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Hydrogen isotope fractionation in the photolysis of formaldehyde

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Abstract. Experiments investigating the isotopic fractionation in the formation of H_2 by the photolysis of CH_2O under tropospheric conditions are reported and discussed. The deuterium (D) depletion in the H_2 produced is 500(±20)‰ with respect to the parent CH_2O. We also observed that complete photolysis of CH_2O under atmospheric conditions produces H_2 that has virtually the same isotope ratio as that of the parent CH_2O. These findings imply that there must be a very strong concomitant isotopic enrichment in the radical channel ($CH_2O+h\nu \rightarrow CHO+H$) as compared to the molecular channel ($CH_2O+h\nu \rightarrow H_2+CO$) of the photolysis of CH_2O in order to balance the relatively small isotopic fractionation in the competing reaction of CH_2O with OH. Using a 1-box photochemistry model we calculated the isotopic fractionation factor for the radical channel to be 0.22(±0.08), which is equivalent to a 780(±80)‰ enrichment in D of the remaining CH_2O. When CH_2O is in photochemical steady state, the isotope ratio of the H_2 produced is determined not only by the isotopic fractionation occurring during the photolytical production of H_2 (α_m) but also by overall fractionation for the removal processes of CH_2O (α_f), and is represented by the ratio of α_m/α_f. Applying the isotopic fractionation factors relevant to CH_2O photolysis obtained in the present study to the troposphere, the ratio of α_m/α_f varies from ~0.8 to ~1.2 depending on the fraction of CH_2O that reacts with OH and that produces H_2. This range of α_m/α_f can render the H_2 produced from the photochemical oxidation of CH_4 to be enriched in D (with respect to the original CH_4) by the factor of 1.2–1.3 as anticipated in the literature.

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1 Introduction

Formaldehyde (CH_2O) is a key carbonyl compound in the atmosphere. Its abundance varies over a wide range from sub-ppb levels to ~100 ppb depending largely on local sources (Warneck, 1999). Its turnover is large in the atmosphere and it is a source of molecular hydrogen (H_2), carbon monoxide (CO), and of the hydroperoxyl radical (HO_2), yet limited measurements are available in various atmospheric regions. Recent satellite observations of CH_2O make it possible to investigate its distribution on regional and global scales (e.g., Martin et al., 2004; Wittrock et al., 2006). While direct emissions from fossil fuel combustion, biomass burning, and also automotive exhaust contribute significantly to the burden of atmospheric CH_2O (Carlier et al., 1986; Garcia et al., 2005), in situ production of CH_2O by photochemical oxidation of volatile organic compounds appears to be the dominant source on a global scale (Carlier et al., 1986; Warneck, 1999). In remote oceanic areas (Wagner et al., 2002; Weller et al., 2000), in the free troposphere (Frost et al., 2002), and in the stratosphere, only the photochemical oxidation of CH_4 serves as the major source. Apart from the importance of the rather simple CH_2O molecule in the Earth's atmosphere and far beyond, it is also subject to fundamental research regarding for instance the exact processes during its photolysis (e.g., Moore and Weisshaar, 1983; Townsend et al., 2004; Troe, 2007).

CH_2O is broken down by photolysis (R1 and R2) and by photochemical oxidation (R3) in the troposphere (Calvert, 1980):

$$CH_2O + h\nu \rightarrow CHO + H \tag{R1}$$

$$CH_2O + h\nu \rightarrow CO + H_2 \tag{R2}$$

$$CH_2O + OH \rightarrow CHO + H_2O \tag{R3}$$

Reaction (R1) produces the HO_2 radical by the rapid reaction of hydrogen (H) and formyl (CHO) radicals with atmospheric oxygen (O_2), which can lead to the formation of the hydroxyl radical (OH) via the reaction with NO or O_3 in the atmosphere. This is an important propagation of the radical chain. Only reaction (R2) yields H_2. All photochemical reactions of CH_2O do produce CO, while solely reaction (R2) forms H_2, which is the topic of our research. In fact, this photochemically produced H_2 constitutes ∼50 to ∼60% of the total source of tropospheric H_2 (Novelli et al., 1999; Rhee et al., 2006b).

In the stratosphere, H_2 originates both from this in situ photolysis process (R2), albeit under photochemically very different conditions, and from tropospheric import. Recently it has been established that stratospheric H_2 is enriched in deuterium (D) along with the decrease of CH_4 mixing ratios whilst the H_2 mixing ratios remain almost constant (Rahn et al., 2003; Rhee et al., 2006a; Röckmann et al., 2003). It appears that the D enrichment of H_2 is much stronger than the concomitant enrichment for CH_4 acompanying its destruction by OH, $O(^1D)$, and Cl radicals. This means that the D enrichment of H_2 occurs not only by the fractionation in the reaction of H_2 with oxidizing radicals (OH, Cl, $O(^1D)$) but is also due to the chain reactions leading from CH_4 to H_2 (Rhee et al., 2006a). Gerst and Quay (2001) discussed potential reactions that may lead to the D enrichment along the photochemical chain reactions of CH_4. However, the detailed mechanism by which the D content of H_2 is accumulated has not yet been elucidated due to the lack of measurements for isotopic fractionation factors at each reaction step and branching, all of which are fundamentally difficult to determine.

To address this question, as a first step we have investigated the isotopic fractionation occurring during the photolysis of CH_2O by which H_2 is produced for the conditions at Earth's surface. In spite of its crucial role in the isotope budget of H_2, as well as CO, in the atmosphere, the isotopic fractionation occurring during photolysis of CH_2O has been rarely investigated in the past (Crounse et al., 2003; Feilberg et al., 2005; Feilberg et al., 2007b). Since CH_2O is a relatively "long-lived" intermediate in the photochemical chain reactions between CH_4 and H_2, the results will provide essential insight into understanding the accumulation of D in H_2 produced.

2 Experiments

Formaldehyde (CH_2O) was prepared by purifying paraformaldehyde (Merck) in a vacuum system following the method of Spence and Wild (1935). Solid paraformaldehyde was heated at ∼420 K under vacuum. For purification the evaporating CH_2O and impurities were forced through a set of glass U-tubes which were partly immersed in an ethanol sludge (∼160 K) made with liquid nitrogen. Purified formaldehyde was then collected in a U-tube dipped in liquid nitrogen (77 K). A given amount of pure CH_2O (∼3 mbar) was released to a 3-L glass bulb and several 0.1-L glass flasks simultaneously, all of which were connected to the same manifold. The pure CH_2O in the 0.1-L glass flasks were used to determine the D/H ratio of the CH_2O (see below). Afterwards pressure inside the manifold was read by a capacitance manometer (MKS10, Baratron). CH_2O-free synthetic air was then introduced into the 3-L glass bulb to reach about ambient pressure and the final pressure was read by another capacitance manometer (MKS1000, Baratron) to determine the CH_2O mixing ratio. Since these pressure readings are essential for determining the CH_2O mixing ratio in the reactors used for the photolysis experiments, the capacitance manometers were calibrated accurately by an absolute manometer (Digiquartz 740, Paroscientific) whenever necessary. The CH_2O-air mixture was used as a stock for a series of CH_2O photolysis experiments. The CH_2O mixing ratios in the stock air were usually around 0.3%.

Aliquots of the CH_2O stock air were transferred to quartz or glass flasks, diluted to the target mixing ratio with CH_2O-free synthetic air, and photolyzed for a few hours to ∼17 days (Table 1). The CH_2O mixing ratios in the reactors were less than ∼2 ppm except in the experiments running for few hours, for which ∼50 ppm of CH_2O was used. After photolysis we measured the H_2 mixing ratio and D/H ratio. The δD values and mixing ratios of the H_2 produced were determined by a recently developed technique involving continuous-flow isotope ratio mass spectrometry (Rhee et al., 2004).

In order to test stability of CH_2O in the reactor, we had once monitored the pressure inside the 3-L glass bulb for 2 days after injecting pure CH_2O at ∼3 mbar. No change in pressure inside was found, indicating no absorption or loss of CH_2O by polymerization or heterogeneous reactions. The same results even at higher pressure of pure CH_2O air have been reported (e.g.,Horowitz and Calvert, 1978).

