Review of quantitative spectroscopy of polyynes

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Abstract

We propose a review of quantitative spectroscopy of polyynes in the infrared and ultraviolet domain focusing on essential spectroscopic parameters for the interpretation of observed spectra in the infrared and ultraviolet domain and for photochemical modeling. We point at the lacking data in both wavelength domains for C_2H_2, C_4H_2, C_6H_2, C_8H_2 and propose downloadable files of the ultraviolet absorption coefficient ready to use for photolysis rate calculations. For longer polyynes, we calculate extrapolated ultraviolet spectra and calculate their photolysis rate. Using a simplified photochemical model of the polyynes in Titan and CRL618, we predict their relative abundance and compare them with the observed ones. This also leads us to predict the abundances of the longer polyynes.
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1. Introduction

Titan is the only solar system body, besides the earth, with a substantial atmosphere mainly composed of molecular nitrogen. The atmosphere obscures the surface leading to intense speculation about Titan's nature. Methane is the second major constituent with an abundance of a few percent, initiating a complex organic chemistry. Several higher hydrocarbons (C_2–C_4) have been detected first during the Voyager fly-by [1], from ISO observations [2] and recently by the CASSINI spacecraft [3,4]. Mixing ratios range from a few ppm (C_2H_6, C_2H_2, C_3H_8) to a few ppb (C_2H_4, C_3H_4, C_4H_2). Diacetylene (C_4H_2) is the only member of the polyyne family (linear molecules with general formula $C_{2n}H_2$) that has been detected in planetary atmospheres. It has also been detected in Saturn's atmosphere using ISO [5] and recently in Uranus' atmosphere by Spitzer [6]. Those detections confirm the predicted production of polyynes in methane-rich atmospheres [7]. Polyynes are also observed outside the solar system in various astrophysical objects as the young proto-planetary nebula CRL 618 where both C_4H_2 and C_6H_2 were monitored [8] and even outside the galaxy in the large Magelanic cloud where C_4H_2 and C_6H_2 have also been detected [9]. Just as for cyanopolyynes (linear molecules with the general formula $HC_{2n+1}N$), longer chains are probably present but the absence of sensitivity in the radio domain, where molecules as long as $HC_{11}N$ have been detected, makes polyynes more difficult to detect. All

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the above-mentioned detections of polyynes have been obtained in the mid-infrared domain, almost exclusively through the strong bending mode around $630 \, cm^{-1}$.

The photochemical mechanism generally used to explain the production of polyynes is

$$C_{2n}H_2 + h\nu \rightarrow C_{2n}H + H, \tag{1}$$

$$C_{2n}H + C_2H_2 \rightarrow C_{2(n+1)}H_2 + H. \tag{2}$$
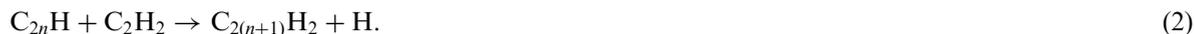
This chemical scheme for the production of long carbon chains has particular importance in photochemical models of planetary atmospheres since those molecules are supposed to be one of the possible links between the gas phase and the solid phase visible as haze at high altitudes in Titan's atmosphere [10] but also in the giant planets [11]. Furthermore, acetylene and longer polyynes are supposed to control the abundance of atomic hydrogen by a competitive mechanism of molecular hydrogen dissociation and H recombination. They are also invoked as one of the major agents of the methane photo-catalysis in the stratosphere. In proto-planetary environments, the polyynes could be the missing blocks that lead to the compounds responsible for unidentified infrared bands (UIR).

In this paper, we are reviewing the status of infrared parameters of the bending modes of C_4H_2, C_6H_2 and C_8H_2, which are needed to retrieve the abundances of the observed species. Since the photolysis rate depends on the absorption coefficient of the molecules of interest, we also discuss the availability of the ultraviolet absorption coefficient for acetylene and polyynes. UV and IR spectroscopic parameters are complementary tools for the study of molecules. UV sounding gives information about the high atmosphere, from the thermosphere down to the high stratosphere, where primary photochemical reactions are initiated, whereas IR observations sound deeper, from the high stratosphere down to the ground, where secondary reactions take place. Coupling both domains lead to the determination of the atmospheric abundance profile of the compounds in the entire atmosphere.

We emphasize on the need for new measurements in particular at low temperature compatible with planetary atmospheres. Finally, we present a model based on the calculation of photolysis rates, which allows us to estimate the abundance of polyynes and conclude on the possibilities to detect longer chains.

