# Branching-chain propagation of parahydrogen-derived nuclear spin order on a catalyst surface

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### Abstract

When a parahydrogen molecule dissociates on a surface of a heterogeneous catalyst (e.g., of a metal nanoparticle), the correlation of the nuclear spins initially inherited by the two surface H atoms may be shared with other surface hydrogens as they diffuse and combine with random H atoms to produce H<sub>2</sub> molecules which subsequently dissociate. This branching-chain-type propagation of nuclear spin order leads to its gradual dilution but at the same time is accompanied by an increase in the number of H atoms that share nuclear spin order. These conclusions, confirmed by the spin density matrix calculations, may be relevant in the context of parahydrogen-induced polarization (PHIP) in heterogeneous hydrogenations catalyzed by supported metal catalysts, observation of which apparently contradicts the accepted non-pairwise mechanism of hydrogen addition to an unsaturated substrate over such catalysts. The potential consequences of the reported findings are discussed in the context of PHIP effects and beyond.

# INTRODUCTION

Hydrogen gas (H<sub>2</sub>) is a unique molecular system, with several scientifically fascinating and practically useful properties. As H<sub>2</sub> is a symmetric molecule, the generalized Pauli principle requires that permutation of its two hydrogen nuclei should lead to the sign change of its total molecular wavefunction. As a result, H<sub>2</sub> exists in two different modifications – orthohydrogen (o-H<sub>2</sub>) with the total nuclear spin of the two hydrogen atoms I=1, and parahydrogen (p-H<sub>2</sub>) with no nuclear spin (I=0)<sup>1</sup>. The two nuclear spin isomers of H<sub>2</sub> were of paramount importance in the development of the principles of quantum mechanics.

Molecular hydrogen is also a key reactant in very important industrial-scale chemical processes<sup>2</sup> such as catalytic hydroprocessing in oil refining, Fischer–Tropsch and ammonia syntheses, removal of alkyne and diene impurities in alkenes prior to their polymerization, etc. To participate in a chemical reaction,  $H_2$  molecule must be activated. In the majority of practical cases, this implies breaking the H-H chemical bond, the process which under typical reaction conditions requires a catalyst. Interaction of molecular hydrogen with metal surfaces, its activation and the subsequent reactivity of the hydrogen atoms produced on a catalyst is thus a highly important area of scientific research and chemical practice, which currently attracts even more attention in the context of chemical energy storage and conversion<sup>3</sup>.

It is remarkable that very soon after the discovery of p-H<sub>2</sub>, it was realized that it can serve as a unique probe of catalytic H<sub>2</sub> activation because the latter leads to a rapid ortho-para conversion of H<sub>2</sub><sup>1</sup>. Indeed, as soon as p-H<sub>2</sub> molecule dissociates, its H atoms rapidly diffuse apart and randomize

on the catalyst surface. Subsequent recombination of random H atoms produces a statistical mixture containing 25% p-H<sub>2</sub> and 75% o-H<sub>2</sub> often termed normal hydrogen (n-H<sub>2</sub>), which corresponds to a thermodynamic equilibrium at room temperature and above. It is thus often assumed that for H<sub>2</sub> the equilibration of ortho-para ratio (OPR) on a metal catalyst surface is essentially instantaneous for all practical purposes.

In addition to the interrogation of catalytic H<sub>2</sub> activation, p-H<sub>2</sub> was also used to explore the mechanisms behind the heterogeneous catalytic hydrogenation processes. Specifically, in a series of studies, A. Farkas et al.<sup>4,5</sup> argued that hydrogenation of unsaturated compounds on metal catalysts proceeds in a pairwise manner, i.e., that the two H atoms from the same H<sub>2</sub> molecule end up in the same product molecule; this was conjectured by comparing the rates of p-H<sub>2</sub> conversion to normal H<sub>2</sub> in the gas phase with or without a concurrent hydrogenation reaction. However, the change in the OPR for H<sub>2</sub> in the gas phase is an indirect, and thus a very unreliable, indicator of what actually happens on the catalyst surface. A more direct approach would require an experimental determination of the nuclear spin states of hydrogen after its chemisorption. Such possibility was clearly lacking at that time.

