FUV Photoionization of Titan Atmospheric Aerosols

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Abstract

Thanks to the Cassini–Huygens mission, it is now established that the first aerosols in Titan’s upper atmosphere are found from an altitude of \( \sim 1200 \) km. Once they are formed and through their descent toward the surface, these nanoparticles are submitted to persistent far-ultraviolet (FUV) radiation that can reach lower atmospheric layers. Such an interaction has an impact, especially on the chemistry and charge budget of the atmospheric compounds. Models are useful to understand this photoprocessing, but they lack important input data such as the photoemission threshold or the absolute photoabsorption/emission cross sections of the aerosols. In order to quantify the photoemission processes, analogs of Titan’s aerosols have been studied with the DESIRS FUV beamline at the synchrotron SOLEIL as isolated substrate-free nanoparticles. We present here the corresponding angle-resolved photoelectron spectroscopy data recorded at different FUV photon energies. The results show a very low photoionization threshold \( (6.0 \pm 0.1 \) eV \( \sim 207 \) nm) and very high absolute ionization cross sections \( (\sim 10^8 \) Mb), indicating that FUV photoemission from aerosols is an intense source of slow electrons that has to be taken into account in photochemical models of Titan’s atmosphere.

Key words: atmospheric effects – methods: laboratory: molecular – methods: laboratory: solid state – molecular processes – planets and satellites: atmospheres – ultraviolet: planetary systems

1. Introduction

Titan’s atmosphere can be considered as a complex chemical reactor and, as such, has been the subject of both space missions and laboratory astrophysical studies. In particular, a rich and fascinating photochemistry involving far-ultraviolet (FUV) photons (defined here as corresponding to the 200–30 nm range, i.e., 6–40 eV), interacting with the main atmospheric gas-phase compounds (molecular nitrogen \( \text{N}_2 \) and methane \( \text{CH}_4 \)), leads to a molecular growth process with the formation of small molecular intermediates up to large solid particles (aerosols), responsible for the brownish haze surrounding Titan.

The Cassini–Huygens mission and its instruments have given some information about the aerosols’ spectral signature from the far infrared up to the FUV range (Porco et al. 2005; Rannou et al. 2010; Anderson & Samuelson 2011; Koskinen et al. 2011; Vinatier et al. 2012), but even if progress on the FUV-induced chemical aging of the aerosols is being made (Carrasco et al. 2018), still not much is known about their FUV photodynamics once they are formed, and especially about their possible photoionization in the atmosphere.

The Cassini Plasma Spectrometer instrument has detected heavy negative ions \( (200 \leq m/z \leq 8000 \) Da) at an altitude of \( \sim 1000 \) km, with a maximum mass peak around 2000 Da. Those negative ions have been identified as embryos of the aerosols, which might have been formed by the aggregation of polyaromatic hydrocarbons (PAHs) with a high electronic affinity in an ionosphere possessing a high electronic density \( (n_e \approx 10^9 \text{ m}^{-3}); \) Waite et al. 2007). From the moment the aerosols get charged, the main growth path will not be by coagulation anymore as the negative charges will repel each other. However, they will attract the positive ions present at the same altitude. This cation capture leads to a fast and efficient growth, starting around 1150 km and reaching a mass of 10,000 Da at an altitude of 950 km. This ionic growth, led by the interaction between heavy anions and lighter cations, appears to be dominant in the upper atmosphere until sedimentation, which is responsible for the haze, begins at altitudes below 600 km (Lavvas et al. 2013). In this way, the presence of aerosols, and more importantly, their development toward nanometric sizes, is mainly due to the presence of both negative and positive ions in the upper layers of the atmosphere, due to ionization of neutrals by the FUV solar light. All of these processes are responsible for the presence of aerosols in the upper layers of Titan’s atmosphere, starting around 1150 km.