2. Laboratory synthesis

While many studies exist about acetylene, there are, on the contrary, very few about longer polyynes because of the synthesis difficulties. Most studies do not deal with absolute absorption intensities because of the problem to obtain and maintain pure samples. A very fine purification procedure is needed to obtain pure samples and so guarantee absolute absorption coefficients both in the ultraviolet and in the infrared range. All the samples are synthesized in the laboratory. The chemical organic synthesis of diacetylene, triacetylene and tetraacetylene have been previously described, respectively, by Khlifi et al. [12], Delpech et al. [13] and Shindo et al. [14]. These chemical protocols always lead to the production of an accompanying chlorated impurity. Moreover, the samples are often mixed with a solvent to ensure the stability as for commercial acetylene and also for the highly unstable tetraacetylene. Otherwise, they need to be kept in a liquid nitrogen-cooled container. Sample contamination is the main concern particularly since the discovery of acetone pollution in former studies on acetylene UV absorption coefficient [15]. Hence, impurities are usually checked by GC–MS analysis and through a pressure-regulated system for all the synthesized molecules. Chlorated impurities can also be tracked by their strong absorption bands in the mid-UV overlapping the polyynes structures. Purification can be achieved by fine distillation, condensing the sample on a cold spot and regulating the temperature. This procedure is very long since the polyynes and the present impurities have very close vapor pressure curves. This requires, for example, a temperature of $-82\,^{\circ}C$ to extract only $1\,mg$ C_6H_2 in a week.

The study of C_8H_2 is an even bigger task, not only because of the difficult synthesis but also because of a very sensitive manipulation due to the very high instability of this compound. A degradation of the C_8H_2 sample can be observed even at $-20\,^{\circ}C$. To overcome the loss of product by polymerization and the possible production of gaseous polymers, tetraacetylene is mixed with a liquid solvent, tetrabutyltin. The properties of this solvent allow one to control the pressure of evaporated C_8H_2 in the gas cell without contributing to the IR spectrum or/and to the total pressure below a temperature of $0\,^{\circ}C$.

3. Polyyne infrared spectroscopy

In the domain from 400 to $4300\,cm^{-1}$, acetylene and polyynes exhibit three intense bands in their vibrational spectra. The position and integrated intensity of these bands are similar for all the studied molecules. These bands are due to $C{\equiv}CH$ bending around $630\,cm^{-1}$, which is the most intense, followed by the CH stretching around $3330\,cm^{-1}$ and a strong combination band of an anti-symmetric and a symmetric bending mode around $1240\,cm^{-1}$. Due to the temperature conditions in planetary atmospheres, the strong bending mode is best suited for the detection of polyynes. But the large abundance of polyynes in CRL618 made the detection of C_4H_2 and C_6H_2 also possible through the combination band [16]. Another active bending mode, due to the bending of the carbon chain, exists for polyynes in the region below $400\,cm^{-1}$. For C_4H_2, this band appears at $220\,cm^{-1}$ (v_9) and has been observed in Titan's atmosphere in addition to the strong v_8 band at $628\,cm^{-1}$. Both have been studied experimentally by Arié and Johns [17] at high resolution providing the line positions that are necessary for astronomers to analyze their spectra. The band intensity of the v_9 band of C_4H_2 at $220\,cm^{-1}$ has been measured once at low resolution [18]. For C_6H_2, the low-energy bending mode has been observed at $105\,cm^{-1}$ and analyzed at high resolution [19]. Those high-resolution studies did not include intensity measurements and no experimental study of the C_6H_2 band intensity at $105\,cm^{-1}$ exists so far. The low-lying band for C_8H_2 is predicted at $62\,cm^{-1}$ but has never been observed experimentally. These low-lying modes and the increasing number of vibrational modes are responsible for the strong hot bands that we will discuss later.

3.1. C_4H_2

The active bending fundamental bands v_8 and v_9 of C_4H_2 have been analyzed at high resolution [17] as well as the combination band $v_6 + v_8$ [20]. The v_8 bending fundamental band has been analyzed together with four hot sub-bands with lower level v_9 ($220\,cm^{-1}$) and four more with lower level $2v_9$ ($440\,cm^{-1}$) [17]. This study does not give any information on the intensities. In fact, no intensity measurement exists at high resolution. The most recent work dealing with intensities has been done by Khlifi et al. [12] at $4\,cm^{-1}$ resolution and gives an absolute intensity of $437\,cm^{-2}\,atm^{-1}$ for the v_8 band. This value has been chosen to interpret the spectra of C_4H_2 observed on CRL 618 [8]. But this value has now appeared to be severely affected by strong saturation. With the help of the high-resolution data, it is possible to calculate a model spectrum using the experimental conditions from Khlifi et al.'s work (10 cm cell length, 14.3 mbar, 1000 mbar N_2) and the average broadening coefficient found for acetylene by Bouanich et al. [21] of $80.10^{-3}\,cm^{-1}\,atm^{-1}$. After convolution of the absorption spectra with the apparatus function, a model spectrum is obtained with about 40% decreased absorption compared with the experimental one. It means that the added nitrogen was not enough to avoid saturation of the spectrum. We therefore now give preference to the intensities measured by Koops et al. [18], who found a value of $708\,cm^{-2}\,atm^{-1}$ for the v_8 band by adding 60 atm of pure nitrogen. Note that in the same paper, Koops et al. were not able to measure the intensity of the v_9 band in the far infrared domain under the same conditions as for v_8. They could not avoid saturation of the absorption for v_9. The value published by Koops et al. for v_9 is $25.5\,cm^{-2}\,atm^{-1}$ and corresponds to an extrapolation to zero sample pressure. New intensity measurements under optimized conditions for v_9 and also for v_8 are therefore strongly required.

