



The long wavelength range temperature variations of the mid-UV acetylene absorption coefficient

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Abstract

In the reductive atmospheres of the giant planets and Titan, acetylene is known to be the major unsaturated hydrocarbon. It is of great importance to determine precisely and to model its abundance profile in order to be able to fully understand the chemistry of these environments. To achieve this task one needs the knowledge of the absorption coefficient in IR and UV which are complementary wavelength ranges for studying atmospheres. The mid-UV absorption coefficient is of special importance when trying to model the photo-dissociation of C_2H_2 because of the rise of the solar flux above 200 nm.

We have previously shown that the most recent data on acetylene cross sections had to be taken with caution because of the presence of acetone bands in the published spectra. Moreover, absolute absorption coefficient of C_2H_2 is poorly known above 200 nm. Consequently, we have measured C_2H_2 absorption coefficient in the 185–235 nm range, at 295 and 173 K. We present the obtained results, putting a special emphasis on their temperature dependence. Then, we discuss the implications of those results on theoretical photochemistry modeling and on future observations of methane rich atmospheres. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

In the cold and dense atmospheres of the outer solar system planets and Titan, the presence of methane as the most abundant carbon bearing molecule leads to a complex organic chemistry. In the high atmosphere, the direct dissociation of methane by energetic photons ($\lambda < 145$ nm) leads to the production of mainly CH_3 and 1CH_2 radicals (Smith and Raulin, 1999). Methyl radicals diffuse downward and will recombine to form ethane in a three body reaction. 1CH_2 radicals are subject to two competing mechanisms. The first produces CH_3 from reaction with H_2 (or CH_4 in Titan's atmosphere) and the second is the quenching to the methylene radical triplet state which eventually leads to the formation of acetylene (Yung et al., 1984).

Energetic photons that could dissociate methane cannot penetrate to the lower atmosphere. Thus, in order to explain the ratio of ethane to acetylene in the stratospheres of giant planets as compared to Titan's (Table 1) where the major gas is N_2 , photo-catalytic mechanisms have been proposed (Yung et al., 1984). It implies the dissociation of acetylene which produces H atoms and, C_2H and C_2 radicals that will then react with methane to regenerate acetylene and produce methyl radicals. Such mechanisms have been proved to take place in the experimental irradiation of $CH_4-C_2H_2$ (1000:1) gas mixtures at 185 nm (Smith et al., 1999). Furthermore, in photochemical models acetylene is thought to control the abundance of atomic hydrogen by competitive mechanisms of molecular hydrogen dissociation and H recombination (Gladstone et al., 1996). Finally, reactions of acetylene photo-products with acetylene initiate the formation of long unsaturated carbon chain species like polyynes ($C_{2n}H_2$, $n > 1$).

All of these mechanisms involve the dissociation of

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acetylene, and to calculate the dissociation coefficient one needs the absorption coefficient, in physical condition as close as possible from the studied environment. Because of the rapid decrease of the solar flux with decreasing wavelength in the ultraviolet, apart from Ly α (121.6 nm), the mid-ultraviolet ($\lambda > 180$ nm) wavelength range is the most important for the determination of dissociation coefficients. Moreover, to constrain models it is necessary to have observations of the studied atmosphere from which we can determine the physical and chemical characteristics of its environment. To analyze UV observations, one again needs the absorption coefficient of expected species under appropriate physical conditions.

Quantitative measurements of the UV absorption coefficient of acetylene together with its temperature variations have been carried out several times (Wu et al., 1989; Chen et al., 1991; Smith et al., 1991). However, we have previously demonstrated that all published spectra determined at room temperature show the signature of acetone (Bénilan et al., 1995). Furthermore, no low temperature absorption cross-sections have been measured above 205 nm. Absorption cross-sections above this wavelength have been obtained (Seki and Okabe, 1993), but at room temperature and rather low resolution (i.e., 1 nm).

We present here the acetylene absorption coefficient in the 195–235 nm range at 295 K, and in the 190–230 nm range at 173 K. The comparison of low and room temperature data shows the presence of “hot bands” predominantly above 200 nm. Using a recently obtained high resolution solar spectrum, we then test the influence of the resolution on acetylene dissociation

rate in planetary atmospheres. We also investigate the influence of incorporating long wavelength and low temperature absorption cross sections in the determination of acetylene dissociation by solar photons. Finally, we conclude on the influence of using low temperature acetylene data for the analysis of planetary albedo spectra.

