

# Absorption cross-sections for some atmospherically important molecules at the H atom Lyman- $\alpha$ wavelength (121.567 nm)

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## Abstract

Absolute values of gas-phase absorption cross-sections for some atmospherically important molecules (HCl, H<sub>2</sub>O, H<sub>2</sub>S, NH<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, HNCO, CH<sub>4</sub>, CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CHF<sub>2</sub>Cl, CHBr<sub>3</sub>, CH<sub>3</sub>CF<sub>2</sub>Cl and CH<sub>3</sub>CFCl<sub>2</sub>) have been measured at the H atom Lyman- $\alpha$  wavelength (121.567 nm) employing narrow band ( $\Delta\lambda = 0.0006$  nm) laser radiation generated by resonant third-order sum-difference frequency conversion. The present values can be used to access the uncertainty associated with Lyman- $\alpha$  absorption cross-section values derived from available literature absorption spectra which usually have been measured with quite different and sometimes with quite low spectral resolutions. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The ultraviolet (UV) solar spectrum is of particular importance in determining the composition, temperature distribution and circulation pattern of the stratosphere, mesosphere and thermosphere. The strongest emission line in the VUV region of the solar spectrum is at the Lyman- $\alpha$  (121.567 nm) wavelength due to neutral atomic hydrogen [1,2]. The energy contained in the solar Lyman- $\alpha$  flux is as large as the total solar flux in the 120–160 nm region [3]. Because the Lyman- $\alpha$  wavelength occurs at a spectral window of molecular oxygen, solar radiation can penetrate down to about 60 km in the earth's atmosphere [4].

Therefore, an accurate knowledge of molecular absorption cross-sections is essential to obtain reliable photodissociation rates in the earth's upper atmosphere as well as in interstellar media. For the sun and other stars with a similar radiation environment, the most important wavelength being the Lyman- $\alpha$  wavelength [5], absolute values of absorption cross-sections at this wavelength are of great significance in the development of chemical dynamical radiative models [6].

Despite such importance, the absolute absorption cross-sections at the Lyman- $\alpha$  wavelength are not yet available for a number of atmospherically important molecules. Although for most of these molecules, absorption spectra covering the range of the Lyman- $\alpha$  wavelength have been reported. However, in most cases absolute values at 121.567 nm are not reported. Also for a number of molecules where absolute values of the Lyman- $\alpha$  absorption cross-sections have been reported, the values obtained by different workers have been

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found to differ depending on the bandwidth of the VUV radiation used in the experiments. In this Letter, we report absolute values for the Lyman- $\alpha$  absorption cross-sections of some atmospheric important molecules which were measured using narrow band VUV laser radiation generated by resonant third-order sum-difference frequency conversion.

## 2. Experimental

The apparatus schematically shown in Fig. 1 was used for measurement of Lyman- $\alpha$  absorption cross-sections and has been described earlier in detail [7–9]. VUV laser light was generated by resonant third-order sum-difference frequency conversion ( $\omega_{\text{VUV}} = 2\omega_{\text{R}} - \omega_{\text{T}}$ ) in a phase-matched Kr–Ar mixture [10,11]. In this scheme  $\omega_{\text{R}} = 212.55$  nm is two-photon resonant with the Kr 4p–5p (1/2, 0) transition and fixed during the measurements. The second frequency  $\omega_{\text{T}}$  could be

tuned over the wavelength region 844–846 nm to generate narrow band VUV laser light tuneable around the H atom Lyman- $\alpha$  transition (121.567 nm). A bandwidth of  $\Delta\lambda = 0.0006$  nm was determined for the VUV laser radiation in separate experiments by recording H atom Doppler profiles under thermalised conditions. In the present measurements the following wavelength calibration was adopted. H atoms produced via laser photolysis of HCl at 193 nm were cooled down to a translational temperature of  $T_{\text{trans}} \approx 300$  K by collisions with room-temperature inert gas argon and the maximum of the H atom Doppler profiles (measured by recording the VUV laser-induced fluorescence spectrum) corresponding to the center-frequency of the H atom Lyman- $\alpha$  transition was determined. In the subsequent absorption measurements  $\omega_{\text{T}}$  was locked at this position.