Also required are new analysis of high-resolution spectra and an accurate line list. The analysis by Arié and Johns [17] is the only accurate study available so far on the bending modes of C_4H_2. Instead of using the outdated GEISA data, a better line list can be obtained from Arié and Johns including the first hot band transitions arising from the lowest excited states v_9 ($220\,cm^{-1}$) and $2v_9$ ($440\,cm^{-1}$). Such a line list has been generated for the v_8 band by Vinatier et al. [22] when analyzing CIRS spectra of Titan. Hot bands play a very important role in C_4H_2 since the vibrational partition function Q_v is equal to 3.5 at 296 K, which means that less than 30% of the molecules are in the ground state at room temperature. Even at 150 K, which is a typical average temperature for planetary atmospheres, 25% of the molecules are still in excited levels. It has been shown recently that transitions arising from excited levels as high as $1300\,cm^{-1}$ play a significant role in the intensity of the v_5 band of HC_3N at room temperature [23]. Since C_4H_2 and HC_3N are very comparable molecules, we believe that including only hot bands from v_9 and $2v_9$ is largely insufficient to model the spectra of C_4H_2 at room temperature. Including more transitions arising from v_7 ($482\,cm^{-1}$), v_6 ($625\,cm^{-1}$) and v_8

($628 \, cm^{-1}$) seems to be necessary even at colder temperature since vibrational factors can enhance specific transitions (see Jolly et al. [23]).

3.2. C_6H_2

The spectra of C_6H_2 are even more complicated than those of C_4H_2 since the number of vibrational modes is higher and the low-frequency mode v_{13} is only at $105 \, cm^{-1}$. The smaller rotational constant also makes the spectra more congested and more difficult to analyze. Several studies investigating C_6H_2 spectrum at high resolution ([19,24–26]) revealed the complexity of polyyne bands as a combination of the cold band and a large set of hot bands. Haas et al. [24] have analyzed the spectra of the bending mode v_{11} at $621 \, cm^{-1}$. Due to the huge density of lines, the sub-bands with lower level v_{13} are the only hot bands associated to v_{11}, which could be reliably analyzed. As can be noticed on the spectra published by Haas et al. just referred to, many other hot bands contribute to the total intensity. At 300 K, the C_6H_2 molecules are less numerous in percentage in the fundamental level than in the first three excited states. And this behavior remains consequent at 200 K. The three first excited states see their population growing when the temperature decreases to 235 K. Even at 100 K, more than 40% of the band intensity arises from transitions starting from excited states.

No work has been done at high resolution concerning the intensities of the bands of C_6H_2 but results at low resolution have been obtained [27]. A band strength of $428 \, atm^{-1} \, cm^{-2}$ was found for the main bending mode v_{11} and it has been shown that the former work by Delpech et al. [13] was in error due to saturation effects. ($312 \, atm^{-1} \, cm^{-2}$). The intensity of v_{13} is unknown. Only an incomplete line list can be obtained from Haas et al.' studies [19,24].

3.3. C_8H_2

Despite huge difficulties of synthesis and stability, the infrared spectra of C_8H_2 could be obtained for the first time by Shindo et al. [14]. The intensity of the three main bands could be measured, among them the $621 \, cm^{-1}$ band and the $1230 \, cm^{-1}$ combination band. One important result was that the bending mode is observed for both C_6H_2 and C_8H_2 at $621 \, cm^{-1}$. This behavior, where the energy of the strong bending mode does converge when the polyyne chain becomes longer, had been predicted by theoretical work [28]. This makes impossible the distinction of both molecules at $0.5 \, cm^{-1}$ resolution and has stringent implications for the detection of longer polyyne chains.

The combination band at $1230 \, cm^{-1}$ has the advantage to give the possibility to estimate the B rotational constant using the separation between the P and the R branches maxima. A value of $B = 1.87 \times 10^{-2} \, cm^{-1}$ was found, which can be compared to $B = 4.4 \times 10^{-2} \, cm^{-1}$ for C_6H_2 and $B = 14.6 \times 10^{-2} \, cm^{-1}$ for C_4H_2. The decreasing energy separation between the branches' maxima could be a useful criterion to distinguish between various polyynes.

