



Universiteit  
Leiden  
The Netherlands

## Isotope effects for formaldehyde plus hydrogen addition and abstraction reactions: rate calculations including tunnelling

Goumans, T.P.M.

### Citation

Goumans, T. P. M. (2011). Isotope effects for formaldehyde plus hydrogen addition and abstraction reactions: rate calculations including tunnelling. *Monthly Notices Of The Royal Astronomical Society*, 413(4), 2615-2620. doi:10.1111/j.1365-2966.2011.18329.x

Version: Not Applicable (or Unknown)

License: [Leiden University Non-exclusive license](#)

Downloaded from: <https://hdl.handle.net/1887/61525>

**Note:** To cite this publication please use the final published version (if applicable).

# Isotope effects for formaldehyde plus hydrogen addition and abstraction reactions: rate calculations including tunnelling

T. P. M. Goumans<sup>★</sup>

*Gorlaeus Laboratories, Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, the Netherlands*

Accepted 2011 January 10. Received 2011 January 10; in original form 2010 September 2

## ABSTRACT

Tunnelling plays a crucial role in the low-temperature chemistry in the interstellar medium (ISM), in particular for reactions involving hydrogen atoms. Using harmonic quantum transition state theory we studied reaction rates down to 20 K including tunnelling effects for the gas phase reaction of formaldehyde with hydrogen atoms, paying particular attention to isotope effects. Hydrogen atoms can either add to formaldehyde, yielding the methoxy radical which is ultimately hydrogenated to form methanol, or they can subtract a hydrogen atom, which could provide a route for deuterium enrichment. The isotope effects are different for the addition and subtraction routes and the relative rates are qualitatively in agreement with previous solid state experiments, although surface effects may also play a decisive role. Therefore, the effect of water molecules and a formaldehyde molecule on the abstraction and addition tunnelling reactions is also studied down to 50 K for selected isotopologues. The gas phase rate calculations indicate that for  $H/D + H_2CO$ , abstraction is preferred over addition, but addition is more favourable than abstraction for the  $H + D_2CO$  reaction. The presence of water molecules enhances the addition reaction and reduces the abstraction reaction, while an extra formaldehyde molecule does not affect the gas phase reaction rates strongly. H addition is preferred over abstraction in water-rich ices, but in apolar ices abstraction is preferred, which could enhance deuteration of formaldehyde and methanol. The calculated reaction rates are in qualitative agreement with recent experimental findings which suggest that H/D exchange in formaldehyde as well as methanol may be contributing to the observed deuterium enrichment in formaldehyde and methanol in the ISM.

**Key words:** astrochemistry – molecular processes – ISM: atoms – ISM: molecules.

## 1 INTRODUCTION

Formaldehyde and methanol are abundant interstellar molecules which can be used to trace local physical parameters. Therefore, their formation, evolution and deuteration are widely studied through observations, laboratory experiments and theoretical modelling. While methanol ice is ubiquitously observed in molecular clouds (Herbst & van Dishoeck 2009), formaldehyde ice has been detected much less frequently (Gibb et al. 2004; Boogert et al. 2008). Nevertheless, both formaldehyde and methanol have been established to form efficiently at low temperatures from the consecutive addition of hydrogen atoms to CO ices (Hiraoka et al. 1994; Watanabe et al. 2004; Fuchs et al. 2009; Pirim et al. 2010), while gas phase formation routes to methanol are thought to be inefficient (Garrod et al. 2006; Geppert et al. 2006).

High degrees of deuteration are observed in gaseous formaldehyde and methanol, which necessitates abstraction reactions in astrochemical networks and indicates that gas–grain chemistry is likely involved (Caselli et al. 2002; Parise et al. 2006). Indeed, experiments have shown that both formaldehyde (Hidaka, Watanabe & Kouchi 2006) and methanol (Nagaoka, Watanabe & Kouchi 2005) display H–D exchange reactions in the solid state upon impingement of H or D atoms, which enhances deuteration in these species. No exchange of the alcoholic hydrogen of methanol was observed (Nagaoka et al. 2005), which is consistent with the interstellar detection of triply deuterated methanol as the  $CD_3OH$  isotopologue (Parise et al. 2004). Recently it has also been found that photolysis of deuterium-rich mixed ices (Weber et al. 2009) or protic H–D exchange of the alcohol group upon heating (Ratajczak et al. 2009) could affect deuteration.