In the absorption cross-sections measurements, the pulse to pulse change in the VUV laser intensity was monitored using a solar blind photomultiplier placed just before the laser light enters the

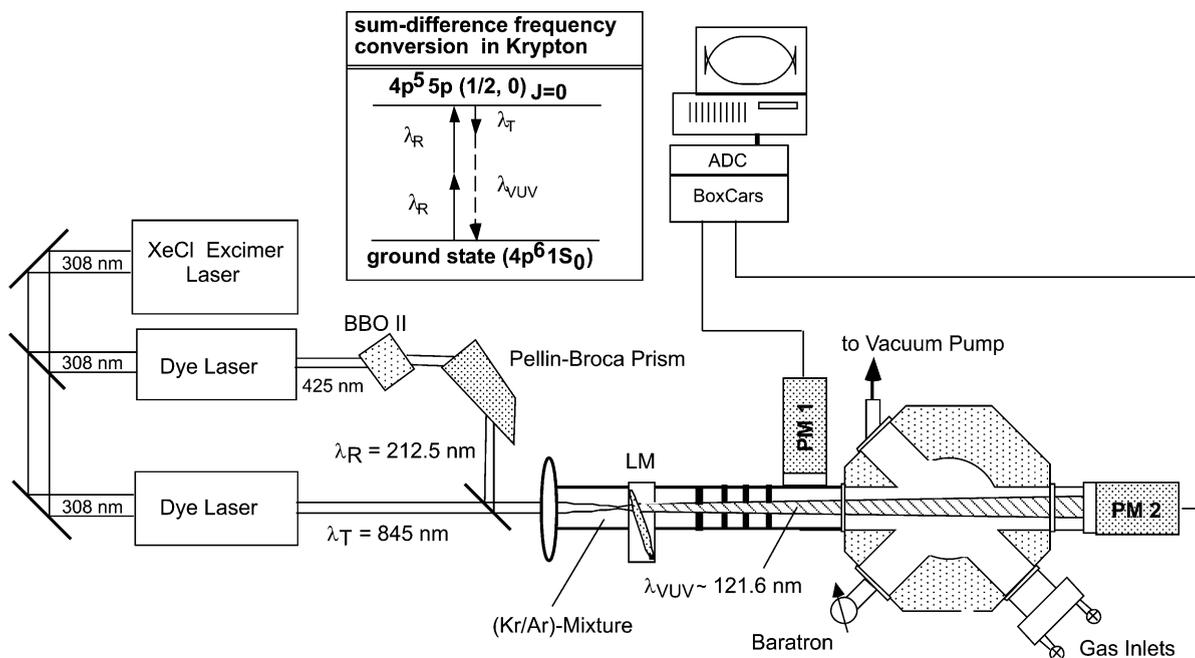


Fig. 1. Schematic diagram of the experimental setup used for the Lyman- $\alpha$  absorption cross-section measurements (PM: photomultiplier, LM: lens monochromator, ADC: analogue to digital converter). The Kr four-wave mixing scheme for the generation of narrow band Lyman- $\alpha$  laser radiation ( $\lambda_{\text{VUV}} = 121.567$  nm,  $\Delta\lambda = 0.0006$  nm) is shown as an inset.

