

Magnetic Field Acceleration of the ortho-para H₂ Conversion on Transition Oxides

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A new electron-nucleus resonant mechanism is shown to increase the ortho-para conversion rate of hydrogen molecules adsorbed on transition metal oxides. This mechanism is suggested to interpret the observed conversion rate accelerations by an external magnetic field and similar effects in a variety of chemical reactions. Since the resonances occur for stringent relations between catalyst and molecular parameters, the magnetic field acceleration is very sensitive to catalyst pretreatments and constitutes a valuable tool to improve the catalytic rates. [S0031-9007(99)08487-2]

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The modification of a chemical reaction by a magnetic field and/or a magnetic catalyst has long been the subject of controversies. Despite the fact that hundreds of magnetic effects have been reported in chemical (and biological) reactions [1,2], although not always reproducible, the weakness of the magnetic energies made their theoretical analysis rather intricate and often uncertain. This paper suggests a new resonant mechanism which might be at the origin of the observed ortho-para hydrogen conversion acceleration, upon the applying of an external magnetic field. Since the hydrogen conversion presents many features common to reactions sensitive to a magnetic field, such as spin singlet-triplet transitions, it is believed that the present interpretation might lead to a theoretical framework able to tackle these magnetic patterns.

The existence of the two nuclear spin isomers of the molecular hydrogen, denoted ortho and para, was associated with the presence of nuclear spins in the early development of quantum mechanics. The ortho (para) variety is characterized by a triplet (singlet) nuclear spin state and by odd (even) rotational states [3]. The conversion process, from one isomer to another, entails the presence of a catalyst. It occurs during the scattering of the hydrogen molecules on the catalyst magnetic impurities. These create strong magnetic field gradients able to uncouple the hydrogen proton spins [4]. This process has important industrial applications, particularly in aerospace, since the conversion is a necessary step in the liquefaction and storage of molecular hydrogen [5].

It was recognized in the 1960s that transition metal oxides provide efficient catalysts [6]. These were built in dispersing *3d* magnetic ions at the surface of a diamagnetic substrate. A typical system, extensively investigated, consists in different concentrations of chromia impurities inserted on alumina. While performing ortho-para (*o-p*) conversion experiments on such catalysts, Misono and Selwood (MS) [7,8] discovered in 1968 the sensitivity of the conversion rates upon the application of an external and homogeneous magnetic field H . The conversion was accelerated and the rate found growing linearly with H at low

field ($H < 1$ kG) and saturating at moderately high field ($H > 5$ kG). At saturation the field acceleration could reach 75% for magnetically diluted chromia catalysts. In 1976, similar results were obtained on cobalt and manganese oxides [9]. On CoO, the acceleration was found slightly negative at low field ($H < 4$ kG) and then grew without reaching saturation, up to 20% at $H = 20$ kG. On MnO, the acceleration was positive and much faster (200% at $H = 20$ kG and not completely saturated). Different patterns were also obtained on rare earth catalysts [10], but in this paper we shall restrict ourselves to *3d* ions.

These observations appeared very surprising and have never been understood. First, a homogeneous magnetic field induces a simultaneous precession of the nuclear spins whereas the ortho-para transition needs their dephasing. Second, the magnetic energy μH of the magnetic moments μ remains negligible compared to the ortho-para fundamental energy ($\mu H \leq 1 \text{ cm}^{-1} \ll h\omega_{op} \approx 120 \text{ cm}^{-1}$). It is also negligible when compared to thermal energies ($\mu H \ll kT$), at the experimental temperatures ($150 < T < 350$ K) and cannot thus affect the nuclear populations. It is the purpose of this paper to suggest a resonant mechanism which, despite the preceding arguments, leads to field accelerations of the conversion process. The general idea is that the transition energy can be drastically reduced when the nuclear *o-p* transition is counterbalanced by an opposite transition within the ionic electron system. In that case, the magnetic field becomes operative in modulating the transition energy.

