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Gas phase ^{1}H NMR studies and kinetic modeling of dihydrogen isotope equilibration catalyzed by Ru-nanoparticles under normal conditions: dissociative vs. associative exchange

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CONTENTS

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7cp

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I. Theoretical Section

We consider the isotopic equilibration process of gaseous dihydrogen isotopologues H_2, HD and D_2 in contact with a solid adsorbent, e.g. a metal surface containing hydrogen isotopes in surface sites. We are interested in the time evolution of the concentrations of all species. As mentioned in the introduction, we consider two different mechanisms, the *dissociative exchange* and the *associative exchange* as illustrated in Figure 1.

A. Dissociative exchange

The main processes occurring in this system is the *dissociative adsorption* of dihydrogen and the reverse reaction, the *associative desorption*. We include the possibility of kinetic and equilibrium isotope effects of the adsorption/desorption as well as the well-known non-statistical distribution of dihydrogen isotopologues in the gas phase. The differential equations obtained can be used to simulate numerically experimental kinetic data and to extract the desired rate constants. If not otherwise mentioned, we follow in this section the nomenclature of usual surface science as described by Chorkendorff et al.[1]

1. Dissociative adsorption of H_2. Adsorption isotherm

The gas phase – surface hydrogen exchange reaction in Figure 1 can be written in the simplified form

$$\mathrm{H}_2 + 2* \underset{k_d^{\mathrm{HH}}}{\overset{k_a^{\mathrm{HH}}}{\rightleftarrows}} 2\,\mathrm{H}*\,, \qquad \backslash*$$

MERGEFORMAT (1)

where * represents the free hydrogen binding sites and H* surface bound hydrogen. Only a single type of adsorption sites is taken into account. k_a^{HH} and k_d^{HH} are the rate constants of dihydrogen adsorption and desorption.

In order to set up the rate law let us define the following quantities. Let M represent the total number of adsorption sites, V the total volume, assumed to be equal to the volume of the gas phase and $N = n_{\mathrm{H2}}$ the total number of dihydrogen molecules in the gas phase at equilibrium. $c_{\mathrm{H2}} = n_{\mathrm{H2}}/V$ represents then the corresponding concentration of H_2 in the gas phase, and p_{H2} the vapor pressure of H_2. $n_{\mathrm{H}*}$ represents the number of occupied adsorption sites, $c_{\mathrm{H}*} = n_{\mathrm{H}*}/V$ the corresponding concentration, and $c_* = n_*/V$ the concentration of the unoccupied sites.

Let $\theta_{\mathrm{H}} = \frac{n_{\mathrm{H}*}}{M}$ be the fraction of adsorption sites covered by H and $\theta_* = (1-\theta_{\mathrm{H}})$ be the fraction of unoccupied adsorption sites. Assuming that the diffusion of dihydrogen in the gas phase is fast, the rate law of the above reaction can be expressed as

$$\frac{dc_{\mathrm{H2}}}{dt} = -k_a^{\mathrm{HH}} p_{\mathrm{H2}} c_* \theta_* + k_d^{\mathrm{HH}} c_{\mathrm{H}*} \theta_{\mathrm{H}} = -\frac{1}{2}\frac{dc_{\mathrm{H}*}}{dt}\,, \qquad \backslash*$$

MERGEFORMAT (2)

where the "mean field" approximation is used.[1] The latter states that the reaction rate of adsorption is proportional to the concentration of the unoccupied sites $c_* = M\theta_* / V = M(1-\theta_\mathrm{H})/V$, times the probability $\theta_* = (1-\theta_\mathrm{H})$ to find an adjacent site also unoccupied. A similar argument holds for the desorption rate. It follows that

$$\frac{dc_\mathrm{H2}}{dt} = -k_a^\mathrm{HH} p_\mathrm{H2} \frac{M}{V}(1-\theta_\mathrm{H})^2 + k_d^\mathrm{HH} \frac{M}{V} \theta_\mathrm{H}{}^2 = -\frac{1}{2}\frac{M}{V}\frac{d\theta_\mathrm{H}}{dt},$$

* MERGEFORMAT (3)

and that

$$V\frac{dc_\mathrm{H2}}{dt} = \frac{dn_\mathrm{H2}}{dt} = -k_a^\mathrm{HH} p_\mathrm{H2} M(1-\theta_\mathrm{H})^2 + k_d^\mathrm{HH} M \theta_\mathrm{H}{}^2 = -\frac{1}{2} M \frac{d\theta_\mathrm{H}}{dt}.$$

* MERGEFORMAT (4)

This equation corresponds to eq (124) in Ref 1. We note that in this reference the factor of ½ is not included. At equilibrium, the reaction rate is zero, leading to the pressure dependent equilibrium constants of adsorption and desorption

$$K_a^\mathrm{HH} = \frac{1}{K_d^\mathrm{HH}} = \frac{k_a^\mathrm{HH}}{k_d^\mathrm{HH}} = \frac{\theta_\mathrm{H}^{\infty 2}}{p_\mathrm{H2}(1-\theta_\mathrm{H}^{\infty 2})^2}.$$

* MERGEFORMAT (5)

Here, the infinity symbol has been used to characterize the equilibrium. It follows that

$$\theta_\mathrm{H}^\infty = \frac{\sqrt{K_a^\mathrm{HH} p_\mathrm{H2}}}{1+\sqrt{K_a^\mathrm{HH} p_\mathrm{H2}}}.$$

* MERGEFORMAT (6)

Eq * MERGEFORMAT (6) represents the Langmuir isotherm of dissociative adsorption. For the case where $K_{\mathrm{H}_2} p_{\mathrm{H}_2} >> 1$, it follows that θ_H^∞ becomes unity and that θ_*^∞ vanishes. Assuming the validity of the ideal gas law as it follows from Eq * MERGEFORMAT (3) that

$$\frac{dn_\mathrm{H2}}{dt} = -\frac{k_a^\mathrm{HH} RT}{V} n_\mathrm{H2} M(1-\theta_\mathrm{H})^2 + k_d^\mathrm{HH} M \theta_\mathrm{H}{}^2 = -\frac{1}{2} M \frac{d\theta_\mathrm{H}}{dt}.$$

* MERGEFORMAT (7)

The term *RT/V* can be included into the rate constant, *i.e.* one can write

$$\begin{aligned}\frac{dn_\mathrm{H2}}{dt} &= -\frac{1}{2}\frac{dn_\mathrm{H*}}{dt} = -\left|\frac{dn_\mathrm{H2 \to H*H*}}{dt}\right| + \left|\frac{dn_\mathrm{H*H* \to H2}}{dt}\right| \\ &= -k_a^\mathrm{HH} n_\mathrm{H2} M(1-\theta_\mathrm{H})^2 + k_d^\mathrm{HH} M \theta_\mathrm{H}{}^2 \;= -k_a^\mathrm{HH} n_\mathrm{H2} M \theta_*{}^2 + k_d^\mathrm{HH} M \left(\frac{n_\mathrm{H*}}{M}\right)^2,\end{aligned}$$

* MERGEFORMAT (8)

where $\frac{dn_\mathrm{H2 \to H*H*}}{dt}$ and $\frac{dn_\mathrm{H*H* \to H2}}{dt}$ represent the number of H_2 molecules which adsorb and desorb per second.

At equilibrium,

$$\frac{dn_{\mathrm{H*H*}\rightarrow\mathrm{H2}}}{dt}=\frac{dn_{\mathrm{H2}\rightarrow\mathrm{H*H*}}}{dt}=k_a^{\mathrm{HH}}n_{\mathrm{H2}}M\theta_*^{\infty 2}=k_d^{\mathrm{HH}}M\left(\frac{n_{\mathrm{H*}}^{\infty}}{M}\right)^2$$ * MERGEFORMAT (9)

from which it follows in analogy to eq * MERGEFORMAT (5) for the mole-dependent equilibrium constants of adsorption or desorption that

$$K_a^{\mathrm{HH}}=\frac{1}{K_d^{\mathrm{HH}}}=\frac{k_a^{\mathrm{HH}}}{k_d^{\mathrm{HH}}}=\frac{\theta_{\mathrm{H}}^{\infty 2}}{n_{\mathrm{H2}}(1-\theta_{\mathrm{H}}^{\infty 2})^2}\,.$$ * MERGEFORMAT (10)

In the following, we will only use the latter constants.