All glass used was Duran glass (Schott), thoroughly evacuated and heated prior to use. Glass bulbs were kept in the dark by wrapping them with aluminum foil or with black cloth to avoid any photochemical reactions prior to commencing CH_2O photolysis experiments. CH_2O photolysis experiments in sunlight were carried out on the roof of a 3-story building of the Max Planck Institute for Chemistry, Mainz (50° N, 8.16° E), in August and September of 2003 and in March, May and June of 2004 (Table 1). We also conducted CH_2O photolysis experiments using a xenon (Xe) short arc lamp (XBO 75W/2). A characteristic intensity spectrum of the light sources and the transmission of the reactor materials are shown in Fig. 1 together with photolytic properties of CH_2O.

The D/H ratio of the original CH_2O in the stock air was determined by analyzing the isotopic composition of the pure CH_2O in the 0.1-L glass flasks, which originated from the same source of CH_2O as that in the stock air (see above). The pure CH_2O sample was photolyzed using a mercury

Table 1. Summary of CH_2O photolysis experiments.

Photolysis			**$[CH_2O]_0$ (ppm)	Light source	Reactor material	$\Psi(H_2)$	δD-H_2 (‰)
Start	End	*Duration (h)					
4-Sep-03	10-Sep-03	91	2.3	Daylight	Glass	0.47	−247
4-Sep-03	10-Sep-03	91	2.5	Daylight	Glass	0.52	−190
4-Sep-03	10-Sep-03	91	2.6	Daylight	Glass	0.49	−252
14-Sep-03	17-Sep-03	51	0.43	Daylight	Glass	0.52	−214
14-Sep-03	17-Sep-03	51	0.46	Daylight	Glass	0.66	−46
14-Sep-03	17-Sep-03	51	0.48	Daylight	Glass	0.56	−205
29-Mar-04	29-Mar-04	1	53	Daylight	Quartz	0.09	−449
29-Mar-04	29-Mar-04	2	50	Daylight	Quartz	0.18	−459
29-Mar-04	29-Mar-04	3	34	Daylight	Quartz	0.21	−415
29-Mar-04	29-Mar-04	7	63	Daylight	Quartz	0.31	−366
29-Mar-04	29-Mar-04	7	36	Daylight	Quartz	0.26	−413
17-May-04	25-May-04	130	2.1	Daylight	Quartz	0.67	3
17-May-04	31-May-04	230	2.0	Daylight	Quartz	0.68	−4
14-Jun-04	18-Jun-04	67	1.4	Daylight	Quartz	0.50	−205
14-Jun-04	18-Jun-04	67	1.8	Daylight	Quartz	0.61	−38
14-Jun-04	18-Jun-04	67	1.8	Daylight	Quartz	0.61	−77
14-Jun-04	18-Jun-04	67	1.1	Daylight	Quartz	0.39	−256
14-Jun-04	30-Jun-04	277	2.1	Daylight	Quartz	0.71	15
14-Jun-04	30-Jun-04	277	1.9	Daylight	Quartz	0.66	−65
30-May-04	4-Jun-04	80	1.6	Daylight	Glass	0.56	−137
30-May-04	4-Jun-04	80	1.6	Daylight	Glass	0.60	−113
5-Jun-04	11-Jun-04	94	1.6	Daylight	Glass	0.54	−132
5-Jun-04	11-Jun-04	94	1.5	Daylight	Glass	0.59	−78
		92	1.5	Xe arc lamp	Quartz	0.44	−12
		244	1.4	Xe arc lamp	Quartz	0.43	5
		10	3 mbar	Hg arc Lamp	Quartz	0.98	7
		10	3 mbar	Hg arc Lamp	Quartz	0.97	−8
		13	3 mbar	Hg arc Lamp	Quartz	1.00	1
		13	3.3 mbar	Hg arc Lamp	Quartz	0.95	0
		12	3.3 mbar	Hg arc Lamp	Quartz	0.99	0

* This is simply a sum of daylight hours calculated using astronomical parameters from the internet (http://aa.usno.navy.mil/data/docs/RS_OneDay.html).
** Initial mixing ratios of CH_2O in a reactor prior to photolysis. For the photolysis of pure CH_2O, unit of pressure is used.

(Hg) short arc lamp (HBO 103W/2, OSRAM). The photolysis of pure CH_2O produces not only CO and H_2 but also H and CHO radicals which further undergo self reactions and reaction with CH_2O, ending up with the production of CO and H_2 (e.g., Calvert, 1980). Thus, the final products of the photolysis are only CO and H_2. Isotopic mass balance requires that for complete conversion the product H_2 has the same isotopic composition as the parent CH_2O. Complete conversion of the CH_2O to CO and H_2 was confirmed by measuring the amount of H_2 produced and its isotopic composition. The deuterium content is as usual expressed as $\delta D=(R_{SPL}/R_{STD}-1)\times 1000$ (‰), where R_{SPL} and R_{STD} represent the D/H of H_2 for sample and a reference material, respectively. For convenience, we express the δD values relative to the isotopic composition of the parent CH_2O.

3 Results

3.1 The yield of H_2 in the photolysis of CH_2O

As mentioned earlier, photolysis of CH_2O has one channel that produces CHO and H radicals (R1) and the other that produces CO and H_2 molecules (R2). The CHO radical reacts rapidly with O_2 in the air, also forming CO. Thus, the amount of CO produced should always be the same as that of CH_2O photolyzed, while the amount of H_2 produced represents the fraction of CH_2O that follows the molecular channel (R2). Thereby, the yield of the molecular channel in the photolysis of CH_2O, given as $\Phi(H_2)$, can be defined by the ratio of H_2 to CO.

However, a portion of the CH_2O in the reactor may react with the radicals, H, OH, and HO_2, as they are produced in the reactor during the photolysis. These reactions produce CO and formic acid (HCOOH). The reaction of

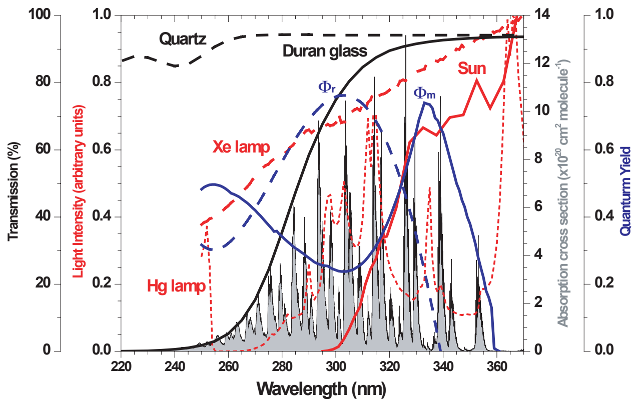

Fig. 1. Absorption cross section (gray shade) (Meller and Moortgat, 2000) and quantum yields (blue lines) (Sander et al., 2006) of CH_2O, light transmission of the reactors, and intensity of the lights used in the experiments. Φ_r and Φ_m indicate the quantum yields of the radical and molecular channels, respectively, in CH_2O photolysis. Light transmissions of quartz (black dashed line) and Duran glass (Schott) (black solid line) are from a company measurement. Spectra of Xe (red dashed line) and Hg (red dotted line) short arc lamps were provided by OSRAM, and normalized actinic flux (red solid line) at the Earth's surface is from Finlayson-Pitts and Pitts (1999).

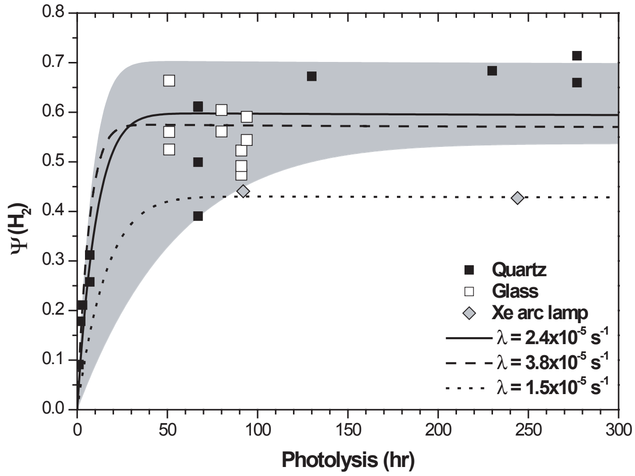

Fig. 2. Evolution of the fraction of H_2 ($\Psi(H_2)$) produced by photolysis of CH_2O in daylight or using a Xe short arc lamp. The gray-shaded area and lines represent model calculations for a given CH_2O photolysis rate and yield of H_2, $\Phi(H_2)$. Solid and dashed lines are the bounds of the most probable evolution of $\Psi(H_2)$ in Mainz using the results from the Tropospheric Ultraviolet and Visible (TUV) radiation model as described in Fig. 3. For photolysis with the Xe lamp, the photolysis rate of $1.5\times10^{-5}\,s^{-1}$ and $\Phi(H_2)$=0.49 are arbitrarily forced to fit the measurements.