sample section (PM 1 in Fig. 1). A second photomultiplier (PM 2 in Fig. 1) kept after the sample compartment was used for measuring the attenuation of Lyman- $\alpha$  radiation by the sample. Typically 50 laser shots were averaged to get absorbance value at a given sample pressure. The absorption path length was  $(20.0 \pm 0.2)$  cm. The pressure range employed in the measurements was 10–500 mTorr depending on the attenuation of the Lyman- $\alpha$  radiation.  $\text{H}_2\text{O}$  used in the measurements was double distilled and deionised. Prior to use in the absorption measurements,  $\text{H}_2\text{O}_2$  (85%, PEROXID Chemie) was pumped through the cell for at least three days until it reached a final concentration of >99.8% (determined by titration). HNCO synthesised using the method described in our earlier work [7,8] was purified by repeated distillation. Its purity was found to be  $\approx 97\%$  as checked by gas chromatography and mass spectrometry. The other samples were obtained from different manufacturers with the following purities: HCl (99.999%, Messer Griesheim: MG),  $\text{CH}_3\text{Cl}$  (>99.8%, MG): the  $\text{CH}_3\text{Cl}$  flow was started several minutes before the experiments in order to ensure the removal of the small amounts of impurities, which were stated by the manufacturer to be mainly HCl and  $\text{CH}_4$ , and higher hydrocarbons, all of them having a considerable higher vapour pressure than  $\text{CH}_3\text{Cl}$ .  $\text{CH}_2\text{Cl}_2$  (>99.5%, Fluka Chemie, amylene-stabilised) and  $\text{CHCl}_3$  (99.8%, Riedel-de Haen, CHROMASOLV, amylene-stabilised): the liquids  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  were degassed prior to the measurements by several freeze-pump-thaw cycles at liquid  $\text{N}_2$  temperature.  $\text{CHBr}_3$  with a purity of >98% was obtained from Merck-Schuchardt and the sample was also degassed prior to the measurements by several freeze-pump-thaw cycles.  $\text{CH}_4$  (>99.998% MG),  $\text{CHF}_2\text{Cl}$  (99.9% MG),  $\text{CH}_3\text{CF}_2\text{Cl}$  (>98%, MG, as stated by the manufacturer, the amount of  $\text{CH}_3\text{CFCl}_2$  in the sample was less than 0.1%, with a water content of less than 5 ppm),  $\text{CH}_3\text{CFCl}_2$  (99.7%, ABCR Chemicals, Karlsruhe) as well as  $\text{H}_2\text{S}$  (UCAR electronic grade, 99.99%) and  $\text{NH}_3$  (99.998 MG) were used without further purification.

Flow rates of the gases were controlled by mass flow controllers (Tylan), which were calibrated

using  $\text{N}_2$  before each measurement. The main source of uncertainty in the measurement of absorption cross-sections apart from sample impurities could come from the pressure measurement, the accumulation of photolysis products and the variations in the intensity of the Lyman- $\alpha$  radiation. As mentioned earlier the purities of most of the compounds were around 99% or more. Accumulation of photolysis products was avoided by measuring under flow conditions. Depending on the actual attenuation of the Lyman- $\alpha$  radiation, sample pressures ranging from 10 to 200 mTorr were employed. The pressure was monitored using a capacitance manometer (MKS Baratron, 10 Torr head) with an accuracy of  $\pm 0.1\%$ . The major uncertainty in the present measurement is due to variations in the VUV light intensity ( $\pm 5\%$  averaged over 50 laser shots). The total cumulative uncertainty in the cross-section value is calculated to be  $\pm 7\%$ . In some runs the Beer–Lambert plots showed small negative intercepts with the  $y$ -axis (see Fig. 2) due to small time-independent pressure offsets of the capacitance manometer. However, this being a constant factor does not affect the value of the slope of the Beer–Lambert plots which yields the absorption cross-section.

### 3. Results and discussion

The optical absorption cross-section  $\sigma$  was determined by measuring the attenuation of the Lyman- $\alpha$  laser radiation and is defined as

$$\sigma = \ln(I_0/I_{\text{trans}})/(n \times l_{\text{abs}}), \quad (1)$$

where  $n$  is the number density of gas molecules,  $l_{\text{abs}}$  is the absorption pathlength and  $I_{\text{trans}}$  and  $I_0$  are the intensities of the Lyman- $\alpha$  radiation measured with and without attenuation by the gas sample. Values for the absorption cross-sections were obtained from the slope of  $\ln(I_0/I_{\text{trans}})$  versus  $(n \times l_{\text{abs}})$  plots as shown in Fig. 2. Absorption cross-sections obtained in the present work are listed in Table 1 and compared – whenever available – with reported literature values or with estimates obtained from absorption spectra reproduced in the literature.