2. H/D Isotope Exchange

In this section, we elucidate the time evolution of a system in which the adsorption/desorption equilibrium of dihydrogen with surface sites is established but not the isotopic equilibrium in the presence of deuterium. Again, it is assumed that gas phase diffusion does not need to be taken into account. We consider the presence of the following isotopic reactions

$$\mathrm{H_2} + 2\,{*} \underset{k_d^{\mathrm{HH}}}{\overset{k_a^{\mathrm{HH}}}{\rightleftarrows}} 2\,\mathrm{H}{*}\,,$$

(*
MERGEFORMAT 11a)

$$\mathrm{HD} + 2\,{*} \underset{k_d^{\mathrm{HD}}}{\overset{k_a^{\mathrm{HD}}}{\rightleftarrows}} \mathrm{H}{*} + \mathrm{D}{*}\,,$$

(*
MERGEFORMAT 11b)

$$\mathrm{D_2} + 2\,{*} \underset{k_d^{\mathrm{DD}}}{\overset{k_a^{\mathrm{DD}}}{\rightleftarrows}} 2\,\mathrm{D}{*}\,.$$

(*
MERGEFORMAT 11c)

The asterisk * indicates again a non-occupied surface site for H or D, and H* and D* a surface hydrogen or deuterium. In the following, we use "L" as general symbol for H and D. $N = n_{\mathrm{H2}} + n_{\mathrm{HD}} + n_{\mathrm{D2}}$ represents now the total number of dihydrogen isotopologues in the gas phase. It is convenient to define the isotope fractions for the adsorption sites as

$$x_{\mathrm{D}*} = \frac{n_{\mathrm{D}*}}{n_{\mathrm{H}*} + n_{\mathrm{D}*}} = \frac{n_{\mathrm{D}*}}{(\theta_{\mathrm{H}} + \theta_{\mathrm{D}})M},\ x_{\mathrm{H}*} = (1 - x_{\mathrm{D}*}) = \frac{n_{\mathrm{H}*}}{(\theta_{\mathrm{H}} + \theta_{\mathrm{D}})M}$$

*
MERGEFORMAT (12)

and for the gas phase as

$$x_{\mathrm{D}} = \frac{n_{\mathrm{HD}} + 2n_{\mathrm{D2}}}{2N},\ 1\text{-}x_{\mathrm{D}} = x_{\mathrm{H}} = \frac{2n_{\mathrm{H2}} + n_{\mathrm{HD}}}{2N}\,.$$

*
MERGEFORMAT (13)

The total deuterium fraction of a sample is then given by

$$X_{\mathrm{D}} = \frac{n_{\mathrm{HD}} + 2n_{\mathrm{D2}} + n_{\mathrm{D}*}}{2n_{\mathrm{H2}} + 2n_{\mathrm{HD}} + 2n_{\mathrm{D2}} + n_{\mathrm{H}*} + n_{\mathrm{D}*}} = \frac{n_{\mathrm{HD}} + 2n_{\mathrm{D2}} + n_{\mathrm{D}*}}{2N + (\theta_{\mathrm{H}} + \theta_{\mathrm{D}})M} = \frac{2Nx_{\mathrm{D}} + x_{\mathrm{D}*}M(\theta_{\mathrm{H}} + \theta_{\mathrm{D}})}{2N + M}\,.$$

*
MERGEFORMAT (14)

In analogy to eq * MERGEFORMAT (8), the rates of desorption of the dihydrogen isotopologues are given by

$$\frac{dn_{\mathrm{H2}}}{dt} = -\left|\frac{dn_{\mathrm{H2}\to\mathrm{H*H*}}}{dt}\right| + \left|\frac{dn_{\mathrm{H*H*}\to\mathrm{H2}}}{dt}\right|,$$

(*
MERGEFORMAT 15a)

$$\frac{dn_{\mathrm{HD}}}{dt} = -\left|\frac{dn_{\mathrm{HD}\to\mathrm{H*D*}}}{dt}\right| + \left|\frac{dn_{\mathrm{H*D*}\to\mathrm{HD}}}{dt},\right|$$

(*
MERGEFORMAT 15b)

$$\frac{dn_{\mathrm{D2}}}{dt} = -\left|\frac{dn_{\mathrm{HD}\to\mathrm{H*D*}}}{dt}\right| + \left|\frac{dn_{\mathrm{D*D*}\to\mathrm{D2}}}{dt}\right|,$$ (*

MERGEFORMAT 15c)

$$\frac{dn_{\mathrm{H*}}}{dt} = M\frac{dx_{\mathrm{H*}}}{dt} = -2\frac{dn_{\mathrm{H2}}}{dt} - \frac{dn_{\mathrm{HD}}}{dt},$$ (*

MERGEFORMAT 15d)

$$\frac{dn_{\mathrm{D*}}}{dt} = M\frac{dx_{\mathrm{D*}}}{dt} = -\frac{dn_{\mathrm{HD}}}{dt} - 2\frac{dn_{\mathrm{D2}}}{dt},$$ (*

MERGEFORMAT 15e)

where

$$\frac{dn_{\mathrm{H2}\to\mathrm{H*H*}}}{dt} = k_a^{\mathrm{HH}}\left(\frac{n_{\mathrm{H2}}}{N}\right)NM\theta_*^2,$$ (*

MERGEFORMAT 16a)

$$\frac{dn_{\mathrm{HD}\to\mathrm{H*D*}}}{dt} = k_a^{\mathrm{HD}}\left(\frac{n_{\mathrm{HD}}}{N}\right)NM\theta_*^2,$$ (*

MERGEFORMAT 16b)

$$\frac{dn_{\mathrm{D2}\to\mathrm{D*D*}}}{dt} = k_a^{\mathrm{DD}}\left(\frac{n_{\mathrm{D2}}}{N}\right)NM\theta_*^2,$$ (*

MERGEFORMAT 16c)

$$\frac{dn_{\mathrm{H*H*}\to\mathrm{H2}}}{dt} = k_d^{\mathrm{HH}}\left(\frac{n_{\mathrm{H*}}}{M}\right)^2 M = k_d^{\mathrm{HH}}\left(1-x_{\mathrm{D*}}\right)^2 M,$$ (*

MERGEFORMAT 16d)

$$\frac{dn_{\mathrm{H*D*}\to\mathrm{HD}}}{dt} = 2k_d^{\mathrm{HD}}\left(\frac{n_{\mathrm{H*}}}{M}\right)\left(\frac{n_{\mathrm{D*}}}{M}\right)M = 2k_d^{\mathrm{HD}}x_{\mathrm{D*}}\left(1-x_{\mathrm{D*}}\right)M,$$ (*

MERGEFORMAT 16e)

$$\frac{dn_{\mathrm{D*D*}\to\mathrm{DD}}}{dt} = k_d^{\mathrm{DD}}\left(\frac{n_{\mathrm{D*}}}{M}\right)^2 M = k_d^{\mathrm{DD}}{x_{\mathrm{D*}}}^2 M,$$ (*

MERGEFORMAT 16f)

The total rates of adsorption and desorption are given by

$$\frac{dN_{\mathrm{LL}\to\mathrm{L*L*}}}{dt} = \frac{dn_{\mathrm{H2}\to\mathrm{H*H*}}}{dt} + \frac{dn_{\mathrm{HD}\to\mathrm{H*D*}}}{dt} + \frac{dn_{\mathrm{D2}\to\mathrm{D*D*}}}{dt},$$ (*

MERGEFORMAT 17a)

$$\frac{dN_{\mathrm{L*L*}\to\mathrm{LL}}}{dt} = \frac{dn_{\mathrm{H*H*}\to\mathrm{H2}}}{dt} + \frac{dn_{\mathrm{H*D*}\to\mathrm{HD}}}{dt} + \frac{dn_{\mathrm{D*D*}\to\mathrm{DD}}}{dt}.$$ (*

MERGEFORMAT 17b)

By combination of eqs (* MERGEFORMAT 16) and (* MERGEFORMAT 17) it follows that

$$\frac{dn_{\mathrm{H2}\to\mathrm{H^*H^*}}}{dt}=\frac{n_{\mathrm{H2}}}{n_{\mathrm{H2}}+\frac{k_a^{\mathrm{HD}}}{k_a^{\mathrm{HH}}}n_{\mathrm{HD}}+\frac{k_a^{\mathrm{DD}}}{k_a^{\mathrm{HH}}}n_{\mathrm{D2}}}\frac{dN_{\mathrm{LL}\to\mathrm{L^*L^*}}}{dt},$$

(*

MERGEFORMAT 18a)

$$\frac{dn_{\mathrm{HD}\to\mathrm{H^*D^*}}}{dt}=\frac{n_{\mathrm{HD}}}{\frac{k_a^{\mathrm{HH}}}{k_a^{\mathrm{HD}}}n_{\mathrm{H2}}+n_{\mathrm{HD}}+\frac{k_a^{\mathrm{DD}}}{k_a^{\mathrm{HD}}}n_{\mathrm{D2}}}\frac{dN_{\mathrm{LL}\to\mathrm{L^*L^*}}}{dt},$$

(*

MERGEFORMAT 18b)

$$\frac{dn_{\mathrm{D2}\to\mathrm{D^*D^*}}}{dt}=\frac{n_{\mathrm{D2}}}{\frac{k_a^{\mathrm{HH}}}{k_a^{\mathrm{DD}}}n_{\mathrm{H2}}+\frac{k_a^{\mathrm{HD}}}{k_a^{\mathrm{DD}}}n_{\mathrm{HD}}+n_{\mathrm{D2}}}\frac{dN_{\mathrm{LL}\to\mathrm{L^*L^*}}}{dt}.$$

(*

MERGEFORMAT 18c)

The equilibrium constants of desorption and adsorption can be expressed as

$$K_d^{\mathrm{HH}}=\frac{k_d^{\mathrm{HH}}}{k_a^{\mathrm{HH}}}=\frac{1}{K_a^{\mathrm{HH}}}=\frac{n_{\mathrm{H2}}^{\infty}\theta_*^{\infty 2}}{\left(\frac{n_{\mathrm{H^*}}^{\infty 2}}{M}\right)^2},$$

(*

MERGEFORMAT 19a)

$$K_d^{\mathrm{HD}}=\frac{k_d^{\mathrm{HD}}}{k_a^{\mathrm{HD}}}=\frac{1}{K_a^{\mathrm{HD}}}=\frac{n_{\mathrm{HD}}^{\infty}\theta_*^{2}}{2\left(\frac{n_{\mathrm{H^*}}^{\infty}}{M}\right)\left(\frac{n_{\mathrm{D^*}}^{\infty}}{M}\right)},$$