CH_2O with HO_2 produces the hydroxymethylperoxy radical ($HOCH_2OO$). This radical is so unstable that it immediately dissociates back to CH_2O. However, a fraction reacts with HO_2 or itself producing HCOOH (Burrows et al., 1989; Su et al., 1979; Veyret et al., 1989) (see Sect. 3.2 for details). In addition, CO and any HCOOH produced can react further with OH to form their oxidized products. These reactions may result in a deficit in the mass balance of CO if only photolysis of CH_2O is considered. Because of such a non-conservation of CO in the reactor, we did not attempt to measure the ratio of the mixing ratios of H_2 to CO for each photolysis run to obtain the value of $\Phi(H_2)$. But, we tracked the actual fraction of H_2 produced by photolysis of CH_2O, given as $\Psi(H_2)$, which represents the ratio of the H_2 mixing ratio in the reactor to the initial CH_2O mixing ratio.

Figure 2 shows the evolution of $\Psi(H_2)$ throughout the periods of photolysis for experiments conducted with different reactor materials or light sources. The period of photolysis is given as number of daylight hours disregarding any parameters that might influence the actual photolysis rates of CH_2O. For the short periods experiments (<12 h), $\Psi(H_2)$ increases rapidly with the increase of photolysis time. At long periods of photolysis (>130 h), $\Psi(H_2)$ converges toward an asymptotic value. By virtue of negligible production of H_2 ($<10^{-8}$ per CH_2O according to the model described below) through reactions other than the CH_2O photolysis and of little reactivity of H_2 in the reactor for the periods of the CH_2O photolysis, $\Psi(H_2)$ approaches an asymptotic value as a function of time. This asymptotic value of $\Psi(H_2)$ is equivalent to $\Phi(H_2)$ when CH_2O is destroyed only by photolysis.

For the photolysis periods from 50 to 100 h, the measurements are scattered. We suspect that this is due mostly to photolytical effects rather than analytical errors. In particular, changes in radiation occurring over the course of the experiments on the roof (e.g., cloudiness, albedo, solar zenith angle (SZA), light scattering due to aerosol content, etc.) may result in such different values. In addition, since the quantum yield of the molecular channel peaks at longer wavelengths compared to the radical channel (Moortgat et al., 1983), $\Psi(H_2)$ increases with the increase of SZA. As an indirect support for this speculation, photolysis of CH_2O performed in the laboratory using Hg and Xe short arc lamps shows that the uncertainty of replicate runs is merely about 2% for the yield of H_2. Provided that the scatter is due to variabilities of the parameters that influence photolysis rate of CH_2O, we did not average the values of $\Psi(H_2)$ for the same period of photolysis, but the individual values were used to determine the isotopic fractionation factors for the CH_2O photolysis.

The CH_2O photolysis experiments conducted with a Xe short arc lamp give an opportunity to qualitatively examine a relation between $\Phi(H_2)$ and the range of wavelengths by which CH_2O is photolyzed. As a Xe short arc lamp emits photons within a broad range of wavelengths, the effective wavelength for the photolysis of CH_2O depends on the cutoff wavelength for transmission through quartz which extends down to ∼200 nm (see Fig. 1). This is shorter than the lower limit of solar wavelengths at the Earth's surface.

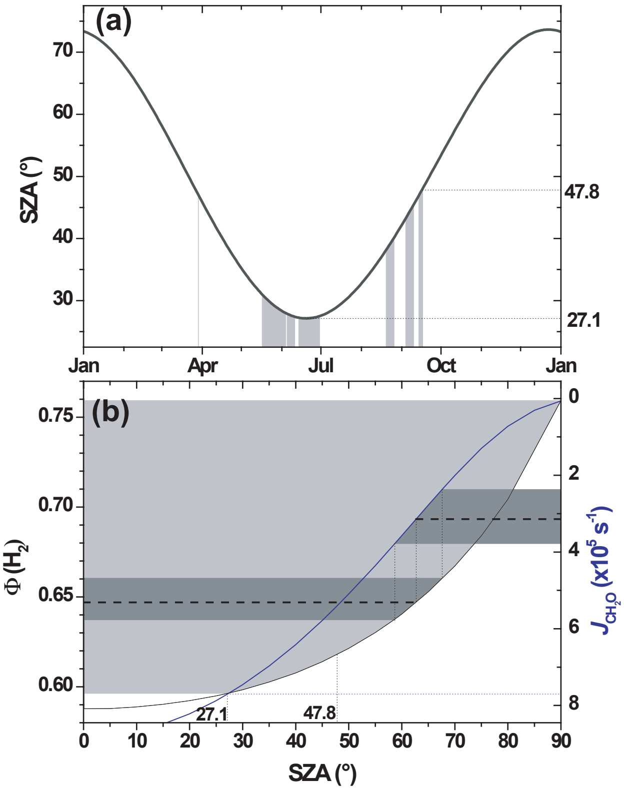

Fig. 3. (a) Solar zenith angle (SZA) at local noon in Mainz (11:00 GMT) in 2004. Gray shaded areas indicate the dates when experiments were conducted. SZA at local noon ranges from 27.1° to 47.8° for the periods of experiment. **(b)** Photolytic yield of H_2 ($\Phi(H_2)$) and photolysis rate of CH_2O (J_{CH_2O}) at a given solar zenith angle calculated with the TUV radiation model. The gray-shaded area indicates a range of $\Phi(H_2)$ for the situation of Mainz, and the blue line represents the photolysis rates at a given SZA. The dark gray area represents daily mean values of $\Phi(H_2)$ and their corresponding values of J_{CH_2O} obtained by weighting the photolysis rates over the range of SZA for the experimental periods. The dashed line indicates the arithmetic mean of minimum and maximum values of these mean values of J_{CH_2O} and its mapping onto values for $\Phi(H_2)$. These two values of J_{CH_2O} and $\Phi(H_2)$ were then used in the 1-box photochemistry model.

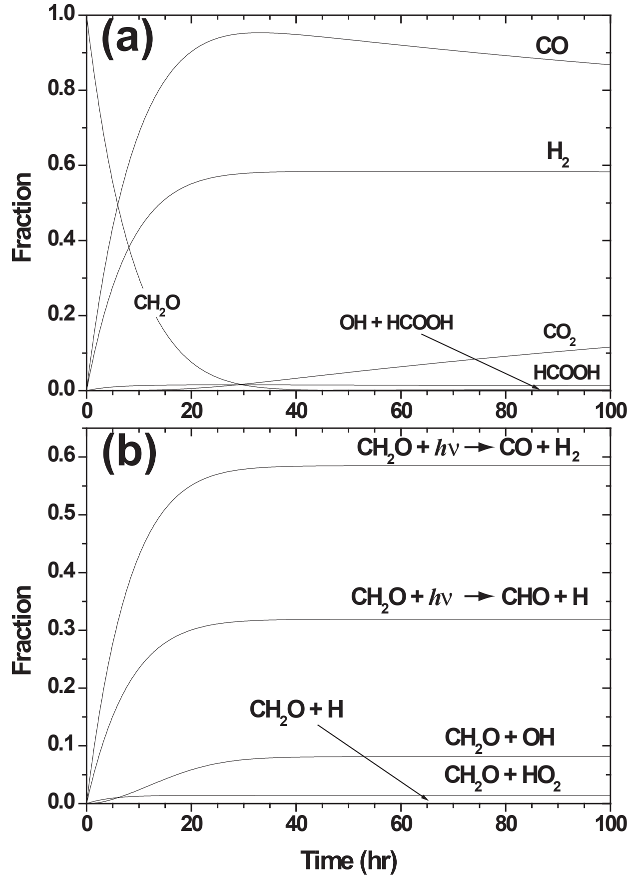

Fig. 4. A 1-box model simulation of CH_2O photochemistry in the reactor. Details of the reactions are given in Appendix A. **(a)** Time evolution of the relative abundances of CH_2O and its photochemical products. "OH+HCOOH" represents the sum of the amounts of any compounds produced by the reaction of formic acid and OH radical. **(b)** Time evolution of the fraction of CH_2O that is photolyzed or reacts with radicals.

