this to be necessary in this work.

In some systems of levels treated here both anharmonic resonances and vibrational \( l \)-resonances contribute to the energy of a given state. The vibrational \( l \)-resonance occurs between levels with \( \Delta l_4 = - \Delta l_5 = \pm 2 \) and \( \Delta k = 0 \). The corresponding off-diagonal matrix elements are given by

\[ \langle v_4^{l_4}, v_5^{l_5}, J, k | \mathcal{H} | v_4^{l_4 \pm 2}, v_5^{l_5 \pm 2}, J, k \rangle = \frac{1}{2} r_{45} \sqrt{(v_4 \pm l_4 + 2)(v_4 \mp l_4)(v_5 \mp l_5 + 2)(v_5 \pm l_5)}. \quad (5) \]

4. Spectral analysis

4.1. Single band analysis

In Table 1 we report the energy centres \( G_c \) of the levels investigated in \( ^{13}\text{C}_2\text{H}_2 \), along with the rotational constants we have determined. (The energy centre \( G_c \) is related to the vibrational origin by the equation \( G_c = G_0 - B_c k^2 - D_c k^4 \).) For the sake of completeness, we also give the results for the dyads \( \nu_1(\Sigma_u^+) / \nu_2 + \nu_4 + \nu_5 (\Sigma_u^+) \) and \( \nu_1 (\Sigma_u^+) / \nu_2 + 2 \nu_5 (\Sigma_u^+) \), whose analyses are reported in Refs. [1,2] respectively.

The \( G_c \) values were calculated by constraining lower state parameters to their literature values [15], and then fitting the upper state energy levels to a power series in \( J(J+1) \). The last column in Table 1 reports the lower states for the bands investigated. In fact, in some cases the same level was detected from various cold and hot transitions, which were analyzed together as a further check of the accuracy of the calibration in different energy regions. A listing of all the observed lines can be obtained from any of the authors.

Single band fits provided a set of perturbed energies, effective rotational constants, and some parameters, i.e. the mean energy for a pair of interacting levels, which could be used as accurate starting values in the subsequent analysis.

To extend the fit to \( J \geq 20 \) terms of order \( \geq [J(J+1)]^2 \) in the expansion were often required. Furthermore, some bands displayed rotational perturbations which could not be accounted for by the rotational dependence of the quartic resonance, because the perturbation was present only in one level of a given polyad. Most of these weak,
Table 1
Energy centres and rotational constants (in cm\(^{-1}\)) determined from single band analyses for higher resonance polyads in \(^{13}\)C\(_2\)H\(_2\)\(^*\)

<table>
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<tr>
<th>Sym.</th>
<th>(v_1)</th>
<th>(v_2)</th>
<th>(v_3)</th>
<th>(v_4^\alpha)</th>
<th>(v_5^\alpha)</th>
<th>(v_4^\beta)</th>
<th>(v_5^\beta)</th>
<th>(G_c)</th>
<th>(B_c)</th>
<th>(\text{Lower states})</th>
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<td></td>
<td></td>
<td></td>
<td>(0^\alpha)</td>
<td>(0^\beta)</td>
<td>(0^\alpha)</td>
<td>(0^\beta)</td>
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<td>(0^\beta)</td>
<td>(1^\pm)</td>
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<td>0</td>
<td>1(^{+1})</td>
<td>1(^{-1})</td>
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<td>1(^{-1})</td>
</tr>
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<td>3(^{\pm1})</td>
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<td>0</td>
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<td>1(^{-1})</td>
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\(^a\) Successive polyads are separated by a blank line.

Localized rotational perturbations are quite difficult to analyze, due to the difficulty of identifying the perturbing level.

We found preliminary single band analyses to be useful in the investigation of the vibrational perturbations. In fact, in the spectra of the stretching-bending combination levels of \(^{13}\)C\(_2\)H\(_2\), relative intensities and separation energies within a single polyad must closely reproduce those found in the corresponding bending combination, unless some strong perturbation affects one or more of these levels. This is expected because the constants which are used to describe the splittings (\(g_{44}, g_{45}, g_{55},\) and \(r_{45}\)) should vary only slowly with the stretching quantum numbers. This also provides a way of tracking down perturbation patterns in a species whose bending spectrum is so well known as in \(^{13}\)C\(_2\)H\(_2\). Thus a test of the efficiency of the deperturbation procedure consists in achieving deperturbed energy gaps close to those observed for the bendings.
Table 2
Results (cm⁻¹) from the analysis of the ν₃ + ν₅ (Πₒ) ← GS and ν₂ + 3 ν₅ (Πₐ) ← GS transitions

