J. Phys. Chem. A **2008,** *112,* 8731–8736

UV Absorption Cross-Sections of a Series of Dimethylbenzaldehydes

G. El Dib,*[†] A. Chakir,[‡,§] and A. Mellouki[||]

Equipe Astrochimie Expérimentale, Institut de Physique de Rennes, UMR 6251 du CNRS - Université de Rennes 1, Bat. 11c, Campus de Beaulieu, 35042 RENNES Cedex, France, Laboratoire GSMA, Campus Moulin de la Housse, Université de Reims, BP 1039, 51687 Reims cedex 02, France, Laboratoire GSMA-UMR 6089, UFR Sciences, CNRS, BP 1039, 51687 Reims cedex 02, France, and 1C avenue de la recherche scientifique, ICARE/CNRS, 45071 Orléans cedex 0, 2, France

Received: May 2, 2008; Revised Manuscript Received: June 26, 2008

The ultraviolet absorption cross-sections of 2,4-, 2,5-, 2,6-, 3,4- and 3,5- dimethylbenzaldehydes are reported in the wavelength range 240−320 nm. The measurements were carried out in the temperature range 318−363 K using two different experimental systems (D_2 lamp−monochromator and D_2 lamp−diode array). The absorption spectra of the five aldehydes have been found to exhibit relatively high absorption cross-sections in the region of the tropospheric interest with maxima around 290 nm. This work provides the first UV cross-section measurements for these aromatic aldehydes. The obtained cross-section values enable us to estimate the tropospheric photolysis lifetimes of these compounds. The results suggest that photolysis could be an important removal process for these species in the troposphere.

I. Introduction

Dimethylbenzaldehydes (DMBs) constitute an important class of the aromatic aldehydes emitted into the atmosphere. They are emitted as primary pollutants from anthropogenic sources.[1] In fact, they are used in several industrial sectors such as pharmaceutical industry and in manufacture of solvents, flavors and perfumes, and they are also produced from the incomplete combustion of automobile fuels.[2] In addition, they are formed in situ through degradation of the trimethylbenzene isomers: e.g., 2,4-, 2,5-, and 3,4-dimethylbenzaldehyde are produced from the hydroxyl radical initiated oxidation of 1,2,4-trimethylbenzene.[3,4] Vegetation constitutes another significant source of DMBs. They are emitted from a variety of arborous plants, shrubs, herbaceous plants and mosses.[5]

In the atmosphere, the potential gas phase removal processes of DMBs are photolysis and chemical reactions with OH, Cl, and NO_3 radicals.[6] Their oxidation could lead to the formation of other photooxidants such as PAN type molecules and ozone. These processes widely affect the chemistry of the air pollution and can have a direct effect on human health. Therefore, to quantify the contribution of these aromatic aldehydes to the photochemical reactions in urban and rural areas and their environmental impact, it is necessary to know the relative importance of the above processes.

Very little information exists in the literature on the atmospheric fate of DMBs. Reaction with OH radicals has been the subject of three kinetic studies.[7−9] They showed that the reactions of OH with these aldehydes are relatively fast and that the lifetimes of these compounds in the atmosphere are relatively short (a few hours). Further, there are several spectroscopic studies carried out on some aromatic aldehydes such as benzaldehyde and the tolualdehyde isomers.[10−12] However, there is no spectroscopic study carried out to date on DMBs. To provide a better knowledge of the atmospheric fate of DMBs, the contribution of the photolysis in their atmospheric removal has to be evaluated. This requires the knowledge of their UV−vis spectra, the photolysis rates and quantum yields.

In this respect, we have determined the UV−visible spectra of five isomers of dimethylbenzaldehyde: 2,4-, 2,5-, 2,6-, 3,4- and 3,5- dimethylbenzaldehyde. Measurements were carried out with a high resolution UV−visible spectrometry using two different experimental systems in the wavelength range 240−320 nm and the temperature range 318−363 K.

The aim of this study is to assess the importance of the photolysis as atmospheric loss process of these species. The absorption cross-sections combined with photolysis quantum yields are used to calculate the photolysis rates of the studied species in the laboratory and in the atmosphere. In fact, the experimental kinetic determinations require the precise knowledge of the absorption cross-sections of these species. In addition, the obtained data are used in the laboratory studies and in the field measurements to detect these species in the atmosphere. The present work reports the first UV spectra of these species.

The data obtained will be presented and compared to those of other aldehydes to assess the structure effect on the UV−visible absorption. The importance of photolysis as loss process of these compounds compared to other gas phase processes in the atmosphere will be discussed as well.

II. Experimental Section

Absorption cross-sections measurements were carried out in two laboratories: GSMA-Reims and ICARE-Orléans. The experimental procedure has been presented in detail in recent papers from both laboratories.[11,13] Therefore, it will be only briefly described here.

A.. D_2 Lamp−Monochromator System at GSMA-Reims. The D_2-lamp beam (30 W) was focused onto the entrance of a spectrometer (Jobin Yvon HR 640) equipped with a 2400 line mm^{-1} grating (dispersion 0.66 nm mm^{-1} for HR 640). At the

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* Corresponding author. Tel.: +33 2 23235680. Fax: +33 2 23236786. E-mail: gisele.eldib@univ-rennes1.fr.