Consequently, $\Phi(H_2)$ from the Xe short arc lamp experiments should be smaller than that obtained with sunlight because of the dominance of the radical channel in CH_2O photolysis at these short wavelengths (Moortgat et al., 1983). As shown in Fig. 2, $\Psi(H_2)$ is almost the same for the two different irradiation periods, indicating that it has reached an asymptote. This asymptotic value is smaller than that obtained in sunlight, which, as expected, reflects a smaller value of $\Phi(H_2)$ using the Xe short arc lamp.

3.2 A box model simulation of CH_2O photolysis

To examine the actual photochemistry in the reactor, we constructed a 1-box model composed of 33 photochemical reactions, including photolysis of CH_2O and H_2O_2 as well as formation of HCOOH (see Appendix A). The model was run under conditions of standard ambient temperature (25°C) and pressure (10^5 Pa) with the other boundary conditions from the results from the Tropospheric Ultraviolet and Visible (TUV) radiation model (http://cprm.acd.ucar.edu/Models/TUV). As shown in Fig. 3, the TUV radiation model predicts that the values of $\Phi(H_2)$ range from 0.6 to 0.76 in Mainz. Since SZA at local noon during the experiments were between 27° and 48°, daily averaged photolysis-rate-weighted mean values of $\Phi(H_2)$ would be 0.64 to 0.66, which correspond to total CH_2O photolysis rates for both channels (J_{CH_2O}) of 2.4×10^{-5} to $3.8\times10^{-5}\,s^{-1}$. For the same range of SZA, the ratio of the photolysis rates of H_2O_2

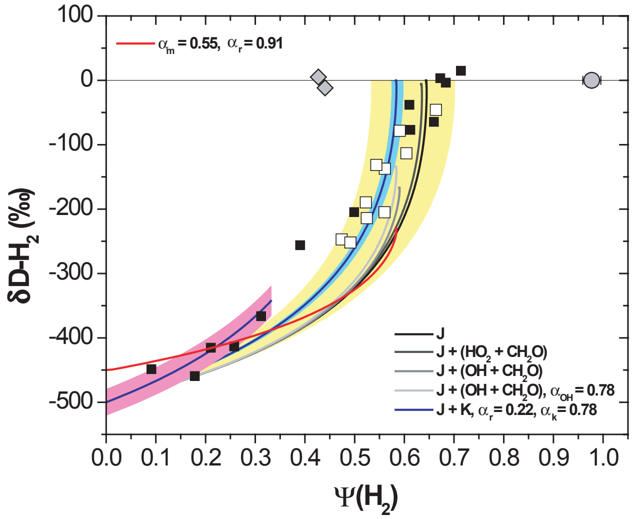

Fig. 5. Evolution of δD-H_2 as a function of the fraction of H_2 produced by photolysis of CH_2O. Symbol keys are the same as in Fig. 2 except the gray circle designating the mean value for photolysis of pure CH_2O using a Hg short arc lamp. Several model sensitivity runs are shown with solid lines. Yellow shading indicates potential isotopic fractionation evolutions for various ranges of $\Phi(H_2)$ for the location of Mainz, and cyan shading represents the isotopic fractionation evolutions using the daily-mean value of $\Phi(H_2)$ during the experiments according to the TUV radiation model described in Fig. 3. For the short duration experiments, we assumed that the initial mixing ratio of CH_2O in the 1-box model was 50 ppm, represented by magenta shading. When calculating the evolution of δD-H_2 using the 1-box model, we constrain the model such that the values of α_m and α_K (see text) are always 0.50 and 0.78, respectively, and that the complete photolysis of CH_2O yields H_2 with a δD value that is the same as that of the initial CH_2O. For comparison, the evolutions of δD-H_2 using the isotopic fractionation factors determined by Feilberg et al. (2007b) is shown as red solid line on the premise that the values of other parameters are the same as those in the present study (see Appendix A).

and CH_2O, $J_{H_2O_2}/J_{CH_2O}$, varies only from 0.089 to 0.090. The initial mixing ratio of CH_2O was assumed to be 1 ppm in synthetic air (78% of N_2 and 22% of O_2). The commercial software package FACSIMILE (MCPA Software, UK) was used to integrate time derivatives of the chemical species in the reactions.

As shown in Fig. 4, while photochemical destruction of CH_2O forms CO and HCOOH, both of which are further oxidized by reacting with the OH radical, H_2 in the reactor is almost entirely produced by CH_2O photolysis to the molecular channel (R2) and is little oxidized by the OH radical within the time periods of the experiments (<0.1% of H_2 has reacted at 99% of CH_2O being oxidized). Hence, a substantial portion of the initial CH_2O is converted to products other than CO, but the H_2 produced is accumulated in the reactor reaching an asymptotic value at full conversion.

The time evolutions of $\Psi(H_2)$ were predicted by applying the values of $\Phi(H_2)$, J_{CH_2O}, and $J_{H_2O_2}$ from the TUV radiation model described above to the 1-box model (Fig. 2). The results appear comparable to the measurements for photolysis periods of <12 h. However, there are substantial differences between the measurements and the model predictions at longer photolysis periods. In particular, the asymptotic value of the measurements differs from the model predictions when the most likely values of parameters under photochemical conditions in Mainz, Germany, are applied (solid and dashed lines in Fig. 2). As shown in Fig. 4b, ~10% of CH_2O is destroyed by the reactions with radicals. This leads to the lower asymptotes of $\Psi(H_2)$ than the value of $\Phi(H_2)$ obtained from the TUV radiation model because this asymptotic value of $\Psi(H_2)$ is smaller than $\Phi(H_2)$ by a factor corresponding to the fraction of CH_2O photolyzed. In order to reproduce the asymptote of $\Psi(H_2)$ from the measurements in the model, a value of $\Phi(H_2)\approx0.74$ is necessary, the value that the TUV radiation model predicts when SZA is near 85° in the location of Mainz. This SZA is larger than the weighted-mean value of 63° predicted by the model. This discrepancy could be associated with feeding the parameters relevant to photochemical reactions in the model without accounting for their variation along the change in radiation as mentioned above.

3.3 Isotope effect of the CH_2O photolysis to the molecular channel

Figure 5 shows the variation of the δD value of H_2 (δD-H_2) as a function of $\Psi(H_2)$. As the isotope ratios are normalized with respect to the δD value of the initial CH_2O, a δD-H_2 value of zero means that the isotope ratio of the H_2 in sample air is the same as that for the initial CH_2O. The air samples whose values of $\Psi(H_2)$ approach the asymptotic values at long photolysis times for both the sunlight and Xe short arc lamp experiments show near-zero values of δD-H_2. This indicates that complete photochemical decomposition of CH_2O yields H_2 that has the same isotope ratios as the initial CH_2O. This observation and the evolution of δD-H_2 as a function of $\Psi(H_2)$ give us crucial information to aid in determining the hydrogen isotopic fractionation processes occurring in (R1) and (R2) as follows.

According to the results from the 1-box model described in Sect. 3.2, most of the CH_2O in the reactor is broken down by photolysis (>90%) with the remainder being destroyed mostly by reaction with OH (<8%) while HO_2 and H radicals play only a minor role (<2%) (see Fig. 4b). The rate of change of the CH_2O mixing ratio in the reactor can thus be described as:

$$\frac{d\,[CH_2O]}{dt} = -\,(J + K)\,[CH_2O] \tag{1}$$

where J is the sum of photolysis rates of (R1) (i.e., j_r) and (R2) (i.e., j_m) and K is the sum of the products of the relevant photochemical reaction rate coefficients (k_i) and radical concentrations (X_i) as follows.

$$J = j_m + j_r \tag{2}$$

$$K = \sum_i k_i \, [X_i] \tag{3}$$

In the same way, for the next abundant isotopologue, CHDO, one obtains:

$$\frac{d\,[\mathrm{CHDO}]}{dt} = -\left(J' + K'\right)[\mathrm{CHDO}] \tag{4}$$

where J' and K' indicate the sums of the photolysis rates and the photochemical reaction rates for CHDO, respectively.