2. Experimental

Acetylene is commercially available and was purchased from Linde (10% C₂H₂ diluted in He). The spectra in the 185–235 nm range were obtained with the SIPAT experimental set-up (Bénilan et al., 1994; Bruston et al., 1991). The pressure regulation system allows us to check the purity of the sample. This is done by recording the absorption intensity versus sample pressure through several successive observations. It can also be done, by looking at the temperature stability of the glass container during the time of vapor pressure regulation. In fact, if we assume that we have a mixture of two products, the temperature at a fixed vapor pressure will be in between that of the two pure products considered separately, depending on the concentration of each species in the mixture. If we regulate the total pressure by adjusting the temperature of the container in which the mixture is stored, we observe a drift in temperature depending on the available amounts of the two products, and on the outgassing velocity of the less abundant compound from the mixed crystalline structure. The consequence is that the partial pressure of the studied compound will not be as stable as expected. To eliminate this effect, we regulate the temperature of the glass container rather than the total pressure of the sample. For spectra recorded below 200 nm, the monochromator was flushed with dry N₂ to remove, as much as possible, the absorption due to H₂O and O₂.

A few years ago, two teams have studied the variations of acetylene spectra with temperature (Wu et al., 1989; Chen et al., 1991; Smith et al., 1991). The authors argue for the presence of hot bands whose intensities decrease when the temperature decreases. Nevertheless, from spectroscopic measurements and thermodynamic studies we have shown that these variations in intensity are rather due to the presence of acetone in their samples (Bénilan et al., 1995). In fact, the presence of less than 1% acetone is enough to explain the observed variations. This is because acetone has absorption bands that are 100 times more intense than those of acetylene in the same wavelength range. Furthermore, the acetone bands show a very good correlation with the observed “hot bands” in acetylene spectra at ambient temperature. Finally, thermodynamical measurements clearly demonstrate that

Table 1
Abundance of main hydrocarbons in the stratosphere of the giant planets and Titan

Jupiter ^a	
CH ₄	2×10^{-3}
C ₂ H ₆	4×10^{-6}
C ₂ H ₂	1×10^{-8}
Saturn ^b	
CH ₄	4×10^{-3}
C ₂ H ₆	4×10^{-6}
C ₂ H ₂	2×10^{-7}
Titan ^c	
CH ₄	2×10^{-2}
C ₂ H ₆	1×10^{-5}
C ₂ H ₂	3×10^{-6}
Neptune ^d	
CH ₄	8×10^{-4}
C ₂ H ₆	1×10^{-6}
C ₂ H ₂	5×10^{-8}

^a Encrenaz et al., 1996.

^b Courtin et al., 1984.

^c Coustenis and Bézard, 1995.

^d Orton et al., 1992.

because of the low vapor pressure of acetone as compared to acetylene, the former will preferentially condense under low temperature conditions.

This has led us to remeasure the acetylene long-wavelength range UV absorption cross sections. We extended the measurements to 235 nm and studied their temperature variations.

3. Results and discussion

Since the absorption coefficient of acetylene varies by more than three orders of magnitude in the 185–235 nm range, the measurements required the use of a wide range of pressure: from a few tenths to several tens of millibars. Thus, the entire spectrum was obtained from the concatenation of five spectra, covering ~ 10 nm each, which overlap by 1 or 2 nm. The entire spectrum was reconstructed studying the correlation and adjusting the phase of the spectra in the overlapping regions. This procedure allowed the verification of the linearity of the absorption as a function of pressure as expected from the Beer–Lambert law. Each part of the spectrum is the sum of three individual scans recorded with a 0.02 nm resolution. A correlation study was made over the three

scans and their phase adjusted before adding them, point to point. This allowed us to check the reproducibility of our measurements: differences were less than 5% in all cases.

The final spectrum is presented in Fig. 1. The absorption bands belong to the well studied $\tilde{A} - \tilde{X}$ electronic transition of acetylene (Watson et al., 1982; Van Craen et al., 1985, 1986). The origin of the transition is at 247 nm. This absorption system is dominated by a long progression in ν_3 (trans-bending mode) and combination bands implying ν_2 (CC stretching) and ν_3 . For each of the stronger bands a progression in the lower state trans-bending mode ν_4 is observed. At high resolution, sub bands can also be distinguished: the principal bands have $\Delta K = \pm 1$ but some satellite sub bands also have $\Delta K = 0, \pm 2$. Furthermore, some LIF studies have shown that some vibrational levels of the singlet state are perturbed due to Fermi interactions and that some coupling exists with an isoenergetic triplet state (Drabbeles et al., 1994). All this leads to a fairly complicated pattern in the 185–235 nm range.

At our 0.02 nm resolution, we cannot distinguish individual rotational lines of rovibrational bands. Only the envelope of those bands can be observed. Nevertheless,