[†] Institut de Physique de Rennes.

[‡] Université de Reims.

[§] CNRS.

[||] ICARE/CNRS.

10.1021/jp803874e CCC: $40.75

exit slit of the monochromator Czerny−Turner, the light was split into a reference beam, and a working beam which passed longitudinally through the absorption cell. The cell is made of Pyrex and equipped with quartz windows. This monochromatic beam minimizes possible photodissociation of the studied gas samples making it unimportant.

The two signals were measured independently by two Hamamatsu R955 photomultiplier tubes. Considering $I_{0,\mathrm{ref}}(\lambda)$ and $I_0(\lambda)$ as, respectively, the intensities of the reference and working beams for a scan with the empty cell, and $I_{\mathrm{ref}}(\lambda)$ and $I(\lambda)$ the corresponding intensities with the filled cell with a known concentration of one of the studied aldehydes. The background was subtracted from the incident and transmitted intensities. The transmittance is obtained from the ratio

$(I_{0,\mathrm{ref}}(\lambda)/I_0(\lambda))/(I_{\mathrm{ref}}(\lambda)/I(\lambda))$. This enables correction for the source fluctuations. Both photomultipliers are connected to a microcomputer for the data acquisition.

The measurements were carried out over the wavelength range 240−320 nm. The wavelength calibration is made by use of the emission lines of a low pressure mercury lamp Hg (313.15, 334.15 nm). The precision of the spectrometer is estimated to be better than ±0.02 nm. The pressure in the cell is measured with a (0−10) Torr MKS Baratron capacitance and the temperature regulation is carried out by resistors. To validate our determined values, the optical length was varied between 49.6 and 180 cm. An entrance slit width between 80 and 180 μm was used providing a resolution varying from 0.05 to 0.20 nm. The control of the spectrometer, the acquisition of the data as well as their treatment is made by computer.

B. D_2 Lamp−Diode Array System at ICARE-Orléans. The major differences between this experimental set up and that described above are the light detection (here a diode array) and the length of the cell (here 100 cm). The studied gas is introduced into a double-jacket Pyrex cell, equipped with quartz windows. The temperature regulation is provided by a fluid circulating between the inner wall and the second jacket. The fluid circulation is commanded by a thermostat that permits better control over the heating power by circulating fluid (water). The temperature control is ±0.5 °C. The collimated output of the D_2 lamp (30 W) passed through the cell and the emerging beam is analyzed by a spectrometer. The UV−visible spectrophotometer (Chromex) is equipped with an 1800 grooves/mm grating and a 1024 element diode array detector (Princeton Instrument, Inc.). Measurements were made over three different spectral regions from 240 to 320 nm ensuring at least a 10 nm overlap between adjacent segments. The spectroscopic data are collected simultaneously over a wide wavelength range, in real time and in three dimensions (time, absorbance and wavelength). Each wavelength region consisted of 45 scans of diode array to minimize the noise effect. The control of the spectrometer, the acquisition of the data, and their treatment are made by computer. The width of the entrance light beam was varying between 40 and 80 μm providing a spectral resolution of 0.2 nm.

The wavelength scale of the spectrometer was calibrated in the wavelength range (200−400) nm using the emission lines from low-pressure Zn (213.8 nm) and Hg (253.7, 313.3, and 365 nm) pen-ray lamps. The accuracy of the wavelength calibration is 0.1 nm. The pressure in the cell is measured with a 0−10 Torr MKS Baratron capacitance.

In addition, experiments are carried out in static and in dynamic range to estimate the phenomena of possible adsorption on the walls of the cell and to be able to take them into account during the treatment of the results. Further, a cutoff filter was mounted between the D_2 lamp and the absorption cell, allowing only radiation at $\lambda > 245$ nm, to prevent any possible photolysis of the studied aldehydes at $\lambda < 240$ nm.

TABLE 1: Experimental Conditions for the Absorption Cross-Section Measurements at Reims and Orléans

	GSMA-Reims		ICARE-Orléans	
compound	pressure (Torr)	temperature (K)	pressure (Torr)	temperature (K)
2,4-DMB	0.09−0.2	340−350	0.06−0.2	330−333
2,5-DMB	0.05−0.2	340−354	0.07−0.12	323−333
2,6-DMB	0.05−0.2	345−360		
3,4-DMB	0.04−0.2	340−350		
3,5-DMB			0.05−0.14	318−333
spectral range (nm):	240−320		240−320	
path length (cm):	49.6 − 180		100	
spectral bandwidth (nm):	0.05 − 0.2		0.2	
optical density OD:	0.05 < OD < 2		0.03 < OD < 2	

Absorption cross-sections have been determined according to Beer−Lambert's law:

$$\sigma(\lambda) = -\ln[I(\lambda)/I_0(\lambda)]/LC \quad (1)$$

where $\sigma(\lambda)$ is the absorption cross-section (cm^2 molecule^{-1}) at wavelength λ, L is the optical-path length (corresponding to the cell length in cm) and C is the concentration of the studied aldehyde (molecule cm^{-3}).