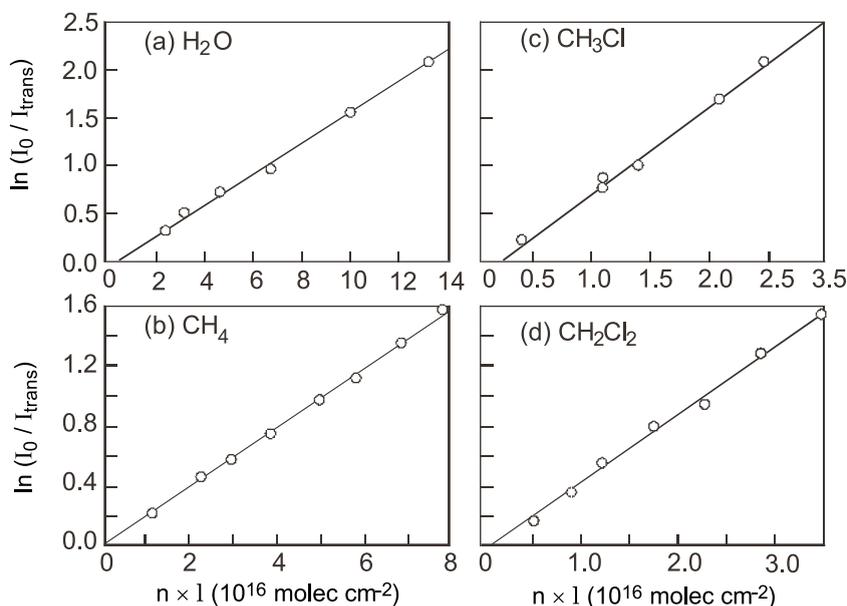


Fig. 2. Beer–Lambert plots for: (a)  $\text{H}_2\text{O}$ , (b)  $\text{CH}_4$ , (c)  $\text{CH}_3\text{Cl}$  and (d)  $\text{CH}_2\text{Cl}_2$ . The corresponding Lyman- $\alpha$  absorption cross-sections derived from the slope of the Beer–Lambert plots (for details see text) are given in Table 1.

For  $\text{CH}_4$ , the absorption spectrum around the Lyman- $\alpha$  wavelength exhibit no pronounced structure [12]. Therefore the influence of the spectral bandwidth of the light source used in the measurement should have only minor influence on the actual value of the Lyman- $\alpha$  absorption cross-section. The fact that the value obtained in the present study,  $(2.0 \pm 0.2) \times 10^{-17} \text{ cm}^2$  (see Table 1), is in good agreement with the value of  $(1.9 \pm 0.1) \times 10^{-17} \text{ cm}^2$  which can be estimated from the spectral data depicted in Fig. 1 of Ref. [13] (spectral resolution 0.2 nm) is in line with this conclusion.

For  $\text{HCl}$ , a VUV absorption spectrum in the 106–185 nm region was recorded by Nee and co-workers with a spectral resolution of 0.05 nm [14]. These authors measured the absorption cross-section close to the Lyman- $\alpha$  wavelength and estimated that the corresponding absorption cross-section is not higher than  $3 \times 10^{-19} \text{ cm}^2$ . This estimate is in general agreement with the present measurement which yielded a value of  $(1.4 \pm 0.1) \times 10^{-19} \text{ cm}^2$  for the Lyman- $\alpha$  absorption cross-section of  $\text{HCl}$ .