(*

MERGEFORMAT 19b)

$$K_d^{\mathrm{DD}}=\frac{k_d^{\mathrm{DD}}}{k_a^{\mathrm{DD}}}=\frac{1}{K_a^{\mathrm{DD}}}=\frac{n_{\mathrm{D2}}^{\infty}\theta_*^{2}}{\left(\frac{n_{\mathrm{D^*}}^{\infty}}{M}\right)^2}.$$

(*

MERGEFORMAT 19c)

In the following, we will assume that the high pressure limit where $\theta_{\mathrm{H}}+\theta_{\mathrm{D}}\approx 1$ is realized, *i.e.*

$$x_{\mathrm{D^*}}=\frac{n_{\mathrm{D^*}}}{M},\ x_{\mathrm{H^*}}=\frac{n_{\mathrm{H^*}}}{M}=1-x_{\mathrm{D^*}}$$

*

MERGEFORMAT (20)

and that the total number of hydrogen molecules in the gas phase and in the surface sites is constant. It follows then from eqs (* MERGEFORMAT 16d) to (* MERGEFORMAT 16f) that

$$\frac{dN_{\mathrm{L^*L^*}\to\mathrm{LL}}}{dt}=\frac{dN_{\mathrm{LL}\to\mathrm{L^*L^*}}}{dt}=k_d^{\mathrm{HH}}\left(1-x_{\mathrm{D^*}}\right)^2M+2k_d^{\mathrm{HD}}x_{\mathrm{D^*}}\left(1-x_{\mathrm{D^*}}\right)M+k_d^{\mathrm{DD}}{x_{\mathrm{D^*}}}^2M$$

*

MERGEFORMAT (21)

As $k_a^{\mathrm{LL}}=k_d^{\mathrm{LL}}/K_d^{\mathrm{LL}}$ we can rewrite eqs (* MERGEFORMAT 18) and * MERGEFORMAT (21) as

$$\frac{dn_{\mathrm{H2\to H^*H^*}}}{dt}=\frac{n_{\mathrm{H2}}}{n_{\mathrm{H2}}+\frac{K_d^{\mathrm{HH}}k_d^{\mathrm{HD}}}{K_d^{\mathrm{HD}}k_d^{\mathrm{HH}}}n_{\mathrm{HD}}+\frac{K_d^{\mathrm{HH}}k_d^{\mathrm{DD}}}{K_d^{\mathrm{DD}}k_d^{\mathrm{HH}}}n_{\mathrm{D2}}}\frac{dN_{\mathrm{LL\to L^*L^*}}}{dt},$$ (*

MERGEFORMAT 22a)

$$\frac{dn_{\mathrm{HD\to H^*D^*}}}{dt}=\frac{n_{\mathrm{HD}}}{\frac{K_d^{\mathrm{HD}}k_d^{\mathrm{HH}}}{K_d^{\mathrm{HH}}k_d^{\mathrm{HD}}}n_{\mathrm{H2}}+n_{\mathrm{HD}}+\frac{K_d^{\mathrm{HD}}k_d^{\mathrm{DD}}}{K_d^{\mathrm{DD}}k_d^{\mathrm{HD}}}n_{\mathrm{D2}}}\frac{dN_{\mathrm{LL\to L^*L^*}}}{dt},$$ (*

MERGEFORMAT 22b)

$$\frac{dn_{\mathrm{D2\to D^*D^*}}}{dt}=\frac{n_{\mathrm{D2}}}{\frac{K_a^{\mathrm{DD}}k_d^{\mathrm{HH}}}{K_d^{\mathrm{HH}}k_d^{\mathrm{DD}}}n_{\mathrm{H2}}+\frac{K_d^{\mathrm{DD}}k_d^{\mathrm{HD}}}{K_a^{\mathrm{HD}}k_d^{\mathrm{DD}}}n_{\mathrm{HD}}+n_{\mathrm{D2}}}\frac{dN_{\mathrm{LL\to L^*L^*}}}{dt},$$ (*

MERGEFORMAT 22c)

$$\frac{dn_{\mathrm{H^*H^*\to H2}}}{dt}=k_d^{\mathrm{HH}}\left(1-x_{\mathrm{D^*}}\right)^2M,$$ (*

MERGEFORMAT 22d)

$$\frac{dn_{\mathrm{H^*D^*\to HD}}}{dt}=2k_d^{\mathrm{HD}}x_{\mathrm{D^*}}\left(1-x_{\mathrm{D^*}}\right)M,$$ (*

MERGEFORMAT 22e)

$$\frac{dn_{\mathrm{D^*D^*\to DD}}}{dt}=k_d^{\mathrm{DD}}x_{\mathrm{D^*}}{}^2M,$$ (*

MERGEFORMAT 22f)

$$\frac{dN_{\mathrm{LL\to L^*L^*}}}{dt}=\frac{dN_{\mathrm{L^*L^*\to LL}}}{dt}=k_d^{\mathrm{HH}}\left(1-x_{\mathrm{D^*}}\right)^2M+2k_d^{\mathrm{HD}}x_{\mathrm{D^*}}\left(1-x_{\mathrm{D^*}}\right)M+k_d^{\mathrm{DD}}x_{\mathrm{D^*}}{}^2M.$$ (*

MERGEFORMAT 22g)

where only rate and equilibrium constants of desorption are included. Using eq (* MERGEFORMAT 19) one can define the "fractionation factors" of dihydrogen desorption

$$\phi_1=\frac{K_d^{\mathrm{HD}}}{K_d^{\mathrm{HH}}}=\frac{K_a^{\mathrm{HH}}}{K_a^{\mathrm{HD}}}=\frac{n_{\mathrm{HD}}n_{\mathrm{H^*}}}{2n_{\mathrm{H2}}n_{\mathrm{D^*}}},\ \ \phi_2=\frac{K_d^{\mathrm{DD}}}{K_d^{\mathrm{HD}}}=\frac{K_a^{\mathrm{HD}}}{K_a^{\mathrm{DD}}}=\frac{2n_{\mathrm{D2}}n_{\mathrm{H^*}}}{n_{\mathrm{HD}}n_{\mathrm{D^*}}},\ \ \frac{K_d^{\mathrm{DD}}}{K_d^{\mathrm{HH}}}=\frac{K_a^{\mathrm{HH}}}{K_a^{\mathrm{DD}}}=\phi_1\phi_2=\frac{n_{\mathrm{D2}}n_{\mathrm{H^*}}{}^2}{n_{\mathrm{H2}}n_{\mathrm{D^*}}{}^2}.$$ *

MERGEFORMAT (23)

If $\phi_1>1$ or $\phi_2>1$, D enriches in the gas phase, and if $\phi_1<1$ or $\phi_2<1$, D enriches in the surface. However, the two fractionation factors are not independent of each other because of the isotopic equilibrium in the gas phase

$$\mathrm{H_2+D_2}\rightleftarrows\mathrm{2\ HD}$$ *

MERGEFORMAT (24)

characterized by the equilibrium constant

$$K_{gas}=K=\frac{n_{\mathrm{HD}}n_{\mathrm{HD}}}{n_{\mathrm{H2}}n_{\mathrm{D2}}}=3.25\ \text{at room temperature.}$$ *

MERGEFORMAT (25)

This value was calculated using isotope theory[2] and has been confirmed experimentally.[3] It means that there is less HD in the gas phase than expected for a statistical distribution where $K = 4$.

By combination with eq * MERGEFORMAT (23) it follows that

$$K_{gas} = \frac{4\left(K_d^{\mathrm{HD}}\right)^2}{K_d^{\mathrm{HH}} K_d^{\mathrm{DD}}} = 4\frac{\phi_1}{\phi_2} \rightarrow \phi_2 = 4\frac{\phi_1}{K_{gas}}, \text{ with } \phi_2 = 1.23\phi_1 \text{ at 298 K.}$$

* MERGEFORMAT (26)

Let us define the kinetic H/D isotope effects of desorption and adsorption as

$$\frac{k_d^{\mathrm{HH}}}{k_d^{\mathrm{HD}}} = P_{1d},\ \frac{k_d^{\mathrm{HD}}}{k_d^{\mathrm{DD}}} = P_{2d},\ \frac{k_d^{\mathrm{HH}}}{k_d^{\mathrm{DD}}} = P_{1d}P_{2d}$$

(* MERGEFORMAT 27a)

$$\frac{k_a^{\mathrm{HH}}}{k_a^{\mathrm{HD}}} = P_{1a},\ \frac{k_a^{\mathrm{HD}}}{k_a^{\mathrm{DD}}} = P_{2a},\ \frac{k_a^{\mathrm{HH}}}{k_a^{\mathrm{DD}}} = P_{1a}P_{2a}$$

(* MERGEFORMAT 27b)

By combination of eqs (* MERGEFORMAT 19), * MERGEFORMAT (23), * MERGEFORMAT (26) and (* MERGEFORMAT 27) one obtains

$$P_{1a} = \phi_1 P_{1d},\ P_{2a} = \phi_2 P_{2d} = \frac{4}{K_{gas}}\phi_1 P_{2d}$$

* MERGEFORMAT (28)

Thus, the pseudo-first order rate constants $k_d^{\mathrm{HH}}, k_d^{\mathrm{HD}}, k_d^{\mathrm{DD}}, k_a^{\mathrm{HH}}, k_a^{\mathrm{HD}}, k_a^{\mathrm{DD}}$ are not independent of each other and can be replaced by the independent quantities $k_d^{\mathrm{HH}}, \phi_1, P_{1d} \equiv P_1$, and $P_{2d} \equiv P_2$ where we drop the subscript d standing for desorption. It follows then that

$$\frac{dn_{\mathrm{H2}\rightarrow\mathrm{H^*H^*}}}{dt} = \frac{n_{\mathrm{H2}}}{n_{\mathrm{H2}} + \frac{n_{\mathrm{HD}}}{\phi_1 P_1} + \frac{n_{\mathrm{D2}}}{\phi_1\phi_2 P_1 P_2}} \frac{dN_{\mathrm{LL}\rightarrow\mathrm{L^*L^*}}}{dt},$$