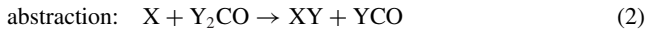
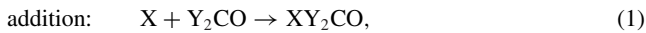
Models predict that high atomic D/H gas phase ratios ( $\sim 0.1$  compared to the average cosmic ratio of  $\sim 1 \times 10^{-5}$ ) are necessary at the time of CO freeze-out to reproduce the high deuteration of formaldehyde and methanol (Roberts, Herbst & Millar 2004). At

<sup>★</sup>E-mail: t.goumans@chem.leidenuniv.nl

There is an Erratum to this article at doi:10.1111/j.1365-2966.2012.20384.x.

these low temperatures, however, D and H can display distinctly different chemistry because of quantum mechanical tunnelling through activation barriers (Andersson, Goumans & Arnaldsson 2011). In particular, reactions that involve the motion of a hydrogen atom will display a huge kinetic isotope effect (KIE),  $k_{\text{H}}/k_{\text{D}}$  (Krishtalik 2000). Therefore, both the addition of H to an unsaturated molecule such as formaldehyde or H abstraction will likely be favoured over the analogous D reactions at temperatures in molecular clouds (10–20 K).

While in principle these kinetic isotope effects can be modelled by including a crude tunnelling model, such as a square barrier of 1 Å (Tielens & Hagen 1982; Hasegawa, Herbst & Leung 1992), the tunnelling path in actual chemical reactions is more complex and multidimensional, which requires a more elaborate approach for accurate rates. Here we employ harmonic quantum transition state theory (HQTST; Arnaldsson 2007; Andersson et al. 2009) to calculate reaction rates that include accurate multidimensional tunnelling corrections, especially at low temperatures for the hydrogen addition and abstraction rates in the hydrogen plus formaldehyde gas phase reactions:



for various isotope combinations of X, Y = H, D. The calculated HQTST rates are fitted to expressions that can be used in astrochemical networks and the trends are compared to recent experiments. The influence of an icy mantle on the tunnelling rates is studied by evaluating the effect of hydrating formaldehyde with two water molecules and by adding an additional formaldehyde molecule.

## 2 METHODOLOGY

HQTST is a reformulation of instanton or ImF theory which uses discretized Feynman paths to optimize the tunnelling path in all dimensions, while treating modes perpendicular to the tunnelling path as harmonic oscillators. The HQTST methodology has been described in great detail before (Arnaldsson 2007; Andersson et al. 2009). Here we employ a direct dynamics approach to optimize the quantum transition state (qTS) with density functional theory (DFT), as recently applied to study the  $\text{O}(^3\text{P}) + \text{CO}$  (Goumans & Andersson 2010), and  $\text{H} + \text{benzene}$  (Goumans & Kaestner 2010) reactions at interstellar temperatures. We do not include rotational partition functions (can be treated classically even at 10 K), which do not play a role for surface reactions and would have only a minor impact on the gas phase reaction rates.

Testing a variety of functionals (BB1K, MPW1K, MPWB1K, B97-1) which usually perform reasonably well for reaction barriers (Zhao & Truhlar 2005) with a combination of basis sets against benchmark high-level *ab initio* calculations (CCSD(T)/CBS), the BB1K/6-311+G\*\* approach seemed to be the most suitable. While the electronic DFT  $\text{H} + \text{H}_2\text{CO} \rightarrow \text{H}_3\text{CO}$  addition barrier is in excellent agreement with the benchmark (CCSD(T)/CBS: 1845 K, BB1K/6-311+G\*\*: 1807 K), the electronic  $\text{H} + \text{H}_2\text{CO} \rightarrow \text{HCO} + \text{H}_2$  abstraction barrier is slightly lower with DFT than the benchmark (CCSD(T)/CBS: 3613 K, BB1K/6-311+G\*\*: 3059 K). Note that quantum mechanical zero-points effects will cause the vibrational adiabatic barriers of the addition and abstraction reactions (1) and (2) to be much closer to each other, with the absolute ordering depending on the isotopes (see results below). CCSD(T) calculations were performed with MOLPRO (Werner et al. 2008), the qTS

was optimized with NWCHEM (Bylaska et al. 2007) and its second derivatives calculated with GAUSSIAN 03 (Frisch et al. 2004).

