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HIGH TEMPERATURE MEASUREMENT OF ACETYLENE UV ABSORPTION CROSS SECTION FOR THE STUDY OF HOT EXOPLANET ATMOSPHERES

B. Fleury¹, M. Poveda^{1,2}, Y. B enilan¹ and O. Venot³

Abstract. The interpretation of exoplanet atmospheres' observations relies on the used of atmospheric models requiring fundamental physico-chemical data as inputs. To improve the accuracy of these models, it is therefore essential to obtain physico-chemical data in conditions relevant to the observed atmospheres. For this purpose, we have studied experimentally the thermal dependency of the ultraviolet (UV) absorption cross section of acetylene (C₂H₂) between 296 and 673 K. Our first results reveal that the absorption cross section of C₂H₂ increases with the temperature, the increase being more important at longer wavelengths ($\lambda > \sim 180$ nm) than at shorter ones.

Keywords: Exoplanet atmospheres, laboratory astrophysics, techniques spectroscopic, planets and satellites: atmospheres

1 Introduction

The understanding of the chemical composition of observed exoplanet atmospheres largely relies on the used of kinetic atmospheric models. This has been illustrated recently with the observation of sulfur dioxide (SO₂) in the atmosphere of the hot Jupiter WASP-39 b by JWST (Alderson et al. 2023). Indeed, the presence of SO₂ in this atmosphere has been explained, thanks to atmospheric 1D thermo-photochemical models, as the result of photochemical reactions (Tsai et al. 2023). To implement photochemistry, these models require fundamental physico-chemical data and in particular the UV absorption cross sections of molecules to calculate their photodissociation rates. Therefore, the use of inaccurate absorption cross sections lead to uncertainties in the calculation of the molecular abundances by these models (Ranjan et al. 2020; Venot et al. 2013, 2018).

Although most observed exoplanets have high equilibrium temperatures (500 - 2000 K), available data of the UV absorption cross sections of molecules of interest for exoplanet atmospheres are generally limited to the relatively low temperatures ($T < 400$ K) encounters in the atmospheres of the Solar System (see e.g., B enilan et al. 2000; Chen & Wu 2004; Wu et al. 2001, 2007; Rufus et al. 2009). However, Venot et al. (2013, 2018) have determined the absorption cross section of carbon dioxide (CO₂) for a wider range of temperature (150 to 800 K) and shown that the absorption cross section of CO₂ increases of several orders of magnitude with the temperature. This increase of the absorption cross section significantly affects the molecular abundances calculated by kinetic model (Venot et al. 2018) and demonstrates the importance of using cross section determined at a temperature relevant for the studied atmospheres. It is therefore essential to study the thermal dependency of the UV absorption cross sections of molecules of interest in order to improve the accuracy of models used to study exoplanet atmospheres.

In this proceeding, we present the study of the thermal dependency of the UV absorption cross section of acetylene from 115 to 230 nm and for temperatures between 296 and 673 K. The experimental methodology is described in Sect. 2 and the first results are presented in Sect. 3.

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2 Experimental methods and protocols

2.1 Measurements of acetylene UV absorption spectra

The thermal dependency of the UV absorption cross section of C₂H₂ was studied thanks to a new UV spectroscopy platform developed at the Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA, France). Briefly, the setup consists in a high temperature absorption cell composed of a quartz tube closed at each extremity by MgF₂ windows. The cell is warmed up by a tube furnace and its temperature is monitored with 3 type-K thermocouples. In this study, spectra of C₂H₂ were measured at 296 (ambient temperature), 373, 473, 573, and 673 K.

UV spectra of C₂H₂ were measured from 115 to 230 nm with an instrumental spectral resolution of 0.046 nm. As acetylene cross section in the 115-230 nm range spans five orders of magnitude (see Fig.1), it is necessary to adjust the pressure of the gas inside the cell (1×10^{-3} to 80 mbar) depending on the region of the spectrum measured in order to avoid any saturation of the absorption bands. For simplicity, we divided the full spectrum (115-230 nm) into 10 spectra covering a few nm each. Then, each spectrum was measured by introducing in the cell gaseous acetylene (purity > 99.5%) at an appropriate pressure.

As shown by Bénilan et al. (1995), acetone inside the gas bottle (used as a stabilizer) can affect the spectra of C₂H₂ recorded in the UV. To prevent this issue, acetone present in the injected gas was trapped by circulating the gas before injection into a cold trap made of a stainless-steel coil immersed in a mixture of liquid nitrogen and acetone at ~183 K.

2.2 Calculation of the absorption cross section

The absolute absorption cross section of C₂H₂ was calculated from the measured spectra using the Beer-Lambert law:

$$\sigma(\lambda, T) = \frac{1}{nL} \times \ln\left(\frac{I}{I_0}\right) \quad (2.1)$$

where $\sigma(\lambda, T)$ is the absorption cross section (cm²) at a given wavelength and temperature, L is the optical pathlength (cm), n the volume density of the gas in the cell (cm⁻³), I_0 the intensity of the light transmitted through an empty cell and I the intensity of the light transmitted through the cell containing a density n of gas. Considering the gas as a perfect gas, the density of the gas in the cell n can be calculated using the equation $n = P / k_b T$ where P is the pressure of C₂H₂ inside the cell (Pa), T the temperature (K), and k_b the Boltzmann constant.