The FUV solar light flux density at the distance of Titan (10 au) does not exceed \( 10^7 \) ph s\(^{-1}\) cm\(^{-2}\) nm\(^{-1}\), except for the Ly\(\alpha\) band (121.6 nm), which is a hundred times more intense with a flux density of \( 10^9 \) ph s\(^{-1}\) cm\(^{-2}\) nm\(^{-1}\) (Figure 1(A) adapted from Thuillier et al. 2004). Since the FUV absorption cross sections and the density profiles of the main gaseous compounds \( (\text{N}_2, \text{CH}_4, \text{C}_2\text{H}_2, \text{C}_2\text{H}_4) \) are known thanks to the Ion and Neutral Mass Spectrometer (INMS) data (Vuitton et al. 2007; Cui et al. 2009; Magee et al. 2009), we can calculate the absorption related to each of them as a function of the altitude together with the resulting total absorption.

The penetration depth of each wavelength of the FUV solar spectrum in the atmosphere of Titan can therefore be estimated as being the altitude corresponding to an optical thickness \( \tau \) such that \( \tau(\lambda) = 1 \) (Figure 1(B); P. Pernot 2017, private communication). If we note \( I_t \) as the transmitted light and \( I_0 \) as the initial intensity before passing through the atmosphere, the Beer–Lambert law states \( I_t/I_0 = e^{-\tau} \). The \( \tau(\lambda) = 1 \) profiles show then where the transmission is no longer significant (\( \sim 37\% \)).

As visible from Figure 1(B), established by taking into account only the absorption by the four main neutral gas-phase
compounds, the FUV radiation penetrates quite far down the atmosphere reaching lower altitudes. In particular, even if radiation with wavelengths below 100 nm never goes further than 900 km because of the absorption by molecular nitrogen, radiation with wavelengths between 100 and 150 nm reaches lower altitudes of 400 km. Note also that photons with wavelengths below 100 km are absorbed by aerosols, mainly through the interaction between freshly formed aerosols and HCN. We can therefore consider the nanoparticles as relevant analogs of the aerosols present in Titan’s atmosphere. Concretely, our samples are analogs of the aerosols present in Titan’s atmosphere, the so-called tholins produced within the PAMPRE dusty plasma reactor, which are described in detail in Szopa et al. (2006). PAMPRE provides an efficient conversion of the initial N₂–CH₄ gas-phase precursors, representative of the atmosphere of Titan, into a solid phase with the synthesis of tholins, which grow in suspension in the plasma. Sciamma-O’Brien et al. (2010) showed that for a pressure inside the reactor around 1 mbar, the tholins production rate becomes optimal for an initial methane concentration of 5%, conditions of which were chosen here in order to collect as many tholins as possible. PAMPRE was operated for 8 hr at a radio frequency power of 30 W to produce 240 mg of aerosol analogs.

Moreover, several analyses have been performed in order to determine if those tholins would be representative analogs of the aerosols present in Titan’s atmosphere. Concretely, different experimental results have been compared to the data gathered during the Cassini-Huygens mission. For example, Coll et al. (2013) compared the data from the instrument Huygens-aerosol collector pyrolyser (ACP) to the results of analyses performed on analogs produced by different Titan-like plasma experiments. More specifically, they found that cold plasmas, just like the one in PAMPRE (i.e., where neutrals remain at room temperature, with a low ionization fraction), are compatible with the composition of tholins measured by ACP, especially regarding the density of volatile species like NH₃ and HCN. We can therefore consider the nanoparticles (NPs) produced by the PAMPRE platform as relevant analogs of the aerosols present in Titan’s upper atmosphere.

### 2. Experimental Methods

#### 2.1. Preparation of the Aerosol Samples

Our samples are analogs of the aerosols present in Titan’s atmosphere, the so-called tholins produced within the PAMPRE dusty plasma reactor, which are described in detail in Szopa et al. (2006). PAMPRE provides an efficient conversion of the initial N₂–CH₄ gas-phase precursors, representative of the atmosphere of Titan, into a solid phase with the synthesis of tholins, which grow in suspension in the plasma. Sciamma-O’Brien et al. (2010) showed that for a pressure inside the reactor around 1 mbar, the tholins production rate becomes optimal for an initial methane concentration of 5%, conditions of which were chosen here in order to collect as many tholins as possible. PAMPRE was operated for 8 hr at a radio frequency power of 30 W to produce 240 mg of aerosol analogs.

