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Deuterium fractionation in formaldehyde photolysis: chamber experiments and RRKM theory

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Abstract

While isotope effects in formaldehyde photolysis are the key link between the δD of methane emissions with the δD of atmospheric in situ hydrogen production, the mechanism and the extent of their pressure dependencies is not adequately described. The pressure dependence of the photolysis rates of the mono- and di-deuterated formaldehyde isotopologues HDCO and D_2CO relative to the parent isotopologue H_2CO was investigated using RRKM theory and experiment. D_2CO and H_2CO were photolysed in a static reaction chamber at bath gas pressures of 50, 200, 400, 600 and 1000 mbar; these experiments compliment and extend our earlier work with HDCO vs. H_2CO. The UV lamps used for photolysis emit light at wavelengths that mainly dissociate formaldehyde into molecular products, CO and H_2 or D_2. A model was constructed using RRKM theory to calculate the lifetime of excited formaldehyde on the S_0 surface to describe the observed pressure dependent photolytic fractionation of deuterium. The effect of deuteration on the RRKM lifetime of the S_0 state is not the main cause of the experimentally observed isotope effect. We propose that there is an additional previously unrecognised isotopic fractionation in the rate of transfer of population from the initially excited S_1 state onto the S_0 surface.

1 Introduction

Formaldehyde is a key intermediate in hydrocarbon oxidation and plays a central role in both atmospheric and combustion chemistry. It enters the atmosphere as a primary emission from combustion engines and biomass burning, and is also formed in the atmosphere, mainly as a result of OH initiated oxidation of methane and larger hydrocarbons. Being a reactive species and an important part of both natural and anthropogenic atmospheric chemistry, the reaction sequences where formaldehyde is an intermediate have consequences for regional air quality and global atmospheric composition (Seinfeld and Pandis, 1998).

As an example of the importance of formaldehyde, over half of atmospheric H_2 is a product of formaldehyde photolysis. The global budget of H_2 has recently been reviewed and modeled (Ehhalt and Rohrer, 2009; Pieterse et al., 2011). In order for these models to give a correct balance between sources and sinks, implementation of an accurate reaction scheme for formaldehyde chemistry is of vital importance. Isotopic composition is an additional observable used to constrain species budgets and atmospheric models. This approach requires information about the isotopic composition of different sources of the compounds, and of the isotopic fractionation in production and loss processes (Brenninkmeijer et al., 2003). Normal formaldehyde, H_2CO, is the main isotopologue while $H_2{}^{13}CO$ is the most common of the minor isotopologues, followed by $H_2C^{18}O$ and $H_2C^{17}O$ (Johnson et al., 2002). Monodeutero formaldehyde, HDCO, has recieved increasing attention as deuterium abundance is a useful tracer in the carbon and hydrogen cycles (Pieterse et al., 2011; Nilsson et al., 2007; Feilberg et al., 2007b, 2005a). Dideutero formaldehyde, D_2CO, is of minor importance in the atmosphere due to its low abundance compared to the other isotopologues, but it can play an important role in investigating mechanism.

The major source of formaldehyde in the atmosphere, methane, is depleted in deuterium, while molecular hydrogen from formaldehyde photolysis is strongly enriched (Gerst and Quay, 2001). It has been shown that there is a large deuterium enrichment in the formation of formaldehyde from the monodeuterated methoxy radical (Nilsson et al., 2010). The kinetic isotope effect in the photolysis of formaldehyde under ambient conditions, HDCO as well as D_2CO, have been determined in several studies summarized in Table 1. For an evaluation of the HDCO results we refer to the discussion in Nilsson et al. (2010).

Modelling studies indicate an altitude dependent deuterium isotope fractionation in the photochemical production of molecular hydrogen (Röckmann et al., 2003; Mar et al., 2007; Pieterse et al., 2011); measurements show increasing deuterium enrichment with altitude (Röckmann et al., 2003; Mar et al., 2007; Batenburg et al., 2012). A pressure dependent isotope effect for monodeutero formaldehyde was confirmed in

a recent publication by our group (Nilsson et al., 2010). This pressure dependence in the isotopic fractionation in formaldehyde photolysis can explain all or part of the altitude dependent deuterium enrichment. Part of the altiude dependence can possibly also stem from a wavelength dependence. The pressure dependence has been implemented in version 5.0 of a global transport model (TM5) (Krol et al., 2005; Pieterse et al., 2011), the first global model with an explicit isotope reaction scheme for photochemical production of H_2. Pieterse et al. (2011) show that they can obtain agreement between modeled and measured atmospheric isotopic composition by varying relevant isotopic parameters within their uncertainty ranges, but that the available data are not sufficient to uniquely constrain the isotope budget. They conclude that further work is needed to quantitatively determine isotopic fractionation in the methane oxidation chain.