In terms of non-equilibrium kinetics, the isotopic fractionation factor is represented as the kinetic isotope effect (or simply isotope effect), which is expressed by the ratio of reaction rates for the different isotopologues, one of which has a rare isotope substituted for the common one (Melander and Saunders, 1980). We define here the isotopic fractionation factor as the ratio of photochemical reaction rates or photolysis rates of an isotopologue which has a single deuterium to that for the most abundant isotopologue. For instance, the isotopic fractionation factor for the molecular channel, α_m is:

$$\alpha_m = \frac{j'_m}{j_m} \tag{5}$$

Hence, J' and K' in Eq. (4) have the following relationship with the corresponding rates for CH_2O by means of isotopic fractionation factor, α_i.

$$\begin{aligned} J' &= j'_r + j'_m \\ &= \alpha_r \, j_r + \alpha_m \, j_m \end{aligned} \tag{6}$$

$$\begin{aligned} K' &= \sum_i k'_i \, [X_i] \\ &= \sum_i \alpha_{k_i} k_i \, [X_i] \\ &= \alpha_K K \end{aligned} \tag{7}$$

By definition, the isotopic fractionation factor for CH_2O, α_f, is

$$\begin{aligned} \alpha_f &= \frac{J' + K'}{J + K} \\ &= \alpha_r \times \frac{j_r}{J} \times \frac{J}{J+K} + \alpha_m \times \frac{j_m}{J} \times \frac{J}{J+K} + \alpha_K \times \frac{K}{J+K} \end{aligned} \tag{8a}$$

In Eq. (8a), the ratio of j_m to J represents the yield of H_2 from photolysis of CH_2O ($\Phi(H_2)$), and the ratio $J/(J+K)$ is the fraction of CH_2O that is photolyzed. Designating the latter as Γ, α_f can be rewritten as

$$\alpha_f = \alpha_r \, (1 - \Phi) \, \Gamma + \alpha_m \Phi \Gamma + \alpha_K \, (1 - \Gamma) \tag{8b}$$

Or simply,

$$\alpha_f = \alpha_{h\nu} \Gamma + \alpha_K \, (1 - \Gamma) \tag{8c}$$

where $\alpha_{h\nu}$ represents the isotopic fractionation factor for photolysis of CH_2O. Since the amount of radicals produced along the experiments is not constant, Γ is not a constant but varies as a function of time. In addition, strictly speaking, $\Phi(H_2)$ varied during the sunlight experiments as did SZA (Fig. 3b). Accordingly α_f is changing along with the CH_2O photolysis and photochemical reactions. Nevertheless, assuming that α_f is constant gives a convenient way to determine the isotopic fractionation factor for the production of H_2, α_m.

Integrating Eqs. (1) and (4) and then dividing [CHDO] by [CH_2O] leads to the well-known Rayleigh equation (Rayleigh, 1902):

$$\frac{R_Q}{R_o} = f^{\alpha_f - 1} \tag{9}$$

where R_o is the isotope ratio of the initial CH_2O,R_Q is that for the remaining CH_2O along the course of experiment, and f the fraction of the remaining CH_2O. Thus, the isotope ratio of the products (R_p) as a function of CH_2O photochemical destruction can be obtained by mass balance:

$$\frac{R_p}{R_o} = \frac{1 - f^{\alpha_f}}{1 - f} \tag{10}$$

Actually R_p is the sum of the isotope ratios of the products formed by CH_2O photolysis and its photochemical reactions with radicals. The isotope ratio of the H_2, R_m, which is produced from CH_2O photolysis to the molecular channel, can be derived from the following derivatives:

$$\frac{d\,[\mathrm{H_2}]}{dt} = j_m \, [\mathrm{CH_2O}] \tag{11}$$

and

$$\frac{d\,[\mathrm{HD}]}{dt} = j'_m \, [\mathrm{CHDO}] \tag{12}$$

Solving Eqs. (11) and (12) with inserting the solutions of Eqs. (1) and (4), respectively, and the definition of α_m in Eq. (5), R_m has the following relation with R_o:

$$\frac{R_m}{R_o} = \frac{\alpha_m}{\alpha_f} \times \frac{1 - f^{\alpha_f}}{1 - f} \tag{13}$$

By dividing (13) by (10), the ratio of the isotope ratios of H_2 (R_m) and all products from CH_2O photochemistry (R_p) is the same as the ratios of their isotopic fractionation factors:

$$\frac{R_m}{R_p} = \frac{\alpha_m}{\alpha_f} \tag{14}$$

Similar experessions can be derived for the radical channel of CH_2O photolysis (15) and for the photochemical reactions (16):

$$\frac{R_r}{R_p} = \frac{\alpha_r}{\alpha_f} \tag{15}$$

Table 2. Sensitivity test of the α_r at a given range of the parameters.

	Prescribed value (Z_i)	Uncertainty of parameter (ΔZ_i)	Sensitivity ($\Delta\alpha_r/\Delta Z_i$)	Uncertainty of α_r ($\Delta\alpha_r$)
$[CH_2O]_0$ (ppm)	1	±1	0.0027*	±0.003
J_{CH_2O} (s^{-1})	3.143×10^{-5}	$+4.53\times10^{-5}$ -3.14×10^{-5}	0.0026*	±0.004
$\Phi(H_2)$	0.647	±0.039	-0.476	∓0.019
$J_{H_2O_2}/J_{CH_2O}$	0.0896	±0.0036	-2.48	∓0.009
α_H for CH_2O+H	0.781	±0.25	~0	~0
α_{OH} for CH_2O+OH	0.781	±0.0061	-0.45	∓0.003
α_{HO_2} for CH_2O+HO_2	0.781	±0.25	-0.036	∓0.009
δD-H_2 of final product (‰)	0	±40	-0.0019	∓0.076
Sum**				0.079

* Sensitivity is calculated by the ratio of a parameter to the prescribed value.
** Quadratic sum of errors.

$$\frac{R_K}{R_p} = \frac{\alpha_K}{\alpha_f} \tag{16}$$

From the relations of Eqs. (14), (15), and (16), it is immediately recognized that R_p is the weighted sum of the isotope ratios of the products from two channels of CH_2O photolysis and its photochemical reactions, similar to the isotopic fractionation factor of CH_2O in Eq. (8b).

$$R_p = R_r\,(1-\Phi)\,\Gamma + R_m\Phi\Gamma + R_K\,(1-\Gamma) \tag{17}$$

Since we measured the evolution of R_m with $\Psi(H_2)$, α_m can be determined from Eq. (13). As f approaches 1 (thus, $\Psi(H_2)$ goes to zero), R_m/R_o in Eq. (13) becomes the value of α_m, which is in turn represented by the value of δD-H_2 as follows:

$$\delta\text{D-H}_2 = (\alpha_m - 1) \times 1000 \text{ (‰)} \tag{18}$$

Accordingly, the intercept in Fig. 5 ($\Psi(H_2)$=0) represents the value of α_m (=0.50($\pm$0.02)) and indicates that H_2 produced by photolysis of CH_2O is 500($\pm$20)‰ depleted with respect to the initial CH_2O. Since the experiments for the photolysis of CH_2O for short periods were conducted with high CH_2O mixing ratios of 50 ppm, a similar amount of initial CH_2O, was applied in the 1-box model to determine the value of α_m. Its uncertainty, 0.02, was determined such that all measurements for the short periods experiments are predicted by the 1-box model within the range of errors (see Fig. 5). The assumption that α_f is constant should be valid during the initial stage of photolysis of CH_2O because the amounts of radicals, in particular the OH radical, produced are too small to affect α_f (see Fig. 4b). Even if α_f were not constant, it would not interfere with the determination of α_m because the α_f's in Eq. (13) cancel for f approaching 1.