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#### 2.2. Aerosol Production and Characterization

Free tholins NPs were produced by nebulizing a 1 g l⁻¹ aqueous solution of the above-described tholins in an atomizer (TSI, model 3076), using two bars of N₂ as the atomizing gas. These NPs were subsequently dried in a 2 m-long (TSI, model 3062) diffusion dryer. In order to fully characterize our aerosol analogs, we measured their size distribution with a scanning mobility particle sizer (SMPS) device available on the DESIRS beamline (model TSI 3080L/3772) as discussed in Gaia-Levrel et al. (2011).
The left and right axis of Figure 2 respectively show the experimentally measured SMPS count size distribution of the airborne tholins and the theoretical (Wang et al. 2005) transmission efficiency of the aerodynamic lens system (see Section 2.4). A bimodal size distribution, with two modal diameters at 60 and 325 nm, was measured with number concentrations of $1.5 \times 10^5$ and $2.1 \times 10^4$ particles cm$^{-3}$ at their maxima, respectively. By taking into account the transmission efficiency, 97% and 99% of these first and second modes, respectively, are theoretically transmitted by the lens system with an overall transmission of 96% of the total distribution.

A second method based upon a scanning electron microscope (SEM; ZEISS Supra55VP) was also used to characterize the produced tholins particles. Two types of samplings were performed: (1) the deposition/evaporation of a colloidal solution droplet on an SEM grid, and (2) the electrostatic precipitation of airborne tholins particles using a nanometer aerosol sampler (NAS; model 3089, TSI) after the nebulization process (Figures 3(a), (b)).

Figure 3(a) presents an SEM picture obtained for the first type of sampling. A count size distribution with a 350 nm modal diameter was measured and corroborates the second mode seen on the SMPS for the same PAMPRE experimental conditions. An earlier study of Hadamcik et al. (2009) showed that, in this reactor, the average grain size increases with the amount of CH$_4$ and, more generally, depends on the plasma parameters such as the gas flow, the discharge power, and the duration of the experiment. As an example, a 300 nm mode diameter was obtained for a gaseous mixture containing 5% of methane in a 30 W radio frequency discharge, which is consistent with our measurements. On the other hand, Figure 3(b) presents an SEM picture obtained for the second type of sampling and confirmed the SMPS bimodal distribution with modal diameters of 50 and 345 nm. The first mode at 50 nm was produced during the nebulization process and should correspond to the SMPS peak at 60 nm. Because the additional family of smaller particles seen in Figures 2 and 3(b)—with diameters in the 50–60 nm range—appears only when going through the nebulization process, we believe that they are most likely a consequence of the violent nature of the atomization. In all cases in the following we will consider that the size distribution of the NPs entering the experimental vacuum chamber is the one given by Figure 2, with 94% of the particles falling into the first mode with a mean size of 60 nm and the 6% remaining onto the second mode at 325 nm.

Finally, note that we used water as a solvent for the tholins prior to their nebulization. Besides being the one with the lowest evaporation rate, water has the highest ionization threshold (12.6 eV against, for example, 10.8 eV for methanol or 12.2 eV for acetonitrile). Therefore, possible residual gas-phase water molecules surrounding the tholins are fully transparent up to 12.6 eV.

2.3. The FUV Ionizing Radiation: The DESIRS Beamline at Synchrotron SOLEIL

Intense tunable synchrotron FUV light was produced by the undulator-based beamline DESIRS at Synchrotron SOLEIL (Gif sur Yvette, France), delivering photons of high brightness in the 4–40 eV range with variable polarization (Nahon et al. 2012). We used a moderate resolution grating (200 groove/mm) providing flux in the $10^{12}$–$10^{13}$ ph s$^{-1}$ range for a bandwidth of $\Delta E/E \sim 0.1 \%$. Note that, thanks to a rare gas filter system, acting as a low-energy pass filter, the radiation provided by DESIRS is free of any undulator-harmonics.