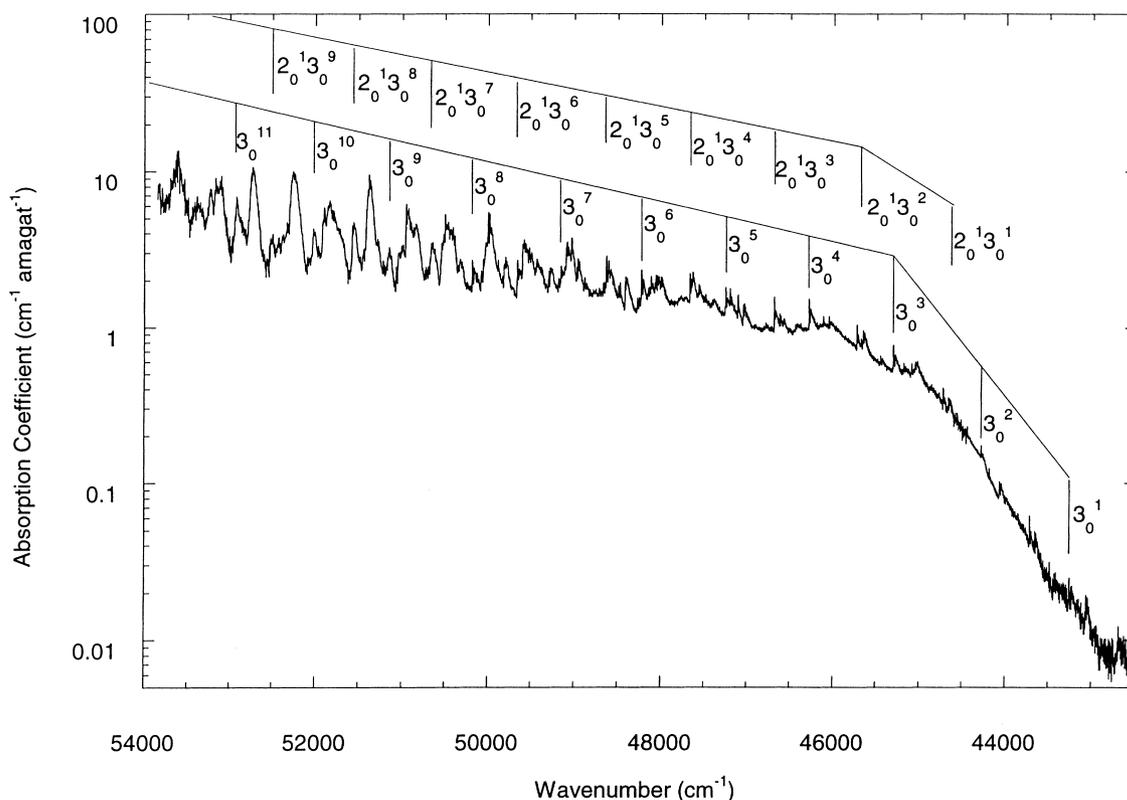


Fig. 1. Absorption coefficient (base e) of C_2H_2 measured at 293 K and 0.02 nm resolution using sample pressure range from 0.2 to 20 mbars. Band identifications are from Watson et al. (1982) and Van Craen et al. (1985, 1986).

R and P/Q branches can be clearly distinguished, at least for wavelengths greater than 200 nm. In Fig. 1, we have superimposed on the spectra the attributions from Watson et al. (1982) and Van Craen et al. (1985, 1986) for the main bands: the ν_3' levels ($n = 1-11$), and the $\nu_2' + \nu_3'$ levels ($n = 1-9$). Because the congestion of the bands becomes much greater in the lower wavelength range, a large number of the structures below 200 nm can not be identified with confidence.

The band system seems to be superimposed on a continuum. The background continuum intensity increases exponentially up to about $46,000 \text{ cm}^{-1}$, then rises almost linearly until $52,000 \text{ cm}^{-1}$ where the continuum starts to increase exponentially again. The first rise of the continuum absorption intensity can possibly be attributed to the increase of energy level density as the energy increases. The second exponential growth is certainly due to the beginning of the $\tilde{B} - \tilde{X}$ transition and to a true continuum belonging to a dissociative electronic state (Wu et al., 1989).

Low temperature absorption coefficients are needed for the interpretation of planetary albedo spectra of cold atmospheres. They are also very useful for spectroscopic analysis of laboratory spectra: low temperature measurements permit the differentiation between hot

and cold bands. Since the integrated intensities of absorption bands are proportional to the population of the level from which the band originates, the integrated intensities of bands involving vibrationally excited levels of the ground electronic state (i.e., hot bands) decrease with temperature. At the same time, integrated intensity of bands involving zero vibration levels of the electronic ground state (i.e., cold bands) increases when the temperature decreases. The band shape will also be modified with the temperature since, at low temperature, mainly rotational levels with low J values are populated.

We have determined the acetylene absorption coefficient at 173 K and 0.02 nm resolution, in the 190–230 nm range. Several changes in the spectra can be observed (Fig. 2). As previously observed for several molecules, the drop in temperature leads to a general decrease of the background continuum. This supports the attribution of this continuum as being due to superimposed hot bands whose intensity decreases with the temperature. Above 200 nm, hot bands are clearly observed. As shown in Fig. 2, a series of hot bands involving the ν_4' bending mode is associated to most cold bands. These hot bands almost disappear in the 173 K spectra, leading to a simplified spectrum. This can easily be explained since the relative population of