Photolysis of formaldehyde has two channels giving molecular products $H_2 + CO$, and radical products $H + HCO$. Experiments show that there is a pressure dependence in the quantum yield of the molecular channel; this dependence has been parameterized by Sander et al. (2006). No pressure dependence is observed in the radical channel. The molecular channel Reaction (R1) has a threshold energy corresponding to a wavelength of about 360 nm, while the radical channel Reaction (R2) has a threshold in the region 330–340 nm (Troe, 2007; Sander et al., 2006). In addition molecular products can also form via the "roaming atom" mechanism Reaction (R3) (Bowman and Zhang, 2006; Townsend et al., 2004).

$$H_2CO + h\nu \rightarrow H_2 + CO \tag{R1}$$

$$H_2CO + h\nu \rightarrow H + HCO \tag{R2}$$

$$H_2CO + h\nu \rightarrow H\cdot HCO \rightarrow H_2 + CO \tag{R3}$$

The photodissociation process has been investigated using experimental as well as theoretical methods, as outlined by Troe (2007) and Herath and Suits (2011). The molecular channel photodissociation occurs in three steps. First the system is excited from the ground state (S_0) to the excited (S_1),

$$H_2CO(S_0, J) + h\nu \rightarrow H_2CO^*(S_1, J'), \quad (R4)$$

where the total angular momentum, J, is subject to the the selection rule,

$$\Delta J = J - J' = 0, \pm 1. \quad (1)$$

Secondly, from S_1 the system undergoes a radiationless transition to S_0 and finally forms products via unimolecular dissociation,

$$H_2CO^*(S_1, J') \rightarrow H_2CO^*(S_0, J') \rightarrow H_2 + CO. \quad (R5)$$

Dissociation into the molecular channel competes with quenching via bath gas collision, and, at energies above the radical channel threshold, Reaction (R2). The extent of the contribution from the "roaming" pathway, Reaction (R3), is not fully understood and is estimated to be < 0.2 of the total photolysis (Herath and Suits, 2011).

The aim of the present work is to further investigate the pressure dependence in the isotope effects in formaldehyde photolysis, confirming and extending our previous work (Nilsson et al., 2010). An experimental study of isotope effects in photodissociation of the dideuterated formaldehyde isotopologue, D_2CO, is presented. The study was carried out in the same way as the previously published study on HDCO (Nilsson et al., 2010). The unimolecular lifetime of excited formaldehyde on the S_0 surface was investigated using RRKM calculations to characterize the mechaism and pressure dependence of the deuterium fractionation via H_2CO, HDCO and D_2CO photolysis under the present experimental conditions.

2 Experimental

The photolysis experiments were carried out in a 2 m long quartz chamber with a volume of 101.4 L, surrounded by 8 UVA lamps with the emission maximum at 350 nm,

emission spectrum shown in Fig. 1. The setup is enclosed in an insulated, temperature controlled housing; for this study the temperature was kept at 293 ± 0.5 K. Loss of reactants was monitored using a Bruker IFS66v/s FTIR spectrometer coupled to a White type optical system in the reaction chamber. The absorption path length was 72 m and a liquid nitrogen cooled InSb detector was used. For further details on the experimental setup we refer to Nilsson et al. (2009b).

The relative photolysis rate of H_2CO versus D_2CO was determined at total pressures of 50, 200, 400, 600 and 1000 mbar, using synthetic air (Air Liquide) as bath gas. The experiments were performed in the same way as for the study of pressure dependence of the monodeuterated formaldehyde isotopologue, as described in Nilsson et al. (2010).

