

IR Spectrum of C₈H₂: Integrated Band Intensities and Some Observational Implications

Fr. Shindo,* Y. Bénilan,* P. Chaquin,† J.-C. Guillemin,‡ A. Jolly,* and Fr. Raulin*

*LISA (Laboratoire Interuniversitaire des Systèmes Atmosphériques), UMR 7583 CNRS, Universités Paris 7 & 12, 61 Av. Gal de Gaulle, 94010 Créteil cedex, France; †Laboratoire de Chimie Théorique, Université Paris VI, 4 place Jussieu, 75005 Paris, France; ‡LSAB (Laboratoire de Synthèse et Activation de Biomolécules), UMR 6052 CNRS, ENSCR, Avenue du Général Leclerc, 35700 Rennes Cedex, France

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Polyynes are of astrophysical interest since they appear to be involved in organic chemistry in very different mediums. In Titan's atmosphere, the lightest polyynes, C₄H₂, was detected by Voyager. Recently C₄H₂ and C₆H₂ have been discovered in a protoplanetary nebula, suggesting polyynes as a possible chemical pathway to PAH (polycyclic aromatic hydrocarbons). Moreover, several experimental simulations and modeling imply their production from the photochemistry of methane and their involvement in the formation of organic aerosols. After the study of C₄H₂ and C₆H₂ spectra in the UV and IR wavelength range, we report here the first spectrum of gaseous C₈H₂ in the range 400–4000 cm⁻¹ at room temperature and low resolution. The task was hardly achieved because of the high instability of this molecule with temperature and pressure. To avoid exothermic polymerization, the compound was mixed with a solvent. We have performed a separate spectroscopic study of the solvent to determine C₈H₂ partial pressure within the mixture. This allowed us to calculate C₈H₂ integrated band intensities. In the studied wavelength range, C₈H₂ presents three main bands similar to those of C₆H₂ in terms of vibrational type, position, and relative intensity. To study the possible identification of these polyynes by spatial observatories (Cassini–Huygens, ISO), we have also measured the C₆H₂ and C₈H₂ infrared spectra in the range 400–1500 cm⁻¹ at 0.35 cm⁻¹ resolution. © 2001 Elsevier Science

Key Words: infrared spectrum; polyynes; tetraacetylene; band intensity.

INTRODUCTION

This work is part of the SCOOP program (Spectroscopie de Composés Organiques Orientée vers la Planétologie), whose purpose is to study the organic chemistry of methane-rich planetary atmospheres (giant planets, Titan), through the analysis of spectroscopic observations. To achieve this task, we developed a detailed spectroscopic database of planetary interest organic compounds, through laboratory measurements. These data are used to detect molecular signatures and to determine abundances from observations. Furthermore, the results are integrated as parameters to constrain planetary atmosphere modeling. Polyynes (H–(C≡C)_n–H) are of particular interest in Titan's atmosphere, where the photolysis of a methane plus nitrogen mixture leads to a rich organic chemistry (1). Polyynes are considered as end-products of this chemistry and are possibly involved in the formation of the haze particles observed in Titan's atmosphere (2). Their presence is confirmed both by observations and by experimental simulations. Indeed, the lightest polyynes, C₄H₂, has been observed on Titan by the infrared interferometer spectrometer (IRIS) of the mission Voyager (3) and experimental simulations of Titan's atmosphere also revealed the presence of gaseous C₆H₂ (4, 5). Moreover, ultraviolet photochemical experiments on diacetylene showed the formation of C₈H₂ (6, 7). All these results strongly support the involvement of polyynes in Titan's organic chemistry.

Concerning the interstellar medium (ISM), the Infrared Spatial Observatory (ISO) observations of the protoplanetary nebula CRL618, in the wavenumber range 220–4200 cm⁻¹, showed infrared absorption bands of two polyynes, C₄H₂ and C₆H₂, and two cyanopolyynes, HC₃N and HC₅N (8). Furthermore, radio survey towards several molecular clouds revealed the presence of longer cyanopolyynes (H–(C≡C)_n–N) (9–14) up to HC₁₁N (15). Both infrared and radio observations strongly suggest the formation of longer polyynes in the ISM (16), although no direct evidence can be obtained by radio detection due to the absence of a permanent electric dipole.

