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The *Q*-branch of $\nu_1+\nu_3+3\nu_4$ band of $^{12}C_2H_2$ located at 8330 cm^{-1}

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Abstract

The *Q*-branch of the $\nu_1+\nu_3+3\nu_4$ cold band of $^{12}C_2H_2$ located at 8330 cm^{-1} has been observed under one kilometer absorption path length. The analysis leads to a line list for this isolated and strong *Q*-branch that is missing from spectroscopic databases. This work completes the large update of acetylene data in the $\Delta P = 13$ spectral region (8200 and 8900 cm^{-1}) made in spectroscopic databases (HITRAN and GEISA) in 2020 edition.

1. Introduction

Acetylene molecule has been extensively studied both from experimental and theoretical point of view. Recent Fourier Transform Spectroscopy (FTS) [1] and Cavity Ring Down Spectroscopy (CRDS) [2] measurements of acetylene in ΔP = 13 region located between 8200 and 8900 cm^{-1} allowed the analysis of line positions and intensities of stronger bands (from FTS) and weaker bands (from CRDS). P is the polyad number defined as $P = 5V_1 + 3V_2 + 5V_3 + V_4 + V_5$, where V_i are the vibrational normal mode quantum numbers, with i = 1−5. Based on Refs. [1,2], a complete line list for around 20 bands of $^{12}C_2H_2$ acetylene is now included in the latest 2020 edition of atmospheric and planetary databases HITRAN [3] and GEISA [4]. Among those bands, the weak $\nu_1+\nu_3+3\nu_4^1$ band present an atypical Q-branch that is reversing around 8330.007 cm^{-1} at $J = 9$. The structure of this Q-branch is consequently quite overlapped leading to difficulties for fitting process. This Q-branch pointed out in Fig. 1 is observed from FTS with absorption path length of around one kilometer. In the previous cited studies [1,2] the experimental conditions did not allow to perform analysis, the Q-branch being saturated on CRDS spectrum recorded at 10 Torr and analyzed in Ref. [2] and on the contrary too weak on FTS spectra [1] recorded with around 50 m absorption path length. The Q-branch of the $\nu_1+\nu_3+3\nu_4^1$ band may be interesting under strong acetylene absorption conditions since the Q-branch is well isolated from main ΔP =13 absorption region (see graphical abstract and a zoom of $\nu_1+\nu_3+3\nu_4^1$ band presented in Fig. 1). Note that except for the studied Q-branch of the $\nu_1+\nu_3+3\nu_4^1$ band missing in HITRAN and GEISA, the whole set of observed transitions belonging to the ΔP =13 spectral region is well reproduced by databases.

(Fig1.)

2. Experimental and analysis details

For the present study, a Fourier transform spectrum was recorded at V.E. Zuev Institute of Atmospheric Optics SB RAS using Bruker IFS-125HR spectrometer connected to a White type cell (base length equal to 27.795 m) allowing to reach an absorption path length of 1057.95 m. The pressure in the cell was measured with Baratron gauge and is equal to 10.88 mbar. The spectral resolution was equal to 0.016 cm^{-1}, corresponding to a maximum optical path difference of 56.25 cm. Note that at 8330 cm^{-1}, the Doppler full-width at half-maximum (FWHM) for $^{12}C_2H_2$ is about 0.020 cm^{-1}. The ILS width (FWHM) can be calculated as (Bruker Res)/(2*0.9). The Bruker resolution of 0.016 cm^{-1} leads to the value of ILS FWHM equal to 0.009 cm^{-1}, around twice smaller than the Doppler FWHM of the studied transitions. Increasing resolution will not significantly help to resolve the congested structure of the *Q*-branch of the $\nu_1+\nu_3+3\nu_4^1$ band. The instrument was fitted with a tungsten source, a 1.50 mm entrance aperture, a CaF2 beam splitter and a 77 K InSb detector. The acetylene commercial sample was used without purification. No optical filter was used and no artificial optical weighting has been performed (boxcar function was selected). A Mertz procedure was used to correct phase of interferogram. 6200 scans have been recorded and accumulated to reach a signal-to-noise ratio (peak to peak) better than 500. The wavenumber calibration has been performed using acetylene and water transitions from HITRAN as etalons. The accuracy on line positions measurements is estimated to be better than 0.001 cm^{-1}.