(* MERGEFORMAT 29a)

$$\frac{dn_{\mathrm{HD}\rightarrow\mathrm{H^*D^*}}}{dt} = \frac{n_{\mathrm{HD}}}{\phi_1 P_1 n_{\mathrm{H2}} + n_{\mathrm{HD}} + \frac{n_{\mathrm{D2}}}{\phi_2 P_2}} \frac{dN_{\mathrm{LL}\rightarrow\mathrm{L^*L^*}}}{dt},$$

(* MERGEFORMAT 29b)

$$\frac{dn_{\mathrm{D2}\rightarrow\mathrm{D^*D^*}}}{dt} = \frac{n_{\mathrm{D2}}}{\phi_1\phi_2 P_1 P_2 n_{\mathrm{H2}} + \phi_2 P_2 n_{\mathrm{HD}} + n_{\mathrm{D2}}} \frac{dN_{\mathrm{LL}\rightarrow\mathrm{L^*L^*}}}{dt},$$

(* MERGEFORMAT 29c)

$$\frac{dn_{\mathrm{H^*H^*}\rightarrow\mathrm{H2}}}{dt} = k_d^{\mathrm{HH}}\left(1 - x_{\mathrm{D^*}}\right)^2 M,$$

(* MERGEFORMAT 29d)

$$\frac{dn_{\mathrm{H^*D^*}\rightarrow\mathrm{HD}}}{dt} = 2k_d^{\mathrm{HH}} P_1^{-1} x_{\mathrm{D^*}}\left(1 - x_{\mathrm{D^*}}\right) M,$$

(* MERGEFORMAT 29e)

$$\frac{dn_{\mathrm{D^*D^*\to DD}}}{dt} = k_d^{\mathrm{HH}} P_1^{-1} P_2^{-1} x_{\mathrm{D^*}}{}^2 M,$$

(* MERGEFORMAT 29f)

$$\frac{dN_{\mathrm{LL\to L^*L^*}}}{dt} = \frac{dN_{\mathrm{L^*L^*\to LL}}}{dt} = k_d^{\mathrm{HH}} \left(1-x_{\mathrm{D^*}}\right)^2 M + 2k_d^{\mathrm{HD}} x_{\mathrm{D^*}} \left(1-x_{\mathrm{D^*}}\right) M + k_d^{\mathrm{DD}} x_{\mathrm{D^*}}{}^2 M,$$

(* MERGEFORMAT 29g)

$$\frac{dn_{\mathrm{LL\to L^*L^*}}}{dt} = \frac{dn_{\mathrm{L^*L^*\to LL}}}{dt} = k_d^{\mathrm{HH}} M \left((1-x_{\mathrm{D^*}})^2 + 2P_1^{-1} x_{\mathrm{D^*}}(1-x_{\mathrm{D^*}}) + P_1^{-1} P_2^{-1} x_{\mathrm{D^*}}{}^2\right).$$

(* MERGEFORMAT 29h)

By combination with eq (* MERGEFORMAT 15), taking into account eq * MERGEFORMAT (20) it follows that

$$\frac{dn_{\mathrm{H2}}}{dt} = \frac{k_d^{\mathrm{HH}}}{M} \left(-n_{\mathrm{H2}} \frac{n_{\mathrm{H^*}}{}^2 + 2P_1^{-1} n_{\mathrm{H^*}} n_{\mathrm{D^*}} + P_1^{-1} P_2^{-1} n_{\mathrm{D^*}}{}^2}{n_{\mathrm{H2}} + \dfrac{n_{\mathrm{HD}}}{\phi_1 P_1} + \dfrac{n_{\mathrm{D2}}}{\phi_1 \phi_2 P_1 P_2}} + n_{\mathrm{H^*}}{}^2 \right),$$

(* MERGEFORMAT 30a)

$$\frac{dn_{\mathrm{HD}}}{dt} = \frac{k_d^{\mathrm{HH}}}{M} \left(-n_{\mathrm{HD}} \frac{n_{\mathrm{H^*}}{}^2 + 2P_1^{-1} n_{\mathrm{H^*}} n_{\mathrm{D^*}} + P_1^{-1} P_2^{-1} n_{\mathrm{D^*}}{}^2}{\phi_1 P_1 n_{\mathrm{H2}} + n_{\mathrm{HD}} + \dfrac{n_{\mathrm{D2}}}{\phi_2 P_2}} + 2P_1^{-1} n_{\mathrm{H^*}} n_{\mathrm{D^*}} \right),$$

(* MERGEFORMAT 30b)

$$\frac{dn_{\mathrm{D2}}}{dt} = -\frac{k_d^{\mathrm{HH}}}{M} \left(n_{\mathrm{D2}} \frac{n_{\mathrm{H^*}}{}^2 + 2P_1^{-1} n_{\mathrm{H^*}} n_{\mathrm{D^*}} + P_1^{-1} P_2^{-1} n_{\mathrm{D^*}}{}^2}{\phi_1 \phi_2 P_1 P_2 n_{\mathrm{H2}} + \phi_2 P_2 n_{\mathrm{HD}} + n_{\mathrm{D2}}} + P_1^{-1} P_2^{-1} n_{\mathrm{D^*}}{}^2 \right),$$

(* MERGEFORMAT 30c)

$$\frac{dn_{\mathrm{H^*}}}{dt} = -2\frac{dn_{\mathrm{H2}}}{dt} - \frac{dn_{\mathrm{HD}}}{dt},$$

(* MERGEFORMAT 30d)

$$\frac{dn_{\mathrm{D^*}}}{dt} = -\frac{dn_{\mathrm{HD}}}{dt} - 2\frac{dn_{\mathrm{D2}}}{dt}.$$

(* MERGEFORMAT 30e)

This set of differential equations allows one to calculate numerically the time evolution of n_{H2}, n_{HD}, n_{D2} and $n_{\mathrm{D^*}}$ or the corresponding mole fractions $x_{\mathrm{D^*}}$ as a function of the total number N of dihydrogen molecules in the gas phase, the number M of hydrogen sites in the solid, the number L of ligand hydrogen sites, the rate constant of desorption $k_{\mathrm{d}}^{\mathrm{HH}}$ and of ligand exchange $k_{\mathrm{c}}^{\mathrm{DH}}$, the equilibrium isotope effect of ligand-surface exchange $K_{\mathrm{c}} = k_{\mathrm{c}}^{\mathrm{DH}} / k_{\mathrm{c}}^{\mathrm{HD}}$, the kinetic isotope effects P_1 and P_2 and the isotopic fractionation factor ϕ_1 of desorption, keeping in mind that $\phi_2 = 4\phi_1 / K_{gas} = 1.23\phi_1$ (eqs * MERGEFORMAT (25) and * MERGEFORMAT (26)).

In order to solve eq (* MERGEFORMAT 30) numerically a MATLAB program was written where the quantities on the left sides of eq (* MERGEFORMAT 30) were calculated as a function of time using sufficiently small time intervals from the corresponding quantities at $t = 0$. Two program versions were written, a simple version with the quantities listed in Table 1 as input parameters, and a second version where the kinetic parameters could be determined by least-squares fitting of the experimental to the calculated data.

B. Associative exchange

In this model, we assume that gaseous dihydrogen molecules can bind to the surface and exchange directly hydrogen isotopes with a neighboring bound hydrogen, releasing again a dihydrogen molecule as illustrated in Figure 1b. The following reaction steps are assumed to occur which are responsible for establishing the isotopic equilibrium in the gas phase. The model is less detailed as illustrated schematically in Figures 2 and 10.

$$\mathrm{H_2} + \mathrm{D}^* \xrightarrow{k_e^{\mathrm{HHD}}} \mathrm{H}^* + \mathrm{HD}\,, \qquad (\backslash *$$

MERGEFORMAT 31a)

$$\mathrm{HD} + \mathrm{D}^* \xrightarrow{k_e^{\mathrm{HDD}}} \mathrm{H}^* + \mathrm{D_2}\ \ , \qquad (\backslash *$$

MERGEFORMAT 31b)

$$\mathrm{DH} + \mathrm{H}^* \xrightarrow{k_e^{\mathrm{DHH}}} \mathrm{D}^* + \mathrm{H_2}\,, \qquad (\backslash *$$

MERGEFORMAT 31c)

$$\mathrm{D_2} + \mathrm{H}^* \xrightarrow{k_e^{\mathrm{DDH}}} \mathrm{D}^* + \mathrm{DH}\,. \qquad (\backslash *$$

MERGEFORMAT 31d)

The first two superscripts of the rate constants k_e^{LLL} stand for the reacting dihydrogen isotopologue and the last superscript for the surface bound hydrogen with which the exchange occurs. The following reactions will also be present

$$\mathrm{H_2} + \mathrm{H}^* \xrightarrow{k_e^{\mathrm{HHH}}} \mathrm{H}^* + \mathrm{H_2}\,, \qquad (\backslash *$$

MERGEFORMAT 32a)

$$\mathrm{HD} + \mathrm{H}^* \xrightarrow{k_e^{\mathrm{HDH}}} \mathrm{H}^* + \mathrm{HD}\,, \qquad (\backslash *$$

MERGEFORMAT 32b)

$$\mathrm{HD} + \mathrm{H}^* \xrightarrow{k_e^{\mathrm{HDH}}} \mathrm{H}^* + \mathrm{DH}\,, \qquad (\backslash *$$