VUV absorption spectra of  $\text{H}_2\text{O}$  have been recorded by different groups [15–22]. For  $\text{H}_2\text{O}$ , the following Lyman- $\alpha$  absorption cross-sections have either been reported [18–20,22] or can be estimated from the literature absorption spectra [17,21]:  $(1.5 \pm 0.1) \times 10^{-17} \text{ cm}^2$  [17] (spectral resolution 0.003 nm),  $(1.4 \pm 0.1) \times 10^{-17} \text{ cm}^2$  [18] (spectral resolution 0.2 nm),  $(1.57 \pm 0.1) \times 10^{-17} \text{ cm}^2$  [19] (spectral resolution 0.005 nm),  $(1.59 \pm 0.1) \times 10^{-17} \text{ cm}^2$  [20] (spectral resolution 0.005 nm),  $(1.3 \pm 0.05) \times 10^{-17} \text{ cm}^2$  [21] (spectral resolution 0.5 nm) and  $(1.4 \pm 0.03) \times 10^{-17} \text{ cm}^2$  [22] (spectral resolution 0.007 nm). In summary, the values for the Lyman- $\alpha$  absorption cross-section reported in the literature are found to range from  $1.3 \times 10^{-17}$  to  $1.6 \times 10^{-17} \text{ cm}^2$  depending on the spectral resolution of the measurement. In the present work, we obtained a value of  $(1.6 \pm 0.1) \times 10^{-17} \text{ cm}^2$  which is in good agreement with the results of the three higher resolution studies [17,19,20].

For  $\text{H}_2\text{S}$ , Watanabe and Jursa recorded an absorption spectrum in the wavelength region 120–160 nm with a resolution of 0.1 nm [23]. From this spectrum (Fig. 3 of Ref. [23]) an absorption cross-

Table 1

Comparison of room-temperature (300 K) gas-phase absorption cross-sections ( $\sigma$ ) for the H atom Lyman- $\alpha$  wavelength (121.567 nm) obtained in the present study with the corresponding values estimated from literature data obtained with various spectral resolutions (for details see text)<sup>a</sup>

Molecule	$\sigma$ in cm <sup>2</sup> (this work)	$\sigma$ in cm <sup>2</sup>	SR in nm	Reference
HCl	$(1.4 \pm 0.1) \times 10^{-19}$	$<3 \times 10^{-19}$	0.05	[14]
H <sub>2</sub> O	$(1.6 \pm 0.1) \times 10^{-17}$	$(1.5 \pm 0.1) \times 10^{-17}$	0.003	[17]
		$(1.4 \pm 0.1) \times 10^{-17}$	0.2	[18]
		$(1.57 \pm 0.1) \times 10^{-17}$	0.005	[19]
		$(1.59 \pm 0.1) \times 10^{-17}$	0.005	[20]
		$(1.3 \pm 0.05) \times 10^{-17}$	0.5	[21]
		$(1.4 \pm 0.03) \times 10^{-17}$	0.007	[22]
H <sub>2</sub> S	$(2.8 \pm 0.2) \times 10^{-17}$	$(2.5 \pm 0.5) \times 10^{-17}$	0.1	[23]
		$(3.0 \pm 0.2) \times 10^{-17}$	~12	[24]
		$3.14 \times 10^{-17}$	~12	[25]
NH <sub>3</sub>	$(7.3 \pm 0.5) \times 10^{-18}$	$(8.0 \pm 0.5) \times 10^{-18}$	0.2	[26]
		$(7.0 \pm 0.5) \times 10^{-18}$	0.007	[27]
H <sub>2</sub> O <sub>2</sub>	$(9.6 \pm 0.7) \times 10^{-18}$			
HNCO	$(2.5 \pm 0.2) \times 10^{-17}$	$(2.0 \pm 0.5) \times 10^{-17}$	0.5	[30]
CH <sub>4</sub>	$(2.0 \pm 0.2) \times 10^{-17}$	$(1.9 \pm 0.1) \times 10^{-17}$	0.2	[13]
CH <sub>3</sub> Cl	$(8.8 \pm 0.6) \times 10^{-17}$	$(5.0 \pm 0.2) \times 10^{-17}$	0.6	[28]
		$(7.5 \pm 0.3) \times 10^{-17}$	0.04	[29]
CH <sub>2</sub> Cl <sub>2</sub>	$(4.0 \pm 0.3) \times 10^{-17}$	$(4.0 \pm 0.2) \times 10^{-17}$	0.04	[29]
CHCl <sub>3</sub>	$(3.5 \pm 0.3) \times 10^{-17}$	$(4.0 \pm 0.2) \times 10^{-17}$	0.4	[29]
CHF <sub>2</sub> Cl	$(1.8 \pm 0.2) \times 10^{-17}$	$(5.8 \pm 0.5) \times 10^{-17}$	Not given	[31]
CHBr <sub>3</sub>	$(7.1 \pm 0.5) \times 10^{-17}$			
CH <sub>3</sub> CF <sub>2</sub> Cl	$(3.1 \pm 0.2) \times 10^{-17}$	$(3.2 \pm 0.3) \times 10^{-17}$	Not given	[32]
CH <sub>3</sub> CFCl <sub>2</sub>	$(6.6 \pm 0.5) \times 10^{-17}$			

