Spectrochimica Acta Part A 72 (2009) 762–765

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Q branch features in the hot parallel bands of $^{13}C_2H_2$ in the three micron region

K.A. Mohamed*

Department of Physics; Aligarh Muslim University, University Main Road, Aligarh 202002, Uttar Pradesh, India

ARTICLE INFO

Article history:
Received 27 June 2008
Accepted 15 November 2008

Keywords:
Fourier transform spectra
Infrared spectra
Rotational constants

ABSTRACT

A systematic study of the high-resolution spectrum of $^{13}C_2H_2$ in the 3 μm spectral region shows Q branch features in five hot parallel bands. These bands are due to the $\nu_3+\nu_4\ (\Pi_u)\leftarrow\nu_4\ (\Pi_g)$, $\nu_3+\nu_5\ (\Pi_g)\leftarrow\nu_5(\Pi_u)$, $\nu_3+2\nu_4\ (\Delta_u)\leftarrow 2\nu_4(\Delta_g)$, $\nu_3+2\nu_5\ (\Delta_u)\leftarrow 2\nu_5(\Delta_g)$ and $\nu_3+\nu_4+\nu_5(\Delta_g)\leftarrow\nu_4+\nu_5(\Delta_u)$ transitions. Sub-Q-branches ($Q_{e\leftarrow f}$ and $Q_{f\leftarrow e}$)are found to be resolved in the first three hot bands. More than 70 Q branch lines have been assigned, spread over the five hot bands. We have applied separate linear least squares fit to the transition wavenumbers of each Q branch/sub-Q-branches, which have yielded values of band origins and rotational constants, in agreement with those derived from the analysis of the P and R branches in earlier work. The analysis of the sub-Q-branches have also provided values of the l-doubling constants. This is the first report on the observation of Q branch lines in $\Delta-\Delta$ hot bands, in the FTIR spectrum of $^{13}C_2H_2$.

1. Introduction

The FTIR spectrum of ^{13}C containing acetylene in the three micron region had been analyzed, and the line positions and rotational constants of various bands belonging to the isotopomers $^{12}C^{13}CH_2$, $^{13}C_2HD$ and $^{13}C_2H_2$ were reported by us in our earlier work [1–4], which essentially involved the analysis of the P and R branches.

In linear molecules, intense Q branches are observed in transitions involving $\Delta l=\pm 1$ (perpendicular bands), while very weak (or sometimes a single line) Q branch is seen in transitions with $\Delta l=0$ (parallel bands with $l\neq 0$) [5,6]. In the case of acetylene isotopomers, Q branches in the perpendicular bands have been reported extensively in the literature. But very little amount of information is available on Q branches being observed and analyzed in the parallel bands.

In the case of $^{12}C_2H_2$, Oomens and Reuss [7] had observed and analyzed Q branches in some $\Pi-\Pi$ and $\Delta-\Delta$ bands in the 3 μm region using the IR–IR double resonance technique, while D'Cunha et al. [8] had reported the analysis of Q-branches in $\Pi-\Pi$ transitions in the same spectral region, using high-resolution FTIR technique. The Q branches associated with $\Delta-\Delta$ bands originating from the doubly excited bending levels $2\nu_4$, $2\nu_5$, and $\nu_4+\nu_5$ to the stretch–bend levels involving the ν_3 mode, in the 3 μm region, were found to be very weak and severely blended, in the FTIR spectrum of $^{12}C_2H_2$,by Sarma et al. [9].