In the (MS) experiments, the hydrogen flows through the catalytic powder, and each molecule experiences many collisions on the grains' surfaces. When a molecule hits a surface, it is adsorbed in the weak physisorption well. The scattering times ($\delta t \approx 10^{-11} - 10^{-12}$ s) being much shorter than the conversion time ($\approx 10^{-3}$ s, [11]), the resulting variation of ortho population during one collision remains infinitesimal ($\delta o \approx 10^{-8}$). One peculiarity of the (MS) experiments was a choice of hydrogen flow and catalyst mass which produced less than a moderate fraction of equilibrium populations. We shall therefore

approximate the exponential return, towards the thermal equilibrium, to its initial slope (linear regime).

The considered quantum system is composed of the impurity (and molecule) electrons and hydrogen nuclei. The whole is embedded in a catalyst electric potential of symmetry group G at the surface. The eigenstates of the unperturbed Hamiltonian (including all interactions except the Zeeman and hyperfine ones) might be labeled, for instance, in the coupled scheme, by the irreducible representations Γ , of G : $|\Gamma\gamma\rangle \equiv |(L, S, J, I, \dots)\Gamma\gamma\rangle$, where the principal quantum numbers refer to the electron orbital (L) and spin (S), and to the nuclear rotation (J) and spin (I), angular momenta. (Intermediate angular couplings should also be added.) γ denotes a particular component of the manifold Γ of energy $E(\Gamma)$. Owing to the values of J and I the eigenstates are divided in two sets: ortho and para, denoted Γ_o and Γ_p . The quantum system is in contact with the thermal bath. By considering the hyperfine interactions represented by a Hamiltonian $H_{h.f.}$, the conversion rate $k = \delta o / \delta t$ can be obtained from the principle of detailed balance that we write in a formal way:

$$k = \sum_{\Gamma_o \Gamma_p} P(\Gamma_o, \Gamma_p) J(\omega_{op}) S(\Gamma_o, \Gamma_p). \quad (1)$$

$P(\Gamma_o, \Gamma_p)$ is a function of the initial and equilibrium populations of the ortho Γ_o and para Γ_p states. $J(\omega)$ is the spectral density which represents the ability of the energy transfer between the thermal bath and the quantum system, and $\hbar\omega_{op} = E(\Gamma_o) - E(\Gamma_p)$ [12–14]. In the following we shall use a Lorentzian form, of width ν , to model the spectral density: $J(\omega) = 2\nu/(\omega^2 + \nu^2)$. The hyperfine coupling between the levels Γ_o and Γ_p is represented by a “conversion strength” (in analogy with optical line strengths), $S(\Gamma_o, \Gamma_p)$, defined and simplified as [15]

$$S(\Gamma_o, \Gamma_p) = \sum_{\gamma_o \gamma_p} |\langle \Gamma_o \gamma_o | H_{h.f.} | \Gamma_p \gamma_p \rangle|^2 = |\langle \Gamma_o || H_{h.f.} || \Gamma_p \rangle|^2. \quad (2)$$

Since the electronic and rotational energy separations are of the order of 100 cm^{-1} or larger, an applied magnetic field will essentially mix the different partners γ inside each manifold. The field eigenstates are obtained from the zero-field ones by applying a unitary transform with field dependent coefficients. However, the conversion strength $S(\Gamma_o, \Gamma_p)$, being invariant under any unitary transform of the wave functions, will remain independent of any applied magnetic field. The magnetic acceleration cannot result from a mixing of states.

The rotational energies of a free hydrogen molecule are those of a free rotor: $BJ(J+1)$ and its eigenstates will be denoted (J, m) . Because the molecule is light, the rotational constant is large $B \cong 60 \text{ cm}^{-1}$, and the ortho-para energy separations fall in the far infrared. When the hydrogen molecule is physisorbed, it experiences the electric potential created by all the oxide charges. Mainly, the

molecular induced dipole couples to the electric field, whereas the molecular quadrupole couples to the electric field gradients. The frustrated molecular rotation at the surface can be described by localized states in the angular degrees of freedom [16]. The consequent splittings of the rotational levels are qualitatively represented in Fig. 1(b). Numerical estimations and chromatographic measurements show that the induced splittings on alumina are of the order of $100\text{--}200 \text{ cm}^{-1}$ [17–19].