The upper level of the band $\nu_1+\nu_3+3\nu_4^1$ was observed through the hot bands in Refs. [5,6]. The $\nu_1+\nu_3+3\nu_4^1-(\nu_4+2\nu_5)^3$ band reported in [6] is very weak. In Ref. [5] many lines of the $\nu_1+\nu_3+3\nu_4^1-\nu_4^1$ band have been observed. But the band manifested perturbed rotational structure and, consequently, was not reported in the supplementary materials. As it can be seen in [7] the Herman-Wallis coefficients and band strength were not defined for the considering $\nu_1+\nu_3+3\nu_4^1$ band. So there is no way to simulate *Q*-branch using isolated band model.

The structure of the *Q*-branch is spreading on a small spectral range (around 0.3 cm^{-1}) and is relatively well predicted by effective Hamiltonian (noted hereafter EH) and effective dipole moment (noted hereafter EDM) operator reported in [8] and used later for the generation of the acetylene database [9]. Due to the difficulties to fit accurately such atypical and overlapped *Q*-branch, we decided to use slightly modified line positions and intensities given by EH and EDM operator from [8] to correctly reproduce the experimental spectrum. A systematic shift of 0.02 cm^{-1} has been applied (calculated wavenumbers have been reduced) and the calculated line intensities have been raised by 10 %. To perform comparison with experimental spectrum, the nominal instrument line shape (sinus cardinal function apodized by effect of the size of the beam) has been used to obtain calculated spectra [10] with a Voigt profile. The calculated *Q*-branch is plotted in Fig.2 together with experimental spectrum. No fit has been performed (except the corrections described previously). The signatures in the residuals from Fig. 2 do not exceed ± 4% and may be due to erroneous line parameters, inaccurate ILS, deviation to Voigt profile, or line mixing effect. Table 1 summarizes the line positions, assignments, intensities and self-broadening coefficients used for the calculation given in Fig. 2 and recommended for databases. Note that the self-broadening coefficients are fixed to those used in HITRAN and GEISA databases, coming from Ref. [11]. According to vibrational numbers used for acetylene, the vibrational code of the $\nu_1+\nu_3+3\nu_4^1$ band is 10130 1

0 _ 00000 0 0 (with V_1, V_2, V_3, V_4, V_5, l_4, l_5 quantum numbers for upper and lower levels).

(Figure 2)

(Table 1)

3. Conclusion

To complete the extensive works [1,2] performed for acetylene in the $\Delta P = 13$ spectral region (8200-8900 cm^{-1}), we propose in this work the recommended line list for the atypical $\nu_1+\nu_3+3\nu_4^1$ *Q*-branch which is well isolated from other acetylene bands and is strong enough to be detected. Modified line positions and intensities calculated using EH and EDM operator from Ref. [8] were checked by comparison with a FT spectrum recorded with a high absorption path length. The data reported in this work are recommended to be added in the HITRAN and GEISA atmospheric line lists [3,4] with accuracy of 0.003 cm^{-1} for line positions and 5-10% for intensities.

Acknowledgements

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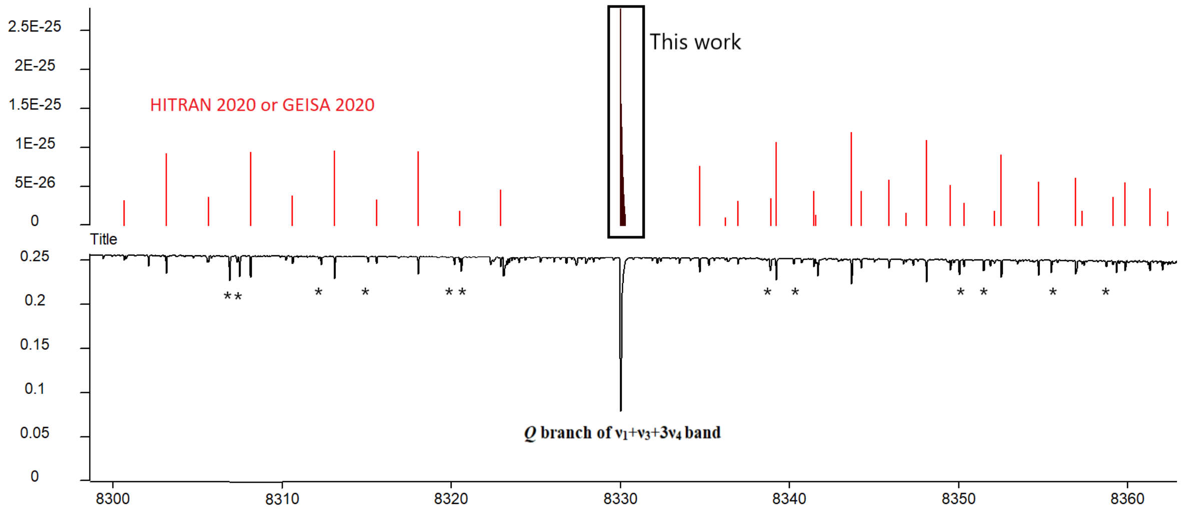