Initial partial pressures of formaldehyde isotopologues for each experiment are given in the third column of Table 2. FTIR spectra were analysed using the spectral fitting program `MALT510` (Griffith, 1996). The experimental spectra were analysed for the formaldehyde isotopologues, and in cases of overlapping absorptions, H_2O, HDO and CO were also included in the analysis. For the formaldehyde isotopologues high resolution reference spectra by Gratien et al. (2007) were used as input for the spectral fitting at 600 mbar and 1000 mbar total pressure. At lower pressures reference spectra were taken in the same reaction chamber under conditions identical to those of the experiments. High resolution line parameters from the HITRAN database were used for H_2O, HDO and CO (Rothman et al., 2009). The natural logarithm of the relative concentrations were plotted for each experiment, as shown in Fig. 2. The slopes of the lines are the relative reaction rates, or the kinetic isotope effects, given in the second column of Table 2.

3 Calculations

3.1 Quantum chemistry calculations

The relevant minima and transition states of the H_2CO electronic ground state were located using the geometry optimization program in `Molpro 2010` (Werner et al., 2010) using the Singles Doubles with perturbed triples Coupled Cluster (CCSD(T)) methodology (Knowles et al., 1993, 2000; Watts et al., 1993; Deegan and Knowles, 1994) and the aug-cc-pVQZ orbital basis set (Dunning, 1989; Woon and Dunning, 1993). The vibrational frequencies at the stationary points were computed using the same level of theory for all isotopologues, H_2CO, HDCO and DHCO (not equivalent at the non-symmetrical transition state), and D_2CO. The electronic energies were refined using the aug-cc-pV5Z orbital basis set. The correlation energy was then extrapolated to the complete basis set limit using the formula of Halkier et al. (1998). The barrier height and vibrational frequencies for H_2CO are in good agreement with the theoretical results of Bowman and Zhang (2006). Energies of the stationary points, vibrational frequencies and zero point energies are available as supporting material.

3.2 Rate calculations

A model was constructed assuming that unimolecular dissociation is the rate determining step. The rate of dissociation into the molecular channel, $k_{\mathrm{dis}}(E_{\mathrm{ph}})$, upon absorbing a photon of energy, E_{ph}, can then, within RRKM theory (Wardlaw and Marcus, 1988; Billing and Mikkelsen, 1996), be written as,

$$k_{\mathrm{dis}}(E_{\mathrm{ph}}) = \sum_J k_{\mathrm{dis}}^{\mathrm{rot}}(E_{\mathrm{ph}},J)(2J+1)e^{-E_J/kT}. \tag{2}$$

We assume that a molecule in the Jth state has an equal probability of being excited into the $(J-1)$, J and $(J+1)$th state. $k_{\mathrm{dis}}^{\mathrm{rot}}(E_{\mathrm{ph}},J)$ is then given by,

$$k_{\mathrm{dis}}^{\mathrm{rot}}(E_{\mathrm{ph}},J) = \frac{1}{3}\sum_{J'=J-1}^{J+1} k_{\mathrm{uni}}(E_{\mathrm{ph}},J'), \tag{3}$$

where $k_{\mathrm{uni}}(E_{\mathrm{ph}},J)$ is the unimolecular (i.e. RRKM) rate constant,

$$k_{\mathrm{uni}}(E_{\mathrm{ph}},J) = \frac{N^{\mathrm{TS}}(E_{\mathrm{ph}},J)}{h\rho(E_{\mathrm{ph}},J)}. \tag{4}$$

Here $N^{\mathrm{TS}}(E,J)$ is the sum of states at the transition state leading to dissociation and $\rho(E,J)$ is the adduct density of states. $N^{\mathrm{TS}}(E,J)$ and $\rho(E,J)$ were evaluated by direct count using the Extended Beyer Swinehart algorithm (Stein and Rabinovitch, 1973) and including Eckart barrier tunneling corrections as described by Miller (1979). The dissociation rate for the different isotopes of formaldehyde is shown in Fig. 3. For H_2CO and D_2CO there are two equivalent dissociation channels, while for HDCO the two channels are different.

Unimolecular dissociation competes with relaxation via bath gas collision. The quantum yield for going into the molecular channel is therefore dependent on pressure and can be approximated as,

$$Y_{\mathrm{mol}}(E_{\mathrm{ph}}) = \left(1 - Y_{\mathrm{rad}}(E_{\mathrm{ph}})\right)\frac{k_{\mathrm{dis}}(E_{\mathrm{ph}})}{k_{\mathrm{dis}}(E_{\mathrm{ph}}) + k_{\mathrm{relax}}\,[M]} \tag{5}$$

where k_{relax}, within the strong collision assumption, is the bi-molecular collision rate, and Y_{rad} is the quantum yield for dissociation into the radical channel (see Fig. 1). Figure 5 shows quantum yields in the molecular channel in the range of pressures studied in the present work, as the pressure decrease the bath gas collions become less important for quenching of the excited formaldehyde molecules, resulting in a yield approaching unity.