<table>
<thead>
<tr>
<th>Vibrational transition</th>
<th>G'_c</th>
<th>Lines analyzed</th>
<th>10^7 σ* (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10001 (Πₒ, e)→00000 (Σ⁺ₐ, e)</td>
<td>4063.1488</td>
<td>(2→21)</td>
<td>(0→19)</td>
</tr>
<tr>
<td>01003 (Πₒ, e)→00000 (Σ⁺ₐ, e)</td>
<td>4072.1974</td>
<td>(2→21)</td>
<td>(0→19)</td>
</tr>
</tbody>
</table>

Fitted upper state parameters

| ⟨E⟩ | 4067.673100(37) | Gₓ(15, Πₒ) | 4066.76652(21) |
| (B) | 1.11414920(52) | Gₓ(2555, Πₐ) | 4068.57979(21) |
| (D) | 1.8389(13) × 10⁻⁶ | Bₚₓ(e) | 1.1138479(29) |
| ΔE | 1.81339(37) | Bₚₓ(Σ⁺ₐ) | 1.1144494(28) |
| ΔB | 5.959(51) × 10⁻⁴ | x₀₁₅ | -10.28447(80) |
| ΔD | 5.47(12) × 10⁻⁷ |

Deduced deperturbed upper state parameters

| ⟨E⟩ | 4067.673100(37) | Gₓ(15, Πₒ) | 4066.76652(21) |
| (B) | 1.11414920(52) | Gₓ(2555, Πₐ) | 4068.57979(21) |
| (D) | 1.8389(13) × 10⁻⁶ | Bₚₓ(e) | 1.1138479(29) |
| ΔE | 1.81339(37) | Bₚₓ(Σ⁺ₐ) | 1.1144494(28) |
| ΔB | 5.959(51) × 10⁻⁴ | x₀₁₅ | -10.28447(80) |
| ΔD | 5.47(12) × 10⁻⁷ |

Constrained upper state parameters

K₁₂₅₅ = 6.268701
K¹₂₅₅ = 13.6388 × 10⁻⁵

r.m.s. = 0.000165 cm⁻¹, number of data in the fit = 77

* σ corresponds to the r.m.s. value of the residuals for the bands analyzed in the simultaneous fit.
  
  b Estimated uncertainties in parentheses are given in units of the last digits quoted.

4.2. Deperturbation procedure

Tables 2–7 show in detail the results from the analysis of all the polyads that we have studied. For each vibrational transition we report the observed values of G', and the deperturbed vibrational and rotational constants and coupling constants in the Hamiltonian matrix, the details of the least-squares refinement, and the root mean square uncertainty in the fit to the observed lines. For the reasons given below the number of lines included in each deperturbation analysis is generally less than the number of lines assigned and analyzed by single band least-squares fits. Furthermore, when a level was observed from more than one transition, we selected the one with stronger and less overlapped lines.

For several of the Π states that we have analysed, only one of the two l-doubled states has been observed (usually the Π(e) state, from the analysis of P and R branches of a Π–Σ⁺ or a Σ⁺–Π band, for example). In these cases we quote the effective rotational constant for the parity state that we have observed.

In all cases the lower state constants were fixed to the values already deduced in the study of the lowest bending excited states [15]. In cases where explicit treatment of the vibrational l-resonance had to be included for the upper state, the constant ν₄₅ responsible for this interaction was fixed to the value found in Ref. [15]. The coupling terms, calculated according to Eqs. (2)–(4), were taken as the K₁₂₅₅, K₂₃₄₅ and K¹₂₅₅ values reported in Refs. [1,2] and constrained in the analysis. The value we use for K₂₃₄₅ is 12.85 cm⁻¹. This is a revised value from that which we previously reported in Ref. [2], 15.79 cm⁻¹; the new value results from a more complete analysis of the ν₃ with ν₃ + ν₅ + ν₆ resonance, which will be reported in Ref. [1]. No rotational dependence was included for the coupling constant K₂₃₄₅ on the ground that the interaction is weak. In fact, in the analysis of the system of levels ν₂ + ν₄ + ν₅ (Σ⁺ₐ), ν₂ + ν₄ + ν₅ (Σ⁺ₐ), ν₂ + ν₄ + ν₅ (Δₐ), and ν₁ (Σ⁺ₐ), where the Σ⁺ₐ levels are coupled, introducing the constant K¹₂₃₄₅ slightly improved the quality of the fit. However, we believe that in that case the constant was acting as an effective parameter, accounting for a more complicated vibrational dependence of the many rotational constants involved in the fit.
Table 3
Results (cm⁻¹) from the analysis of the ν₂ + ν₄ + 2 ν₅ (Π₈) ← ν₅ (Π₀), ν₁ + ν₄ (Π₄) ← ν₄ + ν₅ (Σ₅⁺), and ν₁ + ν₅ (Π₈) ← ν₅ (Π₀) transitions