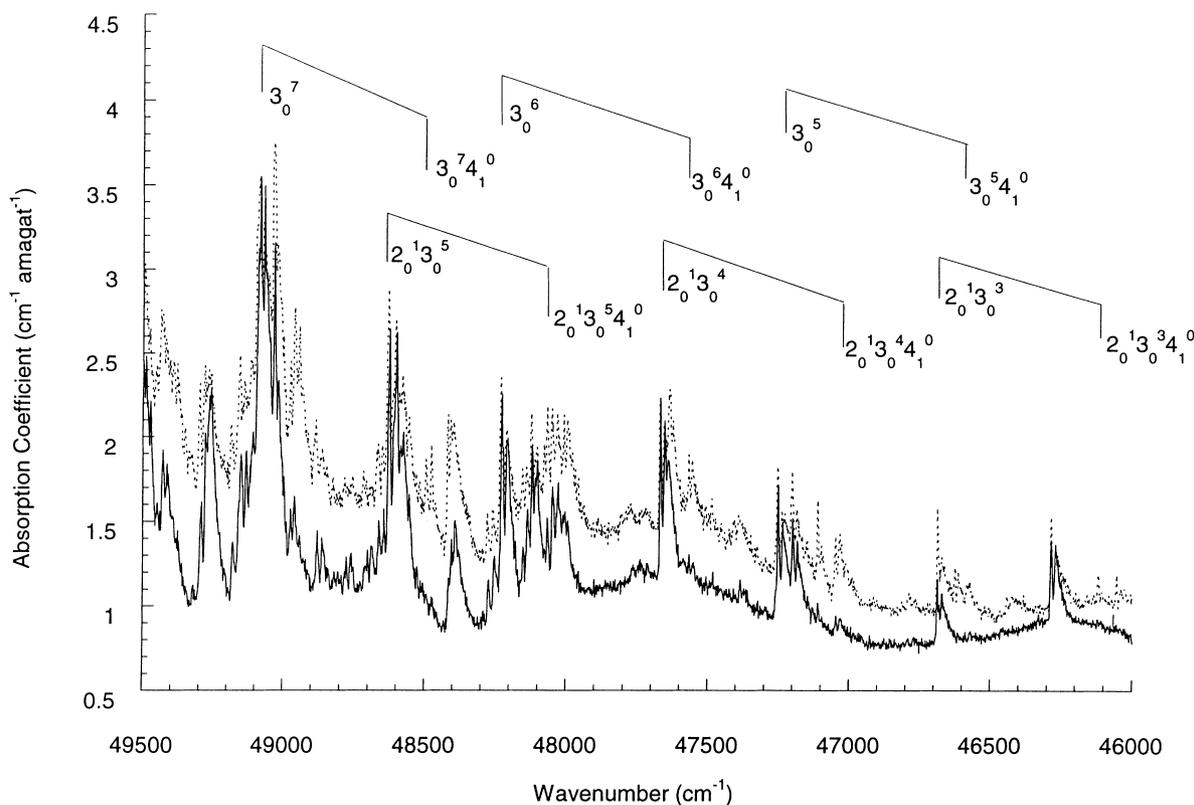


Fig. 2. Comparison between the absorption coefficient (base e) of C_2H_2 measured at 295 K (dashed line) and at 173 K (full line). Hot bands are clearly observable and have been identified.

the $\nu = 1$ level of the ν_4' vibrational bending mode (612 cm^{-1}) decreases by a factor of 8 with respect to the $\nu = 0$ level when the temperature drops from 295 K to 173 K. On the other hand, the zero vibration level of the ground state populates as the temperature decreases so the intensities of bands rising from this level will increase. The band contour also changes when the temperature is reduced. In Fig. 3, we compare the contour of the unblended 3_0^4 band at two temperatures. It can be noticed that the relative intensity between the P/Q branch and the R branch maximum changes with temperature. This is due to the fact that lower rotational levels are favored at low temperature. A complete modeling of the spectra, including the temperature dependence, is underway and will be published elsewhere.

4. Implications for photochemical models and observations

Photochemistry in planetary atmospheres is gener-

ally initiated by the absorption of solar radiation and the subsequent dissociation of molecular species. The classical way to treat these photolysis processes is to introduce a photodissociation coefficient $J_i(z)$, defined as the total number of molecules of the species i dissociated per second at an altitude z :

$$J_i(z) = \int_0^\infty \sigma_i(\lambda) \beta_i(\lambda) \Psi_\odot(z, \lambda) d\lambda, \quad (1)$$

where $\sigma_i(\lambda)$ is the absorption coefficient, $\beta_i(\lambda)$ is the quantum yield for dissociation, and $\Psi_\odot(z, \lambda)$ is the solar flux at altitude z . Uncertainties in each of the three parameters will influence the results obtained by the model. One of the major unknowns is the value of the quantum yields, and especially their wavelength dependencies. The second unknown is the absorption coefficient which also influences the radiative transfer in the atmosphere, and thus the solar flux at a given altitude. Finally, the solar spectrum itself needs to be measured with great accuracy.