Once the molecular channel quantum yield is known the overall rate for production of $H_2 + CO$ can be calculated as,

$$j_{\mathrm{mol}} = \int \mathrm{d}E_{\mathrm{ph}}\, \sigma(E_{\mathrm{ph}})\, I(E_{\mathrm{ph}})\, Y_{\mathrm{mol}}(E_{\mathrm{ph}}) \tag{6}$$

while the rate of dissociation in the radical channel can be calculated as,

$$j_{\mathrm{rad}} = \int \mathrm{d}E_{\mathrm{ph}}\, \sigma(E_{\mathrm{ph}})\, I(E_{\mathrm{ph}})\, Y_{\mathrm{rad}}(E_{\mathrm{ph}}). \tag{7}$$

The total rate of dissociation can be calculated as the sum of the two component terms. The isotope effect is calculated from the total rate.

The rate calculations were performed using the STATRATE program package, previously used for calculations concerning pressure dependence in the isotope effects in the OCS + OH reaction (Schmidt et al., 2012).

4 Results

Relative reaction rates $k(H_2CO)/k(D_2CO)$ determined in each experiment are presented in Table 2 and Fig. 2. This quantity is the rate of photodissociation for the present experimental conditions, inferred from the loss of the two isotopologues throughout the experiments. The photolysis lamps are choosen to mainly photolyze formaldehyde at wavelengths resulting in molecular products.

As can be seen in Fig. 1 there is a tail of the lamp emission spectrum at wavelengths giving radical products. The magnitude of this interference is discussed in our study on HDCO (Nilsson et al., 2010). In summary the experimental results can be corrected for contribution from photolysis into radical products, to yield the isotopic fractionation in the molecular channel; the approach relies on experimental data for the quantum

yields. The available datasets for radical channel quantum yield in the wavelength region of interest (Sander et al., 2006; Atkinson et al., 2006; Troe, 2007) are unfortunately not in good enough agreement to allow a well constrained parameterization. A second complication is the uncertainty regarding the magnitude of the isotope effect in the radical channel. Previous determinations disagree for HDCO (Feilberg et al., 2007b; Rhee et al., 2008). No data on radical channel isotope effects exist for D_2CO. In our previous work (Nilsson et al., 2010) the sensitivity of a parameterization to the different literature values for absorption cross sections and radical channel isotopic fractionation are discussed in detail.

In Fig. 4 the relative removal rates are plotted as a function of chamber pressure, including the atmospheric pressure results from the studies at the European Photoreaction Facility (Feilberg et al., 2005b, 2007a; Nilsson et al., 2009a), and the results from the study on HDCO (Nilsson et al., 2010). The present results at 1000 mbar are in agreement with the results from the previous studies, an agreement that was also seen for the HDCO isotopologue (Nilsson et al., 2010). The isotope effect ranges from about 1.1 at a chamber pressure of 50 mbar, up to about 3 at 1000 mbar. This means that at the lowest pressures the isotope effect for D_2CO is similar to that of HDCO, while at higher pressures the difference is about a factor of two. From Fig. 4 it is seen that in the case of HDCO the ratio $k(H_2CO)/k(HDCO)$ levels out in the region 400–600 mbar; additional pressure increase does not increase the isotope effect. The same trend is not seen for D_2CO.

Figure 5 shows the significant variation of the quantum yield within the pressure range of the present work. At the lowest pressure the yield is one at wavelengths above the radical channel threshold. As the pressure increases the yield rapidly decreases.

The RRKM model assumes that competition between unimolecular decomposition on the S_0 surface and collisional relaxation is the mechanism governing the observed isotope effects. Isotopic substitution results in lower vibrational frequencies and a higher density of states, leading to a longer lifetime via Eq. (4). Comparing the calculated results (lines) with experiments (symbols) in Fig. 4, it is seen that straightforward application of RRKM theory is not sufficient to explainthe experimental observations. It is therefore likely to be working in concert with other processes; the remaining isotope effect could for example be explained by an additional reservoir of population. However, while other isomers of formaldehyde exist, they are higher in energy and are therefore not highly populated. It therefore seems more likely that the remaining isotope effect originates from the non-radiative transition from S_1 to S_0 which is not considered in the present model.