4. Polyyne electronic spectroscopy

Acetylene and polyynes share a similar spectra in the ultraviolet region dominated by a first strong electronic transition peaking at 150 nm for acetylene and gradually increasing to 210 nm for C_8H_2 (Fig. 1). It has been attributed to the first ${}^1A_u - {}^1\Sigma_g^+$ transition for acetylene and to ${}^1\Sigma_u^+ - {}^1\Sigma_g^+$ for all the polyynes. Furthermore, the intensity of the latter transition has been predicted to increase linearly with the length of the chain. At longer wavelength, an extended band about 1000 times weaker is observed for all the molecules discussed here. It has been attributed to the vibrational progressions of two electric dipoles forbidden by overlapping electronic transition ${}^1\Sigma_u^- - {}^1\Sigma_g^+$ and ${}^1\Delta_u - {}^1\Sigma_g^+$.

The mid-UV range between 185 and 300 nm corresponds to the forbidden transition of acetylene but also to the allowed band of tetraacetylene. The domain of interest for planetary atmospheres starts at 120 nm, where the Lyman-α flux is crucial for calculating the photolysis rates in the upper part of the atmosphere. But polyynes also absorb above 200 nm where the solar flux becomes much stronger, which also makes the mid-UV range a very important part of the spectrum to explore.

The possibility to measure spectra at low temperature is of great importance when applied to planetary atmospheres and the ideal temperature range for photolysis calculation is between 150 and 200 K. Mainly
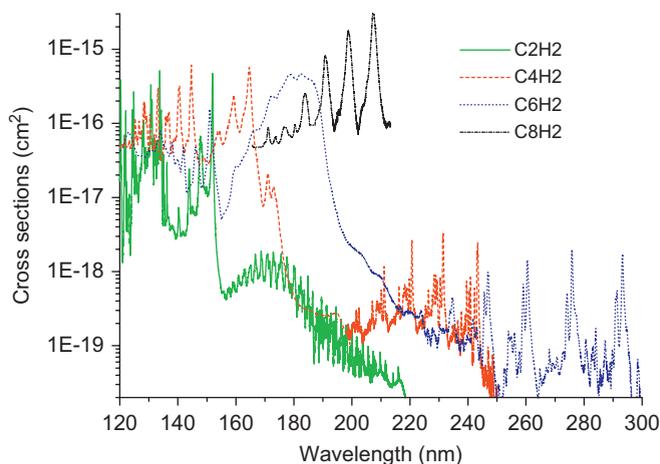
Fig. 1. Compiled low-temperature cross-sections (C_2H_2: Wu et al. [34] up to 190 nm at 150 K and Benilan et al. [33] up to 230 nm at 173 K; C_4H_2: Kloster-Jensen et al. [39] up to 160 nm at 300 K, Fahr and Nayak from 160 to 195 nm at 223 K [35] and Smith et al. [36] from 195 to 260 nm at 195 K; C_6H_2: Kloster-Jensen et al. [39] from 120 to 185 nm at 300 K and Shindo et al. [27] from 185 to 300 nm at 223 K; C_8H_2: Kloster-Jensen et al. [39] from 160 to 185 at 300 K and Shindo [44] between 185 and 210 nm at 223 K).

cross-section measurements at low temperature will be reviewed here. Since most literature studies do not cover the whole wavelength range, we propose downloadable files containing 1 nm interval ultraviolet absorption coefficients compiled from the various studies described below. Those files are intended for photolysis rate calculation and are available from our laboratory database at the following web address: http://www.lisa.univ-paris12.fr/GPCOS/SCOOPweb/SCOOP.html.

4.1. C_2H_2

The formation of polyynes involves the dissociation of acetylene. The work by Wu et al. [29] about the absolute absorption cross-section of acetylene between 153 and 193 nm was usually taken to interpret observation of C_2H_2 also used as input in photochemical models, for instance in Jupiter's atmosphere [30]. It has been previously demonstrated that all published spectra at room temperature show the signature of acetone traces including studies by Wu et al. [29], Chen et al. [31] and Smith et al. [32]. Nevertheless, this has mainly led to the erroneous attribution of hot bands in the room-temperature spectrum [15]. Thanks to the probable condensation of the impurity at low temperature, the work by Wu et al. [29] at 155 K can be considered as almost free of impurities.

More recently, the study has been completed by absorption cross-section measurements above 205 nm at low temperature (173 K), which had not been done before [33]. It has been shown that since the solar flux increases rapidly above 200 nm, absorption above 205 nm is not negligible despite the weakness of the bands and has to be included in photochemical models.