For $^{13}C_2H_2$, none of the previous workers using high-resolution grating spectrographs [10,11] have observed Q branches in the hot parallel bands. Di Lonardo et al. [12] were able to assign few Q lines in the $\nu_3(\Pi_u)\leftarrow\nu_4(\Pi_g)$ band in the 125 cm^{-1} region. A systematic study was therefore undertaken to assign and analyze the Q branch lines observed in the high-resolution spectrum of $^{13}C_2H_2$ in the 3 μm region. Altogether, five parallel hot bands showed Q branches in this region. These are due to $\nu_3+\nu_4\ (\Pi_u)\leftarrow\nu_4(\Pi_g)$, $\nu_3+\nu_5\ (\Pi_g)\leftarrow\nu_5(\Pi_u)$, $\nu_3+2\nu_4\ (\Delta_u)\leftarrow 2\nu_4(\Delta_g)$, $\nu_3+2\nu_5\ (\Delta_u)\leftarrow 2\nu_5(\Delta_g)$ and $\nu_3+\nu_4+\nu_5(\Delta_g)\leftarrow\nu_4+\nu_5(\Delta_u)$ transitions. The accurate line positions of the Q lines, the rotational constants and the l-doubling constants have also been derived from the observed experimental data. This is the first report on the observation and analysis of Q branches of $^{13}C_2H_2$ in the 3 μm region.

2. Experimental details

The absorption spectrum of $^{13}C_2H_2$ in the 3 μm region was recorded on the Bomem DA 3.002 FTIR spectrophotometer available at the Dipartimento di Chimica Fisica ed Inorganica, University of Bologna, Italy, at an apodized resolution of 0.004 cm^{-1}, using a White type multiple reflection gas cell, employing a path length of 5 m and gas pressure of 2 Torr. The necessary details of the experiment including the method of calibration, etc. are given in our earlier work [1,3] and will not be repeated here. The accuracy of the line positions reported in this work is expected to be better than 4×10^{-4} cm^{-1} as reported earlier in Ref. [4].

3. Analysis of data, results and discussion

Our earlier papers [1–4] have described the analysis of the spectra of $^{13}C_2H_2$, $^{12}C^{13}CH_2$ and $^{13}C_2HD$ observed in the 3 μm region.

* Tel.: +91 571 2701001; fax: +91 571 2700093.
E-mail address: kumankattil@yahoo.co.in.

1386-1425/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2008.11.010

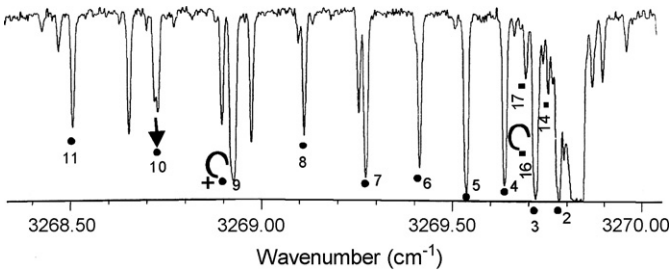

Fig. 1. A part of the hot band spectrum of $^{13}C_2H_2$ in the 3 μm region showing some Q branch lines of the $\nu_3+\nu_4$ (Π_u) ← $\nu_4(\Pi_g)$ band. The sub-Q-branches $Q_{f\leftarrow e}$(J) and $Q_{e\leftarrow f}$ (J) are indicated by ■ and ●, respectively.

The parity labeling *e*/*f* for the rotational levels have been made following the recommendations of Brown et al. [13], according to which, levels with $+(-1)^J$ are called *e* levels and those with $-(-1)^J$ are called *f* levels. In the absence of any interactions, each rotational level is split into two, due to rotational l-type doubling. The *f* levels are assumed to lie higher in energy than the *e* levels. The magnitude of the splitting is given by [14]:

$$\Delta\nu = q_\nu J(J+1) + q_\nu^{(J)} J^2(J+1)^2 \quad (1)$$

where q_ν is the l-doubling constant and $q_\nu^{(J)}$ is the second-order l-doubling constant, such that $q_\nu^{(J)} << q_\nu$.