After the studies of diacetylene and triacetylene in our laboratory (17, 18), we report here the first spectrum of gaseous tetraacetylene in the infrared range (400 cm⁻¹–4000 cm⁻¹) and the integrated intensities obtained for the main bands. In the first section, the organic synthesis of C₈H₂ is briefly described. The encountered experimental constraints and their adopted solutions are then emphasized. The second section presents the main spectral features, their assignments and integrated band intensities. Finally, we discuss the possibility to detect tetraacetylene (i) in Titan's atmosphere through future observations by the composite infrared spectrometer (CIRS) of the Cassini–Huygens mission, and (ii) in the interstellar medium in particular from the already available data of the short-wave spectrometer (SWS) of the Infrared Space Observatory (ISO).

EXPERIMENTAL

(1) Synthesis of C_8H_2

The NMR spectra of the two synthesized molecules are given.

Precursor molecule: 1,8-bistrimethylsilyl-octa-1,3,5,7-tetrayne. It has been prepared as reported by Weng *et al.* (19). 1H NMR ($CDCl_3$, 400 MHz) δ 0.23 (s, 18 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -0.64 ($(SiMe_3)_2$), 62.1, 62.1, 87.8, 88.0.

Octa-1,3,5,7-tetrayne. Octatetrayne (C_8H_2) has been prepared as previously reported by Kloster-Jensen *et al.* (20) from the precursor molecule. To record 1H and ^{13}C NMR spectra, 1 ml of $C_2D_2Cl_4$ has been added to mixture containing C_8H_2 and pentane. The solution was then immersed in a $-40^\circ C$ cold bath and concentrated *in vacuo*. The purification was performed by trap-to-trap distillation: tetrachloroethane and octatetrayne were trapped together at $-40^\circ C$ at a pressure of 10^{-1} mbar. 1H NMR ($C_2D_2Cl_4$, $7^\circ C$) δ : 2.13 (s, 2H). ^{13}C NMR ($C_2D_2Cl_4$, $7^\circ C$) δ : 61.0 (d, $^4J_{CH} = 1.8$ Hz, $C\equiv C-C\equiv C-H$); 61.4 (d, $^3J_{CH} = 7.0$ Hz, $C-C\equiv C-H$); 68.3 (d, $^1J_{CH} = 262.4$ Hz, $C-H$); 68.4 (d, $^2J_{CH} = 51.8$ Hz, $C\equiv C-H$).

(2) Preparation of the Studied Sample

Due to the high instability of C_8H_2 at room temperature (296 K), this compound was mixed with a solvent, namely tetrabutyltin, $(C_4H_9)_4Sn$. The solvent lowers the vapor pressure of C_8H_2 during the vaporization in the cell, preventing polymerization in the tube containing the sample. Moreover, our choice was motivated by the fact that the tetrabutyltin spectrum cannot hide that of tetraacetylene due to a lower vapor pressure. However, the solvent proportion must be adjusted to avoid inhibition of C_8H_2 vaporization. For this purpose, we had to perform cold distillation to remove part of tetrabutyltin. Two tubes were fitted on a vacuum line. The first tube, containing the mixture, was cooled at $0^\circ C$, allowing the vaporization of a sample concentrated in C_8H_2 . The second tube was cooled at $-50^\circ C$ to trap the vapor.

(3) Spectroscopic Protocol

Spectra were measured on an IRTF Perkin-Elmer 1710 equipped with a multireflection Sirocco gas cell, with a variable pathlength fixed here at its maximum: 10.6 m. This long pathlength is essential to the measurement of a spectrum with a low-pressure gas (ranging from 9×10^{-3} to 2×10^{-2} mbar) avoiding exothermic polymerization inside the cell. All the spectra were obtained at a resolution of 2 cm^{-1} between 300 and 4000 cm^{-1} and at 296 K.

The first step of this study was to determine the solvent spectrum from which we were able to correct the spectrum of the mixture and thus reveal the polyyne spectrum. Tetrabutyltin was injected into the cell by vaporization of the solvent at room temperature.