<table>
<thead>
<tr>
<th>Vibrational transition</th>
<th>Gᵋ</th>
<th>Lines analyzed</th>
<th>10⁷ σᵃ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P</td>
<td>R</td>
</tr>
<tr>
<td>01012 (Π₈, e)–000001 (Π₀, e)</td>
<td>3928.4957</td>
<td>(2–24)</td>
<td>(2–23)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Π₈, f)</td>
<td>(Π₀, f)</td>
</tr>
<tr>
<td>10010 (Π₈, e)–00011 (Σ₅⁺, e)</td>
<td>3939.1171</td>
<td>(3–22)</td>
<td>(2–19)</td>
</tr>
<tr>
<td>00101 (Π₈, e)–00001 (Π₀, e)</td>
<td>3998.9412</td>
<td>(2–21)</td>
<td>(1–19)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Π₈, f)</td>
<td>(Π₀, f)</td>
</tr>
</tbody>
</table>

Fitted upper state parameters b

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>β₂₅₅</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gₐ (2455, Π₈)</td>
<td>3937.89597(10)</td>
<td>1.1183475(13)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gₐ (14, Π₄)</td>
<td>3939.24695(15)</td>
<td>1.1146104(19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gₐ (35, Π₄)</td>
<td>3998.49085(24)</td>
<td>1.11607630(32)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D₂₅₅</td>
<td>2.0546(27) × 10⁻⁶</td>
<td>4.5458(25) × 10⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D₁₄</td>
<td>1.3920(51) × 10⁻⁶</td>
<td>5.2683(10) × 10⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D₁₅</td>
<td>1.4884(81) × 10⁻⁶</td>
<td>4.26029(11) × 10⁻³</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Deduced deperturbed upper state parameters b

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>x₁₄</td>
<td>-13.3471(14)</td>
</tr>
<tr>
<td>x₁₅</td>
<td>-7.91341(24)</td>
</tr>
</tbody>
</table>

Constrained upper state parameters

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>K₁₂₅₅ = 6.268701</td>
<td>K'₁₂₅₅ = 13.6388 × 10⁻⁵</td>
</tr>
<tr>
<td>K₂₄₅ = 12.8481</td>
<td>r₅₅ = -6.185526</td>
</tr>
<tr>
<td>g₄₄ = 0.802346</td>
<td>g₅₄ = 6.6155236</td>
</tr>
<tr>
<td>g₅₅ = 3.4368978</td>
<td>r.m.s. = 0.000344 cm⁻¹, number of data in the fit = 185</td>
</tr>
</tbody>
</table>

ᵃ σ corresponds to the r.m.s. value of the residuals for the band analyzed in the simultaneous fit.
ᵇ Estimated uncertainties in parentheses are given in units of the last digits quoted.

In order to minimize the correlation between parameters, whenever possible the mean value and the difference of centre energies and rotational constants were calculated. For the same reason we preferred not to introduce in our calculations rotational parameters of order higher than the quartic centrifugal distortion D, even though in some cases this meant discarding a few high J values.

The simplest interaction studied in this work is given in Table 2, and involves the levels ν₁ + ν₅ (Π₀) and ν₅ + 3 ν₅ (Π₄) as observed from cold bands from the ground state. The system was treated by applying a two-level model, neglecting any interaction with the Φ component of the ν₅ + 3 ν₅ combination. The calculated energy gap between the two unperturbed levels is ≈ 1.81 cm⁻¹, whereas the observed splitting is more than 9 cm⁻¹, giving values for the mixing coefficients a² and b² 0.60 and 0.40 respectively. From the unperturbed energy of the level ν₁ + ν₅ (Π₀) the x₁₅ anharmonic constant has been deduced (Table 2).