In order to observe resonant effects between the nuclear and electron systems, it is necessary that their energy levels be similarly split. Electronic splittings of a few hundreds of cm^{-1} are induced by spin-orbit interactions when the electron orbital momentum is not quenched. We shall therefore assume that the many-electron ground state of the surface ions is degenerate. This implies, in turn, that one among the one-electron orbital states building this ground state is degenerate and only partially filled. This degeneracy can be related to the surface symmetry. A simple example of a two fold degeneracy might be found in the C_{4V} (or in C_{3V}) point group where the two $3d$ orbitals, pointing in two planes perpendicular to the surface, span the irreducible representation E . Introducing the electron spin, the spin-orbit interaction splits the ground state at first order. We shall denote by λ the corresponding energy separation between two neighbor sublevels. In Fig. 1(c) we have represented such a splitting in the simplest case of one electron $3d$. λ is directly related to the strength of the spin-orbit interaction, which for $3d$ ions lies in between 200 and 300 cm^{-1} [20]. When the electron splitting λ equals one

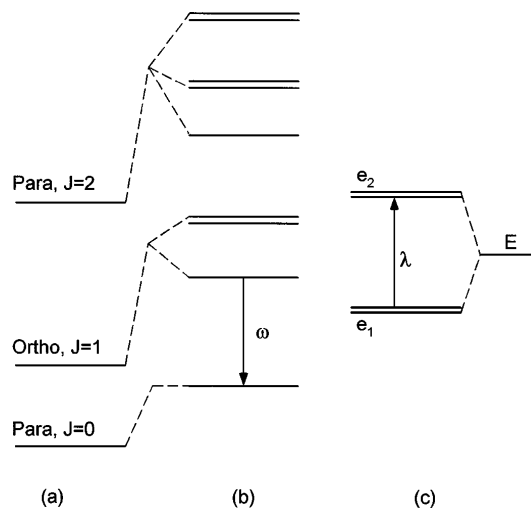


FIG. 1. Nuclear and electron schematic energy levels: (a) the first ($J \leq 2$) rotational levels of a free H₂ molecule; (b) their shifts and splittings by the catalyst surface potential; (c) the spin-orbit splitting of one electron $3d$ in an E state [the levels denoted e_1 (e_2) correspond to $\mu = 0$ ($\mu = \pm 2$), where $\mu = l + 2s$ and l (s) is the projection of the orbital (spin) momentum on the surface normal]. One ortho-para transition $(1, 0) \rightarrow (0, 0)$ is shown to be partially compensated by the electronic transition $e_1 \rightarrow e_2$, when $\lambda \approx \omega$.

of the nuclear o - p energy separations ω , a resonance occurs in the conversion process. In that case, one of the o - p transition is exactly compensated by an opposite transition between two electron states of the catalyst ion, and the thermal bath has no energy to supply (or to absorb), in this global transition. Consequently the conversion rate is resonantly enhanced by 1 or 2 orders of magnitude. [Of course the much stronger electron-phonon interactions maintain permanently the thermodynamical equilibrium within the electron system and the thermal bath will still supply (or absorb) the o - p energy.]

Quite generally the resonance condition $\lambda = \omega$ is not exactly fulfilled, and we shall denote by $\delta = \lambda - \omega$ the energetical deviation from it. Then, the applying of a magnetic field H will bring a subset of levels closer to the resonance. In Fig. 2, we have represented two particular electron-nucleus energy levels, one of which being split by H . When the width ν of the spectral density J is of the order of the magnetic Zeeman energy ($\approx 1 \text{ cm}^{-1}$) and smaller than the initial energy separation δ , the closer approach of one sublevel enhances more the conversion rate than the decrease produced by the remoteness of the other sublevel. The magnetic field acceleration is defined by the relative variation of the conversion rate:

$$\gamma(H) = \frac{\langle k(H) - k(0) \rangle}{\langle k(0) \rangle}, \quad (3)$$

where $k(H)$ represents the conversion rate in the presence of a magnetic field H . The rates' averages must be introduced because the experiments were performed on powders. The surfaces of the grains being rather irregular, the surface potentials above each magnetic site are not necessarily exactly identical. Consequently the separation δ varies from site to site. Moreover, the orientation of the surface normal with respect to the applied magnetic field differs at each site. The important point to stress is that