MERGEFORMAT 32c)

$$\mathrm{D_2} + \mathrm{D}^* \xrightarrow{k_e^{\mathrm{DDD}}} \mathrm{D}^* + \mathrm{D_2}\,, \qquad (\backslash *$$

MERGEFORMAT 32d)

but they are not further considered here as they cannot be monitored because they do not alter the concentrations of the isotopic species. The time dependence of the latter is given by

$$\frac{dn_{\mathrm{D2}}}{dt} = -k_e^{\mathrm{DDH}} n_{\mathrm{DD}} n_{\mathrm{H}^*} + k_e^{\mathrm{HDD}} n_{\mathrm{HD}} n_{\mathrm{D}^*}\,, \qquad (\backslash *$$

MERGEFORMAT 33a)

$$\frac{dn_{\mathrm{HD}}}{dt} = -k_e^{\mathrm{DHH}} n_{\mathrm{HD}} n_{\mathrm{H*}} - k_e^{\mathrm{HDD}} n_{\mathrm{HD}} n_{\mathrm{D*}} + k^{\mathrm{DDH}} n_{\mathrm{DD}} n_{\mathrm{H*}} + k^{\mathrm{HHD}} n_{\mathrm{HH}} n_{\mathrm{D*}},$$

(*

MERGEFORMAT 33b)

$$\frac{dn_{\mathrm{H2}}}{dt} = -k_e^{\mathrm{HHD}} n_{\mathrm{HH}} n_{\mathrm{D*}} + k_e^{\mathrm{DHH}} n_{\mathrm{HD}} n_{\mathrm{H*}},$$

(*

MERGEFORMAT 33c)

$$\frac{dn_{\mathrm{D*}}}{dt} = -\frac{dn_{\mathrm{H*}}}{dt} = k_e^{\mathrm{DDH}} n_{\mathrm{DD}} n_{\mathrm{H*}} - k_e^{\mathrm{HDD}} n_{\mathrm{HD}} n_{\mathrm{D*}} + k_e^{\mathrm{DHH}} n_{\mathrm{HD}} n_{\mathrm{H*}} - k_e^{\mathrm{HHD}} n_{\mathrm{HH}} n_{\mathrm{D*}}.$$

(*

MERGEFORMAT 33d)

At equilibrium

$$\frac{dn_{\mathrm{D2}}^{\infty}}{dt} = 0 = k_e^{\mathrm{DDH}} n_{\mathrm{DD}}^{\infty} n_{\mathrm{H*}}^{\infty} + k_e^{\mathrm{HDD}} n_{\mathrm{HD}}^{\infty} n_{\mathrm{D*}}^{\infty},$$

(*

MERGEFORMAT 34a)

$$\frac{dn_{\mathrm{HD}}}{dt} = 0 = -k_e^{\mathrm{DHH}} n_{\mathrm{HD}} n_{\mathrm{H*}} - k_e^{\mathrm{HDD}} n_{\mathrm{HD}} n_{\mathrm{D*}} + k^{\mathrm{DDH}} n_{\mathrm{DD}} n_{\mathrm{H*}} + k^{\mathrm{HHD}} n_{\mathrm{HH}} n_{\mathrm{D*}},$$

(*

MERGEFORMAT 34b)

$$\frac{dn_{\mathrm{H2}}}{dt} = 0 = -k_e^{\mathrm{HHD}} n_{\mathrm{HH}} n_{\mathrm{D*}} + k_e^{\mathrm{DHH}} n_{\mathrm{HD}} n_{\mathrm{H*}},$$

(*

MERGEFORMAT 34c)

$$\frac{dn_{\mathrm{D*}}}{dt} = -\frac{dn_{\mathrm{H*}}}{dt} = 0 = k_e^{\mathrm{DDH}} n_{\mathrm{DD}} n_{\mathrm{H*}} - k_e^{\mathrm{HDD}} n_{\mathrm{HD}} n_{\mathrm{D*}} + k_e^{\mathrm{DHH}} n_{\mathrm{HD}} n_{\mathrm{H*}} - k_e^{\mathrm{HHD}} n_{\mathrm{HH}} n_{\mathrm{D*}},$$

(*

MERGEFORMAT 34d)

from which it follows that

$$\frac{k_e^{\mathrm{HHD}}}{k_e^{\mathrm{DHH}}} = \frac{n_{\mathrm{HD}}^{\infty} n_{\mathrm{H*}}^{\infty}}{n_{\mathrm{HH}}^{\infty} n_{\mathrm{D*}}^{\infty}} = \phi_1 \text{ and } \frac{k_e^{\mathrm{HDD}}}{k_e^{\mathrm{DDH}}} = \frac{n_{\mathrm{DD}}^{\infty} n_{\mathrm{H*}}^{\infty}}{n_{\mathrm{HD}}^{\infty} n_{\mathrm{D*}}^{\infty}} = \phi_2.$$

*

MERGEFORMAT (35)

ϕ_1 and ϕ_2 are fractionation factors and represent the equilibrium constants of the isotopic reactions

$$\mathrm{H_2} + \mathrm{D*} + \xrightleftharpoons[k_{\mathrm{e}}^{\mathrm{DHH}}]{k_{\mathrm{e}}^{\mathrm{HHD}}} \mathrm{HD} + \mathrm{H*},$$

(*

MERGEFORMAT 36b)

$$\mathrm{HD} + \mathrm{D*} + \xrightleftharpoons[k_{\mathrm{e}}^{\mathrm{DDH}}]{k_{\mathrm{e}}^{\mathrm{HDD}}} \mathrm{D_2} + \mathrm{H*}.$$

(*

MERGEFORMAT 36a)

Attention: These are not the same quantities as those defined in the previous section, but in a similar way they are not independent of each other because of the isotopic equilibrium in the gas phase (eq * MERGEFORMAT (24)). By combination of eqs * MERGEFORMAT (25) and * MERGEFORMAT (35) it follows that

$$K_{gas} = K = \frac{n_{\mathrm{HD}}^{\infty} n_{\mathrm{HD}}^{\infty}}{n_{\mathrm{HH}}^{\infty} n_{\mathrm{DD}}^{\infty}} = \frac{k_e^{\mathrm{HHD}} k_e^{\mathrm{DDH}}}{k_e^{\mathrm{DHH}} k_e^{\mathrm{HDD}}} = \frac{\phi_1}{\phi_2} .$$

*

MERGEFORMAT (37)

Subtraction of eqs (* MERGEFORMAT 33) and (* MERGEFORMAT 34) leads to

$$\frac{dn_{\mathrm{D2}}}{dt} = -k_e^{\mathrm{DDH}}\left(n_{\mathrm{DD}} n_{\mathrm{H*}} - n_{\mathrm{DD}}^{\infty} n_{\mathrm{H*}}^{\infty}\right) + k_e^{\mathrm{HDD}}\left(n_{\mathrm{HD}} n_{\mathrm{D*}} - n_{\mathrm{HD}}^{\infty} n_{\mathrm{D*}}^{\infty}\right),$$

(*

MERGEFORMAT 38a)

$$\begin{aligned}\frac{dn_{\mathrm{HD}}}{dt} = & -k_e^{\mathrm{DHH}}\left(n_{\mathrm{HD}} n_{\mathrm{H*}} - n_{\mathrm{HD}}^{\infty} n_{\mathrm{H*}}^{\infty}\right) - k_e^{\mathrm{HDD}}\left(n_{\mathrm{HD}} n_{\mathrm{D*}} - n_{\mathrm{HD}}^{\infty} n_{\mathrm{D*}}^{\infty}\right) \\ & + k^{\mathrm{DDH}}\left(n_{\mathrm{DD}} n_{\mathrm{H*}} - n_{\mathrm{DD}}^{\infty} n_{\mathrm{H*}}^{\infty}\right) + k^{\mathrm{HHD}}\left(n_{\mathrm{HH}} n_{\mathrm{D*}} - n_{\mathrm{HH}}^{\infty} n_{\mathrm{D*}}^{\infty}\right),\end{aligned}$$

(*

MERGEFORMAT 38b)

$$\frac{dn_{\mathrm{H2}}}{dt} = -k_e^{\mathrm{HHD}}\left(n_{\mathrm{HH}} n_{\mathrm{D*}} - n_{\mathrm{HH}}^{\infty} n_{\mathrm{D*}}^{\infty}\right) + k_e^{\mathrm{DHH}}\left(n_{\mathrm{HD}} n_{\mathrm{H*}} - n_{\mathrm{HD}}^{\infty} n_{\mathrm{H*}}^{\infty}\right),$$

(*

MERGEFORMAT 38c)

$$\begin{aligned}\frac{dn_{\mathrm{D*}}}{dt} = -\frac{dn_{\mathrm{H*}}}{dt} = & \; k_e^{\mathrm{DDH}}\left(n_{\mathrm{DD}} n_{\mathrm{H*}} - n_{\mathrm{DD}}^{\infty} n_{\mathrm{H*}}^{\infty}\right) - k_e^{\mathrm{HDD}}\left(n_{\mathrm{HD}} n_{\mathrm{D*}} - n_{\mathrm{HD}}^{\infty} n_{\mathrm{D*}}^{\infty}\right) \\ & + k_e^{\mathrm{DHH}}\left(n_{\mathrm{HD}} n_{\mathrm{H*}} - n_{\mathrm{HD}}^{\infty} n_{\mathrm{H*}}^{\infty}\right) - k_e^{\mathrm{HHD}}\left(n_{\mathrm{HH}} n_{\mathrm{D*}} - n_{\mathrm{HH}}^{\infty} n_{\mathrm{D*}}^{\infty}\right).\end{aligned}$$

