Identifying signatures of thermal and non-thermal reaction pathways in plasmon induced $\text{H}_2 + \text{D}_2$ exchange reaction – Supporting Information

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SI-1: Diffused reflectance spectrum of Au nanoparticles supported on silica

Characterization of the plasmonic catalyst used in our experiments (Au nanoparticles loaded on silica powder) was done by measuring its absorption spectrum in diffuse reflection mode. Figure 1 shows the diffuse reflectance spectrum of our sample where a strong absorption feature at 520 nm, corresponding to the plasmonic absorption of Au nanoparticles (10 to 20 nm size), can be seen. Catalyst sample was in the same form for both absorption and catalysis measurements (in the form of a dry powder).

Figure 1: Diffuse reflectance spectrum of Au nanoparticles supported on silica, used as catalyst in our experiments. Background signal for silica (without Au nanoparticles) has been subtracted. A strong absorption feature at 520 nm corresponding to the plasmon resonance of the Au nanoparticles is observed. This spectrum was measured on Perkin Elmer UV/VIS Lambda 365 spectrometer, equipped with accessories for diffuse reflectance measurements.
SI-2: Estimating temperatures from equilibrium constant measurements

Relationship among equilibrium constant \( (K_{eq}) \) and temperature \( (T) \) for the reaction
\[
H_2(g) + D_2(g) \rightleftharpoons 2 HD(g)
\]
was evaluated using the following relation:

\[
K_{eq}(T) = K_p = \left( \frac{q_{HD}}{q_{H_2}q_{D_2}} \right) e^{\frac{\Delta E}{k_B T}}
\]  (1)

Here, \( q_{HD} \), \( q_{H_2} \) and \( q_{D_2} \) are molecular partition functions for HD, H\(_2\) and D\(_2\), respectively. \( \Delta E \) corresponds to the difference in dissociation energy (also equivalent to difference in zero point energy in this case), \( k_B \) = Boltzmann constant

The individual partition function of the \( i^{th} \) component was obtained from the following relation:

\[
q_i = q_i^{trans} \times q_i^{rot} \times q_i^{vib}
\]  (2)

Here, \( q_i^{trans} \), \( q_i^{rot} \) and \( q_i^{vib} \) correspond to the translational, rotational and vibrational partition functions for the \( i^{th} \) molecule, respectively. Electronic partition function has been considered as 1, and has a negligible contribution under our experimental conditions. Rotational and vibrational partition functions and zero point energy difference were evaluated using the spectroscopic constants and energy level information available from NIST Chemistry WebBook (https://webbook.nist.gov/chemistry/).

SI-3: Background HD contribution to the reaction

In case of thermal reaction, a relatively large part of the stainless steel reactor body gets heated (compared to the light induced case). In principle, additional HD can form on this heated metal surface (besides the catalyst) and this spurious HD signal needs to be accounted for.

In order to identify this spurious HD signal, we performed control experiments with and without Au nanoparticles under identical conditions at temperatures 393 and 443 K. A difference in HD concentration observed in these two cases allows us to determine the magnitude of this spurious signal.

Our findings clearly show that for the case of thermal reaction, HD contribution is less than 5% of that produced on the catalyst (figure 2 a and b). In case of light induced reaction, it is even smaller (by approximately seven orders of magnitude, figure 2 c). Hence, we conclude that the influence of this additional HD signal is negligibly small and can be safely ignored in our analysis.
SI-4: Estimating gas dependent sensitivity factors for our detection setup

Our mass spectrometer based detection setup has different sensitivity factors for different gases. For a correct evaluation of equilibrium constant in case of light-induced reaction, a correction factor which accounts for gas dependent sensitivity of the detection setup was determined in the following manner:

Estimate based on thermal equilibrium measurements

Thermally-driven reaction with a fixed set temperature (443 K and 458 K) of the catalyst bed was allowed to reach equilibrium and the fractions of H\(_2\), D\(_2\) and HD were noted. Using these fractions the uncorrected value of equilibrium constant (\(K'_{eq}\)) was calculated. Since temperature and hence the actual value of \(K_{eq}\) is known in this case (see SI-2), a comparison of the corrected and uncorrected \(K_{eq}\) gives the correction factor \(\alpha_c\), using the following relation: 
\[ K_{eq} = K'_{eq} \times \alpha_c \]

For laser based experiments, where such a direct temperature measurement is not possible, these correction factors are used to calculate \(K_{eq}\), using which \(T_{eff}\) is estimated. All the \(f_{HD}/(f_{H2}f_{D2})\) and \(K_{eq}\) values presented in the main manuscript for light-induced reaction have been calculated after applying this correction. Figure 3 shows the experimental data using which correction factors were evaluated.