Currently, it is still not feasible to determine the spin states of hydrogen atoms on the surface of a solid catalyst in the operando mode, i.e., under realistic reactive conditions. However, there is now a possibility to interrogate the spin states of hydrogen atoms after they are incorporated in a product molecule. In 1987 it was demonstrated that hydrogenation of a C=C double bond with p-H<sub>2</sub> can lead to a dramatic enhancement of the <sup>1</sup>H NMR signals of the hydrogenation product if the reaction proceeds via pairwise H<sub>2</sub> addition<sup>6</sup>, i.e., if the two H atoms that add to an unsaturated reactant are not random and come from the same p-H<sub>2</sub> molecule. This initial observation resulted in the development of a powerful technique, termed parahydrogen-induced polarization (PHIP), which is currently a key member of the family of modern techniques that provide high levels of spin hyperpolarization<sup>7</sup> for numerous fundamental and practical applications. PHIP effects were originally envisioned for homogeneous hydrogenations in solution<sup>8</sup> since the catalytic cycle often proceeds via formation of a metal dihydride species, thus implementing an intrinsically pairwise hydrogenation mechanism. However, a later observation of such effects in hydrogenations catalyzed by supported metal catalysts<sup>9</sup> was totally unexpected. This is because the generally accepted mechanism of hydrogenation with H<sub>2</sub> on such catalysts, proposed by Horiuti and Polanyi<sup>10</sup>, is entirely nonpairwise (in contrast to the Farkas mechanism mentioned earlier). Thus, observation of PHIP effects, which is expected to require pairwise H<sub>2</sub> addition to an unsaturated substrate, on supported metal catalysts (Fig. 1) and, quite likely, on many other types of heterogeneous catalysts (HET-PHIP) apparently contradicts the widely accepted Horiuti-Polanyi mechanism for hydrogenations over catalytic metal surfaces.

In this study we analyze the behavior of the nuclear spin states of hydrogen atoms produced upon dissociative chemisorption of  $p-H_2$  on a catalyst surface based on spin density matrix formalism (see ESI for details). The results reveal that rapidly diffusing surface hydrogen atoms are able to share their mutual nuclear spin correlation with other (random) H atoms on the catalyst surface in a branching-chain fashion. The key requirement for this phenomenon is that pairs of H atoms can reversibly combine to produce an  $H_2$  molecule which subsequently dissociates so that the participating H atoms remain on the catalyst surface. Through spin density matrix calculations we show that such process gradually dilutes the nuclear spin order of the participating H atoms, but the number of correlated nuclear spins increases after each combination-dissociation event. The potential consequences of this finding are discussed for the field of parahydrogen-based hyperpolarization of nuclear spins and beyond.

## **RESULTS AND DISCUSSION**

Nuclear spins of the two H atoms in an intact p-H<sub>2</sub> molecule are strongly coupled and possess a correlated (in fact, an entangled<sup>11</sup>) spin state. Dissociative chemisorption of H<sub>2</sub> is a facile process on many heterogeneous catalysts, for instance on the surface of platinum group metal particles. As dissociation of an adsorbed p-H<sub>2</sub> molecule proceeds on a subpicosecond timescale, the singlet (I=0) nuclear spin state of p-H<sub>2</sub> is preserved along the reaction coordinate and is initially inherited by the two produced H atoms. The mobility of H atoms on such surfaces is high, with the characteristic jump time between neighboring metal sites being on the order of  $10^{-9}$  s at elevated temperatures<sup>12-14</sup>. This leads to a very rapid separation of H atoms on the metal surface. As a result, the nuclear spins of the two resulting H atoms are no longer coupled, and thus their nuclear-spin-correlated state will be destroyed eventually, either by various chemical processes (reactions with various surface species, spillover from metal to support, etc.) or by uncorrelated nuclear spin dynamics and spin relaxation processes.