The qTS becomes more delocalized with decreasing temperature and consequently more images are necessary to properly resolve the closed Feynman path and therefore rate coefficients need to be converged with respect to increasing the number of images used to discretize the Feynman path. The qTS is optimized at a number of temperatures, starting just below the cross over temperature  $T_c = \hbar\omega^*/2\pi k$ , where tunnelling starts to dominate, down to 20 or 15 K for the gas phase reactions, or down to 50 K for the reactions where extra molecules are included to simulate interstellar ices. We could not obtain converged rates below these temperatures, because of the high dimensionality of the qTS at very low temperatures and the extended delocalization of the qTS leading to numerical inaccuracies with this functional due to the noise in the DFT energies, forces and harmonic frequencies. Therefore, we only fit our HQTST results at temperatures above 20 K for the gas phase reactions. To smoothen the calculated gas phase rate data at higher temperatures, we also include rates at 500, 1000 and 2000 K with a simple Wigner (1938) tunnelling correction  $\kappa = 1/24(\hbar\nu^*/kT)^2$ . Furthermore, we employ a weighted HQTST (0.5) and Wigner (0.5) tunnelling correction near  $T_c$ , because the former appears to overestimate, while the latter seems to underestimate the tunnelling effect near  $T_c$  (Arnaldsson 2007). While in principle the entire temperature range can be fit reasonably well (correlation coefficients 0.992–0.996) to one modified Arrhenius expression, much better fits (correlation coefficients of 0.997–1) are obtained if we fit the temperature ranges  $T > T_c$  and  $T \leq T_c$  separately. The data points at higher  $T$ , where tunnelling does not play a significant role, are better represented by a separate fit above the cross over temperature.

## 3 GAS PHASE REACTION RATES

In Table 1 the vibrational adiabatic barriers, which incorporate zero-point vibrational energies, are reported for the gas phase  $\text{H} + \text{H}_2\text{CO}$ ,  $\text{D} + \text{H}_2\text{CO}$  and  $\text{H} + \text{D}_2\text{CO}$  addition and abstraction reactions and the  $\text{D} + \text{D}_2\text{CO}$  addition reaction. The calculated vibrational adiabatic barriers for H and D addition to  $\text{H}_2\text{CO}$  (2318, 2204 K) are in reasonable agreement with estimates of  $2216 \pm 216$  and  $1957 \pm 144$  K from gas phase experiments combined with unimolecular rate theory (Oehlers et al. 2000). Likewise, the high-temperature gas phase results from Oehlers et al. (2000) show that abstraction is preferred over addition for the reaction of H and D atoms with  $\text{H}_2\text{CO}$ , in agreement with our calculated vibrational adiabatic barriers.

For all reactions studied, the activation barriers are between 1900 and 2500 K. With classical transition state theory (TST), this would give rise to very low reaction rates in molecular clouds, on the order of  $10^{-53}$ – $10^{-61}$   $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  at 20 K (Table 2). A simple Wigner tunnelling correction would only increase these reaction rates by 2 or 3 orders of magnitude at 20 K, which would still render these reactions effectively non-occurring. At these low temperatures the classical reaction rates depend strongly on the activation energies according to the Arrhenius exp ( $-V_{\text{ad}}^*/T$ ) behaviour. The lower

**Table 1.** Calculated vibrational adiabatic barriers  $V_{\text{ad}}^*$  (K) for gas phase addition (add) and abstraction (abstr) reactions of hydrogen plus formaldehyde and isotopologues.

Atom	H	H	D	D	H	H	D
Molecule	$\text{H}_2\text{CO}$	$\text{H}_2\text{CO}$	$\text{H}_2\text{CO}$	$\text{H}_2\text{CO}$	$\text{D}_2\text{CO}$	$\text{D}_2\text{CO}$	$\text{D}_2\text{CO}$
Reaction	add	abstr	add	abstr	add	abstr	add
$V_{\text{ad}}^*$	2318	2234	2204	1935	2253	2499	2128