2.4. The Photoionization Chamber and the Photoelectron Spectrometer

Experiments were performed at the SAPHIRS molecular beam end station (Tang et al. 2015). The exact same method as described in Section 2.2 was used to produce free tholins NPs by nebulization followed by a drying stage before entering, through a 190 $\mu$m limiting aperture, an aerodynamic lens (Gaie-Levrel et al. 2011) that focuses them into a $\sim$400 $\mu$m diameter aerosol beam with a very high transmission (above 90% for NPs ranging from 20 to 1500 nm). The NPs then cross two $\phi = 2$ mm skimmers before reaching the center of the ionization region. Note that the SAPHIRS double-differential vacuum system efficiently removes the gas-phase component of the beam (mostly N$_2$ and H$_2$O in this case since tholins themselves have an extremely low vapor pressure), so that most of the electron signal comes from the NP phase.

Once in the interaction zone, the tholins are photoionized by the FUV synchrotron radiation (Figure 4), releasing a photoelectron with a kinetic energy $E_k$ such that $hv = E_i + E_k$, where $hv$ is the incident energy of the FUV photons and $E_i$ is the ionization energy of a given electronic orbital. Photoelectron spectroscopy (PES) consists of measuring the kinetic energy distribution of the photoelectrons at a given photon energy, which in turn yields the spectroscopy of the cation, i.e., its ionization energies. To do so we used the double-imaging electron/ion coincidence spectrometer ($i^2$PEPICO) DELICIOUS 3 (Garcia et al. 2013), which possesses a velocity map imaging spectrometer (VMI) on the electron side (Eppink & Parker 1997), in which the 3D expending sphere of photoelectrons is imaged onto a 2D position sensitive detector (PSD), providing multiplex radial and angular information. The electrostatic lens formed in the interaction region is such that the impact location on the PSD only depends on the initial momentum of the electrons and not on their precise location of creation. The radius of the circular pattern obtained on the PSD depends on $E_k$ and the electrostatic potentials, which can of course be tuned so that the $4\pi$ distribution of the electron is collected. Provided that there is an axis of symmetry in the 3D photoelectron angular distribution contained in the detector.
plane, the 2D image can be Abel-inversed to retrieve a central cut of the 3D distribution whose angular integration directly leads to PES.

In practice, the VMI concept has already been used to study the angle-resolved PES of salt NPs (Wilson et al. 2007; Goldmann et al. 2015), but only raw images where presented without any image inversion yielding the exact PES. This is due to the fact that in these previous works there was no revolution symmetry axis in the 3D electron distribution. Indeed, the electric field associated with the linear polarization of the FUV light which was used in these studies was perpendicular to the photon propagation axis along which a forward/backward asymmetry is observed in NP photoemission (as seen on Figure 5). This well-documented photon-dependent asymmetry is due to an interplay between the NP size-dependent finite photon penetration depth and electron escape depth. In our case, thanks to the circularly polarized light (CPL) available on DESIRS, the quantification axis is the propagation axis and the revolution symmetry requirement is fulfilled, so that electron images can be Abel inverted. To do so we used the Basex method (Dribinski et al. 2002) providing both radial and angular information, i.e., angle-resolved PES. We focus, in the present study, on the analysis of the radial distribution, by angular integration of the inverted images, providing the PES, i.e., the photoelectron kinetic energy distribution, with an overall relative energy resolution of about 4%.

At each photon energy, the PES experiment on NPs is followed by a similar background measurement with the water solvent alone to quantify and then subtract its residual contribution, in order to provide the pure signal from the tholins only.

3. Results and Discussion

We have used different FUV photon energies from 9 to 11 eV to photoionize the PAMPRE tholins (whose ionization energy was a priori unknown), including, of course, the 121.6 nm (10.2 eV) Lyα emission line, which is the most intense one in the FUV solar spectrum (a hundred times higher than the average, see Figure 1(A)).

The upper limit in energy is set by the activation threshold (100 nm = 12.3 eV) of molecular nitrogen; in the atmosphere of Titan, we assume that below 100 nm, the light will be mainly absorbed by the major gas-phase compounds N2 and CH4 and will marginally interact with the aerosols. As mentioned earlier, after the 11 day solar irradiation time the aerosols have descended to an altitude of 600 km, which corresponds to a lower energy limit of 150 nm (Figure 1(B)). Therefore, the energy range presented in this work, between 9 and 11 eV, represents the photoprocessing of aerosols outside the absorption spectrum of N2, from their formation at high altitudes out into the end of their diurnal continuous irradiation in the thermosphere.