Because of the low vapor pressure of the chemical species studied in this work, the temperature in the cells was varied between 318 and 363 K. For each compound, the concentrations were chosen to obtain an optical density between 0.1 and 2 for which the cross-section is determined with good accuracy. The residual background noise of the spectrometer is measured before every experiment. Following each run, the cell was evacuated and purged with He and the stability of $I_0(\lambda)$ is recorded to check the stability of the light source over the duration of the experiments. It should be noted that the cross-section of the compound as well as its vapor pressure influences the chosen domain of concentrations used for the measurements.

The chemicals were from Aldrich, 2,4-dimethylbenzaldehyde (90%) 2,5-dimethylbenzaldehyde (99%), 2,6-dimethylbenzaldehyde (97%), 3,4-dimethylbenzaldehyde (98%), and 3,5-dimethylbenzaldehyde (97%). They were further purified by repeated freeze−pump−thaw cycles before use. The used experimental conditions are summarized in Table 1.

III. Results and Discussion

The absorption spectra obtained are illustrated in Figures 1 and 2, and the cross-section values are listed in Table 2 in 1 nm intervals. The reported cross-sections were obtained by averaging 8 to 10 independent measurements at several different vapor pressures.

A. Measurements Obtained by D_2 Lamp−Monochromator System at GSMA-Reims. Measurements of the absorption spectra of 2,4-DMB, 2,5-DMB, 2,6-DMB and 3,4-DMB were conducted at different pressures at GSMA in static conditions with a fixed concentration of DMB in the wavelength range 240−320 nm. Experiments were performed in the temperature range of 340−363 K, to minimize the loss of the studied aldehydes on the wall of the cell. The optical length was varied between 49.6 and 180 cm to have an optical density between 0.05 and 2. Our values listed in Table 2 are limited to the spectral region 240−320 nm for all the studied compounds except 2,4-DMB where the corresponding listed cross sections

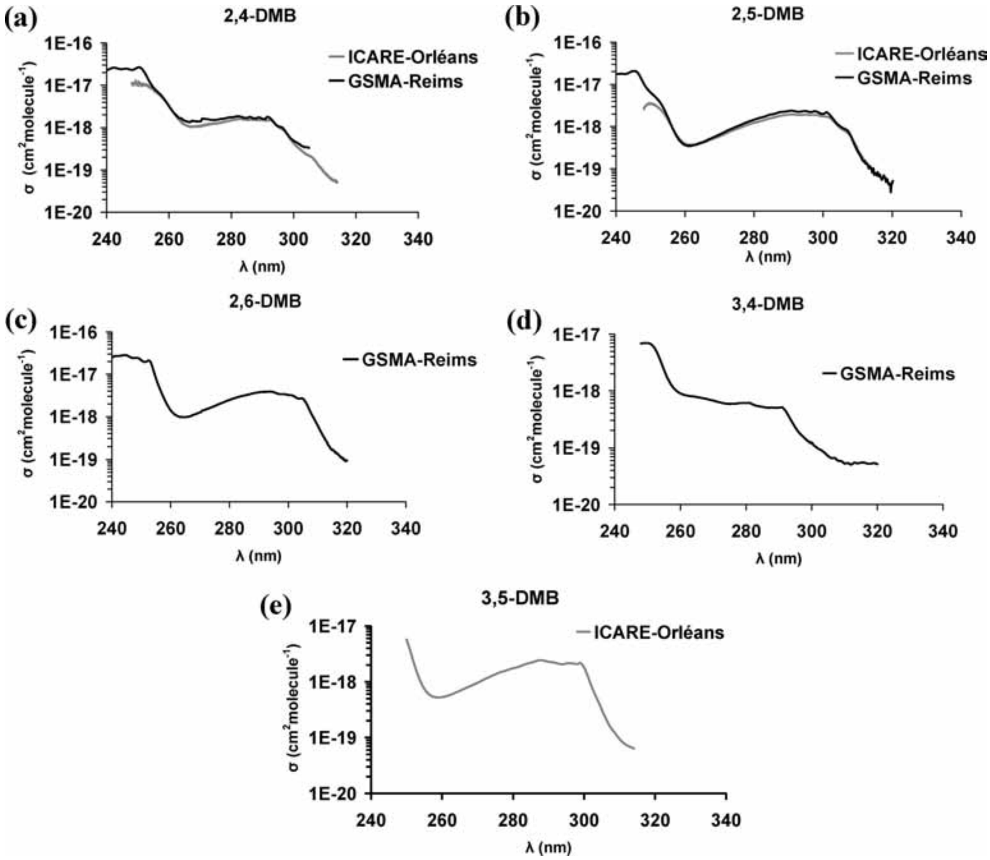

Figure 1. UV−vis spectra of 2,4-, 2,5-, 2,6-, 3,4- and 3,5- dimethylbenzaldehyde obtained using D_2 lamp−monochromator (GSMA) and D_2 lamp−diode array (ICARE) systems.

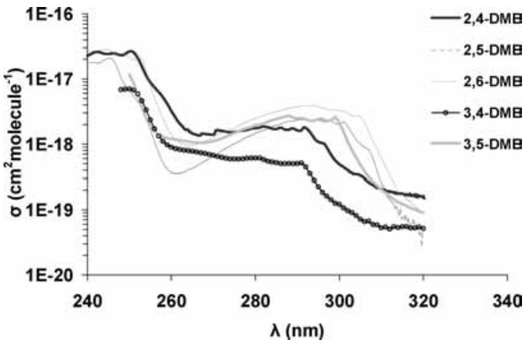

Figure 2. Comparison of the determined UV spectra for the five aldehydes 2,4-, 2,5-, 2,6-, 3,4- and 3,5- dimethylbenzaldehyde.

are limited to 305 nm because of the high uncertainties on the measured data above this limit.