Fig. 1. Overview of the weak $\nu_1+\nu_3+3\nu_4^1$ band with its strong *Q*-branch studied in this work. Experimental spectrum is given in the lower panel. The upper panel presents stick plots of transitions present in HITRAN or GEISA 2020 editions (red sticks) and from line list presented in this work (black sticks). The x-axis corresponds to wavenumbers in cm^{-1}. Stars indicate water transitions appearing due to the presence of a small amount of water inside the cell.

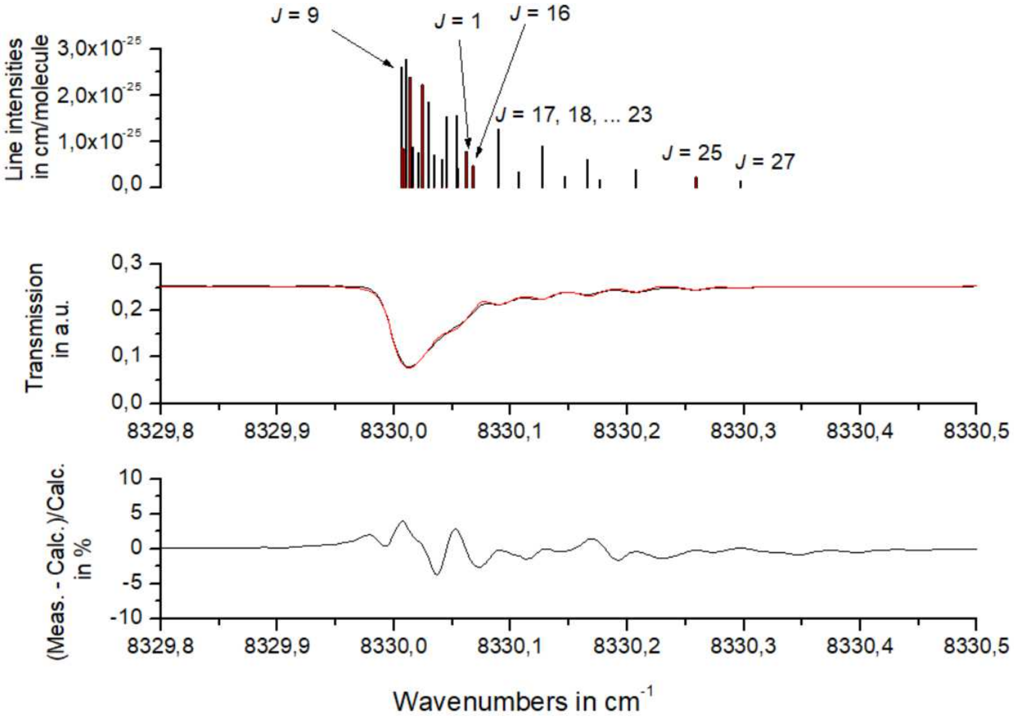
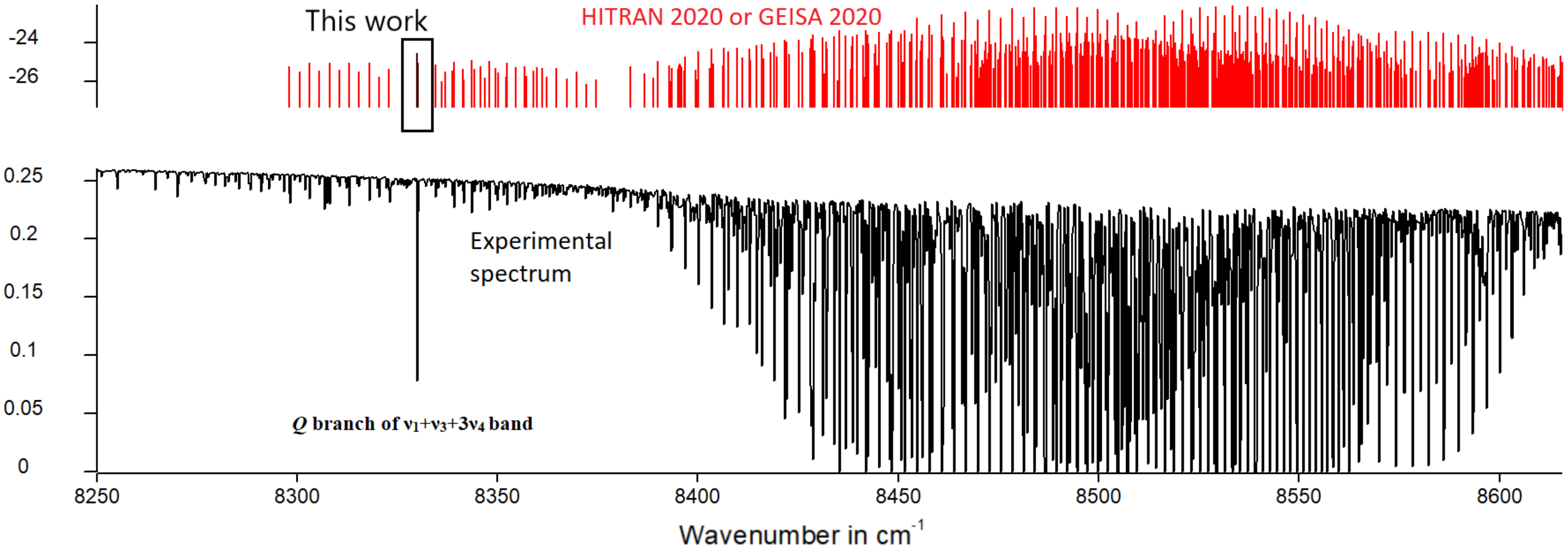