Figure 5 shows the background-corrected noninverted images obtained at various photon energies, images from which are extracted, after inversion, the results presented and discussed hereafter. It is obvious to the naked eye that the forward/backward asymmetry increases with photon energy as the particles become more opaque at wavelengths closer to their diameter (Wilson et al. 2007). There is a relation between angular distributions and physical and optical properties of NPs (Wilson et al. 2007; Goldmann et al. 2015; Signorell et al. 2016; Jacobs et al. 2017). The analysis of this angular information in the case of tholins will be the subject of a forthcoming paper.
3.1. The Ionization Threshold

Figure 6 shows the photoelectron spectra obtained by Abel inversion of the corrected images (Figure 5) and angular integration at different photon energies. We notice that the ionization onset, as estimated by the departure from the baseline signal, appears at a photon energy of $6.0 \pm 0.1 \text{ eV}$ ($\sim 207 \text{ nm}$), regardless of the incident energy. This corresponds then to the ionization threshold of the tholins composed of 5% methane, determined here experimentally and directly for the first time for this kind of material. This means that any photon whose energy is above 6 eV may interact with the tholins leading to their ionization. This value has to be compared to the ionization threshold of the main surrounding neutral gas-phase compounds in Titan atmosphere, which are well above N$_2$ at 15.6 eV, CH$_4$ at 12.6 eV, C$_2$H$_2$ at 11.4 eV, and C$_2$H$_4$ at 10.5 eV.

This is consistent with the predictions of Borucki & Whitten (2008), who state in their study, Borucki & Whitten that the FUV ionization of the aerosols has to start at an energy lower than 7 eV in order to be effective, while higher energies would be absorbed by the gas phase. Mishra et al. (2014) went further in their analysis by making the threshold vary in order to fit the data of the permittivity, waves and altimetry (PWAy) instrument on board Huygens between 160 and 80 km in the atmosphere suggesting that, as the nature of the aerosols changes during their descent through the atmosphere (size, chemical composition, etc.), their ionization threshold might change as well and may vary as a function of the altitude. They managed to satisfactorily reproduce the data obtained by the PWA permittivity instrument by varying the ionization threshold from 6 to 7 eV. Our findings are consistent with their lower-limit energy range. Our experimentally measured value...
is, however, significantly higher than the ~5.1 eV calculated for 3 nm diameter carbonaceous aerosols in Lavvas et al. (2013). This discrepancy might be due to the large amount of nitrogen in our analogs (Sciama-O’Brien et al. 2010) as compared to PAH NPs.

Note that this photoionization threshold measured here for neutral tholins is probably very similar for that of charged tholins. Indeed for large molecular structures, above a size of few nanometers, the charge density is so low that the ionization threshold does not depend on the initial charge (Giuliani et al. 2012).

3.2. Kinetic Energy Distribution of the Photoelectrons

In order to analyze phenomenologically the photoelectron kinetic energy distributions shown in Figure 7, we have extracted the position of the most probable kinetic energy and the FWHM of the PES and these are shown as an insert in the same figure. As the photon energy increases, the most probable kinetic energy shifts toward higher values from 0.6 eV at \( h\nu = 9 \) to 1.5 eV for \( h\nu = 11 \) eV. In parallel, the FWHM of the distribution increases too, from a FWHM of ~1.2 eV at \( h\nu = 9 \) eV to ~1.9 eV at \( h\nu = 11 \) eV. Both trends are expected since an increase in the photon energy leads to, on the one hand, more energetic electrons and on the other hand, to the widening of the energy distribution as more orbitals are being ionized.