For each measured spectrum, data were filtered to eliminate noisy or saturated points and then the absorption cross section was calculated using Eq.2.1. Finally, the 10 spectra obtained were concatenated to reconstruct the full spectrum ranging from 115 to 230 nm.

3 Evolution of C₂H₂ absorption cross section with the temperature

We started our study by measuring the absorption cross section of C₂H₂ at 296 K, which will serve as a reference to compare the evolution of the absorption cross section of C₂H₂ as a function of the temperature. Then, we measured the absorption cross section of C₂H₂ at 373, 473, 573, and 673 K. Fig.1 presents the evolution of the absolute absorption cross section of C₂H₂ as a function of the temperature.

At 296 K, we observe that the spectrum has two components: a background continuum and the band system, which is superimposed on the continuum.

When the temperature of the gas increases, we observe an increase of the background continuum while the intensities of the bands tend to decrease. It results that there is a net increase of the absorption cross section of C₂H₂ with the temperature. This effect varies as a function of the wavelength. For $\lambda < 150$ nm, the increase of the continuum intensity is limited to a factor of ~1.8 when the temperature increases from 296 to 673 K. For longer wavelength, the increase of the continuum intensity is more important with a factor of 2 at 174 nm and of a factor of 5 at 230 nm. Moreover, the decrease of the intensities of the absorption bands is more important at longer wavelength for which less structures are visible at 673 K compared to 296 K.

In addition, a new absorption band appears at ~156.8 nm at high temperatures compared to ambient temperature and its intensity increases when the temperature increases. This can be attributed to the apparition of a "hot band". In the UV, transitions occur between two different electronic states. Each of the electronic

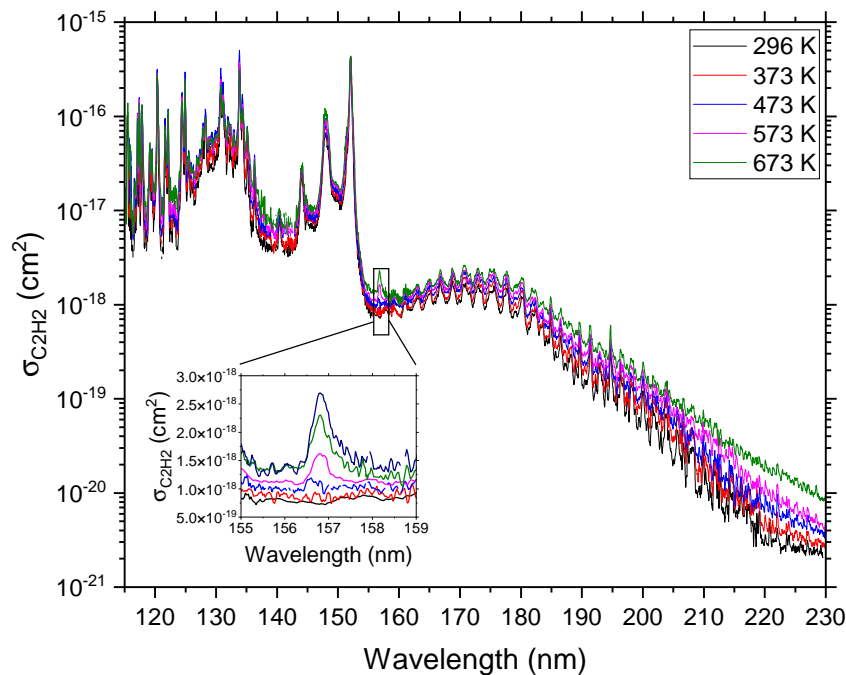


Fig. 1. Evolution of the absolute absorption cross section of C_2H_2 as a function of the temperature. Spectra were measured from 115 to 230 nm at LISA with an instrumental resolution of 0.046 nm.

states is subdivided into vibrational levels. Fundamental transitions occur between the vibrational ground level of the lower electronic state and a vibrational level of the higher electronic state, forming the "cold bands". When the temperature increases, vibrational levels of higher energy of the lower electronic state become more populated, and the intensities of the bands corresponding to transitions from these excited vibrational levels of the lower electronic state to vibrational levels of the higher electronic state increases. These bands are named "hot bands" and their intensities depends on the temperature of the gas.

Additional work will be needed to quantify how the observed increase of the absorption cross section of C_2H_2 with the temperature would affect the abundances calculated by kinetic models (see Fleury et al. in preparation).

4 Conclusions

We have studied experimentally the thermal dependency of the UV absorption cross section of C_2H_2 in a large range of temperatures relevant for exoplanet atmospheres. We determined the absorption cross section of C_2H_2 from 115 to 230 nm and from the ambient temperature to 673 K by increment of 100 K.

We found that the absorption cross section of C_2H_2 increases with the temperature. We also found that this increase is more important at longer wavelengths ($\lambda > 180$ nm) than for shorter ones.

Additional simulations with an atmospheric kinetic model will be done to quantify the impact of the observed increase of the absorption cross section of C_2H_2 with the temperature on the predicted abundances.

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