A general feature of the spectra of ¹³C₂H₂ is that, for a given polyad, usually only the levels at lower energy are observed with sufficiently high intensity. In most cases the failure to detect the higher levels depends both on symmetry selection rules and on transition moments. In the case treated above, for instance, the ν₂ + 3 ν₅ (Φ₅₉) level might be observed in the infrared spectrum from a hot transition starting from a Δ₅ state. (2 ν₅)⁺² and (2 ν₅)⁻² would be both sufficiently populated at room temperature to give weak Φ ← Δ transitions; however we did not observe these bands even in the most dense spectra recorded. In levels coupled by vibrational l-resonance the relative intensity of the transitions depends on the extent of the mixing between the two levels. In the case reported in Table
Table 4  
Results (cm\(^{-1}\)) from the analysis of the \(\nu_2 + \nu_4 + 3 \nu_5 (\Sigma_u^+ \leftarrow \Sigma_u^+) \leftrightarrow \text{GS} (\Sigma_u^+ \leftarrow \Sigma_u^+)\), \(\nu_1 + \nu_4 + \nu_5 (\Sigma_u^+ \leftarrow \Sigma_u^+) \leftrightarrow \text{GS} (\Sigma_u^+ \leftarrow \Sigma_u^+)\), and \(\nu_5 + 2 \nu_5 (\Sigma_u^+ \leftarrow \Sigma_u^+) \leftrightarrow \text{GS} (\Sigma_u^+ \leftarrow \Sigma_u^+)\) transitions

<table>
<thead>
<tr>
<th>Vibrational transition</th>
<th>(G_c^\prime)</th>
<th>Lines analyzed</th>
<th>(10^7 \sigma^a) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>00011 ((\Sigma_u^+ \leftarrow \Sigma_u^+))</td>
<td>4645.5658</td>
<td>(1--11) (0--10)</td>
<td>38</td>
</tr>
<tr>
<td>00102 ((\Sigma_u^+ \leftarrow \Sigma_u^+))</td>
<td>4708.8590</td>
<td>(1--15) (0--14)</td>
<td>45</td>
</tr>
</tbody>
</table>

Fitted upper state parameters \(^b\)

\[
\begin{align*}
\langle E \rangle &= 4639.11580 (19) \\
\langle B \rangle &= 1.1182247 (87) \\
\langle D \rangle &= 1.541 (84) \times 10^{-6} \\
\Delta E &= 9.423246 (53) \\
\Delta B &= -3.626 (23) \times 10^{-3} \\
\Delta D &= -1.225 (23) \times 10^{-5} \\
G_{c} (355, \Sigma_u^+) &= 4708.72053 (16) \\
B_{355} &= 1.1181669 (45) \\
D_{355} &= 3.350 (22) \times 10^{-6} \\
K_{1255} &= 6.268701 \\
K_{1235} &= 13.6388 \times 10^{-5} \\
K_{2345} &= 12.8481 \\
\end{align*}
\]

\(r.m.s. = 0.000454 \text{ cm}^{-1}\), number of data in the fit = 65

\(^b\) \sigma corresponds to the r.m.s. value of the residuals for the bands analyzed in the simultaneous fit.

\(^b\) Estimated uncertainties in parentheses are given in units of the last digits quoted.

3 and illustrated in the energy diagram of Fig. 1 the vibrational \(l\)-resonance is responsible for the mixing of the levels \(|010; 1^{\pm 1}, 2^{0}\rangle\) and \(|010; 1^{\pm 1}, 2^{\pm 2}\rangle\), arising from the combination \(\nu_2 = 1, \nu_4 = 1, \nu_5 = 2\). The former is coupled by anharmonic resonance to the level \(|100; 1^{\pm 1}, 0^{0}\rangle\) and both are coupled with different interaction coefficients to \(|001; 0^{0}, 1^{\pm 1}\rangle\) via the constant \(K_{2345}\). The combination \(\nu_2 = 1, \nu_4 = 1, \nu_5 = 2\) also produces an unobserved \(\Phi\) state neglected in the analysis.