The recorded spectra have been found relatively reproducible. Indeed, for wavelengths lower than 310 nm, the relative error on the obtained cross-section values is lower than 20% but can exceed 30% above 310 nm. Consequently, the spectra are obtained with a high uncertainty in this region.

B. Measurements Obtained by D_2 Lamp−Diode Array System at ICARE-Orléans. At the ICARE laboratory, absorption spectra of 2,4-DMB, 2,5-DMB and 3,5-DMB were measured between 240 and 320 nm under static and dynamic conditions. In the so-called dynamic method, the transmitted beam was measured when a fixed concentration of DMB was flowed through the cell. Numerous experiments were conducted for each compound, at different pressure and at high temperature. To minimize the loss of the studied aldehydes on the wall of the cell, experiments were performed in the temperature range 318 to 333 K. Because of the low vapor pressure of the studied compounds, the pressures during experiments did not exceed 0.2 Torr. Consequently, the obtained optical density below 314 nm varies from 0.03 to 2 and above 314 nm, low values are obtained ($0.01 < \mathrm{OD} \leq 0.03$). Therefore, we report here only the data obtained in the spectral region 240−314 nm (Table 2 and Figures 1 and 2).

The reported data constitute an average of 8−10 independent measurements. Reproducible results are obtained under varied conditions (dynamic conditions, static conditions, temperature and pressure). In the overlapping spectral regions the cross-sections were found to agree within approximately 20% of each other. Reproducible results were thus averaged to produce the reported cross-sections in Table 2. The spectra obtained at the ICARE are presented in Figure 1 where they are compared to those obtained at GSMA. A good agreement is noted for the results obtained by the two techniques.

To our knowledge there is no published study of the UV−vis absorption spectra of dimethylbenzaldehydes in the gas phase so that a comparison of our data is not possible.

C. Sources of Errors. The studied compounds have low vapor pressures and show a tendency to stick to the wall of the absorption cell, which distorts the pressure measurements and entails an error in the calculation of the concentration. To minimize this error, we increased the temperature of the cell (318−363 K) so that the uncertainty in the concentration measurements did not exceed 10%. Other sources of errors in the spectral measurements can result from the calibration wavelength, the temperature, the optical length and the absorbance. The uncertainty due to these parameters does not exceed 1%. To these errors, we shall add the random errors due to the reproducibility of the measurements. The standard deviation, calculated from the measurements was found not to exceed 20%

TABLE 2: Absorption Cross-Section σ (10^{-18} cm^2 molecule^{-1}) of 2,4-, 2,5-, 2,6-, 3,4- and 3,5- Dimethylbenzaldehyde Obtained Using D_2 Lamp−Monochromator (GSMA) and D_2 Lamp−Dode Array (ICARE) Systems in the Temperature Range 313−363 K