**Table 2.** Log of TST and HQTST reaction rate coefficients  $k$  at 20 K, cross over temperature  $T_c$  and fitted modified Arrhenius parameters  $\alpha(>T_c)$ ,  $\beta(>T_c)$ ,  $\gamma(>T_c)$ ,  $\alpha(\leq T_c)$ ,  $\beta(\leq T_c)$  and  $\gamma(\leq T_c)$  for gas phase addition (add) and abstraction (abstr) reactions of hydrogen or deuterium plus (deuterated) formaldehyde.  $\beta$  dimensionless,  $k$  in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $T_c$  and  $\gamma$  in K and  $\alpha$  in  $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Atom	H	H	D	D	H	H	D
Molecule	H <sub>2</sub> CO	H <sub>2</sub> CO	H <sub>2</sub> CO	H <sub>2</sub> CO	D <sub>2</sub> CO	D <sub>2</sub> CO	D <sub>2</sub> CO
Reaction	add	abstr	add	abstr	add	abstr	add
$\log k_{\text{TST}}^{20\text{K}}$	-60.7	-58.8	-58.6	-52.8	-59.2	-64.6	-57.0
$\log k_{\text{HQTST}}^{20\text{K}}$	-20.7	-19.1	-23.9	-21.4	-20.0	-20.4	-23.4
$T_c$	182	340	135	319	181	261	135
$\alpha(>T_c)$	139.1	33.83	108.2	23.92	180.1	270.7	127.1
$\beta(>T_c)$	1.819	2.733	1.630	2.654	1.800	1.124	1.683
$\gamma(>T_c)$	1371	498.1	1567	469.1	1378	1697	1505
$\alpha(\leq T_c)$	0.8461	3.384	0.4518	3.100	0.9238	0.3401	0.6364
$\beta(\leq T_c)$	8.695	6.826	11.47	8.606	8.635	8.078	11.19
$\gamma(\leq T_c)$	-166.8	-100.5	-182.1	-104.3	-198.3	-159.0	-184.3

activation energies for hydrogen abstraction from H<sub>2</sub>CO, make it faster than the addition of either H or D ( $Y = \text{H}$ ,  $X = \text{H}, \text{D}$ ). However, the C–D bond in D<sub>2</sub>CO is stronger and consequently, in the reaction of D<sub>2</sub>CO with H, addition is preferred over D abstraction. Since the abstraction reactions generally have higher cross over temperatures (Table 2) than the additions, tunnelling is more important and in the gas phase abstraction will likely still be favoured at low temperatures where tunnelling dominates.

The tunnelling correction automatically included in the HQTST rate coefficients renders them many orders of magnitude larger than the TST ones (Table 2). The addition of D atoms is markedly slower than any other reaction, because the reaction path mostly involves the motion of the D atom, which therefore tunnels less efficiently than any other reaction where motion of an H atom is involved (H addition, abstraction of an H by an H/D atom or abstraction of H/D by an H atom).

The low-temperature HQTST data points and high-temperature TST plus Wigner correction data points were fit separately above and below the  $T_c$  to the modified Arrhenius expression:

$$k = \alpha \left( \frac{T}{300} \right)^\beta e^{-(\gamma/T)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (3)$$

which is often employed in astrochemical reaction networks. The resulting modified Arrhenius parameters and the cross over temperature that separates the fits are reported in Table 2 alongside the HQTST rate coefficients and the classical TST results at 20 K. All correlation coefficients for the non-linear fits to the low-temperature HQTST data were  $>0.997$ , with an rms error of 0.3–0.9 per cent in  $\log k$ . However, because of the large  $\beta$  coefficient and negative  $\gamma$  arising from the fit below  $T_c$ , the rate expressions blow up at very low  $T$  and can therefore not be applied below the lowest data points included in the fit. Instead, in the 10–20 K temperature regime relevant for the ice chemistry in molecular clouds we suggest to use the 20 K HQTST data tabulated in Table 2, since 20 K is close enough to the deep tunnelling (temperature-independent rate coefficients) regime.