However, quantum correlations do not decay instantaneously. For instance, it is well-known in the field of quantum teleportation<sup>11</sup> that quantum objects can maintain a correlated (entangled) state even when separated by large distances, i.e., with no intrapair interaction whatsoever. All that is required is that their interactions with the surroundings be negligible. The spin state of the two H atoms of a p-H<sub>2</sub> molecule is in fact one of the Bell states considered in quantum information processing<sup>11</sup>. Therefore, to retain nuclear spin correlation upon separation, they should not experience significant out-of-pair interactions either. This is where the rapid diffusion becomes an asset – a very fast diffusive migration of H atoms on the catalyst surface leads to their efficient decoupling from the environment that they traverse. As a result, the separation of the two H atoms on a catalyst surface may not immediately lead to the loss of correlation of their nuclear spins. In fact, the ability of nuclear spin states to survive on a catalyst surface for a time period long enough for them to end up in a hydrogenation product is likely supported by the successful observation of PHIP effects demonstrated for numerous heterogeneous catalysts, including supported and unsupported metals<sup>15,16</sup>.

It is therefore necessary to consider the possible fate of the nuclear-spin-correlated state of the two H atoms produced from the same p-H<sub>2</sub> molecule on a metal surface while it lasts. Specifically, the surface chemistry of H atoms is known to include the following processes<sup>17</sup>: combination of two random adsorbed H atoms,

$$H(ad) + H(ad) \rightarrow H_2(ad), \tag{1}$$

and an exchange process between an H atom and a physisorbed H<sub>2</sub> molecule,

$$H(ad) + H_2(ad) \rightarrow H_2(ad) + H(ad),$$
(2)

where the label 'ad' indicates an adsorbed state. These two processes are well-known in catalysis in the context of H-D exchange and ortho-para conversion of  $H_2$  on catalytic metal surfaces<sup>18</sup>.

Let us consider two hydrogen atoms, H<sup>a</sup> and H<sup>b</sup>, produced upon dissociative chemisorption of a p-H<sub>2</sub> molecule on a catalyst surface (Fig. 2, (ii)). Upon dissociation, H<sup>a</sup> and H<sup>b</sup> retain the mutual singlet spin state of the parent p-H<sub>2</sub> molecule,  $|S\rangle = (|\alpha\beta\rangle - |\beta\alpha\rangle)/\sqrt{2}$ , and then start to diffuse apart while maintaining their correlated spin state as rationalized earlier. Among other possible surface events, let us consider an encounter of H<sup>a</sup> with another H atom on the catalyst surface, H<sup>c</sup> (Fig. 2, (iii)). As mentioned above, combination of random H atoms on the surface (eq. 1) and subsequent desorption of  $H_2$  leads to the equilibration of the OPR for  $H_2$  in the gas phase. But in the context of this study, it is more relevant to consider the effect this process has on the states of nuclear spins of H atoms that stay on the surface.

In fact, the process of eq. 1 is reversible, so that the newly formed adsorbed  $H_2$  molecule can dissociate again into individual adsorbed atoms (Fig. 2, (iv)) instead of desorbing to the gas phase:

$$H^{a} + H^{c} \rightarrow H_{2} \rightarrow H^{a} + H^{c}$$
(3)

Nuclear spin states of H<sup>a</sup> and H<sup>c</sup> were not correlated until these two atoms met and produced an H<sub>2</sub> molecule. However, combination of H<sup>a</sup> and H<sup>c</sup> forces the combined spin system into one of the four nuclear spin eigenstates of the H<sub>2</sub> molecule, namely  $|T_+\rangle = |\alpha\alpha\rangle$ ,  $|T_-\rangle = |\beta\beta\rangle$ ,  $|T_0\rangle = (|\alpha\beta\rangle + |\beta\alpha\rangle)/\sqrt{2}$ , or  $|S\rangle$ . This is essentially the projective measurement exploited in quantum teleportation<sup>11</sup>. As a result, the nuclear spins of H<sup>a</sup> and H<sup>c</sup> in the newly formed H<sub>2</sub> molecule become correlated as each individual H<sub>2</sub> molecule formed this way will be either o-H<sub>2</sub> (for spin states  $|T_+\rangle$ ,  $|T_-\rangle$ , and  $|T_0\rangle$ ) or p-H<sub>2</sub> ( $|S\rangle$ ). This, however, is of no immediate consequence – the correlation disappears once averaging over the large ensemble of H<sub>2</sub> molecules formed in such encounters is done. This is because the OPR for H<sub>2</sub> molecules produced this way will be purely statistical (3:1), i.e., exactly as in n-H<sub>2</sub>.