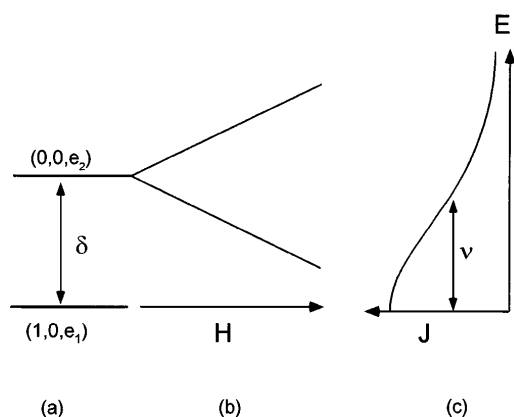


FIG. 2. (a) The two nuclear-electron energy levels corresponding to the initial and final states of the transition indicated in Fig. 1. (b) The ($J = m = 0, e_2$) level is split by an applied magnetic field, whereas the ($J = 1, m = 0, e_1$) one is not ($\mu = 0$). (c) The spectral density J , of width ν , is represented centered on the ortho state as a function of transition energy.

when the electron-nucleus system presents a resonance, all the remaining o - p transitions become negligible compared to the one satisfying even approximately the resonance condition. In other words, the crossing of two electron-nucleus energy levels singles out that particular transition. Consequently the magnetic field acceleration reduces to the relative variation of the spectral density (at the frequency of that particular transition) induced by the application of the magnetic field:

$$\gamma(H) \cong \frac{\langle J(\delta_H) - J(\delta) \rangle}{\langle J(\delta) \rangle}, \quad (4)$$

where $J(\delta_H) = (1/p)\sum_p J(\delta_p)$, and $J(\delta_p)$ are the spectral densities at the frequencies δ_p corresponding to the transitions between the unsplit level and the p sublevels split by H (in the model of Fig. 2, $p = 2$). We have calculated the field accelerations for a variety of fine structures, surface potentials, and by using Gaussian distributions of δ values (and uniform distributions for the field orientations) to represent the site averages. All the calculated accelerations exhibit the following patterns. As a function of δ and for $\delta \ll \nu$, γ is negative since the magnetic sublevels split about symmetrically with respect to the unsplit ones. The field acceleration is positive for $\delta \approx \nu$ and maximum when δ slightly exceeds ν . It becomes negligible when $\delta \gg \nu$. The field acceleration is therefore observable up to about 10 cm^{-1} on each side of the resonance. As a function of the applied magnetic field H , the initial grow of the field acceleration appears quadratic; then it is followed by a linear increase until it reaches a *plateau*. At much higher fields the acceleration decreases until its vanishing. A typical curve $\gamma(H)$ is represented in Fig. 3 and compared to a measured field acceleration observed by Misono and Selwood. Except the quadratic initial increase obtained at very low fields, which is a consequence of our Lorentzian model for the spectral density (the experiments indicate a more linear increase), the concordance appears quite satisfactory. The observed saturation results from a superposition of the different maxima included in the average over the δ values. The width of the plateau can be related to the distribution width of δ .