	2,4-DMB		2,5-DMB				
λ (nm)	GSMA	ICARE	GSMA	ICARE	2,6-DMB GSMA	3,4-DMB GSMA	3,5-DMB ICARE
240	23 ± 4		18 ± 3		26 ± 4		
241	25 ± 5		18 ± 3		27 ± 4		
242	26 ± 5		18 ± 4		27 ± 4		
243	26 ± 5		18 ± 3		28 ± 4		
244	24 ± 5		19 ± 2		28 ± 4		
245	24 ± 5		21 ± 2		28 ± 4		
246	25 ± 5		20 ± 3		26 ± 4		
247	24 ± 5		15 ± 2		24 ± 4		
248	23 ± 4	11 ± 1	11 ± 2	2.6 ± 0.3	25 ± 4	7 ± 1	
249	24 ± 5	11 ± 2	8 ± 1	3.3 ± 0.4	24 ± 4	7 ± 1	
250	27± 5	11 ± 12	6 ± 1	3.5 ± 0.5	22 ± 3	7 ± 1	6 ± 1
251	26 ± 5	11 ± 1	5 ± 1	3.3 ± 0.5	19.5 ± 3.5	7 ± 1	3.7 ± 0.6
252	21 ± 4	10 ± 2	4 ± 0.5	2.9 ± 0.4	20.5 ± 3.5	6 ± 1	2.3± 0.5
253	15 ± 3	10 ± 2	4 ± 0.5	2.5 ± 0.5	20.2 ± 2.5	5 ± 1	1.5 ± 0.3
254	11 ± 3	9 ± 1	2 ± 0.4	2.0 ± 0.4	13.3 ± 1.5	3.4 ± 0.5	1.0 ± 0.2
255	9 ± 2	8 ± 1	2 ± 0.2	1.5 ± 0.2	8.0 ± 0.8	2.4 ± 0.5	0.8 ± 0.4
256	7 ± 2	7 ± 1	1. ± 0.2	1.1 ± 0.2	5.1 ± 0.6	1.7 ± 0.3	0.6 ± 0.1
257	6 ± 1	6 ± 1	0.7 ± 0.1	0.8 ± 0.1	3.5 ± 0.4	1.3 ± 0.3	0.6 ± 0.1
258	5 ± 1	5 ± 1	0.5 ± 0.1	0.6 ± 0.1	2.5 ± 0.3	1.1 ± 0.2	0.5 ± 0.2
259	4.2 ± 0.8	4.1 ± 0.5	0.40 ± 0.08	0.5 ± 0.1	1.8 ± 0.2	1.0 ± 0.2	0.5 ± 0.1
260	3.2 ± 0.5	3.2 ± 0.5	0.40 ± 0.08	0.40 ± 0.05	1.4 ± 0.2	0.9 ± 0.2	0.5 ± 0.1
261	2.5 ± 0.5	2.5 ± 0.5	0.35 ± 0.05	0.35± 0.05	1.2 ± 0.2	0.9 ± 0.2	0.6 ± 0.1
262	2.1 ± 0.4	1.9 ± 0.4	0.36 ± 0.04	0.40 ± 0.05	1.1 ± 0.2	0.8 ± 0.2	0.6 ± 0.1
263	1.8 ± 0.3	1.6 ± 0.3	0.35 ± 0.05	0.35 ± 0.05	1.0 ± 0.2	0.8 ± 0.2	0.6 ± 0.1
264	1.6 ± 0.3	1.3 ± 0.3	0.40 ± 0.05	0.40 ± 0.05	1.0 ± 0.2	0.8 ± 0.2	0.7 ± 0.1
265	1.5 ± 0.3	1.2 ± 0.2	0.40 ± 0.05	0.4 ± 0.1	1.0 ± 0.1	0.8 ± 0.2	0.7 ± 0.1
266	1.4 ± 0.3	1.1 ± 0.2	0.45 ± 0.05	0.40 ± 0.05	1.0 ± 0.1	0.8 ± 0.2	0.7 ± 0.1
267	1.4 ± 0.2	1.1 ± 0.2	0.50 ± 0.04	0.50 ± 0.05	1.0 ± 0.1	0.7 ± 0.2	0.8 ± 0.1
268	1.4 ± 0.2	1.1 ± 0.2	0.55 ± 0.04	0.50 ± 0.05	1.1 ± 0.2	0.7 ± 0.2	0.8 ± 0.1
269	1.4 ± 0.2	1.1 ± 0.3	0.60 ± 0.06	0.6 ± 0.1	1.2 ± 0.2	0.7 ± 0.2	0.9 ± 0.1
270	1.4 ± 0.2	1.1 ± 0.2	0.65 ± 0.08	0.6 ± 0.1	1.3 ± 0.2	0.7 ± 0.2	1.0 ± 0.2
271	1.6 ± 0.3	1.1 ± 0.3	0.7 ± 0.1	0.6 ± 0.1	1.4 ± 0.2	0.7 ± 0.2	1.0 ± 0.2
272	1.6 ± 0.2	1.2 ± 0.2	0.8 ± 0.1	0.7 ± 0.1	1.5 ± 0.2	0.6 ± 0.1	1.1 ± 0.2
273	1.5 ± 0.2	1.2 ± 0.3	0.9 ± 0.1	0.8 ± 0.1	1.6 ± 0.2	0.6 ± 0.2	1.2 ± 0.3
274	1.5 ± 0.3	1.2 ± 0.2	0.9 ± 0.1	0.8 ± 0.1	1.7 ± 0.3	0.6 ± 0.1	1.3 ± 0.2
275	1.5 ± 0.3	1.3 ± 0.1	1.0 ± 0.1	0.9 ± 0.1	1.8 ± 0.3	0.6 ± 0.1	1.4 ± 0.2
276	1.6 ± 0.4	1.3 ± 0.2	1.1 ± 0.1	0.9 ± 0.1	1.9 ± 0.3	0.6 ± 0.1	1.5 ± 0.3