Fig. 2. Comparison of the simulated (using lines given in Table 1) and observed spectra for the *Q*-branch of the weak $\nu_1+\nu_3+3\nu_4^1$ band. Upper panel represents a stick plot of the lines given in Table 1 where the lower *J* quantum number values are indicated for some transitions. Recorded (black) and simulated (red) spectra are given in middle panel. The residual is plotted in the lower panel.

Table 1. The rotational structure of the overlapping *Q*-branch of the $\nu_1+\nu_3+3\nu_4^1$ band.

	J”	*Position*	*Intensity*	γ_{self}	*E”*
Qfe	9	8330.00648	2.588E-25	0.158	105.88464
Qfe	8	8330.00686	8.696E-26	0.162	84.70981
Qfe	10	8330.00881	8.373E-26	0.154	129.41099
Qfe	7	8330.01005	2.778E-25	0.166	65.88686
Qfe	11	8330.01364	2.390E-25	0.150	155.28848
Qfe	6	8330.01597	8.816E-26	0.171	49.41610
Qfe	12	8330.02076	7.445E-26	0.147	183.51668
Qfe	5	8330.02427	2.225E-25	0.176	35.29780
Qfe	13	8330.02994	1.853E-25	0.143	214.09512
Qfe	4	8330.03424	7.063E-26	0.181	23.53219
Qfe	14	8330.04097	6.190E-26	0.140	247.02330
Qfe	3	8330.04477	1.534E-25	0.186	14.11947
Qfe	15	8330.05365	1.554E-25	0.137	282.30067
Qfe	2	8330.05448	4.280E-26	0.192	7.05979
Qfe	1	8330.06196	7.884E-26	0.198	2.35328
Qfe	16	8330.06782	4.843E-26	0.134	319.92665
Qfe	17	8330.08933	1.258E-25	0.131	359.90061
Qfe	18	8330.10703	3.581E-26	0.128	402.22190
Qfe	19	8330.12689	9.043E-26	0.125	446.88981
Qfe	20	8330.14609	2.499E-26	0.122	493.90360
Qfe	21	8330.16600	6.164E-26	0.120	543.26250
Qfe	22	8330.17643	1.663E-26	0.117	594.96570
Qfe	23	8330.20756	3.985E-26	0.114	649.01232
Qfe	25	8330.25909	2.445E-26	0.109	764.13225
Qfe	27	8330.29711	1.424E-26	0.103	888.61466

Note: *e*/*f* symmetry is given for upper and lower states, *J”* – lower state angular moment quantum number, line positions are in cm^{-1}, intensities are in cm/molecule for natural acetylene abundances at 296 K, γ_{self} - self-broadening coefficients in cm^{-1}/atm calculated using polynomial presented by Eq. (5) of the Ref. [10], and *E”* - lower state energies in cm^{-1}


This work
HITRAN 2020 or GEISA 2020
-24
-26
0.25
0.2
0.15
0.1
0.05
0
Experimental spectrum
Q branch of $\nu_1+\nu_3+3\nu_4$ band
8250
8300
8350
8400
8450
8500
8550
8600
Wavenumber in cm^{-1}