Of the two levels of \(\Pi_{u}\) symmetry, labelled \(\Pi_{u}'\) and \(\Pi_{u}''\), only the lower energy combination (\(\Pi_{u}'\)) was observed as a hot band from the \(\nu_5 = 1\) level. This system of levels was analyzed by using a \(4 \times 4\) interaction matrix, whose purely vibrational part is the following:

\[
\begin{pmatrix}
E(010; 1^{\pm 1} 2^{0}) & \sqrt{2} \, r_{45} & \frac{1}{2} K_{1255} & \frac{1}{4} K_{2345} \\
E(010; 1^{\pm 1} 2^{\pm 2}) & 0 & 0 & \frac{1}{4} \sqrt{2} \, K_{2345} \\
E(100; 1^{\pm 1} 0^{0}) & 0 & 0 & 0 \\
E(001; 0^{0} 1^{\pm 1}) & 0 & 0 & 0
\end{pmatrix}
\]

The energy difference between the diagonal terms of \(\Pi_{u}\) symmetry for the combination \(\nu_2 = 1, \nu_4 = 1, \nu_5 = 2\) was constrained according to the values of the constants \(g_{45}, g_{45}\) and \(g_{55}\) fitted in the bending region. Thus, the \(G_c\) value given in Table 3 for the \(\nu_2 + \nu_4 + 2 \nu_5\) \(\Pi_{u}\) state is deperturbed both for the vibrational \(l\)-resonance and for the anharmonic resonances. The overall energy shifts resulting for this scheme of interactions is small, but the eigenvector
Table 5  
Results (cm$^{-1}$) from the analysis of the $\nu_2 + \nu_4 + 3 \nu_5 (\Sigma^-_u) \leftrightarrow \nu_4 (\Pi_g)$ and $\nu_1 + \nu_4 + 3 \nu_5 (\Sigma^-_u) \leftrightarrow \nu_4 (\Pi_g)$ transitions

<table>
<thead>
<tr>
<th>Vibrational transition</th>
<th>$G'_c$</th>
<th>Lines analyzed</th>
<th>$10^3 \sigma^2$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01013 $(\Sigma^-_u, f) \leftrightarrow 00010 (\Pi_g, f)$ ($\Pi_p, e$)</td>
<td>4663.2587</td>
<td>(1–16) (1–13) (8–14)</td>
<td>30</td>
</tr>
<tr>
<td>10011 $(\Sigma^-_u, f) \leftrightarrow 00010 (\Pi_g, f)$ ($\Pi_p, e$)</td>
<td>4653.9760</td>
<td>(2–14) (3–13) (6–10)</td>
<td>27</td>
</tr>
</tbody>
</table>

Fitted upper state parameters$^b$

- $\langle E \rangle$ 4658.61853(28) $G_c (145, \Sigma^-_u)$ 4657.23582(44)
- $\langle B \rangle$ 1.1182537(49) $G_c (2455, \Sigma^-_u)$ 4660.00187(73)
- $\langle D \rangle$ 2.515(20) $\times 10^{-6}$ $B_{145}$ 1.115191(10)
- $\Delta E$ 2.7633(13) $B_{2455}$ 1.121312(11)
- $\Delta B$ 6.003(85) $\times 10^{-3}$

Constrained upper state parameters

- $K_{1255} = 6.268701$ $K'_{1255} = 13.6388 \times 10^{-5}$ $\Delta D = 6.74 \times 10^{-6}$
- r.m.s. = 0.000289 cm$^{-1}$, number of data in the fit = 44

$^a$ $\sigma$ corresponds to the r.m.s. value of the residuals for the bands analyzed in the simultaneous fit.

$^b$ Estimated uncertainties in parentheses are given in units of the last digits quoted.

matrix displays a large mixing between the two $\Pi_g$ levels $\nu_2 + \nu_4 + 2 \nu_5$ and the $\nu_1 + \nu_4$. Two unperturbed anharmonic constants can be deduced: $x_{14}^0$ and $x_{15}^3$.

Tables 4–6 show the results of another scheme of interactions, the system $\nu_2 = 1$, $\nu_4 = 1$, $\nu_5 = 3$ with its partners $\nu_1 = 1$, $\nu_4 = 1$, $\nu_5 = 1$ and $\nu_1 = 1$, $\nu_5 = 2$. In this case also both anharmonic and vibrational $l$-resonances occur, and one level of the $\nu_2 + \nu_4 + 3 \nu_5$ combination ($3 \Delta_u$) has not been observed. Matrices were set up separately for the $\Sigma^-_u$, the $\Sigma^-_u$ and the $\Delta_u$ components (we work in a basis of parity eigenstates, which allows this factorization). This leaves us with only one vibrational $l$-resonance to treat, together with the anharmonic coupling, involving the levels $|010; 1 \pm 1, 3 \pm 1\rangle$, $|010; 1 \pm 1, 3 \pm 3\rangle$, $|100; 1 \pm 1, 1 \pm 1\rangle$, and $|001; 0 \pm 2, 2 \pm 2\rangle$.