<sup>a</sup>The spectral resolution (SR) of the present work was 0.0006 nm.

section of  $(2.5 \pm 0.5) \times 10^{-17}$  can be estimated for the Lyman- $\alpha$  wavelength. Brion et al. [24] applied dipole (e,e) spectroscopy with an energy resolution of 1 eV. From the latter work (Fig. 1 of Ref. [24]) a value of  $(3.0 \pm 0.2) \times 10^{-17}$  cm<sup>2</sup> can be derived for the Lyman- $\alpha$  absorption cross-section. Recently, Feng et al. [25] reported a Lyman- $\alpha$  absorption cross-section of  $3.14 \times 10^{-17}$  cm<sup>2</sup> for a photon energy of 10.2 eV corresponding to a wavelength of 121.55 nm (the energy resolution in their experiment was also 1 eV). Within the combined error limits, the Lyman- $\alpha$  absorption cross-section of  $(2.8 \pm 0.2) \times 10^{-17}$  cm<sup>2</sup> obtained in the present study is in good agreement with the value derived from the spectrum reproduced in [23,24].

For NH<sub>3</sub>, a value of  $(8.0 \pm 0.5) \times 10^{-18}$  cm<sup>2</sup> for the Lyman- $\alpha$  absorption cross-section can be estimated from the spectrum shown in Fig. 1 of Ref. [26] (spectral resolution of 0.2 nm). However, the absorption spectrum reported in Fig. 3 of Ref. [27] (recorded with a higher spectral resolution of 0.007 nm) yields a smaller value of  $(7.0 \pm 0.5) \times 10^{-18}$  cm<sup>2</sup>, which is in better agreement with the value of  $(7.3 \pm 0.5) \times 10^{-18}$  cm<sup>2</sup> obtained in the present work.

In case of CH<sub>3</sub>Cl, a value of  $(5.0 \pm 0.2) \times 10^{-17}$  cm<sup>2</sup> can be estimated from the spectral data depicted in Fig. 3 of Ref. [28]. The latter data have been obtained using dipole (e,e) spectroscopy in the energy range 6–12 eV with a resolution of

0.05 eV (corresponding to a resolution of 0.6 nm at the Lyman- $\alpha$  wavelength of 121.567 nm). Using synchrotron radiation with a spectral resolution of 0.04 nm, Lee and Suto [28] determined a Lyman- $\alpha$  absorption cross-section of  $(7.5 \pm 0.3) \times 10^{-17}$  cm<sup>2</sup>. In the present work we obtained a value of  $(8.8 \pm 0.6) \times 10^{-17}$  cm<sup>2</sup> which is slightly higher than the values derived from the earlier measurements.

For CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>, Lyman- $\alpha$  absorption cross-sections of  $(4.0 \pm 0.2) \times 10^{-17}$  cm<sup>2</sup> and  $(4.0 \pm 0.3) \times 10^{-17}$  cm<sup>2</sup> can be estimated from the absorption spectra given in Fig. 6 (spectral resolution 0.04 nm) and Fig. 3 (spectral resolution 0.4 nm) of Ref. [29]. The values  $(4.0 \pm 0.3) \times 10^{-17}$  cm<sup>2</sup> and  $(3.5 \pm 0.3) \times 10^{-17}$  cm<sup>2</sup> obtained in the present study for CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>, respectively, are within the combined error limits in agreement with these estimates.