In the case of the C_8H_2 /tetrabutyltin mixture, more precautions were taken. The vaporization was controlled by dipping

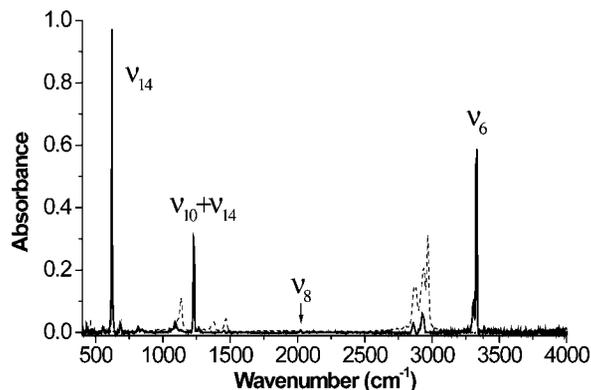


FIG. 1. Solid line: C_8H_2 spectrum in the range $400\text{--}4000\text{ cm}^{-1}$, corrected from the solvent. The spectrum was obtained at 293 K, at a resolution of 2 cm^{-1} , with an optical pathlength of 10.6 m, and at a pressure of 1.8×10^{-2} mbar. Dotted line: the solvent (tetrabutyltin) spectrum at a pressure of 5×10^{-3} mbar.

the mixture into a cold bath at $-20^\circ C$. In addition to its annoying habit of polymerizing, C_8H_2 is strongly adsorbed by the cell walls. Consequently, uncertainty of the pressure was limited to a few percent (about 5%) by averaging 10 scans for each spectrum, corresponding to a total scanning time of about 2 min.

We determine the band intensity S through the relation between the gas pressure p , the pathlength l , and the band integrated absorbance. This relation is linear as long as the compound features are not saturated:

$$\int_{\text{Band}} \ln(I_0/I) dv = S l p. \quad [1]$$

I and I_0 are respectively the spectrum intensity and the background intensity.

The procedure is: (1) to measure spectra at various pressures, (2) to build the diagram of integrated absorbance versus pressure, (3) to define the linear region, and (4) to finally determine the slope S of the observed straight line.

In Figure 1 we show the solvent spectrum as a dotted line. The two bands near 1500 cm^{-1} do not overlap the C_8H_2 features and thus were used to determine the solvent partial pressure in each spectrum of the gaseous mixture containing the polyyne.

RESULTS

C_8H_2 has 17 vibration modes. Eight are degenerated π modes. The nine modes of Σ_g^+ and Π_u symmetry are infrared active. To get the wavelengths of fundamental vibration modes we performed DFT calculations using the SVWN functional and the Dunning cc-pV-TZ basis set. DFT calculations (Table 1) show that within the investigated wavenumber range two fundamental modes with strong intensity, ν_{14} and ν_6 , should be observed experimentally. In the spectrum, three bands stand out clearly by their intensities (Fig. 1). The band observed near 621 cm^{-1} is easily associated to the bending mode ν_{14} regarding its strong

TABLE 1
Theoretical Vibrational Wavenumbers, Normal Modes,
and Symmetry Species for Tetraacetylene

Mode	Symmetry species	SVWN/cc-pvtz (cm ⁻¹)	Int (km · mol ⁻¹)
ν_1	Σ_g^+	3387	0
ν_2		2218	0
ν_3		2138	0
ν_4		1375	0
ν_5		492	0
ν_6	Σ_u^+	3386	454.93
ν_7		2251	2.75
ν_8		2047	4.93
ν_9		955	7.61
ν_{10}	Π_g	600	0
ν_{11}		537	0
ν_{12}		447	0
ν_{13}		164	0
ν_{14}	Π_u	600	91.3
ν_{15}		514	1.07
ν_{16}		289	3.76
ν_{17}		62	2.43

TABLE 2
Experimental Values of Band Positions and Integrated
Intensities for Tetraacetylene

Main bands (cm ⁻¹)	S in atm ⁻¹ · cm ⁻² (±20%)	Mode	Intensities ratio ^a (C ₈ H ₂ /C ₆ H ₂)
621.5 ± 0.2	496	ν_{14}	1.1
{ 1226.7 (P) 1232.6 (R) } ±0.5	256	$\nu_{10} + \nu_{14}$	1.2
{ 3326.6 (P) 3332.2 (R) } ±0.5	595	ν_6	1.1
Minor Bands			
2023.3 ± 0.5	~10 ^b	ν_8	

^a C₆H₂ band intensities from Shindo *et al.* (25).

^b Error of about 50% due to pressure uncertainty and noise level.