The difference between the diagonal energies of the levels $|010; 1 \pm 1, 3 \pm 1\rangle$ and $|010; 1 \pm 1, 3 \pm 3\rangle$, is again constrained to that found in the bending region for the combination $\nu_4 = 1$, $\nu_5 = 3$ and no dependence of the l-vibrational resonance on the vibrational quantum numbers is assumed.

Finally, we have analyzed a perturbation where four excited quanta of $\nu_5$ are involved, between $\nu_1 + 2 \nu_5 (\Sigma^-_u, \Delta_g)$ and $\nu_2 + 4 \nu_5 (\Sigma^+_g, \Delta_g)$ levels. An attempt to fit all these states together failed because of the strong rotational perturbations which affect some components. In the single band analysis, for instance, we observed a strong perturbation in the reduced energy plot of the $\nu_2 + 4 \nu_5 (\Sigma^+_g)$ state, as well as in the $\nu_2 + 4 \nu_5 (\Delta_g, e)$ levels, whereas the f component was unaffected. In the analysis of the levels originating from the $\nu_1 + 2 \nu_5$ combination no perturbations were detected.

The results of the two-level model analyses for this combination are collected in Table 7. This is also the strongest interaction so far observed in these polyads. By setting the coupling terms according to Eq. (2), the energy separation between unperturbed levels is calculated to be $\approx 1.2$ cm$^{-1}$ both for $\Sigma^+_g$ and $\Delta_g$ components, while the observed separations are 12.6 and 10.9 cm$^{-1}$ respectively.
Table 6  
Results (cm$^{-1}$) from the analysis of the $\nu_2 + \nu_4 + 3 \nu_5$ ($^3\Delta_u$) $\leftrightarrow$ $\nu_4$ ($\Pi_u$), $\nu_1 + \nu_4 + \nu_5$ ($\Delta_u$) $\leftrightarrow$ $\nu_4$ ($\Pi_u$), and $\nu_1 + 2 \nu_5$ ($\Delta_u$) $\leftrightarrow$ $2 \nu_5$ ($\Delta_u$) transitions

<table>
<thead>
<tr>
<th>Vibrational transition</th>
<th>$G_0^*$</th>
<th>Lines analyzed</th>
<th>$10^5 \sigma^2$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$01013$ ($^3\Delta_u$, e) $-$ $000010$ ($\Pi_u$, e)</td>
<td>4644.9167</td>
<td>(9-21) (10-21)</td>
<td>333</td>
</tr>
<tr>
<td>$10011$ ($\Delta_u$, e) $-$ $000010$ ($\Pi_u$, e) ($\Delta_u$, e) ($\Pi_u$, f)</td>
<td>4657.9410</td>
<td>(3-8) (1-15) (16-20)</td>
<td>58</td>
</tr>
<tr>
<td>$00102$ ($\Delta_u$, e) $-$ $000020$ ($\Delta_u$, e)</td>
<td>4718.5257</td>
<td>(3-21) (2-19)</td>
<td>50</td>
</tr>
</tbody>
</table>

Fitted upper state parameters $^b$

$G_c$ (24555, $\Delta_u$) 4656.408 (88) $B_{24555}$ 1.118983 (54) $^b$

$G_c$ (145, $\Delta_u$) 4658.108 (17) $B_{355}$ 1.1177504 (90) $^b$

$G_c$ (355, $\Delta_u$) 4717.935 (60) $B_{145}$ 1.116479 (14) $^b$

$D_{24555}$ 5.431 (11) $\times 10^{-6}$

$D_{145}$ $-1.407 (40) \times 10^{-6}$

$D_{355}$ $-3.93 (22) \times 10^{-7}$

Constrained upper state parameters

$K_{1255} = 6.268701 \quad K'_{1255} = 13.6388 \times 10^{-5} \quad K_{2345} = 12.8481 \quad r^2_{45} = -6.185526$

$g_{44} = 0.802346 \quad g_{45} = 6.6155236 \quad g_{55} = 3.4368978$

r.m.s. = 0.001711 cm$^{-1}$, number of data in the fit = 55

$^a$ $\sigma$ corresponds to the r.m.s. value of the residuals for the bands analyzed in the simultaneous fit.