![Figure 3](image)

**Figure 3:** Thermal experiments at (left) 443 K and (right) 458 K, from which the correction factors accounting for different gas sensitivity in our detection setup were estimated. Blue points depict the experimental data, red curve depicts a best fit assuming a second order kinetics. Dashed blue line shows the uncorrected equilibrium constant value.

Based on the results shown in figure 3, correction factor (\(\alpha_c\)) was estimated to be 1.126 (mean of the two \(\alpha_c\) values).

Estimate by comparing signals obtained from gas mixtures with known composition

A further verification of the above gas sensitivity factors for H\(_2\) and D\(_2\) were also obtained by comparing the mass spectrometer signals by sampling a gas mixture with a known composition.

Figure 4 shows the measurements for two such gas mixtures with compositions of 50% H\(_2\) + 50% D\(_2\) (top) and 30% H\(_2\) + 70% D\(_2\) (bottom). The gas mixture was maintained at 300 K (practically no reaction occurs under these conditions) and sampled at different time intervals. Based on the mean signals obtained for H\(_2\) and D\(_2\) in both these cases it can be seen seen that the detection sensitivity of H\(_2\) is 1.9 times higher than that for D\(_2\). Assuming that the detection sensitivity for HD is the mean of that for H\(_2\) and D\(_2\), we obtain a correction factor for \(K_{eq}\) as 1.11, which is not very different from the measurement of thermal equilibrium constants and a known temperature, as discussed above.
Figure 4: H\(_2\) and D\(_2\) signals observed in our setup with repeated sampling for two different gas mixtures, 50% H\(_2\) + 50% D\(_2\) (top) and 30% H\(_2\) + 70% D\(_2\) (bottom). Dashed lines correspond to the background which was subtracted from the observed signal before calculating the mean values. Gas mixture was maintained at 300 K where the forward reaction rate is negligibly small, thereby maintaining a steady concentration of H\(_2\) and D\(_2\). Comparing the mean values of signal, we find that detection sensitivity for H\(_2\) is higher by 1.9 times that of D\(_2\).

**SI-5: Second order kinetics model used for fitting**

The second order kinetics was used to model the progress of the reaction and the relevant expressions are provided below:

\[
\text{H}_2(g) + \text{D}_2(g) \xrightarrow{k_f} \xleftarrow{k_b} 2 \text{HD}(g) \tag{3}
\]

\[
time = 0, \quad \begin{array}{ccc}
a & b & 0 \\
\scriptstyle a-x(t) & \scriptstyle b-x(t) & 2x(t) \\
\end{array}
\]

where, \(a\) and \(b\) are initial concentration of H\(_2\) and D\(_2\), respectively.

\[
\frac{dx}{dt} = k_f(a - x) + k_f(b - x) - 4 k_b x^2 \tag{4}
\]

After simplifying the equation 4, we get

\[
x(t) = \frac{A(1 - e^{(A-B)(K-4) k_b t})}{1 - \frac{A}{2} e^{(A-B)(K-4) k_b t}} \tag{5}
\]
where,

\[ A = \frac{u - \sqrt{u^2 - 4v}}{2} \quad \text{and} \quad B = \frac{u + \sqrt{u^2 - 4v}}{2} \]  

\[ u \text{ and } v \text{ is function of initial concentration of H}_2 \text{ and D}_2, \text{ expression was given following} \]

\[ u = \frac{K(a + b)}{K - 4} \quad \text{and} \quad v = \frac{Kab}{K - 4} \]

we can also write above equation in terms of Reaction Quotient \((K_Q)\)

\[ K_Q = \frac{4x(t)^2}{(a - x(t))(b - x(t))} \]  

Using equation 8, equilibrium constant \((K)\) and rate constant \((k_f \text{ or } k_b)\) can be calculated by knowing the initial concentrations \(a\) and \(b\) and concentration of HD with time.

The rate of change of concentration of HD at time \(t \to 0\), can be estimated from equation 5 ,

\[ \left. \frac{dx}{dt} \right|_{t=0} = Kab k_b = k_{f}ab \]

or,

\[ k_{f} = \frac{1}{ab} \left. \frac{dx}{dt} \right|_{t=0} \]

The above expression for forward rate constant is equivalent to equation 2 in the main manuscript.