Q branch (Fig. 2) characteristic of a Π - Σ transition. The two other bands exhibit intense *P* and *R* branches (Fig. 2) typical of a Σ - Σ transition. There is no doubt that the band near 3320 cm⁻¹ must be assigned to the stretching mode ν_6 . The remaining band at 1220 cm⁻¹ cannot be attributed to a fundamental mode, since theoretical calculations do not forecast any mode close to this value. Previous work on triacetylene (17, 21–25) allows its identification as a very intense combination band, involving π_g and π_u modes. The combination $\pi_g\pi_u$ produces the sum $\Sigma_u^+ + \Sigma_u^- + \Delta_u$ (26), where the term Σ_u^+ allows the Σ - Σ transition. Thus, we assign this band to the combination $\nu_{10} + \nu_{14}$.

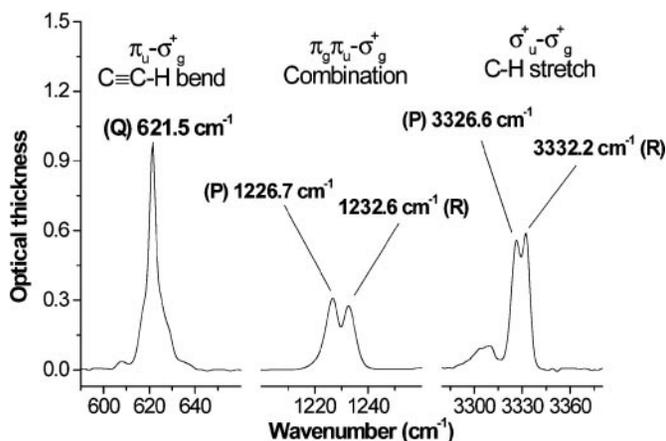


FIG. 2. Main C₈H₂ bands between 400 and 4000 cm⁻¹, at a resolution of 2 cm⁻¹, at room temperature, at a pressure of 1.8 × 10⁻² mbar, and with a pathlength of 10.6 m. The involved vibration and transition symmetries are indicated for each band, as well as the position of *P*, *Q*, and *R* branches.

According to DFT calculations (Table 1), the other fundamental IR-active modes have an intensity 100 times weaker than the two stronger modes. Thus, they are certainly too faint to be detected in our spectrum, except perhaps the ν_8 mode at 2023 cm⁻¹ (Table 2). Besides, all modes below 500 cm⁻¹ lie in a strong noisy area, preventing their detection. As shown in Fig. 1, unassigned features remain after solvent removal from the C₈H₂ spectrum. We were not able to assign them to the polyynes or the solvent, since they could be artifacts due to solvent subtraction. Other minor bands which do not coincide with solvent structures and theoretical location of fundamental modes must be combination involving several modes.

The profile of ν_6 and $\nu_{10} + \nu_{14}$ bands, typical of parallel bands, gives a means to calculate a rough value of the C₈H₂ ground rotational constant B_0 . Indeed, our resolution is sufficient to separate the two branches *P* and *R*, and to measure the wavenumber distance $\Delta\nu$ between their respective maximum. According to Herzberg's formulae (26)[2], $\Delta\bar{\nu}$ and B_0 are related by

$$\Delta\bar{\nu} = \sqrt{\frac{8kTB_0}{hc}} \text{ (cm}^{-1}\text{)}, \quad [2]$$

and from our spectra we deduced a ground rotational constant of $(2.0 \pm 0.3) \times 10^{-2}$ cm⁻¹. We can calculate a theoretical approximation of B_0 from the C₈H₂ moment of inertia through the formulae

$$I_B = \sum m_i r_i^2 \quad [3]$$

and

$$B_0 = \frac{h}{8\pi^2 c I_B} \text{ (cm}^{-1}\text{)}, \quad [4]$$

using the Planck constant h , the speed of light c , atomic mass m_i , and atomic distance from the symmetry center of the molecule r_i . Using the theoretical polyynes bond lengths of Toto *et al.* (27) in Eq. [4] gives for C₈H₂ a B_0 value of 1.87×10^{-2} cm⁻¹,

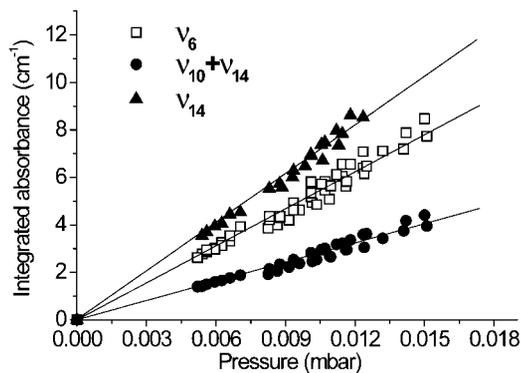


FIG. 3. Integrated absorbance versus pressure for the three main bands. Band intensities are obtained as the slope of linear regression, divided by the pathlength. One can see that despite the dispersion, the spectra were not saturated since each curve seems to be linear (see Eq. [1]).

within the experimental error bar. Comparing the calculated bond lengths of Toto *et al.* to the measurements of Herrera *et al.* (28) on diacetylene leads us to estimate an uncertainty of 2% for this B_0 theoretical value.