$^b$ Estimated uncertainties in parentheses are given in units of the last digits quoted.

5. Discussion and conclusions

The main purpose in deperturbing a series of levels is to remove the effect of the interactions from those quantities which are used to refine harmonic and anharmonic force fields. Even relatively weak interactions, such as the anharmonic quartic resonances described in this work, can deeply affect the values derived for anharmonic constants $x_{ij}^0$ and rotational constants $B_i$. Our analysis appears quite successful for the vibrational resonances, but we have also observed a number of rotational perturbations that we have not been able to analyze. It may be that some of these effects are due to $\Sigma$ with $\Delta$ rotational $l$-resonances (which will generally affect only the $e$ component of a $\Delta$ state) complicated by the anharmonic resonances, but this is not yet clear from our analyses.

In order to provide accurate molecular parameters for $^{13}$C$_2$H$_2$, it was necessary to include in our calculations the effect of high order vibrational perturbations in regions of moderately high energy. At the same time the $l$-type resonance constants were fixed to the values found in the low energy range. This process implies some approximations, such as neglecting the vibrational dependence of all the parameters of the $l$-type interaction or of the anharmonic coupling. However, these should be regarded as minor effects.

The criterion of checking observed and calculated energy separations within a given combination was adopted to verify whether the process of deperturbation performed, with constrained mixing coefficients, worked properly. For instance, the observed energy gap between $\nu_2 + \nu_4 + 3 \nu_5$ ($\Sigma_g^+$) and $\nu_4 + \nu_4 + 3 \nu_5$ ($\Sigma_g^-$) is 0.73 cm$^{-1}$, while the difference between calculated unperturbed energy centres is 26.60 cm$^{-1}$. The unperturbed difference between the related bending combination levels $\nu_4 + 3 \nu_5$ ($\Sigma_g^+$) and $\nu_4 + 3 \nu_5$ ($\Sigma_g^+$) is 25.86 cm$^{-1}$. Correspondingly, the experimental ($\Sigma_g^+$) $-$ ($\Sigma_g^+$) separation in the $\nu_1 + \nu_4 + \nu_5$ system is 8.4 cm$^{-1}$, and this increases to 13.4 cm$^{-1}$ after deperturbation, approaching the predicted value of $2r_{45}^0$. This gives us confidence in our deperturbation analysis.
Table 7
Results (cm$^{-1}$) from the analysis of the pairs $\nu_1 + 2 \nu_5 (\Sigma^+_g) \leftrightarrow \nu_5 (\Pi_u)$, $\nu_2 + 4 \nu_5 (\Sigma^+_g) \leftrightarrow \nu_5 (\Pi_u)$ and $\nu_1 + 2 \nu_5 (\Delta_g) \leftrightarrow \nu_5 (\Pi_u)$, $\nu_2 + 4 \nu_5 (\Delta_g) \leftrightarrow \nu_5 (\Pi_u)$

<table>
<thead>
<tr>
<th>Vibrational transition</th>
<th>$G'_e$</th>
<th>Lines analyzed</th>
<th>$10^5 \sigma^a$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10002 ($\Sigma^+_g$, e)−00001 ($\Pi_u$, e)</td>
<td>4768.8889</td>
<td>(1−18), (1−15)</td>
<td>54</td>
</tr>
<tr>
<td>01004 ($\Sigma^+_g$, e)−00001 ($\Pi_u$, e)</td>
<td>4781.4833</td>
<td>(1−17), (1−15)</td>
<td>57</td>
</tr>
<tr>
<td>10002 ($\Delta_g$, e)−00001 ($\Pi_u$, e)</td>
<td>4778.9630</td>
<td>(1−18), (1−15)</td>
<td>50</td>
</tr>
<tr>
<td>($\Delta_g$, e) ($\Pi_u$, f)</td>
<td></td>
<td>(6−14)</td>
<td></td>
</tr>
<tr>
<td>01004 ($\Delta_g$, e)−00001 ($\Pi_u$, e)</td>
<td>4789.8843</td>
<td>(1−17), (2−15)</td>
<td>51</td>
</tr>
<tr>
<td>($\Delta_g$, e) ($\Pi_u$, f)</td>
<td></td>
<td>(4−14)</td>
<td></td>
</tr>
</tbody>
</table>