5 Conclusions

The pressure dependence in the photolysis of D_2CO has been investigated for the first time. The result at atmospheric pressure is in agreement with data from two previous determinations at another experimental facility, and the overall trend in pressure dependence is analogous to what was recently determined for the HDCO isotopologue. The experimental trend in pressure dependence is to some extent explained by RRKM calculations for both mono- and dideutero formaldehyde, indicating that part of the pressure dependence is a result of competition between unimolecular dissociation and collisional relaxation. The full magnitude of the isotope effect is not reproduced by the calculations and we propose that there are other processes contributing to the isotope effects.

The present work and our previous publication (Nilsson et al., 2010) show that the altitude dependent isotopic fractionation suggested by Röckmann et al. (2003); Mar et al. (2007); Pieterse et al. (2011) likely is a result of pressure dependence. To be able to use this to constrain the isotopic budget a better quantitative determination of the isotope effect is of importance. Due to the overlap between the product channels design of experiments that enable investigation of one channel is a significant challenge. The results presented here can be used to quantify the pressure depence of deuterium isotopic fractionation once the question of the radical channel quantum yield is resolved; currently available estimates conflict. Accurate description of the underlying

mechanism is the key to interpreting the observations and improving trace gas budgets and descriptions of in situ chemistry.

The available experimental laboratory and environmental chamber results, and the model, do not support the large isotope effects reported by Rhee et al. (2008).

Future work should consider the pressure dependence of the photolytic isotope effect for ^{13}C and ^{18}O substituted formaldehyde which will clearly impact the seasonal variation in the isotopic composition of tropospheric CO (Röckmann et al., 2002).

In conclusion only part of the pressure dependence in the photolytic deuterium fractionation in formaldehyde photolysis is due to the longer unimolecular lifetime of the heavy isotopologues. Isotope effects in the rate of S_1 to S_0 transfer is the most likely mechanism for explaining a significant part of the observed fractionation.

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Table 1. Summary of previous experimental results for isotope effects, $k(H_2CO)/k(XDCO)$ (X=H or D), of deuterated formaldehyde at atmospheric pressure, and the results obtained at 1000 mbar in the present study.

Experimental facility	Volume	Light source	Total	Molecular	Radical	Reference
HDCO:						
EUPHORE	200 m^3	Sunlight	1.58 ± 0.03	1.82 ± 0.07	1.1 ± 0.06	Feilberg et al. (2007b)
Glass/quartz vessel	1–3 L	Sunlight	2.50 ± 0.03	2.00 ± 0.02	4.5 ± 0.08	Rhee et al. (2008)
SAPHIRE	370 m^3	Sunlight	1.63 ± 0.03	1.63 ± 0.03	–	Röckmann et al. (2010)
Quartz chamber	101 L	UVA	1.75 ± 0.1	–	–	Nilsson et al. (2010)
D_2CO:						
EUPHORE	200 m^3	Sunlight	3.00 ± 0.50	–	–	Feilberg et al. (2005b, 2007a)
EUPHORE	200 m^3	Sunlight	3.15 ± 0.08	–	–	Nilsson et al. (2009a)
Quartz chamber	101 L	UVA	3.11 ± 0.09	–	–	This work

Table 2. Experimental results at different chamber pressures. The second column presents $k(H_2CO)/k(D_2CO)$ obtained from relative rate plots, errors include the uncertainty in the slope and an additional 3 % error to account for uncertainties in reference spectra. The last two columns give the initial partial pressures of the two isotopologues.

Pressure mbar	$k(H_2CO)/k(D_2CO)$	$[H_2CO]_0$ µbar	$[D_2CO]_0$ µbar
50	1.17 ± 0.04	2.2	0.76
50	1.08 ± 0.03	1.6	0.52
200	1.68 ± 0.05	3.9	2.4
200	1.49 ± 0.05	7.8	2.9
400	1.99 ± 0.06	3.8	2.6
600	2.17 ± 0.07	8.5	4.7
600	2.39 ± 0.07	9.6	3.2
1000	3.11 ± 0.09	15.1	5.7