277	1.6 ± 0.3	1.3 ± 0.2	1.2 ± 0.1	1.0 ± 0.1	2.0 ± 0.4	0.6 ± 0.1	1.5 ± 0.2
278	1.7 ± 0.3	1.4 ± 0.2	1.3 ± 0.1	1.1 ± 0.1	2.2 ± 0.4	0.6 ± 0.1	1.6 ± 0.2
279	1.7 ± 0.3	1.4 ± 0.2	1.4 ± 0.1	1.2 ± 0.1	2.3 ± 0.4	0.6 ± 0.1	1.7 ± 0.2
280	1.7 ± 0.3	1.5 ± 0.2	1.4 ± 0.1	1.3 ± 0.2	2.5 ± 0.4	0.6 ± 0.1	1.7 ± 0.3
281	1.8 ± 0.3	1.5 ± 0.3	1.5 ± 0.1	1.3 ± 0.2	2.6 ± 0.5	0.6 ± 0.1	1.8 ± 0.2
282	1.8 ± 0.4	1.6 ± 0.2	1.6 ± 0.2	1.4 ± 0.2	2.8 ± 0.5	0.6 ± 0.1	1.9 ± 0.3
283	1.8 ± 0.3	1.6 ± 0.1	1.7 ± 0.1	1.4 ± 0.3	2.9 ± 0.5	0.5 ± 0.1	2.0 ± 0.4
284	1.7 ± 0.3	1.6 ± 0.2	1.8 ± 0.2	1.5 ± 0.3	3.0 ± 0.6	0.5 ± 0.1	2.1 ± 0.4
285	1.7 ± 0.2	1.5 ± 0.3	1.9 ± 0.1	1.6 ± 0.3	3.2 ± 0.6	0.5 ± 0.1	2.2 ± 0.4
286	1.8 ± 0.3	1.5 ± 0.2	2.0 ± 0.1	1.6 ± 0.2	3.3 ± 0.6	0.5 ± 0.1	2.3 ± 0.5
287	1.7 ± 0.2	1.5 ± 0.2	2.2 ± 0.1	1.8 ± 0.3	3.4 ± 0.7	0.5 ± 0.1	2.4 ± 0.4
288	1.7 ± 0.3	1.5 ± 0.2	2.2 ± 0.1	1.8 ± 0.2	3.5 ± 0.6	0.5 ± 0.1	2.5 ± 0.4
289	1.7 ± 0.3	1.5 ± 0.2	2.3 ± 0.2	1.9 ± 0.2	3.7 ± 0.7	0.5 ± 0.1	2.4 ± 0.4
290	1.6 ± 0.3	1.5 ± 0.2	2.4 ± 0.1	1.9 ± 0.3	3.7 ± 0.7	0.5 ± 0.1	2.3 ± 0.4
291	1.6 ± 0.3	1.5 ± 0.2	2.4 ± 0.1	2.0 ± 0.3	3.8 ± 0.7	0.5 ± 0.1	2.3 ± 0.5
292	1.8 ± 0.3	1.5 ± 0.2	2.3 ± 0.1	1.9 ± 0.4	3.8 ± 0.7	0.45 ± 0.08	2.2 ± 0.4
293	1.5 ± 0.3	1.4 ± 0.2	2.2 ± 0.1	1.9 ± 0.4	3.9 ± 0.7	0.35 ± 0.08	2.1 ± 0.4
294	1.2 ± 0.2	1.2 ± 0.2	2.3 ± 0.1	1.9 ± 0.4	3.9 ± 0.7	0.30 ± 0.06	2.1 ± 0.4
295	1.1 ± 0.2	1.1 ± 0.3	2.3 ± 0.1	1.9 ± 0.3	3.8 ± 0.7	0.20 ± 0.04	2.1 ± 0.4
296	1.0 ± 0.3	0.9 ± 0.2	2.2 ± 0.1	1.9 ± 0.4	3.6 ± 0.7	0.20 ± 0.04	2.2 ± 0.4
297	0.9 ± 0.2	0.8 ± 0.1	2.2 ± 0.4	1.9 ± 0.4	3.4 ± 0.6	0.20 ± 0.03	2.1 ± 0.4
298	0.7 ± 0.1	0.7 ± 0.1	2.3 ± 0.5	1.9 ± 0.3	3.4 ± 0.6	0.15 ± 0.03	2.1 ± 0.4
299	0.6 ± 0.2	0.5 ± 0.1	2.1 ± 0.4	1.8 ± 0.4	3.4 ± 0.6	0.15 ± 0.02	2.2 ± 0.4
300	0.5 ± 0.1	0.45 ± 0.05	2.0 ± 0.4	1.7 ± 0.3	3.2 ± 0.6	0.10 ± 0.02	1.8 ± 0.4
301	0.4 ± 0.1	0.40 ± 0.07	2.2 ± 0.3	1.7 ± 0.3	3.2 ± 0.6	0.10 ± 0.01	1.3 ± 0.3
302	0.4 ± 0.1	0.30 ± 0.05	1.9 ± 0.3	1.6 ± 0.3	3.0 ± 0.6	0.10 ± 0.02	0.9 ± 0.2
303	0.4 ± 0.1	0.25 ± 0.05	1.5 ± 0.3	1.3 ± 0.2	2.7 ± 0.5	0.09 ± 0.02	0.6 ± 0.2
304	0.35 ± 0.1	0.25 ± 0.08	1.2 ± 0.2	1.1 ± 0.2	2.7 ± 0.5	0.08 ± 0.02	0.4 ± 0.1
305		0.20 ± 0.05	1.0 ± 0.1	0.9 ± 0.1	2.6 ± 0.5	0.07 ± 0.02	0.3 ± 0.1
306		0.19 ± 0.05	0.9 ± 0.2	0.8 ± 0.2	2.1 ± 0.4	0.07 ± 0.02	0.25 ± 0.05
307		0.16 ± 0.05	0.8 ± 0.1	0.7 ± 0.1	1.5 ± 0.3	0.07 ± 0.02	0.20 ± 0.03