3.4 Isotope effect of CH_2O photolysis to the radical channel

Provided that complete photolysis of CH_2O yields H_2 that has the same isotope ratio as that of the initial CH_2O (Fig. 5), we can also determine the isotopic fractionation factor, α_r, which governs the isotopic fractionation occurring in (R1). However, in this case the Rayleigh model cannot be applied because the value of α_f varies with time due to changes in the amounts of radicals (see below). We ran a photochemical 1-box model instead, which consists of the 33 reactions mentioned in Sect. 3.2 as well as critical reactions of CHDO and HD to determine α_r as follows:

$$\text{CHDO} + h\nu \rightarrow \text{products} \tag{R1a}$$

$$\text{CHDO} + h\nu \rightarrow \text{CO} + \text{HD} \tag{R2a}$$

$$\text{CHDO} + \text{OH} \rightarrow \text{products} \tag{R3a}$$

$$\text{CHDO} + \text{H} \rightarrow \text{products} \tag{R4a}$$

$$\text{CHDO} + \text{HO}_2 \rightarrow \text{HOCHDOO} \tag{R5a}$$

$$\text{HD} + \text{OH} \rightarrow \text{products} \tag{R6a}$$

$$\text{HOCHDOO} \rightarrow \text{CHDO} + \text{HO}_2 \tag{R27a}$$

$$\text{HOCHDOO} + \text{HO}_2 \rightarrow \text{products} \tag{R28a}$$

In Fig. 5 several model runs under different conditions are plotted. As an ideal case, we assume that CH_2O is destroyed exclusively by photolysis. Since in this scenario α_f is constant as the reaction proceeds, the Rayleigh model can be applied to determine α_r. In Eq. (13), as f approaches 0, the ratio of R_m to R_o becomes the ratio of α_m to α_f, which is represented by the value of δD-H_2 at the end of photolysis. As the values of δD-H_2 converge at zero, α_f=α_m and thus α_m=α_r

Table 3. Comparison of the isotope effects determined from CH_2O photolysis experiments.

Source	Minor isotopologue	α_m	α_r	*α_{OH}	$\Phi(H_2)$	**Γ	$\alpha_{h\nu}$	α_f	α_m/α_f
This study	[CHDO]	0.50(±0.02)	0.22 (±0.08)	0.781(±0.006)	0.65 (±0.04)	0.69 (±0.28)	0.40 (±0.03)	0.51 (±0.11)	0.97 (±0.21)
Feilberg et al. (2007b)	[CHDO]	0.55(±0.02)	0.91(±0.05)	0.781(±0.006)	***0.77(±0.06)	0.69 (±0.28)	0.63(±0.01)	0.68 (±0.04)	0.81 (±0.06)
Crounse et al. (2003)	[CHDO]	0.8							
Feilberg et al. (2007a)	[CD_2O]						0.333(±0.056)		

* Kinetic isotope effect for CH_2O + OH from Feilberg et al. (2004).
** The value is calculated for the Mainz conditions for the periods of experiments.
*** The value was calculated by the relation $\alpha_{h\nu}=\alpha_m \times \Phi(H_2)+\alpha_r \times (1-\Phi(H_2))$.

according to the relation in Eq. (8b) since Γ=1. This scenario is, however, unlikely considering the substantial production of radicals via the radical channel (R1), which may in turn react with CH_2O in the reactor as described above. Introduction of the reactions of H and/or HO_2 with both CH_2O and CHDO with and without kinetic isotope effect do not significantly change the evolution of δD-H_2 compared to the ideal scenario that only accounts for CH_2O photolysis. However, it is apparent that the reaction of OH and CH_2O is critical for determination of α_r, as the δD-H_2 value for the final product of H_2 reaches only ~-170‰. Taking the kinetic isotope effect for the reaction of CH_2O with OH radicals into account increases the δD-H_2 value for the final product a little to ~-130‰. Applying the kinetic isotope effect for the reaction of HD with OH does not improve the model to simulate the measurements because of too slow reaction rate of H_2+OH. However, decreasing the value of α_r from 0.50 to 0.22 (thus larger isotope effect) makes it possible to reach the δD-H_2 value of the final H_2 to zero and significantly improves the predicted evolution of δD-H_2 compared to the measurements. Therefore, provided that the TUV radiation model and the reaction rates applied in the 1-box model are correct, our best estimate of α_r is 0.22 and the total isotopic fractionation factor of CH_2O due to photolysis ($\alpha_{h\nu}$) results in 0.40 for $\Phi(H_2)$=0.647, the yield of H_2 which is the best estimate from the TUV radiation model for the average conditions of Mainz at the times of the experiments (see Fig. 3).

As the value of α_r in the present study is not determined directly by measurement, but is based on model calculations, we conducted sensitivity runs to estimate the uncertainty of α_r by varying the values of the various parameters used in the 1-box model. These parameters are the mixing ratio of CH_2O in the reactor, $\Phi(H_2)$, photolysis rates of CH_2O and H_2O_2, kinetic isotope effects for the reaction of CHDO with the radicals, and the uncertainty of δD-H_2 for the final product (Table 2). Among them α_r is the most sensitive to the ratio of the photolysis rate of H_2O_2 to that for CH_2O because large production of OH by photolysis of H_2O_2 leads to the increase of the fraction of CH_2O that reacts with OH in the reactor, which in turn lowers the value of α_r to compensate for it (see Eq. 8b). The same effect can be caused by the variation of α_{OH} for CH_2O+OH and by $\Phi(H_2)$. Sensitivity runs for the potential error in the δD-H_2 value of the final product shows the largest impact to α_r among the parameters because of its large potential error of 40‰, which includes the uncertainty of the δD value of the original CH_2O (=4‰). Overall most of the uncertainty for α_r originates from the uncertainties in $\Phi(H_2)$ and the δD-H_2 of the final products. The quadratic sum of the errors incurred by these parameters amounts to 0.08.

4 Discussions

4.1 Comparison with previous research

To our knowledge three experiments have been done in sunlight to determine the isotopic fractionation factor for formaldehyde photolysis (Table 3): One experiment investigated the isotopic fractionation of CH_2O itself by measuring time evolution of the amount of isotopologues, CH_2O and CD_2O using an optical method (Feilberg et al., 2007a; Feilberg et al., 2005), another experiment examined the same isotopic fractionation but for CH_2O and CHDO using the same technique and the D/H ratio of H_2 produced by mass spectrometry (Feilberg et al., 2007b), and the other measured the D/H ratio of H_2 produced from the photolysis of CH_2O which is reported in a conference proceeding abstract (Crounse et al., 2003). In the latter study a similar procedure as in the present study was apparently applied. However, the lack of details of the experiment, in particular the fraction of H_2 ($\Psi(H_2)$) and the δD value of the original CH_2O used for the photolysis experiments, both of which are critical to determine α_m, makes it difficult to infer α_m from this single value of δD. The authors reported that the photolysis of CH_2O produces isotopically light H_2, the δD value of which is ~-200‰. If the authors meant the value to be the degree of enrichment of the H_2 produced, α_m is ~0.8, which is far larger (so less isotopically fractionated) than what we obtained in this study.

In the case of Feilberg et al. (2005)'s experiments, the ratio of photolysis rate of the two isotopologues, J_{CD_2O}/J_{CH_2O}, was determined as 0.333(±0.056) (Feilberg et al., 2007a) using an optical technique. This value is smaller than the value for J_{CHDO}/J_{CH_2O} (=$\alpha_{h\nu}$) of 0.40(±0.03) determined in the present study as expected from the assumption that double-deuterated formaldehyde is more stable than the single-deuterated one due to zero point energy difference.

Recent work reported by the same group (Feilberg et al., 2007b) has a particular interest as the goal of the experiment is the same as the present study, but approaches it in a different way. In this experiment, the authors determined the values of α_m and $\alpha_{h\nu}$ as 0.55(±0.02) and 0.63(±0.01), respectively. The value of α_m is similar to, while that for $\alpha_{h\nu}$ is far larger than, the values determined in the present study. Actually the large discrepancy of $\alpha_{h\nu}$ points to a much larger difference in the value of α_r between Feilberg et al. (2007b) and the present study: 0.91(±0.05) versus 0.22(±0.08). Unlike the previous work (Feilberg et al., 2005), Feilberg et al. (2007b) took into account the CH_2O production in the chamber of the facility in determination of $\alpha_{h\nu}$ in addition to leakage of the experimental chamber. Notwithstanding, there is still such a large discrepancy in the isotopic fractionation factors of CH_2O between the two studies. Besides the discrepancy in the magnitude of α_r, an interesting result of Feilberg et al. (2007b) is that the degree of the isotopic fractionation in CH_2O photolysis to the molecular channel is larger than that for the radical channel, being opposite to the results from the present study and from early results by McQuigg and Calvert (1969).