(*

MERGEFORMAT 38d)

Let us define the kinetic isotope effect

$$P_1 = \frac{k_{\mathrm{e}}^{\mathrm{HHD}}}{k_{\mathrm{e}}^{\mathrm{HDD}}}$$

*

MERGEFORMAT (39)

which corresponds to the rate constant ratio of the H transfer from H_2 to D* and of the D transfer from HD to D*. Using eq * MERGEFORMAT (35) we can then express all rate constants in eq * MERGEFORMAT 38 as

$$k_{\mathrm{e}}^{\mathrm{HDD}} = \frac{k_{\mathrm{e}}^{\mathrm{HHD}}}{P_1},\; k_e^{\mathrm{DHH}} = \frac{k_e^{\mathrm{HHD}}}{\phi_1},\; k_e^{\mathrm{DDH}} = \frac{k_e^{\mathrm{HDD}}}{\phi_2} = \frac{K k_e^{\mathrm{HDD}}}{\phi_1} = \frac{K k_{\mathrm{e}}^{\mathrm{HHD}}}{P_1 \phi_1}.$$

*

MERGEFORMAT (40)

With eq (* MERGEFORMAT 38) it follows then that

$$\frac{dn_{\mathrm{D2}}}{dt} = -\frac{K k_{\mathrm{e}}^{\mathrm{HHD}}}{P_1 \phi_1}\left(n_{\mathrm{DD}} n_{\mathrm{H*}} - n_{\mathrm{DD}}^{\infty} n_{\mathrm{H*}}^{\infty}\right) + \frac{k_{\mathrm{e}}^{\mathrm{HHD}}}{P_1}\left(n_{\mathrm{HD}} n_{\mathrm{D*}} - n_{\mathrm{HD}}^{\infty} n_{\mathrm{D*}}^{\infty}\right),$$

(*

MERGEFORMAT 41a)

$$\begin{aligned}\frac{dn_{\mathrm{HD}}}{dt} = & -\frac{k_e^{\mathrm{HHD}}}{\phi_1}\left(n_{\mathrm{HD}} n_{\mathrm{H*}} - n_{\mathrm{HD}}^{\infty} n_{\mathrm{H*}}^{\infty}\right) - \frac{k_{\mathrm{e}}^{\mathrm{HHD}}}{P_1}\left(n_{\mathrm{HD}} n_{\mathrm{D*}} - n_{\mathrm{HD}}^{\infty} n_{\mathrm{D*}}^{\infty}\right) \\ & + \frac{K k_{\mathrm{e}}^{\mathrm{HHD}}}{P_1 \phi_1}\left(n_{\mathrm{DD}} n_{\mathrm{H*}} - n_{\mathrm{DD}}^{\infty} n_{\mathrm{H*}}^{\infty}\right) + k^{\mathrm{HHD}}\left(n_{\mathrm{HH}} n_{\mathrm{D*}} - n_{\mathrm{HH}}^{\infty} n_{\mathrm{D*}}^{\infty}\right),\end{aligned}$$

(*

MERGEFORMAT 41b)

$$\frac{dn_{\mathrm{H2}}}{dt} = -k_e^{\mathrm{HHD}}\left(n_{\mathrm{HH}} n_{\mathrm{D*}} - n_{\mathrm{HH}}^{\infty} n_{\mathrm{D*}}^{\infty}\right) + \frac{k_e^{\mathrm{HHD}}}{\phi_1}\left(n_{\mathrm{HD}} n_{\mathrm{H*}} - n_{\mathrm{HD}}^{\infty} n_{\mathrm{H*}}^{\infty}\right),$$

(*

MERGEFORMAT 41c)

$$\frac{dn_{\mathrm{D*}}}{dt} = -\frac{dn_{\mathrm{H*}}}{dt} = \frac{Kk_{\mathrm{e}}^{\mathrm{HHD}}}{P_1\phi_1}\left(n_{\mathrm{DD}}n_{\mathrm{H*}} - n_{\mathrm{DD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right) - \frac{k_{\mathrm{e}}^{\mathrm{HHD}}}{P_1}\left(n_{\mathrm{HD}}n_{\mathrm{D*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{D*}}^{\infty}\right) + \frac{k_e^{\mathrm{HHD}}}{\phi_1}\left(n_{\mathrm{HD}}n_{\mathrm{H*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right) - k_e^{\mathrm{HHD}}\left(n_{\mathrm{HH}}n_{\mathrm{D*}} - n_{\mathrm{HH}}^{\infty}n_{\mathrm{D*}}^{\infty}\right),$$

(* MERGEFORMAT 41d)

or

$$\frac{dn_{\mathrm{D2}}}{dt} = k_{\mathrm{e}}^{\mathrm{HHD}}\left\{-\frac{K}{P_1\phi_1}\left(n_{\mathrm{DD}}n_{\mathrm{H*}} - n_{\mathrm{DD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right) + \frac{1}{P_1}\left(n_{\mathrm{HD}}n_{\mathrm{D*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{D*}}^{\infty}\right)\right\},$$

(* MERGEFORMAT 42a)

$$\frac{dn_{\mathrm{HD}}}{dt} = k_{\mathrm{e}}^{\mathrm{HHD}}\left\{-\frac{1}{\phi_1}\left(n_{\mathrm{HD}}n_{\mathrm{H*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right) - \frac{1}{P_1}\left(n_{\mathrm{HD}}n_{\mathrm{D*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{D*}}^{\infty}\right) + \frac{K}{P_1\phi_1}\left(n_{\mathrm{DD}}n_{\mathrm{H*}} - n_{\mathrm{DD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right) + \left(n_{\mathrm{HH}}n_{\mathrm{D*}} - n_{\mathrm{HH}}^{\infty}n_{\mathrm{D*}}^{\infty}\right)\right\},$$

(* MERGEFORMAT 42b)

$$\frac{dn_{\mathrm{H2}}}{dt} = k_{\mathrm{e}}^{\mathrm{HHD}}\left\{-\left(n_{\mathrm{HH}}n_{\mathrm{D*}} - n_{\mathrm{HH}}^{\infty}n_{\mathrm{D*}}^{\infty}\right) + \frac{1}{\phi_1}\left(n_{\mathrm{HD}}n_{\mathrm{H*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right)\right\},$$

(* MERGEFORMAT 42c)

$$\frac{dn_{\mathrm{D*}}}{dt} = -\frac{dn_{\mathrm{H*}}}{dt} = k_{\mathrm{e}}^{\mathrm{HHD}}\left\{\frac{K}{P_1\phi_1}\left(n_{\mathrm{DD}}n_{\mathrm{H*}} - n_{\mathrm{DD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right) - \frac{1}{P_1}\left(n_{\mathrm{HD}}n_{\mathrm{D*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{D*}}^{\infty}\right) + \frac{1}{\phi_1}\left(n_{\mathrm{HD}}n_{\mathrm{H*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right) - \left(n_{\mathrm{HH}}n_{\mathrm{D*}} - n_{\mathrm{HH}}^{\infty}n_{\mathrm{D*}}^{\infty}\right)\right\}.$$

(* MERGEFORMAT 42d)

Using eq * MERGEFORMAT (40) one can also choose k_e^{DDH} as variable leading to

$$\frac{dn_{\mathrm{D2}}}{dt} = k_e^{\mathrm{DDH}}\left\{-\left(n_{\mathrm{DD}}n_{\mathrm{H*}} - n_{\mathrm{DD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right) + \frac{\phi_1}{K}\left(n_{\mathrm{HD}}n_{\mathrm{D*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{D*}}^{\infty}\right)\right\},$$

(* MERGEFORMAT 43a)

$$\frac{dn_{\mathrm{HD}}}{dt} = k_{\mathrm{e}}^{\mathrm{DDH}}\left\{-\frac{P_1}{K}\left(n_{\mathrm{HD}}n_{\mathrm{H*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right) - \frac{\phi_1}{K}\left(n_{\mathrm{HD}}n_{\mathrm{D*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{D*}}^{\infty}\right) + \left(n_{\mathrm{DD}}n_{\mathrm{H*}} - n_{\mathrm{DD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right) + \frac{P_1\phi_1}{K}\left(n_{\mathrm{HH}}n_{\mathrm{D*}} - n_{\mathrm{HH}}^{\infty}n_{\mathrm{D*}}^{\infty}\right)\right\}.$$

(* MERGEFORMAT 43b)

$$\frac{dn_{\mathrm{H2}}}{dt} = k_{\mathrm{e}}^{\mathrm{DDH}}\left\{-\frac{P_1\phi_1}{K}\left(n_{\mathrm{HH}}n_{\mathrm{D*}} - n_{\mathrm{HH}}^{\infty}n_{\mathrm{D*}}^{\infty}\right) + \frac{P_1}{K}\left(n_{\mathrm{HD}}n_{\mathrm{H*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right)\right\},$$

(* MERGEFORMAT 43c)

$$\frac{dn_{\mathrm{D*}}}{dt} = -\frac{dn_{\mathrm{H*}}}{dt} = k_{\mathrm{e}}^{\mathrm{DDH}}\left\{\left(n_{\mathrm{DD}}n_{\mathrm{H*}} - n_{\mathrm{DD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right) - \frac{\phi_1}{K}\left(n_{\mathrm{HD}}n_{\mathrm{D*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{D*}}^{\infty}\right) + \frac{\phi_1}{K}\left(n_{\mathrm{HD}}n_{\mathrm{H*}} - n_{\mathrm{HD}}^{\infty}n_{\mathrm{H*}}^{\infty}\right) - \frac{P_1\phi_1}{K}\left(n_{\mathrm{HH}}n_{\mathrm{D*}} - n_{\mathrm{HH}}^{\infty}n_{\mathrm{D*}}^{\infty}\right)\right\}.$$

(* MERGEFORMAT 43d)

The time dependence of the concentrations of the different species can be calculated as a function of the parameters $k_{\mathrm{e}}^{\mathrm{HHD}}$, P_1, ϕ_1, and of the initial sample composition. The values characterizing the equilibrium sample composition are also needed, but they depend on the initial sample composition as shown in the following.