Integrated band intensities are determined from the slope S of the linear law [1], giving band surface versus pressure. Experimental curves are plotted for the main bands in Fig. 3. Despite dispersion due to adsorption of C_8H_2 on the walls of the gas cell and a small number of spectra involved in each measurement (10 in average), the most intense bands obviously follow a linear law, and no evidence of saturation is detected. The combination band seems to show less dispersion than the two other bands. An explanation could be its location in a much less noisy region of the spectrum. Accounting for adsorption, solvent removal, and noise, a global uncertainty of 20% is estimated, affecting the measured band intensities (Table 2). We were not able to apply our study to the assigned minor ν_8 band because of its weakness in regard to experimental uncertainty. The C_6H_2 and C_8H_2 bands of the same vibration type present similar intensities, with a slight statistical advantage in favor of the heavier polyynes (Table 2).

In the framework of the SCOOP program, we attempt next to give clues to the eventual planetary observations of polyynes. For this purpose, we have measured triacetylene and tetracetylene spectra at a resolution of 0.35 cm^{-1} , which is a little higher than the spectral resolution of the ISO and Cassini–Huygens mission infrared spectrometers. These spectra were acquired with the infrared spectrometer of the atmospheric simulation chamber located at LISA (Laboratoire Interuniversitaire des Systèmes Atmosphériques).

IMPLICATIONS

As pointed out above, diacetylene is the only polyynes detected so far on Titan by the Voyager mission IR spectrometer IRIS, 20 years ago. The Cassini–Huygens mission, which will reach the Saturnian system in 2004, is expected to bring more precise

information on Titan's atmospheric composition and dynamics by remote sensing and *in situ* analysis. The IR spectrometer of this mission, called CIRS, will work in a large wavenumber range ($1500\text{--}10\text{ cm}^{-1}$) with a maximum resolution of 0.5 cm^{-1} . Consequently, among the three intense C_8H_2 bands studied here, only two are of interest: ν_{14} and $\nu_{10} + \nu_{14}$.

Figure 4 presents experimental and theoretical positions of the CCH bending mode near 620 cm^{-1} versus the number of triple bonds in the polyynes chain. Whereas we have no experimental information beyond tetracetylene, two different theoretical calculations have been done up to the polyynes $C_{14}H_2$. The first ones, which are DFT calculations (BP86/ccpV-TZ), are calibrated on measurements by a factor of 1.051, whereas the second ones, which are *ab initio* calculations (MP2/ccpV-DZ), are calibrated by a factor of 1.055. These calculations agree very well with our measurements to highlight a convergence of the bending mode band position with the growth of the molecular chain to a fixed wavenumber. An exponential fit of the experimental data leads to a wavenumber value of 621.09 cm^{-1} . Adding our spectra of C_6H_2 and C_8H_2 obtained at 0.35 cm^{-1} confirms the convergence of the band position to 621 cm^{-1} . This implies that the CIRS resolution will not be high enough to separate the two polyynes (Fig. 5). Even the shape of the resulting feature does not offer an opportunity to guess the presence of more than one compound. The combination band lies in a region where Titan's thermal emission is weak and only methane emission features are discernible due to its stronger abundance. Therefore polyynes heavier than C_4H_2 will only be separated at lower wavenumber, below 300 cm^{-1} . To be more specific, the Π_u symmetry modes related to CCC bending are located at 220 cm^{-1} for C_4H_2 (ν_9), 105 cm^{-1} for C_6H_2 (ν_{13}), and 62 cm^{-1} for C_8H_2 (ν_{17}). These modes are less intense than the CCH bending mode, but they are in a wavelength range where Titan's thermal