It is useful to recall the different experimental conditions in both studies. Feilberg et al. (2007b) performed an isotopic tracer study using similar amounts of CH_2O and CHDO in the EUPHORE reactor in Valencia, Spain, which allowed them to infer $\alpha_{h\nu}$ directly by a spectroscopic method. α_m was then inferred from the isotope-ratio-mass-spectrometric measurements of HD and modeling of the H_2 yield using a given quantum yield for CH_2O photolysis. The direct determination of $\alpha_{h\nu}$ using spectroscopic measurement, however, had to be corrected to account for the losses of CH_2O and CHDO by the reaction with OH radical and large leakage of air in the chamber as well as production of CH_2O from the wall. In addition, their values of α_r and α_m depend on which value of the quantum yield for CH_2O photolysis are applied. In our study, performed at the level of natural deuterium abundance, α_m is the "directly" inferred quantity, and $\alpha_{h\nu}$ follows from the experimental results that the isotopic compositions of the initial CH_2O and of the H_2 that are formed from complete photolysis are virtually the same, but it also requires a correction for reaction with radicals. At present we are not able to identify the reason of the large discrepancy in the isotopic fractionation factors of CH_2O between the two studies. More experiments can resolve this issue.

4.2 Atmospheric implication

The determination of α_m and α_r may provide an important insight to comprehend what causes the enrichment in D throughout the photochemical oxidation pathway from CH_4 to H_2. The overall composite of isotopic fractionation factors from CH_4 to H_2, $\alpha_{CH_4\text{-}H_2}$, may be defined as:

$$\alpha_{CH_4\text{-}H_2} = \frac{R^0_{H_2}}{R_{CH_4}} \tag{19}$$

where $R^0_{H_2}$ represents the isotope ratio of H_2 produced by photochemical oxidation of CH_4 and R_{CH_4} is that for CH_4. Strictly speaking, $\alpha_{CH_4\text{-}H_2}$ differs from the general definition of isotopic fractionation factor in that it is a function of not only thermodynamic conditions but also environmental parameters such as radiation, radical species and their concentrations in the atmosphere. Nonetheless, given a system with these parameters, $\alpha_{CH_4\text{-}H_2}$ can be considered as an isotopic fractionation factor. Rhee et al. (2006a) estimated the value of $\alpha_{CH_4\text{-}H_2}$ to be 1.3 in the troposphere, meaning that the H_2 produced from CH_4 oxidation is enriched in D by 1.3 times as much as the initial CH_4. Gerst and Quay (2001) and Price et al. (2007) also expected D in the H_2 from photochemical oxidation of CH_4 to be enriched by a factor of 1.2–1.3.

As Gerst and Quay (2001) described in detail, $\alpha_{CH_4\text{-}H_2}$ is the product of several factors that are associated with photochemical chain reactions from CH_4 to H_2. These factors include: (1) isotopic fractionation occurring during the reaction of CH_4 with OH (α_{CH_4}), the rate-determining step of the photochemical chain reactions of CH_4, as well as the subsequent isotopic fractionation processes occurring along the way to CH_2O (α_Σ), (2) the branching ratios in the reactions of deuterated species, e.g., CH_3D, CH_2DOOH, and CH_2DO, (3) the factor of 2 brought up by the reduction of the number of hydrogen atoms from CH_4 to CH_2O, and finally (4) isotopic fractionation occurring during the photolytical production of H_2 from CH_2O. Assuming that CH_2O is in a photochemical steady state, as it has a far shorter chemical lifetime than CH_4 and H_2, point (4) is represented by the ratio of the isotopic fractionation factor of the H_2 produced (α_m) to that for CH_2O (α_f), which determines the degree of D enrichment of H_2 (Rhee et al., 2006a). Note that α_f differs from $\alpha_{h\nu}$ by the effect of isotopic fractionation arising from reaction with OH radical (α_{OH}) in the troposphere. Combining all these factors yields:

$$\alpha_{CH_4\text{-}H_2} = 2 \times \alpha_{CH_4} \times \beta_{CH_4} \times \alpha_\Sigma \times \beta_p \times \frac{\alpha_m}{\alpha_f} \tag{20}$$

where β_{CH_4} is the branching ratio for the deuterated product, CH_2D, in the reaction of CH_3D and OH, and β_p is a combined branching ratio for other short-lived intermediates, CH_2DOOH, and CH_2DO.

Regarding the right-hand side of Eq. (20), the value of α_{CH_4} is 0.78(±0.07) at 298 K (Gierczak et al., 1997) and decreases with the decrease of temperature, that for β_{CH_4} is at most unity but most likely is less than unity as Gerst and Quay (2001) speculated, and the same is expected for β_p. In the subsequent reactions, there is no compelling rationale that the more deuterated isotopologues react faster than the lighter ones considering the theoretical view of lower zero point energy for the isotopically heavier isotopologues. Thus, the value of α_Σ may not be larger than unity. The last two parameters in Eq. (20), α_f and α_m, are what we are concerned with here: since α_f is a combined isotopic fractionation factor due to photolysis and photochemical reactions of CH_2O by the fraction of the reaction routes as shown in Eqs. (8), the value is the weighted mean of the isotopic fractionation factors involved in the reactions. As listed in Table 3 under the radiation conditions of Mainz, the best values of α_m and α_r were estimated as 0.50(±0.02) and 0.22(±0.08), respectively, from the present study. Feilberg et al (2004) determined the value of α_{OH} as 0.781(±0.006). The optimal values of $\Phi(H_2)$ and Γ in Mainz were calculated as 0.647(±0.039) and 0.69(±0.28), respectively, for the periods of experiments using the TUV radiation model at a weighted mean SZA of 62.7° (see Fig. 3). In order to determine Γ, we calculated OH radical concentrations and their uncertainties from the relationship between the photolysis rate of O_3 ($J(O^1D)$) and OH concentration by Rohrer and Berresheim (2006) (i.e., $[OH]=2.4\times J(O^1D)+0.13$ and $\sigma=0.07\times10^6+0.33\times[OH]$). By inserting these values into Eq. (8b) the resulting value for α_f is 0.51(±0.11). Most of its uncertainty is carried over from the uncertainty of OH. The resulting ratio of α_m/α_f (=0.97(±0.21)) is slightly lower than unity, but because of its large uncertainty, arising from the uncertainty of the OH concentration, it is not possible to predict with certainty whether the CH_2O photolysis leads to a depletion or enrichment of D in the H_2 produced with respect to the parent CH_2O. When using the values of isotopic fractionation factors determined by Feilberg et al. (2007b), the CH_2O photolysis leads to the depletion of D in the H_2, however, even taking into account the uncertainty of α_m/α_f (see Table 3).

We extend the calculation of the ratio of α_m/α_f to a range of values of $\Phi(H_2)$ and Γ, assuming that the values of α_m, α_r, and α_{OH} determined from the present study and Feilberg et al. (2004) are applicable to the entire troposphere. The potential ranges of $\Phi(H_2)$ for the troposphere were estimated using the TUV radiation model with varying SZA at the altitudes of the US standard atmosphere. In order to estimate Γ for the troposphere, it is necessary to know the reaction rate of CH_2O+OH at a given time and place. The reaction rate coefficient varies by ∼15% in the troposphere due to change in temperature, while the OH concentration varies in the order of magnitude with its peak occurring at local noon. The peak values are well above 10^7 molecules cm^{-3} (e.g., Berresheim et al., 2003), leading to Γ ∼0.45. Thus, the range of Γ is likely to be between 0.4 and 1 in the troposphere. As shown in Fig. 6, the ratios of α_m/α_f vary from ∼0.8 to ∼1.2, which suggests that, depending on the values of Γ and $\Phi(H_2)$ in the troposphere, the H_2 produced from the CH_2O photolysis could be either enriched or depleted in D. For instance, at the Earth's surface the values of α_m/α_f along the track of the sun are likely to be lower than unity, thus yielding the depleted H_2 in D with respect to the parent CH_2O.

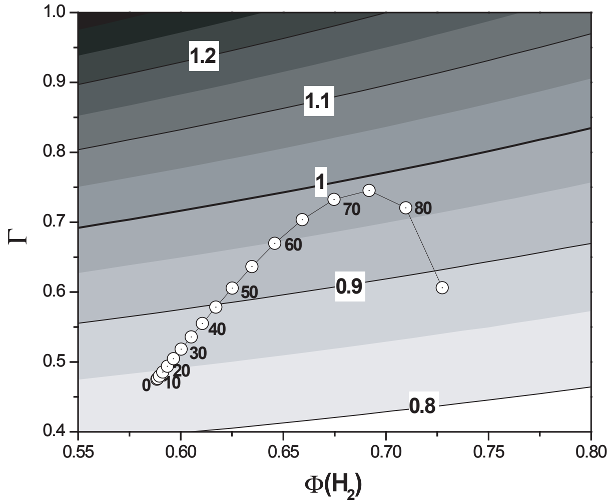

Fig. 6. Contour plot of the ratio α_m/α_f for potential ranges of the yield of H_2 from CH_2O photolysis ($\Phi(H_2)$) and of the fraction of CH_2O that is decomposed by photolysis (Γ) in the troposphere. The symbols track the values of $\Phi(H_2)$ and Γ calculated by the TUV radiation model and Rohrer and Berresheim (2006)'s parameterization of OH concentration at the indicated solar zenith angle (SZA) from 0° to 85° in 5° steps at Earth's surface.