In a new work, Wu et al. [34] have again measured the absorption cross-section of acetylene at 295 and 150 K. The acetone traces were effectively eliminated in this new study, which was extended to the range 120–230 nm. Studies by Wu et al. [34] at 150 K and Benilan et al. [33] at 173 K are very well suited to planetary applications and we propose here a compilation of both studies to obtain the most accurate absorption coefficient of acetylene as shown in Fig. 1. We use Wu et al. [34] up to 190 nm and Benilan et al. [33] up to 230 nm to obtain a preferred set of data recommended for photolysis rate calculations.

4.2. C_4H_2

Fahr and Nayak [35] have been the first to measure the spectrum of C_4H_2 at various temperatures between 333 and 223 K. This study covered the range between 160 and 260 nm. The peak of the first strong electronic transition is observed at 164.6 nm followed by a forbidden transition with many vibrational structures

covering the 200–260 nm domain. Significant temperature dependencies for the cross-section have been observed particularly at absorption peaks and also in the continuum level. The work by Smith et al. [36] on diacetylene cross-sections at 193 and 293 K shows a relatively good agreement for the 195–265 nm domain. It was pointed out in Smith et al. [36] that the small discrepancies observed could be due to C_4H_3Cl, a synthesis impurity possessing a strong absorption in the same wavelength domain as the forbidden diacetylene transition. But a precise comparison between both works is not straightforward since the study by Fahr and Nayak has been done with 0.2 nm intervals while Smith's et al. [36] work was done at 0.02 nm resolution corresponding to 0.0066 nm intervals. As expected, the improved resolution mainly shows lower continuum and higher peak values resulting in sharper structures.

For planetary application the best data available are Fahr and Nayak's data taken at 223 K from 160 to 195 nm and Smith et al.'s taken at 193 K with mainly a better resolution and a colder temperature than Fahr and Nayak's for the 195–265 nm range. Below 160 nm, the only available absorption values so far have been determined at room temperature by Okabe and coworkers [37,38]. Low-temperature measurements do not exist for the domain between 120 and 160 nm where the absorption coefficient is high and thus strongly needed. In addition, the values measured by Okabe and coworkers [37,38], which have been used in all photochemical models and all spectra interpretation, were found to suffer from saturation. This can be easily seen by comparing the shape and relative height of the main peaks in the spectra obtained by Kloster-Jensen et al. [39] and Okabe's spectra. Kloster-Jensen et al. [39] have only measured relative intensities but after rescaling to Fahr and Nayak's [35] absorption value at 160 nm, one can obtain peak absorption values much higher than Okabe's. Finally, it must be highlighted that absolute absorption coefficients of diacetylene below 160 nm have never been accurately measured, including at room temperature.

To see the consequences of the lack of relevant information, we can take as an example the recent detection of C_4H_2 in the atmosphere of Titan through UV observations. Observing the occultation of two stars by the atmosphere of Titan with the CASSINI Ultraviolet Spectral Imager (UVIS), Shemansky et al. [40] could not fit the observed transmission spectra in particular at two wavelength, 144.5 and 164.5 nm. Those features are easily identified as diacetylene's main absorption features but using Okabe's saturated data, Shemansky et al.'s model was not able to reproduce the observed spectra at these positions.

In this particularly important wavelength domain, we adopt Kloster-Jensen's [39] spectra up to 160 nm scaled to Fahr and Nayak's measurements. In the domain between 195 and 265 nm, we prefer the values by Smith et al. [36], which have been corrected from the features due to impurities. A compiled spectrum is shown in Fig. 1 and a 1 nm interval absorption coefficient is made available as mentioned above.

4.3. C_6H_2

The shape of the spectra of C_6H_2 are known since the work by Kloster-Jensen et al. [39]. The first allowed electronic transition is observed to peak at 180 nm and the electric dipole forbidden transitions are observed between 220 and 300 nm. But the first absolute intensity measurements were obtained by Bénilan et al. [41] at 296 and 233 K. Difficulties came from the presence of C_6H_3Cl remaining from the synthesis, which could not be completely removed from the sample. The pure absolute absorption coefficient of C_6H_2 was obtained by subtracting the contribution from the pollutant, which could be measured independently in the same study [41]. Recent measurements done with a purified sample show a smaller absorption coefficient, which can be explained by a contribution of the pollutant not totally taken into account in the previous work [27]. This new study has been done at 300 and 233 K between 185 and 320 nm. The influence of temperature can be observed mainly in the relatively narrow structures observed for the forbidden transitions, which can be attributed to cold or hot bands in view of their behavior with changing temperature. At 233 K, the cold bands have increased peaks but the continuum is lower resulting in a higher contrast.