TABLE 2: Continued

	2,4-DMB		2,5-DMB				
λ (nm)	GSMA	ICARE	GSMA	ICARE	2,6-DMB GSMA	3,4-DMB GSMA	3,5-DMB ICARE
308		0.13 ± 0.03	0.6 ± 0.2	0.6 ± 0.1	1.1 ± 0.2	0.06 ± 0.01	0.15 ± 0.02
309		0.10 ± 0.02	0.40 ± 0.15	0.4 ± 0.1	0.8 ± 0.2	0.06 ± 0.01	0.10 ± 0.03
310		0.09 ± 0.04	0.3 ± 0.1	0.30 ± 0.15	0.6 ± 0.1	0.05 ± 0.01	0.09 ± 0.03
311		0.07 ± 0.05	0.2 ± 0.1	0.2 ± 0.1	0.5 ± 0.1	0.05 ± 0.015	0.08 ± 0.03
312		0.06 ± 0.03	0.15 ± 0.08	0.16 ± 0.08	0.3 ± 0.5	0.05 ± 0.01	0.07 ± 0.02
313		0.06 ± 0.02	0.12 ± 0.06	0.13 ± 0.06	0.3 ± 0.06	0.06 ± 0.01	0.07 ± 0.03
314		0.05 ± 0.02	0.10 ± 0.04	0.10 ± 0.04	0.20 ± 0.06	0.05 ± 0.013	0.06 ± 0.03
315			0.08 ± 0.03		0.17 ± 0.03	0.06 ± 0.01	
316			0.07 ± 0.01		0.15 ± 0.02	0.06 ± 0.01	
317			0.06 ± 0.01		0.13 ± 0.02	0.05 ± 0.01	
318			0.06 ± 0.02		0.11 ± 0.02	0.05 ± 0.01	
319			0.04 ± 0.01		0.10 ± 0.01	0.05 ± 0.02	
320			0.05 ± 0.01		0.09 ± 0.02	0.05 ± 0.02	

in the spectral region 240−310 nm. However, above 310 nm, high inaccuracies in the cross-section values were observed which were attributed to the low vapor pressure of the studied DMBs and their low absorbance compared to the short wavelengths range. The standard deviation in this region can reach up to 30%.

D. General Characteristics of the Obtained Spectra. As can be seen in Figures 1 and 2, the obtained spectra consist of a broad continuum with fine structures between 260 and 310 nm similarly to other aromatic aldehydes.[11] They show band maxima around 290 nm resulting from a dipole forbidden n−π* electronic transition of the C═O group. The absorption of these compounds between 240−320 nm is of the same order of magnitude.

We also notice that the spectra of 2,4-DMB and 3,4-DMB are very similar and do not present a mnimum between 260 and 270 nm unlike the three other compounds. The spectra present a maximum of absorption around 292 nm for 2,4-DMB ($\sigma_{\max} = 1.77 \times 10^{-18}$ cm^2 molecule^{-1}), around 291 nm for 2,5-DMB ($\sigma_{\max} = 2.37 \times 10^{-18}$ cm^2 molecule^{-1}), around 294 nm for 2,6-DMB ($\sigma_{\max} = 3.89 \times 10^{-18}$ cm^2 molecule^{-1}), around 281 nm for 3,4-DMB ($\sigma_{\max} = 6.12 \times 10^{-19}$ cm^2 molecule^{-1}) and around 288 nm for 3,5-DMB ($\sigma_{\max} = 2.51 \times 10^{-18}$ cm^2 molecule^{-1}).

This absorption band is a characteristic of aromatic compounds. The spectra of all the studied DMBs are similar in terms of widths of bands and values of cross-sections and those of 2,4-DMB and 3,4-DMB are shifted to shorter wavelengths. Absorption measurements were also made at several temperatures in the range 318−363 K. At each temperature, at least eight spectra were recorded over a range of pressures and the data averaged to produce the absorption cross-section at that temperature. No temperature dependence was observed within the range 318−363 K of this work. For wavelengths around 290 nm, corresponding to the solar radiation reaching the troposphere, the cross-sections are relatively high (typically $\sigma \sim 5 \times 10^{-19}$ to 4×10^{-18} cm^2 molecule^{-1}). Thus, if the quantum yields are high enough, the photolysis can be an important process of degradation of these compounds within the troposphere.

E. Intercomparison of the ICARE and GSMA Data. The comparison between the spectra obtained at GSMA and the ICARE shows a good spectral agreement for both compounds where no shift in wavelength was observed (Figure 1). Also, the discrepancies between the spectra obtained in both laboratories were found to not exceed 25% and 30% for 2,5-DMB and 2,4-DMB, respectively. The most likely reason for these discrepancies is the difficulties in measuring the concentrations with a good accuracy because the studied DMBs have relatively low vapor pressure. They might also be due to light scattering in the monochromator and the cells.

Moreover, for both compounds, when a difference arises between the measurements conducted in the two laboratories, the cross-sections obtained at the ICARE are lower than those obtained at GSMA. Nevertheless, it should be noted that the fine structures are more visible in the spectra measured at GSMA because of the better resolution of the used monochromator.

The absorption spectra of aromatic aldehydes (benzaldehyde, isomers of tolualdehyde and isomers of dimethylbenzaldehyde) are of the same order of magnitude. Similarly to benzaldehyde and tolualdeyde, the spectra of DMBs show fine structures between 260 and 310 nm.