Finally, at 11 eV, the kinetic energy distribution appears to have a dual component in addition to the fast peak centered around 2 eV, a second weaker slow component around 0.8 eV. The latter contribution is due to electrons that lose energy by inelastic scattering prior to photoemission (Shu et al. 2006; Goldmann et al. 2015), whereas the band observed at higher kinetic energies is the result of the direct photoemission without scattering. This secondary photoemission is also present in the PES obtained for lower photon energies, but the direct photoelectrons are not fast enough to induce a clear separation between both contributions below \( h\nu = 11 \) eV. Note that the secondary photoemission in the FUV domain is a consequence of the finite, yet small, size of the aerosol particles. More specifically, in this configuration the electron-electron scattering length and the absorption length values are comparable with the particle size, leading to commensurate probabilities for both secondary and direct photoemission.

For a given photon energy, a low value of the ionization threshold allows the produced photoelectrons to acquire more kinetic energy as shown above. This kinetic energy makes them mobile in the atmosphere, especially because they are lighter as compared to the surrounding ions. However, their kinetic energy is low enough so that they can recombine efficiently with aerosols even if the maximum number of electrons that an NP can receive depends, generally, on its size, and therefore on the altitude. Lavvas et al. (2013) focused, for example, on the ionization peak at the altitude of 1100 km and found that the aerosols found there are mainly negatively charged, with the ability to capture only one free electron. Moreover, they showed that below the altitude of 1000 km, the electron density decreases while, in parallel, the amount of negatively charged aerosols increases. This effect goes on with decreasing altitude as the aerosols become larger, leading to an increased cross section for electron capture.

In addition, those rather slow photoelectrons, with a kinetic energy below 10 eV, are ideal candidates for dissociative recombination reactions with surrounding gas-phase cations or dissociative electronic attachment reactions on neutrals. Those reactions have high cross sections for electrons with energies \( \lesssim 10 \) eV (Dobrjetic et al. 2016) and need to be considered in order to understand the atmospheric densities of neutrals (Plessis et al. 2012) and negative ions.

3.3. The Absolute Ionization Cross Sections

Another crucial parameter to determine the efficiency of the tholins FUV photoionization is the ionization cross sections and their photon energy dependence. By definition, the ionization cross section \( \sigma \) is given by

\[
\sigma(\lambda) = \frac{\text{photoelectron rate } (\lambda)}{\text{photon flux } (\lambda) \times \text{nanoparticle density } \times \text{interaction length}},
\]

where the photoelectron rate (in \( s^{-1} \)) is the total amount of photoelectrons collected, divided by the total duration of a given measurement corrected by the 60% detector efficiency (corresponding to the open area of the microchannel plate detectors); the interaction length corresponds to the transversal

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**Figure 6.** Photoelectron spectra of tholins aerosols recorded at different photon energies (11, 10.2, 9.5, and 9 eV). The area of the curves has been normalized to the total cross sections derived in Section 3.3. The inset shows a zoom of the ionization onset.

**Figure 7.** Kinetic energy distributions of the electrons coming from the photoionization of tholins at different photon energies. The area of the curves has been normalized to the total cross sections derived in Section 3.3. The inset shows the evolution of the position of the most probable kinetic energy (center) and FWHM as a function of the photon energy.
section of the (cylindrical) NP beam, which has been measured by laser Mie scattering (Gaie-Levrel et al. 2011) to be 420 μm.

The particle concentration is estimated from the convolution of the size distribution and the size-dependent transmission of the aerodynamic lens to $3.5 \times 10^6$ particles cm$^{-3}$. Considering a matter flow via the aerodynamic lens pinholes of 3.17 cm$^2$ s$^{-1}$, one infers a flow of $1.37 \times 10^7$ particles s$^{-1}$ entering the expansion chamber. The aerosol beam volume of 25 cm$^3$ is estimated from a cylinder of 420 μm in diameter and length equal to the beam’s speed, which simulated value is 180 m s$^{-1}$, leading to a particle density of $5.5 \times 10^5$ particles cm$^{-3}$ at the ionization region, if one assumes a 100% transmission via the 2 mm diameter skimmers.

For our measurement conditions, the photon flux of the DESIRS beamline has been determined using a calibrated Si photodiode (IRD, AXUV 100), and ranged from $1.1 \times 10^{12}$ to $7.6 \times 10^{12}$ photon s$^{-1}$.