A comparison with the work by Kloster-Jensen et al. [39] can be obtained by scaling their relative intensity measurements to the absolute intensity study by Shindo et al. [27]. A good agreement is obtained between both works concerning the shape of the bands. Differences appear mainly due to the different spectral resolution of both studies. No other work exists for C_6H_2 below 185 nm. Finally, we show in Fig. 1 the best data available, the most recent work by Shindo et al. [27] from 185 to 320 nm, preferentially at 233 K for planetary
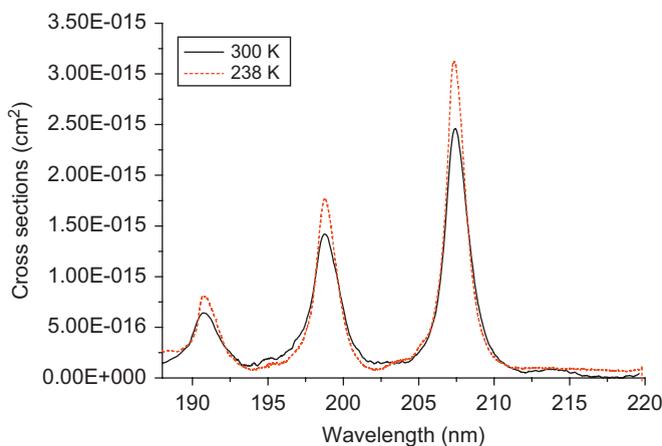
Fig. 2. Absorption cross-sections of C_8H_2 at 238 and 300 K [44].

application, and the scaled relative values of Kloster-Jensen et al. [39] from 120 to 185 nm. Absolute measurements at room and low temperatures are still missing below 185 nm.

4.4. C_8H_2

Eastmond et al. [42] presented a tetraacetylene absolute spectrum in a solution of methanol. However, their absolute absorption intensities are 10 times weaker than the spectra of C_8H_2 that could be measured at LISA [43,44]. On the contrary, the relative intensities measured by Kloster-Jensen et al. [39] from 160 to 210 nm are in good agreement with the absolute absorption coefficients that have been found considering the resolution difference between both studies. The spectrum exhibits three vibronic bands in the 185–210 nm range belonging to the first allowed electronic transition. Fig. 2 represents the obtained spectra at 300 and 238 K [44]. As for triacetylene cold bands, the band maximum increases in intensity with a decreasing temperature and the widths become narrower by the same factor. The relative intensity between the three bands does not seem to vary with the temperature. The narrowing of the bands, which are probably a mixture of hot and cold bands, can be interpreted as mainly due to the narrowing of the rotational distribution.

Only the allowed electronic transition could be observed because, to detect the much weaker forbidden transition structures above 220 nm, high pressure of C_8H_2 is required exceeding the limit where polymerization occurs in the cell. By scaling the spectra measured by Kloster-Jensen et al. below 185 nm, it is possible to obtain spectra of C_8H_2 between 160 and 210 nm (Fig. 1). It is not possible to calculate the true photolysis rate of C_8H_2 because of the missing part of the spectrum between 120 and 160 nm.

5. Applications to observations

Diacetylene (C_4H_2) is the only member of the polyyne family that has been detected in Titan's atmosphere. Actually, polyynes are also observed outside the solar system in the young proto-planetary nebula CRL 618 where, in addition to C_4H_2, C_6H_2 is also observed with an abundance only a factor of 2 lower than that of C_4H_2 [8]. In Titan, the abundance ratio for both species is at least a factor of 10 and one can ask why such a difference is observed.

In the low atmosphere of Titan, the reaction with methane is the dominant loss process of $C_{2n}H$ radicals [45]. This reaction recycles the polyyne so that the production of longer polyynes described by reactions (1) and (2) is inhibited. Nevertheless, reaction (2) becomes the main one at higher altitudes in Titan because the relative abundance of acetylene is high. Thus, at altitudes higher than 600 km, the chemical cycle for the production of polyynes can be described by Eqs. (1) and (2). The limiting factor in this system is the photolysis mechanism in Eq. (1) since it is much slower than the radical reaction from Eq. (2). As an example, the lifetime

of C_4H radical against the reaction with C_2H_2 at 800 km in Titan's upper atmosphere is of the order of 10 s, whereas the photolysis rate of C_4H_2 is $1.5 \times 10^{-6}\,s^{-1}$.