While this conclusion is quite straightforward, it is useful to further confirm it by spin dynamics simulations of the nuclear spin behavior based on the spin density matrix (SDM) formalism. From here on, we exploit the indubitably established fact that if a pair of non-equivalent and weakly coupled H atoms in a molecule is nuclear-spin-correlated, PHIP effects are expected in an NMR experiment<sup>8</sup>, with the two <sup>1</sup>H NMR signals being significantly enhanced and exhibiting the characteristic antiphase lineshape (cf. Fig. 1). In our opinion, this is a much easier-to-grasp way to reveal the presence or absence of any nuclear spin correlation than a cumbersome analysis of the individual elements of an SDM. To this end, the two H atoms that are being interrogated are numerically "placed" in chemically non-equivalent positions of a virtual hydrogenation product with a weak mutual scalar coupling (J) between them. Because NMR usually cannot detect individual molecules or spins as it relies on a bulk measurement, an averaging of the SDM is performed before the resulting <sup>1</sup>H NMR spectrum is extracted (see ESI for further calculational details).

The numerical approach outlined above demonstrates that, as can be expected, nuclear spins of H<sup>a</sup> and H<sup>c</sup> are not correlated both before and after the process of eq. 3. This immediately follows from the absence of any antiphase multiplets in the corresponding modeled <sup>1</sup>H NMR spectra presented in Fig. 3, (ii,iv). It may seem, therefore, that reversible combination of H<sup>a</sup> and H<sup>c</sup> has no useful consequences in the context of nuclear spin correlation, but in fact it does. To understand this, we recall that H<sup>b</sup> may still be present somewhere on the same surface. Nuclear spins of H<sup>a</sup> and H<sup>b</sup> were initially correlated (Fig. 3, (ii)), so the question is: are they still correlated after the combination-dissociation of H<sup>a</sup> and H<sup>c</sup> (eq. 3)? In fact, their correlation is (partially) preserved even when averaging is performed over the large ensemble of such H<sup>a</sup> - H<sup>b</sup> pairs, notwithstanding the fact that they may still be far apart on the catalyst surface. This is demonstrated by the results shown in (Fig. 3, (iv)). Comparison of the data presented in Fig. 3, (ii,iv) reveals that the process shown in eq. 3 reduces the initial correlation of H<sup>a</sup> and H<sup>b</sup> by 50%. However, a much more important consequence of the temporary union of H<sup>a</sup> and H<sup>c</sup> is that it creates a correlation of the nuclear spins of H<sup>c</sup> and H<sup>b</sup>. This may seem rather unexpected because these two H atoms never met and/or interacted. Yet, interestingly, now H<sup>b</sup> with either H<sup>a</sup> or H<sup>c</sup> will produce a product molecule with the antiphase lineshape of NMR signals indicative of their nuclear spin correlation.

Similarly, while  $H^b$  diffuses on the catalyst surface, it can temporarily combine with another random atom,  $H^d$ , so that four pairs of H atoms (a-b, c-b, a-d, c-d) will be in the nuclear-spin-correlated state (see ESI, Fig. S1). This process may continue in a branching-chain manner, with each bifurcation adding new members to the two ensembles – the descendants of  $H^a$  and of  $H^b$ .