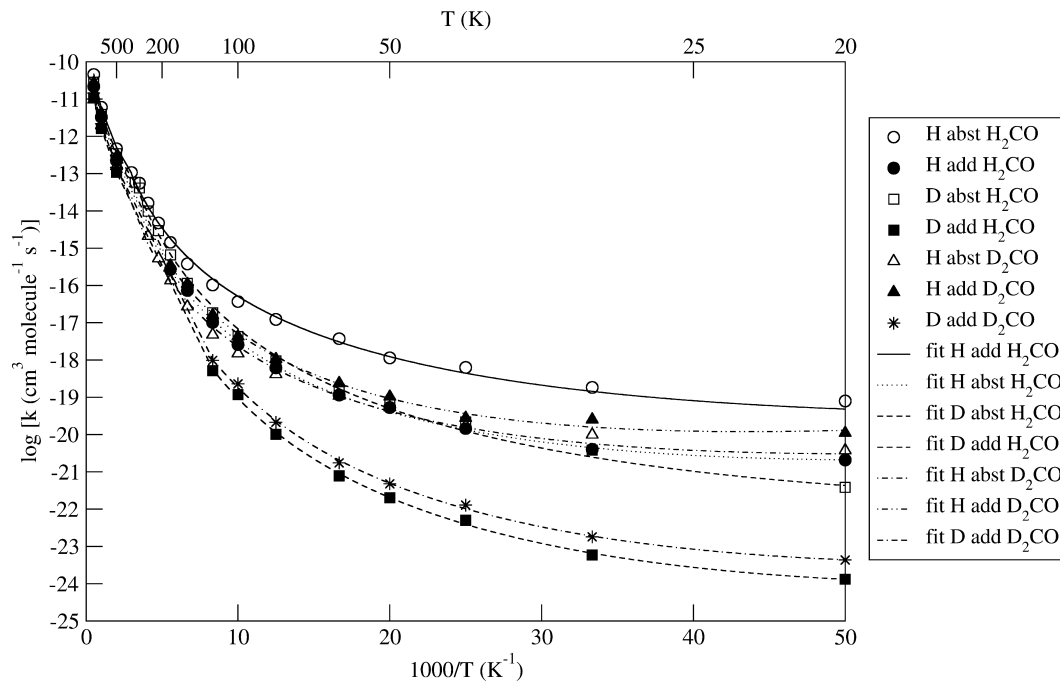
The calculated high-temperature TST plus Wigner (above  $T_c$ ) and low-temperature HQTST (below  $T_c$ ) bimolecular gas phase reaction rate coefficients at various temperatures for the hydrogen plus formaldehyde reactions (1) and (2) are depicted in Fig. 1 in a  $\log k$  versus  $1000/T$  plot together with the fits.

To compare our calculated results with recent experimental results of H and D atoms impinging on formaldehyde ices at low tem-

peratures, we initially focus on the calculated HQTST gas phase rate coefficients at 20 K. Hiraoka et al. (2005) reacted H and D atoms with a 10 K film of solid H<sub>2</sub>CO, finding evidence for abstraction (2) as well as addition reactions (1). For the D + H<sub>2</sub>CO reaction, abstraction is deduced to occur seven times faster than addition. Our gas phase HQTST results predict that the (2)/(1) branching ratio is much larger ( $\sim 300$ ) for this reaction, most likely resulting from the omission of the surface as well as the too low barrier predicted by DFT. The experiments further indicate that the H reaction is much faster than the D reaction, but again our gas phase HQTST results predict a much larger ( $\sim 200$ ) KIE than the solid state experiments ( $\sim 5$ ). A similar discrepancy between a large calculated gas phase KIE (300) and a small experimental solid state KIE ( $\sim 7$ ) has been observed for the addition of H and D to CO (Andersson et al. 2011). At the relatively high atomic flux in lab experiments, other effects such as H/D atom sticking, mobility and hydrogen molecule formation will affect the observed apparent KIE for the addition and abstraction reactions on the surface (see below).

In similar studies, Hidaka et al. (2006, 2009) reacted H with D<sub>2</sub>CO and D with H<sub>2</sub>CO at 15 K. Again both abstraction and addition are indicated from H–D exchange, with abstraction strongly favoured over addition for D + H<sub>2</sub>CO, while addition and abstraction are both observed for H + D<sub>2</sub>CO, with addition about twice as fast as abstraction. Our gas phase HQTST results are in much better quantitative agreement with these experimental results from Hidaka et al. The calculations also predict a strong ( $\sim 300:1$ ) preference for hydrogen abstraction in the D + H<sub>2</sub>CO reaction, and a 2.5:1 preference for H addition to D<sub>2</sub>CO over D abstraction (Table 2). In principle H–D exchange in formaldehyde could either take place via hydrogen abstraction, followed by addition, or by hydrogen addition, followed by abstraction. However, Hidaka et al. (2009) refuted the occurrence of either CH<sub>2</sub>DO or CHD<sub>2</sub>O radical in the D + H<sub>2</sub>CO and H + D<sub>2</sub>CO reactions, thus establishing H–D exchange in formaldehyde to occur via abstraction reactions (2).

To summarize, the low-temperature surface science experiments have established that H is preferentially abstracted from H<sub>2</sub>CO by both H and D atoms, while D atoms are not so easily abstracted from D<sub>2</sub>CO. H atoms add to both H<sub>2</sub>CO and D<sub>2</sub>CO at reasonable rates, while D addition is much slower. Our gas phase HQTST results are not in quantitative agreement with the results of Hiraoka et al. (2005), but are in good agreement with the experiments from Hidaka et al. (2006, 2009).