As discussed by Oomens and Reuss [7], the second term of Eq. (1) can be neglected when only low values of *J* are involved. The transitions involving $2\nu_4$ (Δ_g) and $2\nu_5$ (Δ_g) do not possess a first-order doubling constant q_v (due to $\Delta l = 4$ between the upper and lower components) and hence a second-order doubling constant $q_\nu^{(J)}$ is to be considered [7]. The selection rules permit $e \leftarrow e$ and $f \leftarrow f$ components for the P and R branches, while for the Q branch, $e \leftarrow f$ and $f \leftarrow e$ components are allowed. The wavenumbers of the $Q_{f\leftarrow e}$ components are higher than those of the $Q_{e\leftarrow f}$ components.

Fig. 1 shows a part of the Q branch lines of the $\nu_3+\nu_4$ (Π_u) ← $\nu_4(\Pi_g)$ band of $^{13}C_2H_2$. The assignments of the observed sub-Q-branches are also shown. The $Q_{f\leftarrow e}$ components are heavily blended, but the $Q_{e\leftarrow f}$ components could be easily identified. Fig. 2 shows a part of the Q branch lines of the $\nu_3+\nu_5$ (Π_g) ← $\nu_5(\Pi_u)$ band, in which also the $Q_{f\leftarrow e}$ components are found to be blended while the $Q_{e\leftarrow f}$ components are well separated from each other.

Fig. 3 shows the Q branch lines of the $\nu_3+2\nu_4$ (Δ_u) ← $2\nu_4(\Delta_g)$ band of $^{13}C_2H_2$. Compared to the splittings of Q lines of the $\Pi-\Pi$ bands, the splitting of the Q lines of this band is much smaller. The $Q_{f\leftarrow e}$ and $Q_{e\leftarrow f}$ components are resolved only after $J=6$, and they remain unresolved from $J=2$–5. This is due to the extremely small (second-order) l-doubling of the Δ levels involving $2\nu_4$ upto $J=5$. This observed fact is in conformity with our earlier results [4] on the line positions of the P and R branches of the $\nu_3+2\nu_4$ (Δ_u) ← $2\nu_4(\Delta_g)$ band, where the $e \leftarrow e$ and $f \leftarrow f$ components of R(2)–R(4) and P(3)–P(5) lines were found to be unresolved. Thus,

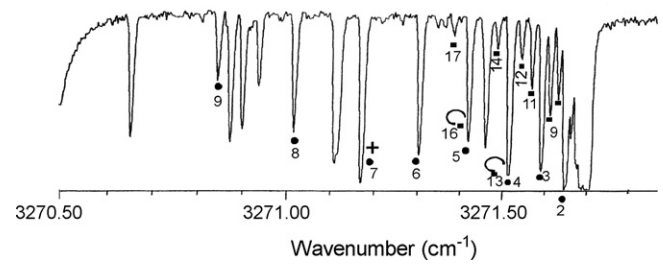

Fig. 2. A part of the hot band spectrum of $^{13}C_2H_2$ showing the sub-Q-branches of the $\nu_3+\nu_5$ (Π_g) ← $\nu_5(\Pi_u)$ band. The sub-Q-branches $Q_{f\leftarrow e}(J)$ and $Q_{e\leftarrow f}$ (*J*) are indicated by ■ and ●, respectively.

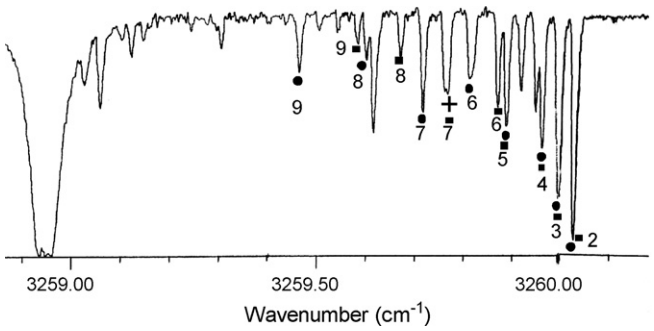

Fig. 3. Q branch lines observed in the $\nu_3+2\nu_4(\Delta_u) \leftarrow 2\nu_4(\Delta_g)$ band of $^{13}C_2H_2$, showing the sub-Q-branches. The sub-Q-branches $Q_{f\leftarrow e}(J)$ and $Q_{e\leftarrow f}$ (*J*) are indicated by ■ and ●, respectively.

