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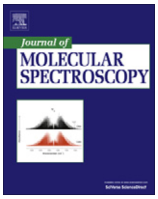

Absolute absorption cross sections for two selected lines of formaldehyde around 6625 cm^{-1}

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ABSTRACT

Absolute absorption cross sections of formaldehyde, CH_2O, have been measured at total pressures of 14.5 and 66 mbar Helium by cw-CRDS for two selected lines at around 6625 cm^{-1}. Absolute CH_2O concentrations have been determined *in situ* by measuring the pseudo-first order decays of OH radicals using high repetition rate laser induced fluorescence (LIF). OH radicals have been generated by laser photolysis of H_2O_2 in the presence of CH_2O and from the well-known rate constant of the reaction of CH_2O with OH radicals, the absolute CH_2O concentration has been determined. Concentrations between 1.5 and 4×10^{14} cm^{-3} have been used. The line strengths for the lines at 6624.779 cm^{-1} and 6625.248 cm^{-1} have been found to be $(9.1 \pm 1.8) \times 10^{-24}$ cm and $(5.3 \pm 1.0) \times 10^{-24}$ cm, respectively. The broadening coefficients in Helium have also been determined for both lines. Converting the line strengths to absorption cross sections it is found that these values are a factor of 2 smaller than the only known determination of these absorption cross sections in the literature (Staak et al., J. Molec. Spectroscopy 229 (2005) 115–121).

1. Introduction

Formaldehyde, CH_2O, is an intermediate in the oxidation of most hydrocarbons and is an important trace gas in the atmosphere. CH_2O plays a key role in atmospheric chemistry by the fact that a major fate is photolysis [1–3], leading to the formation of HO_2 radicals, thus maintaining the oxidizing capacity of the atmosphere. This key role of CH_2O in the chemistry of the atmosphere has triggered large efforts to reliably quantify this species. Two wavelength regions are commonly used for quantification of CH_2O under atmospheric conditions by either ground or airborne instruments: absorption in the UV region between 260 and 350 nm [4–8] and absorption in the infrared region [9–12] either in the 3.5 μm or in the 5–6 μm region. Absorption cross sections in these wavelength regions are rather high and allow obtaining good sensitivity. An excellent overview on data sets of absorption cross sections available in these wavelength ranges can be found at Gratien et al. [13], who have conducted an intercomparison of the absorption cross sections in the two wavelength regions. In many laboratory studies, CH_2O is quantified by either UV-absorption [2,14–16] or using TDLAS in the infrared region [17–20].

Cavity enhanced spectroscopic techniques became increasingly popular in the recent decades. The strong gain in sensitivity by these methods brings another wavelength region into the focus of interest: the near infrared, where transitions due to combination bands or overtone absorption can be found for many species. The absorption cross sections in this wavelength range are rather small, but the high sensitivity of cavity enhanced techniques can compensate for this drawback. As for absorption features of CH_2O in this wavelength range, Barry et al. [21–23] have measured absolute absorption cross sections of selected lines in the $2\nu_5$ transition using two methods, cavity ring down spectroscopy, CRDS, and cavity enhanced absorption spectroscopy (CEAS). They have reported a good agreement between the absorption cross sections obtained by the two different methods. In a more recent work, Staak et al. [24] measured the absorption spectrum of CH_2O in the range 6547–6804 cm^{-1}, where transitions of several combination bands can be found [25]. They employed CEAS for their measurements and have obtained absolute absorption cross sections by calibrating the mirror reflectivity by determining the line strengths of selected absorption lines of CO_2 and H_2O, obtained from the HITRAN data base [26].

Even though the near infrared region is not a wavelength region specifically useful for the quantification of CH_2O in the atmosphere due to the rather small absorption cross sections in this wavelength range, it is nevertheless a wavelength region that finds more and more applications in laboratory studies: availability of cheap and reliable optical components is one of the reasons. CH_2O has been quantified using cw-CRDS at around 6600 cm^{-1} in two recent publications [27,28] and both studies were in rather large disagreement with the absorption cross sections reported by Staak et al. [24]. CH_2O has been identified by Djehiche et al. [27] as a product in the photolysis of CH_3ONO. They have determined the

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absorption cross section of one absorption line under their experimental conditions (24 mbar air) using a commercial, calibrated standard cylinder of CH_2O (Air Liquide): the cylinder was labeled at 100 ppm, however an analysis using the well-known DNPH/HPLC method revealed a concentration of only 40 ± 4 ppm. Extrapolation of the obtained absorption cross section to the conditions used by Staak et al. [24] (2 mbar CH_2O), assuming a Voigt profile and applying the broadening coefficients for N_2 and CH_2O such as obtained by Staak et al. [24], leads to a line strength a factor of 2 smaller. However, broadening coefficients for the different bath gases are not known with high precision, so the comparison is somewhat arguable. In a more recent study, Bahrini et al. [28] have quantified CH_2O as reaction product of CH_4 oxidation in a jet-stirred reactor using cw-CRDS measurements at total pressures of 9–13 mbar He. Since pressure broadening coefficients for He were not known, it was estimated, that the self broadening under the Staak et al. conditions would be of comparable magnitude with the Helium broadening, hence absorption cross sections such as reported by Staak et al. have directly been used. The obtained CH_2O concentration profiles were in poor agreement with model predictions: the measured concentrations were two times lower than the model predicted.