Let N be the number of dihydrogen molecules in the gas phase

$$N = n_{\mathrm{HH}}^{\infty} + n_{\mathrm{HD}}^{\infty} + n_{\mathrm{DD}}^{\infty} .$$ *

MERGEFORMAT (44)

For the isotopic mole fractions it follows that

$$1 = \frac{n_{\mathrm{HH}}^{\infty} + n_{\mathrm{HD}}^{\infty} + n_{\mathrm{DD}}^{\infty}}{N} = x_{\mathrm{HH}}^{\infty} + x_{\mathrm{HD}}^{\infty} + x_{\mathrm{DD}}^{\infty} .$$ *

MERGEFORMAT (45)

The equilibrium gas phase deuterium fraction is given by

$$x_{\mathrm{D}}^{\infty} = \frac{x_{\mathrm{HD}}^{\infty}}{2} + x_{\mathrm{DD}}^{\infty} .$$ *

MERGEFORMAT (46)

It follows that

$$x_{\mathrm{DD}}^{\infty} = x_{\mathrm{D}}^{\infty} - \frac{x_{\mathrm{HD}}^{\infty}}{2} \text{ and that } x_{\mathrm{HH}}^{\infty} = 1 - x_{\mathrm{D}}^{\infty} - \frac{x_{\mathrm{HD}}^{\infty}}{2} .$$ *

MERGEFORMAT (47)

By combination with eq * MERGEFORMAT (35) it follows that

$$K = \frac{x_{\mathrm{HD}}^{\infty} x_{\mathrm{HD}}^{\infty}}{x_{\mathrm{HH}}^{\infty} x_{\mathrm{DD}}^{\infty}} = \frac{x_{\mathrm{HD}}^{\infty} x_{\mathrm{HD}}^{\infty}}{(1 - \frac{x_{\mathrm{HD}}^{\infty}}{2} - x_{\mathrm{D}}^{\infty})(x_{\mathrm{D}}^{\infty} - \frac{x_{\mathrm{HD}}^{\infty}}{2})} .$$ *

MERGEFORMAT (48)

For $K = 4$ one obtains a statistical distribution where

$$x_{\mathrm{HD}}^{\infty} = 2 x_{\mathrm{D}}^{\infty}(1 - x_{\mathrm{D}}^{\infty}),\ x_{\mathrm{HH}}^{\infty} = (1 - x_{\mathrm{D}}^{\infty})^{2},\ x_{\mathrm{DD}}^{\infty} = x_{\mathrm{D}}^{\infty 2}$$ *

MERGEFORMAT (49)

For $K \neq 4$ a simple calculation shows that

$$x_{\mathrm{HD}}^{\infty} = \pm\sqrt{(\frac{K}{4-K})^{2} + \frac{4K x_{\mathrm{D}}^{\infty}(1 - x_{\mathrm{D}}^{\infty})}{4-K}} - \frac{K}{4-K}$$ *

MERGEFORMAT (50)

Let us now discuss the isotopic composition of the surface. Let M be the number of surface H and D

$$M = n_{\mathrm{H*}}^{\infty} + n_{\mathrm{D*}}^{\infty} .$$ *

MERGEFORMAT (51)

The corresponding isotope fractions in the surface are then given by

$$1 = \frac{n_{\mathrm{H*}}^{\infty}}{M} + \frac{n_{\mathrm{D*}}^{\infty}}{M} = x_{\mathrm{H*}}^{\infty} + x_{\mathrm{D*}}^{\infty} .$$ *

MERGEFORMAT (52)

The total deuterium fraction of the combined gas and solid phase is given by

$$X_{\mathrm{D}} = \frac{n_{\mathrm{HD}} + 2n_{\mathrm{DD}} + n_{\mathrm{D*}}}{2n_{\mathrm{HH}} + 2n_{\mathrm{HD}} + 2n_{\mathrm{DD}} + n_{\mathrm{H*}} + n_{\mathrm{D*}}} = \frac{n_{\mathrm{HD}} + 2n_{\mathrm{DD}} + n_{\mathrm{D*}}}{2N + M} = \frac{2Nx_{\mathrm{D}} + x_{\mathrm{D*}}M}{2N + M} .$$ *

MERGEFORMAT (53)

In a closed system, X_{D} is time independent and given by the initial sample composition. For example, if initially there are only D_2 molecules in the gas phase and no D in the surface, then it follows that

$$X_{\mathrm{D}} = \frac{2N}{2N + M} .$$ *

MERGEFORMAT (54)

Using eqs * MERGEFORMAT (35) and * MERGEFORMAT (47) we obtain

$$\frac{k_e^{\mathrm{HDD}}}{k_e^{\mathrm{DDH}}} = \frac{n_{\mathrm{DD}}^{\infty} n_{\mathrm{H*}}^{\infty}}{n_{\mathrm{HD}}^{\infty} n_{\mathrm{D*}}^{\infty}} = \phi_2 \text{ and } \frac{k_e^{\mathrm{HHD}}}{k_e^{\mathrm{DHH}}} = \frac{n_{\mathrm{HD}}^{\infty} n_{\mathrm{H*}}^{\infty}}{n_{\mathrm{HH}}^{\infty} n_{\mathrm{D*}}^{\infty}} = \phi_1 \quad x_{\mathrm{DD}}^{\infty} = x_{\mathrm{D}}^{\infty} - \frac{x_{\mathrm{HD}}^{\infty}}{2} \text{ and that } x_{\mathrm{HH}}^{\infty} = 1 - x_{\mathrm{D}}^{\infty} - \frac{x_{\mathrm{HD}}^{\infty}}{2} \text{ or}$$

$$\frac{x_{\mathrm{DD}}^{\infty} x_{\mathrm{H*}}^{\infty}}{x_{\mathrm{HD}}^{\infty} x_{\mathrm{D*}}^{\infty}} = \phi_2 \text{ and } \frac{x_{\mathrm{HD}}^{\infty} x_{\mathrm{H*}}^{\infty}}{x_{\mathrm{HH}}^{\infty} x_{\mathrm{D*}}^{\infty}} = \phi_1 .$$ *

MERGEFORMAT (55)

For a statistical distribution of hydrogen isotopes in the gas phase with K=4 it follows that $\phi_1 = 2$ and $\phi_2 = 0.5$.

As $x_{\mathrm{HH}}^{\infty} = 1 - x_{\mathrm{D}}^{\infty} - \frac{x_{\mathrm{HD}}^{\infty}}{2}$ it follows that

$$\phi_1 = \frac{x_{\mathrm{HD}}^{\infty}(1 - x_{\mathrm{D*}}^{\infty})}{(1 - x_{\mathrm{D}}^{\infty} - \frac{x_{\mathrm{HD}}^{\infty}}{2}) x_{\mathrm{D*}}^{\infty}} \text{ and } \phi_2 = \frac{(x_{\mathrm{D}}^{\infty} - \frac{x_{\mathrm{HD}}^{\infty}}{2})(1 - x_{\mathrm{D*}}^{\infty})}{x_{\mathrm{HD}}^{\infty} x_{\mathrm{D*}}^{\infty}} .$$ *

MERGEFORMAT (56)

and that

$$x_{\mathrm{HD}}^{\infty} = \frac{2\phi_1 x_{\mathrm{D*}}^{\infty}(1 - x_{\mathrm{D}}^{\infty})}{2(1 - x_{\mathrm{D*}}^{\infty}) + \phi_1 x_{\mathrm{D*}}^{\infty}} = \frac{2x_{\mathrm{D}}^{\infty}(1 - x_{\mathrm{D*}}^{\infty})}{2\phi_2 x_{\mathrm{D*}}^{\infty} + (1 - x_{\mathrm{D*}}^{\infty})} .$$ *

MERGEFORMAT (57)

In the following, we determine the equilibrium fractions of the different isotopic species as a function of the sample composition and the fractionation factors. By rearrangement of eq * MERGEFORMAT (56) it follows that

$$x_{\mathrm{D}}^{\infty} = \frac{\phi_1 x_{\mathrm{D*}}^{\infty}\left(1 - x_{\mathrm{D*}}^{\infty} + 2\phi_2 x_{\mathrm{D*}}^{\infty}\right)}{(1 - x_{\mathrm{D*}}^{\infty})\left(2(1 - x_{\mathrm{D*}}^{\infty}) + \phi_1 x_{\mathrm{D*}}^{\infty}\right) + \phi_1 x_{\mathrm{D*}}^{\infty}\left(1 - x_{\mathrm{D*}}^{\infty} + 2\phi_2 x_{\mathrm{D*}}^{\infty}\right)} .$$ *

MERGEFORMAT (58)

From eq * MERGEFORMAT (53) it also follows for equilibrium conditions that

$$x_{\mathrm{D}}^{\infty} = \frac{X_{\mathrm{D}}(2N + M) - x_{\mathrm{D*}}^{\infty} M}{2N} .$$ *

MERGEFORMAT (59)