Fitted upper state parameters $^b$

\[
\begin{align*}
\langle E \rangle & = 4775.18620(32) \\
\langle B \rangle & = 1.1194856(56) \\
\langle D \rangle & = 4.954(19) \times 10^{-6} \\
\Delta E & = 1.1753(56) \\
\Delta B & = -5.63(39) \times 10^{-4}
\end{align*}
\]

Deduced deperturbed upper state parameters $^b$

\[
\begin{align*}
G_1 (155, \Sigma^+_g) & = 4774.5985(56) \\
G_1 (25555, \Sigma^+_g) & = 4775.7738(56) \\
B_{155} (\Sigma^+_g) & = 1.120049(40) \\
B_{25555} (\Sigma^+_g) & = 1.119204(42)
\end{align*}
\]

r.m.s. = 0.000583 cm$^{-1}$, number of data in the fit = 46

Fitted upper state parameters $^b$

\[
\begin{align*}
\langle E \rangle & = 4784.42330(26) \\
\langle B \rangle & = 1.119073(64) \\
\langle D \rangle & = -1.524(31) \times 10^{-6} \\
\Delta E & = 1.1729(51) \\
\Delta B & = 9.515(38) \times 10^{-3} \\
\Delta D & = 3.20(21) \times 10^{-6}
\end{align*}
\]

Deduced deperturbed upper state parameters $^b$

\[
\begin{align*}
G_1 (155, \Delta_g) & = 4783.8369(56) \\
G_1 (25555, \Delta_g) & = 4785.0100(56) \\
B_{155} (\Delta_g, e) & = 1.114315(40) \\
B_{25555} (\Delta_g, e) & = 1.123830(43)
\end{align*}
\]

Constrained upper stated parameters

\[
\begin{align*}
k_{155} &= 6.268701 \\
k_{25555} &= 13.6388 \times 10^{-5}
\end{align*}
\]

r.m.s. = 0.000511 cm$^{-1}$, number of data in the fit = 46

$^a$ $\sigma$ corresponds to the r.m.s. value of the residuals for the bands analyzed in the simultaneous fit.

$^b$ Estimated uncertainties in parentheses are given in units of the last digit quoted.

The resonance coefficients $K_{155}$ and $K_{25555}$ for the $^{13}$C$_2$H$_2$ isotopomer, defined in Eqs. (1)−(3), have been found to have the values 6.27 and 12.85 cm$^{-1}$, both for the analyses reported earlier on the $V = 5$ polyad containing the $\nu_1$ and $\nu_5$ fundamental bands [1,2], and for the higher polyads reported in this paper. The uncertainty in these values is difficult to estimate, but it is probably at least as large as $\pm 0.01$ cm$^{-1}$ (but we report our results to higher precision so that our calculations may be precisely reproduced). The corresponding value for $K_{2345}$ for the $^{13}$C$_2$H$_2$ isotopomer is 18.29 cm$^{-1}$.

These coefficients may be interpreted as quartic anharmonic resonance coefficients. They have sometimes previously been denoted with a lower case k, as $k_{155}$ and $k_{25555}$, and the implication of some previous discussions [2–4,6,11] has been that they are to be thought of as quartic anharmonic force constants in the potential energy function expressed in the dimensionless normal coordinate representation. However we here draw attention to the fact that the values obtained empirically should be thought of as effective coefficients, which may have both the obvious first order quartic anharmonic force constant contribution, and also various second order cubic contributions which will
appear as a product of two cubic anharmonic force constants with a resonance denominator. The first order quartic and second order cubic contributions are generally comparable in magnitude, and there is often a considerable cancellation between these two contributions to give the total effective coefficient. Pliva [17] and Jonas et al. [10] have previously drawn attention to this situation, which is analogous to the expressions for the Darling–Dennison coefficients presented in the appendix to Mills and Robiette [26]. We follow previous practice in using a capital $K$ to denote the total effective coefficient, and a lower case $k$ to denote the quartic anharmonic force constant which makes up part of the contribution to $K$. We intend to publish the perturbation theory expressions for the total coefficients $K_{1255}$ and $K_{2345}$ in the near future [27].

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References