Since the calculation of the photodissociation coefficient involves the product of the solar spectrum and

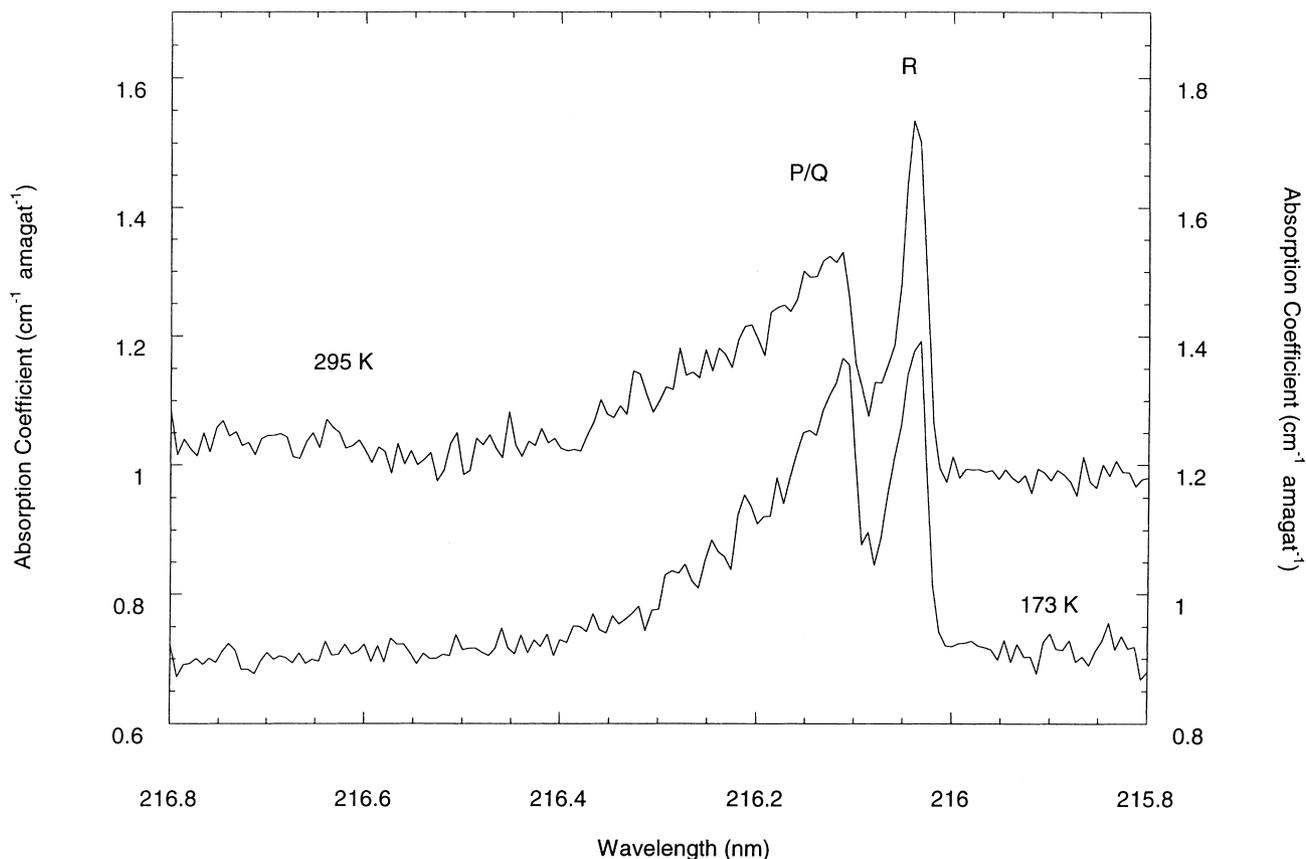


Fig. 3. Comparison of the band structure of the 3_0^4 band at 295 K (left scale) and 173 K (right scale), and at 0.02 nm resolution. R branch has higher intensity than the P/Q branch at 293 K, but these intensities are equal at 173 K.

the absorption coefficient, we wondered how the spectral resolution could influence such a calculation. To test this, we used a high resolution solar spectrum (i.e., 0.01 nm) recently obtained (Tartag et al., 2000) from SMM (Solar Maximum Mission) measurements in the 185–235 nm range. We have calculated the integrated product of the solar spectrum and the acetylene absorption coefficient after having degraded them to a resolution between 0.02 and 2 nm. The results are shown in Fig. 4. One can observe that, even if the photodissociation coefficient decreases when the resolution is poorer, this decrease is small: less than 1% between 0.02 and 2 nm resolutions. We can conclude that the spectral resolution does not introduce much uncertainty to the photodissociation coefficient calculations.

Since no measurements were available above 205 nm and since the dissociation limit is at 217 nm (Mordaunt and Ashfold, 1994), we looked at the influence of including the absorption cross-section up to the dissociation limit in the calculation of the photodissociation rate. Since below 150 nm, dissociation is dominated by Ly α solar radiation flux which is rapidly decreasing with altitude, the computation was performed between 150 and 217 nm. Below 187 nm, we used the absorption coefficient of Smith et al., 1991.