**Figure 1.** Log of calculated TST plus Wigner ( $T > T_c$ ) and QHTST ( $T < T_c$ ) gas phase reaction rate coefficients  $k$  for hydrogen plus formaldehyde addition reactions (closed symbols) and abstraction (open symbols) with various isotopologues plotted against  $1000/T$  and fits above and below  $T_c$  (lines) through the data points with equation (3).

#### 4 SURFACE EFFECTS

We have studied the effect of additional molecules on reactions (1) and (2) to mimic the effect of the solid state. Tunnelling calculations have been performed only down to 50 K because they become computationally very demanding and suffer from numerical noise at lower temperatures. However, the reaction rate coefficients down to 50 K are sufficient to demonstrate the effect of different surfaces.

The energetic effect of water molecules on reactions (1) and (2) was studied previously by an *ab initio* study (Woon 2002). A small reduction of the activation barrier was observed for the addition reaction (1), while the barrier for abstraction reaction (2) was increased significantly. Our DFT calculations predict the same effect on the barriers if two water molecules coordinate to formaldehyde: we predict that the barrier for addition is lowered by 130 K, while the barrier for abstraction is increased by 725 K. These effects are most likely electronic in origin: water stabilizes formaldehyde as well as the transition states (TSs) through dipolar interactions. However, the TS for H addition is more polar ( $\mu = 2.6$  D), while the TS for H abstraction is less polar ( $\mu = 1.9$  D) than formaldehyde ( $\mu = 2.5$  D). Thus, the addition TS is slightly more stabilized than formaldehyde, lowering the barrier, while the abstraction TS is less stabilized than formaldehyde, resulting in a larger barrier.

The combined effect of lowering of the addition barrier and increasing the abstraction barrier by the two water molecules, makes addition more favourable than abstraction for the  $\text{H} + (\text{H}_2\text{CO})(\text{H}_2\text{O})_2$  reaction at all temperatures, as opposed to the gas phase (Fig. 2). We have also calculated the  $\text{D} + (\text{H}_2\text{CO})(\text{H}_2\text{O})_2$  reaction rates and found similar trends in the isotope effects as in the gas phase for both addition and abstraction reactions. Our calculations thus predict that for the reaction of hydrogen atoms with

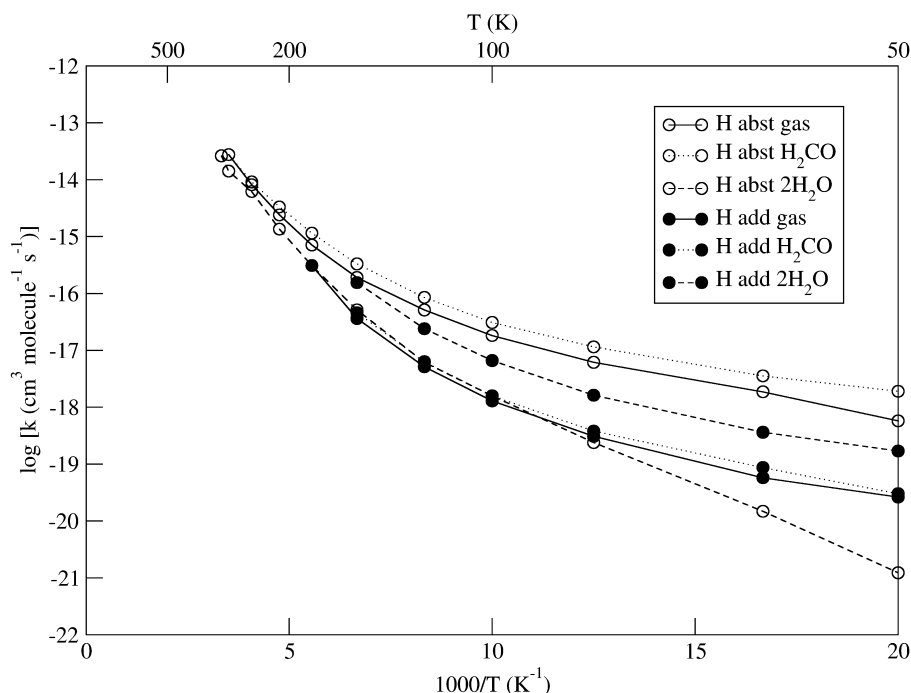
formaldehyde in water-rich ices addition is preferred over abstraction, thus making D enrichment via abstraction–addition reactions less efficient.