The quantification of CH_2O using cw-CDRS in the 6600 cm^{-1} region has been employed increasingly [29]. Therefore we have undertaken a new study on the measurement of absolute absorption cross sections of two selected lines in this wavelength region. A major problem in measuring absolute absorption cross sections for CH_2O is the fact that CH_2O is difficult to handle and tends to polymerize and to adsorb on surfaces. Hence it is difficult to reliably know the absolute concentration of CH_2O in the absorption cell. We have avoided this problem by determining the CH_2O concentration *in situ* within the absorption cell by measuring time resovled OH-decays, a direct measure for the CH_2O concentration.

2. Experiments

There are four main components to the experimental set-up: the photolysis cell, the photolysis laser, the cw-CRDS system and the LIF system. Detailed description of this set-up has already been published [30,31] and an improvement recently made to the acquisition system has been described by Votava et al. [32]. The photolysis cell has three axes and is made of stainless steel, internally coated with Teflon. Photolysis can be achieved along the longest axis with an excimer laser (Lambda Physik LPX 202i) operating at 248 nm. The beam entering the cell through a quartz window has a size of approximately 1.5 × 3.0 cm, with an energy density of around 50 mJ cm^{-2}.

The LIF system has been used in the frame of this work for determining OH decays in order to accurately quantify the absolute CH_2O concentration in the photolysis cell. The LIF system and its acquisition procedure has been described in detail in by Parker et al. [31] and will not be repeated here. The only change compared to the system described by Parker et al. is, that we now use a simple photomultiplier (Hamatsu R928) connected to a boxcar integrator (EG&G 4121B) instead of the photon counting devise.

cw-CRDS (continuous wave-Cavity Ring Down Spectroscopy) can be synchronized to laser photolysis in order to obtain time resolved profiles of species like HO_2 [33] or HONO [34], but was used in this work independent of the laser photolysis, i.e. in a simple non-time resolved manner, for the measurement of the CH_2O absorption spectrum. The principle of this technique has been published previously [30], and recent improvements concerning the synchronization [31] and acquisition [32] can be found in more recent work. The mirrors used in this work (Los Gatos) had a reflectivity of $R = 0.999954$, leading to ring-down times in the empty cavity of around 60 µs. Under our conditions ($[CH_2O]_{max} \approx 5 \times 10^{14}$ cm^{-3}, 70 cm absorption path) a maximal decrease in ring-down time down to around 40 µs was obtained.

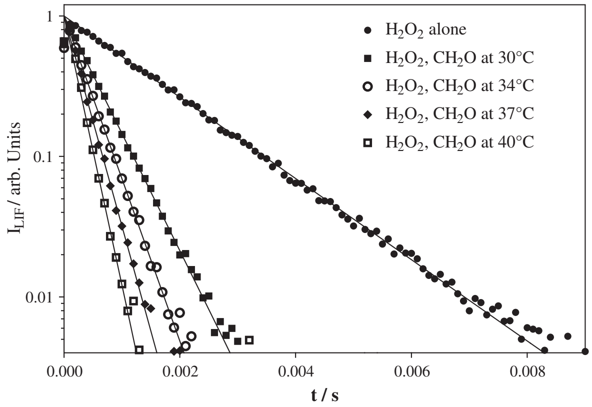

Fig. 1. OH decays in the presence of different CH_2O concentrations.

CH_2O was produced in a continuous manner by gently depolymerizing para-formaldehyde, kept in a trap in a water bath at temperatures between 30 and 40 °C: the gaseous CH_2O was transported directly to the photolysis cell by flushing a small flow of He (100 ccm min^{-1} STP) through the trap. In order to minimize the re-polymerization of the CH_2O monomer, the flow containing the CH_2O was mixed with the main He-flow (400 ccm min^{-1} STP) directly at the exit of the trap. No deposition of re-polymerized CH_2O was visible within the short Teflon tubes, connecting the trap and the photolysis reactor (≈50 cm). The amount of CH_2O reaching the photolysis cell was strongly dependent on the temperature of the water bath, and concentrations between 1.5 and 5×10^{14} cm^{-3} have been obtained by varying the bath-temperature between 30 and 40 °C. In order to be able to generate OH radicals, necessary for determining the CH_2O concentration within the photolysis cell (see next paragraph), a small portion of the main He-flow had been saturated with H_2O_2 vapor prior to the mixing with the CH_2O flow by bubbling through a trap containing a 50% H_2O_2/H_2O solution. In order to check the stability of the CH_2O concentration within the photolysis reactor before starting the experiment, the concentration was directly monitored through its absorption: the wavelength of the cw-CRDS diode was fixed to a wavelength corresponding to the center of an absorption line. This way, variations of the CH_2O concentration within the photolysis reactor can easily be detected through a change in the ring-down time. Once the concentration was stable, i.e. the ring-down time did not change anymore for several minutes, the photolysis laser was started in order to generate OH radicals by 248 nm pulsed laser photolysis of the H_2O_2 and the decay of the OH radicals was measured by high repetition rate LIF (Fig. 1): from this measurement, the absolute CH_2O concentration can be deduced (see next paragraph). Once the OH decay was obtained with a good signal-to-noise ratio (the LIF signals have been averaged over 50–100 photolysis pulses at a repetition rate of 0.5 Hz), the photolysis laser was stopped and the absorption spectrum of both lines was measured continuously with a resolution of around 0.001 cm^{-1} (red[1] line in Fig. 2). Typically 25 ring-down events have been averaged before the cw-CRDS diode laser was tuned to the next wavenumber. Once the absorption spectrum was measured, the photolysis laser was turned on again and the OH decay has been re-measured in order to verify that the CH_2O concentration had not changed during the measurement of the absorption spectrum. Following

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[1] For interpretation of color in Fig. 2, the reader is referred to the web version of this article.