From both equations we obtain

$$1=\frac{2N\phi_1 x_{\mathrm{D}*}^{\infty}\left(1+(2\phi_2-1)x_{\mathrm{D}*}^{\infty}\right)}{\left\{(1-x_{\mathrm{D}*}^{\infty})\left(2+x_{\mathrm{D}*}^{\infty}(\phi_1-2)\right)+\phi_1 x_{\mathrm{D}*}^{\infty}\left(1+(2\phi_2-1)x_{\mathrm{D}*}^{\infty}\right)\right\}\left(X_{\mathrm{D}}(2N+M)-x_{\mathrm{D}*}^{\infty}M\right)}.$$ *

MERGEFORMAT (60)

This equation is of the type

$$1=\frac{ax(1+bx))}{\{(1-x)(2+cx)+dx(1+bx)\}(e-fx)}$$ *

MERGEFORMAT (61)

with

$$x=x_{\mathrm{D}*}^{\infty},\ a=2N\phi_1,\ b=2\phi_2-1,\ c=\phi_1-2,\ d=\phi_1,\ e=X_{\mathrm{D}}(2N+M),\ f=M\ .$$ *

MERGEFORMAT (62)

From eq * MERGEFORMAT (61) it follows that

$$x^3(cf-dbf)+x^2(bde+2f-df-cf-ab-ce)+x(-2f+ce-2e+ed-a)+2e=0\ .$$

This equation is of the form

$$Ax^3+Bx^2+Cx+D=0$$ *

MERGEFORMAT (63)

where

$$A=cf-dbf\ ,\ B=bde+2f-df-cf-ab-ce\ ,\ C=ce+ed-2f-2e-a\ ,\ D=2e\ .$$ *

MERGEFORMAT (64)

Eq * MERGEFORMAT (63) is most conveniently solved numerically using a suitable program. From that we obtain $x_{\mathrm{D}*}^{\infty}$ as a function of N , M ,. ϕ_1, $\phi_2=\frac{\phi_1}{K}$. Using eq * MERGEFORMAT (58) we also can calculate the equilibrium deuterium fraction x_{D}^{∞} in the gas phase, and hence those of HH, HD and DD at equilibrium.

In order to solve eq * MERGEFORMAT (64) numerically again a MATLAB program was written where the quantities on the left sides of eq * MERGEFORMAT (64) were calculated as a function of time using sufficiently small time intervals from the corresponding quantities at $t = 0$.

II. ^{1}H NMR spectra

Figure S1. Line shape analysis of the gas phase 500 MHz ^{1}H NMR spectrum of the Ru/HDA/D+H_2 sample (800 mbar H_2) at 48 min reaction time.

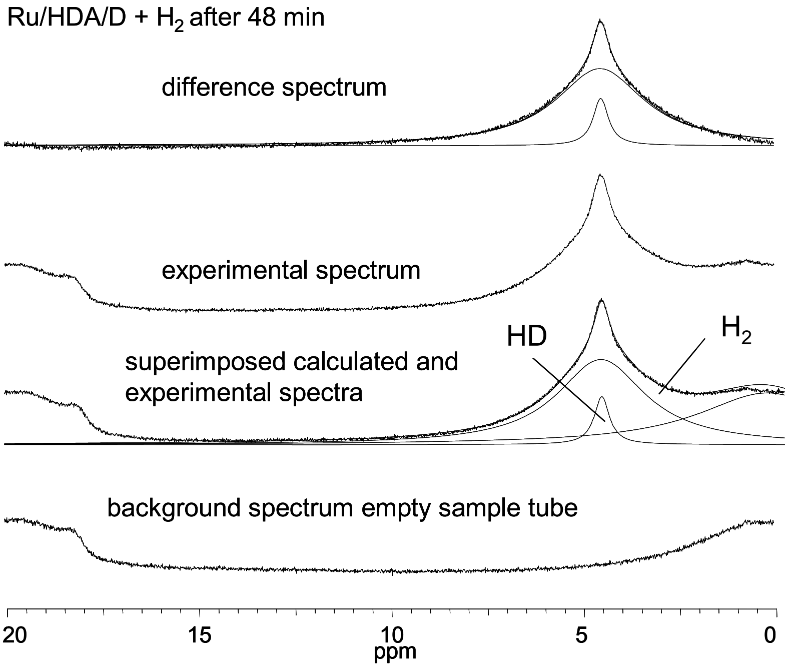
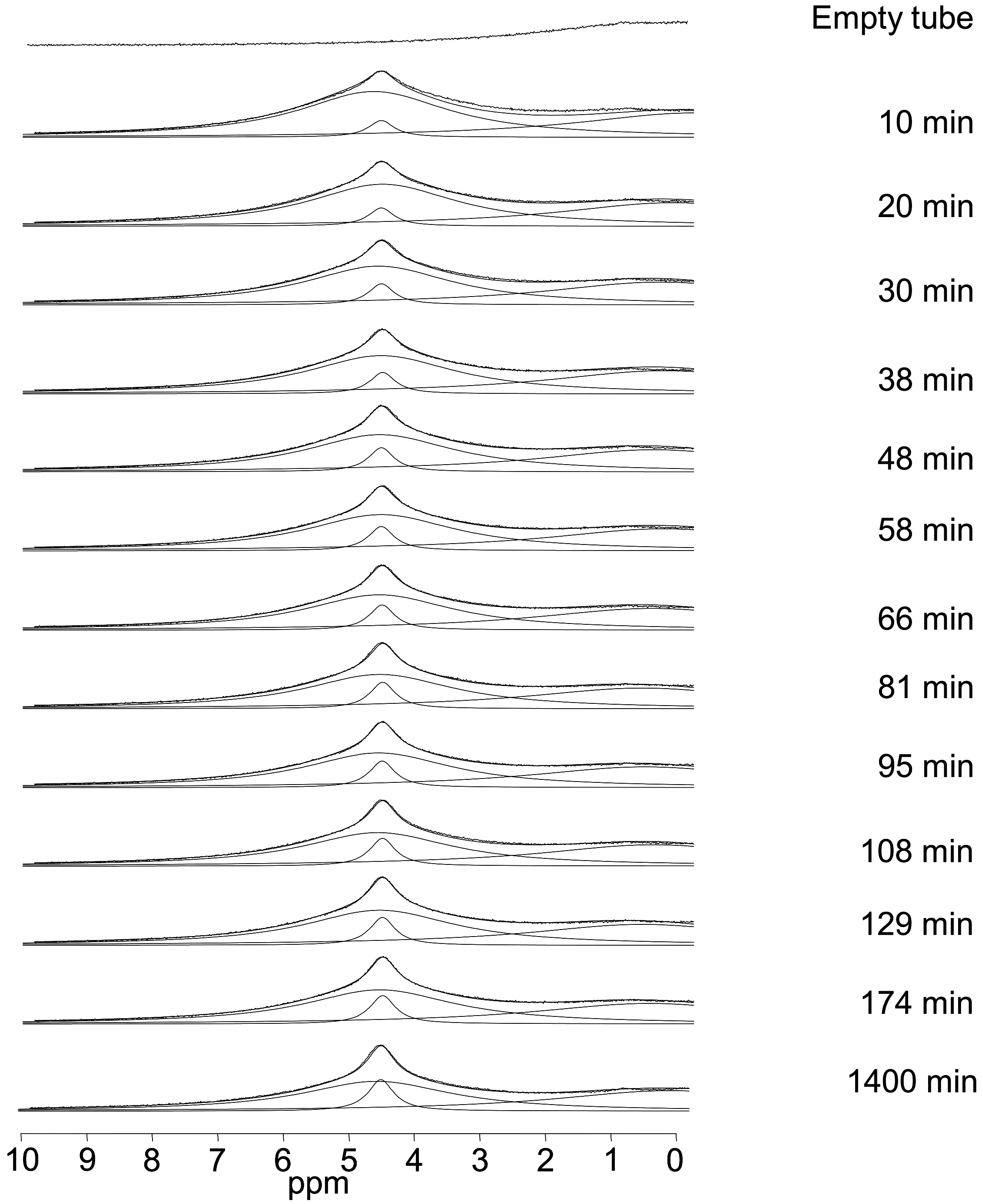


Figure S2. Gas phase 500 MHz ^{1}H NMR spectra of a Ru/HDA/D+H_2 sample (800 mbar H_2) inside a closed NMR glass tube showing the release of HD at different reaction times.



III. Tables

Table S1. ^{1}H signal intensities in units of *Z* for the reaction Ru/HDA/H + 800 mbar D_2.

time / s	[HD] / Z
600	0.18502
1200	0.29914
1680	0.34596
2160	0.36212
2760	0.39583
3660	0.4233
4200	0.42516
8160	0.4741
11700	0.46862
61440	0.54729
63780	0.54548

Table S2. ^{1}H signal intensities in units of *Z* for the reaction Ru/HDA/D + 800 mbar H_2.

time / s	[HD] / Z	2[H_2] / Z
600	0.352	2.24397
1200	0.332	2.2829
2280	0.441	1.96099
3480	0.48635	1.89991
3960	0.48025	2.04092
4860	0.54592	2.0245
5700	0.475	1.853
6480	0.49346	1.94997
7740	0.49128	1.89131
10440	0.525	1.95775
84000	0.57268	1.95952

Table S3. ^{1}H signal intensities in units of *Z* for the reaction Ru/PVP/H + 800 mbar D_2.

time / s	[HD] / Z
480	0.13629
1020	0.18655
1560	0.18793
2160	0.21778
2700	0.239
3480	0.23652
4080	0.26736
10200	0.24226

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