The experiments by Hiraoka et al. (2005) and Hidaka et al. (2006, 2009), however, are performed on a solid film of formaldehyde. We thus also investigated the effect of another formaldehyde molecule on reactions (1) and (2). The second formaldehyde has a much smaller effect on the activation barriers than water, with both barriers slightly increased [(1): 2346 K, (2): 2318 K] with respect to the gas phase. Consequently, an additional formaldehyde molecule does not affect the preference of H abstraction over addition (Fig. 2) and the gas phase results for the reaction coefficients for reactions (1) and (2) are expected to parallel those in a formaldehyde ice.

However, in the lab experiments as well as in the ISM, the surface can affect the apparent reactivity in several ways. Most noticeably, D binds more strongly to ices than H and therefore has longer residence time (Buch & Zhang 1991; Lipshtat, Biham & Herbst 2004) and thus a higher chance to react. Through the same effect, possibly augmented by a tunnel effect, D atoms diffuse slower on and in the ice. In the lab experiments the hydrogen fluxes are about eight orders of magnitude larger than in molecular clouds, and consequently the majority of the hydrogen atoms dimerise (Fuchs et al. 2009). To comprehensively model the reactivity of H and D atoms with a formaldehyde ice both in lab and in space, all these effects should be taken into account with a kinetic Monte Carlo method (Fuchs et al. 2009).

#### 5 DISCUSSION

In the gas phase and in solid formaldehyde H atoms are preferentially abstracted from  $\text{H}_2\text{CO}$  by either D or H, which could be an efficient route for deuterium enrichment in both interstellar formaldehyde and methanol. Conversely, H atoms preferentially



**Figure 2.** Log of calculated HQTST reaction rate coefficients  $k$  for hydrogen plus formaldehyde addition reactions (closed symbols) and abstraction (open symbols) in the gas phase (solid lines), with an additional formaldehyde (dotted lines), and with two water molecules (dashed lines) plotted against  $1000/T$ . Lines are to guide the eye only.

add to  $D_2CO$  so that once deuterated formaldehyde is formed it will likely continue to react to form deuterated methanol. When the reacting formaldehyde is surrounded by two water molecules, however, addition is preferred over abstraction, and consequently deuterium enrichment via H–D exchange in formaldehyde is predicted to be less efficient in water-rich (polar) ices.

Any H atoms attached to the C atom in methanol can be further exchanged for D atoms but not in the OH group (Nagaoka et al. 2005). However, OD can be exchanged for H atoms via protic exchange with  $H_2O$  in the melting and evaporating ice in the warm-up phase near young stellar objects (Ratajczak et al. 2009). The two combined mechanisms of H–D exchange via abstraction of H atoms but not D atoms from formaldehyde and methanol and the protic exchange of OD for OH in the melting ice could explain why formaldehyde and interstellar methanol are heavily deuterated but relatively less so in the alcoholic group of methanol.

We fitted our gas phase rate coefficients between 20 and 1000 K for the abstraction and addition reactions to the standard modified Arrhenius form that is incorporated in astrochemical reaction networks and kinetic Monte Carlo codes. Because of the large tunnelling effect below  $T_c$  we fitted the low and high temperature separately. The low- $T$  parameters are quite different from parameters usually employed and cannot be applied below the fitted temperature range. We suggest employing the tabulated 20 K HQTST rate coefficients for any temperature of 20 K and below. With these phenomenological rate parameters for the hydrogen plus formaldehyde reaction utilized in a reaction network, the effects of adsorption, desorption and competitive reactions can be incorporated to model laboratory (relatively high pressures and shorter time scales) and astrochemical conditions. These may lead to a better understanding of the actual processes involved in the interstellar deuterium fractionation in formaldehyde and methanol. The future computational

study of H–D abstraction rates in methanol will further elaborate these reaction rate networks.

## ACKNOWLEDGMENTS

This work is financially supported by the Netherlands Organisation for Scientific Research (NWO) through a VENI fellowship (700.58.404). Johannes Kaestner is thanked for the direct dynamics implementation of HQTST in CHEMSHELL. The referee is thanked for useful and constructive comments.