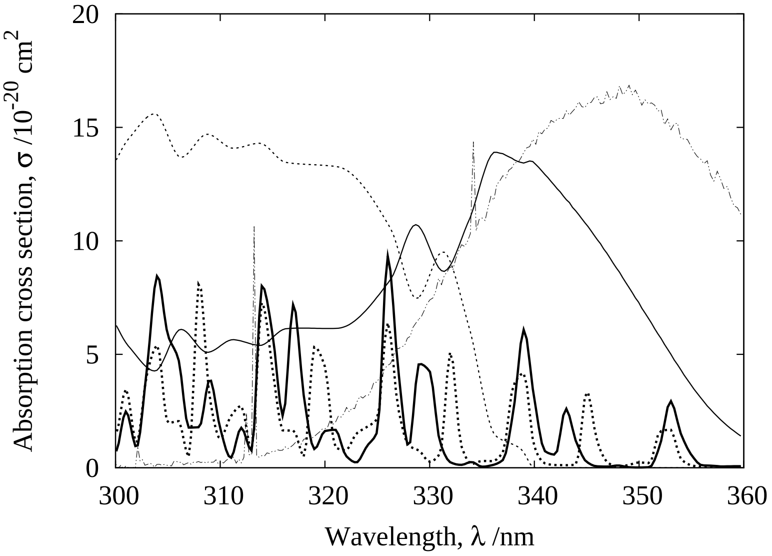

Fig. 1. Absorption cross sections of H_2CO (thick full drawn line) and D_2CO (thick dashed line) from Gratien et al. (2007). Also shown are the quantum yield in the molecular channel (full drawn line), the quantum yield in the radical channel (dashed line) (Atkinson et al., 2006), and the emission spectrum of the photolysis lamp Osram Eversun 100W/79 (dash-dotted line).

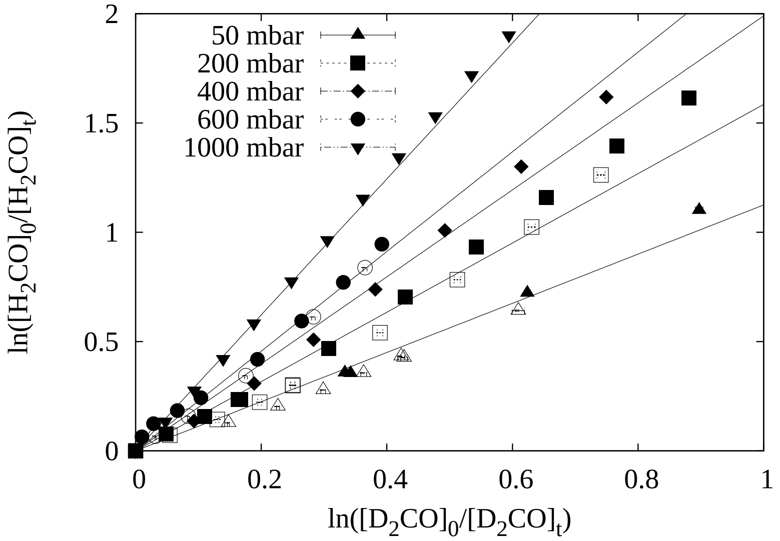

Fig. 2. Relative rate plots of H_2CO vs. D_2CO at the different pressures, closed and open symbols at pressures 50, 200 and 600 mbar are representing different experiments. Error bars are within symbols and include the uncertainty in concentration given from the `MALT` program used for analysis of IR spectra.