The calculation was performed at 0.1 nm resolution using the solar spectrum of Vanhoosier et al., 1988. To simplify the problem, we took a constant quantum yield of dissociation. The normalized running sum of the product of the solar spectrum times the absorption coefficient of acetylene is plotted in Fig. 5. One can see that about half of the dissociation coefficient is due to absorption above 185 nm. Furthermore, about 25% of the dissociation rate is attributed to absorption beyond 205 nm. These surprising results can be explained by the fact that, even if the acetylene absorption decreases by four order of magnitude between 150 and 220 nm, the solar flux increases rapidly in the same wavelength range. Furthermore, this growth is accentuated at the AII discontinuity (205–210 nm) putting more weight on the long wavelength range of the acetylene mid-UV cross-sections. Finally, we repeated this calculation in the 185–220 nm range, using our low temperature acetylene absorption coefficient. The results presented in Fig. 6 show that the dissociation rate decreases by about 20% when the temperature decreases. This is mainly due to the decrease of the underlying continuum.

Several authors have identified the UV signature of C₂H₂ on Jupiter (Owen et al., 1980; Clarke et al., 1982; Wagener et al., 1985; Morrissey et al., 1995),

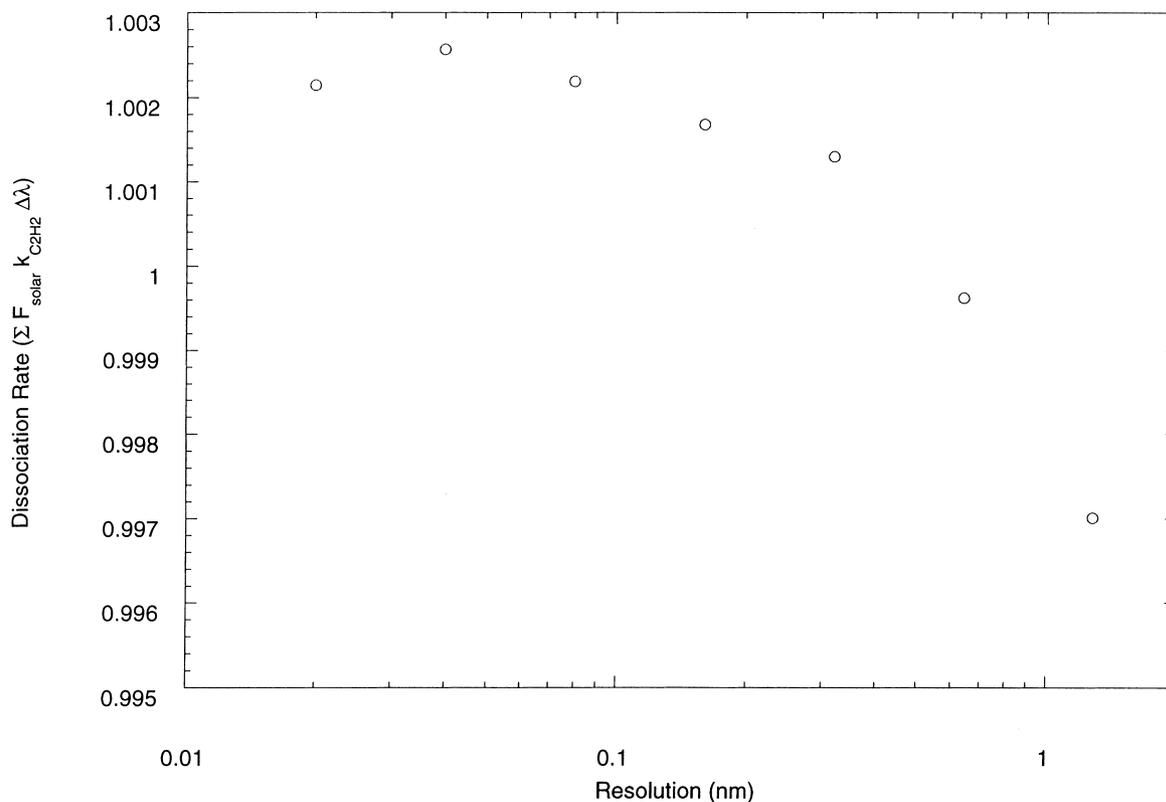


Fig. 4. Dependence of the acetylene dissociation rate on the resolution at ambient temperature. 185–235 nm wavelength range has been used for the calculation. The normalization has been made on the mean value of the dissociation rate.

Saturn (Moos and Clarke, 1979; Clarke et al., 1982), Titan (Smith et al., 1982), Uranus (Encrenaz et al., 1986; Herbert et al., 1987), and Neptune (Yelle et al., 1993). All of these observations reported acetylene signature below 200 nm.