Consequently, in steady-state conditions, the relative abundance of a polyyne can be estimated calculating the ratio of its photolysis rate to the one of C_2H_2: $[C_{2n}H_2]/[C_2H_2] = J_2/J_{2n}$ where J_{2n} is the photolysis rate of $C_{2n}H_2$. The photolysis rate is obtained from

$$J_{2n} = \int \sigma_{2n}(\lambda)I(\lambda)\phi(\lambda)\,d\lambda, \tag{3}$$

where $\sigma_{2n}(\lambda)$ is the absorption cross-section of the polyyne $C_{2n}H_2$, $\phi(\lambda)$ the dissociation quantum yield and $I(\lambda)$ the radiation field. As a first approximation, the quantum yield $\phi(\lambda)$ is taken constant and equal to 1 over the complete wavelength range. Concerning the absorption cross-section $\sigma_{2n}(\lambda)$, for acetylene and polyynes up to C_8H_2, we use the values described in the previous paragraph.

For longer polyynes ($n > 4$), a synthetic cross-section can be calculated as follows: we use the position λ_{0-0} of the $^1\Sigma_u^+ - X^1\Sigma_g^+$ transition measured up to $n = 13$ by Pino et al. [46]. Those data can be reproduced by an exponential function expressed in nm:

$$\lambda_{0-0} = 441.77 - 338.84(0.954)^{2n}. \tag{4}$$

The intensities I of the transitions are taken from theoretical calculations of the oscillator strength f from a paper by Scemama et al. [47] where a convenient analytical function is proposed:

$$I = 2.20467 + 0.41355(2n) - 3.0823\exp(-(0.16048(2n))).$$

After converting to cross-section values using the usual relation:

$$f = 1129.6 \int \sigma_{2n}(\lambda)\,d\lambda/\lambda^2, \tag{5}$$

with λ in nm and σ_{2n} in $10^{-16}\,cm^2$, the oscillator strength is redistributed over the three main bands corresponding to the vibrational progression observed for C_8H_2 in Fig. 2 and for all polyynes up to $C_{26}H_2$ [46]. As described by Pino et al. [46], the frequency v_{CC} of the CC stretch decreases monotonically so that its wavenumber can be modeled using a linear function in cm^{-1}:

$$v_{CC} = 2250 - 17(2n). \tag{6}$$

Finally, the relative intensities and the width of the three bands are fixed to the values taken from the C_8H_2 spectrum: relative intensities are equal to 1/0.5/0.33 and the FWHM $= 350\,cm^{-1}$ (Fig. 2). The absorption cross-sections are calculated with 1 nm intervals.

To calculate the photolysis rate the intensity of the irradiating source is needed. For Titan's atmosphere, we used the SUSIM ATLAS reference spectra [48]. Since the available flux at a given level in the atmosphere requires the computation of radiative transfer including absorption and diffusion, we limit ourselves to high atmospheric levels where diffusion can be neglected. We have computed the available solar flux at 800 km taking into account the absorption by the main hydrocarbons : CH_4, C_2H_2, C_2H_4 and C_2H_6.

The calculated photolysis rates for Titan's atmosphere are presented in Fig. 3. It can be noticed that for the first members of the polyyne family (i.e., $n < 5$) the photolysis rate increases almost linearly, by about one order of magnitude at each step. This is a combined effect of the rapid increase of the solar flux between 150 and 200 nm, where longer polyynes have their maximum absorption shifted to longer wavelength and also show an increase of the oscillator strength. For the longer chains, which have their maximum absorption between 200 and 350 nm, the increase of the photolysis rate is less steep and almost reaches a constant value since the solar flux level above 200 nm becomes flatter and flatter.