Finally, we examine the range of α_m/α_f that can be reconciled with the values of $\alpha_{CH_4\text{-}H_2}$ inferred for tropospheric conditions. In the literature it is reported that $\alpha_{CH_4\text{-}H_2}$ would be between 1.2 and 1.3 in the troposphere (Gerst and Quay, 2001; Price et al., 2007; Rhee et al., 2006a). According to Gierczak et al. (1997), the value of α_{CH_4} at the tropospheric mean temperature of 272 K is 0.77(±0.08). Inserting these values into Eq. (20), the lower bound for α_m/α_f will be ∼0.8 when the branching ratio for deuterated compounds (β_{CH_4} and β_p) and α_Σ are unity. When the values proposed by Gerst and Quay (2001) are applied (i.e., $\beta_{CH_4}\times\alpha_\Sigma\times\beta_p=0.96\times0.77\times0.96$), α_m/α_f is 1.15. These two values of α_m/α_f bound the range which was estimated for the typical values of Γ and $\Phi(H_2)$ in the troposphere (Fig. 6). This suggests that even if α_m/α_f is smaller than unity it is still possible that H_2 formed from the photochemical oxidation of CH_4 is enriched in D with respect to the original CH_4 due to the factor of 2 that arises from the reduction of the number of hydrogen atom. Recent laboratory experiment (Nilsson et al., 2007) reports the branching ratio for CH_2DO reacting with O_2 to be 0.88(±0.01), suggesting β_p to be lower than unity and that α_m/α_f is likely to be larger than unity.

5 Conclusions

CH_2O photolysis experiments conducted in sunlight under ambient conditions allowed us to determine the isotopic fractionation factors for both the radical (R1) and molecular (R2) channels. The H_2 produced is depleted in D by 500(±20)‰ with respect to the initial CH_2O. The radical channel (R1) appears to have a much stronger isotopic fractionation than the molecular channel (R2), resulting in D enrichment of the remaining CH_2O by 780(±80)‰. This isotope effect is significantly larger than the result obtained from the experiments in the EUPHORE reaction chamber by Feilberg et al. (2007b), a difference we do not understand at present.

Applying the isotopic fractionation factors obtained from the present study to the conditions of Mainz, CH_2O photolysis may produce the H_2 that is slightly depleted in D. However, the large uncertainty in the combined isotope effects of the photochemical reactions of CH_2O, which primarily originates from the uncertainty of OH concentration, makes it impossible to precisely define the role of CH_2O photolysis in the D enrichment of H_2. In the troposphere, CH_2O photolysis may produce the H_2 either enriched or depleted in D with respect to the parent CH_2O depending on the fraction of CH_2O that reacts with OH or that is photolyzed to H_2. Nonetheless, our estimated range of α_m/α_f (∼0.8 to ∼1.2) in the troposphere can be reconciled with the production of H_2 enriched in D with respect to the original CH_4 by the factor reported in the literature.

Appendix A

1-box photochemistry model

The 1-box model is composed of 33 reactions (Table A1) running at 25°C and 10^5 Pa of air which is composed of 78% of N_2 and 22% of O_2. Unless otherwise mentioned, the yield of H_2 in the photolysis of CH_2O and the ratio of $J_{H_2O_2}/J_{CH_2O}$ are assumed to be 0.647 and 0.0896, respectively, following the result from the TUV radiation model in Mainz.

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Table A1. Photochemical reactions in the model.

No.*	Reaction	Rate coefficient**	Notes
(R1)	$CH_2O + h\nu \rightarrow CHO + H$	1.109E-5	1
(R2)	$CH_2O + h\nu \rightarrow CO + H_2$	2.033E-5	1
(R3)	$CH_2O + OH \rightarrow CHO + H_2O$	8.6E-12×exp(166/RT)	2
(R3')	$CH_2O + OH \rightarrow HCOOH + H$	2.01E-13	9
(R4)	$CH_2O + H \rightarrow CHO + H_2$	2.14E-12×exp(−9063/RT)×(T/298)$^{1.62}$	8
(R5)	$CH_2O + HO_2 \rightarrow HOCH_2OO$	6.71E-15×exp(4989/RT)	3
(R6)	$H_2 + OH \rightarrow H + H_2O$	5.5E-12×exp(−16629/RT)	3
(R7)	$H_2O_2 + h\nu \rightarrow 2OH$	2.816E-6	1
(R8)	$O_2 + CHO \rightarrow CO + HO_2$	3.5E-12×exp(1164/RT)	3
(R9)	$CHO + CHO \rightarrow CH_2O + CO$	5.0E-11	4
(R9')	$CHO + CHO \rightarrow (CHO)_2$	5.0E-11	5
(R10)	$CHO + H \rightarrow CO + H_2$	1.13E-10	6
(R11)	$CHO + OH \rightarrow CO + H_2O$	1.69E-10	4
(R12)	$CHO + HO_2 \rightarrow$ product	5.0E-11	4
(R13)	$H_2O + CHO \rightarrow CH_2O + OH$	8.54E-13×exp(−108920/RT)	7
(R14)	$H_2O_2 + CHO \rightarrow CH_2O + HO_2$	1.69E-13×exp(−29018/RT)	7
(R15)	$O_2 + H \rightarrow HO_2$	M×5.71E-32×(T/298)$^{-1.6}$	3
(R16)	$H + H \rightarrow H_2$	M×8.85E-33×(T/298)$^{-0.6}$	4
(R17)	$OH + H \rightarrow H_2O$	M×4.38E-30×(T/298)$^{-2.0}$	4
(R18)	$(CHO)_2 + OH \rightarrow$ product	1.1E-11	2
(R19)	$HCOOH + OH \rightarrow$ product	4.0E-13	3
(R20)	$CO + OH \rightarrow CO_2 + H$	1.5E-13×(1+0.6×P/1013.25)	3
(R21)	$CO + HO_2 \rightarrow CO_2 + OH$	5.96E-11×exp(−95616/RT)×(T/298)$^{0.5}$	10
(R22)	$OH + OH \rightarrow H_2O_2$	M×6.20E-31×(T/298)$^{-1}$	3
(R23)	$HO_2 + H \rightarrow$ product	8.10E-11	3
(R24)	$HO_2 + OH \rightarrow H_2O + O_2$	4.8E-11×exp(2079/RT)	3
(R25)	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	M×1.7E-33×exp(8314/RT)	3
(R26)	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	2.91E-12×exp(−1330/RT)	3
(R27)	$HOCH_2OO \rightarrow HO_2 + CH_2O$	2.4E12×exp(−58201/RT)	2
(R28)	$HOCH_2OO + HO_2 \rightarrow HCOOH + H_2O + O_2$	5.6E-15×exp(19123/RT)	2
(R29)	$2HOCH_2OO \rightarrow 2HOCH_2O + O_2$	5.5E-12	11
(R29')	$2HOCH_2OO \rightarrow HCOOH + CH_2(OH)_2 + O_2$	5.71E-14×exp(6236/RT)	11
(R30)	$O_2 + HOCH_2O \rightarrow HCOOH + HO_2$	3.5E-14	12

Notes: 1. TUV radiation model; 2. Atkinson et al. (1997); 3. DeMore et al. (1997); 4. Baulch et al. (1992); 5. Stoeckel et al. (1985); 6. Ziemer et al. (1998); 7. Tang and Hampson (1986); 8. Baulch et al. (1994); 9. Yetter et al. (1989); 10. Volman (1996); 11. Atkinson et al. (1992); 12. Veyret et al. (1982)
* Prime (') designates the second reaction.
** R and T in rate constant designate gas constant and absolute temperature, respectively. M indicates air concentration in termolecular reaction. The units of the rate coefficients for first-, second-, and third-order reactions are s^{-1}, cm^3 $molecule^{-1}$ s^{-1}, and cm^6 $molecule^{-2}$ s^{-1}, respectively.

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