IV. Atmospheric Implications

One of the objectives of this work is to estimate the photolysis rates of these species in the atmosphere to be able to assess the importance of the photolysis as a degradation process even in absence of the direct photolysis studies under atmospheric conditions. The absorption cross-section values obtained in this study can be used to calculate the photodissociation rate constants (J_p) for the aromatic aldehydes by using the following relationship:

$$\sigma(\lambda) = -\ln[I(\lambda)/I_0(\lambda)]/LC$$

where $\sigma(\lambda)$ is the absorption cross-section at wavelength λ (cm^2 molecule^{-1}), $\phi(\lambda)$ is the primary quantum yield for photodissociation at wavelength λ, and $I(\lambda)$ is the actinic flux of solar radiation at wavelength λ (photons cm^{-2} s^{-1}).

The calculations were made under the following conditions: at 10 a.m. of July first, cloudless, at sea level and at latitude of 40° N. The data of the actinic flux at the Earth's surface and zenith angle $\theta = 30°$ for July first are taken from the literature.[14] Because no data on the primary photolysis quantum yields are available, the calculations of J_p were made assuming $\phi(\lambda) = 1$ at all wavelengths. In these conditions, J_p represents the upper limit of the photodissociation rate constant and the deduced lifetimes represent lower limits of the studied compounds. The calculated values of J_p and lifetimes are listed in Table 3. However, it has to be highlighted that the deduced lifetimes of the studied compounds are less than 2 h whatever the photolysis rate value used in the determination of this parameter.

Regarding the atmospheric implication, the high cross-sections found above 290 nm (typically 5×10^{-19} to 4×10^{-18} cm^2 molecule^{-1}) and the relatively short lifetimes obtained show that photolysis could be an important loss process for these

TABLE 3: Photodissociation Rate Constants J_p (Upper Limits) and the Estimated Tropospheric Lifetimes of 2,4-, 2,5-, 2,6-, 3,4- and 3,5-Dimethylbenzaldehyde in the Gas Phase with Respect to Photolysis and Their Reactions with OH Radicals and Cl Atoms

compound	J (s^{-1}) this work	$\tau_{(DMB)photolyze}$ (h) this work	$\tau_{(DMB)OH}$ (h)	$\tau_{(DMB)Cl}$ (h)
2.4 -dimethylbenzaldehyde	1.38×10^{-4}	>2	3.2 h[a] 5.0[b]	32[d]
2,5- dimethylbenzaldehyde	1.46×10^{-4}	>1.9	3.2[a] 5.0[b]	29[d]
2,6- dimethylbenzaldehyde	3.33×10^{-4}	>0.8	4.5[b]	
3,4- dimethylbenzaldehyde	0.40×10^{-4}	>6.9	6.5[a] 5.6[b]	
3,5- dimethylbenzaldehyde	1.60×10^{-4}	>1.7	4.0[c] 4.9[b]	29[d]

[a] Value obtained by using the rate constant measured by Tse et al.[7] [b] Value obtained by using the rate constant measured by Clifford et al.[8] [c] Value obtained by using the rate constant measured by Volkamer et al.[9] [d] Value obtained by using the rate constant measured by El Dib et al. [15]

aldehydes and can be competitive with other atmospheric degradation processes of these compounds. In the atmosphere, DMBs are expected to be removed by photolysis and by reaction with atmospheric radicals such as OH (in day-time), NO_3 (in night-time), Cl (in the marine environment and coastal areas) and O_3. No data are available on the reactions of ozone and NO_3 with DMBs. On the other hand, kinetic determinations of the reaction of DMBs with Cl atoms have been recently published by our group.[15]

In Table 3, are summarized the lifetimes of the studied aldehydes against photolysis and their reactions with OH radical and Cl atoms.[7−9,15] In the calculations, we used an average concentration on 12 h of day of OH equal to 2×10^6 molecules cm^{-316} and a Cl concentration equal to 1×10^5 molecule cm^{-3} corresponding to one morning in marine areas.[17] These calculations suggest that, assuming a photolysis quantum yield of unity ($\phi(\lambda) = 1$), photolysis could be an important loss process of the studied compounds in the troposphere and it could be more important than the reaction with OH radicals and Cl atoms as shown in Table 3. However, these lifetimes have to be considered as lower limits because the photolysis quantum yield could be much lower than unity. Still, once DMBs are emitted into the atmosphere, they can be quickly degraded by the different processes contributing thus to photochemical pollution mainly on local and regional areas.

This work has shown that DMBs are quite difficult to handle; therefore, additional work is required to better measure their cross-sections above 320 nm. Further, their photolysis rates remain to be better defined to accurately assess their tropospheric lifetimes with respect to photolysis. In this respect, there is a need to determine the photolysis quantum yields of these compounds and to measure their photolysis rates under simulated atmospheric conditions.

V. Conclusion

The UV absorption cross-sections of five isomers of dimethylbenzaldehyde have been determined and reported over the wavelength and temperature ranges 240−320 nm and 313−363 K, respectively. This work provides the first spectroscopic determinations of DMBs in the UV−visible domain. Generally, all obtained spectra are similar in shape to those of other aromatic aldehydes with a maximum around 290 nm. Very short photolysis lifetimes of the order of a few hours were calculated for all the studied aldehydes assuming $\phi(\lambda) = 1$. Consequently, photolysis could be an important loss process of these species in the troposphere and comparable to the reaction with OH radicals and Cl atoms in the gas phase.

Acknowledgment. This work was supported by the “Region Champagne Ardenne” and the CNRS through the PNCA (Programme National de Chimie Atmosphérique) for which we are grateful.

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JP803874E