The calculated cross sections, taking into account all of the above-described parameters are given in Mbarn (10$^{-22}$ m$^2$) in Figure 8. The values start at $2.4 \times 10^9$ Mb at 9 eV and increase to reach $1.2 \times 10^9$ Mb at 11 eV. For comparison, the photoionization cross sections of atoms and small molecules, in the few eV range above their ionization threshold, are in general between a few Mb and a few tens of Mb. For instance, these values are between 20 and 25 Mb for molecular nitrogen N$_2$ (Gallagher et al. 1988), or 10 and 25 Mb for methane (Wang et al. 2008). Note that all of these integrated cross sections have been used to normalize the photoelectron kinetic energy distributions presented in Figure 7. Besides, experimental uncertainties relating to tholins partial optical opacity, production and transmission, electron detection efficiency, and photon flux measurements would have a proportional impact on these results. They are hard to quantify, but they would be most likely overestimated, meaning that the absolute cross sections reported here should be taken as lower limits. In all of the cases our measured values correspond to a bimodal size distribution of our aerosols (peaked at 60 and 325 nm in diameter) as shown in Figure 2. Cross sections derived from a simple Mie model strongly depend on the size of the NPs. However the size of our analogs are consistent with the size predicted at a 600 km altitude in Titan’s atmosphere, where 6 eV radiation is still strongly present (see Figure 1).

Figure 8. Experimentally derived absolute photoionization cross sections of the tholins in the near FUV range.

The tholins photoionization cross section appears therefore 5 orders of magnitude higher than the ones of standard molecules. This result, combined with a low ionization threshold at $6.0 \pm 0.1$ eV, make the aerosols FUV photoionization a non-negligible phenomenon in the atmosphere of Titan (as compared to X-ray photoionization for example) and should definitely be taken into account in the overall Titan atmosphere radiative transfer budget.

4. Conclusion

The laboratory experiments of FUV photoionization on Titan’s aerosol analogs reported in this paper constitute the first experimental values for the ionization threshold, ionization cross sections, and kinetic energy distributions of the corresponding photoelectrons. Due to their low ionization threshold of $6.0 \pm 0.1$ eV, associated with very large cross sections, 5 orders of magnitude higher than typical gas-phase molecules, FUV photoionization of aerosols is an important phenomenon and represents a non-negligible source of electrons in the atmosphere that needs to be taken into account in electrical conductivity models. In terms of chemical reactivity, the produced photoelectrons possess a kinetic energy lower than 10 eV and will either recombine with the aerosols from which they originate, heat their environment (by electronic diffusion), or initiate dissociative recombination reactions that become very efficient for low-energy electrons.

This experiment opens opportunities to improve our understanding of planetary aerosols in combination with models, by expanding the range of experimental parameters representative of the Titan atmosphere. One of these parameters is the composition of the tholins, which have been produced here from an initial mixture of 95% N$_2$ + 5% CH$_4$. This ratio could be varied since the tholins composition may impact their photoemission properties. A coating made of ethane or methane might have some effect as well, such as increasing the ionization threshold for example.

Another crucial parameter is the size of the aerosols, which is, as the FUV spectrum, altitude-dependent. One of the caveats of our experiment is that so far we could not preselect their size before transmission and ionization due to the low signal, so that the full size distribution of Figure 2 contributes to the current results. Models appear to be quite sensitive to the size of the aerosols, as it might change their electronic behavior since the larger the NPs, the more surface they offer for interaction with the FUV in order to emit electrons (or capture them). The aerosol radius of Titan’s aerosol is about 10 nm at 600 km (Lavvas et al. 2011), which is significantly smaller than the radius of the aerosol samples synthesized in our study. In order to infer the effective electron production from Titan’s aerosols FUV photoionization in Titan’s ionosphere, a further determination of the aerosols total FUV absorption cross section would be necessary as a normalization scaling factor for the electron production rate obtained in the present study. For future experiments, it would also be interesting to select the size of the NPs and play with their composition/coating in order to test the experimental sensitivity of these parameters to be compared to photochemical models and the permittivity measurements in Titan’s atmosphere. Recent improvements in aerosol transmission at SAPHIRS will allow exploration of the size dependence.

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