Since in Jupiter, altitudes sounded by observations longward of 200 nm should be in the upper troposphere, observable absorption features are not expected on the basis of current photochemical models. Nevertheless, Bar-Nun and Podolak (1985) have proposed that an additional source of acetylene deep in the troposphere might come from lightning induced chemistry. Such phenomena would increase the acetylene mixing ratio in the troposphere and make acetylene features observable. In fact, in recent analyses of HST data for Jupiter acetylene bands have been observed around 207 nm (Betremieux, personal communication). In this context, our low temperature absorption coefficients will be of great help in future analyses.

In Titan's atmosphere, the solar reflected flux below 200 nm is very low and no definite identification of molecular compounds has been achieved (McGrath et

al., 1998). Nevertheless, because our study shows that the contrast of cold bands relative to the background continuum increases at low temperature, and because solar flux increases significantly above the AII discontinuity, one can expect to achieve signal to noise ratio high enough to detect acetylene absorption bands in future observations of Titan.

Finally, we observe that the acetylene absorption band structure is temperature dependent. So, if observations of the giant planets and Titan could be achieved with high enough resolution to distinguish P/Q and R branches of acetylene bands, information on the atmospheric temperature at sounded altitudes could be retrieved. To reach such goal, the resolution should be better than 0.08 nm. We can note that at this resolution the band contrast relative to the continuum increases by almost 50% as compared to the 0.3 nm data.

5. Conclusions

We have determined the absolute absorption coeffi-

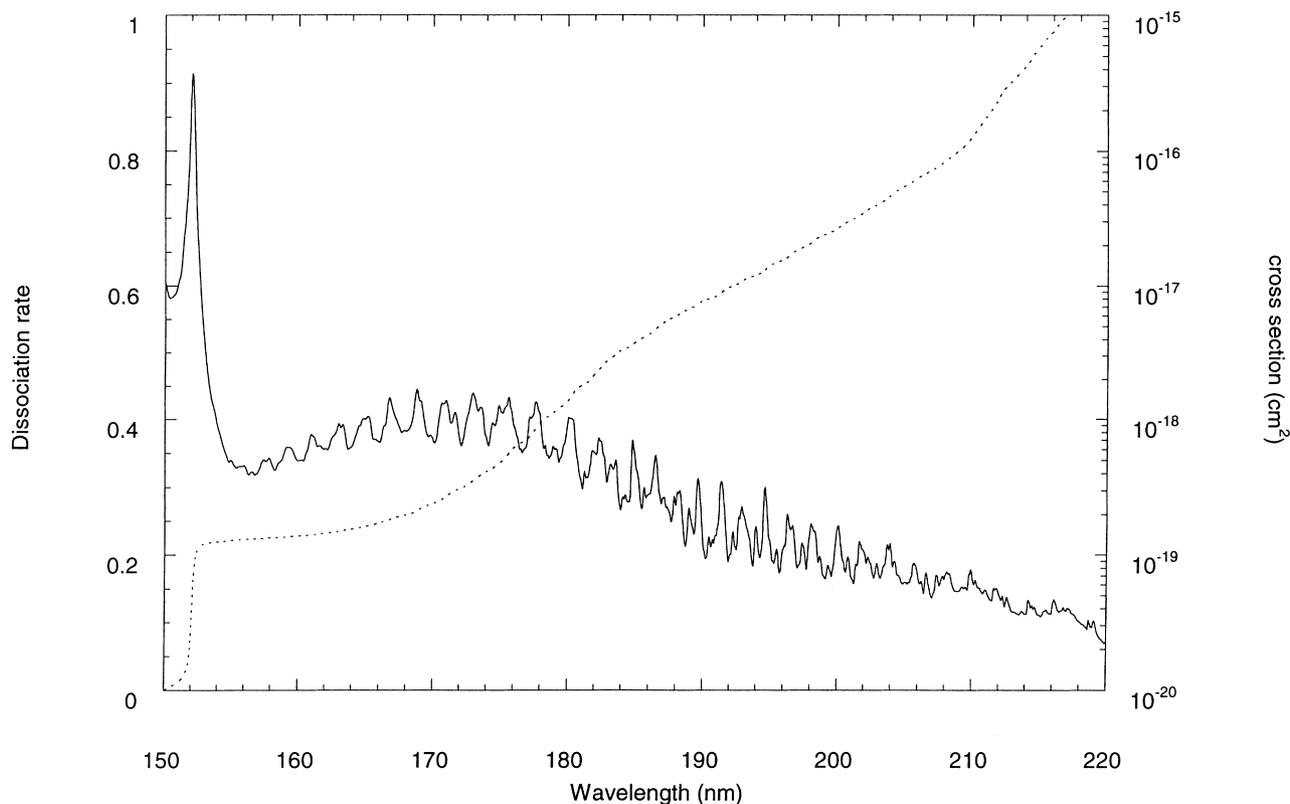


Fig. 5. Acetylene dissociation rate at 295 K (dashed line) normalized to its value at 217 nm (i.e., dissociation limit). Below 185 nm, the absorption cross-sections of Smith et al. (1991) at 293 K have been used.