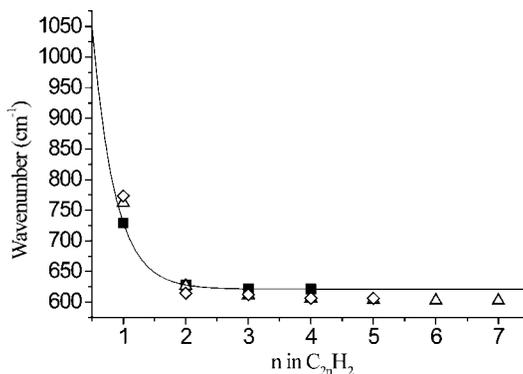


FIG. 4. Position of the $C\equiv CH$ bending mode near 620 cm^{-1} as a function of the number of triple bonds (n) in polyynes. The black squares represent the experimental positions. On the same figure are indicated results from two different theoretical calculations: BP86/ccpV-TZ (open diamond) and MP2/ccpV-DZ (open triangle). A fit of experimental values (solid line) is given by the equation $621.09 + 108 \times \exp[-(n-1)/0.3616]$. Thus, we deduce that the position of this band converges to a constant wavenumber of 621.09 cm^{-1} as the chain grows.

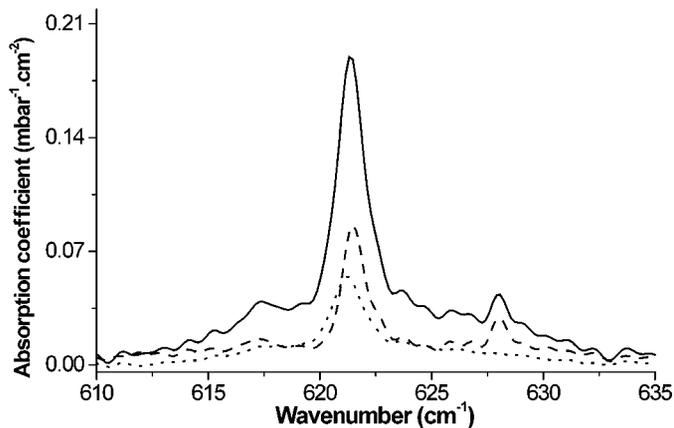


FIG. 5. Experimental absorption coefficient of the 620 cm⁻¹ bands of C₆H₂ (dashed line) and C₈H₂ (dotted line). The latter is multiplied by a factor of 0.5 to distinguish the two bands. The summation of the two polyynes spectra, as a solid line, reveals no detectable separated features. The experimental conditions are a resolution of 0.35 cm⁻¹, a temperature of 296 K, and a pathlength of 130 m.

emission will be more favorable and thus could allow their detection.

In the interstellar medium, C₈H₂ detection could occur eventually through the combination band. Indeed, according to our experimental spectra at 0.35 cm⁻¹, we observe that the C₈H₂ combination band is located just under the P branch of triacetylene combination band. Due to its smaller B_0 , the C₈H₂ band is narrower than the C₆H₂ band. Furthermore, the two polyynes have similar band intensities. Thus, the presence of only a small quantity of C₈H₂ can indeed change the combination band profile of C₆H₂. This is illustrated in Fig. 6, where an asymmetry, growing with the tetraacetylene contribution, occurs between the two branches of triacetylene band in favor of the P branch. Here a contribution of 20% C₈H₂ at room temperature is sufficient to reveal its presence.

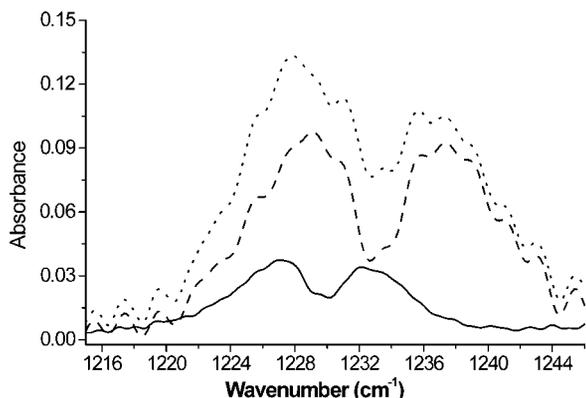


FIG. 6. Experimental spectra of polyynes combination band: in dashed line C₆H₂ (6×10^{-4} mbar) and in straight line C₈H₂ (10^{-4} mbar). A summation of both polyynes spectra (dotted line), involving 20% of C₈H₂ compared to C₆H₂, shows a detectable change in the P branch of triacetylene band. Experimental conditions: 296 K, pathlength of 130 m, resolution of 0.35 cm⁻¹.

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