The environment in which polyynes have been detected in CRL 618 is somewhat different from Titan's high atmosphere. The temperature is about the same (i.e. around 200 K), the density is lower in the circumstellar envelop of CRL 618, but the main difference concerns the energy source. The radiation field, which is illuminating the envelop of CRL 618, comes from a dense and dusty HII region itself illuminated by a central B star. To estimate the relative photolysis rate in CRL 618, we modeled the photon source by a black body radiation at 30 000 K, neglecting the fact that the decrease of the photon flux from the UV to the visible could be less steeper because of the presence of dust.
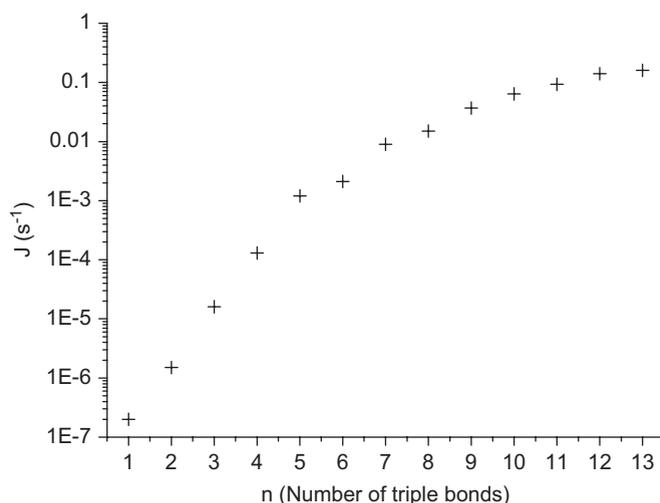
Fig. 3. Photolysis rate of polyynes at 800 km in Titan's atmosphere.
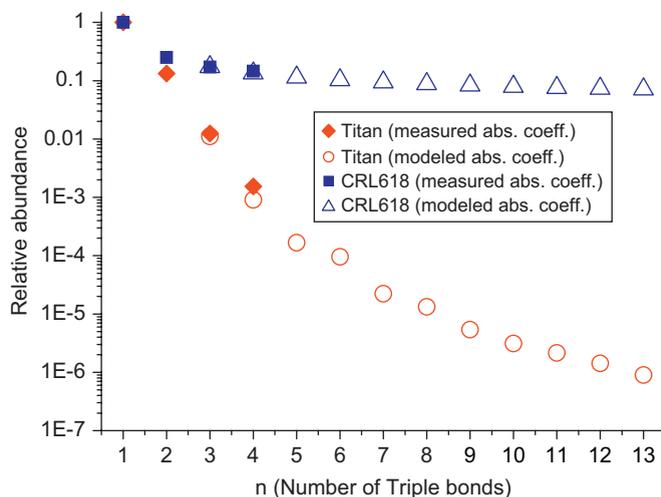
Fig. 4. Relative abundance of polyynes in Titan's atmosphere and in CRL 618. The squares represent the abundances calculated using the measured cross-sections given in Fig. 1. Open figures are calculated using the modeled spectra as described in the text.

Fig. 4 shows the abundance of the polyynes relative to acetylene for both environments Titan and CRL 618. In CRL 618, Cernicharo et al. [8] has determined from the analysis of ISO spectra a relative abundance of diacetylene and triacetylene of 0.6 and 0.3 relatively to acetylene. This is of the same order of magnitude than the 0.25 and 0.17 obtained from our model. The difference might simply be due to the choice of the radiative field. What is striking is the expected abundance of the longer polyynes, around 10% relatively to acetylene. With such large abundances, it should be possible to detect C_8H_2 in the spectra of CRL618 and even longer polyynes but we have to deal with one main barrier. In effect, the frequency of the strong bending mode of C_6H_2 and C_8H_2 and all longer polyynes converges at 620 cm^{-1} so that they cannot be distinguished at the resolution of 0.5 cm^{-1}, though all longer polyynes should contribute to the observed absorption at this wavelength. One way to remove this paradox would be to condense out the higher polyynes.

For Titan's atmosphere, our results from the model can be compared with the values obtained by Shemansky et al. [40] from the analysis of CASSINI-UVIS occultation data. The authors derived at 800 km altitude a column density ratio of 0.12 between acetylene and diacetylene. This is in very good agreement with

what is obtained from the present model. At lower altitude in Titan's atmosphere, the values derived by Vinatier et al. [22] from the analysis of CIRS (Composite InfraRed Spectrograph) limb spectra are much higher. The relative ratio between diacetylene and acetylene abundances varies from 0.03 at 500 km to 0.001 at 200 km. The model we have presented does predict such low relative abundances. Nevertheless, since the Ly α flux will be totally absorbed below 600 km, the lifetime against dissociation will increase much more rapidly for acetylene than for diacetylene. An estimation from the present results for the relative abundance of C_4H_2 at 500 km leads to a value of 0.05, not far from what is measured [22]. Below those altitudes, the approximations in the present simplified model will not be valid anymore and a more complete photochemical model would be needed.

6. Conclusions

While observations become more and more precise and while photochemical models become more and more sophisticated, spectroscopic parameters continuously need to be revised and completed. As we have shown in this review, the available quantitative spectral data for polyynes are not sufficient for most applications as precise abundance determination from infrared and ultraviolet observations in Titan and giant planets. Photolysis rates for polyynes needed for photochemical modeling of planetary atmospheres are approximate due to the lack of UV data, in particular at cold temperature. Experimental efforts are needed for polyynes in particular since those molecules are continuously evoked to be an important link between evolved organic chemistry and the solid phase, which is observed in Titan and all giant planets. In this paper, we have compiled the existing ultraviolet absorption cross-sections for C_2H_2, C_4H_2, C_6H_2 and C_8H_2 and we make available those data ready to use for photolysis rates calculation.

Using those ultraviolet absorption coefficients, we were able to show that the photolysis rate plays a key role to understand the relative abundances of polyynes in various environments by comparing the result of a simplified model to observational results from Titan and CRL618. Predictions for the abundances of longer polyynes are also obtained which show that a very precise knowledge of the photolysis rate is necessary to be able to draw conclusions on the complex chemistry going on, and in particular to deal with the difficult problem of the condensation of the longer carbon chains.

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