The description provided above is certainly oversimplified. During this branching-chain propagation of nuclear spin order on the catalyst surface, other processes will inevitably interfere. Some of the participating H atoms will be intercepted and made irrelevant, for instance via desorption of the formed H<sub>2</sub> molecules, chemical interaction with other species they encounter on the catalyst surface, irreversible spillover from the metal particle to the support<sup>19</sup>, etc. In addition, spin correlation will be gradually reduced by the spin relaxation processes. At the same time, more than one pair of p-H<sub>2</sub>-derived H atoms will be active on the catalyst surface.

We note that the process shown in eq. 2 can also be reversible, which can lead to effects similar to those described above (but not considered in this work). Such processes are not limited to the surface of heterogeneous catalysts but may also take place in solution, for instance in (di)hydride-dihydrogen metal complexes which are known to undergo facile intramolecular hydrogen exchange<sup>20,21</sup>. To the best of our knowledge, the associated transformations of nuclear spin states of the hydride and dihydrogen ligands involved in such exchange were never addressed in the literature.

It is yet to be established in the future studies whether or not the spin order propagation mechanism advanced above contributes measurably to the PHIP effects observed experimentally, both with heterogeneous and with homogeneous catalysts. In either case, it appears useful and appropriate at this time to outline the potential consequences of this new phenomenon to facilitate further research in this area.

First, in contrast to earlier interpretations, observation of PHIP effects in hydrogenations (homogeneous as well as heterogeneous) may not necessarily mean that the reaction mechanism delivers two H atoms of an H<sub>2</sub> molecule to the same product molecule. This is a potentially important piece of information about the active catalytic center and the reaction mechanism that it implements. Note that this is different from the one-H PHIP effect known in homogeneous catalysis<sup>22</sup>, in which only one H atom ends up in the product (e.g., an aldehyde) but the two p-H<sub>2</sub>-derived H atoms still need to stay together in a reaction intermediate. In contrast, the mechanism outlined in this work does not imply the existence of such intermediates. In particular, this could explain why several attempts to utilize p-H<sub>2</sub> for detecting short-lived reaction intermediates in hydrogenations involving supported metal nanoparticles by NMR were unsuccessful<sup>23,24</sup>, while in similar studies of homogeneous processes catalyzed by transition metal complexes in solution the intermediates have been detected owing to a dramatic enhancement of their NMR signals provided by the use of p-H<sub>2</sub><sup>6,25,26</sup>.

Second, and again contrary to the earlier views, the proposed mechanism may reconcile the successful observations of HET-PHIP effects with the widely accepted and dominant Horiuti-Polanyi hydrogenation mechanism which involves addition of random H atoms on a metal surface. While the process described above dilutes the spin order of the participating spins as the ensembles of correlated H atoms increase in size, the original requirement of having H<sup>a</sup> and H<sup>b</sup> in the same product molecule to observe PHIP effects may now be relaxed to having any pair of their descendants, which increases drastically the probability of finding two spin-correlated H atoms in a product molecule. This would imply that HET-PHIP effects may in fact be produced in the main

reaction mechanism and not in a secondary reaction channel, and/or not by the minority active centers. This would provide valuable information on very important industrial catalytic processes. In addition, this may also prove useful for addressing a broader spectrum of chemical processes and producing a wider range of hyperpolarized molecules based on those reactions that are known to be non-pairwise with respect to reactivity of  $H_2$  and thus were never considered earlier in this context.

Third, ortho-para conversion of  $H_2$  on catalytically active metal surfaces may be somewhat less efficient than assumed earlier. Indeed, while combination of either two random H atoms or of two H atoms that belong to the same team of descendants, followed by desorption of the formed  $H_2$  molecule into the gas phase, leads to a complete conversion of p-H<sub>2</sub> to n-H<sub>2</sub>, the conversion efficiency is largely reduced when the two recombining H atoms come from the two different teams.

Finally, we note that the arguments advanced in this work are applicable not only to nuclear spins of hydrogen atoms. Similar effects may be envisioned for electrons in solid materials or for unpaired electron spins in radicals or biradicals (stable or transient) in solution. Interestingly, reversible combination-dissociation of unpaired electron spins may not be required for spin order propagation - a spin state of two electrons can be collapsed onto the singlet-triplet basis by a strong exchange interaction between the two radical centers when they come into close contact but do not recombine, and their subsequent separation will make this process reversible. A similar mechanism is known to drive spin exchange<sup>27,28</sup> for, e.g., a pair of stable free radicals in solution upon their collisions, but the effects of such spin-exchange collisions on additional electron spins may need to be considered.