Uno et al. measured the VUV absorption spectrum (Fig. 1 of Ref. [30]) of HNCO from 107 to 180 nm using synchrotron radiation with a spectral resolution of 0.5 nm which allows to estimate a value of  $(2.0 \pm 0.5) \times 10^{-17}$  cm<sup>2</sup> for the Lyman- $\alpha$  absorption cross-section. The latter value agrees within the combined error limits with the value of  $(2.5 \pm 0.2) \times 10^{-17}$  cm<sup>2</sup> obtained in the present work.

For CF<sub>2</sub>HCl and CH<sub>3</sub>CF<sub>2</sub>Cl, absorption spectra covering the Lyman- $\alpha$  wavelength were recorded and reproduced in Fig. 7 of Ref. [31] and Fig. 4 of Ref. [32], respectively (unfortunately the actual spectral resolution is not given). From the spectrum of [31] the Lyman- $\alpha$  absorption cross-section for CF<sub>2</sub>HCl can be estimated to be  $(5.8 \pm 0.5) \times 10^{-17}$  cm<sup>2</sup>. This value is about three times higher than the value of  $(1.8 \pm 0.2) \times 10^{-17}$  measured in the present work. The reasons of this large difference in the two measurements are not clear as yet. For CH<sub>3</sub>CF<sub>2</sub>Cl, however, the value  $(3.2 \pm 0.3) \times 10^{-17}$  cm<sup>2</sup> estimated from the spectral data of [32] is in good agreement with the value  $(3.1 \pm 0.2) \times 10^{-17}$  cm<sup>2</sup> of the present measurement.

The results of the present study are summarised in Table 1 and compared with the corresponding values/estimates derived from literature absorption spectra. For HCl, H<sub>2</sub>O<sub>2</sub>, CHBr<sub>3</sub> and CH<sub>3</sub>CFCl<sub>2</sub> the present study provided absolute absorption

cross-sections which to best of our knowledge are not yet available in the literature. For the other molecules, apart from CH<sub>3</sub>Cl and CHF<sub>2</sub>Cl, reasonable and in some cases (H<sub>2</sub>O, H<sub>2</sub>S, NH<sub>3</sub>, CH<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>) quite good agreement was found with Lyman- $\alpha$  absorption cross-sections estimated from the presently available literature absorption spectra. For H<sub>2</sub>O, for which a number of optical absorption spectra obtained with different spectral resolutions are available, the data collected in Table 1 suggests that absorption cross-values estimated from spectra recorded with higher spectral resolution [17,19,20] are generally in better agreement with the present results than the values estimated from spectra recorded with lower resolutions [18,21]. At this point it should be noted that all molecules listed in Table 1 except CH<sub>4</sub> exhibit structured absorption spectra near the Lyman- $\alpha$  wavelength. Hence, it can be expected that for these compounds the determination of absolute absorption cross-sections depends on the spectral resolution of the measurement. A similar trend as observed for H<sub>2</sub>O might be present in case of NH<sub>3</sub>, and CH<sub>3</sub>Cl (see Table 1). For CH<sub>3</sub>Cl, the presence of structure in the absorption spectrum which could not be resolved in measurements of [29], would also explain the higher Lyman- $\alpha$  absorption cross-sections obtained in the present study.