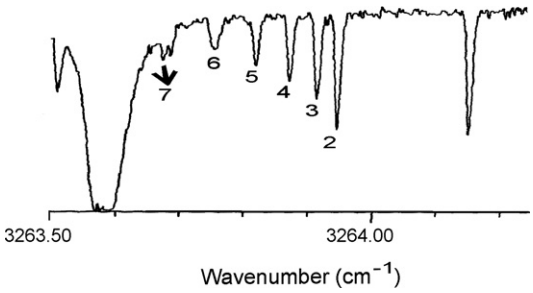

Fig. 4. Q branch lines observed in the $\nu_3+2\nu_5$ (Δ_u) ← $2\nu_5(\Delta_g)$ band of $^{13}C_2H_2$. The sub-Q-branches are not resolved.

the sub-Q-branches from $J=2$–5 are not expected to be resolved for this band.

Figs. 4 and 5 show the Q branches (with unresolved sub-Q-branches) of the $\nu_3+2\nu_5$ (Δ_u) ← $2\nu_5(\Delta_g)$ and $\nu_3+\nu_4+\nu_5(\Delta_g) \leftarrow \nu_4+\nu_5(\Delta_u)$ bands of $^{13}C_2H_2$. Both bands show Q lines from $J=2$–7. From our earlier work [4], it was found that the $e \leftarrow e$ and $f \leftarrow f$ components of the R(2)–R(9) and P(3)–P(10) lines of the $\nu_3+2\nu_5$ (Δ_u) ← $2\nu_5(\Delta_g)$ band were unresolved. Hence, the sub-Q-branches for this band are not expected to be resolved. Similar is the case with the $\nu_3+\nu_4+\nu_5(\Delta_g) \leftarrow \nu_4+\nu_5(\Delta_u)$ band, in which the $e \leftarrow e$ and $f \leftarrow f$ components of the R(2)–R(9) and P(4)–P(13) lines were found to be unresolved [3] and hence the observed Q branches do not show any splitting. (It is mentioned here that in Table 6 of Ref. [3], the wavenumber of the $f \leftarrow f$ component of the R(2) line has to be corrected as 3269.2619 cm^{-1} instead of 3269.2796 cm^{-1}).

Table 1 shows the observed line positions of the Q branches of the $\nu_3+\nu_4$ (Π_u) ← $\nu_4(\Pi_g)$ and $\nu_3+\nu_5$ (Π_g) ← $\nu_5(\Pi_u)$ bands of $^{13}C_2H_2$. It can be seen from the table that the $Q_{e\leftarrow f}$ lines are identified upto $J=16$ for both bands. Due to the heavy blend-

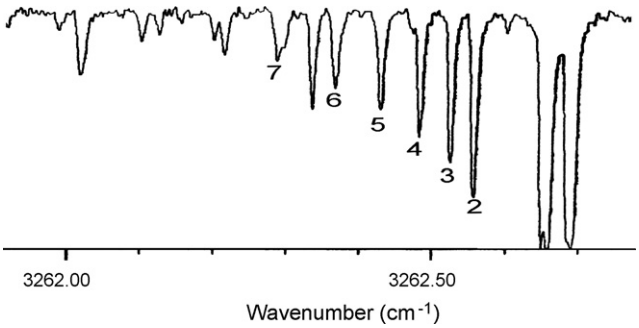

Fig. 5. Q branch lines observed in the $\nu_3+\nu_4+\nu_5(\Delta_g) \leftarrow \nu_4+\nu_5(\Delta_u)$ band of $^{13}C_2H_2$. The sub-Q-branches are not resolved.