Since the position of the resonances is directly related to the surface electric potential, simple pretreatments of the catalyst surface are able to improve the catalyst yield. For instance, in the (MS) experiments [8], a 0.0028% sample of chromia dispersed on alumina, after 2.5 h of pretreatment in H_2 at 490°C , gave an acceleration of 25% in a magnetic field of 7.5 kG (at -150°C). The identical sample after 2 h of pretreatment in H_2 at 535°C gave an acceleration of 75% and a moderately smaller zero field conversion, within identical experimental conditions. From the rate decrease and the field acceleration enhancement, it may be concluded that the second pretreatment has slightly shifted the system away from the resonance. This example displays the sensitivity of the magnetic field acceleration

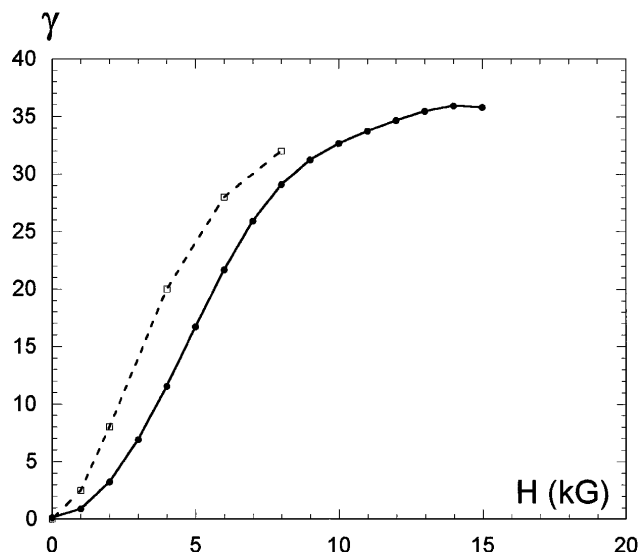


FIG. 3. Conversion acceleration versus the applied magnetic field H (in kG), at $T = 300$ K. The dashed curve represents the experimental acceleration over a sample of (0, 17)% Cr_2O_3 supported on $\alpha\text{-Al}_2\text{O}_3$ (from [8]). The full curve represents the theoretical one calculated with $\lambda = 200$ cm^{-1} , $\nu = 0.42$ cm^{-1} , and a Gaussian distribution of δ values centered around 0.4 cm^{-1} , with a standard deviation of 0.03 cm^{-1} .

upon catalyst pretreatments and its practical usefulness in the selection and preparation of o - p catalysts.

Although the herewith described resonant process has been introduced to interpret o - p conversion experiments, it is believed that similar mechanisms are operative in many catalyzed chemical reactions sensitive to an external magnetic field. Two main arguments are commonly opposed to such a magnetic sensitivity. The first one concerns the magnetic energy which is completely negligible as compared to the electron energies at work in a chemical reaction. The second one is relative to the general lack of reproductiveness of the experimental measurements. But these two apparent paradoxes can be simply understood on the ground basis of our suggested framework. First, in the suggested resonant process, the highly energetic molecular transition is counterbalanced by an inverse catalyst transition. Therefore the magnetic field has to modulate only their energy difference which is beyond compare weaker. Note that, in this process, the molecular reaction energy is first transferred to the catalyst surface electrons and thereafter to the catalyst thermal degrees of freedom (or reciprocally). Second, since the magnetic effects can be observed only in the close vicinity of the resonance, they occur for exacting relationships among the parameters. These can be satisfied accidentally. In o - p conversion, for instance,

there is no reason for an o - p transition energy, modulated by the catalyst surface potential, to be equal to the intraionic spin-orbit interaction strength, and Misono and Selwood had to try empirically many catalyst pretreatments to sift out the magnetic effects. Quite generally the used catalysts are far from being single crystals, their surfaces are loosely defined, and consequently most magnetic effects not easily reproducible.

Inversely if a magnetic field acceleration is observed experimentally it seems likely that the catalyst is operating near a molecule-catalyst resonance. A simple test would be to increase the intensity of the applied magnetic field beyond 20 kG. After the conversion rate has reached its maximum the resonant mechanism predicts a subsequent decrease. Since at exact resonance the catalytic rate is sharply enhanced, the magnetic field effects could be used to determine how efficiently a catalyst is operating and to control its improvement.

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