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**References**

- [1] R.P. Wayne, *Chemistry of Atmospheres*, second ed., Oxford University Press, Oxford, 1994.
- [2] J.S. Levine, *The Photochemistry of Atmospheres*, Academic Press, New York, 1985.
- [3] C.R. Detwiler, D.L. Garrett, J.D. Purcell, R. Tousey, *Ann. Geophys.* 17 (1961) 263.
- [4] J. London, in: H.-J. Bolle (Ed.), *Radiation in the Atmosphere*, Science Press, Princeton, 1977.
- [5] W.M. Jackson, R.J. Price II, D.D. Xu, D. Wrobel, M. Ahmed, D.S. Peterka, A.G. Suits, *J. Chem. Phys.* 109 (1998) 4703.
- [6] G. Brasseur, M.H. Hitchman, S. Walters, M. Dymek, E. Falise, M. Pirre, *J. Geophys. Res.* 95 (1990) 5639.
- [7] R.A. Brownsword, M. Hillenkamp, T. Laurent, R.K. Vatsa, H.-R. Volpp, *J. Wolfrum, Chem. Phys. Lett.* 249 (1996) 162.
- [8] R.A. Brownsword, M. Hillenkamp, T. Laurent, R.K. Vatsa, H.-R. Volpp, *J. Chem. Phys.* 106 (1997) 9563.
- [9] R.A. Brownsword, M. Hillenkamp, T. Laurent, H.-R. Volpp, *J. Wolfrum, R.K. Vatsa, H.S. Yoo, J. Phys. Chem. A* 101 (1997) 6448.
- [10] G. Hilber, A. Lago, R. Wallenstein, *J. Opt. Soc. Am. B* 4 (1987) 1753.
- [11] J.P. Marangos, N. Shen, H. Ma, H.R. Hutchison, J.P. Connerade, *J. Opt. Soc. Am. B* 7 (1990) 1254.
- [12] M.B. Robin, *Higher Excited States of Polyatomic Molecules*, vol. 1, Academic Press, New York, 1974.
- [13] L.C. Lee, C.C. Chiang, *J. Chem. Phys.* 78 (1983) 688.
- [14] J.B. Nee, M. Suto, L.C. Lee, *J. Chem. Phys.* 85 (1986) 719.
- [15] K. Watanabe, M. Zelikoff, *J. Opt. Soc. Am.* 43 (1953) 753.
- [16] A.H. Laufer, J.R. McNesby, *Can. J. Chem.* 43 (1965) 3487.
- [17] P. Guertler, V. Saile, E.E. Koch, *Chem. Phys. Lett.* 51 (1977) 386.
- [18] L.C. Lee, *J. Chem. Phys.* 72 (1980) 4334.
- [19] B.R. Lewis, I.M. Varvadas, J.H. Carver, *J. Geophys. Res.* A 88 (1983) 4935.
- [20] D. Kley, *J. Atmos. Chem.* 2 (1984) 203.
- [21] W.F. Chan, G. Cooper, C.E. Brion, *Chem. Phys.* 178 (1993) 387.
- [22] K. Yoshino, J.R. Esmond, W.H. Parkinson, K. Ito, T. Matsui, *Chem. Phys.* 211 (1996) 387.
- [23] K. Watanabe, A.S. Jursa, *J. Chem. Phys.* 41 (1964) 1650.
- [24] C.E. Brion, Y. Iida, J.P. Thomson, *Chem. Phys.* 101 (1986) 449.
- [25] R. Feng, G. Cooper, C.E. Brion, *Chem. Phys.* 244 (1999) 127.
- [26] M. Suto, L.C. Lee, *J. Chem. Phys.* 78 (1983) 4515.
- [27] T.J. Xia, T.S. Chien, C.Y. Robert Wu, D.L. Judge, *J. Quant. Spectro. Radiat. Trans.* 45 (1991) 77.
- [28] L.C. Lee, M. Suto, *Chem. Phys.* 114 (1987) 423.
- [29] T.N. Olney, G. Cooper, W.F. Chan, G.R. Burton, C.E. Brion, K.H. Tan, *Chem. Phys.* 205 (1996) 421.
- [30] K. Uno, T. Hikida, A. Hiraya, K. Shobatake, *Chem. Phys. Lett.* 166 (1990) 475.
- [31] J. Doucet, P. Sauvageau, C. Sandorfy, *J. Chem. Phys.* 58 (1973) 3708.
- [32] J. Doucet, P. Sauvageau, C. Sandorfy, *J. Chem. Phys.* 62 (1975) 355.