## REFERENCES

- Andersson S., Nyman G., Arnaldsson A., Manthe U., Jónsson H., 2009, *J. Phys. Chemistry A*, 113, 4468
- Andersson S., Goumans T. P. M., Arnaldsson A., 2011, *Chemical Phys. Lett.*, submitted
- Arnaldsson A., 2007, PhD thesis, Univ. Washington
- Boogert A. C. A. et al., 2008, *ApJ*, 678, 985
- Buch V., Zhang Q., 1991, *ApJ*, 379, 647
- Bylaska E. J. et al., 2007, NWChem, A Computational Chemistry Package for Parallel Computers, version 5.1. Pacific Northwest National Laboratory, Richland, WA
- Caselli P., Stantcheva T., Shalabiea O., Shematovich V. I., Herbst E., 2002, *Planet. Space Sci.*, 50, 1257
- Frisch M. J. et al., 2004, Gaussian 03, revision D.01. Gaussian, Inc., Wallington
- Fuchs G. W., Cuppen H. M., Ioppolo S., Romanzin C., Bisschop S. E., Andersson S., van Dishoeck E. F., Linnartz H., 2009, *A&A*, 505, 629
- Garrod R., Park I. H., Caselli P., Herbst E., 2006, *Faraday Discussions*, 133, 51
- Geppert W. D. et al., 2006, *Faraday Discussions*, 133, 177
- Gibb E. L., Whittet D. C. B., Boogert A. C. A., Tielens A., 2004, *ApJS*, 151, 35

- Goumans T. P. M., Andersson S., 2010, *MNRAS*, 406, 2213
- Goumans T. P. M., Kaestner J., 2010, *Angewandte Chemie Int. Ed.*, 49, 7350
- Hasegawa T. I., Herbst E., Leung C. M., 1992, *ApJS*, 82, 167
- Herbst E., van Dishoeck E. F., 2009, *ARA&A*, 47, 427
- Hidaka H., Watanabe N., Kouchi A., 2006, in Kaiser R. I., Bernath P., Mebel A. M., Osamura Y., Petrie S., eds, *AIP Conf. Ser. Vol. 855, Astrochemistry: From Laboratory Studies to Astronomical Observations*. Am. Inst. Phys., Melville, NY, p. 107
- Hidaka H., Watanabe M., Kouchi A., Watanabe N., 2009, *ApJ*, 702, 291
- Hiraoka K., Ohashi N., Kihara Y., Yamamoto K., Sato T., Yamashita A., 1994, *Chemical Phys. Lett.*, 229, 408
- Hiraoka K. et al., 2005, *ApJ*, 620, 542
- Krishtalik L. I., 2000, *Biochimica Biophysica Acta*, 1458, 6
- Lipshtat A., Biham O., Herbst E., 2004, *MNRAS*, 348, 1055
- Nagaoka A., Watanabe N., Kouchi A., 2005, *ApJ*, 624, L29
- Oehlers C., Wagner H. G., Ziemer H., Temps F., Dobe S., 2000, *J. Phys. Chemistry A*, 104, 10500
- Parise B., Castets A., Herbst E., Caux E., Ceccarelli C., Mukhopadhyay I., Tielens A., 2004, *A&A*, 416, 159
- Parise B., Ceccarelli C., Tielens A., Castets A., Caux E., Lefloch B., Maret S., 2006, *A&A*, 453, 949
- Pirim C., Krim L., Laffon C., Parent P., Pauzat F., Pilme J., Ellinger Y., 2010, *J. Phys. Chemistry A*, 114, 3320
- Ratajczak A., Quirico E., Faure A., Schmitt B., Ceccarelli C., 2009, *A&A*, 496, L21
- Roberts H., Herbst E., Millar T. J., 2004, *A&A*, 424, 905
- Tielens A., Hagen W., 1982, *A&A*, 114, 245
- Watanabe N., Nagaoka A., Shiraki T., Kouchi A., 2004, *ApJ*, 616, 638
- Weber A. S., Hodyss R., Johnson P. V., Willacy K., Kanik I., 2009, *ApJ*, 703, 1030
- Werner H. J. et al., 2008, *MOLPRO*, version 2008.1. A package of ab initio programs. Univ. College Cardiff Consultants, Ltd, Cardiff
- Wigner E., 1938, *Trans. Faraday Soc.*, 34, 29
- Woon D. E., 2002, *ApJ*, 569, 541
- Zhao Y., Truhlar D. G., 2005, *J. Phys. Chemistry A*, 109, 5656

This paper has been typeset from a Microsoft Word file prepared by the author.