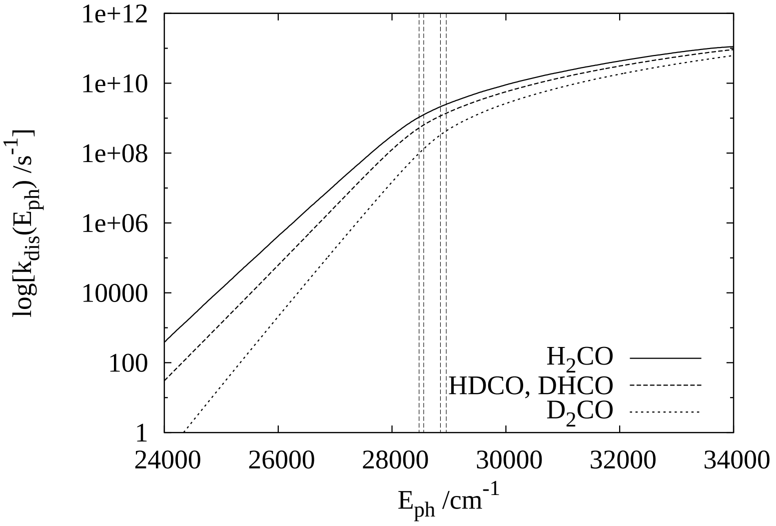

Fig. 3. Dissociation rate as a function of photon energy at $T = 300$ K. The vertical lines mark the position of the barrier for dissociation; 28460 cm^{-1} (H_2–CO), 28 538 cm^{-1} (HD–CO), 28 839 cm^{-1} (DH–CO) and 28 940 cm^{-1} (D_2–CO).

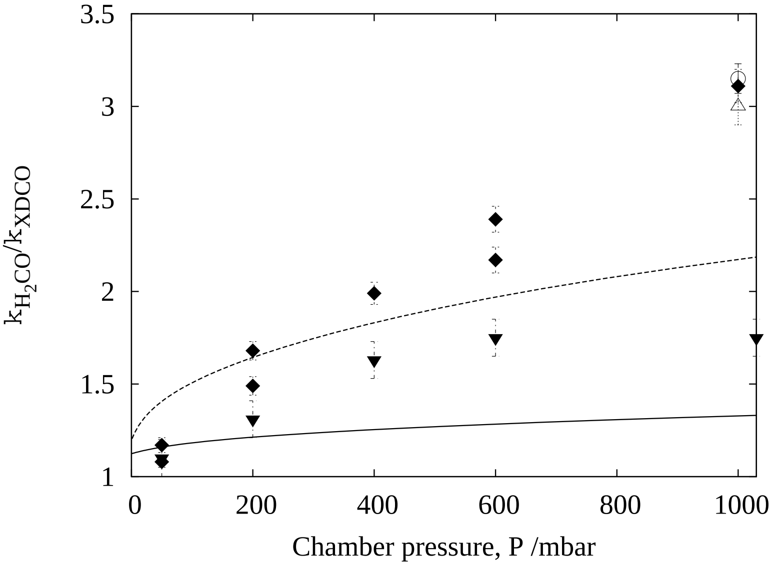

Fig. 4. Relative dissociation rate of formaldehyde $k(H_2CO)/k(XDCO)$(X=H or D) as a function of pressure. The diamonds are the same data as presented in Table 2. Closed triangles represent the corresponding values for the HDCO isotopologue, from Nilsson et al. (2010). Open symbols are previous determinations of $k(H_2CO)/k(D_2CO)$ from Feilberg et al. (2005b, 2007a), triangle, and Nilsson et al. (2009a), circle. Lines represent the calculated isotope effects.

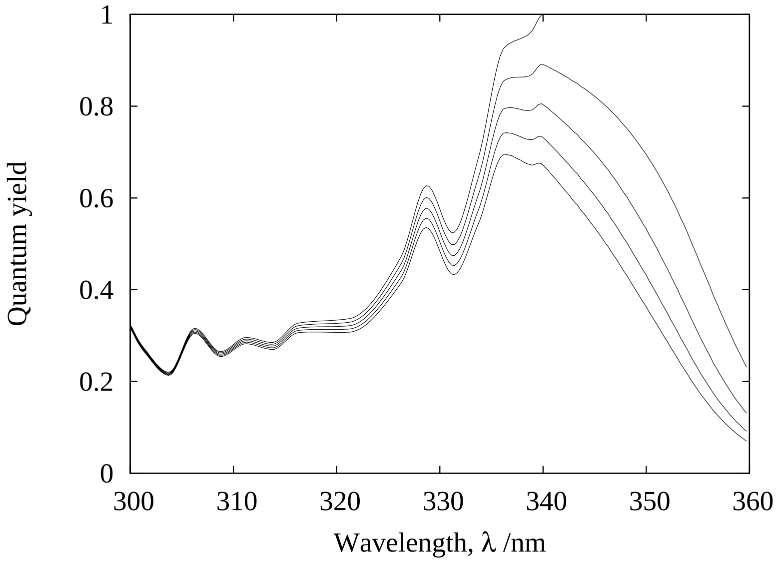

Fig. 5. Molecular channel quantum yield for different pressures. From highest to lowest the lines represent pressures of 0, 250, 500, 750 and 1000 mbar.