# CONCLUSIONS

When two hydrogen atoms are produced on a catalyst surface upon dissociation of a parahydrogen molecule, their initial nuclear spin correlation can propagate in a branching-chain fashion as they diffuse and combine with random H atoms to produce H<sub>2</sub> molecules which subsequently dissociate. This process leads to a gradual dilution of the non-equilibrium nuclear spin order, but at the same time the number of involved H atoms which share the spin order becomes larger. This phenomenon could be the so far missing element required to explain the observations of NMR signal enhancement in heterogeneous hydrogenations with parahydrogen. Such enhancement undoubtedly requires that a pair of H atoms added to an unsaturated substrate must possess a correlated (entangled) nuclear spin state. However, in contrast to the existing paradigm, the results reported in this work suggest that the two H atoms of the correlated pair may not necessarily have to originate from the same p-H<sub>2</sub> molecule. Thus, the proposed mechanism may reconcile the successful observations of such effects with the widely accepted Horiuti-Polanyi hydrogenation mechanism which involves addition of random H atoms on a metal surface. Furthermore, a similar mechanism may be also operative in homogeneous hydrogenations in a liquid phase involving transition metal complexes possessing dihydrogen and hydride ligands in mutual exchange. Overall, this may provide new opportunities for extending the range of catalytic processes which deliver parahydrogen-based NMR signal enhancement by exploring those reactions in in which H<sub>2</sub> chemistry is known to be non-pairwise and which were thus never considered for such applications.

The potential consequences beyond the field of NMR include the currently hot topic of molecular hydrogen activation and reactivity on catalytic surfaces. Specifically, the chemical

ortho-para conversion of  $H_2$  on metal and other catalytic surfaces, which is often used as a probe of  $H_2$  activation and subsequent reactivity, may be affected by the uncovered fine details of nuclear spin order behavior of mobile and reactive H atoms on a catalyst surface. Finally, a similar behavior is envisioned for the spin order of unpaired electron spins which can reversibly couple or come into a close contact at distances where their mutual exchange coupling becomes pronounced. It is expected that this study would stimulate the exploration of the potential importance of the described branching-chain spin order propagation mechanism and its possible experimental manifestations.

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Figure 1. A typical experimental <sup>1</sup>H NMR spectrum (lower trace) detected during the hydrogenation of propylene to propane with  $p-H_2$  over a Rh/TiO<sub>2</sub> heterogeneous catalyst performed in a high magnetic field of an NMR spectrometer (7.05 T, 300 MHz <sup>1</sup>H resonance frequency). The two signals of propane demonstrate the characteristic antiphase PHIP pattern and are significantly enhanced compared to the conventional (thermal; upper trace) <sup>1</sup>H NMR signals.



Figure 2. A sequence of events involving hydrogens on a metal surface. (i) A parahydrogen (p-H<sub>2</sub>) molecule (green) in the gas phase before it adsorbs on the surface, and a surface H atom (grey). (ii) Hydrogens H<sup>a</sup> and H<sup>b</sup> produced on the surface upon dissociative chemisorption of the p-H<sub>2</sub> molecule, and the additional (random) surface atom H<sup>c</sup>. (iii) H<sup>a</sup> and H<sup>b</sup> combine to produce an adsorbed H<sub>2</sub> molecule. (iv) The latter then dissociates again.



Figure 3. Part of the sequence of events involving hydrogens on a metal surface (left), and the corresponding calculated <sup>1</sup>H NMR spectra of the virtual products (right), before (ii) and after (iv)  $H^{a}$  and  $H^{c}$  combine to produce an adsorbed  $H_{2}$  molecule (iii) which then dissociates again. See text for the explanation of spectra.