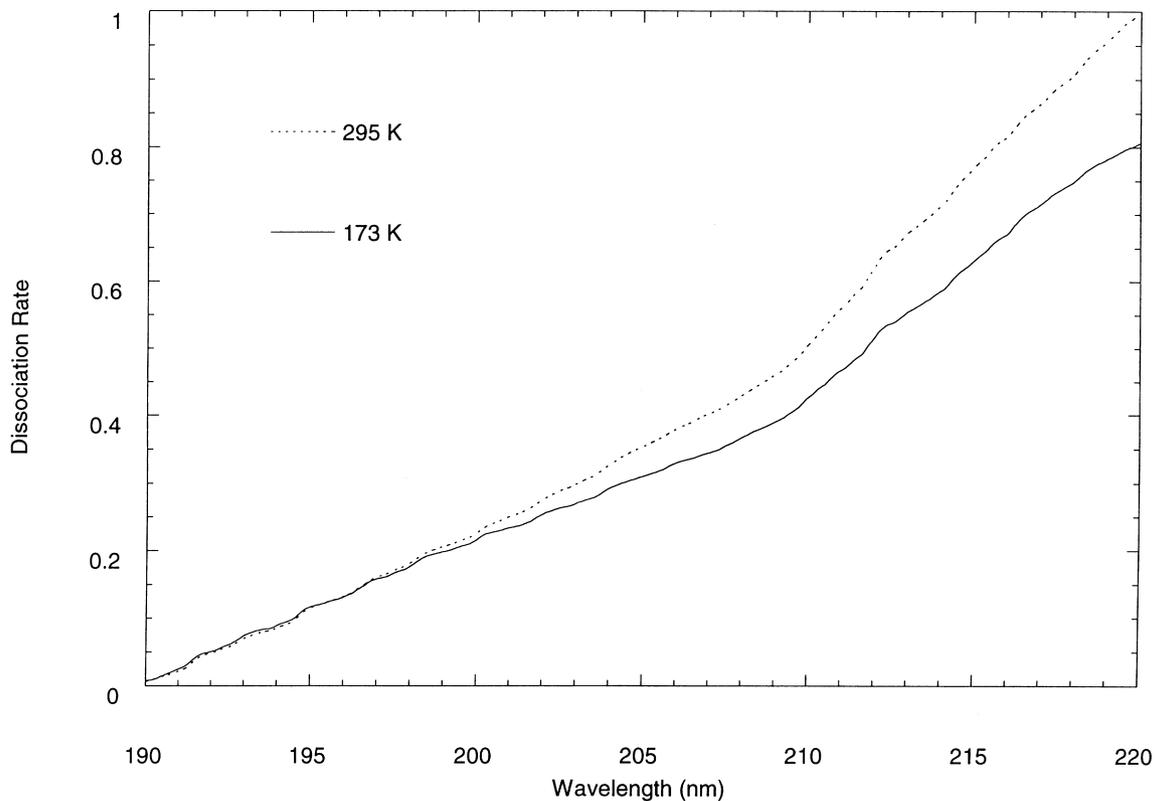


Fig. 6. Temperature dependance of the dissociation rate computed between 185 and 220 nm. In this wavelength range, the total dissociation rate decreases by 25% between 295 K and 173 K.

cient of acetylene in the 190–230 nm range, at 0.02 nm resolution and at two temperatures (293 and 173 K). Special care has been taken to ensure that the sample was free of impurities. A temperature dependence of the absorption coefficient is clearly observed:

- the background continuum on which the band system is superimposed decreases with decreasing temperature;
- hot bands involving the ν_4 vibrational bending mode decrease with decreasing temperature becoming almost unobservable at 173 K;
- cold band intensity increases when the temperature decreases and the structure as observed at our 0.02 nm resolution is also modified.

These changes in the spectrum are attributed to the modification of the rotational and vibrational level populations as the temperature varies. Spectroscopic modeling of these effects is underway.

Based on simple calculations, we have shown the importance of our results for photochemical models. First, we have demonstrated that there should be no need for high resolution absorption cross-sections to calculate photodissociation coefficients in photochemical models. But, we have also shown that since the solar flux increases rapidly above 200 nm,

long wavelength range acetylene cross-sections have to be included in photochemical models. Finally, this omission in current models is somewhat compensated by the decrease of the underlying continuum which reduces the photodissociation rate.

The low temperature measurements presented in this article will be of great help in future analysis of observations of the giant planets and Titan. They should allow a precise determination of the acetylene stratospheric abundance in Jupiter's atmosphere since wavelengths longer than 200 nm sound this region of the atmosphere. Furthermore, since the general and the fine band structure critically depend on temperature, we can expect to use those absorption data as a temperature probe in cold planetary atmospheres. But, this task will only be achieved if high resolution observations can be obtained: resolution should be better than 0.08 nm in order to separate Q and R branches.

Acknowledgements

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